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NSERC for funding this project.

# Abbreviations

| | |
|---|---|
| Ar | aryl |
| $^t$Bu | *tert*-butyl |
| Et | ethyl |
| Me | methyl |
| Ph | phenyl |
| $^i$Pr | *iso*-propyl |
| Cy | cyclohexyl |
| Cp | $\eta^5$-cyclopentadienyl |
| Cp* | $\eta^5$-pentamethylcyclopentadienyl |
| COD | 1,5-cycloctadiene |
| BINAP | 2,2'-*bis*(diphenylphosphino)-1,1'-binaphthyl |
| Tol-BINAP | 2,2'-*bis*(di-*p*-tolylphosphino)-1,1'-binaphthyl |
| dmpe | *bis*(dimethylphosphino)ethane |
| diphoe | *Z*-*bis*(diphenylphosphino)ethene |
| dppb | 1,4-*bis*(diphenylphosphino)butane |
| dppe | 1,2-*bis*(diphenylphosphino)ethane |
| dppm | *bis*(diphenylphosphino)methane |
| dppp | 1,3-*bis*(diphenylphosphino)propane |
| eq. | equation |
| equiv | equivalent |
| L | Generalized 2e ligand |
| $L_nM$ | generalized metal fragment with n ligands |

| | |
|---|---|
| OAc | acetate |
| OTf | triflate |
| POEph | $Ph_2POCHPhCHMeNHMe$ |
| POMeph | $Ph_2POCHPhCHMeNMe_2$ |
| POPheph | $Ph_2POCHPhCHMeNMeCHPh_2$ |
| PPro | 2-(*S*)-diphenylphosphinomethylpyrrolidine |
| PProMe | 2-(*S*)-diphenylphosphinomethyl-*N*-methylpyrrolidine |
| THF | tetrahydrofuran |
| TFA | trifluoroacetic acid |
| X | generalized 1e anionic ligand |

# Abstract

Rhodium complex, $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2]$ containing bridging hydroxo ligands, smoothly reacts with $[HM(CO)_3Cp]$ (M = Cr, Mo, W) to afford the corresponding heterobimetallic complexes, $[(Ph_3P)_2Rh(\mu\text{-}CO)_2M(CO)Cp]$. The reaction of $[Pd_2L_2(Ph)_2(\mu\text{-}OH)_2]$ with an equimolar amount of $[HM(CO)_3Cp]$ gives the organometallic hydroxo clusters $[L_2Pd_2(Ph)_2(\mu\text{-}OH)(\mu\text{-}CO)_2(\mu^3\text{-}CO)MCp]$ in high yield. These reactions can be regarded as the neutralization of an acidic transition metal hydride by a basic transition metal hydroxide. The structure of the $Pd_2Cr$ cluster was determined by single crystal X-ray diffraction study. The trinuclear hydroxo clusters are stable in the solid state but slowly decompose in solution, the decomposition path being strongly dependent on the nature of M. Facile and selective decomposition of the $Pd_2W$ hydroxo complex resulted in the formation of $[Pd_2(PPh_3)_2(Ph)_2(\mu\text{-}OH)_2]$, biphenyl, and the tetranuclear $Pd_2W_2$ cluster. Similar tetranuclear clusters were obtained in high yield when the palladium hydroxo dimers were neutralized with excess $[HM(CO)_3Cp]$ or $[HM(CO)_3Cp^*]$. However these reactions proceed by a different pathway involving Ph/H exchange process, and resulted in the formation of benzene and $[PhM(CO)_3Cp]$ or $[PhM(CO)_3Cp^*]$, respectively. Labeling experiments suggested that the H atoms of the hydrido and hydroxo ligands underwent an exchange which was faster than the neutralization and the concomitant formation of the metal-metal bond. Infrared and NMR studies show that the structures of the trinuclear hydroxo clusters were more rigid than those of the tetranuclear species. Tetranuclear complexes containing three different metals, $Pd_2MoW$ and $Pd_2CrW$ were prepared and characterized.

The reaction of $[Rh(CO)(PPh_3)_2Cl]$ with the sodium salt of (1*S*, 2*R*, 5*S*)-menthol (**NaOMent**) cleanly affords chiral rhodium carbonyl alkoxo complex, $[Rh(CO)(PPh_3)_2OMent]$, which was

characterized by single crystal X-ray diffraction. The similar reaction of $[Rh(PPh_3)_3Cl]$ with **NaOMent** leads to the formation of $[Rh(PPh_3)_3H]$, apparently due to fast decomposition of the intermediate rhodium phosphine alkoxo complex *via* β-H elimination.

The reaction of $[Rh(PPh_3)_3Cl]$ with NaOAr in toluene cleanly affords the corresponding aryloxo complexes $[Rh(PPh_3)_3(OAr)]$ (**4.1**). In solution **4.1** exists in equilibrium with $PPh_3$ and the corresponding $[Rh(PPh_3)_2(\pi\text{–}OAr)]$ (**4.2**) The addition of HOAr shifts the equilibrium completely toward the corresponding adducts **4.2**·2HOAr due to hydrogen bonding between the oxygen atom of the π-coordinated OAr ligand and two molecules of HOAr. Heating **4.1** in toluene at 60-80°C leads to the elimination of HOAr with concomitant cyclometallation of a phenyl ring of one $PPh_3$ ligand, affording mixtures of **4.1**, **4.2**·2HOAr, a cyclometallated Rh complex and $PPh_3$. At room temperature, a reverse reaction slowly occurs to give equilibrium mixtures of **4.1**, **4.2** and $PPh_3$. Complexes **4.1** readily react with water, CO and $H_2$, affording $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2]$, and $[Rh(PPh_3)_3H]$, respectively. The latter complex was also obtained when complexes **4.1** were treated with methanol. The solid state structures of the phenoxo complexes **4.1a**, **4.2**·2PhOH and of *p*-nitrophenoxo species **4.3e** were established by a single crystal X-ray diffraction.

Aminophosphine derivatives of (*S*)-proline (**5.1a,b**) and aminophosphinites prepared from *N*-substituted (1*S*, 2*R*)-ephedrines (**5.2a-c**) cleanly react with $[Rh(CO)_2Cl]_2$ in benzene affording complexes with *P,N*-chelating (**5.3a,b**, **5.4a** and **5.5b**) or monodentate ligands (**5.6b,c** and **5.8c**), depending on the steric bulk of the amino group and metal to ligand ratio. Treatment of the chloro bridged dimer **5.8c** with $AgClO_4$ in methylene chloride gives the cationic complex **5.9c** containing not only *P,N*-chelating aminophosphinite, but also a Ph group of a *N*-(diphenylmethyl) fragment coordinated to Rh in an unusual $\eta^2$ fashion. Formation of the *N*-

based stereocenters occurs selectively and complexes **5.3a,b**, **5.4a** and **5.9c** exist as single diastereomers in the solid state and in solution. The solid state structures of **5.3a,b**, **5.4a** and **5.9c** were established by single crystal X-ray diffraction.

The synthesis of $[Ru_2(OAc)_4]$ by a "one pot" modification of Lindsay's procedure results in increased yield and in the simplification of the preparation. $[Ru_2(OAc)_4]$ reacts with BINAP and Tol-BINAP to give the corresponding Ru(II) bisphosphine complexes. The reaction is exceptionally clean as no side products were detected by $^{31}P$ NMR.

$[Ru_2(OAc)_4]$ reacts with 2-(*S*)-diphenylphosphinomethylpyrrolidine (**PPro**) and 2-(*S*)-diphenylphosphinomethyl-*N*-methylpyrrolidine (**PProMe**) to give *trans, trans, trans*-$[Ru(OAc)_2(PPro)_2]$ (**7.2**) and $[Ru(OAc)_2(PProMe)_2]$, respectively, which possess stereogenic nitrogen atoms. The latter complex exists as the *cis-P,P-cis-P,N-*(Δ)-stereoisomer (Δ-**7.3**) in THF and as the (Λ)-stereoisomer (Λ-**7.5**) with *cis-P,P-trans-N,N* coordination geometry in MeOH. Formation of *N*-based stereocenters occurs selectively and complexes **7.2**, **7.3** and **7.5** are present as single diastereomers in solution and in the solid state. Thermolysis of Δ-**7.3** in boiling dioxane affords (Δ)- and (Λ)-stereoisomers of the carbene ruthenium complex (**7.7**), due to facile dehydrogenation of the *N*-Me groups of the ligand.

# Table of Contents

# General Introduction and Organization of the Thesis

The present thesis can be divided into two parts. The first part describes hydroxo, alkoxo and aryloxo derivatives of Pd and Rh (chapters 1-4), while the other section is devoted to Rh and Ru complexes of *P,N* chelating aminophosphines and aminophosphinites (chapters 5-7). Although seemingly independent, both parts deal with compounds containing "soft" P- and "hard" O- or N-donor ligands in the coordination sphere of a late transition metal. These species possess interesting catalytic properties and reactivity, which make them attractive for application in catalysis and metallorganic synthesis. Hard donors usually bind to soft transition metals relatively weakly and thus can provide a free coordination site upon dissociation. Soft phosphine ligands are normally more strongly attached to a metal and stabilize coordinatively unsaturated species, which are important intermediates in many catalytic processes. The basicity of amino and alkoxo functional groups is sensitive to the nature of the substituents connected to the heteroatom, therefore the coordination properties of N- and O- donor ligands can be readily adjusted by selecting the appropriate substituents. A variety of chiral amines, alcohols, aminoacids and aminoalcohols are available from natural sources in enantiomerically pure form. The application of these natural products and their derivatives as ligands allows for the preparation of chiral metallocomplexes for use in metallorganic synthesis and catalysis.

The following chapter describes the literature data on the synthesis and reactivity of late transition metal hydroxo, alkoxo and aryloxo complexes. The preparation and coordination properties of chiral aminophosphines and aminophosphinites will be discussed later in chapter 5.

# Chapter 1

# Late Transition Metal Hydroxo, Alkoxo and Aryloxo Complexes.

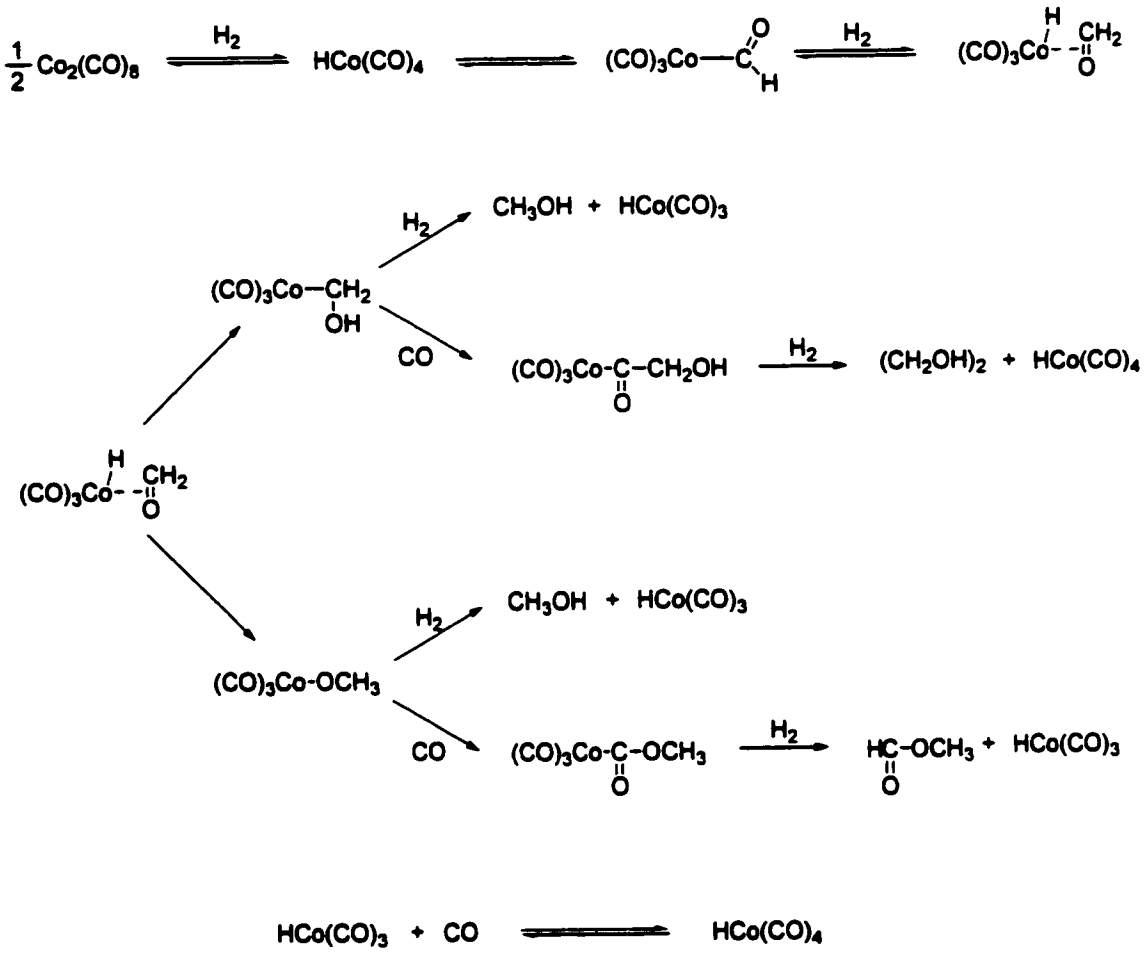
## *1.1 Catalytic Reactions Involving Hydroxo and Alkoxo complexes*

Late transition metal hydroxo and alkoxo complexes were postulated as key intermediates in many metal-catalyzed organic transformations. These include the synthesis of methanol from CO and $H_2$, the water gas shift reaction, the oxidation of organic compounds, hydrogen transfer hydrogenation, the reduction of aldehydes and ketones, the hydroxy / alkoxy carbonylation of alkenes and alkynes, the hydrolysis of phosphates, amides and nitriles and the activation of $O_2$ by metalloproteines.[1-6] Several illustrative examples of these reactions are discussed below.

### *1.1.1 Synthesis of Methanol from CO and $H_2$.*

Methanol is manufactured in bulk quantities from the reaction of synthesis gas (CO + $H_2$) over heterogeneous catalysts. A homogeneous variant of this process has not found an industrial application due to low selectivity for MeOH formation.[3] However, investigations in this field have led to a better understanding of the reaction mechanism. According to Feder and Rathke[7] (Scheme 1.1), the formation of MeOH in the presence of $HCo(CO)_4$ in benzene or dioxane occurs *via* the hydrogenation of the methoxy and hydroxymethylene intermediates formed by the insertion of coordinated formaldehyde into the H-Co bond. Essentially the same mechanism was proposed later by Fahey[8] for a similar Co system and by Dombek[9] for MeOH synthesis catalyzed by $Ru_3(CO)_{12}$ in acetic acid.

**Scheme 1.1**



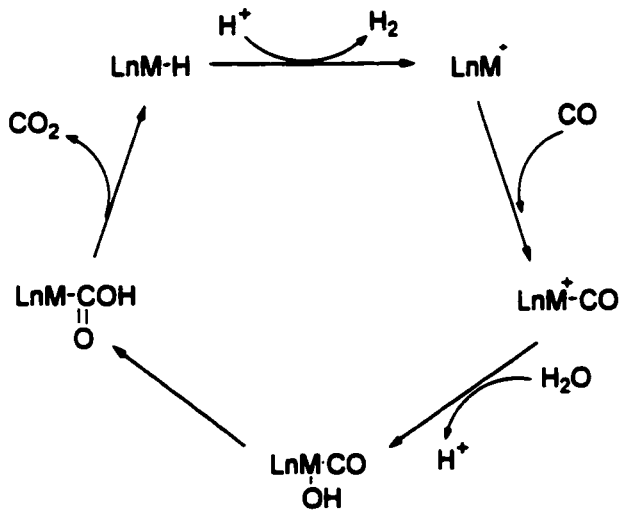
*1.1.2 Water Gas Shift Reaction.*

The water gas shift reaction (eq 1.1) is used to increase the hydrogen content in the synthesis gas (CO + $H_2$) obtained by partial oxidation of methane or steam reforming.[10]

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1.1)$$

In industry, this process is carried out heterogeneously, however homogeneous systems involving $Ru_3(CO)_{12}$, $[Rh(CO)_2I_2]^-$, $[RhH(PEt_3)_3]$ and $[FeH(CO)_4]^-$ are also known.[11,12] The generally accepted mechanism of the reaction is shown in Scheme 1.2 and includes a carbonylhydroxo species as the key intermediate.

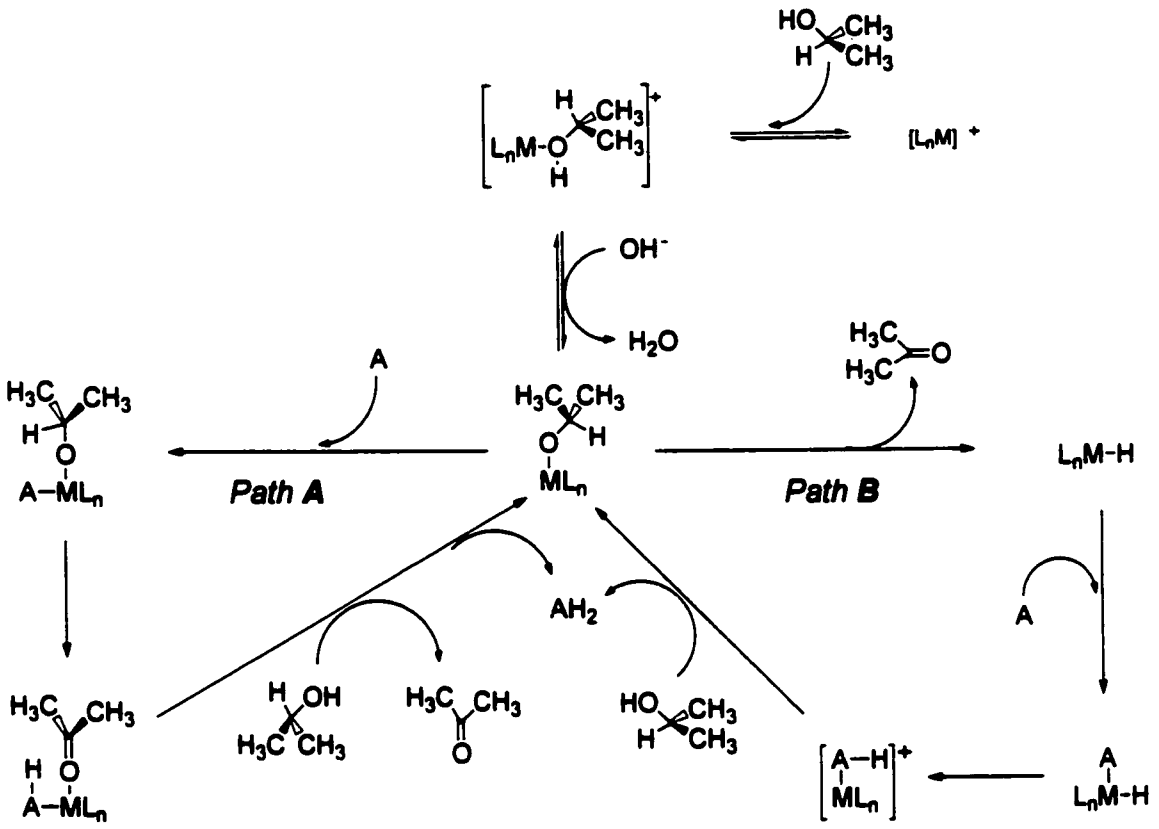
**Scheme 1.2**




### *1.1.3 Hydrogen Transfer Hydrogenation*

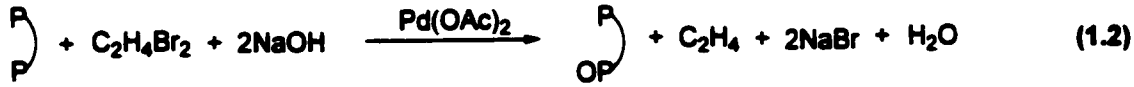
Hydrogen transfer hydrogenation (HTH) is the catalytic reduction of multiple bonds in a substrate by a reducing agent other than $H_2$. The use of a hydrogen donor avoids some of the risks and constraints associated with the use of $H_2$ as well as the necessity of pressure vessels.[13] Various ketones, olefins, imines, epoxides and nitro compounds can be reduced under HTH conditions in the presence of Rh(I), Ir(I) and Ru(II) catalysts.[14] Isopropanol is the most popular hydrogen donor since it is easily handled, nontoxic, inexpensive, dissolves many organic compounds and upon dehydrogenation gives acetone which is readily removable. The mechanism of HTH with isopropanol involves the formation of a transition metal isopropoxy complex which can then reduce a substrate by direct hydrogen transfer (Scheme 1.3, path A) or undergo β-H elimination to give hydride derivatives, followed by hydride transfer from the metal to the substrate (Scheme 1.3, path B).[15]

**Scheme 1.3**




### *1.1.4 Metal Catalyzed Oxidation of Organic Compounds.*

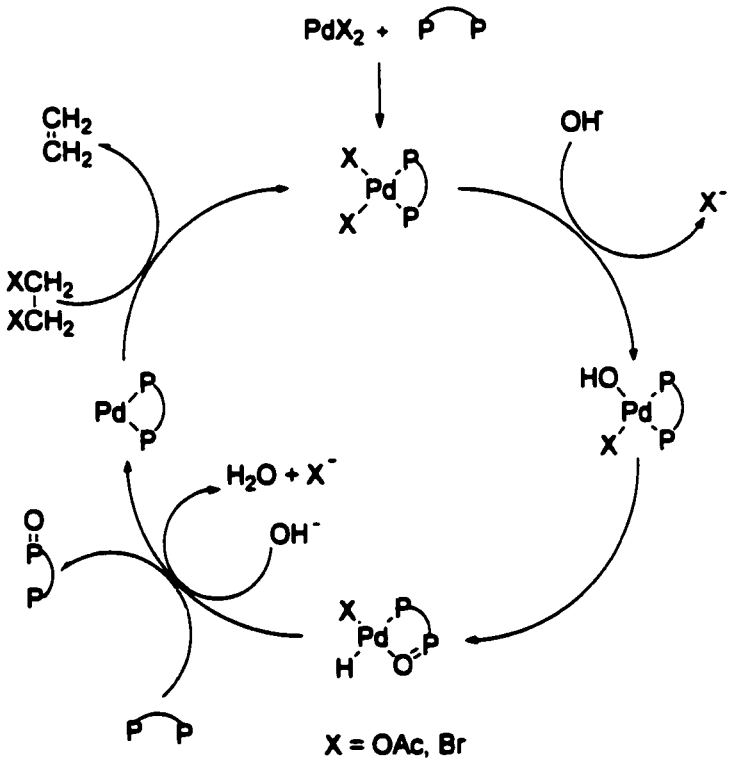
Transition metal hydroxo and alkoxo complexes have been proposed as intermediates in many oxidative organic transformations such as the oxidation of aromatic hydrocarbons[16-23] and the Wacker process.[24-28] An excellent example of a well designed catalytic cycle has been reported recently by Grushin[29] for the selective mono oxidation of bisphosphines to bisphosphine monoxides (BMPO) which are valuable ligands for organometallic synthesis and catalysis. The reaction occurs according to eq1.2.




(1.2)

The mechanism of the catalytic oxidation (Scheme 1.4) involves a bisphosphine-Pd(II)-hydroxo complex which undergoes an intramolecular redox process Pd(II)/P(III) → Pd(0)/P(V)[30] followed by reoxidation of the resulting Pd(0) species back to the catalytically active Pd(II) hydroxo complex. The latter is formed *via* the oxidative addition of dibromoethane to give a bromoethyl intermediate, which subsequently loses $C_2H_4$ and undergoes Br/OH exchange.

**Scheme 1.4**




### *1.2 Synthesis of Late Transition Metal Hydroxo Alkoxo and Aryloxo Complexes.*

The reported synthetic methods can be classified into three groups:

1) Metathesis reactions of $L_nMX$ complexes.
2) Oxidative addition of water, alcohols, phenols and esters to complexes of transition metals in low oxidation states.

3) M-C or M-H bond cleavage by $H_2O$, HOR or HOAr.

### *1.2.1 Metathesis reactions*

The metathesis of transition metal chloro, nitrato or triflato complexes with alkali metal hydroxides, alkoxides and aryloxides is the most common route to the corresponding hydroxo, alkoxo and aryloxo complexes, respectively (eq1.3).

$$L_nMX + NaOR \longrightarrow L_nMOR + NaX \qquad (1.3)$$

X = Cl, $NO_3$, $CF_3SO_3$
R = H, alkyl, aryl

Various Pt(II),[31-36] Pd(II),[37-40] Rh(I),[41-43] Rh(III),[44] Ru(II),[45-47] Ir(I),[48,49] Ir(III),[48,49] Au(I),[50,52] and Au(III)[50] derivatives have been prepared using this synthetic approach. The reactions are usually carried out in a solvent, which dissolves both $L_nMX$ and NaOR reagents (MeCN, THF or ROH), however immiscible solvent systems have also been successfully used. For example, Pd and Rh hydroxo bridged complexes were prepared in a $C_6H_6/H_2O$ mixture according to eqs 1.4 and 1.5 respectively.[40,43]

$$(Ph_3P)_2PdCl_2 + 2NaOH + PhI \xrightarrow[-Ph_3PO]{C_6H_6/H_2O,\ -NaCl,\ -NaI,} \frac{1}{2}\ [(Ph_3P)(Ph)Pd(\mu\text{-}OH)_2Pd(Ph)(PPh_3)] \qquad (1.4)$$

$$(Ph_3P)_3RhCl + NaOH \xrightarrow[-NaCl,\ -PPh_3]{C_6H_6/H_2O} \frac{1}{2}\ [(Ph_3P)_2Rh(\mu\text{-}OH)_2Rh(PPh_3)_2] \qquad (1.5)$$

Substitution of chloro ligands for weakly coordinating anions such as $ClO_4^-$, $BF_4^-$ or $PF_6^-$, by treating the chlorides with the appropriate silver salts, allows for the reaction (1.3)

to be carried out at low temperatures and thus even unstable complexes can often be isolated.[31, 53, 61]

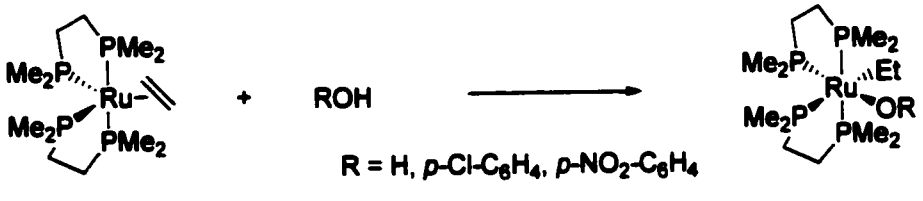
The metathesis of late transition metal amido derivatives with water, alcohols or phenols to give the corresponding hydroxo, alkoxo and phenoxo complexes has also been reported.[62, 63]

### *1.2.2 Oxidative addition of water, alcohols, phenols and esters.*

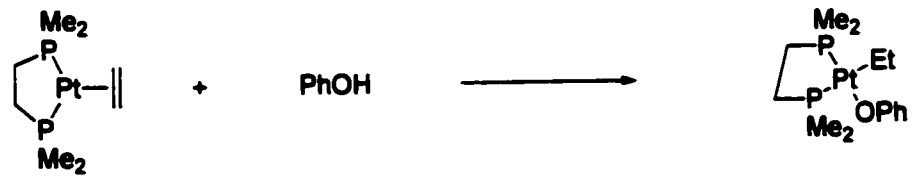
Phosphine complexes of Pt(0), Pd(0), Ru(0) and Ir(I) can oxidatively add water, methanol and phenols (for example, eq. 1.6) to give the corresponding hydroxo, methoxo and aryloxo hydrides of Pt(II),[64] Pd(II),[65] Ru(II)[66, 67] and Ir(III).[68, 69]

(1.6)

$L_nM(C_2H_4)$ complexes of late transition metals often serve as convenient precursors for coordinatively unsaturated species, formed upon the loss of ethylene, however, in reactions with water or alcohols, the coordinated $C_2H_4$ may be involved in the oxidation process. Thus, treating Ru(0) and Pt(0) ethylene complexes with phenols or water affords ethyl aryloxo and ethyl hydroxo complexes of Ru(II)[67] and Pt(II)[64] (eqs 1.7, 1.8).



(1.7)



(1.8)

The reaction of esters with some late transition metal hydrides can also lead to the formation of phenoxo or alkoxo carbonyl complexes. Thus iridium (I) and rhodium (I) alkoxo hydrides were prepared by the treatment of $H_5Ir(PiPr_3)_3$ with $CF_3CO_2CH_2$ (eq 1.13)[70] and $HRh(PPh_3)_4$ with $RCO_2Ar$ (R = Me, Et; Ar = Ph, *p*-$MeOC_6H_4$) (eq 1.14)[71] respectively.

$$H_5Ir(P^iPr_3)_3 + CF_3CO_2CH_2CF_3 \longrightarrow H_2IrOCH_2CF_3 + HOCH_2CF_3 \qquad (1.9)$$

$$HRh(PPh_3)_4 + RCO_2Ar \xrightarrow[-2PPh_3,\ -RH]{} \begin{matrix} PPh_3 \\ | \\ OC\text{-}Rh\text{-}OAr \\ | \\ PPh_3 \end{matrix} \qquad (1.10)$$

The proposed mechanism of the latter transformation involves the oxidative addition of the ester to the Rh(I) center, followed by decarbonylation of the coordinated acyl group and reductive elimination of the alkane (Scheme 1.5).

**Scheme 1.5**

$$[M]\text{-}H \xrightarrow{RCO_2Ar} \begin{matrix} O \\ \| \\ R\text{-}C\text{-}[M]\text{-}H \\ | \\ OAr \end{matrix} \longrightarrow \begin{matrix} OAr \\ | \\ OC\text{-}[M]\text{-}H \\ | \\ R \end{matrix} \xrightarrow[-RH]{} OC\text{-}[M]\text{-}OAr$$

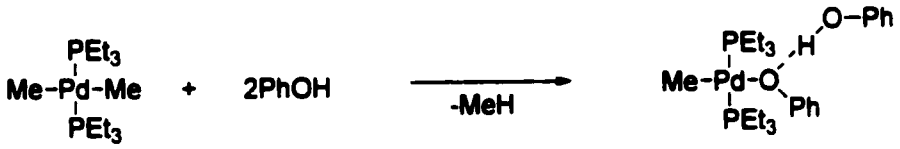
*1.2.3 M-C and M-H bond cleavage by Water, Alcohols and Phenols.*

The reaction of late transition metal hydrides, methyl and σ-phenyl derivatives with water, alcohols or phenols serves as a convenient method for synthesis of the corresponding hydroxo, alkoxo or aryloxo complexes (eq 1.11)

$$L_nMR + HOR' \longrightarrow L_nMOR' + HR \qquad (1.11)$$

R, R' = H, alkyl, aryl

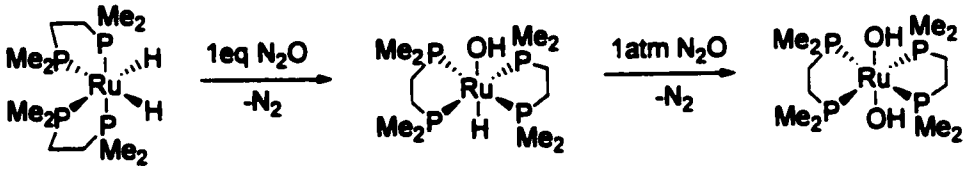
Various rhodium,[72-74] iridium,[72] ruthenium,[66, 75, 76] palladium,[77-82] platinum,[82-84] gold,[85] cobalt[86] and nickel[78-80] HO-, RO- and ArO derivatives were prepared by this method. The alkoxides and aryloxides are often obtained as hydrogen bonded adducts with the corresponding alcohols or phenols (for example, eq1.12).[80] In some cases only the alkoxo and aryloxo complexes coordinated with their respective phenols or alcohols via hydrogen bonding can be isolated and the reaction only goes to completion when the additional amount of phenol or alcohol required for the formation of these adducts is used.[87, 88]



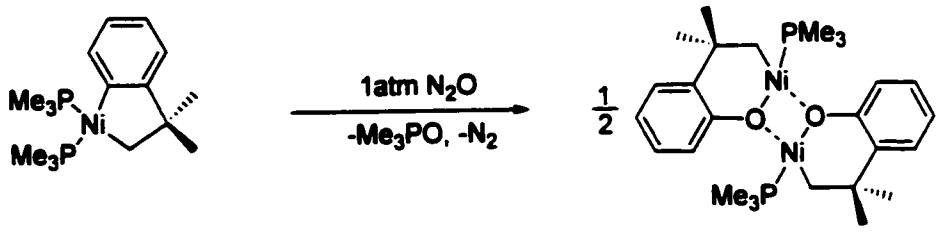

(1.12)

*1.2.4 Direct Oxidation of Hydrido and σ-Aryl Transition Metal Complexes.*

There are only a few examples of these reactions reported in the literature. Thus reaction of $[IrH(NO)(PPh_3)_3]^+$ with $O_2$ affords $[Ir(OH)(NO)(PPh_3)_2]^+$.[89] The ruthenium hydroxo complexes, were prepared by treating $Ru(H)_2(dmpe)_2$ with nitrous oxide (eq 1.13)[90] and oxidation of nickel σ-alkyl-σ-aryl chelate with $N_2O$ led to selective insertion of oxygen into the metal-aryl bond (eq1.14).[91]




(1.13)

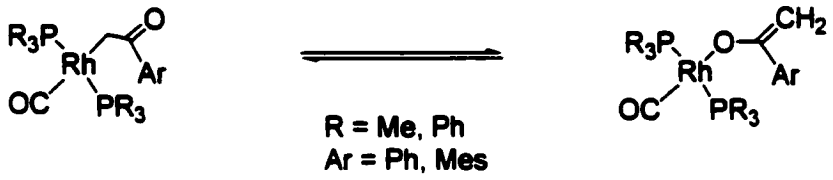



(1.14)

### *1.3 Reactivity and Structure of Hydroxo Alkoxo and Aryloxo Complexes.*

#### *1.3.1 The nature of Late Transition Metal Oxygen Bond.*

The chemistry of late transition metal hydroxo, alkoxo and aryloxo complexes was initially hampered by the early belief that a "soft" metal center has low affinity for "hard" oxygen donors[92] and the intrinsic reactivity of these compounds was explained by the presence of weak M-O bonds. In the past two decades however a number of HO-, OR- and OAr complexes have been prepared for a variety of transition metals, suggesting a sufficient strength of the metal-oxygen bond in these compounds. An NMR investigation of square planar rhodium enolates showed that in solution these species exist in a dynamic equilibrium containing both the oxygen-bound and carbon-bound forms (eq 1.15),[93] and therefore M-O and M-C bonds possess comparable thermodynamic stability.




(1.15)

The relative affinity of the Rh(I) centers towards oxygen and carbon was found to be sensitive to the nature of the phosphine ligands and to the electronic properties of the Ar substituents. Thus the bis-trimethylphosphine complex (R = Me, Ar = Ph) did not show fluxional behavior and existed in solution as the O-bound tautomer, whereas the analogous mesityl substituted enolate (R = Me, Ar = Mes) and bis-triphenylphosphine-σ-phenyl complex (R = Ph, Ar = Ph) both gave equilibrium mixtures of O- and C-bound forms. Mononuclear phosphine hydroxo palladium complexes, reported by Grushin and Alper,[94] exist in solution as equilibrium mixtures with free phosphine and dimeric OH-bridged Pd

species (eq 1.16). These findings suggest that the affinity of OH ligands towards Pd(II) centers in this system is similar to the affinity of phosphines. The relative stability of Pd-O and Pd-P bonds can be adjusted by the appropriate choice of phosphine and σ-C ligands. Thus in contrast to the Ph substituted analogue, the mononuclear $[(Ph_3P)_2Pd(C_6F_5)(OH)]$, reported by Yoshida et al,[31] does not show any tendency to lose $PPh_3$ with concomitant dimerization, and $[(Ph_3P)_2Pd_2(Ph)(\mu\text{-}OH)_2]$ is significantly more stable than the analogous $PCy_3$ and $P^iPr_3$ complexes as indicated by the values of equilibrium constants found for the reaction (1.16).[94]

$$2\,\mathrm{R{-}Pd{-}L{-}OH} \rightleftharpoons \mathrm{R{-}Pd(\mu\text{-}OH)_2{-}Pd{-}R} + 2\,L \qquad (1.16)$$

L = $PPh_3$, $PCy_3$, $P^iPr_3$; R = Ph, Me

An NMR study of MePt(*P,P*)X complexes led to the establishment of a *trans* influence series for a number of X, including OH and OR groups, by measuring $J_{Pt\text{-}P}$ coupling constants. The values found for hydroxo and alkoxo ligands suggested a moderate to weak *trans* influence of these groups as compared with alkyl or aryl substituents, and the M-O bond in alkoxo and hydroxo complexes of Pt(II) is best described as covalent in nature. A relative order of M-X bond energies has been obtained by investigation of the equilibrium between weak organic acids and alkoxo or hydroxo complexes of the type, Pt(Me)(dppe)X and $Ru(X)Cp^*(PMe_3)_2$ (eq 1.17).[47, 95]

$$L_nM\text{-}X + H\text{-}Y \rightleftharpoons L_nM\text{-}Y + H\text{-}X \qquad (1.17)$$

X, Y = H, $CR_3$, $NR_2$, OR, OH

The found order is $L_nM$-(sp)C > $L_nM$-OH > $L_nM$-H > $L_nM$-OR ≈ $L_nM$-($sp^3$)C > $L_nM$-N, and the $L_nM$-X bond strength correlate with H-X bond strength. This suggests that π-interactions (i.e. the repulsion of unshared electron pairs of oxygen and filled d-orbitals of the metal or donation of electron density from oxygen to vacant d-orbitals of the metal) are not significant in the M-O bonds of late transition metal alkoxo or hydroxo complexes. Such interactions however could become important in transition states or intermediates.

### *1.3.2 Structural Features of Pd Hydroxo and Rh Aryloxo Complexes.*

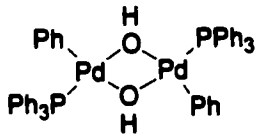
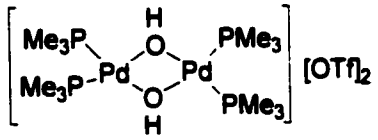
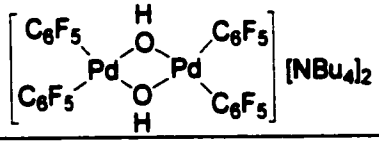
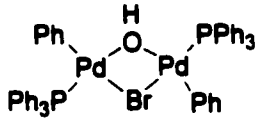
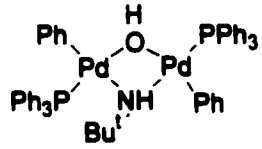
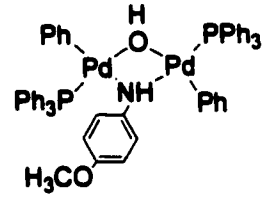
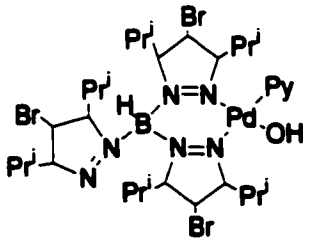
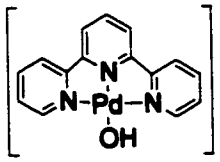
In the last two decades a significant number of late transition metal hydroxo, alkoxo and aryloxo complexes have been characterized by X-ray analysis. Selected structural details for Pd(II) hydroxo and Rh(I) aryloxo species most relevant for the present thesis are compiled in Tables 1.1 and 1.2 respectively.

The metal - oxygen bond distances in Pd hydroxides range from 1.966 Å to 2.140 Å and can be compared with those in Pd carboxylates (1.998 – 2.155 Å) and in aqua complexes (2.106 - 2.301 Å). For the most cases Pd-O distances can be arranged in the following order: Pd-OH (term.) ≈ Pd-OAc (term.) < Pd-OH (bridg.) ≈ Pd-OAc (bridg.) < Pd-$OH_2$. It should be noted, however, that this trend is not always true, as the metal – oxygen bonds in hydroxo-, acetato- and aqua complexes vary significantly in length. Thus Pd-O bonds in some hydroxides are longer than those in some Pd aqua complexes (Table 1.1, *cf.* for example entries 5 and 16). Apparently the metal – oxygen bond length is more sensitive to the nature of the ligands coordinated to the metal than to the nature of substituents attached to the oxygen atom.

In contrast to Pd hydroxides, Rh aryloxides show no tendency to form longer metal – oxygen bonds in bridging species as compared to these in terminal aryloxo complexes. The Rh-O bond distances in structurally characterized Rh(I) aryloxides, hydroxides, alkoxides and carboxylates are all found within the relatively narrow range of 2.044 – 2.124 Å (Table 1.2).

The carbon – oxygen bond in late transition metal alkoxo complexes is often shorter than this type of bond in the corresponding alcohols and esters.[1,2] Interestingly, C-O bonds in bridging Rh aryloxides, although noticeably shorter than these in aryl esters, are comparable in length with C-O bonds in the corresponding phenols. In contrast, the carbon – oxygen bond distances in terminal OAr rhodium complexes are significantly shorter than C-O distances in phenols, but are longer than that found for NaOPh (Table 1.2). The C-O bond lengths in these compounds can therefore be arranged in the following order: NaOAr < RhOAr (term.) < HOAr ≈ RhOAr (bridg.) < ArOAr.

**Table 1.1** Selected Structural Details of Pd(II) Hydroxo Complexes and Related Species

| Entry | Complex | Pd-O (Å) | Pd-O-Pd (deg) | Reference |
|---|---|---|---|---|
| 1 |  | 2.093 | 87.69 | 40 |
| 2 |  | 2.079 | 99.81 | 96 |
| 3 |  | 2.073 | 98.80 | 97 |
| 4 |  | 2.031 | 106.77 | 98 |
| 5 |  | 2.140 | 85.41 | 99 |
| 6 |  | 2.126 | 95.73 | 100 |
| 7 |  | 2.022 | N/A | 101 |
| 8 |  | 1.966 | N/A | 102 |

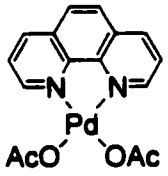
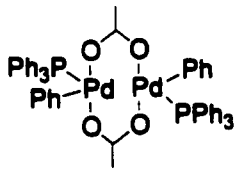
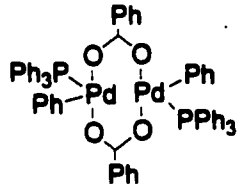
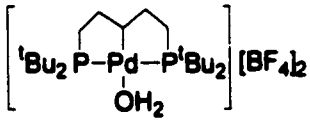
| Table 1.1 Continued | | | | |
|---|---|---|---|---|
| Entry | Complex | Pd-O (Å) | Pd-O-Pd (deg) | Reference |
| 9 |  | 2.008 | N/A | 103 |
| 10 |  | 2.114 | N/A | 104 |
| 11 |  | 2.155 | N/A | 105 |
| 12 | *cis*-$Pd(PPh_3)_2(C(O)OMe)(OAc)$ | 2.071 | N/A | 106 |
| 13 | *trans*-$Pd(OAc)_2Py_2$ | 2.009 | N/A | 107 |
| 14 |  | 2.301 | N/A | 108 |
| 15 | $[(BINAP)Pd(H_2O)_2][BF_4]$ | 2.210 | N/A | 109 |
| 16 | [(dpp)Pd($H_2O$)(OTf)][OTf] | 2.106 | N/A | 110 |

**Table 1.2** Selected Structural Details of Rh(I) Aryloxo Complexes and Related Species

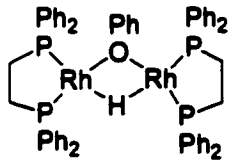
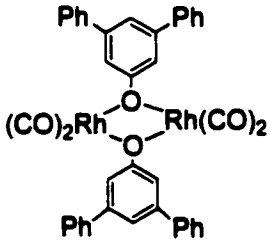
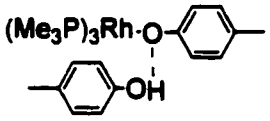
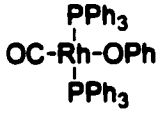
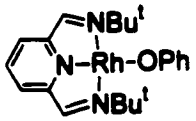
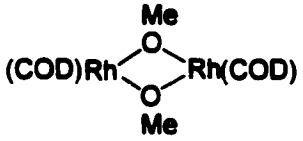
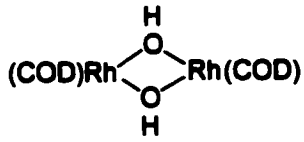
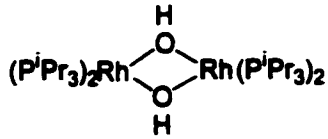
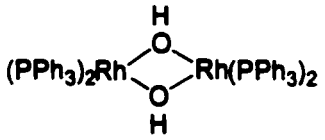
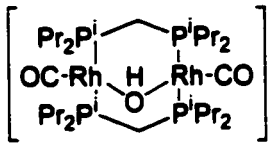
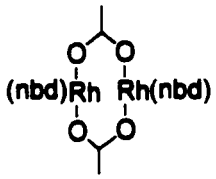
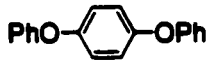
| Entry | Complex | Rh-O (Å) | O-$C_{Ar}$ (Å) | Reference |
|---|---|---|---|---|
| 1 |  | 2.058 | 1.362 | 111 |
| 2 |  | 2.083 | 1.368 | 112 |
| 3 |  | 2.124 | 1.329 (OAr)<br>1.361 (ArOH) | 113 |
| 4 |  | 2.044 | 1.327 | 114 |
| 5 |  | 2.051 | 1.325 | 115 |
| 6 |  | 2.051 | 1.395 | 116 |
| 7 | $(Me_3P)_3RhOCH_2CF_3$ | 2.101 | 1.356 | 113 |
| 8 |  | 2.075 | N/A | 117 |
| 9 |  | 2.117 | N/A | 118 |

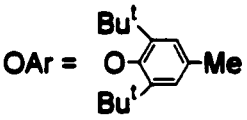
**Table 1.2** Continued

| Entry | Compound | Rh-O (Å) | O-$C_{Ar}$ (Å) | Reference |
|---|---|---|---|---|
| 10 |  | 2.065 | N/A | 119 |
| 11 |  | 2.072 | N/A | 120 |
| 12 |  | 2.107 | N/A | 121 |
| 13 | *cis*-$[Rh(CO)_2(OAc)_2][NBu_4]$ | 2.063 | N/A | 122 |
| 14 | $Rh(PPh_3)_3OOCPh$ | 2.105 | N/A | 123 |
| 15 | *trans*-$Rh(CO)(PPh_3)_2OOCCF_3$ | 2.070 | N/A | 124 |
| 16 | NaOPh·THF | N/A | 1.314 | 125 |
| 17 | HOPh | N/A | 1.369 | 126 |
| 18 |  | N/A | 1.379<br>1.388 | 127 |

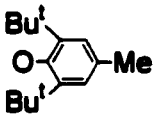
### *1.3.3 Complexes with π-Coordinated Aryloxo Ligands.*

Aryloxo anions are bifunctional ligands and can coordinate a metal either by the phenolic oxygen or by the aromatic system. Complexes with π-coordinated OAr groups are usually prepared by treating the appropriate $L_nMX$ species with phenols or their lithium salts (*e.g.* eqs 1.18, 1.19)[128-132]

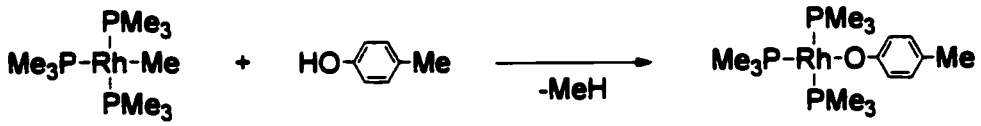
$$Rh\{N(SiMe_3)_2\}(PPh_3)_3 + HOAr \xrightarrow[-LiN(SiMe_3)_2,\ -PPh_3]{} Rh(PPh_3)_2(\pi\text{-}OAr) \qquad (1.18)^{128}$$

OAr = 

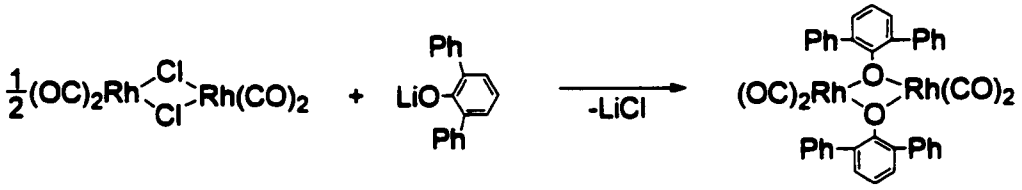
$$\frac{1}{2}L_2Rh(\mu\text{-}Cl)_2RhL_2 + LiOAr \xrightarrow[-LiCl]{} RhL_2(\pi\text{-}OAr) \qquad (1.19)^{129}$$

L = $C_2H_4$, COD; OAr = 

Among the late transition metals, Pd and Pt form only oxygen bound aryloxides, whereas both types of OAr coordination are known for Ru, Os, Rh and Ir. The preferential coordination mode of the OAr group depends on the nature of ligands attached to the metal. Thus $PPh_3$-, COD-, $C_2H_4$- and Cp* containing precursors usually give complexes with π-coordinated OAr anions whereas CO and $PMe_3$ ligands tend to stabilize oxygen bound aryloxides (*cf.* for example eqs 1.20 and 1.21 *vs.* eqs 1.18 and 1.19).

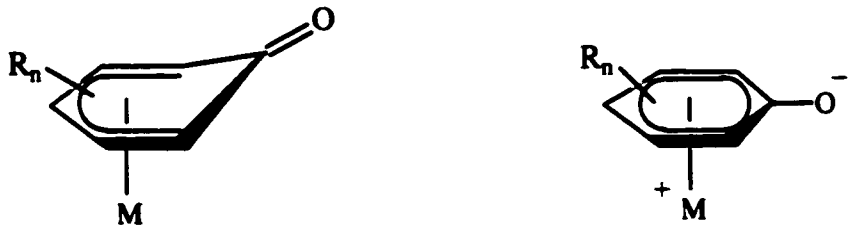


(1.20)[113]



(1.21)[112]

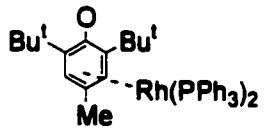
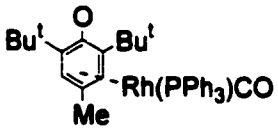
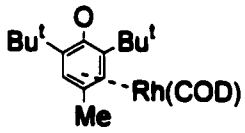
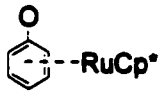
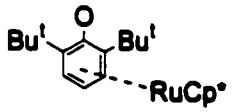
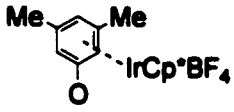
According to X-ray data analysis, available for a number of late transition metal π-aryloxo complexes (Table 1.3), OAr anions usually bind the metal in $\eta^5$-fashion rather than in $\eta^6$-mode commonly observed for π-arene metallocomplexes[133] (Figure 1.1, Structures A and B respectively). The $\eta^5$- hapticity is manifested in substantial elongation of the M-C(*O*) distance (as compared with the distances to the other carbons of the OAr ligand), loss of planarity of the ring and shortening of the C-O bond (as compared with C-O bond in phenols). The OAr anion in π-aryloxides therefore is commonly referred to as $\eta^5$-cyclohexadienonyl ligand.



**(A)** **(B)**

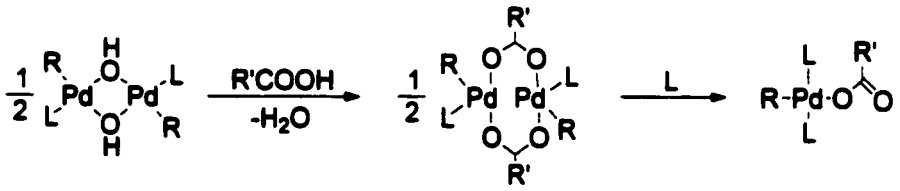
**Figure 1.1** Coordination modes of π-OAr ligand: (A) as $\eta^5$-cyclooctadienonyl, (B) as $\eta^6$-aryloxo anion.

**Table** 1.3 Selected Structural Details of M(π-OAr) Complexes.

| Entry (Ref.) | Complex | Distances, Å | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | C1-O | C1-M | C2-M | C3-M | C4-M | C5-M | C6-M |
| 1 (128) |  | 1.28 | Not reported | 2.65 | 2.43 | 2.19 | 2.26 | 2.46 |
| 2 (129) |  | 1.239 | 2.666 | 2.478 | 2.310 | 2.304 | 2.268 | 2.282 |
| 3 (129) |  | 1.258 | 2.587 | 2.405 | 2.279 | 2.258 | 2.274 | 2.346 |
| 4 (130) |  | 1.236 | 2.483 | 2.244 | 2.236 | 2.229 | 2.219 | 2.246 |
| 5 (134) |  | 1.285 | 2.337 | 2.211 | 2.186 | 2.206 | 2.191 | 2.202 |
| 6 (135) |  | 1.285 | 2.555 | 2.295 | 2.192 | 2.184 | 2.196 | 2.301 |
| 7 (136) |  | 1.230 | 2.511 | 2.244 | 2.210 | 2.216 | 2.204 | 2.214 |
| 8 (137) |  | 1.230 | 2.520 | 2.242 | 2.210 | 2.169 | 2.200 | 2.221 |

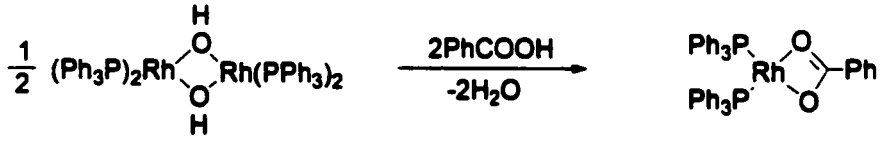
*1.3.4 Reactions of Hydroxo, Alkoxo and Aryloxo Complexes with Strong Protic Acids.*

Strong acids, such as HCl, have been shown to remove the hydroxo and alkoxo groups of many late transition metal hydroxides and alkoxides to give, for example, the corresponding chloro complexes.[138-142] Palladium (II) and rhodium (I) carboxylates were prepared by treating the corresponding dinuclear hydroxides with carboxylic acids (eqs 1.22, 1.23).



L = $PPh_3$; R = Ph, Me; R' = H, Ph

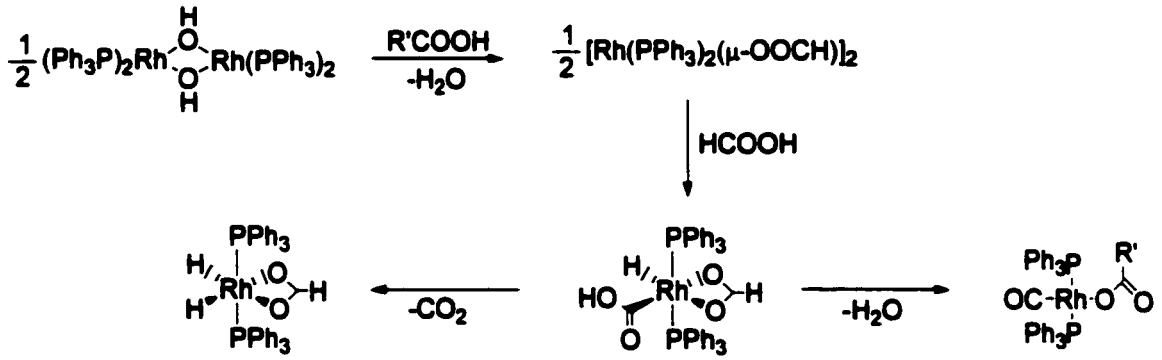
**(1.22)**[105]



**(1.23)**[43]

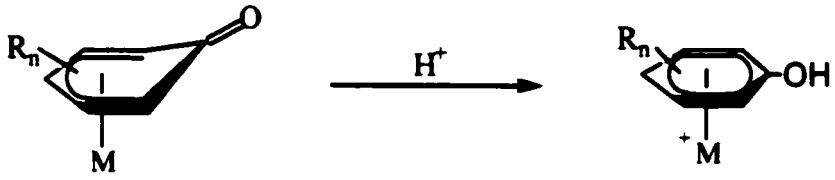
Reaction of $[Rh(PPh_3)_2(\mu\text{-}OH)]_2$ with formic acid affords Rh(I) carbonyl formate and Rh(III) dihydride formate presumably due to facile decarboxylation and dehydration of the intermediate formylformato Rh(III) hydride (Scheme 1.5).[43]

**Scheme 1.6**



Reactions of π-aryloxo complexes of Rh(III),[131] Ru(II)[130] and Ir(III)[132] with strong protic acids lead to the protonation of the OAr ligand and formation of the corresponding complexes with $\eta^6$-coordinated phenols (Scheme 1.7).

