

Rhodium and iridium complexes with thiolate and tertiary phosphine ligands. The synthesis and structures of *trans*-[Ir(SC₆H₃Cl₂-2,6)(CO)(PPh₃)₂], [Rh₂(μ-SC₆H₃Prⁱ₃-2,4,6)₂(CO)₂(PPh₃)₂], [Rh₂H₂(μ-SC₆H₄PPh₂-2)₂(CO)₂(PPh₃)₂][BF₄]₂, and [Rh₂I₆(MeSC₆H₄PPh₂-2)₂]

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Reaction of [MF(CO)(PPh₃)₂] (M = Rh or Ir) with bulky aromatic thiols ArSH gave the binuclear complexes [M₂(μ-SAr)₂(CO)₂(PPh₃)₂] (M = Rh, SAr = SC₆H₂Prⁱ₃-2,4,6 or SC₆H₃Me₂-2,6) and mononuclear complexes [M(SAr)(CO)(PPh₃)₂] (M = Rh or Ir, SAr = SC₆H₃Cl₂-2,6 or SC₆H₄SiPh₃-2; M = Ir, SAr = SC₆H₂Prⁱ₃-2,4,6 or SC₆H₃Me₂-2,6). The crystal structure of [Rh₂(μ-SC₆H₃Prⁱ₃-2,4,6)₂(CO)₂(PPh₃)₂] showed a binuclear thiolate bridged core while that of [Ir(SC₆H₃Cl₂-2,6)(CO)(PPh₃)₂] revealed a conventional square planar geometry with *trans* PPh₃ ligands. Three rhodium complexes were shown to be efficient catalysts for the hydroformylation of hept-1-ene under mild conditions with good selectivity for linear aldehyde for SAr = SC₆H₄SiPh₃-2. Reaction of [MF(CO)(PPh₃)₂] with phosphinothiolate proligands PSH gave the monomeric complexes [M(PS)(CO)(PPh₃)₂] (M = Rh or Ir; PS = SC₆H₄PPh₂-2 or S(CH₂)₃PPh₂; M = Rh, PS = SCH₂CH₂PPh₂ or SCH(CH₃)CH₂PPh₂). The complex [Rh(SC₆H₄PPh₂-2)(CO)(PPh₃)] reacted reversibly with protons (HBF₄) to give the dimeric dication [Rh₂(μ-SC₆H₄PPh₂-2)₂(CO)₂(PPh₃)₂]²⁺, shown by a crystal structure to be a thiolate bridged dimer with an Rh–Rh bond and pseudo-octahedral geometry about each Rh^{III}. Electrophilic attack by [Me₃O][BF₄] on [Rh(SC₆H₄PPh₂-2)(CO)(PPh₃)] occurred at sulfur to give [Rh(MeSC₆H₄PPh₂-2)(CO)(PPh₃)]⁺ and excess of MeI gave [Rh₂I₆(MeSC₆H₄PPh₂-2)₂], with octahedral Rh^{III} linked by a double iodide bridge. Attack at sulfur also occurred in [Rh(SC₆H₄PPh₂-2)(CO)(PPh₃)] with I(CH₂)₃I and ICH₂CO₂H to give [Rh(2-Ph₂PC₆H₄SCH₂CH₂CH₂)(CO)(PPh₃)] and [RhI₂(2-Ph₂PC₆H₄SCH₂CO₂)(PPh₃)] respectively. The complex [RhI₃(CO)(PPh₃)₂] was a by-product and shown by a crystal structure to have a pseudo-octahedral structure with *trans*-PPh₃ ligands.

Introduction

Although thiolate complexes of Rh^I and Ir^I with tertiary phosphine co-ligands are well documented, the majority are polynuclear with bridging thiolates¹ and examples of mononuclear complexes are rare. A wide range of binuclear complexes containing simple di-μ-thiolate bridges are known, and [Ir₂(μ-SCMe₃)₂(CO)₂(P(OMe)₃)₂] is typical. The tridentate trithiol CH₃C(CH₂SH)₃ forms trinuclear thiolate bridged complexes of the type [CH₃C{CH₂SRh(CO)(P(OMe)₃)₃}]₃.² In addition many complexes with mixed bridging ligand systems are also known and exemplified by [Ir₂(μ-pz)(μ-SCMe₃)(CO)₂(P(OMe)₃)₂].³

The chemistry of rhodium and iridium complexes with hybrid phosphorus–sulfur donor chelating ligands is by comparison less well explored.⁴ However such ligands appear to bind very effectively to platinum group metals, and complexes with Rh^I have been shown to be robust and efficient catalysts for the carbonylation of methanol.^{5,6} The thiolate-bridged dimeric complexes [Rh₂(PS)₂(CO)] (PS = Ph₂PCH₂CH₂S, Ph₂PC₆H₁₀S or Ph₂PC₆H₄S-2) and [M₂(Ph₂PC₆H₄S-2)(COD)₂] (M = Rh or Ir; COD = cyclooctadiene) have been known for some time.⁵ Recently the synthesis of the monomeric complexes [M(Ph₂PC₆H₄S-2)(CO)(PPh₃)] (M = Rh or Ir) was also reported,⁷ together with the chemistry of the alkoxide analogues. The PS ligands with aliphatic backbones behave differently, and reaction of [IrCl(CO)(PPh₃)₂] with 2 equivalents of Ph₂PCH₂CH₂SH in the presence of base generated the irid-

ium(III) complex [IrH(Ph₂PC₆H₄S)₂(CO)].⁸ The binucleating phosphinothiol proligand HSC₆H₃(CH₂PPh₂)₂-2,6 (PSHP) reacts with [MCl(CO)(PPh₃)₂] (M = Rh or Ir) to give [Rh₂Cl(PSP)(CO)₂] (with half an equivalent of PSHP) and [Ir₂Cl₂(PSP)₂(μ-CO)]⁹ (with one equivalent).

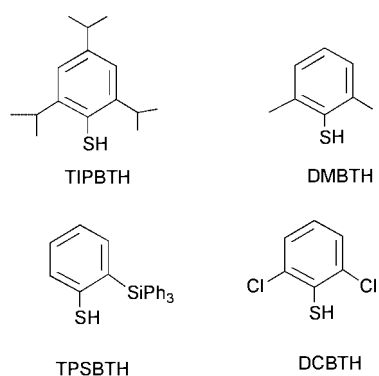
The oxidative addition chemistry of dinuclear thiolate bridged complexes of rhodium and iridium has been studied in some detail. Depending on the binuclear complex used as the starting point, bifunctional agents such as diiodomethane react to give complexes with triple bridges comprising a methylene group and two thiolate sulfurs or a methylene with one bridging thiolate sulfur and another bridging ligand such as pyrazole.^{10,11} Dimethyl acetylene dicarboxylate oxidatively adds to give species such as [Ir₂(μ-pz)(μ-SBu^t)(μ-MeO₂CC=CCO₂-Me)(CO)₂(P(OMe)₃)₂] with a triple bridge including the acetylene molecule, bonded as a dimetallated olefin.² In contrast, tetracyanoethylene adds in asymmetric fashion to [Ir₂(μ-SBu^t)₂(CO)₂(PR₃)₂] (R=Me, Ph or OMe) to give the complexes [(RP₃)₂(OC)Ir(μ-SBu^t)₂Ir(CO)(C₂(CN)₄)].¹² Significant rearrangement also occurs on addition of hexafluoro-2-butyne to [Ir₂(μ-SBu^t)₂(CO)₄] to give trinuclear ‘crown-like’ complexes of the type [Ir₃(μ-SBu^t)₃(μ-C₄F₆)(CO)]₆.¹³

In view of the comparative paucity of data on mononuclear complexes we have investigated the synthesis and reactivities of complexes of the type [Ir(SAr)(CO)(PPh₃)₂] (M = Rh or Ir; Ar = 2,6-disubstituted arene) and [Rh(Ph₂PC₆H₄S-2)(CO)(PPh₃)]. The presence of thiolate ligands in such complexes introduces the possibility of chemistry occurring at sulfur and

