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The Alkylation of Aromatic Amines

by

Kelly Ann Walsh

A thesis submitted to the School of Graduate Studies

in partial fulfillment of the requirements for the

degree of

MASTER of SCIENCE

in the Department of Chemistry

University of Ottawa

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To Antoine
and
my Family

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ABSTRACT

N-alkylated anilines can be obtained in moderate yields from aniline and methyl formate in the presence of $Rh_6(CO)_{16}$ and KI after 72 hours at 180-200°C. $Ru_3(CO)_{12}$ gave similar results to the unpromoted rhodium carbonyl system. Formanilide and N-methylformanilide were also formed in the reaction. The $[HCr(CO)_5]^-$ anion in the form of its PPN^+ and Et_4N^+ salts also catalysed this reaction (under hydrogen) but was selective to the formanilide products. The presence of an electron donating group on the aromatic ring favoured the formation of alkylated products in the presence of bis(triphenylphosphine)iminium (PPN^+) hydridochromiumpentacarbonyl. Several possible mechanisms were tested and the nature of the polynuclear catalysts investigated.

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LIST OF ABBREVIATIONS

acac	acetoacetonate
atm	atmosphere
BASF	Badische Anilin und Soda-Fabrik
Bu	butyl
dct	dibenzocyclooctatetraene
Et	ethyl
GC	gas chromatography
IR	infrared spectroscopy
M	metal centre
Me	methyl
MPa	megapascal
MS	mass spectrometry
m/z	mass per charge
NMP	N-methylpyrrolidone
NMR	nuclear magnetic resonance
(o)	oxidation
OAc	acetate
OBz	benzoate
OHpy	hydroxypyridine
Ph	phenyl
PMR	proton magnetic resonance (ie. ^{1}H NMR)
PPN	(triphenylphosphine)iminium

psi	pounds per square inch
TG	tetraglyme
THF	tetrahydrofuran
tlc	thin layer chromatography

1. INTRODUCTION

1.1. General Introduction

Transition metal complexes are increasingly being used in synthetic organic chemistry.[1,2] Their utility in the activation of simple molecules, such as carbon monoxide, as well as larger organic compounds continues to be of interest to the industrial chemist. The changing electronic nature of the molecule upon complexation increases its susceptibility to other reagents, and possibly increases the regioselectivity of the reaction with a substrate. Coordination of the substrate can also change its geometry, thus exposing specific sites for the reaction.

The reaction involving a transition metal complex can be stoichiometric, that is, employing a 1:1 or greater mixture of the metal species and the reagents, or it may be catalytic. The term catalytic used to describe a system for which the ratio of the reagent to the metal complex is greater than one and although it may participate in the reaction overall the catalyst is left unchanged by it. The catalyst aids the reaction by improving its kinetics but does not alter the thermodynamics of the reagents. The metal species is often used in stoichiometric amounts to model the corresponding catalytic systems. It is impossible to know with complete certainty the mechanism of a catalytic reaction, but the stoichiometric equivalent of the reaction may be studied to gain further insight. The stoichiometric reaction can also be useful in its own right for the design of syntheses.

The fact that the catalyst remains unchanged by the reaction leads to the idea

of a cycle, that is, a system in which the active species complexes with the substrate which is modified and released. Thus, the active metal species is available for further reactions after the first products appear and, theoretically, will continue to react as long as there are starting materials present. In practice, the catalysts are often poisoned by chemicals such as sulphur and phosphines and may decompose slowly under the reaction conditions.

In the past, industrial catalytic systems have been heterogeneous, that is, the catalytic species is in a different phase than the reaction mixture. The active species may interact in the form of a colloid or of a larger surface. The main industrial interest in these catalysts is their ease of separation from the reaction products and thus their recovery for further reactions. The generality of the heterogeneous catalyst, as evidenced by the ubiquitous use of platinum metal in various forms, has also been an advantage. However, with the increased demand for high purity chemicals, and with increased difficulty in the disposal of unwanted by-products, generality may be viewed as a liability.

Drastic conditions are often necessary for systems which are heterogeneous. As well, inherent in these systems is a loss of efficiency as only the top monolayer is active. This problem is at least partially alleviated by the use of colloids of, or supports for the metal. The chemistry at the surface of these catalysts is not well understood and thus, as a consequence, neither are the mechanisms.

The need for greater selectivity and purity of the final products has led to developments in homogeneous catalytic systems. Each metal atom is potentially an active site, therefore increasing the system's efficiency. Spectroscopic studies of the solution are possible and intermediates of the reactions are frequently isolated. This evidence can help to establish at least part of the catalytic cycle. Also with a greater understanding of the reaction mechanism comes greater ease in design of other

catalytic systems with specific requirements. Further, harsh conditions can be undesirable as many of these catalysts are prone to decomposition under harsh conditions. A further asset for the homogeneous system is the possibility of heat dispersal by the solvent during an exothermic reaction, therefore helping to maintain a milder environment than exists in a heterogeneous process.

1.2. Metal Cluster Chemistry

Cluster compounds differ from polynuclear coordination complexes in that they contain metal-metal bonds which have a significant effect on their physical and chemical properties. Although several such compounds were characterized during the first half of this century, it wasn't until the 1960's that the significance of the metal-metal bond was recognized and a new class of compounds emerged.[3]

The bonding in smaller clusters of less than five metal atoms can be explained by the same rules as for coordination compounds, that is, the eighteen electron rule. However, this rule breaks down for larger clusters. Attempts to explain the bonding in clusters with six or more atoms have included the use of comparisons to borane clusters. This technique considers that the cluster is made up of a series of similar mononuclear species, for example, $M(CO)_n$, for which the bonding is understood. Of the nine orbitals of each unit, six would be used for metal-ligand bonding leaving three for skeletal bonding.[4] And, of the three skeletal orbitals, two may be considered to make up "surface" bonds of the polyhedron while the one left points towards the centre of the polyhedron, forming a strong bond at the centre of the cluster.[3] Changes in the geometry of the cluster influence the number of skeletal electron pairs.[4]

There has been interest in recent years in the use of multinuclear catalysts,

metal clusters, as models of heterogeneous systems. Comparisons have been made between the surface behaviour of a metal and the cluster. It was found that, in some cases, the energy of adsorption of carbon monoxide on a metal surface is similar to the M-C bond energy of a metal carbonyl cluster. Also, the photoelectron spectra of an M_3 or M_4 carbonyl species are almost identical to the spectra of CO adsorbed on the surface of their respective metal surfaces. Further, the structure of adsorbed acetylene on a platinum(III) or rhodium(III) surface is the same as the as the corresponding trinuclear ethylidene clusters.[5] These species do tend to be easier to study than their heterogeneous counterparts.

The metal cluster catalyst may offer some distinct advantages over a mononuclear one. The electronic and steric changes in the substrate on complexation with a cluster can be markedly different than those by mononuclear metal species. These changes can lead to enhanced reactivity towards a nucleophile, electrophile, *etc.* Also, the binding of an organic species to more than one metal centre at a time or the transfer of electrons from two or more metal atoms to one substrate molecule would change the electron density and reactivity of the organic moiety drastically. Fragmentation of the substrate onto different metal atoms and the migration of a ligand from one metal centre to another can also be advantageous to the system. The formation of a metal-metal bond can provide the impetus for a reaction such as the departure of the modified organic substrate.

There has been some controversy as to whether these catalysts actually survive under the harsh reaction conditions of some processes. It is possible that the active species is not the cluster but rather a metal surface or colloid which would result from the degradation of the cluster species.[6] Nonetheless, several cases of true cluster catalysis have appeared in the literature.[7] An example is the formation of propion-aldehyde from the hydroformylation of ethylene which is catalysed by the $[HRu_3$-

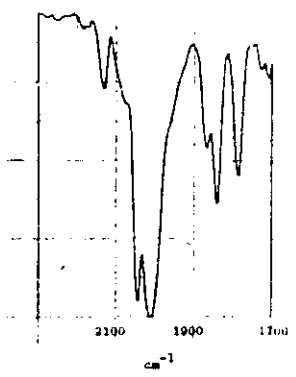
$(CO)_{11}]^-$ anion. Deuterium labelling showed that the cluster remains intact during the reaction. Also, an intermediate of the reaction, $DRu_3(CO)_{10}(COCH_2CH_3)$, was trapped via Equation **1**.[8]

$$HRu_3(CO)_{11}^- \xrightarrow{C_2H_4} HRu_3(CO)_{10}(COEt)^- \xrightarrow{D^+} DRu_3(CO)_{10}(COEt)^- \qquad (1)$$

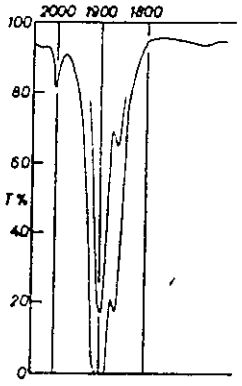
The cluster may not remain intact but may fragment, or catenate, yet the active species could still be a cluster which is dissolved in the reaction medium.[9,10] Rhodium complexes have been used as such precursors for the synthesis of polyols such as ethylene glycol as well as ethanol and methanol.[9,10,11] It was found that the system which included $Rh(CO)_2acac$, cesium benzoate and 2-hydroxypyridine in a solution of N-methylpyrrolidone-tetraglyme under 86 MPa CO/H_2 (1:1) gave good yields of methanol and ethylene glycol after four hours at 503K.[9] There have been

$$CO/H_2 \xrightarrow[\text{2-OHpy / NMP / TG}\\ \text{CsOBz / 503K / 4h}]{Rh(CO)_2acac,} CH_3OH + CH_3CH_2OH + HOCH_2CH_2OH \qquad (2)$$

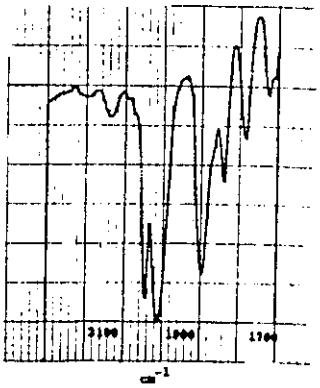
several studies on the nature of the active catalytic species in this reaction.[9,10] The rhodium cluster $[Rh_5(CO)_{15}]^-$ has been invoked as the active catalyst being the only species detected by high-pressure FT-IR at 60.0 MPa and 503K (Equation **2**).[9] This assignment was based on work by Chini et al.[12,13] who found that the CO stretching frequencies for $PPN[Rh_5(CO)_{15}]$, in THF, were: 2045(s), 2010(vs), 1868 (m), 1838(ms) and 1735(ms) ± 10 cm^{-1} (Figure **1**a). Vidal and Walker[10] found that, for a similar system with sulfolane as the solvent, the only species detected up to 180-210°C and 500-1000 atm were $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ (CO stretching frequency at 1895 cm^{-1}, c.f. reference 14). This spectrum is also shown in Figure **1** along with spectra of the two species for comparison. Increasing the temperature



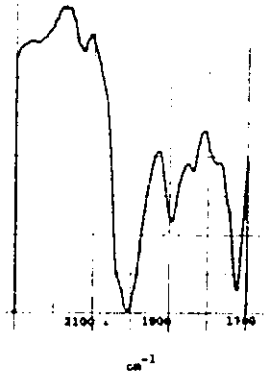
a) $[Rh_5(CO)_{15}]^-$



b)$[Rh(CO)_4]^-$



c) $Rh(CO)_2acac$, $CsPhCO_2$ and NMP in sulfolane at 100-180°C.



d) $Rh(CO)_2acac$, $CsPhCO_2$ and NMP in sulfolane at 250-270°C.

Figure 1: IR Spectra of : a) $[Rh_5(CO)_{15}]^-$; b) $[Rh(CO)_4]^-$ and c) and d): a mixture of $Rh(CO)_2acac$, $CsPhCO_2$ and N-methylpyrrolidone in sulfolane under CO/H_2 (1:1) at c) 100-180°C and d) 250-270°C.

a), c) and d) Taken from J.L. Vidal, W.E. Walker, *Inorg. Chem.*, 1980, 19, 896

b) Taken From P. Chini, S. Martinengo, *Inorg. Chim. Acta*, 1969, 3, 21

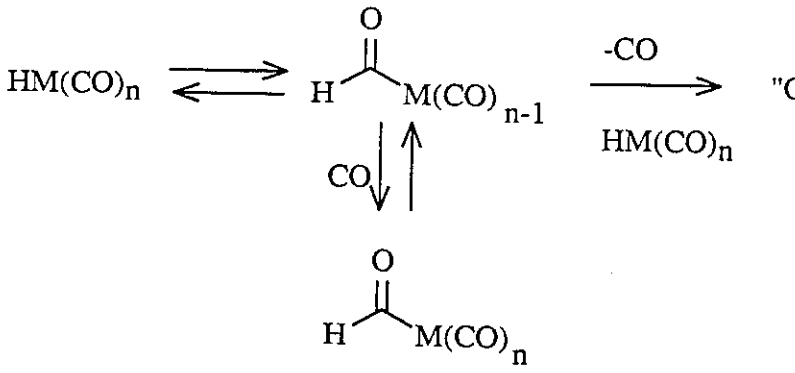
beyond this point broadened the signals and decreased the intensity of the signal attributable to $[Rh(CO)_4]^-$. As catalytic activity was optimum at higher temperatures, and corresponded to a decreased signal for the mononuclear species, it can be assumed that the active catalyst was a cluster such as $[Rh_5(CO)_{15}]^-$ or higher aggregates which would have similar CO stretching frequencies (for example, $[Rh_{13}(CO)_{24}H_3]^{2-}$ with stretching at 2020 and 1845cm^{-1}, c.f. reference 10). The initial spectrum, that is consisting of $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$, was obtained upon cooling the system back down to 180-210°C. This behaviour was the same for other precursors such as $[Rh_m(CO)_n]^{x-}$and $Rh_m(CO)_n$, for example, $Rh_6(CO)_{16}$.[10]

1.3. CO Hydrogenation

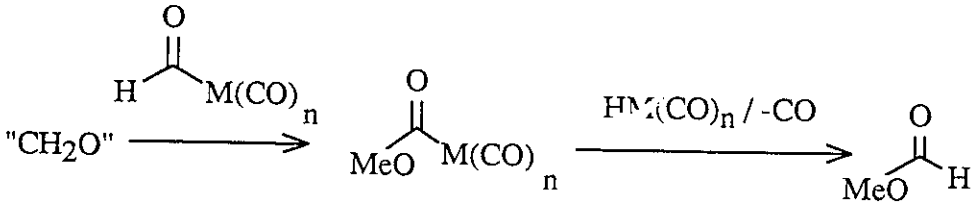
The first attempts to hydrogenate carbon monoxide were carried out heterogeneously at the turn of the century by Sabatier and Senderens, who were reported to have produced methane from carbon monoxide and hydrogen over nickel.[15] Researchers at BASF and Fischer and Tropsch, amongst others, later found that catalysts like alkalized iron, cobalt and compounds containing zinc, could be used to produce hydrocarbons (typically C_4 to C_{10}) and oxygenates (methanol, ethylene glycol, methyl formate, methyl acetate, *etc.).* The pressures of World War II increased interest in the so-called "Fischer-Tropsch" process as fuels were in high demand but this waned after the war as petroleum products became more available. The oil crisis of the early 1970's stimulated investigations of this reaction.[15] Unfortunately, its lack of selectivity limited its usefulness.

