Complexes of 2-Diphenylphosphinobenzenethiol and 2-Diphenylphosphino-6-trimethylsilylbenzenethiol with Rhodium and Iridium. Crystal and Molecular Structures of $[IrCl_2(Ph_2PC_6H_4S)(PMePh_2)_2]$ and $[Ir(Ph_2PC_6H_4S)_3]\cdot0.75CH_2Cl_2$ †

Jonathan R. Dilworth,* Canzhong Lu, John R. Miller and Yifan Zheng
Department of Chemistry and Biological Chemistry, University of Essex, Colchester CO4 3SQ, UK

The reaction between $[IrCl_3(PMePh_2)_3]$ and 2-diphenylphosphinobenzenethiolate in methanol yielded only $[IrCl_2(Ph_2PC_6H_4S)(PMePh_2)_2]$ **1** whereas, with $IrCl_3$, $[Ir(Ph_2PC_6H_4S)_3]$ **2** was formed. The crystal structures of **1** and **2** have been determined. They reveal octahedral geometries about Ir with a *mer* arrangement of P donors in both cases. A similar reaction using $[RhCl(PPh_3)_3]$ as precursor gave an analogous rhodium complex which exists as a mixture of isomers in solution with *mer* and *fac* P donors. However, with the sterically demanding $2\text{-}Ph_2P(6\text{-}Me_3Si)C_6H_3SH$ the complexes $[M\{Ph_2P(Me_3Si)C_6H_3S\}_3]$ (M = Rh or Ir) were generated. Their ^{31}P NMR spectra indicate that these are single species with different structures from those of the $Ph_2PC_6H_4S$ complexes. The reaction between $[IrCl(CO)(PPh_3)_2]$ and the two thiols (HL) yielded the hydride complexes $[IrH(CO)L_2]$ the ^1H and ^{31}P NMR and IR spectra of which confirmed the presence of the hydride ligand and *trans*-P atoms. The $Ph_2PC_6H_4S$ complex isomerises slowly in the solid state and in solution to a species with *cis*-P atoms.

The chemistry of the platinum-group metals with thiolate ligands has not been extensively explored, and this is particularly true for rhodium and iridium. With monodentate thiols and Rh^I and Ir^I it is dominated by complexes with bridging thiolates. Thus $[Rh_2Cl_2(CO)_4]$ gives S-bridged dimers even with sterically demanding thiolates.[1] The catalytic properties of the binuclear complexes with bridging thiolate, pyrazole and diphosphine ligands for hydroformylation have been extensively investigated.[2] The catalytic activity of thiolate-bridged dimers and trimers with monodentate phosphines has also been studied.[3] The complexes $[Rh(SR)(PPh_3)_3]$ (R = Pr^i or C_6F_5) are unstable with respect to formation of $[Rh_2(\mu\text{-}SR)_2(PPh_3)_4]$.[4] However, the complex $[Rh(SC_6H_2Pr^i_3\text{-}2,4,6)(PPh_3)_3]$ with a bulky thiolate is stable and a square-planar geometry has been confirmed by an X-ray analysis.[5] The chemistry of the higher oxidation states is restricted to[6] $[Rh(SC_6H_4SMe\text{-}2)_3]$ and $[Rh(1,2\text{-}S_2C_6H_4)_3]^{3-}$ and the complex $[Rh_2\{\mu\text{-}SC_6H_2Pr^i_2\text{-}4,6\text{-}[C(Me){=}CH_2]\text{-}2\}_2(SC_6H_2Pr^i_3\text{-}2,4,6)_2(MeCN)]$.[7]

We are interested in the possibilities of preparing mononuclear thiolato-complexes of the platinum metals having potential catalytic applications. Reactions of thiolato-complexes with dihydrogen may be complicated by the transfer of hydrogen to sulfur and elimination of the free thiol. We have therefore embarked on a systematic exploration of the chemistry of chelating phosphinothiolate ligands, where the chelate effect should ensure retention of the thiolate. Although the chemistry of 2-diphenylphosphinobenzenethiol with Re, Tc[8] and Ru[9] has been explored, no complexes of Rh and Ir have been reported. The only closely related complexes are $[IrH(Ph_2PCH_2CH_2S)_2]$ and $[Ir(Ph_2PCH_2CH_2S)(CO)(PPh_3)]$.[10] We report here the reactions of a range of rhodium and iridium precursors with 2-diphenylphosphinobenzenethiol and 2-diphenylphosphino-6-trimethylsilylbenzenethiol.

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

Results and Discussion

The known phosphinothiols were prepared using slight modifications of the standard literature procedure involving the lithiation of benzenethiol.[11] Both were obtained as moderately air-stable white crystalline solids.

Complexes.—The physical, analytical and spectroscopic properties of the complexes are summarised in Table 1.

$[IrCl_2(Ph_2PC_6H_4S)(PMePh_2)_2]$ **1** *and* $[Ir(Ph_2PC_6H_4S)_3]\cdot0.75CH_2Cl_2$ **2**. Reaction of $[IrCl_3(PMePh_2)_3]$ with 4 equivalents of $2\text{-}Ph_2PC_6H_4SH$ in methanol under reflux in the presence of triethylamine yielded a yellow solid. The compound is stable in the air in the solid state, and moderately soluble in solvents such as dichloromethane or toluene. The elemental analysis corresponded to $[IrCl_2(Ph_2PC_6H_4S)(PMePh_2)_2]$ **1** and suitable crystals for structure determination were obtained from dichloromethane–methanol. Even prolonged reflux times did not lead to further substitution by the phosphinothiol, but the complex $[Ir(Ph_2PC_6H_4S)_3]$ could be prepared in near-quantitative yield by the direct reaction of $IrCl_3$ with an excess of phosphinothiol in methanol under reflux in the presence of triethylamine. Suitable crystals for structure determination were obtained from dichloromethane–methanol.

Structure of $[IrCl_2(Ph_2PC_6H_4S)(PMePh_2)_2]$ **1**. An ORTEP[12] representation of the structure appears in Fig. 1 together with the atom labelling scheme. Positional parameters are in Table 2 and selected bond lengths and angles in Table 3. The geometry about iridium is as expected pseudo-octahedral with *trans* chloride ligands and a *mer* arrangement of the P donors. The principal distortions from the ideal octahedron are the result of the small bite angle of the phosphinothiolate ligand [S–Ir–P(1) 81.06(3)°] and steric interactions between the $PMePh_2$ ligands which open the P(1)–Ir–P(2) angle to 97.27(3)°. The chelate-ring structure is discussed below in relation to those in compound **2** and the rhenium and technetium analogues.

