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REACTION OF THE RHODIUM AND IRIDIUM COMPLEXES $[C_5Me_5MMe_2(Me_2SO)]$ WITH ALDEHYDES TO GIVE $[C_5Me_5MMe(R)(CO)]$, AND RELATED REACTIONS *

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Summary

The complexes $[C_5Me_5MMe_2(Me_2SO)]$ (**1a**, M = Rh; **1b**, M = Ir) react with aldehydes (RCHO) (cyclohexane, 80°C) to give $[C_5Me_5M(Me)R(CO)]$, methane, and Me_2SO; the reaction is strongly inhibited by dimethyl sulphoxide but is unaffected by addition of di-t-butyl peroxide. Benzaldehyde reacts with the rhodium complex ca. 30 times as fast as with the iridium complex; the relative rates of reaction of tolualdehydes with both **1a** and **1b** are in the ratio, 1/2/2 for the *o*-, *m*- and *p*-isomers. The complexes $[C_5Me_5M(Me)R(CO)]$ are also formed by carbonylation of $[C_5Me_5M(Me)R(Me_2SO)]$. Reaction of $[C_5Me_5IrMe(phenyl)(Me_2SO)]$ with ArCHO gave a mixture of $[C_5Me_5Ir\text{-}Me(Ar)(CO)]$ and $[C_5Me_5Ir(Ar)(phenyl)(CO)]$ (ca. 4/1); replacement of aryl being favoured over replacement of methyl. $[C_5Me_5Ir(phenyl)_2(Me_2SO)]$ gave $[C_5Me_5Ir(phenyl)(tolyl)(CO)]$ on reaction with $p\text{-}MeC_6H_4CHO$. Possible mechanisms are discussed; the evidence favours one involving metal(V) intermediates.

Introduction

We recently reported an unusual aromatic metallation reaction in which the labile dimethyl-rhodium and -iridium dimethyl sulphoxide complexes (**1a** and **1b**) reacted with arenes to give methane and aryl-methyl complexes [1] (eq. 1). The reactivity of **1** was traced to the ease with which the dimethyl sulphoxide could be displaced; it was in fact acting as a "weak protecting group" for a "vacant site".

$$[C_5Me_5M(Me)_2(Me_2SO)] + C_6H_5X \rightarrow [C_5Me_5MMe(C_6H_4X)(Me_2SO)] + CH_4 \quad (1)$$

(**1a**, M = Rh;
1b, M = Ir)

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* Dedicated to Professor Lamberto Malatesta in recognition of the seminal contributions he has made to organometallic chemistry.

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The success of reaction 1 prompted a search for other substrates which would react with **1** in unusual ways. We report here the reactions with aldehydes which lead to alkyl- or aryl-carbonyl complexes.

Results

A solution of the dimethylrhodium complex **1a** [2] dissolved in cyclohexane reacted readily with an excess of benzaldehyde (80°C/4 h) to give, after work-up, red brown crystals of the phenylmethylcarbonyl complex **4a** in high yield. NMR analysis of the reaction solution showed the presence of only dimethyl sulphoxide (uncomplexed) in addition to **4a** and some unreacted **1a**, but mass spectrometry of the gas phase showed that methane was also formed. This indicated that a reaction had taken place according to eq. 2.

$$\underset{(\mathbf{1a})}{[C_5Me_5RhMe_2(Me_2SO)]} + PhCHO \rightarrow \underset{(\mathbf{4a})}{[C_5Me_5Rh(Me)Ph(CO)]} + Me_2SO + CH_4 \qquad (2)$$

TABLE 1

$C_5Me_5MR^1R^2(CO)$ MICROANALYSES, YIELDS, ν(CO)