The use of CO as a C_1 building block in organic synthesis has broadened interest in the Fischer-Tropsch reaction. An increase in the price of petroleum based

feedstocks such as ethylene, as well as a threatened supply, during the last oil crisis were incentives to develop better catalytic systems for the use of synthesis gas, a mixture of CO and H_2, as an alternative feedstock. Research continues in this field because of interest in a secure supply of starting materials for industry in the future.[16,17] Further, the production of oxygenates like those from this process, e.g. ethylene glycol, continues to be of industrial interest.



(3)



(4)

It was found, in the 1950's, that oxygenated products, for example, ethylene glycol and its formate, could be obtained from CO/H_2 mixtures using cobalt complexes, in an apparently homogeneous system under high pressure and relatively high temperatures.[11] Several reports have pointed out the tendency of homogeneous CO hydrogenation processes to yield oxygenates with little or no production of hydrocarbons.[6,18] There have been a number of mechanisms proposed for these homogeneous reactions. Many invoke the formation of a metal-formyl intermediate

from CO insertion into a metal-hydride bond; or a hydride migration onto a coordinated CO.[11,19] There has been some debate as to whether the formaldehyde in the mechanism is "free" or complexed or even if it is actually an intermediate. However, it has been shown that paraformaldehyde, a stable form of formaldehyde, does give a product distribution similar to that of synthesis gas.[20] In the mechanism shown, Equations **3** and **4**, the formation of methyl formate, one of the secondary products of the homogeneous Fischer-Tropsch reaction, is outlined.[11] This compound has been proposed as a source of "activated" CO,[21] being somewhat more stable than the formaldehyde, and thus it was used as a reagent in the research to be described in this thesis.

1.4. Uses of Alkylated Anilines

The main products of the research to be discussed are N-methylaniline and N,N-dimethylaniline; the latter being of greater industrial value. Nonetheless, both amines are used in industry for the production of dyes and dye intermediates. Michler's hydrol, and its analogues are such intermediates used in a variety of dye syntheses. The result of a synthesis of methyl violet from Michler's hydrol is usually a mixture of methyl violet, ***1***, and crystal violet, ***2*** (Figure **2**). Michler's hydrol, ***3***, not only reacts with the N-methylaniline but also with the available N,N-dimethylaniline. To avoid this problem, it is possible to convert the excess N,N-dimethylaniline to N-methylaniline using copper sulphate.[22]

N,N-Dimethylaniline is also used in conjunction with benzoyl peroxide as a promoter for the curing of polyester resins.[23,24] The resins are used in autobody repair kits and other applications for which a discoloured appearance is unimportant.[23,25] A further use for N,N-dimethylaniline has been as a solvent for the

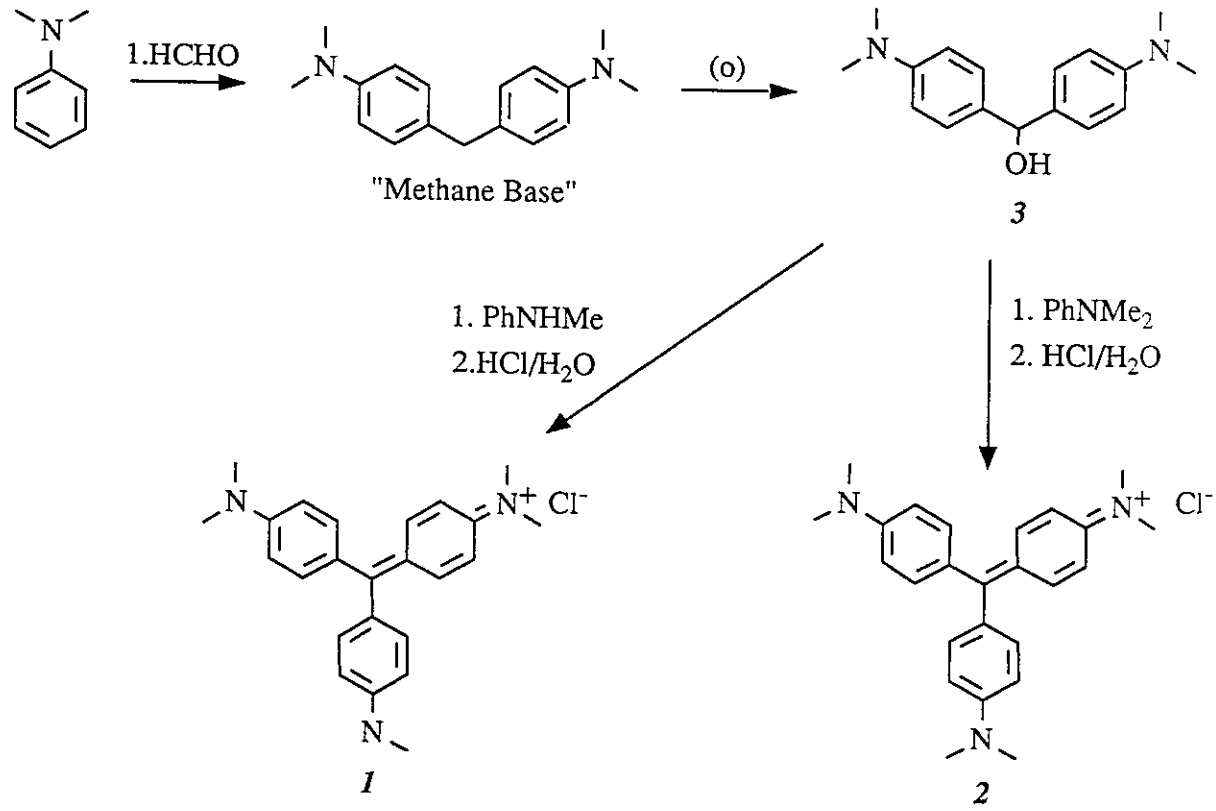
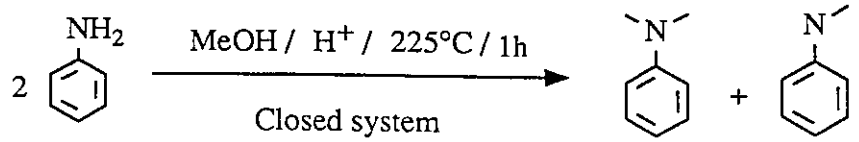


FIGURE 2 The Synthesis of Methyl Violet (*1*) and Crystal Violet (*2*) via N,N-Dimethylaniline and N-Methylaniline.

recovery of $SO_{2(g)}$ wastes and their conversion to $SO_{2(l)}$.[26] N-methylaniline has been used as a starting material for the production of stabilizers and plasticisers for explosives. For example, it has been used, with phosgene, to synthesize N-ethyl-N'-methyl-N,N'-diphenyl urea, one of the components of "Centralite", a stabilizer of smokeless powders.[27]

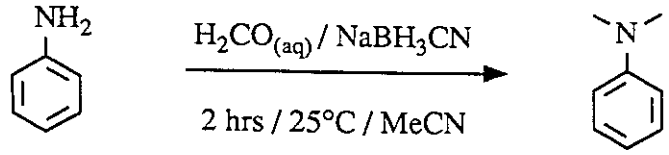
1.5. Previous Syntheses of Alkylated Anilines

The main route to these amines is the methylation of aniline using methanol. The reaction (Equation **5**) is catalysed by an acid such as sulphuric or hydrochloric acid. A mixture of the two amines is produced, the product ratios varying with the concentration of the catalyst, the type of acid used, the temperature, and to some extent pressure of the system.[28]



(**5**)

N,N-Dimethylaniline and N-methylaniline have been synthesized using several organic reagents. For example, a cyanoborohydride anion was used to



(**6**)

catalyse the reaction of aniline with formaldehyde as can be seen in Equation **6**. The yield of N,N-dimethylaniline was quite good (92%) with the reaction conditions being mild and the reaction time fairly short. The best solvent for this system was found to be acetonitrile.[29]

A second method for preparing N-methylaniline uses a trialkyl ortho-carboxylate in combination with aniline (see Figure **3**) with the initial reaction being catalysed by sulphuric acid at 140°C. The alcohol by-product is distilled off and the reaction is continued at 175-180°C giving the N-alkylformanilide, (61% yield for trimethyl orthocarboxylate). Hydrolysis of the formanilide with 10% HCl gives the N-alkylaniline. The authors attributed the low yield of N-methylaniline (44%) to incomplete hydrolysis of the formanilide.[30]

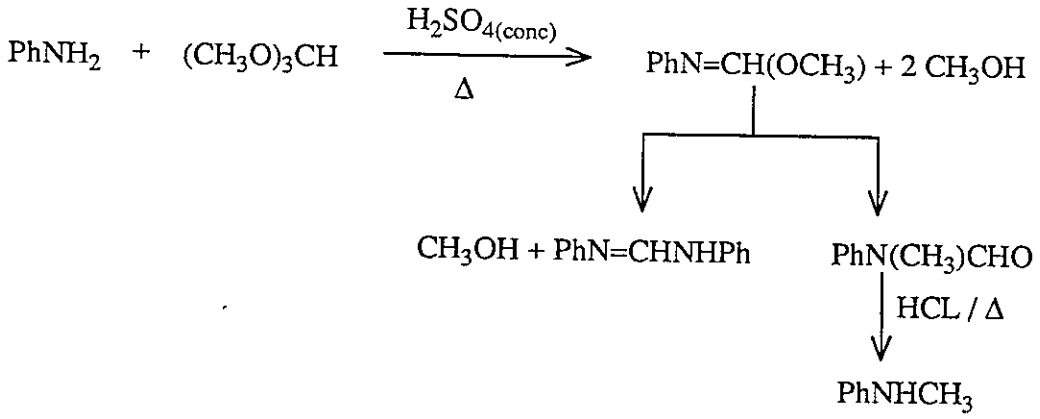
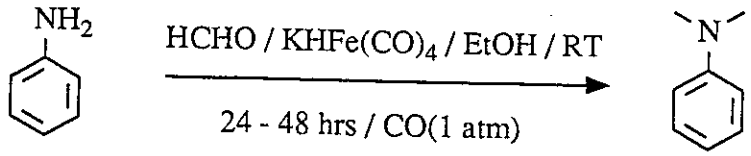


Figure 3 An Alternative Synthesis of N-methylaniline via Aniline and Trimethyl Orthocarboxylate

N-Methyl- and N,N-dimethylaniline have also been synthesized using stoichiometric amounts of a metal complex, potassium hydridotetracarbonyl ferrate, which was produced *in situ.* The system included formaldehyde, a base (i.e. potassium hydroxide), aniline and carbon monoxide (1atm) with iron pentacarbonyl, the catalyst precursor (Equation 7). The reaction proceeded at room temperature with a yield of 91% N-methylaniline (5-10 hrs).[31] If the reaction was allowed to continue for 24-48 hours, the dimethylated amine was produced in almost quantitative yields. It was proposed that the mechanism involved the formation of an imine which was subsequently reduced by the metal species to give the alkyl amine. The fact that the reduction of N-benzylideneaniline proceeded to the expected N-benzylaniline with this metal species supports this proposition.[32]



(7)

Attempts to find a catalyst have been less successful. Watanabe et al.[33]

describe a reaction of aniline with methanol which gives low yields of N-methyl-aniline and N,N-dimethylaniline (12 and 1%, respectively) with the catalyst $RuCl_2(PPh_3)_3$ at 180°C even with 2% (mol) of the metal species after five hours.

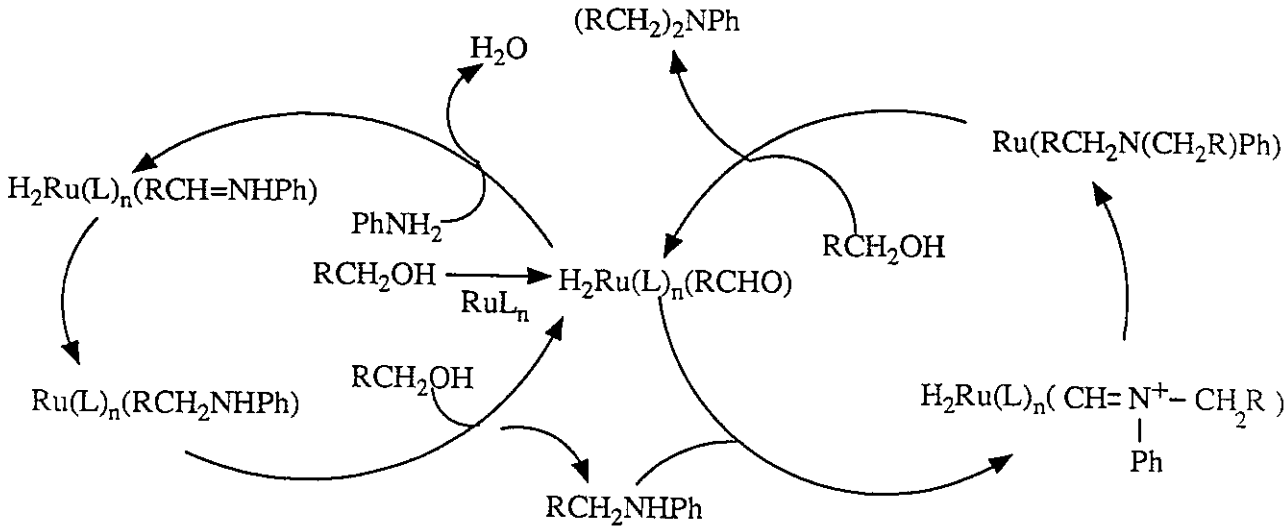


Figure 4: The Synthesis of Alkylanilines from Aniline and an Alcohol

Better results were obtained with larger alcohols; for example, ethanol under the same conditions had a similar conversion but the yield of N-ethylaniline was 53% while that of N,N-diethylaniline was 7%. The authors suggested that the reaction was stepwise and that it followed the scheme pictured in Figure 4. The reductive amination of carbonyl compounds is considered to occur via the formation of a Schiff base (imine) which is then reduced. In this case the reduction occurs via a hydride transfer from the metal. The catalytic reaction of aniline with methanol has been

slightly improved by Jenner and Bitsi.[34] A 15% yield of N-methylaniline and a 3% yield of the dialkylated product was obtained when $RuCl_3 \cdot 3H_2O$ (0.075 mmol) was used at 200°C for 2 hours. The main goal of these authors' research was the synthesis of formamides and this they proposed occurred via the formation of methyl formate from methanol and carbon monoxide which subsequently reacted with aniline via a nucleophilic substitution to give the amide. The synthesis of alkylanilines was incidental and the mechanism of Watanbe, et al., in Figure **4** was invoked to explain their appearance. That is, the dehydrogenation of methanol to formaldehyde followed by the formation of an acylruthenium intermediate.[34]

The following will be a description of our attempts to find a better catalytic system for the exclusive synthesis of one or the other of these amines and to gain a better understanding of the mechanism involved.