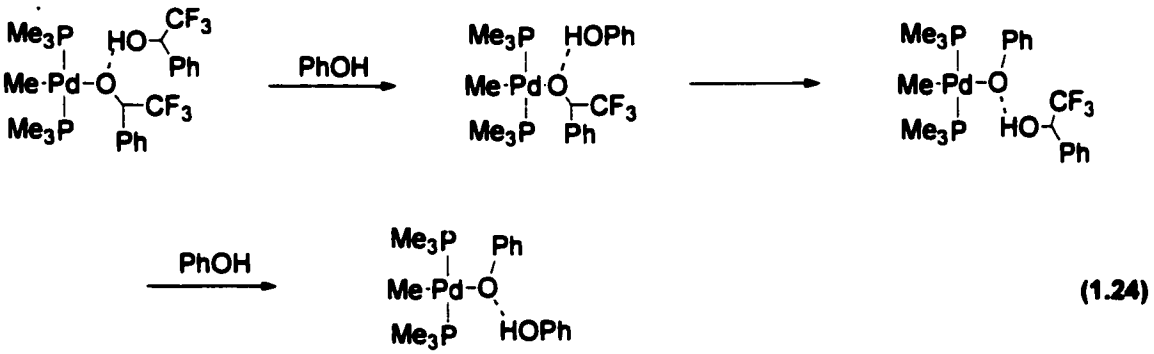
**Scheme 1.7**




*1.3.5 Reactions with Weak Protic Electrophiles.*

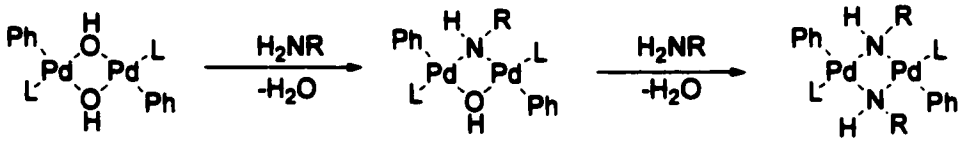
There are many examples of this type of reaction, especially for the interconversion of hydroxides/alkoxides/aryloxides by the addition of an excess of the appropriate alcohol, phenol or water.[1] The equilibrium constants of these reactions are usually close to unity,[47, 143] but as has been found for many syntheses, addition of a large excess of the appropriate reagent can force the equilibrium to one side and allow isolation of the desired product. The reactions of the hydroxo complex, [IrPh(OH)Cp*($PMe_3$)] with *p*-toluidine, phenol, alcohols and silica were driven to completion by the azeotropic removal of water with benzene to afford the corresponding amido, phenoxo, alkoxo and silica-bound complexes respectively.[144-147]

The formation of strong hydrogen bonds between coordinated OH, OR or OAr groups and alcohols or phenols is a well known feature of late transition metal hydroxo, alkoxo and aryloxo complexes.[2] It has been shown that OR/OAr exchange between palladium alkoxides and phenol involves formation of hydrogen bonded [M-OR][HOAr] adducts as the first step and subsequent proton transfer from hydrogen bonded phenol to the alkoxo group of the complex (eq 1.24).[77, 80, 81]



(1.24)

Treating $[PdPh(\mu\text{-}OH)(PPh_3)]_2$ with alkyl and aryl amines affords the corresponding μ-amido bridged Pd(II) species (eq 1.25).[99]

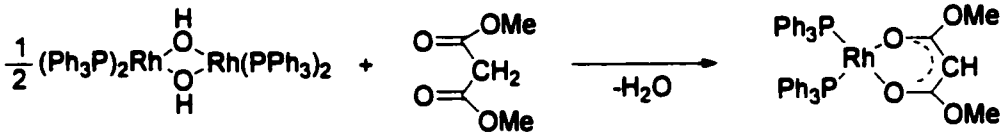


(1.25)

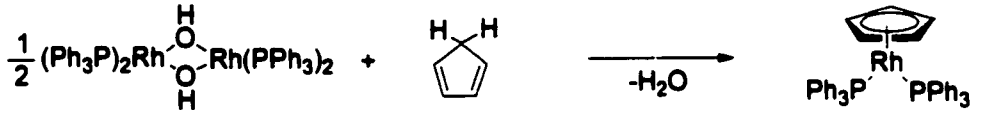
L = $PPh_3$; R = Ph, 2,6-$Me_2C_6H_3$, *t*-Bu, *sec*-Bu

Mechanistic studies of the reaction (1.25) indicated that it proceeds by cleavage of the hydroxo bridges and subsequent coordination of the amine, followed by reversible proton transfer with concomitant formation of the amido ligand and release of water. Similar reactions of $[M(C_6F_5)_2(\mu\text{-}OH)]_2[NBu_4]_2$ (M = Ni, Pd, Pt), with a wide range of primary aromatic amines to give the corresponding binuclear μ-hydroxo-μ-arylamido or di-μ-arylamido complexes have also been reported.[147, 148] $[Pd(C_6F_5)(\mu\text{-}OH)]_2[NBu_4]_2$ also reacts with nitriles such as malonitrile and methyl cyanoacetate, to give the binuclear complexes, $[Pd(C_6F_5)_2\{\mu\text{-}CH(CN)CN\}]_2$ $[NBu_4]_2$ and $[Pd(C_6F_5)_2\{\mu\text{-}CH(CO_2Me)CN\}]_2[NBu_4]_2$ with the concomitant release of water.[148]

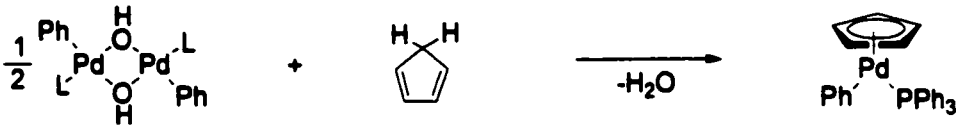
Rhodium and palladium binuclear hydroxo bridged species react with weak C-H acids such as dimethylmalonate and cyclopentadiene affording the corresponding mononuclear cyclopentadienyl and dimethylmalonato complexes (eqs 1.26 – 1.28).



(1.26)[43]

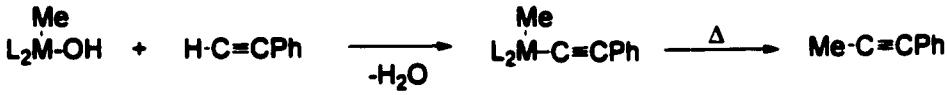


(1.27)[43]



(1.28)[149]

Treatment of methyl-palladium (II) and –platinum (II) hydroxo complexes with phenylacetylene leads to the formation of the corresponding phenylacetylide species, which upon thermolysis liberate MeC≡CPh in quantitative yield (eq1.29).[150]



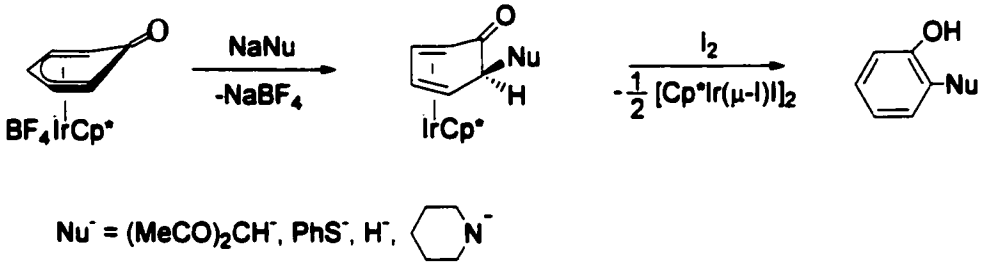
(1.29)

M = Pd, Pt; $L_2$ = dppe, $2PMe_3$; R = $CH(CF_3)_2$, $CH(CF_3)Ph$

### *1.3.6 Reactions with Strong Nucleophiles.*

Iridium (III) π-aryloxides smoothly react with various nucleophiles to give Ir (I) complexes with $\eta^4$-coordinated *ortho*-substituted cyclohexadienones (eq 1.30).[136] Oxidative decomplexation by treatment with $I_2$ leads to tautomerization of the ligand and formation of the corresponding *ortho*-substituted phenols in good yields. Thus, using this methodology, 2-methoxyestradiol was prepared from β-estradiol in three steps with an overall yield of

60%,[132] whereas the conventional organic procedure affords this steroid in 5% yield after five steps.[151]




(1.30)

$Nu^- = (MeCO)_2CH^-, PhS^-, H^-,$ 

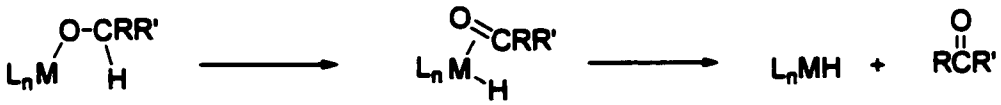
Late transition metal hydroxo and alkoxo complexes react with strong nucleophiles, such as MeLi and MeMgBr to give the corresponding σ-methyl derivatives (eqs 1.31, 1.32).[144, 74]

$IrCp(PMe_3)(Ph)OH \xrightarrow{MeLi} IrCp(PMe_3)(Ph)Me$ (1.31)

$PtMe(OMe)(dppe) \xrightarrow{MeMgBr} PtMe_2(dppe)$ (1.32)

### *1.3.7 β-Hydride Elimination from Metal Alkoxides.*

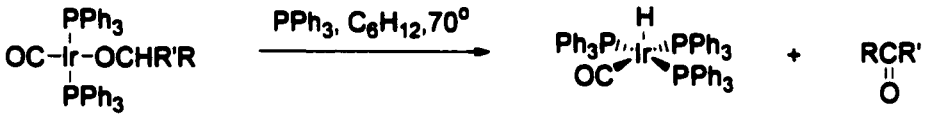
In general alkoxo derivatives of late transition metals are less stable than their hydroxo or aryloxo analogs. This is usually explained by the tendency of $L_nM$-OR (R = alkyl) complexes to decompose *via* β-H elimination to give the corresponding metallohydrides and the appropriate aldehyde or ketone (eq 1.33).[1]




(1.33)

In fact many late transition metal hydrides were prepared by the reactions that may involve initial formation of alkoxo complexes, and in some cases these intermediates were identified.[1]

Iridium alkoxides, *trans*-$Ir(CO)(PPh_3)_2OR$ (R = Me, $^i$Pr, Pr) which contain β-hydrogens smoothly decompose at 70°C (eq 1.34) whereas their analogs possessing no β-H (R = H, $^t$Bu, Ph) are stable under the same conditions.[152]




(1.34)

R = R' = H; R = H, R = Et; R = R' = Me

Studies on the thermolysis reactions of [PtMe(OMe)dppe], [PtEt(OMe)dppe], [$Pt(OCH_2CH_2O)$dppe]and [Pt $(OMe)_2$dppe][34] show that the rate of β-H elimination is much slower in THF than in $CH_2Cl_2$, toluene or α,α′-dimethyltetrahydrofuran. This indicates that a free coordination site is required for β-H elimination in these complexes. X-ray structural analysis of the closely related palladium alkoxide, [$PdMe(OCH(CF_3)_2)$(tmeda)] shows that the proton of the $OCH(CF_3)_2$ unit is oriented towards the palladium atom (Pd....H = 2.89 Å), in a geometry that could be regarded as the incipient stage for β-H elimination.[81] Coordination of a polar solvent may remove this interaction.

The alkoxo complexes, *mer-cis*-[$IrH(OR)Cl(PR'_3)_3$] (R = Me, Et, iPr; R′ = Me, Et) decompose in alcohol/benzene solution to give *mer-cis*-[$Ir(H)_2Cl(PR'_3)_3$] and the appropriate ketone or aldehyde.[153] For these complexes added alcohol acts as a catalyst for the β-H elimination process, presumably by facilitating chloride dissociation by means of H-bonding. Phosphine dissociation was ruled out, as added phosphine did not affect the reaction rate. The

reaction has been shown to proceed *via* chloride dissociation followed by an irreversible rate determining β-C-H cleavage, dissociation of the coordinated aldehyde or ketone and reassociation of the chloro anion.

Attempts to prepare [Ir(Ph)(OR)Cp*($PMe_3$)] (R = Me, $CH_2CMe_3$) by the addition of NaOR to [Ir(Ph)(OTf)Cp*($PMe_3$)] always led to the formation of the corresponding hydride, whereas the reactions of [Ir(Ph)(OH)Cp*($PMe_3$)] with alcohols cleanly afford the corresponding alkoxides, which decompose only slowly by β-H elimination above 60°C.[146] It has been shown that the cationic iridium complex [Ir(Ph)Cp*($PMe_3$)][OTf] catalyses the decomposition of the coordinatively saturated alkoxides to the iridium hydride and appropriate aldehydes, by providing the free coordination site necessary for β-H elimination.

### *1.3.8 Insertion Reactions into Late Transition Metal-Oxygen Bonds.*

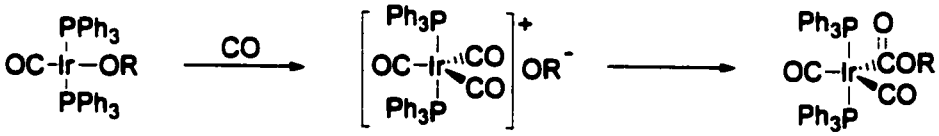
Many late transition metal hydroxides, alkoxides and aryloxides react with carbon monoxide at room temperature and normal pressure to give the corresponding hydroxy-alkoxy- or aryloxycarbonyl complexes (eq 1.35).[1]

$$L_nM\text{-}OR + CO \longrightarrow L_nM\text{-}C(=O)OR \qquad (1.35)$$

In investigation of the elementary steps which comprise the catalytic cycle of the Rh(I) catalysed water gas shift reaction, it was noticed that *trans*-[Rh(OH)(CO)($P^iPr_3$)$_2$] gives [RhH(CO)($P^iPr_3$)$_2$] upon reaction with CO. It was proposed that the reaction proceeds via intermediate formation of [Rh($CO_2H$)CO($P^iPr_3$)$_2$] which than undergoes decarboxylation to afford the hydrido complex. In order to prove this mechanism the reaction of the analogous

methoxo derivarive, $[Rh(OMe)CO(P^iPr_3)_2]$ was studied and found to give the stable methoxycarbonyl complex, $[Rh(CO_2Me)CO(P^iPr_3)_2]$.[12]

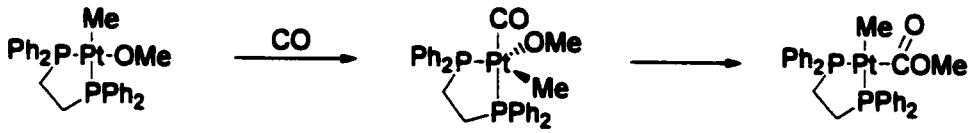
Monitoring the carbonylation of $[Ir(OR)CO(PPh_3)_2]$ (R = Me, Pr, $^t$Bu, Ph) by IR spectroscopy and conductivity measurements indicate that the reaction occurs via alkoxide displacement by CO and subsequent nucleophilic attack of alkoxide anion on a carbonyl ligand of the cation (eq 1.36).[154]




(1.36)

R = Me, Pr, $^t$Bu, Ph

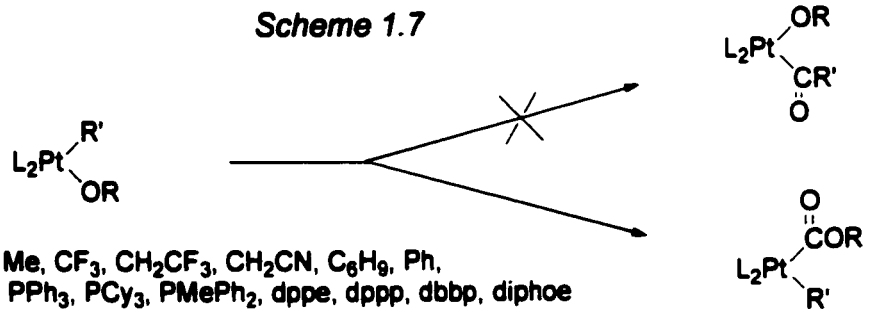
In contrast to the case for iridium (I) complexes, carbonylation of platinum (II) alkoxides has been shown to occur completely by an inner-sphere mechanism. Kinetic measurements for the reaction of [PtMe(OMe)(dppe)] with CO indicate that the overall rate of carbonylation was at least 1000 times faster than that of methoxide dissociation. Low temperature NMR spectroscopic studies showed a rapid interaction of CO with the platinum methoxo complex at –80 to –25°C to give a five-coordinate adduct. The carbonylation carried out in the presence of a ten-fold excess of $CD_3OD$ did not give any incorporation of deuterium into the resulting methoxycarbonyl complex within the limits of detectability. These results are consistent with initial coordination of CO to the metal followed by the migration of an alkoxo ligand onto the coordinated carbonyl (eq 1.37).[33]




(1.37)

Interestingly carbonylation of various platinum (II) species possessing alkoxo or hydroxo and alkyl or aryl ligands in the same coordination sphere always affords alkoxy- or hydroxycarbonyl complexes selectively with no evidence of CO insertion into the M-C bond (Scheme 1.7).[33, 54, 56, 155-162]

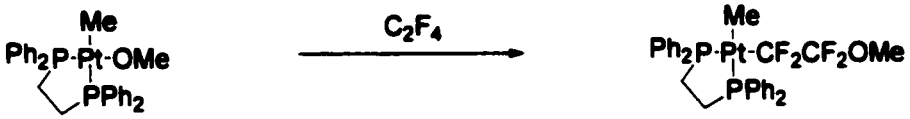
*Scheme 1.7*



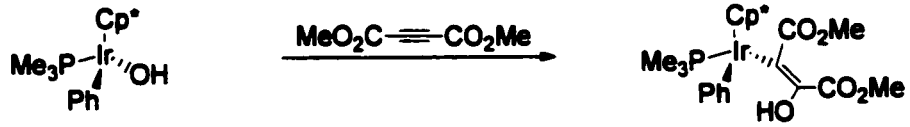

R = H, Me; R' = Me, $CF_3$, $CH_2CF_3$, $CH_2CN$, $C_6H_9$, Ph,
L = $PMe_3$, $PEt_3$, $PPh_3$, $PCy_3$, $PMePh_2$, dppe, dppp, dbbp, diphoe

Bryndza and Tam[1] commented that the higher reactivity of M-OH and M-OR bonds, compared with the metal alkyl or aryl bonds, may be due to an interaction of the lone pairs of oxygen with the $\pi^*$ orbitals of the CO ligand. Thus, substantial O-C bond formation precedes complete M-O bond cleavage, and this can be thought of as an inner-sphere nucleophilic attack of OH or OR ligands on the coordinated carbonyl.

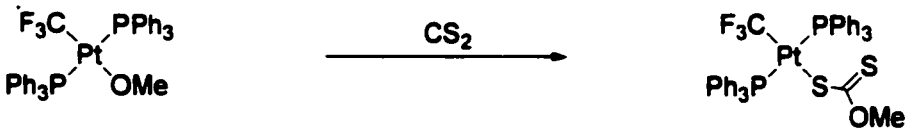
Hydroxo and alkoxo complexes of late transition metals also react with olefins, acetylenes, $CS_2$ and $CO_2$ to give the corresponding products of insertion into the metal oxygen bond (for example eqs 1.38 – 1.41).[163-166]



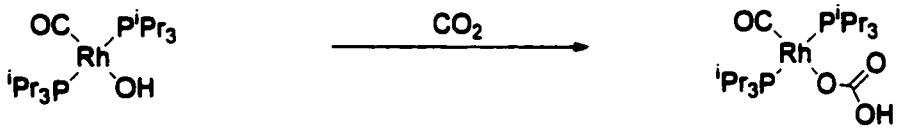

(1.38)




(1.39)




(1.40)




(1.41)

In conclusion, hydroxo, alkoxo and aryloxo complexes of late transition metals possess unique reactivity and interesting structural properties. Investigations in this field have become important, resulting in the rapid development of new chemistry and catalysis.

We were interested in developing new synthetic methods for preparation of heteropolymetallic clusters (Chapter 2), phosphine – Rh complexes with chiral alkoxo ligands (Chapter 3) and phosphine - Rh complexes with π- and σ-coordinated aryloxo ligands (Chapter 4).

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# Chapter 2.

## *Reactions of Phosphine Hydroxo Complexes of Rhodium and Palladium with M-H Acids*

## 2.1 Introduction.

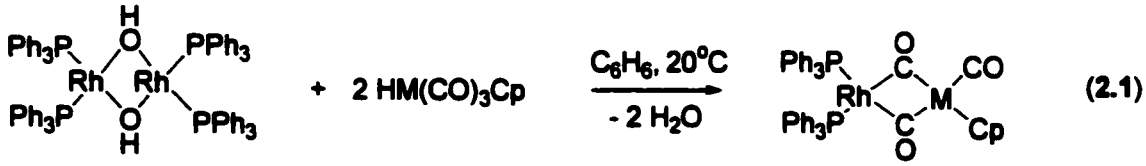
Recently it was shown that the dimeric hydroxo complexes, $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2]$ **(2.1)**[1] and $[Pd_2L_2Ph_2(\mu\text{-}OH)_2]$ (L = $PPh_3$, $PCy_3$) **(2.2)**,[2] react readily with various O-H and C-H acids. It was interesting to investigate the reactivity of these hydroxo complexes towards M-H acids. The Brönsted acidities of some transition metal hydrides are well known.[3] However, no reactions between hydrido and hydroxo complexes of transition metals have been reported in the literature.[4] Cyclopentadienyl tricarbonyl hydrides of chromium, molybdenum and tungsten were chosen as substrates as they are relatively strong M-H acids ($pK_a$ (MeCN, 25°C) = 13.3(1), 13.6(1) and 16.1(1), respectively)[5] and can be readily prepared from the corresponding $M(CO)_6$.[6]

## 2.2 Results and Discussion

### 2.2.1 Reaction of $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2]$ with $[HM(CO)_3Cp]$ (M = Cr, Mo, W).

### Preparation and Characterization of Rh-M Heterobimetallic Complexes 2.3a-c.

When a benzene solution of **2.1** is treated with 2 equiv. of $[HM(CO)_3Cp]$ (M = Cr, Mo, W) bridging carbonyl heterobimetallic complexes, **2.3a-c** are formed (eq. 2.1). According to $^{31}P$ NMR spectra, the reactions are complete within 20 min at room temperature giving **2.3a-c** as the sole metallorganic products even when less than 2 equiv. of the corresponding hydrides were used.




**2.1**

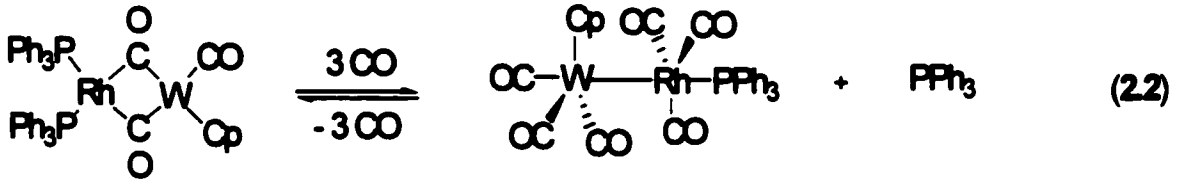
**2.3a**, M = Cr
**2.3b**, M = Mo
**2.3c**, M = W

(2.1)

The complexes **2.3a-c** were isolated in good to excellent yield and characterized by elemental analysis, NMR and IR spectroscopy. The dark red Cr-Rh complex **2.3a** is new, whereas the Mo and W analogs **2.3b,c** have been previously prepared and structurally characterized.[7,8] In terms of simplicity and efficiency the synthesis of **2.3b,c** from **2.1** and the corresponding $[HM(CO)_3Cp]$ is far superior to one of the literature methods[8] and certainly comparable with the other.[7] Moreover, workup of the reaction mixture is exceptionally simple affording analytically pure **2.3a-c** without recrystallization. Comparison of the IR and NMR spectra of **2.3a** with those reported for **2.3b,c**[7-9] indicates that all three complexes are structurally similar. Similarly to **2.3c**,[9] complexes **2.3a,b** display fluxional behavior in solution, associated with the exchange between two nonequivalent phosphines. The sharp doublet observed in the $^{31}P\{^1H\}$ NMR spectra of **2.3a,b** at 20°C transforms to a broad singlet at temperatures below -40°C. The signal did not split or collapse, as was observed for **2.3c**, upon further cooling to -110°C, indicating that the barrier to pseudorotation around the Rh-M bond is even lower than that calculated for **2.3c** ($\Delta G^{\ddagger} = 27.9 \pm 0.8$ kJ/mol at $-108 \pm 8$°C).[9]

Similarly to **2.3c**,[10] complexes **2.3a,b** reversibly react with CO. The reaction leads to fast and efficient exchange between carbon monoxide in the gas phase and all three carbonyl ligands of the heterobimetallic complexes. Stirring dark-brown **2.3c** in toluene under $^{13}CO$ atmosphere for several minutes, with subsequent passing of $N_2$ through the resulting orange solution, gave $[(Ph_3P)_2Rh(\mu\text{-}^{13}CO)_2W(^{13}CO)Cp]$ quantitatively. The IR spectrum of the isolated complex exhibits three carbonyl bands at 1826, 1726 and 1699 $cm^{-1}$ which are 41 – 43 $cm^{-1}$ lower than those in unlabelled **2.3c** (see experimental section). The $^{31}P\{^1H\}$ NMR spectrum of a $^{13}CO$ saturated solution of **2.3c** in toluene-$d_8$ recorded at 20°C shows one broad signal centered at 20 ppm. Upon cooling to -80°C the spectrum displayed a sharp singlet at -7

ppm, tentatively assigned to free $PPh_3$, and a slightly broadened doublet at 37 ppm ($J_{P\text{-}Rh}$ = 105 Hz, $\Delta_{1/2}$ = 35 Hz) in a 1 : 1 ratio. The $^{13}C\{^1H\}$ NMR spectrum of the same sample recorded at 20°C displayed a broad signal at 205.5 ppm. The signal split into three 1 : 2 : 3 resonances at 225.2 (s, $J_{C\text{-}W}$ = 153.5 Hz), 216.6 (s, $J_{C\text{-}W}$ = 165 Hz) and 192.4 ppm (d, $J_{C\text{-}Rh}$ = 70 Hz) when the sample was cooled to -80°C (see Fig 2.1). No tungsten satellites were observed for the upfield carbonyl signal, which appears in the spectrum as a slightly broadened doublet ($\Delta_{1/2}$ = 36 Hz). Taken together these data suggest that the reaction of **2.3c** with CO occurs in accordance with eq 2.2 and the product, complex **2.4c**, should be formulated not as $[Cp(CO)_3WRh(CO)(PPh_3)_2]$[10] but rather $[Cp(CO)_3WRh(CO)_3(PPh_3)]$, assuming that the rotation around W-Rh bond is unhindered.




**2.3c** **2.4c** (2.2)

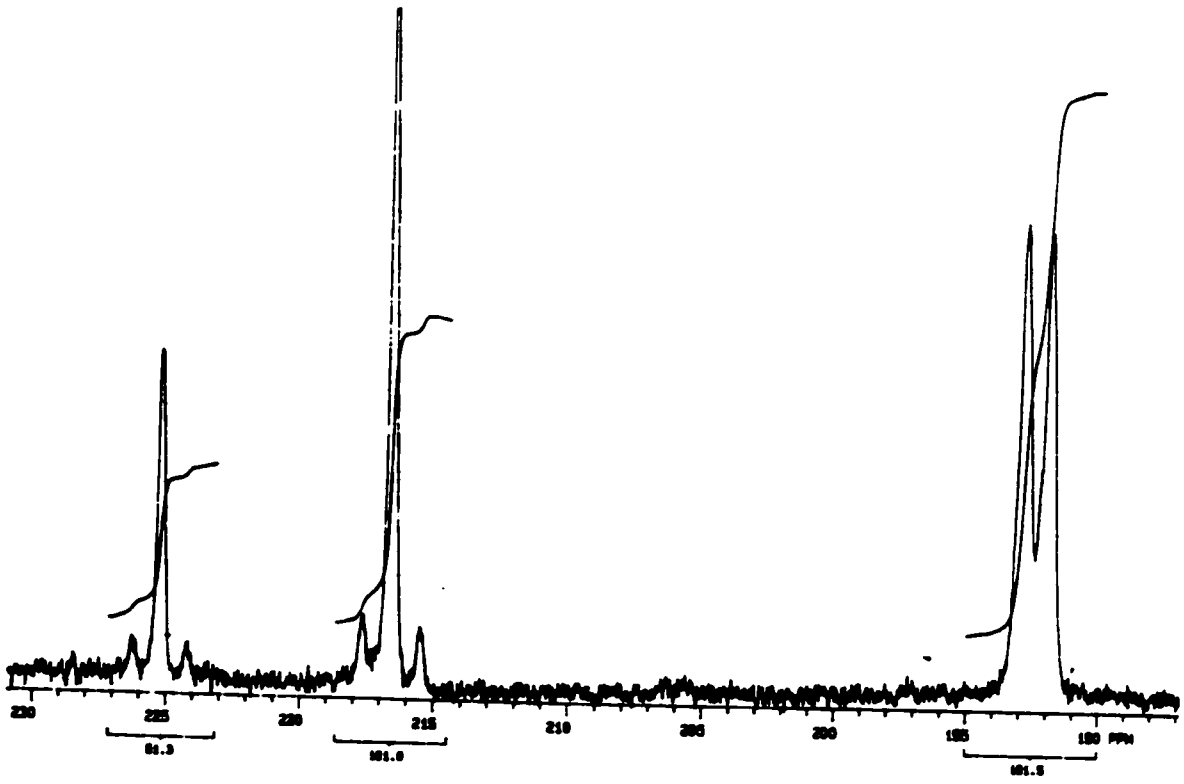
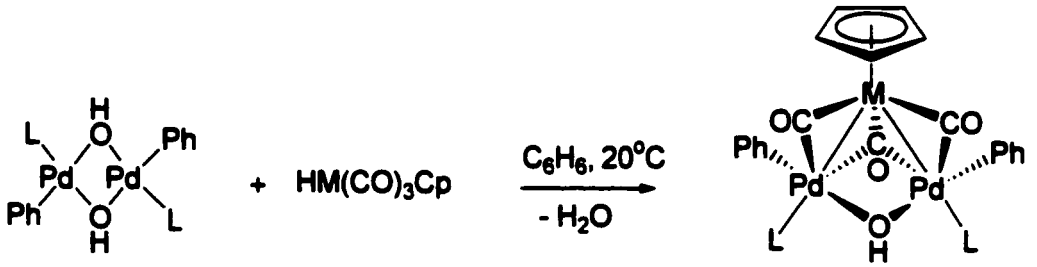


**Figure 2.1**. 193 K $^{13}C\{^1H\}$ NMR spectrum (carbonyl region) of the sample obtained by saturation of toluene-$d_8$ solution of **2.3c** with $^{13}CO$. Measured with $D_1$ = 30s. The same integration ratio was obtained when the spectra were measured with $D_1$ = 10 and 50s.

### 2.2.2 Reaction of $[L_2Pd_2R_2(\mu\text{-}OH)_2]$ with 1 equiv. of $[HM(CO)_3Cp]$ (M = Cr, Mo, W). Preparation and Characterization of Trinuclear $Pd_2M$ Hydroxo Complexes 2.5a-d. X-ray Structure of 2.5a.

The dimeric Pd hydroxides **2.2** react with 1 equiv. of $[HM(CO)_3Cp]$ almost instantaneously, affording the corresponding trinuclear monohydroxo complexes **2.5a-d** in accordance with eq. 2.3.




(2.3)

**2.2**

**2.5a**, M = Cr; L = $PPh_3$
**2.5b**, M = Mo; L = $PPh_3$
**2.5c**, M = W; L = $PPh_3$
**2.5d**, M = W; L = $PCy_3$

The complexes were isolated in high yield as orange (**2.5a**) or yellow (**2.5b-d**) air stable crystalline materials and characterized by elemental analysis, IR- and NMR spectroscopy. The structure of **2.5a** was established by single crystal X-ray diffraction. An ORTEP plot of **2.5a**·MeOH is presented in Figure 2.2. Selected bond distances and angles are given in Table 2.1. The molecule of **2.5a** contains two Pd and one Cr atoms arranged in an open Pd-Cr-Pd triangle. The Pd···Pd separation (3.381(16) Å) is much longer than the sum of the two covalent radii (2.98 Å) indicating that there is no Pd-Pd bond in the complex. The slightly puckered (torsion angles are 9.5(3)° and 10.8(3)°) four membered Pd(1)-O(1)-Pd(2)-C(3) metallocycle assumes a dihedral angle of 49.25(22)° with the $CrPd_2$ frame.

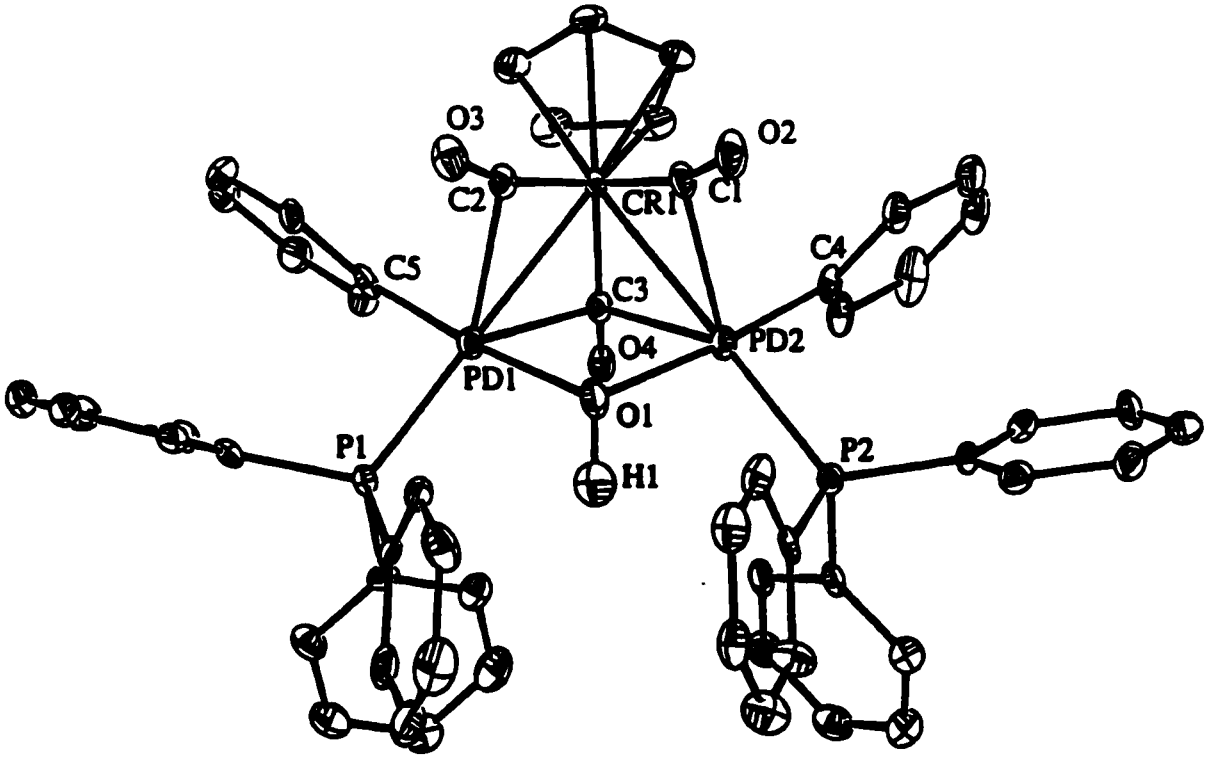



**Figure 2.2.** ORTEP drawing of complex **2.5a** with adopted numbering scheme. Hydrogen atoms (except for OH) are omitted for clarity.

**Table 2.1.** Selected Bond Distances (Å) and Angles (deg) for $[(Ph_3P)_2Pd(\mu\text{-}OH)(\mu\text{-}CO)(\mu^3\text{-}CO)CrCp]\cdot MeOH$

| | | | |
|---|---|---|---|
| Pd(1) - Cr | 2.7523(15) | Pd(1) C(5) | 1.998(9) |
| Pd(2) - Cr | 2.7604(15) | C(2) O(3) | 1.182(10) |
| Pd(1) - P(1) | 2.3035(23) | C(3) O(4) | 1.184(10) |
| Pd(1) - O(1) | 2.125(6) | Cr C(2) | 1.846(9) |
| Pd(1) - C(3) | 2.324(8) | Cr C(3) | 1.889(9) |
| Pd(1) - C(2) | 2.305(9) | Cr - centroid Cp | 1.842(5) |
| C(3) - Pd(1) - O(1) | 79.8(3) | Pd(1) - Cr - C(3) | 56.5(3) |
| Pd(1) - O(1) - Pd(2) | 105.4(3) | C(2) - Cr - C(1) | 79.7(4) |
| Pd(1) - C(3) - Pd(2) | 93.3(3) | C(2) - Cr - C(3) | 112.4(4) |
| Cr - Pd(1) - P(1) | 178.93(7) | O(2) - C(1) - Cr | 164.1(8) |
| Cr - Pd(1) - C(5) | 92.28(24) | O(2) - C(1) - Pd(2) | 113.0(6) |
| O(1) - Pd(1) - C(5) | 174.7(3) | Pd(1) - C(2) - Cr | 82.3(3) |
| P(1) - Pd(1) - O(1) | 97.54(17) | O(4) - C(3) - Cr | 161.6(7) |
| P(1) - Pd(1) - C(5) | 87.74(25) | O(4) - C(3) - Pd(1) | 110.7(6) |
| Pd(1) - Cr - Pd(2) | 75.68(4) | Pd(1) - C(3) - Cr | 80.9(3) |

**Table 2.2.** Bond Distances (Å) and Angles (deg) for the $Pd_2M_2(\mu\text{-}CO)_2(\mu^3\text{-}CO)$ Units in **2.5a** and Relevant Clusters

| bond distance (Å)/angle (deg) | $Pd_2Cr_2$[11] | $Pd_2Mo_2$[12] | **2.5a** |
|---|---|---|---|
| Pd – C (μ-CO) | 2.30(1) | 2.304(7) | 2.305(9) |
| | 2.34(1) | 2.243(6) | |
| Pd – C ($\mu^3$-CO) | 2.34(1) | 2.311(8) | 2.324(8) |
| | 2.26(1) | 2.321(7) | |
| Cr – C (μ-CO) | 1.84(1) | NA | 1.846(9) |
| Cr – C ($\mu^3$-CO) | 1.92(1) | NA | 1.889(9) |
| Pd – C – O (μ-CO) | 114.7(6) | 116.7(5) | 113.0(6) |
| | 117.9(6) | 116.8(7) | |
| Pd – C – O ($\mu^3$-CO) | 118.1(8) | 118.3(5) | 110.7(6) |
| | 117.7(6) | 119.2(5) | |
| Cr – C – O (μ-CO) | 165.7(7) | NA | 164.1(8) |
| | 159.8(7) | | |
| Cr – C – O ($\mu^3$-CO) | 156.6(5) | NA | 161.6(7) |

NA = not applicable

The two phosphines are *syn* and the Pd-P bonds are collinear with the corresponding Pd-Cr bonds. The $\mu^3$-carbonyl is located below and the two $\mu$-carbonyls are situated above the $CrPd_2$ plane in a manner similar to that found in Braunstein's tetranuclear $Pd_2M$ (M = Cr, Mo, W)[11] and Werner's trinuclear $Pd_2Mo$[12] clusters. As can be seen from Table 2.3, the metal-carbonyl cores are structurally similar in $[(Et_3P)_2Pd_2Cr_2(\mu\text{-}CO)(\mu^3\text{-}CO)Cp_2]$,[11] $[(i\text{-}Pr_3P)_2Pd_2Mo(\mu\text{-}CO)_2(\mu_3\text{-}CO)Cp_2]$,[12] and **2.5a**. This suggests similar bonding for the semi-bridging and semi-triply bridging carbonyls[13] to the metals in all three complexes. However, NMR and IR spectra indicates that the metal-carbonyl core in **2.5a-d** is remarkably rigid, while that in Braunstein's $Pd_2M_2$ complexes was shown to be fluxional.[11]

The IR-carbonyl bands for **2.5a-d** being very similar in shape, frequency and intensity to those observed for the tetranuclear $Pd_2M_2$ clusters,[11] are noticeably sharper, pointing to structural rigidity of $[MPd_2(CO)_3]$ frameworks in **2.5a-d**.

The carbonyl region of the $^{13}C$ NMR spectrum of **2.5a-d**, recorded at –30 to 20°C, consists of two separate resonances in a 2 : 1 ratio, suggesting that there is no positional exchange between $\mu$-CO and $\mu^3$-CO ligands in the complexes. In contrast, carbonyls in the closely related tetranuclear $Pd_2M_2$ clusters[11] undergo fast exchange on the NMR time scale, even at –90°C. This remarkable difference in fluxionality may be attributable to the presence of Pd-Pd bond in $Pd_2M_2$ complexes, which is absent in **2.5a-d**. As carbon monoxide is known to insert into the Pd-Pd bond of some complexes,[14,15] the coordinated CO-ligands in $Pd_2M_2$ clusters[11] can reversibly do so, thus undergoing fast positional exchange. Obviously such a mechanism cannot be operational for **2.5a-d**, which possess no Pd-Pd bonding interaction. The downfield carbonyl signal in the $^{13}C\{^1H\}$ NMR spectrum of **2.5a**, tentatively assigned to the chemically equivalent $\mu$-CO groups, appears as a second order AXX′ multiplet. The

pattern can be simulated[16] with the following parameters: $\delta_X = \delta_{X'}$, $J_{AX} = \pm 19$ Hz, $J_{A-X'} = \pm 5$ Hz, $|J_{X-X'}| = 5$ Hz. It should be noted that the relative sign of the coupling constants between the carbon and each magnetically nonequivalent P atom must be different in order to reproduce the experimental spectrum (see Figure 2.3). The upfield carbonyl resonance, which is assigned to the $\mu^3$-CO ligand, appears as a first order triplet ($J_{C-P} = 12.3$ Hz). The *ortho* and *meta* carbons of the $PPh_3$-ligands are also second order multiplets, consistent with $|J_{P-P'}| = 5$ Hz. Both carbonyl signals of complexes **2.5b-d** appear as the first order doublet of doublets ($\mu$-CO) and triplet ($\mu^3$-CO), suggesting that the P-P coupling is significantly weaker. In accordance with this, the signals of *ortho* and *meta* carbons of $PPh_3$ ligands exhibit only very small second order effects. At –25°C, both *ortho* and *meta* carbons of Ph rings $\sigma$-bound to Pd, appear to be nonequivalent within each pair in the $^{13}C\{^1H\}$ NMR spectra of **2.5a-d**, probably because of hindered rotation around the Pd-Ph bond. At room temperature this nonequivalence vanished for **2.5a-c** but was still observed in the spectrum of the tricyclohexylphosphine complex **2.5d**, presumably due to the steric bulk of $Cy_3P$.

It should be noted that complexes **2.5a-d** not only belong to the still very limited group of neutral organopalladium hydroxo complexes,[2,17] but they also represent the first example of heteropolymetallic species containing a Pd-OH unit. No other Pd complexes bearing a set of OH, CO and $\sigma$-aryl (alkyl) ligands have been reported in the literature.[18] It is remarkable that **2.5a-d** are stable, despite the presence of OH, $\sigma$-Ph and CO ligands in the same coordination sphere. In fact, $\sigma$-aryls, $\sigma$-alkyls and especially hydroxo ligands are prone to migratory insertion reactions with the carbonyls coordinated to the metal.[19-24]

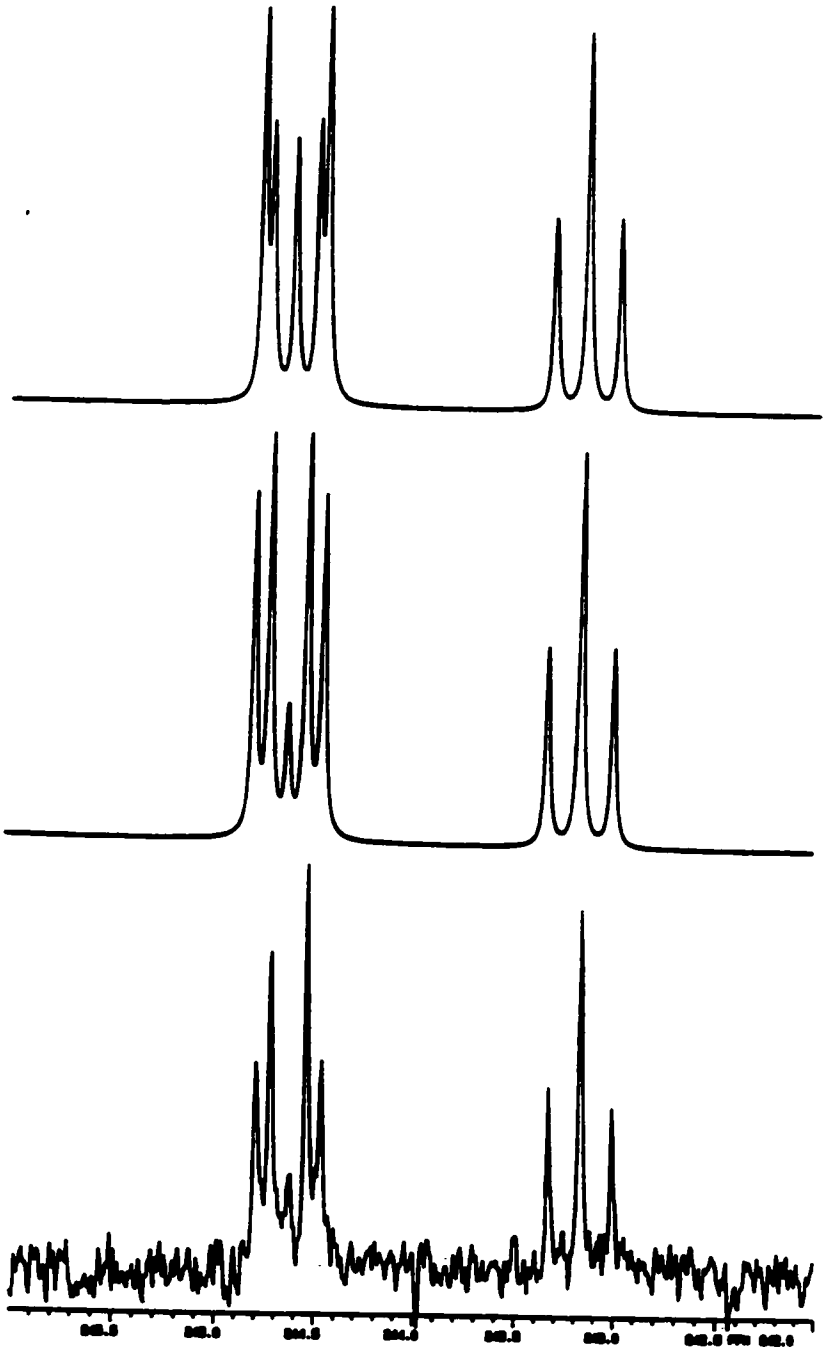


**Figure 2.3.** $^{13}C\{^{1}H\}$ NMR spectrum (carbonyl region) of **2.5a**.

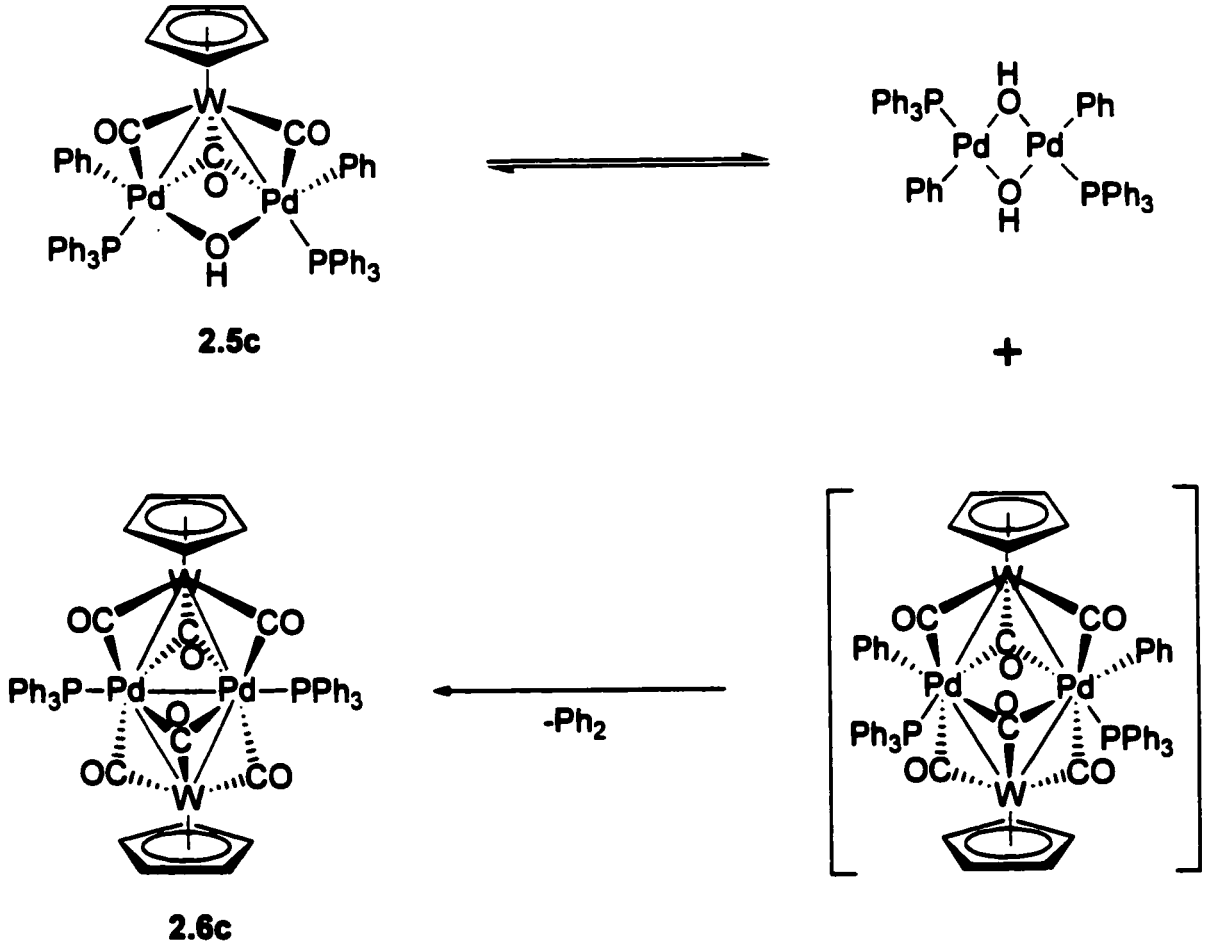
a (bottom) experimental spectrum at –20°C in $CDCl_3$.
b (middle) simulated spectrum with $J_{C\text{-}P1}$ = -19 Hz, $J_{C\text{-}P2}$ =5 Hz, $J_{P1\text{-}P2}$ = 5 Hz.
c (top) simulated spectrum with $J_{C\text{-}P1}$ = 19 Hz, $J_{C\text{-}P2}$ =5 Hz, $J_{P1\text{-}P2}$ = 5 Hz.

The stability of **2.5a-d** is probably associated with the rigidity of their metal-carbonyl cores. The OH and Ph groups are attached to the Pd centers, while the bridging carbonyl ligands are coordinated mainly to Cr, Mo or W. The migratory insertion in such systems would, in fact, require ligand transfer from one metal to a carbonyl group attached to another metal, which is unlikely.

### 2.2.3 Decomposition of Complexes 2.5a-c in Solution.

In the solid state clusters **2.5a,b** can be stored in air for several months The tungsten analog **2.5c** can be handled in air for a few hours without noticeable decomposition. However, the latter is unstable over longer periods in air and should be kept under nitrogen in a freezer. In solution the hydroxo clusters slowly decompose, even in the absence of air; the order of stability is: **2.5a** (Cr) > **2.5b** (Mo) > **2.5c** (W). The decomposition of **2.5c** was monitored by $^{31}$P NMR spectroscopy. The spectra showed the gradual disappearance of **2.5c** (23.4 ppm), accompanied by the simultaneous formation of cluster **2.6c** (21.0 ppm) and the original organopalladium hydroxide (33.2 and 33.9 ppm due to *syn* and *anti* isomers respectively).[2] At room temperature, the complete decomposition of **2.5c** in toluene takes *ca.*20 h, affording the corresponding tetranuclear cluster **2.6c**, the original binuclear Pd hydroxide and biphenyl in a 1 :1 : 1 molar ratio. The absence of benzene and bibenzyl among the products points to a non-radical pathway of the reaction.[25] The mechanism of this transformation remains unclear, but may involve a disproportionation followed by elimination of biphenyl (see Scheme 2.1) although no intermediates were detected. The known examples of binuclear reductive elimination from Pd complexes[26] involve migration of the eliminating fragments to the same metal center, prior to reductive elimination.

