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The Reactions of Dichloro-bis(μ-chloro)-bis(η^6-p-cymene)diosmium(II) and -Diruthenium(II) with Hexamethyldialuminium

JAVIER A. CABEZA*, BRIAN F. TAYLOR and PETER M. MAITLIS

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K.

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Abstract

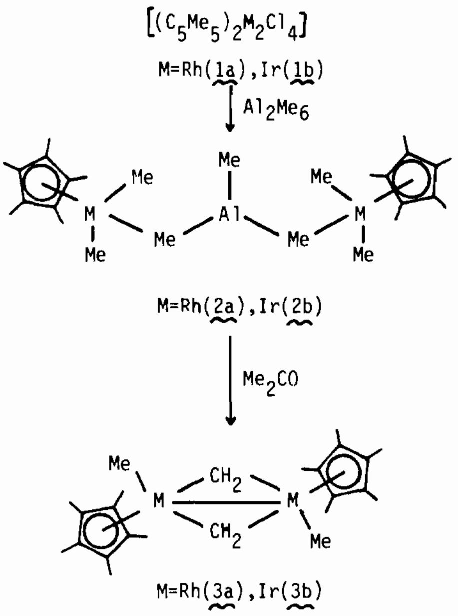
The reactions of $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{M}_2\text{Cl}_4]$ (M = Os, Ru) with Al_2Me_6 in toluene give solutions which contain $\text{Al}_2\text{Me}_4\text{Cl}_2$ and heterometallic species formulated as $[\{(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{MMe}_2\}_2(\text{Al}_2\text{Me}_6)]$ (**4**) on the basis of low-temperature $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy at 62.9 MHz. Reaction of **4** with PPh_3 gives $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{MMe}_2(\text{PPh}_3)]$.

Introduction

Reaction of dichloro-bis(μ-chloro)bis(η^5-pentamethylcyclopentadienyl)dirhodium(III) (**1a**) with Al_2Me_6 followed by reaction with a hydrogen acceptor (acetone) gives the remarkable complex dimethyl-bis(μ-methylene)-bis(η^5-pentamethylcyclopentadienyl)dirhodium(IV) [1–3]. Similar but more complicated reactions occur using the iridium complex (**1b**) [2–4].

Low-temperature $^{13}\text{C}\{^1\text{H}\}$ NMR studies showed that on reaction of **1a** (or **1b**) with Al_2Me_6 in hydrocarbons only one rhodium- (or iridium-) containing species formulated as **2a** (or **2b**) is present [2]. This species gives the bis(μ-methylene) complex **3a** (or **3b**) on reaction with acetone, Scheme 1.

The complexes $[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{M}_2\text{Cl}_4]$ (**1c**, M = Os; **1d**, M = Ru], isoelectronic with **1a** and **1b**, also reacted with Al_2Me_6 in hydrocarbons, but only untractable decomposition products were obtained after addition of acetone or exposing the solutions to air [5]. Since the reasons for this great difference in reactivity were not clear, we decided to carry out a spectroscopic study of the reactions of **1c** and **1d** with Al_2Me_6 in order to identify the species formed.



Scheme 1.

Results and Discussion

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at −70 °C of the red–orange solution formed by reaction of a toluene or perdeuteriotoluene solution of Al_2Me_6 with a suspension of **1c** in perdeuteriotoluene (C_7D_8) (Fig. 1) indicated that only one osmium-containing species was present, since peaks of only one η^6-coordinated p-cymene ligand were observed [δ 102.3(E), 97.5(B), 80.7(C), 79.2(D), 30.7(F), 23.2(G) and 17.9(A), ppm]. Although η^6-coordinated benzene derivatives are much more likely to be attacked by nucleophiles [6] than η^5-pentamethylcyclopentadienyl rings [7], the presence of a normal p-cymene pattern [5] ruled out the possibility of a nucleophilic attack by Al_2Me_6 at the coordinated p-cymene ring as the responsible for the different reactivity of **1c** compared to **1a** or **1b**.

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*Present address: Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain.

