Synthesis of Complexes of Re^{V}, Ru^{II}, Os^{II}, Rh^{I}, Ir^{I} and Ir^{III}. Crystal and Molecular Structures of $[ReO(OH)(SC_6H_4SiPh_3\text{-}2)_2(PPh_3)]$, $[ReH_4(SC_6H_4SiPh_3\text{-}2)(PPh_3)_3]$ and $[IrH(SC_6H_4SiPh_3\text{-}2)_2(PMePh_2)_3]$†

Mustafa T. Ahmet,[a] Canzhong Lu,[a] Jonathan R. Dilworth,*,[a] John R. Miller,[a] Yifan Zheng,[a] David E. Hibbs,[b] Michael B. Hursthouse[b] and K. M. Abdul Malik[b]

[a] *Department of Biological and Chemical Sciences, Central Campus, University of Essex, Colchester CO4 3SQ, UK*

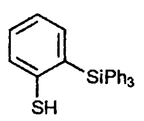
[b] *Department of Chemistry, University of Wales, Cardiff, PO Box 912, Cardiff CF1 3TB, UK*

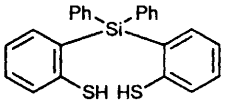
The rhenium(V) precursors $[ReOX_3(PPh_3)_2]$ (X = Cl or Br) reacted with 2-triphenylsilylbenzenethiol in methanol in the presence of base to give $[ReO(Cl)(SC_6H_4SiPh_3\text{-}2)_2(PPh_3)]$ **1** and $[ReO(OH)(SC_6H_4SiPh_3\text{-}2)_2(PPh_3)]$ **2** respectively. In the presence of $NaBH_4$ and no base the blue thiolate polyhydride $[ReH_4(SC_6H_4SiPh_3\text{-}2)(PPh_3)_3]$ **3** was formed in high yield. The crystal structures of **2** and **3** were determined and showed **2** to be monomeric with distorted trigonal-bipyramidal geometry and the oxide and hydroxide ligands in equatorial sites. The thiolate and phosphine ligands of **3** are in a tetrahedral array with the hydride ligands assumed to be in capping sites on the tetrahedral faces. Reaction of the thiol with $[IrCl_3(PMePh_2)_3]$ in methanol in the presence of NEt_3 gave $[IrH(SC_6H_4SiPh_3\text{-}2)_2(PMePh_2)_3]$ **4** in good yield. Its crystal structure revealed the geometry about the Ir to be pseudo-octahedral with *mer* phosphine ligands and *cis* thiolates, and the hydride presumed to be in a vacant site *trans* to a thiolate ligand. The complex $[IrCl(CO)(PPh_3)_2]$ reacted under similar conditions to give monomeric $[Ir(SC_6H_4SiPh_3\text{-}2)(CO)(PPh_3)_2]$ **6** whereas $[RhCl(CO)(PPh_3)_2]$ gave $[Rh_2(\mu\text{-}SC_6H_4SiPh_3\text{-}2)_2(CO)_2(PPh_3)_2]$ **5**; $[OsH(Cl)(PPh_3)_3]$ gave $[OsH(SC_6H_4SiPh_3\text{-}2)(CO)(PPh_3)_3]$ **7** whereas $[RuH(Cl)(PPh_3)_2]$ formed $[Ru(SC_6H_4SiPh_3\text{-}2)(CO)(PPh_3)_2]$ **8**. The potentially bidentate thiol $SiPh_2(C_6H_4SH\text{-}2)_2$ gave a series of products with the same precursors which proved difficult to characterise unequivocally in the absence of X-ray structural data. The geometry adopted by the $SC_6H_4SiPh_3\text{-}2$ ligand was analysed in some detail and contrasted with symmetrically 2,6-disubstituted aromatic thiolates.

The co-ordination chemistry of symmetrical 2,6-disubstituted aromatic thiolate ligands has been explored in considerable detail[1,2] and we were interested to investigate the effect of a single very large group in the 2 position. The thiol 2-$Ph_3SiC_6H_4SH$ has been reported before[3] but its co-ordination chemistry has not apparently been studied. Here we report a systematic investigation of its reactions with a range of tertiary phosphine-containing complexes of Re, Ru, Os, Rh and Ir. We have also studied the analogous reactions of the bis(thiolate) $SiPh_2(C_6H_4SH\text{-}2)_2$[3] in order to determine whether it co-ordinates in a bridging or bidentate manner.

Results and Discussion

Complexes $[ReO(Cl)(SC_6H_4SiPh_3\text{-}2)_2(PPh_3)]$ **1** *and* $[ReO(OH)(SC_6H_4SiPh_3\text{-}2)_2(PPh_3)]$ **2**.—*Preparation.* Reaction of $[ReOX_3(PPh_3)_2]$ (X = Cl) with 2-$Ph_3SiC_6H_4SH$ in methanol under reflux in the presence of base gives the dark green complex $[ReO(Cl)(SC_6H_4SiPh_3\text{-}2)_2(PPh_3)]$ **1**. When X = Br only the oxohydroxo-complex $[ReO(OH)(SC_6H_4SiPh_3\text{-}2)_2(PPh_3)]$ **2** can be isolated, and a bromide ligand is clearly hydrolysed to hydroxide in the course of the reaction, presumably by adventitious water. The reactivity of the thiol is in marked contrast to that of other bulky 2,6-disubstituted aromatic thiols which react with rhenium(V) oxo-precursors to give the oxo-anions $[ReO(SR)_4]^-$.[4] Both





complexes **1** and **2** show a strong IR band at 936 cm^{-1} due to ν(Re=O) and **2** has a weak absorption at about 3500 cm^{-1} assigned to ν(O–H). Details of the analytical and spectroscopic properties of these and other complexes in this paper appear in Table 1. The ^{31}P NMR spectra show singlets at δ 14.2 (**1**) and 19.6 (**2**) consistent with the presence of the single phosphorus donor. A crystal of **2** suitable for X-ray diffraction studies was grown from dichloromethane–methanol.

Crystal structure of complex **2**. A perspective view of the structure of complex **2** appears in Fig. 1 together with a partial atom labelling scheme. Positional parameters and selected bond lengths and angles are in Tables 2 and 3. Details of the structure determination appear in Table 9. Examination of the bond angles at Re and the dihedral angles between ligand atoms taken in threes shows that the geometry about Re can be described as distorted trigonal bipyramidal with P(1) and S(2) apical, or distorted square pyramidal with O(2) in the apical site. This provides the first example of a five-co-ordinate rhenium oxohydroxo-complex, the more common geometry being octahedral with *trans* oxo and hydroxo groups as in $[ReO(OH)(CN)_4]^{2-}$.[6] The crystal structure of the latter has not been determined but it is assumed to be *trans* as in the structurally characterised $[ReO(H_2O)(CN)_4]^-$.[7] The Re–O(2) distance of 1.688(4) Å is assigned to the Re=O bond and is comparable with the Re=O distance in the oxoaqua complex

---

† Co-ordination Chemistry of 2-triphenylsilylbenzene. Part 1.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical and spectroscopic data for 2-triphenylsilylbenzenethiolate complexes

		Analysis (%)[a]			NMR[c] (δ, *J*/Hz)	
Complex	Colour	C	H	IR[b]/cm^{-1}	^{1}H	^{31}P
1 [ReO(Cl)(SC$_6$H$_4$SiPh$_3$-2)$_2$(PPh$_3$)]	Green	64.2 (64.2)	4.4 (4.3)	ν(Re=O) 936	6.6–7.2 (m, Ph)	14.2 (s)
2 [ReO(OH)(SC$_6$H$_4$SiPh$_3$-2)$_2$(PPh$_3$)]·0.5CH$_2$Cl$_2$	Green	63.4 (63.4)	4.5 (4.5)	ν(Re=O) 936	6.3–7.3 (m, Ph)	19.6 (s)
3 [ReH$_4$(SC$_6$H$_4$SiPh$_3$-2)(PPh$_3$)$_3$]·1.5CH$_2$Cl$_2$[d]	Blue	65.1 (64.9)	4.6 (4.7)	ν(Re–H) 2025m, 1968m		
4 [IrH(SC$_6$H$_4$SiPh$_3$-2)$_2$(PMePh$_2$)$_3$]	Yellow	68.6 (68.4)	5.2 (5.1)	ν(Ir–H) 2226	1.75 [t, 6 H, P*Me*Ph$_2$, *J*(PH) = 4.0], 1.61 (d, 3 H, P*Me*Ph$_2$), 7.0–8.1 (m, 68 H, Ph), −16.4 [q, 1 H, hydride, *J*(PH) = 12.1]	19.3 (t), 22.6 (d) [*J*(PP) = 16.7]
5 [Rh$_2$(μ-SC$_6$H$_4$SiPh$_3$-2)$_2$(CO)$_2$(PPh$_3$)$_2$]	Yellow	68.6 (67.9)	4.1 (4.5)	ν(C–O) 1980	6.8–7.9 (m, Ph)	29.9 [d, *J*(RhP) = 134.2]
6 [Ir(SC$_6$H$_4$SiPh$_3$-2)(CO)(PPh$_3$)$_2$]	Yellow	65.3 (65.9)	4.6 (4.7)	ν(C–O) 1960	6.8–7.1 (m, Ph)	
7 [OsH(SC$_6$H$_4$SiPh$_3$-2)(CO)(PPh$_3$)$_3$]·0.5CH$_2$Cl$_2$	Green	67.4 (67.4)	4.6 (4.7)	ν(C–O) 1909, 1891	5.30 (s, CH$_2$Cl$_2$), 6.8–7.9 (m, 64 H, Ph), −7.74 (t), −8.0 (t), [hydride, *J*(PH) = 25.4, 77.1]	−3.89 (t), −5.69 (d) [*J*(RhP) = 16.7]
8 [Ru(SC$_6$H$_4$SiPh$_3$-2)$_2$(CO)(PPh$_3$)$_2$]·2CH$_2$Cl$_2$	Orange	67.8 (67.1)	4.1 (4.1)	ν(C–O) 1923	5.30 (s, 4 H, CH$_2$Cl$_2$), 6.4–7.8 (m, 49 H, Ph)	30.6 (s)
9 [Rh(SC$_6$H$_4$SiPh$_3$-2)(PPh$_3$)$_3$]·CH$_2$Cl$_2$	Red	70.9 (70.2)	4.9 (4.9)	—	*e*	*e*

[a] Calculated values in parentheses. [b] As Nujol mulls. [c] In CDCl$_3$ solution. [d] S 2.7 (2.2)%. [e] Unstable in solution.