Spectroscopic properties of complex **1**. The ^1H NMR spectrum shows doublets at δ 1.2 and 2.1 assigned to the Me

Table 1 Analytical and spectroscopic data for phosphinothiolato-complexes of rhodium and iridium

	Analysis[a] (%)		NMR[b] (δ)	
Complex	C	H	^{1}H	^{31}P
1 $[IrCl_2(Ph_2PC_6H_4S)(PMePh_2)_2]$	54.6 (55.2)	4.2 (4.1)	6.4–7.7 (m, 34 H, Ph), 1.2 (d), 2.1 (d, 6 H, PMe)	δ_1 10.0, δ_2 −41.8, δ_3 −49.1; J_{12} = 14.6, J_{23} = 21.0, J_{13} = 416.4
2 $[Ir(Ph_2PC_6H_4S)_3]\cdot0.75CH_2Cl_2$[c]	57.2 (57.3)	3.9 (3.9)	6.5–8.0 (m, 42 H, Ph)	δ_1 3.69, δ_2 1.06, δ_3 0.531; J_{12} = 380.9, J_{13} = J_{23} = 18.3
3 $[Rh(Ph_2PC_6H_4S)_3]$	65.4 (66.0)	4.3 (4.3)	6.5–8.0 (m, Ph)	$\delta(P^1)$ 35.75, $\delta(P^2)$ 35.78, $\delta(P^3)$ 36.74; J_{12} = 0.00, J_{23} = 28.4, J_{13} = 24.4, $J(RhP^1)$ = 93.0, $J(RhP^2)$ = 93.0, $J(RhP^3)$ = 104.0
4 $[Rh\{Ph_2P(Me_3Si)C_6H_3S\}_3]$	63.4 (63.1)	5.6 (5.5)	7.0–8.0 (m, Ph), −0.15 to −0.86 (Me_3Si)	Unstable in solution
5 $[Ir\{Ph_2P(Me_3Si)C_6H_3S\}_3]$	59.0 (58.7)	5.4 (5.2)	6.7–8.0 (m, 42 H, Ph), −0.15 to −0.86 (27 H, Me_3Si)	−11.92 (s)
6 $[IrH(CO)(Ph_2PC_6H_4S)_2]$[d]	55.0 (55.0)	3.6 (3.5)	6.7–8.0 (m, 28 H, Ph), −11.30 (dd, 1 H, hydride); $J(P_aH)$ = 17.6, $J(P_bH)$ = 16.5	38.53 (d), 25.27 (d); J(PP) = 305
7 $[IrH(CO)\{Ph_2P(Me_3Si)C_6H_3S\}_2]$[e]	54.9 (55.2)	5.0 (4.8)	6.7–8.0 (m, 28 H, Ph), −11.34 (dd, 1 H, hydride); $J(P_aH)$ = 13.2, $J(P_bH)$ = 11.0	36.75 (d), 23.95 (d); J(PP) = 315

[a] Calculated values in parentheses. [b] Recorded in $CDCl_3$ solution J in Hz; m = multiplet, d = doublet, s = singlet. [c] Cl 4.8 (4.7)%. [d] ν(Ir–H) 2080, ν(C–O) 2021 cm^{-1}. [e] ν(Ir–H) 2062, ν(C–O) 2024 cm^{-1}.

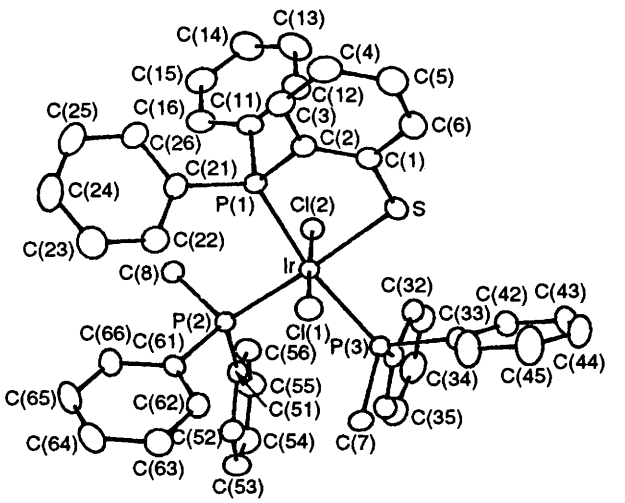


Fig. 1 Structure of $[IrCl_2(Ph_2PC_6H_4S)(PMePh_2)_2]$, with the atom labelling scheme

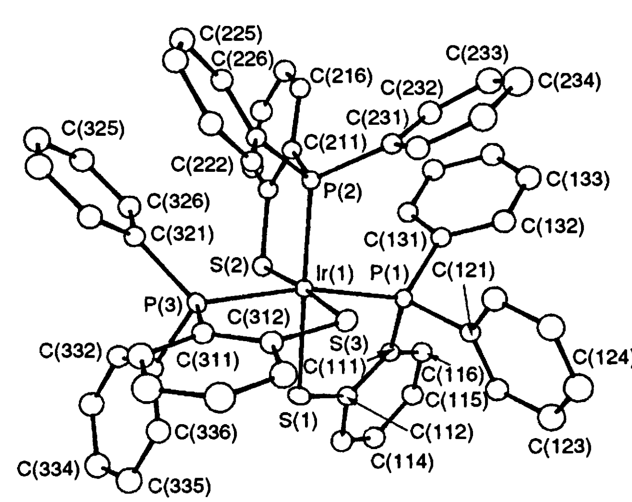


Fig. 2 Representation of the structure of one of the two independent molecules (molecule 1) of $[Ir(Ph_2PC_6H_4S)_3]$, with an atom labelling scheme

groups of the inequivalent $PMePh_2$ ligands, each being coupled to phosphorus. In the ^{31}P NMR spectrum the three inequivalent P donors give rise to three doublets of doublets (see Table 1). That at δ 10 is assigned to P(1) in the phosphinothiolate ligand, and those at δ −41.8 and −49.1 respectively to P(3) and P(2) in the $PMePh_2$ ligands. This is based on the assumption that the large coupling constant between P(1) and P(3) is between P atoms in *trans* positions.

Structure of $[Ir(Ph_2PC_6H_4S)_3]\cdot0.75CH_2Cl_2$ **2**. The structure solution showed there to be two independent molecules in the asymmetric unit, and an ORTEP plot for one is shown in Fig. 2, together with a partial atom labelling scheme. Fractional coordinates for the two independent molecules appear in Table 4 and selected bond lengths and angles in Table 5. Details of the structure determination are presented in Table 6.

The two independent molecules are structurally very similar, and there is a disordered solvent of crystallisation on two independent sites. The complex molecules contain pseudo-octahedrally co-ordinated iridium with the three S and three P atoms in each case in a *mer* configuration. In each molecule the central Ir–P bond is shorter and the central Ir–S bond (*trans* to Ir–P) is longer than the others of the same type, suggesting an enhanced *trans* influence of the central Ir–P bonds on the central Ir–S bonds. The last observation does not apply to the d^4 complexes of Tc and Re.[8] In other respects the bond lengths and angles are normal, but show some interesting small but systematic variations.

