Proceedings of the 2nd Workshop on Catalyst Design

ADVANCES IN CATALYST DESIGN

Vol. 2

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ADVANCES IN CATALYST DESIGN
Volume II

PREFACE

This volume contains the lectures delivered at the second Workshop on Catalyst Design which was held at Trieste from 10 to 14 November 1992. Like the first Workshop on Catalyst Design held in December 1990, this meeting was organized by the International Institute for Pure and Applied Chemistry (IIC). IIC is the chemistry wing of the International Centre for Science and High Technology (ICS). The establishment of the International Centre for Science and High Technology was the brainchild of Professor Abdus Salam, Director of the International Centre for Theoretical Physics (ICTP). In 1989, pilot activities of ICS were started, financed through the Italian contribution to UNIDO. The aim of ICS is to transfer science and technology to developing countries in order to enable industries to develop there and to promote self-reliance. In the light of recent political changes, this support of technology transfer and consequent collaboration is being extended by ICS to include East European countries and those bordering on the Mediterranean as well.

The proposed activities for the International Institute for Pure and Applied Chemistry include technologies and research areas of utmost importance to the chemical industry, such as reactivity, synthesis, macromolecules, combustion chemistry, catalysis and computer chemistry.

Research activities of IIC will be carried out at the "Research Area", a science park just outside the city of Trieste, where several other research institutions are already operating, thus ensuring an effective interdisciplinary approach. Another important activity of IIC is to organize workshops, conferences, and research training programmes, open to scientists from developing countries and East Europe.

It is proposed to hold the third Workshop on Catalyst Design at Trieste in November 1994.

M. Graziani
C. N. R. Rao
Editors

April 1993

CONTENTS

The Use of Spectroscopy, Models, and Labels to Detect Intermediates, Elucidate Mechanisms, and Compare Reactivities in Metal Catalyzed Carbonylation Reactions

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ABSTRACT

Comparisons are made between rhodium and iridium in carbonylation reactions. The previously unknown catalytic intermediate in methanol (and methyl iodide) carbonylation (**B**), has now been spectroscopically detected in the reaction of (**A**) with neat MeI giving (**C**):

$$MeI + [Rh(CO)_2I_2]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [MeRh(CO)_2I_3]^-$$

$$\text{\textbf{A}} \qquad\qquad \text{\textbf{B}}$$

$$\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Rh(CO)(COMe)I_3]^-$$

$$\text{\textbf{C}}$$
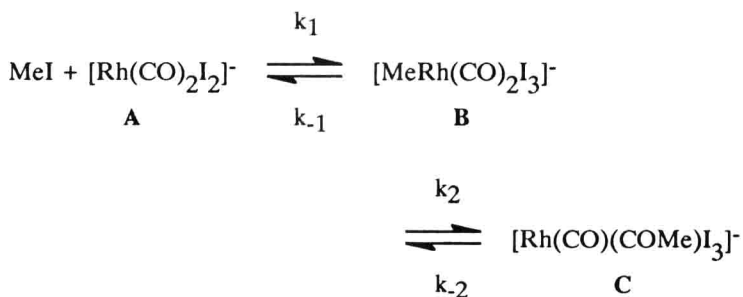
FTIR and low temperature ^{13}C NMR spectroscopic measurements using both ^{13}CO and ^{13}CH$_3$ labelled complexes, and the analogy to $[MeIr(CO)_2I_3]^-$ all favour a *fac-cis*-stereochemistry for **B**. The direct observation of **B** has allowed all the rate constants (k_1, k_{-1}, k_2, and k_{-2}) to be estimated. The rate

constant for the migratory insertion $\mathbf{B} \longrightarrow \mathbf{C}$ (k_2) has been determined over the range 5-35 °C (activation parameters, $\Delta H^{\#} = 63 \pm 2$ kJ mol^{-1}, $\Delta S^{\#} = -59 \pm 9$ J mol^{-1} K^{-1}; $\Delta G^{\#}_{298} = 80 \pm 2$ kJ mol^{-1}).

