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FULL PAPER

Complexes of platinum(II), platinum(IV), rhodium(III) and iridium(III) containing orthometallated triphenylphosphine

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Treatment of $[PtCl_2(SEt_2)_2]$ or $[RhCl_3(SEt_2)_3]$ with 2-$LiC_6H_4PPh_2$ gives four-membered ring chelate arylplatinum(II) or arylrhodium(III) complexes $[Pt\{C_6H_4(PPh_2)\text{-}2\}_2]$ and $[Rh\{C_6H_4(PPh_2)\text{-}2\}_3]$, respectively, whereas the corresponding reaction of $[IrCl_3(SEt_2)_3]$ gives $IrCl\{C_6H_4(PPh_2)\text{-}2\}_2(PPh_3)]$ arising from cleavage of an Ir–$C_6H_4(PPh_2)$ bond. The chemistry of $[Pt\{C_6H_4(PPh_2)\text{-}2\}_2]$ is dominated by the lability of the Pt–P bonds, which are displaced sequentially by ligands at room temperature to give complexes containing monodentate $C_6H_4(PPh_2)$, *i.e.* $[Pt\{C_6H_4(PPh_2)\text{-}2\}\{\eta^1\text{-}C_6H_4(PPh_2)\text{-}2\}(L)]$ [L = PPh_3, $P(OPh)_3$, $P(OMe)_3$ or Bu^tNC] and $[Pt\{\eta^1\text{-}C_6H_4(PPh_2)\text{-}2\}_2(R_2PCH_2CH_2PR_2)]$ (R = Ph, Me or Cy). In the cases of $Me_2PCH_2CH_2PMe_2$ and $Cy_2PCH_2CH_2PCy_2$, binuclear intermediates can be detected in which these ligands bridge two platinum atoms. Oxidative addition of methyl iodide or iodine to $[Pt\{C_6H_4(PPh_2)\text{-}2\}_2]$ gives initially platinum(IV) complexes $[PtI(R)\{C_6H_4(PPh_2)\text{-}2\}_2]$ (R = Me or I) in which the added groups are mutually *trans*; in the final, stable products the added groups and the phosphorus atoms are, separately, mutually *cis*. Oxidative addition of bromine to $[Pt\{C_6H_4(PPh_2)\text{-}2\}_2]$ gives initially *trans*-$[PtBr_2\{C_6H_4(PPh_2)\text{-}2\}_2]$ but subsequent oxidation and hydrolysis at the phosphorus atoms gives chelate tertiary phosphine oxide complexes of platinum(IV). The molecular structures of $[Rh\{C_6H_4(PPh_2)\text{-}2\}_3]$ and *cis*-$[PtI(Me)\{C_6H_4(PPh_2)\text{-}2\}_2]$ have been determined by X-ray crystallography.

Orthometallated complexes containing the unit $M\{C_6H_4(PPh_2)\text{-}2\}$ are commonly made by heating complexes of triphenylphosphine.[1] Although the process of intramolecular C–H activation is usually slow at room temperature, there is evidence for the participation of such complexes in catalytic hydrogen transfer processes, *e.g.* those based on $[RuH(Cl)(PPh_3)_3]$.[2–4] However, other processes, particularly P–Ph cleavage, can compete or occur together with C–H activation,[5] so that the products of thermolysis of a triphenylphosphine complex are unpredictable.

There are remarkably few systematic studies of the basic chemistry of the $M\{C_6H_4(PPh_2)\text{-}2\}$ unit and alternative synthetic procedures are desirable so that a wider range of complexes is available. Lahuerta *et al.* have obtained derivatives of rhodium(III) and palladium(II) containing $C_6H_4(PPh_2)$-2 by oxidative addition of the carbon–halogen bonds of 2-$XC_6H_4PPh_2$ (X = Cl or Br) to rhodium(I) and palladium(0) precursors.[6,7] We have employed transmetallation from 2-$LiC_6H_4PPh_2$, a reagent that is readily obtained from 2-$BrC_6H_4PPh_2$ by treatment with *n*-butyllithium,[8,9] to prepare, for example, the dinuclear gold(I) complex $[Au_2\{\mu\text{-}C_6H_4(PPh_2)\text{-}2\}_2]$.[10] Although this approach has been used frequently to prepare cyclometallated N-donor complexes,[1] it has found only occasional application in the synthesis of analogous P-donor complexes, *e.g.* the formation of the five-membered ring compounds $[M\{CH_2C_6H_4(PPh_2)\text{-}2\}_2]$ and $[M\{C_6H_4(CH_2PPh_2)\text{-}2\}_2]$ (M = Ni, Pd or Pt) by treatment of $K[CH_2C_6H_4(PPh_2)\text{-}2]$ and 2-$LiC_6H_4(CH_2PPh_2)$, respectively, with the appropriate dihalogenometal(II) precursor.[11,12] We report here the preparation and reactions of complexes of platinum(II), platinum(IV), rhodium(III) and iridium(III) containing 2-$C_6H_4PPh_2$. A preliminary communication on some aspects of the chemistry of $[Pt\{C_6H_4(PPh_2)\text{-}2\}_2]$ has appeared.[13]