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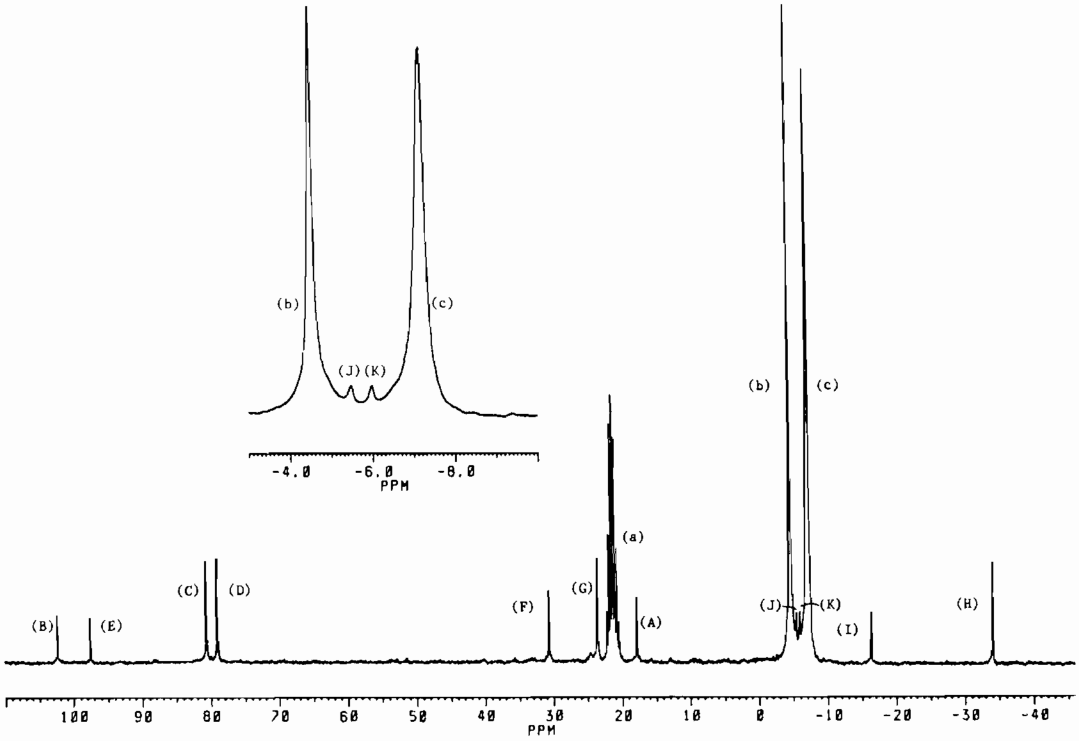


Fig. 1. $^{13}C\{^1H\}$ NMR spectrum of the solution obtained from the reaction of **1c** with excess Al_2Me_6 in deuteriotoluene at −70 ℃. (a) $C_6D_5CD_3$; (b) $Al_2Me_4(\mu\text{-}\mathit{Me})_2$ + $Al_2\mathit{Me}_4Cl_2$; (c) $Al_2\mathit{Me}_4(\mu\text{-}Me)_2$. For carbon atoms labeling see Scheme 2.

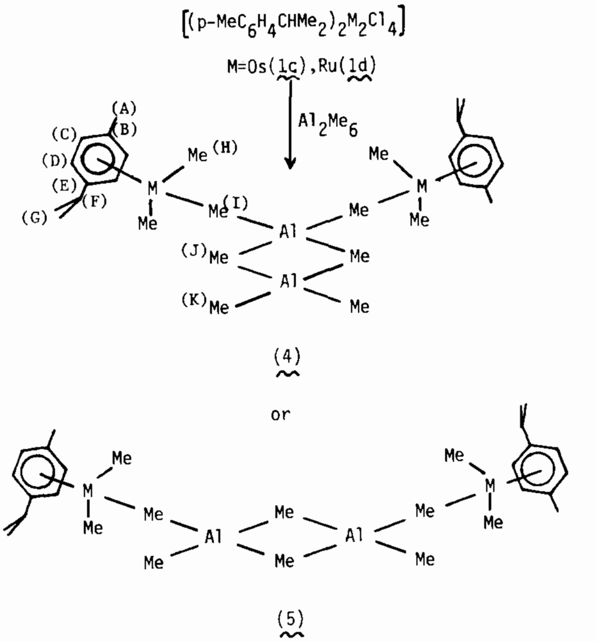
Apart from the *p*-cymene and the solvent peaks, six other resonances appeared in the spectrum, all in the methyl region. Two of these, δ −4.5 and −7.2 ppm, were due to the bridging and terminal methyls respectively of Al_2Me_6 which was present in excess, but the peak at δ −4.5 was some times unexpectedly intense. Spectra run using different concentrations of Al_2Me_6 indicated that the peak at δ −4.5 also included the resonance of the methyls of $Al_2Me_4Cl_2$. The two resonances at very low frequency, δ −16.4 and −34.0 ppm, were certainly due to osmium-bound methyls; their intensities indicated that they were in a 1:2 ratio.