The activation parameters for the oxidative addition of MeI with [Ir(CO)$_2$I$_2$]$^-$, where the product, [MeIr(CO)$_2$I$_3$]$^-$ is stable under ambient conditions, are: $\Delta H^{\#} = 54$ kJ mol^{-1}, $\Delta S^{\#} = -112$ J mol^{-1} K^{-1}; $\Delta G^{\#}_{298} = 87$ kJ mol^{-1}. Thus the oxidative addition step is approximately 120 times faster for iridium than rhodium at 25 °C. Methyl migration only occurs on heating, when the reaction, [MeIr(CO)$_2$I$_3$]$^-$ + CO = [MeCOIr(CO)$_2$I$_3$]$^-$ proceeds slowly (k_{obs} of ca. 2 x 10^{-4} s^{-1} at 115 °C in chlorobenzene under carbon monoxide, 5 bar). Extrapolation of the rate data for methyl migration in the rhodium system to 115 °C (and assuming that CO merely acts to stabilise the acyl iridium complex, and does not affect the intrinsic rate of the migration) shows that methyl migration occurs faster for M = Rh than for M = Ir by a factor of approximately 10^5.

Similar approaches have been used to evaluate the rates of oxidative addition of methyl iodide to [η^5-C$_5$Me$_5$M(CO)$_2$] (M = Rh, Ir) in CH$_2$Cl$_2$, and the subsequent migration. Oxidative addition to the neutral dicarbonyl iridium complex proceeds ca 4 times faster than to its rhodium analogue. Data have been obtained for the reaction [η^5-C$_5$Me$_5$M(CO)MeCl] + L = [η^5-C$_5$Me$_5$M(COMe)Cl(L)] (L = PMePh$_2$ and PMe$_2$Ph), for M = Rh at 283 - 313 K and for M = Ir at 338 K. Extrapolating the rates of the rhodium reactions to 338 K indicates relative rate constants k_{obs}(Rh)/k_{obs}(Ir) = 10^6 for L = PPh$_2$Me and 4 x 10^5 for L = PMe$_2$Ph.

Thus while the oxidative addition of methyl iodide occurs ca 4 - 120 times faster for Ir(I) than Rh(I), methyl migration onto carbonyl in the resulting M(III) complexes is 10^5 - 10^6 times faster for Rh than Ir.

INTRODUCTION

Carbonylation reactions homogeneously catalysed by the Group 8 - 10 metals, cobalt, nickel, ruthenium, rhodium, palladium, and iridium, form a vital part of present day industrial processes. Examples include the hydroformylation of olefins,
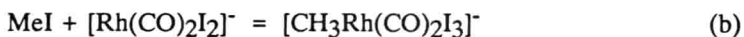
$$RCH=CH_2 + CO + H_2 = RCH_2CH_2CHO$$
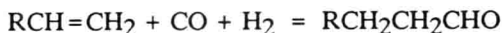
and the carbonylation of methanol to acetic acid,

$$MeOH + CO = MeCOOH$$

Two key steps in catalytic carbonylation are oxidative addition and alkyl migration. Surprisingly little is known about the reactivities of different metals and comparisons of these steps for analogous rhodium and iridium complexes are reported here.

The rhodium-iodide catalysed industrial carbonylation of methanol produces a substantial proportion of the acetic acid made each year[1] (world production *ca.* 4 million tonnes), and the large scale carbonylation of methyl acetate to acetic anhydride also employs similar technology[2]. Studies by Forster[3] and others[4,5,6] led to formulation of the catalytic cycle shown in Scheme 1. High pressure IR spectroscopy showed that the main rhodium species present in catalytic solutions is the square planar Rh^I (d^8) anion, $[Rh(CO)_2I_2]^-$ (A),[7] and the overall rate of carbonylation showed a first order dependence on the concentrations of both rhodium and iodide promoter.