***Scheme 2.1***

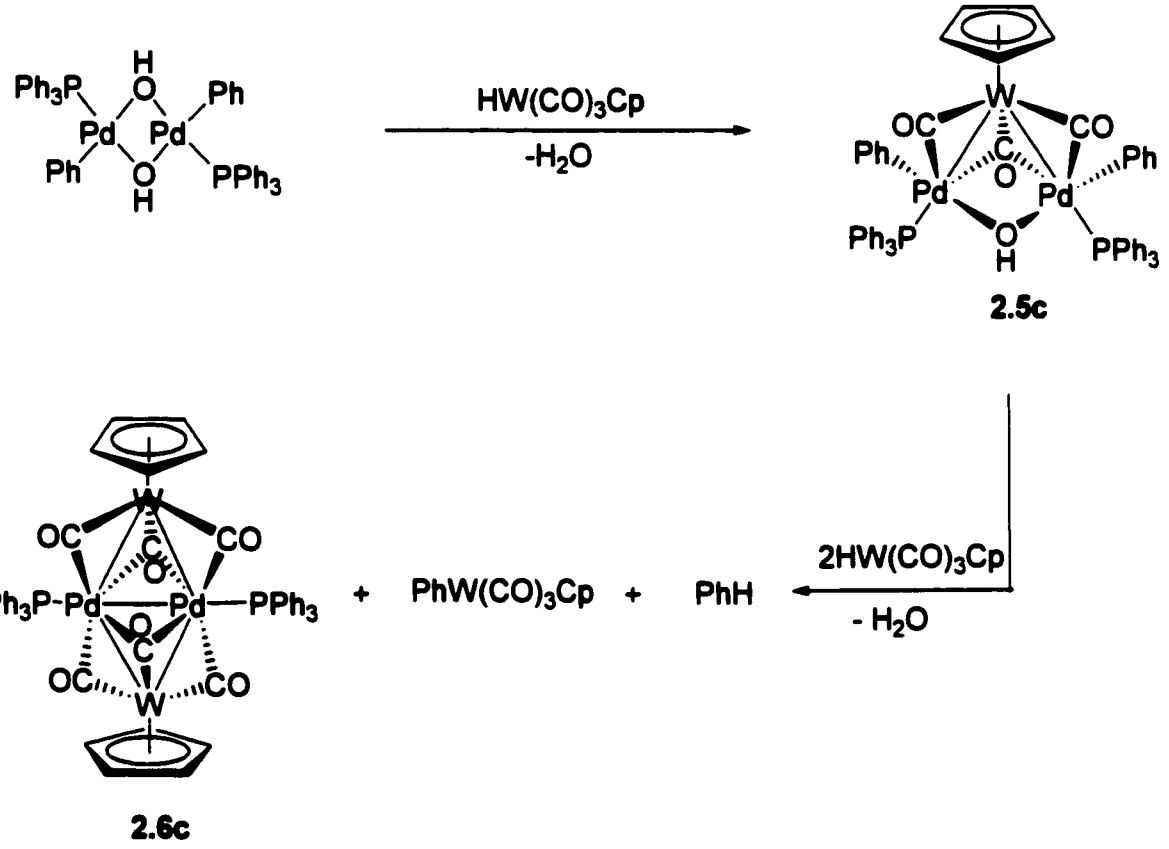



In comparison with the smooth disproportionation of **2.5c**, the decomposition of the chromium analog **2.5a** is slower, taking several days to give a complex mixture of unidentified products. Neither complex **2.6a**, nor **2.2** (L = $PPh_3$) could be detected by $^{31}P$ NMR in the reaction mixture. The palladium-molybdenum hydroxide **2.5b** decomposes faster than **2.5a**, but slower than **2.5c**; the reaction takes *ca.* 48 hours, affording **2.6b** and **2.2** (L = $PPh_3$) in 1 : 1 molar ratio along with other unidentified products.

### 2.2.4 Reaction of $[L_2Pd_2Ph_2(\mu\text{-}OH)_2]$ with Excess $[HM(CO)_3Cp]'$

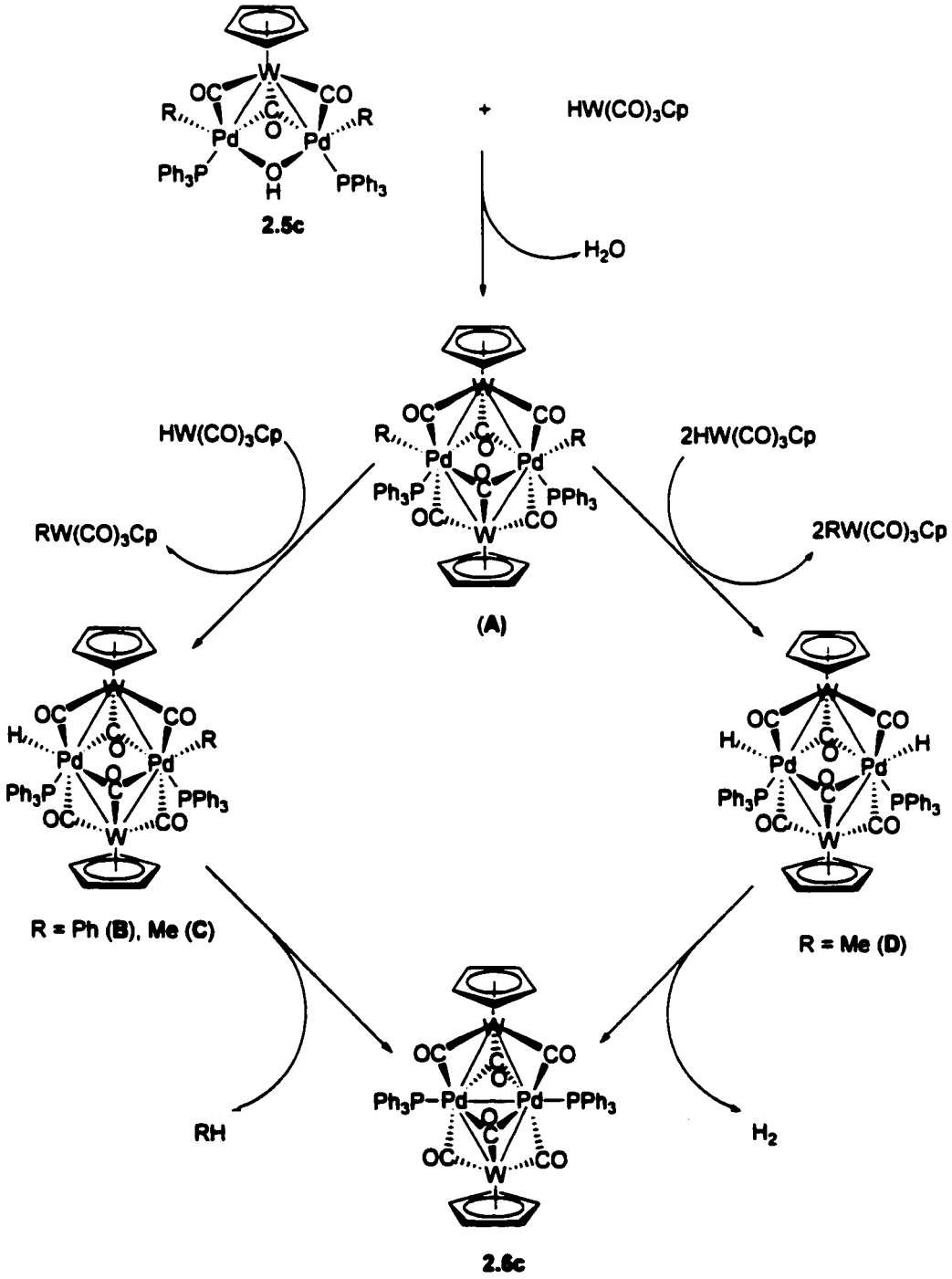
Considering eq. 2.3 and Scheme 2.1 together, it may be expected that the tetranuclear $Pd_2W_2$ cluster **2.6c** can be prepared from $(Ph_3P)_2Pd_2Ph_2(\mu\text{-}OH)_2$ and 2 molar equivalents of $[HW(CO)_3Cp]$ with concomitant formation of biphenyl. However, fast addition of excess tungsten hydride to $(Ph_3P)_2Pd_2Ph_2(\mu\text{-}OH)_2$ affords **2.6c** by an alternative pathway, and the complete conversion of the palladium hydroxide was observed ($^{31}P$ NMR) only when 3 equiv. or more of $[HW(CO)_3Cp]$ were used. In that case, complex **2.6c** (90% isolated yield), benzene (83% GC yield) and $[PhW(CO)_3Cp]$[27] (91% isolated yield) were formed, but neither biphenyl nor bibenzyl were detected. The $^{31}P\{^1H\}$ NMR spectra revealed that the reaction initially gives trinuclear complex **2.5c**, which then gradually disappears from the reaction mixture with the simultaneous formation of cluster **2.6c**. The transformation is complete within *ca.* 30 min, which is much faster than the spontaneous disproportionation of **2.5c** under similar conditions (*ca.* 20 h). These data suggest that the formation of **2.6c** occurs in accordance with Scheme 2.2 and involves the intermediate formation of complex **2.5c** which then further reacts with 2 equiv. of $[HW(CO)_3Cp]$ to give **2.6c**, benzene and $[PhW(CO)_3Cp]$.

***Scheme 2.2***




The formation of benzene and the (σ-phenyl)tungsten complex can be explained by a Ph/H exchange between [$HW(CO)_3Cp$] and one of the two Pd-Ph centers in an intermediate tetranuclear species (Scheme 2.3). The proposed intermediate (**A**), formed upon condensation of the OH group in the complex **2.5c** with [$HW(CO)_3Cp$], may exchange one σ-Ph ligand for H with the still present hydride. The subsequent binuclear elimination from the resulting tetranuclear Pd(H)Pd(Ph) species (**B**) would give benzene and complex **2.6c**. If both σ bound ligands are replaced by hydrides to give (**D**), the elimination might result in the formation of $H_2$ and **2.6c**. Indeed, both $CH_4$ and $H_2$ (6 : 1 molar ratio, GC analysis) were detected among the products of a similar reaction between $[(Ph_3P)_2Pd_2Me_2(\mu\text{-}OH)_2]$[17e] and excess of [$HW(CO)_3Cp$].

***Scheme 2.3***

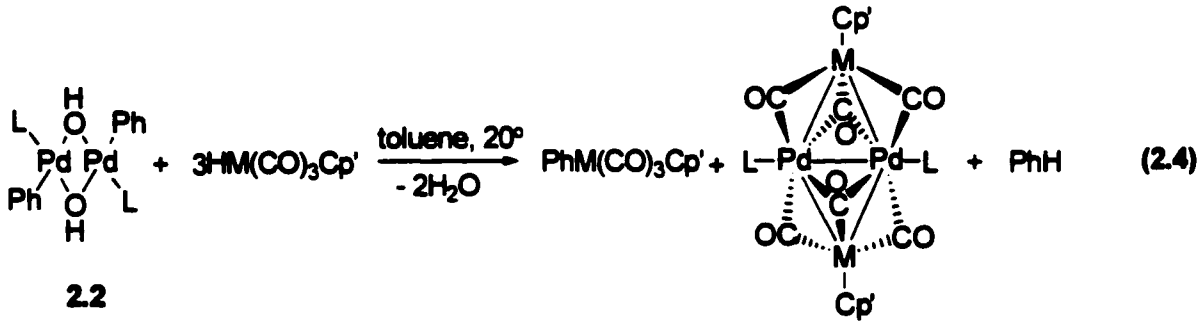

HW(CO)3Cp
H2O
2.5c
HW(CO)3Cp
2HW(CO)3Cp
RW(CO)3Cp
2RW(CO)3Cp
(A)
R = Ph (B), Me (C)
R = Me (D)
RH
H2
2.6c

In that case, complex **2.6c** and $MeW(CO)_3Cp$[28] were isolated in high yield, as the only organometallic products. These results can be rationalized in terms of the mechanism outlined in Scheme 2.3. The details of the W-H/Pd-R exchange remain unclear, but this process may involve oxidative addition of the W-H bond to the Pd-R center, followed by reductive elimination of the W-R compound.[29]

Attempted preparation of the σ-methyl analog of **2.5c** failed, presumably because the desired trinuclear hydroxo complex and the starting hydroxide, $[(Ph_3P)_2Pd_2Me_2(\mu\text{-}OH)]$, possess similar reactivity towards the hydride. When 1 molar equiv. of $[HW(CO)_3Cp]$ was added to $[(Ph_3P)_2Pd_2Me_2(\mu\text{-}OH)]$ in benzene, the $^{31}P\{^1H\}$ NMR spectrum displayed a singlet at 32 ppm which could be assigned to the methyl analog of **2.5c**. The singlet rapidly disappeared, so that within *ca.* 5 min the spectrum contained only signals of the starting Pd hydroxide and the tetranuclear complex **2.6c**.

Treatment of $[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}OH)_2]$ in a toluene solution with 3 equiv. of $DW(CO)_3Cp$ gave $C_6H_6$ and $C_6H_5D$ in an approximately 1 : 1 ratio, determined by GC–MS. When $[(Ph_3P)_2Pd_2Ph_2(\mu\text{-}OD)_2]$ was reacted with $DW(CO)_3Cp$ under analogous conditions, the ratio of $C_6H_6$ : $C_6H_5D$ was *ca.* 1 : 9. These results demonstrate the extensive H/D exchange between the hydrido and hydroxo sites of the reactants. This exchange was found to occur significantly faster than the condensation reaction. When 1 equiv. of $DW(CO)_3Cp$ (90% D) was added to nondeuterated **2.5c** in dry toluene-$d_8$ at –40°C, neither H/D exchange nor formation of **2.6c** was observed by $^1H$ NMR for over 30 min. The hydrido region of the spectrum contained a triplet at –3.7 ppm due to μ-OH and the residual resonance of $[HW(CO)_3Cp]$ at –7.2 ppm. The sample was then quickly warmed to room temperature for *ca.* 1 min, and the $^1H$ NMR spectrum was recorded again at –40°C. The brief exposure to

ambient temperature was sufficient for complete scrambling of the D label over hydrido/hydroxo sites. At the same time the $^1$H- and $^{31}$P{$^1$H} NMR spectra indicated that less than 5% of **2.5c** was converted to **2.6c**. An independent experiment was conducted to show that the H/D exchange between $DW(CO)_3Cp$ and $H_2O$ is very slow, taking hours to reach completion at room temperature. Therefore, water is not required for the observed H/D scrambling, which must result from direct hydrido/hydroxo exchange. Complexes **2.6b-d** were prepared by treating **2.2** with the corresponding hydrides in a 1 : 3 molar ratio according to eq. 2.4. Similarly, the reaction between **2.2** (L = $PPh_3$) and $[HW(CO)_3Cp^*]$ afforded **2.6e** along with $[PhW(CO)_3Cp^*]$ isolated in 60% and 72% yield respectively. The $Cp'M(CO)_3Ph$ byproducts were not isolated in all these cases, but their formation was confirmed by TLC and $^1$H NMR spectroscopy.




**2.2**

**2.6a-e**

**a; M = Cr, L = $PPh_3$, Cp' = $C_5H_5$**
**b; M = Mo, L = $PPh_3$, Cp' = $C_5H_5$**
**c; M = W, L = $PPh_3$, Cp' = $C_5H_5$**
**d; M = W, L = $PCy_3$, Cp' = $C_5H_5$**
**e; M = W, L = $PPh_3$, Cp' = Cp* = $C_5Me_5$**

The NMR and IR spectra obtained for **2.6a-c** were identical to those previously reported.[11] The new clusters **2.6d,e** were characterized by elemental analysis, NMR and IR spectroscopy (see Experimental section).

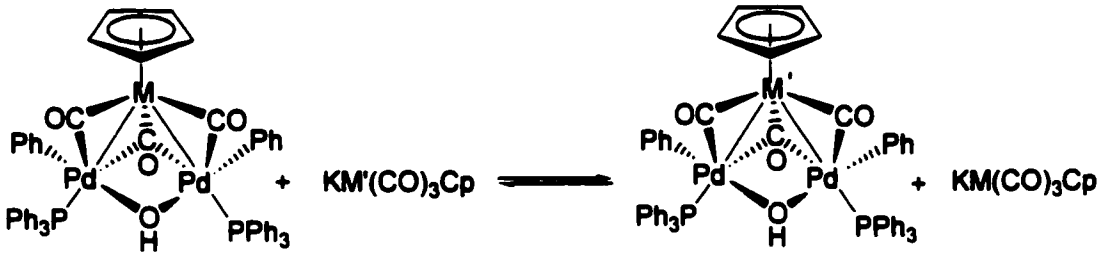
### 2.2.5 Formation of Tetranuclear Trimetallic Clusters.

The fact that the reactions between **2.2** and excess [$HM(CO)_3Cp$] occured *via* the intermediate formation of trinuclear hydroxo complexes **2.5a-d**, implied that other $Pd_2MM'$ tetranuclear heterotrimetallic clusters could be prepared by this method. It should be noted that such clusters cannot be prepared by Braunstein's method.[11] When a 1 : 1 mixture of **2.6a** and **2.6b** in benzene was monitored by $^{31}P$ NMR spectroscopy, no sign of a W/Mo exchange was detected during 2 weeks at room temperature. However, when **2.5c** was treated with 2 equiv. of [$HMo(CO)_3Cp$], a mixture of **2.6b**, **2.6c** and the mixed $Pd_2MoW$ species (**2.7**) was formed in a 1 : 10 : 2 ratio. The reaction between **2.5b** and [$HW(CO)_3Cp$] also resulted in the formation of **2.6b**, **2.6c** and **2.7** in a ratio of 7 : 1 : 10. From this experiment complex **2.7** was isolated by column chromatography in 55% yield and characterized by elemental analysis, NMR and IR spectroscopy. Having been kept in benzene for 24 h, complex **2.7** did not disproportionate or decompose, suggesting that the observed scrambling cannot be explained by the instability of the mixed species. Attempts to prepare $Pd_2WCr$ and $Pd_2MoCr$ mixed clusters by similar methods did not afford the desired complexes selectively; but gave mixtures of all three possible clusters. It has been reported previously that the reaction between [$L_2Pd_2(\mu\text{-}Cl)(\mu\text{-}CO)_2(\mu^3\text{-}CO)MCp$] and Na[$M'(CO)_3Cp$] also gave mixtures of all possible clusters, which were not separated.[12]

Clearly, the observed M/M' scrambling did not result from exchange between the $Pd_2M_2$ and $Pd_2M'_2$ units or disproportionation of $Pd_2MM'$, and it cannot be explained by exchange between $Pd_2MM'$ and unreacted [$HM(CO)_3Cp$]. In fact, although some W/Cr

scrambling was observed when **2.5c** was treated with [HCr(CO)$_3$Cp] in benzene, the reaction was very slow, taking several hours at room temperature before the $Pd_2WCr$ (**2.8**) and $Pd_2W_2$ species could be detected by $^{31}P$ NMR. The complex **2.8** was prepared in this manner and isolated in 34% yield after 70 h. In contrast, all reactions of **2.5a-c** were significantly faster, reaching completion in *ca.* 30 min. Therefore, the M/M' scrambling occurs in the early steps of the reaction.

Unlike [HM(CO)$_3$Cp] (M = Cr, Mo, W), the corresponding potassium salts KM(CO)$_3$Cp readily underwent exchange with **2.6a-c** in *ca.*30 min affording mixtures of $Pd_2M_2$, $Pd_2M'_2$ and $Pd_2MM'$. The trinuclear hydroxo clusters **2.5a-c** also rapidly exchanged with the potassium carbonylates according to eq.2.5. The equilibria were reached within 30 min at room temperature ($^{31}P$ NMR).




(2.5)

Remarkably, two separate singlets were observed in the carbonyl region of the $^{13}C$ NMR spectra of **2.7** and **2.8**, indicating that the μ-CO/$\mu^3$-CO positional exchange occurs only within each $Pd_2M$ unit, with no exchange between the two $Pd_2M$ frameworks. This is probably also true for complexes **2.6a-e**, which display only one carbonyl $^{13}C$ NMR resonance due to symmetry.

## 2.3 Conclusions

The reactions of $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2]$ and $[Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)_2]$ with $[HM(CO)_3Cp]$ (M = Cr, Mo, W) are convenient methods for the preparation of Rh and Pd heterometallic polynuclear clusters and represent the first examples of metal – metal bond formation by the condensation of basic transition metal hydroxides with acidic transition metal hydrides. The mechanisms of these reactions are complex and probably involves a series of oxidative addition – reductive elimination processes. Another aspect, which merits emphasis, is the "peaceful coexistence" of the OH, σ-phenyl and carbonyl ligands, all in the same coordination sphere, in the Pd complexes **2.5a-d**. From this perspective, such polyfunctional complexes are of potential interest in inorganic and organometallic synthesis, as well as in the chemistry of catalytic carbonylation of organic substrates in the presence of alkali-base and homogeneous Pd catalysts.[21-24]

## 2.4 Experimental section

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use. The metal complexes $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2]$,[1] $[Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)_2]$[2], $[Pd_2(PCy_3)_2Ph_2(\mu\text{-}OH)_2]$[2], $[HM(CO)_3Cp]$ (M = Mo, W),[6] $Hg[Cr(CO)_3Cp]_2$[30]and $[HW(CO)_3Cp^*]$ [31] were prepared according to published procedures. Other chemicals were purchased from Strem or Aldrich and were used as received. The following instruments were used: Varian XL 300 ($^1H$-, $^{13}C$- and $^{31}P$ NMR), Hewlett-Packard 5890 Series II Kratos Concept II H (GC-MS), Bomem MB-100 (FT-IR) and Perkin-Elmer 2400 Series II (combustion microanalysis).

**2.4.1 Synthesis of $[(Ph_3P)_2RhCr(CO)_3Cp]$ (2.3a).** A mixture of $Hg[Cr(CO)_3Cp]_2$ (243 mg, 0.40 mmol), THF (5 mL) and K/Na alloy (0.5 mL) was stirred for 1h and then filtered. The filtrate was reduced in volume under vacuum to *ca.* 3 mL, treated with acetic acid (0.2 mL) stirred for 10 min and taken to dryness under vacuum. The yellow-orange crystals of $[HCr(CO)_3Cp]$ were isolated from the residue by vacuum sublimation (1 mm Hg) onto a water cooled probe and added to a solution of $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2] \cdot 2C_6H_6$ (51 mg, 0.035 mmol) in benzene (3mL). The mixture was stirred for 10 min, the resulting dark cherry-red solution was reduced in volume to *ca.* 1 mL, diluted with MeOH (5 mL) and left for 1h. the formed dark red crystals were separated by decantation, washed with MeOH (3 x 5 mL) and dried in vacuum to give analytically pure **2.3a** (45 mg, 77%). Anal. Calcd for $C_{44}H_{35}CrO_3P_2Rh$: C, 63.8; H, 4.3. Found: C, 64.0; H, 4.3. $^1H$ NMR ($C_6D_6$, 20°C), δ: 4.5 (s, 5H, $C_5H_5$), 6.9 (m, 18H, $C_6H_5$), 7.6 (m, 12H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 20°C), δ: 39.4 (d, $J_{P\text{-}Rh}$ = 177 Hz). IR (KBr), $cm^{-1}$: 1876 (vs), 1780 (vs), 1749 (vs).

**2.4.2 Synthesis of $[(Ph_3P)_2RhMo(CO)_3Cp]$ (2.3b).** Solid $[HMo(CO)_3Cp]$ (35 mg, 0.14 mmol) was added to a mixture of $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2] \cdot 2C_6H_6$ (92 mg, 0.06 mmol) and benzene (3 mL). The mixture was stirred for15-20 min until all solids dissolved, reduced in volume to *ca.* 1mL, diluted with MeOH (3 mL) and placed in an ice bath for 1h. The precipitated **2.3b** was separated by decantation, washed with MeOH (3 x 4 mL), pentane (2 x 3 mL) and dried in vacuum to give analytically pure **2.3b** (70 mg, 73 %). Anal. Calcd for $C_{44}H_{35}MoO_3P_2Rh$: C, 60.6; H, 4.0. Found: C, 60.9; H, 4.0. $^1H$ NMR ($C_6D_6$, 20°C), δ: 5.0 (s, 5H, $C_5H_5$), 6.9 (m, 18H, $C_6H_5$), 7.7 (m, 12H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 20°C), δ: 38.1 (d, $J_{P\text{-}Rh}$ = 177 Hz). IR (KBr), $cm^{-1}$: 1873 (vs), 1776 (vs), 1748 (vs).

**2.4.3 Synthesis of $[(Ph_3P)_2RhW(CO)_3Cp]$ (2.3c).** Solid $[HW(CO)_3Cp]$ (70 mg, 0.21 mmol) was added to a mixture of $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2]\cdot 2C_6H_6$ (130 mg, 0.09 mmol) and benzene (5 mL), and the mixture was stirred for 15-20 min until all solids dissolved. Methanol (10 mL) was added to the resulting clear dark-brown solution, and the mixture was kept in an ice bath for 1.5 h. Crystals of **2.3c** were separated, washed with MeOH (4 x 2 mL) and dried in vacuum. The yield of analytically pure **2.3c** was 0.167 mg (97%). Anal. Calcd for $C_{44}H_{35}WO_3P_2Rh$: C, 55.0; H, 3.7. Found: C, 55.0; H, 3.6. $^1H$ NMR ($C_6D_6$, 20°C), δ: 4.9 (s, 5H, $C_5H_5$), 6.9 (m, 18H, $C_6H_5$), 7.7 (m, 12H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 20°C), δ: 31.8 (d, $J_{P\text{-}Rh}$ = 173 Hz). IR (KBr), $cm^{-1}$: 1869 (vs), 1767 (vs), 1738 (vs).

**2.4.4 Synthesis of $[(Ph_3P)_2Pd_2Ph_2(\mu OH)Cr(CO)_3Cp]$ (2.5a).** A mixture of $Hg[Cr(CO)_3Cp]_2$ (210 mg, 0.348mmol), THF (5 mL) and Na/K alloy (1 mL) was stirred for 1h. The THF solution was filtered and treated with acetic acid (1mL). The mixture was stirred for 10 min and evaporated. The residue was washed with water (2 x 5 mL), the bright yellow precipitate was dried in vacuum, dissolved in 5mL of pentane and filtered. Removal of pentane from the filtrate gave 59.7mg (0.295 mmol, 42%) of yellow $[HCr(CO)_3Cp]$. The obtained hydride was dissolved in 4.0 mL of heptane and an aliquot of this solution (1.8 mL, 0.133 mmol of $[HCr(CO)_3Cp]$ ) was added to a stirred solution of $[Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)_2]$ (135mg, 0.146 mmol) in 20 mL of benzene. The resulting clear orange solution was diluted with 20mL of heptane, reduced in volume to c.a. 20 mL and kept first at room temperature (30 min) and then in a fridge at –17°C for 1 hour. The resulting orange crystals were collected, washed with pentane (3 x 10 mL) and dried to give pure **2.5a** (133 mg, 0.120 mmol, 90%). Anal. Calcd for $C_{56}H_{46}CrO_4P_2Pd_2$: C, 60.61; H, 4.18. Found : C, 60.36; H, 4.32.

$^1$H NMR ($CDCl_3$, 20°C), □δ: -4.0 (t, $J_{H-P}$ = 2.0 Hz, 1H, PdOH), 3.7 (s, 5H, $C_5H_5$), 6.5 - 7.6 (m, 40 H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$), δ: 18 (s). $^{13}C\{□H\}$ NMR ($CDCl_3$, -25°C), δ: 89.4 □(s, $C_5H_5$), 121.8 (s, *p*-$C_6H_5$-Pd), 126.4 (s, *m*-$C_6H_5$-Pd), 127.1 (s, *m*-$C_6H_5$-Pd), 128.1(2nd order m, $J_{C-P}$≈10.2 Hz, *m*-$C_6H_5$-P), 129.4 (d, $J_{C-P}$= 41.5 Hz, *q*-$C_6H_5$-P), 129.9 (s, *p*-$C_6H_5$-P), 133.7 (2nd order m, $J_{C-P}$≈ 12.8Hz, *o*-$C_6H_5$-P), 135.3 (s, *o*-$C_6H_5$ -Pd), 142.2 (m, q-$C_6H_5$-Pd), 243.2 (t, $J_{C-P}$ = 12.3 Hz, CO), 244.6 (2nd order m, CO). IR (KBr), $cm^{-1}$: 1859 (vs), 1792 (vs), 1760 (vs).

**2.4.5 Synthesis of $[(Ph_3P)_2Pd_2Ph_2(\mu OH)Mo(CO)_3Cp]$ (2.5b).** A solution of freshly purified $[HMo(CO)_3Cp]$ (33 mg, 0.134 mmol ) in heptane (4 mL) was added to a stirred solution of $[Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)_2]$ (128 mg, 0.138 mmol) in 20 mL of benzene. The resulting yellow-orange solution was diluted with 20 mL of heptane, and reduced in volume to c.a. 20 mL under vacuum. The yellow crystalline precipitate was separated, washed with pentane (3 x 10 mL) and dried to give 138 mg (0.12 mmol, 89%) of analytically pure **2.5b**. Anal. Calcd for $C_{56}H_{46}MoO_4P_2Pd_2$: C, 58.3; H, 4.02. Found C, 58.69; H, 3.87. $^1$H NMR ($CDCl_3$, 20°C), δ: -3.8 (t, $J_{H-P}$ = 2.1 Hz, 1H, PdOH); 4.33 (s, 5H, $C_5H_5$), 6.6 - 7.4 (m, 40 H). $^{31}P\{^1H\}$NMR ($C_6D_6$ 20°C), δ: 18.5 (s). $^{13}C\{□H\}$ NMR ($CDCl_3$, -25°), δ: 102.2 (s, $C_5H_5$), 121.7 (s, *p*-$C_6H_5$-Pd), 126.2 (s, m- $C_6H_5$-Pd), 126.8 (s, m- $C_6H_5$-Pd), 128.0 (2nd order m, $J_{C-P}$≈10.6 Hz, m- $C_6H_5$-P), 129.4 (d, $J_{C-P}$= 40.1 Hz, q- $C_6H_5$-P), 130.7 (s, *p*-$C_6H_5$-P), 133.7 (2nd order m, $J_{C-P}$≈13.0 Hz, *o*-$C_6H_5$-P), 134.0 (s, *o*-$C_6H_5$-Pd); 135.5 (s, *o*-$C_6H_5$-Pd), 139.3 (m, q-

$C_6H_5$-Pd), 233.4 (t, $J_{C-P}$ = 17.1 Hz, CO); 236.1 (d, $J_{C-P}$= 20.5 Hz, CO). IR (KBr), $cm^{-1}$: 1867 (vs); 1799 (vs); 1762 (vs).

**2.4.6 Synthesis of $[(Ph_3P)_2Pd_2Ph_2(\mu OH)W(CO)_3Cp]$ (2.5c)** Solid $[HW(CO)_3Cp]$ (34 mg, 0.102 mmol) was added to a stirred solution of $[Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)_2]$ (100 mg, 0.108 mmol) in 20 mL of benzene. The resulting yellow-brown solution was diluted with 20 mL of heptane and reduced in volume under vacuum until it became turbid. The clear yellow solution was decanted from the dark solid and evaporated until bright yellow crystals were formed and the liquid became almost colorless. The crystals were separated, washed with pentane (3 x 10 mL) and dried under vacuum to give 103 mg (0.083 mmol, 82%) of **2.5c**. The compound was found to be analytically pure. Anal. Calcd for $C_{56}H_{46}O_4P_2Pd_2W$: C, 54.17; H, 3.74. Found: C, 54.29; H, 3.76. $^1H$ NMR ($CDCl_3$, 20°C), δ: -3.74 (t, $J_{H-P}$ = 2.1 Hz, 1H, PdOH), 4.41 (s, 5H, $C_5H_5$), 6.5 - 7.4 (m, 40 H, $C_6H_5$). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 20°C), δ: 23.4(s). $^{13}C\{□H\}$ NMR ($CDCl_3$, -25°C), δ: 91.2 (s, $C_5H_5$), 122.0 (s, p-$C_6H_5$-Pd); 126.4 (s, m- $C_6H_5$-Pd), 127.0 (s, m- $C_6H_5$-Pd), 128.3 (d, $J_{C-P}$=10.4 Hz, *m*-$C_6H_5$-P), 129.5 (d, $J_{C-P}$= 40.Hz, q-$C_6H_5$-P), 130.0 (s, p- $C_6H_5$-P), 133.8 (d, $J_{C-P}$= 12.9Hz, o- $C_6H_5$-P), 135.5 (broad s, *o*-$C_6H_5$-Pd), 139.4 (m, q- $C_6H_5$-Pd), 225.8 (t, $J_{C-P}$= 14.0 Hz, CO), 228.0 (d, $J_{C-P}$= 15.5 Hz, CO). IR (KBr), $cm^{-1}$: 1861 (vs), 1785 (vs), 1750 (vs).

**2.4.7 Synthesis of $[(Cy_3P)_2Pd_2Ph_2(\mu OH)W(CO)_3Cp]$ (2.5d).** Solid $[HW(CO)_3Cp]$ (38 mg, 0.114 mmol) was added to a stirred solution of $[Pd_2(PCy_3)_2Ph_2(\mu\text{-}OH)_2]$ (130 mg, 0.116 mmol) in a mixture of $CH_2Cl_2$ (15 mL), heptane (15 mL) and toluene (2 mL) at 0°C.

The resulting clear yellow solution was stirred at 0°C for 10min, reduced in volume under vacuum to *ca.* 10 mL and kept at –80°C for 3 days. The yellow crystals that precipitated were separated, washed with cold (-80°C) pentane and dried under vacuum to give 110mg (0.086 mmol, 75%) of spectroscopically pure **2.5**·$C_6H_5CH_3$. The compound was recrystallized from a 1:1 mixture of toluene-pentane (8 mL) at –80°C for elemental analysis. Anal. Calcd for $C_{63}H_{90}O_4P_2Pd_2W$: C, 55.2; H, 6.6. Found: C, 55.5; H, 6.6. $^1$H NMR ($C_6D_6$, 20°C), δ: -1.4 (s, 1H, OH); 1.0-2.2 (m, 69H, $C_6H_{11}$ + Me), 4.35 (s, 5H, $C_5H_5$), 6.8 (t, $J_{H-H}$ = 7.1 Hz, 2H, *p*-$C_6H_5$-Pd); 6.99 (m, 4H, m- $C_6H_5$-Pd), 7.1-7.2 (m, 5H, toluene), 7.78 (d, $J_{H-H}$ = 8.0 Hz, 2H, *o*-$C_6H_5$-Pd), 8.17 (d, $J_{H-H}$ = 7.7 Hz, 2H, o- $C_6H_5$-Pd), $^{31}$P{$^1$H} NMR ($CDCl_3$, 20°C), δ: 28.1 (s). $^{13}$C{$^1$H} NMR ($CDCl_3$, -40°C), δ: 23.4 (s, Me), 26.2 (s, $C_6H_{11}$-P), 27.5 (broad s, $C_6H_{11}$-P), 29.0 (m, $C_6H_{11}$-P), 31.2 (broad s, $C_6H_{11}$-P), 91.3 (s, $C_5H_5$), 122.0 (s, *p*-$C_6H_5$-Pd), 125.3 (s, toluene), 125.9 (s, *m*-$C_6H_5$-Pd), 126.7 (s, m- $C_6H_5$-Pd), 128.4 (s, toluene), 129.2 (s, toluene), 134.7 (s, *o*-$C_6H_5$-Pd), 135.3 (s, *o*-$C_6H_5$-Pd), 137.2 (s, toluene); 140.1 (s, q- $C_6H_5$-Pd), 226.7 (t, $J_{C-P}$= 14.0 Hz, CO), 230.4 (d, $J_{C-P}$= 16.5 Hz, CO). IR (KBr), cm$^{-1}$: 2927 (vs), 2850 (m), 1856 (vs), 1783 (vs), 1744 (vs).

**2.4.8 Disproportionation of 2.5c.** (a) The gradual disappearance of **2.5c** (benzene or toluene solutions) and concomitant formation of **2.6c** and [$Pd_2(PPh_3)_2Ph_2(\mu$-$OH)_2$] was monitored by $^{31}$P NMR spectroscopy (see text).

(b) Solid [$HW(CO)_3Cp$] (16 mg, 0.048 mmol) was added to a stirred mixture of [$Pd_2(PPh_3)_2Ph_2(\mu$-$OH)_2$] (64 mg, 0.069 mmol) and toluene (4 mL) at –78°C. The mixture was warmed to room temperature and left for 24 h. The volatiles were vacuum distilled into a

small flask and mixed with *n*-butylbenzene (internal standard, 5 μl). The residue, after distillation, was stirred with hexane (4mL) containing *n*-butylbenzene (internal standard, 5 μl), and the pale yellow solution was decanted from the dark blue precipitate of **2.6c.** Analysis of the liquids by GLC indicated that biphenyl was formed in 73% yield.

**2.4.9 Preparation of [DW(CO)$_3$Cp].** A mixture of [HW(CO)$_3$Cp] (173 mg, 0.518 mmol), THF (5 mL) and K/Na alloy (0.2 mL) was stirred for 1 h. The resulting THF solution was filtered, treated with $CH_3COOD$ (0.5 mL), stirred for 10 min and evaporated in vacuum. The residue was washed with $D_2O$ (2 mL), dried under vacuum and dissolved in pentane (4 mL) The resulting solution was filtered through cotton and evaporated to give white crystalline DW(CO)$_3$Cp (130 mg, 95% D, $^1$HNMR).

**2.4.10 Preparation of [Pd$_2$(PPh$_3$)$_2$Ph$_2$(μ-OD)$_2$]** A mixture of [Pd$_2$(PPh$_3$)$_2$Ph$_2$(μ-OH)$_2$] (100 mg, 0.108 mmol), $CH_2Cl_2$ (5 mL) and $D_2O$ (1 mL) was stirred for 15 min. The organic layer was separated, filtered through cotton, and evaporated to give 94 mg of white [Pd$_2$(PPh$_3$)$_2$Ph$_2$(μ-OD)$_2$].

**2.4.11 Reaction of [Pd$_2$(PPh$_3$)$_2$Ph$_2$(μ-OH)$_2$] with Excess [HW(CO)$_3$Cp]. Isolation of [PhW(CO)$_3$Cp] and Determination of the Amount of Benzene.** A mixture of [Pd$_2$(PPh$_3$)$_2$Ph$_2$(μ-OH)$_2$] (41 mg, 44.4 mmol), [HW(CO)$_3$Cp] (51.8 mg, 155 mmol) and toluene (2 mL) was stirred for 1 h. The volatiles were vacuum distilled into a small flask, *n*-butylbenzene was added (internal standard) and the distillate was analyzed by GLC. The amount of benzene found was 36.9 mmol (83%). Trace amounts of cyclopentadiene, biphenyl

and bibenzyl were also found (GC-MS). The residue after distillation was extracted with pentane (3 x 1 mL) and the resulting yellow solution was chromatographed on silica column (100 x 10 mm, heptane-toluene). The first yellow fraction was collected and taken to dryness to give yellow crystalline [$PhW(CO)_3Cp^*$] (16.6 mg, 40.4 mmol, 91% ). $^1$HNMR ($CDCl_3$, 20°C), δ: 5.49 (s, 5H, $C_5H_5$), 7.02 (m, 3H, $C_6H_5$), 7.68 (m, 2H, $C_6H_5$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20°C),□ δ: 92.4 (s, $C_5H_5$), (124.4 s, q- $C_6H_5$), 124.5 (s, p- $C_6H_5$), 128.4 (s, *m*-$C_6H_5$), 147.3 (s, o- $C_6H_5$), 218.3 (s, $J_{W-C}$ = 158 Hz, CO), 228.2 (s, $J_{W-C}$ = 112 Hz, CO). IR (KBr), $cm^{-1}$: 2017 (m), 1915 (vs), 1896 (vs).

**2.4.12 Reaction of [$DW(CO)_3Cp$] with [$Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)_2$] and with [$Pd_2(PPh_3)_2Ph_2(\mu\text{-}OD)_2$].** These reactions were conducted in absolute toluene, as described above. The benzene-containing distillates were analyzed by GC-MS. The composition of $C_6H_5D/C_6H_6$ mixtures was calculated from the abundances of isotopic peaks in the electron impact mass spectra, using an ISONETA program.[32]

**2.4.13 Synthesis of [$(Ph_3P)_2Pd_2Cp_2Cr_2(\mu\text{-}CO)_4(\mu^3\text{-}CO)_2$] (2.6a).** Solid [$Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)_2$] (100 mg, 0.108 mmol) was added to a solution of [$HCrCO)_3Cp$] (73.3 mg, 0.363 mmol) in benzene (3 mL) and stirred for 30 min. The resulting green-gray solution was reduced in volume to *ca.* 1 mL, diluted with pentane (8 mL) and left overnight. The precipitated solid was washed with methanol (3 x 6 mL), pentane (3 x 6 mL), dried in vacuum and recrystallized from $CH_2Cl_2$/MeOH to give spectroscopically pure **2.6a** (96 mg, 0.0842 mmol, 78%). $^1$HNMR ($CDCl_3$, 20°C), □δ: 4.1 (s, 5H, $C_5H_5$), 7.38 (m, 9H, P- $C_6H_5$),

7.53 (m, 6H, P- $C_6H_5$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C), δ: 26.8 (s). IR (KBr), $cm^{-1}$: 1902 (m ), 1847 (s), 1824 (vs), 1789(s).

**2.4.14 Synthesis of $[Ph_3P)_2Pd_2Cp_2Mo_2(\mu\text{-}CO)_4(\mu^3\text{-}CO)_2]$ (2.6b).** Solid $HMoCO)_3Cp$ (155 mg, 0.63 mmol) was added to a suspension of $[Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)_2]$ (140 mg, 0.151 mmol) in benzene (4 mL) and stirred for 30 min. The resulting deep-green solution was diluted with MeOH (8 mL), stirred for 10 min and filtered. Green solid was washed with copious amount of acetone and dried to give analytically pure **2.6b** (155 mg, 0.126 mmol, 84%). Anal. Calcd for $C_{52}H_{40}Mo_2O_6P_2Pd_2$: C, 50.88; H, 3.28. Found: C, 50.73; H, 3.20. $^1H$ NMR ($CDCl_3$, 20°C), δ: 4.62 (s, 5H, $C_5H_5$), 7.35 (m, 9H, P-$C_6H_5$), 7.55 (m, 6H, P-$C_6H_5$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C), δ: 24.5 (s). IR (KBr), $cm^{-1}$: 1915( m ), 1852 (s), 1829 (vs), 1784 (s).

**2.4.15 Synthesis of $[Ph_3P)_2Pd_2Cp_2W_2(\mu\text{-}CO)_4(\mu^3\text{-}CO)_2]$ (2.6c).** A mixture of $[HW(CO)_3Cp]$ (240 mg, 0.72 mmol), $[Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)_2]$ (138.8 mg, 0.15 mmol) and benzene (10 mL) was stirred for 30 min, diluted with MeOH (10 mL) and left overnight. The precipitated dark blue crystals of **2.6c** were separated by decantation, washed with MeOH (3 x 10 mL), pentane (3 x 10 mL) and dried under vacuum. The yield of analytically pure **2.6c**, thus obtained, was 190 mg (0.135 mmol 90%). Anal. Calcd for $C_{52}H_{40}O_6P_2Pd_2W_2$: C, 44.5; H, 2.87. Found: C, 44.32; H, 2.87. $^1H$ NMR ($CDCl_3$, 20°C), □δ: 4.7 (s, 5H, $C_5H_5$), 7.35 (m, 9H, P-$C_6H_5$), 7.55 (m, 6H, P-$C_6H_5$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20°C), δ: 20.7 (s). IR (KBr), $cm^{-1}$: 1916 ( m ), 1853 (s), 1821 (vs), 1784 (s).

**2.4.16 Synthesis of $[Cy_3P)_2Pd_2Cp_2W_2(\mu\text{-}CO)_4(\mu^3\text{-}CO)_2]$ (2.6d).** A mixture of $[HW(CO)_3Cp]$ (80 mg, 0.239 mmol), $[Pd_2(PCy_3)_2Ph_2(\mu\text{-}OH)_2]$ (50 mg, 0.0519 mmol) and benzene (4 mL) was stirred for 30 min, diluted with MeOH (5 mL) and left overnight. The precipitated solid was separated by decantation, washed with MeOH (3 x 5 mL), pentane (2 x 5 mL) and dried in vacuum to give deep blue powder of analytically pure **2.6d** (71 mg, 0.049 mmol, 95%). Anal. Calcd. for $C_{52}H_{76}O_6P_2Pd_2W_2$: C, 43.38; H, 5.32. Found: C, 43.23; H, 4.95. $^1H$ NMR ($C_6D_6$, 20°C), δ: 1.2-2.2 (m, 33 H, $C_6H_{11}$-P), 5.18 (s, 5H, $C_5H_5$). $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$, 20°C), δ: 33.8 (s). IR (KBr), $cm^{-1}$: 2949 (s), 2824 (m), 1895 (m), 1820(vs), 1795 (vs).

**2.4.17 Synthesis of $[Ph_3P)_2Pd_2Cp^*_2W_2(\mu\text{-}CO)_4(\mu^3\text{-}CO)_2]$ (2.6e).** A mixture of $[HW(CO)_3Cp]$ * (179 mg, 0.443 mmol), $[Pd_2(PPh_3)_2Ph_2(\mu\text{-}OH)_2]$ (115.6 mg, 0.125 mmol) and benzene (4mL) was stirred for one hour and the resulting emerald - green solution was chromatographed on a silica column (250 x 25 mm, toluene - $CH_2Cl_2$ ). The first yellow-orange and emerald green bands were collected. The green fraction was taken to dryness to give 182mg of green-black **2.6e** (90% purity, according to $^{31}P$ NMR) The crude **2.6e** was dissolved in 2 mL of $CH_2Cl_2$, diluted with 10 mL of pentane and kept in a fridge (-17°C) overnight. Long green needles were separated, washed with a cold pentane (2 x 5 mL) and dried to give spectroscopically pure **2.6e** (115 mg, 0.0745 mmol, 60%). Anal. Calcd. for $C_{62}H_{60}O_6P_2Pd_2W_2$: C, 48.24; H, 3.92. Found : C, 49.04; H, 3.97. $^1H$ NMR ($CDCl_3$, 20°C), δ: 1.4 (s, 15H, Me), 7.3 - 7.7 (m, 15H, $C_6H_5$-P). $^{31}P\{^1H\}$ NMR($CDCl_3$, 20°C), δ: 15.1(s).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 20°C), δ: 9.8 (s, Me); 100.5 (s, Cp*), 128.0 (vt., $J_{C-P}$= 4.8 Hz, m-$C_6H_5$-P), 129.2 (s, p- $C_6H_5$-P), 134.3 (vt., $J_{C-P}$= 7.2 Hz, *o*-$C_6H_5$-P), 135.6 (vt., $J_{C-P}$ = 16.1 Hz, *q*-$C_6H_5$-P), 236.1 (s, CO). IR (KBr), $cm^{-1}$: 1887 (m), 1836 (sh), 1811 (sh), 1795 (vs). The yellow-orange fraction was evaporated and chromatographed on a silica column (200 x 25mm, heptane - toluene ) The first yellow fraction was collected and taken to dryness to give [$PhW(CO)_3Cp^*$] (43.2mg, 0.09mmol, 72%) The compound was recrystallized from pentane for elemental analysis. Anal. Calcd. for $C_{19}H_{20}O_3W$: C, 47.52; H, 4.20. Found: C, 47.78; H, 3.85. $^1H$ NMR ($CDCl_3$, 20°C), δ: 1.9 (s, 15H, Me), 7.05 (m, 3H, $C_6H_5$), 7.66 (m, 2H, $C_6H_5$). $^{13}C\{^1H\}$ NMR($CDCl_3$, 20°C), δ: 10.6 (s, Me), 104.5 (s, Cp*), 124.6 (s, p- $C_6H_5$), 128.5 (s, m- $C_6H_5$), 136.8 (s, q- $C_6H_5$), 145.8 (s, *o*-$C_6H_5$), 222.4 (s, CO), 233.1 (s, CO). IR (KBr), $cm^{-1}$: 1999 (s), 1912 (s), 1892 (vs).

**2.4.18 Synthesis of $[Ph_3P)_2Pd_2Cp_2MoW(\mu\text{-}CO)_4(\mu^3\text{-}CO)_2]$ (2.7).** Solid [$HW(CO)_3Cp$] (65 mg, 0.195 mmol) was added to a stirred solution of **2.5b** (101 mg, 0.0875 mmol) in benzene (20 mL), causing the color to change first to brown then to green. The mixture was stirred for 1 h and chromatographed on a silica column (25 x 400 mm, toluene - heptane). The first pink-brown band was discarded. The following bright green, green-blue and violet bands were collected. The green-blue band was evaporated under vacuum to give 57 mg (43 mmol, 49%) of **2.7** as a green solid. Anal. Calcd for $C_{52}H_{40}MoO_6P_2Pd_2W$: C, 47.5; H, 3.1. Found: C, 47.4; H, 2.9. $^1H$ NMR ($CDCl_3$, 20°C), □δ: 4.64 (s, 5H, $C_5H_5$-Mo), 4.69 (s, 5H, $C_5H_5$-W), 7.35 (m, 18H, $C_6H_5$-P), 7.55 (m, 12H, $C_6H_5$-P). $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$), δ:

22.9 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20°C), δ: 87.3 (s, $C_5H_5$-Mo), 90.9 (s, $C_5H_5$-W), 128.1 (vt., $J_{C\text{-}P}$ = 4.5 Hz, *m*-$C_6H_5$-P), 129.8 (s, *p*-$C_6H_5$-P), 134.3 (vt., $J_{C\text{-}P}$ = 7.0 Hz, *o*-$C_6H_5$-P) 134.4 (vt., $J_{C\text{-}P}$ = 17.7 Hz, *q*-$C_6H_5$-P), 228.6 (s, MoCO), 240.3 (s, WCO). IR (KBr), $cm^{-1}$: 1916 (m), 1854 (s), 1825 (vs), 1781 (s). The bright-green and violet fractions gave **2.6b** and **2.6a** (identified by $^{31}P$ NMR) correspondingly. The yields were not determined.

**2.4.19 Synthesis of $[Ph_3P)_2Pd_2Cp_2CrW(\mu\text{-}CO)_4(\mu^3\text{-}CO)_2]$ (2.8).** A mixture of **2.6a** (105 mg, 0.0893 mmol), $[HW(CO)_3Cp]$ (76.5 mg, 0.229 mmol) and benzene (15 mL) was stirred at room temperature (the reaction mixture was monitored by $^{31}P$ NMR). After 70 hrs, when the solution contained **2.8** and **2.6c** in 3:1 ratio and only traces of **2.6a**, the mixture was chromatographed on silica column (250 x 25 mm, $CH_2Cl_2$ - toluene). The first pink-brown band was discarded; the following green and violet fractions were collected. The green fraction was taken to dryness to give analytically pure **2.8** (39.5 mg, 0.030 mmol, 34%). Anal. Calcd for $C_{52}H_{40}CrO_6P_2Pd_2W$: C, 49.1; H, 3.2. Found: C, 48.9; H, 2.9. $^{1}H$ NMR ($CDCl_3$, 20°C), □δ: 3.96 (s, 5H, $C_5H_5$-Cr), 4.69 (s, 5H, $C_5H_5$-W), 7.35 (m, 18H, $C_6H_5$-P), 7.55 (m, 12H, $C_6H_5$-P). $^{31}P\{^{1}H\}$ NMR ($C_6H_6$, 20°C), δ: 24.2 (s). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 20°C), δ: 86.8 (s, $C_5H_5$-Cr), 89.8 (s, $C_5H_5$-W), 128.2 (vt., $J_{C\text{-}P}$ = 4.8 Hz, *m*-$C_6H_5$-P), 129.9 (s, *p*-$C_6H_5$-P), 134.26 (vt., $J_{C\text{-}P}$ = 7.1 Hz, *o*-$C_6H_5$-P); 134.32 (vt., $J_{C\text{-}P}$ = 17.5 Hz, q- $C_6H_5$-P), 227.6 (s, CrCO), 251.9 (s, WCO). IR (KBr), $cm^{-1}$: 1922 (m), 1849 (vs), 1822 (s), 1792 (s). The violet fraction was taken to dryness to give 9.8mg (0.0068 mmol, 8%) of **2.6c**.

**2.4.20 Single-Crystal X-ray Diffraction study of 2.5a·MeOH.** Crystal data and refinement parameters are summarized in Table 2.3. Well shaped transparent orange crystals of the complex were obtained by slow diffusion of pentane into a solution of **2.5a** in dichloromethane containing traces of methanol, over 1 week at –17°C. One of the crystals was mounted on a glass fiber. The data were collected on a Siemens SMART CCD diffractometer. During the data collection standards were measured after every 150 reflections. No crystal decay was noticed. A total of 17590 reflections were collected. The unique set contained 6379 reflections. Using the criterion $I > 2.5\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation derived from the counting statistics, 5328 reflections were used. The data were corrected for Lorentz and polarization effects.[32] No absorption correction was made. The structure was solved by direct methods. All atoms were refined anisotropically, except for hydrogens. The refinement was made on *F*. The hydrogen atoms were calculated. The final cycle of full matrix least squares refinement was based on 5328 observed reflections and 605 variable parameters. Weights based on calculated statistics were used. The maximum and the minimum peaks on the final difference Fourier map corresponded to +0.820 and –0.720 e/Å$^3$ respectively. All the calculations were performed using the NRCWAX crystallographic software package.[33]

**Table 2.1**. Crystallographic data for $[(Ph_3P)_2Pd(\mu\text{-}OH)(\mu\text{-}CO)(\mu^3\text{-}CO)CrCp]\cdot MeOH$

| | |
|---|---|
| Formula | $C_{57}H_{46}CrO_5P_2Pd_2$ |
| F.w. | 1137.72 |
| Cryst. shape | plate |
| Cryst. dimens., mm | 0.3 x 0.2 x 0.1 |
| Cryst. system | monoclinic |
| Lattice parameters | a = 32.9701(4) Å<br>b = 10.6761(1) Å<br>c = 28.9941(2) Å<br>β = 108.405(1)° |
| Space group | C2 / c |
| Z | 8 |
| V | 9683.71(16) $Å^3$ |
| $d_{calc}$ | 1.561 $g/cm^3$ |
| T, K | 123 |
| Radiation (λ) | Mo $K_{\alpha 1}$ (0.70930 Å) |
| μ | 1.03 $mm^{-1}$ |
| R ($R_w$)[a] | 6.1% (7.8%) |

[a] $R = \Sigma(F_0 - F_c)/\Sigma(F_0)$; $R_w = [\Sigma(w(F_0 - F_c)^2/\Sigma(wF_0^2)]^{1/2}$

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# Chapter 3.

## *Reactions of $[Rh(PPh_3)_3Cl]$ and trans-$[Rh(CO)(PPh_3)_2Cl]$ with the sodium salt of (1S,2R,5S)-menthol*

## 3.1 Introduction

$[Rh(PPh_3)_3Cl]$ (**3.1**) has been shown to react with KOH to afford the dinuclear di-μ-hydroxocomplex, $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2]$.[1] The attempted preparation of the corresponding alkoxo complexes by the analogous reaction using NaOR instead of KOH has not been reported. Transition metal alkoxo complexes are often less stable than their hydroxo analogs. This is usually a consequence of facile β-H elimination leading to formation of the corresponding hydrido complexes and the appropriate aldehydes or ketones (Scheme 3.1).[2,3]

*Scheme 3.1*

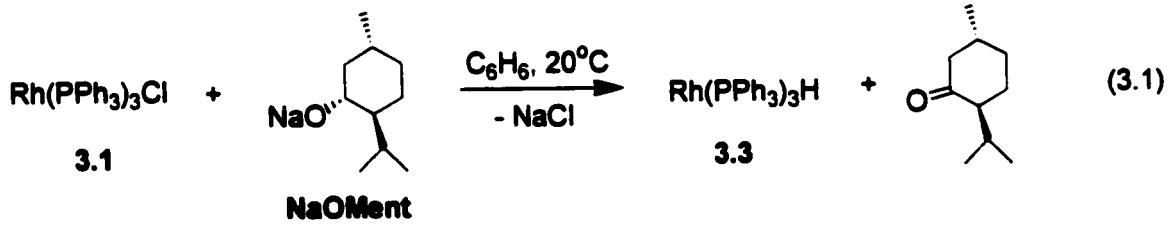

This chapter describes the reactivity of $[Rh(PPh_3)_3Cl]$ (**3.1**) and *trans*-$[Rh(CO)(PPh_3)_2Cl]$ (**3.2**) towards the sodium salt of (*1S,2R,5S*)-menthol (**NaOMent**). Both chlorides are 16e rhodium complexes possessing a vacant orbital and therefore their alkoxo derivatives can in general undergo β-H elimination. The important difference between the two complexes is the presence of carbonyl in **3.2** and its absence in **3.1**. Being a strong π-acceptor the coordinated CO decreases the electron density on Rh and thus can retard the decomposition of alkoxo derivatives of **3.2** via β-elimination pathway. Interestingly, since the discovery of chlorobis(triphenylphosphine)carbonyl rhodium[4] in 1956 and chlorotris(triphenylphosphine) rhodium[5] in 1966, there have been no reports describing the reactions of **3.1** and **3.2** with NaOR (R = alkyl),[6-8] although the reactivity of these complexes towards various compounds has been studied quite extensively.[10,11] Menthol was chosen as an inexpensive chiral alcohol, readily available in enantiomerically pure form and is therefore very attractive for the preparation of chiral metallocomplexes. Chiral alkoxo derivatives of

Al, Mg and early transition metals are widely used as catalysts for many important enantioselective organic transformations.[12] It was hoped therefore that chiral rhodium alkoxo complexes, if isolable might also show interesting reactivity. At the commencement of this project no chiral rhodium alkoxo complexes had been reported.