Results

The $^{31}P\text{-}\{^1H\}$ NMR spectroscopic data for the new complexes are collected in Table 1.

Platinum(II)

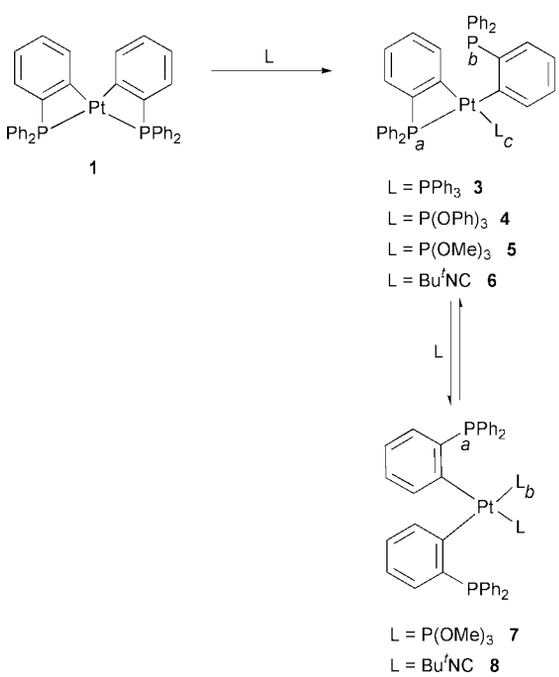
Treatment of either *cis*- or *trans*-$[PtCl_2(SEt_2)_2]$ with 2-$LiC_6H_4PPh_2$ in diethyl ether at −30 °C gives *cis*-$[Pt\{C_6H_4(PPh_2)\text{-}2\}_2]$ **1** as a colourless, microcrystalline solid in 70–80% yield. The monomeric bis(chelate) structure has been confirmed by a single crystal structure analysis.[13] The IR spectrum contains bands at 1560w and 724s cm^{-1} that are characteristic of orthometallated triphenylphosphine complexes[14–16] and the $^{31}P\text{-}\{^1H\}$ NMR spectrum shows a singlet with ^{195}Pt satellites at δ −53.0 ($^1J_{PtP}$ = 1348 Hz). The highly shielded phosphorus resonance is typical of a phosphorus atom in a four-membered chelate ring[17] and the Pt–P coupling constant is even lower than the values of 1400–1800 Hz typically observed for phosphorus *trans* to η^1-phenyl in planar platinum(II) complexes.[18–20] Solutions extracted directly from the reaction mixture often contain an additional singlet at δ −55.6 ($^1J_{PtP}$ = 2376 Hz), which may be due to *trans*-$[Pt\{C_6H_4(PPh_2)\text{-}2\}_2]$ **2**, the Pt–P coupling constant being typical of mutually *trans* P-donors in platinum(II) complexes.[21] Attempts to isolate this isomer gave only complex **1**. In contrast, the analogous five-membered chelate complex $[Pt\{C_6H_4(CH_2PPh_2)\text{-}2\}_2]$ exists as a 1 : 1 mixture of *cis* and *trans* isomers in solution.[12]

One of the co-ordinated phosphorus atoms of complex **1** is easily displaced by the ligands PPh_3, $P(OPh)_3$, $P(OMe)_3$ and Bu^tNC at room temperature to give the colourless 1 : 1 adducts **3**–**6** (Scheme 1) whose structures are established from their $^{31}P\text{-}\{^1H\}$ NMR spectra. The resonances due to the 2-$C_6H_4PPh_2$