The cycle can be broken down into six stoicheiometric reactions which form the closed catalytic loop,

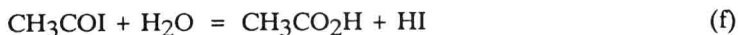$$MeOH + HI = MeI + H_2O \qquad\qquad (a)$$

$$MeI + [Rh(CO)_2I_2]^- = [CH_3Rh(CO)_2I_3]^- \qquad\qquad (b)$$
$$A B$$

$$[CH_3Rh(CO)_2I_3]^- = [CH_3CORh(CO)I_3]^- \qquad\qquad (c)$$
$$B C$$

$$[CH_3CORh(CO)I_3]^- + CO = [CH_3CORh(CO)_2I_3]^- \qquad \text{(d)}$$

$$\text{C} \qquad\qquad\qquad\qquad \text{D}$$

$$[CH_3CORh(CO)_2I_3]^- = [Rh(CO)_2I_2]^- + CH_3COI \qquad \text{(e)}$$

$$\text{D} \qquad\qquad\qquad \text{A}$$

$$CH_3COI + H_2O = CH_3CO_2H + HI \qquad \text{(f)}$$

The first and last steps are entirely organic: (a) the formation of the reactant, methyl iodide, from methanol, and (f) the hydrolysis of the product, acetyl iodide, to acetic acid. The reactions which depend on the metal are: the oxidative addition **A → B**, step (b), the methyl migration, **B → C**, step (c); the carbonylation, **C → D**, step (d); and the reductive elimination of acetyl iodide from **D** and the regeneration of **A**, step (e).

Previous attempts to follow or mimic these reactions have never been able to prove the existence of the methyl-rhodium intermediate **B**, since the first observed product of the oxidative addition was the acetyl complex **C**.[8] We have now detected complex **B**,[9] and have estimated rate constants for both the forward and reverse reactions of steps **A → B** and **B → C**.

We have also studied analogous processes involving iridium.[10] Since the reactions of a *5d* metal are very often considerably slower than those of its *4d* congener, another way of investigating fast processes involving the *4d* metal is to examine the analogous *5d* metal reactions. The oxidative addition and the migration reactions have also been studied for the related pentamethylcyclopentadienyl complexes, where again one would expect modified reactivity arising from the greater steric protection and the higher electron density offered to the metal centre by the pentamethylcyclopentadienyl ligand.

EXPERIMENTAL

All operations were carried out under dry nitrogen. Methyl iodide and dichloromethane were distilled under nitrogen from calcium hydride. WARNING: Methyl iodide is volatile and extremely toxic, and should only be used in an

efficient fume hood or sealed cell. The complexes, $Bu_4N[Rh(CO)_2I_2]$, $Bu_4N[Rh(CO)_2Cl_2]$, $Bu_4N[Rh(CO)(COMe)I_3]$, $Ph_4As[Ir(CO)_2I_2]$, $[\eta^5-C_5Me_5M(CO)_2]$, (M = Rh, Ir) $[\eta^5-C_5Me_5M(CO)(Me)X]$ (M = Rh, Ir), and specifically labelled $Bu_4N[Rh(CO)(^{13}COMe)I_3]$ were prepared as described.[11,12,13,14,15,16] Solutions of isotopically labelled $Bu_4N[Rh(CO)_2I_2]$ were prepared by the reaction of Bu_4NI with ca. 70% ^{13}CO enriched $[Rh(CO)_2I]_2$. Some typical procedures are given. In all cases the spectra of the starting materials and the products were checked to ensure that Beer's law was followed.
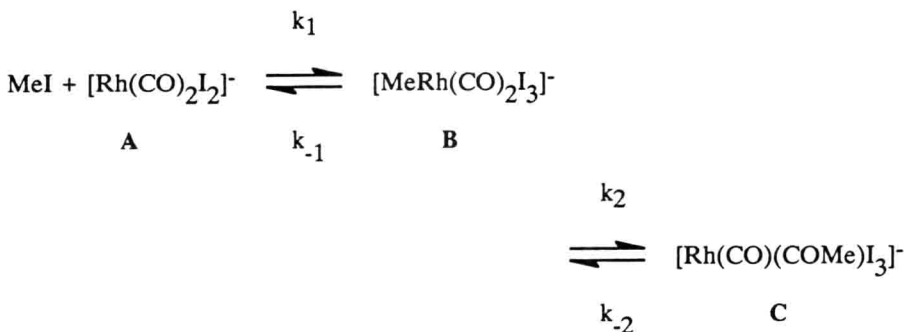
The reaction of $Bu_4N[Rh(CO)_2I_2]$ with methyl iodide was monitored using FTIR spectroscopy in a solution cell fitted with a thermostatted jacket. IR spectra were recorded on a Perkin-Elmer 1710 Fourier Transform spectrometer and stored electronically. A series of spectra were collected with a constant time interval, and stored to disk for subsequent analysis. Data processing involved subtraction of solvent spectrum and extraction of absorbance data for the IR frequency of interest, giving a data set of absorbance against time for each kinetic run. Kinetic measurements were made by following the decay of the low frequency $v(CO)$ absorption of $[Rh(CO)_2I_2]^-$ (1985 cm^{-1} in neat MeI). The pseudo first order rate constants (k_{obs}) were found from the gradient of a plot of $ln(Abs_0/Abs_t)$ against time, where Abs_0 is the initial absorbance and Abs_t the absorbance at time t. The concentration of $Bu_4N[Rh(CO)_2I_2]$ used for IR spectroscopic measurements in neat MeI was typically 0.017 M, but a rhodium concentration of 0.1 M was used for analysis of the initial kinetic behaviour of the weak bands of **B** and **C**. ^{13}C NMR spectra were recorded using a Bruker WH400 spectrometer, at a rhodium concentration of 0.2 M.