## 3.2 Results and Discussion

### 3.2.1 Reaction of $[Rh(PPh_3)_3Cl]$ with the Sodium Salt of (*1S, 2R, 5S*)-Menthol.

Treatment of a suspension of **3.1** in benzene with 1 equiv. of **NaOMent** leads to formation of the known rhodium hydrido complex **3.3** [13] (eq 3.2). According to the $^{31}P$ NMR spectra of the reaction mixture, the conversion of $[Rh(PPh_3)_3Cl]$ to $[Rh(PPh_3)_3H]$ was complete within 10 min at room temperature, and the hydride **3.3** was the only metallorganic product.




(3.1)

The reaction probably occurs *via* intermediate formation of a rhodium menthyloxo complex, which decomposes by the mechanism outlined in Scheme 3.1 to give the hydride **3.3** and menthone (detected in the reaction mixture by GC and identified by GC-Ms). The complex **3.3** was isolated in high yield and characterized by elemental analysis and NMR spectroscopy. The $^1H$ NMR spectrum of **3.3** shows a broad resonance with the value of chemical shift (-7.9 ppm) typical for late transition metal hydrides. The signal turned to a sharp doublet ($J_{H\text{-}P}$ = 8 Hz) when the spectrum was recorded with $^{31}P$ broad band decoupling,

indicating that the line broadening in the $^{1}H$ NMR spectrum was the result of unresolved $^{1}H$-$^{31}P$ coupling.

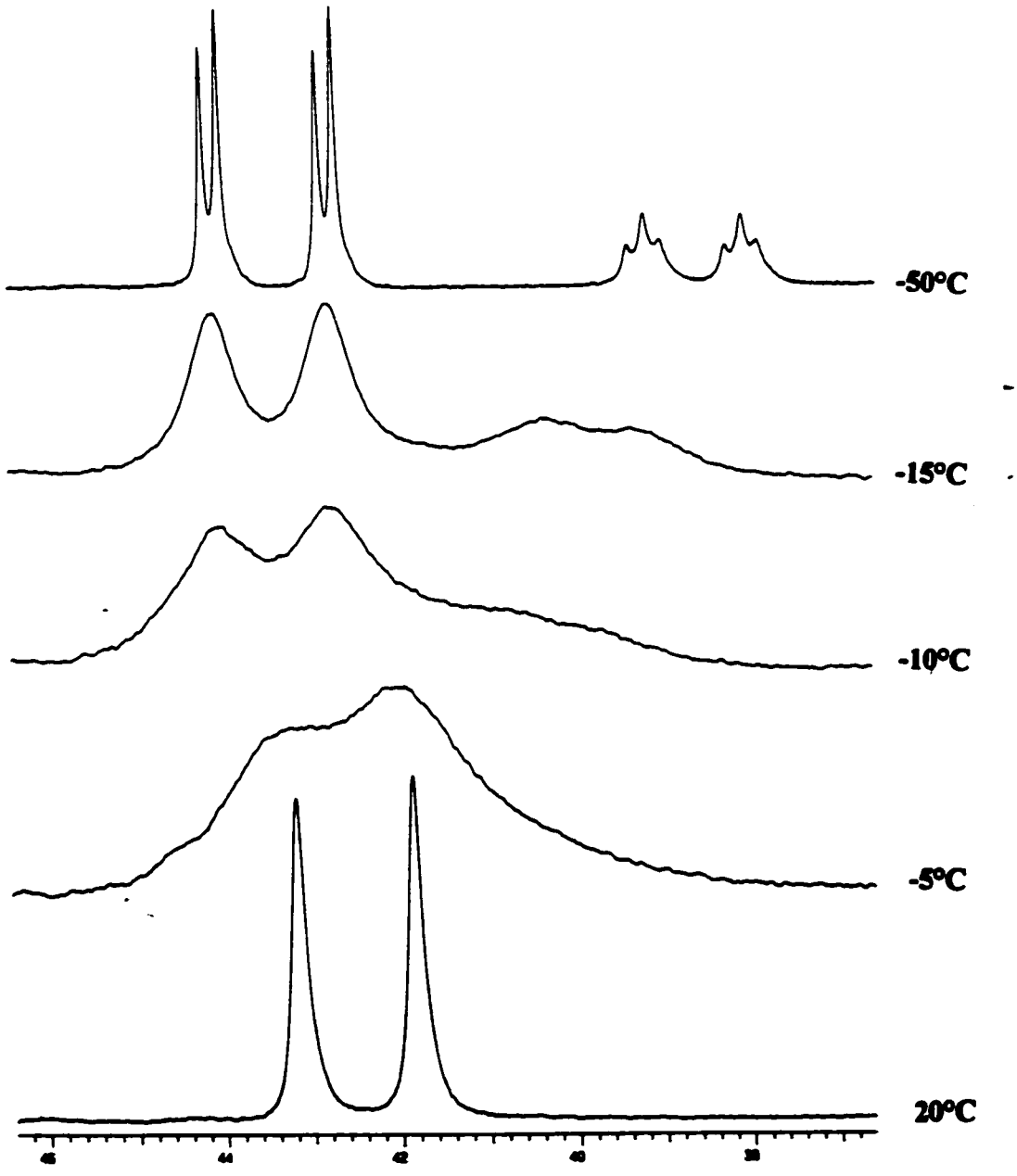
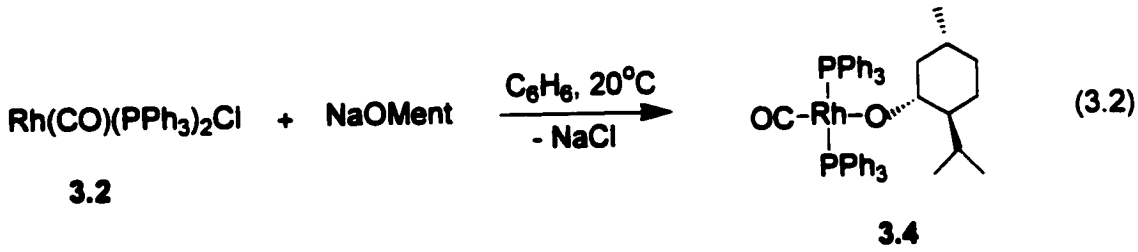



**Figure 3.1** 121 MHz VT $^{31}P\{^{1}H\}$ NMR spectra of **3.3** in toluene-*d8*.

The VT $^{31}P\{^{1}H\}$ NMR spectra of **3.3** (see Fig 3.1) clearly demonstrate that at room temperature all three $PPh_3$ ligands of the complex are equivalent as the result of fast (on the NMR time scale) positional exchange. The exchange can be "frozen" as indicated by a doublet of doublets and a doublet of triplets in a 2 : 1 integral ratio observed in the spectra at temperatures below –50°C, a pattern typical for square planar rhodium complexes with three phosphine ligands. The value of P-Rh coupling constants measured for the doublet of triplets ($J_{P\text{-}Rh}$ = 135 Hz) is significantly lower than that of the doublet of doublets ($J_{P\text{-}Rh}$ = 159 Hz) presumably due to high trans-influence of the hydride *vs.* $PPh_3$ ligands in complex **3.3**.

### 3.2.2 Reaction of [Rh(CO)(PPh$_3$)$_3$Cl] with the Sodium Salt of (1S, 2R, 5S)-Menthol. Preparation and Characterization of [Rh(CO)(PPh$_3$)$_2$(OMent)] (3.4).

**NaOMent** reacts readily with **3.2** in benzene solution at room temperature to afford the rhodium alkoxo complex **3.4** (eq. 3.2) as the sole metallorganic product. The reaction is complete within 10 min ($^{31}P$ NMR control).




**3.2** **3.4** (3.2)

The complex was isolated in high yield as a yellow crystalline solid, that can be stored under nitrogen for several weeks, or in air for several hours without noticeable

decomposition. In solution, however, **3.4** slowly decomposes (half-life *ca.* 36 h, $C_6D_6$, 20°C) even in the absence of air to give a mixture of unidentified products.

The $^{31}P\{^1H\}$ NMR spectrum of **3.4** recorded at room temperature exhibits a sharp doublet at δ 22.5 ($J_{P\text{-}Rh}$ = 147 Hz) indicating that the two $PPh_3$ ligands of the complex are equivalent due to fast (on the NMR time scale) rotation of OMent fragment around the O-Rh and/or the O-C bond. At low temperature (-80 C°) the rotation slows down and the phosphines become nonequivalent, giving rise to a well resolved ABX pattern ($\delta_A$ = 19.4, $\delta_B$ = 21.3, $J_{A\text{-}B}$ = 55 Hz, $J_{A\text{-}X}$ =143 Hz, $J_{B\text{-}X}$ = 146 Hz).

The solid state structure of **3.4** was determined by a single crystal X-ray diffraction study. An ORTEP plot of the molecule of **3.4** is presented in Fig. 3.2, selected bond distances and angles are given in Table 3.1. The central Rh atom of the complex possesses a slightly distorted square planar coordination environment with the *trans* angles P(1)-Rh-P(2) = 169.32(4)° and O(2)-Rh-C(19) = 173.2(1)°. The menthyloxy fragment is *trans* to CO ligand and the Rh-O(2) bond length is 2.027 Å. The short C-O distance is a commonly observed feature of late transition metal alkoxides and aryloxides.[15] In accordance with this observation, the C(20)-O(2) bond of the menthyloxy ligand (1.398 Å) is significantly shorter than the mean value of the corresponding bond in the free alcohols (1.435 Å).[16] The values of other bond lengths and angles in the molecule of **3.4** are unexceptional.

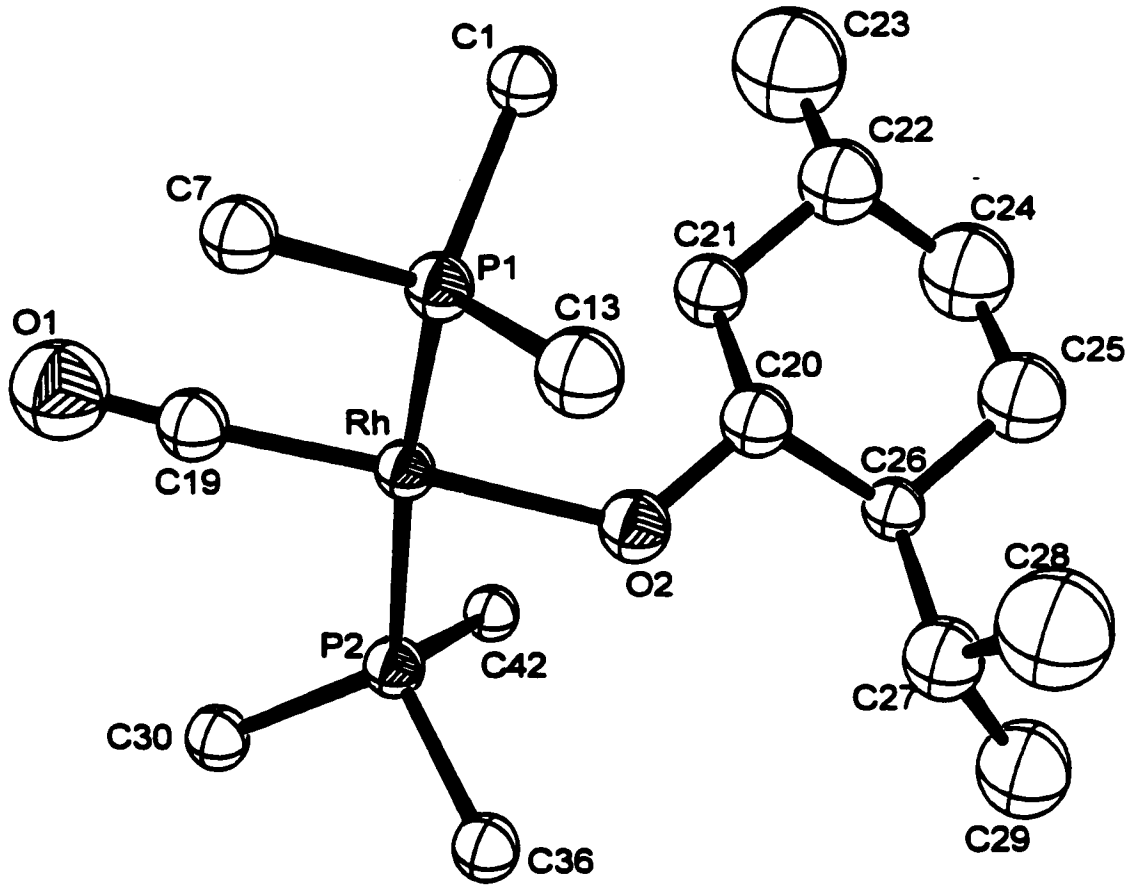



**Figure 3.2.** ORTEP drawing for **3.4** with adopted numbering scheme. Thermal ellipsoids are depicted at 50% probability. Only the *ipso* carbon atoms of $PPh_3$ are shown. Hydrogen atoms are omitted for clarity.

**Table 3.2.** Selected Bond Distances (Å) and Angles (deg) for $[Rh(CO)(Ph_3P)_2OMent]$ (3.4)

| | | | |
|---|---|---|---|
| Rh – P(1) | 2.320(1) | P(1) – Rh – O(2) | 96.94(8) |
| Rh – P(2) | 2.332(1) | P(1) – Rh – C(19) | 89.3(1) |
| Rh – O(2) | 2.027(2) | P(2) – Rh – O(2) | 77.91(8) |
| Rh – C(19) | 1.806(4) | P(2) – Rh – C(19) | 96.46(1) |
| C(19) – O(1) | 1.148(4) | Rh – O(2) – C(20) | 126.7(2) |
| O(2) – C(20) | 1.398(4) | Rh – C(19) – O(1) | 176.1(4) |

## 3.3 Conclusions.

The results presented in this chapter demonstrate that the stability of Rh(I) menthyloxides depends strongly on the nature of ligands attached to the metal. Menthyloxytris(triphenylphosphine) rhodium(I) could not be prepared by the reaction of $[Rh(PPh_3)_3Cl]$ and NaOMent, apparently due to the fast decomposition leading to the formation of $[Rh(PPh_3)_3H]$ and menthone. In a contrast, menthyloxybis(triphenylphosphine) carbonyl rhodium(I) is indefinitely stable in the solid state and only slowly decomposes in solution. Complex **3.4** is the first example of structurally characterized chiral phosphine rhodium alkoxo complex.

## 3.4 Experimental section

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use. All chemicals were purchased from Aldrich and were used as received. The following instruments were used: Varian XL 300 ($^1$H-, $^{13}$C- and $^{31}$P NMR), Bomem MB-100 (FT-IR) Hewlett-Packard 5890 Series II-Kratos Concept II (GC-MS) and Perkin-Elmer 2400 Series II (combustion microanalysis).

**3.4.1 Synthesis of the Sodium Salt of (*1S, 2R, 5S*)-Menthol (NaOMent)** Solid (*1S, 2R, 5S*)-menthol (3.31 g, 21.2 mmol) was added to a stirred suspension of $NaNH_2$ (2.5 g) in THF (10 mL). The mixture was heated to reflux and then cooled to rt. Unreacted $NaNH_2$ was filtered and washed with THF (2 x 3 mL). The volume of the combined filtrates was adjusted to 20.0 mL to give 1.06 M solution of NaOMent. The solution was stored in a Schlenk tube equipped with a Young valve under $N_2$ in a freezer.

**3.4.2 Synthesis of $[Rh(PPh_3)_3H]$** A stirred suspension of $[Rh(PPh_3)_3Cl]$ (260 mg, 0.281 mmol) was treated with NaOMent (0.290 mmol, 1.06 M in THF). The resulting mixture was stirred at rt. for 30 min. evaporated and dried under vacuum. The residue was stirred with benzene (8 mL) and the obtained orange solution was filtered from a white precipitate. The filtrate was diluted with heptane (8 mL), reduced in volume to *c.a.* 10 mL and left overnight. The precipitated orange crystals were separated by decantation, washed with pentane (2 x 5 mL) and dried in vacuum to give 198 mg (0.22 mmol, 79 %) of analytically pure product. Anal. Calcd for $C_{54}H_{46}P_3Rh$: C, 72.81; H, 5.20. Found: C, 72.45; H, 5.12. $^{31}P\{^1H\}$ NMR ($C_6D_6$, 20°C), δ: 42.3 (d, $J_{P\text{-}Rh}$ = 162 Hz). $^1H$ NMR ($C_6D_6$, 20°C),δ: -7.9 (b. s, 1H), 6.8 (m, 27 H), 7.6 (m, 18 H). IR (KBr, $\square_{Rh\text{-}H}$): 1884 $cm^{-1}$ (w).

**3.4.3 Synthesis of $[Rh(CO)(PPh_3)_2(OMent)]$** A mixture of $[Rh(CO)(PPh_3)_2Cl]$ (162 mg, 0.234 mmol), benzene (6 mL) and (*1S,2R,5S*)-$NaOC_{10}H_{19}$ (0.265 mmol, 1.06 M in THF) was stirred for 30 min at room temperature and the resulting yellow turbid solution was evaporated under vacuum. The residue was treated with benzene (2 mL) and heptane (4 mL), the resulting solution was filtered from the white precipitate, diluted with heptane (4 mL) and

kept in a freezer (-17°C) overnight. The precipitated yellow crystals were separated by decantation, washed with pentane (2 x 5 mL) and dried in vacuum to give 142 mg (0.175 mmol, 75 %) of analytically pure product. Anal. Calcd for $C_{47}H_{49}O_2P_2Rh$: C, 69.62, H, 6.09. Found: C, 69.33, H, 6.0. $^{31}P\{^1H\}$ NMR ($C_6D_6$, 20°C), δ: 24.5 (d, $J_{P\text{-}Rh}$ = 147 Hz). $^1H$ NMR ($C_6D_6$, 20°C), δ: 0.75 (d, $J$ = 6.5 Hz, 3H), 0.8 (m, 2H), 0.85 (d, $J$ = 7 Hz, 3H), 1.15 (m, 1H), 1.2 (d, $J$ = 7 Hz, 3H), 1.4 (m, 2H), 1.55 (m, 2H), 1.8 (m, 1H), 3.0 (m, 1H), 7.2 (m, 18 H), 8.2 (m, 12 H). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 20°C), δ: 18.0 (s, Me), 22.8 (s, Me), 23.0 (s, Me), 23.6 (s, $CH_2$), 25.1 (s, $CH_2$), 32.1 (s, $CH_2$), 35.4 (s, CH), 53.2 (s, CH), 54.0 (s, CH), 76.9 (s, CH), 128.3 (vt, $J_{C\text{-}P}$ = 10 Hz, Ph), 129.8 (s, Ph), 134.6 (vt, $J_{C\text{-}P}$ = 42 Hz, Ph), 135.1 (vt,, $J_{C\text{-}P}$ = 13 Hz, Ph), 190.5 (dt, $J_{C\text{-}Rh}$ = 62 Hz, $J_{C\text{-}P}$ = 18.5 Hz, CO). IR (KBr, $\nu_{CO}$): 1945 $cm^{-1}$.

### 3.4.4 Single-Crystal X-ray Diffraction Study of [Rh(CO)(PPh$_3$)$_2$OMent]

Crystal data and refinement parameters are summarized in Table 3.2. Well-shaped transparent yellow crystals of **3.4** were obtained by layering a concentrated solution of the complex in benzene with heptane. One of the crystals was mounted on a glass fiber. The data were collected at –110°C with Mo Kα radiation using a graphite monochromator. During the data collection standards were measured after every 150 reflections. No crystal decay was noticed. A total of 44624 reflections were collected. The unique set contained 9761 reflections. Using the criterion $I > 2.5\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation derived from the counting statistics, 8011 reflections were used. The data were corrected for Lorenz and polarization effects.[17] No absorption correction was made. The structure was solved by direct methods. All atoms were refined anisotropically, except for hydrogens. The refinement was made on $F$. The hydrogen atoms were calculated. The final cycle of full matrix least squares

refinement was based on 8011 observed reflections and 469 variable parameters. Weights based on calculated statistics were used. The maximum and the minimum peaks on the final difference Fourier map corresponded to +0.370 and –0.330 e/Å$^3$ respectively. All the calculations were performed using the NRCWAX crystallographic software package.[18]

**Table 3.2. Crystallographic data for [Rh(CO)($Ph_3P$)$_2$OMent] (3.4)**

| | |
|---|---|
| Formula | $C_{47}H_{49}O_2P_2Rh$ |
| F.w. | 810.75 |
| Cryst. shape | prism |
| Cryst. dimens., mm | 0.2 x 0.2 x 0.2 |
| Cryst. system | orthorhombic |
| Lattice parameters | a = 12.1134(3) Å |
| Space group | P 212121 |
| Z | 4 |
| V | 4075.72(14) Å$^3$ |
| $d_{calc}$ | 1.321 g/cm$^3$ |
| T, K | 123 |
| Radiation (λ) | Mo $K_{\alpha 1}$ (0.70930 Å) |
| μ | 0.53 mm$^{-1}$ |
| R ($R_w$)[a] | 3.5% (3.6%) |

[a] $R = \Sigma(F_0 - F_c)/\Sigma(F_0)$; $R_w = [\Sigma(w(F_0 - F_c)^2/\Sigma(wF_0^2)]^{1/2}$

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# Chapter 4.

## *Phosphine Rhodium Aryloxides.*

## 4.1 Introduction

As was shown in the previous chapter, the rhodium alkoxo complexes readily undergo β-hydrogen elimination, but can be stabilized by introducing the strong π-acceptor ligand, CO, into the coordination sphere of the metal. Another approach for the preparation of stable $[Rh(OR)L_n]$ is to use phenols instead of alcohols. Phenols lack a hydrogen substituent at the α-carbon and therefore, phenoxo complexes cannot decompose *via* a β-hydrogen elimination pathway (see Scheme 3.1, page 42).

The first phosphine rhodium aryloxide was described in 1968.[1] The complex was prepared by the treatment of $[MeRh(PPh_3)_3]$ or $[PhRh(PPh_3)_3]$ with phenol and was formulated as $[Rh(PPh_3)_3OPh]$. This reaction was later reinvestigated and the product was shown to be $[Rh(PPh_3)_2(\pi\text{-}PhO)\cdot 2PhOH]$, containing a π-coordinated phenoxo ligand.[2] In the following two decades a significant number of late transition metal aryloxides were described,[3,24] including Rh-complexes containing CO,[4] cyclooctadiene,[5] and Cp* [6] as stabilizing ligands. However, phosphine rhodium aryloxides are still relatively rare.[7,8]

This chapter describes the preparation and characterization of triphenylphosphine-aryloxo rhodium complexes with σ- and π- coordinated OAr ligands, their behavior in solution and reactivity toward CO, $H_2$, water and methanol.

## 4.2 Results and Discussion.

### 4.2.1 Synthesis and Characterization of $[(Ph_3P)_3RhOAr]$ (4.1a-d). X-ray Structure of 4.1a. Dissociation of 4.1a-d in a Solution

Treatment of Wilkinson's catalyst in toluene with a slight excess of NaOAr for 1h results in clean formation of complexes **4.1a-d** (eq. 4.1).

$$(Ph_3P)_3RhCl + NaOAr \xrightarrow[-NaCl]{\text{toluene, 20°C}} (Ph_3P)_3RhOAr \quad (4.1)$$

**4.1a-d**

a, Ar = Ph
b, Ar = 4-$MeC_6H_4$
c, Ar = 2-Me $C_6H_4$
d, Ar = 4-$MeOC_6H_4$

Slow diffusion of pentane vapors into the corresponding filtered and concentrated reaction solution afforded dark red crystals of **4.1a**. The complex was isolated in 91% yield and characterized by elemental analysis, $^{31}P$ NMR and IR spectroscopy. The complex is moderately air sensitive and should be stored under nitrogen. However, it can be handled in air for a few minutes without significant decomposition. The solid state structure of **4.1a** was determined by X-ray diffraction. An ORTEP plot of the complex is shown in Figure 4.1 and selected bond distances and angles are presented in Table 4.1. The geometry around the Rh atom is substantially distorted from a square planar arrangement (*trans*- P-Rh-P and *trans*-P-Rh-O angles are *ca* 152° and 164° respectively) with the distortion presumably due to the steric bulk of the $PPh_3$ ligands. The phenyl C-O bond of the phenoxide ligand (1.318 Å) is significantly shorter than that of free phenol (1.376Å), and this is typical for late transition metal aryloxides.[9]

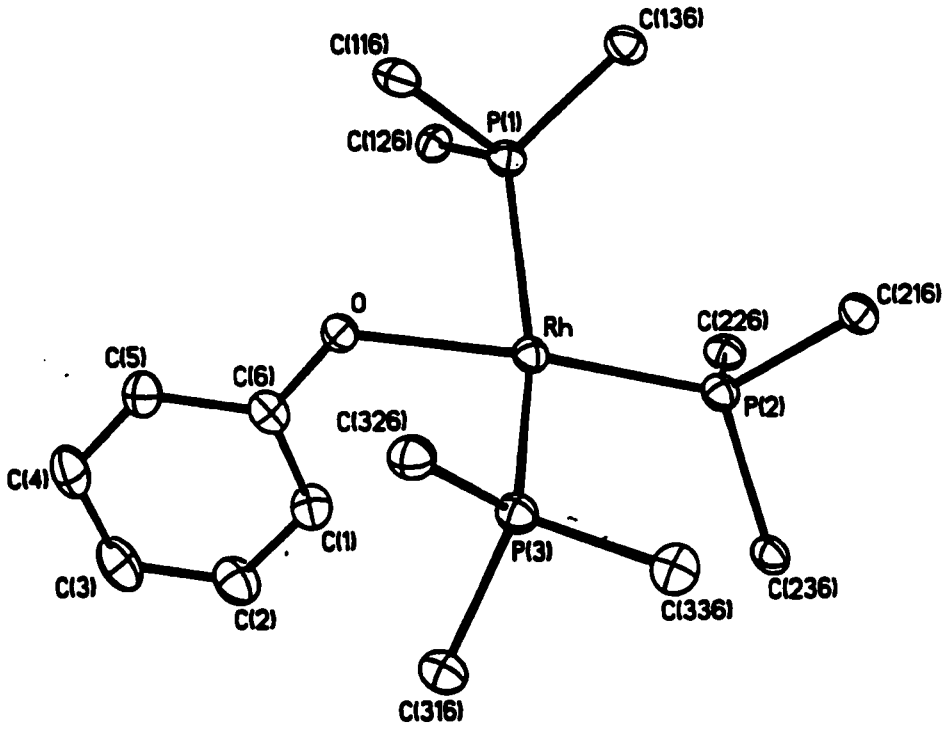



**Figure 4.1.** Perspective drawing for **4.1a** with adopted numbering scheme. Thermal ellipsoids are depicted at 30% probability. Only the *ipso* carbon atoms of $PPh_3$ are shown. Hydrogen atoms are omitted for clarity.

**Table 4.1. Selected Bond Distances (Å) and Angles (deg) for [(Rh(PPh$_3$)$_3$OPh]**

| | | | |
|---|---|---|---|
| P(1) - Rh | 2.348(1) | C(4) – C(5) | 1.381(8) |
| P(2) – Rh | 2.228(1) | C(5) – C(6) | 1.413(7) |
| P(3) – Rh | 2.312(1) | P(1) – Rh – P(2) | 99.07(4) |
| O – Rh | 2.091(3) | P(2) –Rh – P(3) | 99.25(4) |
| O – C(6) | 1.315(6) | P(1) – Rh – O | 79.24(9) |
| C(6) – C(1) | 1.395(7) | P(3) – Rh – O | 88.22(9) |
| C(1) – C(2) | 1.391(8) | P(1) – Rh – P(3) | 152.26(4) |
| C(2) – C(3) | 1.378(8) | O – Rh – P(2) | 164.8(1) |
| C(3) – C(4) | 1.387(8) | C(6) – O - Rh | 123.0(3) |

Complexes **4.1b-d** were not isolated in analytically pure form, but were characterized

by $^{31}P\{^1H\}$ NMR spectra in solution. The data are given in Table 4.2.

**Table 4.2.** $^{31}P\{^1H\}$ NMR data for $[Rh(PPh_3)_3OAr]$ **(4.1a-d).**

| Ar (compound) | Doublet of doublets | | $J_{P-P}$ (Hz) | Doublet of triplets | |
|---|---|---|---|---|---|
| | δ (ppm) | $J_{P-Rh}$ (Hz) | | δ (ppm) | $J_{P-Rh}$ (Hz) |
| Ph (**4.1a**) | 30 | 156 | 39 | 48 | 173 |
| 4-$MeC_6H_4$ (**4.1b**) | 29 | 157 | 40 | 49 | 172 |
| 2-$MeC_6H_4$ (**4.1c**) | 31 | 156 | 40 | 50 | 171 |
| 2-$MeOC_6H_4$ (**4.1d**) | 29 | 158 | 36 | 49 | 172 |

The $^{31}P\{^1H\}$ NMR spectra of **4.1a-d** show a doublet of doublets and doublet of triplets in a 2:1 integral ratio, a pattern characteristic of square planar rhodium complexes with three phosphine ligands. The spectra also contain a singlet at -5 ppm due to free $PPh_3$ and a doublet, which was assigned to rhodium complexes with π-coordinated aryloxide, **4.2a-d** (see below) in a 1:2 ratio. When triphenylphosphine was added to the solution, the intensity of the doublet decreased with an increase of the intensity of signals of **4.1a-d**. This observation suggests that complexes **4.2a-d** are formed by partial dissociation of **4.1a-d** in solution (eq. 4.2).

$$\underset{\textbf{4.1a-d}}{(Ph_3P)_3RhOAr} \rightleftharpoons \underset{\textbf{4.2a-d}}{(Ph_3P)_2Rh(\pi\text{-}ArO)} + PPh_3 \qquad (4.2)$$

### 4.2.2. Synthesis and Characterization of $[Rh(Ph_3P)_2(\pi\text{-}ArO)]$ (4.2a-d).

The formulation of **4.2a-d** as complexes with two $PPh_3$ per rhodium atom and π-coordinated OAr-ligands was established by their preparation from $[Rh(PPh_3)_2Cl]_2$ and the appropriate NaOAr (eq. 4.3).

$$[(Ph_3P)_2Rh(\mu\text{-}Cl)]_2 + 2NaOAr \xrightarrow[-\,2NaCl]{CH_2Cl_2,\ 20^\circ} \underset{\textbf{4.2a-d}}{(Ph_3P)_2Rh(\pi\text{-}ArO)} \qquad (4.3)$$

The $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures showed signals, which were almost identical to those assigned to **4.2 a-d** formed by dissociation of **4.1a-d** (eq 4.2). The complexes were isolated as very air sensitive amorphous light brown solids and characterized by $^{31}P\{^1H\}$ and $^1H$ NMR spectra. The $^{31}P\{^1H\}$ NMR data are given in Table **4.3**.

**Table 4.3.** $^{31}P\{^1H\}$ NMR data for $[Rh(PPh_3)_2(\pi\text{-}OAr)]$ **(4.1a-d).** [a]

| Ar (compound) | δ (ppm) | $J_{P\text{-}Rh}$ (Hz) | Ar (compound) | δ (ppm) | $J_{P\text{-}Rh}$ (Hz) |
|---|---|---|---|---|---|
| Ph (**4.2a**) | 48 | 212 | 2-$MeC_6H_4$ (**4.2c**) | 49 | 216 |
| 4-$MeC_6H_4$ (**4.2b**) | 47 | 210 | 2-$MeOC_6H_4$ (**4.2d**) | 46 | 214 |

[a] Recorded at 121.4 MHz in toluene at 20°C; chemical shifts are relative to external $H_3PO_4$

The $^1H$ NMR spectra confirm that **4.2a-d** contain a phenyl ring π-bonded to rhodium. The proton resonances of the OAr ligands appeared in the region of 4.4 - 5.6 ppm, i.e. they are shifted to significantly higher field as compared to the resonances of the corresponding phenols or O-bonded OAr ligands. This is commonly observed when there is π-coordination of a phenyl ring to a metal. [10]

When $PPh_3$ was added to toluene or methylene chloride solutions of **4.2a-d**, the $^{31}P\{^1H\}$ NMR spectra showed signals assignable to **4.1a-d**. These data confirm that

dissociation of **4.1a-d** in solution is indeed an equilibrium process. The equilibrium constant does not depend on the nature of OAr groups (in the range of accuracy of the measurements), but was sensitive to the nature of the solvent (e. g. the equilibrium constant was estimated as $1 \cdot 10^{-4}$ mol / L in toluene and $2 \cdot 10^{-2}$ mol / L in methylene chloride).

### 4.2.3. Reaction of 4.1a-d with Phenols. Synthesis and Characterization of $[Rh(PPh_3)_2(\pi\text{-}ArO)] \cdot 2HOAr$ (4.2a-d·2HOAr). X-ray Structure of 4.2a·2PhOH.

Strong hydrogen bonding between phenols and aryloxo ligands is a well established feature of transition metal aryloxides.[8, 11] It was of interest to investigate the effect of such bonding with phenols on the equilibrium between **4.1** and **4.2**. Gradual addition of the corresponding phenols to **4.1a-d** in toluene increased the intensity of signals assigned to $PPh_3$ and **4.2a-d**, with a simultaneous decrease in the intensity of the signals assigned to **4.1a-d**, in the $^{31}P\{^1H\}$ NMR spectra. After the addition of two equivalents of HOAr the characteristic pattern of **4.1a-d** had completely disappeared from the spectra and only signals assignable to $PPh_3$ and **4.2a-d** remained in a ratio of 2:1. No change occurred on further addition of HOAr. It is conceivable from these data that hydrogen bonding of phenols with **4.2a-d** is much stronger than with **4.1a-d**, and the formation of strong hydrogen bonds of phenols with π-coordinated OAr ligands of **4.2a-d** drives the equilibrium (eq. 4.2) to the right. The net process can be represented by eq. 4.4

$$(Ph_3P)_3RhOAr + 2HOAr \longrightarrow \underset{\textbf{4.2a-d}2HOAr}{(Ph_3P)_2Rh(\pi\text{-}ArO) \cdot 2HOAr} + PPh_3 \qquad (4.4)$$

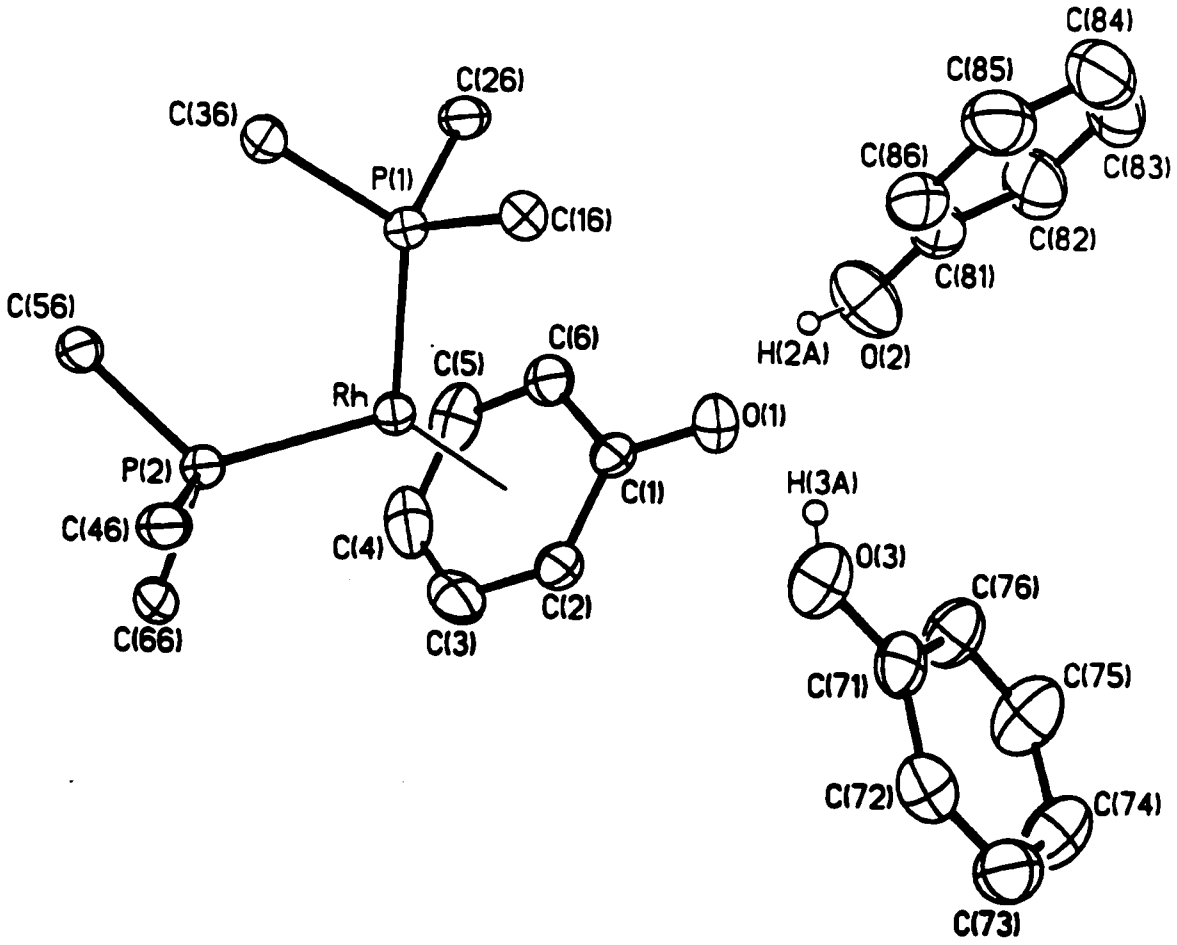



**Figure 4.2.** Perspective drawing for **4.2a**·2PhOH with adopted numbering scheme. Thermal ellipsoids are depicted at 30% probability. Only the *ipso* carbon atoms of $PPh_3$ are shown. Hydrogen atoms (except for O-H) are omitted for clarity.

**Table 4.4.** Selected Bond Distances (Å) and Angles (deg) for [(Rh(PPh$_3$)(π-OPh)]

| | | | |
|---|---|---|---|
| P(1) - Rh | 2.2462(9) | C(1) - C(2) | 1.416(6) |
| O(1) – C(1) | 1.277(5) | C(2) - C(3) | 1.384(7) |
| O(2) – C(81) | 1.355(6) | C(3) - C(4) | 1.405(8) |
| O(3) – C(76 | 1.365(6) | C(4) - C(5) | 1.372(8) |
| O(1) – O(2) | 2.668(1) | C(5) - C(6) | 1.409(6) |
| O(1) – O(3) | 2.608(1) | C(1) - C(6) | 1.420(6) |
| Rh – C(1) | 2.542(4) | C(71) - C(72) | 1.374(8) |
| Rh – C(2) | 2.474(4) | C(72) - C(73) | 1.381(9) |
| Rh - C(3) | 2.327(4) | C(73) - C(74) | 1.365(8) |
| Rh - C(4) | 2.252(4) | C(74) - C(75) | 1.381(8) |
| Rh - C(5) | 2.295(4) | C(75) - C(76) | 1.381(7) |
| Rh - C(6) | 2.298(4) | C(76) - C(71) | 1.367(7) |

Slow diffusion of pentane vapors into concentrated toluene solutions of **4.1a-d**, containing two equivalents of their respective phenols, afforded red crystals of the corresponding **4.2a-d**·2HOAr. Two complexes, **4.2a**·2PhOH and **4.2b**·2(4-Me$C_6H_4$OH) were isolated in high yield and characterized by elemental analysis, NMR and IR spectroscopy. The solid state structure of **4.2a**·2PhOH was determined by X-ray diffraction. An ORTEP plot of the complex is shown in Figure **4.2**; selected bond distances and angles are presented in Table 4.4. The structural arrangement of the complex consists of a $(Ph_3P)_2Rh$ fragment attached to the arene ring of the phenoxo ligand, which in turn is connected *via* two hydrogen bonds to a pair of phenol molecules. Being oriented toward the Rh atom their planes assume an angle of 98° and are almost perpendicular to the plane of the π-coordinated phenoxide. With the exception of the $PPh_3$ ligands, this arrangement is very similar to that found in

$Cp^*Ru(\pi\text{-}PhO)\cdot 2PhOH$.[12] The line bisecting the P1RhP2 triangle is almost perpendicular to the plane of the OPh ligand, which is pivoted around this axis in such a way that the oxygen atom is much closer to P2 (4.075 Å) than to P1 (5.656 Å). The Rh...C(1) and Rh...C(2) separations (2.538 and 2.474 Å respectively) in **4.2a**·2PhOH are clearly longer than the Rh distances to the other carbon atoms of the OPh ligand (2.251 - 2.327 Å). The $C_6$ ring is essentially planar (torsion angles lie in the range 0.4 - 10.6°) and the oxygen atom is only slightly displaced from its mean plane (0.142 Å). The C(1)-O(1) bond (1.277 Å) is shorter than the C-O bond in $NaOPh\cdot 3H_2O$ (1.309 - 1.336 Å),[13] but is substantially longer than the corresponding bond in $[Cp^*Rh(\eta^5\text{-estradienonyl})]BF_4$ (1.20 Å).[6] These data indicate the large contribution from mesomer **A** (Figure 4.3) to the structure of **4.2a**·2PhOH and the complex can therefore be best described as $[(Ph_3P)_2Rh(\eta^4\text{-}PhO)]\cdot 2PhOH$.

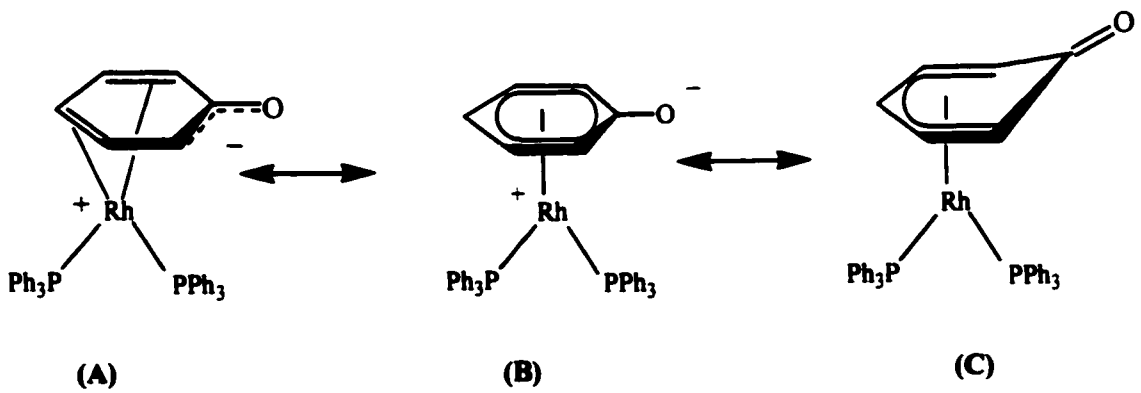



**Figure 4.3.** Mesomeric structures for π-complexing of phenoxo-group: (A) as $\eta^4$-cyclohexadienonyl, (B) as $\eta^6$-phenoxide, (C) as $\eta^5$-cyclohexadienonyl

The unusually long Rh - *ortho* carbon distance (2.65 Å) was also found in the closely related $[(Ph_3P)_2Rh(\pi\text{-}2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2O)]$ complex.[7] It should be noted that only the $\eta^4$-mode of coordination gives the more common 16e configuration of Rh(I), whereas the $\eta^5$-

and $\eta^6$- types both formally give an 18e count. The $\eta^4$-coordination of the OPh ligand in **4.2a**·2PhOH is also supported by the mutual orientation of the $C_6$ ring and the $(Ph_3P)_2Rh$ fragment, which is shifted towards the C3-C4 and C6-C5 bonds presumably to maximize their interaction with the Rh (Figure 4.4). It should be noted, however, that the Rh-C1 and Rh-C2 distances in **4.2a**·2PhOH are probably not long enough to exclude a bonding interaction, therefore it is difficult to assign the definite hapticity to the OPh ligand in complexes **4.2**, and they are further referred to as $[(Ph_3P)_2Rh(\pi\text{-ArO})]$.

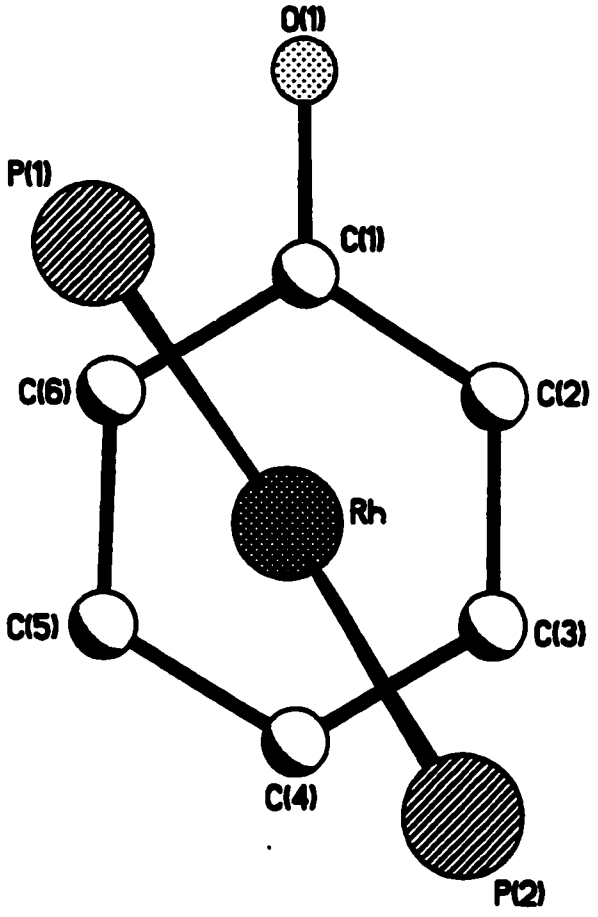



**Figure 4.4.** Top view of **4.2a**·2PhOH. Only the P atoms of $PPh_3$ are shown. Hydrogen atoms are omitted for clarity. Two molecules of hydrogen bonded PhOH are not shown.

The presence of a broad band at 2600-2700 $cm^{-1}$ in the IR- (due to O-H stretch) and a broadened signal at *ca* 11 ppm (due to phenolic protons) in the $^1H$ NMR spectra of **4.2a,b**·2HOAr is indicative of strong hydrogen bonding[14] in the complexes. The proton resonances of π-coordinated OAr ligands appear at higher field, as compared with the resonances of hydrogen bonded phenols, which in turn appear in the aromatic region of the spectra. The presence of the two sets of aromatic resonances clearly shows that exchange between the π-coordinated aryloxide and hydrogen bonded HOAr either does not occur at all, or is slow on the NMR time scale. Addition of PhOH to a solution of **4.2b**·2(4-$MeC_6H_4OH$) resulted in the appearance of a doublet assignable to **4.2a**·2PhOH in the NMR spectrum that slowly increased in intensity for *ca.* 40 min and then remained unchanged. These data indicate that π-OAr/HOAr exchange does occur, although rather slowly. Exchange between hydrogen bonded and free HOAr is rapid as indicated by the observation of a single averaged resonance of the phenolic protons in the $^1H$ NMR spectra when excess HOAr is present.

### 4.2.4. Formation of the Orthometallated Complex $[Rh(C_6H_4PPh_2)(PPh_3)_2]$ (4.4) from 4.1a-d.

Heating solutions of **4.1a-d** in toluene to 60°- 80°C for 5 min led to dramatic changes in the $^{31}P\{^1H\}$ NMR spectra. The signals of **4.1a-d** decreased in intensity, the doublet of **4.2a-d** and singlet of $PPh_3$ increased, and a new pattern consisting of three multiplets centered at -54, 40.8 and 45.8 ppm, appeared in the spectra. Each multiplet of the new pattern contained 8 lines and was interpreted as a doublet of doublets of doublets.[15] The new pattern is assigned to orthometallated square planar Rh complex (**4.4**). The fact that the same pattern was observed in the $^{31}P\{^1H\}$ NMR spectra after heating of various **4.1a-d**, and the absence of

high field resonances in the $^1H$ NMR spectra, suggest that **4.4** contains neither OAr nor hydride ligands. The proposed structure and schematic representation of the $^{31}P\{^1H\}$ NMR spectrum of the complex are shown on Figure 4.5.

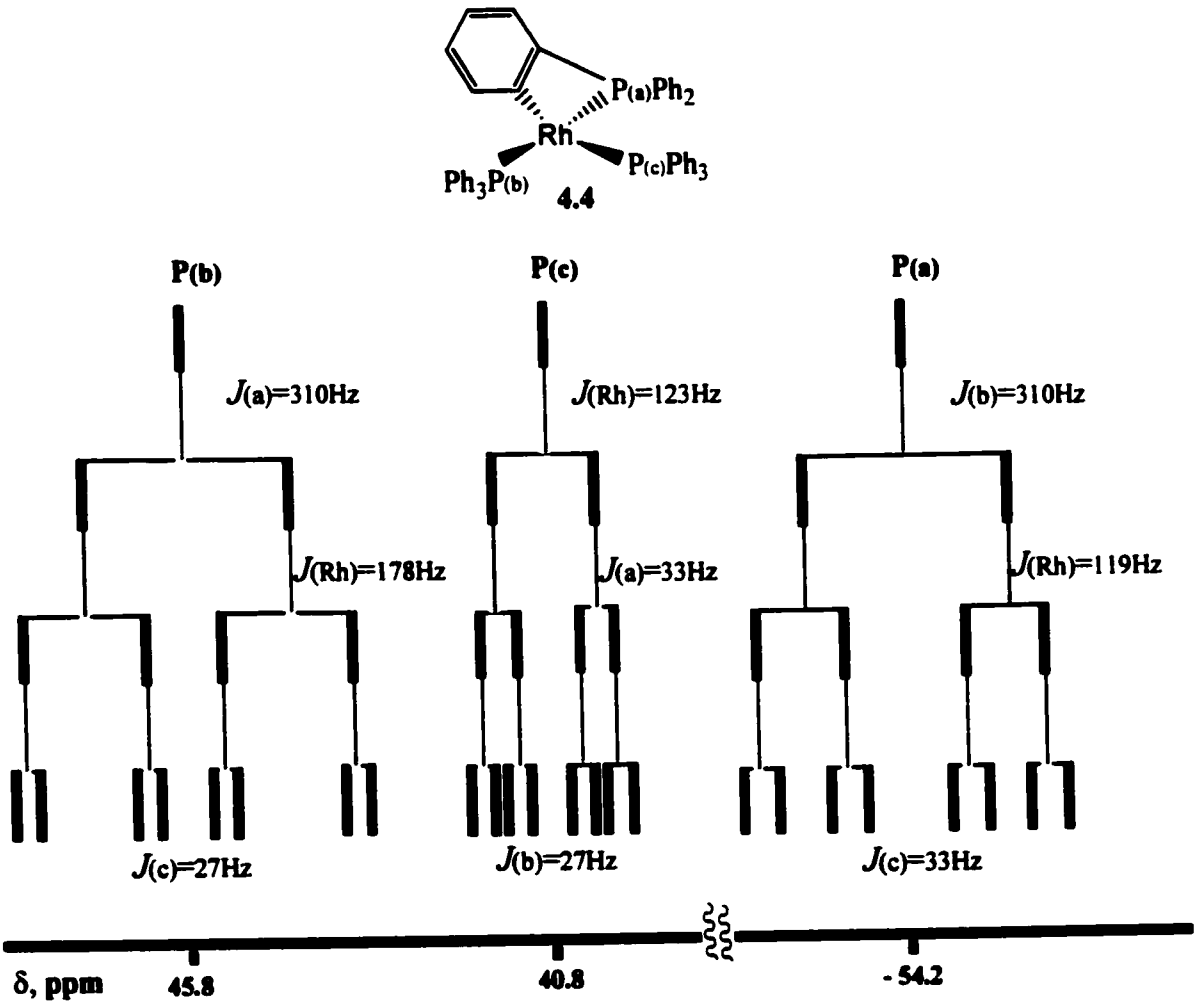
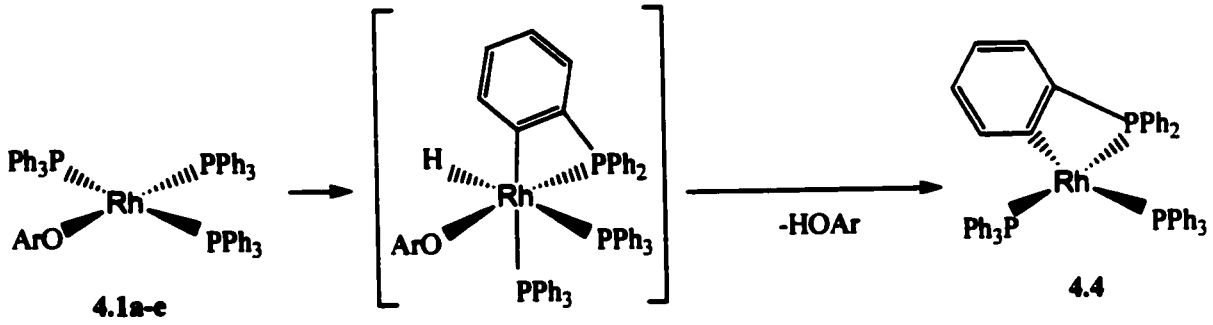



**Figure 4.5.** $^{31}P\{^1H\}$ NMR data for complex **4.4**. Measured in $C_6D_6$ at 20°C. Chemical shifts are relative to 85% $H_3PO_4$ as external standard.

Cyclometallation reactions on metallocomplexes are well known[17] and representative orthometallated compounds are well characterized.[18, 19] The complex **4.4** was described in

1968 by Keim[1] and later used in both catalysis[20] and organometallic synthesis.[21] Although neither X-ray nor $^{31}P$ NMR data were published, there are no doubts about the structure and composition of the complex. The published synthesis of **4.4** involves thermal decomposition of $[MeRh(PPh_3)_3]$ or $[PhRh(PPh_3)_3]$ in solution and was proposed to proceed *via* reductive elimination of methane or benzene from an intermediate hexacoordinated Rh hydride.[1] It seems likely that the formation of **4.4** from **4.1a-d** occurs by a similar mechanism and also involves a Rh(III) hydride as an intermediate, which undergoes reductive elimination of phenol (Scheme 4.1).

Scheme 4.1




The fact, that the formation of **4.4** is accompanied by an increase of the intensity of the signals of **4.2a-d** and $PPh_3$ in the $^{31}P\{^1H\}$ NMR spectra, suggests that HOAr is not released into solution, but reacts with still present **4.1a-d** (cf. eq. 4.4), giving corresponding **4.2a-d**·2HOAr and $PPh_3$. Therefore formation of **4.4** from **4.1a-d** proceeds in accordance with eq. 4.5.

$$3(Ph_3P)_3RhOAr \rightleftharpoons \underset{\textbf{4.4}}{2(PPh_3)_2Rh(C_6H_4PPh_2)} + \textbf{4.2a-d}\cdot 2HOAr + 2PPh_3 \qquad (4.5)$$

The $^{31}P\{^1H\}$ NMR spectra of solutions of **4.1a-d** heated for 1 h showed no change compared with the spectra obtained just after 5 min of heating; *i.e* full conversion of **4.1a-d** to **4.4** could not be obtained and *ca.* 30% of the initial amount of **4.1a-d** still remained in the solution. The characteristic pattern of **4.4** slowly vanished and finally disappeared from the spectra, when the solutions were kept at room temperature for two days. The initial spectra of **4.1a-d** were completely restored after that period of time, but a repeated heating of the solutions again gave rise to the aforementioned changes. It is conceivable from these data, that the formation of **4.4** is an equilibrium process. At elevated temperatures the equilibrium is quickly established and shifted toward the formation of the orthometallated complex. At room temperature the formation of **4.4** is thermodynamically unfavorable, but the equilibrium is established slowly, so that the reverse reaction requires a long time for completion.