Table 1 ^{31}P-$^{1}\{H\}$ NMR data for M{$C_6H_4(PPh_2)$-2} complexes

Complex	Solvent	Chemical shift (multiplicity, J_{PtP})[a–c] P_a	P_b	P_c	J_{PP}
1	CD_2Cl_2	−53.0 (s, 1348)			
2	CD_2Cl_2	−55.6 (s, 2376)			
3	C_6D_6	−58.3 (dd, 1112)	−9.9 (dd, 184)	17.2 (dd, 2112)	*d*
4	C_6D_6	−58.3 (dd, 1146)	−10.4 (dd, 190)	112.7 (dd, 3660)	*e*
5	C_6D_6	−60.2 (dd, 1132)	−10.4 (dd, 220)	130.8 (dd, 3618)	*f*
6	C_6D_6	−58.3 (d, 1114)	−9.3 (d, 256)		4.4
7	C_6D_6	−10.3 (t, 179)	121.4 (t, 3246)		9.6
8	C_6D_6	−7.6 (s, 184)			
9	C_6D_6	−9.6 (t, 170)	32.9 (t, 1762)		7.8
10	C_6D_6	−10.6 (t, 144)	20.8 (t, 1774)		5.1
11	C_6D_6	−7.0 (d, 161)	49.9 (d, 1784)		3.3
12	C_6D_6	−58.8 (m, 1140)	−10.7 (m, 205)	−15.5 (m, 2047)	*g*
13	C_6D_6	−59.5 (dd, 1120)	−14.0 (d, 220)	17.2 (d, 2028)	*h*
14	C_6D_6	−77.8 (s, 921)			
15	CD_2Cl_2	−74.4 (d, 624)	−85.2 (d, 948)		3.7
16	CD_2Cl_2	−68.6 (d, 431)	−83.7 (d, 973)		4.4
17	CD_2Cl_2	−60.8 (d, 513)	−68.2 (d, 977)		4.4
18	CD_2Cl_2	−67.3 (d, 510)	−75.3 (d, 972)		2.8
19	CD_2Cl_2	−83.9 (s, 1026)			
20	CD_2Cl_2	−95.3 (d, 1801)	−98.4 (d, 991)		7.3
21	CD_2Cl_2	−76.3 (d, 2077)	−80.3 (d, 963)		6.1
22	CD_2Cl_2	−66.6 (d, 2114)	62.6 (d, 66)		4.5
23	CD_2Cl_2	55.7 (s, 77)			
24	CD_2Cl_2	−68.4 (s, 926)			
25	CD_2Cl_2	−44.0 (d, 57)			
26	CD_2Cl_2	26.9 (dd, 103)	−28.8 (dt, 110)		18
27	CD_2Cl_2	40.0 (dd, 146)	−40.1 (dd, 114)		34.5
28	CD_2Cl_2	−79.8 (t)	−84.8 (dd)	−2.4 (dd)	*i*

[a] Chemical shifts (δ) in ppm relative to 85% H_3PO_4, coupling constants in Hz. [b] ^{31}P nuclei labelled as shown in text. [c] For platinum(II) complexes, quoted multiplicities exclude ^{195}Pt satellites and J_{PtP} values are in parentheses. [d] $J(P_aP_b) = 6.0$, $J(P_aP_c) = 12.5$, $J(P_bP_c) = 19.4$. [e] $J(P_aP_b) = 5.5$, $J(P_aP_c) = 9.5$, $J(P_bP_c) = 13.0$. [f] $J(P_aP_b) = 4.7$, $J(P_aP_c) = 12.1$, $J(P_bP_c) = 12.1$. [g] Coupling constants could not be measured directly. [h] $J(P_aP_b) = 6.7$, $J(P_aP_c) = 12.3$, $J(P_bP_c) = 0$. [i] $J(P_aP_b) = 14$, $J(P_aP_c) = 14$, $J(P_bP_c) = 398$.



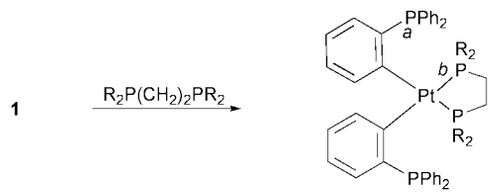
Scheme 1

ligands appear as a pair of doublets, one at δ *ca.* −60 (J_{PtP} = *ca.* 1100 Hz) due to the phosphorus atom in the remaining four-membered ring and one at δ *ca.* −10 (J_{PtP} = *ca.* 190 Hz) due to the dangling phosphorus atom. In the case of the P-donor adducts **3**–**5** these resonances are split further by 5–6 Hz, showing that the two phosphorus atoms are mutually *cis*. The chemical shifts and Pt–P coupling constants for the co-ordinated PPh_3, $P(OPh)_3$ and $P(OMe)_3$ in complexes **3**–**5** are unexceptional. The IR spectrum of complex **6** shows a typical ν(CN) band at 2160 cm^{-1}; there is no evidence for the insertion of Bu^tNC into the platinum(II)–carbon bond.