Table 1 Complexes of rhodium(i) and iridium(i) with bulky aromatic thiolates

Complex	Colour	Elemental analysis (%) ^a		$\tilde{\nu}(\text{CO})^b$	NMR (δ , J/Hz) ^c		MS ^d (<i>m/z</i>)
		C	H		³¹ P	¹ H	
1 <i>trans</i> -[Rh(DCBT)(CO)(PPh ₃) ₂]	Yellow	60.0 (60.0)	3.9 (4.0)	1965	32.2 (d), $J_{\text{P-Rh}} = 133.4$	7.1–7.8 (m) (33 H, aromatic)	804 (M – CO) ⁺
2 <i>trans</i> -[Rh(TPSBT)(CO)(PPh ₃) ₂]	Yellow	70.8 (71.6)	4.8 (4.8)	1978	30.50 (d), $J_{\text{P-Rh}} = 133.6$	6.8–7.8 (m) (49 H, aromatic)	1022 (M ⁺)
3 [Rh ₂ (μ -DMBT) ₂ (CO) ₂ (PPh ₃) ₂]	Yellow	60.2 (60.9)	3.9 (4.0)	1966	34.2 (d), $J_{\text{P-Rh}} = 156.7$	6.5–7.5 (m) (36 H, aromatic), 2.74(s) (6 H, CH ₃), 1.54(s) (6 H, CH ₃)	1060 M ⁺
4 [Rh ₂ (μ -TIPBT) ₂ (CO) ₂ (PPh ₃) ₂]	Yellow	64.5 (65.0)	6.0 (6.1)	1976	35.0 (d), $^1J_{\text{P-Rh}} = 153.6$	6.6–7.7 (m) (34 H, aromatic), 5.6 (m), 4.8 (m), 4.3 (m), 2.7 (m) (4 H, CH), 0.6–1.6 (m) (36 H, CH ₃)	1229 (M + 1 – CO) ⁺
5 <i>trans</i> -[Ir(DCBT)(CO)(PPh ₃) ₂]	Yellow	55.7 (56.9)	3.6 (3.6)	1946	20.8(s)	6.7–7.8 (m) (33 H, aromatic)	945 (M + Na) ⁺
6 <i>trans</i> -[Ir(TPSBT)(CO)(PPh ₃) ₂]	Yellow	66.0 (65.9)	4.4 (4.4)	2004	–3.4(s)	6.4–7.7 (m) (49 H, aromatic)	1111 (M ⁺)
7 <i>trans</i> -[Ir(DMBT)(CO)(PPh ₃) ₂]	Yellow	63.7 (63.7)	4.4 (4.5)	2035	9.31(s)	6.8–7.9 (m) (33 H, aromatic), 2.3(s) (6 H, CH ₃)	853 (M – CO) ⁺
8 <i>trans</i> -[Ir(TIPBT)(CO)(PPh ₃) ₂]	Yellow	61.2 (61.3)	4.4 (4.5)	2035	9.21(s)	6.8–7.9 (m) (32 H, aromatic), 2.6–3.7 (m) (3 H, CH), 0.6–1.4 (m) (18 H, CH ₃)	951 (M – CO) ⁺

^a Calculated values in parentheses. ^b As Nujol mulls, in cm⁻¹. ^c In CDCl₃ solution. ^d FAB mass spectra in 3-nitrobenzyl alcohol matrix.

**Fig. 1** Structures and abbreviations of aromatic thiol proligands.

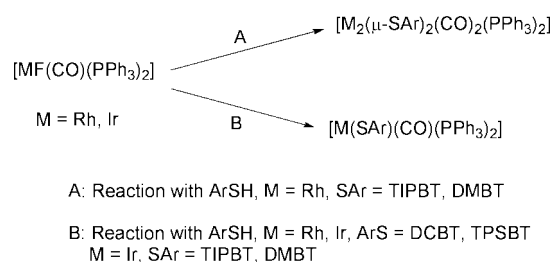
we have explored the balance between electrophilic attack at the metal and sulfur.

Results and discussion

Synthesis of complexes of sterically hindered thiolates

Reaction of [RhCl(CO)(PPh₃)₂] with free thiols RSH gives oxidation addition products and with sodium or lithium salts complex mixtures can be formed. However [RhF(CO)(PPh₃)₂] with bulky aromatic thiols in toluene gives the complexes [M(SAr)(CO)(PPh₃)₂] (M = Rh, SAr = DCBT (**1**) or TPSBT (**2**); M = Ir, SAr = DCBT (**5**), TPSBT (**6**), DMBT (**7**) or TIPBT (**8**)) and [Rh₂(μ -SAr)₂(CO)₂(PPh₃)₂] (SAr = TIPBT (**4**) or DMBT (**3**)). The structures and abbreviations for the thiols are summarised in Fig. 1, and the syntheses are summarised in Scheme 1. The complexes were isolated as moderately air-stable bright yellow solids, and analytical and spectroscopic data are summarised in Table 1.

The spectroscopic properties of the monomeric complexes were generally entirely consistent with a planar structure. Two thiols DCBTH and TIPBTH gave dimeric complexes with Rh, reflecting the greater steric constraints exerted by the 2,6-isopropyl or 2,6-chloro substituents, which cause loss of a triphenylphosphine ligand. The greater kinetic stability of iridium leads to monomeric iridium(i) complexes as triphenylphosphine is not lost. The ¹H NMR of complex **7** indicates that both Me groups are equivalent, indicating a symmetrical

**Scheme 1** Synthesis of thiolate complexes of Ir^I and Rh^I.

disposition of the aromatic thiolate groups. In the dimeric rhodium complex **3** the two thiolates are presumably equivalent in the *anti* configuration (see structure of **4** below), but the Me groups are inequivalent, and appear as two singlets. For the rhodium complexes **1** and **2** the Rh–P coupling constants of *ca.* 134 Hz are consistent with a *trans* arrangement of the tertiary phosphine ligands.

The crystal and molecular structure of [Rh₂(μ -TIPBT)₂(CO)₂(PPh₃)₂] **4**

A ZORTEP¹⁴ representation of the structure appears in Fig. 2 and selected bond lengths and angles are shown in Table 2. The two square planar rhodium(i) units are bridged by two arenethiolate sulfurs with the arene groups adopting an *anti* arrangement with respect to the Rh₂S₂ core. The observation of only two singlets in the ¹H NMR of the DMTB analogue suggests free rotation about the C–S bond in solution. The Rh–S distances are very similar to those observed for *anti*-[Rh₂(μ -S^tBu)₂(CO)₂(PPh₃)₂]¹⁵ (2.357(1) and 2.391(6) Å) and [Rh₂(μ -S^{Ph})₂(CO)₂(PPh₃)₂]¹⁶ (2.375(7) and 2.400(7) Å). The slightly longer Rh–S distances observed in **4** are ascribable to the steric effects exerted by the 2,6-substituents in the arenethiolate group. The Rh₂S₂ has a characteristic ‘butterfly’ configuration and the Rh···Rh distance of 3.522(1) Å indicates the absence of a Rh–Rh bond.

The crystal and molecular structure of [Ir(DCBT)(CO)(PPh₃)₂] **5**

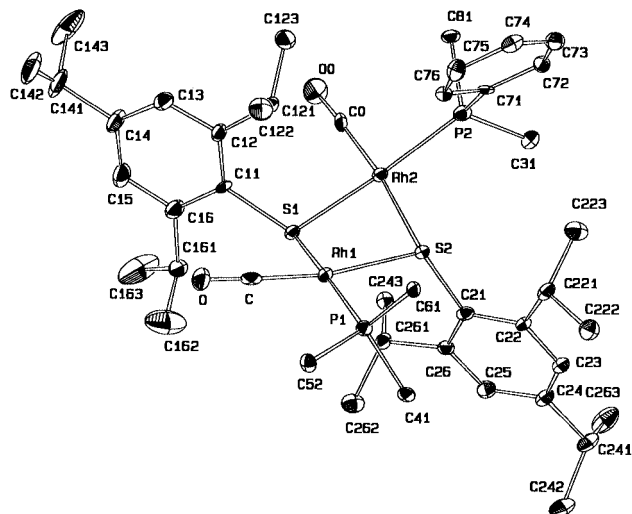
A ZORTEP representation of the molecular structure of complex **5** is shown in Fig. 3, and selected bond lengths and angles are shown in Table 3. The geometry about iridium is slightly