Complex				Yield (%)	Analysis (Found (calcd.)(%))			ν(CO) (cm^{-1})
M	R^1	R^2			C	H	Other	
Rh	Me	Me	**2a**	75	52.5 (52.7)	7.0 (7.1)	–	1995
Ir	Me	Me	**2b**	85	40.2 (40.5)	5.5 (5.3)	–	1975
Rh	Me	Et	**3a**	–	–	–	–	1990
Ir	Me	Et	**3b**	–	–	–	–	1975
Rh	Me	Ph	**4a**	65	60.4 (60.3)	6.5 (6.5)	–	1985
Ir	Me	Ph	**4b**	85	48.5 (48.3)	5.2 (5.2)	–	1988
Rh	Me	*o*-To	**5a**	8	61.8 (61.3)	7.0 (6.8)	–	1992
Ir	Me	*o*-To	**5b**	30	49.6 (49.4)	5.5 (5.5)	–	1962
Rh	Me	*m*-To	**6a**	42	61.6 (61.3)	7.1 (6.8)	–	1992
Ir	Me	*m*-To	**6b**	45	49.0 (49.4)	5.5 (5.5)	–	1962
Rh	Me	*p*-To	**7a**	35	61.3 (61.3)	7.0 (6.8)	–	1995
Ir	Me	*p*-To	**7b**	32	50.1 (49.4)	5.9 (5.5)	–	1980
Ir	Me	C_6H_4I	**11b**	92	37.5 (37.7)	3.8 (3.9)	I, 22.0 22.1	1993
Ir	Me	$C_6H_4NO_2$	**12b**	95	43.8 (43.9)	4.5 (4.5)	N, 2.9 2.8	1995
Ir	C_6H_5	*p*-To	**14b**	32	54.3 (55.0)	5.3 (5.2)	–	1975

TABLE 2

^{1}H NMR SPECTRA FOR $C_5Me_5MR^1R^2(CO)$ ($CDCl_3$), J(Rh–H) IN [] Hz AND J(H–H) IN () (Hz)

Complex	C_5Me_5	R^1 (Me)	R^2
2a	1.78	0.17d [2.3]	–
2b	1.83	0.32s	
3a	1.77	0.17d [2]	Et, 1.24b,m
3b	1.82	0.36s	Et, 1.31b,m
4a	1.72	0.53d [2.3]	Ph, 7.1m, H-3/4/5; 7.7d, H-2/6 (7.5)
4b	1.77	0.65s	Ph, 6.96m, H-3/4/5; 7.16d, H-2/6 (7.4)
5a	1.67	0.53d [2.5]	*o*-To, 2.41s (Me); 6.90m, 7.06m
5b	1.80	0.75s	*o*-To, 2.48s (Me); 6.92m, 7.11m
6a	1.68	0.50d [2.5]	*m*-To, 2.25s (Me); 6.77d, 6.92m
6b	1.76	0.64s	*m*-To, 2.23s (Me); 7.00s, H-2; 6.93d, H-4 (7.0); 6.85t, H-5 (7.2); 6.75d, H-6 (7.0)
7a	1.69	0.50d [2.5]	*p*-To, 2.25s (Me); 6.86dd, H-3 (1; 8); 7.03dd, H-2 (1.5; 8)
7b	1.78	0.60	*p*-To, 2.19s (Me); 6.81d, H-2/6, H-2/6 (7.0); 7.03d, H-3/5 (7.0)
11b	1.77 1.86	0.62	*m*- and *p*-C_6H_4I, 6.8t, 7.05d, 7.18m, 7.34bd, 7.48bd
12b	1.8	0.61 0.64	*m*- and *p*-$C_6H_4NO_2$, 7.18t, 7.45m, 7.58m, 7.84d, 7.98bd
14b	1.80		Ph, *p*-To; 2.21s (Me); 6.76d, 6.91m, 7.13d, 7.20–7.62m

Similar products, $[C_5Me_5Rh(Me)R(CO)]$ where R = Me (**2a**), Et (**3a**), *o*-tolyl (**5a**), *m*-tolyl (**6a**), and *p*-tolyl (**7a**), were obtained from reaction of **1a** with other aldehydes RCHO; the occasional low yield quoted in Table 1 is due to the difficulty in isolating some of the products from an excess of the aldehyde, rather than to the production of other complexes.

The complexes were identified by microanalysis and spectroscopically (IR: terminal metal-CO bands at 1990 ∓ 5 cm^{-1} for the rhodium and rather lower for the iridium complexes, Table 1, and ^{1}H and ^{13}C NMR spectra, Table 2).

$$\underset{(\mathbf{1b})}{[C_5Me_5IrMe_2(Me_2SO)]} + PhCHO \rightarrow \underset{(\mathbf{4b})}{[C_5Me_5Ir(Me)Ph(CO)]} + Me_2SO + CH_4 \quad (3)$$