The chelation of the PS ring systems varies in that the Ir atoms lie out of the least-squares planes of the P–C–C–S units by different amounts. This is similar to, but not so marked as, differences found in the structures of the $[Tc(Ph_2PC_6H_4S)_3]$ and $[Re(Ph_2PC_6H_4S)_3]$ analogues.[8] The chelate rings are inherently distinguishable, and may be classified as (c, e), (e, c) and (e, e) according to whether the P and S atoms are central (c) or end-positioned (e) in the *mer* configurations. The (e, c) chelate rings show the greatest displacements of Ir, and additionally show both the smallest bite angles at Ir and the longest Ir–P and Ir–S distances within one chelate ring. These

Table 2 Fractional coordinates for $[IrCl_2(Ph_2PC_6H_4S)(PMePh_2)_2]$

Atom	*x*	*y*	*z*
Ir	0.194 15(1)	0.228 64(1)	0.339 51(1)
Cl(1)	0.023 35(8)	0.336 77(7)	0.333 12(4)
Cl(2)	0.354 94(8)	0.113 16(6)	0.345 35(4)
S	0.050 43(9)	0.122 04(7)	0.285 62(4)
P(1)	0.116 61(8)	0.150 19(7)	0.407 74(4)
P(2)	0.346 69(8)	0.321 44(7)	0.394 91(3)
P(3)	0.232 88(8)	0.294 86(6)	0.258 42(3)
C(1)	−0.065 4(3)	0.100 3(3)	0.324 0(2)
C(2)	−0.043 0(3)	0.115 2(3)	0.379 1(1)
C(3)	−0.134 1(4)	0.097 0(3)	0.408 1(2)
C(4)	−0.250 6(4)	0.061 5(3)	0.383 3(2)
C(5)	−0.272 2(4)	0.044 6(4)	0.328 8(2)
C(6)	−0.183 7(4)	0.064 4(3)	0.299 8(2)
C(7)	0.230 4(4)	0.423 5(3)	0.256 1(2)
C(8)	0.421 9(4)	0.254 2(3)	0.453 1(2)
C(11)	0.191 3(3)	0.036 9(3)	0.428 1(2)
C(12)	0.153 2(4)	−0.042 7(3)	0.400 1(2)
C(13)	0.208 8(5)	−0.128 9(3)	0.412 8(2)
C(14)	0.310 1(5)	−0.134 8(3)	0.454 3(2)
C(15)	0.350 2(4)	−0.058 2(3)	0.483 7(2)
C(16)	0.293 4(4)	0.029 3(3)	0.471 2(2)
C(21)	0.103 9(3)	0.208 1(3)	0.470 2(1)
C(22)	0.090 1(4)	0.305 5(3)	0.471 4(2)
C(23)	0.079 7(4)	0.349 5(4)	0.518 5(2)
C(24)	0.082 9(4)	0.298 1(4)	0.563 7(2)
C(25)	0.091 3(4)	0.203 2(4)	0.562 8(2)
C(26)	0.102 0(4)	0.156 3(3)	0.516 3(2)
C(31)	0.379 0(3)	0.263 6(3)	0.237 8(1)
C(32)	0.405 7(3)	0.167 9(3)	0.231 4(1)
C(33)	0.518 1(4)	0.142 9(3)	0.215 6(2)
C(34)	0.601 5(4)	0.210 4(4)	0.207 4(2)
C(35)	0.575 5(4)	0.304 4(4)	0.213 6(2)
C(36)	0.463 6(4)	0.330 7(3)	0.228 6(2)
C(41)	0.110 7(3)	0.269 1(3)	0.199 7(1)
C(42)	0.129 0(4)	0.209 4(3)	0.159 5(2)
C(43)	0.034 6(4)	0.195 4(3)	0.114 7(2)
C(44)	−0.078 2(4)	0.239 3(4)	0.109 9(2)
C(45)	−0.098 6(4)	0.297 8(4)	0.150 1(2)
C(46)	−0.005 8(4)	0.312 1(4)	0.194 5(2)
C(51)	0.486 0(3)	0.359 2(3)	0.369 5(1)
C(52)	0.505 2(3)	0.453 4(3)	0.357 8(2)
C(53)	0.615 4(4)	0.481 9(3)	0.342 7(2)
C(54)	0.708 7(3)	0.417 1(4)	0.340 4(2)
C(55)	0.690 2(3)	0.323 5(3)	0.351 7(2)
C(56)	0.580 4(4)	0.294 4(3)	0.365 9(2)
C(61)	0.301 4(3)	0.430 9(3)	0.424 7(1)
C(62)	0.220 7(3)	0.495 3(3)	0.394 9(1)
C(63)	0.186 8(4)	0.578 0(3)	0.416 7(2)
C(64)	0.232 3(4)	0.597 8(3)	0.470 4(2)
C(65)	0.311 5(4)	0.535 3(3)	0.500 3(2)
C(66)	0.345 6(4)	0.452 5(3)	0.478 2(2)

Table 3 Selected bond lengths (Å) and angles (°) for $[IrCl_2(Ph_2PC_6H_4S)(PMePh_2)_2]$

Ir–Cl(1)	2.3842(9)	Ir–P(1)	2.361(1)
Ir–Cl(2)	2.3736(9)	Ir–P(2)	2.3563(9)
Ir–S	2.401(1)	Ir–P(3)	2.390(9)
Cl(1)–Ir–Cl(2)	176.42(3)	Cl(2)–Ir–P(3)	94.04
Cl(1)–Ir–S	87.36(4)	S–Ir–P(1)	81.06(3)
Cl(1)–Ir–P(1)	88.02(3)	S–Ir–P(2)	174.87(3)
Cl(1)–Ir–P(2)	97.46(3)	S–Ir–P(3)	87.24(3)
Cl(1)–Ir–P(3)	87.55(3)	P(1)–Ir–P(2)	97.27(3)
Cl(2)–Ir–S	89.52(3)	P(1)–Ir–P(3)	167.67(3)
Cl(2)–Ir–P(1)	89.77(3)	P(2)–Ir–P(3)	94.71(3)
Cl(2)–Ir–P(2)	85.62(3)		

data are collected in Table 7, together with some data for $[IrCl_2(Ph_2PC_6H_4S)(PMePh_2)_2]$. The PS co-ordination in complex **1** is most similar to the (e, c) chelate in molecule 1 of $[Ir(Ph_2PC_6H_4S)_3]$. In the absence of any obvious steric effects in complex **1** to affect the bonding of the phosphinothiolate ligand [the shortest intramolecular contact between non-hydrogen atoms is C(22) ··· C(61) 3.305(6) Å, and there are no non-hydrogen intermolecular contacts less than 3.5 Å] it appears that the (e, c) ligands in complex **2** are bound in their natural formation. The (c, e) and (e, e) ligands are affected either by interphenyl steric factors or by very sensitive electronic factors. In the $[Tc(Ph_2PC_6H_4S)_3]$ and $[Re(Ph_2PC_6H_4S)_3]$ complexes[8] the (c, e) ligands show the longest M–P and M–S distances and the smallest bite angles, and the (e, e) the shortest distances and largest angles. This suggests strongly that the electron configuration of the metal (d^4 for Tc and Re, d^6 for Ir) plays a significant role in the details of the geometry.

In general the phosphinothiolate ligand, when acting in its chelate mode, has an element of adaptability in that the metal atom can take up a position in the P–C_6H_4–S plane or may move up to 1 Å out of this plane; the direction of the phosphorus lone pair is altered by torsional movement of the two PPh rings.

