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Reactions of Dichlorobis(μ-chloro)bis(pentamethylcyclopentadienyl)dirhodium and -diiridium with Hexamethyldialuminum

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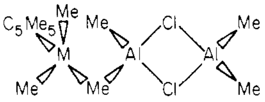
Reaction of [$(C_5Me_5M)_2Cl_4$] (M = Rh or Ir) with Al_2Me_6 gives a yellow solution that has been analyzed by low-temperature ^{13}C NMR spectroscopy at 25 and 100 MHz and has been shown to contain $Al_2Me_4Cl_2$ and heterotrimetallic species formulated as [$(C_5Me_5MMe_3)_2AlMe$], for which structures **3** are suggested. Reaction of **3a** (M = Rh) with acetone gives the *trans*-bis(μ-methylene) complex **2**, and a mechanism for this transformation is proposed. The complexes **3a** and **3b** react with other ligands L [dimethyl sulfoxide (Me_2SO), triphenylphosphine, and bis(diphenylphosphino)methane (dppm)] to give the complexes [$C_5Me_5MMe_2L$].

Introduction

We have recently described the formation of the novel complex dimethylbis(μ-methylene)bis(pentamethylcyclopentadienyl)dirhodium (**2**) from the reaction of dichlorobis(μ-chloro)bis(pentamethylcyclopentadienyl)dirhodium (**1a**) with hexamethyldialuminum followed by reaction with an oxidizer (air) or a hydrogen acceptor (acetone).[1,2] Similar but more complex reactions take place when the iridium complex **1b** is reacted with hexamethyldialuminum.[1b,3]

We have also briefly reported that, on reaction of **1a** or **1b** with Al_2Me_6 in hydrocarbons at low temperature and before workup or addition of other reagents, only one rhodium- (or iridium-) containing species is present, as shown by detailed ^{13}C NMR studies. This species was originally formulated as A based on results obtained at −90 °C and a ^{13}C frequency of 25 MHz. The data have now been supplemented by ^{13}C studies at 100 MHz which, together with the improved integration facilities, have caused us to make a change in some details of the proposed structure. These studies form the subject of this paper.



A

Results and Discussion

Low-Temperature NMR Spectra. The ^1H NMR spectrum of the yellow solution formed by reaction of a solution of Al_2Me_6 with a suspension of **1a** in perdeuteriotoluene (C_7D_8) was not very informative, even at low temperature, owing to the overlap of signals in the metal–methyl region. However, the single C_5Me_5 resonance at δ 1.34 (at −90 °C) suggested the presence of only one rhodium complex.

The $^{13}C\{^1H\}$ spectra in C_7D_8 (or cyclopentane) at −90 °C were simple (Figure 1) and indicated that only one rhodium-containing species (**3a**) was present. This was characterized by sharp resonances at δ −17.98 [d, J(Rh–C) = 28.1 Hz], +2.61 [d, J(Rh–C) = 23.3Hz], 8.52 (s), and 97.89 [d, J(Rh–C) = 2.7 Hz]. Off-resonance decoupling showed the signals at δ −17.98, 2.61, and 8.52 to arise from methyl groups; the signal at δ 97.89 came from the carbons of a single C_5Me_5 ring. Assuming similar NOE's for the three methyl resonances, the relative intensities of the signals, 2:1:5, indicate a "$C_5Me_5RhMe_3$" unit in which one of the rhodium-bound methyls is different from the other two. These relative intensities remained constant over a large number of integrations involving some 20 different experiments carried out on two different instruments; pulse widths and repetition times were chosen to ensure that the spectra were measured under fully equilibrated conditions in order to optimize accuracy of integration. The magnitudes of the coupling constants are consistent with these methyls being bound to rhodium[4] (see also values for **4a**, **5a**, and **6a** in Table I) and the splitting into doublets shows that they are only associated with one rhodium.

Four other resonances may be distinguished in the metal–methyl region. Two of these (δ −4.54 and −7.19) are due to the bridging and terminal methyls respectively of Al_2Me_6, which is present in excess. The other two resonances (δ −5.03 and −5.89) are assigned to other Me–Al species. The δ −5.03 resonance is sufficiently close to that for the four equivalent terminal methyls of $Al_2Me_4Cl_2$ (normally at δ −5.12 under similar conditions[5,6]) for us to identify it with the presence of this molecule. This leaves only one resonance, at δ −5.89, to be accounted for. The relative intensities also of these resonances (other than those of Al_2Me_6) remained quite constant from one experiment to another and on varying the molar ratio of **1a**:Al_2Me_6 from 2.5 to 10:1. Integration shows the δ −5.03 and −5.89 resonances to be in the ratio of 4:0.5 taking the Rh–Me at δ 2.61 as unity. This indicates an empirical formula for the species of $(C_5Me_5RhMe_2Me)_2AlMe$ (**3a**) plus $2(Al_2Me_4Cl_2)$.

Above about −60 °C the three resonances due to Al_2Me_6 and $Al_2Me_4Cl_2$ begin to broaden and coalesce. The small resonance at δ −5.89 appears not to participate in the exchange at this temperature and remains separate and reasonably sharp up to ca. −30 °C. Spin saturation transfer

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(1) (a) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 809. (b) Vázquez de Miguel, A.; Isobe, K.; Taylor, B. F.; Nutton, A.; Maitlis, P. M. *Ibid.* **1982**, 758.

(2) Isobe, K.; Vázquez de Miguel, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1441.

(3) (a) Isobe, K.; Andrews, D. G.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 809. (b) Isobe, K.; Maitlis, P. M. *J. Organomet. Chem.* **1983**, *250*, C25.

(4) Mann, B. E.; Taylor, B. F. "^{13}C NMR Data for Organometallic Compounds"; Academic Press: New York, 1981; p 44.

