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N-HETEROCYCLIC CARBENES AS ACTIVATING LIGANDS IN HYDROGENATION CATALYSTS: SYNTHETIC AND CATALYTIC STUDIES

By

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ABSTRACT

Novel hydridochlorocarbonyl ruthenium complexes containing N-heterocyclic carbene (NHC) ligands were prepared in order to explore the effect of the NHC ligand class in hydrogenation chemistry. Routes were developed to $RuHCl(CO)(NHC)(PPh_3)$ (NHC = IMes, H_2IMes) from $RuHCl(CO)(PPh_3)_3$, and the hydrogenation activities of these complexes were screened against that of the known complexes $RuHCl(CO)(PCy_3)_2$ and $RuHCl(CO)(IMes)(PCy_3)$. The combination of the donor ability of the NHC ligand, in conjunction with the lability of the PPh_3 group, increased activity for the challenging hydrogenation of sterically hindered trans internal olefins, but also led to competing isomerization of terminal olefins and polymerization of strained cycloolefins.

In the course of this work, high yield, efficient new routes were also developed to the known complexes $RuHCl(CO)(PCy_3)_2$ and $RuHCl(CO)(NHC)(PCy_3)$ from $RuHCl(CO)(PPh_3)_3$. The lability of the phosphine groups in the latter precursor complex enabled milder reaction conditions than had been possible in the literature methods.

In an effort to gain access to carbonyl-free analogues, synthesis of a ruthenium hydride complex containing a cyclometalated IMes ligand was undertaken. However, the product obtained using the reported method was a novel complex, formulated as $RuHCl(IMes)_2$ on the basis of extensive NMR and MALDI-MS analysis.

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TABLE OF COMPOUND NUMBERS

Number	**Compound**
1	$RuCl_2(PPh_3)_3$
2	$RuHCl(PPh_3)_3$
3	$RuCl_2(CHPh)(PCy_3)_2$
4	$RuCl_2(NHC)(PCy_3)(CHPh)$
	(**a**: NHC = IMes; **b**: NHC = H_2IMes)
5	$RuCl_2(NHC)(py)_2(CHPh)$
	(**a**: NHC = IMes; **b**: NHC = H_2IMes)
6	$RuCl_2(NHC)(3\text{-}Brpy)_2(CHPh)$
	(**a**: NHC = IMes; **b**: NHC = H_2IMes)
7	$RuHCl(CO)(PPh_3)_3$
8	$RuHCl(H_2)(PCy_3)_2$
9	$RuHCl(CO)(PCy_3)_2$
10	$RuCl_2(CO)_2(PCy_3)_2$
11	$RuCl_2(CO)(PCy_3)_2$
12	$RuHCl(CO)(IMes)(PPh_3)$
	(**a**: NHC = IMes; **b**: NHC = H_2IMes)
13	$RuHCl(CO)(IMes)(PCy_3)$
	(**a**: NHC = IMes; **b**: NHC = H_2IMes)
14	$RuHCl(CO)(IMes)_2$
15	(**a**: $RuHCl(IMes)_2$; **b**: $[RuHCl(IMes)_2]_2$)

16	hydridobis(triphenyl)ruthenium complex with cyclometalated IMes ligand to produce Ru-CH_2-aryl linkage
17	$[RuCl\{2\text{-}[(2, 6\text{-}{}^{i}Pr_2C_6H_3)\text{-}N{=}CH\}C_4H_3N](PCy_3)(CHPh)$
18	$RuCl(dcypb)(\mu\text{-}Cl)_3Ru(dcypb)(N_2)$
19	$[RuCl\{2\text{-}[(2, 6\text{-}{}^{i}Pr_2C_6H_3)\text{-}N{=}CH]C_4H_3N\}(PPh_3)]_2$
20	10-[3-*tert*-butyl-dimethyl-silanyloxy)-propylidene]-6-(*tert*-butyl-diphenyl-silanyloxymethyl)-2,2-dimethyl-octahydro-naphtho[1,8a-d][1,3]dioxole

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LIST OF ABBREVIATIONS

Å	Angstrom
Ar	aryl
atm	atmosphere (1 atm = 760 mmHg, 101.3 kPa, 14.696 psi
br	broad
3-Brpy	3-Bromo Pyridine
c	cis
$^{13}C\{^1H\}$	proton-decoupled carbon-13 (NMR)
CDA	cyclododecane
CDE	cyclododecene
CM	Cross metathesis
COE	cyclooctene
Cy	cyclohexyl
d	doublet
GC-FID	Gas chromatography- flame ionization detector
GPC	Gel permeation chromotography
H_2IMes	1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene
H_2IMes·HCl	1,3-bis-(2,4,6-trimethylphenyl)imidazolinium chloride
IMes	bis(1,3-(2,4,6-trimethylphenyl)imidazol-2-ylidene
IR	Infrared
J	coupling constant
L	ligand
$M^{+\cdot}$	molecular ion
M	central metal atom in a complex
MALDI-MS	Matrix-assisted laser desorption ionization mass spectrometry
m	multiplet (NMR)
m	meta
min	minutes
Me	methyl

Mes	Mesityl
m/z	mass-to-charge ratio
NHC	N-heterocyclic carbene
NMR	Nuclear Magnetic Resonance
o	ortho
ORTEP	Oak Ridge Thermal Ellipsoid Projection
p	para
$^{31}P\{^{1}H\}$	proton-decoupled phosphorus-31 (NMR)
PCy_3	tricyclohexyl phosphine
Ph	phenyl
PPh_3	triphenyl phosphine
py	pyridine
q	quartet (NMR)
RCM	Ring Closing Metathesis
ROMP	Ring Opening Metathesis Polymerization
RT	Room Temperature
s	Singlet (NMR)
t	Triplet (NMR)
THF	tetrahydrofuran
TOF	Turnover frequency
T_1	Longitudinal relaxation time (NMR)
XRD	X-ray diffraction
η	Descriptor hapticity
λ	wavelength

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PUBLICATIONS FROM THESIS WORK

- U. L. Dharmasena, S. D. Drouin, H. A. Jenkins, D. E. Fogg. "Hydridocarbonyl Complexes of Ruthenium with Phosphine and Mixed Phosphine - NHC groups: High-yield, Efficient, New Routes for Old Complexes" manuscript in preparation.

- U. D. Dharmasena, H. M. Foucault, E. N. dos Santos, D. E. Fogg, S. P. Nolan, "N-Heterocyclic Carbenes as Activating Ligands for Hydrogenation and Isomerization of Unactivated Olefins" *Organometallics* 2005, *24*, 1056.

CHAPTER 1

Introduction

1.1. Homogeneous Catalysis

Catalytic processes are more economical and environmentally friendly compared to non-catalytic processes: increases in process efficiency and minimizing of energy requirements help to reduce environment hazards.[1] Heterogeneous catalysis, in which a solid catalyst interacts with a liquid or gaseous substrate,[2] is long established in chemical industry.[3] Heterogeneous catalysts offer high durability and low cost, but because they are ill-defined at the molecular level, they exhibit low selectivity.[3] Homogeneous catalysis by well-defined, soluble metal complexes acting in solution phase[2] offers higher selectivity, though the catalysts are less robust, more expensive and sometimes difficult to separate from reactants or products. Homogeneous catalysts generally consist of a central metal ion bonded to ancillary ligands, the steric and electronic properties of which control the environment of the active site, and hence catalyst activity and selectivity. Fine-tuning of the ligands enables chemoselectivity (discrimination between possible functional groups), regioselectivity (selectivity in the site of attack), and in some cases stereoselectivity (discrimination between two possible enantiomeric products).[4] At present a tremendous amount of research work is focused on characterizing catalysts spectroscopically and chemically, understanding reaction kinetics, and creating tailor-made catalysts that are specially designed for individual reactions. This increased understanding of homogeneous catalysts at the molecular level has increased the applications in chemical industries.[3]

1.2. Homogeneous Hydrogenation by Ru Catalysts

In synthetic organic chemistry, by far the most significant catalytic method is hydrogenation, and the cleanest possible reducing agent is hydrogen.[5] While addition of H_2 to an alkene or alkyne is thermodynamically feasible, the uncatalyzed reaction is symmetry-forbidden in the ground state via concerted cis addition. Since there is no net overlap, electrons cannot flow from H_2 to the empty π^*-orbital of the alkene. However, the d-orbitals of transition metals posses the correct symmetry to overlap directly with H_2. Electrons can thus flow from the filled metal d-orbitals into the empty σ^*-orbital of H_2, dissociating the H-H bond and forming two metal hydride bonds. The H atom can now be transferred, at least in principle, in one step to the alkene (Figure 1.1).[6]

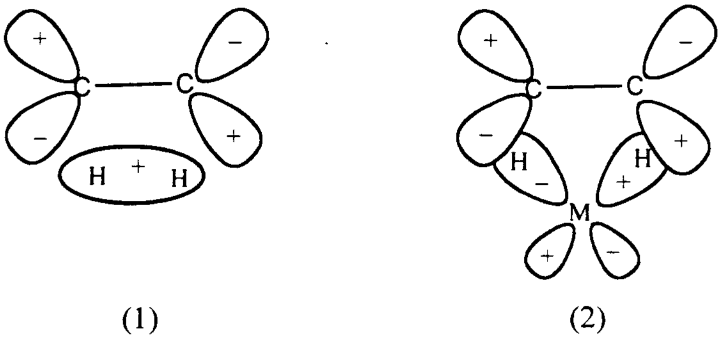


Figure 1.1 Schematic presentation of (1) symmetry–forbidden addition of H_2 and (2) metal catalyzed allowed concerted addition of two H atoms to a double bond.

Homogeneous hydrogenation by Ru complexes has a long history. The first well-characterized example of homogeneous hydrogenation of an alkene (the activated alkene maleic acid) by a Ru(II) system was reported in 1961.[6] Utilization of ruthenium complexes as homogeneous catalysis significantly expanded following the discovery of

$RuHCl(PPh_3)_3$ by Wilkinson's group in 1965.[7] More recently, the application of ruthenium chemistry in catalytic reactions and organic synthesis has been widely studied. Owing to the efficiency, selectivity and low cost of Ru-catalyzed processes relative to reactions promoted by other precious metals such as palladium and rhodium, ruthenium is widely used in industrial applications.[8] In addition, a breadth of chemistry is suggested by the fact that ruthenium possesses the widest scope of oxidation states of all the elements of the periodic table (from -2 in $Ru(CO)_4^{2-}$ to +8 in RuO_4). A great variety of possible coordination geometries is possible in each electronic configuration,[8] each with variable catalytic properties. These catalytic activities arise from the following distinctive properties of ruthenium which persist through quite drastic ligand changes:

1. A propensity for π-back-bonding, reflected in the stability of Ru-CO, $Ru(\eta^1\text{-}N_2)$, and $Ru(\eta^2\text{- }H_2)$ bonds.
2. A tendency to undergo intra- and inter-molecular metallation.
3. A tendency to form polyhydride complexes.[9]

The rich catalytic properties of ruthenium complexes cover a wide range of organic transformations, including not only hydrogenation,[10-28] but oxidation,[29-32] isomerization,[5,12,16] nucleophilic addition to carbon-carbon[33-37] and carbon-heteroatom multiple bonds,[38,39] carbon-carbon bond formation (metathesis related reactions,[40,41] cyclopropanation,[42] radical reactions,[43-46]) decarbonylation,[47-51] and reactions of CO and CO_2.[6,52-54] In homogeneous hydrogenation alone, substrates include alkenes,[10-16] alkynes,[15,17] carbonyls[13,15,18-21], polynuclear heteroatomic compounds,[22,23] arenes,[24] nitro compounds,[25] and new developments have recently opened the door to tandem hydrogenation.[26-28] Ruthenium catalysts, as compared to complexes of rhodium, iridium and cobalt, are sometimes less effective for homogeneous hydrogenation of simple and functionalized olefins.[9,55] However, this mild reactivity can be useful for chemoselective hydrogenation of polyolefins.[8]

1.3. N-Heterocyclic Carbene Ligands (NHCs)

Pioneering work by Arduengo and co- workers led to the isolation of stable N-heterocyclic carbenes, of which the first example was 1,3-di-1-adamantyl-imidazol-2-ylidene.[56] NHC ligands have subsequently evoked considerable interest in coordination chemistry, organometallic chemistry and organic chemistry. Interest in these ligands derives from their high stability and donor ability, which was manifested in a strong activating effect at the metal center in many complexes.[57] The extraordinary stability of these singlet carbenes arises from their ground- state multiplicity, governed by electronic effects, in particular mesomeric and inductive effects associated with the nitrogen substituents on the carbene carbon. In these diaminocarbenes, electron deficiency is reduced by donation of two nitrogen lone pairs, while the carbene lone pair is inductively stabilized by the electronegative nitrogen atoms. Although structural, thermodynamic and magnetic criteria suggest electron delocalization in imidazol-2-ylidenes, the interaction of the carbene center with the π-donating, σ-attracting amino substituents is the major stabilizing factor, not aromaticity.[57]

N-heterocyclic carbenes are typical σ-donors and poor π-acceptors and thus can substitute classical two-electron donor ligands such as amines, ethers and phosphanes in metal coordination chemistry. NHC ligands have similar bonding properties to those of phosphines.[57-59] In NHC complexes, the metal-carbene bond lengths are longer than the classical Fischer and Schrock carbenes, which have some backbonding or double bond nature.[59] NHC ligands thus have greater freedom to rotate around the metal center, depending on the steric environment.

a b

Figure 1.2 **a**: IMes (1-3-bis-(2-4-6-trimethylphenyl)imidazol-2-ylidene), **b**: H_2IMes (1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene.

The application of N-heterocyclic carbene ligands in transition metal chemistry has led to significant advances in catalytic transformations ranging from olefin metathesis chemistry[40,60] to Pd-catalyzed coupling reactions,[61] hydrogenation,[10,11,62,63] isomerizaton,[10,11,16] polymerization,[64] hydroboration,[65] hydroformylation,[66,67] hydrosilylation[68-71] and allylic substitution.[72] Particularly notable is the high reactivity of NHC derivatives in the fields of metathesis and Pd-catalyzed coupling reactions. The discovery that replacement of a phosphine group of the well-known Grubbs catalyst, $RuCl_2(PCy_3)_2(CHPh)$, with IMes (1-3-bis-(2-4-6-trimethylphenyl)imidazol-2-ylidene)[40] or H_2IMes (1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene[36] (Figure 1.2) led to much more active "second generation" catalysts (Figure 1.3) opened a new era of the field of olefin metathesis. These NHC catalysts display superior activity in ROMP (ring opening metathesis polymerization) and ADMET (acyclic diene metathesis), and played a major role in opening up the fields of RCM (ring closing metathesis), CM (cross metathesis).[60] Very high rates have been reported for ROMP of low-strain and sterically hindered substrates in the presence of $RuCl_2(CHPh)(PCy_3)(IMes)$ (**4a**) and $RuCl_2(CHPh)(PCy_3)(H_2IMes)$ (**4b**).[73] Both **4a** and **4b** are capable of performing RCM of sterically demanding dienes to form tri-substituted olefins.[41,74] Incorporation of NHC ligands in ruthenium center has made ruthenium "the most versatile olefin metathesis metal", due to the combination of high activity with tolerance to functional groups.[59]

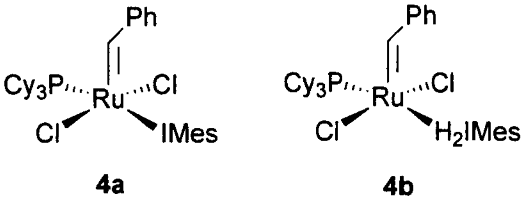
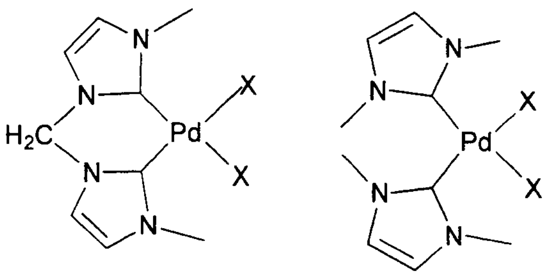


Figure 1.3 Second generation ruthenium catalysts for olefin metathesis.

NHC complexes are also superior to their phosphine analogue in many Pd-catalyzed coupling reactions. In the first application of NHC ligands in coupling reactions, Herrmann and co-workers explored the complexes shown in Figure 1.4 in Heck coupling.[75] The high activity obtained in these reactions is due to the ability of the NHC ligands to stabilize low-valent Pd species.[58] The phosphine-free NHC catalyst shown in Figure 1.5 (either the isolated complex or that generated in situ), represents the most active coupling agent now used in the Suzuki cross-coupling reaction.[76]



X = Cl, Br, I

Figure 1.4 Type of complexes used in Heck coupling.[75]

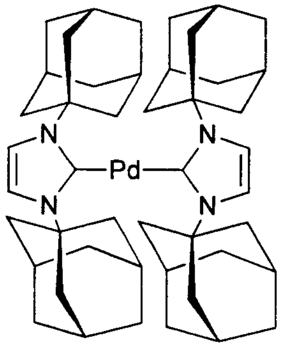


Figure 1.5 Phosphine-free NHC complexes used in Suzuki cross-coupling reaction. [76]

1.4. Scope of Thesis

This thesis describes explorations of the utility of NHC ligands in ruthenium-catalyzed hydrogenation chemistry. Experimental procedures are discussed in Chapter 2. Chapter 3 describes the synthesis, characterization and hydrogenation activity of new NHC complexes, RuHCl(CO)(NHC)(PPh_3) (**12a**: NHC = IMes; **12b**: NHC = H_2IMes). The enhanced hydrogenation activity of these complexes stems from the activating effect of the NHC ligand, in conjunction with the lability of the PPh_3 group. Chapter 4 discloses new synthetic routes that were developed for the known complexes RuHCl(CO)L(PCy_3)

(**9**: L = PCy_3; **13a**: L = IMes; **13b**: L = H_2IMes), and which overcome many of the drawbacks associated with the reported methods. Isolation of a new ruthenium bis(IMes) (**15a**) complex, which is formulated as $RuHCl(IMes)_2$, is described in Chapter 5. General conclusions and suggestions for future work are presented in Chapter 6.

1.5. References

(1) Gates, B. C. *Catalytic Chemistry*; John Wiley and Sons: New York, 1992.

(2) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; 3rd ed.; Wiley-Interscience: Toronto, 1994.

(3) Cornils, B.; Herrmann, W. A. *J. Catal.* **2003**, *216*, 23-31.

(4) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; 2nd ed.; Wiley-Interscience: Toronto, 1992.

(5) Blaser, H.-U.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M. *Adv. Synth. Catal.* **2003**, *345*, 103.

(6) James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 8, Chapter 51, and references therein.

(7) Evans, D.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *Nature* **1965**, *208*, 1203.

(8) Naota, T.; Takaya, H.; Murahashi, S.-I. *Chem. Rev.* **1998**, *98*, 2599.

(9) Chaloner, P. A.; Esteruelas, M. A.; Joo, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer: Boston, 1994.

