Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 17.[1] Complexes with Sulphur-containing Ligands†

By **Michael J. H. Russell, Colin White, Alan Yates,** and **Peter M. Maitlis,*** Department of Chemistry, The University, Sheffield S3 7HF

Preparations and properties of the following η^5-pentamethylcyclopentadienyl-rhodium and -iridium complexes are reported: $[\{Rh(C_5Me_5)\}_2Cl_4(SMe_2)]$, $[Rh(C_5Me_5)(SMe_2)_3][PF_6]_2$, $[Rh(C_5Me_5)(MeCN)(dithian)][PF_6]_2$, $[\{Rh(C_5Me_5)\}_2(SS)Cl_4]$ (SS = 1,4-dithian, 2,5-dithiahexane), $[Rh(C_5Me_5)(2,5\text{-dithiahexane})_2][PF_6]_2$, $[Rh(C_5Me_5)Cl(SR)]_n$ (R = Me, Ph, and $PhCH_2$), $[Rh(C_5Me_5)Cl(S_2CNEt_2)]$, $[Rh(C_5Me_5)(S_2CNMe_2)_2]$, $[Rh(C_5Me_5)(S_2CMe)_2]$, $[Rh(C_5Me_5)\{S_2C_2(CN)_2\}]$, $[\{Rh(C_5Me_5)(3,4\text{-}S_2C_6H_3Me)\}_2]$, $[Ir(C_5Me_5)(S_2CNMe_2)_2]$, and $[Ir(C_5Me_5)\{S_2C_2(CN)_2\}]$. The complexes $[Rh(C_5Me_5)(S_2CNMe_2)_2]$, $[Rh(C_5Me_5)(S_2CMe)_2]$, and $[Ir(C_5Me_5)(S_2CNMe_2)_2]$ have one uni- and one bi-dentate dithio-ligand.

A range of Rh^I and Pd^{II} 1,4-dithian (dt) complexes have also been prepared including $[\{RhCl(dt)\}_n]$-$[\{PdX_2(dt)\}_n]$ (X = Cl or Br), $[\{RhL_2(dt)\}_n][PF_6]$ [$n = 2$, L = PPh_3, $P(OPh)_3$; $n = 1$, L_2 = cyclo-octa-1,5-diene or norbornadiene] and $[Pd(L)(dt)][PF_6]$ (L = η^3-2-methylallyl and η^3-1-phenylallyl). The poisoning of the $[\{Rh(C_5Me_5)Cl_2\}_2]$-catalysed olefin hydrogenation by S-containing ligands is contrasted with the ability of some of the above sulphur complexes to catalyse olefin hydrogenation under certain conditions.

DURING our examination of pentamethylcyclopentadienyl-rhodium and -iridium complexes as hydrogenation catalysts [1] we observed that the $[\{Rh(C_5Me_5)Cl_2\}_2]$-catalysed hydrogenation of cyclohexene was markedly inhibited by other ligands, in particular those containing sulphur as donor atom. These ligands, however, showed rather variable levels of inhibition; to reduce the activity by 90% required some 3.4 equivalents of PhSH, 16 of SMe_2 but only 1.0 equivalents of thiophen per molecule of $[\{Rh(C_5Me_5)Cl_2\}_2]$ (1).

These observations led us to investigate the types of complexes that were actually formed when the pentamethylcyclopentadienylrhodium complexes were allowed to react with sulphur-containing ligands. This paper describes the products of the reactions with thiols, thioethers and chelating dithioethers, dithiocarbamates, dithiolates, and 3,4-dithiotoluene (Scheme 1). *S*-Bonding occurred in all these cases; however, although no products could be isolated from thiophen itself, the di- and tetra-methylthiophens gave η^5-bonded π-complexes, which are discussed in the following paper.[2]

RESULTS AND DISCUSSION

Thioether (R_2S) *Complexes*.—The simplest complex was obtained when the rhodium complex (1) was refluxed in ethanol with a large excess (27 equiv.) of dimethyl sulphide. This complex (2) had the empirical formula $[\{Rh(C_5Me_5)\}_2Cl_4(SMe_2)]$; the ^1H n.m.r. spectrum showed only two singlets in the ratio 30 : 6, but in the ^{13}C spectrum the asymmetry of the complex was indicated by two doublets [$J(^{13}C-^{103}Rh) < 2$ Hz] arising from two different types of C_5Me_5 carbons. The observed molecular weight in chloroform was low which may indicate that the molecule is either ion-paired [as for formula (2a)] or, less probably, that it has the chlorine bridged structure as in (2b) and that partial dissociation is occurring.

We have described the preparation of a variety of tris-solvent complexes $[Rh(C_5Me_5)(sol)_3]^{2+}$ (3) by the reaction of the dichloride (1) with $AgPF_6$ in the presence of a weakly binding ligand (sol) (where sol = MeCN, Me_2SO, py, thf, and Me_2CO).[3] When the MeCN, the acetone, or the thf complex was treated with dimethyl sulphide the dicationic tris(dimethyl sulphide) complex (4) was isolated; analyses and spectroscopic properties fully substantiate the structure shown. The sulphide ligands are relatively easily displaced, for example, reaction with trimethyl phosphite gave the known [4] $[Rh(C_5Me_5)\{P(OMe)_3\}_3][PF_6]_2$.

It should also be noted that a solvent complex, $[Rh(C_5Me_5)(CS_2)_n]^{2+}$, presumably analogous to (3), is formed when (1) is treated with $AgPF_6$ in CS_2. A stable yellow solution was obtained, which could be evaporated down to an oil and which showed bands at 840 [$\nu(PF_6)$], 1 020 and 1 070 [ν(C–S)], and 1 420 [ν(C=S)] cm^{-1} but all attempts to crystallise this material led to decomposition. The ^1H n.m.r. spectrum in CS_2 showed only a singlet at δ 2.03 (C_5Me_5).

Complexes of Chelating Dithioethers ($RSCH_2CH_2SR$).—The best characterised complex of a chelating disulphide ligand was obtained by reaction of the acetonitrile solvent complex (3; sol = MeCN) with dithian (1,4-dithiacyclohexane, dt). The dithian replaces two acetonitrile ligands, and the complex is formulated as shown with a chelating dithian. The mononuclear structure (5) shown is consistent with the observed molar conductivity (210 Ω^{-1} cm^2 mol^{-1}) in acetone which is in the same region (204—231 Ω^{-1} cm^2 mol^{-1}) as other 1 : 2 electrolytes of this type.

Other dithian complexes were less tractable (but see below); for example, reaction of the dichloride complex (1) with dithian gave a compound (6a) which analysed