2. DEVELOPMENT OF A CATALYTIC SYSTEM

2.1. Reactions Catalysed by $Rh_6(CO)_{16}$

The research discussed herein may be divided into two sections. The first will discuss the development of a catalytic system for the alkylation of aromatic amines using a rhodium carbonyl cluster or hydridochromiumpentacarbonyl anion (refer to Equation (**8**)). An investigation of the mechanism involved as well as the scope of these reaction will be considered later in Section 3.

$$4\ PhNH_2 \xrightarrow[HCO_2Me\ /\ 180°C\text{-}200°C\ /\ 72h]{Rh_6(CO)_{16}\ or\ [HCr(CO)_5]^-} PhNHMe + PhNMe_2 + PhNHCHO + PhNMeCHO \quad (8)$$

For the most part, the conditions for the reaction were previously determined by another in our laboratory and these results are presented in Table IA. Several reactions were repeated and gave values within 5%. The optimum temperature was found to be in the range 180°C to 220°C.[35] This value is only slightly lower than the temperature necessary for the industrial conversion of aniline to dimethylaniline which was established to give the best results at 225°C with acid catalysis.[28] The reaction time was established to be three days as the results of experiments with shorter reaction times gave unsatisfactory yields of the alkylated products. A reaction time of eighteen hours gave mostly the formanilide with a moderate amount of

TABLE IA: Development of a Catalytic System: The Determination of Reaction Conditions with $Rh_6(CO)_{16}$ as Catalyst.[a,b,c]

ENTRY No.	CONDITIONS	$PhNH_2$ (%)	PhNHMe (%)	$PhNMe_2$ (%)	PhNHCHO (%)	PhNMeCHO (%)	COMMENTS
1	210°C 70h	14	8	15	19	42	Standard Reaction; Unidentified products (2)[d]: 2%
2	190°C 18h	4	1	2	71	22	
3	210°C 68.5h	9	5	6	38	42	Purged with N_2
4	190°C 72.5h	10	4	8	20	35	N_2 pressure: 100 psi; Unidentified products (2): 23%
5	205°C 73h	1	3	12	26	38	CO pressure: 100 psi; Unidentified products (2): 20%
6	215°C 72h	10	8	6	19	39	Syngas Pressure: 105 psi; Unidentified products (3): 18%
7	210°C 72h	6	5	7	7	23	H_2 Pressure: 100 psi; Unidentified products (3): 52%
8	200°C 70.5h	5	3	8	18	26	$Rh_6(CO)_{16}$ (0.11 mmol); Unidentified products (2): 40%
9	200°C 67h	12	3	5	33	24	HCO_2Me (58 mmol); Unidentified products (3): 23%
10	210°C 72h	40	13	3	10	9	*i*-PrOH (1.0 mL) was used as a solvent; Unidentified products (5): 25%

a) Taken from reference 35

b) Reagents: $PhNH_2$ (10 mmol); HCO_2Me (19 mmol); Catalyst: $Rh_6(CO)_{16}$ (0.05 mmol) unless otherwise noted.

c) These reactions were carried out without a glass insert and the data was not corrected for response factors.

N-methylformanilide (Entry 2) while at seventy hours there was a marked decrease in the proportion of formanilide and a twofold increase in N-methylformanilide (Entry 1). There was also a large increase in N-methylaniline and N,N-dimethylaniline (1% and 2% versus 8% and 15%, respectively).[35] This was similar to results obtained by Watanabe et al. who found that prolonging the reaction time favoured the formation of diethylaniline and who concluded that N-alkylation in their system was stepwise.[33] If the system of Jenner and Bitsi[34], mentioned in section 1.5, operated under the same mechanism as that of Watanabe et al.[33], it seems likely that an increased reaction time would result in a greater proportion of alkylated products.

Changing the amount of catalyst in the reaction did not increase its selectivity towards N,N-dimethylaniline or N-methylaniline. As can be seen from Table IA, Entry 8, the proportion of these two products in the reaction mixture actually decreased with about a twofold increase in catalyst concentration while the activity of the reaction was only slightly improved.[35]

Several different gases were studied for their effects on this system. It was found that the presence of nitrogen enhanced the production of formamides at the expense of alkylated products (Entry 3), and to some extent, the activity of the system. Higher pressures of nitrogen, 100 psi versus simply purging the reaction vessel, had similar results (Entry 4). Carbon monoxide (Entry 5) and synthesis gas (Entry 6) slightly suppressed the formation of alkylated products and increased the reaction's activity and amide formation. It was noted by Jenner and Bitsi[34] that carbon monoxide pressure had an effect on the selectivity of a similar reaction involving methanol and aniline. They found that this reaction under carbon monoxide, with ruthenium chloride as the catalyst, produced more formamide at higher pressures while at lower pressures alkylation of the amino group was favoured. However, they were using much higher pressures of carbon monoxide than were used

for the current system, the lowest of these was 1.6 times greater than those tried in the present system. Hydrogen also affected the selectivity of the reaction towards alkylated products (Entry 7). The only significant difference from the results with the other gases was the large proportion of an unidentified product produced and the small amount of formanilide detected.[35] Because the gases mentioned did not have a beneficial effect on the system, the reactions were carried out without purging. An exception was the system involving the hydridochromiumpentacarbonyl anion, which will be discussed later in this Section. This metal species, being moisture and air sensitive, necessitated that the reaction vessel be purged of air. Hydrogen was chosen because it produced the least amount of amide product for those reactions including $Rh_6(CO)_{16}$.

The previous work carried out in our laboratory did not provide a suitable solvent for this system. The solvent considered was *iso*-propanol which was used previously in similar reactions. However, it was found that this species inhibited the reaction, lowering its selectivity towards N,N-dimethylaniline and N-methylformanilide (Entry 10) but slightly enhancing the formation of N-methylaniline. The large number of unidentified products leads one to wonder whether the alcohol was participating in the reaction to give, for example, N-*iso*-propylaniline. Work by Watanabe, et al., revealed that this alcohol did react with aniline in their catalytic system.[33] Any search for a solvent for the present system is hindered by the low solubility of the catalyst and possible side reactions of the solvent with aniline or methyl formate. Several other groups have used one of their reagents as the solvent. For example, Watanabe, et al.[33] and Jenner and Bitsi[34] used higher alcohols and methanol, respectively, for both solvent and reagent. Laine, et al.[21] used formamides, like N-methylpiperidine, in the same role. However, it was found that in the present system, an approximately sixfold excess of the formate decreased the selectivity of the reaction

towards the alkylated products including N-methylformanilide (Entry 9).[35] This decrease was accompanied by an enhanced yield of formanilide and unidentified products. Further, Jenner and Bitsi discovered that the use of aprotic solvents, like dioxane, lowered the extent of conversion in their system. This effect was attributed to dilution.[34]

Migratory reactions are often aided by solvents which are good donors and in some cases, the solvent effect is quite marked. The addition of a nucleophile to methylmanganese pentacarbonyl showed a very strong solvent dependence. A difference in the reaction rate of 10^4 between mesitylene and dimethylformamide was observed which could not be fully accounted for by the differences in the dielectric constant. The authors speculated that the migration involves the methyl group and that attack of the donor solvent is needed during the migration, therefore, the reaction involves "solvent catalysis".[36] Their work was supported by a study of migratory carbon monoxide insertions performed by Wax and Bergman[37] who found that there was a marked difference in the rate constants for the insertion of a CO ligand into the metal-alkyl bond of cyclopentadienyltricarbonyl(alkyl)molybdenum for a series of substituted tetrahydrofurans. While the dielectric constants for these solvents are similar, the rate constant attributed to insertion decreases in the order: THF > 2-MeTHF > 3-MeTHF > 2,5-Me_2THF. Thus the differences in the rate constants are probably due to steric hindrance experienced during solvent coordination.

A further example of the importance of the solvent in migratory insertions is the hydroformylation of formaldehyde to give glycolaldehyde which is selective to the aldehyde only if tertiary amides, such as dimethylformamide, are used as the solvent. The proposed mechanism involves the coordination of the solvent through the oxygen, to replace the migratory species, which are carbon monoxide and hydrogen.[38]

If the metal hydride species undergoes hydrogen transfer in the present

TABLE 1B: Development of a Catalytic System: Promoted Reactions Catalysed by $Rh_6(CO)_{16}$.[a]

RXN No.	$PhNH_2$ (%)	PhNHMe (%)	$PhNMe_2$ (%)	PhNHCHO (%)	PhNMeCHO (%)	COMMENTS
1	59	11	trace	11	19	Standard reaction for comparison
2[b]	4	3	4	81	6	Solvent: $Me_2NCONMe_2$: 7.2mL; Unidentified Product[c]: 2%
3[b]	1	2	13	60	24	Promoter: KI (0.3 mmol); H_2 pressure: 120 psi.
4[b]	5	1	5	66	23	Promoter: KI (0.9 mmol); H_2 pressure: 120 psi; Internal std.: *p*-xylene; Conversion: 86%
5	3	5	45	4	38	Promoter: KI (3 mmol); Unidentified Product: 5%
6	3	10	32	11	39	Promoter: KI (0.3 mmol); Unidentified Products(2): 5%
7[b]	3	2	24	43	13	Promoter: KI (0.9 mmol); Unidentified products(2): 15%

a) Reaction conditions: $PhNH_2$(10 mmol), HCO_2Me (20 mmol); catalyst: $Rh_6(CO)_{16}$(0.05 mmol); temperature: 180-200°C; reaction time: 72h.

b) A glass sleeve was introduced into the reaction vessel. The reagent amounts were adjusted accordingly. Refer to Experimental Section 6.2 for details.

c) The number of unidentified products observed is given in brackets and percentage is of reaction mixture.

system, then a donor solvent such as an amide should enhance alkylation not only

through the ability of the metal to refill its coordination sphere but also through support of any anionic metal species in solution. The use of excess methyl formate as the solvent was precluded, as was discussed earlier. Thus the test solvent tetramethylurea was chosen because as an amide, it is a good donor and there is no possibility for side-reactions at the carbonyl groups or nitrogen. The results, shown in Table IB, entry 2, indicated that the solvent, and probably other similar solvents, was ineffective. While the proportion of reacted aniline increased with the use of tetramethylurea, the selectivity of the reaction towards alkylated products was diminished. Indeed, there was a marked increase in the amount of formanilide produced. It should be noted that the formanilide would be expected even if no catalyst were present. As there was no success with this solvent no further attempts were made to find one. There was little problem with solubility and no precipitation of the catalyst (or decomposition products) for reactions involving the hydridochromiumpentacarbonyl anion.

During the development of the reaction system under discussion, the use of a promoter, the iodide ion, was considered. This ion is a good nucleophile, a good leaving group, a weak base and is known to form complexes with the platinum group metals. It has been shown that salts containing iodide promote several other systems for which a rhodium complex is a catalyst. Of these systems, probably the best known is the Monsanto acetic acid synthesis (Figure 5).[39] The fact that iodide is known to activate Rh(I) to oxidative addition was exploited in this synthesis whose initial step is the formation of methyl iodide from methanol and HI. The active catalyst is formed *in situ* from a soluble rhodium complex such as $RhCl_3 \cdot 3H_2O$ along with CO and the iodide ion. Methyl iodide oxidatively adds to the active metal species and then the intermediate isomerizes via a CO insertion into the metal-alkyl bond to give a 5-coordinate complex. The addition of a further CO completes the

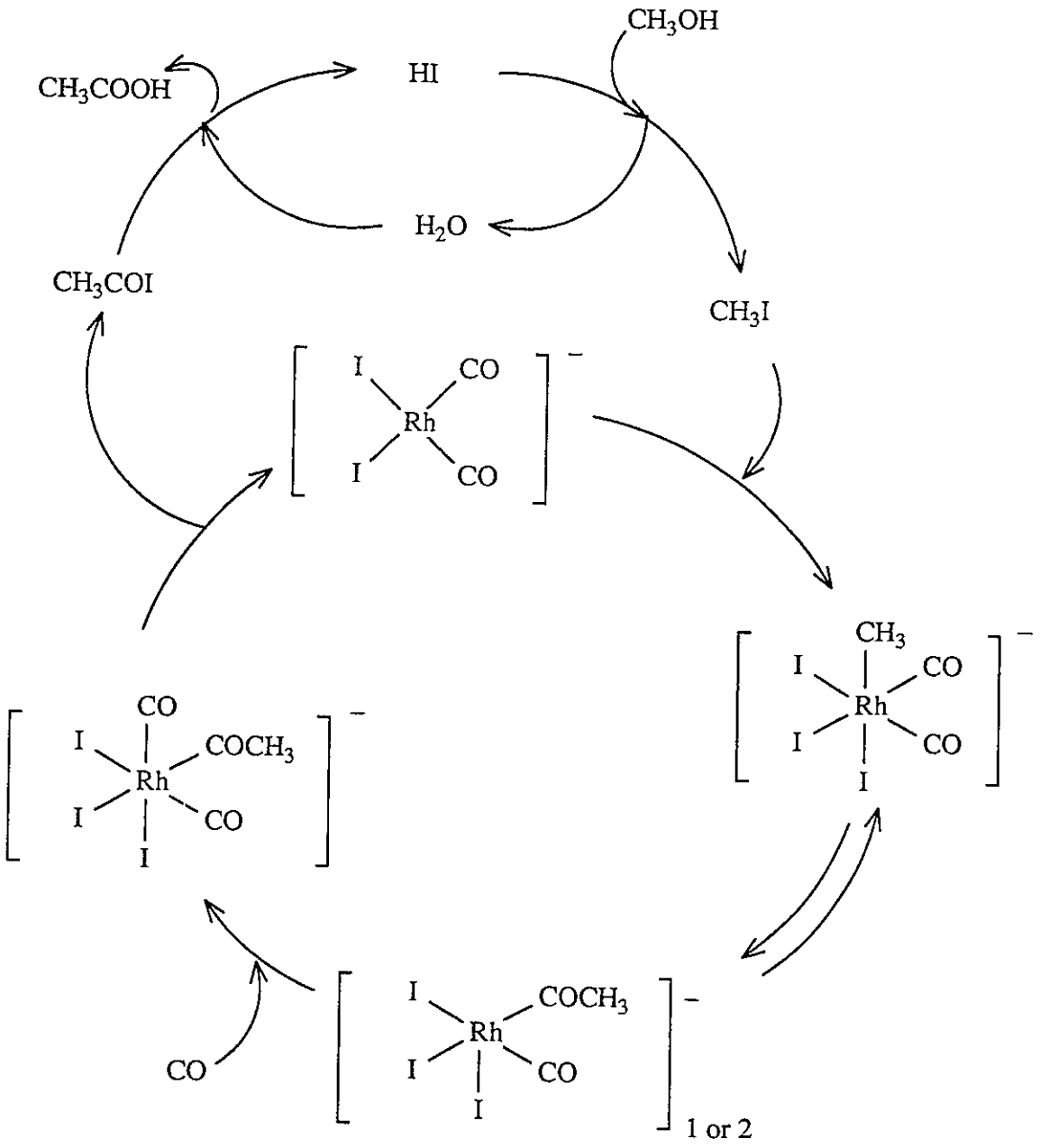


Figure 5: The Monsanto Process: Demonstrating the role of $[I]^-$ in this promoted system.