(5) Gómez, M.; Spencer, C. M.; Maitlis, P. M., unpublished results.

(6) (a) For discussions of organoaluminum chemistry, see: Mole, T.; Jeffery, E. A. "Organoaluminum Compounds"; Elsevier: New York, 1972. (b) Eisch, J. J. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, pp 555 et seq.

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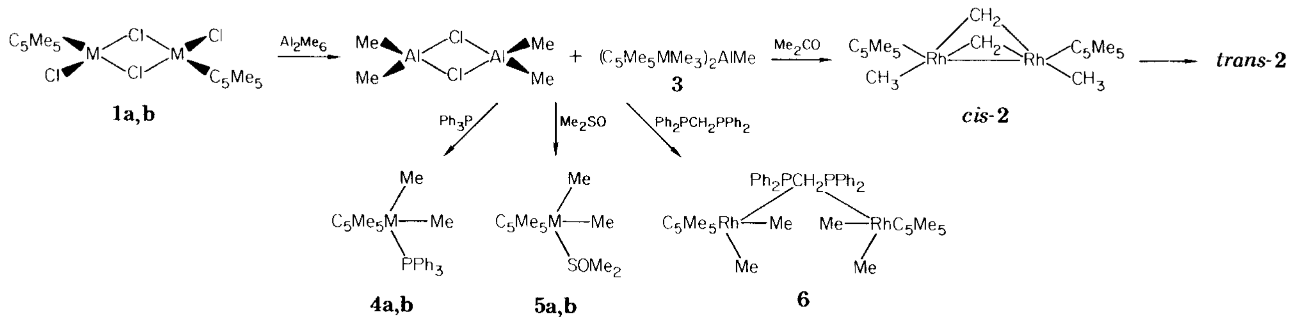
Table I

	% yield (method)	microanalysis[a]			IR, cm^{-1}	^1H NMR ($CDCl_3$, δ)[b,c]				^{13}C NMR ($CDCl_3$, δ)[b,c]			
		C	H	other		C_5Me_5	MMe_1	Me_2SO	Ph	C_5*Me*$_5$	C_5Me_5	MMe_2	other
$[C_5Me_5RhCl_2(Me_2SO)]$	80	37.5 (37.2)	5.4 (5.5)	Cl, 18.5 (18.4) S, 8.4 (8.3)	(SO) 1085 vs 1105 vs (RhCl) 280 s 265 s	1.72		2.98		8.5	98.7 [6.1]		41.6 (Me_2SO)
$[C_5Me_5IrCl_2(Me_2SO)]$	80	30.0 (30.3)	4.4 (4.4)	Cl, 15.1 (14.9) S, 6.8 (6.7)	(SO) 1112 vs 1080 sh (IrCl) 290 vs 270 vs	1.77		3.16		8.7	92.7		41.9 (Me_2SO)
$[C_5Me_5RhMe_2(Me_2SO)]$ (5a)	80 (A)	48.4 (48.6)	7.8 (7.9)	S, 9.2 (9.3) mol wt, 356 (346)	(SO) 1082 vs 1097 s	1.70	−0.05 [2]	2.78		8.6	97.8 [3.8]	−1.74 [29.8]	43.4 (Me_2SO)
$[C_5Me_5IrMe_2(Me_2SO)]$ (5b)	50 (A) 85 (B)	38.6 (38.6)	6.1 (6.2)	S, 7.3 (7.4) mol wt, 438 (436)	(SO) 1085 vs 1097 vs	1.70	0.04	2.91		8.3	93.3	−19.7	42.8 (Me_2SO)
$[C_5Me_5RhMe_2(PPh_3)]$ (4a)	49 (A) 95 (C)	67.6 (67.9)	6.9 (6.8)			1.41 (2.3)	−0.18 [2.3] (4.7)		7.28, 7.36 m	8.8	97.3 [4.6]	−1.76 [29.5] (13.7)	124-137 (Ph, m)
$[C_5Me_5IrMe_2(PPh_3)]$ (4b)	39 (A) 70 (C)	57.8 (58.1)	5.8 (5.9)			1.46 (1.7)	0.07 (5.3)		7.31 bd				
$[(C_5Me_5RhMe_2)_2(dppm)]$ (6)	80 (A) 75 (C)	63.9 (63.9)	7.0 (7.0)			1.28 (2.2)	−0.01 [2.3] (4.0)	CH_2P_2 −3.34 bd	7.07 bd				

[a] Calculated in parentheses. [b] J(Rh-H) and J(Rh-C) (Hz) expressed in brackets. [c] J(P-H) and J(P-C) (Hz) expressed in parentheses.

Scheme I



a, M = Rh; B, M = Ir

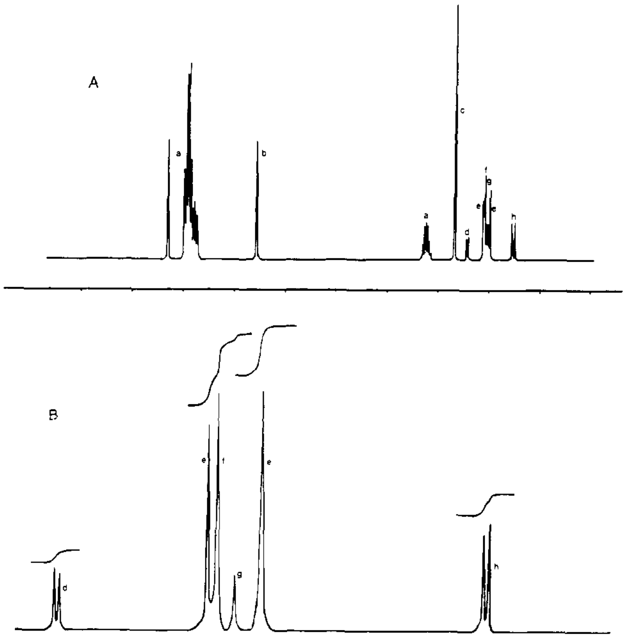


Figure 1. ^{13}C NMR spectrum of the solution obtained from reaction of $[(C_5Me_5Rh)_2Cl_4]$ with Al_2Me_6 in toluene-d_8 at -90 °C: (A) at 25 MHz, (B) at 100 MHz. Key: (a) C_7D_8 solvent, (b) C_5Me_5, (c) $C_5\mathit{Me}_5$, (d) RhMe, (e) Al_2Me_6, (f) $Al_2Me_4Cl_2$, (g) "lone" Me–Al, (h) $RhMe_2$.

