

# Binuclear complexes with ligands based on the 2,6-bis(diphenylphosphinomethyl)benzene framework. Syntheses and crystal structures of $[\text{Ir}_2\text{Cl}_2(\mu\text{-CO})\{2,6\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3\text{S}\}_2]\cdot 2\text{CH}_2\text{Cl}_2$ , $[\text{Ni}_2\{2,6\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_4\text{S}\}_2][\text{PF}_6]_2\cdot \text{Et}_2\text{O}\cdot 0.5\text{CH}_2\text{Cl}_2$ and $[\text{Rh}_2\text{Cl}_2(\text{CO})_2\{1,3\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_4\}_2]$

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The new binucleating phosphinothiolate proligand 2,6-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SH (L3H) was prepared from bromo-2,6-dimethylbenzene in a 4 step synthesis. Reaction with [IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] in MeCN gave the carbonyl and thiolate bridged dimer [Ir<sub>2</sub>Cl<sub>2</sub>(μ-CO)(L3)] **1**. Reaction of [{RhCl(CO)<sub>2</sub>}]<sub>2</sub> with half an equivalent of L3H resulted in formation of the dimeric species [Rh<sub>2</sub>Cl(CO)<sub>2</sub>(L3)] **2** with one bridging thiolate and one bridging chloride. The dimeric species [Ni<sub>2</sub>(L3)<sub>2</sub>]<sup>2+</sup> **3** was formed in high yield from reaction of [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] with L3H in MeCN. The diphosphine 1,3-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (L4) gave the dimeric species [Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>2</sub>(L4)] **4** with [RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] with no evidence for metallation at the bridging aryl group. The crystal structures of complexes **1**, **3** and **4** are discussed.

## Introduction

There is considerable current interest in proligands involving the general structural motif 2,6-(R<sub>2</sub>ECH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>X (E = P, X = H; E = N, X = SH; R = Ph or Bu<sup>t</sup>).<sup>1,2</sup> In the case where E = P and R = Bu<sup>t</sup>, the facile metallation of the central aryl group at the 1 position was first demonstrated for Rh, Ir, Ni, Pd and Pt in 1976.<sup>3</sup> Recent examples involving R<sub>2</sub>PCH<sub>2</sub> substituents include the iridium complex [IrH<sub>2</sub>{2,6-(Bu<sup>t</sup>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}]<sup>4</sup> which is an active catalyst for cycloalkane dehydrogenation, and the facile C–O bond cleavage of 2,6-(Bu<sup>t</sup>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OME by Rh<sup>I</sup> to give [RhH(Cl){2,6-(Bu<sup>t</sup>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}] with a Rh–C σ bond to the central phenyl group.<sup>5</sup>

The concept of using an aromatic phenol or thiol with potential donor atoms on substituents in the 2 and 6 positions (as above with X = OH or SH) to generate binuclear complexes is now well established, both for acyclic and macrocyclic<sup>6</sup> compounds. However there are few if any examples where the non-bridging ligands in such systems are tertiary phosphines. We have shown previously that phosphinothiolate ligands are not only very versatile, but are also robust enough when coordinated to survive carbonylation catalysis conditions and provide highly active catalysts.<sup>7</sup> We now report the synthesis and a preliminary investigation of the co-ordination chemistry of a new phosphinothiol proligand designed to stabilize binuclear systems, and the crystal and molecular structures of dimeric complexes of Ir<sup>III</sup> and Ni<sup>II</sup>. We also describe the synthesis of a binuclear complex of Rh formed from the 1,3-bis(diphenylphosphinomethyl)benzene ligand, where in contrast to the chemistry so far reported for this type of ligand, there is no M–C bond formation.

## Results and discussion

### Ligand synthesis

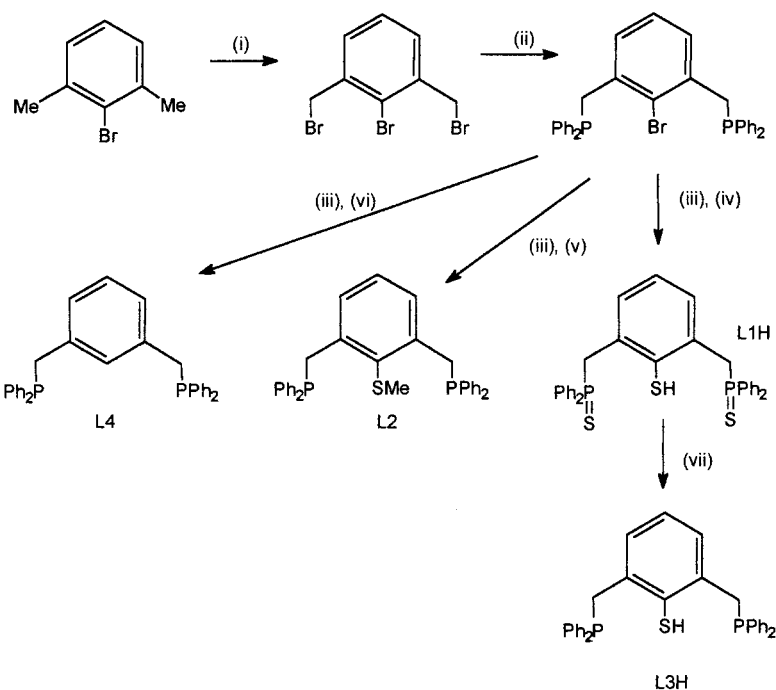
The proligand 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>SH can be prepared readily by direct lithiation of 2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and subsequent