---

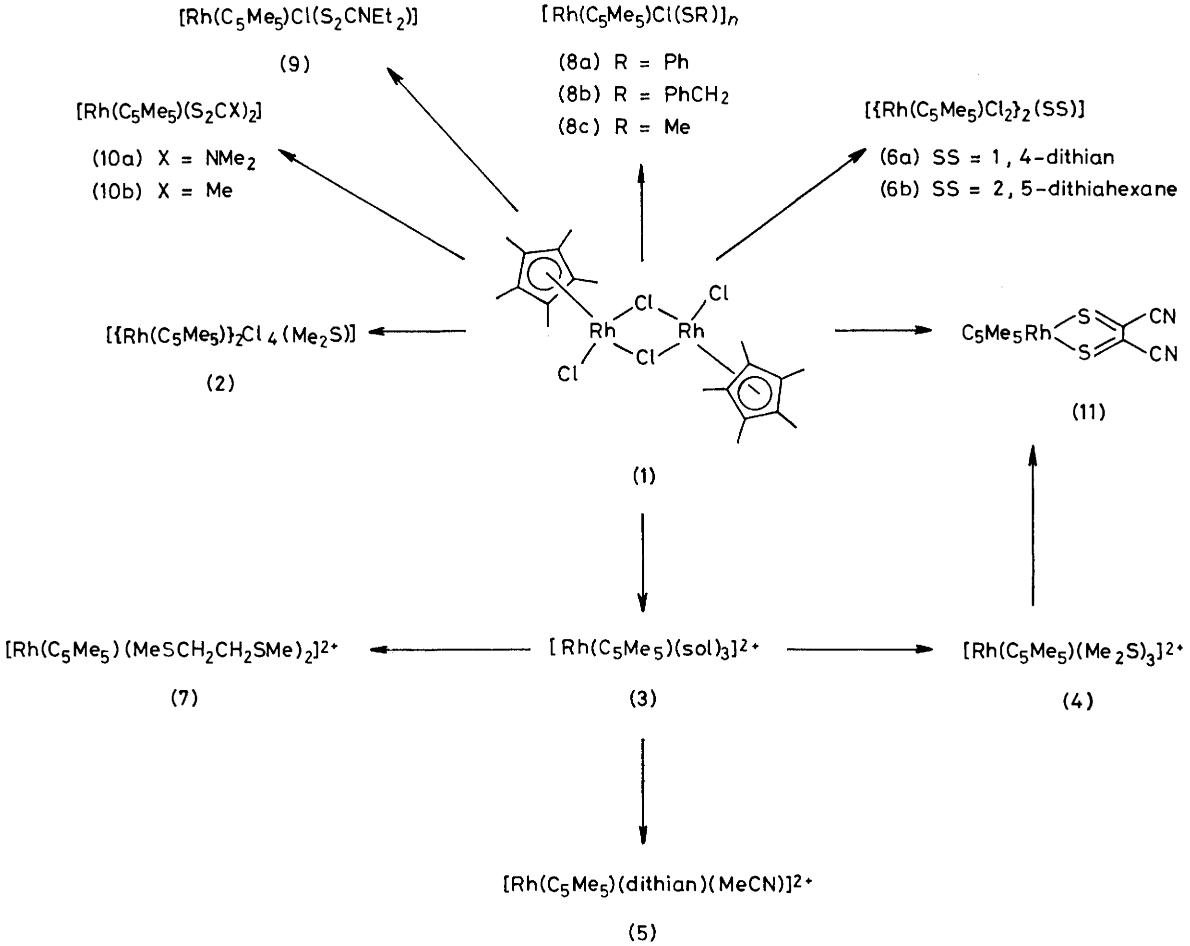
† No reprints available.

[1] Part 16, D. S. Gill, C. White, and P. M. Maitlis, *J.C.S. Dalton*, 1978, 617.

[2] M. J. H. Russell, C. White, and P. M. Maitlis, following paper.

[3] C. White, S. J. Thompson, and P. M. Maitlis, *J.C.S. Dalton*, 1977, 1654.

[4] C. White, S. J. Thompson, and P. M. Maitlis, *J. Organometallic Chem.*, 1977, **136**, 87.



SCHEME 1

TABLE 1

Microanalytical and molecular-weight data (calculated values in parentheses)

Complex	% Composition					M [a]
	C	H	S	N	Cl	
$[\{Rh(C_5Me_5)\}_2Cl_4(SMe_2)]$ (2)	33.7 (33.8)	4.8 (5.3)	4.4 (4.7)		20.3 (20.8)	562 (680)
$[Rh(C_5Me_5)(SMe_2)_3][PF_6]_2$ (4)	26.9 (26.9)	4.7 (4.7)	13.7 (13.5)			
$[Rh(C_5Me_5)(NCMe)(dt)][PF_6]_2$ (5)	27.9 (27.9)	3.9 (3.8)	11.7 (9.3)	2.0 (2.0)		[c]
$[\{Rh(C_5Me_5)\}_2Cl_4(dt)]_n$ (6a)	38.5 (39.0)	5.1 (5.2)	9.1 (8.7)		23.3 (19.2)	
$[\{Rh(C_5Me_5)\}_2Cl_4(dithiahexane)]_n$ (6b)	38.4 (38.9)	5.7 (5.5)	8.7 (8.7)		19.8 (19.3)	
$[Rh(C_5Me_5)(dithiahexane)_2][PF_6]_2$ (7)	28.0 (28.0)	4.6 (4.6)	16.7 (16.6)			
$[Rh(C_5Me_5)Cl(SPh)]_n$ (8a)	50.1 (50.2)	5.5 (5.3)	9.4 (8.4)		8.8 (9.3)	1 284 (1 148) [b]
$[Rh(C_5Me_5)Cl(SCH_2Ph)]_n$ (8b)	51.2 (51.5)	5.8 (5.6)	8.3 (8.1)		9.1 (8.9)	1 121 (1 190) [b]
$[\{Rh(C_5Me_5)\}_2Cl_2(SMe)_2{\cdot}MeSH]_n$ (8c)	39.7 (40.1)	6.4 (5.8)	14.0 (14.0)		10.1 (10.3)	1 240
$[Rh(C_5Me_5)Cl(S_2CNEt_2)]$ (9)	42.2 (42.7)	5.8 (6.0)	15.6 (15.2)	3.3 (3.3)	8.8 (8.4)	449 (421)
$[Rh(C_5Me_5)(S_2CNMe_2)_2]$ (10a)	39.9 (40.1)	5.5 (5.7)	26.8 (26.8)	5.5 (5.9)		483 (478)
$[Ir(C_5Me_5)(S_2CNMe_2)_2]$	33.7 (33.8)	4.8 (4.8)	23.3 (22.6)	4.9 (4.9)		568 (566)
$[Rh(C_5Me_5)(S_2CMe)_2]$ (10b)	40.1 (40.0)	5.0 (5.0)	30.4 (30.5)			443 (420)
$[Rh(C_5Me_5)\{S_2C_2(CN)_2\}]$ (11)	44.0 (44.4)	4.2 (4.0)	15.8 (16.9)	7.7 (7.4)		359 (376)
$[Ir(C_5Me_5)\{S_2C_2(CN)_2\}]$	35.8 (35.9)	3.3 (3.2)	11.2 (13.7)	5.8 (6.0)		
$[Rh(C_5Me_5)(S_2C_6H_3Me)]_2$ (12)	51.6 (52.0)	5.5 (5.4)	16.3 (16.3)			794 (784)
$[RhCl(dt)]_n$ (13)	18.7 (18.6)	3.3 (3.1)	22.5 (24.8)		12.3 (13.7)	
$[PdCl_2(dt)(0.1\ Me_2CO)]_n$ (14a)	17.3 (17.0)	2.9 (2.9)	21.5 (21.1)		24.3 (23.4)	
$[PdBr_2(dt)(0.1\ Me_2CO)]_n$ (14b)	13.6 (13.2)	2.0 (2.2)	16.6 (16.4)		Br, 40.0 (40.7)	
$[Rh(cod)(dt)][PF_6]$ (15)	30.4 (30.3)	4.2 (4.2)	13.7 (13.5)			[d]
$[Rh(C_7H_8)(dt)][PF_6]$	28.7 (38.7)	3.8 (3.5)	11.6 (13.9)			[e]
$[\{Rh(dt)(PPh_3)_2\}_2][PF_6]_2$ (16a)	53.1 (53.8)	4.4 (4.3)	9.0 (7.2)			[f]
$[\{Rh(dt)[P(OPh)_3]_2\}_2][PF_6]_2$ (16b)	48.2 (38.6)	4.0 (3.9)	7.6 (6.5)			[g]
$[Pd(2\text{-}Me\text{-}C_3H_4)(dt)][PF_6]$ (17a)	22.4 (22.5)	3.6 (3.5)	17.9 (15.0)			[h]
$[Pd(1\text{-}Ph\text{-}C_3H_4)(dt)][PF_6]$ (17b)	32.3 (32.0)	3.7 (3.5)	14.8 (13.1)			
1,4-Dithian (dt)	39.7 (40.0)	6.7 (6.7)	53.1 (53.3)			

[a] In chloroform by osmometry. [b] Calculated for $n = 2$. Molar conductivities (Λ_M) in acetone: [c] 210, [d] 145, [e] 140, [f] 239, [g] 231, [h] 156 Ω^{-1} cm^2 mol^{-1}. Reference, $[Rh(C_5Me_5)(tetramethylthiophen)][PF_6]_2$, Λ_M 204 Ω^{-1} cm^2 mol^{-1}.