coordination sphere after which, the acyl group can reductively eliminate to give acetyl iodide and the active catalyst. The acetyl iodide subsequently undergoes hydrolysis to give the desired product, that is, acetic acid, as well as HI, which is recycled.[40]

A further example of an iodide promoted system, this time involving a ruthenium complex, is a "Fischer-Tropsch"-type of reaction. Although, it was generally understood that ruthenium complexes did not give products with more than one carbon in Fischer-Tropsch systems, the use of a carboxylic acid, as a solvent and promoter, led to the formation of a glycol ester.[41] The author also found that a variety

$$H_2/CO \xrightarrow{Ru_3(CO)_{12}/I^-} CH_3OH + HOCH_2CH_2OH + CH_3CH_2OH \qquad (9)$$

of iodides promoted the reaction further to give, along with methanol, ethanol and ethylene glycol (refer to Equation **9**). The main interest in the reaction was the glycol; the ethanol was produced in less significant quantities. Several other oxygenates were also present as minor fractions. Again the counterion for the iodide had little effect on the results and the iodide was the best promoter tried. Also, there was an optimum I^-/Ru ratio which was similar for the production of both ethylene glycol and methanol. This was explained in terms of Equation **10** since there was a ratio, 0.43, below which the amount of active species in solution decreased. The metal

$$7/3\ Ru_3(CO)_{12} + 3I^- + H_2 \longrightarrow 2HRu_3(CO)_{11}^- + Ru(CO)_3I^-_3 + 3CO \qquad (10)$$

species $HRu_3(CO)_{11}^-$ and $Ru(CO)_3I_3^-$ were found in the reaction mixture at the end of the process and although they had relatively low activity individually (as their PPN salts), they showed a marked activity when used in conjunction with each other.[42] A later publication by Dombek proposed that the active species are actually

fragmentation products of the species described above. The fragments would appear to be $HRu(CO)_4^-$ and $Ru(CO)_3I_3^-$.[43] The systems, described by this author, in which a carboxylic acid acted as a promoter, or which was unpromoted, were considered to have, as the active species, $Ru(CO)_5$. However, this species was not detected in the reactions promoted by iodide. It is probable that the reactions without a promoter and those promoted by a carboxylic acid do not have the same mechanism as those involving the iodide. The formation of one of the metal cluster hydrides is proposed to occur as shown in Equation **10.** [41,42]

As can be seen in Table IB, the presence of potassium iodide had a marked effect on the selectivity of the reaction as well as on the proportion of aniline reacted. The greater the iodide concentration, the greater the selectivity of the reaction to alkylated products, particularly, N,N-dimethylaniline (compare Entry 1 in Table IB with Entries 5, 6 and 7). A tenfold increase in $[I^-]$ increased the amount of N,N-dimethylaniline produced from 32% to 45% (refer to Entries 5 and 6), while the proportions of N-methylaniline and formanilide in the mixture dropped. The slightly anomalous result between reactions 6 and 7 in the Table is due to the introduction of a glass sleeve to the reaction vessel. Nonetheless, the effect of the promoter can be seen (comparing Entry 1 with 7) regardless of the presence of the sleeve, in the marked increase in the amount of N,N-dimethylaniline produced, that is, from a trace to 24%. As in earlier reactions[35], for which the addition of hydrogen had some effect on the course of the reaction, its presence in those reactions including iodide was detrimental to selectivity (for example, Entry 3). The addition of an internal standard only slightly changed the effectiveness of the promoter and the conversion of the reaction including potassium iodide (0.9 mmol) was calculated to be 86% with *p*-xylene as the internal standard (Entry 4).

2.2. Reactions Catalysed by the $[HCr(CO)_5]^-$ Anion

In several processes, metal hydride intermediates have been implicated. For example, the mechanism considered in Section 1.3, Equations **3** and **4**, wherein the hydrogenation of carbon monoxide was described. This mechanism included a metal hydride which undergoes a "CO insertion" or a "hydride shift", to give a metal-formyl species.[11] Further, a more specific example can be found in the ruthenium promoted system discussed *vide supra* for which the hydride species $[HRu(CO)_4]^-$ is considered to be one of the active catalysts.[43]

The inclusion of these species in several proposed mechanisms led to an interest in the exploitation of these hydrides, particularly the anions, in catalysis. Indeed, the hydrides of several metal compounds were found to catalyse reactions in either stoichiometric or catalytic amounts. The reactions of Watanabe et al.[31], as have already been discussed in Section 1.5, rely on $HFe(CO)_4^-$ for the synthesis of N-alkyl-amines. Previous work[35] included an initial look at the hydridochromiumpenta-carbonyl anion in the present system. Two salts of the anion were considered for the continuing investigation of this system.

The metal species $[HCr(CO)_5]^-$ is accepted to be less reactive than other substituted anionic hydrides such as $[HCr(CO)_4PR_3]^-$.[44] Nonetheless, the former anionic hydride was investigated because it should lead to less complications in mechanistic studies and was more interesting for its relative ease of preparation. The systems involving such an anion tend to be less active, and selective, than rhodium or ruthenium catalysts but the generation of these species from relatively inexpensive materials increases their attractiveness. Chromium hydrides have been used for catal-ysis by Darensbourg, et al.,in the reduction of aldehydes and ketones.[45] The active species was proposed to be the mononuclear hydride anion which adds to

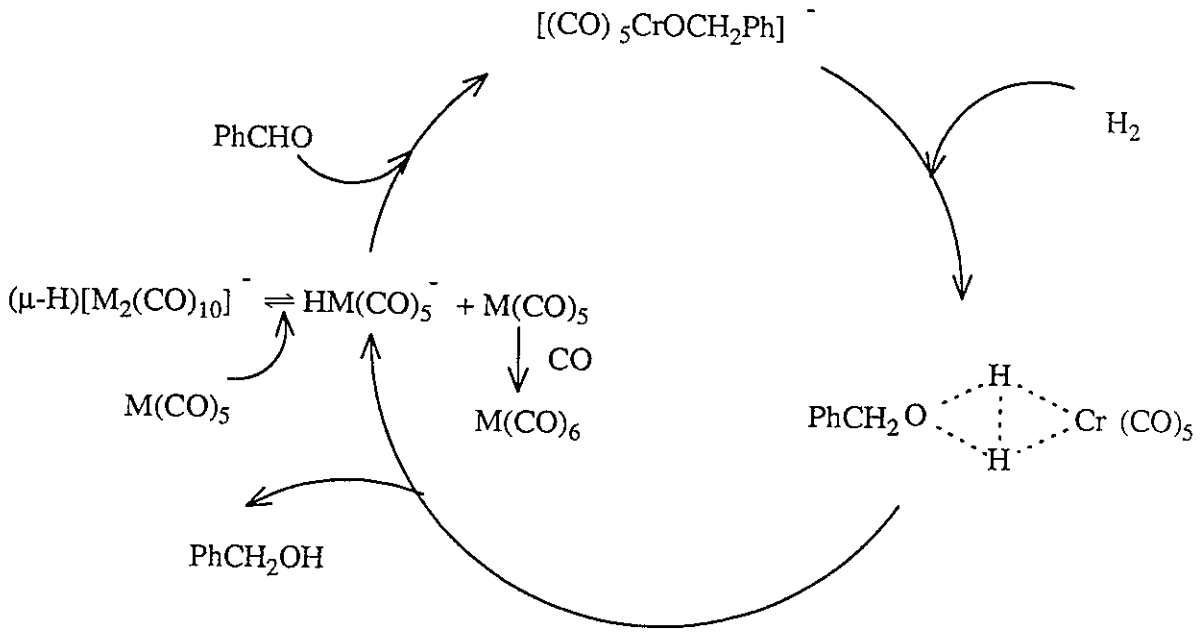


Figure 6: Reduction of Benzaldehyde via a Hydridochromiumcarbonyl Anion

benzaldehyde to give an alkoxide. The bridged complex $(\mu\text{-H})[Cr_2(CO)_{10}]^-$ is known to undergo cleavage to give the monomeric hydride, mentioned above. As the bridged species is easier to manipulate than $[HCr(CO)_5]^-$, it was used as the catalyst precursors and the turnover for it was good (~15). The mechanism of the reaction is shown in Figure 6.

The major problem to be overcome if these salts are to be exploited is their air sensitivity and the resultant difficulty in handling these compounds, as was recognized by Darensbourg, et al., who used the PPN^+ salt of the dimeric species. To this end, it was thought that a larger cation should increase the stability of the salt.

Therefore, the utility of the bis(triphenylphosphino)iminium (PPN^+) salt was also explored. In general, as expected, the proportion of aniline recovered was higher and selectivity to alkylanilines was lower for the system involving the $[HCr(CO)_5]^-$ salts as compared to the promoted rhodium carbonyl system. As can be seen in Table II, an unpromoted reaction (Entry 1) with tetraethylammonium hydridochromiumpenta-carbonyl, under 120 psi of hydrogen, gave: formanilide, 23%; N-methylformanilide, 7%; N-methylaniline, 14%; and N,N-dimethylaniline, 4%. Lowering the pressure slightly and using freshly prepared catalyst, as in Entry 2 (see Experimental Section 6 for full explanation), gave no trace of N,N-dimethylaniline and a greater amount of unreacted aniline, while the addition of a promoter, potassium iodide, (see Entries 3-5) increased the activity of the system. However, the only effect the promoter had on the selectivity of the reaction was to increase the proportion of formanilide produced. Catalyst concentration seems to have some small effect on the system since a decrease in the amount of catalyst used resulted in a decrease in the activity of the system and in its selectivity towards N-methylaniline (Entry 3 versus Entry 5) while the proportion of formanilide produced increased slightly. The catalyst in Entry 4 was probably partially decomposed to the hydrogen bridged dimer, $(\mu\text{-H})\text{-}[Cr_2(CO)_{10}]^-$, which is relatively stable. The result was a slightly lower activity and selectivity towards alkylated products than was observed for Entry 3. The hydrogen in this dimer is not thought to be labile[44]; nonetheless, this species has been shown to catalyse hydrogenation of a variety of functionalities.[46] On the other hand, it is known that this type of metal complex thermally decomposes to give the $Cr(CO)_5$ and $[HCr(CO)_5]^-$ which in turn reacts with CO to give $Cr(CO)_6$ and hydrogen.[44,45]

As expected, the PPN^+salt was found to be easier to manipulate and tolerated short exposures to air. The use of the larger cation seems to have had little effect on the activity of the reaction as can be seen in Entry 6, Table II; the proportion of

TABLE II: Development of a Catalytic System: Reactions Catalysed by the $[HCr(CO)_5]^-$ Anion.[a]

Entry No.	CATALYST	$PhNH_2$ (%)	PhNHMe (%)	$PhNMe_2$ (%)	PhNHCHO	PhNMeCHO (%)	COMMENTS
1	$Et_4NHCr(CO)_5$ (0.27mmol)	52	14	4	23	7	H_2 pressure: 120 psi
2	" (0.26 mmol)	64	8	-	25	3	H_2 pressure: 100 psi
3	" (0.24 mmol)	15	13	3	60	9	H_2 pressure: 100 psi; Promoter: KI (0.3 mmol)
4	" (83 mg)[c]	29	trace	1	65	5	H_2 pressure: 100 psi; Promoter: KI (0.3 mmol)
5	" (0.14 mmol)	19	3	1	67	9	H_2 pressure: 100 psi; Promoter: KI (0.3 mmol); Unidentified Products (3)[b]: 1%
6	$PPNHCr(CO)_5$ (0.24 mmol)	21	2	4	52	21	Purged with H_2; Promoter: KI (0.7 mmol)

a) Reaction conditions: $PhNH_2$ (10 mmol); HCO_2Me (19 mmol); temperature: 180-200°C; reaction time: 72 hours.
b) The number of unidentified products observed is given in brackets and percentage is of reaction mixture.
c) The catalyst was deliberately left to partially decompose therefore no accurate amount of catalyst can be given.

recovered aniline was comparable to, or slightly larger than, the other promoted reactions catalysed by $[HCr(CO)_5]^-$, that is, 21%. Notable is the proportion of N-methylformanilide obtained (21%), which was the highest found for aniline with the hydridochromiumpentacarbonyl anion. Of the reactions promoted by potassium iodide, the ratio of formanilide in this reaction mixture was slightly smaller (52%),

while that of N,N-dimethylaniline was similar (compare with Entry 3). The amount of N-methylaniline from this reaction was comparable with that of Entry 5 while being less than that obtained in Entry 3. The reaction vessel was merely purged with hydrogen for Entry 6, and, as well, the concentration of promoter was higher (0.74 mmol). These changes seemed to have little effect on the results, the only substantial difference being the amount of N-methylformanilide and N-methylaniline detected.