### 4.2.5. Reaction of $[(PPh_3)_4Rh(\mu\text{-}OH)_2]$ with *p*-nitrophenol in the Presence of $PPh_3$. Preparation and Characterization of $[(PPh_3)_3RhOC_6H_4NO_2]$ (4.1e).

Recently it was reported that the binuclear rhodium hydroxo complex $[(PPh_3)_2Rh(\mu\text{-}OH)]_2$, can be "neutralized" by various carboxylic acids and even relatively weak C-H and M-H acids to give water and the corresponding complexes with Rh-O, Rh-C and Rh-M bonds.[22]. Since phenols are stronger acids ($pK_a \approx 10$) than water, it seemed reasonable to expect that the reactions with $[(PPh_3)_2Rh(\mu\text{-}OH)]_2$ will lead to the corresponding rhodium aryloxides. Surprisingly, no reaction was observed when the complex was treated with various HOAr in toluene or methylene chloride. Even *p*-nitrophenol, which is quite acidic ($pK_a = 7.14$), did not give any products. However, when 2 molar equivalents of $PPh_3$ were added to the solution a fast and clean transformation occurred to, give $(PPh_3)_3RhOC_6H_4NO_2$ **(4.1e)** as the sole

metalloorganic product (eq 4.6). In contrast, phenol, anisole, *o*- and *p*-cresol were not reactive even in the presence of $PPh_3$.

$$[(Ph_3P)_2Rh(\mu\text{-}OH)]_2 + 2HOC_6H_4NO_2 + 2PPh_3 \xrightarrow[-2H_2O]{} \underset{\textbf{4.1e}}{2(Ph_3P)_3RhOC_6H_4NO_2} \qquad (4.6)$$

Complex **4.1e** was isolated as a 1:2 benzene solvate and characterized by elemental analysis, IR- and NMR spectroscopy. The orange crystals of **4.1e**·$2C_6H_6$ can be handled in air for several minutes without noticeable decomposition, however they slowly darken upon longer exposure to air. The analytical and spectral data (see experimental section) are in agreement with the structure of **4.1e** as a square planar Rh complex with three triphenylphosphine ligands and the $OC_6H_4NO_2$ moiety coordinated to the metal *via* the phenolic oxygen. The $^1H$ NMR spectrum of **4.1e** in $C_6D_6$ at 20°C shows two sharp doublets for the *o*- and *m*-protons of the $OC_6H_4NO_2$ ligand at 6.4 and 7.9 ppm respectively. Upon heating to 60°C the signals become very broad, indicating a dynamic exchange process. Sharp doublets centered at 6.1 and 7.3 ppm were observed in the spectrum of **4.1e** in $CD_2Cl_2$ at -20°C, but the signals became very broad at room temperature. Signals of the $PPh_3$ ligands appear as sharp lines in the $^{31}P\{^1H\}$ NMR spectrum of **4.1e** in $CD_2Cl_2$ at 20°C. The lines do not become broader when triphenylphosphine is added to the solution, indicating that exchange between free and coordinated $PPh_3$ is slow on the NMR time scale under these conditions and line broadening in the $^1H$ NMR is not caused by *cis/trans* exchange of the $PPh_3$ ligands. These data suggest that the dynamic process, which occurs in solutions of **4.1e**, probably involves a reversible dissociation of *p*-nitrophenoxy anion from the complex. The degree of dissociation is probably low, and thus no new signals are detected in the $^1H$- and

$^{31}P\{^1H\}$ NMR spectra. Line broadening in the $^1H$ NMR spectra probably occurs due to shortening of the spin - spin relaxation time.

When 2 molar equivalents of *p*-nitrophenol was added to a $C_6D_6$solution of **4.1e**, the $^1H$ NMR spectrum showed a broad signal at 10.6 ppm, which was assigned to the phenolic protons of hydrogen bonded p-nitrophenol. The aromatic protons of the $OC_6H_4NO_2$ ligand were indistinguishable from the corresponding protons of *p*-nitrophenol and appeared as very broad resonances at 6.3 and 7.7 ppm. Further addition of *p*-nitrophenol led to a gradual shift of the signal of the phenolic protons to lower frequency. These data indicate that *p*-nitrophenol forms strong hydrogen bonds with the $OC_6H_4NO_2$ ligand of **4.1e**, and that the *p*-nitrophenoxo ligand undergoes fast exchange with free and hydrogen bonded *p*-nitrophenol in solution.

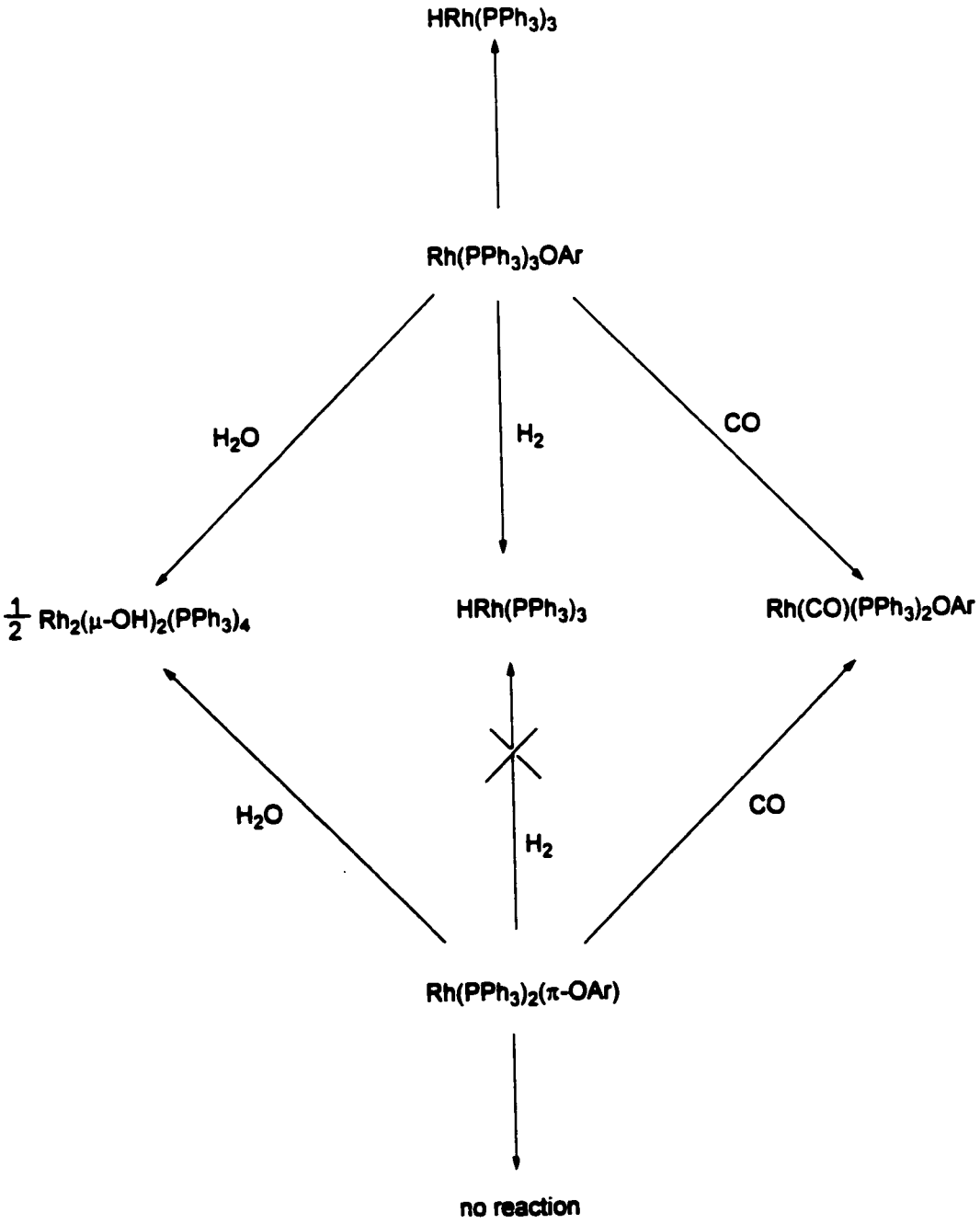
Although **4.1e** and **4.1a-d** have the same molecular arrangement, their behavior in solution is very different. According to $^{31}P\{^1H\}$ NMR spectra, **4.1e** shows no tendency to eliminate $PPh_3$ and form a complex with π-coordinated $OC_6H_4NO_2$ ligand, unlike **4.1a-d** (see. eq 4.2). Moreover, **4.1e** does not give any orthometallated species in observable concentrations even under prolonged heating in solution. Such behavior may be attributable to the electron withdrawing effect of the $NO_2$ group which makes the aromatic ring of the ligand electron poor and unlikely to undergo coordination to the Rh in a π-fashion.

### 4.2.6. Reactivity of 4.1a-e and 4.2a-d towards $H_2O$, MeOH, $H_2$ and CO. Preparation of $(Ph_3P)_2Rh(CO)(OAr)$ (4.3a-e) X-ray Structure of 4.3e.

Since transition metal alkoxides/aryloxides are regarded as important intermediates in various metal catalyzed organic reactions,[23, 24] it was of interest to investigate and compare

the reactivity of the Rh aryloxides, **4.1a-e** and **4.2a-d** toward CO, $H_2$, water and alcohols. The transformations described further in this section are presented in Scheme 4.2

**Scheme 4.2**



**Reaction with $H_2O$.** Complexes **4.1a-d** are very moisture sensitive. In solution they react immediately with water to give $[(PPh_3)_2Rh(\mu\text{-}OH)]_2$ and $PPh_3$ which were identified by $^{31}P$ NMR, and the corresponding phenols. Hydrolysis of **4.2a-d**·2HOAr occurs similarly, but requires *ca* 30 min for complete reaction. The *p*-nitrophenoxo Rh complex, **4.1e** did not give any products, detectable by $^{31}P$ NMR when it was stirred with water in benzene or dissolved in wet THF.

**Reaction with MeOH.** The addition of MeOH to toluene solution of **4.1a-d** results in clean formation of $[HRh(PPh_3)_3]$, which was identified by comparison of its $^{31}P\{^1H\}$ NMR spectrum with that of an authentic sample.[25] The reaction probably proceeds *via* β- hydrogen elimination from an intermediate Rh methoxy complex with the formation of formaldehyde and the Rh hydride. According to $^{31}P\{^1H\}$ NMR spectra, complexes **4.1e** and **4.2a-d** do not give any products when treated with methanol in toluene solution.

**Reaction with $H_2$.** When toluene solutions of **4.1a-d** are saturated with hydrogen, $[HRh(PPh_3)_3]$ is formed within several min. Under the same conditions complexes **4.2a-d** were unreactive. Passing $H_2$ through a solution of **4.1e** in toluene produced a mixture of unidentified products, but no $[HRh(PPh_3)_3]$ was detected by $^{31}P$ NMR.

**Reaction with CO.** Bubbling CO into a toluene or benzene solution of **4.1a-e** or **4.2a-d**·2HOAr for several min cleanly affords the corresponding rhodium carbonyl aryloxides, $(Ph_3P)_2Rh(CO)(OAr)$ (**4.3a-e**) (eq. 4.7 and 4.8).

$$\underset{\textbf{4.1a-e}}{(Ph_3P)_3RhOAr} + CO \longrightarrow \underset{\textbf{4.3a-e}}{(Ph_3P)_2Rh(CO)OAr} + PPh_3 \qquad (4.7)$$

$$\underset{\textbf{4.2a-d}\cdot 2HOAr}{(Ph_3P)_2Rh(\pi\text{-}ArO)\cdot 2HOAr} + CO \longrightarrow \underset{\textbf{4.3a-d}}{(Ph_3P)_2Rh(CO)OAr} + 2HOAr \qquad (4.8)$$

In general, it might be expected that CO would insert into Rh-O bond of rhodium aryloxides to give the corresponding (aryloxy)carbonyls, as it has been observed for $[Pt(triphos)(OAr)]PF_6$[3a] and $[(ArO)Ir(CO)(PPh_3)_2]$.[26] This reaction, however, did not occur in the case of **4.1a-e** or **4.2a-d**·2HOAr and transformations 4.7 and 4.8 were quantitative according to $^{31}P\{^1H\}$NMR spectra. Complex **4.3e** was isolated in high yield as air stable yellow crystals and characterized by elemental analysis, IR- and NMR spectroscopy and an X-ray diffraction study. The structures of **4.3a-d** were confirmed by their alternative synthesis from $[RhCl(CO)(PPh_3)_2]$ and the appropriate NaOAr. The complexes were isolated as air stable yellow crystals and characterized by elemental analysis, NMR and IR spectroscopy (see experimental section)[27]. An ORTEP plot of **4.3e** and selected bond lengths and angles are presented in Figure 4.6 and Table 4.5 respectively. The central Rh atom in **4.3e** has an essentially square planar geometry, with the *trans* angles being 173.5° and 176.8° for P1-Rh-P2 and O1-Rh-C43, respectively. The *p*-nitrophenoxy fragment is *trans* to the CO ligand and bonded to the metal *via* the phenolic oxygen. The values of the C-C, C-O, C-N and O-N bond lengths for the $OC_6H_4NO_2$ ligand (Table 4.6) are unexceptional and lie within the range of values reported for *p*-nitrophenol[28] and its potassium salt.[29]

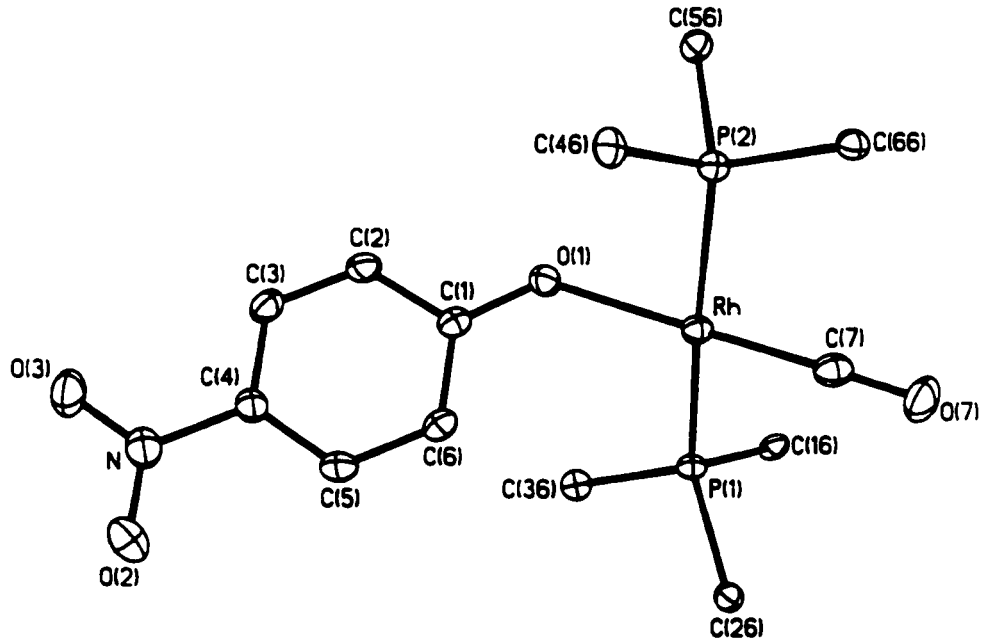



**Fig 4.6.** Perspective drawing for **4.3e** with adopted numbering scheme. Thermal ellipsoids are depicted at 30% probability. Only the *ipso* carbon atoms of $PPh_3$ are shown. Hydrogen atoms are omitted for clarity.

**Table 4.5.** Selected Bond Distances (Å) and Angles (deg) for $[(Rh(PPh_3)_3(CO)(OC_6H_4NO_2)]$

| | | | |
|---|---|---|---|
| P(1) - Rh | 2.3346(8) | P(1) – Rh - O(1) | 94.66(5) |
| P(2) - Rh | 2.3403(8) | P(1) – Rh – C(7) | 88.16(8) |
| Rh(7) – Rh | 1.814(3) | C(7) – Rh – P(2) | 90.79(8) |
| C(7) – O(7) | 1.156(3) | O(1) – Rh – P(2) | 86.55(5) |
| O(1) – Rh | 2.069(2) | O(7) - C(7) – Rh | 178.2(2) |
| C(1) – O(1) | 1.307(3) | Rh- O(1) – C(1) | 130.2(2) |

**Table 4.6.** Bond Distances (Å) in 4-$NO_2C_6H_4O$ units of *p*-nitrophenol, **4.3e** and 4-$NO_2$-$C_6H_4OK \cdot H_2O$

| Bond distance | *p*-nitrophenol | **4.3e** | 4-$NO_2C_6H_4OK \cdot H_2O$ |
|---|---|---|---|
| C(1) - C2 | 1.393(4) | 1.417(3) | 1.424(2) |
| C(2) - C(3) | 1.380(6) | 1.374(3) | 1.373(2) |
| C(3)-C (4) | 1.383(6) | 1.398(3) | 1.400(2) |
| C(4) – C(5) | 1.388(6) | 1.390(3) | 1.400(2) |
| C(5) - C(6) | 1.377(6) | 1.374(3) | 1.373(2) |
| C(1) - C(6) | 1.387(6) | 1.422(3) | 1.428(2) |
| C(1) – O(1) | 1.351(6) | 1.306(3) | 1.292(2) |
| C(4) – N | 1.442(6) | 1.446(3) | 1.418(2) |
| N – O(2) | 1.232(6) | 1.235(3) | 1.341(2) |
| N – O(3) | 1.236(6) | 1.248(3) | 1.247(2) |

## 4.3 Conclusions

The present study shows that the properties of rhodium aryloxo complexes of general formula $[(Ph_3P)_3Rh(OC_6H_4R)]$ are quite sensitive to the nature of the substituents in the aromatic ring of the aryloxo ligand. Complexes **4.1a-d**, containing electron donor substituents, are very labile, and readily react with $H_2O$, MeOH, $H_2$ and CO. In solution they exist as equilibrium mixtures with $PPh_3$ and the corresponding $[(PPh_3)_2Rh(\pi\text{-ArO})]$. In the presence of phenols the equilibrium is completely shifted towards the complexes with π-coordinated OAr due to the formation of strong hydrogen bonds between the oxygen atom of the ligand and two molecules of HOAr. Upon heating in solution **4.1a-d** eliminate the corresponding phenol with orthometallation of the aromatic ring of a triphenylphosphine ligand. Unlike **1a-d**, complex **4.1e**, which contains an electron withdrawing $NO_2$ group, is

relatively inert. In solution it shows no tendency to dissociate to $PPh_3$ and the corresponding complex with a π-coordinated OAr ligand. The complex does not give any orthometallated species even upon prolonged heating in solution. Although **4.1e** reacts with CO in the same way like complexes **4.1a-d** do, it is inert towards water and methanol.

## 4.4 Experimental Section

All manipulations were carried out under inert atmosphere using standard Schlenk techniques. The solvents were dried and distilled prior to use. The rhodium complexes $[(Ph_3P)_3RhCl]$,[31] $[(Ph_3P)_2RhCl]_2$,[31] $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2]$[22] and $[(Ph_3P)_2Rh(CO)Cl]$[31] were prepared as described elsewhere. The NaOAr reagents were prepared from the corresponding phenols and a 3-fold excess of $NaNH_2$ in THF. The stirred mixture was heated to reflux, cooled, unreacted $NaNH_2$ was filtered, and the filtrates were used as stock solutions. The other chemicals were purchased from Aldrich and were used as received. The following instruments were used: Varian XL-300 (NMR), Bomem MB-100 (FT-IR) and Perkin-Elmer 2400 Series II (combustion microanalysis).

**4.4.1 Synthesis of $[(Ph_3P)_3RhOPh]$ (4.1a)** A mixture of $[(Ph_3P)_3RhCl]$ (410 mg; 0.443 mmol), toluene (8 ml) and NaOPh (0.9 M solution in THF, 0.5 mmol) was stirred for 1h at room temperature. The resulting brown solution was filtered and reduced in volume to *ca.* 3 ml. Pentane vapors were allowed to diffuse into the solution overnight. The precipitated dark red crystals were separated, washed with toluene (2 x 2 ml), pentane (2 x 6 ml) and vacuum dried to give 398 mg (91%) of analytically pure **4.1a.** $^{31}P\{^1H\}$ NMR: see Table 4.2. IR (KBr), selected bands, $cm^{-1}$: 1586 (m), 1482 (s), 1433 (s), 1295 (s), 1090 (m).

Anal. Calcd for $C_{60}H_{50}OP_3Rh$: C, 73.3; H, 5.1. Found: C, 73.2; H, 5.2.

**4.4.2 Synthesis of $[(Ph_3P)_3RhOC_6H_4NO_2]$ (4.1e)** $[(Ph_3P)_3RhCl]$ (205 mg; 0.221 mmol) was added to a mixture of KOH (2g), water (3 ml) and benzene (10 ml), and the reaction mixture was refluxed with stirring for 2h. The orange organic layer was filtered through cotton wool, the aqueous phase was washed with benzene (3x2 ml), the washings were filtered, and *p*-nitrophenol (31 mg; 0.223 mmol) was added to the combined filtrates. The resulting red solution was stirred for 30min, diluted with heptane (6 ml), reduced in volume under vacuum to *ca* 8 ml and left overnight. The precipitated orange crystals were rinsed with benzene, washed with copious amount of pentane and vacuum dried. The yield of spectroscopically pure **4.1e** $\cdot 2C_6H_6$ was 210 mg (92%). $^{31}P\{^1H\}$ NMR($C_6D_6$), δ: 31.3 (dd, $J_{P-Rh}$ = 151 Hz, $J_{P-P}$ = 40 Hz), 51.1 (dt, $J_{P-Rh}$ = 176 Hz, $J_{P-P}$ = 40 Hz). $^1H$ NMR ($C_6D_6$), δ: 6.5 (d, $J$ = 8.8 Hz, 2H), 6.8 (m, 27 H), 7.6 (m, 18 H), 7.95 (d, $J$ = 8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR ($C_6D_6$), δ: 120.5 (s, $OC_6H_4NO_2$), 125 (s, $OC_6H_4NO_2$), 127.35 (d, $J_{C-P}$ =10 Hz, *trans*-$PC_6H_5$), 127.6 (vt, $J_{C-P}$ = 9.5 Hz, *cis*-$PC_6H_5$), 129.15 (s, *trans*-$PC_6H_5$), 129.2 (s, *cis*-$PC_6H_5$), 134.1 (vt, $J_{C-P}$ = 39.5 Hz, *cis*-$PC_6H_5$), 134.7 (s, $OC_6H_4NO_2$), 134.9 (d, $J_{C-P}$ = 11 Hz, *trans*-$PC_6H_5$), 135.1(vt, $J_{C-P}$ = 12 Hz, *cis*-$PC_6H_5$), 137 (d, $J_{C-P}$ = 44.5 Hz, *trans*-$PC_6H_5$), 177.3 (s, $OC_6H_4NO_2$). IR (KBr), selected bands, $cm^{-1}$: 1577 (s), 1485 (m), 1433 (m), 1288 (vs), 1106 (m), 1090 (m). The compound was recrystallised from toluene for elemental analysis. Anal. Calcd. for $C_{74}H_{65}NO_3P_3Rh$ (**4.1e** $\cdot 2MeC_6H_5$): C, 73.3; H, 5.4; N, 1.2. Found: C, 73.4; H, 5.2; N, 1.1.

### 4.4.3 Synthesis of $[(Ph_3P)_2Rh(\pi\text{-}ArO)]\cdot 2ArOH$ (4.2a,b·2ArOH)

(a) **4.2a·2PhOH.** A mixture of $[(Ph_3P)_3RhCl]$ (113 mg; 0.122 mmol), toluene (6 ml) and NaOPh (0.9 M solution in THF, 0.25 mmol) was stirred for 1 h at room temperature and then filtered. Solid PhOH (30mg; 0.32 mmol) was added to the filtrate, and the resulting solution was reduced in volume to *ca* 3 ml. Pentane vapors were allowed to diffuse into the solution for two days. The precipitated dark red crystals were separated, washed with toluene (2 x 2ml), pentane (2 x 6 ml) and vacuum dried to give 92 mg (83%) of **2a**·2PhOH. The compound was recrystallised from benzene. $^{31}P\{^1H\}$ NMR ($C_6D_6$), δ: 47.5 (d, $J_{P\text{-}Rh}$ = 213 Hz). $^1H$ NMR ($C_6D_6$), δ: 4.4 (t, $J$ = 5.9 Hz, 1H), 5.15(m, 2H), 5.6 (d, $J$ = 7 Hz, 2H), 6.8 (m, 2H), 6.9 (m, 18H), 7.2 (m, 8H), 7.5 (m, 12H), 10.7 (broad s, 2H). $^{13}C\{^{1H}\}$ NMR ($C_6D_6$), δ: 84.3 (s, π–$C_6H_5O$), 97.3 (s, π–$C_6H_5O$), 104.9 (s, π–$C_6H_5O$), 116.3 (s, PhOH), 119.1 (s, PhOH), 127.8 (vt, $J_{C\text{-}P}$ = 10 Hz, $PC_6H_5$), 129.5 (s, $PC_6H_5$), 129.7 (s, PhOH), 134.3 (vt, $J_{C\text{-}P}$ = 12 Hz, $PC_6H_5$), 136.4 (vt, $J_{C\text{-}P}$ = 46 Hz, $PC_6H_5$), 158.7 (s, PhOH), 164.6 (s, π–$OC_6H_5$). IR (KBr), selected bands, $cm^{-1}$: 2700 (v broad), 1602 (w), 1589 (m), 1541 (s), 1478 (vs), 1468(vs), 1434 (s), 1271 (m), 1247 (s), 1093 (s). Anal. Calcd for $C_{54}H_{47}O_3P_2Rh$: C, 71.4; H, 5.2. Found: C, 71.8; H, 5.2.

(b) **4.2b·2(4-Me$C_6H_4$OH).** The complex was prepared in the similar way and recrystallised from toluene. The yield was 89%. $^{31}P\{^1H\}$ NMR ($C_6D_6$), δ: 46 (d, $J_{P\text{-}Rh}$ = 209 Hz). $^1H$ NMR ($C_6D_6$), δ: 1.55 (s, 3H), 2.15 (s, 6H), 4.5 (d, $J$ = 7.2 Hz, 2H), 5.5 (d, $J$ = 7.2Hz, 2H), 6.9 (m, 18H), 6.98 (d, $J$ = 8.5 Hz, 4H), 7.33 (d, $J$ = 8.5 Hz, 4H), 7.5 (m, 12H), 11.4 (s, 2H). $^{13}C\{^1H\}$ NMR ($C_6D_6$), δ: 18.7 (s, π-$\underline{C}H_3C_6H_4O$), 20.7 (s, $HOC_6H_4\underline{C}H_3$), 92.8 (s, π-$CH_3\underline{C}_6H_4O$), 102.6 (s, π-$CH_3\underline{C}_6H_4O$), 105.2 (s, $HO\underline{C}_6H_4CH_3$), 117.4 (s, $HO\underline{C}_6H_4CH_3$), 127.2

(s, π-$CH_3\underline{C}_6H_4O$), 127.8 (vt, $J_{C\text{-}P}$ = 10 Hz, $PC_6H_5$), 129.5 (s, $PC_6H_5$), 130.2 (s, $HO\underline{C}_6H_4CH_3$), 134.3 (vt, $J_{C\text{-}P}$ = 12 Hz, $PC_6H_5$), 136.4 (vt, $J_{C\text{-}P}$ = 46.5 Hz, $PC_6H_5$), 157.2 (s, $HO\underline{C}_6H_4CH_3$), 163.4 (s, π-$CH_3\underline{C}_6H_4O$). IR (KBr), selected bands, $cm^{-1}$: 2660 (v broad), 1610 (m), 1591 (w), 1545 (s), 1513 (s), 1497 (vs), 1485 (s), 1433 (s), 1267 (s), 1247 (s), 1091 (s). Anal. Calcd for $C_{57}H_{53}O_3P_2Rh$: C, 72.0; H, 5.6. Found: C, 71.7; H, 5.5.

**4.4.4 Reaction of 4.1a-d and 4.2a-d with $H_2O$.** 0.6 mL of the solution of **4.3a-d** obtained by stirring [$(Ph_3P)_3RhCl$] (100mg; 0.108 mmol), and the corresponding NaOAr (0.115 mmol) in toluene (5 mL) for 1 h at room temperature was placed into an NMR tube, treated with water (50μL) and shaken for several seconds. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicated quantitative formation of $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2]$[22] and $PPh_3$ in a 1 : 2 molar ratio. The reaction of **4.2a-d** with $H_2O$ was studied in a similar manner.

**4.4.5 Reaction of 4.1 a-d with MeOH** 0.6 mL of the solution of **4.3a-d** obtained by stirring [$(Ph_3P)_3RhCl$] (100mg; 0.108 mmol), and the corresponding NaOAr (0.115 mmol) in toluene (5 mL) for 1 h at room temperature was placed into an NMR tube, treated with methanol (100μL) and shaken for several seconds. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicated quantitative formation of $[HRh(PPh_3)_3]$.[25]

**4.4.6 Reaction of 4.1 a-d with $H_2$** 0.6 mL of the solution of **4.3a-d** obtained by stirring [$(Ph_3P)_3RhCl$] (100mg; 0.108 mmol), and the corresponding NaOAr (0.115 mmol) in toluene (5 mL) for 1 h at room temperature was placed into an NMR tube. Hydrogen was bubbled through the solution for 5 min. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicated quantitative formation of

$[HRh(PPh_3)_3]$.[25]

**4.4.7 Reaction of 4.1 a-d with CO** 0.6 mL of the solution of **4.3a-d** obtained by stirring $[(Ph_3P)_3RhCl]$ (100mg; 0.108 mmol), and the corresponding NaOAr (0.115 mmol) in toluene (5 mL) for 1 h at room temperature was placed into an NMR tube. Carbon monoxide was bubbled through the solution for 5 min. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicated quantitative formation of the corresponding $[Rh(CO)(PPh_3)_2OAr]$ (**4.3a-d**). The reaction of **4.2a-d** with CO was studied in a similar manner.

**4.4.8 Synthesis of $[(Ph_3P)_2Rh(CO)OAr]$ (4.3a-d).** A mixture of $[(Ph_3P)_2Rh(CO)Cl]$ (104mg; 0.150 mmol), NaOAr (THF solution, 0.2 mmol) and benzene (6 ml) was stirred for 1h at room temperature and then filtered. The filtrate was diluted with heptane, reduced in volume to *ca* 8ml and left for 2 h. The precipitated yellow crystals were washed with benzene (2x2 ml), pentane (2x6 ml) and dried to give **4.3a-d**. The complexes were found to be analytically pure without recrystallization.

**4.3a**. Yield 95%. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 28 (d, $J_{P\text{-}Rh}$ = 139.5 Hz). $^1H$ NMR ($CDCl_3$), δ: 6.1 (t, $J$ = 7.2 Hz, 1H), 6.2 (d, $J$ = 7.9 Hz, 2H), 6.5 (m, 2H), 7.1 (m, 18H), 7.6 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 112 (s, OPh), 120.6 (s, OPh), 127.5 (s, OPh), 128.2 (vt, $J_{C\text{-}P}$ = 10 Hz, $PC_6H_5$), 130 (s, $PC_6H_5$), 132.4 (vt, $J_{C\text{-}P}$ = 44 Hz, $PC_6H_5$), 134.5 (vt, $J_{C\text{-}P}$ = 13.5 Hz, $PC_6H_5$), 167 (s, OPh), 189.4 (dt, $J_{C\text{-}Rh}$= 67 Hz, $J_{C\text{-}P}$= 17.5Hz, CO). IR (KBr), selected bands, $cm^{-1}$: 1953 (vs), 1587 (m), 1483 (m), 1433 (m), 1290 (m), 1093 (m). Anal. Calcd for $C_{43}H_{35}O_2P_2Rh$: C, 69.0; H, 4.7. Found: C, 69.0; H, 4.7.

**4.3b**. Yield 97%. $^{31}P\{^1H\}$ NMR ($C_6D_6$), δ: 27 (d, $J_{P\text{-}Rh}$ = 140 Hz). $^1H$ NMR ($C_6D_6$), δ:

2.1 (s, 3H), 6.6 (m, 4H), 7.0 (m, 18H), 7.9 (m, 12H). $^{13}C\{^1H\}$ NMR ($C_6D_6$), δ: 20.8 (s, $OC_6H_4\underline{C}H_3$), 120.7 (s, $O\underline{C}_6H_4CH_3$), 121 (s, $O\underline{C}_6H_4CH_3$), 128.4 (vt, $J_{C\text{-}P}$ = 10 Hz, $PC_6H_5$), 128.8 (s, $O\underline{C}_6H_4CH_3$), 130.1 (s, $PC_6H_5$), 133.3 (vt, $J_{C\text{-}P}$ = 43.5 Hz, $PC_6H_5$), 134.9 (vt, $J_{C\text{-}P}$ = 13 Hz, $PC_6H_5$), 166 (s, $O\underline{C}_6H_4CH_3$), 191 (dt, $J_{C\text{-}Rh}$= 66 Hz, $J_{C\text{-}P}$ = 17 Hz, CO). IR (KBr), selected bands, $cm^{-1}$: 1954 (vs), 1601 (m), 1497 (s), 1478 (m), 1433 (s), 1278 (s), 1096 (m). Anal. Calcd for $C_{44}H_{37}O_2P_2Rh$: C, 69.3; H, 4.9. Found: C, 69.7; H, 5.1.

**4.3c**. Yield 88%. $^{31}P\{^1H\}$ NMR ($C_6D_6$), δ: 29.5 (d, $J_{P\text{-}Rh}$ = 140.5 Hz). $^1H$ NMR ($C_6D_6$), δ: 1.9 (s, 3H), 6.4 (dt, $^1J$ = 7.2 Hz, $^2J$ = 1.2 Hz, 1H), 6.7 (dt, $^1J$ = 7.2 Hz, $^2J$ = 1.8 Hz, 1H), 6.85 (m, 2H), 7.0 (m, 18H), 7.9 (m, 12H). $^{13}C\{^1H\}$ NMR ($C_6D_6$), δ: 18.1 (s, $OC_6H_4\underline{C}H_3$), 113 (s, $O\underline{C}_6H_4CH_3$), 120.8 (s, $O\underline{C}_6H_4CH_3$), 126 (s, $O\underline{C}_6H_4CH_3$), 128.3 (vt, $J_{C\text{-}P}$ = 9.5 Hz, $PC_6H_5$), 129 (s, $O\underline{C}_6H_4CH_3$), 132.5 (s, $PC_6H_5$), 133.2 (vt, $J_{C\text{-}P}$ = 43.5 Hz, $PC_6H_5$), 134.8 (vt, $J_{C\text{-}P}$ = 12.5 Hz, $PC_6H_5$), 166 (s, $O\underline{C}_6H_4CH_3$), 191 (dt, $J_{C\text{-}Rh}$ = 66 Hz, $J_{C\text{-}P}$ = 17 Hz, CO). IR (KBr), selected bands, $cm^{-1}$: 1953 (vs), 1588 (m), 1477 (s), 1433 (s), 1284 (s), 1095 (m). Anal. Calcd for $C_{44}H_{37}O_2P_2Rh$: C, 69.3; H, 4.9. Found: C, 69.7; H, 4.8.

**4.3d**. Yield 95%. $^{31}P\{^1H\}$ NMR ($C_6D_6$), δ: 27.5 (d, $J_{P\text{-}Rh}$ = 139.5 Hz). $^1H$ NMR ($C_6D_6$), δ: 3.4 (s, 3H), 6.4 (m, 4H), 7.0 (m, 18H), 7.9 (m, 12H). $^{13}C\{^1H\}$ NMR ($C_6D_6$), δ: 55 (s, $OC_6H_4O\underline{C}H_3$), 113.6 (s, $O\underline{C}_6H_4OCH_3$), 120.2 (s, $O\underline{C}_6H_4OCH_3$), 127.8 (vt, $J_{C\text{-}P}$ = 9 Hz, $PC_6H_5$), 131.5 (s, $PC_6H_5$), 132.7 (vt, $J_{C\text{-}P}$ = 43 Hz, $PC_6H_5$), 134.3 (vt, $J_{C\text{-}P}$ = 12 Hz, $PC_6H_5$), 148.6 (s, $O\underline{C}_6H_4OCH_3$), 161.8 (s, $O\underline{C}_6H_4OCH_3$), 190.5 (dt, $J_{C\text{-}Rh}$ = 66 Hz, $J_{C\text{-}P}$ = 17.5 Hz, CO). IR (KBr), selected bands, $cm^{-1}$: 1965 (vs), 1491 (s), 1433 (m), 1224 (m), 1096 (m). Anal. Calcd for $C_{44}H_{37}O_3P_2Rh$: C, 67.9; H, 4.8. Found: C, 68.1; H, 4.6.

**4.3.9 Synthesis of $[(Ph_3P)_2Rh(CO)OC_6H_4NO_2]$ (4.3e)** Carbon monoxide was bubbled through a solution of $[(Ph_3P)_3RhOC_6H_4NO_2]\cdot 2CH_3Ph$ (48 mg, 0.040 mmol) in benzene (6 ml) for 5 min. The resulting pale yellow solution was diluted with heptane (6 ml), reduced in volume to *ca* 6 ml under vacuum and left overnight. The precipitated yellow crystals were washed with benzene (2x2 ml), pentane (2x6 ml) and vacuum dried to give 28 mg (0.036 mmol, 91%) of **4.3e.** $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 29.5 (d, $J_{P\text{-}Rh}$ = 134.5 Hz). $^1H$ NMR ($CDCl_3$), δ: 6.1 (m, 2H), 6.9 (m, 18H), 7.65 (m, 12H), 7.75 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 119.6 (s, $OC_6H_4NO_2$), 125.2 (s, $OC_6H_4NO_2$), 128.4 (vt, $J_{C\text{-}P}$ = 8.5 Hz, $PC_6H_5$), 130.5 (s, $PC_6H_5$), 131.5 (vt, $J_{C\text{-}P}$ = 45 Hz, $PC_6H_5$), 134 (s, $OC_6H_4NO_2$), 134.3 (vt, $J_{C\text{-}P}$ = 13 Hz, $PC_6H_5$), 175 (s, $OC_6H_4NO_2$), 189.7 (dt, $J_{C\text{-}Rh}$ = 70 Hz, $J_{C\text{-}P}$ = 17 Hz, CO). IR (KBr), selected bands, $cm^{-1}$: 1980 (s), 1580 (s), 1489 (m), 1467 (m), 1433 (m), 1289 (vs), 1097 (s). Anal. Calcd. for $C_{43}H_{34}NO_4P_2Rh$: C, 66.4; H, 4.4; N, 1.8. Found: C, 66.5; H, 4.6; N, 1.8.

**4.3.10 Single-Crystal X-ray Diffraction Study of $[(Ph_3P)_3RhOPh]$ (4.1a), $[(Ph_3P)_2RhOPh]\cdot 2PhOH$ (4.2a·2PhOH) and $[(Ph_3P)_2Rh(CO)OC_6H_4NO_2]$ (4.3e)**

Crystal data and refinement parameters are summarized in Table 4.7. Crystals suitable for X-ray analysis were obtained by crystallization from concentrated toluene solutions. The crystals were mounted on glass fibers. All measurements were made at -110°C on a Siemens Smart CCD diffractometer with Mo $K\alpha_1$ radiation. Systematic absences in the diffraction data and unit-cell parameters are uniquely consistent with the reported space groups for **4.1a** and **4.3e**. No symmetry higher than triclinic was observed for **4.2a**·2PhOH. Solution in the centric space group option yielded chemically reasonable and computationally stable results.

During the data collection standards were measured after every 150 reflections. No crystal decay was noticed. Each structure was solved by direct methods, completed by Fourier synthesis and refined by full-matrix least squares procedures based on $F^2$. The data were corrected for absorption by using redundant data at different effective azimutal angles. Two symmetrically-unique but chemically equivalent, cocrystallysed phenol molecules were located in the asymmetric unit of **4.2a**·2PhOH. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The phenolic hydrogen atoms of **4.2a**·2PhOHwere initially located from the difference map but were treated as rigid groups with idealized geometry in subsequent refinement. All other hydrogen atoms were treated as idealized contributions. All software and sources of atomic scattering factors are contained in the SHEXTL(5.03) program library.[32]

**Table 4.7.** Summary of crystallographic data for **4.1a**, **4.2a** · 2PhOH and **4.3e**.

| Complex | **4.1a** | **4.2a** · 2PhOH | **4.3e** |
|---|---|---|---|
| Formula | $C_{60}H_{50}OP_3Rh$ | $C_{54}H_{47}O_3P_2Rh$ | $C_{43}H_{34}NO_4P_2Rh$ |
| Fotmula weight | 982.82 | 908.77 | 793.56 |
| Cryst. Dimens. (mm) | 0.2x0.1x0.08 | 0.2x0.2x0.2 | 0.2x0.2x0.2 |
| Crystal system | orthorhombic | triclinic | monoclinic |
| a(Å) | 12.3095(3) | 10.5639(1) | 15.7469(3) |
| b(Å) | 20.7943(6) | 12.4749(1) | 14.6046(2) |
| c(Å) | 37.7345(9) | 18.3573(2) | 17.4164(1) |
| α(°) | | 70.821 | |
| β(°) | | 85.859 | 112.862(1) |
| γ(°) | | 81.396(1) | |
| Space group | *Pbca* | *P*-1 | $P2_1/n$ |
| Z | 8 | 2 | 4 |
| V(Å) | 9658.8(4) | 2258.53(1) | 3690.73(9) |
| $d_{calc}$ (g/cm$^3$) | 1.352 | 1.333 | 1.428 |
| T (K) | 163 | 163 | 163 |
| Radiation (λ) | Mo $K_{\alpha 1}$ (0.71073 Å) | Mo $K_{\alpha 1}$ (0.71073 Å) | Mo $K_{\alpha 1}$ (0.71073 Å) |
| μ (MoKα) (cm$^{-1}$) | 4.95 | 4.92 | 5.93 |
| R ($R_w$)[a] | 5.79%(11.34%) | 4.22%(10.72%) | 2.29%(10.4%) |

[a] $R = \Sigma(F_o - F_c)/\Sigma(F_o)$; $R_w = [\Sigma(w(F_o - F_c)^2/\Sigma(wF_o^2)]^{1/2}$

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# Chapter 5.

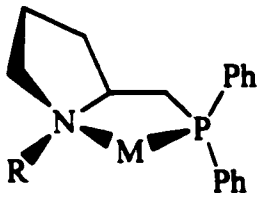
## *Rhodium Complexes with Chiral Aminophosphine Derivatives of Proline and Chiral Aminophosphinite Derivatives of Ephedrine.*

## *5.1 Introduction*

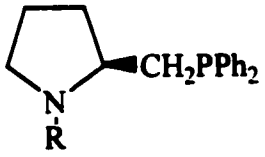
Metallocomplexes containing *P,N*-chelating ligands possess interesting structural, chemical and catalytic properties and have been the subject of recent reviews.[1,2] The affinity of "soft" transition metals toward N-donors is generally considered to be lower than toward phosphorus and the strength of the M-N bond is affected much more by steric effects than that of the corresponding M-P bond.[3] As a result, depending on the steric bulk of the *N*-substituents, aminophosphines and aminophosphinites may act as *P,N* chelating or monodentate *P* bound ligands.[3] The chemistry of an amino group is well developed, so it is possible to introduce virtually any substituent at the nitrogen[4,5] therefore allowing for fine tuning of the coordination properties of these ligands. Metallocomplexes with chiral *P,N* ligands are of special interest due to their possible application as catalysts for many important enantioselective organic transformations.[1,6] The vast majority of these complexes possess chirality associated with carbon and sometimes phosphorus atoms, while the nitrogen is $sp^2$ hybridized or bears identical substituents and therefore cannot be chiral. It is well known that the N atom in an amino group undergoes fast inversion of configuration. However donation of the lone pair to a metal retards the inversion and the coordinated nitrogen becomes stereogenic. The formation of chiral N centers was proposed or implied in a number of publications.[7] Structurally characterized complexes featuring stereogenic nitrogen are rare.[6a,8,9] Chiral aminoacids, such as proline, and aminoalcohols, such as ephedrine, are attractive for applications in metalloorganic chemistry. They are inexpensive, readily available in enantiomerically pure form and can be easily transformed to the corresponding aminophosphines[10,11] and aminophosphinites.[12]. Chiral aminophosphines prepared from (*S*)-proline were used as chiral auxiliaries in Pd-catalyzed asymmetric allylation[10] and Grignard

cross coupling.[11] The application of the aminophosphinite derivative of (*1S, 2S*)-ephedrine for the nickel catalyzed linear dimerization of butadiene has been communicated.[13] However, to the best of our knowledge no structurally characterized metallocomplexes of these ligands have been reported. Coordination of the aminophosphines **5.1a,b** (Chart 5.1) to a metal results in the formation of stereogenic nitrogen centers incorporated into [3.3.0] bicyclic systems which are either *cis*- or *trans*-fused and can be considered as analogs of *cis*- and *trans*-bicyclooctanes. Since *cis*-$C_8H_{14}$ is thermodynamically more stable than the corresponding *trans*-isomer,[14] preferential formation of metallocomplexes possessing type **A** structural fragments with the *S*-absolute configuration of the nitrogen would be expected.

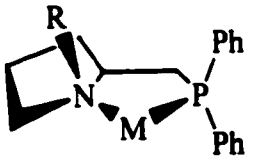
**Chart 5.1**



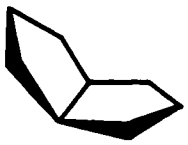

**(A)**



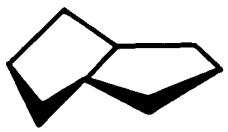

**1a,b**
**a, R = H (PPro)**
**b, R = Me (PProMe)**




**(B)**



*cis*-$C_8H_{14}$

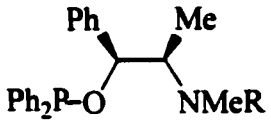


*trans*-$C_8H_{14}$

$\Delta G^{\circ}_{(cis\text{-}C_8H_{14})} - \Delta G^{\circ}_{(trans\text{-}C_8H_{14})} = -26.8$ kJ/ mol

The absolute configuration of the *N*-chiral centers formed upon coordination of **2a,c** (Chart 5.2) to a metal should depend on steric interactions among the substituents of the resulting six-membered chelate cycle.

## Chart 5.2




**a**, R = H (**POEph**)
**b**, R = Me (**POMePh**)
**c**, R = $Ph_2CH$ (**POPheph**)

**5.2 a - c**

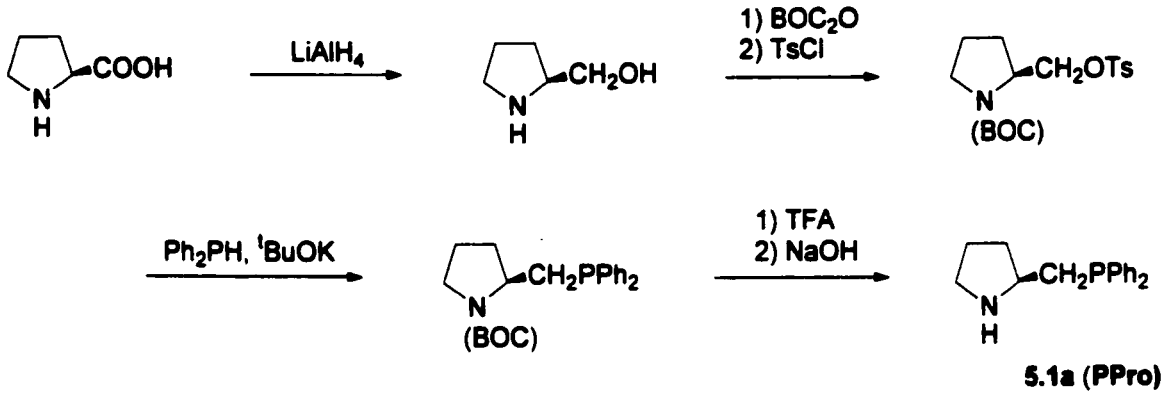
The following chapter describes the preparation and characterization of Rh complexes with aminophosphine derivatives of (S)-proline (**5.1a,b**) and aminophosphinite derivatives of ephedrine, (**5.2a-c**) emphasizing the factors, which affect the structure of the complexes and the selectivity for the formation of chiral centers at nitrogen.

### *5.2 Results and Discussion*

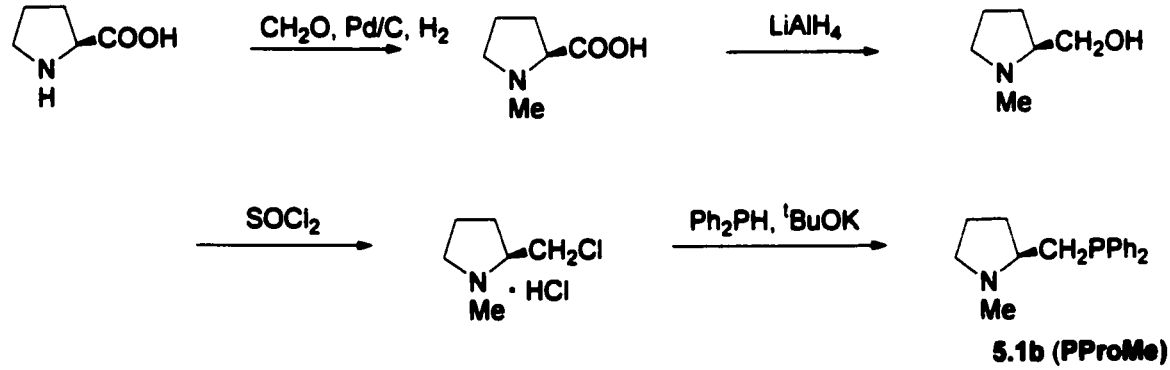
#### 5.2.1 Preparation of Aminophosphines 1a,b.

The aminophosphine ligands **5.1a,b** were both prepared starting from (*S*)-proline by slight modifications of the published procedures (Scheme 5.1 and 5.2, respectively).[10,11] Reduction of (*S*)-proline with $LiAlH_4$ affords (*S*)-prolinol, which was reacted subsequently with BOC-anhydride and tosyl chloride to give (*S*)-1-(*tert*-butylcarbonato)-2-(chloromethyl)pyrrolidine. The latter was converted to **5.1a** by treatment with $Ph_2PH$ and $Bu^tOK$ and subsequent deprotection of the amino group with trifluoroacetic acid (Scheme 5.1).[10] Methylation of (*S*)-proline by reductive condensation with formaldehyde in the presence of Pd/C under hydrogen affords (*S*)-methylproline,[4] which was reduced by $LiAlH_4$ to (*S*)-1-methyl-2-hydroxymethyl pyrrolidine and then reacted with thionyl chloride in chloroform to give (*S*)-1-methyl-2-(chloromethyl)pyrrolidine. The latter was converted to **5.1b** by treatment with $Ph_2PCl$ and $Bu^tOK$ (Scheme 5.2).[11]

## Scheme 5.1

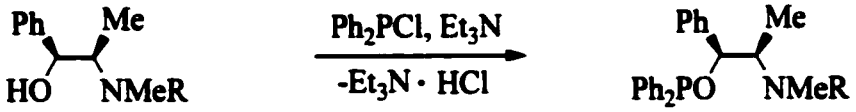



## Scheme 5.2




### 5.2.2 Preparation of Aminophosphinites 5.2a-c.

The aminophosphinite ligands were prepared by treatment of *N*-substituted ephedrines with $Ph_2PCl$ in the presence of $Et_3N$ in benzene (eq 5.1) in a way similar to that described for prolinol based aminophosphinites.[12] The compounds were isolated as colorless oils and characterized by $^{31}P$, $^{1}H$ and $^{13}C$ NMR spectra.




(5.1)

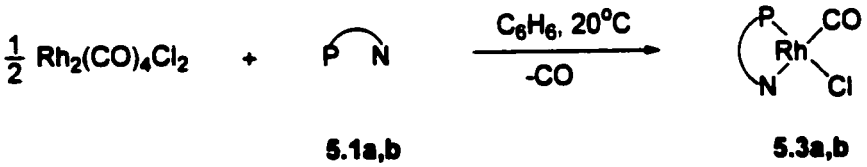
**5.2 a - c**

**a**, R = H (**POEph**)
**b**, R = Me (**POMePh**)
**c**, R = $Ph_2CH$ (**POPheph**)

According to $^{31}P\{^1H\}$ NMR spectra of the reaction mixture, the formation of **5.2b** was very clean and took less than 5 min. at room temperature. Under the same conditions *N*-(diphenylmethyl)ephedrine reacted more slowly (*ca.* 6 h at rt). No intermediates were observed during this time. The $^{31}P\{^1H\}$ NMR spectra showed only the signals of **5.2c** and unreacted $Ph_2PCl$ (δ 113 and 82.5, respectively). Similar reaction of **1a** and $Ph_2PCl$ at 20°C led predominantly to the formation of *N*-(diphenylphosphino)ephedrine (identified by a signal at δ 60.5 in $^{31}P\{^1H\}$ NMR spectrum),[12,15] however heating the reaction mixture to reflux for *ca.* 30 min led to complete rearrangement to the desired **5.2a**. The reaction was accompanied by formation of unidentified side products (*ca.* 20%) and therefore column chromatography was employed in order to purify **5.2a**.

### 5.2.3 Reaction of 5.1a,b with $[Rh_2(CO)_4Cl_2]$. X-Ray Structure of [Rh(CO)(PProMe)Cl] (5.3b)

Treating a benzene solution of $[Rh_2(CO)_4Cl_2]$ with 1 equiv of **5.1a,b** at room temperature leads to the evolution of CO and formation of the corresponding **5.3a,b** (eq 5.2). Similar reaction of $[Rh_2(CO)_4Cl_2]$ with 2 equiv of **5.1a,b** afforded intractable mixtures of unidentified products and was not therefore further investigated.




**5.1a,b** **5.3a,b** (5.2)

Complexes **5.3a,b** were isolated in high yield as air stable yellow crystalline solids soluble in common organic solvents, except for saturated hydrocarbons and were characterized by elemental analysis, IR- and NMR spectroscopy (see experimental section).

The solid state structure of **5.3b** was determined by single crystal X-ray diffraction. An ORTEP plot of the complex is given in Figure 5.1; selected bond distances and angles are compiled in Table 5.1. The square planar coordination environment of the central Rh atom consists of a *cis*-chelating aminophosphine, a chloro ligand and a carbonyl group, which is trans to the nitrogen. As expected the [3.3.0] bicyclic system of the chelate is *cis*-fused and the chiral N-center of the chelate adopts an (*S*)-configuration. The values of Rh-P, Rh-N and the other bond lengths are unexceptional.

