Metal Complexes of Sulphur Ligands. Part 15.[1] Reaction of Bis[(η-arene)dichlororuthenium] and Bis[dichloro(η-pentamethylcyclopentadienyl)metal] Complexes of Rhodium and Iridium with Various Dithioacid Ligands

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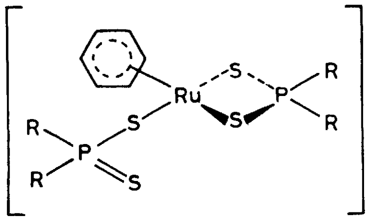
Reaction of the complexes $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ (1) (arene = C_6H_6 or $C_6H_3Me_3$) and $[\{M(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (2) (M = Rh or Ir) with excess of various dithioacid anions gives monomeric $[Ru(\eta\text{-arene})(S\text{-}S)_2]$ (3: $S\text{-}S^- = [S_2PR_2]^-$) and $[M(\eta\text{-}C_5Me_5)(S\text{-}S)_2]$ (4: M = Rh, $S\text{-}S^- = [S_2PR_2]^-$, $[S_2CNR_2]^-$, or $[S_2COR]^-$; M = Ir, $S\text{-}S^- = [S_2CNMe_2]^-$ or $[S_2PMe_2]^-$) respectively. Analytical data together with i.r. and ^1H, ^{13}C, and ^{31}P n.m.r. studies show that these complexes contain both bi- and uni-dentate dithioacid groups both in the solid state and in solution. For $[M(\eta\text{-}C_5Me_5)(S_2CNMe_2)_2]$ (M = Rh or Ir) and $[Rh(\eta\text{-}C_5Me_5)(S_2COEt)_2]$ in solution at higher temperatures, however, kinetic line-shape analysis indicates the occurrence of uni- and bi-dentate dithioacid exchange probably *via* a dissociatively controlled intramolecular mechanism. Reaction of (1; arene = C_6H_6) and (2; M = Rh) with $[S\text{-}S]^-$ (1 : 1 mol ratio) gives $[Ru(\eta\text{-}C_6H_6)Cl(S_2PPh_2)]$ and $[Rh(\eta\text{-}C_5Me_5)Cl(S\text{-}S)]$ (5; $S\text{-}S^- = [S_2CNMe_2]^-$, $[S_2PMe_2]^-$, or $[S_2PPh_2]^-$) respectively which are useful precursors for synthesising a range of complexes such as $[Rh(\eta\text{-}C_5Me_5)X(S_2CNMe_2)]$ ($X = Br^-$, I^-, or SCN^-) and the mixed dithioacid complexes $[Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)(S\text{-}S)]$ (6; $S\text{-}S^- = [S_2PMe_2]^-$, $[S_2PPh_2]^-$, or $[S_2COMe]^-$). In methanol, (5; $S\text{-}S^- = [S_2CNMe_2]^-$) gives the solvated cation $[Rh(\eta\text{-}C_5Me_5)(HOMe)(S_2CNMe_2)]^+$ which reacts with various Lewis bases (L) to give $[Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)L][BPh_4]$ (L = PPh_3, $PMePh_2$, CO, $AsPh_3$, or C_5H_5N). Similar complexes can also be made by reaction of $[Ru(arene)Cl_2(NC_5H_5)]$ or $[Rh(\eta\text{-}C_5Me_5)Cl_2(PPh_3)]$ with $[S\text{-}S]^-$ (1 : 1 mol ratio) and excess of $Na[BPh_4]$. However, reaction of (5; $S\text{-}S^- = [S_2CNMe_2]^-$) with excess of $Ph_2P[CH_2]_2PPh_2$ (dppe) or $Ph_2PCH_2PPh_2$ (dppm) in methanol gives the dimeric cations $[\{Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)\}_2(\text{dppe or dppm})]^{2+}$ (7), and with $C_2(CN)_4$ and $Na[BPh_4]$ in methanol the cyanotriphenylborate complex $[Rh(\eta\text{-}C_5Me_5)(NCBPh_3)(S_2CNMe_2)]$ (8) is formed.

In previous papers on dithioacid complexes of the rarer platinum metals ruthenium,[2-6] rhodium,[7] and osmium[8] we have examined the reactions of *mer*-$[MCl_3(PMe_2Ph)_3]$ and various ruthenium(II) tertiary phosphine, phosphinite, phosphonite, and phosphite complexes with dithioacid ligands, and also the reaction with $[\{RuCl_2(diene)\}_n]$ which gave the complexes *cis*-$[Ru(diene)(S_2PMe_2)_2]$ (diene = bicyclo[2.2.1]hepta-2,5-diene or cyclo-octa-1,5-diene).

In this paper, we report the full results[9] of reactions of the related $[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$ (1; arene = C_6H_6 or $C_6H_3Me_3$) and $[\{M(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (2; M = Rh or Ir) complexes with some dithioacid anions. Although several reactions of (1) with unidentate Lewis bases have been reported,[10,11] this is only the second study involving ligands capable of bidentate co-ordination. Earlier[10] reaction of (1) with $Ph_2PCH_2PPh_2$ (dppm) gave $[Ru(\eta\text{-}C_6H_6)Cl_2(dppm)]$ with the dppm ligand bound in a unidentate fashion whereas with $Ph_2P[CH_2]_4PPh_2$ (dppb) the dimeric $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2(dppb)]$ with a bridging dppb group was formed. Similarly, with (2; M = Rh), $Ph_2P[CH_2]_2PPh_2$ (dppe) gave $[Rh(\eta\text{-}C_5Me_5)Cl_2(dppe)]$ and $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2(dppe)]$ with excess and 1 : 1 mol ratios of (2) : dppe respectively. The complex $[Rh(\eta\text{-}C_5Me_5)Cl_2(dppe)]$ then reacted readily with $[NH_4][PF_6]$ in ethanol to give $[Rh(\eta\text{-}C_5Me_5)Cl(dppe)][PF_6]$.[12]

RESULTS AND DISCUSSION

Reaction of (1; arene = C_6H_6) in aqueous media with an excess of $Na[S_2PR_2]$ (R = Me, OMe, or OEt) or $[NH_4][S_2PPh_2]$ gave an immediate colour change from orange to deep red, and, after extraction with diethyl ether or methylene chloride, red crystalline solids were isolated. On the basis of analytical and molecular-weight data † together with ^1H and ^{31}P n.m.r. (Tables 1 and 2 respectively) and i.r. studies (see Experimental section) these solids are best formulated as monomeric $[Ru(\eta\text{-}C_6H_6)(S_2PR_2)_2]$ (3) with one bi- and one uni-



(3) R = Me, Ph, OMe, or OEt

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dentate $[S_2PR_2]^-$ group. Thus, the positions of ν(PS_2) in the i.r. spectra of the methyl- and phenyl-substituted $[S_2PR_2]^-$ complexes were diagnostic of the presence of both bi- and uni-dentate co-ordination (see refs. 13 and 14 respectively). Furthermore, the ^1H n.m.r. spectrum in $CDCl_3$ at 301 K of $[Ru(\eta\text{-}C_6H_6)(S_2PMe_2)_2]$ consisted of a singlet at δ 5.88 p.p.m. due to the co-ordinated benzene ring and three doublets of relative intensity 2 : 1 : 1 at 2.10, 1.95, and 1.89 p.p.m. respectively [^2J(PH) 12.0 Hz] from the methyl groups of the $[S_2PMe_2]^-$ ligands. This indicated three magnetically inequivalent methyl groups as expected for structure (3; R = Me). Similarly, the ^1H n.m.r. spectrum of $[Ru(\eta\text{-}C_6H_6)\{S_2P(OMe)_2\}_2]$ at 301 K showed three methyl doublets of relative intensity 2 : 1 : 1, and the

TABLE 1

Hydrogen-1 n.m.r. data for various ruthenium(II) dithioacid complexes at 301 K [a]

Complex	δ ±0.01 p.p.m.[b] Dithio-ligand	η-Arene	Other resonances
$[Ru(\eta\text{-}C_6H_6)(S_2PMe_2)_2]$	2.10 (d) (12.0) [2] 1.95 (d) (12.0) [1], 1.89 (d) (12.0) [1],	5.88 (s) [2]	
$[Ru(\eta\text{-}C_6H_6)(S_2PPh_2)_2]$	7.0—8.3 (m) [10]	5.48 (s) [3]	
$[Ru(\eta\text{-}C_6H_6)\{S_2P(OMe)_2\}_2]$	3.79 (d) (14.0) [1] 3.75 (d) (14.0) [2] 3.68 (d) (14.0) [1]	5.80 (s) [2]	
$[Ru(\eta\text{-}C_6H_6)\{S_2P(OEt)_2\}_2]$	4.15 (m) [4], 1.35 (m) [6]	5.76 (s) [3]	
$[Ru(\eta\text{-}C_6H_3Me_3)(S_2PMe_2)_2]$	2.14 (d) (12.0) [2], 1.98 (d) (12.0) [1], 1.92 (d) (12.0) [1]	5.51 (s) [1], 2.21 (s) [3] [c]	
$[Ru(\eta\text{-}C_6H_3Me_3)(S_2PPh_2)_2]$	6.9—8.3 (m) [20]	5.10 (s) [3], 1.98 (s) [9] [c]	
$[Ru(\eta\text{-}C_6H_6)Cl(S_2PPh_2)]$	7.2—8.2 (m) [5]	5.50 (s) [3]	
$[Ru(\eta\text{-}C_6H_6)(NC_5H_5)(S_2PMe_2)][BPh_4]$ [d]	2.02 (d) (12.0) [3], 1.32 (d) (12.0) [3]	5.41 (s) [6]	8.82 (d),[e] 6.7—7.8 (m) [25]
$[Ru(\eta\text{-}C_6H_3Me_3)(NC_5H_5)(S_2PMe_2)][BPh_4]$	1.05 (d) (12.0) [3], 1.70 (d) (12.0) [3]	4.43 (s) [3] 1.60 (s) [9] [c]	8.48 (d),[e] 6.7—7.8 (m) [25]
$[Ru(\eta\text{-}C_6H_6)(PPh_3)(S_2PPh_2)][PF_6]$	7.2—8.2 (m) [25] [f]	5.40 (s) [6]	
$[Ru(\eta\text{-}C_6H_6)(PMePh_2)(S_2PPh_2)][PF_6]$	7.2—8.2 (m) [20] [f]	5.45 (s) [6]	2.25 (d) (10.0) [g] [3]
$[Ru(\eta\text{-}C_6H_3Me_3)(NC_5H_5)(S_2PPh_2)][BPh_4]$ [h]	6.0—7.6 (m) [35] [f]	4.80 (s) [3], 1.62 (s) [9] [c]	8.52 (d),[e] 6.0—7.6 (m)
$[Ru(\eta\text{-}C_6H_6)\{P(OMe)_3\}(S_2PPh_2)][PF_6]$	7.2—8.2 (m) [10]	5.78 (s) [6]	3.75 (d) (11.0) [i] [9]
$[Ru(\eta\text{-}C_6H_6)(NC_5H_5)(S_2PPh_2)][PF_6]$ [h]	7.0—8.0 (m) [15] [f]	5.93 (s) [6]	9.10 (d),[e] 7.0—8.0 (m)
$[Ru(\eta\text{-}C_6H_6)(S_2PPh_2)(SbPh_3)][PF_6]$ [h]	7.2—8.0 (m) [25] [f]	6.00 (2) [6]	