reaction with elemental sulfur, utilizing the neighbouring group effect of the amine nitrogens to control the site of metallation.<sup>2</sup> The corresponding bis(tertiary phosphine) cannot be site specifically lithiated and the bis(phosphino)thiol proligand (L3H) requires a much more involved synthesis. It can however be made in moderate yield (overall about 20%) according to Scheme 1. The selection of PBU<sup>n</sup><sub>3</sub> as reducing agent in step (vii) is crucial, as all other reducing agents lead to species with intramolecular P···S interactions which do not form metal complexes. The 2,6-bis(phosphinothiomethyl)benzenethiol (L1H) is also an effective proligand for metal ions, behaving as a tridentate non-bridging donor, and details of these complexes will be presented elsewhere. The 1,3-bis(diphenylphosphinomethyl)benzene L4 was prepared by hydrolysis of the lithium compound as shown in the scheme, but is more conveniently made direct from 1,3-(BrCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>.

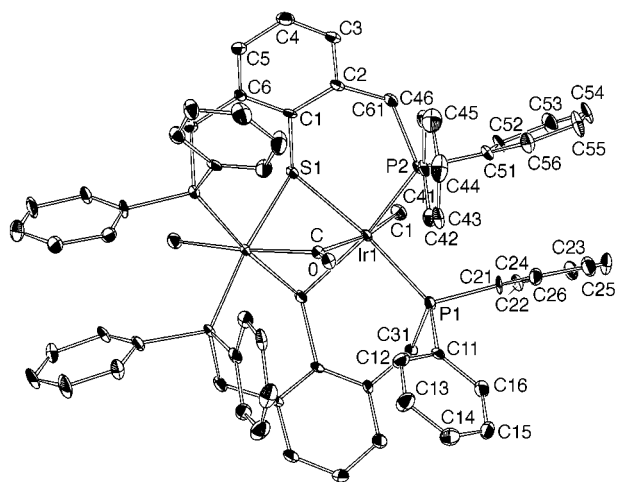
### Synthesis of metal complexes

**Of 2,6-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>S<sup>−</sup> (L3).** The iridium complex [Ir<sub>2</sub>Cl<sub>2</sub>(μ-CO){2,6-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>S}<sub>2</sub>] **1** was synthesized in low yield as a moderately air stable yellow solid by reaction of [IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] with one equivalent of L3H in MeCN at room temperature. The reaction produces a mixture of products as indicated by IR and <sup>31</sup>P NMR and **1** was obtained in low yield by recrystallization of the crude product. The complex is a non-electrolyte in dichloromethane solution and the IR spectrum shows ν(CO) at 1714 cm<sup>−1</sup>, consistent with the presence of a bridging CO ligand. The presence of both chloride and thiolate ligands suggests a formal oxidation state of at least two for the metal, and the bridging CO appears the more likely. The <sup>31</sup>P NMR spectrum showed a singlet at δ −23.3 indicating two equivalent P atoms.

The crystal and molecular structure of complex **1** was determined and a ZORTEP<sup>8</sup> representation of the structure appears in Fig. 1. Selected bond lengths and angles appear in Table 1 and a summary of the details of data collection and structure solution in Table 4. Both iridium atoms are in a



**Scheme 1** Synthesis of ligands. (i) NBS/(PhCO)<sub>2</sub>O<sub>2</sub>, (ii) NaPPh<sub>2</sub>/liquid NH<sub>3</sub>, (iii) BuLi/thf/−78 °C, (iv) S<sub>8</sub>/thf, (v) MeSSMe, (vi) water and (vii) Bu<sup>n</sup><sub>3</sub>P/180 °C.



**Fig. 1** A ZORTEP representation of the structure of complex 1.

pseudo-octahedral environment, the six co-ordination sites being occupied by the two bridging sulfurs, a carbon atom of the bridging CO, a terminal chloride and two phosphorus atoms from different PSP ligands. The Ir⋯Ir distance is 3.1035(13) Å which is a little shorter than the literature value in the related complex [Ir<sub>2</sub>(μ-SBu<sup>t</sup>)<sub>2</sub>(μ-CO)(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>I<sub>2</sub>]<sup>9</sup> [Ir⋯Ir 3.1980(4) Å], and indicates little or no Ir–Ir bonding. Other bond distances are Ir–C 2.048(13), Ir–P 2.294(3) and 2.297(4); Ir–S 2.439(4) and 2.446(3) Å and Ir–Cl 2.563(4) Å and are unremarkable. Although CO bridged iridium complexes are well documented, the combination of a bridging CO with two bridging thiolates is restricted to [Ir<sub>2</sub>(μ-SBu<sup>t</sup>)<sub>2</sub>(μ-CO)(CO)<sub>2</sub>R<sub>2</sub>I<sub>2</sub>] (R = PMe<sub>3</sub> or PMe<sub>2</sub>Ph).<sup>9</sup> This last complex was formulated as containing two iridium(III) centres with a bridging dianionic ketonic ligand and the same formalism can be adopted for complex **1**. The presence of a hydride ligand is ruled out as there is no evidence for it in the IR or NMR spectra, and there is no obvious location for it within the co-ordination sphere.