The spectrum was thus quite similar to those obtained from the reactions of **1a** (and **1b**) with Al_2Me_6 [2]. This indicated the presence in the osmium species of the moiety $(p\text{-}MeC_6H_4CHMe_2)$-$OsMe'Me_2''$, where Me' and Me" are inequivalent methyls. In the reaction of **1a** (or **1b**) the spectrum also showed another singlet assigned to the 'lone methyl' on the bridging aluminium of complex **2a** (or **2b**) [2]. In the case of the osmium reaction there were two more peaks, at δ −5.6 and −6.0 ppm, both with the same intensity as the peak at δ −16.4 ppm.

Above −60 ℃ the resonances due to Al_2Me_6 and $Al_2Me_4Cl_2$ began to broaden and they coalesced at about −40 ℃, with the two resonances at δ −5.6 and −6.0 ppm participating in the interchange (this did not happen with the 'lone methyl' resonance of the rhodium and iridium species which remained sharp up to *ca* −30 ℃ [2]). Above −40 ℃ all the methyls only bound to aluminium gave rise to a singlet at δ −5.7 ppm. The signals due to the osmium-bound methyls only started to broaden above *ca.* −30 ℃, and coalesced at *ca.* 0 ℃. At 25 ℃ all the methyl resonances were broad and only the *p*-cymene peaks remained reasonably sharp. The low-temperature spectrum could be reproduced on recooling.

The fact that the low-temperature spectrum shows the two unknown resonances very close to those of Al_2Me_6, that they are fluxional at approximately the same temperature range as Al_2Me_6, and that both of them have the same intensity as the peak at δ −16.4 ppm regardless of the excess of Al_2Me_6 used, suggested **4** as a possible structure for this species, Scheme 2. The alternative structure **5** is also possible, but this might be expected to exist in both *cis* and *trans* isomers.

The mechanism [2] proposed for the transformation of the rhodium and iridium species **2a** and **2b** to the corresponding bis(μ-methylene) complexes using acetone as hydrogen acceptor requires a coordinatively unsaturated '$AlMe_3$' moiety bridging the two metals. If this mechanism is correct, the proposed structure **4** (or **5**) for the osmium species explain why it does not react with acetone in the same way as the rhodium or iridium species do, since in **4** or



Scheme 2.

5 all the aluminium atoms are coordinatively saturated and then incapable to activate the osmium-bound methyls.

Further evidence concerning the nature of this species comes from its reaction with PPh_3. Monitoring the reaction by $^{13}C\{^1H\}$ NMR spectroscopy pointed out that the trimethylaluminium adduct of triphenylphosphine Ph_3PAlMe_3 (δ −6.3, doublet, $J = 17$ Hz) was immediately formed, even at −70 °C. However, reaction with the osmium species only occurred at temperatures above 0 °C, giving the known complex $[(p\text{-}MeC_6H_4CHMe_2)OsMe_2(PPh_3)]$ [5] quantitatively. Once this complex is formed the reaction cannot be reversed on recooling.

Solubility problems prevented a complete low-temperature $^{13}C\{^1H\}$ NMR study of the reaction of the ruthenium complex **1d** with Al_2Me_6. Below −40 °C an oil was deposited on the walls of the NMR tube; above that temperature all the methyls only bonded to aluminium were fluxional, and thus only the resonances due to the *p*-cymene ligand [δ 109.0(B), 102.7(E), 89.2(C), 88.8(D), 30.9(F), 23.5(G) and 18.2(A) ppm] and to the ruthenium-bound methyls [δ −15.0(I) and −24.7(H) ppm] could be observed. The similarity of this spectrum to the osmium one (and the fact that the ruthenium species neither forms methylene bridges upon reaction with acetone) suggested that it may also have the structure **4** (or **5**).