(10) Dharmasena, U. L.; Foucault, H. M.; dos Santos, E. N.; Fogg, D. E.; Nolan, S. P. *Organometallics* **2005**, *24*, 1056.

(11) Lee, H. M.; Smith, D. C., Jr.; He, Z.; Stevens, E. D.; Yi, C. S.; Nolan, S. P. *Organometallics* **2001**, *20*, 794.

(12) Yi, C. S.; Lee, D. W. *Organometallics* **1999**, *18*, 5152.

(13) Noyori, R. *Adv. Synth. & Catal.* **2003**, *345*, 15.

(14) Dell'Amico, D. B.; Calderazzo, F.; Englert, U.; Labella, L.; Marchetti, F.; Specos, M. *Eru. J. Inorg. Chem.* **2004**, 3938.

(15) Frediani, P.; Bianchi, M.; Salvini, A.; Guarducci, R.; Carluccio, L. C.; Piacenti, F. *J. Organomet. Chem.* **1995**, *498*, 187.

(16) Dinger, M. B.; Mol, J. C. *Eur. J. Inorg. Chem.* **2003**, 2827.

(17) Cabeza, J. A. *Metal Clusters in Chemistry* **1999**, *2*, 715.

(18) Genet, J.-P. *Acc. Chem. Res.* **2003**, *36*, 908.

(19) Salvini, A.; Frediani, P.; Giannelli, C.; Rosi, L. *J. Organomet. Chem.* **2005**, *690*, 371.

(20) Drouin, S. D.; Amoroso, D.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2002**, 1042.

(21) Sanchez-Delgado, R. A.; Valencia, N.; Marquez-Silva, R.; Andriollo, A.; Medina, M. *Inorg. Chem.* **1986**, *25*, 1106.

(22) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *Organometallics* **1985**, *4*, 1743.

(23) Fish, R. H.; Thormodsen, A. D.; Cremer, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 5234.

(24) Halpern, J. *Pure Appl. Chem.* **1987**, *59*, 173.

(25) Knifton, J. F. *J. Org. Chem* **1975**, *40*, 519.

(26) Borsting, P.; Nielsen, P. *Chem. Comm.* **2002**, 2140.

(27) Louie, J.; Bielawski, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 11312.

(28) Drouin, S. D.; Zamanian, F.; Fogg, D. E. *Organometallics* **2001**, *20*, 5495.

(29) Murahashi, S.-I.; Naota, T. *Adv. Met.-Org. Chem* **1994**, *3*, 225.

(30) Murahashi, S.-I.; Naota, T.; Nakajima, N. *Tetrahedron Lett.* **1985**, *26*, 925.

(31) Murahashi, S.-I.; Naota, T. *Synthesis* **1993**, 433.

(32) Tanaka, M.; Kobayashi, T.; Sakakura, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 518.

(33) Ruppin, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1986**, *27*, 6323.

(34) Mitsudo, T.; Hori, Y.; Watanabe, Y. *J. Org. Chem* **1985**, *50*, 1566.

(35) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron, Lett* **1986**, *27*, 2125.

(36) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *J. Org. Chem* **1987**, *52*, 2230.

(37) Hori, Y.; Mitsudo, T.; Watanabe, Y. *Tetrahedron Lett* **1986**, *27*, 5389.

(38) Murahashi, S.-I.; Sasao, S.; Saito, E.; Naota, T. *J. Org. Chem* **1992**, *57*, 2521.

(39) Murahashi, S.-I.; Sasao, S.; Saito, E.; Naota, T. *Tetrahedron* **1993**, *49*, 8805.

(40) Huang, J.; Stevens, E. D.; Nolan, S. P.; Peterson, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674.

(41) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953.

(42) Demonceau, A.; Lemoine, C. A.; Noels, A. F.; Chizhevsky, I. T.; Sorokin, P. V. *Tetrahedron Lett* **1995**, *36*, 8419.

(43) Matsumoto, H.; Nikaido, T.; Nagai, Y. *Tetrahedron Lett* **1975**, 899.

(44) Matsumoto, H.; Nakano, T.; Takasu, K.; Nagai, Y. *J. Org. Chem* **1978**, *43*, 1734.

(45) Bland, W. J.; Davis, R.; Durrant, J. L. A. *J. Orgnomet. Chem.* **1985**, *280*, 397.

(46) Nakano, T.; Shimada, Y.; Sako, R.; Kayama, M.; Matsumoto, H.; Nagai, Y. *Chem. Lett.* **1982**, 1255.

(47) Drouin, S. D.; Monfette, S.; Amoroso, D.; Yap, G. P. A.; Fogg, D. E. In *Organometallics*, 2005, ASAP article.

(48) Gottschalk-Gaudig, T.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1999**, *38*, 5241.

(49) Marchenko, A. V.; Huffman, J. C.; Valerga, P.; Jimenez Tenorio, M.; Puerta, M. C.; Caulton, K. G. *Inorg. Chem.* **2001**, *40*, 6444.

(50) Barnard, C. F. J.; Daniels, J. A.; Jeffery, J.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1861.

(51) Krassowski, D. W.; Nelson, J. H.; Brower, K. R.; Hauenstein, D.; Jacobson, R. A. *Inorg. Chem.* **1988**, *27*, 4294.

(52) Laine, R. M. *J. Am. Chem. Soc* **1978**, *100*, 6451.

(53) King, A.; King, R. B.; Yang, D. B. *J. Chem. Soc., Chem. Comm* **1980**, 529.

(54) Bricker, J. C.; Nagel, C. C.; Bhattacharyya, A. A.; Shore, S. G. *J. Am. Chem. Soc* **1985**, *107*, 377.

(55) Halpern, J.; Harrod, J. F.; James, B. R. *J. Am. Chem. Soc* **1966**, *88*, 5150.

(56) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(57) Bourissou, D.; Guerret, O.; Gabbaie, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

(58) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247.

(59) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1291.

(60) (a) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2490. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 262. (c) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953.

(61) (a) Navarro, O.; Kelly, R. A., III ; Nolan S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194, and references therein. (b) Herrmann, W. A.; Öfele, K.; Preysing, D. V.; Schneider, S. K. *J. Organomet. Chem.* **2003**, *687*, 229, and references therein.

(62) Perry, M. C.; Cui, X. H.; Powell, M. T.; Hou, D. R.; Reibenspies, J. H.; Burgess, K. *J. Am. Chem. Soc.* **2003**, *125*, 113.

(63) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 48.

(64) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239.

(65) Grasa, G. A.; Moore, Z.; Martin, K. L.; Stevens, E. D.; Nolan, S. P.; Paquet, V.; Lebel, H. *J. Organomet. Chem.* **2002**, *658*, 126.

(66) van Rensburg, H.; Tooze Robert, P.; Foster Douglas, F.; Slawin Alexandra, M. Z. *Inorg. Chem.* **2004**, *43*, 2468.

(67) Chen, A. C.; Ren, L.; Decken, A.; Crudden, C. M. *Organometallics* **2000**, *19*, 3459.

(68) Mas-Marza, E.; Poyatos, M.; Sanau, M.; Peris, E. *Inorg. Chem.* **2004**, *43*, 2213.

(69) Kaur, H.; Zinn, F. K.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2004**, *23*, 1157.

(70) Duan, W.-L.; Shi, M.; Rong, G.-B. *Chem. Comm.* **2003**, 2916.

(71) Sprengers, J. W.; Mars, M. J.; Duin, M. A.; Cavell, K. J.; Elsevier, C. J. *J. Organomet. Chem.* **2003**, *679*, 149.

(72) Sato, Y.; Yoshino, T.; Mori, M. *Org. Lett.* **2003**, *5*, 31.

(73) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2903.

(74) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247.

(75) Herrmann, W. A.; Elison, M.; Fischer, J.; Kocher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371.

(76) Gstottmayr, C. W. K.; Bohm, V. P. W.; Herdtweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1363.

CHAPTER 2

Experimental

2.1. Materials

Solvents. Reagent grade tetrahydrofuran, hexanes, toluene, benzene, dichloromethane and diethyl ether were dried and degassed using an Anhydrous Engineering solvent purification system. Other solvents were refluxed over and distilled from an appropriate drying agent under nitrogen atmosphere: pentane over sodium; pyridine, n-propanol and 2- propanol over CaH_2; methanol and EtOH over Mg/I_2; acetone over Drierite (anhydrous $CaSO_4$). All solvents (with the exception of methanol and 2-propanol) were stored over Linde 4Å molecular sieves under an atmosphere of N_2. 2-Methoxyethanol (Alfa-Aesar) was used without further purification. All deuterated solvents ($CDCl_3$, CD_2Cl_2, and C_6D_6) were obtained from Cambridge Isotope Laboratories Ltd and stored under N_2. $CDCl_3$ was refluxed over and distilled from Drierite under an atmosphere of N_2. C_6D_6 was deoxygenated by consecutive freeze/pump/thaw cycles and stored over Linde 4Å molecular sieves. Ampoules of CD_2Cl_2 and toluene-d_8 were used as received.

Gases. Hydrogen (Praxair UHP Grade) was passed through a Deoxo cartridge and a Drierite column in series for procedures at 1 atm, or used without further purification for reactions above atmospheric pressure. Argon (Research Grade) was passed through a Drierite column.

Other Materials. The following materials were purchased from Aldrich Chemical Co. and used as received: potassium hydride (KH), potassium *tert*-butoxide, ammonium chloride, lithium *tert*-butoxide, triethylorthoformate, aqueous formaldehyde, 2,4,6-trimethylphenylamine, chloromethylethyl ether (95%) and glyoxal (40 wt%) solution in water. Hydrated $RuCl_3$ (38-43% Ru), $[RuCl_2(COD)]_x$, $RuCl_2(PCy_3)_2(CHPh)$ ("Grubbs' Catalyst") and triphenylphosphine were obtained from Strem Chemical Co. and used as received. Cyclooctene, cyclododecene and allylbenezene (Aldrich) were vacuum-distilled and stored under N_2. Triethylamine (Aldrich) was distilled from $CaSO_4$ and stored under N_2. Diethyl diallylmalonate (Aldrich, 98%) was deoxygenated by consecutive freeze/pump/thaw cycles and stored under N_2. Tricyclohexylphosphine (Aldrich) was stored under N_2 atmosphere. $RuCl_2(H_2IMes)(PCy_3)(CHPh)$ was generously supplied by Professor Steven Nolan of the University of New Orleans; 10-[(3-*tert*-butyl-dimethyl-silanyloxy)-propylidene]-6-(*tert*-butyl-diphenyl-silanyloxymethyl)-2,2-dimethyl-octahydro-naphtho[1,8a-d][1,3]dioxole[1] by Mr. Louis Morency of the Barriault research group at the University of Ottawa.

2.2. Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on Varian Gemini 200 (200 MHz for ^1H), or a Bruker Avance 300 (300 MHz for ^1H, 121 MHz ^{31}P, 75 MHz for ^{13}C) or a Bruker AMX-500 (500 MHz for ^1H, 202 MHz ^{31}P, 125 MHz for ^{13}C) FT-NMR spectrometer. For ^1H and ^{13}C NMR spectra, the residual proton and carbon signals of the deuterated solvents were used as internal standards. ^{31}P NMR spectra were referenced against internal or external PPh_3 (δ_P -5.06, C_6D_6; -5.46, $CDCl_3$; -5.64, CD_2Cl_2): shifts are reported relative to external 85% H_3PO_4. Downfield shifts are taken as positive for all nuclei. Variable-temperature and 2D NMR experiments were carried out on the Bruker Avance 300 or the Bruker Avance 500 instrument. IR spectra were measured on a Bomem MB100 IR spectrometer. Inert-atmosphere MALDI-MS analyses were performed using a Bruker OmniFlex MALDI-TOF mass spectrometer equipped with a nitrogen laser (337 nm), and interfaced to an MBraun glovebox. Data were collected in positive reflectron mode, with the accelerating voltage held at 20 kV. Matrix (anthracene) and analyte solutions were prepared in CH_2Cl_2 at concentrations of 20 mg/mL and 1 mg/mL, respectively. Samples were mixed in a matrix:analyte ratio of 20:1. Microanalyses were carried out by Guelph Chemical Laboratories Ltd., Guelph, Ontario. Single crystal X-ray diffraction studies were carried out by Professor Hilary A. Jenkin of Saint Mary's University, Halifax, Nova Scotia.

2.3. Laboratory Techniques

Unless otherwise stated, all reactions were carried out at room temperature (RT, ~22 °C), and all manipulations involving air-sensitive compounds were performed using standard Schlenk or drybox techniques. High-pressure reactions were conducted in machined steel autoclaves (Parr) equipped with glass liners and charged in an N_2-filled drybox.

2.4. Literature Preparations

The following precursors were prepared according to the literature methods: glyoxal-bis(2,4,6-trimethylphenyl)imine, IMes·HCl (1,3- bis-(2,4,6-

trimethylphenyl)imidazolium chloride), IMes (1-3-bis-(2-4-6-trimethylphenyl)imidazol-2-ylidene), N,N'-bis-(2-4-6-trimethylphenylamino)ethane dihydrochloride, H_2IMes·HCl (1,3-bis-(2,4,6-trimethylphenyl)imidazolinium chloride) and H_2IMes (1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene.[2] The following ruthenium complexes were prepared according to the reported methods: $RuCl_2(PPh_3)_3$ (**1**),[3,4] $RuHCl(PPh_3)_3$ (**2**),[5] $RuCl_2$(IMes)(PCy_3)(CHPh) (**4a**),[6] $RuCl_2$(IMes)$(py)_2$(CHPh) (**5a**),[7] $RuCl_2$(H_2IMes)$(py)_2$(CHPh) (**5b**),[8] $RuCl_2$(IMes)(3-Brpy)$_2$(CHPh) (**6a**),[9] $RuCl_2$(H_2IMes)(3-Brpy)$_2$(CHPh) (**6b**),[10] $RuHCl(CO)(PPh_3)_3$ (**7**)[11] and $RuHCl(H_2)(PCy_3)_2$ (**8**).[12]

2.5. New Complexes and New Synthetic Routes to Known Complexes

2.5.1. $RuHCl(CO)(PCy_3)_2$ (9)

In our hands, the literature procedure[13] gave a mixture of **9**, contaminated by $RuCl_2(CO)_2(PCy_3)_2$ (**10**) and $RuCl_2(CO)(PCy_3)_2$ (**11**), removal of which leads to low yields (see Chapter 4). We therefore undertook preparation of **9** by an alternative route. Solid PCy_3 (88 mg, 0.32 mmol) was added to a pale pink suspension of $RuHCl(CO)(PPh_3)_3$ (**7**; 100 mg, 0.11 mmol) in 80 mL benzene. The reaction mixture immediately turned pale yellow. Stirring was continued for 3 h at 40 °C, yielding a bright yellow, homogeneous solution. An aliquot removed at this time showed solely the $^{31}P\{^1H\}$ NMR singlet for the product. The solvent was concentrated under vacuum, treated with Et_2O, and chilled to –35 °C to precipitate bright yellow, microcrystalline **9**. The solid was filtered off, washed with Et_2O (3 × 3 mL), EtOH (3 × 3 mL), and dried under vacuum. Yield 67 mg (88%). NMR data were measured in C_6D_6, rather than

CD_2Cl_2 as reported[13] therefore, data agree with those reported with the exception of the minor variation of the location of the peaks. ^{1}H NMR (C_6D_6, 298K): δ 2.55 – 1.23 (m, 66H, Cy), -24.21 (t, $^2J_{HP}$ = 18.0 Hz, 1H, Ru*H*). ^{31}P{^{1}H} NMR (C_6D_6, 298K): δ 46.86 (s).

2.5.2. RuHCl(CO)(IMes)(PPh_3) (12a)[14]

A colorless solution of IMes (188 mg, 0.62 mmol) in 8 mL toluene was added to a pink suspension of RuHCl(CO)(PPh_3)$_3$ (**7**; 420 mg, 0.44 mmol) in 8 mL toluene, and the reaction was stirred at 22 °C. An orange, homogeneous solution was observed after one hour. After a further two hours, formation of **12a** was complete (^{31}P NMR). The solution was concentrated, treated with hexanes, and chilled to –35 °C to precipitate the orange-yellow, microcrystalline product. This was filtered off, washed with cold hexanes (3 × 5 mL) and dried under vacuum. Yield 0.275 g (85%). ^{1}H NMR (C_6D_6, 298K): δ 7.53-7.49 and 7.02 - 6.94 (m, 15H, Ph), 6.78 (s, 2H, IMes Ar, *m*-C*H*), 6.73 (s, 2H, IMes Ar, *m*-C*H*), 6.24 (s, 2H, IMes C*H*), 2.44 (s, 6H, Mes C*H*$_3$), 2.32 (s, 6H, Mes C*H*$_3$), 2.10 (s, 6H, Mes C*H*$_3$), –23.89 (d, $^2J_{PH}$ = 24.3 Hz, 1H, Ru*H*). ^{31}P{^{1}H} NMR (C_6D_6, 298K): δ 42.1 (s, PPh_3). ^{13}C{^{1}H} NMR (C_6D_6, 298K): δ 201.4 (d, $^2J_{PC}$ = 14.4 Hz, *C*O), 189.7 (d, $^2J_{PC}$ = 103.6 Hz, N*C*N,), 138.2 – 127.5 (s, *i-C*, *C*H of Mes and Ph *C*H), 122.1 (s, N*C*H*C*HN), 20.8 (s, Mes *C*H$_3$), 18.7 (s, Mes *C*H$_3$), 18.6 (s, Mes *C*H$_3$). IR (Nujol): ν(CO) 1913, ν(Ru-H) 1897 cm^{-1}. MALDI-MS, m/z: Found, 731.109; Calcd for $[M-H]^{+\cdot}$, 731.260. Anal. Calcd. for $C_{40}H_{40}ClN_2OPRu$: C, 65.61; H, 5.51; N, 3.82%. Found: C, 65.13; H, 5.21; N, 3.39%.