3. STUDIES WITH SUBSTITUTED ANILINES

3.1. Reactions Catalysed by $Rh_6(CO)_{16}$ and $Ru_3(CO)_{12}$

The generality of the process was previously explored using a variety of substituted anilines. The sensitivity of the reaction to changes in the electron density around the aromatic ring and its implications for the reaction mechanism may also be determined in this study. Under standard conditions, *p*-toluidine provided product distributions which were quite different from those of a standard reaction with $Rh_6(CO)_{16}$ (Entry 2 versus 1, Table III). The addition of a donor substituent to the aromatic ring increased the activity of the system, decreased the selectivity of the reaction towards alkylated products, and increased the production of unidentified products. The methyl groups in 3,5-dimethylaniline suppressed the activity as well as selectivity of the system (Entry 4, Table III). The number and proportion of unidentified products for this species were higher than for both those of aniline and *p*-toluidine (41% (8) versus 2% (2) and 24% (2)). A decrease in activity relative to that of aniline was noted for the same species using $Ru_3(CO)_{12}$ as the catalyst (Entry 4, Table IV), but the loss of activity (based on recovered starting material) for the smaller cluster was less significant (23% for $Rh_6(CO)_{16}$ versus 8% for $Ru_3(CO)_{12}$). Thus, the lower conversion for both catalytic systems may be, at least in part, due to steric interactions. Interestingly, the proportions of monomethylated amine detected

TABLE III: The Effect of Ring Substitution on the Reaction of Aniline with Methyl Formate Catalysed by $Rh_6(CO)_{16}$.[a,b]

RXN No.	AMINE	RNH_2 (%)	RNHMe (%)	$RNMe_2$ (%)	RNHCHO (%)	RNMeCHO (%)	COMMENTS
1	$PhNH_2$ 10 mmol	14	8	15	19	42	Unidentified products (2)[c]: 2% Shown in Table IA
2	*p*-$MePhNH_2$ 9.5 mmol	7	6	12	13	38	Unidentified products (2): 24%
3	" 10 mmol	1	2	5	5	34	H_2 pressure: 100 psi; Unidentified products (3): 53%
4	3,5-Me_2PhNH_2 8 mmol	37	10	1	10	1	Unidentified products (8): 41%
5	*p*-$ClPhNH_2$ 8 mmol	3	5	3	trace	9	Unidentified products (7): 80%
6	*p*-$MeOPhNH_2$ 8 mmol	0	0	25	25	0	Unidentified products(3): 50%

a) Reaction conditions unless otherwise noted:
Catalyst: $Rh_6(CO)_{16}$ (0.05 mmol); HCO_2Me (20 mmol); Time: 72 hours;
Temperature: 200-210°C; These reactions were carried out without a glass insert and the data reported does not include corrections for response factors.

b) Taken from reference 35

c) The number of unidentified products observed is given in brackets and percentage is of reaction mixture.

for both the aniline and 3,5-dimethylaniline reactions were almost the same (within 2%) while that of the *p*-toluidine experiment was only slightly lower. It appears from the results in the Table that the electronic nature of the amine has only a small effect on the system.

The study was then extended to include π-donors like *p*-chloroaniline (Entry 5, Table III). While the activity increased in contrast to that of aniline or *p*-toluidine, there was a further suppression of the formation of known products; however, the ratio of the N-methylaniline analogue was unchanged from that of *p*-toluidine. A

significant proportion of unidentified products (80%), possibly by-products from dehalogenation, were produced. Dehalogenation may account for the low ratios of known products. One other substrate considered was *p*-anisidine which followed the trend of an increase in unidentified products (50% (3 unknowns in all)) and activity (>99%) (Entry 6, Table III). However, the results for the N,N-dimethylaniline and formanilide analogues were unexpected. The proportions of both species in the reaction mixture were 25% while the proportion of N-methylanisidine dropped to zero.[35]

The presence of hydrogen in the reaction of *p*-toluidine (Entry 3, Table IV) was found to enhance the conversion of the amine while suppressing the formation of known products (53% unidentified products (3)).[35] This was in contrast to experiments with $Ru_3(CO)_{12}$ for which the activity was much lower, the ratio of alkylated products relatively high, and the unidentified products were less significant or not detected. Therefore, the use of $Ru_3(CO)_{12}$ as a catalyst was investigated further. This included the reaction of aniline with methyl formate catalysed by triruthenium dodecacarbonyl (Entry 1, Table IV). This catalyst was reported to give a reaction mixture which was similar to that obtained for a standard reaction with hexarhodium hexadodecacarbonyl (Entry 1, Table IB). The conversion of aniline with $Ru_3(CO)_{12}$ was higher than that with $Rh_6(CO)_{16}$, however, the increase in conversion was matched by an increase in amide products rather than alkylated ones with the exception of the dimethylated product. The use of *p*-toluidine instead of aniline (Entry 2, Table IV) gave product ratios similar to those of entry 1, but there was more recovered toluidine than aniline. This drop in activity for the toluidine was matched by a decrease in amide formation. The ratios of alkylated products were within 3% of each other, thus the addition of this substituent and the presence of hydrogen gas had a minimal effect on the reaction. A second reaction with *p*-toluidine was also

TABLE IV: The Effect of Ring Substitution on the Reaction of Aniline with Methyl Formate Catalysed by $Ru_3(CO)_{12}$.[a]

RXN No.	AMINE	RNH_2 (%)	RNHMe (%)	$RNMe_2$ (%)	RNHCHO (%)	RNMeCHO (%)	COMMENTS
1[b]	$PhNH_2$	19	9	11	25	30	Unidentified products (2)[c]: 6%
2[b]	p-$MePhNH_2$	35	9	12	17	27	H_2 pressure: 100 psi
3[b]	"	1	2	5	5	34	Catalyst: $Rh_6CO)_{16}$ (0.05 mmol); H_2 pressure: 100 psi; Unidentified products (3): 53%; Shown in Table III
4	3,5-Me_2PhNH_2	27	9	13	21	27	$Ru_3(CO)_{12}$: 0.08 mmol; Amine: 8 mmol; Unidentified products (2): 3%

a) Reaction conditions unless otherwise noted:
Catalyst: $Ru_3(CO)_{12}$ (0.09 mmol); amine (10 mmol); HCO_2Me (19 mmol);
Time: 72 hours; Temperature: 200°C.

b) taken from reference 35

c) The number of unidentified products observed is given in brackets and percentage is of reaction mixture.

reported for which the catalyst was not $Ru_3(CO)_{12}$, but rather, $Et_4NHCr(CO)_5$ (Entry 2, Table V). This catalyst effected a better proportion of reacted amine (87% vs. 65%) but produced even less alkyl amines than for $Ru_3(CO)_{12}$ (4% less for both alkylated amines). The results for the hydridochromiumpentacarbonyl anion are discussed in the following section which will deal with the reactions catalysed by $PPNHCr(CO)_5$ and similar species.

If the electronic nature of the aromatic ring is important, then 3,5-dimethylaniline should give results similar to those of aniline and differing from those of *p*-toluidine. In the current work, 3,5-dimethylaniline (Entry 4, Table IV) gave product ratios

similar to the former two reactions, but the activity was slightly lower than that for aniline. As mentioned earlier, this may be due in part to some steric hindrance from the *meta* methyl groups. The proportion of each alkyl amine produced was within 1% of their *p*-toluidine analogues while 21% of 3,5-dimethylformanilide was produced, an increase of 4% over the value for *p*-methylformanilide. It may be concluded that the system can be extended to include substituted anilines and that electron donating groups on the aromatic ring have little effect on the selectivity and slightly suppress the activity of the system including $Ru_3(CO)_{12}$. As will be discussed later, this suppression may be due to the enhancement of competing decarbonylation.

3.2 Reactions Catalysed by $[HCr(CO)_5]^-$ and Analogues

A reaction was carried out with the *p*-toluidine in the presence of $RuCl_2(PPh_3)_4$ (Entry 1, Table V) to bridge the reactions catalysed by $Ru_3(CO)_{12}$ and those by $[HCr(CO)_5]^-$. The catalyst, $RuCl_2(PPh_3)_4$, while being a ruthenium complex, is isoelectronic with the chromium species. The products of the reaction resembled those obtained in the presence of the chromium catalyst (Entry 2, Table V) rather than those in the presence of triruthenium dodecacarbonyl (Entry 2, Table IV). The product mixture consisted almost entirely of amides: *p*-methylformanilide, 77%, and N,4-dimethylformanilide, 21%. The starting material was detected in trace quantities and only 2% of N-methyl-*p*-toluidine was obtained. It seems possible that the current reaction is more dependent on the electronic configuration of the catalyst than on its other characteristics. The differences between a mononuclear complex and a cluster may also give rise to differing results. The use of these two ruthenium compounds may result in different reaction mechanisms.

TABLE V: The Effect of Ring Substitution on the Reaction of Aniline with Methyl Formate in the Presence of $PPNHCr(CO)_5$ and Analogues.[a]

RXN No.	CATALYST	AMINE	RNH_2 (%)	RNHMe (%)	$RNMe_2$ (%)	RNHCHO (%)	RNMeCHO (%)	COMMENTS
1	$RuCl_2(PPH_3)_4$ (0.058 mmol)	*p*-$MePhNH_2$ (9.3 mmol)	trace	2	-	77	21	H_2 presssure: 100 psi
2[b]	$Et_4NHCr(CO)_5$ (0.25 mmol)	" (9.7 mmol)	13	5	8	40	34	H_2 pressure: 100 psi;
3	$PPNHCr(CO)_5$ (0.24 mmol)	$PhNH_2$ (9.8 mmol)	21	2	4	52	21	Purged with H_2; Promoter: KI (0.7 mmol); Shown in Table II
4	" (0.25 mmol)	*m*-$MePhNH_2$ (10 mmol)	2	2	7	61	28	H_2 pressure: 100 psi; Promoter: KI (0.7 mmol)
5	" (0.26 mmol)	*p*-$ClPhNH_2$ (17 mmol)	-	-	-	trace	43	H_2 pressure: 100 psi; Promoter: KI (0.7 mmol); Ratio of $PhNMe_2$: 11%; Ratio of PhNMeCHO: 38%; Unidentified product[c]: 8%
6	" (0.11 mmol)	*o*-(OMe)$PhNH_2$ (9.7 mmol)	100	-	-	-	-	H_2 pressure: 100 psi; Promoter: KI (0.3 mmol);
7	" (0.26 mmol)	*p*-(OMe)PhNH2 (10 mmol)	5	2	34	29	30	H_2 presssure: 100 psi; Promoter: KI (0.7 mmol)

a) Reaction conditions unless otherwise noted: HCO_2Me (19 mmol); Time 72 hours; Temp. 180-200°C;
b) Taken from reference 35
c) Percentage is of reaction mixture.

Jenner and Bitsi have reported a reaction with aniline and methyl formate in the presence of $RuCl_3 \cdot 3H_2O$ under CO (510 bar).[34] Although the results are quite similar to those found in the presence of $RuCl_2(PPh_3)_4$, no conclusions can be drawn

from this report as their reaction time was much shorter than for the current system. As these authors were beginning to explore the same system being discussed here, further plans to develop a ruthenium system were dropped.

The reactions of a series of substituted anilines catalysed by $[HCr(CO)_5]^-$ showed that this system was quite susceptible to changes in the electronic character of the substrate. A methyl group *meta* to the amino substituent should affect neighbouring carbons only. The use of *m*-toluidine increased the proportion of alkylated products in the reaction mixture (Entry 3 vs. 4, Table V) as evidenced by a 7% rise in the ratio of the N-methylformanilide analogue and 3% rise in that of the analogue of N,N-dimethylaniline. The activity of the system also increased. Localized changes in the electron density of the ring would appear to have some effect on the system. Shifting the methyl group to the *para* position further increased the selectivity of the reaction towards alkylated products, and, in particular, N,4-dimethylformanilide (Entry 2 vs. 4, Table V) which increased 6% over the *meta* isomer. Very slight increases in the N-methylaniline and N,N-dimethylaniline analogues were also observed (3% and 4% from those of aniline and 3% and 1% from those of *p*-toluidine). While the presence of a promoter increased activity it had little effect on the formation of alkylated products. The drop in proportion of *p*-methylformanilide (to 40%) may be due, in part, to enhancement of the decarbonylation as will be discussed in Section **4** pages 41 and 42. This effect was also evident for the reactions catalysed by $Ru_3(CO)_{12}$ (Table IV) but not those catalysed by $Rh_6(CO)_{16}$ (Table III). It should be noted that, for the latter, decarbonylation was in the order of 5%. Do the former two catalysts aid decarbonylation of *p*-methylformanilide more effectively than the latter?

The above data leads to the conclusion that the presence of electron donating groups on the aromatic ring increase the activity of the system as well as the

selectivity towards reduced products. To confirm this trend, consideration was then given to π-donors such as *p*-chloroaniline. The selectivity of the reaction with this species was greatly increased over those of either aniline or the toluidines (Entry 5, Table V). A marked increase in reduced products was obtained and only trace quantities of *p*-chloroformanilide were detected. The product mixture consisted mainly of the methylated amides *p*-chloro-N-methylformanilide (43%) and N-methylformanilide (38%) both of which amounts are greater than was produced by aniline. Dehalogenation occurred but formanilide was not detected in the reaction mixture although a significant proportion of N,N-dimethylaniline (11%) was produced. Unlike the results of aniline and the toluidines, there was no starting material found in the reaction mixture nor any N-methyl- or N,N-dimethyl-*p*-chloroaniline. An unidentified product (8%) was also formed in this system.

The chloro substituent enhances both the activity and selectivity of the system. Two competing paths to the observed products can be envisaged; either through the formation of formanilide from its *p*-chloro analogue, which should lead to the N-methylformanilide via the same path as the standard reaction, or the formation of methylated products followed by dehalogenation. The lack of formanilide and increased amounts of N,N-dimethylaniline and N-methylformanilide detected leads one to conclude that the loss of the chloro substituent occurs later in the reaction. One possible mechanism for the dehalogenation is the oxidative addition of the aryl halide across the metal followed by reductive elimination of the aryl group with the hydride resulting in the corresponding monosubstituted aromatic ring. Dehalogenation of aryl halides has been reported to occur with the a variety of hydridometalcarbonyl anions including the $[HCr(CO)_5]^-$ anion.[47] It was found that although the reaction proceeded well for a variety of iodides, their system was less effective for chlorides like n-butyl chloride and/or less reactive substrates, for example a *t*-butyl halide. Therefore, while

the authors invoked a radical mechanism for their system, it seems likely that the present reaction follows a different pathway.

The last π-donor considered was a methoxy group. With *o*-anisidine there was no apparent reaction (Entry 6, Table V), not even the formation of the corresponding formanilide. An ^1H NMR of the crude reaction mixture showed only unreacted starting material along with methyl formate. Steric hindrance was thought to be the major factor in the failure since products were detected for the *p*-anisidine (Entry 7, Table V). The amount of amide in the reaction mixture obtained from *p*-anisidine was greater than in the reaction with *p*-chloroaniline. *p*-Methoxyformanilide was obtained in a ratio of 29%, in contrast to only a trace for the *p*-chloro analogue, which was accompanied by 5% of unreacted starting material, and a little N-methyl-*p*-anisidine (2%). However, the most striking result was the 34% yield of the dimethylated product, N,N-dimethyl-*p*-anisidine. The presence of so much of the end product demonstrates that the suggested trend towards greater selectivity with the addition of donor substituents is valid. The ratio of the methylated amide, was also high, 30% of N-methyl-*p*-methoxyformanilide. Indeed, this system was the most successful of the substituted anilines using $[HCr(CO)_5]^-$ as the catalyst for the synthesis of the N,N-dimethylaniline analogue. It can be concluded from these results that not only is the system general for a variety of substituted anilines, but also definite increases in activity and selectivity result from electron donating groups on the aromatic ring.

