

Di- μ -iododi- η^1 -methylbis(η^5 -pentamethylcyclopentadienylrhodium) and related complexes

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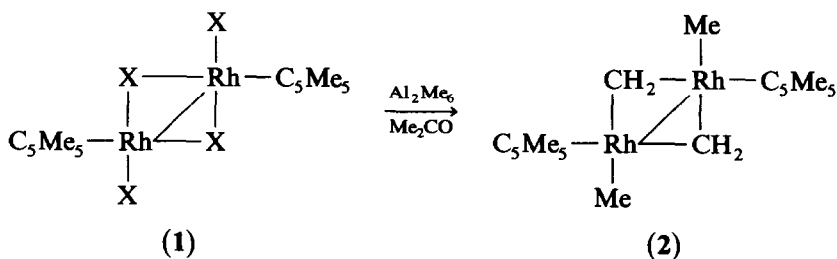
Abstract

$[(C_5Me_5RhI)_2]$ has been found to react with excess Al_2Me_6 to give the dinuclear $[(C_5Me_5RhMe)_2(\mu-I)_2]$ (3), which in turn exchanges organic ligands on reaction with $HgPh_2$ to give $[(C_5Me_5RhPh)_2(\mu-I)_2]$ (6). Complexes 3 and 6 were converted into the mononuclear $[C_5Me_5RhR(Me_2SO)(I)]$ (with Me_2SO) and $[C_5Me_5RhR(CO)(I)]$ on carbonylation ($R = Me, Ph$).

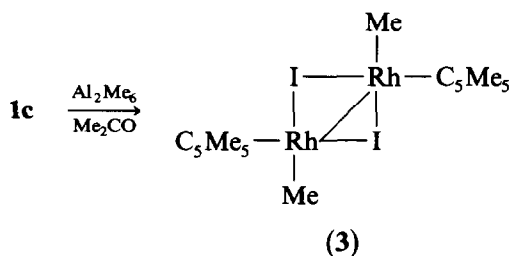
Introduction

We have reported the remarkable transformation of the pentamethylcyclopentadienylrhodium chloride complex (1a, $X = Cl$) into di- μ -methylenedimethyl-dirhodium complex 2 on reaction with Al_2Me_6 , followed by acetone [1]. The course of this reaction depends quite subtly on the halide (leaving ligand) and we here report on the interaction of the iodo-complex 1c with Al_2Me_6 , to give $[(C_5Me_5RhMe)_2(\mu-I)_2]$ rather than 2, and on some related reactions.

Results



(a, $X = Cl$; b, $X = Br$; c, $X = I$)



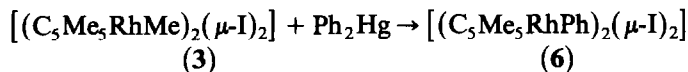
A large excess of trimethylaluminium in toluene was added to a suspension of the iodo-complex **1c** [2] in toluene (-70°C). The brown suspension was allowed to warm up; excess trimethylaluminium was then destroyed with acetone, and water. Work-up gave brown complex **3**, which was only sparingly soluble in solvents in which it did not react. It was identified as the dimeric $[(\text{C}_5\text{Me}_5\text{Rh}(\text{Me})\text{I})_2]$ by microanalysis, FAB mass-spectrum, and spectroscopically.

An unexpected characteristic of the complex is the surprisingly low field (high frequency) rhodium methyl signal in the ^1H NMR spectrum (δ 2.45 in C_6D_6), which is not far from the position of the acyl methyl signal in **5**, below. The position of the $\text{Rh}-\text{Me}$ resonance was solvent-dependent; it appeared at δ 1.88 in CDCl_3 and at 1.80 in CD_2Cl_2 . By contrast, the position of the methyl in the ^{13}C NMR spectrum is normal (δ 0.1); since the methyl is somewhat on the molecular periphery its hydrogens may be subject to unusually strong solvation effects.

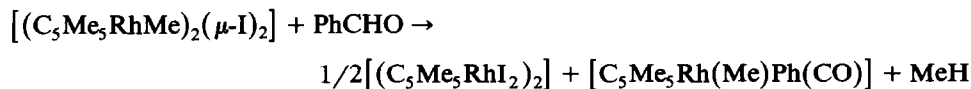
The formulation of the complex as **3** was confirmed by reaction with dimethyl sulphoxide to give $[\text{C}_5\text{Me}_5\text{Rh}(\text{Me}_2\text{SO})(\text{Me})\text{I}]$ (**4**), and with CO to give $[\text{C}_5\text{Me}_5\text{Rh}(\text{CO})(\text{COMe})\text{I}]$ (**5**) [4].