Table 2 Positional parameters for [ReO(OH)(SC$_6$H$_4$SiPh$_3$-2)$_2$(PPh$_3$)]·0.75CH$_2$Cl$_2$ **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	0.148 77(2)	0.062 13(2)	0.310 58(1)	C(43)	0.271 0(7)	0.343 1(7)	0.332 0(7)
S(1)	0.247 8(1)	0.014 5(1)	0.178 73(8)	C(44)	0.331 8(7)	0.337 4(8)	0.253 5(9)
S(2)	0.015 6(1)	0.215 5(1)	0.287 84(9)	C(45)	0.280 7(8)	0.367 8(9)	0.191 6(7)
P	0.323 5(1)	−0.064 8(1)	0.335 83(9)	C(46)	0.173 5(6)	0.400 3(6)	0.209 1(5)
Si(1)	−0.049 5(1)	0.461 8(1)	0.312 9(1)	C(51)	−0.099 6(5)	0.470 0(5)	0.221 4(4)
Si(2)	0.242 4(1)	−0.111 1(1)	0.026 8(1)	C(52)	−0.158 0(5)	0.418 9(5)	0.211 5(5)
O(1)	0.180 9(3)	0.137 8(3)	0.380 0(3)	C(53)	−0.199 2(6)	0.431 9(6)	0.145 4(5)
O(2)	0.079 3(3)	−0.007 5(3)	0.344 1(3)	C(54)	−0.178 1(7)	0.498 0(7)	0.087 2(5)
C(1)	0.185 1(4)	0.084 4(4)	0.104 4(3)	C(55)	−0.121 7(8)	0.545 1(7)	0.097 9(5)
C(1′)	−0.062 2(4)	0.283 1(4)	0.383 9(4)	C(56)	−0.082 1(7)	0.531 6(6)	0.164 5(5)
C(2)	0.181 5(4)	0.030 5(4)	0.040 6(3)	C(61)	−0.109 1(5)	0.597 1(5)	0.358 2(4)
C(2′)	−0.097 1(5)	0.389 0(4)	0.393 0(4)	C(62)	−0.053 3(6)	0.627 7(5)	0.400 1(5)
C(3′)	−0.165 6(6)	0.440 3(5)	0.469 5(4)	C(63)	−0.094 8(7)	0.719 7(6)	0.434 6(5)
C(3)	0.134 6(5)	0.088 5(5)	−0.018 2(4)	C(64)	−0.200 5(8)	0.790 7(6)	0.434 3(6)
C(4)	0.094 0(5)	0.193 8(5)	−0.011 3(4)	C(65)	−0.255 2(8)	0.763 8(7)	0.391 0(8)
C(4′)	−0.196 4(7)	0.391 5(6)	0.533 6(5)	C(66)	−0.209 0(7)	0.666 8(6)	0.355 3(7)
C(5)	0.101 8(6)	0.242 1(4)	0.049 2(4)	C(71)	0.442 2(5)	−0.042 4(5)	0.285 3(4)
C(5′)	−0.160 2(6)	0.286 4(5)	0.523 9(5)	C(72)	0.530 9(6)	−0.112 1(6)	0.223 6(5)
C(6)	0.149 8(5)	0.189 4(4)	0.107 3(4)	C(73)	0.617 8(7)	−0.090 2(7)	0.183 7(6)
C(6′)	−0.094 8(6)	0.234 2(5)	0.447 9(5)	C(74)	0.621 6(6)	−0.006 7(7)	0.207 0(5)
C(11)	0.158 5(4)	−0.165 1(4)	0.101 0(4)	C(75)	0.532 9(6)	0.065 0(6)	0.267 0(5)
C(12)	0.073 8(5)	−0.108 1(5)	0.168 9(4)	C(76)	0.443 7(5)	0.046 5(5)	0.305 2(4)
C(13)	0.014 3(6)	−0.151 7(6)	0.222 4(5)	C(81)	0.363 1(5)	−0.197 4(5)	0.308 5(4)
C(14)	0.038 6(6)	−0.251 0(6)	0.207 9(5)	C(82)	0.459 7(7)	−0.271 9(6)	0.321 9(5)
C(15)	0.122 7(7)	−0.309 1(6)	0.137 9(6)	C(83)	0.491 0(8)	−0.372 3(7)	0.303 9(6)
C(16)	0.181 1(6)	−0.265 6(5)	0.086 8(5)	C(84)	0.427 7(9)	−0.399 1(6)	0.275 4(6)
C(21)	0.390 4(5)	−0.163 9(5)	0.027 4(4)	C(85)	0.328 4(7)	−0.326 1(5)	0.261 4(5)
C(22)	0.438 8(5)	−0.247 9(5)	0.068 3(4)	C(86)	0.297 4(6)	−0.224 6(5)	0.277 8(4)
C(23)	0.552 0(6)	−0.282 7(6)	0.065 4(5)	C(91)	0.314 2(4)	−0.060 4(4)	0.443 1(3)
C(24)	0.613 2(5)	−0.239 7(7)	0.022 8(5)	C(92)	0.402 4(5)	−0.070 2(5)	0.470 2(4)
C(25)	0.567 5(5)	−0.158 4(6)	−0.016 4(5)	C(93)	0.390 0(5)	−0.067 8(6)	0.552 9(4)
C(26)	0.457 5(5)	−0.117 4(5)	−0.014 4(4)	C(94)	0.290 1(6)	−0.056 6(6)	0.606 9(4)
C(31)	0.240 1(4)	−0.151 3(4)	−0.074 3(3)	C(95)	0.204 6(5)	−0.046 9(5)	0.579 7(4)
C(32)	0.137 3(5)	−0.125 8(6)	−0.088 3(4)	C(96)	0.215 1(5)	−0.048 1(5)	0.498 3(4)
C(33)	0.132 8(6)	−0.155 1(6)	−0.160 9(5)	Cl(1)	0.378 4(4)	0.602 6(3)	0.604 3(3)
C(34)	0.226 7(5)	−0.206 9(5)	−0.222 0(4)	Cl(2)	0.447 7(3)	0.346 5(4)	0.483 4(4)
C(35)	0.327 1(6)	−0.232 9(6)	−0.209 1(4)	Cl(3)	0.464 5(5)	0.539 1(5)	0.932 2(4)
C(36)	0.333 7(5)	−0.205 7(5)	−0.135 9(4)	C(0)	0.422(1)	0.658(1)	0.530 9(9)
C(41)	0.103 8(5)	0.407 5(4)	0.286 8(4)	C(01)	0.547(1)	0.515(1)	0.940(1)
C(42)	0.155 9(6)	0.379 1(6)	0.348 6(5)				

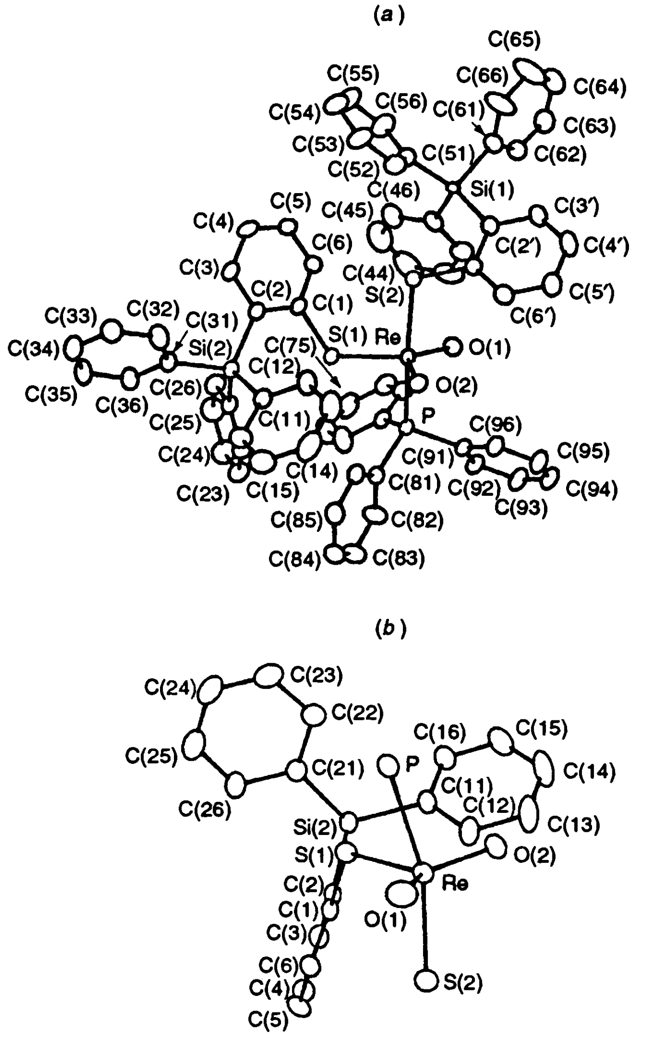


Fig. 1 Structure of [ReO(OH)($SC_6H_4SiPh_3$-2)$_2$(PPh_3)]: (*a*) an ORTEP[5] view showing the atom labelling scheme, (*b*) a reduced view showing the orientation of two of the phenyl groups attached to Si

[1.667(8) Å]. The Re–O(1) distance of 1.931(4) Å is too short for a Re–OH_2 bond (generally *ca.* 2.1 Å) and is attributed to Re–OH. This is also consistent with the observed diamagnetism of the complex (Re^V), and the presence of a sharp IR absorption at 3500 cm^{-1}.