4 MECHANISTIC STUDIES

4.1 General Studies

Several mechanisms can be proposed for reactions described in Section 2, particularly those involving $Rh_6(CO)_{16}$. Figures **7** and **8** contain two plausible mechanisms. In Scheme 1, the reaction begins with formylation of aniline to give

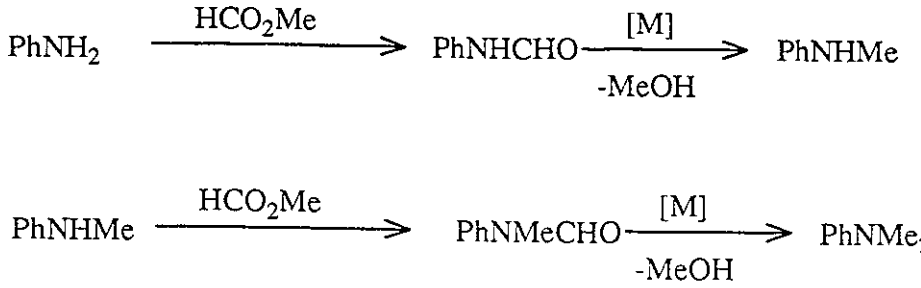


Figure **7**: Possible Reaction Pathway: Scheme 1.

formanilide. This type of reaction is known to occur without a catalyst (for example, references 34 and 48). As was discussed in the Section 2, pages 25-26, metal hydrides are thought to be active in the reduction of various substrates. According to this scheme, the product N-methylaniline should arise from the reduction of formanilide probably via a metal hydride species. The other products should then

result from acylation of N-methylaniline and subsequent reduction of N-methylformanilide to give N,N-dimethylaniline.

The second mechanism would start with the decomposition of methyl formate

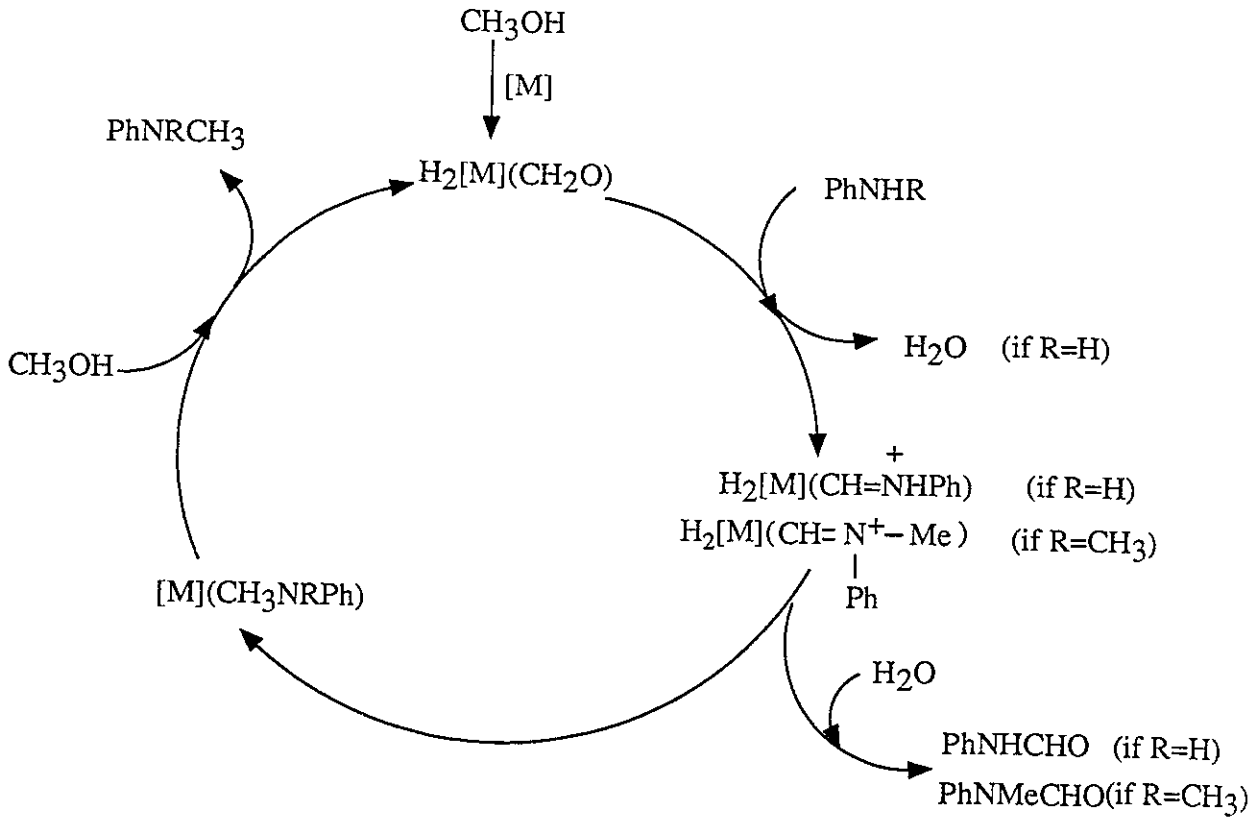


Figure 8: Possible Reaction Pathway: Scheme 2.[a]
a) Based on mechanism proposed in reference 33.
In this scheme, R=H or Me.

to give methanol. Methanol has been used in a similar system by Watanabe et al.[33], who proposed the transformations shown in Figure 8. In Scheme 2, the oxidative addition of methanol to a metal complex followed by hydrogen transfer gives a

coordinated formyl species. The addition of aniline to the coordinated "formaldehyde" gives a Schiff base which is then reduced to N-methylaniline. When N-methylaniline follows the same cycle (fig. **8**, R=Me), N,N-dimethylaniline is the expected product. Hydrolysis of the two Schiff bases produces the observed amides.

A third option involves carbonylation of the amine with carbon monoxide produced from the decomposition of the metal complex and/or the formate followed by reduction of the carbonylated species. The carbonylation reaction is known to occur for alkyl amines[49,50] but it is unlikely to be a viable alernative in this case since aniline was not found to react under the same conditions.[49]

The validity of the first scheme was tested by conducting a series of reactions, under standard conditions, using proposed intermediates as starting materials. An experiment with formanilide gave the expected product mixture, however, the yields of methylated amines did not increase markedly as might have been expected.[35] The most significant increase was in the ratio of N,N-dimethylaniline obtained (from a trace in Entry 1, Table IB to 4%). Nonetheless, while 39% of the formanilide did not react, an increase in the proportion of N-methylformanilide was observed. Interestingly, the production of N-methylaniline was inhibited, dropping 9% from the standard reaction in Table IB. The presence of some aniline (5%) in the reaction mixture was due to decarbonylation.

During the current work, the reaction of N-methylformanilide with a catalyst: amide molar ratio of 1:390 and an amide:formate ratio of 2:1 was unsuccessful (<1% conversion). Furthermore, it produced only trace quantities of N,N-dimethylaniline, as did the standard reaction (Entry 1, Table IB). Varying the ratio of methyl formate to N-methylformanilide gave results comparable to those of formanilide. The

percentage of N,N-dimethylaniline produced by a reaction in which the catalyst: amide ratio was 1:160 and the amide:formate, 1:2; was 3%, which was only slightly higher than the standard reaction. As with formanilide, decarbonylation appears to have also occurred with N-methylformanilide as evidenced by the formation of small amounts of N-methylaniline (only a trace under the former conditions and 1% under the latter). A similar reaction, the decarbonylation of dimethylformamide, is known to occur in the presence of iridium halides and triphenylphosphine to give dimethylamine and $IrCl(CO)(PPh_3)_2$. However, this reaction is not catalytic; rather, its major aim is the synthesis of the iridium compound known as Vaska's complex.[50] A catalytic decarbonylation of dimethylformamide is known to proceed with a ruthenium porphyrin complex but when such a complex is involved the reaction is unlikely to proceed via the known route for decarbonylation (that is, oxidative addition of the carbonyl containing substrate, migration of the CO to the metal, and reductive elimination of the product) because of saturation of the coordination sphere. It was speculated that instead a photoprocess was involved.[52] The above results for the present system were inconclusive.

Methanol was used instead of methyl formate to test the second reaction sequence. The reaction was run under standard conditions (refer to Section 7.2) except it was under ~10 psi of nitrogen. Nitrogen was used to ensure that the alkylation was indeed due to methanol and not some other process such as carbonylation via carbon monoxide or methyl formate, which could arise from the reaction of methanol with carbon monoxide. The results indicate that alkylation via methanol is not a likely (certainly not major) pathway under standard conditions. The only measurable product was formanilide, 1%. This was detected along with traces of

N,N-dimethylaniline. When $Ru_3(CO)_{12}$ was used instead of the rhodium complex, similar results were obtained. The reaction, under ~20 psi nitrogen, produced small amounts of N-methylaniline (3%) and traces of N,N-dimethylaniline and N-methylformanilide while most of the aniline was recovered (97%). It is likely that methanol deactivates the metal. During the experiment with methanol a great deal of black solid was produced. This was not seen when methyl formate was used as the substrate; on the contrary, an orange solution with no apparent solid was observed at the end of the reaction. This reaction with $Ru_3(CO)_{12}$ and methyl formate under nitrogen produced a mixture of 66% formanilide, 13% N-methylformanilide, 6% N,N-dimethylaniline and 5% N-methylaniline along with 10% aniline. The results are markedly different from those observed in the presence of methanol and are comparable to those of the standard reaction with $Rh_6(CO)_{16}$ (Entry 1, Table IB). The use of methanol with aniline in a system without a catalyst and under CO (100 psi) with standard reaction time and temperature gave results similar to the other reactions of methanol. The amount of aniline recovered was greater than 99% and there were only traces of formanilide and N-methylformanilide.

The investigation of the reaction mechanism was extended to include the use of carbon monoxide itself, rather than one of its activated forms. So that the third option discussed could be ruled out. The use of CO (120 psi) with aniline and $Rh_6(CO)_{16}$ at 195°C for 70 hours, gave the same results as with methanol; 99% of the unreacted aniline was recovered. Only a very small amount of N,N-dimethylaniline (1%) was obtained by increasing the reaction time to 80.5 hours. Therefore, the contributions from this path to the system were discounted.

Butyl formate was also used instead of methyl formate to test the generality of

the system and shed some light on the path of the reaction. If the first scheme (Figure 7) is operative, then butyl formate should give the same alkylated products as methyl formate. The reaction of butyl formate and aniline in the presence of $PPNHCr(CO)_5$ did not give the expected methylated products but a series of butylated ones. Formanilide was again observed but with it were detected N-butylaniline and N-butyl-formanilide, as well as unreacted aniline and an unidentified species. There was no indication that any dibutylaniline was produced. These results render the first scheme suspect, at least for those reactions catalysed by $[HCr(CO)_5]^-$. Although formanilide was formed, it would seem that the butylation of the amide and perhaps of aniline was the major path for this reaction.

An investigation of the role of methyl formate in the current system should provide some insight into the mechanism. The decarbonylation of methyl formate was reported for a system involving $Rh_6(CO)_{16}$ with 2-methoxyethanol as the solvent[53] and one involving $Ru_3(CO)_{12}$ promoted by tricyclohexylphosphine.[54] It seems likely that the same reaction is occurring in the current system. In such a case, the methanol produced could undergo the reaction shown in Figure 8. An attempt was made to determine if the decarbonylation proceeded with the hydridochromium-pentacarbonyl anion, since the use of this species would ensure that the reaction did occur via a homogeneous pathway. Approximately one atmosphere of hydrogen was used for the reaction with 0.28 mol of the formate and 0.017 mmol of the catalyst. About two-thirds of the formate remained after the reaction (66%). Methanol, as expected, was detected (33%) along with a small amount dimethylcarbonate (1%). The presence of the carbonate was indicated by GC/MS and confirmed by the addition of an authentic sample of the carbonate to the reaction mixture. The

presence of methanol was also confirmed by adding a standard to the reaction mixture. Although methanol is produced during the reaction, its role in the process, if there is one, is unclear since the scheme involving alkylation by methanol has been ruled out as a major pathway (pages 42 and 43).

4.2. Investigation of the Nature of the Polynuclear Catalysts

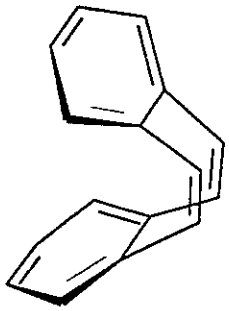
The presence of a mirror on the glass sleeve at the end of one of the experiments cast some doubt on the true nature of the rhodium catalyst, suggesting a more in depth look at the catalyst was appropriate. The work of Vidal and Walker[9], discussed in Section 1.2, demonstrated that related clusters are stable at temperatures used in this reaction. Their conditions, like those of the present system, were weakly basic. A trend towards higher aggregates, or clusters, was noted but no mention of deposited metal was made. Moreover, initial studies on this system[35] showed that rhodium black was not as effective as the cluster compound in this reaction. However, the question remained as to whether the present system was homogeneous or heterogeneous, or a combination of the two, consequently, it was decided to test the heterogeneity of the system using selective poisoning.

It has been known for some time that mercury can poison heterogeneous catalysts consisting of the platinum group metals and others.[55,56,57] The poisoning is probably due to the coverage of active sites on the catalyst surface with mercury, that is, interactions like physisorption or amalgamation. In systems for which a heterogeneous reaction is competing with a desired homogenous reaction, mercury has been

used as a selective poison to enhance yield.[58] Homogeneous systems are generally not as strongly affected by this type of poison. Tests for the heterogeneous vs. homogenous nature of a catalytic system have been proposed which would include an experiment with mercury.[58,59] It was found that a slight molar excess of mercury did have an effect on the present system. The percentage of recovered aniline was high (97%) and the only product was formanilide, 3%. It is possible to conclude from these results that at least one step in the mechanism of the reaction involves a heterogeneous species.

The mercury test, while appropriate in most cases, may sometimes be inconclusive. For example, a situation can be envisaged wherein the catalyst precusor is heterogeneous and inactive. An equilibrium between such a precursor and the active homogeneous species would provide sufficient quantities of the homogeneous catalyst for the reaction to occur. The introduction of mercury to such a system would tie up the precursor, preventing the formation of the catalyst and giving the mercury test a false positive result. Also, the effect of mercury on a cluster is unclear. Does a cluster behave more like a mononuclear species in solution or like a colloid?

The introduction of a homogeneous poison to verify the mercury results is a logical next step. Dibenzo[a,e]cyclooctatetraene (dct), ***4***, was the inhibitor chosen. The platinum group metals have an affinity to olefinic functionalities such as in ***4***. The resultant metal-dct complex should hinder the approach of any substrate, as well as change its electronic nature, thus eliminating the catalytic reaction. A metal surface should not be as greatly affected by dct because the "tub" shape precludes the formation of strong bonds with the metal surface. In order to bond to a surface, dct would have to adopt an unfavourable planar geometry. Indeed, Anton and Crabtree



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found that dct had very little effect on supported Pd and Rh and no effect on their colloids.[59] Fortunately, the reactions considered were hydrogenations as is the case in the present system. A 2:1 mole ratio of dct:$Rh_6(CO)_{16}$ was used, in a standard reaction with no promoter, and this gave 2% of N,N-dimethylaniline, and a moderate amount of N-methylaniline (17%). The conversion (81%) was greater than for the standard reaction but was still lower than was noted for the iodide promoted reactions discussed in Section 2, Table IB (Entries 5-7). Formanilide production was fairly high (60%) and there was 2% of N-methylformanilide in the reaction mixture. Surprisingly, dct actually enhances the activity of the reaction and its selectivity towards alkylated amines, particularly N-methylaniline. A possible explanation is the stabilization of the cluster by dct with respect to decomposition to the metal. Anton and Crabtree[60] also found that a hydridoiridium complex of dct was stable to at least 180°C in air. Further, it has been reported that excess ligand is displaced by dct only if the metal is rhodium.[59] Therefore, it is likely that the affinity of rhodium for dct is even greater than that of iridium.