Complexes **3** and **4** are unaffected by addition of an excess of PPh_3 and $P(OPh)_3$, respectively. In contrast, addition of an excess of $P(OMe)_3$ or Bu^tNC to **5** and **6** causes displacement of the remaining phosphorus atom to give bis(aryl)platinum(II) complexes containing two dangling phosphorus atoms, **7** and **8** (Scheme 1). These were identified *in situ* by their ^{31}P-$\{^1H\}$ NMR spectra, which show only a resonance at δ *ca.* −7 to −10 (J_{PtP} = *ca.* 180 Hz) arising from the unco-ordinated phosphorus atoms; the highly shielded resonance characteristic of the four-membered ring is absent. Attempts to isolate these compounds led to partial or complete formation of the precursors **5** and **6**.

If a solution of complex **1** in C_6D_6 is treated with an equimolar amount of Bu^tNC and the ^{31}P-$\{^1H\}$ NMR spectrum is measured immediately the signals due to complexes **1**, **6** and **8** are observed, but over a period of hours those due to **1** and **8** disappear while that due to **6** increases. Clearly, the second chelate ring of complex **1** is opened by Bu^tNC more rapidly than the first but the process is reversible.

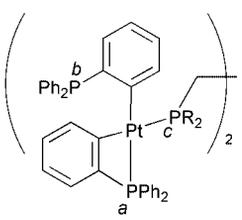
Treatment of complex **1** with the bidentate ligands $R_2PCH_2CH_2PR_2$ [R = Ph (dppe), Me (dmpe) or cyclohexyl(Cy) (dcpe)] gives stable, colourless bis(aryl)platinum(II) complexes **9**–**11** containing two dangling phosphorus atoms and the chelate ditertiary phosphine (Scheme 2), whose structure is evident from the ^{31}P-$\{^1H\}$ NMR spectra (Table 1). In the reactions with dmpe and dcpe it is possible to detect intermediates **12** and **13** in solution in which these ligands appear to bridge a pair of $\overline{Pt\{C_6H_4(PPh_2)\text{-}2\}}\{\eta^1\text{-}C_6H_4(PPh_2)\text{-}2\}$ moieties. Thus, the ^{31}P-$\{^1H\}$ NMR spectrum of a solution containing equimolar amounts of complex **1** and dmpe shows, in addition to the signals arising from these species, multiplet resonances at δ −58.8 ($^1J_{PtP}$ = 1140 Hz) due to η^2-$C_6H_4(PPh_2)$-2, −10.7



R = Ph **9**, Me **10**, Cy **11**

Scheme 2

(J_{PtP} = 205 Hz) due to η^1-$C_6H_4(PPh_2)$-2, and −15.5 ($^1J_{PtP}$ = 2047 Hz). The last signal is assigned to μ-dmpe on the basis of its chemical shift,[17] which is much more shielded than that of complex **10** (δ 20.8) in which dmpe acts as a bidentate chelate ligand. The same complex **12** is formed on mixing solutions of **1** and **10**. The spectroscopic parameters for the corresponding dcpe intermediate **13** are similar, though this compound is not regenerated by addition of complex **11** to **1**.



R = Me **12**, Cy **13**

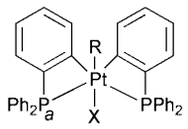
Attempts to generate bi- or tri-metallic complexes by addition of $[PtCl_2(SEt_2)_2]$ to the unco-ordinated phosphorus atoms of **9**–**11** only re-formed **1** together with $[PtCl_2(R_2PCH_2CH_2PR_2)]$.