TABLE 2

^{1}H and ^{13}C N.m.r. spectroscopic data (in $\mathrm{CDCl_3}$)

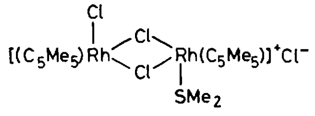
	^{1}H N.m.r.			^{13}C N.m.r.		
Complex	Assignment	δ		Assignment	δ	
$[\{\mathrm{Rh(C_5Me_5)}\}_2\mathrm{Cl_4(SMe_2)}]$ (2)	$\mathrm{C_5Me_5}$	1.67 (30 H)	s	$\mathrm{C_5}\mathit{Me}_5$	9.3	s
	$\mathrm{SMe_2}$	2.45 (6 H)	s	$\mathrm{S}\mathit{Me}_2$	21.7	s
				$\mathit{C}_5\mathrm{Me}_5$	94.0	d
				$\mathit{C}_5\mathrm{Me}_5$	96.2	d, 2[b]
$[\mathrm{Rh(C_5Me_5)(SMe_2)_3][PF_6]_2}$[a] (4)	$\mathrm{C_5Me_5}$	2.0 (15 H)	s	$\mathrm{C_5}\mathit{Me}_5$	9.3	s
	$\mathrm{SMe_2}$	2.77 (18 H)	d, 1[c]	$\mathit{Me}_2\mathrm{S}$	21.7	s
				$\mathit{C}_5\mathrm{Me}_5$	106.5	d, 7.6[b]
$[\mathrm{Rh(C_5Me_5)(NCMe)(dt)][PF_6]_2}$ (5)				$\mathit{Me}\mathrm{CN}$	4.1	s
	$\mathrm{C_5Me_5}$	2.18 (15 H)	s	$\mathrm{C_5}\mathit{Me}_5$	9.6	s
	MeCN	2.69 (3 H)	s	$\mathit{C}\mathrm{H_2}$	34.6	s
	$\mathrm{CH_2}$	3.44 (4 H)	s	$\mathit{C}\mathrm{H_2}$	38.6	s
	$\mathrm{CH_2}$	3.56 (4 H)	s	$\mathit{C}_5\mathrm{Me}_5$	105.3	d, 6.1[b]
				$\mathrm{Me}\mathit{C}\mathrm{N}$	129.6	d, 6.1[d]
$[\mathrm{Rh(C_5Me_5)(dithiahexane)_2][PF_6]_2}$ (7)[a]	$\mathrm{C_5Me_5}$	1.89 (15 H)	s	$\mathrm{C_5}\mathit{Me}_5$	9.2	s
	MeS	2.36 (6 H)	s	$\mathit{Me}\mathrm{S}$	16.3	s
	MeS	2.59 (6 H)	s	$\mathit{Me}\mathrm{S}$	18.6	s
	$\mathrm{CH_2}$	3.15 (8 H)	s	$\mathit{C}\mathrm{H_2}$	33.1	s
				$\mathit{C}\mathrm{H_2}$	38.2	s
				$\mathit{C}_5\mathrm{Me}_5$	102.2	d, 7.6[b]
$[\mathrm{Rh(C_5Me_5)Cl(SPh)}]_n$ (8a)	$\mathrm{C_5Me_5}$	1.33 (15 H)	s	$\mathrm{C_5}\mathit{Me}_5$	8.7	s
		7.22 (3 H)	broad	$\mathit{C}_5\mathrm{Me}_5$	97.9	d, 7.6[b]
	SPh	7.64 (2 H)	broad	Phenyl	128.1	s
					128.7	s
					132.4	s
					133.1	s
$[\mathrm{Rh(C_5Me_5)(SCH_2Ph)Cl}]_n$ (8b)	$\mathrm{C_5Me_5}$	1.40 (15 H)	s	$\mathrm{C_5}\mathit{Me}_5$	8.5	s
	$\mathrm{CH_2}$	3.79 (2 H)	s	$\mathit{C}\mathrm{H_2}$	34.5	s
		7.20 (3 H)	broad	$\mathit{C}_5\mathrm{Me}_5$	89.4	d, 6.1[b]
		7.50 (3 H)	broad	Phenyl	125.8	s
					127.7	s
					130.7	s
					141.3	
$[\{\mathrm{Rh(C_5Me_5)}\}_2\mathrm{Cl_2(SMe_2)_2{\cdot}MeSH}]_n$ (8c)	$\mathrm{C_5Me_5}$	1.80 (30 H)	s	$\mathrm{C_5}\mathit{Me}_5$	9.3	s
	SMe	1.93 (6 H)	s	$\mathrm{S}\mathit{Me}$	13.2	s
	$\mathit{Me}\mathrm{SH}$	2.11 (3 H)	s	$\mathit{C}_5\mathrm{Me}_5$	97.4	d, 6.1[b]
	$\mathrm{MeS}\mathit{H}$	2.39 (1 H)	s			
$[\mathrm{Rh(C_5Me_5)Cl(S_2CNEt_2)}]$ (9)	$\mathrm{S_2CNCH_2}\mathit{Me}$	1.42 (6 H)	t J(H–H) = 7	$\mathrm{C_5}\mathit{Me}_5$	9.2	s
	$\mathrm{C_5Me_5}$	2.21 (15 H)	s	$\mathrm{S_2CN(CH_2}\mathit{Me})_2$	12.4	s
	$\mathrm{S_2CN}\mathit{C}\mathrm{H_2Me}$	2.75 (4 H)	m	$\mathrm{S_2CN(}\mathit{C}\mathrm{H_2Me)_2}$	43.4	s
				$\mathit{C}_5\mathrm{Me}_5$	96.4	d, 6.1[b]
				$\mathrm{S_2}\mathit{C}\mathrm{NEt_2}$	207.6	d, 4.6
$[\mathrm{Rh(C_5Me_5)(S_2CNMe_2)_2}]$ (10a)	$\mathrm{C_5Me_5}$	1.66 (15 H)	s	$\mathrm{C_5}\mathit{Me}_5$	9.3	s
	$\mathrm{S_2CNMe_2}$	3.20 (6 H)	s		38.3	s
				$\mathrm{S_2CN}\mathit{Me}_2$	44.6	s
					45.9	s
	$\mathrm{S_2CNMe_2}$	3.60 (6 H)	s	$\mathit{C}_5\mathrm{Me}_5$	96.4	d, 7.6[b]
				$\mathrm{S_2}\mathit{C}\mathrm{NMe_2}$	208.4	s
					209.1	d, 4.6[b]
$[\mathrm{Ir(C_5Me_5)(S_2CNMe_2)_2}]$	$\mathrm{C_5Me_5}$	1.80 (15 H)	s	$\mathrm{C_5}\mathit{Me}_5$	9.0	s
	$\mathrm{S_2CNMe_2}$	3.36 (6 H)		$\mathrm{S_2CN}\mathit{Me}_2$	37.7	s
		3.88 (6 H)			46.0	b
				$\mathit{C}_5\mathrm{Me}_5$	89.7	s
				$\mathrm{S_2}\mathit{C}\mathrm{NMe_2}$	207.6	s
					210.8	s
$[\mathrm{Rh(C_5Me_5)(S_2CMe)_2}]$ (10b)	$\mathrm{C_5Me_5}$	1.91 (15 H)	s	$\mathrm{C_5}\mathit{Me}_5$	9.5	s
	$\mathrm{S_2CMe}$	2.57 (3 H)	s	$\mathrm{S_2C}\mathit{Me}$	41.6	s
		3.06 (3 H)	s	$\mathrm{S_2C}\mathit{Me}$	44.0	s
				$\mathit{C}_5\mathrm{Me}_5$	97.6	d, 6.1[b]
				$\mathit{C}\mathrm{Me}$	209.8	d, 6.1[b]
					216.4	s

TABLE 2 (*Continued*)