The two thiolate ligands are in *cis* positions, and the *S*-bonded carbons of the thiolate ligands lie close to the Re–S(1)–S(2) plane. The phenylene ring on S(1) twists to bring the $SiPh_3$ group to the same side of the Re as O(2), the other twisting to take its $SiPh_3$ group away from O(2). The dihedral angles of the C_6H_4 rings with the least-squares plane through Re, S(1), C(1), S(2), C(2') are 43.0(2) and 41.1(1)° for the S(1) and S(2) rings respectively.

The oxohydroxo-complex might be viewed as a precursor to the more familiar $Re_2O_3^{4+}$ core which would be formed by the elimination of water. However in this instance the formation of the μ-oxo dimer is precluded by the bulk of the thiolate and phosphine ligands.

Solvent dichloromethane was found with partial occupation in two sites. The first [Cl(1), C(0), Cl(2)] was refined with site-occupation factors of 0.5. The second [Cl(3), C(01)] was very near the centre of symmetry and Cl(3) is disordered across this centre; these atoms also have site-occupation factors of 0.5 giving a total of 1.5 molecules of dichloromethane in the unit cell.

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Re–S(1)	2.278(1)	Re–S(2)	2.328(2)
Re–O(1)	1.931(4)	Re–O(2)	1.688(4)
Re–P	2.492(2)	S(1)–C(1)	1.792(6)
S(2)–C(1')	1.776(6)	P–C(71)	1.813(7)
P–C(81)	1.833(7)	P–C(91)	1.829(6)
Si(1)–C(2')	1.875(7)	Si(1)–C(41)	1.856(8)
Si(1)–C(51)	1.878(8)	Si(1)–C(61)	1.906(7)
Si(2)–C(2)	1.883(6)	Si(2)–C(11)	1.889(7)
Si(2)–C(21)	1.869(7)	Si(2)–C(31)	1.883(6)
S(1)–Re–S(2)	95.75(5)	S(1)–Re–P	83.57(5)
S(1)–Re–O(1)	122.1(2)	S(1)–Re–O(2)	110.8(2)
S(2)–Re–P	160.33(6)	S(2)–Re–O(1)	87.4(1)
S(2)–Re–O(2)	104.7(2)	P–Re–O(1)	76.5(1)
P–Re–O(2)	93.8(2)	O(1)–Re–O(2)	124.1(2)
Re–S(1)–C(1)	117.6(2)	Re–S(2)–C(1')	106.4(2)
Re–P–C(71)	112.5(2)	Re–P–C(81)	116.6(2)
Re–P–C(91)	110.9(2)	C(71)–P–C(81)	106.3(3)
C(71)–P–C(91)	105.8(3)	C(81)–P–C(91)	103.9(3)
C(2')–Si(1)–C(41)	108.2(3)	C(2')–Si(1)–C(51)	114.8(3)
C(2')–Si(1)–C(61)	107.5(3)	C(41)–Si(1)–C(51)	112.1(4)
C(41)–Si(1)–C(61)	108.1(3)	C(51)–Si(1)–C(61)	105.9(3)
C(2)–Si(2)–C(11)	113.3(3)	C(2)–Si(2)–C(21)	108.2(3)
C(2)–Si(2)–C(31)	109.7(3)	C(11)–Si(2)–C(21)	113.8(3)
C(11)–Si(2)–C(31)	103.9(3)	C(21)–Si(2)–C(31)	107.7(3)

Complex [ReH_4($SC_6H_4SiPh_3$-2)(PPh_3)$_3$] **3**.—Reaction of [$ReOBr_3(PPh_3)_2$] with 2-$Ph_3SiC_6H_4SH$ in methanol in the presence of $NaBH_4$ gives the blue complex **3** in high yield. It is moderately stable in the air in the solid state but decomposes rapidly in solution. Suitable crystals for a structure determination were grown from dichloromethane–isopropyl alcohol.

Crystal structure. A graphical representation of the structure of complex **3** appears in Fig. 2, together with a partial atom labelling scheme. Positional parameters and selected bond lengths and angles are given in Tables 4 and 5. Details of the structure determination appear in Table 9.

The three P atoms and the S of the $SC_6H_4SiPh_3$-2 ligand form a distorted tetrahedron around the Re. The Re–P(1) and Re–P(2) bond are of equal length, but Re–P(3) is noticeably longer. All the Re–P distances are shorter than that in compound **2**. The Re–S distance is almost equal to the larger of two in **2**. The principal distortion involves an opening of the opposite S–Re–P(2) and P(1)–Re–P(2) angles, and the S–Re–P(3) angle is relatively small. The hydrogen atoms detected by IR and NMR spectroscopy are not located in the crystal structure, but are assumed to be bound to Re in angular positions roughly capping the four faces of the S, P(1), P(2), P(3) tetrahedron. There are no particularly short C–C distances between atoms on adjacent ligands, but distances in the range of 3.3–3.5 Å between the SC_6H_4 ring and C(25)–C(30) on P(1) suggest some steric interaction. There are contacts of about 3.5 Å between S and C(73), C(74) and C(78). A single molecule of dichloromethane of crystallisation was located in the lattice.

Complex [$IrH(SC_6H_4SiPh_3$-2)$_2$($PMePh_2$)$_3$] **4**.—*Preparation.* Complex **4** was prepared as a pale yellow air-stable solid by the reaction of [$IrCl_3(PMePh_2)_3$] with 4 equivalents of 2-$Ph_3SiC_6H_4SH$ in refluxing methanol in the presence of triethylamine. A crystal suitable for a structure determination was grown from dichloromethane–methanol.

Crystal structure. Representations of the complete structure are shown in Figs. 3 and 4, together with the atom numbering scheme. Two views are presented with different phenyl groups omitted for clarity as the complete views are highly congested. Atomic coordinates appear in Table 6 and selected bond lengths and angles in Table 7. Full details of the structure determination are presented in Table 9. The overall geometry about the Ir is pseudo-octahedral, with the phosphines in a *mer* configuration and the thiolates *cis*. The thiolate aromatic rings are disposed so

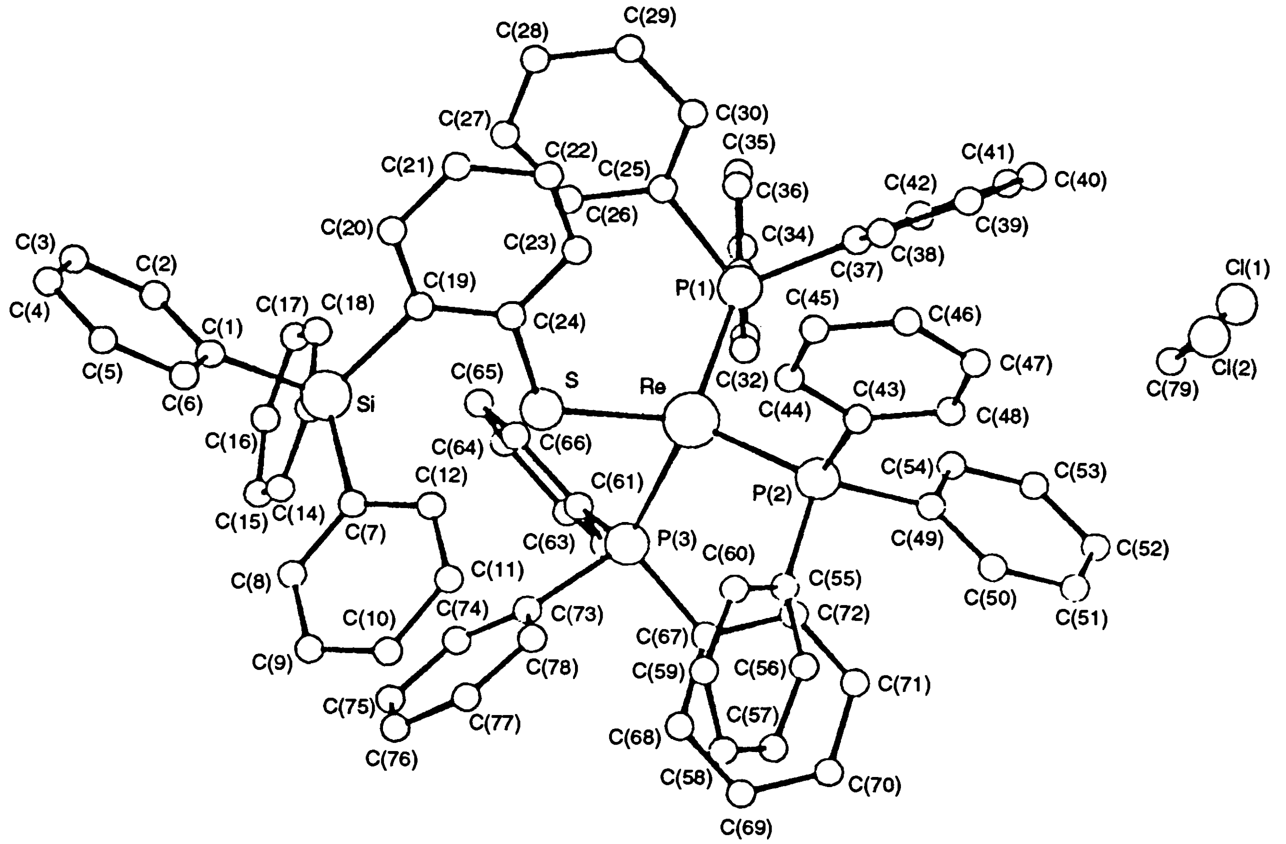


Fig. 2 An ORTEP view of the structure of $[ReH_4(SC_6H_4SiPh_3\text{-}2)(PPh_3)_3]\cdot CH_2Cl_2$, with an atom labelling scheme

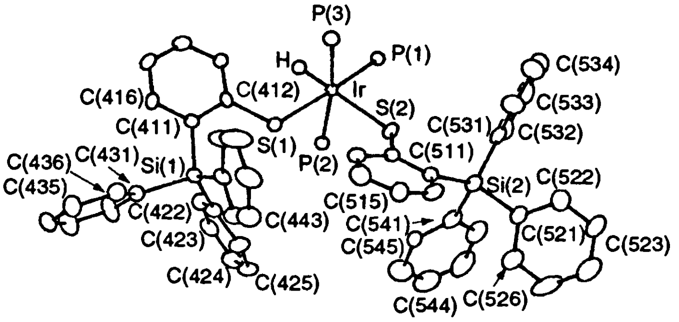


Fig. 3 An ORTEP view of the structure of $[IrH(SC_6H_4SiPh_3\text{-}2)_2(PMePh_2)_3]$ showing an atom labelling scheme, and omitting phosphine methyl and phenyl groups for clarity

as to move the bulky $SiPh_3$ substituents as far as possible away from one another and the phosphine phenyl groups. The hydride ligand is assumed to be located in the vacant site *trans* to S(2). The Ir–P distances are unremarkable and lie in the range found for other iridium phosphine complexes. The Ir–S distances are significantly different with Ir–S(1) 2.439(2) and Ir–S(2) 2.520(3) Å. The long Ir–S(2) distance presumably reflects the *trans* influence of the hydride ligand. The S(1)-Ir-S(2) angle is opened up to 98.00(9)° compared to the ideal octahedral value of 90° due to steric repulsions between the bulky thiolate groups.