NMR spectra of complex **2**. The ^1H NMR spectrum in $CDCl_3$ is unremarkable, showing multiplet resonances in the range δ 6.5–8.0 due to phenyl groups and a single peak at δ 5.30 due to the CH_2Cl_2 of crystallisation. The ^{31}P NMR spectrum (see Fig. 3) can be completely assigned and simulated on the basis of a second-order spectrum with three inequivalent P donors. The relevant shifts are δ_1 3.69, δ_2 1.06 and δ_3 0.531 and the coupling constants are J_{12} = 380.87 and J_{13} = J_{23} = 18.31 Hz. By

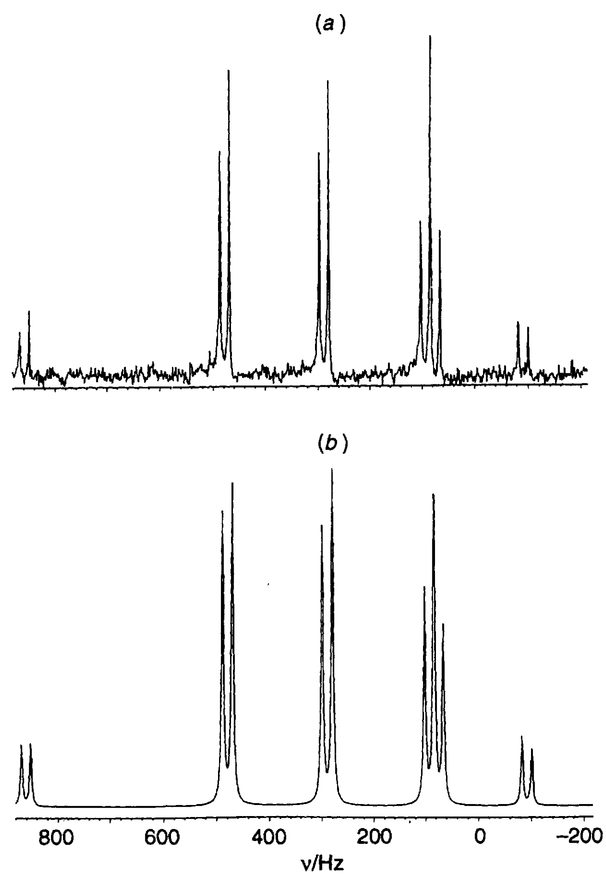


Fig. 3 Actual (*a*) and simulated (*b*) ^{31}P NMR spectrum of $[Ir(Ph_2PC_6H_4S)_3]$

Table 4 Positional parameters for $[Ir(Ph_2PC_6H_4S)_3]$ (molecules 1 and 2)

Molecule 1

Atom	*x*	*y*	*z*
Ir(1)	0.216 12(2)	0.026 96(1)	0.250 82(1)
S(1)	0.346 0(2)	−0.013 7(1)	0.174 7(1)
S(2)	0.175 9(2)	−0.099 9(1)	0.238 66(9)
S(3)	0.269 0(2)	0.152 6(1)	0.263 06(9)
P(1)	0.111 8(2)	0.018 1(1)	0.152 68(9)
P(2)	0.081 7(1)	0.052 0(1)	0.316 19(8)
P(3)	0.351 3(1)	0.028 9(1)	0.333 37(9)
C(111)	0.165 0(6)	−0.055 4(4)	0.093 2(4)
C(112)	0.273 2(6)	−0.063 4(4)	0.103 7(4)
C(113)	0.321 8(7)	−0.112 7(5)	0.054 4(4)
C(114)	0.263 8(7)	−0.154 6(5)	0.000 6(4)
C(115)	0.157 6(7)	−0.149 0(5)	−0.008 5(4)
C(116)	0.107 7(6)	−0.098 4(5)	0.037 8(4)
C(121)	0.124 0(6)	0.099 8(4)	0.121 3(4)
C(122)	0.165 4(7)	0.095 7(5)	0.063 3(4)
C(123)	0.175 6(8)	0.160 2(6)	0.042 4(5)
C(124)	0.145 4(8)	0.225 8(6)	0.078 5(5)
C(125)	0.104 0(8)	0.230 1(5)	0.135 2(5)
C(126)	0.092 6(7)	0.166 8(5)	0.157 5(4)
C(131)	−0.029 2(6)	−0.005 3(4)	0.139 9(4)
C(132)	−0.101 5(7)	0.037 6(5)	0.116 4(4)
C(133)	−0.207 5(8)	0.015 3(6)	0.105 0(5)
C(134)	−0.240 1(8)	−0.048 9(5)	0.117 0(5)
C(135)	−0.169 8(7)	−0.092 8(5)	0.139 7(4)
C(136)	−0.064 2(6)	−0.072 3(5)	0.149 3(4)
C(211)	0.014 2(6)	−0.035 8(4)	0.309 8(3)
C(212)	0.062 4(6)	−0.100 0(4)	0.278 3(4)
C(213)	0.015 1(7)	−0.168 5(5)	0.275 5(4)
C(214)	−0.079 4(7)	−0.172 9(5)	0.300 4(4)
C(215)	−0.082 2(6)	−0.042 1(4)	0.335 6(4)
C(216)	−0.129 0(7)	−0.108 9(5)	0.330 5(4)
C(221)	0.111 8(5)	0.095 2(4)	0.403 0(3)
C(222)	0.178 7(6)	0.157 8(4)	0.421 2(3)
C(223)	0.196 9(6)	0.196 9(4)	0.485 2(4)
C(224)	0.149 0(6)	0.174 0(5)	0.532 2(4)
C(225)	0.084 9(7)	0.111 6(5)	0.515 2(4)
C(226)	0.066 9(6)	0.072 2(4)	0.450 3(4)
C(231)	−0.020 0(6)	0.115 1(4)	0.299 3(4)
C(232)	−0.121 1(7)	0.090 4(5)	0.271 7(4)
C(233)	−0.196 3(8)	0.141 0(6)	0.263 5(5)
C(234)	−0.169 9(8)	0.214 4(6)	0.279 3(5)
C(235)	−0.069 7(8)	0.240 4(5)	0.303 9(5)
C(236)	0.004 3(7)	0.190 6(5)	0.314 2(4)
C(311)	0.415 8(6)	0.120 1(4)	0.354 7(4)
C(312)	0.378 3(6)	0.170 5(4)	0.320 9(4)
C(313)	0.432 1(7)	0.239 8(5)	0.332 4(4)
C(314)	0.519 5(8)	0.255 8(6)	0.375 8(5)
C(315)	0.557 6(8)	0.206 1(5)	0.407 8(5)
C(316)	0.507 1(7)	0.138 4(5)	0.397 2(4)
C(321)	0.323 3(6)	0.004 8(4)	0.408 2(4)
C(322)	0.360 6(7)	0.047 5(5)	0.469 4(4)
C(323)	0.341 9(7)	0.024 9(5)	0.524 6(5)
C(324)	0.286 1(7)	−0.038 6(5)	0.519 2(5)
C(325)	0.247 0(7)	−0.081 1(5)	0.460 1(4)
C(326)	0.265 6(6)	−0.059 8(5)	0.404 0(4)
C(331)	0.459 6(6)	−0.031 2(4)	0.306 8(4)
C(332)	0.458 6(7)	−0.105 0(5)	0.309 3(4)
C(333)	0.538 3(7)	−0.149 9(5)	0.285 5(5)
C(334)	0.618 8(8)	−0.122 2(5)	0.259 4(5)
C(335)	0.621 7(7)	−0.050 6(5)	0.257 5(5)
C(336)	0.541 5(7)	−0.004 1(5)	0.281 3(4)