2.5.3. RuHCl(CO)(H_2IMes)(PPh_3) (12b)[14]

Low isolated yields were encountered in preparing free H_2IMes. Thus, a solution of H_2IMes was generated in situ by addition of lithium *tert*-butoxide (101 mg, 1.26 mmol) to a solution of H_2IMes·HCl (305 mg, 1.26 mmol) in 25 mL THF. The colorless solution was stirred at 22 °C for 2 h, then added dropwise to a stirred pink suspension of RuHCl(CO)$(PPh_3)_3$ (**7**; 600 mg, 0.629 mmol) in 30 mL THF. After 3 h at 22 °C, a bright yellow homogeneous solution had formed, and formation of **12b** was complete (^{31}P NMR). The solution was filtered through Celite, concentrated, treated with hexanes, and chilled to –35 °C to precipitate the bright yellow microcrystalline product. This was filtered off, washed with cold hexanes (3 × 5 mL), and dried under vacuum. Yield 376 mg (82%). ^{1}H NMR (C_6D_6, 298K): δ 7.38 – 7.45 and 6.88 – 6.93 (m, 15H, Ph), 6.80 (s, 2H, H_2IMes Ar, m-C*H*), 6.76 (s, 2H, H_2IMes Ar, m-C*H*), 3.25 (s, 4H, H_2IMes CH_2), 2.63 (s, 6H, Mes CH_3), 2.49 (s, 6H, Mes CH_3), 2.10 (s, 6H, Mes CH_3), –23.50 (d, $^2J_{PH}$ = 24.0 Hz, 1H, Ru*H*). ^{31}P{^{1}H} NMR (C_6D_6, 298K): δ 41.0 (s, PPh_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 298K): δ 216.0 (d, $^2J_{PC}$ = 95.8 Hz, N*C*N), 200.8 (d, $^2J_{PC}$ = 14.0 Hz, *C*O), 137.7 – 127.6 (s, *i-C*, *C*H of Mes and Ph *C*H), 51.3 (s, NCH_2CH_2N), 51.2 (s, NCH_2CH_2N), 21.2 (s, Mes CH_3), 18.9 (s, Mes CH_3). IR (Nujol): ν(CO) 1911, ν(Ru-H) 1865 cm^{-1}. MALDI-MS, m/z: Found, 734.059; Calcd for $[M]^{+\cdot}$, 734.284. Anal. Calcd. for $C_{40}H_{42}ClN_2OPRu$: C, 65.43; H, 5.76; N, 3.82%. Found: C, 65.40; H, 5.57; N, 3.84%.

2.5.4. RuHCl(CO)(IMes)(PCy_3) (13a)

We developed a new route to **13a**, as the literature method required prolonged heating and gives a low yield.[15] Solid PCy_3 (77 mg, 0.27 mmol) was added to a stirred solution of RuHCl(CO)(IMes)(PPh_3) (**13a**; 100 mg, 0.14 mmol) in 3 mL toluene. The yellow-orange solution underwent no apparent color change on heating for 2 h at 80 °C, but reaction was complete at this time (^{31}P NMR). Concentration, addition of EtOH, and chilling to –35 °C caused deposition of a yellow-orange microcrystalline product. This was filtered off, washed with cold EtOH (3 × 4 mL) and dried under vacuum. A second crop was isolated by repeating this procedure. Combined yield: 80 mg (78%). ^{1}H NMR data agree with values reported,[15] with the minor exception of the multiplicity of the aromatic protons of the mesityl group and $^{31}P\{^{1}H\}$ NMR data were measured in C_6D_6, rather than CD_2Cl_2 as reported.[15] ^{1}H NMR (C_6D_6, 298K): δ 6.83 (s 2H, IMes Ar, m-C*H*), 6.79 (s, 2H, IMes Ar, m-C*H*), 6.22 (s, 2H, IMes C*H*), 2.49 (s, 6H, Mes C*H₃*), 2.38 (s, 6H, Mes C*H₃*), 2.21-1.14 (m, 33 H, Cy), 2.12 (s, 6H, Mes C*H₃*), –24.82 (d, $^{2}J_{PH}$ = 21.0 Hz, 1H, Ru*H*). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 298K): δ 47.8 (s, PCy_3).

2.5.5. RuHCl(CO)(H_2IMes)(PCy_3) (13b)

While this work was in progress, a report appeared of the formation of **13b** by reaction of H_2IMes (generated in situ) with **9**.[16] Crystallization of the product from a yellow oil containing 75% **13b** was unsuccessful, however. Our synthesis involved addition of solid PCy_3 (92 mg, 0.327 mmol) to a stirred solution of RuHCl(CO)(H_2IMes)(PPh_3) (**12b**; 120 mg, 0.163 mmol) in 5 mL toluene. Reaction was complete after 2 h at 80 °C (^{31}P NMR). Concentration, addition of hexanes, and chilling to –35 °C precipitated orange-yellow, microcrystalline **13b**, which was filtered off, washed with cold hexanes (3 × 1 mL) and dried under vacuum. A second crop was isolated by repeating this procedure. Combined yield: 74 mg (60%). Yields are limited by the high solubility of the product in common organic solvents, including hexanes. NMR data were measured in C_6D_6, rather than CD_2Cl_2 as reported.[16] ^{1}H NMR (C_6D_6, 298K): δ 6.85 (s, 2H, H_2IMes Ar, *m*-C*H*), 6.81 (s, 2H, H_2IMes Ar, *m*-C*H*), 3.25 (s, 4H, H_2IMes CH_2), 2.67-2.55 (overlapping s, 12H, Mes CH_3), 2.22-2.20 and 1.89-1.09 (m, 33H, Cy), 2.13 (s, 6H, Mes CH_3), -24.90 (d, $^2J_{PH}$ = 21.3 Hz, 1H, Ru*H*). ^{31}P{^{1}H} NMR (C_6D_6, 298K): δ 46.8 (s, PCy_3). ^{13}C NMR (C_6D_6, 298K): δ 217.8 (d, $^2J_{PC}$ = 89.7 Hz, N*C*N), 202.1 (d, $^2J_{PC}$ = 13.5 Hz, *C*O), 137.5 - 129.5 (s, *i-C*, *C*H of Mes), 50.9 (overlapping s, N*C*H_2*C*H_2N), 34.4-26.9 (m, *C*H_2, *C*H of PCy_3), 21.1 (s, Mes *C*H_3), 18.9 (s, Mes *C*H_3). MALDI-MS, m/z: Found, 731.11; Calcd for $[M-H]^{+\cdot}$, 731.26. Anal. Calcd. for $C_{40}H_{60}ClN_2OPRu$: C, 63.87; H, 8.04; N, 3.72%. Found: C, 64.32; H, 8.30; N, 3.85%.

2.5.6. RuHCl(CO)(IMes)$_2$ (14)

Solid IMes (83 mg, 0.27 mmol) was added to a yellow solution of RuHCl(CO)(IMes)(PPh_3) (**12a**; 100 mg, 0.14 mmol) in 3 mL benzene, in a small Kontes flask. The yellow solution was heated to 70 °C in an oil bath. No color change was apparent over two days of reaction. Over this time, the progress of reaction was conveniently monitored by ^{31}P NMR analysis. Disappearance of the phosphine singlet for **12a** was observed, and appearance of singlet for free phosphine: no intermediates were noted. The reaction was complete after 39 h (^{31}P NMR and ^{1}H NMR). Concentration, addition of hexanes, and chilling to –35 °C precipitated a yellow-orange, microcrystalline product. The solid was filtered off, washed with hexanes (3 × 3 mL), and dried under vacuum. Yield 85 mg (81%). ^{1}H NMR (C_6D_6, 298K): δ 6.82 (s, 4H, IMes Ar, *m*-C*H*), 6.78 (s, 4H, IMes Ar, *m*-C*H*), 6.16 (s, 4H, IMes C*H*), 2.32 (s, 12H, Mes CH_3), 2.17 (s, 12H, Mes CH_3), 2.05 (s, 12H, Mes CH_3), -25.39 (s, 1H, Ru*H*). ^{13}C{^{1}H} NMR (C_6D_6, 298K): δ 202.1 (s, *C*O), 195.2 (s, N*C*N), 137.0 - 129.0 (s, *i-C*, *C*H of Mes), 121.6 (s, N*C*H*C*HN), 21.3 (s, Mes *C*H$_3$), 19.0 (s, Mes *C*H$_3$) 18.9 (s, Mes *C*H$_3$). IR (Nujol): ν(CO) 1883, ν(Ru-H) 1839 cm^{-1}. MALDI-MS, m/z: Found, 744.34; Calcd for $[M\text{-}H\text{-}CO]^{+\cdot}$, 745.07. Anal. Calcd. for $C_{43}H_{49}ClN_4ORu$: C, 66.69; H, 6.38; N, 7.23%. Found: C, 67.02; H, 6.79; N, 6.95%.

2.5.7. RuHCl(IMes)$_2$ (15a)

Attempts to synthesize a ruthenium-IMes complex in which one mesityl group was activated (**16**) by the reported procedure[17] afforded previously unreported **15a**. Solid IMes (54 mg, 0.18 mmol) was added to a purple suspension of RuHCl(PPh$_3$)$_3$ (**2**; 65 mg, 0.07 mmol) in 2 mL THF. As in the literature procedure, the suspension was stirred at 66 °C for 12 h in a Kontes flask under N_2. ^{31}P{^{1}H} NMR analysis revealed the AB pattern for **16** (δp, 59.7, 59.1; $^2J_{PP}$ = 15.3 Hz) as ca. 20% of the total integrated intensity, the balance being due to free PPh$_3$. The solution was filtered through Celite, concentrated, and treated with hexanes. The orange-brown precipitate was filtered off, washed with hexanes (3 × 2 mL), and dried under vacuum. It consisted of solely **15a**, as judged by NMR analysis. (The chemical shift of the hydride singlet for **15a** is identical to that for the doublet of doublets reported for **16**). Yield 37 mg (71%). ^{1}H NMR (C_6D_6, 298K): δ 6.83 and 6.81 (2 overlapping s, 8H, IMes Ar, *m*-C*H*), 6.23 (s, 4H, IMes C*H*), 2.32 (s, 12H, *p*-C*H*$_3$), 2.12-2.07 (br, 24H, *o*-C*H*$_3$), -28.04 (s, 1H, Ru*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 298K): δ 198.3 (s, N*C*N), 136.8, 129.1 (s, *i-C*, *C*H of Mes), 121.6 (s, NCH*C*HN), 30.2 (s, Mes *C*H$_3$), 21.3 (s, Mes *C*H$_3$). IR (Nujol): ν(Ru-H) 1992 cm^{-1}. MALDI-MS, m/z: Found, 744.58; Calcd for RuCl(IMes)(IMes-H)$^{+\cdot}$, 744.25. Identical results were obtained under argon atmosphere.

2.6. Hydrogenation: General Procedures

2.6.1. Hydrogenation of Cyclododecene

A representative procedure is given for hydrogenation of cyclododecene. In a glove box, a Parr autoclave was charged with cyclododecene (333 mg, 2.00 mmol), toluene (15 mL) and RuHCl(CO)(H_2IMes)(PPh_3) (**12b**; 0.73 mg, 1.00 μmol). The autoclave was removed from the drybox, purged with H_2 (while stirring), pressurized to 140 psi, and heated to 80 °C. The sample reached thermal equilibrium in seven minutes, at which point the sample designated as t_o was removed. Subsequent samples were taken at 30 min, 1 h and 2 h. Product yields were determined by GC-FID analysis and integrated against tetralin as an internal standard. The average of two trials is reported.

2.6.2. Hydrogenation of a Tri–Substituted Olefine (20)[1]

A solution of $RuCl_2$(H_2IMes)$(py)_2$(CHPh)((**5b**; 1 mg, 1.375 μmol) in C_6H_6 (1 mL) was added to 10-[3-*tert*-butyl-dimethyl-silanyloxy)-propylidene]-6-(*tert*-butyl-diphenyl-silanyloxymethyl)-2,2-dimethyl-octahydro-naphtho[1,8a-d][1,3]dioxole (**20**) (14 mg, 20 μmol), diluted with MeOH to 2 mL and NEt_3 (9.1 μL, 65 μmol) was added. The solution was transferred to a glass-lined autoclave, then purged with H_2, pressurized to 1350 psi and stirred at 80 °C for 5 days. The solvent was then removed, and conversions were determined by ^{1}H NMR ($CDCl_3$), based on the integration of aliphatic peak at δ_H 4.06 (t, 1H) relative to the aliphatic peak at δ_H 4.20 - 4.19 (m, 1H) (Figure 2.1).

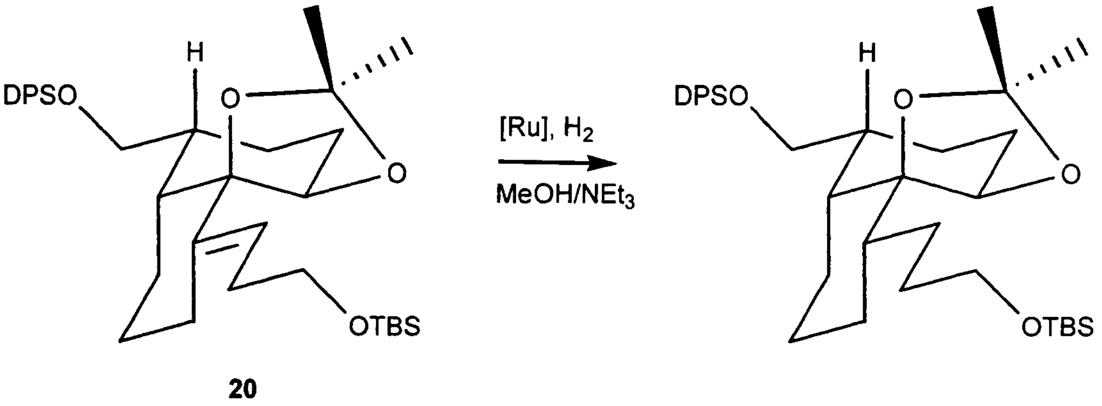


Figure 2.1 Hydrogenation of **20** by Ru benzylidene (**5b**) in the presence of MeOH and NEt_3

2.7. Tandem Metathesis-Hydrogenation: General Procedures

2.7.1. Tandem ROMP- Hydrogenation

A solution of $RuCl_2(IMes)(PCy_3)(CHPh)$ (**4a**; 2.0 mg, 2.4 μmol) in CH_2Cl_2 (2 mL) was stirred rapidly as cyclooctene (64 μL, 490 μmol) ([S]:[C] = 204) was added. Stirring was continued at 22 °C for 10 minutes, until ROMP was complete. The solution was then diluted to 10 mL (CH_2Cl_2, 6 mL; MeOH, 2 mL) and NEt_3 (1.6 μL, 12 μmol) was added. Further reaction was then carried out as in Section 2.6.2, but at 60 °C and 1 atm. Conversions were determined by ^{1}H NMR ($CDCl_3$), based on the integration of the olefinic signals (δ 5.31, m, 2H) relative to the aliphatic signals (δ_H 2.03 and 1.33, m, 18H). The average of three trials (±3%) is reported.

2.7.2. Tandem RCM-Hydrogenation

A solution of $RuCl_2(H_2IMes)(py)_2(CHPh)$ (**5b**; 3.6 mg, 5 μmol) in C_6D_6 (1 mL) was added to a stirring solution of diethyl diallylmalonate (DDM) (24 μL, 100 μmol) ([S]:[C] = 20). RCM was complete after 1h, after which the solution was diluted with MeOH to 2 mL and NEt_3 (3.3 μL, 25 μmol) was added. Further reaction was then carried out as in Section 2.6.2, but at 22 °C and 1 atm. Conversions were determined at 20 minutes and 1 h, by ^1H NMR (C_6D_6), based on the integration of aliphatic peak at δ_H 3.12 (s, 4H), relative to the aliphatic peaks at δ_H 2.31 (t, 4H). The average of three trials (±3%) is reported.

2.8. References

(1) Morency, L.; Barriault, L. *J. Org. Chem.* **2005**, accepted.

(2) Arduengo, A. J.; Krafczyk, R. W. J.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523.

(3) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. **1970**, *12*, 237.

(4) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 237.

(5) Amoroso, D.; Snelgrove, J. L.; Conrad, J. C.; Drouin, S. D.; Yap, G. P. A.; Fogg, D. E. *Adv. Synth. Catal.* **2002**, *344*, 757.

(6) Huang, J.; Stevens, E. D.; Nolan, S. P.; Peterson, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674.

(7) Conrad, J. C.; Parnas, H. H.; Snelgrove, J. L.; Fogg, D. E. *J. Am. Chem. Soc.* **2005**, *127*, 11882.

(8) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314.

(9) Complex **6a** was prepared in a similar procedure to complex **5a**.

(10) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 4035.

(11) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 48.

(12) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867.

(13) Yi, C. S.; Lee, D. W. *Organometallics* **1999**, *18*, 5152.

(14) Dharmasena, U. L.; Foucault, H. M.; dos Santos, E. N.; Fogg, D. E.; Nolan, S. P. *Organometallics* **2005**, *24*, 1056.

(15) Lee, H. M.; Smith, D. C., Jr.; He, Z.; Stevens, E. D.; Yi, C. S.; Nolan, S. P. *Organometallics* **2001**, *20*, 794.

(16) Dinger, M. B.; Mol, J. C. *Eur. J. Inorg. Chem.* **2003**, 2827.

(17) Abdur-Rashid, K.; Fedorkiw, T.; Lough, A. J.; Morris, R. H. *Organometallics* **2004**, *23*, 86.

CHAPTER 3*

Synthesis and Catalytic Activity of Ruthenium Hydridocarbonyl Complexes containing an N-heterocyclic carbene and a labile phosphine donor

3.1. Introduction

Hydridocarbonyl complexes of ruthenium (II) are of interest for their ability to promote a wide range of catalytic processes, and arylphosphine complexes such as $RuHCl(CO)(PPh_3)_3$ (**7**) have a long history of use.[1] Our interest in complexes containing strongly electron-donating ligands such as alkylphosphine and N-heterocyclic carbene (NHC) groups stems from the potential for enhanced olefin binding and activation.[2] Recent studies involving the well-known hydridocarbonyl catalyst $RuHCl(CO)(PCy_3)_2$ (**9**), reveal high activity in hydrogenation of olefinic[3] and carbonyl[4] functionalities, as well as in isomerization,[3,5-7] hydrovinylation,[8-11] dehydrosilylation,[12] and silylative coupling of olefins,[13-18] and intermolecular coupling of alkenes and amines.[19]

N-heterocyclic carbene (NHC) ligands have emerged as an exceptionally versatile class of ligands for transition metal catalysis. Owing to their enhanced sigma-donating ability and thermal stability,[20,21] NHC complexes display higher reactivity than the corresponding phosphine complexes in many Ru-catalyzed olefin metathesis[22-26] and Pd-catalyzed coupling reactions.[27] They can also offer advantages over the important but thermally sensitive Crabtree catalyst, $[(Ir(cod)(PCy_3)(py)]PF_6$, in H_2-hydrogenation of olefins.[28,29] While good to excellent activity, typically at high catalyst loadings, has been reported in transfer hydrogenation via NHC complexes of iridium,[29,30] nickel,[31] and ruthenium,[32] deployment of this ligand class in Ru-

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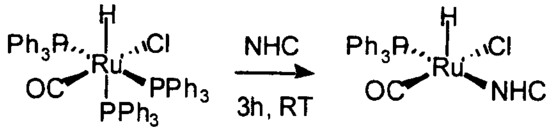
catalysed H_2-hydrogenation has so far met with less spectacular success. Yi, Nolan and co-workers[6] recently pointed out that RuHCl(CO)(IMes)(PCy_3) (**13a**) (IMes = (1-3-bis-(2-4-6-trimethylphenyl)imidazol-2-ylidene) is considerably less active for olefin hydrogenation than the known, highly active[3,33-35] catalyst RuHCl(CO)(PCy_3)$_2$ (**9**) at room temperature, and is only marginally more active than **9** at 100 °C. This finding was surprising, as it might be anticipated that the enhanced donor ability and two-dimensional steric demand of the IMes ligand should promote olefin binding and activation via **13a**, relative to **9**. (It may be noted, however, that oxidative addition of C-H and H-H bonds is not necessarily promoted by Ru-NHC derivatives, relative to Ru-PPh_3 analogues).[36] Given the dissociative pathway established for hydrogenation via **9**,[3,33] we speculated that the poor performance of **13a** might reflect a decrease in the lability of PCy_3 trans to an NHC group, vs. a second PCy_3 ligand. Such a decrease is noted in olefin metathesis via $RuCl_2$(L)(PCy_3)(CHPh), for L = NHC vs. PCy_3.[37] We thus considered the possibility that incorporating a labile donor ligand, in addition to an NHC ligand, might increase the hydrogenation activity of these complexes. This chapter describes the synthesis, characterization, and hydrogenation activity of new ruthenium hydride complexes of the type RuHCl(CO)(NHC)(PPh_3).