experiments indicate that the rhodium-bound methyls at δ -17.98 and +2.61 exchange only with each other (at rather higher temperature, broadening becomes marked only above ca. -30 °C), and the aluminum-bound methyls only exchange with each other. Exchange is slow, at least at the lower temperatures, between Rh- and Al-bound methyls. The complex is reasonably stable to ca. +40 °C, by which temperature all the methyl resonances are broadened, and the low-temperature spectra can be reproduced exactly on recooling.

Further evidence concerning the nature of this species **3a** comes from trapping experiments (Scheme I). A variety of ligands was added to these solutions at low temperatures, and the NMR spectra were examined. Ether ligands caused collapse and fast exchange of all the methyl resonances even at -90 °C (but see below), and amines and hexamethylphosphoramide had similar effects. Reaction with triphenylphosphine gave $[C_5Me_5RhMe_2(PPh_3)]$ (**4a**) in 49% yield, but solubility problems precluded NMR monitoring of the reaction. The best ligand for this purpose turned out to be dimethyl sulfoxide (Me_2SO) since the reaction could be monitored at low temperature and a stable soluble complex, $[C_5Me_5RhMe_2(Me_2SO)]$ (**5a**), could then be isolated from the reaction in 95% yield. The properties of these and related complexes are described below. When Me_2SO was added to the yellow solution at very low temperature, only signals due to **3** and to the Me_2SO complex **5a** could be detected in the NMR spectrum. Addition of further Me_2SO converted the spectrum into that of **5a** together with that of an (uncharacterized) aluminum–Me_2SO complex, possibly $AlMe_2Cl(Me_2SO)$. These experiments suggest that the rhodium in the yellow solution is still in the +3 oxidation state and that no reduction (or oxidation) has yet occurred.

It should also be noted that, when the reaction of Al_2Me_6 with complex **1a** is carried out very carefully at low temperatures (to give the yellow solution), no methane is liberated. Further, the ^{13}C NMR spectra of the yellow solution show absolutely no sign of low-field (high-frequency) signals such as bridging or terminal CH or CH_2 ligands give rise to. This result may be contrasted with the formation of methane and of the trinuclear bis(μ_3-methyne) cluster $[(C_5Me_5Rh)_3(\mu\text{-}CH)_2]$[7] which occurs when the same reactants are mixed at ambient temperature and in very concentrated solution. This reaction at low temperature may also be contrasted with the reaction to give **7** described by Tebbe et al.[8]

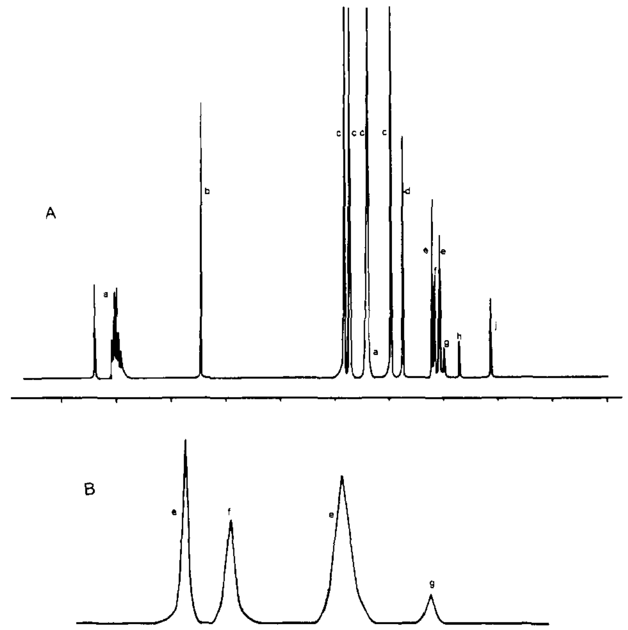
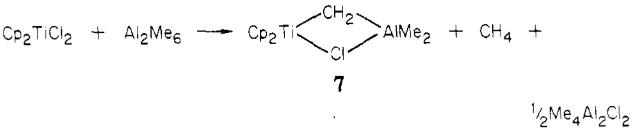


Figure 2. ^{13}C NMR spectrum of the solution obtained from reaction of $[(C_5Me_5Ir)_2Cl_4]$ with Al_2Me_6 in 2-methylbutane at -120 °C and 25 MHz: (A) entire spectrum, (B) Al–methyl region. Key: (a) toluene reference, (b) C_5Me_5, (c) 2-methylbutane solvent, (d) $C_5\mathit{Me}_5$, (e) Al_2Me_6, (f) $Al_2Me_4Cl_2$, (g) "lone" methyl, Me–Al, (h) IrMe, (j) $IrMe_2$.