Molecule 2

Atom	*x*	*y*	*z*
Ir(2)	0.220 01(2)	0.531 57(2)	0.255 61(1)
S(4)	0.064 6(2)	0.465 0(1)	0.268 6(1)
S(5)	0.135 1(2)	0.645 6(1)	0.291 03(9)
S(6)	0.296 3(2)	0.414 8(1)	0.228 7(1)
P(4)	0.141 0(2)	0.513 9(1)	0.148 43(9)
P(5)	0.263 2(1)	0.540 5(1)	0.365 89(9)
P(6)	0.378 2(1)	0.582 2(1)	0.240 65(9)
C(411)	0.039 7(6)	0.441 2(4)	0.135 6(4)
C(412)	0.003 3(6)	0.427 8(4)	0.190 9(4)
C(413)	−0.083 9(7)	0.378 8(5)	0.183 0(4)
C(414)	−0.129 6(7)	0.343 9(5)	0.122 1(4)
C(415)	−0.090 7(7)	0.356 2(5)	0.067 6(4)
C(416)	−0.007 0(6)	0.405 4(5)	0.073 8(4)
C(421)	0.070 6(6)	0.593 8(4)	0.134 2(4)
C(422)	0.124 5(7)	0.654 9(5)	0.128 4(5)
C(423)	0.073 9(8)	0.715 2(6)	0.115 9(5)
C(424)	−0.0308(9)	0.713 3(7)	0.107 7(6)
C(425)	−0.087(1)	0.656 7(8)	0.115 1(7)
C(426)	−0.0357(9)	0.593 2(6)	0.127 3(5)
C(431)	0.212 1(6)	0.483 3(4)	0.076 6(4)
C(432)	0.206 5(7)	0.517 4(5)	0.0272(5)
C(433)	0.263 5(9)	0.493 6(6)	−0.0267(5)
C(434)	0.326 1(9)	0.434 7(7)	−0.0297(6)
C(435)	0.330 9(8)	0.397 2(6)	0.017 2(5)
C(436)	0.273 1(7)	0.421 9(5)	0.070 6(4)
C(511)	0.204 9(6)	0.622 5(4)	0.411 2(3)
C(512)	0.147 6(6)	0.664 6(4)	0.376 3(4)
C(513)	0.098 2(6)	0.726 8(4)	0.411 9(4)
C(514)	0.103 8(7)	0.744 2(5)	0.477 5(4)
C(515)	0.157 9(7)	0.701 9(5)	0.512 2(4)
C(516)	0.207 1(6)	0.640 1(4)	0.478 6(4)
C(521)	0.203 2(6)	0.467 3(4)	0.395 0(3)
C(522)	0.249 0(6)	0.398 9(4)	0.387 5(4)
C(523)	0.202 2(7)	0.343 7(5)	0.408 1(4)
C(524)	0.109 6(7)	0.355 0(5)	0.436 0(4)
C(525)	0.062 1(7)	0.421 8(5)	0.441 9(5)
C(526)	0.108 2(6)	0.477 3(5)	0.421 5(4)
C(531)	0.401 2(6)	0.541 8(4)	0.399 8(3)
C(532)	0.464 0(6)	0.485 3(4)	0.371 7(4)
C(533)	0.566 9(7)	0.483 5(5)	0.398 3(4)
C(534)	0.606 5(7)	0.536 5(5)	0.451 3(4)
C(535)	0.544 6(7)	0.593 7(5)	0.478 8(4)
C(536)	0.442 7(6)	0.596 5(4)	0.452 5(4)
C(611)	0.462 0(6)	0.504 3(4)	0.213 8(4)
C(612)	0.421 7(6)	0.433 2(4)	0.210 2(4)
C(613)	0.487 3(8)	0.373 8(5)	0.191 2(5)
C(614)	0.586 5(9)	0.385 4(6)	0.176 8(5)
C(615)	0.626 2(8)	0.454 2(5)	0.178 1(5)
C(616)	0.562 1(7)	0.515 0(5)	0.196 5(4)
C(621)	0.388 1(6)	0.635 1(4)	0.180 1(4)
C(622)	0.367 9(7)	0.710 3(5)	0.195 3(4)
C(623)	0.376 2(8)	0.750 7(6)	0.149 9(5)
C(624)	0.402 4(8)	0.715 5(6)	0.088 4(5)
C(625)	0.420 0(7)	0.641 5(5)	0.072 6(5)
C(626)	0.413 3(7)	0.601 2(5)	0.118 0(4)
C(631)	0.448 8(6)	0.648 3(4)	0.311 2(4)
C(632)	0.392 6(6)	0.706 0(4)	0.346 8(4)
C(633)	0.442 7(7)	0.759 0(5)	0.398 6(4)
C(634)	0.548 9(8)	0.754 6(5)	0.415 0(5)
C(635)	0.604 2(7)	0.697 9(5)	0.381 1(5)
C(636)	0.554 6(6)	0.643 8(5)	0.3294 (4)
Cl(1)	0.554 0(4)	0.168 1(3)	0.168 9(3)
Cl(2)*	0.449 7(7)	0.180 1(5)	0.051 5(5)
Cl(2′)*	0.464(1)	0.087 3(7)	0.04 65(7)
Cl(3)*	0.196 4(8)	0.368 1(6)	0.73 42(5)
Cl(4)*	0.144 8(9)	0.410 2(6)	0.620 1(6)
C	0.434(1)	0.144 6(8)	0.121 1(7)
C(2)*	0.144(2)	0.400(2)	0.687(1)

* Atoms with site occupation 0.5.

analogy with complex **1**, shifts 1 and 2 can be assigned to the *trans*-P atoms because of the large J_{12} coupling constant. Shift 3 is therefore assigned unambiguously to the central P atom [P(2) in molecule 1 and P(6) in 2], but it has not proved possible to assign shifts 1 and 2 to individual P atoms.

Table 5 Selected bond lengths (Å) and angles (°) for $[Ir(Ph_2PC_6H_4S)_3]$ (molecules 1 and 2)