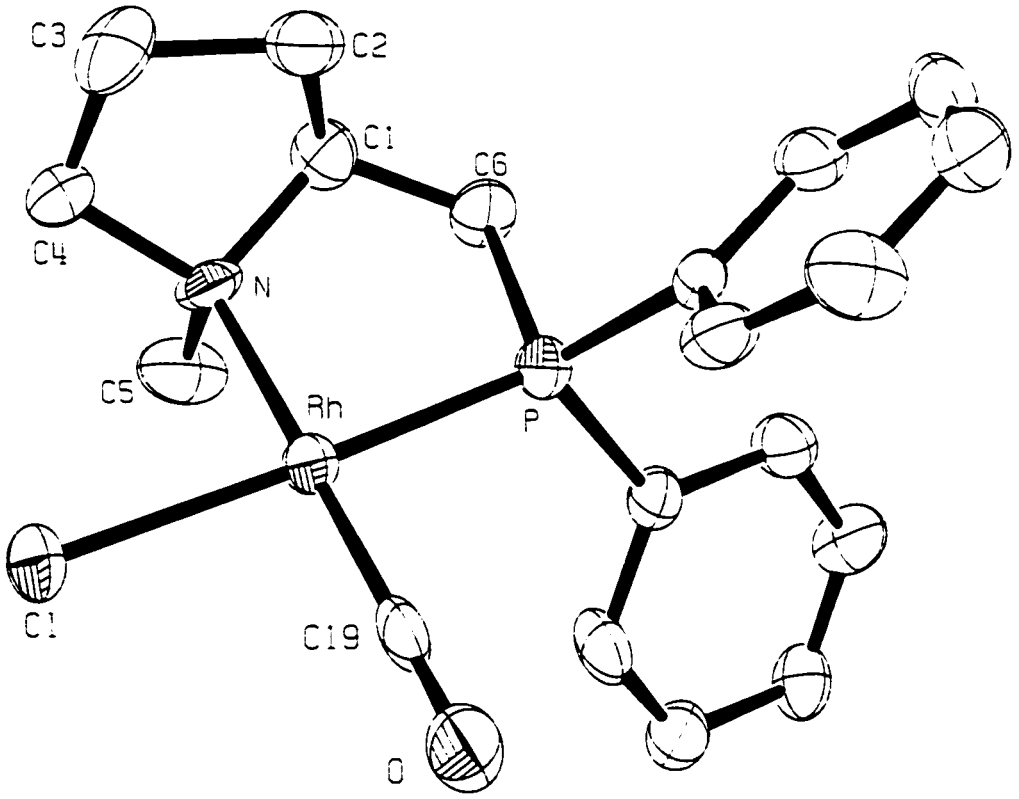



**Figure 5.1.** Perspective diagram of **5.3b** with 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

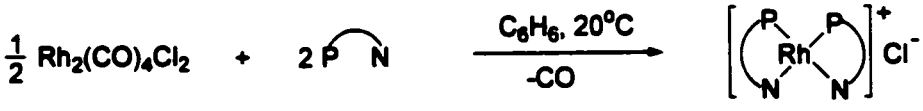
**Table 5.1** Selected Bond Distances (Å) and angles (deg) for **5.3b**.

| | | | |
|---|---|---|---|
| Rh-N | 2.186(5) | Rh-Cl | 2.378(2) |
| Rh-P | 2.217(2) | C(19)-O | 1.151(7) |
| Rh-C(19) | 1.792(7) | | |
| | | | |
| N-Rh-P | 85.01(16) | Rh-N-C(1) | 109.6(5) |
| P-Rh-C(19) | 94.1(2) | Rh-N-C(4) | 117.0(5) |
| C(19)-Rh-Cl | 89.4(2) | Rh-N-C(5) | 106.8(4) |
| Cl-Rh-N | 91.31(16) | C(4)-N-C(5) | 110.4(6) |

The $^{31}P\{^{1}H\}$ NMR spectra of **5.3a,b** in toluene display doublets (δ 59, $J_{P\text{-}Rh}$ = 172 Hz and δ 61, $J_{P\text{-}Rh}$ = 173 Hz respectively) which remained sharp and did not split when the spectra were recorded from –80 to 110°C. This suggests that the formation of the *N*-chiral centers occurs selectively and the complexes **5.3a,b** exist in solution as single epimers.

### 5.2.4. Reaction of POEph with $[Rh_2(CO)_4Cl_2]$. X-ray structure of $[Rh(POEph)_2]^+Cl^-$ (5.4a).

Treatment of a benzene solution of $[Rh_2(CO)_4Cl_2]$ with 2 equiv of **5.2a** led to the evolution of CO and formation of complex **5.4a** according to eq 5.3.




**5.2a** **5.4a** **(5.3)**

According to the $^{31}P\{^{1}H\}$ NMR spectra, complex **5.4a** was the only metalloorganic product

even when less than 2 equiv of the aminophosphinite were used. The signal of unreacted **5.2a** appeared in the spectrum only when more than 2 equiv of the ligand were added. The complex was isolated in high yield as air stable yellow crystals soluble in benzene, $CH_2Cl_2$ and methanol, but insoluble in $Et_2O$ and saturated hydrocarbons. The structure of **5.4a** was established by single crystal X-ray diffraction. An ORTEP plot of the complex is shown in Figure 5.2, selected bond distances and angles are presented in Table 5.2.

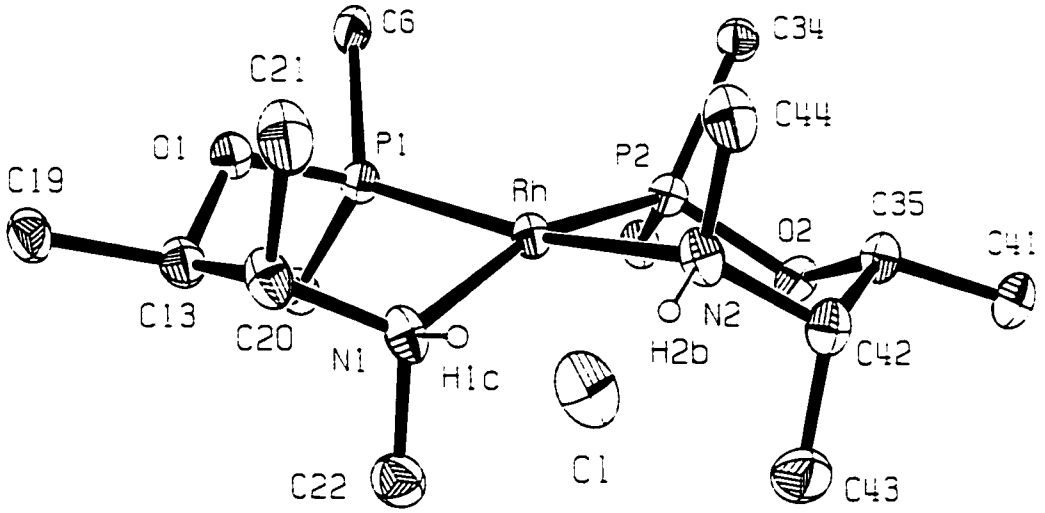



**Figure 5.2.** Perspective diagram of **5.4a** with 30% probability ellipsoids. The hydrogen atoms (except for *N*-H) and phenyl carbon atoms (except for *ipso*) are omitted for clarity.

**Table 5.2.** Selected Bond Distances (Å) and Angles (deg) for **5.4a**.

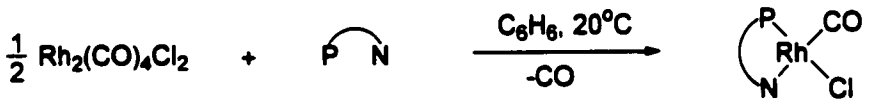
| | | | |
|---|---|---|---|
| Rh-N(1) | 2.182(3) | N(1)-Rh-N(2) | 85.77(10) |
| Rh-N(2) | 2.201(3) | N(2)-Rh-P(2) | 88.98(7) |
| Rh-P(1) | 2.1855(9) | P(1)-Rh-P(2) | 98.74(3) |
| Rh-P(2) | 2.1887(8) | C(22)-N(1)-Rh | 106.7(2) |
| O(1)-P(1) | 1.633(3) | C(22)-N(1)-C(20) | 111.1(3) |
| N(1)-Rh-P(1) | 89.34(8) | C(20)-N(1)-Rh | 123.3(3) |

The coordination environment of the Rh is noticeably distorted from a square planar geometry (the *trans*-P-Rh-N angles are 164.9 and 166.4°), with the distortion presumably due to steric repulsion between the *cis*-$PPh_2$ fragments. The observed arrangement with two phosphorus atoms *cis* to each other seems to be quite common for bis *P,N*-chelated metallocomplexes and was reported for closely related $[Rh(PN)_2]PF_6$, PN = 1-(2-pyridyl)-2-(diphenylphosphino)ethane[16] and some Ru complexes.[17] The six-membered chelate rings of the complex adopt the thermodynamically more stable chair conformation with the bulky Ph groups at C(13) and C(35) in equatorial positions, while the sterically less demanding Me substituents at C(20) and C(42) occupy axial sites (chirality of the ligands dictates *cis*-orientation of the neighboring Ph and Me groups). Both nitrogen atoms possess the *(R)*-configuration with the attached Me substituents in axial positions. It should be noted that the chiral centers at the N atoms in **5.4a** arise only upon coordination to the metal, therefore another diastereomer with a sterically more favorable equatorial orientation of the *N*-Me groups could be formed. Since this does not happen, it seems reasonable to assume that the selective formation of the *(R)*-diastereomer, which occurs despite unfavorable 1,3-diaxial interaction of the *N*-Me and *P*-Ph groups, is explained by the strong hydrogen bonding between the Cl-anion and the two equatorial protons attached to the nitrogens. The *N*(H)...Cl interatomic separation (3.158(5) and 3.176(5) Å) in **5.4a** is consistent with strong Cl-H hydrogen bonds, while the hypothetical *(S)*-diastereomer would possess two *trans*-*N*-H substituents in axial positions. The latter is unsuitable for simultaneous formation of two hydrogen bonds with the Cl-anion. The $^1$H NMR spectrum of **5.4a** displays a broad resonance at 8.3 ppm which is typical for hydrogen bonded *N*-H protons. It should be noted that formation of the chiral centers occurs stereoselectively and **5.4a** exists as a single

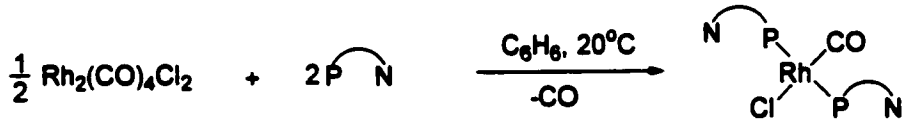
diastereomer, not only in the solid state but also in solution, as follows from the $^{31}P\{^1H\}$ NMR of the reaction mixture (sharp doublet at 141 ppm) and $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and $^1H$ NMR spectra of the isolated complex.[18]

### 5.2.5 Reaction of POMeph with $[Rh_2(CO)_4Cl_2]$. Characterization of [Rh(POMeph)(CO)Cl] (5.5b) and $Rh(POMeph)_2(CO)Cl$ (5.6b).

In comparison with **5.2a**, aminophosphinite **5.2b** gives two different products depending on the metal to ligand ratio employed. The reactions are very clean and occur easily at room temperature according to eqs 5.4 and 5.5.




**5.2b** **5.5b** (5.4)




**5.2b,c** **5.6b,c** (5.5)

The complexes **5.5b** and **5.6b** were isolated in high yield and characterized by elemental analysis, IR and NMR spectra. The carbonyl group of the complex **5.5b** appears as a doublet of doublets in the $^{13}C\{^1H\}$ NMR spectrum ($J_{C\text{-}P}$ = 18 Hz; $J_{C\text{-}Rh}$ = 71 Hz) indicating that there is only one phosphinite ligand in the molecule and that CO is *cis* to the phosphorus. The diastereotopic *N*-Me groups of the complex give two signals in the spectrum. Coordination of the nitrogen to the metal was unequivocally confirmed by the $^{15}N\{^1H\}$ NMR spectrum, which showed a doublet of doublets, due to coupling with Rh ($J_{N\text{-}Rh}$ = 11.5 Hz) and phosphorus ($J_{N\text{-}P}$ = 3.5 Hz). In contrast to **5.5b**, complex **5.6b** shows a doublet of triplets in

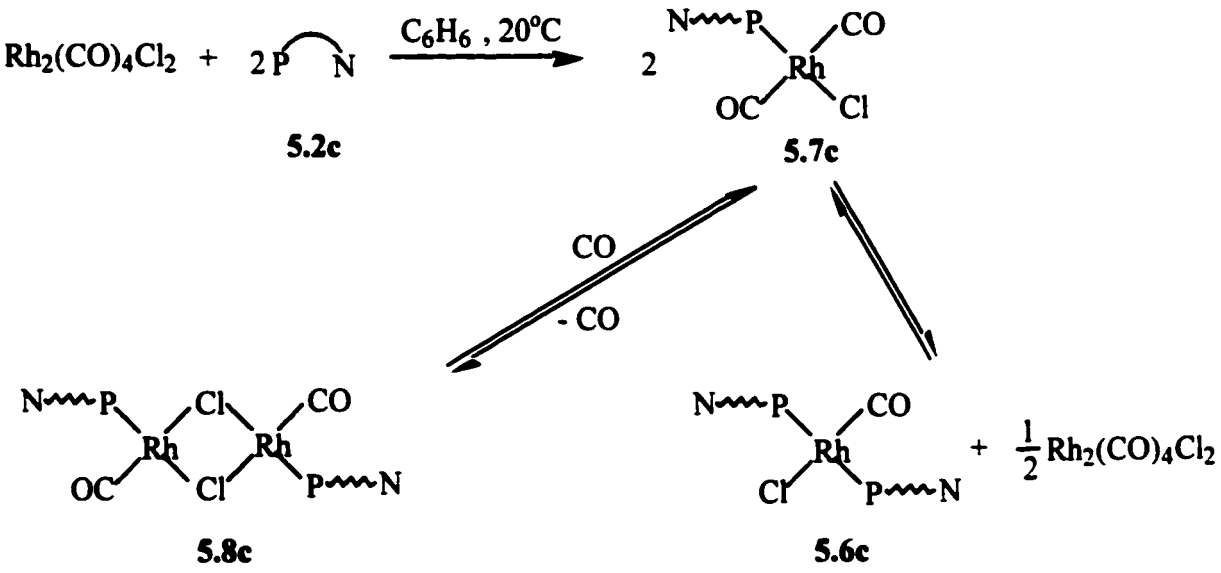
the carbonyl region of the $^{13}C\{^1H\}$ NMR spectrum as a result of CO carbon coupling with Rh ($J_{C\text{-}Rh}$ = 74.5 Hz) and with two P-ligands ($J_{C\text{-}P}$ = 17 Hz). The two phosphinites are equivalent (sharp doublet in $^{31}P\{^1H\}$ NMR) and hence are *trans* to each other. The *N*-Me groups of the complex appear as a single line in the $^{13}C\{^1H\}$ NMR spectrum indicating that the two nitrogens of **5.6b** are equivalent and not coordinated to the metal.

### 5.2.6 Reaction of POPheph with $[Rh_2(CO)_4Cl_2]$. Characterization of $[Rh_2(POPheph)_2(CO)_2Cl_2]$ (5.8c). X-ray structure of $[Rh(POPheph)CO]^+ClO_4^-$ (5.9c).

The reaction of $[Rh_2(CO)_4\ Cl_2]$ and 2 equivalents of **5.2c** occurs according to eq 5.5 in the same way as described for **5.2b**. The resulting **5.6c** was isolated in high yield as an air stable orange solid and characterized by elemental analysis, IR and NMR spectroscopy (see experimental section).

Treatment of $[Rh_2(CO)_4\ Cl_2]$ with 1 equiv of **5.2c** in benzene at room temperature leads to the appearance of two broad doublets at δ 125 ($J_{P\text{-}Rh}$ = 192 Hz), 110 ($J_{P\text{-}Rh}$ = 144 Hz) and a sharp doublet at 116 ppm ($J_{P\text{-}Rh}$ = 136 Hz) in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture. The sharp doublet was identified as the signal of **5.6c** on the basis of its chemical shift and coupling constant. It seemed reasonable to assume that the reaction involves a set of equilibria shown in Scheme 5.3.

**Scheme 5.3**




**5.2c** **5.7c** **5.8c** **5.6c**

The removal of CO from the solution with a stream of inert gas resulted in the disappearance of the doublets of **5.6c** (116 ppm) and **5.7c** (110 ppm) from the NMR spectrum while the doublet corresponding to **5.8c** became sharp. Bubbling CO through the solution restored the original equilibrium. Complex **5.8c** was isolated from the degassed reaction mixture in high yield and characterized by elemental analysis, IR and NMR spectra. The carbonyl groups of the complex appear as a doublet of doublets (δ 183.5, $J_{C\text{-}P}$ = 19 Hz, $J_{C\text{-}Rh}$ = 82 Hz) with the value of the C-P coupling constant indicative of a *cis* relationship between the CO and phosphorus. The amino groups of **5.8c** are equivalent and not coordinated to rhodium as indicated by a sharp singlet at - 342 ppm in the $^{15}N\{^{1}H\}$ NMR spectrum. The available spectral data do not contradict the proposed structure of **5.8c** as a dimer with two phosphinites coordinated in an *anti* fashion. We cannot exclude, however, that these ligands occupy *syn* positions in the dimer or that the complex exists as a mixture of both isomers.

It seemed conceivable that substitution of the bridging chlorides with weakly

coordinating anions such as perchlorate would destroy the dimeric structure of **5.8c** bringing about coordination of the pendant amino group to the metal. Indeed treatment of **5.8c** with $AgClO_4$ leads to precipitation of silver chloride and the formation of a cationic complex **5.9c** containing *P,N*-chelating aminophosphinite and, surprisingly, a Ph group of the *N*-(diphenylmethyl) fragment coordinated to rhodium in an unusual $\eta^2$ fashion. The complex was isolated in high yield as yellow air stable crystals soluble in $CH_2Cl_2$ and methanol, insoluble in THF and aromatic hydrocarbons. The structure of **5.9c** was established by single crystal X-ray diffraction. An ORTEP plot as well as selected bond distances and angles of the complex cation, are shown in Figure 5.3 and Table 5.3, respectively.

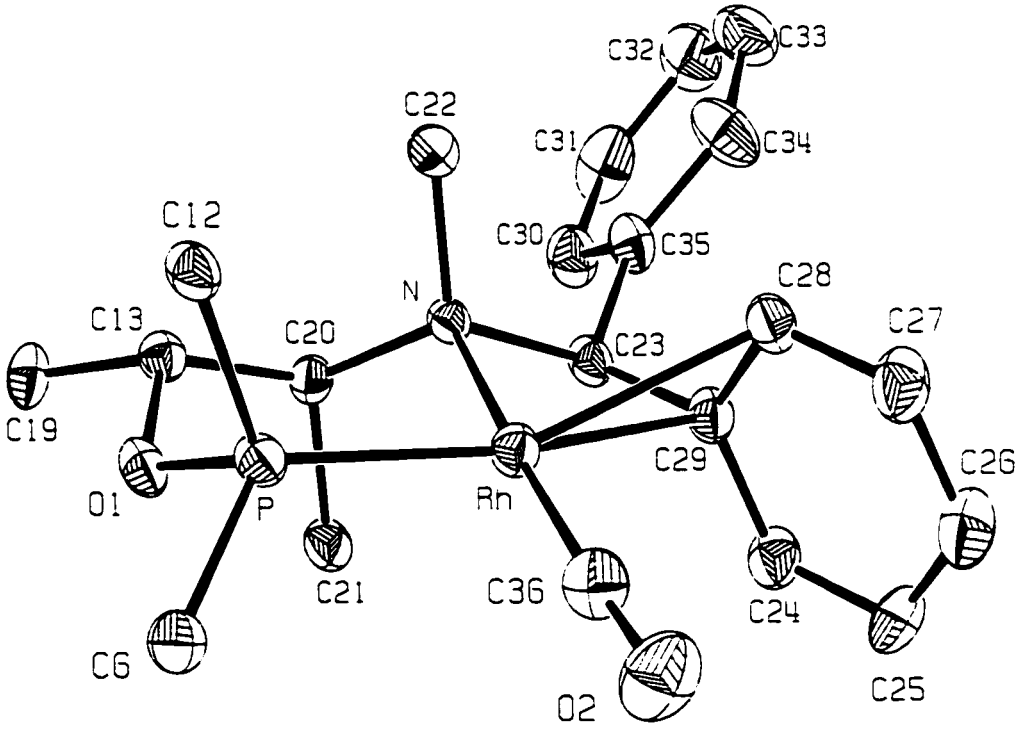



**Figure 5.3.** Perspective diagram of the cation **5.9c** with 30% probability ellipsoids. All hydrogen atoms and non-*ipso*-phenyl carbon atoms on P and C(13) are omitted for clarity.

**Table 5.3.** Selected Bond Distances (Å) and Angles (deg) for **5.9c**.

| | | | |
|---|---|---|---|
| Rh-N | 2.127(5) | C(27)-C(28) | 1.405(12) |
| Rh-P | 2.2015(16) | P-O(1) | 1.605(5) |
| Rh-C(36) | 1.835(9) | N-Rh-P | 92.34(13) |
| C(36)-O(2) | 1.146(10) | N-Rh-C(36) | 174.4(3) |
| Rh-C(29) | 2.334(6) | C(36)-Rh-P | 92.4(3) |
| Rh-C(28) | 2.449(7) | C(20)-N-C(22) | 109.9(5) |
| C(23)-C(35) | 1.546(10) | C(22)-N-C(23) | 111.9(5) |
| C(23)-C(29) | 1.514(10) | C(22)-N-Rh | 113.0(4) |
| C(28)-C(29) | 1.434(11) | C(20)-N-Rh | 114.9(4) |
| C(24)-C(29) | 1.383(11) | C(23)-N-Rh | 95.2(3) |
| C(24)-C(25) | 1.370(12) | Rh-C(29)-C(28) | 77.0(4) |
| C(25)-C(26) | 1.404(13) | Rh-C(29)-C(24) | 106.6(5) |
| C(26)-C(27) | 1.337(12) | Rh-C(29)-C(23) | 88.4(3) |

The coordination environment of the Rh is formed by a *cis* *P,N*-chelating aminophosphinite, a carbonyl group which is *trans* to the nitrogen and a Ph group coordinated to the metal *via* the *ipso* and *ortho* carbons. The phenyl ring remains approximately planar (rms. deviation = 0.02 Å) and assumes a dihedral angle of 104° with the plane defined by the two coordinated carbons and the Rh atom. The Rh-*ipso*-C distance (2.334(6) Å) is very close to the average value for π-arene Rh complexes (2.33(5) Å)[19], while the distance to the coordinated *ortho* carbon (2.449(7) Å) is substantially longer. A similar situation was reported for $[\eta^3\text{-}CH_2C_6Me_5Rh(P(OPr^i)_3)_2]$, which was described as the benzyl analog of π-allyl Rh complexes[20]. The Rh-C(23) separation (2.746(7) Å) in **5.9c**, however is too long for any bonding interaction and **5.9c** thus represents a new example of still quite rare

$\eta^2$-arene metallocomplexes.[21-23]

The six membered P-N-Rh chelate is in a chair conformation. As anticipated, the bulky diphenylmethyl group at the nitrogen, and Ph at C(13), occupy equatorial positions, rendering the sterically less demanding methyl substituents at C(20) and at the nitrogen in axial sites. The stereogenic N-center thus adopts the (*S*)-absolute configuration. Coordination of Rh to one of the two Ph groups of the diphenylmethyl fragment brings about formation of a chiral center at C(23) with the absolute configuration depending on which phenyl is coordinated. The two possible diastereomers should differ from each other by the position of the uncoordinated Ph group relative to Me substituents at the N and C(20). The observed structure of **5.9c** displays an *(S)*-configuration at C(23) with the uncoordinated Ph group *cis* to the *N*-Me unit, while the hypothetical *(R)*-diastereomer would possess the uncoordinated Ph *cis* to the Me group at C(20). The *cis* interaction in **5.9c** is relieved to some extent by pivoting of the diphenylmethyl group around the C(23)-N bond (C(22)-N-C(23)-C(35) torsion angle is 31.8(5)°), while the *cis* interaction between the uncoordinated Ph and Me at C(20) is probably severe enough to prevent formation of the *R*-diastereomer. The structure of **5.9c** thus incorporates six stereogenic centers. Two of them (C(13) and C(20)) were present in the ligand, while the others (C(23), C(28), C(29) and N) arise upon coordination of the $\eta^2$-Ph and amino group to the metal. Formation of the new chiral centers occurs stereoselectively and **5.9c** exists as a single diastereomer, not only in the solid state but also in solution ($^{31}P\{^1H\}$ NMR of the reaction mixture[24] and $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and $^1H$ NMR spectra of the isolated complex).

### 5.2.7 Fluxional behavior of 5.9c in solution.

The $\eta^2$ coordinated Ph group of **5.9c** gives six sharp resonances in the 125 MHz $^{13}C\{^1H\}$NMR spectra[25] recorded below 260 K (see Fig. 5.4). At higher temperatures the signals of the *ortho* and *meta* carbons become broad and cannot be observed at 285 K. The *meta* carbons show a broad averaged resonance (δ 134.3) at 310 K, while the *ortho* carbons still cannot be seen in the spectrum. The signals of the *ipso* and *para* carbon atoms of the $\eta^2$-Ph remain sharp in the temperature interval 210 - 310 K. Taken together these data suggest that the observed fluxional behavior of **5.9c** is explained by restricted rotation of the coordinated Ph group around the σ-bond (C(23) - C(29) on Fig.5.3). It should be noted that the other Ph groups of the complex have low rotational barriers as indicated by the pairwise equivalence of the *ortho* and *meta* carbons in the VT $^{13}C\{^1H\}$ NMR spectra.

The *ortho* protons of the $\eta^2$-Ph are nonequivalent and well separated from the other aromatic protons in the $^1H$ NMR spectra of the complex (see Fig 4). At 260 K they appear as sharp doublets centered at 8.6 and 7.9 ppm. Increasing the temperature leads to broadening and finally collapse of the signals at 305 ± 5 K. The value of the rotational barrier of the $\eta^2$-Ph group calculated for **5.9c** .(13.7 ± 0.3 kcal/mol) compares well with the value obtained for "ring whizzing" in $\eta^2$-arene- pentammineosmium (II) complexes (11.8 - 17.2 kcal/mol)[26] and is significantly higher than the corresponding value[20] for $[\eta^3\text{-}CH_2C_6Me_5Rh(P(OPr^i)_3)_2]$, where two sides of the benzyl ligand appear to be equivalent even at 193 K.

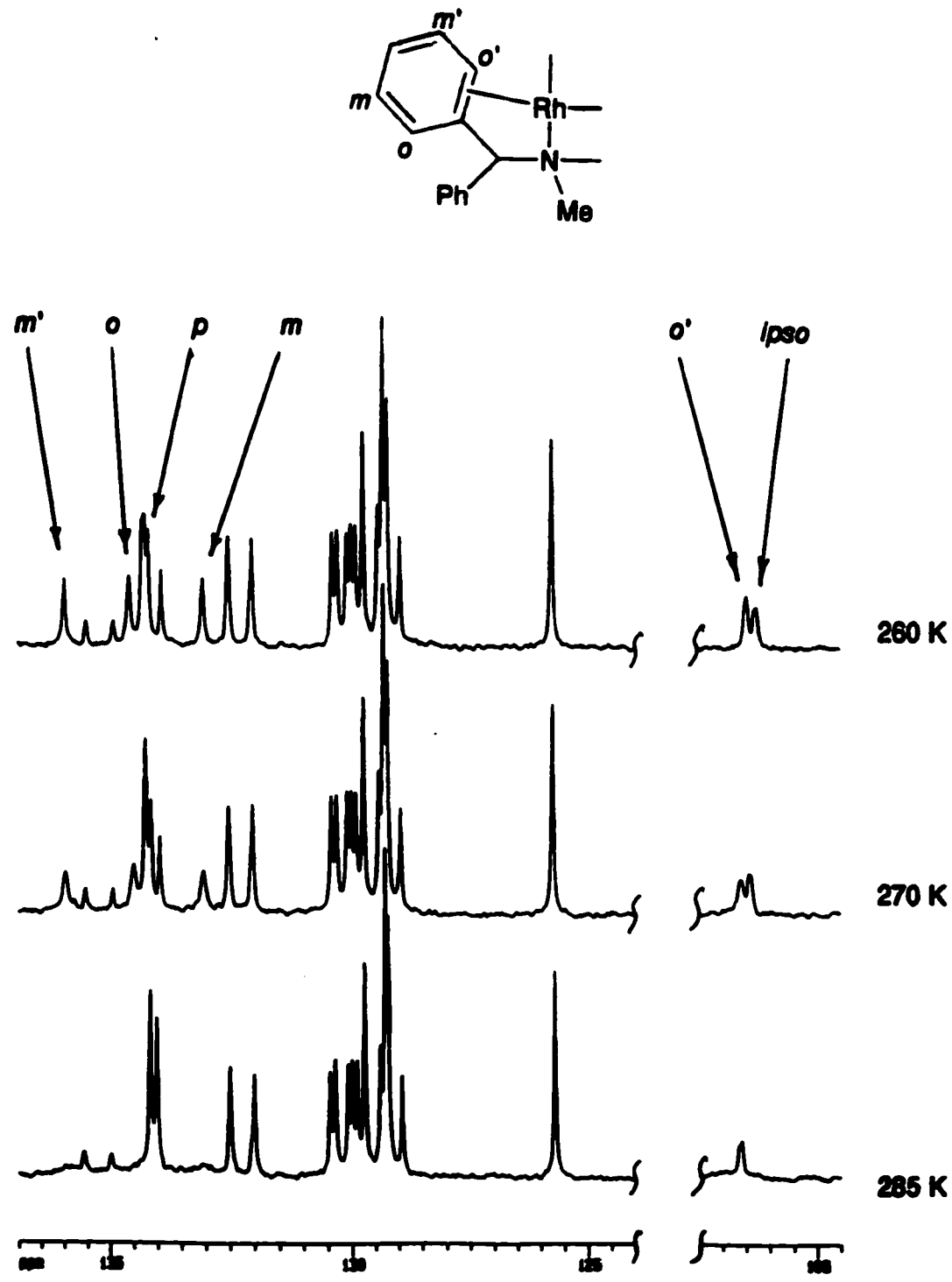



**Figure 5.4** 125 MHz VT $^{13}C\{^1H\}$ NMR spectra (aromatic region) of 5.9c in $CD_2Cl_2$.

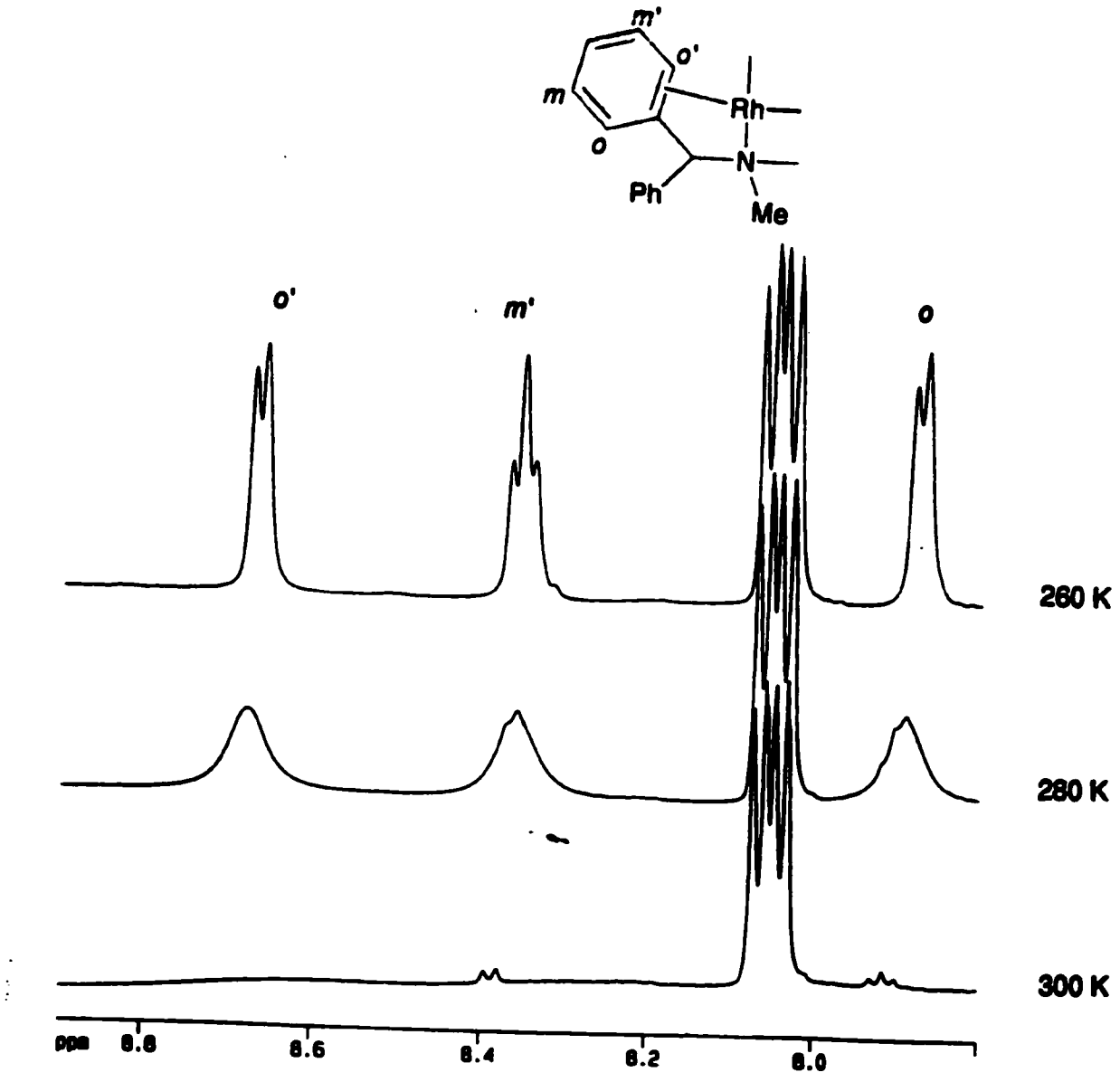



**Figure 5.5.** 500 MHz VT $^1$H NMR spectra (fragment of aromatic region) of **5.9c** in $CD_2Cl_2$.

## 5.3 Conclusions

The present study demonstrates that coordination properties of aminophosphinites are very sensitive to the steric bulk of the amino group. Reaction of **5.2a** and $[Rh_2(CO)_4Cl_2]$ occurs with displacement of the Cl-anion and all carbonyls from the coordination sphere of Rh(I). The two *P,N*-chelate cycles of the resulting complex **5.4a** remain intact in the presence of excess ligand, indicating high affinity of the NHMe fragment to the metal. The $NMe_2$ terminus of **5.2b** easily cleaves the Cl-bridges, but is not able to displace carbonyl, and the chelate ring in the formed **5.5b** can be opened by an excess of the ligand. The amino group of **5.2c**, which possesses a rather large *N*-(diphenylmethyl) substituent, is not able to cleave the relatively weak Cl-bridges. The *P,N*-ligand in **5.8** is connected to Rh only *via* phosphorus. It does not mean, however, that the $NMeCHPh_2$ fragment cannot be coordinated, and treatment of the complex with $AgClO_4$ does lead to the formation of a chelate cycle. The affinity of the amino group of **5.2a-c** toward Rh(I) thus can be arranged in the following order: -NHMe > CO > $-OPPh_2$ > $-NMe_2$ > $\mu$-$Cl^-$ > $-NMeCHPh_2$ > $ClO_4^-$.

The superior stability of the *P,N*-chelate in **5.4a** is probably explained by the formation of strong hydrogen bonds between the Cl anion and the two *N*-H protons. The hydrogen bonds render the *N*-H protons of the six membered chelate rings in equatorial positions, and thus define the configuration of the stereogenic nitrogen atoms in the complex. The selective formation of the chiral centers at the nitrogen in **5.9c** is governed by the well known tendency of non-rigid six membered rings to adopt a chair conformation with the sterically more demanding substituents in equatorial positions. The selective formation of N-chiral centers in **5.3a,b** is explained by the higher thermodynamic stability of *cis* (as compared to *trans*) fused [3.3.0] bicyclic systems arising upon chelation of **5.1a,b** to a metal.

## 5.3.Experimental Section.

All manipulations were carried out under inert atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. Aminophosphine PProMe (**5.1b**)[11] and (1*R*, 2*S*)-*N*-(diphenylmethyl)ephedrine[5] were prepared according to the published procedures. Other chemicals were purchased from Aldrich, and were used as received. The following instruments were used: Varian XL-300 and Bruker AMX 500 (NMR), Bomem MB-100 (FT-IR) and Perkin-Elmer 2400 Series II (combustion microanalysis). The natural abundance $^{15}N\{^1H\}$ NMR spectra were acquired using 0.5 - 0.7 M solutions of the Rh complexes, 10 mm probe, $CH_3NO_2$ as external standard, D1 = 12s, gated decoupling. Spectra with acceptable (20:1) signal to noise ratio were observed after 12 - 24 h.

**5.3.1 Synthesis of PPro (5.1a)** (*S*)-Proline (10.0 g, 86.8 mmol) was added by small portions to a stirred suspension of $LiAlH_4$ (3.3 g, 86.8 mmol) in THF (170 mL) under $N_2$ at –78°C. After the addition was complete the cooling bath was removed, the mixture was allowed to warm up to room temperature and stirred for 12 h. The stirred reaction mixture was cooled in an ice bath and subsequently treated with water (5.0 ml) and 15% NaOH (5.0 mL). The obtained suspension was stirred at room temperature for 1 h and filtered. The solid was washed with hot THF (4 x 20 mL) and the combined filtrates were evaporated to give crude (*S*)-prolinol as a slightly yellow oil (8.15 g, 80.7 mmol), which was used for another step without purification.

BOC-anhydride (19.0 ml, 84.0 mmol) was added dropwise to a stirred solution of crude (*S*)-prolinol (8.15 g, 80.7 mmol) in a mixture of $Et_3N$ (18 ml) and $CH_2Cl_2$ (50 mL) at 0°C. The reaction mixture was stirred at room temperature for 2 h, cooled to 0°C and treated

with tosyl chloride (18.2 g, 95 mmol), added as a solid. The resulting solution was stirred overnight at room temperature, diluted with $Et_2O$ (200 ml) and treated with 10% HCl. The organic phase was separated, washed with water, saturated $NaHCO_3$, dried over $Na_2SO_4$ and evaporated. The obtained residue was chromatographed on a silica column (400 x 40 mm, $Et_2O$ : hexanes 1:2 – 1:4) to give (*S*)-*N*-*tert*-butoxycarbonylprolinol-p-toluenesulfonate (21.2 g, 59.6 mmol, 69%).

$Ph_2PH$ (0.713 mL, 4.1 mmol) was added to a solution of potassium *tert*-butoxide in THF (20 ml) The resulting red-orange solution was stirred for 30 min and treated with a solution of (*S*)-*N*-*tert*-butoxycarbonylprolinol-p-toluenesulfonate (1.44 g, 4.05 mmol) in THF (10 mL). The reaction mixture was stirred for 1 h at room temperature and evaporated. The residue was stirred with a mixture of water (20mL) and ether (20 mL). The ethereal extract was separated, washed with sat. NaCl, dried over $Na_2SO_4$ and evaporated. The obtained yellow oil was stirred with trifluoroacetic acid (15 mL) for 2 h and the resulting solution was evaporated. The residue was dissolved in $Et_2O$ (20 mL) and treated at 0°C with 10% aqueous ammonia (20 mL) The organic layer was separated, washed with sat. NaCl, dried over $Na_2SO_4$ and evaporated. The obtained yellow oil was chromatographed on basic alumina column (100 x 25 mm, hexanes : $Et_2O$ = 4:1 – 2:1) to give **5.1a** (935 mg, 3.47 mmol, 86%) as a colorless oil. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: -19.7 (s). $^1H$ NMR ($CDCl_3$), δ: 1.2-1.4 (m, 1H); 1.5-1.8 (m, 2H); 1.8-1.9 (m, 1H); 2.0 (s, 1H); 2.2 (m, 1H); 2.3 (m, 1H); 2.7-2.8 (m, 1H); 2.9-3.0 (m, 2H); 7.1-7.9 (m, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 25.1 (s, $CH_2$); 32.8 (d, $J_{C\text{-}P}$ = 7.5 Hz, $CH_2$); 35.7 (d, $J_{C\text{-}P}$ = 13 Hz, $CH_2$); 46.1 (s, $CH_2$); 56.2 (d, $J_{C\text{-}P}$ = 16 Hz, CH); 127.9 (s, Ph); 128.0 (s, Ph); 128.1 (s, Ph); 128.2 (s, Ph); 132.2 (d, $J_{C\text{-}P}$ = 12 Hz, Ph); 132.5 (d, $J_{C\text{-}P}$ = 11 Hz, Ph); 138.2 (d, $J_{C\text{-}P}$ = 29 Hz, Ph); 138.3 (d, $J_{C\text{-}P}$ = 29 Hz, Ph). $[\alpha]_D^{20}$-28.2° (c = 3.1,

toluene) [lit.* $[\alpha]_D^{20}$-27.9° (c = 2.9, EtOH)].

**5.3.2 Synthesis of Aminophosphinites (5.2a-c).** A solution of $Ph_2PCl$ (2.0 mL, 11.14 mmol ) and $Et_3N$ (4 mL) in 30 mL of benzene was added to a stirred solution of the corresponding ephedrine (11.16 mmol) in 30 mL of benzene. The resulting suspension was heated to reflux for 1 h, allowed to cool and filtered. The filtered white solid was washed with benzene (3 x 10 mL), and the combined filtrates were evaporated and dried in vacuum at 100°C. The oily residue was stirred with heptane : $Et_2O$ (4 : 1, 15 mL), a white precipitate which formed was filtered off, and the filtrate was passed through a short column with basic alumina (50 x 25 mm) and eluted with 30 mL of heptane : $Et_2O$ (1 : 2 for **5.2a**, or 2 : 1 for **5.2b,c**). Removal of the solvent in vacuum afforded the corresponding **5.2a-c** as a colorless oil.

**5.2a** (POEph).[27] The compound was purified by column chromatography on basic alumina (250 x 25 mm, heptane - 2 : 1 heptane/$Et_2O$).Yield 63%. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 113.1 (s). $^1H$ NMR ($CDCl_3$), δ: 1.1 (d, $J$ = 6.4 Hz, 3H); 2.3 (s, 3H); 2.9 (m, 1H); 5.0 (dd, $J_{H-H}$ = 4.6 Hz, $J_{H-P}$ = 9.7 Hz, 1H); 7.2 - 7.7 (m, 15H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 15.2 (s, Me); 33.8 (s, Me); 60.6 (d, $J_{C-P}$ = 5.5 Hz, CH); 83.9 (d, $J_{C-P}$ = 18.7 Hz, CH); 127.0 - 131.1 (12 lines, Ph); 140.1 (d, $J_{C-P}$ = 2.5 Hz, Ph); 142.05 (d, $J_{C-P}$ = 15.4 Hz, Ph); 142.15 (d, $J_{C-P}$ = 20 Hz, Ph). $[\alpha]_D^{20}$-5.9° (c = 3.9, toluene)

**2b** (POMeph). Yield 81%. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 112.8 (s). $^1H$ NMR ($CDCl_3$), δ: 1.2 (d, $J$ = 6.7 Hz, 3H); 2.3 (s, 6H); 3.0 (m, 1H); 5.1 (dd, $J_{H-H}$ = 5.5 Hz, $J_{H-P}$ = 8.9 Hz, 1H); 7.3 - 7.8 (m, 15H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 9.6 (s, Me); 41.4 (s, Me); 65.1 (d, $J_{C-P}$ = 6.2 Hz, CH); 85.4 (d, $J_{C-P}$ = 18.6 Hz, CH); 127.0 - 131.2 (12 lines, Ph); 141.6 (d, $J_{C-P}$ = 2 Hz, Ph);

142.1 (d, $J_{C\text{-}P}$ = 14Hz, Ph); 142.4 (d, $J_{C\text{-}P}$ = 17Hz, Ph). $[\alpha]_D^{20}$+21.4° (c = 22.5, benzene).

**2c** (POPheph).[27] Yield 71%. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 112.2 (s). $^1H$ NMR ($CDCl_3$), δ: 1.1 (d, $J$ = 6.7 Hz, 3H); 2.1 (s, 3H); 3.2 (m, 1H); 4.4 (s, 1H); 4.8 (apparent t, $J_{H\text{-}H} \approx J_{H\text{-}P} \approx$ 8.5 Hz, 1H); 6.8 - 7.6 (m, 25H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 9.5 (s, Me); 34.2 (s, Me); 59.3 (d, $J_{C\text{-}P}$ = 7.4 Hz, CH); 74.1 (s, CH); 85.1 (d, $J_{C\text{-}P}$ = 18.6 Hz, CH); 126.6 - 131.4 (18 lines, Ph); 141.8 - 142.1 (6 lines, Ph); 142.9 (s, Ph); 143.9 (s, Ph). $[\alpha]_D^{20}$+105° (c = 2.1, benzene).

**5.3.3 Synthesis of [ClRh(CO)(PPro)] (5.3a)** **PPro** (1.822 mmol, 0.251 M in $C_6H_6$) was added to a stirred solution of $[Rh_2(CO)_4Cl_2]$ (177 mg, 0.455 mmol) in 10 mL of benzene. The resulting light yellow solution was reduced in volume to *ca.* 6 mL and set aside for 2 h. The formed crystals were separated by decantation, rinsed with benzene (2 mL) and dried in vacuum to give 220 mg of [ClRh(CO)(PPro)] as pale yellow crystals. The additional 108 mg of the product was obtained upon the concentration of the mother liquor. The total yield was 328 mg (0.753 mmol, 83%). . Anal. Calcd. for $C_{18}H_{20}ClNOPRh$ : C, 49.6; H, 4.6; N, 3.2. Found: C, 49.8; H, 4.6; N, 3.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 58.8 (d, $J_{P\text{-}Rh}$ = 172 Hz). $^1H$ NMR ($CDCl_3$), δ: 1.5 (m, 1H); 1.7 – 2.0 (m, 3H); 2.5 (m, 1H); 2.8 (m, 1H); 3.1 (m, 1H); 3.3 (m, 1H); 3.7 (m, 1H); 4.7 (m, 1H); 7.2 – 7.8 (m, 10H); 8.7 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 24.3 (s, $CH_2$); 29.7 (d, $J_{C\text{-}P}$ = 12 Hz, $CH_2$); 38.8, (d, $J_{C\text{-}P}$ = 28 Hz, $CH_2$); 48.9 (s, $CH_2$); 60.4 (d, $J_{C\text{-}P}$ = 6 Hz, CH); 128.6 (d, $J_{C\text{-}P}$ = 11 Hz, Ph); 128.7 (d, $J_{C\text{-}P}$ = 11 Hz, Ph); 130.6 (d, $J_{C\text{-}P}$ = 17 Hz, Ph); 130.7 (d, $J_{C\text{-}P}$ = 17 Hz, Ph); 132.6 (s, Ph); 132.8 (s, Ph); 133.7 (dd, $J_{C\text{-}P}$ = 71 Hz, $J_{C\text{-}Rh}$ = 2 Hz, Ph); 133.9 (dd, $J_{C\text{-}P}$ = 72 Hz, $J_{C\text{-}Rh}$ = 2 Hz, Ph); 188.7 (dd, $J_{C\text{-}P}$ = 18 Hz, $J_{C\text{-}Rh}$ = 70 Hz, CO); IR (KBr), $\nu_{CO}$ : 1968 $cm^{-1}$

**5.3.4 Synthesis of [ClRh(CO)(PProMe)] (5.3b).** **PProMe** (0.556 mmol, 0.411 M in $C_6H_6$) was added to a stirred solution of $[Rh_2(CO)_4Cl_2]$ (108 mg, 0.278 mmol) in 10 mL of benzene. The resulting light yellow solution was reduced in volume to *ca.* 6 mL and left overnight. The formed crystals were separated by decantation, rinsed with benzene (2 mL) and dried in vacuum to give 207 mg (0.460 mmol, 83%) of [ClRh(CO)(PPro)] as pale yellow crystals. Anal. Calcd. for $C_{19}H_{22}ClNOPRh$ : C, 50.7; H, 4.9; N, 3.1. Found: C, 50.9; H, 4.9; N, 3.1. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 61.3 (d, $J_{P\text{-}Rh}$ = 173 Hz). $^1H$ NMR ($CDCl_3$), δ: 1.3 – 1.9 (m, 4H); 2.2 (m, 1H); 2.5 (m, 1H); 2.6 (s, 3H); 2.8 (m, 1H); 4.1 (m, 1H); 7.2 – 7.4 (m, 6H); 7.6 (m, 2H); 7.8 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 21.3 (s, $CH_2$); 28.5 (d, $J_{C\text{-}P}$ = 6 Hz, $CH_2$); 34.1, (d, $J_{C\text{-}P}$ = 25 Hz, $CH_2$); 45.0 (s, $CH_3$); 59.2 (s, $CH_2$); 70.5 (d, $J_{C\text{-}P}$ = 5 Hz, CH); 128.5 (d, $J_{C\text{-}P}$ = 11 Hz, Ph); 128.8 (d, $J_{C\text{-}P}$ = 11 Hz, Ph); 130.4 (d, $J_{C\text{-}P}$ = 2 Hz, Ph); 130.9 (d, $J_{C\text{-}P}$ = 2 Hz, Ph); 131.8 (d, $J_{C\text{-}P}$ = 14 Hz, Ph); 132.9 (d, $J_{C\text{-}P}$ = 14 Hz, Ph); 132.7 (dd, $J_{C\text{-}P}$ = 57 Hz, $J_{C\text{-}Rh}$= 2 Hz, Ph); 133.9 (dd, $J_{C\text{-}P}$ = 58 Hz, $J_{C\text{-}Rh}$ = 2Hz, Ph); 187.8 (dd, $J_{C\text{-}P}$ = 18 Hz, $J_{C\text{-}Rh}$= 70 Hz, CO); IR (KBr), $\nu_{CO}$: 1975cm$^{-1}$.

**5.3.5 Synthesis of [ClRh(POEph)$_2$] (5.4a).** POEph (1.8 mmol, 0.313 M in $C_6H_6$) was added to a stirred solution of $[Rh_2(CO)_4Cl_2]$ (170 mg, 0.437 mmol) in 6 mL of benzene. The resulting bright yellow solution was reduced in volume to *ca.* 5 mL under vacuum and diluted with 6 mL of heptane to form a voluminous yellow precipitate. Heating the reaction flask in boiling water led to transformation of the precipitate into a yellow oil which spontaneously crystallized. The flask was allowed to stay at rt. for 1 h, the crystals were separated, washed with plenty of pentane and dried in vacuum to give 670 mg (0.800 mmol, 91%) of analytically pure **5.4a** as a light yellow microcrystalline solid. Anal. Calcd. for

$C_{44}H_{48}ClN_2O_2P_2Rh$ : C, 63.1; H, 5.8; N, 3.3. Found: C, 62.8; H, 5.6; N, 3.1. $^{31}P\{^1H\}$ NMR ($C_6D_6$), δ: 141 (d, $J_{P\text{-}Rh}$ = 189.5 Hz). $^1H$ NMR ($C_6D_6$), δ: 1.8 (d, $J$ = 6.3 Hz, 3H); 2.8 (m, 4H); 4.7 (s, 1H); 6.7 - 7.8 (m, 21H); 8.3 (broad s, 1H). $^{13}C\{^1H\}$ NMR ($C_6D_6$), δ: 14.8 (s, Me); 39.7 (s, Me); 61.2 (s, CH); 73.8 (s, CH); 126 - 141 (Ph). $^{15}N\{^1H\}$ NMR ($C_6D_6$ : $C_6H_6$ = 1 : 10), δ: -364.3 (second order m). $[\alpha]_D^{20}$+28° (c = 1.0, toluene).

**5.3.6 Synthesis of ClRh(CO)(POMeph) (5.5b).** **POMeph** (2.6 mmol, 0.618 M in $C_6H_6$) was added to a stirred solution of $[Rh_2(CO)_4Cl_2]$ (505 mg, 1.3 mmol) in 12 mL of benzene. The resulting orange solution was evaporated and the pale yellow mass was dissolved in 10mL of hot MeOH and allowed to stay at rt for 1 h and then in a freezer (-17°) overnight. The precipitated yellow crystals were separated, rinsed with cold MeOH and dried under vacuum to give analytically pure **5.5b** (1174 mg, 2.219 mmol, 85%). Anal. Calcd. for $C_{24}H_{26}ClNO_2PRh$ : C, 54.4; H, 5.0; N, 2.6. Found: C, 54.4; H, 5.0; N, 2.5. $^{31}P\{^1H\}$ NMR ($C_6D_6$), δ: 134 (d, $J_{P\text{-}Rh}$ = 184 Hz). $^1H$ NMR ($C_6D_6$), δ: 0.8 (d, $J$ = 6.4 Hz, 3H); 1.75 (m, 1H); 2.5 (s, 6H); 5.2 (d, $J$ = 7.7 Hz, 1H); 6.8 - 7.9 (m, 15H). $^{13}C\{^1H\}$ NMR ($C_6D_6$), δ: 12.2 (s, Me); 47.7 (s, Me); 48.1 (s, Me); 70.8 (d, $J_{C\text{-}P}$ = 3.8 Hz, CH); 77 (s, CH); 125.3 - 138.7 (Ph); 187.9 (dd, $J_{C\text{-}Rh}$ = 71 Hz, $J_{C\text{-}P}$ = 18 Hz, CO). $^{15}N\{^1H\}$ NMR ($C_6D_6$ : $C_6H_6$ = 1 : 10), δ: -355.4 (dd, $J_{N\text{-}Rh}$ = 11.5 Hz, $J_{N\text{-}P}$ = 3.6 Hz). IR (KBr), $\nu_{CO}$: 1985 $cm^{-1}$. $[\alpha]_D^{20}$ +38.7° (c = 0.506, $C_6H_6$).

**5.3.7 Synthesis of [ClRh(CO)(POMeph)$_2$] (5.6b).** **POMeph** (0.804 mmol, 0.618 M in $C_6H_6$) was added to a stirred solution of $[Rh_2(CO)_4Cl_2]$ (77 mg, 0.198 mmol) in 10 mL of benzene. The reaction mixture was evaporated under vacuum and the resulting yellow oil

was stirred with 10 mL of methanol to give a yellow precipitate which was separated, washed with MeOH (2 x 5 mL) and vacuum dried to form 312 mg ( 0.349 mmol, 88%) of **5.6b** as a yellow microcrystalline solid. Anal. Calcd. for $C_{47}H_{52}ClN_2O_3P_2Rh$ : C, 63.2; H, 5.9; N, 3.1. Found: C, 63.5; H, 6.1; N, 3.0. $^{31}P\{^1H\}$ NMR ($C_6D_6$), δ: 114 (d, $J_{P\text{-}Rh}$ = 136.5 Hz). $^1H$ NMR ($C_6D_6$), δ: 1.3 (d, $J$ = 6.6 Hz, 3H); 2.1 (s, 6H); 3.1 ( quint, $J$ = 6.9 Hz, 1H); 6.3 (m, 1H); 6.8 - 8.1 (m, 15H). $^{13}C\{^1H\}$ NMR ($C_6D_6$), δ: 10.6 (s, Me); 42.1 (s, Me); 65.3 (v.t, $J_{C\text{-}P}$ = 6.5 Hz, CH); 84.2 (s, CH); 127.8 - 141.8 (Ph); 186.8 (dt, $J_{C\text{-}Rh}$ = 74.5 Hz, $J_{C\text{-}P}$ = 17 Hz, CO). IR (KBr), $\nu_{CO}$: 1992 $cm^{-1}$.