The iridium analogue of **3**, $[(\text{C}_5\text{Me}_5\text{Ir}(\text{Me})\text{I})_2]$ was formed on reaction of $[(\text{C}_5\text{Me}_5\text{IrI}_2)_2]$ with Al_2Me_6 , but was difficult to purify. It was converted into the carbonyl and characterised as $[\text{C}_5\text{Me}_5\text{Ir}(\text{Me})(\text{CO})\text{I}]$.

An unexpected reaction occurred between **3** and diphenylmercury; instead of replacing the second iodine on the rhodium, the reaction gave the phenyl analogue **6** of **3** in good yield. This was again established by analysis, and spectroscopy, and also by the formation of the monomeric adducts $[\text{C}_5\text{Me}_5\text{Rh}(\text{Me}_2\text{SO})(\text{Ph})\text{I}]$ (**7**) by reaction with dimethyl sulphoxide, and $[\text{C}_5\text{Me}_5\text{Rh}(\text{CO})(\text{COPh})\text{I}]$ (**8**) from carbonylation [5]; these are the analogues of **4** and **5**.



Complex **3** also underwent unexpected reactions with benzaldehyde and with methyl iodide. Thus it reacted with benzaldehyde in cyclohexane at 50°C to give **1c**, methane and $[\text{C}_5\text{Me}_5\text{Rh}(\text{Me})(\text{CO})(\text{Ph})]$ [6], approximately in accordance with the equation,



When **3** was treated with methyl iodide, the products were **1c**, methane and ethane in the ratio 7.5 : 1, and a trace of ethylene. GC-MS analysis of the gases from the reaction with CD_3I showed that most of the gases were protio-labelled; only small amounts of deuterium were incorporated. Thus their formation did not

involve the added methyl iodide and they must have been formed by a reaction involving a redistribution of the rhodium–methyl.

A similar result was obtained on heating **3** in C_6D_6 ; in this case the methane:ethane ratio was ca. 17:1. GC-MS analysis showed that the gases were > 95% CH_4 and C_2H_6 and negligible deuterium incorporation had occurred. When complex **3** was reacted with diazomethane in diethyl ether, the only products detectable were the iodide dimer **1c** and some white polymethylene.

Discussion

There seem to have been no systematic comparisons between different anions on transition metals as leaving groups in alkylation reactions. However, one might expect that for the heavier platinum group metals, iodide would be more difficult to displace than chloride. Indeed we find that in the reaction of Al_2Me_6 with complex **1** the chloride **1a** gave only $[(C_5Me_5Rh-\mu-CH_2)_2(Me)_2]$ (**2**) [**2**], and by contrast, the iodide gave mainly **3**. However, NMR spectroscopy of the mother liquors of the crude product showed the presence of small amounts of **2** [**1**] and $[(C_5Me_5Rh-\mu-CH_2)_2(Me)I]$ [**3**], in addition to **3**. Further, reaction of the bromide (**1b**, X = Br) with Al_2Me_6 gave an intermediate result, a mixture of **2** and the mono-bromide, $[(C_5Me_5Rh-\mu-CH_2)_2(Me)Br]$, in the ratio 3:1, by 1H NMR spectroscopy. This indicates that the Rh–I bond is very much more inert to substitution by Me–Al, than is the Rh–Cl bond and that the Rh–Br bond is closer to Rh–Cl. Iodide probably bridge-bonds more strongly than chloride or bromide, and thus displacement is less favoured.

The various reactions of **3** (with MeI in cyclohexane, or with C_6D_6) give rise to methane and ethane. No significant amount of label is incorporated with deuterio-reagents, hence the gases arise solely from the Rh–Me; presumably the ethane is formed via a redistribution to a $RhMe_2$ species which then reductively eliminates. There seems little tendency for the methyls in **3** to undergo reactions leading to carbene-type reactivity, i.e. the equilibrium $Rh-CH_3 \rightleftharpoons Rh(H)(CH_2)$ is well over to the left.

Experimental

All reactions were carried out under nitrogen by standard Schlenk techniques. Microanalyses are by the University of Sheffield Microanalysis Service; NMR spectra were run on PE-220 (1H) and Bruker AM-250 (1H and ^{13}C); IR spectra were recorded on a PE-1710 FT-IR spectrometer.