s = Singlet, d = doublet, and m = multiplet.

[a] In $CDCl_3$ unless otherwise stated. [b] J(PH) (in Hz) values are given in parentheses. Numbers in square brackets indicate normalised integrated intensities. [c] Methyl resonance of $C_6H_3Me_3$. [d] In CD_2Cl_2. [e] Pyridine resonance; others masked by phenyl resonances. [f] Intensity includes aromatic resonances from other ligands. [g] Methyl resonance of $PMePh_2$. [h] In $(CD_3)_2CO$. [i] Methyl resonance of $P(OMe)_3$.

TABLE 2

Phosphorus-31 n.m.r. data (proton-noise decoupled) for various ruthenium(II) and rhodium(III) dithioacid complexes in $CDCl_3$

Complex	T/K	δ [a]/p.p.m. $[S_2PR_2]$	Other resonances
$[Ru(\eta\text{-}C_6H_6)(S_2PMe_2)_2]$ [b]	303	106.6 (s), 62.6 (s)	
$[Ru(\eta\text{-}C_6H_6)(S_2PPh_2)_2]$	303	85.9 (s), 68.9 (s)	
$[Ru(\eta\text{-}C_6H_6)Cl(S_2PPh_2)]$	298	91.7 (s)	
$[Ru(\eta\text{-}C_6H_6)(PMePh_2)(S_2PPh_2)][PF_6]$ [c]	298	85.0 (d) (16.5) [d]	24.6 (d) (16.5) [d]
$[Ru(\eta\text{-}C_6H_6)\{P(OMe)_3\}(S_2PPh_2)][PF_6]$ [c]	298	95.7 (d) (19.0) [d]	123.9 (d) (19.0) [d]
$[Rh(\eta\text{-}C_5Me_5)(S_2PMe_2)_2]$	233	93.9 (d) (10.1),[e] 57.5 (d) (3.6) [e]	
	273	92.9 (d) (10.1),[e] 57.2 (d) (3.6) [e]	
	298	92.2 (d) (9.8),[e] 56.9	
	343	91.3 (br), 56.8 (br)	
	298 [f]	90.3 (d) (8.8),[e] 54.4 (d) (1.5) [e]	
	405 [f]	70.9 (br)	
$[Rh(\eta\text{-}C_5Me_5)(S_2PPh_2)_2]$	298	80.8 (d) (10.8),[e] 64.2	
	343	81.5 (br), 64.5 (br)	
$[Rh(\eta\text{-}C_5Me_5)Cl(S_2PMe_2)]$	298	87.6 (d) (10.8) [e]	
$[Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)(S_2PMe_2)]$	298	66.6 (d) (3.9) [e]	
$[Rh(\eta\text{-}C_5Me_5)(PPh_3)(S_2PMe_2)][BPh_4]$	298	103.3 [g] (9.2),[e] (9.7) [d]	35.9 [h] (9.7) [d] (144.8) [i]
$[Rh(\eta\text{-}C_5Me_5)(PPh_3)(S_2PPh_2)][PF_6]$ [c]	298	88.4 [g] (10.5),[e] (11.3) [d]	34.9 [h] (11.3) [d] (143.8) [i]
$[Rh(\eta\text{-}C_5Me_5)(NCBPh_3)(S_2PMe_2)]$	303	97.7 (d) (8.9) [e]	

[a] Chemical shifts reported to high frequency of 85% H_3PO_4. [b] On standing, an additional peak appears at 54.4 p.p.m. ($[S_2PMe_2]^-$). [c] $^{31}P\text{-}\{^1H\}$ n.m.r. of $[PF_6]^-$ ion; multiplet at *ca.* 144 p.p.m. [^1J(PF) 712 Hz]. [d] ^3J(PP) in Hz. [e] ^2J(RhP) in Hz. [f] In chlorobenzene–$[^2H_8]$toluene. [g] Overlapping doublet of doublets. [h] Doublet of doublets. [i] ^1J(RhP) in Hz.

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^{31}P n.m.r. spectra of the $[S_2PMe_2]^-$ and $[S_2PPh_2]^-$ complexes at 303 K each showed two resonances consistent with structure (3).

Thus, this spectroscopic evidence indicated stereochemical rigidity of these complexes in solution at ambient temperature, *i.e.* no rapid scrambling of the uni- and bi-dentate $[S_2PR_2]^-$ groups was observed {*cf.*[13] $[Pt(PR'_3)(S_2PR_2)_2]$}. However, on leaving as a solid in air (for R = Me) or in solution (all R) for several days some decomposition occurred as indicated by the appearance of free benzene in the ^1H n.m.r. spectra and of $[S_2PR_2]^-$ ion in the ^{31}P n.m.r. spectra. Decomposition also readily occurred on warming the freshly prepared solutions and, therefore, no detailed investigation could be undertaken of any fluxional processes which might be exhibited by these complexes in solution.

TABLE 3

Hydrogen-1 n.m.r. data for various rhodium(III) and iridium(III) dithioacid complexes [a]

Complex	T/K	$\delta \pm 0.01$ p.p.m.[b] Dithio-ligand	 η-C_5Me_5	 Other resonances
$[Rh(\eta-C_5Me_5)(S_2PMe_2)_2]$	343	2.02 (d) (12.5) [4]	1.71 (s) [5]	
	301	1.8—2.3 (m) (br) [4]		
	273	2.11 (d) (12.5) [2], 1.90 (d) (12.5) [1], 1.93 (d) (12.5) [1]		
$[Rh(\eta-C_5Me_5)(S_2PPh_2)_2]$	301	7.1—8.0 (m) [4]	1.52 (s) [3]	
$[Rh(\eta-C_5Me_5)(S_2CNMe_2)_2]$	301	3.58 (s) [2], 3.15 (s) [2]	1.73 (s) [5]	
	301 ^{c}	3.62 (s) [2], 2.80 (s) [2]		
	387 ^{c}	3.29 (s) [4]		
$[Rh(\eta-C_5Me_5)(S_2CNEt_2)_2]$	253	4.17 (dq) (7.0) ^{d} [4], 3.66 ^{n} (7.0) [4], 1.20 (m) (7.0) ^{d} [12],	1.75 (s) [15]	
	301	4.12 (q) (7.0) ^{d} [4], 3.61 ^{o} (7.0) ^{d} [4], 1.20 (m) (7.0) ^{d} [12],		
	343	4.13 (br), 3.68 (br), 1.29 (t) (7.0) ^{d}		
	359 ^{c}	3.77 (br), 1.29 (t) (7.0) ^{d}		
$[Rh(\eta-C_5Me_5)(S_2COMe)_2]$	301	4.03 (s) [1], 4.00 (s) [1]	1.79 (s) [5]	
$[Rh(\eta-C_5Me_5)(S_2COEt)_2]$	301	4.50 (q), 4.48 (q) (7.0) ^{d} [4], 1.40 (t), 1.33 (t) (7.0) ^{d} [6]	1.78 (s) [15]	
$[Rh(\eta-C_5Me_5)Cl(S_2CNMe_2)]$	301	3.20 (s) [2]	1.73 (s) [5]	
$[Rh(\eta-C_5Me_5Cl(S_2PMe_2)]$	301	2.00 (d) (13.0) ^{c} [2]	1.67 (s) [5]	
$[Rh(\eta-C_5Me_5)(S_2CNMe_2)(S_2PMe_2)]$	301	3.21 (s) [2], 2.00 (d) (13.0) [2]	1.79 (s) [5]	
$[Rh(\eta-C_5Me_5)(S_2CNMe_2)(S_2PPh_2)]$	301	8.0 (m), 7.1 (m) [10], 2.69 (s) [6]	1.78 (s) [15]	
$[Rh(\eta-C_5Me_5)(S_2CNMe_2)(S_2COMe)]$	301	4.05 (s) [1], 3.28 (s) [2]	1.78 (s) [5]	
$[Rh(\eta-C_5Me_5)(HOMe)(S_2CNMe_2)][BPh_4]$	301 ^{e,f}	2.20 (s)	1.78 (s)	6.7—7.3 (m)
$[Rh(\eta-C_5Me_5)(PPh_3)(S_2PMe_2)][BPh_4]$	301	1.69 (d) (13.0) [3], 0.52 (d) (13.0) [3]	1.32 (d) (4.0) ^{g} [15]	7.0—7.5 (m) [35]
$[Rh(\eta-C_5Me_5)(PMePh_2)(S_2CNMe_2)][BPh_4]$	301	2.60 (s) [6]	1.50 (d) (4.0) ^{g} [15]	1.92 (d) (10.0) ^{h} [3], 7.0—7.5 (m) [10]
$[Rh(\eta-C_5Me_5)(NC_5H_5)(S_2CNMe_2)][BPh_4]$	301	2.92 (s) [6]	1.54 (s) [15]	8.23(d),^{i} 6.0—7.4 (m) [25]
$[Rh(\eta-C_5Me_5)(CO)(S_2CNMe_2)][BPh_4]$	301 ^{j}	3.28 (s) [6]	2.01 (s) [15]	7.0—7.4 (m) [20]
$[Rh(\eta-C_5Me_5)(PMePh_2)(S_2PPh_2)][PF_6]$	301	7.0—7.8 (m) [20] ^{k}	1.34 (d) (4.0) ^{g} [15]	2.10 (d) (10.0) ^{h} [3]
$[\{Rh(\eta-C_5Me_5)(S_2CNMe_2)\}_2(dppe)][BPh_4]_2$	301 ^{e,l}	2.98 (s) [6]	1.32 (d) (3.0) ^{g} [15]	6.7—7.8 (m) [40]
$[\{Rh(\eta-C_5Me_5)(S_2CNMe_2)\}_2(dppm)][BPh_4]_2$	301 ^{e}	2.95 (s) [6]	1.44 (d) (4.0) ^{g} [15]	3.20 (q), 6.7—7.7 (m) [40]
$[Rh(\eta-C_5Me_5)(PMePh_2)(S_2PMe_2)][S_2PMe_2]$	301	2.12 (d) (12.5) [3], 2.05 (d) (12.5) [6], 0.89 (d) (12.5) [3]	1.60 (d) (4.0) ^{g} [15]	2.34 (d) (10.0) ^{h} [3], 7.0—7.5 (m) [10]
$[Rh(\eta-C_5Me_5)(PMePh_2)(S_2PMe_2)][BPh_4]$	301	1.72 (d) (13.0) [1], 0.75 (d) (13.0) [1]	1.48 (d) (4.0) ^{g} [5]	2.04 (d) (10.0) ^{h} [1], 6.8—7.6 (m) [10]
$[Rh(\eta-C_5Me_5)(NCBPh_3)(S_2CNMe_2)]$	301	3.17 (s) [2]	1.79 (s) [5]	7.0—7.5 (m) [5]
$[Ir(\eta-C_5Me_5)(S_2CNMe_2)_2]$	301	3.80 (s) [2], 3.28 (s) [2]	1.73 (s) 5	
	357 ^{c}	3.23 (s) [2], 2.36 (s) [2] ^{m}		
	402 ^{c}	3.17 (s) (br), 2.47 (s) (br) ^{m}		