**5.3.8 Synthesis of $[Rh_2(\mu\text{-}Cl)_2(CO)_2(POPheph)_2]$.(5.8c).** **POPheph** (1.028 mmol, 0.381 M in $C_6H_6$) was added to a stirred solution of $[Rh_2(CO)_4Cl_2]$ (200 mg, 0.514 mmol) in 15 mL of benzene and nitrogen was passed through the homogeneous reaction mixture for 15 min. The resulting orange solution was diluted with 40 mL of heptane and reduced in volume to *ca.* 30 mL under vacuum to give a yellow precipitate and a pale yellow solution. The precipitate was separated by decantation, washed with pentane (2 x 20 mL) and dried under vacuum to give 575 mg ( 0.421 mmol, 82%) of **7c** as a yellow microcrystalline solid. Anal. Calcd. for $C_{72}H_{68}Cl_2N_2O_4P_2Rh_2$ : C, 63.4; H, 5.0; N, 2.0. Found: C, 63.9; H, 5.2; N, 1.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 123 (d, $J_{P\text{-}Rh}$ = 192 Hz). $^1H$ NMR ($CDCl_3$), δ: 1.5 (d, $J$ = 6.5 Hz, 3H); 2.5 (s, 3H); 3.8 (m, 1H); 4.5 (s, 1H); 6.6 (dt, $J_{H\text{-}H}$ = 9.5 Hz, $J_{H\text{-}P}$ = 11.7 Hz, 1H); 6.8 - 8.0 (m, 25H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 10.2 (s, Me); 34.2 (s, Me); 59.1 (d, $J_{C\text{-}P}$ = 8 Hz, CH); 74.1 (s, CH); 85.9 (s, CH); 126.7 - 143.9 (Ph); 183.5 (dd, $J_{C\text{-}Rh}$ = 82 Hz, $J_{C\text{-}P}$ = 19 Hz, CO). $^{15}N\{^1H\}$ NMR ($C_6D_6$ : $C_6H_6$ = 1 : 10), δ: - 341.6 (s). IR (KBr), $\nu CO$ : 1993 $cm^{-1}$.

**5.3.9 Synthesis of [ClRh(CO)(POPheph)$_2$] (5.6c).** **POPheph** (0.721 mmol, 0.381 M in $C_6H_6$) was added to a solution of [$Rh_2(CO)_4Cl_2$] (70 mg, 0.180 mmol) in 10 mL of benzene and the reaction mixture was evaporated under vacuum. The obtained yellow mass was stirred with MeOH, a pale yellow solid was separated and vacuum dried to give 387 mg (0.323 mmol, 90%) of **5.6c** as a light yellow powder. Anal. Calcd. for $C_{71}H_{68}ClN_2O_3P_2Rh$ : C, 71.2; H, 5.7; N, 2.3. Found: C, 71.1; H, 5.9; N, 2.3. $^{31}P\{^1H\}$ NMR ($C_6D_6$), δ: 115 (d, $J_{P\text{-}Rh}$ = 136 Hz). $^1H$ NMR ($C_6D_6$), δ: 1.5 (d, $J$ = 6.2 Hz, 3H); 2.4 (s, 3H); 3.7 (m, 1H); 4.5 (s, 1H); 6.6 (m, 1H); 6.8 - 8.1 (m, 25H). $^{13}C\{^1H\}$ NMR ($C_6D_6$), δ: 10.2 (s, Me); 34.6 (s, Me); 59.6 (v.t, $J_{C\text{-}P}$ = 8 Hz, CH); 74.4 (s, CH); 85.1 (s, CH); 126.8 - 144.4 (Ph); 186.8 (dt, $J_{C\text{-}Rh}$ = 74.5 Hz, $J_{C\text{-}P}$ = 17 Hz, CO). IR (KBr), $\nu_{CO}$ : 1986 $cm^{-1}$.

**5.3.10 Synthesis of [Rh(CO)(POPheph)] $ClO_4$ (5.9c).** $AgClO_4$ (0.733 mmol, 0.218 M in toluene ) was added to a stirred solution of [$Rh_2(\mu\text{-}Cl)_2(CO)_2$(POPheph)$_2$] (500 mg, 0.366 mmol) in 10 mL of $CH_2Cl_2$. The bright yellow solution was filtered from precipitated AgCl diluted with 8 mL of benzene and reduced in volume to *ca.* 10 mL to give a brown oil and pale-yellow solution. The oil crystallized upon standing overnight. The formed crystals were separated, washed with THF (3 x 10mL) and dried under vacuum to give 526 mg of crude **5.9c**· $C_6H_6$ as green-yellow crystals. Recrystallization from $CH_2Cl_2$ - $C_6H_6$ afforded analytically pure **5.9c**· $C_6H_6$ (482 mg, 0.584 mmol, 80%) as yellow crystals with a green tint. Anal. Calcd. for $C_{42}H_{40}ClNO_6PRh$ : C, 61.2; H, 4.9; N, 1.7. Found: C, 61.2; H, 4.7; N, 1.6. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$), δ: 128 (d, $J_{P\text{-}Rh}$ = 209 Hz). $^1H$ NMR ($CD_2Cl_2$), δ: 2.1 (d, $J$ = 6.3 Hz, 3H); 2.8 (s, 3H); 3.05 (m, 1H); 5.3 (m, 1H); 6.3 (s, 1H); 7.1 - 8.2 (m, 28H). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$), δ: 14.3 (s, Me); 46.2 (s, Me); 68.1 (d, $J_{C\text{-}P}$ = 2.3 Hz, CH); 71.8 (s, CH); 77.1

(s, CH); 110.2 (d, $J$ = 7.5 Hz, Ph); 126.1 (s, Ph); 129.2 - 138.1 (Ph); 187.1 (dd, $J_{C\text{-}Rh}$ = 73 Hz, $J_{C\text{-}P}$ = 21 Hz, CO). $^{15}N\{^1H\}$ NMR ($CD_2Cl_2$ : $CH_2Cl_2$ = 1 : 10), δ: - 356.7 (d, $J_{N\text{-}Rh}$ = 10.5 Hz). IR (KBr), $\nu_{CO}$ : 2014 $cm^{-1}$. $[\alpha]_D^{20}$+45.1° (c = 1.35, $CH_2Cl_2$).

**5.3.11 Single Crystal X-ray Diffraction Study of 5.3b, 5.4.a and 5.9c.** Crystal data and refinement parameters are summarized in Table 5.4. The crystals suitable for X-ray analysis were obtained by slow diffusion of heptane into a benzene solution of **5.3b**, $Et_2O$ into a benzene solution of **5.4a**, or THF into a solution of **5.9c** in $CH_2Cl_2$, respectively. The crystals were mounted on glass fibers with viscous oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω - scans at 0°, 90° and 180° in ϕ. Unit cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.[28] Systematic absences in the diffraction data and unit cell parameters were consistent uniquely with the reported space group for **5.3b** and **5.9c** and with *$P4_1$, $P4_3$,, $P4_122$ and $P4_322$* for **5.4a**. Only the solution in *$P4_3$* yielded chemically reasonable and computationally stable results for the refinement of **5.4a**. The structures were solved by direct methods, completed with difference Fourier synthesis and refined with full matrix least squares procedures based on $F^2$. Refinement of the Flack parameter yielded nil values indicating that the true hands of the data sets were determined correctly. All non hydrogen atoms were refined with anisotropic refinement parameters. All hydrogen atoms were treated as idealized contributions. All atomic scattering and anomalous dispersion factors are contained in the SHEXTL 5.1 program library.[29]

**Table 3.3. Summary of Crystallographic data for 5.3b, 5.4a and 5.9c**

| complex | **5.3b** | **5.4a** | **5.9c** |
|---|---|---|---|
| formula | $C_{19}H_{22}ClNOPRh$ | $C_{46}H_{48}ClN_2O_2P_2Rh$ | $C_{36}H_{34}ClNO_6PRh$ |
| fw | 449.71 | 915.31 | 746.01 |
| cryst dimens, mm | 0.1 x 0.1 x 0.1 | 0.1 x 0.1 x 0.1 | 0.4 x 0.1 x 0.1 |
| cryst syst | orthorhombic | orthorhombic | tetragonal |
| lattice params (Å) | a = 11.359(5) | a = 10.9890(5) | a = 10.6135(4) |
| | b = 12.209(5) | b = 19.4833(9) | b = 10.6135(4) |
| | c = 13.461(7) | c = 20.1668(9) | c = 34.797(2) |
| space group | $P2_12_12_1$ | $P2_12_12_1$ | $P4_3$ |
| $Z$ | 4 | 4 | 4 |
| $V$, Å$^3$ | 1866.9(9) | 4317.8(4) | 3919.8(3) |
| $d_{calc}$, g/cm$^3$ | 1.600 | 1.291 | 1.264 |
| $T$, K | 293(2) | 203(2) | 204(2) |
| radiation (λ) | | MoKα (0.71073Å) | |
| abs. coeff, mm$^{-1}$ | 1.149 | 0.568 | 0.585 |
| transmission (max./ min.) | 0.928072 / 0.695530 | 0.801520 / 0.609815 | 0.928077 / 0.778905 |
| $R(F)$,% | 4.31 | 4.07 | 3.96 |
| $R(wF^2)$,% | 7.01 | 9.55 | 10.75 |
| G.o.F. | 1.022 | 1.058 | 1.015 |
| Flack parameter | -0.21(6) | -0.03(3) | 0.02(4) |

Quantity minimised = $R(wF^2) = \Sigma[(w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^2)^{1/2}$;
$R(F) = \Sigma\Delta / \Sigma(F_o)$, $\Delta = |(F_o - F_c)|$

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(24) The spectrum shows a sharp doublet for **8c** and other unidentified signals were of low intensity (*ca.* 5% altogether ).

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# Chapter 6.

***A Practical Synthesis of $[Ru_2(OAc)_4]\cdot 2THF$, a Convenient Precursor for the Preparation of Ru (II) Complexes with Atropisomeric Diphosphines.***

## 6.1 Introduction.

Ruthenium acetate serves as a starting material for the synthesis of various dimeric Ru carboxylates, some of which possess interesting mesogenic and magnetic properties.[1] Several methods were developed for the preparation of $[Ru_2(OAc)_4]$ and some other Ru carboxylates.[1, 2]. Unfortunately, the published procedures are somewhat laborious and provide the product in only low to moderate yield.

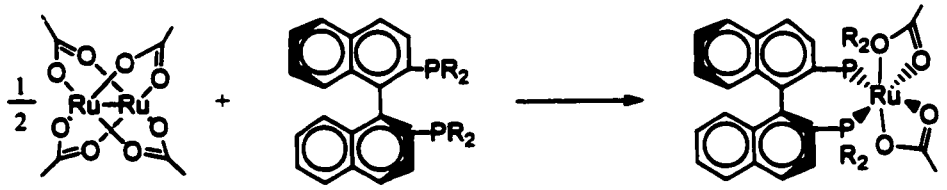
As shown in early publications by Lindsay *et al.*, $[Ru_2(OAc)_4]$ is a suitable precursor for the synthesis of various complexes with O-, S-, N- and P-donor ligands.[3] This application, however, seems to have been forgotten in the past years. Thus, ruthenium acetato complexes with atropisomeric diphosphines, such as BINAP [4] and Tol-BINAP [5] which are highly efficient catalysts for enantioselective hydrogenation [6-10], were prepared using $[(COD)RuCl_2]_n$,[11] $[(\eta^6\text{-cymene})Ru(OAc)_2]$[12] and $[(COD)Ru(\eta^3\text{-allyl})_2]$[10] as starting materials. Surprisingly, a straightforward and simple approach, utilizing ruthenium acetate as the precursor has not yet been reported in the literature. This may be a consequence, at least in part, of the lack of a convenient procedure for the preparation of $[Ru_2(OAc)_4]$. The following chapter describes a simple and efficient synthesis of ruthenium acetate and its complexes with BINAP and Tol-BINAP.

## 6.2 Results and Discussion.

The synthesis described here, being a "one pot" modification of Lindsay's procedure[13] results in the simplification of the preparation and increases the yield of ruthenium acetate up to 81% (from 47%, previously reported). A mixture of $RuCl_3 \cdot xH_2O$ and LiOAc was heated in methanol under 3 - 4 atm of $H_2$ in the presence of a catalytic

amount of platinum on carbon. Several batches of Ru (III) chloride hydrate containing 40.38, 41.6, 41.21 and 38.86% Ru were successfully used, affording ruthenium acetate in 72–81% yield.[14] The reaction seems to be sensitive to the presence of water, and the yield dropped significantly if methanol or LiOAc were not dried prior to use. The isolated ruthenium acetate is air sensitive and should be stored under nitrogen in a freezer. The complex may be handled in air for a few minutes without noticeable decomposition.

Ruthenium acetate reacts smoothly with BINAP or Tol-BINAP in boiling toluene, according to eq 6.1, to form known Ru complexes **6.2a,b**[10-12] with the corresponding bisphosphines. The reactions are exceptionally clean (no side products were detected by $^{31}P$ NMR) and require 2-3 hours for completion. The obtained solutions can be stored for several days and used directly for enantioselective hydrogenation.[6-10] The analytically pure complexes were isolated as yellow powders, which can be kept in air for several hours without decomposition. Both compounds are air sensitive in solution. Highly crystalline [Ru(OOCC$(CH_3)_3)_2$((*R*)-BINAP)][11] was prepared by the treatment of Ru-BINAP-acetate with sodium pivaloate in methanol. The complex shows the same activity and enantioselectivity for the hydrogenation of atropic acid as was observed for the corresponding Ru-BINAP-acetate,[8] but is more convenient for handling and storage.




(6.1)

**6.1a, R = Ph (BINAP)**
**6.1b, R = 4-MeC$_6$H$_4$ (Tol-BINAP)**

**6.2a,b**

((*S*)-configuration of the ligands is shown)

## 6.3 Experimental Section

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Methanol and THF were dried and distilled according to standard procedures. Other solvents were deoxygenated by passing a stream of nitrogen for 5–10 min. Anhydrous lithium acetate and sodium pivaloate were prepared by heating $LiOAc{\cdot}2H_2O$ or *t*-$BuCOONa{\cdot}xH_2O$ respectively in vacuum at 100-120° for 2h (the solid "boils", therefore a glass filter was used to prevent the dust from entering the vacuum line). Other chemicals were purchased from Strem or Aldrich and used as received.

**6.3.1 Synthesis of $[Ru_2(OAc)_4]{\cdot}2THF$.** Method A. Ruthenium (III) chloride hydrate (41.6% Ru, 600 mg, 2.469 mmol), lithium acetate (1.2 g, 18.2 mmol) and platinum on carbon (10% Pt, 30 mg) were placed in a 100 mL glass autoclave, which was purged with nitrogen and charged with methanol (16 mL), acetic anhydride (1 mL) and hydrogen (4 atm). The reaction mixture was stirred for 2 h at ambient temperature, then 1h at 120°- 130° ($t_{bath}$) and then allowed to cool to rt. The formed brown precipitate was separated by filtration, washed with methanol (4 x 10 mL), dried in vacuum and dissolved in hot THF(10 mL). The brown solution was filtered, the residue was washed with THF (5 mL) and the combined filtrates were taken to dryness under vacuum at room temperature to give $Ru_2(OAc)_4{\cdot}2THF$ (583 mg, 1.0 mmol, 81%) as black-brown shining crystals[15]. Anal. Calcd for $C_{16}H_{28}O_{10}Ru_2$: C, 32.99; H, 4.85. Found: C, 32.69, 32.60; H, 4.74, 4.66.

Method B Hydrogen was slowly bubbled through a stirred mixture of ruthenium(III) chloride hydrate (41.21% Ru, 600 mg, 2.446 mmol), LiOAc (1.2 g, 18.2

mmol), platinum on carbon (10% Pt, 30 mg), MeOH (16 mL) and acetic anhydride (1 mL) while the mixture was heated to reflux. After 4h the reaction mixture was cooled to rt. and $[Ru_2(OAc)_4]\cdot 2THF$ (418 mg, 0.717 mmol, 58%) was isolated in the same way as described for method A.

**6.3.2 Synthesis of [Ru(OAc)$_2$((*R*)-BINAP)].** A stirred mixture of $[Ru_2(OAc)_4]\cdot 2THF$ (234 mg, 0.402 mmol), (*R*)-BINAP (500 mg, 0.803 mmol) and toluene (6 mL) was heated to reflux for 3h. The resulting brown-orange solution was evaporated under vacuum. The residue was dissolved in $CH_2Cl_2$ (5 mL) and diluted with MeOH (10 mL). The obtained solution was reduced in volume under vacuum until it became turbid and some dark colored matter precipitated, filtered, evaporated and dried in vacuum to give 622 mg (0.739 mmol, 92%) of [Ru(OAc)((*R*)-BINAP)] as a yellow powder. Anal. Calcd for $C_{48}H_{38}O_4P_2Ru$: C, 68.48; H, 4.55. Found: C, 68.21, 68.23; H, 4.70, 4.69. $[\alpha]_D^{20} = 1562°$(c = 0.237, toluene).[16]

**6.3.3 Synthesis of [Ru(OAc)$_2$((S)-Tol-BINAP** A stirred mixture of $[Ru_2(OAc)_4]\cdot 2THF$ (215 mg, 0.369 mmol), (*S*)-Tol-BINAP (500 mg, 0.737 mmol) and toluene (6 mL) was heated to reflux for 3h. The resulting brown-orange solution was evaporated under vacuum, the residue was dissolved in $Et_2O$ (6 mL) and diluted with heptane (6 mL). The obtained solution was reduced in volume until it became turbid and some dark colored matter precipitated, filtered through cotton wool, evaporated and dried in vacuum to give 622 mg (0.693 mmol, 94%) of [Ru(OAc)$_2$((*S*)-Tol-BINAP)] as an orange powder. Anal. Calcd for $C_{52}H_{46}O_4P_2Ru$: C, 69.55; H, 5.16. Found: C, 69.27,

69.32; H, 5.54, 5.51. $[\alpha]_D^{20}$ = -1322°(c = 0.177, toluene).[16]

**6.3.4 Synthesis of Ru[OOCC(CH$_3$)$_3$]$_2$[(R)-BINAP]** A stirred mixture of [Ru$_2$(OAc)$_4$]·2THF (234 mg, 0.402 mmol), (*R*)-BINAP (500 mg, 0.803 mmol) and toluene (6 mL) was heated to reflux for 3h. The resulting brown-orange solution was evaporated under vacuum. Anhydrous sodium pivaloate (1.2 g, 9.7 mmol) and methanol (20 mL) were added to the residue, the stirred mixture was heated to reflux for 30 min and taken to dryness under vacuum. The residue was stirred with 12 mL of hot ethyl acetate and filtered. The dark orange solution was reduced in volume to c.a. 8 mL and allowed to stay at rt. for 3 h. The formed large orange-brown crystals were separated by decantation, washed with 50% methanol (2 x 5 mL) and dried to give 419 mg of [Ru(OOCCCH$_3$)$_3$)$_2$((*R*)-BINAP)]. The additional 205 mg of the complex was isolated upon concentration of the mother liquor. The total yield 624 mg (0.674 mmol, 84%). Anal. Calcd for $C_{54}H_{50}O_4P_2Ru$: C, 70.04; H, 5.44. Found: C, 70.04; H, 5.44. $[\alpha]_D^{20}$ = 1169°(c = 0.29, toluene).[16]

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(14) One sample (42.98% Ru) repeatedly gave substantially lower (ca. 50%) yield. This sample was only partially soluble in water, which suggests the presence of some anhydrous $RuCl_3$ or metallic ruthenium.

(15) The complex easily loses THF upon heating in vacuum affording amorphous brown $Ru_2(OAc)_4$.

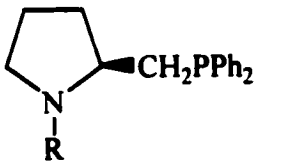
(16) $P\{^1H\}$-, $^1H$- and $^{13}C\{^1H\}$ NMR data were reported.[4, 6]

# Chapter 7.

## *Chiral Ruthenium Complexes with P,N-ligands Derived from (S)-Proline.*

## 7.1 Introduction

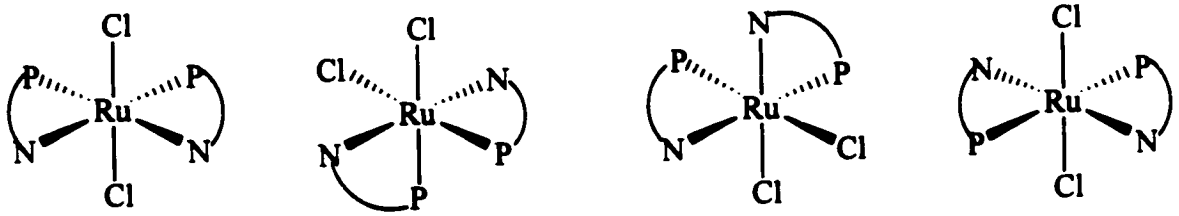
As was demonstrated in the previous chapter $[Ru_2(OAc)_4]$ is a convenient precursor for the preparation of ruthenium complexes with chiral bisphosphines. It was of interest to investigate the reactivity of ruthenium acetate towards *P,N*-chelating ligands such as aminophosphine derivatives of (S)-proline (**7.1a,b**) described in chapter 5.



**7.1a,b**
**a, R = H (PPro)**
**b, R = Me (PProMe)**

Ruthenium complexes with *P,N* chelating ligands demonstrate remarkable structural diversity. Thus, compounds displaying *P,P-cis, N,N-cis*;[1,2,3] *P,P-cis, N,N-trans*;[4,5] all *cis*[5,6] and all *trans*[7,8] coordination geometries (Chart 1) have been prepared and characterized by X-ray diffraction.

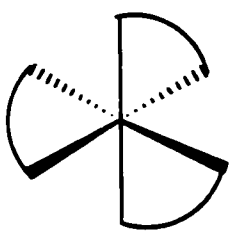
**Chart 7.1**



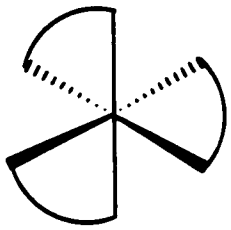
*P,P-cis, N,N-cis* *P,P-cis, N,N-trans* all *cis* all *trans*

Octahedral metallocomplexes featuring three, or at least two non-coplanar chelate cycles, are chiral and usually exist as racemic mixtures of (Δ)- and (Λ)-enantiomers (Chart 2). Application of chiral ligands, however, may lead to the selective formation of one diastereomer. For instance $[Ru(OAc)_2(BINAP)]$ has the (Δ,*R*)- or (Λ,*S*)-configuration whereas the corresponding (Λ,*R*)- or (Δ,*S*)-epimer was not obtained.[9]

**Chart 7.2**



Δ



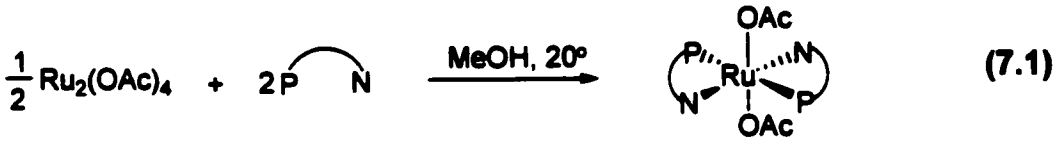
Λ

The following chapter describes the structure and properties of chiral Ru complexes prepared from **7.1a,b** and $[Ru_2(OAc)_4]$. To the best of our knowledge no Ru complexes of these ligands have been reported previously.

## 7.2. Results and Discussion

### 7.2.1 Reaction of PPro with $[Ru_2(OAc)_4]$. X-ray Structure of $[Ru(OAc)_2(PPro)_2]$.

Treatment of a methanol suspension of $[Ru_2(OAc)_4]$ with 2 equiv of PPro leads to the formation of complex **7.2** (eq 6.1), along with *ca.* 5% of unidentified side-products.[10,11] According to $^{31}P$ NMR spectra, the reaction is complete in 5 min at room temperature.




(7.1)

**7.1a** **7.2**

The complex was isolated in high yield as air stable yellow crystals (1:1 methanol solvate) which are soluble in $CH_2Cl_2$, moderately soluble in THF and benzene and slightly soluble in MeOH and $Et_2O$. The solid state structure of **7.2** (1:1 $Et_2O$ solvate) was established by single crystal X-ray diffraction. An ORTEP plot of the complex is shown in Figure 6.1;

selected bond distances and angles are presented in Table 7.1.

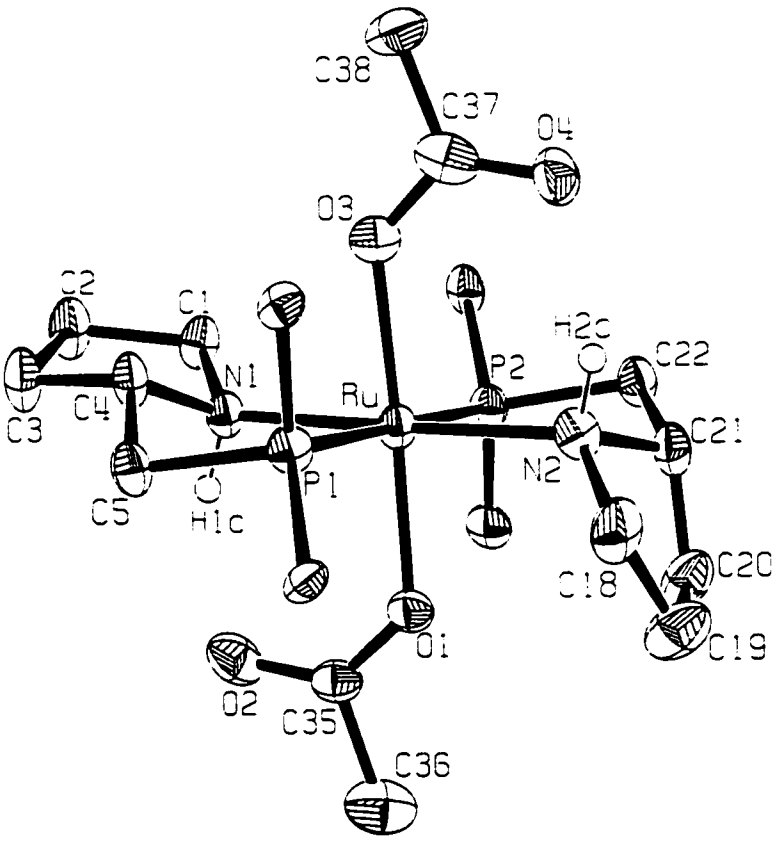



**Figure 7.1.** Perspective diagram of **6.2** with 50% probability ellipsoids. The hydrogen atoms (except for *N*-H) and phenyl carbon atoms (except for *ipso*) are omitted for clarity.

**Table 7.1. Selected Bond Distances (Å) and Angles (deg) for 7.2·$Et_2O$.**

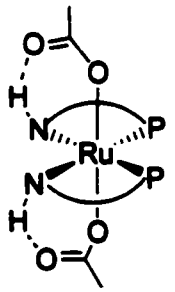
| | | | |
|---|---|---|---|
| N(1)-Ru | 2.142(5) | C(1)-N(1)-Ru | 122.9(3) |
| N(2)-Ru | 2.163(5) | C(1)-N(1)-C(4) | 103.1(5) |
| O(1)-Ru | 2.098(4) | C(4)-N(1)-Ru | 113.7(3) |
| O(3)-Ru | 2.118(4) | C(18)-N(2)-Ru | 119.6(4) |
| P(1)-Ru | 2.363(2) | C(18)-N(2)-C(21) | 101.4(5) |
| P(2)-Ru | 2.309(2) | C(21)-N(2)-Ru | 117.8(4) |

The octahedral coordination environment of the central Ru atom consists of two *P,N*-chelating aminophosphines and a pair of mutually *trans*-monodentate acetates. The two phosphorus atoms are *trans* to each other and lie in the same plane with the two *trans*-nitrogen atoms of the chelates. In such an arrangement the ruthenium is not stereogenic. One of the two bicyclic [3.3.0] systems of **7.2** is *cis*-fused, whereas another adopts the thermodynamically less stable *trans*-conformation, presumably due to hydrogen bonding between the coordinated acetate and amino groups (the H(1c)...O(2) and H(2c)...O(4) separations are 1.985 and 2.04 Å respectively). In order to form hydrogen bonds with the two mutually *trans*-OAc ligands one of the two *N*-H protons should lie above while another lies below the P-N-P-N equatorial plane of the molecule, as a result the two N-based stereocenters of the complex possess opposite absolute configurations.

The $^{31}P\{^{1}H\}$ NMR spectrum of **7.2** in toluene at 20°C displays a well-resolved AB pattern typical for complexes with two non-equivalent *trans*-phosphine ligands. The lines neither collapsed nor broadened significantly when the spectrum was recorded from –80 to +110°C. Therefore, it appears that the structure of **7.2** remains intact in solution and pseudorotation of chelates, which could proceed *via* decoordination - inversion of configuration - recoordination of amino groups does not occur or it is slow on the NMR time scale. The lack of fluxional behavior demonstrated by **7.2** is probably attributable to the strong NH-OAc hydrogen bonding, which not only induces the thermodynamically unfavorable *trans*-fusion of the [3.3.0] bicyclic system, but also makes the whole structure robust.

It should be noted that hydrogen bonding alone cannot explain the presence of a *trans*-fused bicyclic system in **7.2**. Indeed, amino groups of the hypothetical *cis-P,P, cis- N,N,*

*trans-O,O* isomer could also form hydrogen bonds with two mutually *trans* OAc ligands but both [3.3.0] ring systems of the molecule would possess *cis*-configuration. Therefore the observed *trans-P,P, trans-N,N* arrangement of chelates in **7.2** arises despite concomitant formation of the thermodynamically less stable *trans*-fused bicyclic system.



Hypothetical *cis, cis, trans*- $Ru(OAc)_2(PPro)_2$

Unfortunately the available experimental data do not allow us to ascertain whether the structure of **7.2** corresponds to the most thermodynamically stable configuration, or **7.2** is just the kinetic product which possesses rigid structure and therefore is not prone to rearrangement even at elevated temperatures.

### 7.2.2 Reaction of PProMe with $[Ru_2(OAc)_4]$. X-ray Structure of $[Ru(OAc)_2(PProMe)_2]$.

Ruthenium acetate readily reacts with 2 equiv of PProMe affording complex Δ-**3** selectively (eq. 7.2).[12] According to $^{31}P$ NMR spectra, the reaction is complete in 5 min at room temperature.


(7.2)

**7.1b** Δ -**7.3**

.The analytically pure complex was isolated in high yield by crystallization from cyclopentane as a 1:1 $C_5H_{10}$ solvate. The large orange crystals of Δ-**7.3**·$C_5H_{10}$ are air stable and soluble in common organic solvents. The solid state structure of the complex was established by single crystal X-ray diffraction. The asymmetric unit of the crystalline Δ-**7.3**·$C_5H_{10}$ contains two independent molecules of the complex. Although crystallographically important, the difference between the two molecules is chemically insignificant (both are (Δ)-stereoisomers possessing the same spatial arrangement of the atoms and very close values of the corresponding bond lengths and angles). The ORTEP plot (Figure 7.2) shows only one arbitrarily chosen molecule of the asymmetric unit. The selected bond lengths and angles are given in Table 7.2.

In contrast to the case for complex **7.2**, only one of the two aminophosphine ligands of Δ-**7.3** is *P,N*-chelating, while another is attached to Ru only *via* phosphorus. The two P-atoms are *cis* to each other and lie in the same plane with the coordinated nitrogen. As expected the [3.3.0] bicyclic system of the molecule is *cis*-fused and the *N* based stereocenter adopts an *(S)*-configuration.

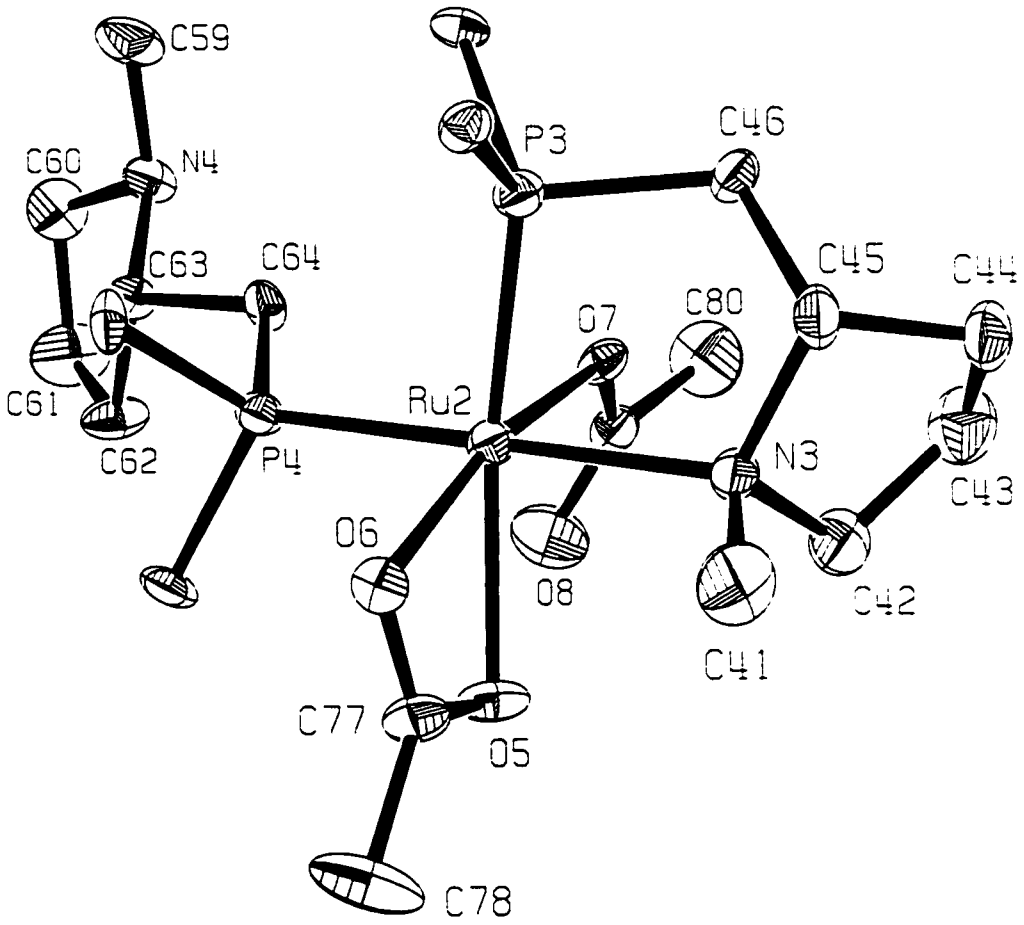


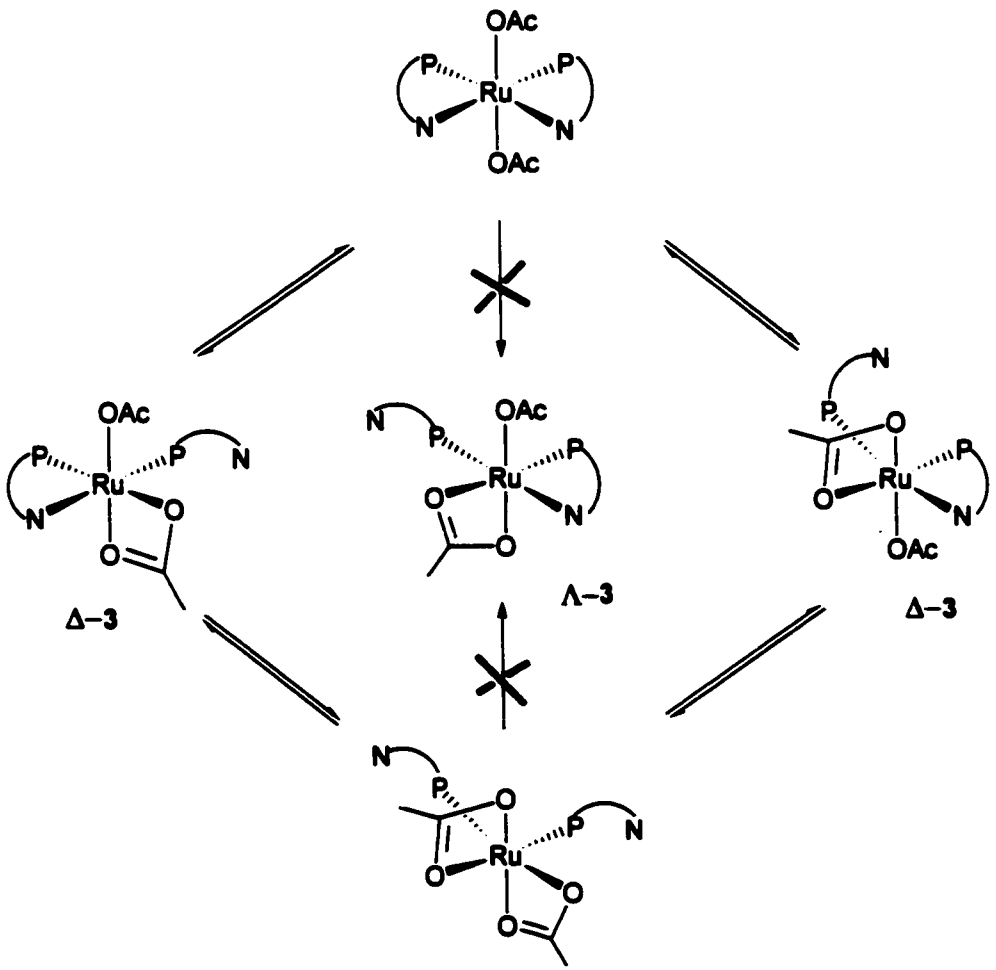

**Figure 7.2.** Perspective diagram of Δ-7.3 with 30% probability ellipsoids. All hydrogen atoms and non *ipso*-phenyl carbon atoms are omitted for clarity.

**Table 7.2. Selected Bond Distances (Å) and Angles (deg) for Δ-7.3·$C_5H_{10}$.**

| | | | |
|---|---|---|---|
| O(5)-Ru(2) | 2.214(9) | O(5)-Ru(2)-O(6) | 61.0(3) |
| O(6)-Ru(2) | 2.139(8) | C(41)-N(3)-C(42) | 111.1(11) |
| O(7)-Ru(2) | 2.062(8) | C(41)-N(3)-C(45) | 105.6(11) |
| N(3)-Ru(2) | 2.270(10) | C(41)-N(3)-Ru(2) | 111.2(8) |
| P(3)-Ru(2) | 2.207(4) | C(42)-N(3)-C(45) | 104.8(10) |
| P(4)-Ru(2) | 2.264(4) | C(60)-N(4)-C(63) | 104.6(10) |

The $^{31}P\{^{1}H\}$ NMR spectrum of Δ-**7.3** in toluene exhibits two doublets with $J_{P\text{-}P}$ = 37 Hz, which is typical for complexes with two non-equivalent *cis*-phosphine ligands. The lines remain sharp and do not split in the temperature interval 180-300 K, indicating that in solution the complex exists as a single epimer. Increasing the temperature above 300 K leads to gradual broadening and finally collapse of the signals at 370 ± 5 K. The observed fluxional behavior can be explained in terms of the mechanism outlined in Scheme 7.1, with the calculated barrier of activation $\Delta G^{\neq}$ = 15.6 ± 0.3 kcal/mol.

**Scheme 7.1**

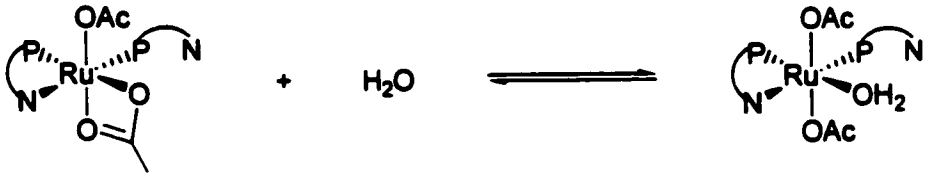


Cross peaks observed in $^{31}P\{^{1}H\}$ ECSY NMR spectrum at 20°C indicate that this process slowly occurs even at room temperature. No signals attributable to Λ-7.3 or other products were detected in the $^{31}P\{^{1}H\}$ NMR spectra when Δ-7.3 was kept for several days in a THF or toluene solution. It is conceivable therefore that the selective formation of Δ-7.3 in the reaction (7.2) is thermodynamically controlled and Δ-7.3 is more stable than the corresponding (Λ)-stereoisomer.

In comparison with complex 7.2, which is rather inert, $[Ru(OAc)_2(PProMe)_2]$ readily reacts with water, undergoes facile isomerization in methanol and smoothly transforms to carbene-ruthenium complexes upon thermolysis (see below).

### 7.2.3 Reaction of $[Ru(OAc)_2(PProMe)_2]$ with $H_2O$. X-ray Structure of $[Ru(OAc)_2(H_2O)(PProMe)_2]$.

In solution complex Δ-7.3 is extremely moisture sensitive and reacts readily with adventitious water, in accordance with eq 7.3.




(7.3)

Δ -7.3 7.4

It is common that ruthenium species containing chelating sulfonato[13] or acetato[14] ligands are very reactive with water to give the corresponding aqua complexes. There are also many examples of the Ru(II) aqua complexes stabilized by a combination of P and N donor ligands.[15]

Yellow crystalline $7.4 \cdot C_5H_{10}$ (1:1 cyclopentane solvate) was isolated by recrystal-

lization of Δ-7.3·$C_5H_{10}$ from wet cyclopentane and characterized by elemental analysis, NMR spectroscopy and single crystal X-ray diffraction. An ORTEP plot of the complex is shown in Figure 7.3, while selected bonds distances and angles are given in Table 7.3.

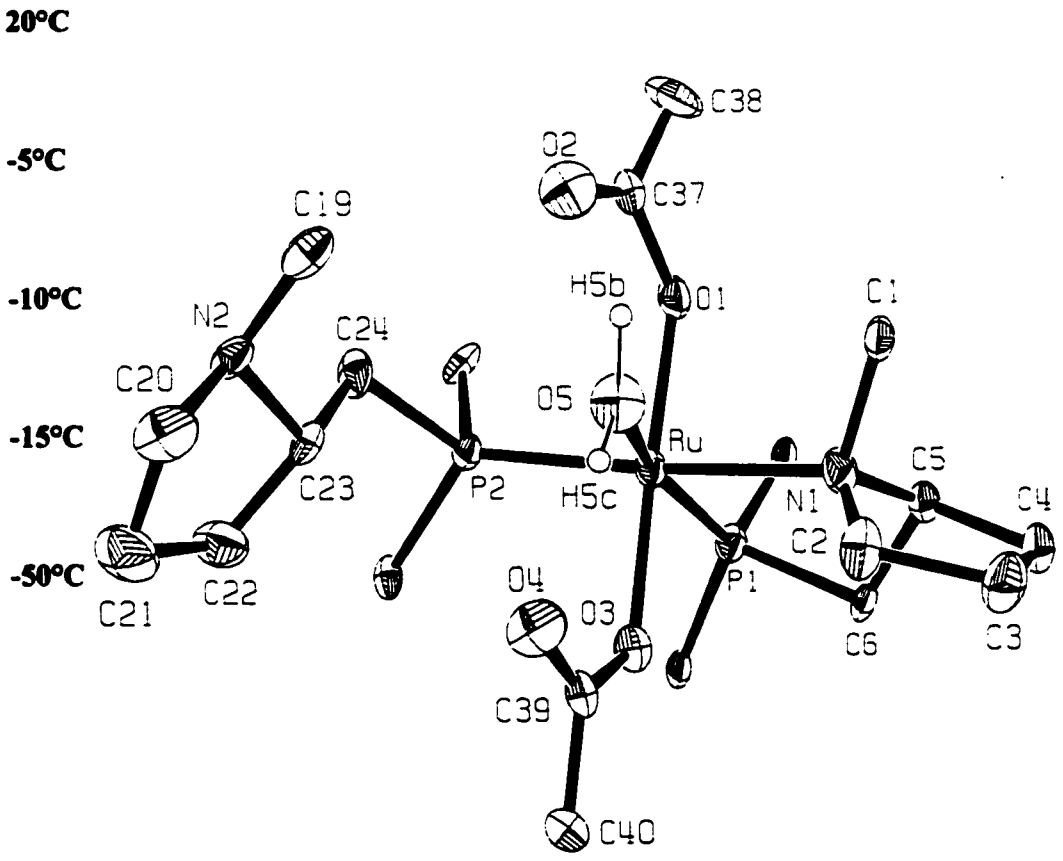



**Figure 7.3.** Perspective diagram of **7.4** with 30% probability ellipsoids. Hydrogen atoms (except for *O*-H) and non *ipso*-phenyl carbon atoms are omitted for clarity.

**Table 7.3. Selected Bond Distances (Å) and Angles (deg) for 7.4·$C_5H_{10}$.**

| | | | |
|---|---|---|---|
| O(1)-Ru | 2.054(15) | N(1)-Ru | 2.27(2) |
| O(3)-Ru | 2.110(14) | P(1)-Ru | 2.255(6) |
| O(5)-Ru | 2.138(13) | P(2)-Ru | 2.288(7) |
| | | | |
| C(1)-N(1)-C(2) | 110.2(2) | C(1)-N(1)-Ru | 109.9(13) |
| C(1)-N(1)-C(5) | 102.9(17) | C(2)-N(1)-C(5) | 108.5(18) |

The acetate ligands of **7.4** are monodentate and *trans* to each other. They lie essentially in plane with the aqua ligand. The short O(2)····O(5) and O(4)····O(5) interatomic separations (2.607 and 2.595 Å respectively) suggest strong –C=O····HOH····O=C- hydrogen bonding. The mutual arrangement and coordination mode of the two aminophosphine ligands in **7.4** are exactly the same as those of complex Δ-**7.3**. The molecule of **7.4**, however, possesses only one bidentate ligand and therefore the ruthenium is not stereogenic.

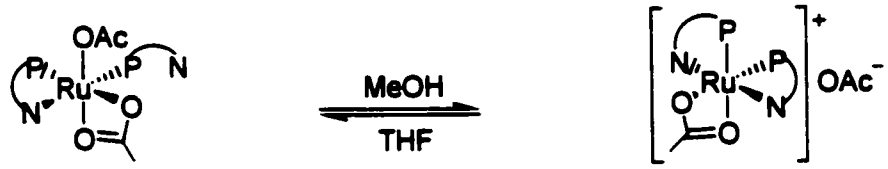
The $^{31}P\{^{1}H\}$ NMR spectrum of **7.4**·$C_5H_{10}$ (dry THF,–40°C) displays two intense doublets (46.5 and 55.8 ppm, $J_{P\text{-}P}$ = 37 Hz) assigned to **7.4** along with two weak doublets (47.7 and 63.8 ppm, $J_{P\text{-}P}$ = 37 Hz) belonging to Δ-**7.3**. The four doublets collapsed into two resonances, a broad doublet at 48 ppm ($J_{P\text{-}P}$ = 37 Hz, $\Delta_{1/2}$ = 18 Hz) and a broad signal centered at 58 ppm ($\Delta_{1/2}$ = 116 Hz), when the spectrum was recorded at 20°C. Addition of excess water led to disappearance of the signals of Δ-**7.3** from the –40°C spectrum and transformed the signals of **7.4** into two sharp doublets in the spectrum recorded at 20°C. These data indicate that in solution complex **7.4** undergoes partial dissociation to Δ-**7.3** and water and the reaction (7.3) is indeed an equilibrium process ($K_{eq} \approx 1.5x10^3$)[16] which is fast on the NMR time scale.

### 7.2.4 Isomerization of [Ru(OAc)$_2$(PProMe)$_2$] in Methanol.

### X-ray Structure of [Ru(OAc)(PProMe)$_2$]PF$_6$

In methanol solution complex Δ-**7.3** undergoes spontaneous rearrangement to the cationic complex Λ-**7.5** (eq 7.4). The complete transformation takes *ca.* 1.5 h at room temperature and can be conveniently monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy. The signals of Δ-**7.3** gradually decrease in intensity while the singlet at 55 ppm, assigned to Λ-**7.5**

simultaneously grows. The reaction (7.4) is reversible and complex Λ-**7.5** completely reverts back to Δ-**7.3** within 1.5 h when dissolved in THF or toluene.




(7.4)

Δ -**7.3** Λ-**7.5**

The $^{31}P\{^{1}H\}$ NMR spectra of Λ-**7.5** in methanol recorded from –80 to 60°C display a sharp singlet, indicating that in solution the complex exists as a single epimer. Attempts to obtain Λ-**7.5** in a crystalline form failed, so the complex was treated with $NaPF_6$ in methanol to afford the hexafluorophosphate salt (Λ-**7.6**), which precipitates from the solution as crystals suitable for X-ray analysis. Comparison of the NMR spectra of Λ-**7.5** and Λ-**7.6** (see experimental section) indicates that the structure of the complex cation is identical in both compounds.

The asymmetric unit of crystalline Λ-**7.6** consists of two octahedral Ru cations and two $PF_6$ anions. Although crystallographically distinct, the two cationic fragments are chemically indistinguishable (both are (Λ)- stereoisomers with the same spatial arrangement of atoms and have almost identical values for corresponding bond lengths and angles). An ORTEP plot showing an arbitrarily chosen complex cation of Λ-**7.6** is given in Figure 7.4. The selected bond distances and angles are presented in Table 7.4.

The octahedral coordination environment of ruthenium in Λ-**7.6** consists of a chelating acetato ligand and two *P,N*-chelating aminophosphines. The two P atoms are mutually *cis*, while the coordinated amino groups are *trans* to each other. Both [3.3.0] bicyclic systems of

Λ-7.6 are fused in the thermodynamically favorable *cis*-fashion, consequently both *N*-stereocenters of the complex adopt an *(S)*-configuration.

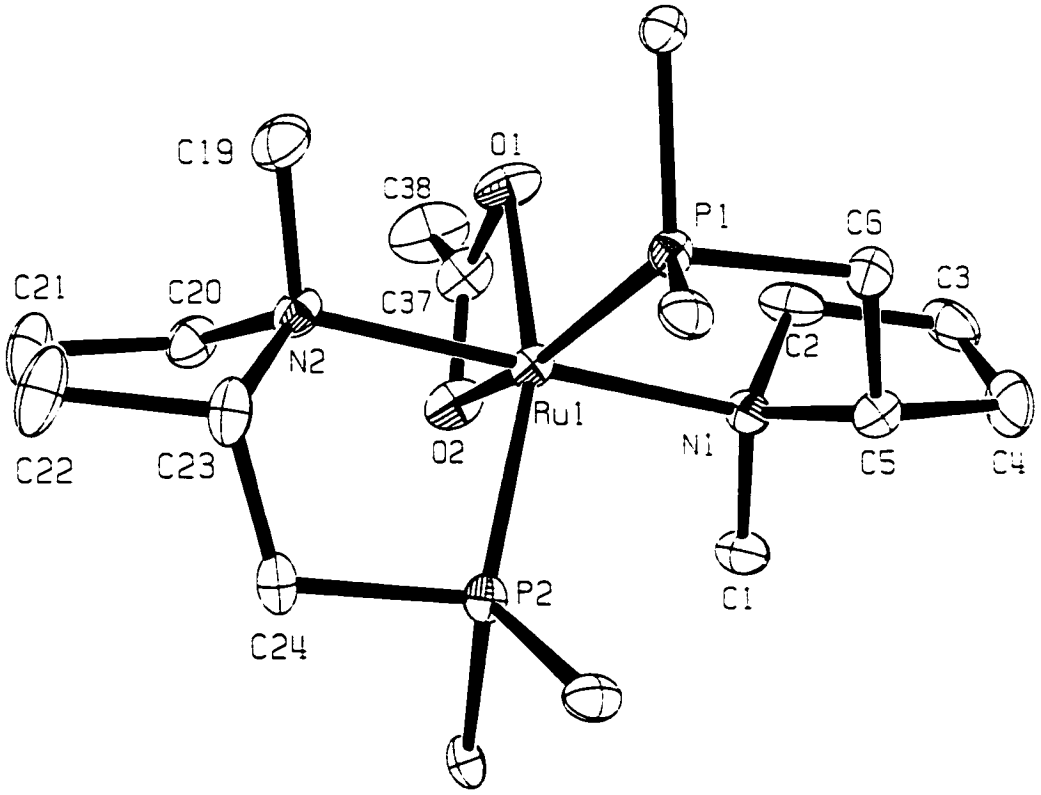



**Figure 7.4.** Perspective diagram of the complex cation of Λ-7.6 with 30% probability ellipsoids. All hydrogen atoms and non *ipso*-phenyl carbon atoms are omitted for clarity.

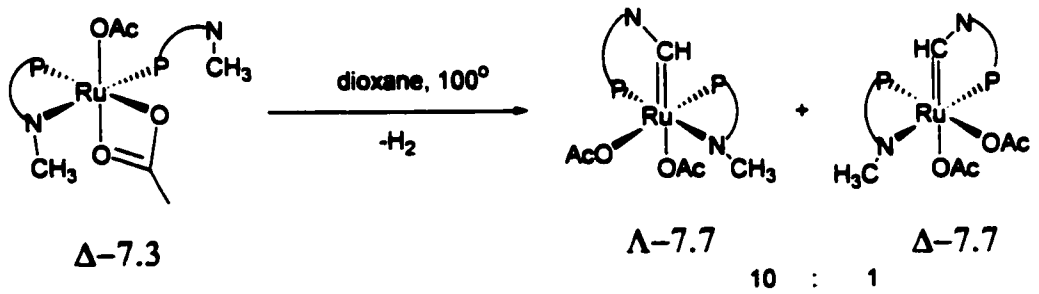
**Table 7.4. Selected Bond Distances (Å) and Angles (deg) for Λ-7.6.**

| | | | |
|---|---|---|---|
| O(1)-Ru(1) | 2.213(5) | O(1)-Ru(1)-O(2) | 59.84(17) |
| O(2)-Ru(1) | 2.180(5) | P(1)-Ru(1)-P(2) | 97.73(6) |
| N(1)-Ru(1) | 2.191(5) | C(1)-N(1)-C(2) | 106.0(5) |
| N(2)-Ru(1) | 2.201(5) | C(1)-N(1)-C(5) | 109.2(5) |
| P(1)-Ru(1) | 2.2778(18) | C(1)-N(1)-Ru(1) | 109.7(4) |
| P(2)-Ru(1) | 2.2645(17) | C(2)-N(1)-C(5) | 102.3(5) |

The detailed mechanism of the isomerization (7.4) remains unclear, but perhaps it involves dissociation of one OAc ligand and rearrangement of the resulting penta-coordinate intermediate.

### 7.2.5 Formation of ruthenium carbene complexes (Λ-7.7) and (Δ-7.7) upon thermolysis of [Ru(OAc)$_2$(PProMe)$_2$]. X-ray Structure of Δ-7.7.

Refluxing Δ-7.3 in dioxane or toluene solution leads to the evolution of hydrogen[17] and formation of the carbene complexes Λ-7.7 and Δ-7.7 in a 10:1 ratio (eq 7.5), along with *ca.* 10% of unidentified side products. According to $^{31}$P NMR spectra the reaction is complete in 5 h.




Δ–7.3 Λ–7.7 Δ–7.7

10 : 1

(7.5)

In contrast to the (Λ)-diastereomer, Δ-7.7 is only sparingly soluble in dioxane or toluene and precipitates upon concentration and cooling to room temperature. The complex was isolated as a yellow air stable crystalline solid soluble in methanol or chlorinated hydrocarbons and characterized by elemental analysis and NMR spectroscopy. The solid state structure of Δ-7.7 was established by a single crystal X-ray diffraction study. An ORTEP plot of the complex is shown in Figure 7.5; the selected bond distances and angles are compiled in Table 7.5.