Reaction of dichlorobis(μ-chloro)bis(pentamethylcyclopentadienyl)diiridium (**1b**) with Al_2Me_6 followed a quite parallel path at low temperature. Again a solution (very pale yellow-orange, in this case) was readily formed when a suspension of **1b** was reacted in a hydrocarbon solvent. Since the species present in this solution reacted slowly with aromatic compounds (toluene, benzene[3]), the solvents of choice, especially for the low-temperature ^{13}C NMR experiments, were aliphatic hydrocarbons such as 2-methylbutane or cyclopentane. (Parallel studies on the rhodium systems showed that the same species were formed in cyclopentane as in toluene.)

The ^{13}C NMR spectra at -90 °C (Figure 2) showed resonances at δ -29.0 (2) and -15.7 (1) (relative intensities of the methyl resonances in parentheses), which we assign to the $IrMe_3$, at δ 8.23 (5) and 93.2, assigned to the single C_5Me_5Ir, as well as methylaluminum resonances at δ -3.9 and -8.0 (excess Al_2Me_6), -5.5 (8, $Al_2Me_4Cl_2$), and -9.9 (0.5), assigned again to the lone methyl. These relative intensities were the same as those observed for the rhodium analogue. For this system the spectrum was also determined in 2-methylbutane at -120 °C. The chemical shifts

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[7] Vâzquez de Miguel, A.; Isobe, K.; Bailey, P. M.; Meanwell, N. J.; Maitlis, P. M. *Organometallics* **1982**, *1*, 1604.

[8] Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

of all the resonances were within 0.5 ppm of the values in cyclopentane at −90 °C, and thus the low temperature limiting spectrum appears to have been reached, at least so far as gross changes are concerned. Again, only a single iridium-containing species, [($C_5Me_5IrMe_3)_2(AlMe)$] (**3b**), is present.

When diethyl ether was added and the solution recooled to −118 °C, the ^{13}C NMR spectrum showed resonances due to **3b** virtually unshifted and still clearly recognizable as such. However the other methylaluminum resonances had all coalesced into a single sharp peak at δ −6.8. The fact that the peak at δ −9.9, assigned to the "lone" methyl, is still clearly visible and not exchanging with the Al_2Me_6 and $Al_2Me_4Cl_2$ resonances is highly significant in the assignment of a structure to **3**. Addition of Me_2SO simply and cleanly produced the [$C_5Me_5IrMe_2(Me_2SO)$] complex (**5b**) in high yield.

When toluene or benzene was added to solutions of **3b**, new resonances very soon appeared, consistent with our observation that these molecules reacted with the intermediate.[3]

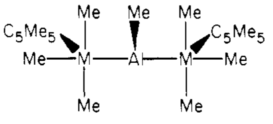
To sum up, both the rhodium and the iridium chloro complexes **1a** and **1b**, respectively, react easily at low temperatures with Al_2Me_6 to give a stoichiometric amount of $Al_2Me_4Cl_2$ and a thermally relatively stable species that is then defined as [($C_5Me_5MMe_3)_2AlMe$] (**3**) produced according to

$$2[(C_5Me_5M)_2Cl_4] + 5Al_2Me_6 = \underset{\mathbf{3}}{2[(C_5Me_5MMe_3)_2AlMe]} + 4Al_2Me_4Cl_2$$

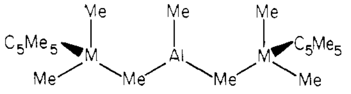
One of the chief reasons for proposing this formula rather than the one suggested before, (A),[1b] is that the 100-MHz ^{13}C NMR spectra strongly indicate that the intensity of the "lone" methyl is only half of that of the smaller of the Rh- (or Ir-) bound methyls. This points to a structure in which two Rh (or Ir) atoms and one Al are in the unit.

Further experiments were carried out with the aim of generating **3a** from a different starting material. This was accomplished when a solution of the Me_2SO complex **5a** was reacted with Al_2Me_6. The reaction proceeded quite slowly and required a large excess of Al_2Me_6 and gentle warming. In C_7D_8 at −90 °C signals were seen at δ −0.6 (d, J = 28 Hz), 8.23 (s), and 98.4 (d, J = 3 Hz) due to complex **5a**, at δ −5.8 which is where the dmso adduct of $AlMe_3$ resonates, at δ −4.7 and −6.9 (assigned to Al_2Me_6), and at δ −19.0 (d, J = 28 Hz), 1.6 (d, J = 23 Hz), 7.6, and 97.1. These last four resonances are very close to four of the five resonances found for **3a** and we therefore assign them accordingly; the missing signal of the lone Al-bound methyl is probably under the $AlMe_3(Me_2SO)$ resonance at δ −5.8. This experiment showed that complex **3a** could also be generated by a different route.

Structure of Complex 3. It is most unlikely that **3**, or indeed any other species formed under these conditions, has any appreciable ionic character in view of the very high solubility in solvents such as 2-methylbutane at temperatures as low as −120 °C. Indeed this observation strongly suggests that the molecules present must have a very "solvent-like" appearance—that is they must be relatively small and have an essentially all-hydrocarbon outer shell. The question then arises as to the disposition of the two types of rhodium- (or iridium-) bound methyls. One obvious solution to the problem is that they occupy three (two equivalent cis and one trans) sites in the base of a square pyramid. The four-legged piano stool geometry has been shown to occur in the Ir(V) complex [$C_5Me_5IrMe_4$].[3] However, since addition of Me_2SO and similar ligands gives rise to well-defined M(III) complexes, the fourth ligand would then have to be cationic in order to balance the charge, assuming the 18-electron rule continues to be obeyed. This implies the formation of a metal–metal bond (Al–Rh or Al–Ir; not Rh–Rh since that would result in a more complex spin-multiplicity for the attached methyls) and can be represented by structure **3-i**.