3.2.1. Routes to RuHCl(CO)(NHC)(PPh_3) (12a: NHC = IMes; 12b: NHC = H_2IMes)

Complexes **12a** and **12b** were prepared by the room-temperature reaction of RuHCl(CO)(PPh_3)$_3$ (**7**) with one equivalent of the appropriate NHC ligand (Figure 3.1). Thus, treatment of a suspension of RuHCl(CO)(PPh_3)$_3$ (**7**) in toluene with a solution of IMes in toluene effected quantitative conversion to **12a** over 3 h at room temperature, as judged by in situ ^{31}P NMR analysis. The orange-yellow microcrystalline product was isolated in 85% yield. Attempts to isolate free H$_2$IMes resulted in low yields. As we suspected that the problem might arise from the lower stability of the free carbene, we modified the protocol to generate the carbene in situ. Addition of base to the H$_2$IMes·HCl salt in THF, followed by addition of **7**, resulted in complete conversion to **12b** within 3 hours at room temperature. The product was isolated in 82% yield. The identity of **12a** and **12b** is supported by MALDI-MS, NMR and elemental analysis, and X-ray crystallography in the case of **12a**.



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12a, NHC = IMes
12b, NHC = H$_2$IMes

Figure 3.1 Proposed synthesis of target complexes.

Retention of a single phosphine ligand in **12a** and **12b** is confirmed by NMR analysis. Key spectroscopic data are summarized in Table 3.1. Both complexes give rise to a singlet in the ^{31}P{^{1}H} NMR spectrum, and the doublet multiplicity of the hydride signal, as well as the carbonyl and carbene carbon signals, confirms the presence of a single ^{31}P nucleus. The upfield location of the hydride doublet is also a valuable clue, indicating that the hydride ligand is trans to a vacant site. Other ^{1}H NMR signals for the IMes ligand show the expected multiplicities and integration values, although rotation of the IMes group at room temperature causes equilibration of the NHC resonances, which requires cooling to –63 °C to resolve. At this temperature, two singlets are observed for the olefinic protons of the carbene ring, four singlets for the aromatic protons of the mesityl group and six singlets for the methyl groups of the mesityl ring. The presence of the hydride and carbonyl entities is also evident from the infrared spectra, in which two bands are observed near 1900 cm^{-1}.

Table 3.1 Key spectroscopic parameters for **12a, 12b** and **14.**[a]

Complex	δ_P	δ_H ($^2J_{PH}$, Hz)	δ_{CO} ($^2J_{PC}$, Hz)	ν_{CO}, $\nu_{Ru\text{-}H}$
RuHCl(CO)(IMes)(PPh$_3$), **12a**	42.1 (s)	-23.9 (d, 24)	201.4 (d, 14)	1913, 1897
RuHCl(CO)(H$_2$IMes)(PPh$_3$), **12b**	41.0 (s)	-24.0 (d, 24)	200.8 (d, 14)[b]	1911, 1865
RuHCl(CO)(IMes)$_2$, **14**	-	-25.4 (s)	202.1	1883, 1839

[a] NMR spectra measured in C_6D_6, except where noted; IR spectra as Nujol mulls.
[b] Spectrum measured in $CDCl_3$ solvent, in order to improve solubility.

3.2.2. Preparation of RuHCl(CO)(IMes)$_2$ (14)

The PPh$_3$ ligand in **12a** can be displaced by a second NHC group, as we discovered on crystallization of RuHCl(CO)(IMes)$_2$ **(14)**. This complex was unexpectedly obtained during synthesis of **12a** according to our standard protocol (see above), on allowing the crude reaction mixture to crystallize over several weeks. Complex **14** was subsequently synthesized deliberately, in quantitative yields, by reaction of **12a** with two equivalents of IMes in toluene (Figure 3.2). Reaction was rather slow, even at 70 °C, requiring 39 hours to go to completion, as judged by in situ ^{31}P NMR analysis. The identity of the product is confirmed by NMR, IR, MALDI-MS and elemental analysis, as well as X-ray crystallography. The spectroscopic evidence includes observation of singlets for the hydride, carbonyl, and IMes carbene nuclei, confirming loss of the phosphine ligand, and an integration ratio of 1:4 for the hydride singlet, relative to that for the IMes "olefinic" protons, or 1:8, relative to the mesitylene aromatic CH group, confirming the presence of two IMes ligands (Table 3.1). Interestingly, no activation of the NHC ligand is observed under these rather forcing conditions, despite precedents for such behavior in other ruthenium-NHC complexes.[38,39]

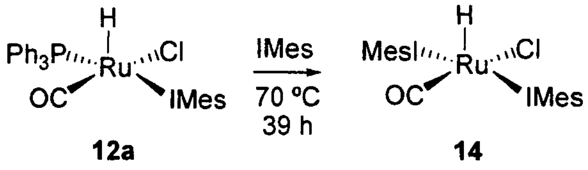


Figure 3.2 Synthesis of **14** by phosphine exchange of **12a**.

A number of ruthenium bis(NHC) complexes have previously been reported,[40-42] among them several bis(IMes) complexes. Whittlesey and co-workers reported *trans*-dihydro aqua and ethanol complexes[43] and hydrogen sulfide dihydride derivatives,[44] while our own group reported formation of $RuCl_2(IMes)_2(CHCH{=}CMe_2)$ and $RuCl_2(IMes)_2(CHPh)$ on reaction of Ru-alkylidene precursors with excess IMes.[45] A $RuH_2(H_2)_2(IMes)_2$ complex was also reported by Giunta et al.[46] Of interest is the fact that all of the bis(IMes) complexes containing hydride or dihydride ligands, including **14**, were obtained under rather forcing conditions, while the bis(IMes) complexes of ruthenium benzylidene and vinylidene were accessible at room temperature.

3.2.3. Molecular Structures of $RuHCl(CO)(IMes)(PPh_3)$ (12a) and $RuHCl(CO)(IMes)_2$ (14)

X-ray quality crystals of **12a** and **14** were obtained by slow evaporation of a benzene solution. ORTEP representations are shown in Figures 3.3 and 3.4, with relevant bond lengths and angles in Table 3.2. In both cases, the geometry about ruthenium is a slightly distorted square pyramid, presuming the presence of the hydride ligand, which is not observed. In both complexes, Cl/CO disorder renders the Ru-CO and C-O bond distances meaningless. The Ru-P bond distance in **12a** (2.3557(8) Å), however, is shorter than the corresponding values in **7** (2.371(8), 2.411(9) Å).[47] Yi, Nolan and co-workers reported a similar effect in comparing the Ru-P bond distances in **13a** vs. **9**.[6] This finding lends support to the suggestion that the NHC ligand exerts some attraction on a trans phosphine group, presumably reflecting some degree of π-back bonding.

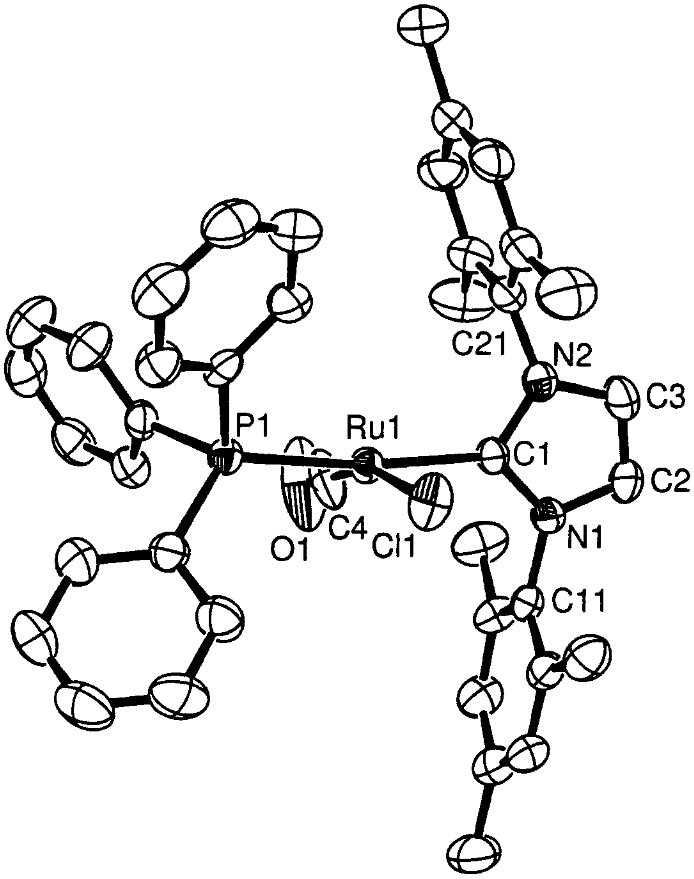


Figure 3.3 ORTEP diagram for RuHCl(CO)(IMes)(PPh_3) (**12a**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

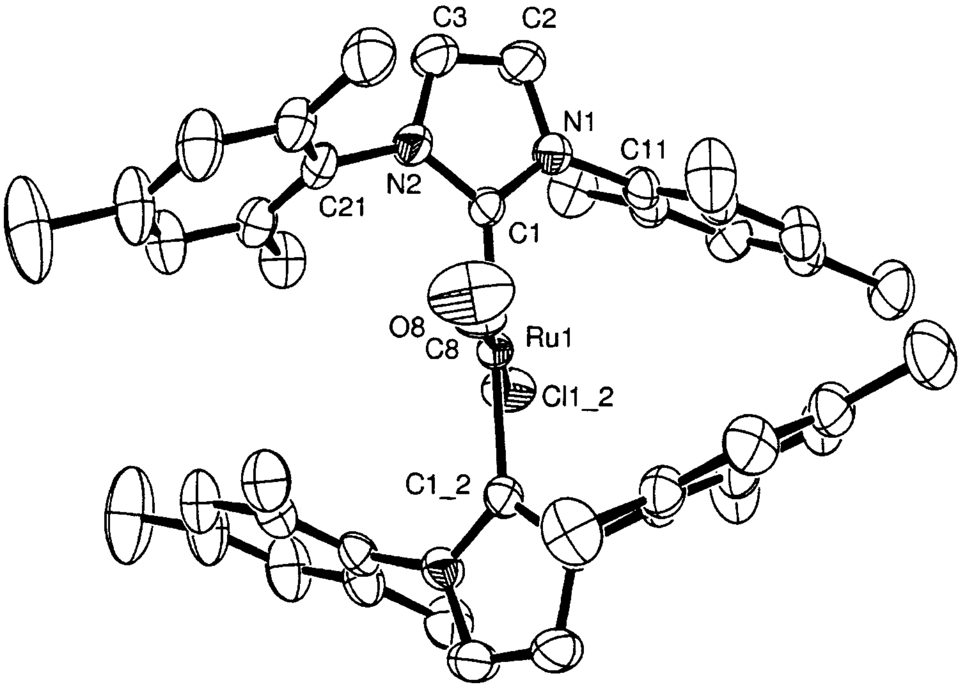


Figure 3.4 ORTEP diagram for RuHCl(CO)(IMes)$_2$ (**14**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 3.2 Selected bond lengths (Å) and Angles (deg) for RuHCl(CO)(IMes)(PPh$_3$) (**12a**) and RuHCl(CO)(IMes)$_2$ (**14**)

	12a	**14**
Ru 1-C 1	2.079(3)	2.077(3)
Ru 1-P 1	2.3557(8)	-
Ru 1-C 1_2	-	2.074(3)
P 1-Ru 1-C 1	170.75(8)	-
C 1_2-Ru 1-C 1	-	179.78(13)
Cl 1-Ru 1-C 1	86.65(8)	-
Cl 1_2-Ru 1-C 1	-	90.14(10)
Cl 1-Ru 1-P 1	89.79(3)	-
Cl 1_2-Ru 1-C 1_2	-	90.38(7)
C 4-Ru 1-C 1	92.5(3)	-
C 8-Ru 1-C 1	-	90.4(3)
C 4-Ru 1-P 1	93.8(3)	-
C 8-Ru 1- C 1_2	-	89.62(7)

3.3. Catalytic Activities of Complexes, 9, 12a, 12b and 13a.

Comparative studies of catalytic activity initially focused on hydrogenation using $RuHCl(CO)(PCy_3)_2$ (**9**), $RuHCl(CO)(NHC)(PPh_3)$ (**12a**, NHC = IMes; **12b**, NHC = H_2IMes), and $RuHCl(CO)(IMes)(PCy_3)$ (**13a**). In addition, some activity for polymerization and isomerization of olefins emerged in the course of these experiments. As the high hydrogenation activity of **9** is well established,[3,33-35] we chose as our targets for comparative catalytic studies internal, unactivated olefins, a class of substrates for which few catalysts are effective.[48] Hydrogenation was carried out at low catalyst loadings (0.05 mol% Ru), to which the Ir systems are not generally amenable.

Unexpectedly, in light of the earlier findings, reduction of cyclooctene (COE) suggested the trend **12a** ~ **13a** > **9** (Table 3.3), with the NHC catalysts effecting complete consumption of substrate within 10 minutes at 50 psi and 80 °C (GC analysis). The integrated intensity of the cyclooctane signal is low relative to internal standard, however, and closer examination revealed that both **12a** and **13a** trigger competing polymerization of cyclooctene. Nearly 20% polymer was isolated by removal of solvent, unreacted COE, and cyclooctane product under vacuum. While the polymeric material proved too insoluble for NMR or GPC analysis, IR characterization indicated complete hydrogenation of the unsaturated polymer (a challenging, sterically hindered substrate)[49] by catalyst **12a**. Ruthenium hydrides have previously been found to be effective ROMP catalysts, though typically for highly strained, bicyclic monomers.[50,51] The implied balance between the hydrogenation and ROMP activities of **12** suggests that these catalysts may have broadest applicability in hydrogenation of low-strain cycloolefins or acyclic olefins. Of particular interest in the former category are macrocyclic rings, with potential relevance to the synthesis of saturated odiferous or organoleptic compounds[52] by tandem RCM-hydrogenation.[53,54] We thus undertook reduction of cyclododecene (CDE), as a representative substrate with a slightly lower degree of ring strain than COE.[55] CDE and other macrocyclic substrates pose a twofold challenge for hydrogenation: not only is reduction more difficult with increasing ring size, but macrocycles frequently exist as mixtures of the cis and the sterically encumbered trans internal olefins. The results are summarized in Table 3.3.

Table 3.3 Hydrogenation of selected internal olefins[a]

catalyst	substrate	TOF[b]	time (min)	conversion[c]
9	cyclooctene (COE)	138	10	69[d]
13a		164[e]	10	100
12a		164[e]	10	100
9	cyclododecene (CDE)	740	60	33
13a		235	60	8
12a		3,228	60	96[d]
12b		3,280	60	97[d]

[a] Conditions: 0.05 mol % Ru, 50 psi H_2 (COE); 140 psi of H_2 (CDE), 80 °C; toluene. [b] Turnover frequency calculated at 10 min (COE), 30 min (CDE). Values are in units of min^{-1} for COE and h^{-1} for (CDE). [c] Conversions determined by GC; ±3% in replicate runs. Thermal equilibration period was 7 min for 80 °C (t_o). [d] The conversion was 100% within 30 min (COE) and 2 h (CDE). [e] TOF corrected for ROMP contribution (18%).

The resistance of *trans*-CDE to hydrogenation is illustrated by the product distributions shown in Figure 3.5: for catalysts **9** or **13a**, the proportion of the trans isomer at 1 h is little changed from that in the starting material. Catalysts **12a** and **12b**, in contrast, efficiently reduce both cis and trans olefins. These catalysts effect conversion to cyclododecane (CDA) over ten times faster than **13a**, and three to four times faster than **9**. Essentially identical activity is found for the IMes (**12a**) and H_2IMes (**12b**) catalysts; no polymerization is observed in either case.

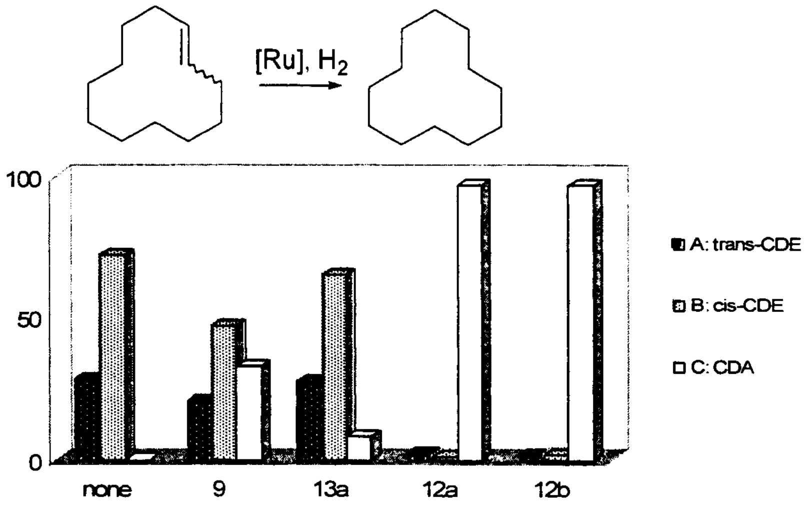


Figure 3.5 Product distribution at 1 h for reduction of cyclododecene (for conditions see Table 3.3).

Electron-rich Ru alkylidene complexes containing NHC ligands frequently promote olefin isomerization, and metal hydrides are proposed as the catalytically-relevant species.[56] Such behavior has important implications for hydrogenation of *terminal* olefins by catalysts of type **12a** and **12b**, if conversion to internal olefins occurs over the timescale of hydrogenation. In order to quantify the reduction, vs. isomerization, capabilities of the well-defined hydride complexes **9**,[57] **13a**, **12a**, and **12b**, allylbenzene was chosen as a probe substrate. Owing to the high stability of the di-substituted, isomerized products (Figure 3.6), this terminal olefin affords a sensitive probe of isomerization capabilities. Catalyst **9** effects ca. 70% reduction of allylbenzene within 30 min under 50 psi H_2 at 80 °C, accompanied by 9% isomerization (Table 3.4). Comparable isomerization activity is found for **13a**, though the hydrogenation efficiency is ~20% lower. While conversion profiles indicate that both catalysts reduce cis-propenylbenzene (Figure 3.6) at appreciable rates, neither is effective for reduction of the trans olefin under these conditions. Indeed, the olefin remaining after 2 h is almost entirely trans-propenylbenzene, which is reduced very slowly even on raising the hydrogen pressure to 140 psi. Consistent with the earlier report on reduction of 1-hexene,[6] NHC catalyst **13a** outperforms **9** under the more forcing conditions. More surprisingly, use of **12a** offers no improvement. The higher hydrogenation activity of **12a** is clearly offset, for this α-olefin substrate, by its high isomerization activity: at "t_o", nearly 20% internal olefin is already present, and this rises to 40% within 30 min *under 50 psi H_2*. Reduction of the trans olefin is effected, although slowly, at 50 psi; it can be efficiently reduced at 140 psi. Interestingly, catalyst **12b** proves significantly more active for isomerization, even at 140 psi, and is thus less effective for reduction of allylbenzene.