Di- μ -iododimethylbis(pentamethylcyclopentadienylrhodium) (3)

A solution of Al_2Me_6 in toluene (10% v/v; 10 cm^3) was added to a vigorously stirred suspension of $[(C_5Me_5RhI_2)_2]$ [**2**] (**1c**; 1.12 g, 2.76 mmol; molar ratio Al:Rh = 4.4) in toluene (20 cm^3) at $-70^\circ C$. The brown suspension was stirred (50 min; $-70^\circ C$) and then allowed to warm to $-40^\circ C$; an excess of acetone (5 cm^3) was then added, giving a deep brown solution, which was allowed to warm to $0^\circ C$. The aluminium compounds were hydrolysed by slow addition of water (5 cm^3). More toluene (2×10 cm^3) was added; the toluene extracts washed with water, dried, filtered, and evaporated to dryness to give **3** as a brown solid (yield, 0.76 g,

72%) which was, with some difficulty, crystallised from benzene-pentane. Anal. Found: C, 34.8; H, 4.9; I, 33.8; M^+ (FAB-MS), 760. $C_{12}H_{36}I_4Rh_2$ calcd.: C, 34.8; H, 4.7; I, 33.4%; M , 760. 1H NMR δ 1.50 (s, C_5Me_5), 2.45 [d, Me, $J(Rh-H)$ 3 Hz] in C_6D_6 ; the resonances were shifted to 1.61 and 1.80 (CD_2Cl_2), and 1.68 and 1.88 ($CDCl_3$) respectively. ^{13}C NMR δ 0.1 [d, Me, $J(Rh-C)$ 23 Hz], 9.6 (C_5Me_5), 94.0 [d, C_5Me_5 , $J(C-Rh)$ 6.5 Hz].

Di- μ -iododiphenylbis(pentamethylcyclopentadienylrhodium) (6)

Diphenylmercury (0.46 g, 1.3 mmol) was added to a solution of complex **3** (1 g, 2.63 mmol) in cyclohexane (150 cm^3). The solution was stirred (25 min, 50 °C), filtered, and the solvent removed in vacuo to leave a brown solid, which was washed with pentane and dried to give complex **6** (yield, 0.78 g, 68%). Anal. Found: C, 43.6; H, 4.7; I, 28.4; M (FAB-MS), 885 ($M + H^+$). $C_{32}H_{40}I_4Rh_2$ calcd.: C, 43.5; H, 4.5; I, 28.7%; M , 884. 1H NMR (CD_2Cl_2) δ 1.36 (d, C_5Me_5 , $J(Rh-H)$ 0.5 Hz), 6.88 (m, 7.61 dd [phenyl, $J(H-H)$ 8, 3 Hz]. ^{13}C NMR δ 9.5 (C_5Me_5), 96.5 [d, C_5Me_5 , $J(C-Rh)$ 6 Hz]; 121.9, 127.0, 144.9, 163.9 d [$J(C-Rh)$ 31 Hz] phenyl.

Carbonylation of di- μ -iododimethylbis(pentamethylcyclopentadienylrhodium) (3) to give [$C_5Me_5Rh(CO)I(COMe)$] (5)

A slow stream of carbon monoxide (1 atm, 3 h, 20 °C) was passed through a solution of complex **3** (0.1 g, 0.26 mmol) in cyclohexane (10 cm^3). Removal of solvent left pale brown complex **5** (yield, 0.11 g, 96%). Anal. Found: C, 35.6; H, 4.3; I, 28.7; M (FAB-MS) 437 ($M + H^+$). $C_{13}H_{18}IO_2Rh$ calcd.: C, 35.8; H, 4.1; I, 29.1%; M 436. IR $\nu(CO)$ 1685, 2035 cm^{-1} . 1H NMR (CD_2Cl_2) δ 1.89 (C_5Me_5), 2.69 (MeCO). ^{13}C NMR δ 10.2 and 106.7 d [C_5Me_5 , $J(Rh-C)$ 4 Hz], 52.7 (MeCO), 189.8 d [CO, $J(Rh-C)$ 80 Hz], 226.1 d [COMe, $J(Rh-C)$ 23 Hz].

Complex [$C_5Me_5Rh(CO)I(COPh)$] (**8**) was prepared similarly from **6** (yield, 90%). Anal. Found: C, 43.2; H, 4.1; I, 25.4; M (FAB-MS) 499 ($M + H^+$). $C_{13}H_{18}IO_2Rh$ calcd.: C, 43.4; H, 4.0; I, 25.5%; M 498. IR $\nu(CO)$ 1663, 2039 cm^{-1} . 1H NMR (CD_2Cl_2) δ 2.15 (C_5Me_5), 7.59 (m, Ph). ^{13}C NMR δ 10.5 and 106.9 d [C_5Me_5 , $J(Rh-C)$ 4 Hz], 127.1, 128.4, 131.0, 150.6 (phenyl), 189.8 d [CO, $J(Rh-C)$ 80 Hz], 230.0 d [COPh, $J(Rh-C)$ 25 Hz].