3-i



3-ii

One (indirect) analogy for structure **3-i** comes from the complexes [$Cp_2(C_5H_4)Mo_2(\mu\text{-}H)_2(\mu\text{-}AlMe_2)_2(\mu\text{-}AlMe)$] and [$Cp_2(C_5H_4)_2Mo_2(\mu\text{-}AlMe_2)(\mu\text{-}AlMe)$] that both have two metal atoms held together by a bridging AlMe ligand.[9,10] However, in these molecules the aluminums also bind to the C_5 rings, a feature for which the NMR spectra of **3** provide no evidence.

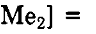
A closer analogy is provided by the trimetallic complex **8** which arises from the reaction of [$CpMo(CO)_3H$] and $GaMe_3$.[11]

$$[CpMo(CO)_3H] + GaMe_3 = [CpMo(CO)_3\text{–}GaMe_2] + CH_4$$

$$6[CpMo(CO)_3\text{–}GaMe_2] = \underset{\mathbf{8}}{3[CpMo(CO)_3\text{–}GaMe\text{–}Mo(CO)_3Cp]} + 3GaMe_3$$

For structure **3-i** the lower intensity of the Rh- (or Ir-) bound methyl resonance would be due to the methyl trans to the Al, while the $RhMe_2$ (or $IrMe_2$) resonance would arise from the two equivalent methyls cis to the Al.

Alternatively, either the pair of (equivalent) methyls or the single metal methyl could be bridging to the aluminum. Since the coupling to rhodium of the lower intensity doublet in **3a** is smaller (23.3 Hz) than that of the larger doublet (28.1 Hz), which in turn is similar to that of the terminal methyls in **4a** (29.5 Hz) or **5a** (29 Hz), this suggests that the Me_2 ligands in **3a** are also terminal and hence that it is the single methyl which bridges to aluminum as in structure **3-ii**. This assignment is also consistent with the assignments for Al_2Me_6, where the bridging methyls resonate at lower field (higher frequency) than the terminal ones,[12] and also for such complexes as [$Cp_2Sc(\mu\text{-}Me_2)\text{-}AlMe_2$] (**9a**), where again the methyls bridging Sc and Al resonate at substantially lower field (δ 20.7) than the terminal methyls (δ −6.3).[13]



9a, M = Sc
b, M = Yb
c, M = Ti
d, M = Lu

One immediately obvious point of difference between **3-ii** and the lanthanide complexes is that in the latter the metals are bridged by two methyls; this has been confirmed

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[9] Forder, R.; Prout, C. K. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2312.

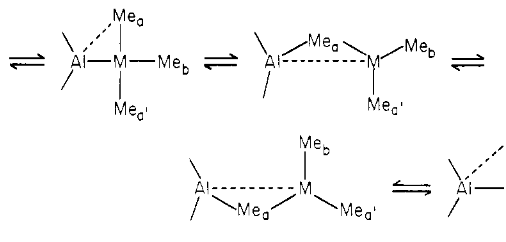
[10] Rettig, S. J.; Storr, A.; Thomas, B. S.; Trotter, J. *Acta Crystallogr., Sect. B* **1974**, *B30*, 666.

[11] (a) St. Denis, J. N.; Butler, W.; Glick, M. D.; Oliver, J. D. *J. Organomet. Chem.* **1977**, *129*, 1. (b) Conway, A. J.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1945.

[12] Muller, N. *Chem. Phys.* **1962**, *36*, 359. Olah, G. A.; Prakash, G. K. S.; Liange, G.; Henold, K. L.; Haigh, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 5217.

[13] Holton, J. A.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45 and 54.

Scheme II



by an X-ray structure determination of the Yb analogue **9b**.[13] A double bridge has also been proposed for $[Cp_2Ti(\mu\text{-}Me)_2AlMe_2]$ (**9c**),[13] $[(C_5Me_5)_2Lu(\mu\text{-}Me)_2AlMe_2]$ (**9d**),[14] and $[(\eta^3\text{-allyl})Ni(\mu\text{-}Me)_2AlMe_2]$.[15]

Structures **3-i** and **3-ii** formally leave the Al in the trimetallic unit three-coordinate. This can be justified because of the bulk of the attached substituents; it is also possible that in solution there is some weaker interaction either between two units or between one and $Al_2Me_4Cl_2$.

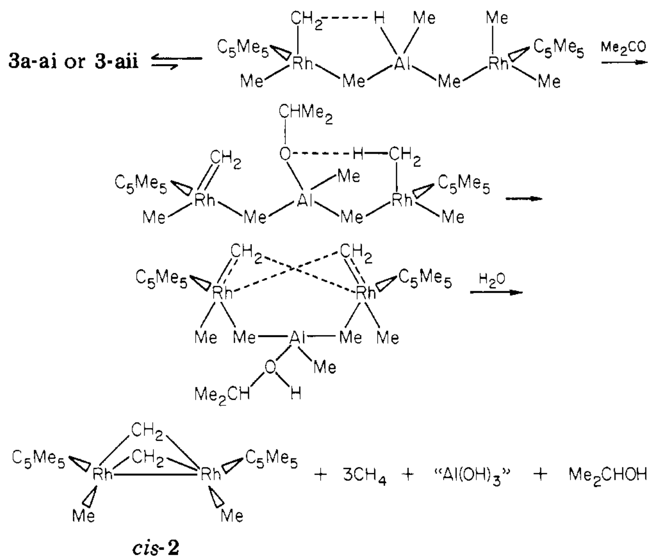
The two representations **3-i** and **3-ii** are to some extent equivalent since in molecules such as Al_2Me_6 which contain bridging methyls, at least some Al–Al interaction must also exist;[16] this will also apply to heterotrimetallic systems with bridging methyls. Further, if the ground state of **3** is closer to the metal–metal bonded form **3-i**, then the reactivity of the molecule, in particular that with Me_2SO at low temperature, suggests that the binding is quite weak. Indeed, the fact that on addition of an ether to a solution of **3a** all the methyl resonances collapse even at −90 °C indicates that all the methyl–metal bonds are very labile.