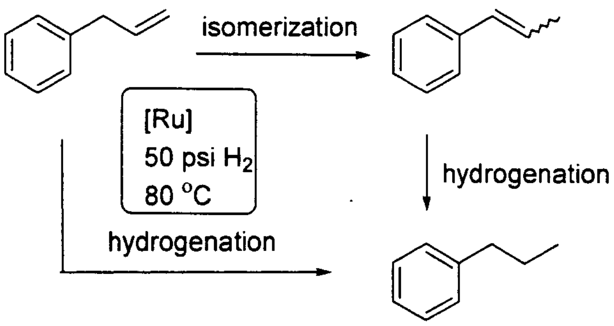


Figure 3.6 Reaction of allylbenzene with Ru-hydride complexes under H_2 atmosphere.

Table 3.4 Reduction vs. isomerization of allylbenzene.[a]

Catalyst	pH_2 (psi)	% propyl-benzene	PhCH=CHMe (%) cis	trans	TOF (h^{-1})[b]
9	50	72	0	9	2880 (360)
	140	86	0	9	3440 (360)
13a	50	51	1	6	2040 (280)
	140	94	0	6	3760 (240)
12a	50	60	0	40	2400 (1600)
	140	89[c]	0	11	3560 (440)
12b	140	49	10	37	1960 (1880)

[a] Conditions: 0.05 mol % Ru, 2.00 mmol of allylbenzene in toluene, 80 °C; 30 min reaction time following "t_o". Conversions were determined by GC; ±3% in replicate runs. [b]Turnover frequency for hydrogenation; TOF values for isomerization are given in parentheses. [c] 100% at 2 h.

3.4. Conclusions

The work described in this chapter expands the synthesis and hydrogenation activity of novel Ru-NHC complexes to include five-coordinate ruthenium hydridocarbonyl complexes containing a labile PPh_3 ligand. The new complexes are effective catalysts for the challenging problem of hydrogenating sterically hindered trans-internal olefins, although their reactivity was less than initially expected. (As this point emerges even more clearly in the synthetic chemistry presented in the next chapter, discussion will be deferred until then). Both hazards and opportunities can be inferred from the activity of the new complexes for isomerization of terminal olefins, and polymerization of strained cycloolefins. The poorer performance of PCy_3 analogue **13a** is notable: the presence of a labile phosphine donor in the precatalyst is clearly fundamental to the activity of the NHC complexes, consistent with a dissociative mechanism[3] involving phosphine loss prior to olefin binding. Indeed, this synergy between an activating N-heterocyclic carbene (NHC) ligand and a labile PPh_3 donor is likewise responsible for the exceptionally high metathesis activity of "mixed ligand" catalysts $RuCl_2(NHC)(PPh_3)(CHR)$.[22,45] A clear parallel thus exists between the requirements for maximum activity in metathesis, isomerization, and hydrogenation catalysis.

3.5. References.

(1) Naota, T.; Takaya, H.; Murahashi, S.-I. *Chem. Rev.* **1998**, *98*, 2599, and references therein.

(2) Valentine, D. H.; Hillhouse, J. H. *Synthesis* **2003**, 2437.

(3) Yi, C. S.; Lee, D. W. *Organometallics* **1999**, *18*, 5152.

(4) Sanchez-Delgado, R. A.; Valencia, N.; Marquez-Silva, R.; Andriollo, A.; Medina, M. *Inorg. Chem.* **1986**, *25*, 1106.

(5) Dinger, M. B.; Mol, J. C. *Eur. J. Inorg. Chem.* **2003**, 2827.

(6) Lee, H. M.; Smith, D. C., Jr.; He, Z.; Stevens, E. D.; Yi, C. S.; Nolan, S. P. *Organometallics* **2001**, *20*, 794.

(7) Martin, P.; McManus, N. T.; Rempel, G. L. *J. Mol. Catal. A* **1997**, *126*, 115.

(8) He, Z.; Yi, C. S.; Donaldson, W. A. *Synlett* **2004**, 1312.

(9) He, Z.; Yi, C. S.; Donaldson, W. A. *Org. Lett.* **2003**, *5*, 1567.

(10) Yi, C. S.; He, Z.; Lee, D. W. *Organometallics* **2001**, *20*, 802.

(11) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043.

(12) Yi, C. S.; He, Z.; Lee, D. W.; Rheingold, A. L.; Lam, K.-C. *Organometallics* **2000**, *19*, 2036.

(13) Marciniec, B.; Chadyniak, D.; Krompiec, S. *Tetrahedron Lett.* **2004**, *45*, 4065.

(14) Jankowska, M.; Marciniec, B.; Pietraszuk, C.; Cytarska, J.; Zaidlewicz, M. *Tetrahedron Lett.* **2004**, *45*, 6615.

(15) Itami, Y.; Marciniec, B.; Kubicki, M. *Chem. Eur. J.* **2004**, *10*, 1239.

(16) Marciniec, B.; Majchrzak, M. *J. Organomet. Chem.* **2003**, *686*, 228.

(17) Itami, Y.; Marciniec, B.; Majchrzak, M.; Kubicki, M. *Organometallics* **2003**, *22*, 1835.

(18) Itami, Y.; Marciniec, B.; Kubicki, M. *Organometallics* **2003**, *22*, 3717.

(19) Yi, C. S.; Yun, S. Y.; Guzei, I. A. *Organometallics* **2004**, *23*, 5392.

(20) Arduengo, A. J.; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

(21) That this stability is not invariable is illustrated by a recent overview of reactions involving activation of NHC ligands. See: Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247.

(22) (a) Huang, J.; Stevens, E. D.; Nolan, S. P.; Peterson, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674. (b) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 5375.

(23) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.*, **1999**, *40*, 2247.

(24) (a) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1998**, 37, 2490. (b) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 262.

(25) Grela, K.; Harutyunyan, S.; Michrowska, A. In *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 4038.

(26) Wakamatsu, H.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 2403.

(27) (a) Navarro, O.; Kelly, R. A., III ; Nolan S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194, and references therein. (b) Herrmann, W. A.; Öfele, K.; Preysing, D. V.; Schneider, S. K. *J. Organomet. Chem.* **2003**, *687*, 229, and references therein.

(28) (a) Lee, H. M.; Jiang, T.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 1255. (b) Vazques-Serrano, L. D.; Owens, B. T.; Buriak, J. M. *Chem. Commun.* **2002**, 2528.

(29) Perry, M. C.; Cui, X.; Powell, M. T.; Hou, D.-R.; Reibenspies, J. H.; Burgess, K. *J. Am. Chem. Soc.* **2003**, *125*, 113.

(30) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 3596.

(31) Kuhl, S.; Schneider, R.; Fort, Y. *Organometallics* **2003**, *22*, 4184.

(32) Edwards, M. G.; Jazzar, R. F. R.; Paine, B. M.; Shermer, D. J.; Whittlesey, M. K.; Williams, J. M. J.; Edney, D. D. *Chem. Commun.*. **2004**, 90.

(33) Yi, C. S.; Lee, D. W.; He, Z.; Rheingold, A. L.; Lam, K.-C.; Concolino, T. E. *Organometallics* **2000**, *19*, 2909.

(34) (a) McManus, N. T.; Rempel, G. L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1995**, *C35*, 239. (b) Martin, P.; McManus, N. T.; Rempel, G. L. *J. Mol. Catal. A* **1997**, *126*, 115.

(35) Other leading references: (a) Sanchez-Delgado, R. A.; De Ochoa, O. L. *J. Organomet. Chem.* **1980**, 427. (b) Sanchez-Delgado, R. A.; Valencia, N.; Marquez-Silva, R.-L.; Andriollo, A.; Medina, M. *Inorg. Chem.* **1986**, *25*, 1106. (c) Huh, S.; Cho, Y.; Jun, M.-J.; Whang, D.; Kim, K. *Polyhedron* **1994**, *13*, 1887. (d) Yoshida, Y.; Yoshinari, M.; Iko, A.; Komiya, Z. *Polymer J.* **1998**, *30*, 819.

(36) Diggle, R. A.; Macgregor, S. A.; Whittlesey, M. K. *Organometallics* **2004**, *23*, 1857.

(37) Sanford, M. S.; Love, J. A.; Grubbs, R. H. In *J. Am. Chem. Soc.*, **2001**, *123*, 6543.

(38) Abdur-Rashid, K.; Fedorkiw, T.; Lough, A. J.; Morris, R. H. *Organometallics* **2004**, *23*, 86.

(39) Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944.

(40) Herrmann, W. A. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 1291.

(41) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T. L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546.

(42) Chaumonnot, A.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B.; Buron, C.; Bertrand, G.; Metivier, P. *Organometallics* **2001**, *20*, 5614.

(43) Jazzar, R. F. R.; Bhatia, P. H.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2003**, *22*, 670.

(44) Chatwin, S. L.; Diggle, R. A.; Jazzar, R. F. R.; MacGregor, S. A.; Mahon, M. F.; Whittlesey, M. K. *Inorg. Chem.* **2003**, *42*, 7695.

(45) Conrad, J. C.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2003**, *22*, 1986.

(46) Giunta, D.; Hoelscher, M.; Lehmann, C. W.; Mynott, R.; Wirtz, C.; Leitner, W. *Adv. Synth. Catal.* **2003**, *345*, 1139.

(47) Snelgrove, J. L.; Conrad, J. C.; Yap, G. P. A.; Fogg, D. E. *Inorg. Chim. Acta* **2003**, *345*, 268.

(48) Blaser, H.-U.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M. *Adv. Synth. Catal.* **2003**, *345*, 103.

(49) (a) McLain, S. J.; McCord, E. F.; Arthur, S. D.; Hauptman, E.; Feldman, J.; Nugent, W. A.; Johnson, L. K.; Mecking, S.; Brookhart, M. *Polym. Mater. Sci. Eng.* **1997**, *76*, 246.

(b) Bielawski, C. W.; Morita, T.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 678. (c) Drouin, S. D.; Zamanian, F.; Fogg, D. E. *Organometallics* **2001**, *20*, 5495.

(50) Mutch, A.; Leconte, M.; Lefebvre, F.; Basset, J.-M. *J. Mol. Catal. A* **1998**, *133*, 191, and references therein.

(51) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: New York, 1997.

(52) (a) Fürstner, A.; Langemann, K. *J. Org. Chem.* **1996**, *61*, 3942. (b) Fürstner, A.; Langemann, K. *Synthesis* **1997**, 792. (c) Jafarpour, L.; Heck, M.-P.; Baylon, C.; Lee, H. M.; Mioskowski, C.; Nolan, S. P. *Organometallics* **2002**, *21*, 671.

(53) Louie, J.; Bielawski, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 11312.

(54) For a review of tandem catalysis, see: Fogg, D. E.; dos Santos, E. N. *Coord. Chem. Rev.* **2004**, *248*, 2365.

(55) Ring strain vs. cyclohexene: COE, 9.6 kcal/mol; CDE, 4.0 kcal/mol. See G. Rousseau, *Tetrahedron* **1995**, *51*, 2777.

(56) Leading references: (a) Fürstner, A.; Thiel, O. R.; Ackermann, L.; Schanz, H.-J.; Nolan, S. P. *J. Org. Chem.* **2000**, *65*, 2204. (b) Bourgeois, D.; Pancrazi, A.; Nolan, S. P.; Prunet, J. *J. Organomet. Chem.* **2002**, *643-644*, 247. (c) Cadot, C.; Dalko, P. I.; Cossy, J. *Tetrahedron Lett.* **2002**, *43*, 1839. (d) Kinderman, S. S.; van Maarseveen, J. H.; Schoemaker, H. E.; Hiemstra, H.; Rutjes, F. P. J. T. *Org. Lett.* **2001**, *3*, 2045.

(57) For a recent report on isomerization and hydrogenation of 1-octene via **9** and related catalysts, see: Dinger, M. B.; Mol, J. C. *Eur. J. Inorg. Chem.* **2003**, 2827. This work suggests that turnover numbers obtained for reduction or isomerization in the presence of a solvent should be regarded as minimum figures for activity.

CHAPTER 4

High yield, efficient, new synthetic routes to complexes RuHCl(CO)LL' (9: L = L' = PCy_3; 13a: L = IMes, L' = PCy_3; 13b: L = H_2IMes, L' = PCy_3)

4.1. Introduction

The synthesis of novel Ru-NHC complexes containing a labile PPh_3 ligand, and evaluation of their hydrogenation and isomerization activities, relative to the known complexes RuHCl(CO)LL' (**9**: L = L' = PCy_3; **13a**: L = IMes, L' = PCy_3), were discussed in Chapter 3. In the course of that work, we undertook synthesis of the known complexes by the literature methods. The practical difficulties we encountered led us to explore new synthetic routes to these species, which are described in this Chapter.

Prior routes to RuHCl(CO)(NHC)(PCy_3) (**13a**: NHC = IMes;[1] **13b**: NHC = H_2IMes[2]) rely on displacement of a phosphine ligand from RuHCl(CO)$(PCy_3)_2$ (**9**). An inherent limitation is the low lability of the PCy_3 group, which necessitates use of long reaction times and forcing conditions. As well, we find that the literature routes to the precursor complex **9**, whether based on $RuCl_3 \cdot 3H_2O$[3,4] or $RuCl_2[(COD)]_x$,[5] afford limited yields of pure product, owing to difficulties in separation of unidentified side-products. In exploring alternative, more convenient routes to complexes **9, 13a** and **13b** we began by seeking a precursor accessible in high yields and purity (preferably from the ultimate starting material $RuCl_3$), that contains both a pre-installed hydride ligand, and neutral donor ligands sufficiently labile to undergo exchange under mild conditions, and that is highly soluble in a range of solvents, including aromatics. These criteria led us to the classic hydride complex RuHCl(CO)$(PPh_3)_3$ (**7**).[6] Complex **7** meets all the conditions above, save that of high solubility in aromatic solvents, and proves a valuable precursor to the target complexes.

$RuHCl(CO)(PCy_3)_3$ (**9**) was originally synthesized three decades ago, by prolonged thermolysis of $RuCl_3.xH_2O$ with excess PCy_3 in 2-methoxyethanol[3] (48 h; Table 4.1). Less forcing conditions can be used where sodium borohydride is added as a reducing agent, but yields are then limited to 75%.[4] More recently, Yi and co-workers prepared **9** by thermolysis of $[RuCl_2(COD)]_n$ in ethanol.[5] The insolubility of $[RuCl_2(COD)]_n$ necessitates long reaction times even in a sealed tube at 90-95 °C. We find that reaction at the normal boiling point of the solvent, at reflux in an open vessel, results in contamination by a side-product which we identify as the double carbonylation product $RuCl_2(CO)_2(PCy_3)_2$ **10**, on the basis of NMR analysis and comparison with reported IR data.[7,8] The high solubility of **10** in diethyl ether permits its removal by exhaustive extraction, although yields of clean **9** are limited to < 40%.

In our hands, reaction under the Yi conditions (i.e. at 95 °C in a pressure vessel) afforded **9** in higher yields, but side-products include **10** and another complex, which we identify as the corresponding monocarbonyl species, $RuCl_2(CO)(PCy_3)_2$ (**11**).[7] This byproduct was also observed by Moers et al. in their 1972 synthesis of **9** from $RuCl_3$ (see above), and was obtained as a principal product after 72 hours reaction time.[8] Ample precedents exist for both carbonylation[9,10] and decarbonylation[9,10,12-14] of related Ru species by refluxing in the presence of alcohols. Complex **11** may thus be formed by decarbonylation of **10** under the forcing reaction conditions. Extensive washing of the crude product with ethanol and diethyl ether afforded **9** in ca. 65% isolated yield, albeit with traces of **11** remaining. Attempts to purify the product further, by reprecipitation from hot benzene, resulted in extensive decomposition.

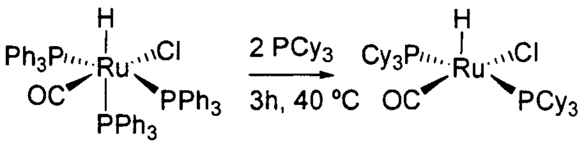
Table 4.1 Comparison of New and Literature Routes to RuHCl(CO)LL' Complexes.

Complex	Precursor	Conditions	Yield (%)	Ref
$RuHCl(CO)(PCy_3)_2$, **9**	$RuCl_3$	2 d, 130 °C	N/G	3
	$RuCl_3$	10 min, 78 °C	75	4
	$RuCl_2(COD)_x$	2 d, 90 °C	85[a]	5
	7	3 h, 40 °C	88	This work
$RuHCl(CO)(NHC)(PCy_3)$, **13**				
a: NHC = IMes	**9**	2h, 80 °C	69	1
	12a	2 h, 80 °C	78	This work
b: NHC = H_2IMes	**9**	3 h, 100 °C	75[b]	2
	12b	2 h, 80 °C	60[c]	This work

[a] Isolated product contaminated by **10** and **11**; see text. [b]Reported as an impure oil, in which **13b** accounts for 75% of total NMR integration. [c]Isolated yield limited by high solubility.

4.2. Preparation of $RuHCl(CO)(PCy_3)_2$ (9)

In contrast with the forcing conditions common to the literature methods cited above,[3-5] we find that treating a suspension of $RuHCl(CO)(PPh_3)_3$ (**7**) in benzene with excess PCy_3 (3 equiv) effected quantitative conversion to **9** within 3 h at 40 °C. The product was isolated in 88% yield following precipitation from Et_2O (Figure 4.1). NMR analysis showed the expected hydride triplet (δ_H -24.21; $^2J_{PH}$ = 18.0 Hz) and $^{31}P\{^1H\}$ NMR singlet (46.86 ppm). Other data agree with published values[5] (Table 4.2). Advantages of this route over the literature procedures are the high yield and purity of the product, as well as the experimental convenience associated with the mild reaction conditions and short reaction times.



7 **9**

Figure 4.1 Synthesis of $RuHCl(CO)(PCy_3)_2$ (**9**).