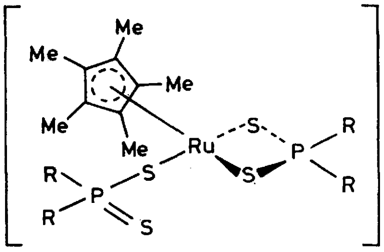
t = Triplet, q = quartet.

[a] In $CDCl_3$ unless otherwise stated. [b] J(PH) (in Hz) values are given in parentheses. Numbers in square brackets indicate normalised integrated intensities. [c] In chlorobenzene. [d] $J(CH_2CH_3)$ in Hz. [e] In $(CD_3)_2SO$. [f] Contaminated by some $[Rh(\eta-C_5Me_5)(SMe_2O)(S_2CNMe_2)][BPh_4]$ (integration not exact). [g] $J[PH(C_5Me_5)]$ in Hz. [h] Methyl resonance of $PMePh_2$. [i] Pyridine resonance; others masked by phenyl resonances. [j] In $(CD_3)_2CO$. [k] Intensity includes aromatic resonances from other ligands. [l] C_2H_4 protons in dppe too weak for accurate measurement. [m] Silicone-oil capillary as external reference. [n] ABM_3 system with J(AB) 14.0 Hz, δ(AB) 19.5 Hz. [o] ABM_3 system with J(AB) 14.0 Hz, δ(AB) 16.4 Hz.

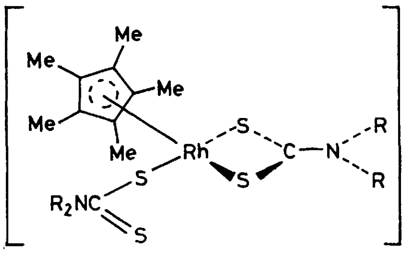
Furthermore, attempts to synthesise the related complexes $[Ru(\eta-C_6H_6)(S\text{-}S)_2]$ ($S\text{-}S^- = [S_2COR]^-$ or $[S_2CNR_2]^-$) by the same methods were unsuccessful. Instead, greenish brown paramagnetic solids were obtained which contained no co-ordinated benzene ring (n.m.r. evidence) and therefore were not investigated further, although most probably mixtures of species such as $[Ru(S_2CNR_2)_3]$, $[Ru_2(S_2CNR_2)_5]Cl$,[15] *etc.* were formed.

In an attempt to retain the arene ring, the methyl-substituted arene dimer $[\{Ru(\eta\text{-}C_6H_3Me_3)Cl_2\}_2]$ was treated with $Na[S_2CNR_2]$ and $K[S_2COR]$ but again ring displacement accompanied chloride-ion substitution in each case. However, with the less nucleophilic $[S_2PR_2]^-$ (R = Me or Ph), $[Ru(\eta\text{-}C_6H_3Me_3)(S_2PR_2)_2]$ were isolated and characterised as above (Tables 1 and 2). For R = Me, the complex is more stable than $[Ru(\eta\text{-}C_6H_6)(S_2PMe_2)_2]$ since it can be heated to 320 K in $CDCl_3$ without decomposition, although no fluxional behaviour was observed up to this temperature.

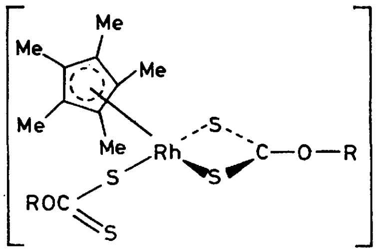
Since the reactions of (1) with dithioacid ligands did not generate a very wide range of stable η-bonded benzene ruthenium(II)–sulphur complexes, it was decided to investigate the reactions of the isoelectronic $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (2) with these ligands because earlier studies[12] had indicated the inertness of the Rh–C_5Me_5 bond towards a range of nucleophiles. Thus (2) was dissolved in either water or methyl cyanide and treated with an excess of $[S\text{–}S]^-$ ion ($[S\text{–}S]^- = [S_2PMe_2]^-$, $[S_2PPh_2]^-$, $[S_2CNMe_2]^-$, $[S_2CNEt_2]^-$, $[S_2COMe]^-$, or $[S_2COEt]^-$) to give either orange-red solutions which could be extracted with diethyl ether or methylene chloride or orange-red precipitates directly which were readily recrystallised. From analytical and molecular-weight data and i.r. and n.m.r. spectroscopy (Tables 2—4) these products were formulated as monomeric $[Rh(\eta\text{-}C_5Me_5)(S\text{–}S)_2]$ (4) containing one bi- and one unidentate $[S\text{–}S]^-$ group. As expected, these complexes were much more stable thermally than the isoelectronic $[Ru(arene)(S_2PR_2)_2]$ and showed little sign of decomposition on leaving in solution for prolonged periods.



(4a) R = Me or Ph



(4b)



(4c)

R = Me or Et

Thus, at ambient temperature, the ^1H n.m.r. spectrum of $[Rh(\eta\text{-}C_5Me_5)(S_2PMe_2)_2]$ in $CDCl_3$ consisted of a singlet at δ 1.71 p.p.m. (from the C_5Me_5 ring) and a rather complicated multiplet between 1.8 and 2.3 p.p.m. On cooling, this multiplet was resolved into three doublets of relative intensity 2 : 1 : 1 at 2.11, 1.93, and 1.90 p.p.m. respectively [^2J(PH) 12.5 Hz] as expected for structure (4a; R = Me). On warming the solution, the doublets broadened and coalesced at 333 K giving a single doublet centred at 2.02 p.p.m. [^2J(PH) 12.5 Hz] (Table 3). This phenomenon, which is concentration independent and reversible with temperature, suggested that rapid intramolecular scrambling of dithioacid groups [see equation (1)] was occurring at higher temperatures {*cf.*[13] $[Pt(PR'_3)(S_2PR_2)_2]$}. The fluxional behaviour of this complex was also monitored by ^{31}P

TABLE 4

Carbon-13 n.m.r. spectrum (proton-noise decoupled) for $[Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)_2]$ in $CDCl_3$ at 318 K [a]

δ [b]/p.p.m.		Assignment
209.7 (d)	[^2J(RhC) 3.8 Hz]	$S_2\mathit{C}NMe_2$ (bidentate) [c]
209.0 (s)		$S_2\mathit{C}NMe_2$ (unidentate)
96.6 (d)	[^1J(RhC) 7.3 Hz]	C_5Me_5
45.4br (s)		$S_2CN\mathit{Me}_2$ (unidentate)
38.4 (s)		$S_2CN\mathit{Me}_2$ (bidentate) [d]
9.3 (s)		$C_5\mathit{Me}_5$

[a] A small amount of tris(pentane-2,4-dionato)chromium was added. [b] Chemical shifts to high frequency of $SiMe_4$. [c] Assigned to bi- rather than uni-dentate $[S_2\mathit{C}NMe_2]^-$ because of larger ^2J(RhC) (see text), and also $[Rh(\eta\text{-}C_5Me_5)(NCBPh_3)(S_2CNMe_2)]$ with bidentate $[S_2\mathit{C}NMe_2]^-$ resonance at 206.2 p.p.m. [^2J(RhC) 4.0 Hz]. [d] *cf.* $[Rh(\eta\text{-}C_5Me_5)(NCBPh_3)(S_2CNMe_2)]$ with bidentate $[S_2CN\mathit{Me}_2]^-$ resonance at 36.9 p.p.m.