Platinum(IV)

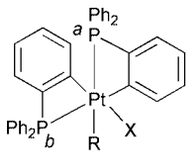
Complex **1** behaves as a typical platinum(II) complex in undergoing oxidative addition reactions. It reacts with neat methyl iodide at room temperature over a period of hours to give a colourless 1 : 1 adduct **14**, which shows a singlet ^{31}P resonance at δ −77.8 ($^1J_{PtP}$ = 921 Hz) arising from equivalent four-membered rings. The Pt–H coupling constant of 70 Hz to the triplet methyl resonance at δ 1.25 is in the expected range for methyl *trans* to halide in octahedral platinum(IV) complexes[22,23] and the Pt–P coupling constant is about two-thirds of that of the platinum(II) precursor **1**, as expected for a platinum(IV) complex.[21] Although stable as a solid, complex **14** isomerises slowly in benzene, and more rapidly in CH_2Cl_2, to a yellow, more unsymmetrical complex **15** which shows in its ^{31}P-{^{1}H} NMR spectrum two closely spaced doublets ($^2J_{PP}$ = 3.7 Hz) at δ −85.2 and −74.4 with couplings to ^{195}Pt of 948 and 624 Hz, respectively. The small P–P coupling points to mutually *cis*-phosphorus atoms; this feature has been confirmed by a single crystal X-ray study (see below), which also shows the metal–carbon σ bonds to be mutually *cis*.

Other halides, such as ethyl iodide, allyl chloride and benzyl bromide, also add to complex **1**. The ^{31}P-{^{1}H} NMR spectra of the adducts **16**–**18** are similar to those of **15** indicating that the organo groups and the halide are mutually *cis*. The products of *trans*-oxidative addition could not be detected. In the reactions of ethyl iodide and benzyl bromide small amount of the corresponding dihalogenoplatinum(IV) complexes (see below) are also formed, as shown by ^{31}P-{^{1}H} NMR spectroscopy.

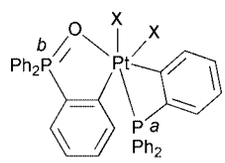
The reaction of complex **1** with iodine is similar to that with methyl iodide, but occurs more rapidly. The initially formed *trans*-diiodo complex **19** rearranges over a period of days in CH_2Cl_2 to the *cis*-diiodo complex **20**, which shows in its ^{31}P-{^{1}H} NMR spectrum resonances at δ −95.3 ($^1J_{PtP}$ = 1801 Hz) and −98.4 ($^1J_{PtP}$ = 991 Hz) assigned to phosphorus atoms *trans* to iodide and phenyl, respectively. The isomerisation is reversible to a small extent: traces of **19** can be detected by ^{31}P-{^{1}H} NMR spectroscopy in CD_2Cl_2 solutions of pure **20** that have been allowed to stand for a week at room temperature. The effects of solvent on the isomerisation of **14** to **15** and **19** to **20** have not been studied further; the process is probably initiated by halide ion dissociation.



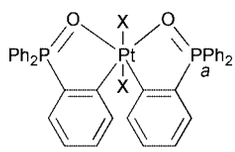
R = Me, X = I **14**
R = X = I **19**
R = X = OH **24**



R = Me, X = I **15**
R = Et, X = I **16**
R = C_3H_5, X = Cl **17**
R = $PhCH_2$, X = Br **18**
R = X = I **20**
R = X = Br **21**



X = Br **22**



X = Br **23**

The ^{31}P-{^{1}H} NMR spectrum of the solution obtained by treatment of complex **1** with an approximately equimolar amount of bromine in CH_2Cl_2 shows the presence of two new species in addition to unchanged **1**. One of these is believed to be the *cis*-dibromo oxidative addition product **21** because its ^{31}P NMR parameters (Table 1) are similar to those of the *cis*-diiodo complex **20**. Although **21** is stable in CH_2Cl_2 over a period of days, we have been unable to isolate it because it reacts with bromine to give the second product at least as fast as it is formed from **1**.

The second species can be isolated as a pale yellow solid from the reaction of complex **1** with a large excess of bromine. The highest mass peak in its FAB-mass spectrum at *m*/*z* 734 corresponds to the addition of one oxygen atom and the loss of two bromide ions from $PtBr_2(C_6H_4PPh_2)_2$, and the IR spectrum contains a strong band at 1062 cm^{-1} assignable to ν(P=O). The ^{31}P-{^{1}H} NMR spectrum contains a highly shielded resonance at δ −66.6 ($^1J_{PtP}$ = 2114 Hz) and a less shielded resonance at δ 62.6 (J_{PtP} = 66 Hz), implying the presence of one four-membered chelate $Pt\{C_6H_4(PPh_2)$-2$\}$ ring and a five-membered ring containing an unco-ordinated phosphorus atom. The spectroscopic data are consistent with structure **22**, which contains a bidentate σ-aryl tertiary phosphine oxide co-ordinated to platinum(IV). This novel ligand is probably formed by initial addition of bromine to a readily displaced phosphorus atom in complex **21** and subsequent hydrolysis of the resulting dibromophosphorane by traces of water. There are few examples of tertiary phosphine oxide or alkyl phosphonate complexes of palladium or platinum and they are restricted to the divalent elements.[24–26]

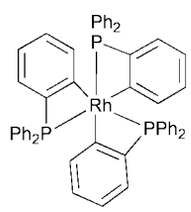
The reaction of complex **1** with an excess of bromine also gave a small amount of a compound which is believed to have structure **23** with two five-membered chelate rings derived by oxidation of the phosphorus atoms. As expected, the ^{31}P-{^{1}H} NMR spectrum shows only a deshielded singlet with a small Pt–P coupling constant and the FAB-mass spectrum confirms that two oxygen atoms have been added.