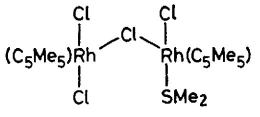
	^{1}H N.m.r.			^{13}C N.m.r.		
Complex	Assignment	δ		Assignment	δ	
$[\mathrm{Rh(C_5Me_5)\{S_2C_2(CN)_2\}}]$ (11)	$\mathrm{C_5Me_5}$	2.05	s	$\mathrm{C_5}Me_5$	10.7	s
				$C_5\mathrm{Me_5}$	101.4	d, 7.1 [b]
				$\mathrm{S_2}C_2\mathrm{(CN)_2}$	122.7	
				$\mathrm{S_2C_2(}CN\mathrm{)_2}$	146.7	
$[\mathrm{Ir(C_5Me_5)\{S_2C_2(CN)_2\}}]$	$\mathrm{C_5Me_5}$	2.14	s	$\mathrm{C_5}Me_5$	10.6	s
				$C_5\mathrm{Me_5}$	95.4	s
				$\mathrm{S_2}C_2\mathrm{(CN)_2}$	116.5	s
				$\mathrm{S_2C_2(}CN\mathrm{)_2}$	137.2	s
$[\mathrm{\{Rh(C_5Me_5)(S_2C_6H_3Me)\}_2}]$ (12)	$\mathrm{C_5Me_5}$	1.98 (15 H)	s	$\mathrm{C_5}Me_5$	8.0, 10.7	
	$\mathrm{S_2C_6H_3Me}$	2.20 (2 H)	s	$\mathrm{S_2C_6H_3}Me$	20.4, 20.7	
		2.36 (1 H)	s		20.9, 21.2	
	$\mathrm{S_2C_6}H_3\mathrm{Me}$	7.20 (3 H)	m	$C_5\mathrm{Me_5}$	96.5 (4.6 [b])	
					98.2 (6.1 [b])	
				$\mathrm{S_2}C_6\mathrm{H_3Me}$	121.1, 123.9,	
					126.1, 128.2	
					129.4, 130.4,	
					131.4, 134.8	
$[\mathrm{Rh(cod)(dt)][PF_6]}$ [a] (15)	$CH_2\mathrm{(cod)}$	2.32 (8 H)	broad	$C\mathrm{H_2(cod)}$	30.8	s
	$\mathrm{C}H_2\mathrm{(dt)}$	3.42 (8 H) [e]	broad	$C\mathrm{H_2(dt)}$	33.4	s
	$\mathrm{C}H\mathrm{(cod)}$	5.23 (4 H)	s	$C\mathrm{H(cod)}$	89.6	d, 10.7 [b]
$[\mathrm{\{Rh(dt)(PPh_3)_2\}_2][PF_6]_2}$ [d] (16a)	$\mathrm{CH_2}$	3.60 (8 H)	broad	$C\mathrm{H_2}$	35.0	s
	Ph	7.40 (30 H)	s		129.2	s
				Phenyl	131.1	s
					132.6	s
					134.6	s
$[\mathrm{\{Rh(dt)[P(OPh)_3]_2\}_2][PF_6]_2}$ [d] (16b)	$\mathrm{CH_2}$	3.60 (8 H)	broad	$C\mathrm{H_2}$	32.9	s
	Ph	7.48 (30 H)	s		122.1	s
				Phenyl	127	s
					131.2	s
					151.7	s
$[\mathrm{Pd(2\text{-}Me\text{-}C_3H_4)(dt)][PF_6]}$ [a] (17a)	Me	2.07 (3 H)	s	$Me\mathrm{\text{-}C_3H_4}$	23.2	s
	syn $\mathrm{CH_2}$	2.70 (2 H)	s	$C\mathrm{H_2(dt)}$	32.3	s
	$\mathrm{CH_2(dt)}$	3.15 (8 H)	s	C_1, C_3	68.7	s
	anti $\mathrm{CH_2}$	3.36 (2 H)	s	C_2	137.9	s
$[\mathrm{Pd(1\text{-}Ph\text{-}C_3H_4)(dt)][PF_6]}$ [a] (17b)	$\mathrm{C}H_2\mathrm{(dt)}$	3.38 (8 H)	s	$C\mathrm{H_2(dt)}$	32.7	s
	anti $\mathrm{CH_2}$	3.69 (4 H)	m	C_1	66.3	s
	syn $\mathrm{CH_2}$	4.78	m	C_3	90.9	s
	CH	5.60	m		128.4	s
	Ph	7.60 (5 H)	m	Phenyl	129.5	s
					130.0	s

[a] In [^{2}H$_6$]acetone. [b] *J*(C–Rh) in Hz. [c] *J*(H–Rh) in Hz. [d] In [^{2}H$_3$]acetonitrile at −30 °C. [e] Free 1,4-dithian shows ^{1}H resonance at δ 2.87.

correctly for $[\mathrm{\{Rh(C_5Me_5)\}_2Cl_4(dithian)}]$ but the total insolubility of this compound precluded molecular-weight measurements or solution spectroscopic studies.



(2a)



(2b)

The far-i.r. spectrum is consistent with a polymeric structure with both terminal and bridging chlorines.

2,5-Dithiahexane forms similar complexes to those of 1,4-dithian. Reaction of the dichloride (1) with a 12-fold excess of dithiahexane gave a 1 : 2 adduct (6b) which appeared to be completely analogous to the dithian complex (6a).

When the tris-acetone solvent complex (3; sol = Me$_2$CO) was treated with dithiahexane, the complex $[\mathrm{Rh(C_5Me_5)(MeSCH_2CH_2SMe)_2][PF_6]_2}$ (7) was obtained. In acetone or dimethyl sulphoxide solution this complex showed two types of *Me*S and CH_2–S resonances in a 1 : 1 ratio, neither set of which appeared at the same position as the free dithiahexane ligand. The ^{1}H n.m.r. spectrum was unchanged down to −70 °C and it therefore appears likely that the observed spectrum arises from a solvated complex with both dithiahexanes being unidentate, $[\mathrm{Rh(C_5Me_5)(MeSCH_2CH_2SMe)_2(sol)][PF_6]_2}$. The solid-state structure of unsolvated (7) is not known but it may well have one chelated and one unidentate ligand.

Thiolato (RS-) *Complexes*.—The dichloro-complex (1) reacted with thiolate ion, RS$^-$, under a variety of conditions (LiSR or NaSR in thf; RSH and sodium carbonate in dichloromethane or toluene) to replace one chloride by SR giving $[\mathrm{Rh(C_5Me_5)Cl(SR)}]_n$ (8a, R = Ph; 8b, R = PhCH$_2$; or 8c, R = Me). In the formation of the phenyl- and benzyl-thiolato-complexes the reactions were complicated (and the isolation procedure made difficult) by the formation of the disulphides, RSSR.* All the complexes are associated in chloroform solution

---

* Coupling products are frequently observed from metal-catalysed oxidations of thiols under alkaline conditions.[5]

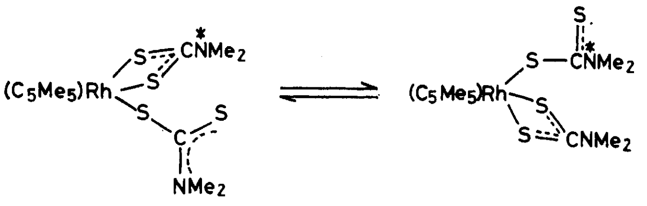
[5] See, for example, M. Ahmad, R. Bruce, and G. R. Knox, *J. Organometallic Chem.*, 1966, **6**, 1.

and molecular-weight measurements indicated $n \approx 3$ for (8a) and (8b). The methylthiolato-complex (8c) crystallised with 0.5n MeSH as shown by analysis and the ^{1}H n.m.r. spectrum. The structures of these complexes remain speculative.