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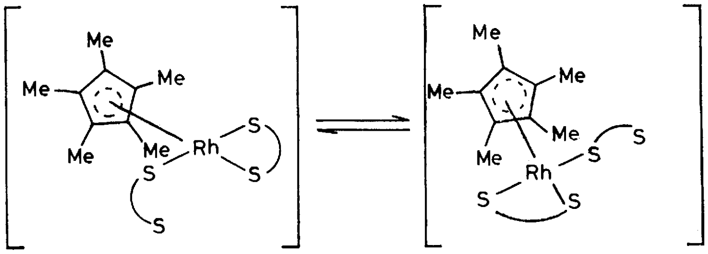
[15] See A. R. Hendrickson, J. M. Hope, and R. L. Martin, *J.C.S. Dalton*, 1976, 2032 and refs. therein for better methods of preparation of these complexes.

n.m.r. spectroscopy (Table 2). At ambient temperatures the spectra consisted of two sharp resonances which broadened on warming. Although coalescence of the peaks was not achieved in $CDCl_3$ [because of their large separation (1 474 Hz) and the low boiling point of $CDCl_3$], use of chlorobenzene as solvent produced a single ^{31}P n.m.r. resonance, indicative of fast uni- and bi-dentate $[S_2PMe_2]^-$ exchange at 405 K.



(1)

For $[Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)_2]$, the ^1H n.m.r. spectrum in $CDCl_3$ at $\leqslant$301 K consisted of two singlets of equal intensity at δ 3.58 and 3.15 p.p.m. (from $[S_2CNMe_2]^-$) in addition to the singlet at 1.73 p.p.m. from the C_5Me_5 ring. Here the two methyl groups on the bidentate $[S_2CNMe_2]^-$ group will be magnetically equivalent as shown in structure (4b; R = Me) assuming rapid rotation of the unidentate $[S_2CNMe_2]^-$ group about the Rh–S and/or C–S bonds. The ^{13}C n.m.r. spectrum of this complex in $CDCl_3$ at 318 K was also consistent with the proposed structure (4b) (see Table 4). Note that unequivocal assignment of the signals of the methyl groups arising from bi- and uni-dentate $[S_2CNMe_2]^-$ ligands in this spectrum was possible by comparison with the ^{13}C n.m.r. spectrum of $[Rh(\eta\text{-}C_5Me_5)(NCBPh_3)\text{-}(S_2CNMe_2)]$ (see later) which contained only a bidentate $[S_2CNMe_2]^-$ resonance at 36.9 p.p.m.

On increasing the temperature, broadening of the two methyl singlets in the ^1H n.m.r. spectrum occurred followed by coalescence and the appearance of a singlet situated midway between the original signals (see Table 3). A full line-shape analysis on this data gave the rate constants and associated activation parameters for the kinetic process shown in equation (1) (Table 5). Similarly, the ^1H n.m.r. spectrum of $[Rh(\eta\text{-}C_5Me_5)(S_2COEt)_2]$ in $CDCl_3$ at 301 K consisted of two quartets (CH_2) and two triplets (CH_3) as expected for structure (4c; R = Et). At higher temperatures, coalescence and averaging of these signals was observed and the results of a line-shape analysis on the methylene resonances are given in Table 5. For $[Rh(\eta\text{-}C_5Me_5)(S_2COMe)_2]$, although two methyl singlets were observed in the ^1H n.m.r. spectrum at 301 K, decomposition occurred before coalescence of these signals was observed (<345 K).

Interestingly, for $[Rh(\eta\text{-}C_5Me_5)(S_2CNEt_2)_2]$, the ^1H n.m.r. spectrum in $CDCl_3$ at 253 K for the methylene region consisted of an overlapping doublet of quartets centred at δ 4.17 p.p.m. and a multiplet centred at 3.66 p.p.m. which was readily analysed as arising from an ABM_3 spin system (Table 3). On increasing the temperature to 343 K, the doublet first became a single quartet and then broadened, whereas for the multiplet δ(AB) first decreased and then broadening occurred. In chlorobenzene, at >350 K, coalescence of these resonances occurred to give a broad averaged resonance at 3.77 p.p.m.

TABLE 5

Rates and activation parameters obtained by line-shape analysis for some rhodium(III) and iridium(III) dithioacid complexes in PhCl

Complex	$\ln(k_{298}/s^{-1})$	$E^‡$ kJ mol^{-1}	$\Delta H_{298}^‡$ kJ mol^{-1}	$\Delta S_{298}^‡$ J K^{-1} mol^{-1}	$\Delta G_{298}^‡$ kJ mol^{-1}
$[Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)_2]$	−0.74	86.3 ± 6	83.8 ± 6	30.5 ± 43	74.7 ± 7 [a]
$[Rh(\eta\text{-}C_5Me_5)(S_2COEt)_2]$ [b]	−1.63	88.1 ± 3	85.6 ± 3	28.8 ± 20	77.0 ± 3 [c]
$[Ir(\eta\text{-}C_5Me_5)(S_2CNMe_2)_2]$	−4.66	95.1 ± 4	92.6 ± 4	27.5 ± 23	84.4 ± 3 [d]

[a] $\Delta G_{T_c}^‡$ = 72.0 kJ mol^{-1} (T_c = 359 K). [b] Obtained from monitoring methylene resonances. [c] $\Delta G_{T_c}^‡$ = 75.2 ± 3 kJ mol^{-1} (T_c = 361 K for methylene resonances). [d] T_c >402 K.

This behaviour can be rationalised on the basis of a 'frozen-out' structure (4b; R = Et) in solution at lower temperature with the two protons of each CH_2 group in the *bidentate* $[S_2CNEt_2]^-$ ligand forming a diastereotopic pair, thus producing an ABM_3 spin system for these ethyl groups. Similar patterns have been observed elsewhere.[16] The methylene protons of the *unidentate* $[S_2CNEt_2]^-$ ligands should also produce diastereotopic pairs and hence an ABM_3 spin system for the ethyl groups. However, in this instance, the difference in chemical environment was probably so slight because of ready rotation about the Rh–S and/or C–S bonds that the *outer* lines of the ABM_3 pattern were *too weak* to be observed. Increasing the temperature then led to both rapid rotation about the –CN bonds and uni- and bi-dentate exchange which produced equivalence of *all* the methylene protons on the n.m.r. time scale.

Although the error limits for the kinetic line-shape

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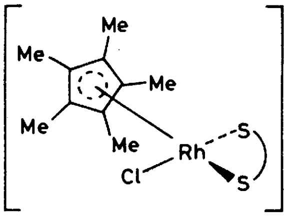
[16] See, for example, R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Dalton*, 1976, 1150.

data given in Table 5 are rather large, especially for the $\Delta S^\ddagger$ values, comparisons with kinetic data obtained for the related [Pt(S–S)$_2$L] complexes[13] are of interest. In the latter, the negative $\Delta S^\ddagger$ values and the dependence of rate on both dithioacid ligand and L group were interpreted in terms of an associative intramolecular mechanism. In this instance, the positive $\Delta S^\ddagger$ values indicate an essentially dissociative intramolecular process which is consistent with other kinetic studies on rhodium(III) complexes.[17]

For completion, the analogous [Ir(η-C_5Me_5)(S_2CNMe_2)$_2$] was synthesised from [{Ir(η-C_5Me_5)Cl_2}$_2$][12] and an excess of Na[S_2CNMe_2]·2H_2O. A line-shape analysis performed on the ^1H n.m.r. spectra of this complex gave the kinetic parameters shown in Table 5. Again, an essentially dissociatively controlled, intramolecular, exchange process was suggested (positive $\Delta S^\ddagger$ value) and the considerably larger $\Delta G_{298}^\ddagger$ value compared to the rhodium analogue was in keeping with the more inert co-ordination sphere expected for a third-row compared to a second-row transition-metal complex belonging to the same triad. Finally, the excellent agreement between $\Delta G_{298}^\ddagger$ and $\Delta G_{T_c}^\ddagger$ (T_c = coalescence temperature) for these complexes provided a good internal check on the validity of this line-shape data.

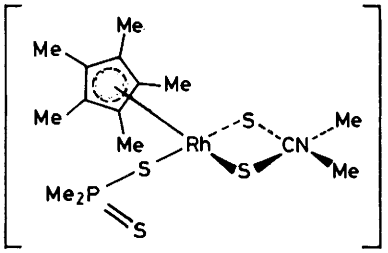


(5) S–S⁻ = [S_2CNMe_2]⁻, [S_2PMe_2]⁻ or [S_2PPh_2]⁻

If (2; M = Rh) was treated with either Na[S_2CNMe_2]·2H_2O, Na[S_2PMe_2]·2H_2O, or [NH_4][S_2PPh_2] in a 1 : 2 mol ratio, then the monomeric complexes [Rh(η-C_5Me_5)Cl(S–S)] (5) were formed. Similarly, reaction of (1; arene = C_6H_6) with [NH_4][S_2PPh_2] (1 : 2 mol ratio) in methanol gave [Ru(η-C_6H_6)Cl(S_2PPh_2)], although with Na[S_2PMe_2]·2H_2O only [Ru(η-C_6H_6)(S_2PMe_2)$_2$] could be isolated. Attempts to make [Rh(η-C_5Me_5)Cl(S_2COR)] were also unsuccessful due to the formation of inseparable mixtures whose i.r. spectra indicated the formation of some dithiocarbonate [S_2CO]$^{2-}$ as well as alkyl dithiocarbonate complexes.