The iridium complex **1b** reacted similarly to **1a** (eq. 3), but this reaction was significantly slower than reaction 2. Comparisons between reactions 2 and 3 are complicated due to the release of the dimethyl sulphoxide which inhibits each reaction but to differing extents. (Addition of one equivalent of dimethyl sulphoxide inhibited the rhodium reaction (eq. 2) at 50°C by a factor of approximately 4.5 and the iridium reaction (eq. 3) at 80°C by a factor of approximately 6.) Under comparable conditions (70°C; 1/2 complex **1**: benzaldehyde in cyclohexane-d_{12}), $t_{\frac{1}{2}}$ was 0.5 h for the rhodium reaction 2 and ca. 16 h for the iridium reaction 3. With benzaldehyde under these conditions the rhodium complex **1a** reacts effectively ca. 30 times as fast as **1b**. This result is in marked contrast to that found for the reactions of **1** with arenes (eq. 1) where the iridium complex reacted approximately 400 times faster than the rhodium complex [1].

Reaction of the complexes **1a** and **1b** with carbon monoxide in cyclohexane (8 atm, 55°C) gave the dimethylcarbonyl complexes **2a** and **2b** in good yields (ν(CO) 1995 and 1975 cm^{-1}, respectively). These products were also formed by reaction of **1a** or **1b** with acetaldehyde, which therefore effectively acted here simply as a source of CO.

Propionaldehyde appeared to react similarly to acetaldehyde and benzaldehyde, but the resultant ethylmethylcarbonyl complexes (**3a** and **3b**) were very unstable and were only characterised by NMR and IR spectroscopy in situ.

The arylmethylcarbonyliridium complexes (**4b**, **11b**, and **12b**) were also made by reaction of the appropriate arylmethyl dimethylsulphoxide complexes, **8b**, **9b**, and **10b**, respectively, with CO (5 atm/60°C; eq. 4).

$$[C_5Me_5IrMe(R)(Me_2SO)] + CO \rightarrow [C_5Me_5IrMe(R)(CO)] + Me_2SO \qquad (4)$$

^{13}C NMR studies of the complexes **11b** and **12b**, which had been made from the *m-/p-* isomer mixtures $[C_5Me_5IrMe(C_6H_4X)Me_2SO)]$ (**9b**, X = I; **10b**, X = NO_2) obtained by treating **1b** with either iodo- or nitro-benzene [1], showed that the same relative proportions of *m-* and *p-*isomers were present in the carbonyls as were in the arylmethyl dimethyl sulphoxide complexes (3/1 for X = I, 1/1 for X = NO_2). Reaction 4 is thus simply a replacement of the labile Me_2SO by CO.