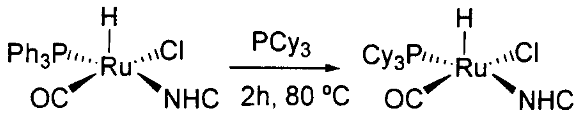
Table 4.2 Key Spectroscopic Parameters for **9-14**.[a]

Complex	δ_P	δ_H ($^2J_{PH}$, Hz)	δ_{CO} ($^2J_{PC}$, Hz)	ν_{CO}, $\nu_{Ru\text{-}H}$
$RuHCl(CO)(PPh_3)_3$, **7**[b]	40.9, 14.8 (br)	-7.2 (dt, 105, 23)	N/G	2020, 1922[6]
$RuHCl(CO)(PCy_3)_2$, **9**	46.9 (s)	-24.2 (t, 18)	201.9 (t,14)[5]	1905, 2030[3]
$RuCl_2(CO)_2(PCy_3)_2$, **10**[c]	27.2 (s)	—	N/G	tct: 2035, 1965 ttt: 1984[8]
$RuCl_2(CO)(PCy_3)_2$, **11**	35.2 (s)	—	N/G	1934[15]
$RuHCl(CO)(NHC)(PPh_3)$, **12**				
a: NHC = IMes	42.1 (s)	-23.9 (d, 24)	201.4 (d, 14)	1913, 1897
b: NHC = H_2IMes	41.0 (s)	-24.0 (d, 24)	200.8 (d, 14)[b]	1911, 1865
$RuHCl(CO)(NHC)(PCy_3)$, **13**				
a: NHC = IMes	47.8 (s)	-24.8 (d, 21)	N/G	1896[1]
b: NHC = H_2IMes	46.8 (s)	-24.9 (d, 21)	202.1 (d, 14)	N/G
$RuHCl(CO)(IMes)_2$, **14**	-	-25.4 (s)	202.1	1883, 1839

[a] NMR spectra measured at 300 MHz, 298 K, in C_6D_6 and IR measurements in Nujol unless otherwise specified. [b] $CDCl_3$ solvent. [c] Only IR data are reported for **10**.

4.3. Syntheses of $RuHCl(CO)(NHC)(PCy)_3$ (13a: NHC = IMes; 13b: NHC = H_2IMes)

The literature route to **13a** involves reaction of **9** with IMes in toluene at 80 °C for 2 h, followed by 18 h further reaction at RT.[1] Limitations to this synthesis are the inconveniently long reaction time, as well as the difficulties in purification of the precursor **9**, as noted above. Mol and co-workers recently reported that **13b** is likewise accessible by this approach, and that reaction times can be reduced to 3 h by carrying out the thermolysis at 100 °C (Table 4.1; Figure 4.2).[2] However, ca. 25% contamination by unidentified side-products was noted, and clean **13b** could not be isolated from the yellow oil obtained. In contrast, the PPh_3 ligand in **12a** or **21b** undergoes exchange with an NHC ligand within 2 h at 80 °C, yielding **13a** or **13b** respectively, as the sole product (NMR analysis). The complexes were isolated as yellow, crystalline powders by precipitation from hexanes, though yields are limited, particularly for **13b**, by high solubility (**13a**: ca. 80%; **13b**: 60%). Product identities are confirmed by comparison to the reported NMR values (Table 4.2), supported by MALDI-MS and elemental analysis for **13b**. In both cases, retention of a phosphine ligand is indicated by ^{31}P NMR analysis, and observation of a hydride doublet confirms that a single phosphine ligand is present. Signals for the NHC ligand show the expected multiplicities and integration values, indicating that the mesityl group remains intact. Two recent reports describe activation of a mesityl methyl[16] or α-carbon[17] group on thermolysis of $RuHCl(PPh_3)_3$ or $RuH_2(CO)(PPh_3)_3$, respectively, with IMes.



12a, NHC = IMes
12b, NHC = H_2IMes

13a, NHC = IMes
13b, NHC = H_2IMes

Figure 4.2 Synthesis of $RuHCl(CO)(NHC)(PCy_3)$ complexes.

The attenuated reactivity of **12a** and **12b** relative to **7** (**12a**, for example, shows <10% exchange with PCy_3 over 12 h in benzene at 22 °C) was somewhat unexpected, and presumably reflects the lower lability of the PPh_3 ligand in the NHC complexes. In a related observation, the Grubbs group earlier reported a dramatic reduction in the lability of a PCy_3 ligand trans to an N-heterocyclic carbene within complexes of the type $RuCl_2(NHC)(PR_3)(CHPh)$.[18] We speculate that this behavior may be a general characteristic of phosphine ligands trans to an NHC group, possibly owing to π-backbonding of the metal into the d orbital on phosphorus. It should be noted, however, that the Grubbs study also demonstrated a 50-fold increase in the rate of phosphine exchange on replacing the PCy_3 group by a more weakly donating PPh_3 ligand. Consistent with this is the higher reactivity for the PPh_3 complexes **12a** and **12b**, relative to their PCy_3 analogues, described in Chapter 3.[11]

4.4. Conclusions

The foregoing describes high-yield synthetic routes to an important class of Ru complexes bearing electron-rich phosphine and NHC ligands. $RuHCl(CO)(PPh_3)_3$ (**7**) proved a valuable precursor to these complexes, owing largely to the lability of its triphenylphosphine ligands. Reactions of **7** with excess PCy_3 afforded **9** in quantitative yields. Key advantages of this new method over the literature routes lie in the high yield of clean **9**, the short reaction times, and mild, its experimentally convenient conditions. Similarly, the relative lability of the PPh_3 ligand in **12a** and **12b**, relative to the PCy_3 ligand present in **9**, facilitates replacement of phosphine by an NHC ligand to yield **13a** and **13b**. Thus, **13a** and **13b** were isolated in high yield, using shorter reaction times and milder conditions than those possible in the literature route from **9**, though thermolytic conditions were still required, owing to the attenuated lability of PPh_3 trans to an NHC ligand. Probably owing to the short reaction times, no activation of the NHC mesityl group was observed, in contrast to the literature precedents.[16,17] The foregoing underlines the importance of selecting a precursor with pre-installed or appropriately labile ancillary ligands in designing convenient and efficient routes to the target complexes.

4.5. References

(1) Lee, H. M.; Smith, D. C., Jr.; He, Z.; Stevens, E. D.; Yi, C. S.; Nolan, S. P. *Organometallics* **2001**, *20*, 794.

(2) Dinger, M. B.; Mol, J. C. *Eur. J. Inorg. Chem.* **2003**, 2827.

(3) Moers, F. G.; Langhout, J. P. *RECUEIL* **1972**, *91*, 591.

(4) James, B. R.; Preece, M.; Robinson, S. D. *Adv. Chem. Ser.* **1982**, *196*, 145.

(5) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043.

(6) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 48.

(7) Drouin, S. D. **2002**, Ph.D. Thesis, University of Ottawa, 2004.

(8) Moers, F. G.; Hoedt, R. W. M. T.; Langhout, J. P. *J. Organomet. Chem.* **1974**, *65*, 93.

(9) Drouin, S. D.; Monfette, S.; Amoroso, D.; Yap, G. P. A.; Fogg, D. E. *Organometallics*, 2005, ASAP article.

(10) Gottschalk-Gaudig, T.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1999**, *38*, 5241.

(11) Dharmasena, U. L.; Foucault, H. M.; dos Santos, E. N.; Fogg, D. E.; Nolan, S. P. *Organometallics* **2005**, *24*, 1056.

(12) Marchenko, A. V.; Huffman, J. C.; Valerga, P.; Jimenez Tenorio, M.; Puerta, M. C.; Caulton, K. G. *Inorg. Chem.* **2001**, *40*, 6444.

(13) Barnard, C. F. J.; Daniels, J. A.; Jeffery, J.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1861.

(14) Krassowski, D. W.; Nelson, J. H.; Brower, K. R.; Hauenstein, D.; Jacobson, R. A. *Inorg. Chem.* **1988**, *27*, 4294.

(15) Drouin, S. D.; Amoroso, D.; Yap, G. P. A.; Fogg, D. E. *Organometallics* **2002**, *21*, 1042.

(16) Abdur-Rashid, K.; Fedorkiw, T.; Lough, A. J.; Morris, R. H. *Organometallics* **2004**, *23*, 86.

(17) Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944.

(18) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543.

CHAPTER 5

Attempted Replacement of CO by H_2 in $RuHCl(CO)(NHC)(PPh_3)$: Unexpected Synthesis of a Bis(Carbene) Complex

5.1. Introduction

The studies described in this chapter began with an attempt to investigate the effect on hydrogenation activity of the carbonyl ligand in electron-rich ruthenium complexes of the type described in Chapter 3. There are suggestions in the literature that a CO ligand is *deactivating* in less electron-rich systems. Arylphosphine complexes of Ru, Rh, and Ir show reduced activity for olefin hydrogenation when π-acid ligands such as CO are incorporated.[1,2] π-Acid ligands are thought to increase the activation energy barrier for oxidative addition of H_2, which is favored by greater electron density on the metal center, as well as coordinative unsaturation.[3] In contrast, preliminary results from our group suggested that $RuHCl(CO)(PCy_3)_2$ (**9**) is more active than $RuHCl(H_2)(PCy_3)_2$ (**8**).[4] In order to examine the generality of this behavior, we wished to replace the CO ligand of $RuHCl(CO)(NHC)(PPh_3)$ with a dihydrogen ligand. In the course of our search for suitable precursors for the target complex $RuHCl(H_2)(NHC)(PPh_3)$, the Morris group reported a ruthenium-IMes complex in which one mesityl group was activated (**16**, Figure 5.1).[5] Complex **16** contains a pre-installed hydride, the activated IMes group, and two labile PPh_3 ligands, and thus appears an attractive entry point into the desired chemistry. This chapter describes the attempted synthesis of the Morris compound and $RuHCl(H_2)(L)(NHC)$, and the characterization of an unexpected product.

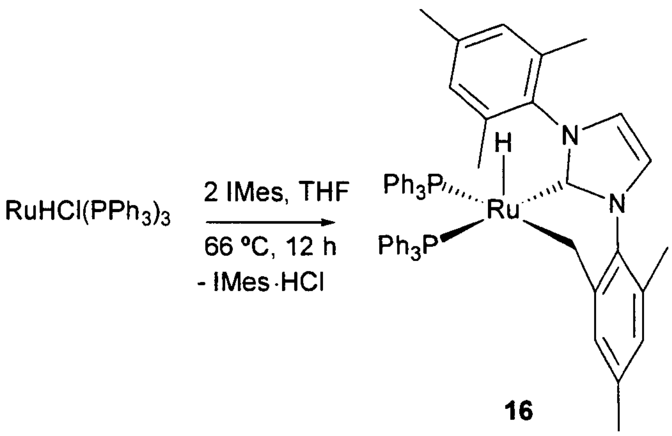
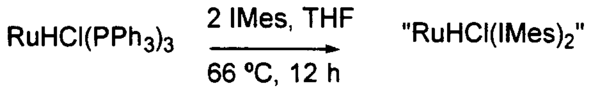


Figure 5.1 Synthesis of **16** from **2** by Morris and co-workers.[5]

5.2. Preparation of $RuHCl(IMes)_2$ (15a)

The literature route to **16** involves reaction of a suspension of $RuHCl(PPh_3)_3$ (**2**) in THF with two equivalents of IMes at 66 °C for 12 h under argon. Use of a second equivalent of IMes is rationalized as providing the base necessary to take up the HCl generated by activation of a mesityl methyl proton.[5] A precipitate identified as IMes·HCl was filtered off at the end of the reaction, prior to precipitation of the red product with hexanes. The product identity was suggested on the basis of NMR and IR analysis, though the microanalytical data were poor.

In our hands, this reaction (N_2 atmosphere) yielded a dark orange-brown solution. As judged by ^{31}P NMR analysis, complex **16** was present in minor amounts (20% of total integrated intensity), the balance being due to free phosphine. Large excess of free phosphine suggested the presence of a second species. The majority product being a new species identified as **15** (Figure 5.2) on the basis of extensive spectroscopic analysis. Following workup by filtering through Celite, concentrating, and treating with hexane, the orange-brown product showed only NMR signals for **15**. (The chemical shift of the hydride singlet for **15** is identical to that for the doublet of doublets reported for **16**). Extensive NMR and MALDI (Figure 5.3) analysis suggest the empirical formula RuHCl(IMes)$_2$, although we are unable to conclusively distinguish between structure **15a**, with an agostic interaction between the metal and the methyl protons of the IMes mesityl groups, and dimeric [RuHCl(IMes)$_2$]$_2$ (**15b**).



$$\mathrm{RuHCl(PPh_3)_3} \xrightarrow[66\ ^\circ\mathrm{C},\ 12\ \mathrm{h}]{2\ \mathrm{IMes,\ THF}} \text{"}\mathrm{RuHCl(IMes)_2}\text{"}$$

Figure 5.2 Formation of **15** from **2** under the literature conditions.

Complete loss of PPh$_3$ is deduced from the null ^{31}P NMR spectrum for **15**, in conjunction with the singlet multiplicity of the IMes carbene carbon and the hydride signals evident from the ^{13}C and ^{1}H NMR spectra. The upfield location of the hydride singlet (δ_H -28.04 ppm) indicates that the hydride ligand is trans to a vacant site, while its integration, relative to that for the IMes “olefinic” protons (1:4) or the mesitylene aromatic CH groups (1:8), confirms the presence of two IMes ligands per hydride ligand. At room temperature, two overlapping singlets were observed for the mesityl aryl protons, while the olefinic protons of the carbene ring appeared as a singlet. The *p*-methyl protons of the mesityl group appeared as a singlet, and the *o*-methyl protons as a broad peak, suggesting some fluxionality associated with rotation of the IMes ligand about the metal-carbon bond. At -63 °C, these signals are resolved into three singlets for the mesityl protons (two of these peaks being coincident) and six singlets for the mesityl methyl groups. No change in the hydride signal was observed.

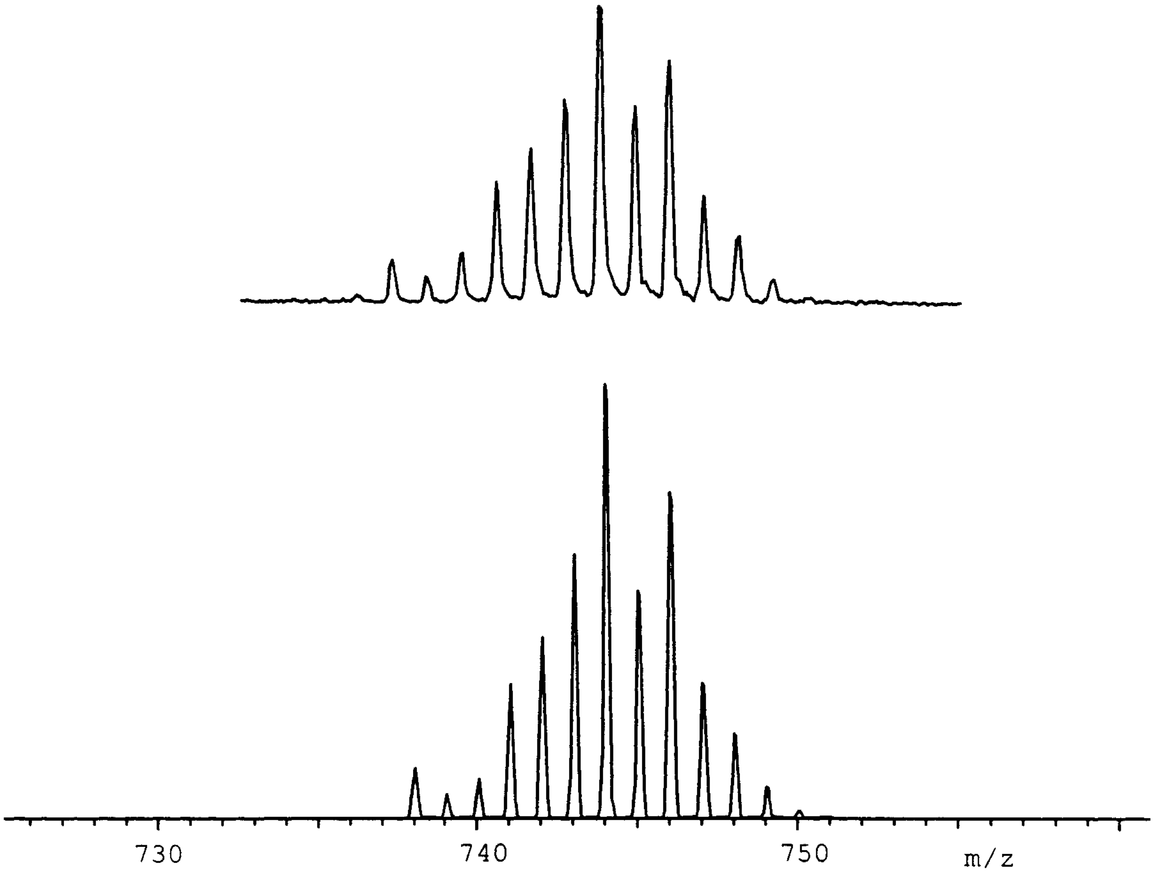


Figure 5.3 MALDI-MS spectra (anthracene matrix), showing observed (top; m/z 744.58) and simulated (bottom; m/z 744.25) isotope patterns for $[RuCl(IMes)(IMes\text{-}H)]^{+\cdot}$ within **15**.

These data confirm that the NHC ligand remains intact, despite the original report.[5] We exclude the possibility that the fifth coordination site in the presumed square pyramidal complex is taken up by bound N_2, as identical NMR features are observed whether reaction is carried out under argon or N_2. We thus tentatively formulated the structure as either agostic **15a** or dimeric **15b.** Elucidation by X-ray diffraction could not be undertaken, as attempts to grow crystals in a variety of solvents (benzene, toluene and THF) proved unsuccessful.