Dithiolato- (Dithiocarbamato-, Dithioacetato-, Toluene-3,4-dithiolato-, and 1,2-Dicyanoethylene-1,2-dithiolato-) Complexes.—Reaction of the dichloride dimer complex with NaS_2CX ($X = NEt_2$, NMe_2, or Me) (or the free acid in the presence of base) gave the chloro(diethyldithiocarbamato) complex (9), where only one Cl had been substituted by S_2CNEt_2, or the bis-dithiocarbamato- or -dithioacetato-complexes (10a) and (10b) with the smaller S_2CNMe_2 and S_2CMe ligands. The dimethyldithiocarbamato-iridium complex $[Ir(C_5Me_5)(S_2CNMe_2)_2]$ was also prepared from $[\{Ir(C_5Me_5)Cl_2\}_2]$.*

All these complexes were monomeric in solution and the isolation of $[Rh(C_5Me_5)Cl(S_2CNEt_2)]$, (9), where the dithiocarbamate is bidentate, suggests strongly that in the bis-complexes both chelating and unidentate S_2CX groups are to be found. This is confirmed by the i.r. spectrum of (10a) which shows strong ν(CN) bands at 1 392 and 1 530 cm^{-1} and by the i.r. spectrum of (9) which shows only one strong ν(CN) at 1 510 cm^{-1}. Bands above 1 470 cm^{-1} have been assigned to ν(CN) in bidentate and those below to ν(CN) in unidentate dithiocarbamates.[6]

At ambient temperature the ^{1}H n.m.r. spectra of both (10a) and $[Ir(C_5Me_5)(S_2CNMe_2)_2]$ show two singlets for the S_2CNMe_2 methyl resonances in a 1 : 1 ratio and these are assigned to the bi- and uni-dentate dithiocarbamate methyls. In the rhodium complex (10a) these signals coalesced on heating and this is ascribed to the exchange process shown in Scheme 2.

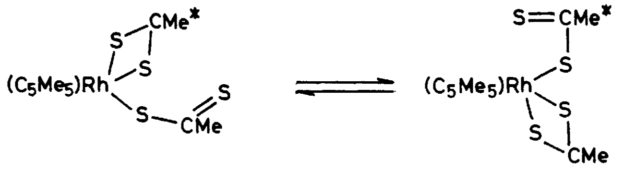


SCHEME 2

The ^{13}C n.m.r. spectrum of the rhodium complex (10a) at +30 °C shows the presence of one sharp dithiocarbamate methyl (δ 38.3) and two broad ones (δ 44.6, 45.9). The latter are assigned to the two inequivalent methyls of the unidentate dithiocarbamate which are already beginning to exchange by rotation about the partial $S_2C \overset{...}{-} NMe_2$ double bond. In $[Ir(C_5Me_5)(S_2CNMe_2)_2]$ these methyl signals have already coalesced to a broad singlet at δ 46.0.

One other observation which aids in structure assignment is that for the chelating dithiocarbamate of both the bis-complex (10a) and the mono-complex (9) the ^{13}C spectrum shows S_2CNR_2 as a doublet [$J(^{13}C-^{103}Rh) = 4.6$ Hz] whereas the same carbon in the unidentate ligand is a singlet; both carbons are of course singlets in the iridium analogue $[Ir(C_5Me_5)(S_2CNMe_2)_2]$. One possible explanation for the observation of these couplings is that in a unidentate ligand the through-space C–Rh coupling cancels out the two-bond C–Rh coupling whereas in the chelated ligand there are two two-bond C–Rh couplings which reinforce each other so that J(C–Rh) is observed.

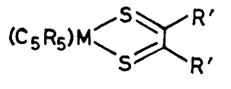
A similar phenomenon is observed in the rhodium bis-dithioacetate complex (10b) where the ^{13}C spectrum again shows a singlet at δ 216.4 and a doublet at δ 209.8, J(C–Rh) = 6.1 Hz, arising from the uni- and bi-dentate S_2CMe carbons respectively. The presence of chelating and unidentate $MeCS_2$ ligands is again confirmed by the i.r. spectrum which shows ν(CS) at 1 030 m and 940 m.[6] In the ^{1}H n.m.r. spectrum the two types of dithioacetate were distinguished by two singlets which coalesced on heating. This is again ascribed to an exchange (see Scheme 3).



SCHEME 3

Either the rhodium dichloride dimer (1) and the tris(dimethyl sulphide) complex (4) reacted with sodium 1,2-dicyanoethylene-1,2-dithiolate to give the monomeric 1,2-dithiolate (11); the iridium analogue was obtained similarly from $[\{Ir(C_5Me_5)Cl_2\}_2]$. By analogy to $[Co(C_5H_5)\{S_2C_2(CF_3)_2\}]$, the structure of which is shown and which approximates best to a Co^I complex (A, R = H; R′ = CF_3, M = Co),[7] (11) and its iridium analogue are best considered as Rh^I and Ir^I complexes respectively.

A different situation arises in (12), obtained from sodium toluene-3,4-dithiolate and (1). This complex is dimeric in chloroform, but the n.m.r. spectra in this solvent suggest that at least two isomers are present. This is most clearly shown by the ^{13}C spectrum where five tolyl methyls may be distinguished and where two signals show coupling to ^{103}Rh and are assigned to two distinct C_5Me_5 groups. Three geometrically isomeric dimers of this type are possible.



(A)

It is interesting to note that the most appropriate oxidation state for the Rh in (12) is (+III) in contrast to that

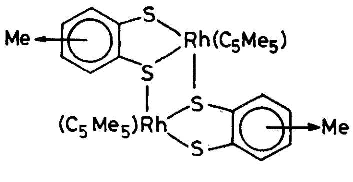
---

* The complexes $[Rh(C_5Me_5)(S_2CNMe_2)_2]$ and $[Ir(C_5Me_5)(S_2CNMe_2)_2]$ have been independently prepared and their exchange processes studied (D. R. Robertson and T. A. Stephenson, *J. Organometallic Chem.*, 1976, **107**, C46; *J.C.S. Dalton*, in the press).

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

[7] H. W. Baird and B. M. White, *J. Amer. Chem. Soc.*, 1966, **88**, 4744.

in the monomeric (11); this is presumably due to the greater reluctance of the organic moiety in (12) to adopt the *o*-quinonoid form, analogous to that in (A), and which is apparently needed to stabilise a monomeric complex.



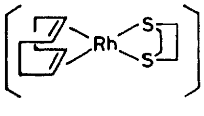
(12)

1,4-*Dithian Complexes of* Rh^I *and* Pd^{II}.—Relatively few 1,4-dithian complexes have been prepared and even fewer have been spectroscopically characterised [8,9] and it was, therefore, of interest to prepare some and to investigate their properties.

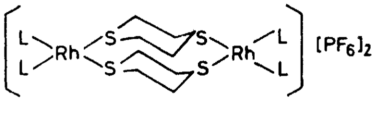
Neutral complexes were obtained by reaction of $[\{Rh(cyclo\text{-}octene)_2Cl\}_2]$, $[Pd(PhCN)_2Cl_2]$, or $[Pd(PhCN)_2Br_2]$ with dithian (dt) to give $[Rh(dt)Cl]_n$ (13), and $[Pd(dt)X_2(0.1\ acetone)]$ (14a, X = Cl; 14b, X = Br) respectively. All these complexes were totally insoluble and very unreactive. The presence of acetone in (14a) and (14b) was indicated by analysis and by ν(CO) at 1 700 cm^{-1} in the i.r. spectrum, and this could not be removed even on extensive drying *in vacuo*. The structures of these complexes are not known but the far-i.r. spectra suggest the presence of bridging halides in (13) and bridging and terminal halides in (14a) and (14b).

The cationic complexes $[Rh(L_2)(dt)]^+$ and $[Pd(allyl)(dt)]^+$ were more tractable. Reaction of $[\{Rh(cod)Cl\}_2]$ (cod = cyclo-octa-1,5-diene) with dithian in the presence of $AgPF_6$ gave $[Rh(cod)(dt)][PF_6]$ (15). The conductivity of this salt was consistent with a 1 : 1 electrolyte and the field desorption mass-spectrum showed *m/e* at 331 and the isotope pattern, in particular the absence of a peak at *m/e* 331.5, indicated that the cation was mononuclear. Both the ^1H and ^{13}C n.m.r. spectra were consistent with the structure shown containing a chelating dithian ligand. A similar complex, $[Rh(nor\text{-}C_7H_8)(dt)][PF_6]$, was obtained from dithian and $[\{Rh(norbornadiene)Cl\}_2]$ in the presence of $AgPF_6$ but lack of solubility precluded useful n.m.r. measurements.