The reaction of $[Ir(CO)_2(Me)I_3]^-$ with CO was carried out in chlorobenzene at 115 °C in a Fisher-Porter tube; samples were withdrawn at regular intervals and analysed on a Perkin-Elmer 1640 FTIR spectrometer.

The kinetics of the reactions of $[C_5Me_5M(CO)(Me)Cl]$ with phosphines were measured by UV-visible spectroscopy on a Varian Cary 219 spectrometer.

RESULTS

i) The identification of the catalytic intermediate $[MeRh(CO)_2I_3]^-$, **B** by IR
    spectroscopy

$$MeI + [Rh(CO)_2I_2]^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [MeRh(CO)_2I_3]^-$$

$$\quad\quad\quad\text{A}\quad\quad\quad\quad\quad\quad\quad\text{B}$$

$$\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Rh(CO)(COMe)I_3]^-$$

$$\quad\quad\quad\quad\quad\text{C}$$

Scheme 2

A kinetic analysis, based on Scheme 2, and applying the steady state
approximation to the intermediate **B**, with the assumption that k_{-2} is small, leads to
the following relationship between the concentrations of **A** and **B**:

$$[B]/[A] = (k_1 [MeI])/(k_{-1} + k_2) \tag{1}$$

At steady state the concentration of **B** is therefore directly proportional to the
concentration of methyl iodide; thus, to generate detectable amounts of **B**,
experiments were carried out using neat methyl iodide as both reactant and solvent.
Since it has been found in other systems[17] that the rates of migratory insertion in
non-polar solvents are slowed down by factors of more than 10^4, the use of a
medium of low polarity such as MeI should also favour accumulation of **B** by
reducing k_2.

In the reaction of $Bu_4N[Rh(CO)_2I_2]$ with neat MeI at 25 °C, the two terminal
$v(CO)$ bands of **A** at 2055 and 1985 cm^{-1} were replaced by the terminal and acyl
$v(CO)$ absorptions of **C** at 2061 and 1740 cm^{-1} respectively (Figure 1). However,
careful inspection of the bands revealed the presence of a much weaker absorption
at 2104 cm^{-1}, not present in either **A** or **C**, and which did not correspond to any

known rhodium carbonyl iodide species which might be formed as by-products. The kinetic traces in Figure 2 show that during the reaction the weak absorption decays in direct proportion to the band due to **A** at 1985 cm^{-1}. The ratio of the absorbances, R_{Abs} ($= Abs_{2104}/Abs_{1985}$), both in neat MeI, and in MeI diluted with dichloromethane, was found to be directly proportional to [MeI]. According to the Beer-Lambert law, R_{Abs} is directly proportional to the ratio of concentrations of the species responsible for the two absorptions. Therefore, the absorption at 2104 cm^{-1} behaved exactly as predicted for a $v(CO)$ mode of **B** by the steady state approximation (equation 1).

