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REACTIONS OF DIMETHYL(DIMETHYLSULPHOXIDE)PENTAMETHYLCYCLOPENTADIENYL-RHODIUM AND -IRIDIUM WITH ACIDS

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Summary

The complexes $[C_5Me_5MMe_2(Me_2SO)]$ (Ia, M = Rh; Ib, M = Ir) react with *p*-toluenesulphonic acid in acetonitrile to give $[C_5Me_5MMe(Me_2SO)(MeCN)]^+$, (II), and with trifluoroacetic acid to give first $[C_5Me_5MMe(Me_2SO)(O_2CCF_3)]$ and then $[C_5Me_5M(Me_2SO)(O_2CCF_3)_2]$. Complexes II react with halide (X^-) to give the halomethyl complexes $[C_5Me_5MMe(X)(Me_2SO)]$. The IR, far-IR, ^1H and ^{13}C NMR spectra are all in agreement with the structures proposed.

Introduction

The chemistry of a large number of pentamethylcyclopentadienyl-rhodium and -iridium complexes have been investigated [1]. These now also include the dimethyl complexes $[C_5Me_5MMe_2L]$ [2,3] and their diethyl analogues, [4], but we have so far only touched on the reactions. We here report on the reactions of $[C_5Me_5MMe_2(Me_2SO)]$ with acids to give $[C_5Me_5MMe(Me_2SO)L]^+$ and $[C_5Me_5MMe(Me_2SO)X]$. Werner and coworkers have published the syntheses and properties of $[CpRhMeL_2]^+$ [5], $[CpRh(CH_2X)L(X)]$ [6], some of their C_5Me_5 analogues, and related complexes.

Results and discussion

$[C_5Me_5MMe(Me_2SO)(MeCN)]PF_6$ (II)

Reaction of I [2] with one equivalent of *p*-toluenesulphonic acid in acetonitrile in the presence of KPF_6 gave II. This presumably occurs by protonation of one methyl

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and its removal as methane and replacement by acetonitrile.

$$\underset{\text{(I)}}{[(C_5Me_5MMe_2(Me_2SO)]} + H^+ + PF_6^- \rightarrow \underset{\text{(II)}}{[C_5Me_5MMe(Me_2SO)(MeCN)]}PF_6 + CH_4$$

$$(a, M = Rh; b, M = Ir) \qquad (1)$$

The complexes II are stable to air and are soluble in polar organic solvents. Their IR spectra showed ν(CN) at 2250 and 2295 (IIa), and at 2290 and 2315 (IIb) cm^{-1}, compared to 2254 and 2295 cm^{-1} for free MeCN. The small increase in ν(CN) on coordination for IIb indicates that the MeCN is functioning chiefly as a σ-donor, as has previously been observed in $[M(C_8H_{12})(MeCN)_3]BF_4$ (C_8H_{12} = cycloocta-1,5-diene, M = Rh or Ir) [7]. The spectra also showed ν(SO) at 1080 (IIa) and 1075 (IIb) cm^{-1}. Studies of dimethylsulphoxide (DMSO) complexes have indicated that ν(SO) > 1040 cm^{-1} is diagnostic of the presence of an S-bonded DMSO [8,9]. Hence we may conclude that the DMSO in IIa and IIb is S-bonded.

The ^{1}H and the ^{13}C NMR spectra both show separate resonances for the two magnetically inequivalent coordinated DMSO methyls (Table 2); by contrast, they appear as single resonances in I [3].

$[C_5Me_5MMe(Me_2SO)(O_2CCF_3)]$ (III)

Reaction of the dimethyl complexes I with one equivalent of trifluoroacetic acid in acetone gave methane and III, according to eq. 2.

$$\underset{\text{(I)}}{[C_5Me_5MMe_2(Me_2SO)]} + CF_3CO_2H \rightarrow \underset{\text{(III)}}{[C_5Me_5MMe(Me_2SO)(O_2CCF_3)]} + CH_4 \qquad (2)$$

The IR spectra showed strong bands due to $\nu_{asym}(CO_2)$ in the region 1680–1712 cm^{-1} and rather weaker ones, due to $\nu_{sym}(CO_2)$ in the region 1310–1430 cm^{-1}. This pattern is quite characteristic [11] for monodentate carboxylate ligands, as expected. Again the presence of ν(SO) > 1040 cm^{-1} implies that the DMSO is S-bound. The NMR spectra show the inequivalent DMSO methyls as two resonances; however in IIIa they overlap.