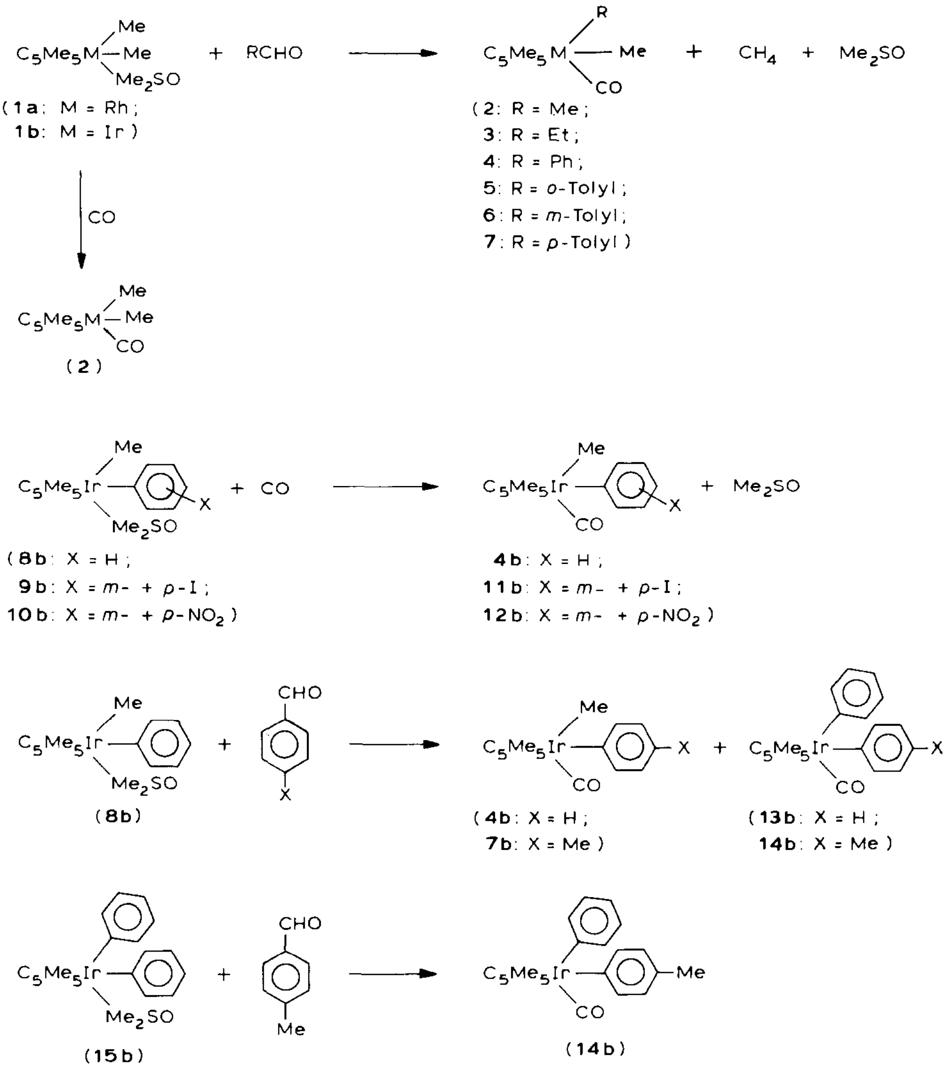
Reaction of the complexes **1a** or **1b** with *o-*, *m-*, or *p-*tolualdehyde (MeC_6H_4CHO) gave the corresponding *o-*, *m-* or *p-*tolyl complexes $[C_5Me_5M(Me)(C_6H_4Me)(CO)]$ (**5**–**7**). *o-*Tolualdehyde reacted with greatest difficulty. Competitive experiments wherein one equivalent of **1a** or **1b** was treated with a mixture containing one equivalent of each of the three tolualdehydes showed that the products were formed in the ratios *o-*, *m-* and *p-*, of ca. 1/2/2 for both rhodium and iridium. This implies that a methyl *meta* or *para* to the aldehyde has roughly the same effect, and that this is approximately half that for a methyl *ortho* to the aldehyde. One may presume that the effect on the *ortho* position will be very largely steric; this implies that the steric effect of a substituent in the *meta* and *para* positions is very small indeed.

Reaction of $[C_5Me_5IrMe(Ph)(Me_2SO)]$ (**8b**) with benzaldehyde gave not only the diphenyl complex $[C_5Me_5IrPh_2(CO)]$ (**13b**). Contrary to expectations **13b** proved to be the minor product, the major one (in the ratio of ca. 1/4) being the methylphenylcarbonyl complex $[C_5Me_5IrMe(Ph)(CO)]$ (**4b**). Similarly, reaction of **8b** with *p-*tolualdehyde gave an approximately 4/1 mixture of $[C_5Me_5IrMe(p\text{-}MeC_6H_4)(CO)]$ (**7b**) and $[C_5Me_5IrPh(p\text{-}MeC_6H_4)(CO)]$ (**14b**). It was also shown that reaction of the iridium diphenyl complex $[C_5Me_5IrPh_2(Me_2SO)]$ (**15b**) with *p-*tolualdehyde gave $[C_5Me_5IrPh(p\text{-}MeC_6H_4)(CO)]$ (**14b**).

The reactions carried out are summarised in Scheme 1.

Discussion

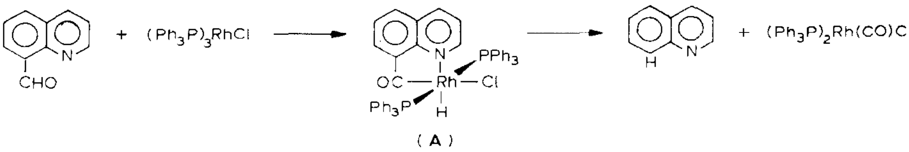
Although the reaction with aldehydes does not appear to have previously been used for the synthesis of transition metal σ-alkyl or σ-aryl complexes, the metal complex-induced decarbonylation of aldehydes to the hydrocarbon (frequently using



SCHEME 1

$[Rh(PPh_3)_3Cl]$), has been accomplished both stoicheiometrically [3] and catalytically [4]. The generally agreed reaction path involves oxidative addition of the aldehyde C–H to the low valent metal centre to give an acylmetal intermediate, followed by migration, decarbonylation, and reductive elimination steps. From studies using optically active aldehydes, it was suggested that caged radicals were involved during the decomposition of an intermediate acylrhodium(III) complex, in the stoicheiometric reaction [5].