The observation that at −30 °C the Rh-bound methyls exchange only with each other and not with the Al-bound methyls is easily understood on the basis of the structures proposed and a facile interconversion between them as shown (Scheme II).

We also attempted to measure the ^{27}Al NMR spectra of such solutions; however, at temperatures below ca. −50 °C the resonances were so broad as to be unrecognizable. Since the molecules showed fast-exchange behavior already below this temperature, such measurements seemed rather unproductive. This effect arises from the high quadrupole moment of ^{27}Al which also made a more quantitative treatment of the ^{13}C exchange rates of doubtful value.

The Formation of $[(C_5Me_5RhMe)_2(\mu\text{-}CH_2)_2]$ (2). We have previously described the reaction of the yellow solution containing **3a** with acetone to give complex **2**.[2] It was of considerable importance to determine whether the aluminum played a vital role in the conversion of **3** into **2** or whether this could be achieved simply by hydrogen transfer from a "$C_5Me_5RhMe_2$" species. We have shown elsewhere[17] that the Me_2SO ligand in complex **5** is quite labile and that these complexes can be used as convenient sources of "$C_5Me_5MMe_2$". In fact, when **5a** was heated with acetone (and a variety of other hydrogen-acceptor molecules), no reaction took place and no formation of **2** could be observed. By contrast, when **3a** had been formed by prior reaction of **5a** with Al_2Me_6, complex **2** was obtained in good yield on addition of acetone. This indicates that the aluminum plays an essential role in the conversion. The low-temperature ^{13}C NMR spectrum of the solution obtained on addition of a small amount of acetone to a solution of **3a** in deuteriotoluene at low temperature showed the presence of only **3a** and **2**; no intermediates were detectable by NMR spectroscopy. Similarly, when the reaction was carried out in the cavity of an ESR spectrometer, no radical species could be detected either. This indicates a very facile reaction sequence from **3a** to **2**, and a proposal is made in Scheme III. It will be noted that this sequence leads to the formation of *cis*-**2** which is indeed the observed initial product, since the subsequent isomerization to *trans*-**2** is promoted by Lewis acids.[2]

Scheme III



The reaction of **3b** with acetone also gives some of the iridium analogue of **2**, presumably formed by a similar reaction; however this is complicated by the formation of a variety of other products.[3,18]

The formation of $[(C_5Me_5Rh)_3(\mu_3\text{-}CH)_2]$[7] and of its iridium analogue, together with methane from the reaction of (Al_2Me_6) with complex **1** in excess, can also be understood in terms of the reaction represented by

$$2[(C_5Me_5MMe_3)_2AlMe] + [(C_5Me_5M)_2Cl_4] = 2[(C_5Me_5M)_3(\mu_3\text{-}CH)_2] + Al_2Me_2Cl_4 + CH_4$$

Complexes $[C_5Me_5M(Me)_2L]$ (L = Me_2SO, PPh_3, and dppm/2). The Me_2SO complexes **5a** and **5b** were obtained in very high yield by reaction of **1a** or **1b** with Al_2Me_6 and Me_2SO; the precise yields depended somewhat on the exact conditions used. For preparative purposes it was convenient to make $[C_5Me_5MCl_2(Me_2SO)]$ in situ by reaction of **1** with Me_2SO and to then react this with Al_2Me_6 in toluene for **5a** or pentane for **5b**. The complexes were characterized by microanalysis and spectroscopic methods. The presence of a strong band in the IR at 1085 cm^{-1} in both is consistent with the presence of an S-bonded Me_2SO ligand.[19] This was confirmed by a careful analysis of the ^1H NMR spectrum of **5a** which showed a small coupling (0.68 Hz) of the Me_2SO methyls to rhodium, characteristic of a three-bond H–C–S–Rh coupling.[20]

The triphenylphosphine complexes **4a** and **4b** were similarly characterized, in particular by their ^1H NMR

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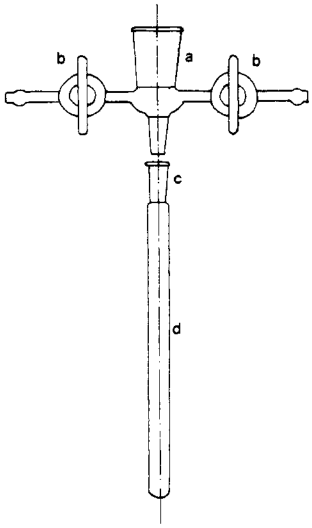

Figure 3. Manifold used for loading NMR tubes (d) with Al_2Me_6 solutions under argon: (a) RB-19, (b) stopcocks, (c) RB-10 joint.

spectra which showed the iridium-bonded methyls, in **4b**, as a doublet [J(P–H) = 5.3 Hz], and the rhodium-bonded methyls, in **4a**, as a double doublet [J(P–H) = 4.7 Hz, J(Rh–H) = 2.3 Hz]. Complexes **4a** and **4b** were also conveniently formed by reaction of **5a** and **5b** respectively, with triphenylphosphine in refluxing benzene.

The bis(diphenylphosphino)methane ligand reacted with either **3a** or the Me_2SO complex **5a** to give the bridged dinuclear complex **6**. The proton NMR spectrum was normal (Table I), but the ^{31}P NMR showed two "triplets" which arose from an $[AX]_2$ spin system owing to the magnetically inequivalent phosphorus nuclei. This could be analyzed in a conventional manner[21] to give ^2J(P–P) = 45.2, ^1J(Rh–P) = 171.9, and ^3J(Rh–P) = 4.3 Hz at a chemical shift of δ 45.4 with respect to external phosphoric acid.