Table 2 Selected bond lengths (Å) and angles (°) for compound **4**

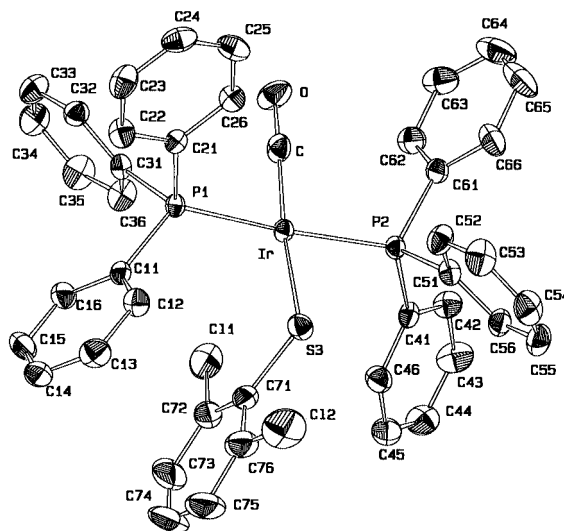
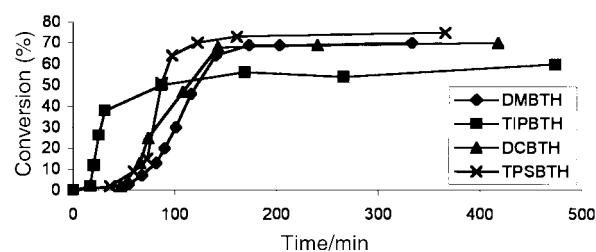
Rh(1)–C	1.764(8)	S(2)–C(21)	1.803(7)
Rh(1)–P(1)	2.266(2)	P(1)–C(41)	1.813(7)
Rh(1)–S(1)	2.369(2)	P(1)–C(61)	1.813(8)
Rh(1)–S(2)	2.415(2)	P(1)–C(52)	1.876(7)
Rh(2)–C(0)	1.814(8)	P(2)–C(31)	1.812(7)
Rh(2)–P(2)	2.267(2)	P(2)–C(81)	1.842(7)
Rh(2)–S(1)	2.368(2)	P(2)–C(71)	1.851(8)
Rh(2)–S(2)	2.448(2)	C–O	1.217(8)
S(1)–C(11)	1.798(7)	C(0)–O(0)	1.150(9)
C–Rh(1)–P(1)	92.1(2)	P(2)–Rh(2)–S(2)	96.65(7)
C–Rh(1)–S(1)	93.5(2)	S(1)–Rh(2)–S(2)	80.76(6)
P(1)–Rh(1)–S(1)	169.90(7)	C(11)–S(1)–Rh(1)	116.2(2)
C–Rh(1)–S(2)	171.1(2)	C(11)–S(1)–Rh(2)	114.1(2)
P(1)–Rh(1)–S(2)	94.03(7)	Rh(1)–S(1)–Rh(2)	96.05(7)
S(1)–Rh(1)–S(2)	81.45(6)	C(21)–S(2)–Rh(1)	119.1(2)
C(0)–Rh(2)–P(2)	89.9(2)	C(21)–S(2)–Rh(2)	117.7(3)
C(0)–Rh(2)–S(1)	92.7(2)	Rh(1)–S(2)–Rh(2)	92.81(6)
P(2)–Rh(2)–S(1)	170.69(7)	O–C–Rh(1)	177.1(6)
C(0)–Rh(2)–S(2)	173.4(2)	O(0)–C(0)–Rh(2)	177.3(8)

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

Ir–C	1.824(4)	P(2)–C(41)	1.833(3)
Ir–P(2)	2.3238(9)	P(2)–C(61)	1.835(3)
Ir–P(1)	2.3335(8)	S(3)–C(71)	1.756(4)
Ir–S(3)	2.3933(9)	Cl(1)–C(72)	1.737(5)
P(1)–C(21)	1.828(3)	Cl(2)–C(76)	1.733(6)
P(1)–C(11)	1.827(3)	O–C	1.153(5)
P(2)–C(51)	1.824(3)		
C–Ir–P(2)	92.25(11)	P(2)–Ir–S(3)	85.66(3)
C–Ir–P(1)	86.42(11)	P(1)–Ir–S(3)	94.68(3)
P(2)–Ir–P(1)	174.31(3)	O–C–Ir	177.0(3)
C–Ir–S(3)	169.67(12)		

**Fig. 2** A ZORTEP representation of the structure of $[\text{Rh}_2(\mu\text{-TIPBT})_2(\text{CO})_2(\text{PPh}_3)_2]$ **4** showing the atom labelling scheme. The tertiary phosphine phenyl groups are omitted for clarity.

distorted square planar with C–Ir–P(2) 92.25(11), C–Ir–P(1) 86.42(11)°, P(2)–Ir–S(3) 85.67(5)° and P(1)–Ir–S(3) 94.68(3). The orientation of the DCBT ligand is such as to bring one Cl substituent close to the metal with an $\text{Ir}\cdots\text{Cl}(1)$ distance of 3.197(1) Å. This suggests weak donation of electron density of the Cl lone pairs to the iridium, which may explain the lower value for $\nu(\text{CO})$ for this complex compared to those of the other monomeric iridium(i) complexes. The Ir–S bond length of 2.393(2) Å is somewhat longer than that observed for other monomeric thiolate complexes such as $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{SC}_6\text{F}_4\text{H})_2]$.¹⁶ However the variations in ligands and oxidation states make a precise comparison difficult.

**Fig. 3** A ZORTEP representation of the structure of $[\text{Ir}(\text{DCBT})(\text{CO})(\text{PPh}_3)_2]$ **5** showing the atom labelling scheme.**Fig. 4** Percentage conversion of olefin into linear aldehyde for the hydroformylation of 1-heptene (70 °C, 5 bar forming gas) for a range of rhodium(i) aromatic thiolate complexes.

Catalytic activity of rhodium thiolate complexes

The catalytic activity of binuclear complexes such as $[\text{Rh}_2(\mu\text{-SR})_2(\text{CO})_2\text{P}_2]$ ($\text{R} = \text{Bu}^t$ or $\text{Me}_2\text{NCH}_2\text{CH}_2$, $\text{P} =$ tertiary phosphine), particularly for hydroformylation or aminomethylation, has been explored in some detail.^{18–20} *In situ* IR experiments showed the formation of mononuclear hydrides such as $[\text{RhHP}]$ under hydroformylation conditions (80 °C, 5–30 bar). Deuterioformylation experiments provided no evidence for the involvement of binuclear species.²¹ Similar results were obtained in water using sulfonated triphenylphosphine to confer solubility.²² Generally conversion rates are reasonably high and use of chiral diphosphines provides high regioselectivity and medium to high enantiomeric excesses.²³ Asymmetric hydroformylation of styrene has also been achieved using 1,1'-binaphthalene-2,2'-dithiol complexes of Rh^I .²⁴

Here both monomeric and dimeric rhodium complexes **1**, **2** and **4** were tested for hydroformylation catalysis activity for 1-heptene, and the results are presented in Fig. 4. High conversion rates are obtained under the mild conditions (70 °C, 5 bar forming gas) with reasonable to good regioselectivities for formation of linear as opposed to branched aldehydes. Maximum selectivity for linear aldehyde was observed for complex **2** of the asymmetrically substituted thiol TPSBTH where the single large Ph_3Si group is clearly able to exert steric influence on the reaction stereochemistry at the olefin insertion step. There is no discernible difference in rate or selectivity between the dimeric and monomeric complexes and in view of the results obtained above it seems likely that both give rise to monomeric intermediates. The overall conversion rates are comparable with those for $[\text{RhCl}(\text{PPh}_3)_3]$ and the selectivity to linear aldehyde formation is approximately twice that for Wilkinson's complex. The strong dependence of conversion yield and stereochemistry on the thiolate suggests that thiolate

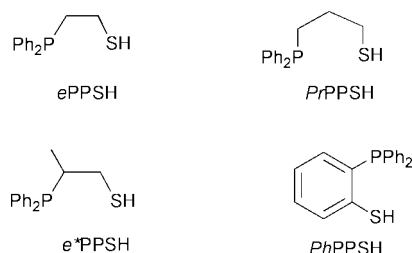


Fig. 5 Structures and abbreviations for phosphinothiol proligands.

co-ordination may be retained in the active catalyst under the conditions used, although involvement as a non-co-ordinated anion cannot be excluded.

Synthesis of phosphinothiolate complexes

We describe here the convenient high yield (*ca.* 90%) syntheses of complexes of the type $[M(PS)(CO)(PPh_3)_2]$ **9–14** ($M = Rh$ or Ir ; $PS = PhPPS$, $ePPS$, $PrPPS$; abbreviations and structures summarised in Fig. 5) by direct reaction of $[RhF(CO)(PPh_3)_2]$ with PSH in toluene, Et_3N being added for $M = Ir$. We also describe oxidative addition reactions with a range of electrophiles with the objective of establishing if electrophilic attack occurred at sulfur or the metal and if replacement of chloride by thiolate in $[RhCl(CO)P]$ ($P =$ tertiary phosphine) type complexes modified the chemistry.