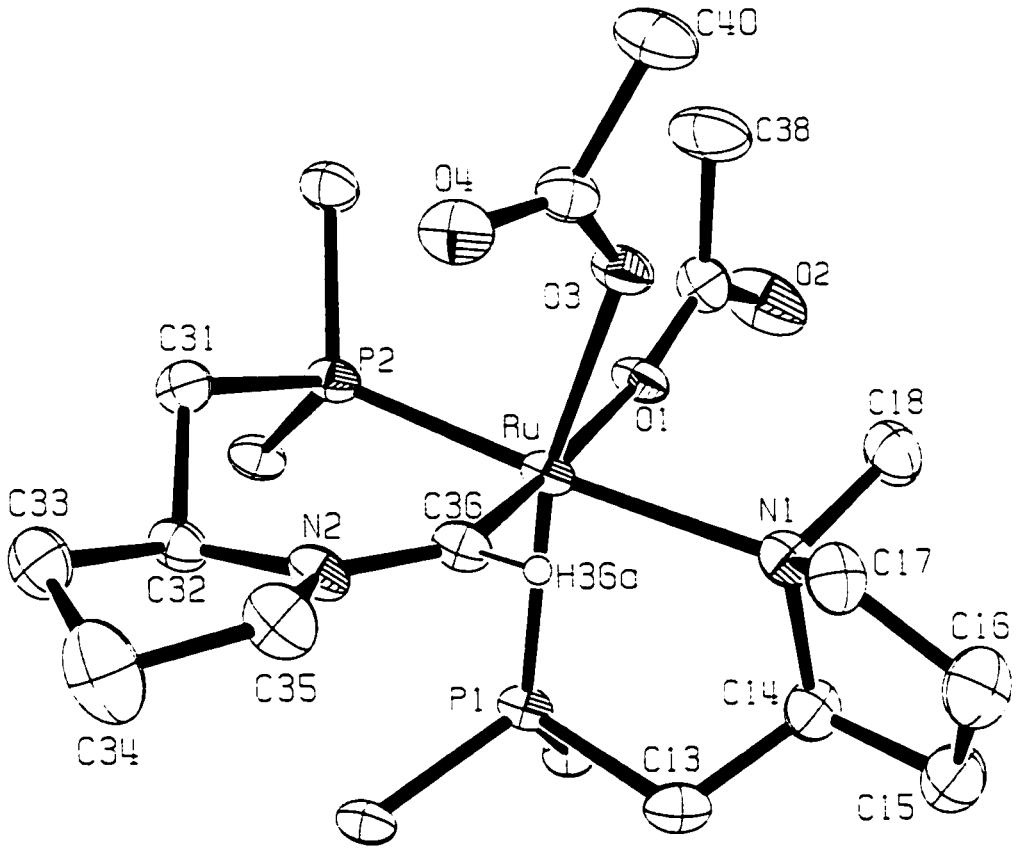



**Figure 7.5.** Perspective diagram of Δ-**7.7** with 30% probability ellipsoids. All hydrogen atoms (except for carbene-H) and non *ipso*-phenyl carbon atoms are omitted for clarity.

The octahedral coordination environment of the central Ru atom in Δ-**7.7** is formed by a *P,N*-chelating aminophosphine, the phosphine-carbene chelate and two mutually *cis* monodentate OAc ligands. The coordinated amino group is *trans* to one of the two phosphorus atoms, which in turn are *cis* to each other and to the carbene moiety. The C(32)-C(35)-N(2)-C(36)-Ru fragment is essentially planar, which indicates a high degree of conjugation in the Ru-carbene-nitrogen system. Thus, the carbene-nitrogen bond (1.324 Å) is significantly shorter than the corresponding methyl-nitrogen bond (1.492 Å) in the *P,N*-

chelating aminophosphine. The ruthenium-carbene carbon distance is comparable to those of other Fisher type carbene–Ru complexes reported in the literature.[18] As expected the [3.3.0] bicyclic system of Δ-**7.7** adopts the thermodynamically more stable *cis*-fused configuration and the stereogenic nitrogen of *P,N*-chelate is of *(S)*-absolute configuration.

**Table 7.5. Selected Bond Distances (Å) and Angles (deg) for Δ-7.7·$C_6H_6$.**

| | | | |
|---|---|---|---|
| Ru-C(36) | 1.939(3) | C(36)-N(2) | 1.324(4) |
| Ru-N(1) | 2.313(3) | C(18)-N(1) | 1.492(5) |
| Ru-O(1) | 2.220(3) | C(32)-N(2) | 1.476(5) |
| Ru-O(3) | 2.117(2) | C(35)-N(2) | 1.489(4) |
| Ru-P(1) | 2.2915(9) | C(14)-N(1) | 1.488(5) |
| Ru-P(2) | 2.2427(11) | C(17)-N(1) | 1.505(5) |
| | | | |
| C(36)-Ru-N(1) | 93.23(13) | C(32)-N(2)-C(35) | 111.7(3) |
| C(36)-Ru-O(3) | 90.76(12) | N(2)-C(36)-Ru | 134.3(3) |
| C(36)-Ru-P(1) | 87.35(10) | C(14)-N(1)-Ru | 112.5(2) |
| C(36)-Ru-P(2) | 90.75(11) | C(17)-N(1)-Ru | 117.0(2) |
| N(1)-Ru-P(1) | 81.70(8) | C(18)-N(1)-Ru | 109.2(3) |
| P(1)-Ru-P(2) | 100.16(4) | C(14)-N(1)-C(17) | 102.9(3) |
| C(36)-N(2)-C(32) | 127.4(3) | C(14)-N(1)-C(18) | 108.3(3) |
| C(36)-N(2)-C(35) | 120.5(3) | C(17)-N(1)-C(18) | 106.5(3) |

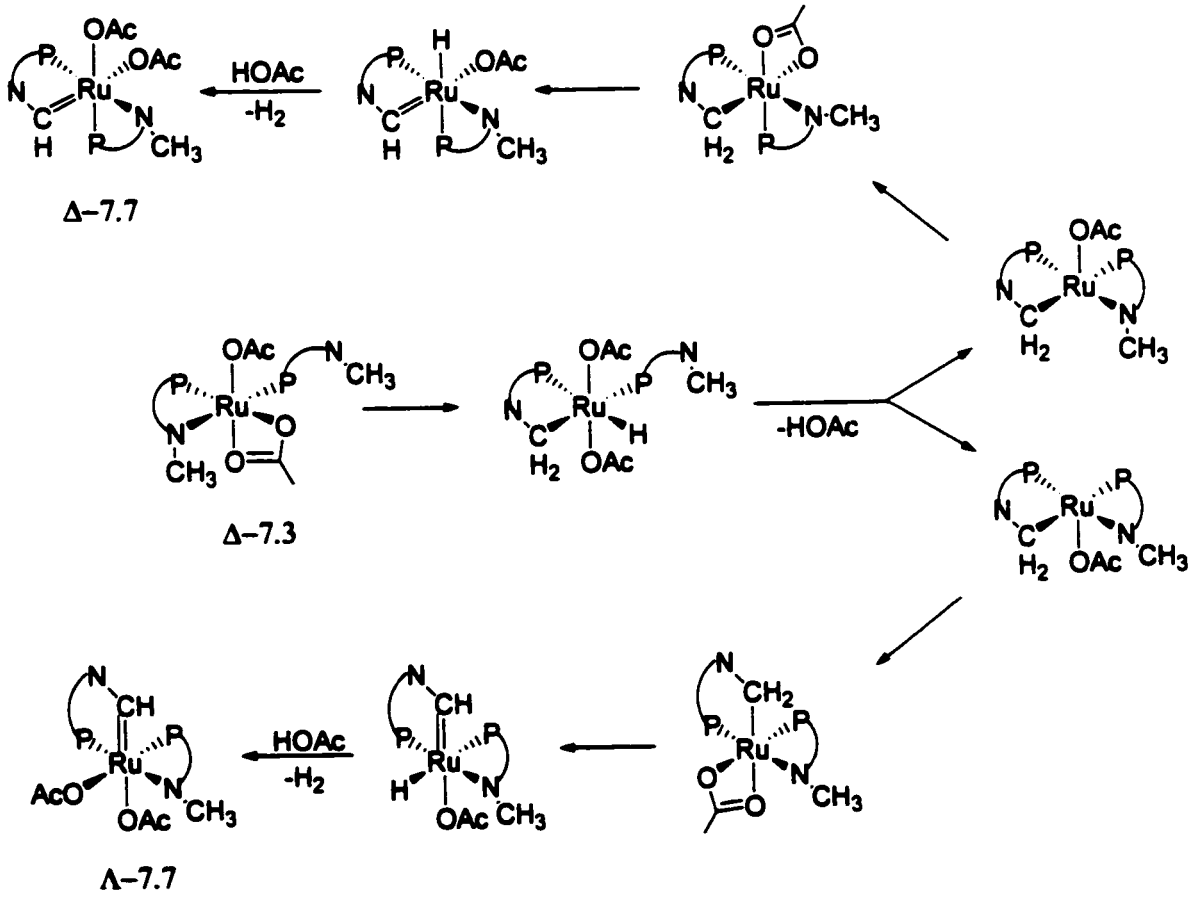
The main product of the reaction (7.5), complex Λ-**7.7**, was isolated as an air stable yellow-orange solid, soluble in common organic solvents except for saturated hydrocarbons. Attempts to obtain Λ-**7.7** in crystalline form were unsuccessful, however, its composition and stereochemistry were deduced from NMR data. Comparison of the NMR spectra of Λ-**7.7** with those of the (Δ)-diastereomer indicates that these complexes possess similar structures. Both compounds display a pair of doublets in their $^{31}P\{^1H\}$ NMR spectra at 50.4 and 55.8 ppm ($J_{P\text{-}P}$ = 32 Hz) for Δ-**7**, and at 45.4 and 64.5 ppm ($J_{P\text{-}P}$ = 32 Hz) for Λ-**7**, due to non-

equivalent *cis*-phosphines. The values of the $J_{C\text{-}P}$ coupling constants for low field triplets observed in the $^{13}C\{^1H\}$ NMR spectra at 242.5 ppm ($J_{C\text{-}P1} \approx J_{C\text{-}P2}$ = 15 Hz) for Δ-**7.7**, and at 242.8 ppm ($J_{C\text{-}P1} \approx J_{C\text{-}P2}$ = 15 Hz) for Λ-**7.7** indicate that the carbene ligand is *cis* to both P atoms in both complexes. Other carbons of Λ-**7.7** give $^{13}C$ NMR signals with close values of chemical shifts to those for the corresponding carbons of Δ-**7** (see experimental section). The coordinated amino group of Λ-**7.7** gives a doublet in the $^{15}N\{^1H\}$ NMR spectrum at δ –320.4 ($J_{N\text{-}P}$ = 32 Hz). The value of the coupling constant[19] is indicative of a *trans* relationship between the nitrogen and one of the two phosphorus atoms (the *cis* N-P coupling constants are often smaller than 1 Hz and therefore not observed). Taken together these data suggest that the two complexes relate to each other as a pair of epimers. Since the configurations of the corresponding stereocenters at nitrogen and carbon atoms are the same in both compounds and one of them is the structurally characterized (Δ)-stereoisomer, the other complex should possess the (Λ)-configuration.

According to $^{31}P$ NMR no (Δ-Λ) or (Λ-Δ) interconversion occurred when the isolated Δ-**7.7** or Λ-**7.7** were kept in methanol or dioxane solution for 1 week at room temperature. However, when heated in sealed NMR tubes immersed in an oil bath ($t_{bath}$ 130°C) as dioxane solutions, both complexes underwent fast epimerization affording *ca.* 1:8 mixture of (Δ)- and (Λ)-stereoisomers. This ratio was attained in 2 h and then remained constant under prolonged (up to 24 h) heating. In boiling dioxane (b.p. 101°C) the epimerization is sluggish. When isolated Δ-**7.7** is heated under these conditions, *ca.* 20:1, 8:1, 3:1 and 1:1 Δ/Λ ratios were observed after 3, 5, 12 and 24 h, respectively. These data show that Λ-**7.7** is thermodynamically more stable than the corresponding (Δ)-stereoisomer. The preferential formation of Λ-**7.7** however is kinetically controlled and cannot be explained by simultaneous

epimerization, since it occurs significantly slower than the thermolysis of Δ-7.3. The possible mechanism for reaction (7.5) may involve β-H abstraction from the coordinated amino group of Δ-7.3 followed by reductive elimination of HOAc (Scheme 7.2). The subsequent α-H abstraction from the resulting alkyl-ruthenium intermediates may lead either to Δ-7.7 or to Λ-7.7, depending on which of the two acetate ligands remains coordinated.

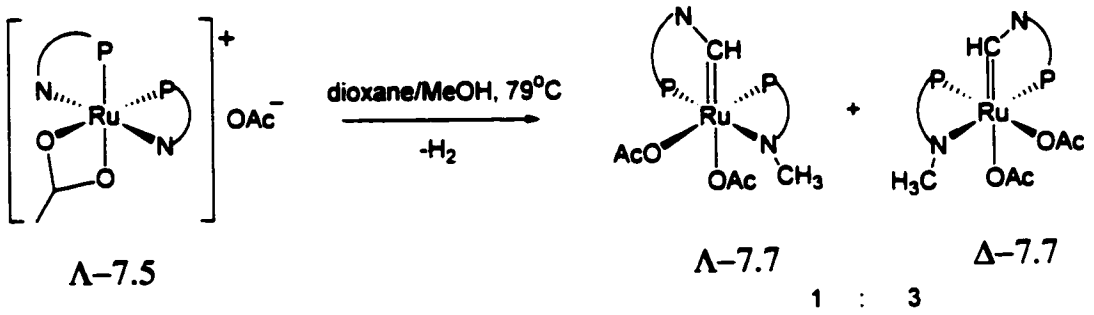
**Scheme 7.2**




A similar sequence of β-H and α-H elimination from the coordinated $NMe_2$ fragment leading to the formation of a carbene tantalum complex has been reported[20] and intramolecular C-H bond activation of *N*-Me group in Ru complexes is a well documented

process.[21,22] It should be noted, however, that mechanisms other than that proposed in Scheme 7.2 are possible. For example, oxidative addition of the C-H bond is not strictly necessary. An alternative pathway may include deprotonation of the coordinated *N*-Me group by acetate ligand. Moreover, the uncoordinated amino group may also react *via* agostic C-H bonding after the OAc ligand has vacated a coordination site by changing from chelating to monodentate. We cannot rule out any of these possibilities, but the latter appears to be less probable as the thermolysis of Λ-**7.5**, which possesses no pendant amino groups, occurs significantly faster than that of Δ-**7.3** (see below).

Thermolysis of Δ-**7.3** in a 6:1 dioxane-methanol solution affords the thermodynamically less stable Δ-**7.7** as the major product. The reaction is complete in 3 h to give Δ-**7.7** and Λ-**7.7** in approximately a 3:1 ratio, along with *ca.* 10% of unidentified products. Such reversed selectivity is not the result of the lower reaction temperature. Indeed thermolysis of Δ-**3** in a 2:1 dioxane-THF solution, which has the same boiling point (79°C) as the 6:1 dioxane-methanol mixture, proceeded significantly slower (ca. 10 h for complete conversion) and led to formation of Δ-**7.7** and Λ-**7.7** in the same 1:10 ratio as was observed for thermolysis in neat dioxane. The $^{31}P$ NMR monitoring of the reaction in dioxane-methanol shows that on refluxing for 10 minutes the signals of Δ-**7.3** completely disappeared from the spectra. At this point the spectra displayed an intense singlet at 55 ppm assigned to complex Λ-**7.5** (see eq 7.4) along with weak signals of Δ-**7.7** and Λ-**7.7**. Further heating led to the gradual disappearance of the singlet accompanied by an increase of the signals due to Δ-**7.7** and Λ-**7.7**. These data suggest that under the reaction conditions Δ-**7.3** is initially transformed into the cationic species Λ-**7.5**, which then undergoes thermolysis in accordance with eq 7.6.



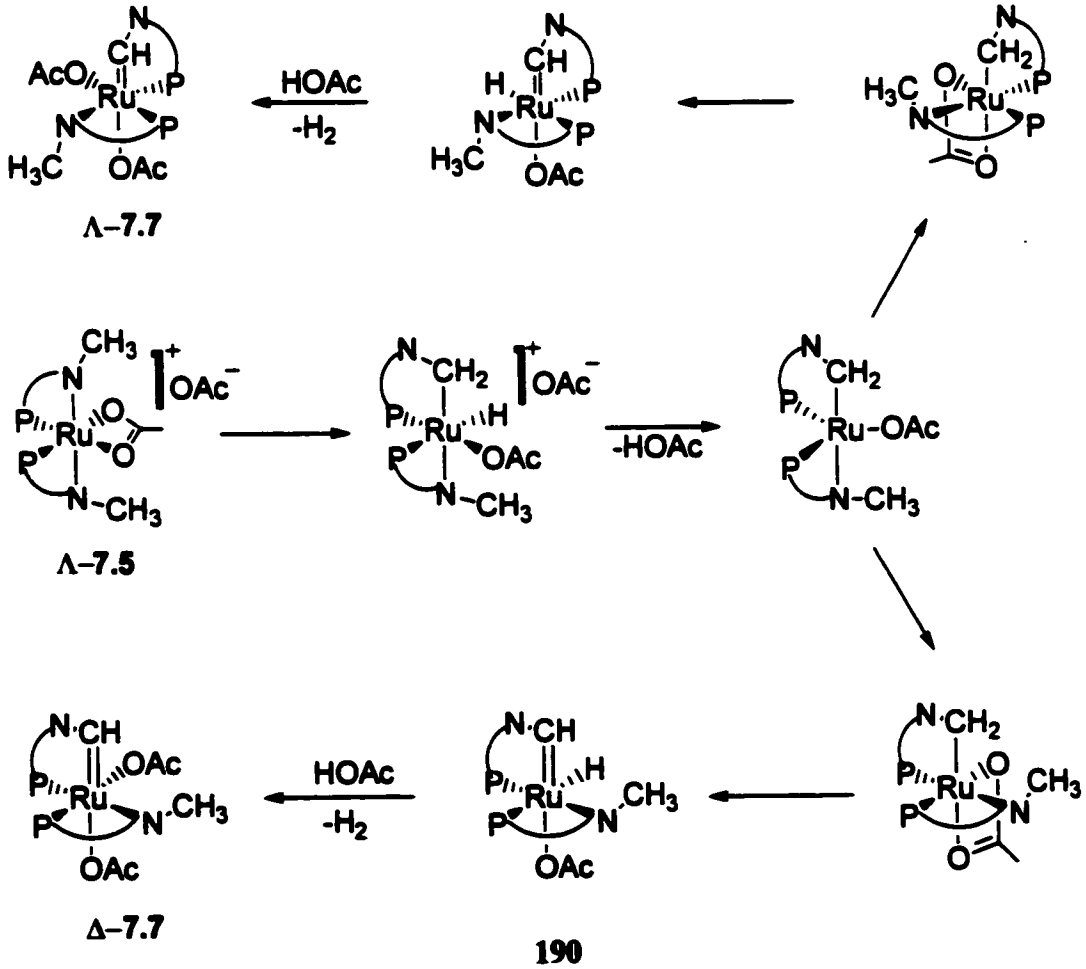

Λ–7.5 Λ–7.7 Δ–7.7

1 : 3

(7.6)

Analogous to reaction (7.5), several mechanisms can be proposed for the thermolysis of Λ-7.5. One possible mechanism is shown in Scheme 7.3 and includes key steps similar to those suggested for reaction (7.5). The penta-coordinate intermediate can be formed via C-H

**Scheme 7.3**



oxidative addition / HOAc reductive elimination, as is shown in Scheme 7.3, or alternatively, by deprotonation of the *N*-Me group by an OAc ligand or OAc anion. The preferential formation of Δ-**7.7** is kinetically controlled. Perhaps the rearrangement of the penta-coordinate intermediate leading to the formation of Δ-**7.7** has a lower activation barrier than that of a Berry pseudorotation or turnstile rotation[23] leading to Λ-**7.7**.

## 7.3 Conclusions

Ruthenium complexes of general formula $[Ru(OAc)_2(P,N)_2]$ can be readily prepared from ruthenium acetate and aminophosphines **7.1a,b**. The balance of electronic and steric factors, which defines the structure of these complexes, is very delicate and easily affected by solvation or intramolecular hydrogen bonding. Thus $[Ru(OAc)_2(PPro)_2]$ displays *trans-P,P*, *trans-N,N* coordination geometry, whereas $[Ru(OAc)_2(PProMe)_2]$ exists as the *cis-P,P*, *cis-P,N* (Δ)-stereoisomer in THF and as the (Λ)-stereoisomer with a *cis-P,P*, *trans-N,N* configuration in methanol. The selective formation of *N*-based stereocenters in $[Ru(OAc)_2(PProMe)_2]$ is explained by the higher thermodynamic stability of *cis* (as compared to *trans*) fused [3.3.0] bicyclic systems arising upon chelation to Ru. The relative stability of *cis*- and *trans*-fused ring systems is not important in the case of $[Ru(OAc)_2(PPro)_2]$, where hydrogen bonding renders *N*-H protons in the opposite sides of P-N-N-P equatorial plane of the molecule, and thus defines the absolute configuration of the *N*-stereocenters.

## 7.4 Experimental Section.

All manipulations were carried out under inert atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. Aminophosphine **PProMe** was

prepared by slight modifications of the published procedure.[24] The synthesis of **PPro** and $[Ru_2(OAc)_4]\cdot 2THF$ was described in the Chapters 5 and 6 respectively. Other chemicals were purchased from Strem or Aldrich and were used as received. The following instruments were used: Varian XL-300 and Bruker AMX 500 (NMR) and Perkin-Elmer 2400 Series II (combustion microanalysis). The natural abundance $^{15}N\{^1H\}$ NMR spectrum of Λ-7.7 was acquired using 0.9 M solution of the complex in a 1:10 $C_6D_6/C_6H_6$ mixture, 10 mm probe, $CH_3NO_2$ as external standard, D1 = 12 s, gated decoupling. The spectrum with acceptable (10:1) signal to noise ratio was observed after 18 h.

**7.4.1 Synthesis of $[Ru(OAc)_2(PPro)_2]\cdot MeOH$.** **PPro** (1.245 mmol, 0.344 M in toluene) was added to a suspension of $[Ru_2(OAc)_4]\cdot 2THF$ (164 mg, 0.281 mmol) in methanol (10 mL). The mixture was stirred for 15 min, the resulting clear yellow solution was evaporated under vacuum and the residue was dissolved in $CH_2Cl_2$ (5 mL). The resulting solution was diluted with MeOH (10 mL), reduced in volume to *ca.* 8 mL under vacuum and left overnight at room temperature. The precipitated crystalline yellow solid was separated by decantation, washed with methanol (2 x 3 mL) and dried in vacuum to give 298 mg of analytically pure $[Ru(OAc)_2(Ph_2PPro)_2]\cdot MeOH$. An additional 48 mg of the complex was isolated upon concentration of the mother liquor. The total yield was 346 mg (0.438 mmol, 78%). Anal. Calcd for $C_{39}H_{50}N_2O_5P_2Ru$: C, 59.31; H, 6.38; N, 3.55. Found: C, 59.12; H, 6.52; N, 3.48. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 41.9 (d, $J$ = 334 Hz); 45.6 (d, $J$ = 334 Hz). $^1H$ NMR ($CDCl_3$), δ: 0.9 (s, 3H); 1.4-1.9 (m, 4H); 1.6 (s, 3H); 2.1 (m, 4H); 2.3-3.1 (m, 9H); 3.3 (s, 3H, MeOH), 3.7 (m, 1H); 7.2-7.6 (m, 20H); 8.5 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 24.4 (s, $CH_3$); 24.9 (s, $CH_2$); 25.8 (s, $CH_3$); 27.5 (s, $CH_2$); 30.2 (d, $J_{C\text{-}P}$ = 15 Hz, $CH_2$); 31.9 (d, $J_{C\text{-}P}$ =

13 Hz, $CH_2$); 32.2 (d, $J_{C\text{-}P}$ = 16 Hz, $CH_2$); 38.2 (d, $J_{C\text{-}P}$ = 21 Hz, $CH_2$); 50.3 (s, MeOH); 52.1 (s, $CH_2$); 52.3 (s, $CH_2$); 61.2 (m, CH); 64.9 (m, CH); 127.8-129.2 (18 lines, Ph); 132.3-137.4 (31 line, Ph); 182.7 (s, OAc); 184.5 (s, OAc).

**7.4.2 Synthesis of $[Ru(OAc)_2(PProMe)_2]\cdot C_5H_{10}$.** **PProMe** (0.950 mmol, 0.465 M in toluene) was added to a stirred solution of $[Ru_2(OAc)_4]\cdot 2THF$ (138 mg, 0.237 mmol) in THF (8 mL). The mixture was stirred for 15 min and the resulting clear orange solution was evaporated under vacuum. The residue was dissolved in cyclopentane (8 mL), the solution was filtered and kept at room temperature until a dark orange crystalline mass precipitated.[25] The crystals were separated by decantation, washed with cyclopentane (2 x 3 mL) and dried in vacuum to give 297 mg of analytically pure $[Ru(OAc)_2(PProMe)_2]\cdot C_5H_{10}$. An additional 45 mg of the complex were isolated upon concentration of mother liquor. The total yield was 342 mg, 0.399 mmol, 84%. Anal. Calcd for $C_{45}H_{60}N_2O_4P_2Ru$: C, 63.14; H, 7.06; N, 3.27. Found: C, 63.15; H, 7.14; N, 3.26. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 48.9 (d, $J$ = 37 Hz); 63 (d, $J$ = 37 Hz). $^1H$ NMR ($CDCl_3$),δ: 0.6 (m, 1H); 0.9 (m, 1H); 1.1-2.0 (m, 10H); 1.2 (s, 3H); 1.3 (m, 10H, $C_5H_{10}$); 1.7 (s, 3H); 1.9 (s, 3H); 2.1(s, 3H); 2.3 (m, 1H); 2.5-3.0 (m, 4H); 3.4 (m, 1H); 6.9-7.4 (m, 20H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 21.1 (s, Me); 23.5 (s, $CH_2$); 23.9 (s, Me); 25.1 (s, $CH_2$); 25.4 (s, $C_5H_{10}$); 28.0 (d, $J_{C\text{-}P}$ = 13 Hz, $CH_2$); 29.0 (d, $J_{C\text{-}P}$ = 21 Hz, $CH_2$); 31.2 (s, $CH_2$); 39.8 (s, Me); 40.3 (d, $J_{C\text{-}P}$ = 27 Hz, $CH_2$); 47.8 (s, Me); 56.0 (s, $CH_2$); 56.7 (s, $CH_2$); 61.5 (d, $J_{C\text{-}P}$ = 7.5 Hz, CH); 68.1 (s, CH); 126.4-136.8 (Ph); 180.0 (s, OAc); 186.2 (s, OAc). $^{31}P\{^1H\}$ NMR ($CD_3OD$), δ: 55.0 (s). $^1H$ NMR ($CD_3OD$), δ: 1.3 (m, 10H, $C_5H_{10}$); 1.7-2.0 (m, 8H); 1.9 (s, 3H); 2.2 (m, 2H); 2.3 (s, 3H); 2.5 (s, 6H); 2.7 (m, 2H); 2.9 (m, 2H); 3.2-3.5 (m, 4H); 7.0 (m, 4H); 7.2 (t, $J$ = 7.5 Hz, 4H); 7.3-7.4 (m, 8H); 7.7 (m, 4H).$^{13}C\{^1H\}$ NMR

($CD_3OD$), δ: 20.1 (s, $CH_2$); 24.5 (s, $CH_3$); 25.3 (s, $CH_3$); 25.6 (s, $C_5H_{10}$); 26.8 (vt, $J_{C\text{-}P}$ = 13 Hz, $CH_2$); 42.3 (m, $CH_2$); 54.2 (s, $CH_3$); 59.5 (s, $CH_2$); 74.4 (s, CH); 129.5 (vt, $J_{C\text{-}P}$ = 10 Hz, Ph);130.3 (vt, $J_{C\text{-}P}$ = 9 Hz, Ph); 130.5 (s, Ph); 130.7 (s, Ph); 132.1 (vt, $J_{C\text{-}P}$ = 8 Hz, Ph); 133.6 (vt, $J_{C\text{-}P}$ = 9 Hz, Ph); 133.7 (vt, $J_{C\text{-}P}$ = 43 Hz, Ph); 140.6 (second order m, Ph); 179.6 (s, OAc); 192.0 (t, $J_{C\text{-}P}$ = 2.5 Hz, OAc). $^{15}N\{^1H\}$ NMR ($CD_3OD$:$CH_3OH$ = 1:10), δ: -345.1 (s).

**7.4.3 Synthesis of $[Ru(OAc)(PProMe)_2]PF_6$.** **PProMe** (1.98 mmol, 0.465 M in toluene) was added to a stirred suspension of $[Ru_2(OAc)_4]\cdot 2THF$ (286 mg, 0.572 mmol) in MeOH (10 mL). The resulting orange solution was treated with solid $NaPF_6$ (200 mg, 1.19 mmol), stirred for 15 min, filtered through cotton wool, reduced in volume to ca. 5 mL and allowed to stay at 5°C for 2 h. The formed orange crystalline solid was separated by decantation, rinsed with cold MeOH (3 mL) and dried in vacuum to give analytically pure $[Ru(OAc)(PProMe)_2]PF_6$ (499 mg, 0.572 mmol, 58%). Anal. Calcd for $C_{38}H_{47}F_6N_2O_2P_3Ru$: C, 52.35; H, 5.43; N, 3.21. Found: C, 52.26; H, 5.28; N, 3.12. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$), δ: -143.8 (sept, $J_{P\text{-}F}$ = 713 Hz); 51.6 (s). $^1H$ NMR ($CD_2Cl_2$), δ: 1.8-2.3 (m, 10H); 2.4 (s, 3H); 2.6 (s, 6H); 2.7 (m, 2H); 2.9 (m, 2H); 3.1 (m, 2H); 3.4 (m, 2H); 6.9 (m, 4H); 7.1 (t, $J$ = 7.5 Hz, 4H); 7.3 (m, 8H); 7.6 (m, 4H).$^{13}C\{^1H\}$ NMR ($CD_2Cl_2$), δ: 19.3 (s, $CH_2$); 25.2 (s, $CH_3$); 26.1 (vt, $J_{C\text{-}P}$ = 13 Hz, $CH_2$); 43.3 (m, $CH_2$); 56.4 (s, $CH_3$); 57.3 (s, $CH_2$); 73.2 (s, CH); 128.6 (vt, $J_{C\text{-}P}$ = 10 Hz, Ph);129.2 (vt, $J_{C\text{-}P}$ = 9 Hz, Ph); 129.4 (s, Ph); 129.8 (s, Ph); 130.5 (vt, $J_{C\text{-}P}$ = 7 Hz, Ph); 132.4 (vt, $J_{C\text{-}P}$ = 8 Hz, Ph); 138.9 (vt, $J_{C\text{-}P}$ = 44 Hz, Ph); 139.4 (vt, $J_{C\text{-}P}$ = 44 Hz, Ph); 190.1 (t, $J_{C\text{-}P}$ = 2.5 Hz, OAc);

**7.4.4 Synthesis of $[Ru(OAc)_2(H_2O)(Ph_2PProMe)_2]\cdot C_5H_{10}$.** Water (50 μL, 2.77 mmol) was added to a stirred solution of **7.3**·$C_5H_{10}$ (1.29 g, 1.51 mmol) in warm cyclopentane (15 mL) causing an immediate color change from orange to light yellow. The resulting solution was reduced in volume to *ca.* 8 mL under vacuum and left overnight. The precipitated yellow crystals were separated by decantation, washed with $C_5H_{10}$ and dried in vacuum to give 735 mg of analytically pure **7.4**·$C_5H_{10}$; an additional 446 mg were isolated upon concentration of the mother liquor. The total yield of **7.4**·$C_5H_{10}$ was 1.18 g (1.35 mmol, 89 %). Anal. Calcd for $C_{45}H_{62}N_2O_5P_2Ru$: C, 61.84; H, 7.15; N, 3.21. Found: C, 61.53; H, 7.28; N, 3.12. $^{31}P\{^1H\}$ NMR (toluene-$d_8$, -40°C), δ: 49.5 (d, $J$ = 37 Hz); 58.4 (d, $J$ = 37 Hz). $^1H$ NMR (toluene-$d_8$, -40°C), δ: 0.9 (m, 2H); 1.2 (m, 2H); 1.4-1.9 (m, 5H); 1.6 (s, 10H); 1.8 (s, 3H); 2.1 (s, 3H); 2.3 (m, 2H); 2.4 (s, 3H); 2.5 (s, 3H); 2.6-3.1 (m, 5H); 3.4 (m, 1H); 3.6 (m, 1H); 5.3 (b.s, 2H); 7.0-7.4 (m, 16H); 7.8 (m, 4H). $^{13}C\{^1H\}$ NMR (toluene-$d_8$, -40°C), δ: 22.2 (s, $CH_2$); 22.4 (s, $CH_2$); 25.4 (s, $CH_3$); 26.0 (s, $CH_3$); 26.2 (s, $C_5H_{10}$); 28.01 (d, $J_{C\text{-}P}$ = 13 Hz, $CH_2$); 32.6 (s, $CH_2$); 33.7 (d, $J_{C\text{-}P}$ = 19 Hz, $CH_2$); 40.3 (s, $CH_3$); 41.8 (d, $J_{C\text{-}P}$ = 27 Hz, $CH_2$); 46.1 (s, $CH_3$); 54.9 (s, $CH_2$); 56.1 (s, $CH_2$); 62.3 (d, $J_{C\text{-}P}$ = 7 Hz, CH); 68.4 (d, $J_{C\text{-}P}$ = 5 Hz, CH); 127.4-129.8 (Ph); 133.6-138.1 (Ph); 183.2 (s, OAc); 183.4 (s, OAc).

**7.4.5 Synthesis of Δ-7.7. Method A.** A stirred solution of $[Ru(OAc)_2(ProMe)_2]\cdot C_5H_{10}$ (3.14 g, 3.66 mmol) in a mixture of dioxane (18 mL) and MeOH (3 mL) was heated to reflux for 3 h, reduced in volume to *ca.* 16 mL and cooled to room temperature. The formed voluminous precipitate was separated by filtration, washed with benzene (2 x 4 mL) and dried in vacuum to give 1.08 g of analytically pure Δ-7.7. An additional 323 mg were isolated upon concentration of the mother liquor. The total yield of Δ-

7.7 was 1.40 g, 1.79 mmol, 49%. Anal. Calcd for $C_{40}H_{48}N_2O_4P_2Ru$: C, 61.21; H, 6.17; N, 3.57. Found: C, 61.29; H, 6.23; N, 3.40. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 50.4 (d, $J$ = 32 Hz); 55.8 (d, $J$ = 32 Hz). $^1H$ NMR ($CDCl_3$),δ: 1.0 (s, 3H); 1.4-2.2 (m, 9H); 1.9 (s, 3H); 2.4 (s, 3 H); 2.6 (m, 2H); 3.0 (m, 2H); 3.7 (m, 1H); 4.3 (m, 1H); 4.9 (m, 1H); 6.3 (m, 2H); 6.8-7.7 (m, 20H); 12.4 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 22.6 (s, $CH_3$); 23.4 (s, $CH_2$); 23.5 (s, $CH_2$); 25.1 (s, $CH_2$); 26.5 (d, $J_{C\text{-}P}$ = 14 Hz, $CH_2$); 31.9 (d, $J_{C\text{-}P}$ = 32 Hz, $CH_2$); 34.8 (d, $J_{C\text{-}P}$ = 13 Hz, $CH_2$); 43.0 (d, $J_{C\text{-}P}$ = 34 Hz, $CH_2$); 47.0 (s, $CH_3$); 57.2 (s, $CH_2$); 57.8 (s, CH); 60.8 (s, $CH_2$); 66.3 (s, CH); 127.2-133.4 (Ph); 175.8 (s, OAc); 186.5 (s, OAc); 242.5 (t, $J_{C\text{-}P}$ = 15 Hz, CH).

**Method B.** A stirred solution of $[Ru(OAc)_2(ProMe)_2]\cdot C_5H_{10}$ (2.12 g, 2.48 mmol) in dioxane (20 mL) was heated to reflux for 6 h and then evaporated to dryness. The residue was dissolved in benzene (10 mL) and the resulting orange-brown solution was set aside for 2 h. The formed voluminous precipitate was separated by filtration, washed with benzene (2 x 2 mL) and dried in vacuum to give 146 mg of Δ-7.7. The combined washings and filtrate were diluted with heptane (10 mL) and reduced in volume to *ca.* 10 mL under vacuum to give orange solution and brown oily residue. The solution was discarded, the residue was washed with heptane (2 x 10 mL) and dissolved in benzene. The resulting solution was left at room temperature overnight. The formed yellow crystals were separated by filtration, washed with benzene (2 x 2 mL), and dried in vacuum to give an additional 32 mg of Δ-7.7. The total yield was 178 mg, 0.227 mmol, 9 %.

**7.4.6 Synthesis of Λ-7.7.** The supernatant and washings collected after the separation of complex Δ-7.7 by method B (see above) were evaporated to dryness under vacuum. The residue was stirred with cyclopentane (10 mL) to give a yellow solid and

yellow solution. The solid was separated by decantation and dried in vacuum to give 1.43 g of crude Λ-**7.7**. The complex was *ca.* 90% pure ($^{31}$P NMR) and contained a non-stoichiometric amount of benzene ($^{13}$C- and $^{1}$H NMR). $^{31}$P{$^{1}$H} NMR ($C_6D_6$), δ: 45.4 (d, $J$ = 32 Hz); 54.5 (d, $J$ = 32 Hz). $^{1}$H NMR ($C_6D_6$),δ: 0.7 (m, 2H); 1.1 (m, 3H); 1.3-1.6 (m, 4H); 1.5 (s, 3H); 1.8 (m, 1H); 2.2 (m, 1H); 2.3 (s, 3H); 2.6 (m, 1H); 3.0 (s, 3H); 3.2 (m,1H); 3.5 (m, 2H); 4.4 (m, 2H); 5.4 (m, 1H); 6.9-7.7 (m, 20H); 12.8 (s,1H). $^{13}$C{$^{1}$H} NMR ($C_6D_6$), δ: 21.1 (s, $CH_2$); 22.1 (s, $CH_2$); 24.4 (s, $CH_3$); 24.5 (s, $CH_3$); 27.9 (d, $J_{C\text{-}P}$ = 11 Hz, $CH_2$); 28.8 (d, $J_{C\text{-}P}$ = 31 Hz, $CH_2$); 35.0 (d, $J_{C\text{-}P}$ = 12 Hz, $CH_2$); 44.0 (d, $J_{C\text{-}P}$ = 29 Hz, $CH_2$);45.8 (s, $CH_3$); 58.6 (s, $CH_2$); 59.5 (s, CH); 60.7 (s, $CH_2$); 68.4 (s, CH); 128.2-136.7 (Ph); 175.1 (s, OAc); 185.9 (d, $J_{C\text{-}P}$ = 2 Hz, OAc); 242.8 (t, $J_{C\text{-}P}$ = 15 Hz, CH). $^{15}$N{$^{1}$H} NMR ($C_6D_6$ : $C_6H_6$ = 1 : 10), δ: -320.4 (d $J_{N\text{-}P}$ = 32.6 Hz); -165.8 (s).

**7.4.7 Single-Crystal X-ray Diffraction Study of 7.2·$Et_2O$, Δ-7.3·$C_5H_{10}$, 7.4·$C_5H_{10}$, Λ-7.6 and Δ-7.7·$C_6H_6$.** Crystals of **7.2**·$Et_2O$, suitable for X-ray analysis, were obtained by slow diffusion of ether into a $CH_2Cl_2$ solution of **7.2**·MeOH. Single crystals of Δ-**7.3**·$C_5H_{10}$, **7.4**·$C_5H_{10}$ Λ-**7.6** and Δ-**7.7**·$C_6H_6$ were obtained by slow crystallization of the corresponding complexes from concentrated solutions in $C_5H_{10}$, wet $C_5H_{10}$, MeOH and $C_6H_6$, respectively. Compound **7.4**·$C_5H_{10}$ consistently crystallized as thin stacked plates and the reported diffraction data represents the best result of several attempts. The crystals were mounted on thin glass fibers using viscous oil and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on

equivalent reflections were applied.[26] Systematic absences in the diffraction data and unit-cell parameters were consistent for space groups $P2_1$ and $P2_1/m$ for Δ-**7.3**·$C_5H_{10}$, Λ-**7.6** and **7.4**·$C_5H_{10}$; *C*2, *Cm* and *C*2/*m* for **7.2**·$Et_2O$; and, uniquely, $P2_12_12_1$ for Δ-**7.7**·$C_6H_6$. Solutions in the acentric space groups are consistent with the enantiomerically pure compounds. Only the space group *C*2 yielded chemically reasonable and computationally stable results of refinement for **7.2**·$Et_2O$. The structures were solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on $F^2$. An inspection of the resulting packing diagrams did not suggest any overlooked symmetry. Refinement of the Flack parameter in each case yielded nil indicating that the true hands of the data sets have been determined. Two symmetry-unique compound molecules were located in the asymmetric unit of Δ-**7.3**·$C_5H_{10}$ and Λ-**7.6**. Two molecules of cyclopentane, two half-molecules of diethyl ether, a cyclopentane molecule and two half-occupied molecules of benzene, treated as idealized, rigid, flat hexagons, were located in the asymmetric units of Δ-**7.3**·$C_5H_{10}$, **7.2**·$Et_2O$, **7.4**·$C_5H_{10}$ and Δ-**7.7**·$C_6H_6$, respectively. The benzene and cyclopentane carbon atoms were refined isotropically. All other non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.10 program library.[27] ORTEP plots were made using ORTEP-III (1.0.3) software [28] downloaded from the Internet at http://www.chem.gla.ac.uk/~louis/ortep3/.

**Table 7.6.** Summary of Crystallographic data for **2·$Et_2O$**, **Δ-3·$C_5H_{10}$**, **4·$C_5H_{10}$**, **Λ-6** and **Δ-7·$C_6H_6$**

| complex | 2·$Et_2O$ | Δ-3·$C_5H_{10}$ | 4·$C_5H_{10}$ | Λ-6 | Δ-7·$C_6H_6$ |
|---|---|---|---|---|---|
| formula | $C_{42}H_{56}N_2O_5P_2Ru$ | $C_{45}H_{60}N_2O_4P_2Ru$ | $C_{45}H_{62}N_2O_5P_2Ru$ | $C_{38}H_{47}F_6N_2O_2P_3Ru$ | $C_{46}H_{54}N_2O_4P_2Ru$ |
| fw | 831.90 | 855.96 | 873.97 | 871.76 | 861.92 |
| cryst dimens, mm | 0.2x0.1x0.1 | 0.1x0.1x0.1 | 0.3x0.3x0.1 | 0.1x0.1x0.2 | 0.3x0.2x0.2 |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic | orthorhombic |
| *a*, Å | 15.373(1) | 10.216(3) | 9.790(5) | 9.9950(7) | 15.431(2) |
| *b*, Å | 15.911(1) | 21.508(6) | 20.021(9) | 39.365(3) | 16.229(2) |
| *c*, Å | 16.641(1) | 19.816(5) | 12.838(9) | 10.0685(7) | 17.424(2) |
| β, deg | 108.044(1) | 98.556(3) | 101.32(1) | 98.6570(10) | 90 |
| space group | *C*2 | $P2_1$ | $P2_1$ | $P2_1$ | $P2_12_12_1$ |
| *Z* | 4 | 4 | 2 | 4 | 4 |
| *V* Å$^3$ | 3870.1(5) | 4306(2) | 2467(2) | 3916.3(5) | 4363.2(7) |
| $d_{calc}$, g/cm$^3$ | 1.428 | 1.329 | 1.178 | 1.479 | 1.312 |
| *T*, K | 203(2) | 293(2) | 203(2) | 203(2) | 203(2) |
| radiation (λ) | MoKα (0.71073 Å) | | | | |
| abs. coeff., mm$^{-1}$ | 0.535 | 0.482 | 0.423 | 0.587 | 0.476 |
| transmissn (max/min.) | 1.33580 | 1.59535 | 1.33198 | 1.39534 | 1.33187 |
| $R(F)$,% | 4.33 | 5.68 | 8.60 | 6.09 | 4.12 |
| $R(wF^2)$,% | 10.06 | 12.34 | 22.38 | 12.60 | 9.47 |
| GOF | 1.070 | 1.040 | 1.043 | 1.009 | 1.002 |
| Flack param. | -0.01(4) | 0.05(5) | -0.05 | -0.01(3) | -0.04 |

Quantity minimised = $R(wF^2) = \Sigma[(w(F_O^2 - F_C^2)^2]/\Sigma(wF_O^2)^{1/2}$;

$R(F) = \Sigma\Delta / \Sigma(F_O)$, $\Delta = |(F_O - F_C)|$

## 7.5 References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10. The reaction in THF or $CH_2Cl_2$ gives **2** along with *ca.* 30% of unidentified side-products.

11. Attempts to prepare a 1:1 Ru-PPro complex by treating of $[Ru_2(OAc)_4]$ with 1 equiv of **1a** were unsuccessful. A complex mixture of unidentified products, along with traces of **2**, was observed by $^{31}P$ NMR

12. Reaction of $[Ru_2(OAc)_4]$ with 1equiv of PPrOMe afforded a product of unknown structure, which shows a singlet at 87 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The complex was not isolated due to fast decomposition in solution (half-life *ca.* 6 h in

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16. Calculated for 0.176 M solution of $4{\cdot}C_5H_{10}$ in THF at –40°C.

17. Formation of *ca.* 1 equiv $H_2$ was confirmed by collecting the released gas and GC analysis.

18. See for example Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1998**, *17*, 827 and references therein.

19. The values of *cis* P-N and *trans* P-N constants in metallocomplexes normally lie within 0-6 Hz and 25–95 Hz respectively. See for example: (a) Kuznetsov, V. F. Facey, G. A.; Yap, G. P. A.; Alper, H. *Organometallics*, **1999**, *18*, 4706. (b) Carlton, L. Weber, R. *Inorg. Chem.* **1996**, *35*, 5843. (c) Heaton, B. T.; Jacob, C.; Monks, G. L.; Hursthouse M. B.; Ghatak, I.; Somervile R. G.; Heggie, W.; Page, P. R.; Villax, I. *J. Chem. Soc. Dalton Trans.* **1996**, 61. (d) Carlton, L. De Sousa, G. *Polyhedron*, **1993**, *12*, 1377.

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# Claims to Original Research.

1) It has been shown that the rhodium and palladium hydroxo complexes $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2]$ and $[Pd_2(Ph)_2(PPh_3)_2(\mu\text{-}OH)_2]$ react with acidic transition metal hydrides to give the corresponding heterobimetallic clusters.

2) The first palladium complexes containing aryl/alkyl, hydroxo and carbonyl ligands all in the same coordination sphere have been prepared and characterized. Stepwise "neutralization" of $[Pd_2(Ph)_2(PPh_3)_2(\mu\text{-}OH)_2]$ with $[M(CO)_3Cp]$, (M = Cr, Mo, W) allows for the preparation of tetranuclear heterotrimetallic complexes.

3) The reaction of $[ClRh(PPh_3)_3]$ and $[ClRh(CO)(PPh_3)_2]$ with the sodium salt of (1*S*,2*R*,5*S*)-menthol has been investigated. The first chiral phosphine rhodium alkoxo complex has been prepared and structurally characterized.

4) It has been shown for the first time that phosphine rhodium aryloxo complexes, $[Rh(PPh_3)_3(OAr)]$, can exist in solution in equilibrium with the corresponding $\pi$-aryloxo complexes, $[Rh(PPh_3)_2(\pi\text{-}OAr)]$, and triphenylphosphine. In the presence of HOAr the equilibrium is shifted toward the complexes with $\pi$-coordinated OAr due to the formation of strong hydrogen bonds between the oxygen atom of the OAr ligand and two molecules of HOAr.

5) It has been shown that the phosphine rhodium aryloxo complexes, $[Rh(PPh_3)_2(\pi\text{-}OAr)]$, are best described as $\eta^4$-aryloxides, rather than $\eta^5$-aryloxides, as they have been often referred before.

6) The reactivity of chiral aminophosphinites derived from *N*-substituted ephedrines with $[Rh_2(CO)_4Cl_2]$ has been investigated. It has been demonstrated that the affinity of the

amino group toward Rh(I) depends strongly on the steric bulk of the *N*-substituents; *i.e* -NHMe > CO > -$OPPh_2$ > -$NMe_2$ > $\mu$-$Cl^-$ > -$NMeCHPh_2$ > $ClO_4^-$.

7) The formation of *N*-based stereocenters arising upon chelation of the Rh(I) by the aminophosphinites is governed by the tendency of non-rigid six-membered rings to adopt a chair conformation, with the sterically more demanding substituents in equatorial positions.

8) It has been shown that [$Ru_2(OAc)_4$] is an excellent precursor for the preparation of Ru(II) complexes containing chiral chelating bisphosphines and aminophosphines. Factors affecting the selectivity for the formation of the *N*- and *Ru*-based stereocenters, arising upon chelation of the aminophosphines derived from (*S*)-proline to Ru, have been investigated.

# List of Publications

(1) A Simple and Convenient Preparation of $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2]$ and Its Reactions with C-H, O-H and M-H acides. Grushin, V. V.; **Kuznetsov, V. F.**, Bensimon, C.; Alper. H. *Organometallics*, **1995**, *14*, 3927.

(2) "Neutralization" of Palladium Hydroxides, $[L_2Pd_2(R)_2(\mu\text{-}0H)_2]$, by M-H Acids, $[CpM(CO)_3H]$ (M = W, Mo, Cr). **Kuznetsov, V. F.**; Bensimon, C.; Facey, G. A.; Grushin, V. V.; Alper, H. *Organometallics*, **1997**, *16*, 97.

(3) Preparation, Structure and Properties of Triphenylphosphine Rhodium Aryloxides. **Kuznetsov, V. F.**; Yap, G. P. A.; Bensimon, C.; Alper, H. *Inorg. Chim. Acta* **1998**, *280*, 172.

(4) Rhodium Complexes with Chiral Aminophosphine Derivatives of Ephedrine. **Kuznetsov, V. F.**; Facey, G. A.; Yap, G. P. A.; Alper, H. *Organometallics*, **1999**, *18*, 4706.

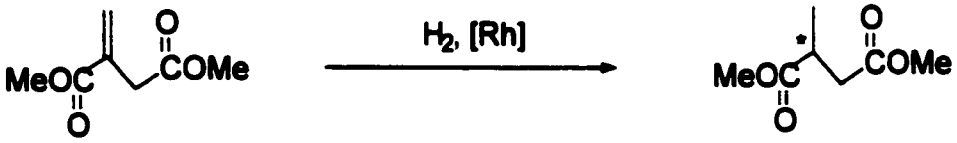
(5) Chiral Ruthenium Complexes with Aminophosphine Derivatives of (*S*)-Proline. **Kuznetsov, V. F.**; Yap, G. P. A.; Alper, H. *Organometallics*. In press.

# Appendix 1.

## Catalytic Activity of Chiral Rhodium Complexes in Hydrogenation of Dimethylitaconate

Catalytic activity of the chiral Rh complexes **5.3a,b**, **5.4a** and **5.9c** in hydrogenation of dimethyl itaconate (eq A.1) was investigated using the following procedure.

Rh complex (0.015 mmol), dimethyl itaconate (475 mg, 3.0 mmol) and a magnetic stirring bar were placed into a 100 mL glass autoclave. The autoclave was evacuated, filled with hydrogen, charged with 5.0 mL of the solvent (dried and distilled under $N_2$ prior to use) and pressurized with hydrogen. The mixture was stirred at the reaction temperature for 2 – 20 h, cooled to room temperature, hydrogen pressure was released and the resulting solution was distilled on Kugelrohr apparatus. The distillate was analyzed by chiral GC (capillary column with cyclodextrin, l = 20 m, t = 75°C). The results are presented in Table A.1.




A.1

**Table A.1.** Catalytic Activity of Chiral Rhodium Complexes in Hydrogenation of Dimethylitaconate (eq A.1).

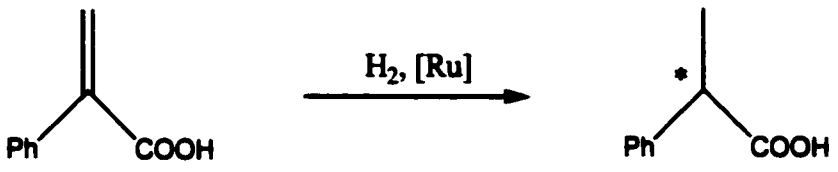
| Complex | Solvent | T, °C | Time, h | $pH_2$, atm | Conversion, % | e.e, % |
|---|---|---|---|---|---|---|
| $[Rh(CO)(PPh_3)_2(OMent)]$ **3.4** | $C_6H_6$ | 20 | 6 | 5 | 28 | 0 |
| | $CH_2Cl_2$ | 20 | 6 | 5 | 32 | 0 |
| | MeOH | 20 | 6 | 5 | 49 | 0 |
| [Rh(CO)(PPro)Cl] **5.3a** | $CH_2Cl_2$ | 20 | 12 | 4 | 85 | 11 |
| | $CH_2Cl_2$ | 80 | 2 | 4 | 22 | 18 |
| | MeOH | 20 | 12 | 4 | 100 | 0 |
| [Rh(CO)(PProMe)Cl] **5.3b** | $C_6H_6$ | 20 | 20 | 4 | 5 | 18 |
| | $C_6H_6$ | 80 | 2 | 4 | 15 | 48 |
| | THF | 60 | 4 | 4 | 42 | 42 |
| | MeOH | 60 | 3 | 4 | 62 | 0 |
| | $CH_2Cl_2$ | 40 | 3 | 4 | 28 | 39 |
| | $CH_2Cl_2$ | 60 | 3 | 4 | 46 | 71 |
| | $CH_2Cl_2$ | 80 | 3 | 4 | 98 | 71 |
| $[Rh(POEph)_2]Cl$ **5.4a** | $CH_2Cl_2$ | 20 | 8 | 4 | 0 | - |
| | $CH_2Cl_2$ | 60 | 8 | 4 | 5 | 0 |
| | MeOH | 20 | 8 | 4 | 0 | - |
| | MeOH | 60 | 8 | 4 | 7 | 0 |
| $[Rh(POPheph)CO]ClO_4$ **5.9c** | $CH_2Cl_2$ | 20 | 3 | 4 | 58 | 0 |
| | $CH_2Cl_2$ | 60 | 3 | 4 | 100 | 0 |
| | MeOH | 20 | 3 | 4 | 70 | 0 |
| | MeOH | 60 | 3 | 4 | 100 | 0 |

# Appendix 2.

## Catalytic Activity of Aminophosphine Ruthenium Complexes in Hydrogenation of Atropic Acid.

Catalytic activity of the chiral Ru complexes **7.2** and **7.3** in hydrogenation of atropic acid (eq A.2) was investigated using the following procedure.

Ru complex (0.015 mmol), atropic acid (445 mg, 3.0 mmol) and a magnetic stirring bar were placed into a 50 mL stainless steel autoclave. The autoclave was flushed with hydrogen, charged with 6.0 mL of the solvent (dried and distilled under $N_2$ prior to use) and pressurized with hydrogen. The mixture was stirred at the reaction temperature for 3 – 24 h, cooled to room temperature, hydrogen pressure was released, the resulting solution was evaporated on rotovap and the residue was distilled on Kugelrohr apparatus. The distillate was diluted with methanol (6 mL), treated with 3 drops of conc. $H_2SO_4$ and heated to reflux for 1 h. The resulting solution was cooled to room temperature and diluted with $H_2O$ (10 mL) and ether (15 mL). The upper layer was separated, washed with $H_2O$ (10 mL), dried over $Na_2SO_4$ and analyzed by chiral GC (capillary column with cyclodextrin, l = 20 m, t = 75°C). The results are presented in Table A.2.




**A.2**

**Table A.2.** Catalytic Activity of Aminophosphine Ruthenium Complexes in Hydrogenation of Atropic Acid (eq A.2)

| Complex | Solvent | $pH_2$, atm | T, °C | Time, h | Conversion, % | e.e, % |
|---|---|---|---|---|---|---|
| $[Ru(OAc)_2(PPro)_2]$ 7.2 | $CH_2Cl_2$ | 50 | 20 | 16 | 2 | 0 |
| | $CH_2Cl_2$ | 50 | 60 | 24 | 23 | 0 |
| | MeOH | 50 | 20 | 16 | 0 | - |
| | MeOH | 50 | 60 | 24 | 18 | 0 |
| $[Ru(OAc)_2(PProMe)_2]$ 7.3 | $CH_2Cl_2$ | 50 | 20 | 24 | 47 | 16 |
| | $CH_2Cl_2$ | 50 | 60 | 3 | 92 | 4 |
| | MeOH | 50 | 20 | 24 | 63 | 0 |
| | MeOH | 50 | 60 | 3 | 100 | 0 |