The presence of the three bridging ligands in the iridium dimer **1** will restrict the possibilities for catalytic activity, and we have also prepared the complex [Rh<sub>2</sub>(μ-Cl)(CO)<sub>2</sub>(L3)] **2** by the reaction of [Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub>] with one equivalent of L3H in tolu-

**Table 1** Selected bond distances (Å) and angles (°) for [Ir<sub>2</sub>Cl<sub>2</sub>(μ-CO){2,6-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>S<sub>2</sub>}] **1**

Ir(1)–C	2.048(13)	Ir(1)⋯Ir(1')	3.1035(13)
Ir(1)–P(2)	2.294(3)	S(1)–C(1)	1.818(14)
Ir(1)–P(1)	2.297(4)	S(1)–Ir(1')	2.446(3)
Ir(1)–S(1)	2.439(4)	C–O	1.20(2)
Ir(1)–S(1')	2.446(3)	C–Ir(1')	2.048(13)
Ir(1)–Cl	2.563(4)		
C–Ir(1)–P(2)	99.3(3)	S(1')–Ir(1)–Cl	87.67(12)
C–Ir(1)–P(1)	104.7(3)	C–Ir(1)–Ir(1')	40.7(4)
P(2)–Ir(1)–P(1)	97.03(13)	P(2)–Ir(1)–Ir(1')	123.18(10)
C–Ir(1)–S(1)	78.9(3)	P(1)–Ir(1)–Ir(1')	126.06(10)
P(2)–Ir(1)–S(1)	92.58(12)	S(1)–Ir(1)–Ir(1')	50.66(8)
P(1)–Ir(1)–S(1)	169.00(12)	S(1')–Ir(1)–Ir(1')	50.46(9)
C–Ir(1)–S(1')	78.7(3)	Cl–Ir(1)–Ir(1')	121.25(10)
P(2)–Ir(1)–S(1')	171.40(12)	C(1)–S(1)–Ir(1)	114.9(5)
P(1)–Ir(1)–S(1')	91.56(12)	C(1)–S(1)–Ir(1')	109.4(5)
S(1)–Ir(1)–S(1')	78.83(13)	Ir(1)–S(1)–Ir(1')	78.88(10)
C–Ir(1)–Cl	162.0(4)	O–C–Ir(1')	130.7(4)
P(2)–Ir(1)–Cl	92.37(13)	O–C–Ir(1)	130.7(4)
P(1)–Ir(1)–Cl	87.27(13)	Ir(1')–C–Ir(1)	98.5(9)
S(1)–Ir(1)–Cl	87.01(13)		

Symmetry relation: 1 – x, y, –z + ½

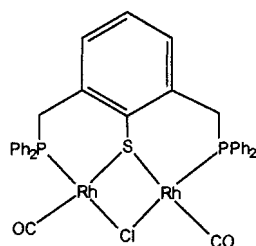
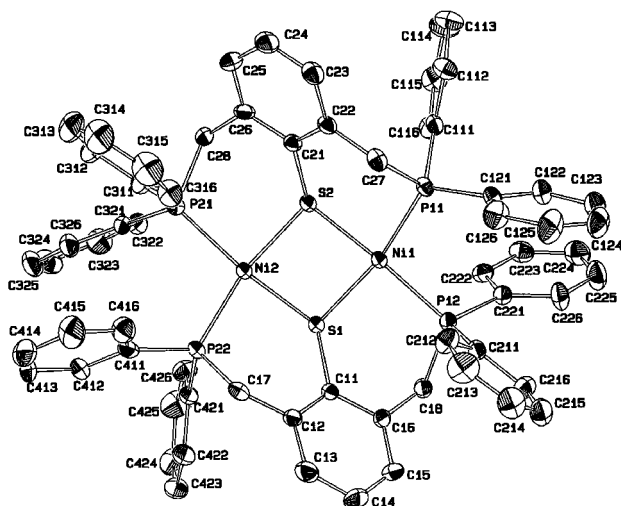
ene. The complex is isolated as a yellow, moderately air stable solid. The IR spectrum shows two strong bands at 1976 and 2060 cm<sup>−1</sup> assigned to ν(CO), a peak in the FAB mass spectrum at *m/z* 802 corresponding to a dimeric structure, and a singlet in the <sup>31</sup>P NMR indicating equivalent phosphorus donors. The complex is assigned the structure shown in Fig. 2.