Experimental Section

All manipulations involving the use of organoaluminum compounds were carried out under a protective atmosphere of argon in carefully dried equipment. Standard Schlenk apparatus was used and liquids were transferred by syringe or cannulae. Samples for NMR measurements (5-mm tubes for ^1H, 10-mm tubes for ^{13}C) were made up under argon by using a simple piece of equipment as shown in Figure 3. NMR spectra were measured at 60 (R-12B) and 400 MHz (WH-400) for ^1H and at 25 (PFT-100) and 100 MHz (WH-400) for ^{13}C. The ^{13}C spectra measured in hydrocarbon solvents were referenced against the toluene resonance at δ 21.34 as internal standard; other spectra were referenced against tetramethylsilane (δ 0) or dichloromethane (δ 5.33 for ^1H) as appropriate. IR spectra were measured on a P.E. 157 or on a P.E. 180 with a far-IR attachment. Microanalyses were carried out by the University of Sheffield Microanalytical Unit. Analytical and spectroscopic data for all the new complexes isolated are given in Table I.

Preparation of Complex 3a. Complex **1a** (0.24 g, 0.38 mmol) was transferred into a 10-mm diameter NMR tube (d, Figure 3; usually of quartz, for extra strength) fitted with a RB-10 joint (c) attached to the manifold containing two stopcocks (b) and a RB-19 joint (a) covered with a Suba-seal (Figure 3). The tube containing **1a** was heated to 80 °C and alternately evacuated and filled with pure argon some 10–12 times during 1 h. It was then cooled to 20 °C, solvent (deuteriotoluene, cyclopentane, etc. *Caution: Solutions of Al_2Me_6 in low boiling solvents are unusually pyrophoric and dangerous*) added, the mixture injected onto the solid sample and then cooled further at −78 °C under a flow of argon. A solution of Al_2Me_6 (usually 10 % w/w in the same solvent, 2.5:1 molar ratio) was then added dropwise over 10 min. The solid dissolved to give a pale yellow solution that was briefly shaken at −78 °C to complete the reaction. The manifold was removed under a steady stream of argon and quickly replaced by a Suba seal to cap the NMR tube. With only a little practice it is possible to prepare in this manner clear solutions containing Al_2Me_6 that show no trace of the $Al_3Me_6(OMe)_3$[22] resonances at δ −9.3 and 51.6 (in toluene) and that are quite free of contamination by moisture or oxygen.

At −90 °C in deuteriotoluene (reference δ 21.32) the solution showed resonances at δ 97.89 (d, J = 2.7 Hz), 8.52, 2.61 (d, J = 23.3 Hz), −4.54, −5.03, −5.89, −7.19, and −17.98 (d, J = 28.1 Hz). The relative intensities and the assignments of the peaks are discussed in the text. When the same solution was made up in cyclopentane (containing a small amount of toluene as reference), the same resonances appeared at δ 97.87, 8.72, 2.50 (d, J = 22.9 Hz), −4.09, −5.42, −6.94, −8.03, and −17.92 (d, J = 27.5 Hz). For comparison the resonances of pure Al_2Me_6 appeared at δ −4.60 and −7.15 (toluene) and at δ −4.09 and −7.73 (cyclopentane) under the same conditions. When a small amount of deuterioacetone was added to a solution of **3a** in deuteriotoluene, all the resonances decreased and two new resonances, due to the cis isomer of complex **2**, appeared at δ 9.7 and 100.0; no other resonances were observable. Similarly, when Me_2SO was added to a solution of **3a** at low temperatures, only the resonances due to **5a** and to **3a** could be observed. When a small amount of tetrahydrofuran was added to a solution of **3a** in deuteriotoluene, the spectra at −80 °C (and at −50 °C) showed resonances due to two C_5Me_5Rh species, at δ 98.85 (d, J = 3.8 Hz) and 9.45 and at δ 99.35 (d, J = 3 Hz) and 10.85. However all the methyl resonances had collapsed to a singlet at δ −8.55.

A solution of the rhodium–Me_2SO complex **5a** was made up in deuteriotoluene, and a large (7–8 fold) excess of Al_2Me_6 was added; the solution was then warmed to +40 °C before cooling to −90 °C to measure the ^{13}C spectrum. This showed resonances at δ 98.35 (d, J = 3.1 Hz), 8.23, and −0.61 (d, J = 28.2 Hz) due to unreacted **5a**, at δ −4.75 and −6.85 due to Al_2Me_6, and at δ −5.85 due to $Al(Me_2SO)Me_3$, as well as the following peaks assigned to **3a**: δ 97.1 (d, J = 3.8 Hz), 7.62, 1.57 (d, J = 23.7 Hz), −8.24, and −19.0 (d, J = 28.2 Hz).

Preparation of Complex 3b. This was prepared, in cyclopentane containing a small amount of toluene as reference, in exactly the manner described for the preparation of 3a. At −90 °C this showed the following resonances: δ 93.23, 8.23, −9.91, −15.73, and −29.02 due to **3b**, δ −3.90 and −7.97 due to Al_2Me_6, and at −5.48 due to $Al_2Me_4Cl_2$. The ^{13}C NMR spectrum in 2-methylbutane at −120 °C was similar and showed resonances at δ 93.74, 8.99, −8.51, −14.98, and −28.32 due to **3b** as well as at δ −3.51, −4.42, and −6.69 due to the organoaluminum species. On addition of diethyl ether and remeasuring the spectrum at −118 °C the resonances due to **3b** remained (at δ 93.62, 8.72, −9.03, −15.65, and −28.75) but the methylaluminum resonances had all coalesced to a singlet at δ −6.76.