The comparative lability of the fluoride ligand in the complexes $[MF(CO)(PPh_3)_2]$ permits high yield syntheses of the complexes $[M(PS)(CO)(PPh_3)_2]$ by direct reaction with one equivalent of the thiol. In our hands reaction of the chloro-complexes with lithium or sodium salts of the phosphinothiol gave mixtures and significantly lower yields of the required product. The complexes **9** to **14** were isolated as moderately air-stable yellow solids and analytical and spectroscopic data are summarised in Table 4.

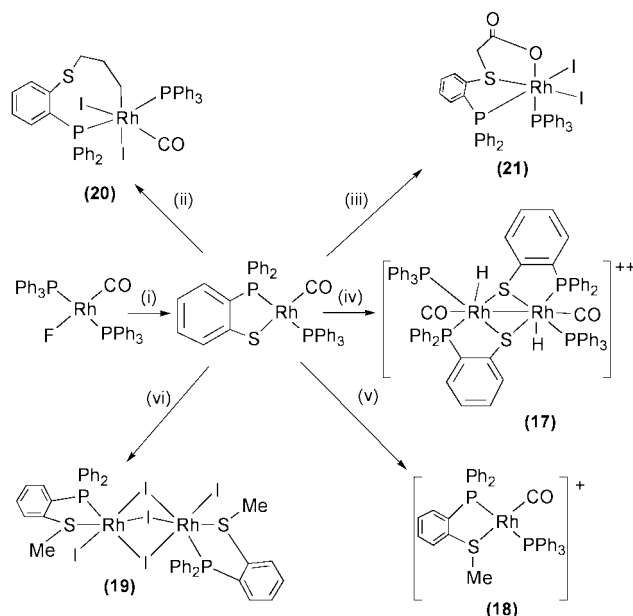
The IR spectra show strong absorptions in the range 1947–1976 cm^{-1} assigned to $\nu(CO)$. It is at first sight somewhat surprising that the CO stretching frequency is higher for the complexes with PS ligands with ethylene or trimethylene backbones than for those with a phenyl group linking P and S ($PhPPS$). This may be due to the saturated hydrogen backbones conferring more flexibility on the ligand. A similar effect is observed for $[Ir(PrPPS)(CO)(PPh_3)_2]$ **14** and $[Ir(PhPPS)(CO)(PPh_3)_2]$ **13**, where $\nu(CO)$ is 50 cm^{-1} higher for the complex with the trimethylene bridge. The 1H and ^{31}P NMR spectra were in accord with a square planar geometry of the complexes with *trans* phosphorus donors, as shown by X-ray crystallography.⁶

Syntheses of complexes of the type $[IrH(PS)_2(CO)]$ ($PS = PhPPS$ **15** or $PrPPS$ **16**)

Reaction of $[IrF(CO)(PPh_3)_2]$ with 2 equivalents of $PhPPSH$ or $ePPSH$ in the presence of diethylamine as base gave the complexes $[IrH(PhPPS)_2(CO)]$ **15** or $[IrH(PrPPS)_2(CO)]$ **16** in good yield as pale yellow powders. Complex **15** was identical to that prepared earlier from $[IrCl(CO)(PPh_3)_2]$, and **16** is directly analogous. Analytical and spectroscopic data for (Table 4) **16** are consistent with its formulation as an octahedral iridium(III) complex.

Reactions of $[Rh(PhPPS)(CO)(PPh_3)]$ **9**

Reactions of complex **9** with a range of electrophiles have been investigated, and these are summarised in Scheme 2. The reaction with HCl gave a complex, intractable mixture of products that could not be separated. However with excess of $HBF_4 \cdot OEt_2$ in dry CH_2Cl_2 at room temperature a near quantitative yield was obtained of the deep purple dimeric cation $[Rh_2H_2(PhPPS)_2(CO)_2(PPh_3)_2]^{2+}$ **17** isolated as the $[BF_4]^-$ salt. The complex is moderately stable in air both as a solid and in



Scheme 2 Summary of the synthesis and reactions of $[Rh(Ph_2PC_6H_4-S-2)(CO)(PPh_3)_2]$ **9**. (i) $ArSH$ in toluene. (ii) $I(CH_2)_3I$ in CH_2Cl_2 . (iii) Excess of ICH_2CO_2H in benzene. (iv) $HBF_4 \cdot Et_2O$ in CH_2Cl_2 . (v) $[MeO][BF_4]$ in CH_2Cl_2 . (vi) Excess of MeI in benzene. All reactions at room temperature.

solution. The IR spectrum shows a single intense band at 2050 cm^{-1} assigned to $\nu(CO)$ and a broad band at around 1090 cm^{-1} due to the $[BF_4]^-$ counter ion. The FAB mass spectrum displays a peak at $m/z = 687$ due to $[M]^{2+}$ and also peaks at $m/z = 1082$ ($[M - H - CO - PPh_3]^+$) and 658 ($[M - 2CO]^{2+}$). Reaction of **17** with Et_3N in methanol results in the quantitative regeneration of complex **9**, confirming an unusual example of reversible, pH-dependent formation of a thiolate-bridged metal–metal bond. However despite the clear evidence for the presence of protons from the reaction with base, we were unable to detect any 1H NMR resonances attributable to metal hydride in the range $\delta +10$ to -30 . This may be due to a rapid hydrogen exchange process between the metal and sulfur sites, but the hydride resonances still could not be detected at lower temperatures. It is also possible that they are obscured by other intense peaks in the spectrum. The ^{31}P NMR revealed a complex second order spectrum which was consistent with the solid state structure discussed below.

The formation of the dimeric cation **17** presumably occurs *via* initial protonation at the metal to give $[RhH(FBF_3)(PhPPS)(CO)(PPh_3)]$ followed by displacement of the weakly bound $[BF_4]^-$ anion by the thiolate sulfur of an adjacent molecule. A precedent is found in the complex $[IrH(FBF_3)Cl(CO)(PPh_3)_2]$ where a crystal structure confirmed the presence of an F-bound $[BF_4]^-$ anion.²⁵ Further support for the possibility of bridging hydrides in **17** comes from protonation of the complex $[Ir_2H_2(SBu^t)_2(CO)_2(PPh_3)_2]$ that gave $[Ir_2H_2(\mu-H)(SBu^t)_2(CO)_2(PPh_3)_2]^+$ in which there is a single hydride bridging between the two iridiums.²⁶

The crystal structure of $[Rh_2H_2(PhPPS)_2(CO)_2(PPh_3)_2]^{2+}$ **17.** A ZORTEP representation of the molecular structure of complex **17** is shown in Fig. 6 and selected bond lengths and angles are displayed in Table 5. The geometry about each Rh is distorted octahedral (including the Rh–Rh bond) with each Rh atom lying above the P,P,S,S plane. There are vacant sites approximately *trans* to P(2) and P(4) which could accommodate the hydride ligands. The molecule is folded about the S–S vector to give a butterfly type structure, and the Rh–Rh distance is typical for a metal–metal single bond. The Rh–S distances for the bridging thiolates are significantly different $[Rh(1)–S(1)$ 2.309(2), $Rh(2)–S(1)$ 2.376(2), $Rh(1)–S(2)$ 2.412(2), $Rh(2)–S(2)$

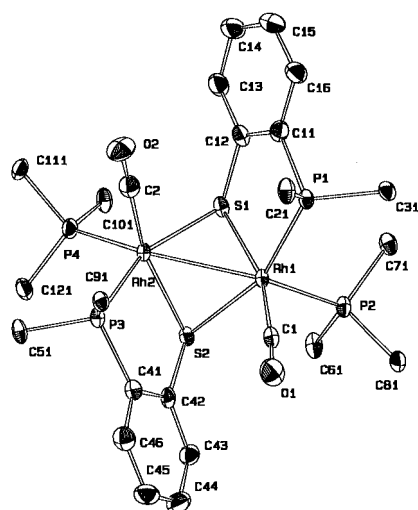
Table 4 Phosphinothiolate complexes of rhodium(I) and iridium(I)