Suggs showed that the probable path for the stoicheiometric decarbonylation reaction using the potential chelate quinoline-8-aldehyde and $[Rh(PPh_3)_3Cl]$ was as illustrated in Scheme 2 [6]. A stable intermediate (**A**) was isolated and shown to bear a rhodium-bonded hydride and an aroyl ligand; on heating, **A** decarbonylated and



SCHEME 2

reductively eliminated to give quinoline and [Rh(PPh$_3$)$_2$(CO)Cl]. The formation of the acylrhodium(III) hydride intermediate, **A**, implies that an oxidative addition of the aldehyde C–H bond to a rhodium(I) has occurred.

There are several possible mechanisms for the reactions of **1** with aldehydes. The fact that even very small amounts of added dimethyl sulphoxide (one equivalent per mole of **1**) inhibit the reaction with aldehydes so very strongly points clearly to the initial step being the loss of dimethyl sulphoxide and the creation of a vacant site.

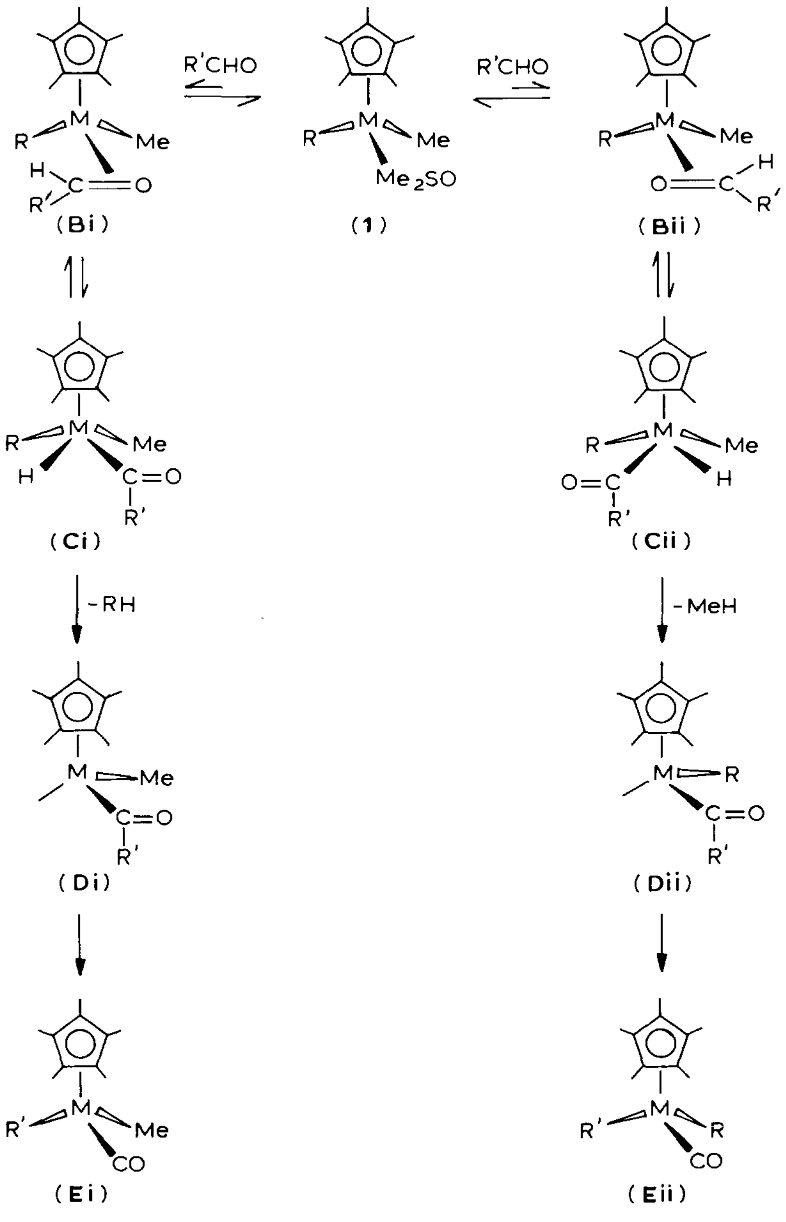
One plausible mechanism for the reactions is via a radical process. The most reasonable would involve attack by RCO$^\cdot$ at the metal, presumably at the site occupied by the Me$_2$SO. However, addition of di-t-butyl peroxide to the reactions of benzaldehyde with both **1a** (at 50°C) and **1b** (at 80°C) caused no detectable changes in rate. Furthermore the reactions are quite clean and the products are formed virtually quantitatively. Although it is difficult to completely exclude all radical processes, such as the participation of caged radical pairs during the decomposition steps, these facts discount any major involvement of free radical species during the early part of the reaction.