$[C_5Me_5M(Me_2SO)(O_2CCF_3)_2]$ (IV)

Reaction of the dimethyl complexes I with an excess of trifluoroacetic acid gives the bis(trifluoroacetato)dimethylsulphoxide complexes IV (eq. 3).

$$\underset{\text{(I)}}{[C_5Me_5MMe_2(Me_2SO)]} + 2CF_3CO_2H \rightarrow \underset{\text{(IV)}}{[C_5Me_5M(Me_2SO)(O_2CCF_3)_2]} + 2CH_4 \qquad (3)$$

Remarkably, even here the DMSO remains firmly bound (again through S) to the metals. The trifluoroacetates are again monodentate (Table 1) and since the DMSO methyls are now equivalent they appear as singlets in the NMR spectra (Table 2).

$[C_5Me_5MMe(X)(Me_2SO)]$ (V–VII)

Reaction of the cationic complexes IIa or IIb with halide salts (conveniently as tetraphenylarsonium chloride or iodide or tetrabutylammonium bromide) in acetone gave the appropriate halomethyl-DMSO complexes V–VII (eq. 4).

$$\underset{\text{(II)}}{[C_5Me_5MMe(Me_2SO)(MeCN)]PF_6} + X^- \rightarrow [C_5Me_5MMe(X)(Me_2SO)] + MeCN + PF_6^- \quad (4)$$

$$\begin{array}{l}(\text{V}, X = Cl;\\ \text{VI}, X = Br;\\ \text{VII}, X = I)\end{array}$$

Again the IR spectra (Table 1) showed the DMSO to remain S-bonded throughout. The far-IR spectra each showed a single ν(MX) consistent with the presence of a single metal-bonded halide. As expected the ν(MX) decreased in the order M = Cl > Br > I; for example for Va, VIa and VIIa at 283, 278 and 270 cm^{-1}. It is unexpected that the values are so close to each other, though the similarity between the Rh and Ir complexes is less surprising. The NMR spectra again showed the DMSO methyls to be magnetically inequivalent, though at low field the ^1H resonances of Va and Vb were coincident. All the ^1H resonances in both the Rh and the Ir complexes were displaced to higher frequency (lower field) on changing the halogen from Cl to Br to I. This also applied to the C_5Me_5 and the DMSO resonances in the ^{13}C NMR but not to the metal-methyl resonances which experienced shifts in the opposite direction. A similar phenomenon has been noted in the triethyltin halides where the CH_3 resonance increased in frequency from Cl (δ 9.4 ppm) to Br (δ 10.4 ppm) to I (δ 11.4 ppm) while the CH_2 resonance moved in the opposite direction (δ 9.3 → 9.0 → 7.9 ppm) for the same three halides [12].

Gas evolution experiments

Careful analyses were carried on the gases evolved when the dimethylrhodium complex Ia was treated with an excess of a variety of reagents in acetonitrile. These showed that acids (*p*-toluenesulphonic, sulphuric, or tetrafluoroboric) gave largely methane (95–99%) with a small amount of ethane (1–5%). Similar results were obtained when Ia was treated with cerium(IV) but the very good one-electron oxidisers I_2, $AgBF_4$, and $IrCl_6^{2-}$ gave much more ethane (45%, Ag^+; 98%, Ir^{IV}). Iodine gave largely methyl iodide but the gases produced were 90% ethane. Both the organic one-electron oxidants triphenylmethyl and tropylium (as their BF_4 salts) caused some decomposition (35 and 20%, respectively) to give methane and ethane (7 and 35%, respectively. In all cases we suggest that the ethane arises by an electrophile-induced methyl–methyl coupling [13].

Experimental

Reactions were generally carried out in air. Solvents were distilled under nitrogen before use. The details for experiments are given below; microanalytical, yields, Ir and NMR (^1H and ^{13}C) spectroscopic data are collected in Tables 1 and 2. Microanalytical data were determined by the University of Sheffield Microanalytical Services, Ir and far-IR spectra were determined on a PE-180 spectrometer and NMR spectra on PE R-12B (60 MHz, ^1H) and JEOL PFT-100 (25 MHz, ^{13}C).