Complex	Colour	Elemental analysis (%) ^a		$\nu(\text{CO})^b$	NMR (δ , J/Hz) ^c		MS ^d (m/z)
		C	H		³¹ P	¹ H	
9 [Rh(<i>Ph</i> PPS)(CO)(PPh ₃)]	Pale yellow	64.9 (64.7)	4.1 (4.3)	1962	63.5 (dd), 33.4 (dd), $J_{\text{Rh-P}} = 130.4$, $J_{\text{P-P}} = 301.1$	6.8–7.8 (m) (29 H, phenyl group)	687 (M ⁺)
10 [Rh(<i>Pr</i> PPS)(CO)(PPh ₃)]	Yellow orange	60.1 (60.2)	5.4 (5.4)	1952	87.5 (dd), 32.8 (dd), $J_{\text{Rh-P}} = 127.3$, $J_{\text{P-P}} = 287.6$	6.8–7.8 (m) (19 H, aromatic), 2.5–2.7 (br) (2 H, CH), 1.37 (d), 1.31 (d), 1.20 (d), 1.14 (d) (12 H, CH ₃)	653 (M ⁺)
11 [Rh(<i>e</i> PPS)(CO)(PPh ₃)]	Yellow	62.1 (62.1)	4.5 (4.6)	1976		6.8–8.4 (m) (25 H, aromatic), 2.2–3.7 (br) (4 H, CH ₂)	639 (M ⁺)
12 [Rh(<i>e</i> *PPS)(CO)(PPh ₃)]	Yellow	62.5 (62.5)	5.0 (4.9)	1951	68.2 (dd), 59.9 (dd), $J_{\text{Rh-P}} = 133.4$, $J_{\text{P-P}} = 304.2$	7.0–8.0 (m) (25 H, aromatic), 2.9–3.2 (m) (2 H, CH ₂), 2.4–2.7 (m) (1 H, CH), 1.3–1.5 (d) (3 H, CH ₃)	653 (M ⁺)
13 [Ir(<i>Ph</i> PPS)(CO)(PPh ₃)]	Yellow	57.2 (57.3)	3.8 (3.8)	1947	55.0 (d), 25.9 (d), $J_{\text{P-P}} = 303.1$	6.7–6.9 (m) (29 H, aromatic)	776 (M ⁺)
14 [Ir(<i>Pr</i> PPS)(CO)(PPh ₃)]	Yellow	52.5 (52.6)	4.6 (4.7)	1997	53.1 (d), 6.84 (d), $J_{\text{P-P}} = 380.0$	6.7–7.9 (m) (19 H, aromatic), 2.3–3.0 (br) (2 H, CH), 0.8–1.5 (m) (12 H, CH ₃)	708 (M ⁺)
15 [Ir(H)(<i>Ph</i> PPS) ₂ (CO)]	Yellow	55.1 (55.0)	3.6 (3.6)	2026, $\nu(\text{Ir-H})$ 2098w	37.08 (d), 23.84 (d), $^2J_{\text{P-P}} = 307.2$	6.7–8.0 (m) (28 H, aromatic), –11.29 (dd) (1 H, hydride), $^2J_{\text{H-P}} = 8.85$	778 (M – CO – H) ⁺
16 [Ir(H)(<i>Pr</i> PPS) ₂ (CO)]	Yellow	50.3 (50.3)	4.5 (4.5)	2018, $\nu(\text{Ir-H})$ 2112w	–28.3(s)	7.2–8.2 (m) (20 H, aromatic), 2.0–3.9 (m) (12 H, CH ₂), –11.6 (d) (1 H, hydride), $J_{\text{P-H}} = 11.2$	740 (M ⁺)
17 [Rh ₂ (<i>Ph</i> PPS) ₂ (CO) ₂ (PPh ₃) ₂][BF ₄] ₂	Purple	56.2 (56.8)	3.9 (3.9)	2050	62.0 (d), 15.5 (d)	6.4–8.0 (m) (aromatic)	1082 (M – CO – PPh ₃ – H) ⁺
18 [Rh(<i>Ph</i> PPSMe)(CO)(PPh ₃)] [BF ₄]	Purple	57.9 (57.9)	4.1 (4.1)	2014	61.8 (dd), $^1J_{\text{P-Rh}} = 115.2$, 27.5 (dd), $^1J_{\text{P-Rh}} = 123.3$, $^2J_{\text{P-P}} = 272.9$	6.5–8.0 (m) (29 H, aromatic), 1.8 (s) (3 H, SCH ₃)	701 (M ⁺)
19 [Rh ₂ (μ -I) ₂ (I) ₄ (<i>Ph</i> PPSMe) ₂]	Deep red	29.0 (28.8)	2.2 (2.2)		70.5 (dd), $^1J_{\text{P-Rh}} = 115.2$	6.7–8.2 (m) (20 H, aromatic), 1.8 (s) (3 H, CH ₃)	701 (M ⁺)
20 [RhI ₂ (<i>Ph</i> PPS(CH ₂) ₃)(CO)(PPh ₃)]	Bright red	54.1 (54.3)	3.7 (3.6)	2062	61.2 (dd), $^1J_{\text{P-Rh}} = 136.4$, 25.8 (dd), $^1J_{\text{P-Rh}} = 121.2$, $^2J_{\text{P-P}} = 16.2$	6.7–8.1 (m) (29 H, aromatic), 0.7–2.4 (m, br) (6 H, CH ₂)	730 (M – 2I) ⁺
21 [RhI ₂ (<i>Ph</i> PPSCH ₂ CO ₂)(PPh ₃)]	Deep red	46.9 (47.0)	3.3 (3.3)	1652	48.2 (dd), 4.9 (dd), $^2J_{\text{P-P}} = 545.7$	6.8–7.5 (m) (29 H, aromatic), 2.75 (d) (1 H, CH ₂), 2.20 (d) (1 H, CH ₂), $^2J_{\text{H-H}} = 17.3$	971 (M ⁺)
22 <i>trans</i> -[RhI ₃ (CO)(PPh ₃) ₂]	Deep orange	43.0 (42.9)	2.9 (2.9)	2082	48.2 (d), $^1J_{\text{P-Rh}} = 76.8$	6.8–8.5 (m) (aromatic)	881 (M – CO – I) ⁺

^a Calculated values in parentheses. ^b As Nujol mulls, in cm⁻¹. ^c In CDCl₃ solution. ^d FAB mass spectra in 3-nitrobenzyl alcohol matrix.

Table 5 Selected bond lengths (Å) and angles (°) for compound **17**

Rh(1)–C(1)	1.933(9)	P(1)–C(21)	1.828(8)
Rh(1)–S(1)	2.309(2)	P(1)–C(31)	1.840(8)
Rh(1)–P(1)	2.320(2)	P(2)–C(81)	1.833(9)
Rh(1)–P(2)	2.395(2)	P(2)–C(61)	1.833(8)
Rh(1)–S(2)	2.412(2)	P(2)–C(71)	1.836(8)
Rh(1)–Rh(2)	2.746(2)	S(2)–C(42)	1.784(8)
Rh(2)–C(2)	1.886(9)	P(3)–C(41)	1.815(8)
Rh(2)–P(3)	2.320(2)	P(3)–C(51)	1.816(8)
Rh(2)–S(2)	2.321(2)	P(3)–C(91)	1.829(8)
Rh(2)–S(1)	2.376(2)	P(4)–C(111)	1.814(8)
Rh(2)–P(4)	2.440(2)	P(4)–C(101)	1.830(8)
S(1)–C(12)	1.777(8)	C(1)–O(1)	1.090(10)
P(1)–C(11)	1.816(8)	C(2)–O(2)	1.136(11)
C(1)–Rh(1)–S(1)	161.7(2)	C(2)–Rh(2)–P(3)	91.0(3)
C(1)–Rh(1)–P(1)	96.5(2)	C(2)–Rh(2)–S(2)	161.9(3)
S(1)–Rh(1)–P(1)	86.75(7)	P(3)–Rh(2)–S(2)	87.02(8)
C(1)–Rh(1)–P(2)	99.2(2)	C(2)–Rh(2)–S(1)	97.2(3)
S(1)–Rh(1)–P(2)	98.08(7)	P(3)–Rh(2)–S(1)	158.88(7)
P(1)–Rh(1)–P(2)	98.70(8)	S(2)–Rh(2)–S(1)	79.16(8)
C(1)–Rh(1)–S(2)	92.9(2)	C(2)–Rh(2)–P(4)	98.3(3)
S(1)–Rh(1)–S(2)	78.68(7)	P(3)–Rh(2)–P(4)	105.13(8)
P(1)–Rh(1)–S(2)	159.14(7)	S(2)–Rh(2)–P(4)	99.54(7)
P(2)–Rh(2)–S(2)	98.07(8)	S(1)–Rh(2)–P(4)	92.96(8)
C(1)–Rh(1)–Rh(2)	106.7(2)	C(2)–Rh(2)–Rh(1)	107.6(3)
S(1)–Rh(1)–Rh(2)	55.27(5)	P(3)–Rh(2)–Rh(1)	105.98(6)
P(1)–Rh(1)–Rh(2)	106.32(6)	S(2)–Rh(2)–Rh(1)	56.09(5)
P(2)–Rh(1)–Rh(2)	141.18(6)	S(1)–Rh(2)–Rh(1)	52.97(6)
S(2)–Rh(1)–Rh(2)	52.99(5)	P(4)–Rh(2)–Rh(1)	138.71(6)

**Fig. 6** A ZORTEP representation of the structure of $[\text{Rh}_2\text{H}_2(\mu\text{-Ph}_2\text{PC}_6\text{H}_4\text{S-2})_2(\text{CO})_2(\text{PPh}_3)_2]^{2+}$ **17** showing the atom labelling scheme. The tertiary phosphine phenyl groups are omitted for clarity.