Spectroscopic properties. The IR spectrum of complex **4** as a Nujol mull shows a medium-intensity band at 2226 cm^{-1} assigned to Ir–H. The ^1H NMR spectrum of a fresh solution in $CDCl_3$ shows an overlapping doublet and triplet at δ 1.75 due to the phosphine methyls, consistent with their *mer* configuration. The high-field region of the spectrum shows an apparent quartet at δ −16.38 due to coupling with the three phosphorus ligands. In view of the fact that the ^{31}P NMR spectrum shows a triplet and a doublet [Fig. 5(*a*)], indicating that there are inequivalent phosphines, the ^1H NMR hydride region might be expected to comprise a doublet of triplets. The observed quartet indicates that P–H couplings to the *cis*-P atoms may be virtually identical, and the complex is assigned the structure **A**. An alternative possibility is that the molecule is fluxional, but in view of the apparent rigidity shown in Fig. 5(*b*) we prefer the explanation that the coupling constants are the same.

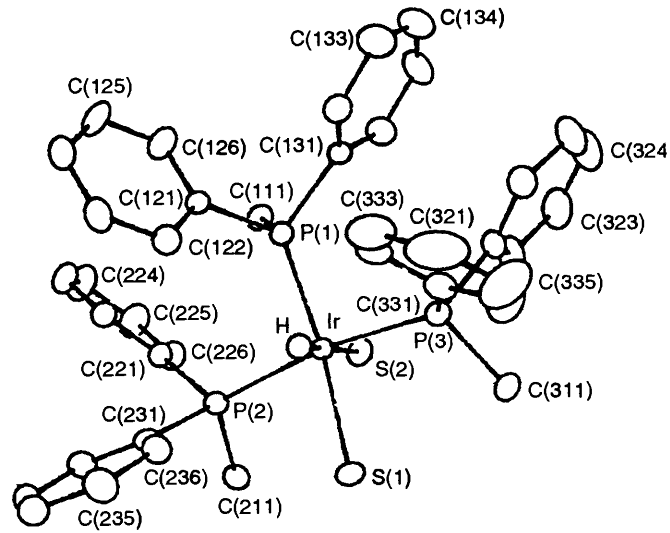


Fig. 4 An ORTEP view of the structure of $[IrH(SC_6H_4SiPh_3\text{-}2)_2(PMePh_2)_3]$ with the triphenylsilylphenyl groups omitted for clarity

After 30 min in solution the ^1H and ^{31}P NMR spectra show the emergence of a second species. The ^{31}P NMR spectrum of

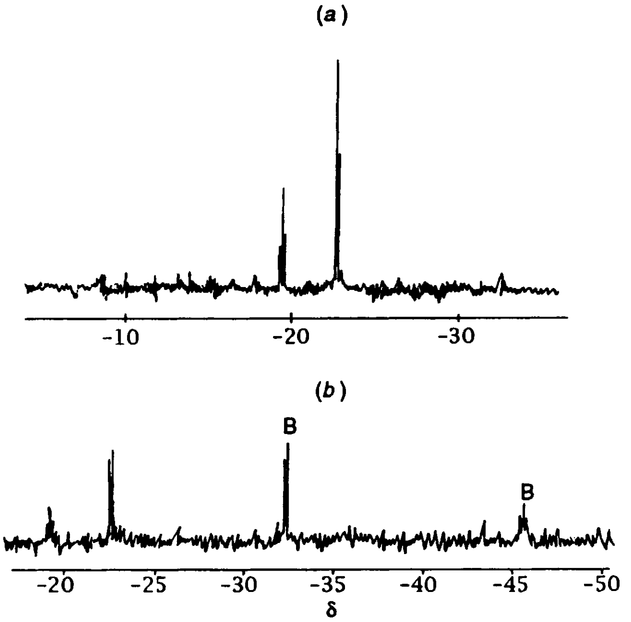
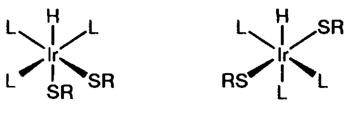


Fig. 5 The ^{31}P NMR spectra of $[IrH(SC_6H_4SiPh_3\text{-}2)_2(PMePh_2)_3]$ recorded in $CDCl_3$: (*a*) fresh solution, (*b*) after standing for 30 min under dinitrogen



A **B**

L = PMePh$_2$
R = 2-Ph$_3$SiC$_6$H$_4$

the new species (labelled B) in Fig. 5(*b*) indicates retention of the meridional configuration for the P atoms. A doublet of triplets is apparent in the hydride region [Fig. 5(*b*)] consistent with coupling to three P atoms in a *mer* arrangement. Complex **4** is isomerising in solution to give a second species in which the P–H coupling constants to the hydride hydrogen are no longer the same. This isomer is assigned the structure **B** with the two bulky thiolate ligands now *trans*.

General Comments on the Co-ordination of the $SC_6H_4SiPh_3\text{-}2$ *Ligand.*—The principal reason for investigating the co-ordination chemistry of the $SC_6H_4SiPh_3\text{-}2$ ligand is to determine to what extent the single bulky $SiPh_3$ group is able to control it, and the effect of the asymmetric substituent pattern. None of its complexes structurally characterised to date have bridging thiolates, but analysis of the eight structures below indicates how the substituent orientation will permit bridging provided the steric demands from the other ligands around the metal are minimal. The structures analysed cover five different $M\text{–}SC_6H_4SiPh_3\text{-}2$ types of co-ordination and those of $(2\text{-}Ph_3SiC_6H_4S)_2$ and $[2\text{-}Ph_3SiC_6H_4S\text{–}PPh_3]^+$ provide three further environments, albeit not at a metal site.

Fig. 6 shows the distribution in space of the atoms A in species of the type $2\text{-}Ph_3SiC_6H_4S\text{–}A$ relative to the common SiC_6H_4S unit. The coordinate system is defined in the legend. The C_6H_4 ring lies in the *zx* plane with all *x* values positive. The atoms A all lie close to the *zy* plane *i.e.* in a plane orthogonal to the SiC_6H_4S plane, and in three cases (Re in complex **3** and both iridium positions in **4**) the A atom is in the *zx* plane giving a linear Si–S–A arrangement. This moves the $SiPh_3$ group as far as possible from the metal and occurs for the complexes with higher co-ordination numbers and bulky co-ligands. In each of the other five cases the complexes are less sterically crowded, and A lies well out of the SiC_6H_4S (*zx*) plane. In all cases one of the $SiPh_3$ phenyls is arranged with the Si-bound C almost opposite the S. The two other phenyl groups form a pair of wings on either side of the phenylene ring which completely shield one side of the S atom. This is illustrated in Fig. 1(*b*). Table 8 provides additional geometric data for the complete series of derivatives discussed above.

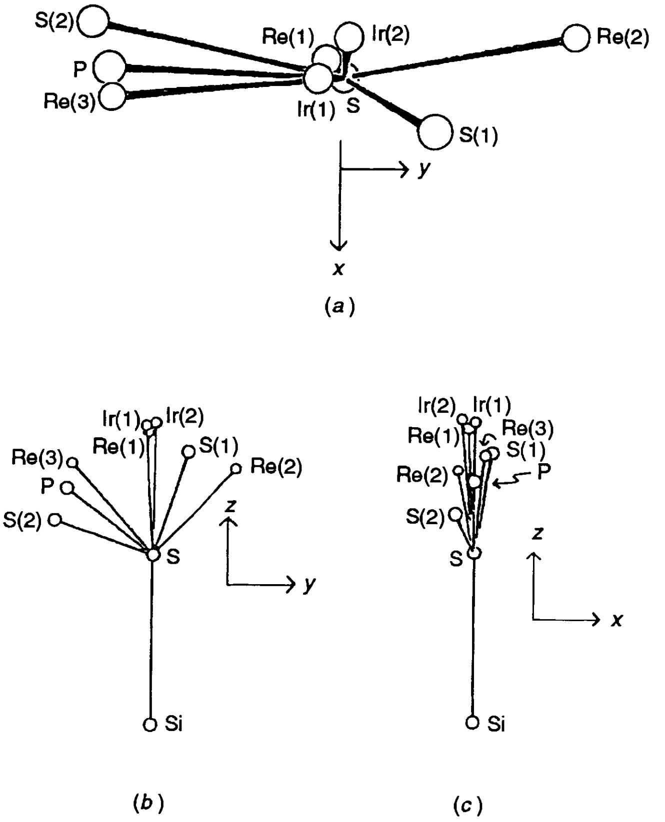


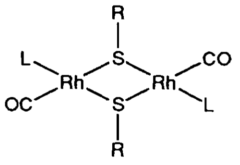
Fig. 6 Diagrams summarising the orientations of the $SC_6H_4SiPh_3\text{-}2$ ligand projected down the *z* (*a*), *x* (*b*) and *y* axis (*c*). Coordinate system: *z* = Si–S direction, *y* = nomal to $SC_6H_4SiPh_3$ least-squares plane and *x* = third orthogonal coordinate ($y \times z$). The A atoms are S(1), S(2) from $(2\text{-}Ph_3SiC_6H_4S)_2$, P from $[2\text{-}Ph_3SiC_6H_4S\text{–}PPh_3]^+$, Re(2), Re(3) from complex **2** Re(1) from **3** and Ir(1), Ir(2) from **4**