The above complexes have been fully characterised by analytical data, i.r. [$\nu(PS_2)$ and $\nu(CN)$ positions], and ^1H and ^{31}P n.m.r. studies (Tables 2—4). For example, the ^{31}P n.m.r. spectrum of [Rh(η-C_5Me_5)Cl(S_2PMe_2)] in $CDCl_3$ at 298 K contained a doublet at δ 87.6 p.p.m. [^2J(RhP) 10.8 Hz] {*cf.* [Rh(η-C_5Me_5)(S_2PMe_2)$_2$] whose ^{31}P n.m.r. spectrum at 233 K had two doublets at 93.9 [^2J(RhP) 10.1] and 57.5 p.p.m. [^2J(RhP) 3.6 Hz]}. This clearly showed that the higher-frequency resonances were due to bidentate [S_2PMe_2]⁻ groups and that these could also be differentiated from unidentate [S_2PMe_2]⁻ groups by virtue of their larger ^2J(RhP) coupling constants. Similarly, for [Pt(PMe_2Ph)(S_2PPh_2)$_2$], it was found that at 218 K the ^{31}P n.m.r. signal of the bidentate [S_2PPh_2]⁻ group was a triplet at 87.8 p.p.m. [^2J(PtP) 276.6 Hz] and the unidentate [S_2PPh_2]⁻ group gave a triplet at 57.1 p.p.m. [^2J(PtP) 105.3 Hz].[18] Further examples include [Ru(η-C_6H_6)Cl(S_2PPh_2)] (^{31}P n.m.r. at 298 K showed a singlet at 91.7 p.p.m.) compared to [Ru(η-C_6H_6)(S_2PPh_2)$_2$] (singlets at 85.9 and 68.9 p.p.m.) and [Pt(PPh_3)$_2$(S_2PPh_2)][PF_6] whose ^{31}P n.m.r. spectrum had a triplet at 92.1 p.p.m. [^2J(PtP) 254.7 Hz] from the bidentate [S_2PPh_2]⁻ group.[18] Thus, ^{31}P n.m.r. chemical shifts and coupling constants (where appropriate) in these [S_2PR_2]⁻ complexes are, like $\nu(PS_2)$ values,[13,14] *diagnostic* of the type(s) of co-ordination present.

The complexes [Rh(η-C_5Me_5)Cl(S–S)] (5) were useful starting materials for synthesising a variety of complexes. Thus, reaction of (5; S–S⁻ = [S_2CNMe_2]⁻) in methanol with an excess of either LiBr, NaI, or K[SCN] led to replacement of the chloride group to give [Rh(η-C_5Me_5)X(S_2CNMe_2)] (X = Br⁻, I⁻, or SCN⁻), whereas reaction with Na[S_2PMe_2]·2H_2O (1 : 1 mol ratio) in methyl cyanide gave the mixed dithioacid complex [Rh(η-C_5Me_5)(S_2CNMe_2)(S_2PMe_2)] (6). The i.r. spectrum of this complex had bands at 1 524 and 600 cm^{-1} indicative of bidentate [S_2CNMe_2]⁻ (ref. 19) and unidentate [S_2PMe_2]⁻ co-ordination[13] respectively. Like the analogous [Pt(PR_3)(S_2CNEt_2)(S_2PMe_2)] (PR_3 = $PMePh_2$[18] or PPh_3[20]), ^1H n.m.r. studies show that (6) was stereochemically rigid at elevated temperatures, a fact attributed to the low nucleophilicity of [S_2PMe_2]⁻ compared to [S_2CNMe_2]⁻. Similarly, reaction of (5; S–S⁻ = [S_2CNMe_2]⁻) with [NH_4][S_2PPh_2] and K[S_2COMe] (1 : 1 mol ratio) gave [Rh(η-C_5Me_5)(S_2CNMe_2)(S_2PPh_2)] and [Rh(η-C_5Me_5)(S_2CNMe_2)(S_2COMe)] respectively. Again, i.r. studies on [Rh(η-C_5Me_5)(S_2CNMe_2)(S_2PPh_2)] clearly indicated unidentate [S_2PPh_2]⁻ [$\nu(PS_2)$ at 646 and 535 cm^{-1}][14] and bidentate [S_2CNMe_2]⁻ [$\nu(CN)$ at 1 520 cm^{-1}][19] co-ordination. For [Rh(η-C_5Me_5)(S_2CNMe_2)(S_2COMe)] the



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[17] See 'Inorganic Reaction Mechanisms,' vol. 2, *Specialist Periodical Rep.*, The Chemical Society, London, 1972, p. 170.

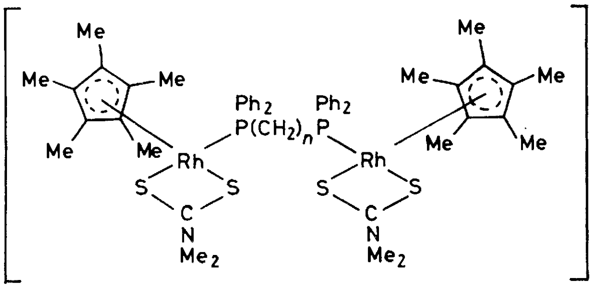
[18] M. C. Cornock and T. A. Stephenson, *J.C.S. Dalton*, 1977, 501.

[19] See D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc.* (*A*), 1969, 1152 and refs. therein.

[20] M. C. Cornock and T. A. Stephenson, *J.C.S. Dalton*, 1977, 683.

value of ν(CN) (1 530 cm^{-1}), together with the position of the methyl singlet (3.28 p.p.m.) in its ^{1}H n.m.r. spectrum {which compared favourably with those in $[Rh(\eta\text{-}C_5Me_5)Cl(S_2CNMe_2)]$ (3.20) and $[Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)(S_2PMe_2)]$ (3.21 p.p.m.)}, also supported bidentate $[S_2CNMe_2]$ co-ordination.

If $[Rh(\eta\text{-}C_5Me_5)Cl(S_2CNMe)_2)]$ was dissolved in methanol a conducting solution was obtained and addition of $Na[BPh_4]$ precipitated solvated $[Rh(\eta\text{-}C_5Me_5)(HOMe)(S_2CNMe_2)][BPh_4]$. The latter was then used as a precursor for synthesising a range of cationic complexes of the type $[Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)L][BPh_4]$ ($L = PPh_3$, $PMePh_2$, CO, $AsPh_3$, or C_5H_5N). Similarly, reaction of $[Rh(\eta\text{-}C_5Me_5)Cl(S_2PPh_2)]$ and $[Ru(\eta\text{-}C_6H_6)Cl(S_2PPh_2)]$ in alcoholic media with excess of L followed by addition of $[NH_4][PF_6]$ gave the analogous $[Rh(\eta\text{-}C_5Me_5)(S_2PPh_2)L][PF_6]$ ($L = PMePh_2$ or PPh_3) and $[Ru(\eta\text{-}C_6H_6)(S_2PPh_2)L][PF_6]$ [$L = PPh_3$, $PMePh_2$, $P(OMe)_3$, $SbPh_3$, or C_5H_5N] respectively. Alternatively, this type of complex could be prepared by shaking either $[Ru(arene)Cl_2(NC_5H_5)]$ (arene = C_6H_6[10] or $C_6H_3Me_3$[11]), $Na[S_2PMe_2]\cdot 2H_2O$ (or $[NH_4][S_2PPh_2]$) (1 : 1 mol ratio), and excess of $Na[BPh_4]$ in acetone to give $[Ru(arene)(NC_5H_5)(S\text{–}S)][BPh_4]$, or $[Rh(\eta\text{-}C_5Me_5)Cl_2(PPh_3)]$,[12] $Na[S_2PMe_2]\cdot 2H_2O$ (or $Na[S_2CNMe_2]\cdot 2H_2O$) (1 : 1 mol ratio), and excess of $Na[BPh_4]$ in ethanol to give $[Rh(\eta\text{-}C_5Me_5)(PPh_3)(S\text{–}S)][BPh_4]$.

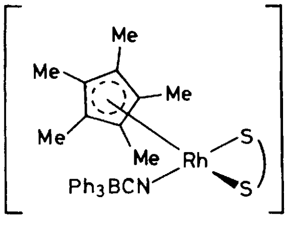


(7) n = 1 or 2

All these complexes, which are 1 : 1 electrolytes in methylene chloride, have been fully characterised by elemental analyses, and i.r. (which showed bidentate dithioacid co-ordination), ^{1}H, and, in certain cases, ^{31}P n.m.r. spectroscopy (Tables 2—4). For example, the ^{31}P n.m.r. spectrum of $[Rh(\eta\text{-}C_5Me_5)(PPh_3)(S_2PMe_2)][BPh_4]$ in $CDCl_3$ at 298 K consisted of an overlapping doublet of doublets at δ 103.3 p.p.m. (bidentate $[S_2PMe_2]^-$ resonance) due to the fortuitously similar values of $^2J(RhP)$ 9.2 and $^3J(PP)$ 9.7 Hz, and a doublet of doublets at 35.9 p.p.m. (PPh_3) with $^1J(RhP)$ 144.8 and $^3J(PP)$ 9.7 Hz.

Attempts to make related cationic complexes by reaction of (5; $S\text{–}S^- = [S_2CNMe_2]^-$), a large anion, and potentially bidentate ligands such as 2,2′-bipyridyl, 1,10-phenanthroline, and cyclo-octa-1,5-diene were unsuccessful. However, treatment of (5; $S\text{–}S^- = [S_2CNMe_2]^-$) with an excess of dppe in methanol, followed by addition of $Na[BPh_4]$ to the resulting yellow solution, gave a yellow precipitate which analysed closely for the dimeric $[\{Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)\}_2(dppe)][BPh_4]_2$. Support for this formulation came from the conductivity value in methylene chloride which was considerably higher than the values found earlier, and elsewhere,[13] for 1 : 1 electrolytes containing similar anions. The i.r. spectrum indicated bidentate $[S_2CNMe_2]^-$ co-ordination, and the ^{1}H n.m.r. spectrum integrated for one dppe to two $[S_2CNMe_2]^-$ to two C_5Me_5 groups. Furthermore, the small doublet splitting of 3.0 Hz of the latter resonance, arising from coupling of a phosphorus ligand to the C_5Me_5 protons, indicated that only one P atom was bound to each rhodium atom. On the basis of this evidence the complex was formulated with structure (7) (*cf.*[12] the related $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2(dppe)]$). Likewise (5; $S\text{–}S^- = [S_2CNMe_2]^-$) reacted with excess of dppm and $Na[BPh_4]$ in methanol to give $[\{Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)\}_2(dppm)][BPh_4]_2$ and $[Rh(\eta\text{-}C_5Me_5)Cl(S_2PPh_2)]$, dppe, and $Na[BPh_4]$ gave $[\{Rh(\eta\text{-}C_5Me_5)(S_2PPh_2)\}_2(dppe)][BPh_4]_2$.