It is interesting that in the reactions of rhodium and iridium precursors with L3H we did not observe any sign of a mononuclear species with L3 functioning as an extremely strained tridentate ligand as proposed for the reaction of the phenolic analogue of L3H with [{RhCl(COD)}<sub>2</sub>]<sup>3</sup> or in the strained methylene complex [RhH(Cl)(PP<sup>r</sup><sub>2</sub>CH<sub>2</sub>Et){2,6-(Bu<sup>t</sup>PCH<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>}].<sup>10</sup> The reasons for this difference in reactivity may well relate to the precursor used, and we are currently investigating the chemistry of L3H with other iridium(I) or rhodium(I) starting materials.

The dimeric dicationic complex [Ni<sub>2</sub>(L3)<sub>2</sub>]<sup>2+</sup> was isolated as a brown hexafluorophosphate salt **3** from the reaction of

**Table 2** Selected bond lengths (Å) and angles (°) for  $[\text{Ni}_2\{\mu\text{-}2,6\text{-Ph}_2\text{-PCH}_2\text{C}_6\text{H}_4\text{S}\}_2][\text{PF}_6]_2 \mathbf{3}$ 

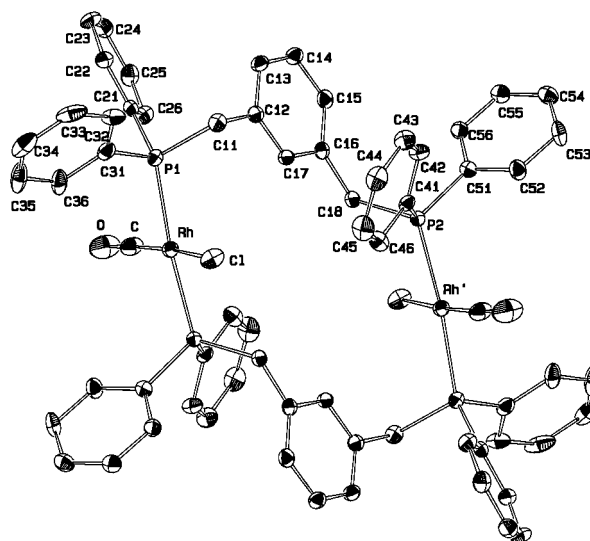
Ni(1)–S(2)	2.1748(19)	Ni(2)–P(22)	2.1736(19)
Ni(1)–P(12)	2.178(2)	Ni(2)–P(21)	2.192(2)
Ni(1)–P(11)	2.185(2)	Ni(2)–S(1)	2.1972(18)
Ni(1)–S(1)	2.2128(18)	Ni(2)–S(2)	2.1978(17)
Ni(1)–Ni(2)	3.1959(12)		
S(2)–Ni(1)–P(12)	161.56(8)	P(22)–Ni(2)–S(2)	167.61(8)
S(2)–Ni(1)–P(11)	90.02(7)	P(21)–Ni(2)–S(2)	90.82(7)
P(12)–Ni(1)–P(11)	100.41(7)	S(1)–Ni(2)–S(2)	79.78(7)
S(2)–Ni(1)–S(1)	79.94(6)	P(22)–Ni(2)–Ni(1)	124.88(6)
P(12)–Ni(1)–S(1)	91.38(7)	P(21)–Ni(2)–Ni(1)	132.75(6)
P(11)–Ni(1)–S(1)	167.28(8)	S(1)–Ni(2)–Ni(1)	43.75(5)
S(2)–Ni(1)–Ni(2)	43.32(5)	S(2)–Ni(2)–Ni(1)	42.76(5)
P(12)–Ni(1)–Ni(2)	133.74(6)	C(11)–S(1)–Ni(2)	120.4(2)
P(11)–Ni(1)–Ni(2)	124.10(6)	C(11)–S(1)–Ni(1)	108.9(2)
S(1)–Ni(1)–Ni(2)	43.36(5)	Ni(2)–S(1)–Ni(1)	92.89(7)
P(22)–Ni(2)–P(21)	101.52(7)	C(21)–S(2)–Ni(1)	120.1(2)
P(22)–Ni(2)–S(1)	88.81(7)	C(21)–S(2)–Ni(2)	108.3(7)
P(21)–Ni(2)–S(1)	160.20(8)	Ni(1)–S(2)–Ni(2)	93.92(7)

**Fig. 2** Proposed structure for  $[\text{Rh}_2\text{Cl}(\text{CO})_2(\text{L}3)]_2$ .**Fig. 3** A ZORTEP representation of the structure of complex **3**.