On reaction of the cod complex (15) with triphenylphosphine or triphenyl phosphite the cod was displaced and the complexes $[RhL_2(dt)]_n[PF_6]_{2n}$ [16a, L = PPh_3; 16b, L = $P(OPh)_3$] were obtained. The conductivities of these salts in acetone were consistent with their being 1 : 2 electrolytes, and they are most appropriately formulated as shown with bridging dithian ligands. The n.m.r. spectra of both (16a) and (16b) at ambient temperatures were very broad and indicated a dynamic process to be occurring; at −30 °C this process had slowed down sufficiently to give sharper spectra which agreed with the proposed structures.

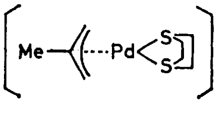


(15)



(16)

Reaction of $[\{Pd(\eta^3\text{-}C_3H_4R)Cl\}_2]$ with dithian in the presence of $AgPF_6$ gave $[Pd(\eta^3\text{-}C_3H_4R)(dt)]_n[PF_6]_n$ (17a, C_3H_4R = 2-methylallyl; 17b, C_3H_4R = 1-phenylallyl). The ^1H and ^{13}C n.m.r. spectra were in agreement with the proposed structures and showed that the C_3H_4R ligand was still η^3-bonded; however complex (17a) underwent a dynamic process at ambient temperature which only slowed down sufficiently at −30 °C for sharp n.m.r. spectra to be observed. The conductivity in acetone of complex (17a) was in the range expected for a 1 : 1 electrolyte; this is consistent with the structure shown where the dithian is chelating. The complex (17b) slowly decomposed when attempts to measure the conductivity were made.



(17a)

TABLE 3

The activity of sulphur complexes as catalysts for the hydrogenation of cyclohexene [a]

Complex	% Cyclohexane formed Base present	 Base absent
$[\{Rh(C_5Me_5)\}_2Cl_4(SMe_2)]$ (2)	95	100
$[Rh(C_5Me_5)(SMe_2)_3][PF_6]_2$ (4)	95	100
$[Rh(C_5Me_5)(NCMe)(dt)][PF_6]_2$ (5)	28	54
$[Rh_2(C_5Me_5)_2Cl_4(dt)]_n$ (6a)	44	94
$[\{Rh(C_5Me_5)\}_2Cl_4(dithiahexane)]$ (6b)	30	20
$[Rh(C_5Me_5)(dithiahexane)_2][PF_6]_2$ (7)	6	20
$[Rh(C_5Me_5)Cl(SPh)]_n$ (8a)	5	35
$[Rh(C_5Me_5)(SCH_2Ph)Cl]_n$ (8b)	35	15
$[\{Rh(C_5Me_5)\}_2Cl_2(SMe)_2\cdot MeSH]_n$ (8c)	20	30
$[Rh(C_5Me_5)Cl(S_2CNEt_2)]$ (9)	12	0
$[Rh(C_5Me_5)(S_2CNMe_2)_2]$ (10a)	3	2
$[Ir(C_5Me_5)(S_2CNMe_2)_2]$	0	1
$[Rh(C_5Me_5)(S_2CMe)_2]$ (10b)	0	0
$[Rh(C_5Me_5)\{S_2C_2(CN)_2\}]$ (11)	15	0
$[Ir(C_5Me_5)\{S_2C_2(CN)_2\}]$	52	0
$[\{Rh(C_5Me_5)(S_2C_6H_3Me)\}_2]$ (12)	15	12
$[Rh(dt)Cl]_n$ (13)	10	0
$[Pd(dt)Cl]_n$ (14a)	29 [b]	16 [b]
$[Rh(cod)(dt)][PF_6]$ (15)	35 [b]	30 [b]
$[Rh(C_7H_8)(dt)][PF_6]$	30	5 [b]
$[Rh_2(dt)_2(PPh_3)_4][PF_6]_2$ (16a)	44	93
$[Rh_2(dt)_2\{P(OPh)_3\}_4][PF_6]_2$ (16b)	96	3
$[Pd(2\text{-}Me\text{-}C_3H_4)(dt)][PF_6]$ (17a)	2	26 [b]
$[Pd(1\text{-}Ph\text{-}C_3H_4)(dt)][PF_6]$ (17b)	17	35 [b]

[a] 0.05 mmol of catalyst, cyclohexene (2 ml, 20 mmol), propan-2-ol (18 ml) at 50 bar hydrogen, 50 °C over a 24 h period. The added base was Et_3N (0.2 ml, 1.5 mmol). [b] Decomposition to metal.

In agreement with earlier authors [8] we also found reliable sulphur analyses to be very difficult to obtain for dithian complexes; other microanalytical data were, however, satisfactory.

---

[8] H. Londahl, *Acta Universitatis Lundensis*, 1892, **27**, 1.

[9] See, for example, D. A. Rice, and R. A. Walton, *Spectrochim. Acta*, 1971, **27A**, 279; E. A. Allen, N. P. Johnson, D. T. Rosevear, and G. Wilkinson, *J. Chem. Soc. (A)*, 1969, 78.

Catalytic Hydrogenation.—In view of the sulphur-poisoning experiments reported above, it was of interest to find out whether any of the complexes prepared here were catalysts for olefin hydrogenation under the conditions where [$\{Rh(C_5Me_5)Cl_2\}_2$] was active. The results are summarised in Table 3. Complexes with chelating sulphur ligands [(9), (10b), and (11)] showed zero activity towards cyclohexene at 20 °C and 1 atm H_2, but the dimethyl sulphide cationic complex (4), although also inactive under these conditions, did catalyse the hydrogenation of hex-1-ene, cyclohexene, and styrene (to hexane, cyclohexane, and ethylbenzene respectively) at 50 °C and 50 atm H_2. Under these conditions the complexes (2), (16a), (16b), and (6a) had approximately the same activity while [$Ir(C_5Me_5)\{S_2C_2(CN)_2\}$], (8), (6b), and (5), also showed some activity. The dithian rhodium(I) complex (15) and the dithianpalladium complexes (17a) and (17b) were catalysts but decomposed to the metal.

It appears from these results that, while sulphur-containing ligands are very effective poisons toward catalytic hydrogenation, some complexes containing sulphur ligands can, under more vigorous conditions, act as catalysts. This suggests that these sulphur ligands are first displaced under such conditions.

We have also attempted, but without success, to make hydrido-complexes, for example from [$Rh(C_5Me_5)(S_2CMe)_2$]. The analogous acetate complex [$Rh(C_5Me_5)(OCOMe)_2]_n$ very readily activates H_2 heterolytically, even in the absence of base, to give the mono-μ-hydrido-complex, [$\{Rh(C_5Me_5)\}_2H(OCOMe)_2]^+$ [10] but no such reaction occurred with either complex (10b) or (9). The cationic dimethyl sulphide complex (4) reacted neither with H_2 nor with $NaBH_4$ or LiH. A further reason for the low catalytic activity of sulphur-containing complexes such as (10a) or (10b) may, therefore, be found in the low tendency to form hydrides and indeed few transition-metal hydrides with S-containing co-ligands are known.

EXPERIMENTAL

All reactions were carried out under nitrogen. Microanalytical data are collected in Table 1, n.m.r. spectroscopic data in Table 2, and the results of hydrogenation experiments in Table 3.

[$\{Rh(C_5Me_5)\}_2Cl_4(SMe_2)$] (2).—Dimethyl sulphide (1 ml) was added to a solution of [$\{Rh(C_5Me_5)Cl_2\}_2$] (0.30 g, 0.49 mmol) in ethanol (20 ml) and the mixture was refluxed for 5 h. The solution was concentrated to 5 ml under reduced pressure and diethyl ether (20 ml) was added. The precipitate was filtered off and washed with diethyl ether to give complex (2) as an orange microcrystalline solid (0.27 g, 73%).