Since the gas given off during the reaction is methane, we can also exclude a mechanism involving the primary reduction of **1** to a lower oxidation state species (e.g., Rh^I, which then oxidatively added RCOH) since that should lead to co-production of ethane.

We prefer, by analogy to the arene activation reactions described before [1], to consider that the aldehyde reactions also proceed by a primary η^2-coordination of the reactant in the site vacated by the dimethyl sulphoxide (**B** in Scheme 3), followed by a C–H activation as shown. This is basically similar to the mechanism proposed by Suggs for reactions promoted by Rh^I, except that the metal in the intermediate **B** is in the higher formal oxidation state of +3. In the case of the reactions described by eq. 1 an η^2-bonding of the arene was presumed to precede oxidative addition of an aryl C–H. Here we suggest that the aldehyde initially binds η^2 through the C=O, as in **B**. This type of bonding has been found in a number of molecules, most notably in [Ni((cyclo-C$_6$H$_{11}$)$_3$P)$_2$(PhCHO)], the X-ray structure of which shows η^2-coordination of the C=O [7]. This molecule can also be regarded as having an oxanickelacyclopropane ring.

More information and further support for Scheme 3 comes from the reactions of [C$_5$Me$_5$IrMe(C$_6$H$_5$)(Me$_2$SO)] (**8b**) with benzaldehyde and with *p*-tolualdehyde. Both these reactions gave a mixture of two products, both approximately in the ratio of 1/4, identified as [C$_5$Me$_5$Ir(C$_6$H$_5$)(XC$_6$H$_4$)(CO)] (**13b**, X = H or **14b**, X = *p*-Me) and [C$_5$Me$_5$IrMe(XC$_6$H$_4$)(CO)] (**4b**, X = H, or **7b**, X = *p*-Me), respectively. We must conclude that the methyl on the iridium in **8b** is not eliminated preferentially.

Since the driving force for the reactions involving **1** must be the loss of methane, why is the loss of methane not the dominant force in the experiments with **8b**? The



SCHEME 3

reason must be that the reaction path which is followed does not especially lend itself to loss of methane. To accommodate this we suggest that the key intermediate/transition state (**C** in Scheme 3) involves a square pyramidally based complex in which the metal formally has the +5 oxidation state. Such a geometry has been found for three M^V complexes, $[C_5Me_5IrMe_4]$ [8], $[C_5Me_5Rh(H)_2(SiEt_3)_2]$ [9], and $[C_5Me_5Ir(H)_2(SiEt_3)_2]$ [10].

In Scheme 3, when R = Me, intermediate **Bi** is identical to **Bii** and **Ci** is identical to **Cii**. However, for reactions of complex **8b**, R = Ph, there are two orientations of the aldehyde (R'CHO) with respect to the phenyl and methyl groups on the metal, if we assume that the geometry of **B**, where the aldehyde is bonded η^2 to the metal in the site previously occupied by the Me_2SO, is a rigid one. The R' can be on the same side as the phenyl (R), as in **Bii**, or on the same side as the methyl, as in **Bi**. (It is assumed that, to minimise non-bonded interactions of the aldehyde with the C_5-ring, the aldehyde coordination with the aldehydic hydrogen pointing "up" towards the ring will be strongly favoured over the alternatives, with either the R or the CO group pointing up.)