$[\text{NiCl}_2(\text{PPh}_3)_2]$  with 1 equivalent of L3H in MeCN at room temperature. The  $^{31}\text{P}$  NMR spectrum of the cation showed a singlet at  $\delta$  147.3 due to the four equivalent phosphorus donors. Suitable crystals for structure determination were grown from dichloromethane–methanol, and a ZORTEP representation of the structure appears in Fig. 3. Selected bond lengths and angles appear in Table 2, and details of the data collection and structure solution in Table 4. The geometry at each Ni atom is approximately square planar with a slight fold along the S–S vector providing an overall butterfly type structure. The Ni–S distances [2.1748(19) to 2.2128(18) Å] lie in the range formed for other nickel(II) thiolate bridged complexes.<sup>11–13</sup> The Ni–Ni distance of 3.1959(12) Å indicates a relatively weak Ni–Ni interaction, and the Ni–S–Ni angles are correspondingly greater at 92.89(7) and 93.92(7)° than for species with strong metal–metal bonding. Other reported bi- and tri-nuclear complexes of Ni<sup>II</sup> involving phosphinothiolate ligands, such as

**Table 3** Selected bond lengths (Å) and angles (°) for  $[\text{Rh}_2\text{Cl}_2(\text{CO})_2\{\mu\text{-}1,3\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_4\}_2] \mathbf{4}$ 

Rh–C	1.789(10)	Rh–Cl	2.376(2)
Rh–P(2')	2.313(2)	P(2)–Rh'	2.313(2)
Rh–P(1)	2.330(2)	C–O	1.155(11)
C–Rh–P(2')	90.1(3)	P(2')–Rh–Cl	89.27(8)
C–Rh–P(1)	94.5(3)	P(1)–Rh–Cl	86.57(8)
P(2')–Rh–P(1)	174.23(8)	O–C–Rh	176.1(10)
C–Rh–Cl	172.8(4)		

Symmetry relation:  $1 - x, -y, -z$ .**Fig. 4** A ZORTEP representation of the structure of complex **4**.

$[\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{S}-\mu)_2\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{S})]$ ,<sup>14</sup>  $[\{\text{Ni}(\text{Et}_2\text{PCH}_2\text{CH}_2\text{S}-\mu)_2\text{Ni}\}^{2+}]^{15}$  and  $[\text{Ni}_2\{\text{P}(\text{C}_6\text{H}_4\text{S}-2)_2(\text{C}_6\text{H}_4\text{S}-2-\mu)\}_2]^{2-}$ <sup>13</sup> have similar Ni–S and Ni–P distances.

#### Synthesis of $[\text{Rh}_2\text{Cl}_2(\text{CO})_2\{\mu\text{-}1,3\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_4\}_2] \mathbf{4}$

The predominant reaction reported for the diphosphine L4 in Scheme 1 with platinum group metal precursors (Ni, Pd, Pt, Rh and Ir) is the formation of an M–C bond at C-2 of the central aryl group as discussed in the Introduction. The only reported dimeric complexes have either involved blockage of this position with a methyl group as in  $[\text{M}_2\text{Cl}_4\{\mu\text{-}2,6\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{HMe}_3\text{-}1,3,5\}_2]^{16}$  (M = Pd or Pt) or silver(I) complexes of the type  $[\{\text{Ag}(\mu\text{-X})[\mu\text{-}1,3\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_4\}_2]$  (where X = Cl, I or NO<sub>3</sub>).<sup>17</sup>

However, reaction of  $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$  with L4 in methanol at room temperature gives the binuclear complex  $[\text{Rh}_2\text{Cl}_2(\text{CO})_2\{\mu\text{-}1,3\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_4\}_2] \mathbf{4}$  as a pale yellow solid in good yield. The IR spectrum shows a single strong band at 1957 cm<sup>-1</sup> assigned to  $\nu(\text{CO})$  and the  $^{31}\text{P}$  NMR shows a single resonance due to the PPh<sub>2</sub> groups, suggesting they are magnetically equivalent. Suitable crystals for a structure determination were obtained from dichloromethane–methanol.

#### Crystal structure of $[\text{Rh}_2\text{Cl}_2(\text{CO})_2\{\mu\text{-}1,3\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_4\}_2] \mathbf{4}$

A ZORTEP representation of the structure of complex **4** appears in Fig. 4. Selected bond lengths and angles are summarised in Table 3 and details of the data collection and structure solution in Table 4. The overall structure is of the double A-frame type with the two diphosphine ligands both acting as bridging ligands between the square planar rhodium(I) units forming 16-membered dimetallacycles. The Cl–Rh–CO systems are in an eclipsed orientation with the CO groups disposed above and below the plane of the metallocycle. The Rh···Rh

distance is 7.119(2) Å. As has been discussed previously<sup>16</sup> the use of mild reaction conditions, as in this case, will favour the formation of dimers rather than the metallated product, although the nature of the co-ligands on the precursor is also important. We are currently investigating if there is any cooperativity between the rhodium centres in catalysis.

## Experimental

All manipulations were carried out under an atmosphere of dinitrogen using conventional Schlenk-type apparatus. Solvents were dried according to established procedures and redistilled immediately prior to use. The NMR spectra were measured in CDCl<sub>3</sub> solution using a JEOL EX270 (270 MHz) spectrometer. The complexes [RhCl(CO)<sub>2</sub>]<sub>2</sub>,<sup>18</sup> [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>19</sup> and [IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>20</sup> were prepared by reported procedures.