2.321(2) Å] probably as a consequence of the presence of the chelated P,S ring system.

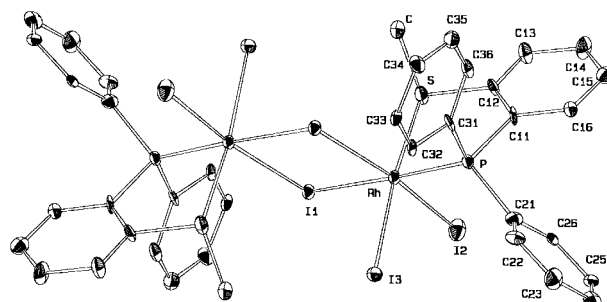
With $[\text{Me}_3\text{O}][\text{BF}_4]$ or MeI. Reaction of complex **9** with $[\text{Me}_3\text{O}][\text{BF}_4]$ in dry CH_2Cl_2 gave the purple rhodium(i) cation $[\text{Rh}(\text{PhPPSMe})(\text{CO})(\text{PPh}_3)]^+$ **18** in high yield, isolated as the $[\text{BF}_4]^-$ salt. The IR spectrum showed an intense band due to $\nu(\text{CO})$ at 2014 cm^{-1} (see Table 4). This is 36 cm^{-1} lower than the value for complex **17**, consistent with alkylation taking place at sulfur rather than the metal and retention of the rhodium(i) oxidation state.

The oxidative addition of MeI is a crucial step in the carbonylation of methanol in the Monsanto process, and we have investigated the reaction of complex **9** with an excess of methyl iodide. In benzene at room temperature the deep red dimeric complex $[\text{Rh}_2\text{I}_6(\text{PhPPSMe})_2]$ **19** is formed in high yield. GC analysis of the reaction mixture indicated that acetone had been formed in virtually quantitative yield, presumably *via* methylation of an acetyl intermediate. The formation of acetone is not

Table 6 Selected bond lengths (Å) and angles (°) for compound **19**

Rh–P	2.272(3)	I(1)–Rh#1	2.7602(14)
Rh–S	2.355(4)	S–C(12)	1.801(12)
Rh–I(2)	2.659(2)	S–C	1.831(14)
Rh–I(3)	2.6603(14)	P–C(11)	1.808(13)
Rh–I(1)	2.683(2)	Rh–C(31)	1.807(13)
Rh–I(1)#1	2.7602(14)	P–C(21)	1.828(14)
P–Rh–S	86.10(12)	P–Rh–I(1)#1	176.02(10)
P–Rh–I(2)	91.93(10)	S–Rh–I(1)#1	90.09(9)
S–Rh–I(2)	84.12(10)	I(2)–Rh–I(1)#1	86.53(4)
P–Rh–I(3)	89.75(10)	I(3)–Rh–I(1)#1	93.97(4)
S–Rh–I(3)	174.11(10)	I(1)–Rh–I(1)#1	81.62(4)
I(2)–Rh–I(3)	91.85(5)	Rh–I(1)–Rh#1	98.38(4)
P–Rh–I(1)	99.88(9)	C(12)–S–C	96.5(6)
S–Rh–I(1)	95.65(10)	C(12)–S–Rh	103.4(5)
I(2)–Rh–I(1)	168.16(5)	C–S–Rh	114.0(5)
I(3)–Rh–I(1)	89.17(4)		

Symmetry relation: #1 $-x, -y, -z$.

**Fig. 7** A ZORTEP representation of the structure of $[\text{Rh}_2\text{I}_6(\text{Ph}_2\text{PC}_6\text{H}_4\text{SMe-2})_2]$ **19**, showing the atom labelling scheme.

unexpected for these systems, and is observed as a by-product in the carbonylation of methanol.²⁷ The availability of sulfur as an additional site for alkylation has a significant effect on the course of the reaction, and little or no acetone is formed when $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ is treated with an excess of MeI under similar conditions.

Crystal structure of $[\text{Rh}_2\text{I}_6(\text{PhPPSMe})_2]$ **19.** The X-ray crystal structure is shown in Fig. 7 and selected bond lengths and angles appear in Table 6. The geometry about each rhodium(III) atom of the dimer is approximately octahedral with a double iodide bridge. The bond distances and angles for the Rh_2I_6 unit are similar to those reported for $[\text{Rh}_2(\text{MeCO})_2\text{I}_6(\text{CO})_2]^{2-}$.²⁸ The phosphinothiolate ligand has been alkylated at sulfur to give the corresponding bidentate thioether and the Rh–P and Rh–S distances are very similar to those found in $[\text{Rh}(\text{ePPSMe})_2]\text{BF}_4$.²⁹

With 1,3-diiodopropane. Reaction of complex **9** with an excess of $\text{I}(\text{CH}_2)_3\text{I}$ in dry dichloromethane for 24 h at room temperature gave **20** as a bright orange powder in *ca.* 55% yield. The elemental analysis suggested the stoichiometry 'Rh(PhPSS)(CH_2)₃I₂(CO)(PPh₃)' consistent with oxidative addition of the diiodopropane unit. The IR showed a single strong band at 2062 cm^{-1} , the increase from that found in **9** being consistent with oxidative addition at the metal. The ³¹P NMR showed two doublets of doublets at δ 61.2 and 25.8 consistent with two inequivalent phosphine ligands. The FAB mass spectrum shows a strong peak at $m/z = 658$ corresponding to $[\text{M} - (\text{CH}_2)_3 - 2\text{I} - \text{CO}]^+$ with appropriate isotope distribution.

The first step of the reaction is presumably oxidative addition of one end of the diiodopropane to the Rh^{I} or at S to give $[\text{Rh}(\text{CH}_2\text{CH}_2\text{CH}_2\text{I})(\text{PhPPS})(\text{CO})(\text{PPh}_3)_2]$ or $[\text{Rh}(\text{PhPPSCH}_2\text{CH}_2\text{CH}_2\text{I})(\text{CO})(\text{PPh}_3)_2]^+\text{I}^-$. These possibilities cannot be distinguished, but the fact that no CO insertion product is

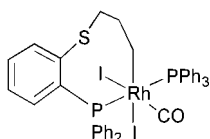


Fig. 8 Proposed structure for $[\text{RhI}_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{S}(\text{CH}_2)_3)(\text{CO})(\text{PPh}_3)]$ **20**.

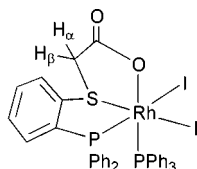


Fig. 9 Proposed structure for $[\text{RhI}_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{SCH}_2\text{CO}_2)(\text{PPh}_3)]$ **21**.

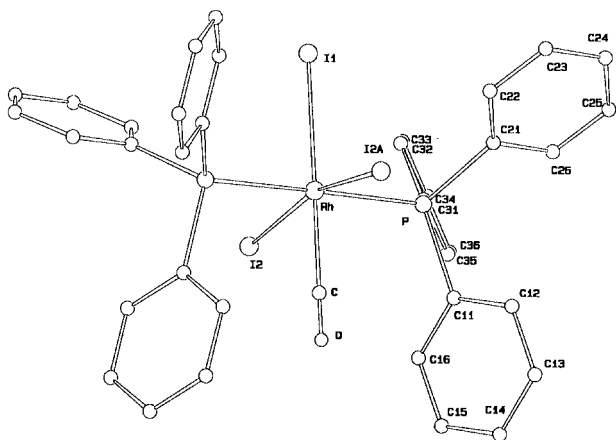


Fig. 10 A ZORTEP representation of the structure of $[\text{RhI}_3(\text{CO})(\text{PPh}_3)_2]$ **22**, showing the atom labelling scheme.

observed, and the nature of the product **19** of the reaction with $\text{Me}_3\text{O}^+\text{BF}_4^-$, suggest initial attack may be at sulfur. Oxidative addition of the second CH_2I group and co-ordination of the iodide counter ion gives the final product **20**, for which we propose the structure shown in Fig. 8. The formation of the chelated alkyl derivative presumably prevents insertion of CO to give a co-ordinated acetyl group.