In summary we suggest that when atom A bears three or more bulky ligands additional to $2\text{-}Ph_3SiC_6H_4S$ then A is forced into the SiC_6H_4S plane. This has the effect of bringing the hydrogen *ortho* to S closer to the metal, and although not detected in these structures, agostic interactions or ortho-metallation should be favoured. The orientation of the phenylene ring means that the bulk of the $SiPh_3$ group lies further from the metal than for thiols symmetrically substituted with bulky groups. Nevertheless $2\text{-}Ph_3SiC_6H_4S$ is able to produce unusual low-co-ordination-number complexes as illustrated in this paper. For the less-crowded complexes A lies well out of the SiC_6H_4S plane and the *o*-hydrogen is consequently further from A. Another feature of the analysis is that the $SiPh_3$ group does permit the $2\text{-}Ph_3SiC_6H_4S$ ligand to bridge two metal atoms, as in complex **6** (see below), where there is only one other bulky ligand on the metal. In **5** and **7**–**9** there are three other phenyl-bearing ligands, and the complexes are monomeric.

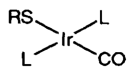
Complexes $[Rh_2(\mu\text{-}SC_6H_4SiPh_3\text{-}2)_2(CO)_2(PPh_3)_2]$ **5** *and* $[Ir(SC_6H_4SiPh_3\text{-}2)(CO)(PPh_3)_2]$ **6**.—*Preparation.* Complexes **5** and **6** were prepared in good yield from $[MCl(CO)(PPh_3)_2]$ (M = Rh or Ir) and $2\text{-}Ph_3SiC_6H_4SH$ (4 equivalents) in methanol under reflux. They were isolated as yellow

Table 4 Positional parameters for $[ReH_4(SC_6H_4SiPh_3\text{-}2)(PPh_3)_3]\cdot CH_2Cl_2$ **3**

Atom	x	y	z	Atom	x	y	z
Re	3659.0(1)	2953.8(1)	4018.8(1)	C(39)	3155(1)	2610(3)	1412(3)
S	4133.1(5)	2532(1)	4614(1)	C(40)	2955(1)	3326(4)	1054(2)
P(1)	3610.5(5)	4076(1)	3168(1)	C(41)	2952(1)	4282(4)	1325(3)
P(2)	3292.0(5)	1814(1)	3617(1)	C(42)	3149(1)	4522(3)	1954(3)
P(3)	3646.1(5)	3503(1)	5114(1)	C(43)	3317(1)	888(3)	2968(2)
Si	4809.0(5)	2078(2)	5518(1)	C(44)	3589(1)	567(3)	3023(2)
C(1)	5210(1)	1897(4)	5807(3)	C(45)	3623(1)	−90(3)	2548(3)
C(2)	5389(1)	2716(3)	5840(3)	C(46)	3386(1)	−425(3)	2018(2)
C(3)	5681(1)	2562(3)	6006(3)	C(47)	3113(1)	−105(3)	1964(2)
C(4)	5793(1)	1589(4)	6138(3)	C(48)	3079(1)	552(3)	2438(3)
C(5)	5614(1)	770(3)	6105(3)	C(49)	2904(1)	2147(4)	3275(3)
C(6)	5322(1)	925(3)	5940(3)	C(50)	2691(1)	1457(3)	3258(3)
C(7)	4667(1)	958(3)	5882(3)	C(51)	2406(1)	1755(4)	3021(3)
C(8)	4761(1)	777(4)	6567(3)	C(52)	2333(1)	2743(5)	2800(3)
C(9)	4672(1)	−85(4)	6810(2)	C(53)	2546(1)	3433(3)	2817(3)
C(10)	4487(1)	−767(3)	6367(3)	C(54)	2831(1)	3135(4)	3054(3)
C(11)	4393(1)	−586(3)	5682(3)	C(55)	3306(1)	905(3)	4301(2)
C(12)	4483(1)	276(4)	5439(2)	C(56)	3136(1)	1063(3)	4683(3)
C(13)	4754(1)	3365(3)	5820(3)	C(57)	3161(1)	431(4)	5222(3)
C(14)	4727(1)	3485(4)	6442(3)	C(58)	3357(1)	−360(4)	5379(2)
C(15)	4719(2)	4451(5)	6694(2)	C(59)	3528(1)	−519(3)	4996(3)
C(16)	4738(1)	5297(3)	6324(3)	C(60)	3502(1)	114(4)	4457(3)
C(17)	4765(1)	5177(3)	5703(3)	C(61)	3743(1)	4858(2)	5280(3)
C(18)	4773(1)	4211(4)	5451(2)	C(62)	3572(1)	5541(4)	5462(3)
C(19)	4657(1)	2030(3)	4561(2)	C(63)	3653(1)	6552(3)	5574(3)
C(20)	4849(1)	1799(3)	4244(3)	C(64)	3905(1)	6880(2)	5504(3)
C(21)	4751(1)	1682(3)	3552(3)	C(65)	4076(1)	6197(4)	5322(3)
C(22)	4462(1)	1796(3)	3177(2)	C(66)	3995(1)	5186(3)	5210(3)
C(23)	4271(1)	2028(3)	3494(2)	C(67)	3300(1)	3426(3)	5263(3)
C(24)	4368(1)	2144(3)	4186(2)	C(68)	3286(1)	3033(3)	5855(2)
C(25)	3950(1)	4249(3)	3006(3)	C(69)	3025(1)	2961(3)	5943(2)
C(26)	4189(1)	4537(3)	3548(2)	C(70)	2776(1)	3282(3)	5437(3)
C(27)	4456(1)	4580(3)	3482(2)	C(71)	2790(1)	3675(3)	4845(2)
C(28)	4483(1)	4335(3)	2875(3)	C(72)	3052(1)	3747(3)	4758(2)
C(29)	4244(1)	4047(3)	2332(2)	C(73)	3885(1)	2908(4)	5900(2)
C(30)	3977(1)	4004(3)	2398(2)	C(74)	4015(1)	3464(3)	6483(3)
C(31)	3534(1)	5456(2)	3255(3)	C(75)	4165(1)	2969(4)	7079(2)
C(32)	3404(1)	5777(3)	3697(3)	C(76)	4185(1)	1918(4)	7093(2)
C(33)	3347(1)	6800(4)	3744(3)	C(77)	4055(1)	1362(3)	6510(3)
C(34)	3421(1)	7502(2)	3347(3)	C(78)	3905(1)	1858(3)	5914(2)
C(35)	3551(1)	7181(3)	2904(3)	C(79)	2390(2)	2226(6)	1296(5)
C(36)	3607(1)	6158(4)	2858(2)	Cl(1)	2202(1)	3205(2)	769(2)
C(37)	3348(1)	3806(4)	2312(2)	Cl(2)	2384(1)	1121(2)	836(2)
C(38)	3351(1)	2850(3)	2041(3)				



5



6

L = PPh_3, R = 2-$Ph_3SiC_6H_4$

precipitates, stable in air both in the solid state and solution. The catalytic activity of these complexes and others reported below will be described elsewhere.

Spectroscopic properties. The IR spectra of both complexes showed strong sharp absorptions in the range 1960–1980 cm^{-1} assigned to ν(C–O). The ^{31}P NMR spectrum of **6** shows a singlet indicating equivalent phosphines, and **5** exhibits a doublet [J(Rh–P) = 134.2 Hz] again consistent with equivalent phosphine donors. The ^1H NMR spectra are uninformative with only complex multiplets due to phenyl protons visible at around δ 7. The proposed structures of the complexes are as shown.

Complex $[OsH(SC_6H_4SiPh_3\text{-}2)(CO)(PPh_3)_3]$ **7**.—The complex $[OsH(CO)(PPh_3)_3]$ was heated under reflux in methanol with an excess of 2-$Ph_3SiC_6H_4SH$ in methanol to precipitate **7** as a yellow solid. The complex is stable in the solid state, but decomposes in solution in the air.

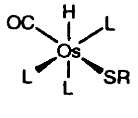
Spectroscopic properties. The IR spectrum shows a sharp medium-intensity band at 2153 cm^{-1} due to ν(Os–H) and a strong band at 1909 cm^{-1} with a shoulder at 1891 cm^{-1} assigned to ν(C–O). The ^{31}P NMR spectrum of a fresh solution shows a doublet and triplet indicative of two sets of inequivalent phosphine ligands. A peak is also observed at δ 32.1 characteristic of $Ph_3P{=}O$, consistent with oxidation of the complex in solution. The ^1H NMR spectrum showed the expected doublet of triplets (δ −7.74t, −8.0t) due to the coupling of the hydride hydrogen to three phosphines in a *mer*-configuration. A singlet is also observed at δ 5.30 due to the CH_2Cl_2 of crystallisation. On the basis of the above the complex may have any of the three structures **C**–**E**.