A dicarbonyl complex such as B, is expected to exhibit two IR active $v(CO)$ modes, but only one $v(CO)$ band assignable to **B** was observable. It is suggested that the second absorption is also weak and obscured by the intense bands of **A** and **C** close to 2060 cm^{-1}; this is supported by the analogous iridium MeIr(CO)$_2$I$_3^-$ (made analogously, but which is stable under ambient conditions), the $v(CO)$ of which are very similar.

We have also monitored the reaction of *ca.* 70% ^{13}CO enriched Bu$_4$N[Rh(CO)$_2$I$_2$] with neat MeI, and have assigned a weak absorption at 2090 cm^{-1}, to the isotopomer of **B**, [MeRh(^{12}CO)(^{13}CO)I$_3$]$^-$. Observation of the two frequencies allows the calculation of the two CO factored force constants of the M(CO)$_2$ unit, and hence an estimate of the frequencies of hidden bands. Using this method, the low frequency band of the M(^{12}CO)$_2$ species is predicted to occur at 2057 ± 6 cm^{-1},[18] very close to the high frequency bands of **A** and **C**, which would easily obscure a weak band in the same region.

Thus the intermediate has two $v(CO)$ bands which are shifted to high frequency relative to those of **A**. This shift indicates a decrease of electron density at the metal centre, characteristic of Rh(III).

ii)   The identification of the catalytic intermediate [MeRh(CO)$_2$I$_3$]$^-$, **B** by NMR spectroscopy

The characterisation has been confirmed by ^{13}C NMR spectroscopy on solutions of **B** generated by low temperature reaction of **A** in MeI, using ^{13}C

labelling in both methyl and carbonyl positions. Thus, for example, a solution of
$Bu_4N[Rh(CO)_2I_2]$ in $^{13}CH_3I$ showed a weak new doublet at δ -0.65 ppm,
(characteristic of a Rh-Me, $^1J(^{103}Rh-^{13}C)$ 14.7 Hz; ^{103}Rh, 100%, I = 1/2), and an
^1H chemical shift (δ 2.08 ppm), again typical of a rhodium-methyl species.

After brief warming of a sample of *ca.* 70% ^{13}CO enriched $Bu_4N[Rh(CO)_2I_2]$
in unenriched MeI, the spectrum contains two new weak rhodium carbonyl
doublets, at δ 180.2 ($^1J(^{103}Rh-^{13}C)$ = 66 Hz; due to the terminal carbonyl of the
rhodium acyl complex, **C**), and at δ 175.9 ppm [$^1J(^{103}Rh-^{13}C)$ = 60 Hz] due to the
carbonyls of the intermediate, **B**. The relative ^{13}C intensities for the carbonyls of **A**
and **B** suggest that the concentration of **B** is *ca.* 1% that of **A**, in agreement with the
IR data. On allowing the reaction of **A** with MeI to reach completion, the methyl
and carbonyl ^{13}C signals assigned to **B** could no longer be detected, as expected for
an intermediate species.

Of the three possible structures for $[MeRh(CO)_2I_3]^-$, the one in best accord
with the spectroscopic data is the *fac,cis-* isomer illustrated; this structure is also
adopted by the iridium analogue, $[MeIr(CO)_2I_3]^-$.

iii)   The kinetic behaviour of the catalytic intermediate $[MeRh(CO)_2I_3]^-$, **B**

The kinetic behaviour of **B** has been monitored by FTIR spectroscopy, at high
MeI concentrations, where pseudo first order conditions apply. Experimentally
determined values of k_{obs} and R_{Abs} and derived values of k_2 over the range 5 -
35 °C allow the construction of an Arrhenius plot of the k_2 data yielding activation
parameters for migratory insertion ($\Delta H^\# = 63 \pm 2$ kJ mol^{-1}, $\Delta S^\# = -59 \pm 9$ J
mol^{-1} K^{-1}; $\Delta G^\#_{298} = 80 \pm 2$ kJ mol^{-1}).