Complex **1** also reacts with aqueous hydrogen peroxide. Although a number of products are formed, the ^{31}P-{^{1}H} NMR spectrum of the main species is very similar to those of **14**

and **19**, indicative of the *trans*-bis(hydroxo) structure **24**. The isolated solid shows bands in its IR spectrum at 3590 and 1662 cm^{-1} due to water and the mass spectrum confirms the incorporation of two oxygen atoms, but attempts to purify the compound by chromatography caused decomposition.

Rhodium(III) and iridium(III)

From the reaction of *mer*-$[RhCl_3(SEt_2)_3]$ with 2-$LiC_6H_4PPh_2$ in *ca.* 3.5:1 mol ratio, the colourless, crystalline tris(chelate) complex $[Rh\{C_6H_4(PPh_2)\text{-}2\}_3]$ **25** can be isolated in *ca.* 20% yield. The other products of the reaction have not been identified. The structure determined by X-ray crystallography (see below) shows that the phosphorus atoms and the σ-bonded aryl carbon atoms are mutually *cis* in a distorted octahedral coordination about the metal atom. The IR spectrum is similar to that of the bis(chelate)platinum(II) complex **1** and the highest mass peak in the EI-mass spectrum corresponds to $[M - C_6H_5]^+$. The $^{31}P\text{-}\{^1H\}$ NMR spectrum contains just one characteristically shielded doublet, the coupling constant to ^{103}Rh of 57 Hz being one of the lowest ever observed (typical values are 90–150 Hz).[21] Although this datum would appear to suggest that the Rh–P bond is weak, the compound is remarkably stable: it survives heating in benzene in the absence of air at 140 °C and decomposes only slowly in air in refluxing toluene. There is no reaction with CO, ^tBuNC, H_2, or PPh_3, either in toluene or THF, at room temperature or on heating.



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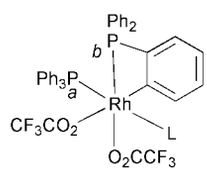
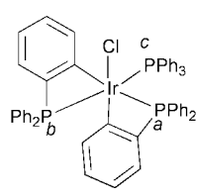


L = PPh_3 **26**
L = CF_3CO_2H **27**



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The metal–carbon σ bonds of complex **25** are not cleaved by an excess of benzoic acid, by an equivalent amount of HCl in ether, or by a threefold excess of trifluoroacetic acid. Treatment with a much larger amount (*ca.* 300-fold excess) of CF_3CO_2H cleaves two of the Rh–C bonds. The products could not be isolated in a pure state but have been identified tentatively on the basis of $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. The first species, formed within 10 min, shows a doublet at δ 26.9 and a triplet at −28.8 ($^2J_{PP}$ = 18 Hz), with couplings to ^{103}Rh of 103 Hz and 110 Hz, respectively. The ^1H NMR spectrum contains no hydride resonances. When the solution is set aside in the presence of the excess of CF_3CO_2H the ^{31}P signals disappear and are replaced by a pair of doublets at δ 40.0 and −40.1 ($^2J_{PP}$ = 34.5 Hz) with couplings to ^{103}Rh of 146 and 114 Hz, respectively. There is also a peak at δ 7.85, which a gated spectrum showed to be due to $[HPPh_3]^+$. These data suggest that the first-formed compound contains two PPh_3 ligands *cis* to the phosphorus atom of 2-$C_6H_4PPh_2$, consistent with structure **26**, and that the second compound, **27**, is derived from it by replacement of one of the PPh_3 ligands by trifluoroacetate or trifluoroacetic acid. A compound whose $^{31}P\text{-}\{^1H\}$ NMR spectrum resembles that of **27** is observed in the solution obtained by treatment of **25** with an excess of HCl; other unidentified peaks were also present.