Complex $[Ru(SC_6H_4SiPh_3\text{-}2)_2(CO)(PPh_3)_2]$ **8**.—Complex **8** was prepared analogously to **6** starting from $[RuH(Cl)(PPh_3)_3]$, and isolated as an orange precipitate. This was recrystallised as a dichloromethane solvate from dichloro-

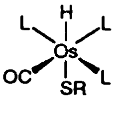
Table 5 Selected bond lengths (Å) and angles (°) for complex **3**

Re–P(1)	2.289(2)	Re–P(2)	2.291(2)
Re–P(3)	2.470(2)	Re–S	2.326(2)
S–C(24)	1.800(4)	P(1)–C(25)	1.864(4)
P(1)–C(31)	1.844(4)	P(1)–C(37)	1.865(5)
P(2)–C(43)	1.885(4)	P(2)–C(49)	1.869(5)
P(2)–C(55)	1.870(4)	P(3)–C(61)	1.855(4)
P(3)–C(67)	1.871(4)	P(3)–C(73)	1.853(5)
Si–C(1)	1.890(4)	Si–C(7)	1.918(4)
Si–C(13)	1.871(4)	Si–C(19)	1.911(4)
C(79)–Cl(1)	1.751(8)	C(79)–Cl(2)	1.751(8)
P(1)–Re–P(2)	106.4(1)	P(1)–Re–S	112.9(1)
P(2)–Re–S	125.0(1)	P(1)–Re–P(3)	122.0(1)
P(2)–Re–P(3)	105.1(1)	S–Re–P(3)	85.3(1)
C(24)–S–Re	120.9(2)	C(25)–P(1)–C(37)	102.3(3)
C(25)–P(1)–C(31)	97.6(2)	C(37)–P(1)–C(31)	100.6(3)
C(25)–P(1)–Re	112.3(2)	C(37)–P(1)–Re	119.5(2)
C(31)–P(1)–Re	121.0(2)	C(49)–P(2)–C(55)	101.7(3)
C(49)–P(2)–C(43)	101.3(3)	C(55)–P(2)–C(43)	99.4(2)
C(49)–P(2)–Re	125.1(2)	C(55)–P(2)–Re	109.0(2)
C(43)–P(2)–Re	116.6(2)	C(73)–P(3)–C(61)	101.2(3)
C(73)–P(3)–C(67)	99.3(3)	C(61)–P(3)–C(67)	102.4(2)
C(73)–P(3)–Re	120.4(2)	C(61)–P(3)–Re	111.7(2)
C(67)–P(3)–Re	118.8(2)	C(13)–Si–C(1)	105.6(3)
C(13)–Si–C(19)	110.3(3)	C(1)–Si–C(19)	108.6(3)
C(13)–Si–C(7)	116.1(3)	C(1)–Si–C(7)	105.8(3)
C(19)–Si–C(7)	110.0(2)		

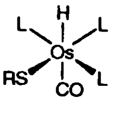
Non-bonded angle Re–S–Si 176.1(1)



C



D



E

L = PPh$_3$, R = 2-Ph$_3$SiC$_6$H$_4$

methane–methanol. The complex is stable in air in the solid state and moderately stable in solution even in air.

Spectroscopy. A strong IR band at 1923 cm^{-1} is assigned to ν(C–O). The ^{31}P NMR spectrum shows a singlet at δ 30.6, consistent with equivalent environments for the two phosphine ligands. The ^{1}H NMR spectrum showed the expected multiplet for phenyl protons and a sharp singlet at δ 5.3 due to the CH$_2$Cl$_2$ of crystallisation. The complex is formally five-co-ordinate Ru^{II} with 16 valence electrons. It is highly probable that, as found for other 16-electron ruthenium(II) thiolates, there is an agostic interaction of a phenyl hydrogen with the metal to give pseudo-octahedral co-ordination.

Reactions of [RuCl$_2$(PPh$_3$)$_3$] *and* [RhCl(PPh$_3$)$_3$].—Reaction of [RhCl(PPh$_3$)$_3$] with 2-Ph$_3$SiC$_6$H$_4$SH in methanol in the presence of triethylamine gives a dark red complex **9** the elemental analysis of which (see Table 1) suggests the formulation [Rh(SC$_6$H$_4$SiPh$_3$-2)(PPh$_3$)$_3$]. Due to rapid decomposition in solution even under dinitrogen it was not possible to record the ^{1}H or ^{31}P NMR spectra. However, the colour suggests the complex may well be monomeric, as dimeric species are generally yellow or orange (see complex **5**). Crystals apparently suitable for a structure determination were obtained, but these decomposed during data collection, despite being sealed in a capillary tube under dinitrogen. Many of these thiolate complexes of Rh and Ru are active for a number of catalytic processes, and the results of these studies will be reported elsewhere.

Analogous reaction of [RuCl$_2$(PPh$_3$)$_3$] with 2-Ph$_3$SiC$_6$H$_4$SH in methanol under reflux in the presence of triethylamine gave a dark green solid. However this decomposed on attempted recrystallisation and was not fully characterised.

Complexes of SiPh$_2$(C$_6$H$_4$SH-2)$_2$.—This compound was synthesised by a straightforward modification of the literature route *via* the lithiation of benzenethiol. Consideration of molecular models suggested that it might be capable of spanning *trans* sites in a square-planar complex, and we therefore directed our investigations towards d^8 metal complex precursors. Although a number of solid complexes were isolated, these could not be satisfactorily characterised in the absence of crystal structural information.

Experimental

All reactions were carried out under dinitrogen using conventional Schlenk tube and syringe techniques. All solvents were freshly distilled from appropriate drying agents under dinitrogen. Analytical data were obtained from the Microanalysis Laboratory, University of Manchester. Infrared spectra were recorded as Nujol mulls between NaCl plates using a Perkin-Elmer 1330 spectrophotometer, ^{1}H and ^{31}P NMR on an EX-270 JEOL spectrometer.

The compounds [ReOX$_3$(PPh$_3$)$_2$][9] (X = Cl or Br), [RhCl(PPh$_3$)$_3$],[10] [IrCl(CO)(PPh$_3$)$_2$],[11] [RuCl$_2$(PPh$_3$)$_3$],[12] [OsH(Cl)(CO)(PPh$_3$)$_3$],[13] [RhCl(CO)(PPh$_3$)$_2$],[14] 2-triphenylsilylthiophenol[2] and diphenylbis(2-sulfanylphenyl)silane[2] were prepared by literature methods.

Preparations.—[ReO(Cl)(SC$_6$H$_4$SiPh$_3$-2)$_2$(PPh$_3$)] **1**. To a suspension of [ReOCl$_3$(PPh$_3$)$_2$] (0.15 g, 0.18 mmol) in methanol (30 cm^3) was added 2-Ph$_3$SiC$_6$H$_4$SH (0.13 g, 0.36 mmol) and lithium methoxide (0.014 g, 0.36 mmol). The suspension was heated under reflux for 4 h to give a dark green complex. This was filtered off in air and washed with methanol and diethyl ether. Yield 0.12 g, 54%.

[ReO(OH)(SC$_6$H$_4$SiPh$_3$-2)$_2$(PPh$_3$)] **2**. This complex was prepared in an analogous manner to **1** above, using [ReOBr$_3$(PPh$_3$)$_2$] (0.20 g) and triethylamine as the base, as a dark green solid (0.11g, 45%). Deep green crystals suitable for a structure determination were obtained by recrystallisation from dichloromethane–methanol.

[ReH$_4$(SC$_6$H$_4$SiPh$_3$-2)(PPh$_3$)$_3$] **3**. The complex [ReOBr$_3$(PPh$_3$)$_2$] (0.1 g, 0.1 mmol), 2-Ph$_3$SiC$_6$H$_4$SH (0.12 g, 0.3 mmol) and NaBH$_4$ (0.1 g, 2.5 mmol) were heated under reflux in ethanol (30 cm^3) for 5 h to give a deep blue solid (0.08 g, 55%). Blue crystals suitable for a structure dermination were obtained from dichloromethane–methanol.

[IrH(SC$_6$H$_4$SiPh$_3$-2)$_2$(PMePh$_2$)$_3$] **4**. To a suspension of [IrCl$_3$(PMePh$_2$)$_3$] (0.11 g, 0.12 mmol) in methanol (25 cm^3) was added 4 mole equivalents of 2-Ph$_3$SiC$_6$H$_4$SH (0.18 g, 0.49 mmol) and about an equivalent of triethylamine (0.15 cm^3). The suspension was heated under reflux for 3 h. The pale yellow precipitate was filtered off and washed with methanol and ether. Yield 0.13 g, 71%.

A pale yellow suspension of the above crude compound (0.06 g) in CH$_2$Cl$_2$ was stirred for a few minutes in air until it dissolved completely to give a pale yellow solution. A layer of methanol was carefully placed on the surface. A small amount of pale yellow crystals suitable for an X-ray determination were obtained after 1 d at room temperature.

[Rh$_2$(μ-SC$_6$H$_4$SiPh$_3$-2)$_2$(CO)$_2$(PPh$_3$)$_2$] **5**. A suspension of [RhCl(CO)(PPh$_3$)$_2$] (0.08 g, 0.12 mmol) in methanol (25 cm^3) was treated with 2-Ph$_3$SiC$_6$H$_4$SH and triethylamine as for complex **4**. The suspension was heated under reflux for 2 h. The yellow precipitate was filtered off immediately and washed with methanol and ether. Yield 0.08 g, 88%.