In an agostic C-H bond,[6] the proton is often highly fluxional, undergoing rapid exchange with geminal protons. The NMR signals therefore coalesce into a singlet: that is, the signal is indistinguishable from a classical methyl group. Even at the lowest attainable temperatures, it is not unusual to observe a singlet for agostic methyl groups.[6,7] Observation of singlets for the methyl protons of **15a** even at -63 °C thus does not exclude the possible presence of agostic interactions in **15a**. Reduced $^1J_{(C\text{-}H)}$ coupling values are also diagnostic for agostic interactions, but these are averaged in a fluxional system. Rapid exchange of hydride ligands with agostic protons is also noted in the literature,[8] and can sometimes be observed by measurements of minimum T_1 values. For **15a**, the T_1(min) value for the hydride group is 724 ms (250K, 500 MHz), and T_1(min) values for the methyl protons of the mesityl groups range from 737.023–788.955 ms (270K, 500 MHz), suggesting the absence of such an interaction. (In general, T_1 values are less than 100 ms for a dihydrogen ligand, and greater than 300 ms for a classical hydride).[9,10]

As none of these data provide positive evidence for the presence of an agostic interaction in **15a**, we attempted instead to answer the fundamental question of whether **15** was mononuclear (**15a**) or dinuclear (**15b**). Pulsed Field Gradient Spin Echo (PGSE) measurements of molecular diffusion constants provide insight into molecular size that have been used to identify polynuclear complexes, ion pairs, and aggregated species.[11-13] PGSE studies can likewise be used to discriminate between monomeric and dimeric species.[12] The experiment involves pulsing a spatial volume of the sample in the NMR tube over some gradient, and measuring the decrease in signal intensity over time as the molecules diffuse out of that region. The rate of movement (and hence the diffusion constant; see below) of any given molecule is proportional to its hydrodynamic radius, as shown by the Stokes-Einstein equation (Eqn. 1).

$$D = \frac{kT}{6\pi\eta r_H} \qquad (1)$$

k = Boltzmann constant, T = absolute temperature, η = viscosity, r_H = hydrodynamic radius

Smaller molecules have smaller hydrodynamic radii, and hence move faster. Their diffusion rate depends on a number of factors in addition to size, including the magnetogyric ratio of the nucleus involved, the duration of the pulse, the gradient strength, and the delay between the midpoints of the gradients. Equation 2 shows the relationship between signal intensity (ln I/I_0; observed spin-echo intensity without gradients) and the diffusion coefficient.

$$\ln\left(\frac{I}{I_0}\right) = -\gamma^2\delta^2G^2\left(\Delta - \frac{\delta}{3}\right)D \qquad (2)$$

γ = magnetogyric ratio of hydrogen, δ = duration of gradient pulse (4 ms), G = gradient strength, Δ = delay between the midpoints of the gradients (10 ms), D = diffusion coefficient.

As this expression takes the form y = mx + b, the diffusion constant can be extracted from the slope of a plot of the gradient strength versus the intensity ratios. The absolute value of the slope decreases with increasing molecular weight (which approximates hydrodynamic ratio): that is, smaller molecules give rise to steep slopes (larger *D* values). PGSE analysis of **15**, relative to four other ruthenium complexes of known molecular weight (Figure 5.4), was carried out by Heather Foucault of the Fogg group.

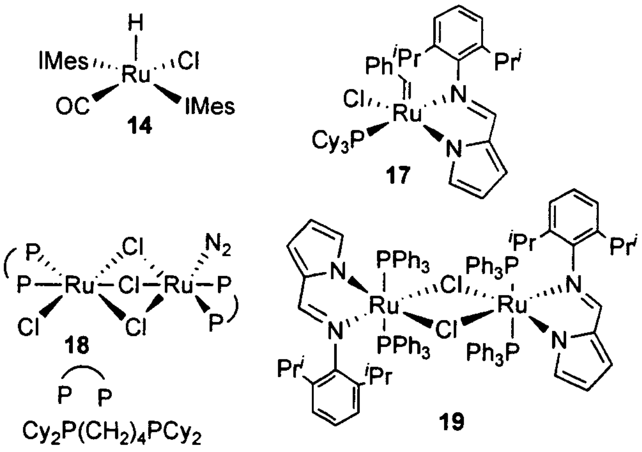


Figure 5.4 Reference complexes employed in PGSE study.

The PGSE data (collected in Table 5.1) indicate that the diffusion constant for **15** lies between that of the two monoruthenium complexes **14** and **17**, with greatest similarity in slopes, and hence similar *D* values, for **15** and **14**. This strongly suggests that **15** is a monoruthenium complex, and it is thus identified as the agostic complex $RuHCl(IMes)_2$ **15a**.

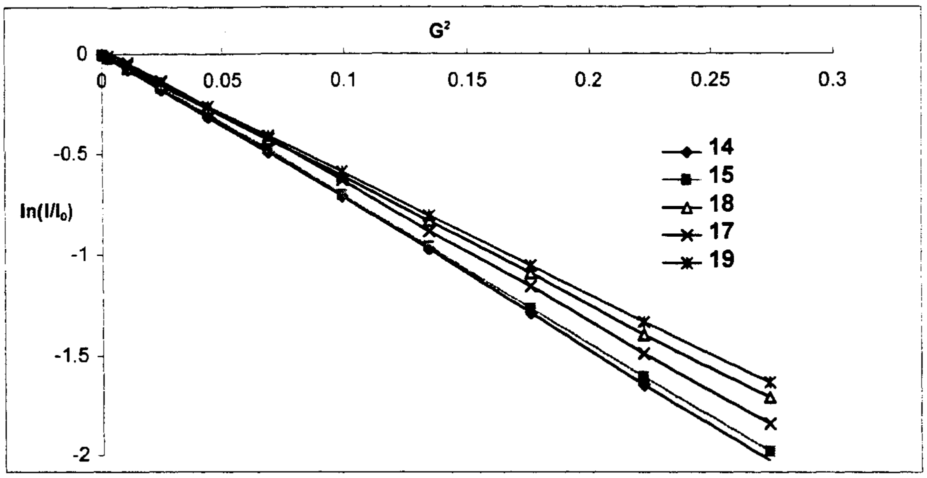


Figure 5.5 Plot of $\ln(I/I_0)$ vs the square of the gradient amplitude. The slope is related to the diffusion constant *D*. Molecular weight increases in the order **14** < **17** < **18** < **19**.

Table 5.1 Molecular weights, slopes of the lines of Figure 5.2 and *D* values for **14**, **15**, **17-19**.[a]

complex	MW (g mol^{-1})	slope	D (10^{-10} m^2 s^{-1})
14	774.27	-7.3995	7.382
15	746.26/1492.52	-7.2529	7.281
17	842.40	-6.8064	6.86
18	1273.78	-6.2483	6.296
19	1828.62	-5.9982	6.04

[a] All PGSE measurements are at 22 °C in $CDCl_3$.

5.3. Conclusions

The foregoing describes the synthesis of the new Ru hydride complex, **15a**, during attempts to prepare a complex containing an activated mesityl group. While absolute confirmation of the final structure has not been achieved, the basis for identification of **15** as a monoruthenium complex of formula $RuHCl(IMes)_2$ is strong. Crystallographic analysis[7,8,14] could aid in confirming the proposed agostic interaction:

even where the location of the C-H hydrogen is uncertain, its position can often be deduced with reasonable certainty from the known positions of the other substituents on an agostic carbon.[7] Also potentially beneficial would be isotopic perturbation of resonance (IPR), a valuable technique for discriminating between an agostic methyl group and a classical methyl group in fluxional systems.[15-18]

The ultimate goal of this work, however, was to synthesize a CO-free molecule of the type $RuHCl(H_2)(NHC)(PPh_3)$, in order to study the effect of a CO ligand on hydrogenation activity. The foregoing indicates that new routes to such complexes must be sought.

5.4. References

(1) James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 8, Chapter 51, and references therein.

(2) James, B. R. *Homogeneous Hydrogenation*; John Wiley & Sons: Toronto, 1973.

(3) Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386.

(4) Drouin, S. D. **2002**, Ph.D. Thesis, University of Ottawa, 2004.

(5) Abdur-Rashid, K.; Fedorkiw, T.; Lough, A. J.; Morris, R. H. *Organometallics* **2004**, *23*, 86.

(6) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(7) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

(8) Gusev, D. G.; Madott, M.; Dolgushin, F. M.; Lyssenko, K. A.; Antipin, M. Y. *Organometallics* **2000**, *19*, 1734.

(9) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032.

(10) Antoniutti, S.; Albertin, G.; Amendola, P.; Bordignon, E. *J. Chem. Soc. Chem. Commun.* **1989**, 229.

(11) Valentini, M.; Pregosin, P. S.; Ruegger, H. *Organometallics* **2000**, *19*, 2551.

(12) Valentini, M.; Ruegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **2001**, *84*, 2833.

(13) Pregosin, P. S.; Martinez-Viviente, E.; Kumar, P. G. A. *Dalton Trans.* **2003**, 4007.

(14) Abdur-Rashid, K.; Fedorkiw, T.; Lough, A. J.; Morris, R. H. *Organometallics* **2004**, *23*, 86.

(15) Lawes, D. J.; Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **2005**, *127*, 4134.

(16) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

(17) Trepanier, S. J.; McDonald, R.; Cowie, M. *Organometallics* **2003**, *22*, 2638.

(18) Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 1602.

CHAPTER 6

Conclusions and Recommendations for Future Work

The work presented in this thesis documents the utility of NHC ligands as a versatile class of ligands in ruthenium-catalyzed hydrogenation. Synthesis of new hydridocarbonyl complexes of ruthenium, and their increased hydrogenation activities, were discussed in Chapter 3. The high activity of the NHC complexes rests on the choice of a labile PPh_3 group as the ancillary "placeholder" ligand, which is displaced by incoming olefin. Their additional activity toward both isomerization and polymerization is noteworthy, as this carries both limitations and opportunities. Future work in this area will focus on exploration of these structural motifs in context of tandem metathesis-hydrogenation chemistry.

$RuHCl(CO)(PPh_3)_3$ emerged as a valuable precursor for a range of complexes of the type RuHCl(CO)LL' type. The lability of the PPh_3 groups in the precursor is fundamental to the efficiency of these ligand substitution reactions. While the $RuHCl(CO)(NHC)(PPh_3)$ complexes likewise showed higher reactivity than their PCy_3 analogues, the lability of the phosphine groups appeared to be attenuated when trans to a NHC ligand. NMR studies involving ^{31}P magnetization transfer would be valuable in quantifying the phosphine exchange rates within these complexes. This issue may be important in catalyst redesign. Substitution of the phosphine group present in the NHC derivatives with a pyridine group, for example (in which no d orbitals are present that would support back-donation from the metal) may enable us to understand whether the NHC ligands amplify back-bonding of the metal onto a *trans*-phosphine group.

The attempted synthesis of a carbonyl-free complex containing a cyclometaled IMes ligand led to a new complex, formulated as RuHCl(IMes)$_2$. Crystallographic confirmation of the proposed agostic structure should be pursued; we note that the stability of this complex provides a strong argument against the possibility that it is a genuinely 14-electron ruthenium(II) species. The initial objective, evaluation of the effect of the CO ligand in electron–rich Ru(II) systems, remains unmet, and may be pursued more readily by computational analysis. However, future work should also target synthesis of the novel complexes RuHCl(H$_2$)(NHC)(PPh$_3$) (perhaps by hydrogenolysis of the benzylidene complex) and comparing their catalytic activity towards hydrogenation with respect to their carbonyl analogues. Alternatively, a comparison of RuHCl(CO)(NHC)(PCy$_3$) and RuHCl(NHC)(PCy$_3$)(H$_2$) may be more straightforward, as the latter complex may be readily accessible by reaction of the known complex RuHCl(H$_2$)(PCy$_3$)$_2$ with an NHC ligand.

APPENDICES

APPENDIX A

Crystallographic information for RuHCl(CO)(IMes)(PPh$_3$)·C$_6$H$_6$ (12a·C$_6$H$_6$)

Crystals of **12a** were grown from benzene. A suitable crystal was selected and mounted on a glass fibre and transferred to a Siemens (Bruker) SMART-1K X-ray diffractometer. Data were collected at -50°C using Mo-Kα radiation, and structure solution (direct methods) and refinement (full-matrix least squares on F^2) were carried out using the SHELXTL suite of programs. (reference: SHELXTL Version 5.1, Bruker AXS Inc. Madison, WI, 2001.) The structure was solved in the centrosymmetric orthorhombic space group Pbca, All non-hydrogen atoms were refined anisotropically while H atoms were placed in geometrically reasonable positions and refined as riding atoms. The CO group was disordered over two positions, both of which result in a slight distortion from ideal square planar geometry at Ru1. In the final stages of refinement wR^2 = 6.78% and R^1= 3.30%.

Table A.1. Crystal data and structure refinement for $RuHCl(CO)(IMes)(PPh_3)\cdot C_6H_6$ (**12a**$\cdot C_6H_6$)

empirical formula	$C_{46}H_{45}ClN_2OPRu$	
formula weight	809.33	
temperature	223(2) K	
wavelength	0.71073 Å	
crystal system	orthorhombic	
space group	*Pbca*	
unit cell dimensions	a = 15.5763(8) Å	α = 90°
	b = 21.9626(12) Å	β = 90°
	c = 23.6577(13) Å	γ = 90°
volume	8093.2(8) $Å^3$	
Z	8	
density (calcd)	1.328 mg/cm^3	
abs coeff	0.530 mm^{-1}	
$F(000)$	3352	
crystal size	0.18 × 0.35 × 0.4 mm^3	
θ range for data collection	1.72 to 25.00°	
reflections collected	57572	
independent reflections	7135 [R(int) = 0.0591]	
completeness to θ = 25.00°	100.0%	
absorption correction	none	
refinement method	full-matrix least-squares on F^2	
data/restraints/parameters	7135 / 0 / 488	
goodness-of-fit on F^2	1.022	
final R indices [$I > 2\sigma(I)$]	R1 = 0.0330, wR2 = 0.0678	
R indices (all data)	R1 = 0.0684, wR2 = 0.0710	
largest diff. peak and hole	0.384 and -0.318 e $Å^{-3}$	

Table A.2. Bond lengths [Å] and angles [deg] for $RuHCl(CO)(IMes)(PPh_3)\cdot C_6H_6$ (**12a**$\cdot C_6H_6$)

Ru(1)-C(4')	1.754(8)
Ru(1)-C(4)	1.780(11)
Ru(1)-C(1)	2.079(3)
Ru(1)-P(1)	2.3557(8)
Ru(1)-Cl(1)	2.4073(8)
P(1)-C(41)	1.832(3)
P(1)-C(31)	1.835(3)
P(1)-C(51)	1.843(3)
C(4)-O(1)	1.195(12)
C(4')-O(1')	1.175(9)
N(1)-C(1)	1.353(3)
N(1)-C(2)	1.386(3)
N(1)-C(11)	1.454(3)
N(2)-C(1)	1.370(3)
N(2)-C(3)	1.382(3)
N(2)-C(21)	1.441(3)
C(2)-C(3)	1.332(4)
C(2)-H(2A)	0.9400
C(3)-H(3A)	0.9400
C(11)-C(16)	1.380(4)
C(11)-C(12)	1.396(4)
C(12)-C(13)	1.395(4)
C(12)-C(17)	1.508(4)
C(13)-C(14)	1.382(4)
C(13)-H(13A)	0.9400
C(14)-C(15)	1.388(4)
C(14)-C(18)	1.518(4)
C(15)-C(16)	1.394(4)
C(15)-H(15A)	0.9400
C(16)-C(19)	1.494(4)
C(17)-H(17A)	0.9700

C(17)-H(17B)	0.9700
C(17)-H(17C)	0.9700
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(18)-H(18C)	0.9700
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(19)-H(19C)	0.9700
C(21)-C(26)	1.385(4)
C(21)-C(22)	1.397(4)
C(22)-C(23)	1.397(4)
C(22)-C(27)	1.503(4)
C(23)-C(24)	1.381(4)
C(23)-H(23A)	0.9400
C(24)-C(25)	1.379(4)
C(24)-C(28)	1.514(4)
C(25)-C(26)	1.395(4)
C(25)-H(25A)	0.9400
C(26)-C(29)	1.513(4)
C(27)-H(27A)	0.9700
C(27)-H(27B)	0.9700
C(27)-H(27C)	0.9700
C(28)-H(28A)	0.9700
C(28)-H(28B)	0.9700
C(28)-H(28C)	0.9700
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(29)-H(29C)	0.9700
C(31)-C(36)	1.381(4)
C(31)-C(32)	1.382(4)
C(32)-C(33)	1.387(4)
C(32)-H(32A)	0.9400
C(33)-C(34)	1.362(4)
C(33)-H(33A)	0.9400
C(34)-C(35)	1.378(4)
C(34)-H(34A)	0.9400

C(35)-C(36)	1.388(4)
C(35)-H(35A)	0.9400
C(36)-H(36A)	0.9400
C(41)-C(42)	1.377(4)
C(41)-C(46)	1.389(4)
C(42)-C(43)	1.387(4)
C(42)-H(42A)	0.9400
C(43)-C(44)	1.376(4)
C(43)-H(43A)	0.9400
C(44)-C(45)	1.366(4)
C(44)-H(44A)	0.9400
C(45)-C(46)	1.390(4)
C(45)-H(45A)	0.9400
C(46)-H(46A)	0.9400
C(51)-C(52)	1.373(4)
C(51)-C(56)	1.383(4)
C(52)-C(53)	1.386(4)
C(52)-H(52A)	0.9400
C(53)-C(54)	1.371(5)
C(53)-H(53A)	0.9400
C(54)-C(55)	1.373(5)
C(54)-H(54A)	0.9400
C(55)-C(56)	1.385(4)
C(55)-H(55A)	0.9400
C(56)-H(56A)	0.9400
C(61)-C(66)	1.331(7)
C(61)-C(62)	1.367(7)
C(61)-H(61A)	0.9400
C(62)-C(63)	1.380(7)
C(62)-H(62A)	0.9400
C(63)-C(64)	1.351(6)
C(63)-H(63A)	0.9400
C(64)-C(65)	1.346(6)
C(64)-H(64A)	0.9400
C(65)-C(66)	1.355(6)
C(65)-H(65A)	0.9400

C(66)-H(66A)	0.9400
C(4')-Ru(1)-C(4)	30.9(3)
C(4')-Ru(1)-C(1)	91.4(2)
C(4)-Ru(1)-C(1)	92.5(3)
C(4')-Ru(1)-P(1)	90.5(3)
C(4)-Ru(1)-P(1)	93.8(3)
C(1)-Ru(1)-P(1)	170.75(8)
C(4')-Ru(1)-Cl(1)	169.2(5)
C(4)-Ru(1)-Cl(1)	159.7(7)
C(1)-Ru(1)-Cl(1)	86.65(8)
P(1)-Ru(1)-Cl(1)	89.79(3)
C(41)-P(1)-C(31)	103.61(13)
C(41)-P(1)-C(51)	100.94(14)
C(31)-P(1)-C(51)	102.88(13)
C(41)-P(1)-Ru(1)	115.46(9)
C(31)-P(1)-Ru(1)	108.75(10)
C(51)-P(1)-Ru(1)	122.98(10)
O(1)-C(4)-Ru(1)	175.7(12)
O(1')-C(4')-Ru(1)	179.3(9)
C(1)-N(1)-C(2)	111.8(2)
C(1)-N(1)-C(11)	126.1(2)
C(2)-N(1)-C(11)	121.5(2)
C(1)-N(2)-C(3)	110.9(2)
C(1)-N(2)-C(21)	125.8(2)
C(3)-N(2)-C(21)	122.7(2)
N(1)-C(1)-N(2)	103.4(2)
N(1)-C(1)-Ru(1)	131.5(2)
N(2)-C(1)-Ru(1)	124.8(2)
C(3)-C(2)-N(1)	106.5(3)
C(3)-C(2)-H(2A)	126.8
N(1)-C(2)-H(2A)	126.8
C(2)-C(3)-N(2)	107.3(3)
C(2)-C(3)-H(3A)	126.3
N(2)-C(3)-H(3A)	126.3
C(16)-C(11)-C(12)	123.0(3)
C(16)-C(11)-N(1)	119.3(3)