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TABLE 1

MICROANALYTICAL AND IR SPECTROSCOPIC DATA

Complex	Analysis (Found (calcd.) (%))					Yield (%)	IR (cm^{-1})		
	C	H	N	S	X		ν(PF$_6^-$)	ν(SO)	ν(CN)
IIa	34.9 (34.8)	5.2 (5.3)	2.6. (2.7)	6.3 (6.2)	–	86	845vs	1080vs	2295, 2250w
IIb	28.7 (28.7)	4.3 (4.3)	2.2 (2.2)	13.8 (13.9)	–	75	830vs	1075vs	2315w, 2290w
							ν(O$_2$CR)		
IIIa	40.3 (40.5)	5.4 (5.4)	–	7.1 (7.2)	–	80	1685vs, 1310s, 1410w	1100vs	
IIIb	33.7 (33.8)	4.5 (4.5)	–	6.0 (6.0)	–	85	1690vs, 1425s, 1315m	1090vs	
IVa	35.2 (35.4)	3.8 (3.9)	–	5.8 (5.9)	–	80	1680vs, 1430m, 1310m	1060vs	
IVb	30.4 (30.4)	3.5 (3.4)	–	5.2 (5.1)	–	82	1695vs, 1402s, 1310w	1080vs	
							ν(M–X)		
Va	42.4 (42.6)	6.4 (6.6)	–	8.5 (8.7)	9.6 (9.7)	75	283s	1082vs	
VIa	38.1 (38.0)	5.7 (5.9)	–	7.6 (7.8)	19.2 (19.4)	70	278m	1090vs	
VIIa	34.4 (34.1)	5.2 (5.3)	–	–	–	80	270w	1095vs	
Vb	34.2 (34.2)	5.3 (5.3)	–	6.9 (7.0)	7.6 (7.7)	85	280s	1110vs	
VIb	31.0 (31.2)	4.9 (4.8)	–	6.5 (6.4)	15.8 (16.0)	80	273m	1108vs	
VIIb	28.3 (28.5)	4.4 (4.4)	–	–	–	85	262m	1100vs	

TABLE 2

^{1}H AND ^{13}C NMR DATA (Recorded in $CDCl_3$; $J(^{103}Rh-^1H)$ (Hz) in square parentheses; $J(^{103}Rh-^{13}C)$ (Hz) in round brackets.)

Complex	^{1}H NMR (δ scale)				$^{13}C\{^1H\}$ NMR (δ scale)					
	$(CH_3)_2SO$	C_5Me_5	MMe	Other	$\mathit{C}_5\mathrm{Me}_5$	$(CH_3)_2SO$	$\mathrm{C}_5\mathit{Me}_5$	M–Me	Other	
				CH_3–CN					$\mathrm{CH_3}$–CN	$\mathit{C}\mathrm{H_3}$–CN
IIa	3.12s 2.86s	1.7s	0.82d [2.7]	2.42s	101.3d (6.1)	46.6s 42.7s	8.7s	4.9d (21.4)	125.0s	3.4s
IIb	3.36s 3.08s	1.76s	0.68s	2.91s	95.5s	46.7s 42.3s	8.3s	−14.7s	[a]	3.6s
									$\mathit{C}\mathrm{F_3}$–COO	$\mathrm{CF_3}$–COO
IIIa	2.94b	1.62s	0.93d [2.6]		98.5d (5.3)	44.4s 41.2s	8.9s	7.2d (23.65)	[a]	159.8q
IIIb	3.21s 2.93s	1.71s	0.74s		92.1s	43.0s 41.1s	8.6s	−10.2s	114.0d [289.9][b]	162.6q
IVa	2.75	1.62s			93.7d (9.9)	39.3s	8.2s		115.4d [289.9][b]	162.3q [38.1][b]
									$\mathit{C}\mathrm{F_3}$–COO	$\mathrm{CF_3}$–COO
IVb	3.06s	1.72s			91.4s	41.2s	9.4s		115.2dd [298.6][b]	161.6q [32.6][b]
Va	2.94b	1.68s	0.96d [2.7]		98.1d (6.8)	45.2s 41.2s	8.7s	4.1d (22.9)		
VIIa	3.08b	1.70s	0.96d [2.7]		99.4d (5.3)	47.0s 41.5s	8.9s	2.0d (22.9)		
VIIIa	3.42b 3.06b	1.81s	1.07d [2.7]		99.9d (5.3)	50.3s 49.2s	9.5s	−1.5d (22.9)		
Vb	3.32b 2.4b	1.7s	0.82s		93.2s	45.1s 39.8s	8.4s	−13.1s		
VIb	3.44b 3.06b	1.74s	0.95s		93.6s	47.3s 40.1s	8.6s	−15.3s		
VIIb	3.62s 3.22s	1.86s	1.18s		94.2s	51.0s 40.9s	9.1s	−19.3s		