Molecule 1			
Ir(1)–S(1)	2.428(2)	Ir(1)–S(2)	2.370(2)
Ir(1)–S(3)	2.385(2)	Ir(1)–P(1)	2.360(2)
Ir(1)–P(2)	2.296(2)	Ir(1)–P(3)	2.360(2)
S(1)–C(112)	1.748(8)	S(2)–C(212)	1.750(8)
S(3)–C(312)	1.756(8)	P(1)–C(111)	1.807(8)
P(1)–C(121)	1.835(8)	P(1)–C(131)	1.835(8)
P(2)–C(211)	1.817(7)	P(2)–C(221)	1.833(7)
P(2)–C(231)	1.850(8)	P(3)–C(311)	1.817(8)
P(3)–C(321)	1.840(8)	P(3)–C(331)	1.839(8)
S(1)–Ir(1)–S(2)	86.58(7)	S(1)–Ir(1)–S(3)	90.41(8)
S(1)–Ir(1)–P(1)	80.42(7)	S(1)–Ir(1)–P(2)	172.84(7)
S(1)–Ir(1)–P(3)	86.57(7)	S(2)–Ir(1)–S(3)	176.04(7)
S(2)–Ir(1)–P(1)	88.43(7)	S(2)–Ir(1)–P(2)	87.21(7)
S(2)–Ir(1)–P(3)	91.76(7)	S(3)–Ir(1)–P(1)	93.60(7)
S(3)–Ir(1)–P(2)	95.96(7)	S(3)–Ir(1)–P(3)	85.49(7)
P(1)–Ir(1)–P(2)	95.88(7)	P(1)–Ir(1)–P(3)	166.95(7)
P(2)–Ir(1)–P(3)	97.16(7)		
Molecule 2			
Ir(2)–S(4)	2.411(2)	Ir(2)–S(5)	2.390(2)
Ir(2)–S(6)	2.366(2)	Ir(2)–P(4)	2.367(2)
Ir(2)–P(5)	2.343(2)	Ir(2)–P(6)	2.310(2)
S(4)–C(412)	1.743(8)	S(5)–C(512)	1.763(8)
S(6)–C(612)	1.740(8)	P(4)–C(411)	1.820(8)
P(4)–C(421)	1.839(8)	P(4)–C(431)	1.827(8)
P(5)–C(511)	1.806(8)	P(5)–C(521)	1.832(8)
P(5)–C(531)	1.852(7)	P(6)–C(611)	1.829(8)
P(6)–C(621)	1.838(8)	P(6)–C(631)	1.844(8)
S(4)–Ir(2)–S(5)	89.94(8)	S(4)–Ir(2)–S(6)	85.77(8)
S(4)–Ir(2)–P(4)	83.23(7)	S(4)–Ir(2)–P(5)	84.80(7)
S(4)–Ir(2)–P(6)	173.27(8)	S(5)–Ir(2)–S(6)	174.33(7)
S(5)–Ir(2)–P(4)	91.41(7)	S(5)–Ir(2)–P(5)	86.05(7)
S(5)–Ir(2)–P(6)	96.75(7)	S(6)–Ir(2)–P(4)	91.75(7)
S(6)–Ir(2)–P(5)	89.88(7)	S(6)–Ir(2)–P(6)	87.44(7)
P(4)–Ir(2)–P(5)	167.77(7)	P(4)–Ir(2)–P(6)	97.30(7)
P(5)–Ir(2)–P(6)	94.89(7)		

Electrochemistry. The cyclic voltammetry of complex **2** was studied under the conditions specified in the Experimental section. The complex showed a rather broad irreversible oxidation at +0.89 V *vs.* saturated calomel electrode (SCE) and no identifiable reduction processes. This behaviour is in marked contrast to $[Re(Ph_2PC_6H_4S)_3]$ which shows two reversible oxidations and one reversible reduction,[6] and shows that the corresponding iridium(IV) (d^5) species is not as stable as those of Re^{VI} (d^3) and Re^{V} (d^2).

Synthesis of $[Rh(Ph_2PC_6H_4S)_3]$ **3**. This complex was prepared in a directly analogous manner to that of **1** by reaction of $[RhCl(PPh_3)_3]$ with 4 equivalents of 2-$Ph_2PC_6H_4SH$ in the presence of triethylamine. There is a formal oxidation of the Rh^{I} to Rh^{III}, and such oxidations are common in reactions of thiolates. There was no evidence for the formation of complexes such as $[Rh(Ph_2PC_6H_4S)_2]^-$ at lower thiol:metal ratios or shorter reaction times. The orange product is stable in the solid state, and moderately soluble in dichloromethane or toluene. The elemental analysis was consistent with the proposed formulation.

NMR spectroscopy of complex **3**. The ^1H NMR spectrum in $CDCl_3$ shows the expected resonances for phenyl protons as a series of complex multiplets in the region δ 6.5–8. The ^{31}P NMR spectrum in $CDCl_3$ shows both Rh–P and P–P coupling and has been assigned as in Table 1 and simulated (Fig. 4). The presence of the three non-equivalent P atoms supports the presence of the *mer* form in solution. In a freshly prepared solution there is a doublet (δ 47.25, J_{RhP} = 102.6 Hz) in addition to the shifts reported in Table 1. This gradually loses intensity over 1 week and is assigned to an unstable *fac* isomer with three equivalent P atoms.

Syntheses of $[Rh\{Ph_2P(Me_3Si)C_6H_3S\}_3]$ **4** *and* $[Ir\{Ph_2P(Me_3Si)C_6H_3S\}_3]$ **5**. These complexes were prepared as for **2** and **3**, using the silylated phosphine thiolate, and were isolated as air-stable yellow solids. Their elemental analyses were in accord with the proposed formulation $[M\{Ph_2P(Me_3Si)C_6H_3S\}_3]$.

NMR spectroscopy of complexes **4** *and* **5**. The ^1H NMR spectra of the complexes in $CDCl_3$ show resonances due to the

Table 6 Summary of crystal data, data collection and structure refinement for $[IrCl_2(Ph_2PC_6H_4S)(PMePh_2)_2]$ and $[Ir(Ph_2PC_6H_4S)_3]\cdot 0.75CH_2Cl_2$ *

Empirical formula	$C_{44}H_{40}Cl_2IrPS_3$	$C_{108}H_{84}Ir_2P_6S_6 \cdot 1.5CH_2Cl_2$
Colour, system	Yellow, monoclinic	Yellow, triclinic
Crystal size/mm	0.70 × 0.30 × 0.17	0.18 × 0.35 × 0.17
Space group	$P2_1/n$	$P\bar{1}$
a/Å	10.863(7)	12.8292(7)
b/Å	14.134(3)	18.758(1)
c/Å	25.62(2)	21.4504(9)
α/°	90	104.968(4)
β/°	101.38(3)	95.021(4)
γ/°	90	90.863(4)
U/Å^3	3856(6)	4963.9(4)
Z	4	2
D_c/g cm^{-3}	1.65	1.52
μ/mm^{-1}	3.79	3.01
F(000)	1 904	2 276
hkl ranges	0–12, 0–16, −30 to 30	0–15, −22 to <22, −25 to <25
Reflections collected	7466	18 057
Reflections observed ($F_o > 3\sigma F_o$)	5794	13 751
Weighting scheme, w	$1/[\sigma^2(F_o) + (0.0125F_o)^2]$	$1/[\sigma^2(F_o) + (0.02F_o)^2 + 1]$
R (observed data)	0.023	0.050
R'	0.031	0.056
Goodness of fit	1.64	1.07

* Details in common: Enraf-Nonius CAD4 diffractometer; Mo-Kα radiation (λ 0.710 73 Å); 291 K; graphite-crystal monochromator; 2θ 3–50°; scan speed 1–7° min^{-1}; background 25% above and below range; three standard reflections, every 120 min; empirical absorption correction based on ψ scans; Patterson method; full-matrix least-squares refinement on F; quantity minimised $\Sigma w(|F_o| - |F_c|)^2$; H atoms included, but not refined.