These results may be contrasted with the formation of the trinuclear bis-(μ_3-methyne) cluster $[(C_5Me_5)_3Rh_3(\mu_3\text{-}CH)_2]$ [8], which occurs when **1a** and Al_2Me_6 are mixed at room temperature in very concentrated solutions; and also with the formation of the μ-methylene-μ-chloro complex $[Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)AlMe_2]$ by reaction of $[Cp_2TiCl_2]$ with Al_2Me_6 [9].

Experimental

$[(p\text{-}MeC_6H_4CHMe_2)_2Os_2Cl_4]$ [5] and $[(p\text{-}MeC_6H_4CHMe_2)_2Ru_2Cl_4]$ [10] were prepared as described elsewhere. All manipulations involving the use of Al_2Me_6 were carried out under argon in carefully dried equipment. The $^{13}C\{^1H\}$ NMR spectra were measured on a Bruker AM-250 instrument at 62.9 MHz, using the deuteriotoluene resonance at δ 21.34 ppm as internal standard.

In a typical experiment, **1c** (130 mg, 0.16 mmol) was placed into a 10 mm diameter NMR tube fitted with a joint attached to a manifold containing two stopcocks and an additional joint covered with a Suba-seal [2]. The tube was alternatively evacuated and filled with argon some 10–12 times during 30 min and 0.5 cm^3 of perdeuteriotoluene was injected. The resultant suspension was cooled at −78 °C under a flow of argon and a solution of Al_2Me_6 in toluene or perdeuteriotoluene (2 cm^3, 0.42 M, 0.84 mmol) was then dropwise injected over 10 min. The solid dissolved to give a red–orange solution that was briefly shaken to complete the reaction, the manifold was removed from the tube under a steady stream of argon and quickly replaced by a Suba-seal. The tube was then transfered to the NMR spectrometer probe and spectra were run at different temperatures.

Solutions of the ruthenium derivative of **4** were prepared by the same method.

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References

1 K. Isobe, P. M. Bailey and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 809 (1981); K. Isobe, A. Vázquez de Miguel, P. M. Bailey and P. M. Maitlis, *J. Chem. Soc. Dalton Trans.*, 1441 (1983).

2 A. Vázquez de Miguel, M. Gómez, K. Isobe, B. F Taylor, B. E. Mann and P. M. Maitlis, *Organometallics*, *2*, 1724 (1983).

3 A. Vázquez de Miguel, K. Isobe, B. F. Taylor, A. Nutton and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 758 (1982).

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

K. Isobe, A. Vázquez de Miguel, A. Nutton and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 929 (1984).

5 J. A. Cabeza and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 573 (1985).

6 S. D. Robertson, I. W. Robertson and T. A. Stephenson, *J. Organomet. Chem.*, *202*, 30 (1980); S. L. Grundy and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 379 (1982); H. Werner, R. Werner and C. Burscha, *Chem. Ber.*, *117*, 152 (1984); H. Werner and R. Werner, *Chem. Ber.*, *117*, 142 and 161 (1984); H. Werner and R. Werner, *J. Organomet. Chem.*, *210*, C11 (1981); R. J. Restivo, G. Ferguson, D. J. O'Sullivan and F. J. Lalor, *Inorg. Chem.*, *14*, 3046 (1975).

7 N. J. Meanwell, A. J. Smith and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1419 (1986).

7 A. Vázquez de Miguel, K. Isobe, P. M. Bailey, N. J. Meanwell and P. M. Maitlis, *Organometallics*, *1*, 1604 (1982).

9 F. N. Tebbe, G. W. Parshall and G. S. Reddy, *J. Am. Chem. Soc.*, *100*, 3611 (1978).

10 M. A. Bennett, T. N. Huang, T. W. Matheson and A K. Smith, *Inorg. Synth.*, *21*, 74 (1983).