[a] Not observed. [b] J(C–F) in Hz.

Acetonitrile(dimethylsulphoxide)methyl(pentamethylcyclopentadienyl)-rhodium and -iridium(III) hexafluorophosphates (IIa and IIb)

KPF_6 (0.49 mmol) was added to a solution of Ia or Ib (0.46 mmol) in acetonitrile (15 cm^3). After a few minutes a freshly prepared *p*-toluenesulphonic acid solution in acetonitrile (0.46 mmol in 5 cm^3) was added dropwise. The resultant suspension was stirred (20°C, 1 h). The precipitated potassium *p*-toluenesulphonate was filtered off and the solvent removed in vacuo to leave a residue. This was crystallised from dichloromethane/pentane to give yellow-orange crystals of IIa (0.2 g, 86%) or yellow crystals of IIb (0.22 g, 75%).

Methyltrifluoroacetato(dimethylsulphoxide)(pentamethylcyclopentadienyl)-rhodium and -iridium (IIIa and IIIb)

Trifluoroacetic acid (0.019 cm^3, 0.248 mmol) was added to a solution of Ia or Ib (0.248 mmol) in dry acetone (15 cm^3). The solution was stirred (20°C, 1.5 h) and then evaporated to dryness. The residue was extracted with CH_2Cl_2 (2×15 cm^3), the solution concentrated and pentane (5 cm^3) added. On cooling, orange crystals of IIIa (0.08 g, 75%) or IIIb (0.11 g, 85%) were obtained.

Bis(trifluoroacetato)dimethylsulphoxide(pentamethylcyclopentadienyl)-rhodium and -iridium (IVa and IVb)

Trifluoroacetic acid in slight excess (0.92 mmol) was added to a solution of Ia or Ib (0.45 mmol) in dry acetone (20 cm^3). The solution was stirred (20°C, 5 h, Ia and 48 h, Ib) and then evaporated to dryness. The residue was crystallised from dichloromethane/pentane to give red crystals of IVa (0.19 g, 80%) or yellow crystals of IVb (0.23 g, 82%).

Halo(methyl)dimethylsulphoxide(pentamethylcyclopentadienyl)-rhodium and -iridium (V–VII)

The quaternary halide [$(Ph_4As)Cl$, $(n\text{-}Bu_4N)Br$ or $(Ph_4As)I$] (0.29 mmol) was added to a solution of IIa or IIb (0.15 g, 0.29 mmol) in acetone and the resultant suspension was stirred (20°C, 30 min). The precipitated hexafluorophosphate salt was filtered off and the solvent removed in vacuo to leave a residue which on crystallisation from dichloromethane and pentane gave the rhodium complexes Va–VIIa as red crystals and the iridium complexes Vb–VIIb as yellow or yellow-orange crystals.

Gas analyses

All reactions were carried out in 5 cm^3 flasks sealed with a Suba-seal under N_2 atmosphere. Complex Ia (10 mg) and the appropriate reagent (5–10 molar excess) of dry acetonitrile (2 cm^3) (or a mixture of acetonitrile (1.5 cm^3) and aqueous mineral acid (9 *M*, 0.5 cm^3)). The solutions were stirred and briefly heated to 55°C to complete the reaction. For each reagent six identical reactions were carried out and the gas from each analysed twice. Gas analyses were carried out using a Porapak Q column at 100°C on a Carlo Erba 4100 chromatograph fitted with F.I.D.

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