In view of the above studies, a surprising reaction occurred when (5; $S\text{–}S^- = [S_2PMe_2]^-$, $[S_2PPh_2]^-$, or $[S_2CNMe_2]^-$) were treated with $C_2(CN)_4$ in methanol, followed by addition of $Na[BPh_4]$. Instead of the expected $[Rh(\eta\text{-}C_5Me_5)\{C_2(CN)_4\}(S\text{–}S)][BPh_4]$, yellow non-conducting solids were isolated whose analytical data were consistent with the formulation $[Rh(\eta\text{-}C_5Me_5)(NCBPh_3)(S\text{–}S)]$ (8). Additional evidence for the formulation of (8) as zwitterionic complexes containing the cyanotriphenylborate anion was based on spectroscopic data. Thus, the i.r. spectra of all complexes (8) contained a CN stretching band at *ca.* 2 180 cm^{-1}, indicative of cyanide rather than isocyanide co-ordination of the $[BPh_3(CN)]^-$ group[21] and all showed bands characteristic of bidentate co-ordination of the dithioacid ligands. The mass spectrum of (8; $S\text{–}S^- = [S_2CNMe_2]^-$) had a



(8) $S\text{–}S^- = [S_2PMe_2]^-, [S_2PPh_2]^-$ or $[S_2CNMe_2]^-$

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[21] S. J. Lippard and P. S. Welcker, *Inorg. Chem.*, 1972, **11**, 6.

peak at *m/e* 626 corresponding to $[Rh(\eta\text{-}C_5Me_5)(NCBPh_3)(S_2CNMe_2)]^+$ together with a fragmentation pattern consistent with this formulation. Furthermore, the ^1H n.m.r. spectrum of (8; $S\text{-}S^- = [S_2CNMe_2]^-$) in $CDCl_3$ at 303 K had the expected three signals at 1.79 (s) (C_5Me_5), 3.17 (s) ($[S_2CNMe_2]^-$), and 7.0—7.5 (m) p.p.m. $[Ph_3BCN]^-$) of relative intensity 5 : 2 : 5.

However, unequivocal proof of the solid-state structure of (8; $S\text{-}S^- = [S_2PMe_2]^-$) came from a preliminary *X*-ray structural analysis [22] which showed a Rh–N distance of 2.00 Å. In fact, only a few examples of transition-metal complexes of cyanotriphenylborate have been found in the literature {*viz.* $[M(\eta\text{-}C_5H_5)(NCBPh_3)(PPh_3)_2]$ (M = Fe or Ru),[23] $[Ru(\eta\text{-}C_5H_5)(CNBPh_3)(PPh_3)_2]$,[23] and $[Cu(NCBPh_3)(PPh_3)]\cdot CHCl_3$ [21]} and all these were prepared by means of *direct* reaction with $Na[BPh_3(CN)]$.* Here, the $[BPh_3(CN)]^-$ anion was generated *in situ*, possibly by reaction of hydrogen cyanide with $[BPh_4]^-$, since earlier studies on $C_2(CN)_4$ have shown that HCN was readily released on its reaction with alkoxide ions in the presence of certain catalysts.[26]

However, it should be noted that this rather unusual reaction is not confined to rhodium. Thus, reaction of $[Ru(\eta\text{-}C_6H_6)Cl(S_2PPh_2)]$ with a methanolic solution of $C_2(CN)_4$ and $Na[BPh_4]$ gave $[Ru(\eta\text{-}C_6H_6)(NCBPh_3)(S_2PPh_2)]$; also $[PdCl(PMe_2Ph)(S_2CNEt_2)]$ on treatment with $Ag[BF_4]$–tetrahydrofuran (thf) {which gave [18] $[Pd(PMe_2Ph)(S_2CNEt_2)(thf)]$}, followed by $C_2(CN)_4$ and $Na[BPh_4]$ in methanol gave $[Pd(NCBPh_3)(PMe_2Ph)(S_2CNEt_2)]$.

Finally, by analogy with earlier studies on complexes of type *cis*-$[M(PMe_2Ph)_2(S_2PMe_2)_2]$ (M = Ru or Os), which underwent ready cleavage of M–S bonds with CO to give complexes such as $[M(CO)(PMe_2Ph)_2(S_2PMe_2)_2]$ containing a unidentate $[S_2PMe_2]^-$ linkage,[2,8] it was hoped to generate $[Rh(\eta\text{-}C_5Me_5)(S_2PMe_2)_2L]$ containing *two* unidentate $[S_2PMe_2]^-$ ligands by reaction of $[Rh(\eta\text{-}C_5Me_5)(S_2PMe_2)_2]$ with various L in non-polar solvents. However, even in benzene with $PMePh_2$, the only product isolated was $[Rh(\eta\text{-}C_5Me_5)(PMePh_2)(S_2PMe_2)][S_2PMe_2]$ indicating that loss of the unidentate $[S_2PMe_2]$ group here is always the preferred process. This complex, which was fully characterised by analytical and spectroscopic data (see Table 3), showed no evidence for bidentate–ionic dithioacid exchange up to 343 K (*cf.* the related $[Pt(PR_3)_2(S\text{-}S)][S\text{-}S]$ {$S\text{-}S^- = [S_2CNR_2]^-$ (ref. 27) or $[S_2PMe_2]^-$ (ref. 13)}.

EXPERIMENTAL

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab model 301A vapour-pressure osmometer calibrated with benzil. Infrared spectra were recorded in the 250—4 000 cm^{-1} region on a Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Conductivity measurements were made on a Portland Electronics 310 conductivity bridge at 298 K. Hydrogen-1 n.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe and on a Varian EM-360 spectrometer. Phosphorus-31 n.m.r. spectra (proton-noise decoupled) were obtained on a Varian XL-100 spectrometer operating in the pulse and Fourier-transform modes at 40.5 MHz (^{31}P chemical shifts quoted in p.p.m. to high frequency of 85% H_3PO_4), and ^{13}C n.m.r. spectra (proton-noise decoupled) on a Varian CFT-20 spectrometer operating at 20 MHz (^{13}C chemical shifts quoted in p.p.m. to high frequency of $SiMe_4$). Mass spectra were recorded on an A.E.I. MS9 spectrometer. Melting points were determined with a Köfler hot-stage microscope and are uncorrected. The kinetic line-shape analysis was carried out as detailed in ref. 13 and $\Delta G_{T_c}^{\ddagger}$ calculated by use of equation (2) where T_c = coalescence

$$\Delta G_{T_c}^{\ddagger} = 19.06\,T_c[10.319 + \log T_c/k_{T_c}]\ \text{[28]} \qquad (2)$$

temperature and k_{T_c} = rate constant at temperature T_c ($= \pi\Delta\nu_0/2^{\frac{1}{2}}$) where $\Delta\nu_0$ = separation of peaks in the absence of exchange.

Analytical, molecular weight, and conductivity data are given in Supplementary Publication No. SUP 22220, and ^1H n.m.r. data for ruthenium, and selected rhodium and iridium complexes in Tables 1 and 3,† and ^{31}P n.m.r. data in Table 2. Infrared bands diagnostic of the mode of coordination of $[S_2PMe_2]^-$ (ref. 13) and $[S_2PPh_2]^-$ ligands [14] are listed for the various complexes (b = bidentate, u = unidentate, i = ionic). Finally, all the reactions under reflux were carried out in degassed solvents under an atmosphere of nitrogen.

Ruthenium Complexes.—*(η-Benzene)bis(dimethylphosphinodithioato)ruthenium*(II). The complex $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ [10] (0.20 g, 0.4 mmol) was dissolved in water with gentle warming. Excess of $Na[S_2PMe_2]\cdot 2H_2O$ (0.55 g, 3 mmol) was then added to the orange solution, producing an immediate colour change to deep red. Extraction with diethyl ether, followed by separation and drying over anhydrous sodium sulphate gave a red ether solution. Concentration of this solution gave a dark red crystalline precipitate, m.p. 140 °C (decomp.), $\nu(PS_2)$ at 603(u) and 584(b) cm^{-1}. *(η-Benzene)bis(OO′-dimethyl dithiophosphato)ruthenium*(II) was similarly prepared as a dark red crystalline *solid*, m.p. 110 °C (decomp.), from $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ and $Na[S_2P(OMe)_2]$.

(η-Benzene)bis(OO′-diethyl dithiophosphato)ruthenium(II). A similar preparation gave an oil on concentration of the

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* Very recently, some platinum(II) complexes containing both $NCBPh_3$ and $CNBPh_3$ linkages have been prepared, both by reaction [24] of the cyano-complexes with BPh_3 and by reaction of $[PtH(Cl)(PEt_3)_2]$ with $Na[BPh_3(CN)]$.[25]

† Hydrogen-1 spectral data for other rhodium(III) dithioacid complexes are given in the Supplementary Publication.

[22] For details, see M. C. Cornock, D. R. Robertson, T. A. Stephenson, C. L. Jones, G. H. W. Milburn, and L. Sawyer, *J. Organometallic Chem.*, 1977, **135**, C50.

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[24] L. E. Manzer and G. W. Parshall, *Inorg. Chem.*, 1976, **15**, 3114.

[25] L. E. Manzer and M. F. Anton, *Inorg. Chem.*, 1977, **16**, 1229.

[26] W. J. Middleton and V. A. Engelhardt, *J. Amer. Chem. Soc.*, 1958, **80**, 2788.

[27] J. M. C. Alison and T. A. Stephenson, *J.C.S. Dalton*, 1973, 254.