The rate at which the steady state was attained was measured at + 5 °C, when
it was found that the 2104 cm^{-1} absorption, due to **B**, did not attain its maximum
intensity until *ca.* 6 minutes after mixing. Thereafter, the absorption decayed at the
same rate as that of **A** at 1985 cm^{-1} decreased and the rate of formation of **C**
reached its maximum, showing that the rate of product formation is proportional to
the concentration of the intermediate species. This gave a first order rate constant
$(k_{-1} + k_2)$ of $(8.5 \pm 0.2) \times 10^{-3}$ s^{-1} very close to that obtained for k_2 (8.3×10^{-3} s^{-1}

at 5 °C), indicating that $(k_{-1} + k_2)$ is dominated by k_2 under these conditions. This unambiguously establishes that the previous non-observation of **B** is primarily due to rapid migratory insertion, rather than rapid reductive elimination of MeI.

iv) Other kinetic investigations on the rhodium cycle

From the observed rate of the overall reaction **A** $\longrightarrow$ **C** (oxidative addition plus migration), k_{obs} ($= 9.78 \times 10^{-4}$ s^{-1} at 35 °C in neat methyl iodide), a value for the second order rate constant, k_1 ($= 6.8 \times 10^{-5}$ M^{-1} s^{-1}) for the oxidative addition has been calculated.

An investigation of the solution behavior of labelled **C** [Rh(^{12}CO)(^{13}COMe)I$_3$]$^-$, has allowed the determination of k_{-2} (the rate constant for migratory de-insertion in **C**, $4.0 \pm 0.2 \times 10^{-5}$ s^{-1} at 35 °C), and the ratio k_2/k_{-1} (*ca.* 9 in CH$_2$Cl$_2$ at 35 °C) which defines the relative importance of the two modes of reaction for **B**. This gives k_{-1} as 1.5×10^{-2} (in CH$_2$Cl$_2$ at 35 °C).

These data show that migratory insertion is fast compared to reductive elimination, as previously suggested, and is the reason why **B** had not been detected before.

Comparison of k_{-1} (estimated) with k_1 (measured) shows that the methyl complex, **B**, is also unstable with respect to loss of MeI, even in methyl iodide as solvent. Thus, even if migratory insertion were not so facile for **B**, the molecule would still decompose via reductive elimination of MeI, with a half life of < 1 min at 35 °C.

v) Kinetic investigations on [MeIr(CO)$_2$I$_3$]$^-$

The high reactivity of the rhodium complex **B** contrasts sharply with its iridium analogue, [MeIr(CO)$_2$I$_3$]$^-$, which is rather inert and only undergoes migratory insertion at elevated temperature, in the presence of carbon monoxide,[19] and is also relatively stable towards reductive elimination of MeI. The oxidative addition of MeI to [Ir(CO)$_2$I$_2$]$^-$ to give [MeIr(CO)$_2$I$_3$]$^-$ was followed by monitoring the decrease in [v(CO) at 1969 cm^{-1}].[20] In the presence of excess methyl iodide pseudo-first order kinetics were obeyed, leading to activation parameters $\Delta H^{\#}$ =

54 ± 2 kJ mol^{-1}, $\Delta S^{\#} = -112 \pm 9$ J mol^{-1} K^{-1}; $\Delta G^{\#}_{298} = 87$ kJ mol^{-1} in dichloromethane. Thus under comparable conditions the oxidative addition step is approximately 120 times faster for iridium than rhodium at 25 °C.[20]

Only on heating did the migration reaction, $[MeIr(CO)_2I_3]^- + CO = [MeCOIr(CO)_2I_3]^-$ proceed at a useful rate (k_{obs} of *ca.* 2×10^{-4} s^{-1} at 115 °C in chlorobenzene under carbon monoxide, 5 bar). Extrapolation of the rate data for the rhodium system to 115 °C (and assuming that CO merely acts to stabilise the acyl iridium complex, and does not affect the intrinsic rate of migration) shows that methyl migration occurs faster for M = Rh than for M = Ir by a factor of approximately 10^5.[20]

vi) Oxidative addition and migration reactions in pentamethylcyclopentadienyl-rhodium and -iridium complexes

In order to see how general the reactivity ratios were between rhodium and iridium, we have also carried out some studies on a completely different system, the pentamethylcyclopentadienyl complexes of these metals.[15,20] The η^5-C$_5$Me$_5$ ring is quite bulky and is expected to shield the metal from attacking nucleophiles; since it is also an electron-donating ligand that should again strongly influence reactions at the metal centre. It should therefore allow an estimation of the intrinsic differences in behaviour of the two metals.