Preparation of the Iridium–Me_2SO Complex 5b. Method A. Complex **1b** (0.50 g, 0.63 mmol) and a small magnetic stirrer were placed into a dry Schlenk tube and heated (5 min/60 °C); the tube was then filled with dry argon. This procedure was repeated six times over 30 min. The tube was then cooled to 20 °C and dry *n*-pentane (25 cm^3) added to the solid; the suspension was stirred and cooled to −78 °C. A freshly prepared solution of hexamethyldialuminum in *n*-pentane (2.6 cm^3 of a 26.5% w/w solution; 6.3 mmol) was added dropwise with stirring at −78 °C. The orange suspension gradually dissolved to give a pale yellow-orange solution. After the solution was stirred (10 min at −78 °C), excess dimethyl sulfoxide (0.3 cm^3) was added dropwise over 20 min; the solution was allowed to warm to 20 °C and all volatiles were removed in vacuo. The yellow-orange residue was extracted with wet pentane (3 × 40 cm^3); this solution was filtered and evaporated to dryness, and the extraction was repeated to give a pentane solution of complex **5b** which deposited yellow crystals of the complex (0.27 g, 50%) on cooling.

Method B. A suspension of complex **1b** (0.50 g) in *n*-pentane (25 cm^3) was prepared as described above. To this was added

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Me_2SO (0.2 cm^3, 2.8 mmol); after the solution was stirred for a few minutes, the suspension was cooled to −78 °C and hexamethyldialuminum (2.1 cm^3 of a 26.5% w/w solution in pentane, 5.0 mmol) was added dropwise. The suspension slowly turned yellow and after 30 min was allowed to warm to 20 °C. This solution was worked up as described above to give yellow crystals of **5b** (0.47 g, 80%). This complex could also be made from [$C_5Me_5IrCl_2(Me_2SO)$] if this was isolated from the reaction of Me_2SO with complex **1b**.

The rhodium complex **5a** as well as the complexes **4a**, **4b**, and **6** was all prepared by method A and are detailed in Table I. In addition complexes **4a**, **6**, and also **4b** were prepared by reaction of the Me_2SO complexes 5a and **5b**, respectively, with the appropriate ligand (method C).

Preparation of Complex 6. Method C. A solution of bis(diphenylphosphino)methane (0.11 g, 0.29 mmol) was added to a solution of complex **5a** (0.10 g, 0.29 mmol) in dry benzene (15 cm^3). The solution was refluxed (1 h), the solvent removed, and the residue extracted with wet pentane. On cooling, the pentane solution slowly gave yellow crystals of complex 6 (0.20 g, 75%).

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Registry No. **1a**, 12354-85-7; **1b**, 12354-84-6; **3a**, 87174-69-4; **3b**, 87174-70-7; **4a**, 87174-71-8; **4b**, 87174-72-9; **5a**, 87183-26-4; **5b**, 87183-27-5; **6a**, 87174-73-0; Al_2Me_6, 15632-54-9; Ph_3P, 603-35-0; Me_2SO, 67-68-5; $Al_2Me_4Cl_2$, 14281-95-9; dppm, 2071-20-7; Al, 7429-90-5; Rh, 7440-16-6; Ir, 7439-88-5; acetone, 67-64-1.

Kinetics and Mechanism of the Phase-Transfer-Catalyzed Carbonylation of Benzyl Bromide by the Cobalt Tetracarbonyl Anion

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The carbonylation of benzyl bromide with the cobalt carbonyl anion according to eq 1 and 2 was studied in a liquid–liquid two-phase system (H_2O/CH_2Cl_2, $H_2O/i\text{-}Pr_2O$, H_2O/C_6H_6). The disappearance of benzyl bromide was found to follow a second-order kinetic law under stoichiometric conditions. In these experiments, the concentration of the cobalt carbonyl anion in the organic phase remained constant throughout the reaction, owing to rapid pairing with the tetrabutylammonium cation used as a cationic carrier. Under catalytic conditions, the kinetics depended strongly on the stirring speed (which was not the case under stoichiometric conditions). A catalytic cycle is proposed for this liquid–liquid system, in which it is shown that the catalyst ($Bu_4N^+Co(CO)_4^-$) stays in the organic phase, and the product (the phenylacetate anion) is expelled into the aqueous phase. It is also shown that the rate-limiting reaction is not the nucleophilic displacement (1) (reaction of benzyl bromide with the cobalt carbonyl anion) but the cleavage of the acylcobalt carbonyl 4 by the ion pair $Bu_4N^+OH^-$ at the liquid–liquid interface. The presence of byproducts such as toluene and diphenylethane is accounted for in terms of the decomposition of a transient hydroxycarbonyl species **13** through loss of carbon dioxide.

One of the main challenges in the field of catalysis is to combine the advantages of heterogeneous and homogeneous catalysis. The former (mostly solid–gas) is very efficient, securing a good separation between the catalyst and the product, but lacks selectivity. The latter proceeds under mild conditions and is more selective, but catalyst and products are mixed in the same liquid phase. Several years ago, Bailar[1] suggested a liquid–liquid biphasic system which, in principle, should secure separation between the catalyst and the products by a proper choice of two immiscible liquids A and B. Useful combinations of catalyst, reagents, and products in such a liquid–liquid two-phase system are given in Scheme I.

Scheme I

liquid A catalyst

liquid B reagents + products

liquid A catalyst + reagents

liquid B products

Recent applications of phase-transfer catalysis[2] to organotransition-metal reactions[3] represent a step in this direction. Expected effects are as follows: (1) good separation between the catalyst and the product; (2) increased efficiency; (3) new selectivity due to the unusual conditions met within two-phase systems.

A number of experimental results have already been reviewed,[4] but, so far, no mechanistic investigation has been attempted. We report here a study of the catalytic carbonylation of benzyl bromide, run in a liquid–liquid phase-transfer system, with the cobalt carbonyl anion as

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