With iodoacetic acid. An excess of iodoacetic acid reacted with complex **9** in benzene at room temperature to give **21** as a deep red powder in about 50% isolated yield. The complex is stable in air both in the solid state and in solution, the elemental analysis being consistent with the stoichiometry $[\text{RhI}_2(\text{PhPPS})(\text{CH}_2\text{CO}_2)(\text{PPh}_3)]$. The IR spectrum shows a strong band at 1652 cm^{-1} assigned to a carboxyl group, but no band attributable to a terminally bonded carbonyl ligand. ^1H NMR showed the expected multiplet for the aromatic protons and a pair of doublets at δ 2.20 and 2.75 assigned to the methylene protons and suggests metal binding by the carboxylate oxygen. The ^{31}P NMR comprised two doublets of doublets at δ 48.2 and 4.9 consistent with two inequivalent phosphine ligands bound to Rh. An intense peak in the MS at $m/z = 971$ corresponds to $[\text{M}]^+$ and a weaker peak at $m/z = 844$ to $[\text{M} - \text{I}]^+$. Based on the analytical and spectroscopic data we assign the structure shown in Fig. 9. The loss of the CO ligand suggests a multiple series of insertion/addition reactions, as with methyl iodide, but we were unable to identify the eventual fate of the CO in this case.

A by-product of the reaction, isolated by recrystallisation as a red solid in ca. 15% yield, is $[\text{RhI}_3(\text{CO})(\text{PPh}_3)_2]$ **22**. Crystals suitable for structure determination were grown from dichloromethane–methanol.³⁰ A ZORTEP representation of the structure appears in Fig. 10. The geometry about the Rh is pseudo octahedral with the two phosphorus donors in *trans* locations. Such trihalogenorhodium(III) complexes have been observed before³¹ but isolated in very low yield and identified

by NMR spectroscopy. The Rh–P distances are closely similar to those in $[\text{Rh}(\text{CH}_3)_2(\text{PPh}_3)_2]$ ³² and the Rh–I distances are close to those found in $[\text{Rh}(\text{COCH}_3)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$.³³

Conclusion

We have shown that reaction of a fluoro precursor with bulky aromatic thiolates provides a convenient high yield route to complexes of the types $[\text{M}(\text{SAr})(\text{CO})(\text{PPh}_3)_2]$ ($\text{M} = \text{Ir}$) and $[\text{M}_2(\mu\text{-SAr})_2(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{M} = \text{Rh}$). These have been shown to be effective hydroformylation catalysts. The monomeric phosphinothiolate complex $[\text{Rh}(\text{PhPPS})(\text{CO})(\text{PPh}_3)]$ can be prepared analogously and its reactions clearly show that, with the exception of the proton, electrophilic attack takes place at the thiolate sulfur. This causes such reactions to take a quite different course from that for complexes where thiolate is replaced by halide or the thiolate is bridging and much less susceptible to electrophilic attack. By contrast, protonation with acids with weakly co-ordinating anions occurs at the metal with an unusual example of reversible thiolate bridge formation.

Experimental

Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using conventional Schlenk glassware and solvents were dried using established procedures and distilled under dinitrogen immediately prior to use. IR spectra were recorded on a Perkin-Elmer Paragon FT-IR spectrometer as Nujol mulls and ^1H and ^{31}P NMR spectra on a JEOL EX270 spectrometer in CDCl_3 solution. Elemental analyses were determined on a Perkin-Elmer 240 instrument at the University of Essex. The complexes $[\text{MF}(\text{CO})(\text{PPh}_3)_2]$ ($\text{M} = \text{Rh}$ or Ir) were made by the literature method.³⁴ The thiols, TIPBTH,³⁵ DMBTH³⁵ and TPSBTH³⁶ and phosphinothiols *PhPPSH*, *ePPSH*,³⁷ *e*PPSH*³⁷ and *PrPPSH*³⁷ were also prepared by published routes.

Preparations

***trans*-[Rh(DCBT)(CO)(PPh₃)₂] 1.** *trans*-[RhF(CO)(PPh₃)₂] (0.10 g, 0.15 mmol) and the thiol DCBTH (0.027 g, 15 mmol) were stirred at room temperature in toluene (30 ml) for 45 min to give an orange solution. The solvent was removed under reduced pressure and the residue crystallised from CH_2Cl_2 –MeOH as a yellow-orange microcrystalline powder in 85% yield.

***trans*-[Rh(TPSBT)(CO)(PPh₃)₂] 2.** This compound was prepared in a similar manner to **1** from *trans*-[RhF(CO)(PPh₃)₂] (0.1 g, 0.15 mmol) and the thiol TPSBTH (0.055 g, 0.15 mmol). Yield 70%.

[Rh(μ-DMBT)₂(CO)₂(PPh₃)₂] 3. This compound was prepared in a similar manner to **1** from *trans*-[RhF(CO)(PPh₃)₂] (0.1 g, 0.15 mmol) and the thiol DMBTH (0.020 g, 0.15 mmol). Yield 80%.

[Rh(μ-TIPBT)₂(CO)₂(PPh₃)₂] 4. This compound was prepared in a similar manner to compound **1** from *trans*-[RhF(CO)(PPh₃)₂] (0.1 g, 0.15 mmol) and the thiol TIPBTH (0.035 g, 0.15 mmol). Yield 83%.

***trans*-[Ir(DCBT)(CO)(PPh₃)₂] 5.** To a solution of *trans*-[IrF(CO)(PPh₃)₂] (0.1 g, 0.13 mmol) in toluene (25 cm³) was added 1 equivalent of the thiol DCBTH (0.023 g, 0.13 mmol). The solution was stirred at room temperature for 45 min. The volume was reduced under vacuum and the residue recrystallised from CH_2Cl_2 –MeOH. Yield 95%.

***trans*-[Ir(TPSBT)(CO)(PPh₃)₂] 6.** This compound was prepared in a similar manner to **5** from *trans*-[IrF(CO)(PPh₃)₂] (0.1 g, 0.13 mmol) and the thiol TPSBTH (0.048 g, 0.13 mmol). Yield 90%.

***trans*-[Ir(DMBT)(CO)(PPh₃)₂] 7.** This compound was prepared in a similar manner to **5** from *trans*-[IrF(CO)(PPh₃)₂] (0.1 g, 0.13 mmol) and the thiol DMBTH (0.018 g, 0.13 mmol). Yield 40%.

***trans*-[Ir(TIPBT)(CO)(PPh₃)₂] 8.** To a solution of *trans*-[IrF(CO)(PPh₃)₂] (0.1 g, 0.13 mmol), TIPBTH (0.031 g, 0.13 mmol) was added. After stirring in toluene (25 ml) for 1 hour a green solution was obtained. Reduction of the solvent under vacuum yielded a green oily product. The crude material was then redissolved in the minimum amount of CH₂Cl₂ and chromatographed on a column using silica gel as the stationary phase (Kieselgel 60, Fluka) and eluted with CH₂Cl₂. The green solution was collected and impurities remained at the top of the column. Yield 43% as a yellow solid.

[Rh(*Ph*PPS)(CO)(PPh₃)] 9. To a solution of *trans*-[RhF(CO)(PPh₃)₂] (0.1 g, 0.15 mmol) in toluene (25 cm³) was added 1 equivalent of the phosphinothiol *Ph*PPSH (0.044 g, 0.15 mmol). The solution was stirred for 45 min, the volume reduced under reduced pressure and the residue recrystallised as a pale yellow solid from CH₂Cl₂-MeOH. Yield 95%.

[Rh(*Pr*PPS)(CO)(PPh₃)] 10. This compound was prepared in a similar manner to **9** from *trans*-[RhF(CO)(PPh₃)₂] (0.1 g, 0.15 mmol) and the phosphinothiol *Pr*PPSH (0.039 g, 0.15 mmol), yield 90%.

[Rh(*e*PPS)(CO)(PPh₃)] 11. This compound was prepared in a similar manner to **9** from *trans*-[RhF(CO)(PPh₃)₂] (0.1 g, 0.15 mmol) and the phosphinothiol *e*PPSH (0.037 g, 0.15 mmol), yield 80%.

[Rh(*ePPS)(CO)(PPh₃)] 12.** This compound was prepared in a similar manner to **9** from *trans*-[RhF(CO)(PPh₃)₂] (0.1 g, 0.15 mmol) and the phosphinothiol *e**PPSH (0.039 g, 0.15 mmol), yield 87%.