We have studied the second order rates of oxidative addition of methyl iodide to $[\eta^5\text{-C}_5\text{Me}_5\text{M(CO)}_2]$ (M = Rh, Ir) in CH$_2$Cl$_2$, and the subsequent migration reaction. For rhodium the first observed product of oxidative addition is again an acyl, $[C_5Me_5Rh(COMe)(CO)I]$[14] and, although the intermediate methyl complex was not detected by IR spectroscopy, there is circumstantial evidence favouring it. The activation parameters were $\Delta H^{\#} = 40 \pm 4$ kJ mol^{-1}, $\Delta S^{\#} = -180 \pm 11$ J mol^{-1} K^{-1}; $\Delta G^{\#}_{298} = 90 \pm 6$ kJ mol^{-1}.

The parallel reaction with iridium yields the ionic iodide in an equilibrium,

$$[C_5Me_5Ir(CO)_2] + MeI \rightleftharpoons [C_5Me_5Ir(CO)_2Me]I$$

That reaction was also first order in both [MeI] and [C$_5$Me$_5$Ir(CO)$_2$], but the data are complicated due to that equilibrium, and to an equilibrium with the acyl, [C$_5$Me$_5$Ir(COMe)(CO)I], which is formed to a small but detectable extent [n(CO$_{acyl}$) 1673 cm^{-1}].

The pseudo-first order rate constants found for these reactions were k$_{(Ir)}$ 1.8 x 10^{-3} s^{-1} and k$_{(Rh)}$ 4.6 x 10^{-4} s^{-1} (0.8 M MeI in CH$_2$Cl$_2$, 25 °C). Thus, under comparable conditions the neutral dicarbonyl iridium complex oxidatively adds methyl iodide *ca.* 4 times faster than its rhodium analogue.[20]

Hart-Davis and Graham[21], found second order rate constants, k$_{(Rh)}$ 3.5 x 10^{-3} M^{-1} s^{-1} and k$_{(Ir)}$ 21 x 10^{-3} M^{-1} s^{-1} (CH$_2$Cl$_2$, 25 °C) for the oxidative addition of MeI to [η^5-C$_5$H$_5$M(CO)(PPh$_3$)]. Again here, the product from the iridium reaction was the ionic iodide, [η^5-C$_5$H$_5$Ir(CO)(Me)(PPh$_3$)]I, whereas the rhodium reaction proceeded through to the acyl, [η^5-C$_5$H$_5$Rh(COMe)(PPh$_3$)I]. This implies a rate difference factor of 6 between iridium and rhodium for the oxidative addition, very close to the value we found for [η^5-C$_5$Me$_5$M(CO)$_2$].

The iodo rhodium complex undergoes the bimolecular reaction,

$$[C_5Me_5Rh(CO)Me(I)] + PPh_3 \longrightarrow [C_5Me_5Rh(COMe)I(PPh_3)]$$
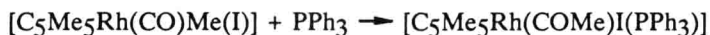
but the same reaction did not proceed for the iridium analogue. However, the chloride complex [η^5-C$_5$Me$_5$Ir(CO)Me(Cl)] shows some reactivity with PPh$_3$ in toluene at high temperature, and the second order rate constants for the reaction

$$[C_5Me_5M(CO)MeCl] + L \longrightarrow [C_5Me_5M(COMe)Cl(L)]$$
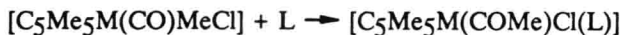
with the more basic phosphines, L = PMePh$_2$ and PMe$_2$Ph, have been measured for both Rh and Ir by UV-visible spectroscopy (k$_{(Rh)}$ = 3.7 M^{-1} s^{-1} for L = PMePh$_2$ and 8.4 M^{-1} s^{-1} for L = PMe$_2$PhCH$_2$Cl$_2$, 20 °C, in the range [L] = 5 x