## Preparation

**BrC<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>Br)<sub>2</sub>-2,6.** The compounds BrC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6 (60 g, 0.32 mol) and *N*-bromosuccinimide (116 g, 0.65 mol) in chlorobenzene (200 ml) were stirred at room temperature and benzoyl peroxide (2.6 g) was added. The suspension was heated under reflux for half an hour, further benzoyl peroxide (1.6 g) was added, and the heating continued for 5 h. The brown solution was cooled to room temperature and left to stand overnight. The white solid was filtered off and discarded and the brown filtrate evaporated to dryness on a rotary evaporator. The residue was dissolved in the minimum volume of acetone (*ca.* 20 ml) and stored in a freezer overnight. This gave a white crystalline solid which was filtered off, washed with the minimum amount of cooled acetone and dried. Yield 50 g (45%). Mass spectrum (FAB): *m/z* 342 (M<sup>+</sup>) (Calc. for C<sub>8</sub>H<sub>7</sub>Br<sub>3</sub>: C, 28.0; H, 2.1. Found: C, 27.8; H, 2.0%). <sup>1</sup>H NMR: δ 7.19–7.42 (m, Ph, 4 H) and 4.64 (s, CH<sub>2</sub>-Br, 4 H). <sup>13</sup>C NMR: δ 138.43, 131.37, 128.01, 126.60 and 33.83.

**BrC<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-2,6.** Liquid ammonia (*ca.* 150 ml) was introduced into a 500 ml three-necked Quickfit flask equipped with a solid CO<sub>2</sub> condenser and stirrer and immersed in a solid CO<sub>2</sub>-acetone bath. Sodium (5.2 g, 0.23 mmol), cut into small pieces, was added to give a deep blue solution. After stirring for 15 min, triphenylphosphine (30 g, 0.12 mmol) was slowly added with vigorous stirring. Stirring was continued for 2 h, the cooling bath being removed for the second hour, permitting the liquid NH<sub>3</sub> to reflux gently. The resulting mixture was dark orange. The cooling bath was replaced, dry NH<sub>4</sub>Br (11.2 g) added slowly, and the solution stirred in the cooling bath for 1 h to give a paler orange solution. The cooling was maintained and a solution of BrC<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>Br)<sub>2</sub>-2,6 (19.6 g, 0.06 mol) in degassed THF (60 ml) was added dropwise, completely decolorizing the solution. The cooling bath was removed and the liquid NH<sub>3</sub> allowed to evaporate to leave a white solid. Water (200 ml) was added to the residue and the suspension stirred vigorously to dissolve any inorganic salts. The residue was filtered off in air and washed by acetone. Yield 16 g (50.1%). Mass spectrum (FAB): *m/z* 555 (M<sup>+</sup> + 1) and 473 (M<sup>+</sup> - Br) with appropriate isotope distributions (Calc. for C<sub>32</sub>H<sub>27</sub>BrP<sub>2</sub>: C, 69.5; H, 4.9. Found: C, 69.2; H, 4.7%). <sup>1</sup>H NMR: δ 6.56–7.44 (m, Ph, 23 H) and 3.60 (s, CH<sub>2</sub>P, 4 H). <sup>31</sup>P NMR: δ -11.9. <sup>13</sup>C NMR: δ 126–138 (m, Ph) and 37.48 (d, *J*<sub>P-C</sub> = 14 Hz, CH<sub>2</sub>P).

**MeSC<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-2,6.** The compound BrC<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-2,6 (2.6 g, 4.7 mmol) in dry THF (30 ml) was cooled in a solid CO<sub>2</sub>-acetone bath, Bu<sup>n</sup>Li (1.65 ml, 2.5 M in hexane) added and the mixture stirred for 6 h in a solid CO<sub>2</sub>-acetone bath. Excess of MeS-SMe (1.2 ml) was then added to the cooled brown solution, and the mixture slowly warmed to room temperature and stirred overnight. The solvent was then removed under reduced pressure and the residue treated with

MeOH. Yield 1.8 g (73.8%). Mass spectrum (FAB): *m/z* 521 (M<sup>+</sup> + 1) and 505 (M<sup>+</sup> - Me) with appropriate isotope distributions (Calc. for C<sub>33</sub>H<sub>30</sub>P<sub>2</sub>S: C, 76.1; H, 5.8. Found: C, 76.3; H, 5.9%). <sup>1</sup>H NMR: δ 6.66–7.45 (m, Ph, 23 H), 3.80 (s, CH<sub>2</sub>P, 4 H) and 2.27 (s, MeS, 3 H). <sup>31</sup>P NMR: δ -7.8. <sup>13</sup>C NMR: δ 122–138 (m, Ph), 35.397 (d, *J*<sub>P-C</sub> = 16 Hz, CH<sub>2</sub>P) and 22.33 (s, MeS).