C(12)-C(11)-N(1)	117.5(3)
C(13)-C(12)-C(11)	117.2(3)
C(13)-C(12)-C(17)	121.2(3)
C(11)-C(12)-C(17)	121.7(3)
C(14)-C(13)-C(12)	122.0(3)
C(14)-C(13)-H(13A)	119.0
C(12)-C(13)-H(13A)	119.0
C(13)-C(14)-C(15)	118.4(3)
C(13)-C(14)-C(18)	120.5(3)
C(15)-C(14)-C(18)	121.0(3)
C(14)-C(15)-C(16)	122.1(3)
C(14)-C(15)-H(15A)	118.9
C(16)-C(15)-H(15A)	118.9
C(11)-C(16)-C(15)	117.3(3)
C(11)-C(16)-C(19)	122.2(3)
C(15)-C(16)-C(19)	120.5(3)
C(12)-C(17)-H(17A)	109.5
C(12)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(12)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(14)-C(18)-H(18A)	109.5
C(14)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(14)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(26)-C(21)-C(22)	121.8(3)
C(26)-C(21)-N(2)	118.4(3)

C(22)-C(21)-N(2)	119.5(3)
C(23)-C(22)-C(21)	117.1(3)
C(23)-C(22)-C(27)	121.4(3)
C(21)-C(22)-C(27)	121.5(3)
C(24)-C(23)-C(22)	123.1(3)
C(24)-C(23)-H(23A)	118.5
C(22)-C(23)-H(23A)	118.5
C(25)-C(24)-C(23)	117.4(3)
C(25)-C(24)-C(28)	121.7(3)
C(23)-C(24)-C(28)	120.9(3)
C(24)-C(25)-C(26)	122.5(3)
C(24)-C(25)-H(25A)	118.8
C(26)-C(25)-H(25A)	118.8
C(21)-C(26)-C(25)	118.1(3)
C(21)-C(26)-C(29)	121.9(3)
C(25)-C(26)-C(29)	120.0(3)
C(22)-C(27)-H(27A)	109.5
C(22)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(22)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(24)-C(28)-H(28A)	109.5
C(24)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(24)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(26)-C(29)-H(29A)	109.5
C(26)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(26)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(36)-C(31)-C(32)	118.2(3)
C(36)-C(31)-P(1)	123.7(2)

C(32)-C(31)-P(1)	118.1(2)
C(31)-C(32)-C(33)	121.2(3)
C(31)-C(32)-H(32A)	119.4
C(33)-C(32)-H(32A)	119.4
C(34)-C(33)-C(32)	119.9(3)
C(34)-C(33)-H(33A)	120.0
C(32)-C(33)-H(33A)	120.0
C(33)-C(34)-C(35)	119.9(3)
C(33)-C(34)-H(34A)	120.1
C(35)-C(34)-H(34A)	120.1
C(34)-C(35)-C(36)	120.2(3)
C(34)-C(35)-H(35A)	119.9
C(36)-C(35)-H(35A)	119.9
C(31)-C(36)-C(35)	120.6(3)
C(31)-C(36)-H(36A)	119.7
C(35)-C(36)-H(36A)	119.7
C(42)-C(41)-C(46)	118.3(3)
C(42)-C(41)-P(1)	123.3(2)
C(46)-C(41)-P(1)	118.4(2)
C(41)-C(42)-C(43)	120.9(3)
C(41)-C(42)-H(42A)	119.5
C(43)-C(42)-H(42A)	119.5
C(44)-C(43)-C(42)	120.1(3)
C(44)-C(43)-H(43A)	119.9
C(42)-C(43)-H(43A)	119.9
C(45)-C(44)-C(43)	119.8(3)
C(45)-C(44)-H(44A)	120.1
C(43)-C(44)-H(44A)	120.1
C(44)-C(45)-C(46)	120.2(3)
C(44)-C(45)-H(45A)	119.9
C(46)-C(45)-H(45A)	119.9
C(45)-C(46)-C(41)	120.7(3)
C(45)-C(46)-H(46A)	119.6
C(41)-C(46)-H(46A)	119.6
C(52)-C(51)-C(56)	118.4(3)
C(52)-C(51)-P(1)	122.2(3)

C(56)-C(51)-P(1)	119.4(2)
C(51)-C(52)-C(53)	120.8(3)
C(51)-C(52)-H(52A)	119.6
C(53)-C(52)-H(52A)	119.6
C(54)-C(53)-C(52)	120.4(4)
C(54)-C(53)-H(53A)	119.8
C(52)-C(53)-H(53A)	119.8
C(53)-C(54)-C(55)	119.4(3)
C(53)-C(54)-H(54A)	120.3
C(55)-C(54)-H(54A)	120.3
C(54)-C(55)-C(56)	120.2(4)
C(54)-C(55)-H(55A)	119.9
C(56)-C(55)-H(55A)	119.9
C(51)-C(56)-C(55)	120.8(3)
C(51)-C(56)-H(56A)	119.6
C(55)-C(56)-H(56A)	119.6
C(66)-C(61)-C(62)	120.2(6)
C(66)-C(61)-H(61A)	119.9
C(62)-C(61)-H(61A)	119.9
C(61)-C(62)-C(63)	119.9(5)
C(61)-C(62)-H(62A)	120.0
C(63)-C(62)-H(62A)	120.0
C(64)-C(63)-C(62)	118.3(5)
C(64)-C(63)-H(63A)	120.8
C(62)-C(63)-H(63A)	120.8
C(63)-C(64)-C(65)	121.1(5)
C(63)-C(64)-H(64A)	119.5
C(65)-C(64)-H(64A)	119.5
C(64)-C(65)-C(66)	120.2(5)
C(64)-C(65)-H(65A)	119.9
C(66)-C(65)-H(65A)	119.9
C(61)-C(66)-C(65)	120.2(6)
C(61)-C(66)-H(66A)	119.9
C(65)-C(66)-H(66A)	119.9

Symmetry transformations used to generate equivalent atoms:

APPENDIX B

Crystallographic information for RuHCl(CO)(IMes)$_2$ (14)

Crystals of **14** were grown from benzene. A suitable crystal was selected and mounted on a glass fibre and transferred to a Siemens (Bruker) SMART-1000 X-ray diffractometer. Data were collected at -50°C using Mo-Kα radiation, and structure solution (direct methods) and refinement (full-matrix least squares on F^2) were carried out using the SHELXTL suite of programs. (reference: SHELXTL Version 5.1, Bruker AXS Inc. Madison, WI, 2001.) The structure was solved in the monoclinic space group C2/c, and two independent half-molecules were solved in the unit cell: the Ru1 fragment sits upon an inversion centre and Ru2 on a mirror plane. In both cases all non-hydrogen atoms were refine anisotropically while H atoms were placed in geometrically reasonable positions and refined as riding atoms. Both Ru atoms have the same square planar coordination sphere: two IMes ligands, one chloride, and one carbonyl. Cl-CO disorder occurred in both molecules, and in order to reduce this effect Ru-C distances were restrained to 2.0Å, C-O distances to 1.2 Å and Ru-Cl distances to 2.45 Å. In the final stages of refinement $R^2 = 10.97\%$ and $R^1 = 3.27\%$.

Table B.1. Crystal data and structure refinement details for $RuHCl(CO)(IMes)_2$ (**14**)

empirical formula	$C_{22}H_{24}ClN_2ORu.1/18C_6H_6$	
formula weight	473.52	
temperature	213(2) K	
wavelength	0.71073 Å	
crystal system	monoclinic	
space group	*C*2/*c*	
unit cell dimensions	$a = 21.0039(14)$ Å	$\alpha = 90^\circ$
	$b = 21.0003(14)$ Å	$\beta = 109.4160(10)^\circ$
	$c = 19.5653(13)$ Å	$\gamma = 90^\circ$
volume	8139.2(9) $Å^3$	
Z	16	
density (calcd)	1.546 g/cm^3	
abs coeff	0.916 mm^{-1}	
F(000)	3867	
crystal size	0.35 × 0.30 × 0.20 mm^3	
θ range for data collection	1.41 to 25.00°	
index ranges	$-24 \leq h \leq 24$, $-24 \leq k \leq 24$, $-23 \leq l \leq 23$	
reflections collected	29632	
independent reflections	7176 [*R*(int) = 0.0220]	
completeness to $\theta = 25.00°$	99.9%	
absorption correction	none	
refinement method	full-matrix least-squares on F^2	
data/restraints/parameters	7176 / 9 / 540	
goodness-of-fit on F^2	1.079	
final R indices $[I > 2\sigma(I)]$	R1 = 0.0327, wR2 = 0.1002	
R indices (all data)	R1 = 0.0500, wR2 = 0.1097	
largest diff. peak and hole	0.387 and -0.479 e $Å^{-3}$	

Table B.2. Bond lengths [Å] and angles [deg] for RuHCl(CO)(IMes)$_2$ (**14**)

Ru(1)-C(8)	1.817(8)
Ru(1)-C(8)#1	1.817(8)
Ru(1)-C(1)	2.077(3)
Ru(1)-C(1)#1	2.077(3)
Ru(1)-Cl(1)#1	2.447(3)
Ru(1)-Cl(1)	2.447(3)
Cl(1)-O(8)	0.525(7)
Cl(1)-C(8)	0.631(6)
C(8)-O(8)	1.154(9)
N(1)-C(1)	1.364(3)
N(1)-C(2)	1.385(4)
N(1)-C(11)	1.449(3)
N(2)-C(1)	1.366(3)
N(2)-C(3)	1.382(4)
N(2)-C(21)	1.443(3)
C(2)-C(3)	1.330(5)
C(11)-C(16)	1.395(4)
C(11)-C(12)	1.400(4)
C(12)-C(13)	1.391(4)
C(12)-C(17)	1.507(4)
C(13)-C(14)	1.377(4)
C(14)-C(15)	1.386(5)
C(14)-C(18)	1.517(4)
C(15)-C(16)	1.384(4)
C(16)-C(19)	1.512(4)
C(21)-C(26)	1.397(4)
C(21)-C(22)	1.394(4)
C(22)-C(23)	1.394(4)
C(22)-C(27)	1.507(4)
C(23)-C(24)	1.384(5)
C(24)-C(25)	1.392(5)
C(24)-C(28)	1.526(5)
C(25)-C(26)	1.381(5)
C(26)-C(29)	1.504(4)

Ru(2)-C(10)	1.846(12)
Ru(2)-C(9)	1.841(11)
Ru(2)-C(5)	2.074(3)
Ru(2)-C(5)#1	2.074(3)
Ru(2)-Cl(2)	2.464(4)
Ru(2)-Cl(3)	2.454(6)
O(9)-C(9)	1.114(15)
C(10)-O(10)	1.149(17)
N(3)-C(5)	1.368(4)
N(3)-C(6)	1.380(4)
N(3)-C(31)	1.448(3)
N(4)-C(5)	1.369(3)
N(4)-C(7)	1.383(4)
N(4)-C(41)	1.441(3)
C(6)-C(7)	1.333(5)
C(31)-C(32)	1.389(4)
C(31)-C(36)	1.398(4)
C(32)-C(33)	1.391(5)
C(32)-C(37)	1.507(5)
C(33)-C(34)	1.385(5)
C(34)-C(35)	1.379(5)
C(34)-C(38)	1.528(5)
C(35)-C(36)	1.393(4)
C(36)-C(39)	1.498(4)
C(41)-C(42)	1.390(4)
C(41)-C(46)	1.401(4)
C(42)-C(43)	1.389(4)
C(42)-C(47)	1.512(4)
C(43)-C(44)	1.390(5)
C(44)-C(45)	1.383(5)
C(44)-C(48)	1.514(4)
C(45)-C(46)	1.381(4)
C(46)-C(49)	1.510(4)
C(101)-C(100)	1.35(3)
C(101)-C(102)	1.40(3)
C(100)-C(102)#2	1.34(2)

C(102)-C(100)#2	1.34(2)
C(201)-C(200)	1.33(4)
C(201)-C(202)	1.33(4)
C(202)-C(200)#3	1.44(4)
C(200)-C(202)#3	1.44(4)

C(8)-Ru(1)-C(8)#1	177.6(7)
C(8)-Ru(1)-C(1)	90.4(3)
C(8)#1-Ru(1)-C(1)	89.6(3)
C(8)-Ru(1)-C(1)#1	89.6(3)
C(8)#1-Ru(1)-C(1)#1	90.4(3)
C(1)-Ru(1)-C(1)#1	179.78(13)
C(8)-Ru(1)-Cl(1)#1	178.3(3)
C(8)#1-Ru(1)-Cl(1)#1	1.0(4)
C(1)-Ru(1)-Cl(1)#1	90.14(10)
C(1)#1-Ru(1)-Cl(1)#1	89.86(10)
C(8)-Ru(1)-Cl(1)	1.0(4)
C(8)#1-Ru(1)-Cl(1)	178.3(3)
C(1)-Ru(1)-Cl(1)	89.86(10)
C(1)#1-Ru(1)-Cl(1)	90.14(10)
Cl(1)#1-Ru(1)-Cl(1)	179.29(13)
O(8)-Cl(1)-C(8)	174.9(15)
O(8)-Cl(1)-Ru(1)	176.1(16)
C(8)-Cl(1)-Ru(1)	2.9(10)
Cl(1)-C(8)-O(8)	2.3(7)
Cl(1)-C(8)-Ru(1)	176.0(14)
O(8)-C(8)-Ru(1)	176.9(14)
Cl(1)-O(8)-C(8)	2.8(8)
C(1)-N(1)-C(2)	111.9(2)
C(1)-N(1)-C(11)	124.7(2)
C(2)-N(1)-C(11)	123.4(2)
C(1)-N(2)-C(3)	111.7(2)
C(1)-N(2)-C(21)	125.3(2)
C(3)-N(2)-C(21)	123.0(2)
N(1)-C(1)-N(2)	102.7(2)
N(1)-C(1)-Ru(1)	128.97(19)

N(2)-C(1)-Ru(1)	128.32(19)
C(3)-C(2)-N(1)	106.6(3)
C(2)-C(3)-N(2)	107.1(3)
C(16)-C(11)-C(12)	122.0(3)
C(16)-C(11)-N(1)	118.6(3)
C(12)-C(11)-N(1)	119.4(3)
C(13)-C(12)-C(11)	117.4(3)
C(13)-C(12)-C(17)	120.8(3)
C(11)-C(12)-C(17)	121.8(3)
C(14)-C(13)-C(12)	122.1(3)
C(13)-C(14)-C(15)	118.6(3)
C(13)-C(14)-C(18)	120.3(3)
C(15)-C(14)-C(18)	121.1(3)
C(16)-C(15)-C(14)	122.1(3)
C(15)-C(16)-C(11)	117.6(3)
C(15)-C(16)-C(19)	121.3(3)
C(11)-C(16)-C(19)	121.1(3)
C(26)-C(21)-C(22)	122.4(3)
C(26)-C(21)-N(2)	118.1(3)
C(22)-C(21)-N(2)	119.6(3)
C(23)-C(22)-C(21)	117.7(3)
C(23)-C(22)-C(27)	120.1(3)
C(21)-C(22)-C(27)	122.2(3)
C(24)-C(23)-C(22)	121.4(3)
C(23)-C(24)-C(25)	119.1(3)
C(23)-C(24)-C(28)	120.0(4)
C(25)-C(24)-C(28)	120.9(4)
C(26)-C(25)-C(24)	121.6(3)
C(25)-C(26)-C(21)	117.8(3)
C(25)-C(26)-C(29)	120.6(3)
C(21)-C(26)-C(29)	121.6(3)
C(10)-Ru(2)-C(9)	180.000(1)
C(10)-Ru(2)-C(5)	90.38(7)
C(9)-Ru(2)-C(5)	89.62(7)
C(10)-Ru(2)-C(5)#1	90.38(7)
C(9)-Ru(2)-C(5)#1	89.62(7)

C(5)-Ru(2)-C(5)#1	179.24(14)
C(10)-Ru(2)-Cl(2)	0.0
C(9)-Ru(2)-Cl(2)	180.0
C(5)-Ru(2)-Cl(2)	90.38(7)
C(5)#1-Ru(2)-Cl(2)	90.38(7)
C(10)-Ru(2)-Cl(3)	180.0
C(9)-Ru(2)-Cl(3)	0.0
C(5)-Ru(2)-Cl(3)	89.62(7)
C(5)#1-Ru(2)-Cl(3)	89.62(7)
Cl(2)-Ru(2)-Cl(3)	180.0
O(9)-C(9)-Ru(2)	180.0
O(10)-C(10)-Ru(2)	180.000(1)
C(5)-N(3)-C(6)	112.0(2)
C(5)-N(3)-C(31)	124.4(2)
C(6)-N(3)-C(31)	123.5(2)
C(5)-N(4)-C(7)	111.5(2)
C(5)-N(4)-C(41)	125.2(2)
C(7)-N(4)-C(41)	123.3(2)
N(3)-C(5)-N(4)	102.6(2)
N(3)-C(5)-Ru(2)	128.8(2)
N(4)-C(5)-Ru(2)	128.6(2)
C(7)-C(6)-N(3)	106.7(3)
C(6)-C(7)-N(4)	107.1(3)
C(32)-C(31)-C(36)	122.7(3)
C(32)-C(31)-N(3)	118.1(3)
C(36)-C(31)-N(3)	119.3(3)
C(33)-C(32)-C(31)	117.3(3)
C(33)-C(32)-C(37)	120.6(3)
C(31)-C(32)-C(37)	122.1(3)
C(34)-C(33)-C(32)	121.9(3)
C(35)-C(34)-C(33)	119.0(3)
C(35)-C(34)-C(38)	120.2(4)
C(33)-C(34)-C(38)	120.8(4)
C(34)-C(35)-C(36)	121.7(3)
C(35)-C(36)-C(31)	117.4(3)
C(35)-C(36)-C(39)	120.3(3)

C(31)-C(36)-C(39)	122.3(3)
C(42)-C(41)-C(46)	122.0(3)
C(42)-C(41)-N(4)	118.5(3)
C(46)-C(41)-N(4)	119.5(3)
C(41)-C(42)-C(43)	117.9(3)
C(41)-C(42)-C(47)	121.3(3)
C(43)-C(42)-C(47)	120.8(3)
C(42)-C(43)-C(44)	121.7(3)
C(45)-C(44)-C(43)	118.4(3)
C(45)-C(44)-C(48)	121.0(3)
C(43)-C(44)-C(48)	120.7(3)
C(46)-C(45)-C(44)	122.3(3)
C(45)-C(46)-C(41)	117.7(3)
C(45)-C(46)-C(49)	120.7(3)
C(41)-C(46)-C(49)	121.6(3)
C(100)-C(101)-C(102)	120.4(16)
C(102)#2-C(100)-C(101)	121.3(18)
C(100)#2-C(102)-C(101)	118.2(18)
C(200)-C(201)-C(202)	122(2)
C(201)-C(202)-C(200)#3	123(2)
C(201)-C(200)-C(202)#3	115(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2 #2 -x-1/2,-y-1/2,-z+1 #3 -x+1/2,-y-1/2,-z+1