[Ir(SC$_6$H$_4$SiPh$_3$-2)(CO)(PPh$_3$)$_2$] **6**. A suspension of [IrCl(CO)(PPh$_3$)$_2$] (0.09 g, 0.12 mmol) in methanol (25 cm^3) was

Table 6 Positional parameters for $[IrH(SC_6H_4SiPh_3\text{-}2)_2(PMePh_2)_3]$ **4**

Atom	*x*	*y*	*z*
Ir	−0.002 88(1)	0.280 03(3)	0.254 30(1)
S(1)	0.062 90(9)	0.138 5(2)	0.269 8(1)
S(2)	−0.083 65(9)	0.182 2(2)	0.181 4(1)
P(1)	−0.060 44(9)	0.418 1(2)	0.253 4(1)
P(2)	−0.018 88(9)	0.181 9(2)	0.332 6(1)
P(3)	0.024 84(9)	0.354 6(2)	0.178 6(1)
Si(1)	0.151 0(1)	−0.051 5(2)	0.299 7(1)
Si(2)	−0.194 2(1)	0.070 8(2)	0.093 1(1)
C(111)	−0.129 9(4)	0.381 7(8)	0.236 3(4)
C(121)	−0.042 9(4)	0.492 9(7)	0.326 6(4)
C(122)	0.006 9(4)	0.484 4(8)	0.374 2(4)
C(123)	0.017 5(4)	0.539 1(8)	0.429 0(4)
C(124)	−0.021 9(5)	0.602 9(8)	0.435 8(4)
C(125)	−0.070 5(5)	0.612 5(9)	0.388 6(5)
C(126)	−0.079 7(4)	0.558 9(9)	0.334 5(5)
C(131)	−0.072 7(4)	0.530 6(7)	0.199 7(4)
C(132)	−0.044 5(4)	0.624 9(8)	0.215 0(4)
C(133)	−0.056 8(5)	0.716(1)	0.177 3(6)
C(134)	−0.101 4(5)	0.706(1)	0.121 4(5)
C(135)	−0.129 5(5)	0.613(1)	0.104 5(5)
C(136)	−0.115 0(4)	0.525 1(9)	0.143 1(5)
C(211)	−0.024 8(4)	0.040 4(7)	0.316 8(4)
C(221)	−0.078 6(3)	0.207 6(7)	0.348 2(4)
C(222)	−0.079 3(3)	0.284 6(8)	0.391 7(4)
C(223)	−0.125 8(4)	0.305 3(9)	0.401 8(4)
C(224)	−0.172 5(4)	0.249(1)	0.370 2(5)
C(225)	−0.172 4(4)	0.174(1)	0.328 1(5)
C(226)	−0.126 3(4)	0.153 9(9)	0.317 5(4)
C(231)	0.032 2(3)	0.185 1(7)	0.411 2(4)
C(232)	0.020 3(4)	0.136 1(8)	0.458 5(4)
C(233)	0.058 9(4)	0.130 1(9)	0.517 6(4)
C(234)	0.108 0(4)	0.170 9(9)	0.531 6(4)
C(235)	0.120 5(4)	0.219(1)	0.485 5(5)
C(236)	0.082 5(4)	0.227 1(9)	0.425 8(4)
C(311)	0.055 4(4)	0.257 8(8)	0.143 3(4)
C(321)	−0.021 5(4)	0.414 6(8)	0.107 6(4)
C(322)	−0.063 3(4)	0.354(1)	0.067 9(5)
C(323)	−0.096 9(5)	0.393(1)	0.010 1(5)
C(324)	−0.088 2(5)	0.496(1)	−0.006 6(5)
C(325)	−0.047 3(5)	0.556(1)	0.031 9(5)
C(326)	−0.013 1(4)	0.517 9(9)	0.091 2(5)
C(331)	0.078 2(4)	0.452 7(8)	0.207 6(4)
C(332)	0.082 3(4)	0.516 7(8)	0.258 2(5)
C(333)	0.125 0(5)	0.586 8(9)	0.283 6(6)
C(334)	0.164 2(5)	0.592(1)	0.259 6(8)
C(335)	0.159 7(5)	0.532(1)	0.2093(7)
C(336)	0.116 5(5)	0.464(1)	0.182 6(6)
C(411)	0.168 8(3)	0.093 2(7)	0.315 4(4)
C(412)	0.130 6(3)	0.176 2(7)	0.303 9(3)
C(413)	0.148 4(3)	0.282 4(8)	0.318 6(4)
C(414)	0.203 1(4)	0.303 9(8)	0.343 5(4)
C(415)	0.239 9(4)	0.227 3(9)	0.353 4(4)
C(416)	0.223 5(3)	0.121 1(8)	0.340 7(4)
C(421)	0.110 6(4)	−0.095 7(7)	0.345 1(4)
C(422)	0.124 7(4)	−0.054 7(8)	0.404 1(4)
C(423)	0.099 7(4)	−0.092 7(8)	0.443 1(4)
C(424)	0.060 2(4)	−0.167 8(9)	0.423 3(4)
C(425)	0.043 9(4)	−0.207 1(8)	0.364 0(4)
C(426)	0.068 5(4)	−0.171 3(8)	0.325 2(4)
C(431)	0.215 5(3)	−0.130 4(7)	0.331 3(4)
C(432)	0.239 7(4)	−0.161(1)	0.393 7(5)
C(433)	0.285 9(5)	−0.218(1)	0.416 2(5)
C(434)	0.311 0(4)	−0.250 9(8)	0.377 7(5)
C(435)	0.289 2(4)	−0.222(1)	0.316 7(4)
C(436)	0.241 9(4)	−0.163 2(9)	0.294 3(4)
C(441)	0.123 6(4)	−0.078 5(7)	0.214 2(4)
C(442)	0.100 9(4)	−0.175 3(9)	0.188 7(4)
C(443)	0.091 0(4)	−0.199 0(8)	0.127 2(5)
C(444)	0.106 3(5)	−0.129 3(9)	0.092 0(5)
C(445)	0.128 7(6)	−0.036(1)	0.116 5(5)
C(446)	0.137 6(5)	−0.009 4(9)	0.176 7(4)
C(511)	−0.128 1(4)	0.044 4(7)	0.086 6(4)
C(512)	−0.079 6(3)	0.084 4(7)	0.128 6(4)
C(513)	−0.031 6(4)	0.047 4(8)	0.129 0(5)
C(514)	−0.031 7(4)	−0.028 4(9)	0.083 1(5)
C(515)	−0.078 1(4)	−0.060 4(8)	0.039 8(4)
C(516)	−0.124 6(4)	−0.027 0(8)	0.042 2(4)
C(521)	−0.248 0(4)	−0.006 0(9)	0.032 6(4)
C(522)	−0.288 6(5)	0.039(1)	−0.017 6(6)
C(523)	−0.331 8(5)	−0.019(1)	−0.056 5(6)
C(524)	−0.333 5(5)	−0.127(1)	−0.048 9(5)
C(525)	−0.293 4(5)	−0.175(1)	0.000 5(5)
C(526)	−0.251 7(4)	−0.118(1)	0.039 6(5)
C(531)	−0.215 6(3)	0.214 3(9)	0.082 8(4)
C(532)	−0.237 2(4)	0.269 9(9)	0.118 6(5)
C(533)	−0.253 9(4)	0.378(1)	0.103 8(6)
C(534)	−0.250 9(5)	0.429(1)	0.054 1(5)
C(535)	−0.231 0(5)	0.373(1)	0.018 5(6)
C(536)	−0.214 2(5)	0.269(1)	0.031 1(5)
C(541)	−0.192 5(4)	0.005 7(9)	0.166 5(4)
C(542)	−0.150 5(4)	−0.064 1(8)	0.197 4(4)
C(543)	−0.151 2(5)	−0.132(1)	0.246 2(5)
C(544)	−0.196 6(6)	−0.127(1)	0.260 1(6)
C(545)	−0.238 6(5)	−0.063(1)	0.229 9(6)
C(546)	−0.237 4(5)	0.007(1)	0.181 9(5)

Table 7 Selected bond lengths (Å) and angles (°) for complex **4**

Ir–S(1)	2.439(2)	Ir–S(2)	2.520(3)
Ir–P(1)	2.322(3)	Ir–P(2)	2.382(3)
Ir–P(3)	2.363(3)	S–C(412)	1.757(9)
S(2)–C(512)	1.77(1)	P(1)–C(111)	1.82(1)
P(1)–C(121)	1.85(1)	P(1)–C(131)	1.84(1)
P(2)–C(211)	1.81(1)	P(2)–C(221)	1.811(9)
P(2)–C(231)	1.83(1)	P(3)–C(311)	1.83(1)
P(3)–C(321)	1.82(1)	P(3)–C(331)	1.82(1)
S(1)–Ir–S(2)	98.00(9)	S(1)–Ir–P(1)	172.50(9)
S(1)–Ir–P(2)	80.96(9)	S(1)–Ir–P(3)	88.88(9)
S(2)–Ir–P(1)	87.39(9)	S(2)–Ir–P(2)	84.71(9)
S(2)–Ir–P(3)	97.02(9)	P(1)–Ir–P(2)	94.41(9)
P(1)–Ir–P(3)	95.67(9)	P(2)–Ir–P(3)	169.84(9)
Ir–S(1)–C(412)	116.3(3)	Ir–S(2)–C(512)	122.9(3)
Non-bonded angles (°)			
Ir–S(1)–Si(1)	176.2(1)	Ir–S(1)–Si(2)	174.4(1)

Table 8 Summary of structural data for $SC_6H_4SiPh_3\text{-}2$ complexes

Compound	Si–S–A unit	S–A/Å	δ/°
$(2\text{-}Ph_3SiC_6H_4S)_2$*	Si(1)–S(1)–S(2)	2.037(1)	70.7(1)
	Si(2)–S(2)–S(1)	2.037(1)	20.2(1)
$[2\text{-}Ph_3SiC_6H_4S{\cdot}PPh_3]$*	Si–S–P	2.082(4)	52.8(5)
$[ReH_4(SC_6H_4SiPh_3\text{-}2)(PPh_3)_3]$	Si–S–Re	2.326(2)	3.9(1)
$[ReO(OH)(SC_6H_4SiPh_3\text{-}2)_2\text{-}(PPh_3)]$	Si(2)–S(1)–Re	2.278(1)	44.2(1)
	Si(1)–S(2)–Re	2.328(2)	42.2(1)
$[IrH(SC_6H_4SiPh_3\text{-}2)_2(PMePh_2)_3]$	Si(1)–S(1)–Ir	2.439(2)	3.8(1)
	Si(2)–S(2)–Ir	2.520(3)	5.6(1)

* The details of these structures are to be published elsewhere.[8] δ = Polar angle between Si–S and S–A vectors = 180° − (Si–S–A). The *z* coordinate axis of Fig. 6 is related by $z = r(\text{S–A}) \times \cos\delta$.

treated with $2\text{-}Ph_3SiC_6H_4SH$ and triethylamine as for complex **4**. The suspension was heated under reflux for 3 h. The pale yellow precipitate was filtered off whilst hot and washed with methanol and ether. Yield 0.10 g, 75%.