**HSC<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>PSPPh<sub>2</sub>)<sub>2</sub>-2,6 (L1H).** The compound BrC<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-2,6 (4 g, 7.2 mmol) in dry THF (30 ml) was cooled in a solid CO<sub>2</sub>-acetone bath and Bu<sup>n</sup>Li (3.3 ml, 2.5 M in hexane) added slowly. After stirring for 6 h in the cooling bath, S<sub>8</sub> (1.8 g, 7.0 mmol) was added to the cold brown solution, the mixture slowly warmed to room temperature and then stirred overnight. This solution was then added to a suspension of LiAlH<sub>4</sub> (3.6 g) in dry degassed diethyl ether. The suspension was stirred for 4 h, and any excess of LiAlH<sub>4</sub> was filtered off. To the filtrate was added water (50 ml) and hydrochloric acid (50 ml, 10%), the organic phase was separated, and the aqueous phase extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 100 ml). The combined organic phase was dried over MgSO<sub>4</sub> and evaporated to dryness under reduced pressure. Yield 3.0 g (72.9%) of white solid. Mass spectrum (FAB): *m/z* 571 (M<sup>+</sup> + 1) with appropriate isotope distribution (Calc. for C<sub>32</sub>H<sub>28</sub>P<sub>2</sub>S<sub>3</sub>: C, 67.4; H, 5.0. Found: C, 67.2; H, 4.9%). <sup>1</sup>H NMR: δ 6.73–7.85 (m, Ph, 23 H), 4.34 (d, *J*<sub>P-H</sub> = 13 Hz, CH<sub>2</sub>P, 4 H) and 5.11 (s, SH, 1 H). <sup>31</sup>P NMR: δ 42.8. <sup>13</sup>C NMR: δ 120–140 (m, Ph) and 39.743 (d, *J*<sub>P-C</sub> = 52 Hz, CH<sub>2</sub>P).

**HSC<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-2,6 (L3H).** The compound HSC<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>PSPPh<sub>2</sub>)<sub>2</sub>-2,6 (4 g, 7.0 mmol) in Bu<sup>n</sup>P (4.8 ml) under N<sub>2</sub> was slowly heated to 195 °C for 3 h, then cooled to room temperature and the excess of phosphine removed under reduced pressure to give an oily residue, which was treated with methanol. The resulting white solid was filtered off under nitrogen, yield 2 g (56.4%). Mass spectrum (FAB): *m/z* 506 (M<sup>+</sup> + 1) (Calc. for C<sub>32</sub>H<sub>28</sub>P<sub>2</sub>S: C, 75.9; H, 5.6. Found: C, 76.1; H, 5.7%). <sup>1</sup>H NMR: δ 6.52–7.42 (m, Ph, 23 H), 3.65 (s, CH<sub>2</sub>P, 4 H) and 3.95 (t, *J* = Hz, SH, 1 H). <sup>31</sup>P NMR: δ -14.599. <sup>13</sup>C NMR: δ 123–141 (m, Ph) and 36.36 (d, *J*<sub>P-C</sub> = 16.62 Hz, CH<sub>2</sub>P).

**[Ir<sub>2</sub>Cl<sub>2</sub>(μ-CO){2,6-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>S<sub>2</sub>}] 1.** To a solution of [IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (0.13 g, 0.117 mmol) in MeCN (25 ml) was added (L3H) (0.1 g, 0.2 mmol). The solution was stirred for 12 h, giving a yellow solid which was washed with diethyl ether (30 ml), then recrystallized from dichloromethane-diethyl ether as yellow prisms (9%) (Calc. for C<sub>67</sub>H<sub>58</sub>Cl<sub>6</sub>Ir<sub>2</sub>OP<sub>4</sub>S<sub>2</sub>: C, 48.4; H, 3.5. Found: C, 48.1; H, 3.6%). <sup>1</sup>H NMR: δ 6.35–7.77 (m, Ph, 46 H), 4.02 (br, CH<sub>2</sub>P, 8 H) and 5.32 (s, CH<sub>2</sub>Cl<sub>2</sub>, 4 H). <sup>31</sup>P NMR: δ -23.3 (s).

**[Rh<sub>2</sub>Cl(CO)<sub>2</sub>{2,6-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>S}] 2.** To a solution of [RhCl(CO)<sub>2</sub>]<sub>2</sub> (0.04 g, 0.1 mmol) in toluene (20 ml) under N<sub>2</sub> was added L3H (0.05 g, 0.1 mmol), and the resulting solution stirred overnight to give a clear yellow solution. The solvent was reduced to 3 ml and hexane (30 ml) added to precipitate the complex as a yellow solid, yield 0.05 g (62%) (Calc. for C<sub>34</sub>H<sub>27</sub>ClO<sub>2</sub>P<sub>2</sub>Rh<sub>2</sub>S: C, 50.9; H, 3.4. Found: C, 50.7; H, 3.5%). Mass spectrum (FAB): *m/z* 802 (M<sup>+</sup>), 774 (M - CO), 746 (M - 2CO) and 711 (M - Cl - 2CO). FTIR: ν(CO) 1976s and 2060m cm<sup>-1</sup>.