Reaction of di- μ -iododimethylbis(pentamethylcyclopentadienylrhodium) (3) with Me_2SO to give [$C_5Me_5Rh(Me_2SO)(Me)I$] (4)

Dimethyl sulphoxide (18.7 μ l, 0.26 mmol) was added to a solution of complex **3** (0.1 g, 0.26 mmol) in cyclohexane (20 cm^3). The solution was stirred (1 h, 20 °C); the solvent was removed in vacuo, the residue washed with water to remove remaining dimethyl sulphoxide and then dried (yield, 0.118 g, 98%). Anal. Found: C, 34.1; H, 5.1; I, 27.4. $C_{13}H_{24}IORhS$ calcd.: C, 34.1; H, 5.2; I, 27.7%. IR $\nu(SO)$ 1100 cm^{-1} . 1H NMR (CD_2Cl_2) δ 0.96 d [Me-Rh, $J(Rh-H)$ 2 Hz]; 1.74 (s, C_5Me_5); 2.98, 3.43 (Me_2SO). ^{13}C NMR δ -1.7 [d, Me, $J(Rh-C)$ 23 Hz]; 9.7 (C_5Me_5); 43.4, 50.7 (Me_2SO); 100.3 [d, C_5Me_5 , $J(C-Rh)$ 5 Hz].

Complex [$C_5Me_5Rh(Me_2SO)(Ph)I$] (**7**) was made similarly from complex **6** and dimethyl sulphoxide [79% yield, $\nu(SO)$ 1103 cm^{-1}]. Anal. Found: C, 41.6; H, 5.3; I, 24.3. $C_{18}H_{26}IORhS$ calcd.: C, 41.5; H, 5.0; I, 24.4%. IR $\nu(SO)$ 1100 cm^{-1} . 1H NMR (CD_2Cl_2) δ 1.66 (s, C_5Me_5); 2.85, 3.43 (Me_2SO); 6.96, 7.68 (m, Ph). ^{13}C NMR δ

9.9 (C_5Me_5); 46.4, 50.0 (Me_2SO); 101.5 [d, C_5Me_5 , $J(C-Rh)$ 5 Hz]; 123.5, 128.9, 157.1d, $J(Rh-C)$ 30 Hz, phenyls.

The analogous chloro-complex $[C_5Me_5Rh(Me_2SO)(Ph)Cl]$ was prepared (92%) by Dr. G.J. Sunley by reaction of $[C_5Me_5Rh(Me_2SO)Cl_2]$ with $HgPh_2$ in CH_2Cl_2 . Anal. Found: C, 50.9; H, 5.9; Cl, 7.7; S, 8.5. $C_{18}H_{26}ClORhS$ calcd.: C, 50.4; H, 6.1; Cl, 7.5; S, 8.3%. 1H NMR ($CDCl_3$) δ 1.58 (s, C_5Me_5); 2.57, 3.27 (Me_2SO); 7.02, 7.50 (mm, Ph). ^{13}C NMR δ 8.8 (C_5Me_5); 43.4, 44.9 (Me_2SO); 100.4 [d, C_5Me_5 , $J(C-Rh)$ 5 Hz]; 123.3, 128.1, 159.0d, $J(Rh-C)$ 30 Hz, phenyls.

Reaction of $[(C_5Me_5RhMe)_2(\mu-I)_2]$ with benzaldehyde

Benzaldehyde (28 μ l, 0.26 mmol) was added to a solution of complex 3 (0.1 g, 0.26 mmol) in cyclohexane (10 cm^3). The mixture was stirred (50 °C, 20 h); the precipitated $[(C_5Me_5RhI_2)_2]$ (**1c**) was filtered off (0.058 g, 90%) and identified by 1H NMR spectroscopy and FAB-MS. The filtrate was evaporated to leave a pale brown solid (0.042 g, 89%) which, after crystallisation was identified as $[C_5Me_5Rh(Me)(CO)(Ph)]$ [**6**] by 1H NMR spectroscopy. Analysis of the gas phase of the reaction by GC showed the presence of methane.

Reaction of di- μ -iododiiodobis(pentamethylcyclopentadienyliridium) with hexamethyldialuminium

The iridium complex $[(C_5Me_5IrI_2)_2]$ was reacted with Al_2Me_6 as described above for **3**. The product was shown by 1H NMR spectroscopy to contain $[(C_5Me_5Ir(Me)I)_2]$ [20%; δ ($CDCl_3$) 1.63 (C_5Me_5) and 2.18 (Me)] as well as $[(C_5Me_5IrI_2)_2]$ (δ 1.73, C_5Me_5). The crude product was treated with CO (1 atm, 20 °C, 1.5 h); solid $[C_5Me_5Ir(CO)I_2]$ precipitated, and the solution was chromatographed to yield $[C_5Me_5Ir(Me)(CO)I]$ [**7**]; 1H NMR, δ (CD_2Cl_2) 1.13 (Me), 1.46 (C_5Me_5); FAB, m/z 496, 498.

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