Table 7 Geometrical data for PS chelate rings of complexes 1 and 2

		$[Ir(Ph_2PC_6H_4S)_3]$ **2**	
Ligand type[a]	Geometric data[b]	Molecule 1 P(1), S(1)	Molecule 2 P(4), S(4)
(e, c)	d/Å	0.985(1)	0.498(1)
	β/°	80.42(7)	83.23(7)
	r_P/Å	2.360(2)	2.369(2)
	r_S/Å	2.428(2)	2.411(2)
		P(2), S(2)	P(6), S(6)
(c, e)	d/Å	0.238(1)	0.089(1)
	β/°	87.21(7)	87.51(7)
	r_P/Å	2.296(2)	2.310(2)
	r_S/Å	2.370(2)	2.366(2)
		P(3), S(3)	P(5), S(5)
(e, e)	d/Å	0.082(1)	0.100(1)
	β/°	85.49(7)	86.05(7)
	r_P/Å	2.360(2)	2.344(2)
	r_S/Å	2.385(2)	2.390(2)

For complex **1**, ligand (e, c), atoms P(1), S: d = 0.950(1) Å, β = 81.06(3)°, r_P = 2.361(1) and r_S = 2.401(1) Å.
[a](e, c) = End P atom, central S atom, *etc.* [b]d = Perpendicular distance of Ir atom from P–C–C–S plane; β = P–Ir–S angle, r_P = Ir–P distance, r_S = Ir–S distance.

phenyl protons (12 H) and a series of peaks between δ −0.15 and −0.86 integrating at 27 H. This multiplicity indicates that steric interactions result in restricted rotation about the Si–C bond with each Me group in a different environment. The ^{31}P NMR spectrum of **5** shows a singlet at δ −11.92 indicating a single species with equivalent phosphorus atoms. The negative value of the shift is atypical for ligated $Ph_2P(Me_3Si)C_6H_3S$ (see complex **7** below), and suggests the P atoms may not be ligated. Complex **4** appears to be unstable in solution over the time to record a ^{31}P NMR spectrum which only has a singlet at δ 31.05 and the lack of Rh–P coupling suggests strongly that the P atoms are not co-ordinated, and the value of the shift could indicate oxidation of unco-ordinated P donors to P=O in solution. However, there is X-ray diffraction confirmation for S-bonding only of the $Ph_2PC_6H_4S$ ligand in complex $[Re(Ph_2PC_6H_4S)_3(MeCN)(PPh_3)]$[13], and the unco-ordinated and unoxidised P atoms give rise to ^{31}P NMR peaks at δ −9.5. We therefore favour a monodentate S-bonded structure for **4** and **5** with oxidation of the unco-ordinated P atoms to P=O in the case of complex **4**. The co-ordination number of the metal is unlikely to be three, and agostic interactions with hydrogens could complete the co-ordination sphere. The ^1H NMR spectrum was however too complex to confirm this. Also, attempts to grow crystals of complexes **4** and **5** suitable for an X-ray determination were not successful and the exact structure of these complexes remains unclear.

Syntheses of $[IrH(CO)(Ph_2PC_6H_4S)_2]$ **6** *and* $[IrH(CO)\{Ph_2P(Me_3Si)C_6H_3S\}_2]$ **7**. These neutral, yellow complexes were prepared by reaction of $[IrCl(CO)(PPh_3)_2]$ with 4 equivalents of the appropriate thiol in methanol under reflux in the presence of triethylamine. The elemental analysis was in accord with the formulations. They are stable as solids for some time in air, but **6** becomes orange after 3 weeks in air.

Spectroscopy of complexes **6** *and* **7**. The IR spectra of the complexes show sharp absorptions at 2080 (**6**) and 2062 cm^{-1} (**7**) due to Ir–H and at 2021 or 2024 cm^{-1} respectively due to C=O. The ^1H NMR spectra of fresh solutions of **6** and **7** were very similar with a doublet of doublets at around δ −11.3 due to the hydridic hydrogen. The observed pattern is consistent with coupling to two inequivalent P atoms, and the coupling constants suggest the H and P atoms are *cis*. Possible structures

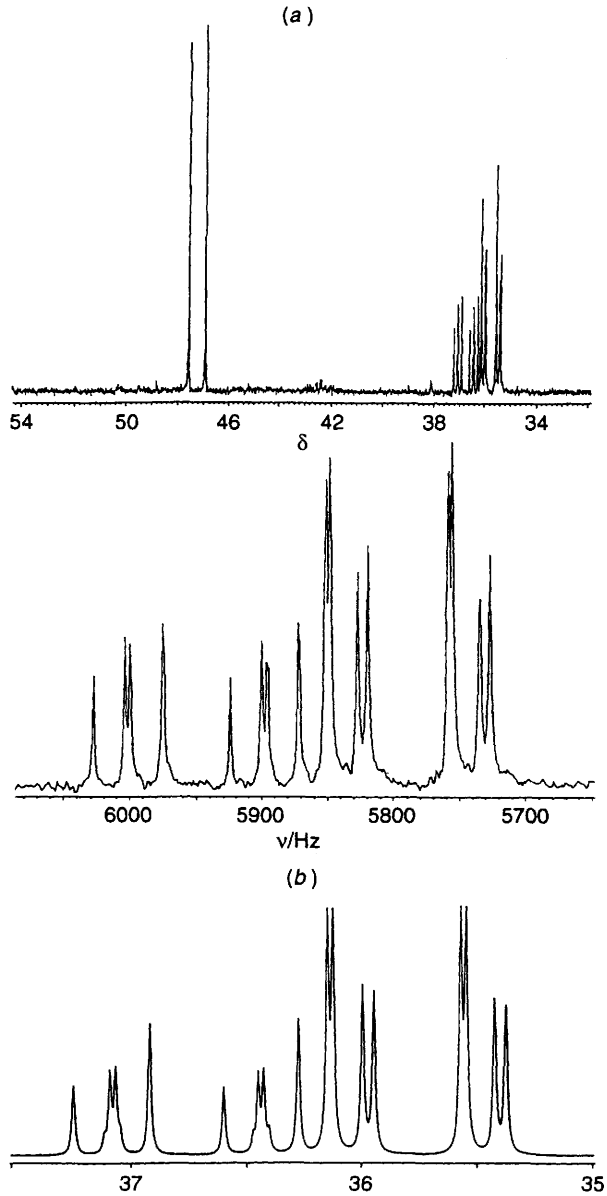
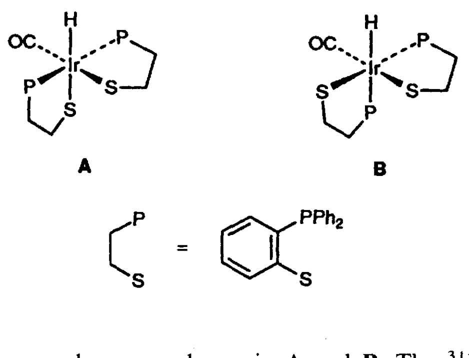


Fig. 4 Actual (*a*) and simulated (*b*) ^{31}P NMR spectrum of $[Rh(Ph_2PC_6H_4S)_3]$



A **B**

for these complexes are shown in **A** and **B**. The ^{31}P NMR spectra comprise the expected two doublets due to two inequivalent P atoms. The large values of the coupling constants suggests *trans* P atoms.

The ^1H NMR spectrum of the orange complex formed on standing **6** in air shows the persistence of the species described above and an additional species with a doublet of doublets at δ −9.68. The ^{31}P NMR spectrum showed two new doublets at δ 37.35 and 12.20, and the coupling constant is now consistent with *cis*, inequivalent P atoms. These data suggest slow isomerisation of **6** to a second species with the structure **B**.

Solutions of complex **7** are completely unchanged even on standing for 1 year, which suggests that the increased steric hindrance prevents isomerisation.