The above results demonstrate that dct does not inhibit catalytic (homo-

geneous?) reactions with this cluster. One of several potential explanations is that dct binds to one or two of the metal atoms of the cluster thereby sterically blocking several faces of the cluster but leaving at least one face free for the reaction to take place. If this occurred, the dct might stabilize the cluster thermodynamically while still allowing some reaction to occur. It is also possible that the olefin changes the electronic nature of the complexed metal atom, thus, stabilization of the cluster or fragments may result without a change in remote metal atoms of the cluster or fragment. This would explain the increase in products observed. On the other hand, the dct may serve to solubilize the cluster in the reaction medium as does 2,3-dimethyl-1,3-butadiene in the clusters $Rh_6(CO)_{12}(\eta^4\text{-}CH_2C(Me)C(Me)CH_2)_2$ and $Rh_6(CO)_{14}(\eta^4\text{-}CH_2C(Me)C(Me)CH_2)$.[61] These results support the argument for a homogeneous system. In fact, it seems possible that the situation described previously, in which mercury poisons precursor of the active catalyst(s), is occurring in this system.

5 CONCLUSION

The syntheses of methylated anilines from aniline and methyl formate were best achieved in the presence of $Rh_6(CO)_{16}$ and potassium iodide. An increase in $[I^-]$ led to a greater proportion of N,N-dimethylaniline in the reaction products. Addition of solvent was found to be detrimental to the system as was an increase in catalyst concentration. The hydridochromiumpentacarbonyl anion was also found to be an effective catalyst in this system. Although the use of this catalyst led to increased activity, its selectivity was mainly for the amide product, formanilide. Changing the counterion for this species from the tetraethylammonium to the bis(triphenylphosphine)iminium cation or changing the pressure of hydrogen from ~1 atm to 100 psi had only a small effect on the system.

The scope of the reaction was extended to include several substituted anilines. The addition of electron donors to the ring had a small effect on the systems catalysed by $Rh_6(CO)_{16}$ and $Ru_3(CO)_{12}$. There was an increase in activity for the reactions catalysed by the rhodium complex which was accompanied by a decrease in selectivity, while for the ruthenium complex a drop in activity was observed. The lower conversion of the latter was explained as resulting from enhanced decarbonylation. The use of *p*-chloroaniline instead of aniline in the presence of $Rh_6(CO)_{16}$ also returned less unreacted amine which was accompanied by a decrease in selectivity but

this may have arisen from dehalogenation. The increase in the ratio of the N,N-dimethylaniline and formanilide analogues obtained from *p*-anisidine in the presence of $Rh_6(CO)_{16}$ is not understood. The addition of methyl groups *m*- to the amino group did cause some steric interference for both catalysts.

The ruthenium complex, $RuCl_2(PPh_3)_4$, behaved more like the isoelectronic species, $[HCr(CO)_5]^-$, than like the other ruthenium catalyst. Indeed, no N-methyl- nor N,N-dimethylaniline were produced with this species. The system involving $[HCr(CO)_5]^-$ was markedly more susceptible to changes in the electronic nature of the aromatic ring than the reactions catalysed by $Ru_3(CO)_{12}$. There was an increase in the proportion of methylated products upon addition of a methyl group, even if the substituent was in the *m*- position. The results for *p*-toluidine were better again than those for *m*-toluidine.

The addition of a π-donor increased further the selectivity of the reaction to the methylated products. A *p*-methoxy substituent gave the best yields of dimethylated amine while *p*-chloroaniline gave the most methylated products overall. Dehalogenation occurred with the latter species, probably later in the reaction sequence as there was more alkylated products produced than for aniline itself. The lack of a reaction for *o*-anisidine, which was suspected to arise from steric interactions, was the only exception to the observed trend

Several attempts were made to determine the mechanism of these reactions. The replacement of aniline by formanilide and N-methylformanilide in the standard system gave inconclusive results and decarbonylation was noted to occur.

It was determined that the reaction path did not involve the reaction of only methanol with aniline, as the lack of reaction under nitrogen demonstrated. Triruthenium dodecacarbonyl was no more effective than $Rh_6(CO)_{16}$ under nitrogen. Indeed, the catalyst seemed to decompose under the reaction conditions with

methanol and nitrogen.

The path via carbonylation with CO was also ruled out as aniline did not undergo a significant reaction with or without the rhodium catalyst. Increasing the reaction time to 80.5 hours did not give better results.

The decomposition of methyl formate in the presence of $[HCr(CO)_5]^-$ gave methanol and a trace of dimethyl carbonate as well as carbon monoxide.

The use of butyl formate rather than methyl formate led to puzzling results. The products indicated that the expected pathway via reduction of the amides formed from the reaction of aniline with the formate was not valid, at least if the catalyst is $[HCr(CO)_5]^-$, since only butylated products were obtained.

Several tests were performed to determine the nature of the catalytic system. It was concluded that since mercury poisoned the system involving $Rh_6(CO)_{16}$, the mechanism likely included at least one heterogeneous species. This compound could be the catalyst precursor which may have been prevented from dissolving in the reaction medium and giving the active catalyst. The addition of dct enhanced the selectivity of the system, thus one may conclude that the active species is homogeneous. It was proposed that the dct aids the catalyst by either increasing its solubility or stability.

6. Suggestions for Further Research

There were several areas of this study for which further research would seem appropriate. These include a further look at the reaction of N-methylformanilide with methyl formate this time in the presence of potassium iodide as well as consideration of rhodium diene carbonyl clusters as potential catalysts. Also it is necessary to isolate the metallic species at the end of the reactions with and without KI, DCT and Hg.

Although initial results suggest that there is little effect due to changes in hydrogen pressure for those reactions catalysed by $[HCr(CO)_5]^-$, it seems that this area has not been sufficiently explored. Also the effect of temperature on the reactions catalysed by $Rh_6(CO)_{16}$, in the presence of mercury may warrant further study.

The lack of reaction for *o*-anisidine was surprising. Would this effect be seen also for *o*-toluidine. If so then the problem is obviously steric in nature and the effct should be lessened for *m*-anisidine, also the sensitivity of the reaction to donors may be verified by the results from the *m*- isomer.

The decarbonylation of formate esters has recieved some attention of late because of an interest in the formation of pure carbon monoxide and alcohols as well

as applications in organic synthesis, for example reference 53. The authors described a system in which methanol is formed in ~70% yield from methyl formate, with a catalyst concentration of 200:1/formate:$Rh_6(CO)_{16}$. The reaction temperature was 220°C with a reaction time of 22 hours (or 8 hours in the presence of 2-methoxy-ethanol). As described in Section 4.1, the decarbonylation of methyl formate can also be effected by the use of $PPNHCr(CO)_5$. The reaction time was considerably longer, but the catalyst concentration was markedly lower (that is, 1500:1 / formate:catalyst). The reaction temperature was lower as well, being 180°C. Nonetheless, a significant amount of methanol was produced (33%), with little by-products. An increase in the catalyst concentration may allow for a reduction in reaation time as well as possibly increasing the yield. It appears that further research in this area could be quite fruitful.

7 EXPERIMENTAL

7.1 General Comments

Infrared spectra were obtained on a Perkin-Elmer 783 spectrometer and were calibrated with polystyrene. KBr pellets or sodium chloride solution cells were used to run the spectra.

Proton NMR spectra were recorded on a Varian EM360 or T60 NMR spectrometer and were referenced to tetramethylsilane. Hydride shifts were obtained on a Varian XL300 NMR spectrometer. Samples for GC/MS spectra were run on a Varian 3300 Chromatograph fitted with a megabore DB5 capillary column in tandem with a VG micromass 7070E spectrometer equipped with a Digital Equipment Corp. PDP8A data system. Mass spectra were obtained on the VG micromass 7070E spectrometer. The reactions were carried out in 45 mL-series 4700 high pressure stainless steel, screw cap, autoclaves manufactured by Parr Instruments.

The results of this research were obtained from GC analysis on a programmable Varian Vista 6000 chromatograph which was fitted with a 3m glass column packed with 5% carbowax 20M on Chromosorb G, AW-DMCS, 80-100 mesh. A flame ionization detector was used and the signals were integrated with a Varian 4270 integrator. Retention times and response factors were determined using authentic samples and an standard mix of the same. Preparative thin layer chromatography was

run on silica gel and neutral alumina plates which were purchased from Terochem Ltd. Neutral alumina was purchased from E. Merck Co.

Of the several internal standards considered, only *p*-xylene had an appropriate retention time. However, the use of *p*-xylene was not without problems. In several instances the conversions calculated from the internal standard were obviously flawed. Indeed, in one case the use of the internal standard resulted in a negative conversion. Thus only one example was reported.

Several unknowns were reported in the initial work on this system. The addition of a glass sleeve to the reaction vessel lessened their occurrence. A GC/MS of a standard reaction, with a glass sleeve, showed all the expected products excepting formanilide. Instead, the last peak of the trace had a molecular ion peak of m/z 151, while fragmentation was as expected. Such an $[M]^+$ mass could correspond to the empirical formula: $C_8H_9NO_2$. Attempts were made to separate the mixture, however, the resultant streaking did not allow for isolation of any of the components excepting the most polar. This was sent for MS and was found to be formanilide, with an M^+ of m/z 121. Further, doping the reaction mixture with an authentic sample of the formanilide confirmed that the last peak of the chromatograph was due to formanilide.

Reagents and catalysts were purchased from Aldrich Chemical Company, Inc., J.T. Baker Chemical Co., Eastman Kodak Co., BDH, Inc. and Strem Chemicals Co. The chemicals were used "as is" with the exception of aniline, which was vacuum distilled for the reactions catalysed by $[HCr(CO)_5]^-$, and *o*-anisidine, which was cleaned by preparative tlc with silica gel. Methanol was dried over activated molecular sieves. Carbon monoxide, hydrogen and nitrogen were obtained from Air Products Co.

7.2 General Procedure for the Methylation of Aromatic Amines

Aniline (7 mmol) and methyl formate (13 mmol) were added to the high pressure reactor and a glass sleeve was inserted. (Please note that the amount of reagents added at this stage changed with the autoclave and glass sleeve used, however, the molar ratio of the two was maintained. Also, the ratios of methanol and butyl formate to aniline were maintained in the same manner). Inside the glass sleeve were introduced aniline (10 mmol) and methyl formate (20 mmol), the catalyst and a stir bar. The vessel was closed and at this point a gas was introduced if there was to be any in the system. The gas was added in the following manner: the system was purged three times with the gas and then the vessel was filled to the required pressure. The autoclave was placed in an oil bath which had been heated to 180-200°C. The reaction was carried out over three days and was monitored over this period for changes in temperature and pressure. At the end of the reaction time, the vessel was allowed to cool to room temperature. Any residual pressure was released slowly. The product mixture was filtered through a small plug of glass wool and neutral alumina and analysed by GC. Product ratios were calculated after the data was corrected for the response factors.

Note: The following reactions are classified by catalyst.

7.3 The Reactions Catalysed by $Rh_6(CO)_{16}$

The amount of hexarhodium hexadodecacarbonyl used in these reactions was

0.05 mmol unless otherwise noted. The general procedure was followed for these reactions with the noted modifications.

7.3.1 The Standard Reaction

This reaction was performed without a glass sleeve. Resultant reaction mixture: $PhNH_2$, 59%; PhNHMe, 11%; $PhNMe_2$, trace; PhNHCHO, 11%; PhNMeCHO, 19%.

7.3.2 The Reaction in the Presence of a Solvent

Tetramethylurea (2.2 mL) was used, instead of a mixture of reagents, outside of the glass sleeve. Inside the sleeve, 5 mL of the solvent was added to the reaction. A mirror was found on the glass insert at the end of this reaction. Resultant reaction mixture: $PhNH_2$, 4%; PhNHMe, 3%; $PhNMe_2$, 4%; PhNHCHO, 81%; PhNMeCHO, 6%; unknown, 2%.

7.3.3 The Reactions Including Potassium Iodide as Promoter

(i) Table IB, Entry 3: Potassium iodide (0.32 mmol) was added to the reaction mixture along with the catalyst. Hydrogen gas (120 psi) was used. Resultant reaction mixture: $PhNH_2$, 1%; PhNHMe, 2%; $PhNMe_2$, 13%; PhNHCHO, 60%; PhNMeCHO, 24%.

(ii) Table IB, Entry 4: Potassium iodide (0.93 mmol) was added with the catalyst and p-xylene was added to the mixture of reagents inside and outside the glass sleeve (9.8 mmol and 6.5 mmol, respectively). Hydrogen gas (120 psi) was used. Conversion: 86%. Resultant reaction mixture: $PhNH_2$, 5%; PhNHMe, 1%; $PhNMe_2$, 5%; PhNHCHO, 66%; PhNMeCHO, 23%.

(iii) Table IB, Entry 7: Potassium iodide (0.94 mmol) was added with the catalyst. Resultant reaction mixture: $PhNH_2$, 3%; PhNHMe, 2%; $PhNMe_2$, 24%; PhNHCHO, 43%; PhNMeCHO, 13%; unknowns (2), 15%.

(iv) Table IB, Entry 5: This reaction and the following one were performed without a glass insert. The data was included to demonstrate a trend towards more methylated products with an increase in potassium iodide concentration. Potassium iodide (3.1 mmol) was added. Resultant reaction mixture: $PhNH_2$, 3%; PhNHMe, 5%; $PhNMe_2$, 45%; PhNHCHO, 4%; PhNMeCHO, 38%; unknown, 5%.

(v) Table IB, Entry 6: Potassium iodide (0.34 mmol) was added with the catalyst. Resultant reaction mixture: $PhNH_2$, 3%; PhNHMe, 10%; $PhNMe_2$, 32%; PhNHCHO, 11%; PhNMeCHO, 39%; unknowns (2), 5%.

7.3.4 The Reactions of N-Methylformanilide with Methyl Formate

(i) N-methylformanilide (19.5 mmol) was combined with methyl formate (10.5 mmol) in this reaction. Resultant reaction mixture: PhNMeCHO, >99%. Trace quantities of N-methylaniline and N,N-dimethylaniline were detected.