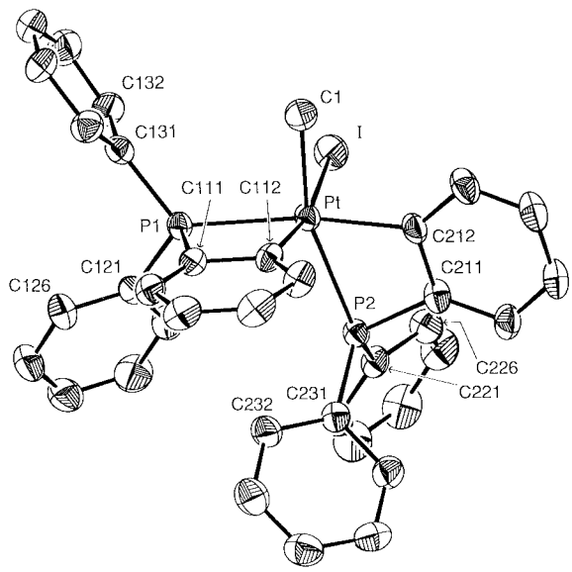

Fig. 1 Molecular structure of *cis*-$PtI(Me)\{C_6H_4(PPh_2)\text{-}2\}_2]\cdot C_6H_6$ **15**. Ellipsoids represent 30% probability levels.

The reaction of *mer*-$[IrCl_3(SEt_2)_3]$ with 2-$LiC_6H_4PPh_2$ gives only traces of the iridium(III) analogue of **25**, identified tentatively on the basis of a singlet in the $^{31}P\text{-}\{^1H\}$ NMR spectrum at δ −73.8. The main product is the pale yellow bis(ortho-metallated) complex $[IrCl\{C_6H_4(PPh_2)\text{-}2\}_2(PPh_3)]$ **28**, which is evidently formed by cleavage of an intermediate Ir–$C_6H_4PPh_2$ species during the reaction; the source of the protons has not been established. The isolated solid retains variable amounts of CH_2Cl_2, so elemental analyses were not completely satisfactory, but the structure shown follows unambiguously from spectroscopic data. The FAB-mass spectrum shows a parent ion peak and the $^{31}P\text{-}\{^1H\}$ NMR spectrum displays an ABX pattern arising from two inequivalent, highly shielded phosphorus atoms A and B belonging to $C_6H_4PPh_2$ groups (δ *ca.* −80) and the phosphorus atom of PPh_3 (X) (δ −2.4). The magnitude of $^2J_{BX}$, 398 Hz, shows that PPh_3 is *trans* to one of the phosphorus atoms of a four-membered ring;[21] the other two P–P couplings are small (*ca.* 14 Hz). The IR spectrum contains a band at 260 cm^{-1} assignable to ν(IrCl), the value being in the range expected for Cl *trans* to σ-bonded carbon.[27] The ^{31}P chemical shifts for **28** are similar to those reported for the structurally characterised hydrido-complex $[IrH\{C_6H_4(PPh_2)\text{-}2\}_2(PPh_3)]$, although the phosphorus atoms in this compound are mutually *cis*.[28,29] Complex **28** is inert towards H_2 or CO (1 bar) in CH_2Cl_2.

Molecular structures

The molecular structures of *cis*-$[PtI(Me)\{C_6H_4(PPh_2)\text{-}2\}_2]$ **15** and $[Rh\{C_6H_4(PPh_2)\text{-}2\}_3]$ **25** are shown in Figs. 1 and 2, respectively, together with atom numbering. Selected interatomic distances and angles are listed in Tables 2 and 3. In both complexes the chelate four-membered rings subtend angles of only 68–69° at the metal atoms, similar to the values found in complex **1** (69°), $[IrH(Br)\{C_6H_4(PPh_2)\text{-}2\}_2(PPh_3)_2]$ (67°),[30] $[IrH\{C_6H_4(PPh_2)\text{-}2\}_2(PPh_3)]$ (67, 68°),[29] $[Mn(CO)_4\{C_6H_3Me\text{-}5\text{-}(P\{C_6H_4Me\text{-}p\}_2\text{-}2)\}]$ (67°),[31] and *cis*-$[Pt\{C_6H_4(PPh_2)\text{-}2\}(R)(PPh_3)]$ [R = η^1-$C(CO_2Me)$=$CH(CO_2Me)$ (68°),[32] η^1-C_6H_5 (69°)[33] or η^1-C_6H_9 (69°)[33]]. The small bite angle of the four-membered rings causes marked deviations from octahedral geometry, *e.g.* in **15** the angles P(2)–Pt–C(1), I–Pt–C(112) and P(1)–Pt–C(212) are up to 20° less than the ideal value of 180°. The deviations from linearity of the