[$Rh(C_5Me_5)(SMe_2)_3][PF_6]_2$ (4).—Silver hexafluorophosphate (0.42 g, 1.67 mmol) was added to a suspension of [$\{Rh(C_5Me_5)Cl_2\}_2$] (0.20 g, 0.32 mmol) in acetonitrile (5 ml). The reaction mixture was stirred for 10 min and was then filtered through a short cellulose-filled column into dimethyl sulphide (2 ml). The solvent was removed under reduced pressure, and the residue was crystallised from acetone–diethyl ether to give yellow crystals of complex (4) (0.40 g, 87%).

[$Rh(C_5Me_5)(SMe_2)_3][PF_6]_2$ was obtained in lower yields when the reaction was carried out in acetone (74%), in dimethyl sulphide (68%), or in thf (35%).

[$Rh(C_5Me_5)(SMe_2)_3][PF_6]_2$ (0.40 g, 0.61 mmol) and trimethyl phosphite were stirred in acetone (20 ml) for 16 h. The solvent was removed under reduced pressure; crystallisation of the residue from acetone–ether gave [$Rh(C_5Me_5)\{P(OMe)_3\}_3][PF_6]_2$ as pale yellow crystals (0.42 g, 77%). The compound was characterised by a comparison of the ^1H n.m.r. and i.r. spectra with those of the reported compound.[4]

Reaction of [$\{Rh(C_5Me_5)Cl_2\}_2$] *with Silver Hexafluorophosphate in Carbon Disulphide.*—Complex (1) (0.23 g, 0.37 mmol) and silver hexafluorophosphate (0.40 g, 1.58 mmol) were stirred together for 10 min in a mixture of carbon disulphide (5 ml) and acetone (5 ml). The reaction mixture was filtered through a short cellulose-filled column and the solution was taken to dryness under reduced pressure to leave a yellow-green oil [^1H n.m.r. spectrum in CS_2, δ 2.03 (s, C_5Me_5)]. Attempts to crystallise a solid from an acetone solution of the oil led to decomposition.

[$Rh(C_5Me_5)(NCMe)(dithian)][PF_6]_2$ (5).—1,4-Dithian [11] (0.15 g, 1.25 mmol) was added to a solution of [$Rh(C_5Me_5)(NCMe)_3][PF_6]_2$ (0.40 g, 0.61 mmol) in acetone (10 ml). The mixture was stirred for 15 min and then taken to dryness under reduced pressure. Crystallisation of the residue from acetone–diethyl ether gave complex (5) as yellow crystals (0.40 g, 95%).

[$\{Rh(C_5Me_5)\}_2Cl_4(dithian)]_n$ (6a).—Complex (1) (0.30 g, 0.48 mmol) and 1,4-dithian (0.12 g, 1 mmol) were dissolved in dichloromethane (10 ml) and the solution was stirred for 10 min. An orange precipitate formed which was filtered off and washed with chloroform (10 ml) and diethyl ether (10 ml) to give complex (6a) (0.31 g, 74%). Far-i.r. spectrum: 375w, 344w, 315w, 278s, 258s, 220s, 198w, and 153w cm^{-1}.

[$\{Rh(C_5Me_5)\}_2Cl_4(dithiahexane)]_n$ (6b).—2,5-Dithiahexane [12] (1.0 g, 4.1 mmol) was added to a solution of [$\{Rh(C_5Me_5)Cl_2\}_2$] (0.2 g, 0.32 mmol) in thf (20 ml). The mixture was stirred for 16 h; the resultant precipitate was then filtered off and washed with diethyl ether to leave complex (6b) as a red powder (0.21 g, 89%). Far-i.r. spectrum: 342vw, 327m, 304s, 282m, 262m, 241s, and 218w cm^{-1}.

[$Rh(C_5Me_5)(dithiahexane)_2][PF_6]_2$ (7).—Silver hexafluorophosphate (0.33 g, 1.30 mmol) was added to a suspension of complex (1) (0.26 g, 0.42 mmol) in 2,5-dithiahexane (3 ml). The mixture was stirred for 10 min and filtered through a short cellulose-filled column. The solution was taken to dryness under reduced pressure; crystallisation of the residue from acetone–light petroleum (b.p. 40—60 °C) gave complex (7) as orange crystals (0.58 g, 67%). This complex was obtained in 59% yield when the reaction was carried out in acetonitrile as solvent.

[$Rh(C_5Me_5)Cl(SPh)]_n$ (8a).—*Method* (*a*). Benzenethiol (0.33 g, 3 mmol) was added to a suspension of lithium hydride (0.05 g, 6 mmol) in dry thf (20 ml) to give a solution of lithium thiophenoxide. A suspension of complex (1) (0.20 g, 0.32 mmol) in dry thf was added dropwise and the mixture was stirred for 2 h. The solvent was removed under reduced pressure and the residue was crystallised from

---

[10] C. White, A. J. Oliver, and P. M. Maitlis, *J.C.S. Dalton*, 1973, 1901.

[11] R. G. Gillis and A. B. Lacey, *Org. Synth.*, 1963, **4**, 396.

[12] D. S. C. Black and I. A. McLean, *Austral. J. Chem.*, 1971, **24**, 1409.

acetone–diethyl ether to give complex (8a) as orange, hygroscopic crystals (0.23 g, 93%), m.p. 172—176 °C.

Soxhlet extraction of the residue with diethyl ether gave white crystals of PhSSPh[13] (0.1 g). Mass spectrum: parent peak *m/e* 218: ^{1}H n.m.r. spectrum ($CDCl_3$): δ 7.30 (s).

Complex (8a) was also obtained in 73% yield from the reaction of sodium thiophenoxide with complex (1) in thf [*Method* (*b*)]; in 81% yield from the reaction of benzenethiol with complex (1) in dichloromethane in the presence of sodium carbonate [*Method* (*c*)]; in 70% yield by reaction of lithium thiophenoxide with $[\{Rh(C_5Me_5)\}_2HCl_3]$ in benzene [*Method* (*d*)]; and in 85% yield by reaction of $[Rh_2Cl_4(C_5Me_5)_2]$ with benzenethiol and sodium carbonate in toluene [*Method* (*e*)].

$[Rh(C_5Me_5)(SCH_2Ph)Cl]_n$ (8b).—Orange hygroscopic crystals of this complex were obtained from the reaction of toluene-α-thiol with complex (1) in 95% [Method (c) above], 91% [Method (e)], or 81% yield [Method (a)].

The crude product from the reaction giving complex (8b) in thf solution was Soxhlet-extracted with diethyl ether. The solvent was removed under reduced pressure to give white crystals (0.1 g) of dibenzyl disulphide[14] (Found: C, 68.2; H, 5.8; S, 26.3. $C_{14}H_{16}S_2$ requires C, 68.2; H, 5.7; S, 26.0%); ^{1}H n.m.r. ($CDCl_3$) δ 3.55 (s, 4 H) and 7.34 (s, 10 H).

The crude product from the reaction giving complex (8b) in dichloromethane solution was Soxhlet-extracted with diethyl ether. The solvent was removed under reduced pressure to give white crystals of di(benzylthio)methane[15] (0.12 g, m.p. 50 °C) [Found: C, 69.0; H, 6.0; S, 24.5%; *M* (mass-spectroscopic) 260. $C_{15}H_{14}S_2$ requires C, 69.2; H, 6.2; S, 24.6%; *M* 260]. ^{1}H N.m.r. ($CDCl_3$): δ 3.41 (s, 2 H), 3.84 (s, 4 H), and 7.31 (s, 10 H).

$[Rh(C_5Me_5)Cl(SMe)]_n\cdot0.5n$ MeSH (8c).—Yellow crystals of this compound were obtained in 86% yield from the reaction of methanethiol with complex (1) using method (e) above.