$[OsH(SC_6H_4SiPh_3\text{-}2)(CO)(PPh_3)_3]{\cdot}0.5CH_2Cl_2$ **7**. A suspension of $[OsH(Cl)(CO)(PPh_3)_3]$ (0.13 g, 0.12 mmol) in methanol

Table 9 Summary of crystal structure data for complexes **2–4** *

	2	**3**	**4**
Chemical formula	$C_{66}H_{54}O_2PReS_2Si_2{\cdot}0.75CH_2Cl_2$	$C_{77}H_{68}P_2ReSi_2{\cdot}CH_2Cl_2$	$C_{87}H_{78}IrP_3S_2Si_2$
M_r	1282.84	1429.51	1517.9
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$
a/Å	13.964(2)	50.025(4)	26.9718(42)
b/Å	14.774(2)	13.198(8)	12.5527(8)
c/Å	17.317(4)	21.343(5)	23.4349(31)
α/°	87.69(1)	90	90
β/°	74.21(1)	110.80(4)	112.283(6)
γ/°	64.31(1)	90	90
U/Å^3	3085.3(9)	13 173(9)	7342(3)
Z	2	8	4
D_c/g cm^{-3}	1.381	1.442	1.37
μ/mm^{-1}	2.23	2.094	2.01
Crystal colour	Green	Blue	Yellow
Crystal description	Plate	Prism	Prism
Crystal size/mm	0.1 × 0.3 × 0.8	0.2 × 0.25 × 0.35	0.2 × 0.2 × 0.3
T/K	291	120(2)	291
No. reflections for lattice parameters	25	250	25
θ Range for lattice parameters/°	22–25	1.82–25.04	13–18
No. reflections measured	11 345	23 286	12 728
No. independent reflections	10 847	9672	12 238
No. observed reflections	9633 [$F > 3.0\sigma(F_o)$]	4487 [$I > 2\sigma(I_o)$]	5726 [$I > 3\sigma(I_o)$]
R_{int}	0.012	0.0853	0.046
Absorption correction, T_{min}	0.73	0.889	0.74
h, k, l Ranges	0–16, −17 to 17, −20 to 20	−49 to 49, −14 to 10, −23 to 19	0–31, 0–14, −27 to 25
Variation of standards	−0.532		−0.003
F(000)	1297	5688	3084
No. parameters refined	697	628	856
No. reflections used	9633	9672	5726
R	0.046	0.110	0.040
R'	0.075	0.083	0.048
S	2.9	0.587	1.50
$(\Delta/\sigma)_{max}$	< 0.01	0.04	0.01
Maximum, minimum $\Delta\rho$/e Å^{-3}	2.30, −0.09	1.370, −0.839	1.22, −0.20

* Details in common: θ_{max} 25°; no extinction coefficient; weighting schemes $w = 1/[\sigma^2(F_o) + (0.02F_o)^2]$ for **2** and **4**, $1/\sigma^2(F_o)^2$ for **3**.

(25 cm^3) was treated with 2-$Ph_3SiC_6H_4SH$ and triethylamine as for complex **4**. The suspension was heated under reflux for 3 h. The green precipitate was filtered off whilst hot and washed with methanol and ether. Yield 0.10 g, 59%.

[$Ru(SC_6H_4SiPh_3$-2$)_2(CO)(PPh_3)_2]{\cdot}2CH_2Cl_2$ **8**. A suspension of [$RuH(Cl)(PPh_3)_3$] (0.11 g, 0.12 mmol) in methanol (25 cm^3) was treated with 2-$Ph_3SiC_6H_4SH$ and triethylamine as for complex **4**. The suspension was heated under reflux for 3 h. The yellow precipitate was filtered off whilst hot and washed with methanol and ether. Yield 0.10 g, 53%.

Other Reactions of 2-$Ph_3SiC_6H_4SH$.—*With* [$RhCl(PPh_3)_3$]. A suspension of [$RhCl(PPh_3)_3$] (0.11 g, 0.12 mmol) in methanol (25 cm^3) was treated with the thiol and triethylamine as for complex **4**. The reaction mixture was then heated under reflux for 3 h to give a dark red precipitate which was filtered off and recrystallised from dichloromethane–methanol as dark red crystals.

With [$RuCl_2(PPh_3)_3$]. A suspension of [$RuCl_2(PPh_3)_3$] (0.11 g, 0.12 mmol) in methanol (25 cm^3), was treated as above. The brown precipitate was filtered off under N_2 and washed with methanol and ether. The brown solid was recrystallised from a mixture of CH_2Cl_2 and MeOH under N_2 at −20 °C. When exposed to the air for a few minutes it gave a green solid.

With [$OsCl_2(PPh_3)_3$]. A suspension of [$OsCl_2(PPh_3)_3$] (0.13 g, 0.12 mmol) in methanol (25 cm^3) was treated as above. The green precipitate was filtered off under N_2 and washed with methanol and ether. When exposed to the air for a few minutes it gave a brown solid.

Crystallography.—The details of the crystal structure determinations are summarised in Table 9.

[$ReO(OH)(SC_6H_4SiPh_3$-2$)_2(PPh_3)]{\cdot}0.75CH_2Cl_2$ **2**. *Data collection.* Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Cell constants were obtained from least-squares refinement of the setting angles of 25 centred reflections in the range 22 < θ < 25°. The data were collected in the ω–2θ scan mode and three standard reflections were measured every hour of exposure; 53.2% loss of intensity was observed which was linearly corrected during processing. Three standard reflections were measured every 200 to check the crystal orientation. The data were corrected for Lorentz and polarisation factors and an absorption correction was applied using ψ scans of nine reflections.

Structure solution and refinement. The structure was solved using the Patterson heavy-atom method (MOLEN software[15]). Remaining non-hydrogen atoms were located in subsequent cycles of Fourier difference syntheses and least-squares refinement. Full-matrix least-squares refinement on F converged with R = 0.04, R' = 0.075, maximum shift/error < 0.01, and S = 2.9. Hydrogen atoms were added in calculated positions with $B_{eq} = 1.3B_{eq}$ of the attached atom; they were included in structure-factor calculations but were not refined. Neutral atom scattering factors were used.[16]

[$ReH_4(SC_6H_4SiPh_3$-2$)(PPh_3)_4]{\cdot}CH_2Cl_2$ **3**. *Data collection.* Intensity data were collected on a Delft Instruments FAST area detector diffractometer (rotating anode) and graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) by following previously described procedures.[17] Cell constants were obtained from least-squares refinement of the setting angles of 250 reflections in the range $1.82 < \theta < 25.04°$. The data were corrected for Lorentz and polarisation factors and an absorption correction was applied using DIFABS.[18]

Structure solution and refinement. The structure was solved using the Patterson heavy-atom method (SHELXS)[19] and difference map, subsequently refined on F^2 by full-matrix least squares (SHELXL 93)[20] using all unique data above background. All non-hydrogen atoms were anisotropic, phenyl rings idealised [C–C 1.390 Å, C–C–C (internal) 120°]. The hydrogen atoms were included in the riding model with $U_{iso} = 1.2U_{eq}$ of the parent. Final R (on F) and R' (on F^2) were 0.110 and 0.083 for all data, 0.040 and 0.074 for data with $F_o > 4\sigma(F_o)$. Neutral atom scattering factors were used.[20]

$[IrH(SC_6H_4SiPh_3\text{-}2)_2(PMePh_2)_3]$ **4**. *Data collection.* Intensity data were collected as for complex **2**, except as follows: 25 centred reflections in the range $13 < \theta < 18°$ three standard reflections measured every 2 h of exposure, 0.3% loss of intensity observed.

Structure solution and refinement. As for complex **2**, except as follows: $R = 0.040$, $R' = 0.048$, maximum shift/error 0.01, and $S = 1.50$.

Acknowledgements

We are indebted to Johnson-Matthey for the loan of ruthenium, osmium, rhodium and iridium salts and to the Committee of Vice Chancellors and Principals for the award of Overseas Research Student fellowships (to C. L. and Y. Z.).

References

1 P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, 1987, **76**, 121.
2 J. R. Dilworth and J. Hu, *Adv. Inorg. Chem. Radiochem.*, 1994, **40**, 411.
3 E. Block, G. Ofori-Okai and J. Zubieta, *J. Am. Chem. Soc.*, 1989, **111**, 2327; G. D. Figuly, C. K. Loop and J. C. Martin, *J. Am. Chem. Soc.*, 1989, **111**, 654.
4 P. J. Blower and J. R. Dilworth, *Inorg. Chim. Acta*, 1984, **90**, L27.
5 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
6 J. G. Leipoldt, S. S. Basson, A. Roodt and W. Purcell, *Transition Met. Chem.*, 1987, **12**, 209.
7 W. Purcell, A. Roodt, S. S. Basson and J. G. Leipoldt, *Transition Met. Chem.*, 1990, **15**, 239.
8 J. R. Miller, J. R. Dilworth and Y. Zheng, unpublished work.
9 N. P. Johnson, C. J. L. Lock and G. Wilkinson, *J. Chem. Soc.*, 1964, 1054.
10 J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1967, **10**, 67.
11 K. Vrieze, J. P. Collman, C. T. Sears and M. Kubota, *Inorg. Synth.*, 1964, **7**, 102.
12 P. S. Hollman, B. R. Stephenson and G. Wilkinson, *Inorg. Chem.*, 1970, **12**, 237.
13 N. Ahmad, J. J. Levison, S. D. Robinson and M. F. Uttley, *Inorg. Synth.*, 1973, **15**, 1973.
14 D. Evans, J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1964, **7**, 99.
15 MOLEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, 1990.
16 D. T. Cromer and J. T. Weber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
17 J. A. Darr, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.*, 1993, **32**, 5704.
18 N. P. C. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158; adapted for FAST geometry by A. I. Karaulov, University of Wales, Cardiff, 1991.
19 G. M. Sheldrick, SHELXS, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
20 G. M. Sheldrick, SHELXL 93, Program for Crystal Structure Refinement, University of Göttingen, 1993.

Received 3rd *February* 1995; *Paper* 5/00643K