(ii) N-methylformanilide (8.1 mmol) was combined with methyl formate (16.2 mmol) in this reaction. Resultant reaction mixture: PhNMeCHO, 96%; PhNHMe, 1%; $PhNMe_2$, 3%.

7.3.5 The Reaction of Aniline with Methanol

The reaction of aniline (9.9 mmol) with methanol (20 mmol) included a slight pressure of nitrogen (~10 psi). Resultant reaction mixture: $PhNH_2$, 99%; PhNHCHO, 1%; $PhNMe_2$, trace.

7.3.6 The Carbonylation of Aniline

The reactions of aniline with carbon monoxide were charged to 100 psi with CO.

(i) The reaction time was 70 hours. Resultant reaction mixture: $PhNH_2$, >99%; PhNHCHO, trace; PhNMeCHO, trace.

(ii) The reaction time was 80.5 hours. Resultant reaction mixture: $PhNH_2$, 99%; $PhNMe_2$, 1%.

7.3.7 The Reaction of Aniline with Methyl Formate in the Presence of Mercury

Mercury (0.052 mmol) was added along with the catalyst. Resultant reaction mixture: $PhNH_2$, 97%; PhNHCHO, 3%.

7.3.8 The Reaction of Aniline with Methyl Formate in the Presence of Dibenzocyclooctatetraene

The dibenzocyclooctatetraene (dct) as prepared following the synthesis of C.E. Griffin, et. al..[62,63] The quantity of reagents was reduced proportionally to the amount of dct used. The reaction mixture contained as follows: $PhNH_2$, 5 mmol; HCO_2Me, 16.2 mmol; dct, 0.04 mmol and catalyst, 0.02 mmol. Resultant reaction mixture: $PhNH_2$, 19%; PhNHMe, 17%; $PhNMe_2$, 2%; PhNHCHO, 60%; PhNMeCHO, 2%.

7.4 The Reactions Catalysed by $[HCr(CO)_5]^-$

These reactions were carried out as for the general procedure except as noted. The amount of catalyst present was approximately 0.25 mmol for both $Et_4NHCr(CO)_5$ and $PPNHCr(CO)_5$. The catalysts were freshly prepared before each reaction unless

otherwise noted. All of these reactions were carried out under hydrogen (at various pressures). For each reaction, the catalyst was added immediately before flushing the system and after being weighed under nitrogen. The catalyst was obtained in the following manner immediately before use: the salts of the hydridochromiumpenta-carbonyl anion were prepared according to the synthesis described by D.H Gibson, et. al.,[64] with the following modifications: (i) a cannula adapted with a small paper filter was used instead of a Schlenck-type filter aided by Celite; (ii) PPNCl (2.4 mmol) was used instead of Et_4NHSO_4 to prepare the corresponding salt.

7.4.1 The Reactions Catalysed by $Et_4NHCr(CO)_5$

(i) Table II, Entry 1: The initial pressure of hydrogen was 120 psi. There was a marked increase in pressure during the course of the reaction; the final pressure was 620 psi before cooling. The catalyst (0.27 mmol) in this instance was not freshly prepared. Resultant reaction mixture: $PhNH_2$, 52%; PhNHMe, 14%; $PhNMe_2$, 4%; PhNHCHO, 23 %; PhNMeCHO, 7%.

(ii) Table II, Entry 2: The vessel was filled to 100 psi with hydrogen and the amount of catalyst used was 0.26 mmol. Resultant reaction mixture: $PhNH_2$, 64%; PhNHMe, 8%; PhNHCHO, 25%; PhNMeCHO, 3%.

(iii) Table II, Entry 3: Potassium iodide (0.35 mmol) was used while the hydrogen pressure was 100 psi and the amount of catalyst used 0.24 mmol. Resultant reaction mixture: $PhNH_2$, 15%; PhNHMe, 13%;

$PhNMe_2$, 3%; PhNHCHO, 60%; PhNMeCHO, 9%.

(iv) Table II, Entry 4: Potassium iodide (0.35 mmol) was present and the hydrogen pressure used was 100 psi. The catalyst (83 mg) for this reaction was not freshly prepared, but rather deliberately left to partially decompose. Resultant reaction mixture: $PhNH_2$, 29%; PhNHMe, trace; $PhNMe_2$, 1%; PhNHCHO, 65%; PhNMeCHO, 5%.

(v) Table II, Entry 5: Potassium iodide (0.3 mmol), was used and the hydrogen pressure was 100 psi. The catalyst for this reaction (0.14 mmol) was not freshly prepared. Resultant reaction mixture: $PhNH_2$, 19%; PhNHMe, 3%; $PhNMe_2$, 1%; PhNHCHO, 67%; PhNMeCHO, 9%; unknowns (3), 1%.

7.4.2 The Reactions Catalysed by $PPNHCr(CO)_5$

(i) Table II, Entry 6: Potassium iodide (0.74 mmol) was used. Hydrogen pressure was ~1 atm and the the amount of catalyst used 0.24 mmol. Resultant reaction mixture: $PhNH_2$, 21%; PhNHMe, 2%; $PhNMe_2$, 4%; PhNHCHO, 52%; PhNMeHCO, 21%.

7.4.2.1 The Reaction of Butyl Formate with Aniline

Butyl formate (12 mmol) and aniline (9.8 mmol) were combined with potassium iodide (0.8 mmol). The catalyst was added and the vessel flushed and

charged with hydrogen (100 psi). The product ratios were not available.

GC/MS data:

PhNHCHO:	m/z 121 [M^+].
PhNHBu:	m/z 149 [M^+], 121(-C_2H_3), 106(-C_3H_7, $C_6H_5NCH_3$).
$PhNH_2$:	m/z 93 [M^+].
PhNBuCHO:	m/z 177 [M^+], 134(-C_3H_7), 106($C_6H_5NCH_3$).

7.4.2.2 The Decomposition of Methyl Formate in the Presence of $PPNHCr(CO)_5$

Methyl formate was placed in an autoclave (17 mL inside glass sleeve and 3 mL outside) along with a stir bar and the catalyst. Hydrogen pressure was ~1 atm. The vessel was cooled in ice at the end of the reaction. The GC/MS of the reaction mixture indicated the presence of not only methyl formate but also potentially dimethyl carbonate. The MS spectrum of this componenet did not have an [M^+] peak but the fragmentation pattern was highly suggestive of the carbonate. The identity of this fraction was confirmed to be dimethyl carbonate by doping the mixture with an authentic sample. Methyl formate and methanol were also verified with authentic samples. Response factors were calculated from a standard mixture and the results corrected. Carbon monoxide was also detected and, when most of the methyl formate had been distilled off, an unknown was found. Resultant reaction mixture: HCO_2Me, 66%; MeOH, 33%, $CH_3OCO_2CH_3$, 1%.

GC/MS data:

HCO_2Me:	m/z 60 [M^+], 31(OCH_3, -CHO), 29(CHO, -OCH_3).
$CH_3OCO_2CH_3$:	m/z 75, 47 (-CO), 31 (OCH_3, -CO_2).
unknown:	m/z 108, 96, 80, 73, 52.

7.4.3 The Reactions of Other Aromatic Amines with Methyl Formate

The results for these amines have not been corrected. The general procedure for aniline was followed here with the noted modifications.

(i) **The reaction of *m*-toluidine with methyl formate** (Table V, Entry 4). *m*-Toluidine (10 mmol) replaced aniline in the reaction and the amount of catalyst used was 0.25 mmol. Potassium iodide (0.70 mmol) was present and the hydrogen pressure was 100 psi. Resultant reaction mixture: *m*-$MePhNH_2$, 2%; *m*-MePhNHMe, 2%; *m*-$MePhNMe_2$, 7%; *m*-MePhNHCHO, 61%; *m*-MePhNMeCHO, 28%.

GC/MS data:

m-$MePhNH_2$:	m/z 107 [M^+], 106(-H).
m-MePhNHMe:	m/z 121 [M^+], 120(-H).
m-$MePhNMe_2$:	m/z 135 [M^+], 134(-H).
m-MePhNHCHO:	m/z 135 [M^+], 106(-CHO, $CH_3C_6H_4NH$).
m-MePhNMeCHO:	m/z 149 [M^+].

(ii) **The reaction of *p*-chloroaniline with methyl formate** (Table V, Entry 5). *p*-Chloroaniline (16.7 mmol) was used instead of aniline and the amount of catalyst used was 0.26 mmol. Potassium iodide (0.68 mmol) was present as well as 100 psi of hydrogen. It was demonstrated by doping that there was no starting material was left in the reaction mixture. Resultant reaction mixture: $PhNMe_2$, 11%; PhNMeCHO, 38%; *p*-ClPhNHCHO, trace; *p*-ClPhNMeCHO, 43%; unknown (not picked up in MS), 8%.

GC/MS data:

$PhNMe_2$:	m/z 121 [M^+], 120(-H). There was no M+2 peak as expected for a chloro substituent.
PhNMeCHO:	m/z 135 [M^+], 106(-CHO). There was no M+2 peak as expected for a chloro substituent.
p-ClPhNHCHO:	m/z 157(M+2), 155 [M^+], 154(-H).
p-ClPhNMeCHO:	m/z 171(M+2), 169 [M^+], 140(-CHO).

(iii) **The reaction of *o*-anisidine with methyl formate** (Table V, Entry 6). *o*-Anisidine (9.7 mmol) replaced aniline. Potassium iodide (0.3 mmol) and 0.11 mmol of catalyst were used. Hydrogen pressure was 100 psi. The PMR spectrum indicated that the only species in the reaction mixture were *o*-anisidine and methyl formate.

(iv) **The reaction of *p*-anisidine with methyl formate** (Table V, Entry 7). *p*-Anisidine (10 mmol) was placed in the glass insert along with the methyl formate which was also used to fill the space between the glass sleeve and the autoclave (3 mL outside sleeve). Potassium iodide (0.70 mmol) was used while the hydrogen pressure was 100 psi and the amount of catalyst used was 0.26 mmol. The first two components were not separated by the GC/MS. However, these two were compared with authentic samples and were thus considered to be the mono- and dimethylated amines. The samples were prepared in the following manner: *p*-anisidine (0.48g) was dissolved in ether and to this solution was dropped slowly a solution of MeOBF (0.76g) in ether. The mixture was allowed to stir for 30 minutes and was then basified with $NaOH_{(aq)}$ (50% solution). The basic solution was extracted with ether and the ether was then evaporated under a flow of nitrogen. The crude product (0.44g) had three components, which were, by PMR, the amine and the mono- and dimethylated products. These were separated using a chromatotron (EtOAc:hexanes/5:1). The separation was not complete but sufficient to demonstrate the retention time of each component. The GC peak due to starting material was confirmed by doping the reaction mixture. Resultant reaction mixture: *p*-$OMePhNH_2$, 5%; *p*-OMePhNHMe, 2%; *p*-$OMePhNMe_2$, 34%; *p*-OMePhNHCHO, 29 %; *p*-OMePhNMeCHO, 30%.

GC/MS data:

p-OMePhNHCHO: m/z 151 [M^+], 136(-CH_3),

120(-OCH_3).

p-OMePhNMeCHO: m/z 165 [M^+], 122(-NCHO).

7.5 The Reactions Catalysed by Complexes of Ruthenium

These reactions were carried out as for the general procedure Section 7.2

7.5.1 The Reactions Catalysed by $Ru_3(CO)_{12}$

The amount of catalyst used was 0.08 mmol.

(i) **The reaction of aniline with methyl formate.** The same amounts of reagents were used as for the standard reaction catalysed by $Rh_6(CO)_{16}$ and the reaction was carried out under nitrogen (~40 psi). There was no precipitate found in the reaction mixture. Resultant reaction mixture: $PhNH_2$, 10%; PhNHMe, 5%; $PhNMe_2$, 6%; PhNHCHO, 66%; PhNMeCHO, 13%.

(ii) **The reaction of aniline with methanol.** The reaction was again carried out under nitrogen (~20 psi) but methanol (20 mmol) replaced methyl formate. A large amount of black solid was found suspended in the reaction mixture. Resultant reaction mixture: $PhNH_2$, 97%; PhNHMe, 3%; $PhNMe_2$, trace; PhNMeCHO, trace.

(iii) **The reaction of 3,5-dimethylaniline with methyl formate** (Table IV,

Entry 3). The amount of 3,5-dimethylaniline used was 8 mmol. This reaction did not include a glass insert and the results have not been corrected. Resultant reaction mixture: 3,5-Me_2PhNH_2, 27%; 3,5-$Me_2PhNHMe$, 9%; 3,5-Me_2PhNMe_2, 13%; 3,5-$Me_2PhNHCHO$, 21%; 3,5-$Me_2PhNMeCHO$, 27%; unknowns (2), 3%.

GC/MS data:

3,5-Me_2PhNH_2:	m/z 121 [M^+].
3,5-$Me_2PhNHMe$:	m/z 135 [M^+].
3,5-Me_2PhNMe_2:	m/z 149 [M^+], 148(-H).
3,5-$Me_2PhNHCHO$:	m/z 149 [M^+], 120(-CHO), 106(-C_2H_3O).
3,5-$Me_2PhNMeCHO$:	m/z 163 [M^+], 134(-CHO).
unknown:	m/z 163, 162(-H).
unknown:	m/z 177.

The unknown with m/z of 177 may have the empirical formula: $C_{10}H_{13}NO_2$. It is possible that this is the product of a second carbonylation of the formanilide and/or it may be related to the unknown discussed in Section 7.1.

7.5.2 The Reaction of *p*-Toluidine with Methyl Formate in the Presence of $RuCl_2(PPh_3)_4$

The reaction mixture included 0.058 mmol of the catalyst, $RuCl_2(PPh_3)_4$, and 9.3 mmol of *p*-toluidine. The reaction was carried out under hydrogen (100 psi). Assignments were based on previous results[28] and the data was not corrected. The

starting material was detected in trace quantities. Resultant reaction mixture: *p*-$MePhNH_2$, trace; *p*-MePhNHMe, 2%; *p*-MePhNHCHO, 77%; *p*-MePhNMeCHO, 21%.

7.6 Miscellaneous

The reaction of aniline with methanol without a catalyst. Methanol (19.8 mmol) and aniline (9.9 mmol) were placed under CO (100 psi). The reaction was carried out according to the general procedure in Section 6.2. Resultant reaction mixture: $PhNH_2$, >99%; PhNHCHO and PhNMeCHO were detected in trace quantities.

8. CLAIMS TO ORIGINAL RESEARCH

1. The synthesis of N-methylated anilines from aniline and methyl formate was achieved most selectively via a catalytic reaction with $Rh_6(CO)_{16}$ promoted by potassium iodide. $Ru_3(CO)_{12}$ and $[HCr(CO)_5]^-$ were also found to be active for this reaction and the best results for the latter were obtained from substituted anilines.

2. The mechanism of the process and the nature of the rhodium cluster catalyst were investigated.

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