$[Rh(C_5Me_5)Cl(S_2CNEt_2)]$ (9).—Complex (1) (0.20 g, 0.32 mmol) and sodium diethyldithiocarbamate (0.20 g, 1.17 mmol) were stirred in dichloromethane (10 ml) for 18 h. The mixture was filtered and the filtrate was taken to dryness under reduced pressure. Crystallisation of the residue from dichloromethane–light petroleum (b.p. 60—80 °C) gave orange crystals of complex (9) (0.17 g, 63%).

$[Rh(C_5Me_5)(S_2CNMe_2)_2]$ (10a).—NaS_2CNMe_2 (0.37 g, 2.6 mmol) was added to a solution of complex (1) (0.40 g, 0.65 mmol) in dichloromethane (10 ml). The reaction mixture was stirred for 18 h, filtered, and the solution taken to dryness under reduced pressure. The residue crystallised as a red microcrystalline powder from chloroform–diethyl ether (0.5 g, 81%).

$[Ir(C_5Me_5)(S_2CNMe_2)_2]$.—This compound was prepared as a yellow powder in 62% yield by the method used for complex (10a).

$[Rh(C_5Me_5)(S_2CMe)_2]$ (10b).—Dithioacetic acid[16] (4 ml) was added to a stirred suspension of complex (1) (0.40 g, 2 mmol) and an excess of Na_2CO_3 in dichloromethane (5 ml). The mixture was stirred for 18 h, filtered, and the solution was evaporated to dryness under reduced pressure. Crystallisation of the residue from diethyl ether followed by washing with light petroleum (b.p. 30—40 °C) gave orange crystals of complex (10b) (0.39 g, 64%).

$[Rh(C_5Me_5)\{S_2C_2(CN)_2\}]$ (11).—*Method* (*i*). A solution of $Na_2S_2C_2(CN)_2$[17] (0.12 g, 0.67 mmol) in acetone (5 ml) was added to a solution of complex (1) (0.20 g, 0.32 mmol) in dichloromethane (5 ml). The solution was stirred 18 h at 20 °C and filtered. The filtrate was taken to dryness under reduced pressure and recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C) to give red crystals of complex (11) (0.19 g, 79%).

Method (*ii*). A solution of $Na_2S_2C_2(CN)_2$ (0.11 g, 0.61 mmol) and $[Rh(C_5Me_5)(SMe_2)_3][PF_6]_2$ (4) (0.40 g, 0.61 mmol) in acetone (10 ml) was stirred for 16 h. The mixture was evaporated to dryness under reduced pressure, dichloromethane was added, and the mixture was filtered. The solution was concentrated under reduced pressure to 2 ml; on addition of light petroleum the complex (11) was precipitated as a red powder (0.16 g, 69%).

$[Ir(C_5Me_5)\{S_2C_2(CN)_2\}]$.—This compound was prepared as orange crystals in 80% yield by Method (i) for compound (11).

$[\{Rh(C_5Me_5)(S_2C_6H_3CH_3)\}_2]$ (12).—Red crystals of complex (12) were obtained in 66% yield from $[Rh_2Cl_4(C_5Me_5)_2]$, toluene-3,4-dithiol and sodium carbonate by Method (e) for complex (8a).

$[RhCl(dt)]_n$ (13).—$[Rh_2Cl_2(\text{cyclo-octane})_4]$[18] (14) (0.80 g, 1.1 mmol) and 1,4-dithian (0.3 g, 2.5 mmol) were stirred in acetone (10 ml) for 16 h. The yellow precipitate was filtered off and washed with acetone (10 ml) and diethyl ether (10 ml) and dried *in vacuo* at 56 °C to give complex (13) (0.35 g, 64%). Far-i.r. spectrum: 380w, 320w, 248s, and 148s cm^{-1}.

$[PdCl_2(dt)(0.1Me_2CO)]_n$ (14a).—$[Pd(PhCN)_2Cl_2]$ (0.2 g, 0.52 mmol) and 1,4-dithian (0.19 g, 1.6 mmol) were stirred in acetone (10 ml) for 16 h. The yellow precipitate was filtered off, washed with acetone (10 ml) and diethyl ether (10 ml), and dried *in vacuo* at 56 °C to give complex (14a) (0.11 g, 80%). Far-i.r. spectrum: 348s, 288s, 243sh, and 233m cm^{-1}.

$[PdBr_2(dt)(0.1Me_2CO)]_n$ (14b).—A mixture of $[Pd(PhCN)_2Cl_2]$ (0.20 g, 0.52 mmol) and an excess of lithium bromide were stirred in acetone (10 ml) for 24 h and filtered. Dithian (0.19 g, 1.6 mmol) in acetone (10 ml) was added to the solution which was then stirred for a further 16 h. An orange solid precipitated which was collected, washed with acetone (10 ml) and diethyl ether (10 ml), and dried *in vacuo* at 56 °C to give complex (14b) (0.15 g, 75% yield). Far-i.r. spectrum: 325m, 285s, 265s, 240sh, 230m, and 154s cm^{-1}.

$[Rh(cod)(dt)][PF_6]$ (15).—Silver hexafluorophosphate (0.26 g, 1 mmol) in dichloromethane (3 ml) was added to a suspension of $[\{Rh(cod)Cl\}_2]$ (0.25 g, 0.5 mmol) in dichloromethane (3 ml) solution containing dithian (0.3 g). The mixture was stirred for 10 min, filtered, and the filtrate was taken to dryness *in vacuo*. Crystallisation of the residue from acetone–diethyl ether gave complex (15) as a yellow powder (98%).

$[Rh(C_7H_8)(dt)][PF_6]$.—This complex was obtained as an orange powder in 90% yield by the reaction of $[Rh_2Cl_2(C_7H_8)_2]$ with silver hexafluorophosphate and 1,4-dithian in dichloromethane by the method used for complex (15).

$[Rh(dt)(PPh_3)_2][PF_6]$ (16a).—A solution of triphenyl-

---

[13] E. M. Rodd, 'Chemistry of Carbon Compounds,' Elsevier Publishing, 1971, Vol. IIIA, p. 434.

[14] J. A. Smythe, *J. Chem. Soc.*, 1909, 349.

[15] E. Fromm, A. Forster, and B. Scherschewitzki, *Annalen*, 1912, **394**, 343.

[16] J. Houben and H. Pohl, *Chem Ber.*, 1907, **40**, 1303.

[17] G. Bähr and G. Schleitzer, *Chem. Ber.*, 1955, **88**, 1771.

[18] A. van der Ent and A. L. Onderdelinden, *Inorg. Synth.*, 1973, **14**, 93.

phosphine (0.22 g, 0.84 mmol) in acetone (10 ml) was added to a solution of [Rh(cod)(dithian)][PF_6] (0.20 g, 0.42 mmol) in acetone (10 ml), and the mixture was stirred for 4 h; the solvent was then removed under reduced pressure. Crystallisation of the residue from acetone–diethyl ether gave complex (16a) as a yellow microcrystalline compound (0.32 g, 85%).

[Rh(dt){$P(OPh)_3$}$_2$][PF_6] (16b).—Complex (16b) was obtained as pale yellow crystals in 74% yield from the reaction of triphenyl phosphite with complex (15) by the method used for complex (16a).

[Pd(dt)(2-Me-C_3H_4)][PF_6] (17a).—Complex (17a) was obtained as white crystals in 82% yield from the reaction of 1,4-dithian with [Pd_2Cl_2(η^3-2-MeC_3H_4)$_2$] and silver hexafluorophosphate in acetone by the method used for complex (15).

[Pd(dt)(1-Ph-C_3H_4)][PF_6] (17b).—Complex (17b) was obtained as white crystals in 92% yield from the reaction of 1,4-dithian with [Pd_2Cl_2(η^3-1-Ph-C_3H_4)$_2$] in acetone by the method used for complex (17a).

We thank the S.R.C. and British Petroleum for the award of a CASE Studentship (to M. J. H. R.), Dr. B. E. Mann for helpful discussion, Dr. D. E. Games (University College, Cardiff) for the f.i.d. mass-spectrum, and Mr. Alan Yates and Mr. Albert Wright for experimental assistance.

[7/1619 *Received, 12th September,* 1977]