**[Ni<sub>2</sub>{(2,6-Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>S<sub>2</sub>}] [PF<sub>6</sub>]<sub>2</sub> 3.** To a solution of [NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.10 g, 0.15 mmol) in MeCN (25 ml) was added L3H (0.1 g, 0.2 mmol), and the resulting solution stirred for 6 h to give a deep brown solution. The solvent was removed in vacuum, the residue dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) and NaPF<sub>6</sub> (0.09 g) added. The complex was precipitated as a brown solid with diethyl ether and washed with methanol and ether, yield 0.10 g (94%). Suitable crystals for the structure determination were grown from CH<sub>2</sub>Cl<sub>2</sub>-methanol (Calc. for C<sub>68</sub>H<sub>65</sub>ClF<sub>12</sub>Ni<sub>2</sub>-

**Table 4** Summary of structural data for complexes **1**, **3** and **4**

	<b>1</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>67</sub> H <sub>38</sub> Cl <sub>6</sub> Ir <sub>2</sub> OP <sub>4</sub> S <sub>2</sub>	C <sub>68.5</sub> H <sub>65</sub> ClF <sub>12</sub> Ni <sub>2</sub> OP <sub>6</sub> S <sub>2</sub>	C <sub>66</sub> H <sub>56</sub> Cl <sub>2</sub> O <sub>2</sub> P <sub>4</sub> Rh <sub>2</sub>
<i>M</i>	1664.24	1535.01	1281.70
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P2<sub>1</sub>/a</i>
<i>a</i> /Å	25.060(7)	38.985(12)	12.094(5)
<i>b</i> /Å	13.434(3)	22.435(5)	16.450(3)
<i>c</i> /Å	19.625(5)	16.460(2)	14.604(5)
$\beta$ /°	104.95(4)	105.56(2)	90.20(2)
<i>V</i> /Å <sup>3</sup>	6383(3)	13869(5)	2905.5(16)
<i>Z</i>	4	8	2
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	4.625	0.855	0.815
<i>T</i> /K	293(2)	293(2)	293(2)
Reflections collected	6071	9750	6431
Independent reflections	5926 ( <i>R</i> <sub>int</sub> = 0.0524)	9587 ( <i>R</i> <sub>int</sub> = 0.0346)	5225 ( <i>R</i> <sub>int</sub> = 0.1440)
Reflections observed	3864	5507	2560
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0850, 0.2062	0.0616, 0.1666	0.0609, 0.1496

OP<sub>6</sub>S<sub>2</sub>: C, 53.6; H, 4.3. Found: C, 53.0; H, 4.1%). <sup>1</sup>H NMR:  $\delta$  6.39–7.74 (m, Ph, 46 H), 4.04 (br, CH<sub>2</sub>P, 8 H) and 5.32 (s, CH<sub>2</sub>Cl<sub>2</sub>, 1 H). <sup>31</sup>P NMR:  $\delta$  147.3 (s) and –148.9 (seven, *J*<sub>F-P</sub> = 713 Hz).

[Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>2</sub>{1,3-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>}<sub>2</sub>] **4**. The compound 1,3-(Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (0.15 g, 0.36 mmol) was added to [RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] (0.15 g, 0.22 mmol) in MeCN (25 ml) and the mixture stirred at room temperature for 4 h. The resulting yellow microcrystalline solid was filtered off and recrystallized from dichloromethane–methanol. Yield 0.12 g, 86% (Calc. for C<sub>33</sub>H<sub>28</sub>ClOP<sub>2</sub>Rh: C, 61.9; H, 4.4. Found: C, 61.8; H, 4.3%). IR:  $\nu$ (CO) 1957 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  6.65–7.53 (m, Ph, 48 H) and 4.10 (m, CH<sub>2</sub>, 8 H). <sup>31</sup>P NMR:  $\delta$  29.6 (d, *J*<sub>Rh-P</sub> = 125 Hz).

#### Crystal structure determinations

The relevant numerical data are summarized in Table 4. All three sets of intensity data were collected on an Enraf-Nonius diffractometer using monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å).<sup>21</sup> Cell constants were obtained from least squares refinement of one of the setting angles of 25 centred reflections. The data were collected in the  $\omega$ -2 $\theta$  mode, and three standard reflections were measured every three hours of exposure; no loss of intensity was observed for complexes **2** and **4**. There was ca. 25% loss of intensity for **1** and a correction was applied, but the data quality resulted in a relatively high *R* value. Three standard reflections were measured every 200 scans to check the crystal orientation. The data were corrected for Lorentz-polarization factors and an absorption correction applied using  $\psi$  scans of 9 reflections. All structures were solved via direct methods (core atoms)<sup>22</sup> and refined on *F*<sub>o</sub><sup>2</sup> by full matrix least squares.<sup>23</sup> The weighting schemes gave satisfactory agreement. All the residual peaks higher than 1.0 e Å<sup>-3</sup> are located less than 1.0 Å from the heavy metal atoms.

CCDC reference number 186/1432.

See <http://www.rsc.org/suppdata/dt/1999/1877/> for crystallographic files in .cif format.

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