[28] See T. R. Jack and J. Powell, *Canad. J. Chem.*, 1975, **53**, 2558.

ether solution. This was dissolved in the minimum volume of methanol and addition of water then precipitated slowly an orange crystalline *solid*, m.p. 132 °C (decomp.).

(η-Benzene)bis(diphenylphosphinodithioato)ruthenium(II). The product from reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ and excess of $[NH_4][S_2PPh_2]$ in water was extracted with methylene chloride. Addition of light petroleum (b.p. 60—80 °C) to this solution then gave a brick-red *solid*, m.p. 175 °C, $\nu(PS_2)$ at 643 and 548(u) and 610 and 575(b) cm^{-1}.

Bis(dimethylphosphinodithioato)(η-mesitylene)ruthenium(II), red, m.p. 145 °C (decomp.), $\nu(PS_2)$ at 601(u) and 585(b) cm^{-1}, and *bis(diphenylphosphinodithioato)(η-mesitylene)ruthenium*(II), orange-red, m.p. 186 °C, $\nu(PS_2)$ at 647 and 541(u), and 604 and 580(b) cm^{-1}, were prepared as above using $[\{Ru(\eta\text{-}C_6H_3Me_3)Cl_2\}_2]$ and an excess of $Na[S_2PMe_2]\cdot 2H_2O$ or $[NH_4][S_2PPh_2]$ respectively, the products precipitating directly from the aqueous media.

(η-Benzene)chloro(diphenylphosphinodithioato)ruthenium(II). The complex $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.20 g, 0.4 mmol) was stirred in methanol (15 cm^3) with $[NH_4][S_2PPh_2]$ (0.21 g, 0.8 mmol) (1 : 2 mol ratio) for several hours. After removal of solvent, the residue was recrystallised from methylene chloride–hexane to give a red *solid*, m.p. 190 °C (decomp.), $\nu(PS_2)$ at 608 and 587(b) cm^{-1}.

(η-Benzene)(dimethylphosphinodithioato)pyridineruthenium(II) *tetraphenylborate*. The complex $[Ru(\eta\text{-}C_6H_6)Cl_2(NC_5H_5)]$ [10] (0.066 g, 0.2 mmol), $Na[S_2PMe_2]\cdot 2H_2O$ (0.037 g, 0.2 mmol), and excess of $Na[BPh_4]$ (0.12 g, 0.4 mmol) were shaken in acetone (25 cm^3) for 3 h. A white precipitate of NaCl was filtered off and the orange solution was concentrated at *ca.* 5 cm^3. Addition of diethyl ether then gave a yellow *precipitate* which was washed with warm water and diethyl ether and recrystallised from methylene chloride–hexane, m.p. 220 °C (decomp.), $\nu(PS_2)$ at 582(b) cm^{-1}.

Similarly prepared were *(diphenylphosphinodithioato)(η-mesitylene)pyridineruthenium*(II) *tetraphenylborate* from $[Ru(\eta\text{-}C_6H_3Me_3)Cl_2(NC_5H_5)]$,[11] $[NH_4][S_2PPh_2]$, and $Na[BPh_4]$ as a yellow *solid*, m.p. 199 °C (decomp.), $\nu(PS_2)$ at 604 and 580(b) cm^{-1} and *(dimethylphosphinodithioato)(η-mesitylene)pyridineruthenium*(II) *tetraphenylborate*, $\nu(PS_2)$ at 582(b) cm^{-1}, from $[Ru(\eta\text{-}C_6H_3Me_3)Cl_2(NC_5H_5)]$, $Na[S_2PMe_2]\cdot 2H_2O$, and $Na[BPh_4]$.

(η-Benzene)(diphenylphosphinodithioato)(triphenylphosphine)ruthenium(II) *hexafluorophosphate*. The complex $[Ru(\eta\text{-}C_6H_6)Cl(S_2PPh_2)]$ (0.09 g, 0.2 mmol) was shaken in ethanol with excess of triphenylphosphine (0.10 g, 0.4 mmol) and $[NH_4][PF_6]$ (0.06 g, 0.4 mmol) for several hours. The solvent was removed, the residue dissolved in acetone, and the solution filtered. Addition of diethyl ether then gave a yellow *precipitate* which was washed with warm water then diethyl ether and dried in air, m.p. 215 °C (decomp.), $\nu(PS_2)$ at 605 and 580(b) cm^{-1}. The following yellow complexes were prepared similarly: $[Ru(\eta\text{-}C_6H_6)(PMePh_2)(S_2PPh_2)][PF_6]$, m.p. 129 °C, $\nu(PS_2)$ at 602 and 580(b) cm^{-1}; $[Ru(\eta\text{-}C_6H_6)\{P(OMe)_3\}(S_2PPh_2)][PF_6]$, m.p. 190 °C, $\nu(PS_2)$ at 603 and 580(b) cm^{-1}; $[Ru(\eta\text{-}C_6H_6)(S_2PPh_2)(SbPh_3)][PF_6]$, m.p. 211 °C, $\nu(PS_2)$ at 600 and 577(b) cm^{-1}; and $[Ru(\eta\text{-}C_6H_6)(NC_5H_5)(S_2PPh_2)][PF_6]$, m.p. 202 °C, $\nu(PS_2)$ at 605 and 580(b) cm^{-1}.

(η-Benzene)(cyanotriphenylborato)(diphenylphosphinodithioato)ruthenium(II). The complex $[Ru(\eta\text{-}C_6H_6)Cl(S_2PPh_2)]$ (0.09 g, 0.2 mmol) dissolved in methanol on addition of tetracyanoethylene (0.13 g, 1.0 mmol) to give a yellow solution. Addition of excess of $Na[BPh_4]$ to this solution then gave a yellow *precipitate*, m.p. 210 °C (decomp.), $\nu(PS_2)$ at 602 and 580(b) cm^{-1}.

Rhodium Complexes.—Bis(dimethylphosphinodithioato)(η-pentamethylcyclopentadienyl)rhodium(III). The complex $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ [12] (0.12 g, 0.2 mmol) was dissolved in water (20 cm^3) by warming and excess of $Na[S_2PMe_2]\cdot 2H_2O$ (0.28 g, 1.5 mmol) added to the filtered solution. The resulting dark red solution was extracted with methylene chloride, and the organic layer separated and dried over anhydrous $Na_2[SO_4]$. Hexane was then added and the methylene chloride allowed to evaporate off slowly giving a red crystalline *solid*, m.p. 181 °C, $\nu(PS_2)$ at 600(u) and 588(b) cm^{-1}. *Bis(diphenylphosphinodithioato)(η-pentamethylcyclopentadienyl)rhodium*(III), m.p. 214 °C, $\nu(PS_2)$ at 648 and 539(u), and 603 and 575(b) cm^{-1}, was similarly prepared from $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (0.12 g) and $[NH_4][S_2PPh_2]$ (0.42 g).

Bis(dimethyldithiocarbamato)(η-pentamethylcyclopentadienyl)rhodium(III). The complex $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (0.12 g, 0.2 mmol) was dissolved in water (20 cm^3). Addition of excess of $Na[S_2CNMe_2]\cdot 2H_2O$ (0.28 g, 1.6 mmol) gave a red *precipitate* which was recrystallised from methylene chloride–light petroleum (b.p. 60—80 °C), m.p. 218 °C. *Bis(diethyldithiocarbamato)(η-pentamethylcyclopentadienyl)rhodium*(III), m.p. 223 °C, was similarly prepared from $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (0.12 g) and $Na[S_2CNEt_2]\cdot 3H_2O$ (0.33 g).

Bis(O-methyl dithiocarbonato)(η-pentamethylcyclopentadienyl)rhodium(III). The complex $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (0.12 g, 0.2 mmol) was dissolved in water (20 cm^3). Addition of excess of $K[S_2COMe]$ (0.23 g, 1.6 mmol) gave an oily bright orange precipitate which was extracted from aqueous solution by diethyl ether. The orange ether solution was then concentrated to dryness and the residue recrystallised from acetone–water. *Bis(O-ethyl dithiocarbonato)(η-pentamethylcyclopentadienyl)rhodium*(III), m.p. 120 °C, was similarly prepared from $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (0.12 g) and excess of $K[S_2COEt]$ (0.26 g).

Chloro(dimethyldithiocarbamato)(η-pentamethylcyclopentadienyl)rhodium(III). The complex $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (0.12 g, 0.2 mmol) was dissolved in methyl cyanide (20 cm^3), $Na[S_2CNMe_2]\cdot 2H_2O$ (0.072 g, 0.4 mmol) added (1 : 2 molar ratio), and the solution stirred for several hours. After filtering to remove NaCl, the solution was evaporated to dryness and the residue recrystallised from methylene chloride–hexane, m.p. 273 °C, $\nu(RhCl)$ at 270 cm^{-1}. *Chloro(dimethylphosphinodithioato)(η-pentamethylcyclopentadienyl)rhodium*(III), $\nu(PS_2)$ at 588(b) cm^{-1} and $\nu(RhCl)$ at 265 cm^{-1}, and *chloro(diphenylphosphinodithioato)(η-pentamethylcyclopentadienyl)rhodium*(III), m.p. 247 °C, $\nu(PS_2)$ at 603 and 574(b) cm^{-1}, $\nu(RhCl)$ at 270 cm^{-1}, were similarly prepared using $Na[S_2PMe_2]\cdot 2H_2O$ and $[NH_4][S_2PPh_2]$ respectively and recrystallising from chloroform–light petroleum (b.p. 60—80 °C).

Bromo(dimethyldithiocarbamato)(η-pentamethylcyclopentadienyl)rhodium(III). The complex $[Rh(\eta\text{-}C_5Me_5)Cl(S_2CNMe_2)]$ was shaken with excess of lithium bromide for several hours in methanol. The solution was then evaporated to dryness and the residue extracted with methylene chloride. After filtering through Celite and adding hexane, slow evaporation of methylene chloride gave a dark red crystalline *precipitate*, m.p. 235 °C. The analogous $[Rh(\eta\text{-}C_5Me_5)I(S_2CNMe_2)]$, m.p. 247 °C, and $[Rh(\eta\text{-}C_5Me_5)(SCN)(S_2CNMe_2)]$, m.p. 151 °C, $\nu(CN)$ at 2 085 cm^{-1}, were similarly prepared from $[Rh(\eta\text{-}C_5Me_5)Cl(S_2CNMe_2)]$ and NaI or K[SCN] respectively.