[Ir(*Ph*PPS)(CO)(PPh₃)] 13. To a solution of *trans*-[IrF(CO)(PPh₃)₂] (0.1 g, 0.13 mmol) in toluene (25 cm³) was added 1 equivalent of the phosphinothiol *Ph*PPSH (0.039 g, 0.13 mmol). The solution was stirred for 45 min in the presence of NEt₃, the volume reduced under reduced pressure and the residue recrystallised as a pale yellow solid from CH₂Cl₂-MeOH. Yield 72%.

[Ir(*Pr*PPS)(CO)(PPh₃)] 14. This compound was prepared in a similar manner to **13** from *trans*-[IrF(CO)(PPh₃)₂] (0.1 g, 0.13 mmol) and the phosphinothiol *Pr*PPSH (0.034 g, 0.13 mmol), yield 90%.

[Ir(H)(*Ph*PPS)₂(CO)] 15. This compound was prepared in a similar manner to **13** from *trans*-[IrF(CO)(PPh₃)₂] (0.1 g, 0.13 mmol) and the phosphinothiol *Ph*PPSH (0.039 g, 0.13 mmol), but no NEt₃ was added, yield 87%.

[Ir(H)(*Pr*PPS)₂(CO)] 16. This compound was prepared in a similar manner to **15** from *trans*-[IrF(CO)(PPh₃)₂] (0.1 g, 0.13 mmol) and the phosphinothiol *Pr*PPSH (0.034 g, 0.13 mmol), yield 87%.

[Rh₂(*Ph*PPS)₂(CO)₂(PPh₃)₂][BF₄]₂ 17. To a CH₂Cl₂ solution (20 cm³) of complex **9** (0.1 g, 0.146 mmol) was added an excess of HBF₄ (0.03 mg, 0.35 mmol); an immediate change from a bright yellow to a dark purple was observed. The mixture was stirred for 1 hour and then the solvent removed under vacuum. The residue was redissolved in the minimum amount of CH₂Cl₂ and precipitated with *n*-pentane as a fine, dark red-purple powder **17**, yield 80%.

[Rh(*Ph*PPSMe)(CO)(PPh₃)][BF₄] 18. To a benzene solution (25 ml) of complex **9** (0.1 g, 0.146 mmol) was added an excess of [Me₃O][BF₄] (0.05 g, 0.350 mmol). After stirring for 30 min a precipitate started to form and a change from a bright yellow to a dark purple was observed. The mixture was stirred for one hour and then the deep purple precipitate filtered off, redissolved in the minimum amount of CH₂Cl₂ and precipitated with *n*-pentane as a fine, deep purple powder **18**, yield 65%.

[Rh₂(μ-I)₂(I)₄(*Ph*PPSMe)₂] 19. To a solution of complex **9** (0.1 g, 0.146 mmol) in benzene (10 cm³), was added MeI (0.8 cm³) and the mixture allowed to stir for 24 hours. During this time a change from bright yellow to deep red was observed. The solvent was removed under vacuum to give a reddish black residue, which was redissolved in the minimum of CH₂Cl₂ and layered with MeOH. On standing for 24 hours a deep red microcrystalline product **19** was isolated. Yield 52%.

[RhI₂(*Ph*PPS(CH₂)₃(CO)(PPh₃)] 20. To a CH₂Cl₂ solution (25 ml) of complex **9** (0.1 g, 0.146 mmol) was added 1,3-diiodopropane (0.8 cm³) and the mixture stirred for 24 hours. The solvent was then removed *in vacuo* and the orange residue redissolved in the minimum amount of CH₂Cl₂ and precipitated with *n*-pentane yielding the compound **20** as a bright orange powder. Yield 55%.

[RhI₂(*Ph*PPSCH₂CO₂)(PPh₃)] 21. This compound was synthesized analogously to **20** using an excess of iodoacetic acid, yield 52%.

***trans*-[RhI₃(CO)(PPh₃)₂] 22.** This compound was obtained from the previous reaction as a by-product. Purification was achieved by recrystallisation from CH₂Cl₂-MeOH, final yield 15%.

Catalysis experiments

Hydroformylation experiments were carried out at the Instituto de Catalisis y Petroleoquimica, Consejo Superior de Investigaciones Cientificas, (C.S.I.C.), Madrid, Spain, in a 150 cm³ stainless steel autoclave with a magnetic stirrer and a glass inlet. The temperature was kept constant at 70 °C by using a double jacket water system circulate. Syngas (H₂:CO = 1:1) was introduced at a constant pressure of 5 bar from a gas reservoir. The fall of pressure in the autoclave was monitored with a transducer connected to an electric recorder. A solution of the precursor containing the substrate was placed in the evacuated autoclave and then heated to the required temperature. When thermal equilibrium was reached Syngas was introduced at 5 bar, and stirring was initiated. After each run the solution was analysed by GLC with a Hewlett-Packard 5940A chromatograph equipped with a 6 m × 1/8 in column of OV-17 on Chromosorb WHP.

X-Ray data collection

For complexes 5 and 17. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer³⁸ with monochromated Mo-Kα radiation (λ = 0.71073 Å). Cell constants were obtained from least squares refinement of the setting angles of 25 centred reflections in the range 1.87 < θ < 24.97°. The data were collected in the ω-2θ scan mode and three standard reflections were measured every 2 hours of exposure. 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 psi scans of nine reflections.

For complexes 4 and 19. Intensity data were collected at the EPSRC service, Cardiff on a Delft-Instrument FAST-TV area detector diffractometer with graphite-monochromated Mo-Kα

Table 7 Summary of X-ray structural data for complexes **4**, **5**, **17** and **19**

	4 [Rh ₂ (μ-TIPBT) ₂ - (CO) ₂ (PPh ₃) ₂]	5 <i>trans</i> -[Ir(DCBT)- (CO)(PPh ₃) ₂]	17 [RhH ₂ (PhPPS) ₂ - (CO) ₂ (PPh ₃) ₂][BF ₄] ₂	19 [Rh ₂ (μ-I) ₂ (I) ₄ - (PhPPSMe) ₂]
Empirical formula	C ₆₈ H ₇₆ O ₂ P ₂ Rh ₂ S ₂	C ₄₃ H ₃₃ Cl ₂ IrOP ₂ S	C ₇₄ H ₆₀ B ₂ F ₈ O ₂ P ₄ Rh ₂ S ₂	C ₁₉ H ₁₇ I ₃ PRhS
<i>M</i>	1257.17	922.79	1548.66	791.97
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	13.529(4)	9.2039(10)	11.931(2)	12.503(2)
<i>b</i> /Å	33.568(10)	11.600(2)	13.554(9)	12.982(5)
<i>c</i> /Å	14.134(5)	19.014(3)	22.814(4)	14.481(3)
<i>α</i> /°		99.934(10)	97.70(3)	
<i>β</i> /°	104.69(5)	95.243(10)	97.870(10)	92.51(5)
<i>γ</i> /°		106.744(10)	97.41(4)	
<i>V</i> /Å ³	6209(3)	1893.3(5)	3581(3)	2348.2(11)
<i>Z</i>	4	2	2	4
<i>μ</i> (Mo-Kα)/mm ⁻¹	0.693	3.840	0.674	4.829
<i>T</i> /K	293	293	293	293
Reflections collected	20978	7071	13194	6872
Independent reflections (<i>R</i> _{int})	8986(0.1085)	6616(0.0121)	12610(0.0701)	3276(0.0757)
Reflections observed	5682	6098	9358	1980
<i>R</i> 1, <i>wR</i> 2	0.0637, 0.1356	0.0222, 0.0575	0.0685, 0.1951	0.430, 0.0925

radiation ($\lambda = 0.71069 \text{ \AA}$).³⁹ Cell constants were obtained from least squares refinement of the setting angles of 250 reflections having $\theta = 2.34\text{--}25.09^\circ$.

Structure analysis and refinement. The structures were all solved *via* direct methods⁴⁰ and refined on F_o^2 by full-matrix least squares.⁴¹ All non-hydrogen atoms were anisotropic. The hydrogen atoms were included in idealised positions with U_{iso} free to refine. The weighting scheme gave satisfactory results. The structure diagrams were produced by ZORTEP.¹⁴ Crystallographic data for all four compounds are presented in Table 7.

CCDC reference number 186/2095.

See <http://www.rsc.org/suppdata/dt/b0/b005588n/> for crystallographic files in .cif format.

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