If **Bi** and **Bii** do not easily interconvert in the lifetime of the intermediate, then oxidative addition of the aldehyde C–H to the metal will yield **Ci** and **Cii**, respectively, where a small distance slide of the C=O–metal interaction has occurred. If R is bulkier than Me, then **Bi**, and **Ci**, where R and R'CO are *trans* (diametrically opposite in the base of the square pyramid) may be expected to be favoured over **Bii** and **Cii** (R and R'CO *cis*). This means that in the favoured geometry **Ci**, the hydride will be *cis* to the phenyl and *trans* to the methyl and therefore the reductive elimination, which is expected to be between the hydride and a *cis*-ligand, will favour loss of benzene (Ph....H) over loss of methane (Me....H). Thus, **Ci** will give **Di**, which can undergo migration of R' back onto the metal to give **Ei**; analogously, **Eii** arises from **Cii** via **Dii**.

We also know from the chemistry of the rhodium(V) complex $[C_5Me_5Rh(H)_2(Et_3Si)_2]$ that the most common reaction is reductive elimination of Et_3SiH. Since the bond energy of a C–H bond is substantially greater than that of an Si–H bond, the driving force towards reductive elimination of benzene or methane from the intermediate **C** is likely to be much greater.

One question remains, why is the reactivity of the rhodium complex **1a** ca. 30 times that for the iridium complex **1b** in reaction 5, while it is one-four hundredth of that for **1b** in reaction 6?

$$[C_5Me_5MMe_2(Me_2SO)] + PhCHO \rightarrow [C_5Me_5M(Me)Ph(CO)] + Me_2SO + CH_4 \quad (5)$$

$$[C_5Me_5MMe_2(Me_2SO)] + C_6H_6 \rightarrow [C_5Me_5M(Me)Ph(Me_2SO)] + CH_4 \quad (6)$$

It is probable that the answer lies in the relative facility with which rhodium and iridium η^2-coordinate to the benzene and the aldehyde, respectively. Work in our laboratories has shown that C_5Me_5Ir is a softer centre than C_5Me_5Rh and binds more strongly to olefins and arenes [11–13]. Thus, if the stability of the η^2-arene complex plays an important role in determining the overall rate of reaction 6, the Ir complex will be expected to react faster than Rh.

There is also evidence that C_5Me_5Rh binds better to oxy ligands than does C_5Me_5Ir, for example in the complexes with Me_2SO [13]. Analogously then, since the η^2 binding of the aldehyde is expected to be stronger to Rh than to Ir, the reaction with **1a** may be anticipated to be faster than that with **1b** if the stability of **B** plays an important role in the overall reaction 5.

Experimental

Yields, microanalytical data (University of Sheffield Microanalytical Service), and ^1H and ^{13}C NMR spectroscopic data (Perkin–Elmer R-12B, R-34, Jeol PFT-100,

TABLE 3

$^{13}C\{^1H\}$ NMR SPECTRA FOR $C_5Me_5MR^1R^2(CO)$ J(Rh–C) IN [] (Hz)

Complex	C_5Me_5	CO	R^1 (Me)	R^2						
2a	8.9; 100.0	193.2	−5.6							
	[4.9]	[78.1]	[24.4]							
2b	8.6; 96.8	173.3	−24.3							
3b	8.6; 97.4	173.9	−23.2	Et	−6.6	+20.5				
4a	9.1; 101.7	192.8	−2.7	Ph	*i*-	*o*-	*m*-	*p*-		
	[2.5]	[77.0]	[25.0]		152.4	139.1	127.8	122.9		
					[37.2]					
4b	8.7; 98.3	172.7	−22.0		130.8	139.7	127.9	122.7		
5a	9.0; 101.7	192.9	−0.8	*o*-To	153.0	144.5 138.1	128.6 124.9	123.1	Me,	27.9
		[77.0]	[25.2]		[34.7]					
5b	8.6; 98.1	172.8	−20.1	*o*-To	145.5	132.0 138.1	128.0 124.9	123.0	Me,	28.4
6a	9.1; 101.6	192.9	−2.8	*m*-To	152.1	139.8 135.9	136.7 123.8	127.4	Me,	21.4
	[2.9]	[78.0]	[25.4]		[33.8]					
6b	8.7; 98.2	172.8	−22.0	*m*-To	130.7	123.5 140.6	136.6 127.5	136.5	Me,	31.3
7a	9.1; 101.6	192.9	−2.8	*p*-To	147.4	138.7	128.8	132.1	Me,	41.4
	[2.6]	[77.5]	[25.2]		[33.7]					
7b	8.8; 98.2	172.8	−22.1	*p*-To	131.8	139.4	129.0	125.9	Me,	20.7
11b *m*-C_6H_4I	8.7; 98.3	172.3	−21.8	*m*-C_6H_4I	134.8	147.6 139.0	95.4 129.6	131.5		
p-C_6H_4I	8.7; 98.8	170.8	−21.9	*p*-C_6H_4I	n.o.	142.0	136.5	88.5		
12b *m*-$C_6H_4NO_2$	8.7; 98.6	172.0	−21.5	*m*-$C_6H_4NO_2$	n.o.	133.5 146.7	147.5 127.7	118.0		
p-$C_6H_4NO_2$	8.7; 98.5	171.9	−21.7	*p*-$C_6H_4NO_2$	144.8	140.3	121.6	n.o.		
14b	9.1; 100.2	172.3	–	Ph	127.0	140.1	128.0	122.5		
				p-To	131.6	139.8	129.1	125.0	Me,	20.6