Experimental

Materials and Methods.—All experimental manipulations were carried out under an atmosphere of dry nitrogen gas unless stated otherwise. Standard Schlenk-tube, vacuum-line and syringe techniques were employed throughout where appropriate. Melting points were determined using an Electrothermal apparatus. Elemental analyses were carried out by the Microanalytical Laboratories at Manchester and Sussex Universities. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrophotometer in the range 200–4000 cm^{-1} as Nujol mulls on KBr plates, ^1H and ^{13}C NMR spectra on JEOL PMX 60SYS, 270, or Bruker WP80SY spectrometers with $SiMe_4$ as an internal standard using the solvents indicated, ^{31}P NMR spectra on Bruker WP80SY and Varian U400 400MHz spectrometers using trimethyl phosphate as the internal standard or H_3PO_4 as external standard and electronic spectra on a Beckman DU-7 spectrophotometer. Solvents were dried by standard methods. All other methods and reagents were obtained commercially (Fisons, Aldrich) and used without further purification, $[IrCl_3(PMePh_2)_3]$, $[IrCl(CO)(PPh_3)_2]$,[14] $[RhCl(PPh_3)_3]$,[15] 2-$Ph_2PC_6H_4SH$ and 2-Ph_2P-6-$Me_3SiC_6H_3$-SH[11] were prepared by literature methods.

Electrochemical Measurements.—Cyclic voltammetry experiments were typically carried out in 0.2 mol dm^{-3} solutions of $[NBu_4][BF_4]$ in either CH_2Cl_2 or dimethylformamide under a nitrogen atmosphere at room temperature using a three-electrode cell configuration. The working electrode was either a gold or platinum disc, and the reference electrode was usually a silver wire arranged such that a luggin capillary was in close proximity to the working electrode. The $E_{\frac{1}{2}}$ values are quoted *versus* the SCE against which the ferrocene–ferrocenium couple has an $E_{\frac{1}{2}}$ value of 0.54 V in tetrahydrofuran–0.2 mol dm^{-3} $[NBu_4][BF_4]$. Cyclic voltammetric measurements were made on an EG & G Par model 362 scanning potentiostat. The current and potential values were stored on floppy disk *via* the EG & G twin-channel data recorder. The data were manipulated on an OPUS™ microcomputer using EG & G CONDECON 300™ software.

Syntheses of Complexes.—$[IrCl_2(Ph_2PC_6H_4S)(PMePh_2)_2]$ **1**. The complex $[IrCl_3(PMePh_2)_3]$ (0.11 g, 0.12 mmol) was added to a solution of 2-$Ph_2PC_6H_4SH$ (0.15 g, 0.48 mmol) and NEt_3 (0.10 cm^3) in methanol (25 cm^3) and the reaction mixture heated under reflux for 3 h. The complex precipitated as a yellow solid (0.08 g, 83%).

$[Ir(Ph_2PC_6H_4S)_3]\cdot 0.75CH_2Cl_2$ **2**. Iridium(III) chloride (0.06 g, 0.2 mmol) was added to a solution of 2-$Ph_2PC_6H_4SH$ (0.24 g, 0.8 mmol) and NEt_3 (0.1 cm^3) in methanol (25 cm^3) and the mixture heated under reflux under N_2 for 4 h. The complex precipitated as a pale yellow solid (0.1 g, 80%).

$[Rh(Ph_2PC_6H_4S)_3]$ **3**. To a suspension of $[RhCl(PPh_3)_3]$ (0.11 g, 0.12 mmol) in methanol (25 cm^3) was added 4 mole equivalents of 2-$Ph_2PC_6H_4SH$ (0.14 g, 0.48 mmol) and an equivalent amount of triethylamine (0.07 cm^3). The suspension was heated under reflux for 3 h to give an orange precipitate which was filtered off and washed with methanol and diethyl ether. Yield 0.09 g (76%).

$[Rh\{Ph_2P(Me_3Si)C_6H_3S\}_3]$ **4**. To a suspension of $[RhCl(PPh_3)_3]$ (0.11 g, 0.12 mmol) in methanol (25 cm^3) was added 4 mole equivalents of 2-$Ph_2P(6$-$Me_3Si)C_6H_3SH$ (0.18 g, 0.48 mmol) and an equivalent amount of triethylamine (0.07 cm^3). The suspension was heated under reflux for 3 h to give a yellow precipitate which was filtered off and washed with methanol and ether. Yield 0.03 g (20%).

$[Ir\{Ph_2P(Me_3Si)C_6H_3S\}_3]$ **5**. 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 the phosphinothiol (0.18 g, 0.48 mmol) and an equivalent amount of triethylamine (0.07 cm^3). The suspension was heated under reflux for 3 h to give a yellow precipitate which was filtered off and washed with methanol and ether. Yield 0.03 g (20%).

$[IrH(CO)(Ph_2PC_6H_4S)_2]$ **6**. To a suspension of $[IrCl(CO)(PPh_3)_2]$ (0.09 g, 0.12 mmol) in methanol (25 cm^3) was added 4 mole equivalents of 2-$Ph_2PC_6H_4SH$ (0.14 g, 0.48 mmol) and an equivalent amount of triethylamine (0.07 cm^3). The suspension was heated under reflux for 3 h to give a white precipitate which was filtered off and washed with methanol and ether. Yield 0.08 g (83%).

$[IrH(CO)\{Ph_2P(Me_3Si)C_6H_3S\}_2]$ **7**. To a suspension of $[IrCl(CO)(PPh_3)_2]$ (0.09 g, 0.12 mmol) in methanol (25 cm^3) was added 4 mole equivalents of 2-$Ph_2P(6$-$Me_3Si)C_6H_3SH$ (0.18 g, 0.48 mmol) and an equivalent amount of triethylamine (0.07 cm^3). The suspension was heated under reflux for 3 h to give a white precipitate which was filtered off and washed with methanol and ether. Yield 0.06 g (53%).

Crystallography.—The details of the crystal structure determinations are summarised in Table 6.

Complex **1**. *Data collection.* Cell constants were obtained from least-squares refinement of the setting angles of 24 centred reflections in the range 23 < θ < 25. The data were collected in the ω–2θ scan mode and three standard reflections were measured every 2 h of exposure. No loss of intensity was observed. Three standard reflections were measured every 200 to check the crystal orientation. The data were corrected for Lorentz and polarisation factors.

Structure solution and refinement. The structure was solved using the Patterson heavy atom method (MOLEN).[16] Remaining non-hydrogen atoms were located in subsequent cycles of Fourier-difference syntheses and least-squares refinement. Hydrogen atoms were added in calculated positions with B_{eq} = 1.3 times B_{eq} of the attached atom; they were included in structure factor calculations but were not refined. Neutral atom scattering factors were used.[17]

Complex **2**. *Data collection.* Cell constants were obtained from least-squares refinement of the setting angles of 24 centred reflections in the range 21 < θ < 23. The data were collected in the ω–2θ scan mode and three standard reflections were measured every 2 h of exposure. A 3% 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.

Structure solution and refinement. The structure was solved using the Patterson heavy atom method (MOLEN).[16] Remaining non-hydrogen atoms were located in subsequent cycles of Fourier-difference syntheses and least-squares refinement. Hydrogen atoms were added in calculated positions with B_{eq} = 1.3 times B_{eq} of the attached atom; they were included in structure factor calculations but were not refined. Neutral atom scattering factors were used.[17]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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