(Dimethyldithiocarbamato)(dimethylphosphinodithioato)-(η-pentamethylcyclopentadienyl)rhodium(III). The complex $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl(S_2CNMe_2)}]$ (0.153 g, 0.4 mmol) and $\mathrm{Na[S_2PMe_2]\cdot 2H_2O}$ (0.074 g, 0.4 mmol) (1 : 1 mol ratio) were stirred in methyl cyanide for 3 h. The solution was filtered to remove NaCl, concentrated to dryness, and the residue recrystallised from methylene chloride–pentane, m.p. 157 °C, $\nu(\mathrm{PS_2})$ at 600(u) cm^{-1}. Similarly, *(dimethyldithiocarbamato)(diphenylphosphinodithioato)(η-pentamethylcyclopentadienyl)rhodium*(III), m.p. 224 °C, $\nu(\mathrm{PS_2})$ at 646 and 535(u) cm^{-1}, and *(dimethyldithiocarbamato)(O-methyl dithiocarbonato)(η-pentamethylcyclopentadienyl)rhodium*(III), m.p. 181 °C, were prepared from $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl(S_2CNMe_2)}]$ and $\mathrm{[NH_4][S_2PPh_2]}$ or $\mathrm{K[S_2COMe]}$ respectively.

(Dimethyldithiocarbamato)(methanol)(η-pentamethylcyclopentadienyl)rhodium(III) *tetraphenylborate*. The complex $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl(S_2CNMe_2)}]$ was dissolved in methanol and addition of excess of $\mathrm{Na[BPh_4]}$ precipitated an orange *solid*, m.p. 197 °C.

(Dimethyldithiocarbamato)(η-pentamethylcyclopentadienyl)-(triphenylphosphine)rhodium(III) *tetraphenylborate. Method A*. The complex $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl_2(PPh_3)}]$ [12] (0.11 g, 0.2 mmol) was shaken in ethanol with excess of $\mathrm{Na[S_2CNMe_2]\cdot 2H_2O}$ (0.09 g, 0.5 mmol) and $\mathrm{Na[BPh_4]}$ (0.17 g, 0.5 mmol) for 24 h. The resulting orange solid was filtered off and washed thoroughly with warm water, ethanol, and diethyl ether, m.p. 205 °C. The analogous $[\mathrm{Rh(\eta\text{-}C_5Me_5)(PPh_3)(S_2PMe_2)}][\mathrm{BPh_4}]$, m.p. 216 °C (decomp.), was prepared by the same method, using $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl_2(PPh_3)}]$ and excess of $\mathrm{Na[S_2PMe_2]\cdot 2H_2O}$ [$\nu(\mathrm{PS_2})$ at 573(b) cm^{-1}].

Method B. The complex $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl(S_2CNMe_2)}]$ (0.08 g, 0.2 mmol) was dissolved in methanol and excess of $\mathrm{PPh_3}$ (0.13 g, 0.5 mmol) added. The solution became orange-yellow on gentle warming and addition of $\mathrm{Na[BPh_4]}$ gave an orange crystalline *product* on cooling. Similar methods were used to prepare the analogous $[\mathrm{Rh(\eta\text{-}C_5Me_5)(PMePh_2)(S_2CNMe_2)}][\mathrm{PF_6}]$, $[\mathrm{Rh(\eta\text{-}C_5Me_5)(NC_5H_5)(S_2CNMe_2)}][\mathrm{BPh_4}]$, m.p. 97 °C, and $[\mathrm{Rh(AsPh_3)(\eta\text{-}C_5Me_5)(S_2CNMe_2)}][\mathrm{BPh_4}]$, m.p. 192 °C.

Carbonyl(dimethyldithiocarbamato)(η-pentamethylcyclopentadienyl)rhodium(III) *tetraphenylborate*. The complex $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl(S_2CNMe_2)}]$ (0.10 g, 0.25 mmol) was dissolved in methanol (50 cm^3) and carbon monoxide bubbled through the solution for 4 h. Addition of $\mathrm{Na[BPh_4]}$ to the resulting yellow solution gave a crystalline yellow solid, m.p. 183 °C, $\nu(\mathrm{CO})$ at 2 070 cm^{-1}.

(Diphenylphosphinodithioato)(methyldiphenylphosphine)-(η-pentamethylcyclopentadienyl)rhodium(III) *hexafluorophosphate*. The complex $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl(S_2PPh_2)}]$ (0.10 g, 0.2 mmol) was dissolved in methanol (15 cm^3). On addition of several drops of $\mathrm{PMePh_2}$, the solution became yellow and addition of excess of $\mathrm{[NH_4][PF_6]}$ then gave an orange-yellow crystalline solid, $\nu(\mathrm{PS_2})$ at 603 and 577(b) cm^{-1}. *(Diphenylphosphinodithioato)(η-pentamethylcyclopentadienyl)(triphenylphosphine)rhodium*(III) *hexafluorophosphate* was similarly prepared, m.p. 214 °C, $\nu(\mathrm{PS_2})$ at 608 and 572(b) cm^{-1}.

μ-[1,2-Bis(diphenylphosphino)ethane]-bis[dimethyldithiocarbamato)(η-pentamethylcyclopentadienyl)rhodium(III)] *bis(tetraphenylborate)*. The complex $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl(S_2CNMe_2)}]$ (0.08 g) was dissolved in methanol. Addition of excess of $\mathrm{Ph_2PCH_2CH_2PPh_2}$ (dppe) (0.15 g) accompanied by gentle warming gave a yellow solution from which a yellow solid was precipitated on addition of $\mathrm{Na[BPh_4]}$, m.p. 217 °C. The complex $[\{\mathrm{Rh(\eta\text{-}C_5Me_5)(S_2CNMe_2)}\}_2\text{-}\mathrm{Ph_2PCH_2PPh_2}][\mathrm{BPh_4}]_2$, m.p. 200 °C, was similarly prepared. *μ-[1,2-Bis(diphenylphosphino)ethane]-bis[(diphenylphosphinodithioato)(η-pentamethylcyclopentadienyl)rhodium*(III)] *bis(tetraphenylborate)*, $\nu(\mathrm{PS_2})$ at 603 and 574(b) cm^{-1}, was also prepared as above from $[\mathrm{Rh(C_5Me_5)Cl(S_2PPh_2)}]$, dppe, and $\mathrm{Na[BPh_4]}$.

(Dimethylphosphinodithioato)(methyldiphenylphosphine)-(η-pentamethylcyclopentadienyl)rhodium(III) *dimethylphosphinodithioate*. The complex $[\mathrm{Rh(\eta\text{-}C_5Me_5)(S_2PMe_2)_2}]$ was dissolved in benzene and several drops of $\mathrm{PMePh_2}$ were added to give a yellow solution which, on standing, deposited a yellow crystalline solid, m.p. 226 °C, $\nu(\mathrm{PS_2})$ at 610(i) and 575(b) cm^{-1}.

(Cyanotriphenylborato)(dimethyldithiocarbonato)(η-pentamethylcyclopentadienyl)rhodium(III). The complex $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl(S_2CNMe_2)}]$ (0.10 g, 0.25 mmol) was dissolved in methanol (10 cm^3) and treated with tetracyanoethylene (0.13 g, 1.0 mmol). On gentle warming a yellow solution was formed which on treatment with $\mathrm{Na[BPh_4]}$ gave an orange-yellow crystalline *solid* on cooling, m.p. 221 °C, $\nu(\mathrm{CN})$ at 2 180 cm^{-1}. The analogous complexes $[\mathrm{Rh(\eta\text{-}C_5Me_5)(NCBPh_3)(S_2PMe_2)}]$, m.p. 225 °C, $\nu(\mathrm{CN})$ at 2 180, $\nu(\mathrm{PS_2})$ at 577(b) cm^{-1}, and $[\mathrm{Rh(\eta\text{-}C_5Me_5)(NCBPh_3)(S_2PPh_2)}]$, m.p. 237 °C, $\nu(\mathrm{CN})$ at 2 180, $\nu(\mathrm{PS_2})$ at 603 and 575(b) cm^{-1}, were prepared from $\mathrm{C_2(CN)_4}$, $\mathrm{Na[BPh_4]}$, and $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl(S_2PMe_2)}]$ or $[\mathrm{Rh(\eta\text{-}C_5Me_5)Cl(S_2PPh_2)}]$ respectively.

Iridium Complexes.—Bis(dimethyldithiocarbamato)-(η-pentamethylcyclopentadienyl)iridium(III). The complex $[\{\mathrm{Ir(\eta\text{-}C_5Me_5)Cl_2}\}_2]$ [12] (0.16 g, 0.2 mmol) was dissolved in methyl cyanide (20 cm^3) together with $\mathrm{Na[S_2CNMe_2]\cdot 2H_2O}$ (0.28 g, 1.6 mmol) and the resulting yellow solution stirred for 2 h. After filtering off NaCl, the filtrate was evaporated to dryness and the residue extracted with methylene chloride. Excess of $\mathrm{Na[S_2CNMe_2]\cdot 2H_2O}$ was filtered off and addition of hexane gave the yellow *product*, m.p. 242 °C. *Bis(dimethylphosphinodithioato)(η-pentamethylcyclopentadienyl)iridium*(II), $\nu(\mathrm{PS_2})$ at 602(u) and 590(b) cm^{-1}, was similarly prepared from $[\{\mathrm{Ir(\eta\text{-}C_5Me_5)Cl_2}\}_2]$ and excess of $\mathrm{Na[S_2PMe_2]\cdot 2H_2O}$.

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