and Bruker AB 250) are collected and presented in Tables 1–3. Brief descriptions of typical experiments are give below. Rates were measured by following changes in the ^{1}H NMR spectra of reactions of **1** and benzaldehyde in cyclohexane-d_{12} (at 50°C for **1a** and at 80°C for **1b**), except where stated).

*[$C_5Me_5Rh(Me)(C_6H_5)(CO)$] (**4a**)*

Benzaldehyde (0.03 cm^3, 0.31 mmol) was added to a solution of [$C_5Me_5RhMe_2$-(Me_2SO)] (**1a**) [2] (0.10 g, 0.29 mmol) in cyclohexane (5 cm^3) in a Schlenk tube under argon (or nitrogen). The tube was heated (80°C, 4 h); the brownish-red solution was then filtered and evaporated to dryness on a rotary evaporator. The red residue was extracted with pentane (2 × 10 cm^3) and water (to remove excess dimethyl sulphoxide, 3 cm^3). The pentane solution was dried, and concentrated to give, on standing, red-brown crystals of complex **4a** (65 mg, 65%).

The identical reaction with complex **1b**, yielded 85% **4b** after 24 h at 80°C and similar work-up; complexes **2a**, **2b**, **5a**, **5b**, **6a**, **6b**, **7a**, and **7b** were prepared similarly from **1** and the appropriate aldehyde.

The ethylmethyl complexes [$C_5Me_5MMe(Et)(CO)$] (**3a** and **3b**) were obtained in solution by reaction of **1** with propionaldehyde in C_6D_6 at 54°C, the reaction being monitored by ^{1}H NMR spectroscopy.

*Reactions of [$C_5Me_5IrMe(phenyl)(Me_2SO)$] (**8b**)*

(i) with CO. A solution of [$C_5Me_5IrMe(phenyl)(Me_2SO)$] (**8b**) [1] (50 mg, 0.1 mmol) dissolved in cyclohexane (15 cm^3) was treated with CO (5 atm, 60°C, 15 h) in a Fisher–Porter glass pressure tube. The reaction was then stopped, the solvent removed in vacuo, and the residue extracted with wet pentane (10 cm^3); after drying and concentration, the pentane solution yielded yellow crystals of complex **4b** (42 mg, 95%).

The reactions of **9b**, and **10b** (mixtures of isomers obtained as described previously [1]) and of **1a** and **1b** with CO were conducted entirely analogously.

(ii) with benzaldehyde. A solution of [$C_5Me_5IrMe(phenyl)(Me_2SO)$] (**8b**) (0.27 g, 0.52 mmol) in cyclohexane (10 cm^3) containing benzaldehyde (0.06 cm^3, 0.6 mmol) was heated (70°C/20 h) under argon. The solution was filtered, and the solvent removed. The residue (**a**) was extracted with dichloromethane, which was then washed with water to remove dimethyl suphoxide, dried, and the solvent removed. Crystallisation of the residue from aqueous methanol gave a yellow solid (**b**, 50 mg). The mass spectrum of (**b**) showed the presence of molecular ions due to both [$C_5Me_5IrMe(phenyl)(CO)$] (**4b**), and [$C_5Me_5Ir(phenyl)_2(CO)$] (**13b**) (m/e 448 and 509 respectively). HPLC analysis showed the presence of the same two compounds, by reference to authentic samples, and the ^{1}H NMR spectrum also showed the presence of these two compounds, in the ratio of ca. 4/1. The ratio was essentially the same in the NMR spectrum of (**a**).

The reactions of **8b** and of **15b** with *p*-tolualdehyde were conducted analogously.

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