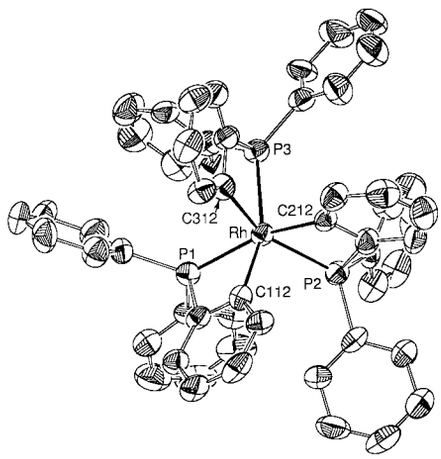

Fig. 2 Molecular structure of $[Rh\{C_6H_4(PPh_2)\text{-}2\}_3]\cdot CHCl_2$ **25**. Ellipsoids represent 50% probability levels.

trans-P–Rh–C angles in **25** are even greater and, although the C–Rh–C angles are close to 90°, the P–Rh–P angles range from 101 to 109°.

In complex **15** the Pt–P distances *trans* to the σ-aryl and methyl carbon atoms [2.370(2), 2.439(2) Å, respectively] indicate that the methyl group has the higher *trans* influence. The Pt–I bond length [2.742(1) Å] is similar to the Pt–I distances for I *trans* to aryl carbon [2.755(1), 2.814(2) Å] in the 9,10-dihydroplatinaanthracene derivative $[PtI_2(PEt_3)_2(\eta^1,\eta^1\text{-}C_6H_4CH_2C_6H_4)]$.[34]

The Pt–C(aryl) distance *trans* to I in complex **15** [2.027(8) Å] is significantly shorter than that *trans* to P(1) [2.052(8) Å], as expected on the basis of the *trans* influences of these donor atoms. The Rh–C(aryl) distances in **25** [2.06(1), 2.06(1), 2.03(1) Å] are comparable with those observed in several five- and six-co-ordinate phenylrhodium(III) complexes containing heavier Group 15 donor atoms, *e.g.* $[RhCl_2(Ph)(PPh_3)_2]$ [2.016(3) Å],[35] $[RhCl_2(Ph)(SbPh_3)_3]$ [2.090(22) Å],[36] and $[RhCl_2(Ph)(NCMe)(SbPh_3)_2]$ [2.027(14) Å,[37] 2.044(10) Å[38]]; they are significantly greater than the Rh–C(aryl) distances in cyclometallated N-donor complexes, such as $[RhI(Me)\{C_6H_4(NMe_2)_2\text{-}2,5\}]$ [1.940(8) Å][39] and $[RhCl_2(H_2O)\{C_6H_4(NMe_2)_2\text{-}2,5\}]$ [1.913(3) Å][40] or in the ligand-free σ-mesityl $[Rh(C_6H_2Me_3\text{-}2,4,6)_3]$ [1.97 Å (av.)],[41] indicating the importance of steric effects in determining these metal–carbon bond lengths.

Table 2 Selected bond distances (Å) and angles (°) for *cis*-$[PtI(Me)\{C_6H_4(PPh_2)\text{-}2\}_2]$ **15**

Pt–P(1)	2.370(2)	Pt–P(2)	2.439(2)
Pt–I	2.742(1)	Pt–C(1)	2.097(10)
Pt–C(112)	2.027(8)	Pt–C(212)	2.052(8)
P(1)–C(111)	1.789(8)	P(2)–C(211)	1.809(9)
C(111)–C(112)	1.43(1)	C(211)–C(212)	1.41(1)
I–Pt–P(1)	100.24(6)	I–Pt–P(2)	93.15(5)
I–Pt–C(1)	89.9(3)	I–Pt–C(112)	168.5(2)
I–Pt–C(212)	95.5(2)	P(1)–Pt–P(2)	107.71(7)
P(1)–Pt–C(1)	90.8(3)	P(1)–Pt–C(112)	68.9(2)
P(1)–Pt–C(212)	164.0(2)	P(2)–Pt–C(1)	160.3(3)
P(2)–Pt–C(112)	93.9(2)	P(2)–Pt–C(212)	68.0(2)
C(1)–Pt–C(112)	86.5(4)	C(1)–Pt–C(212)	92.3(4)
C(112)–Pt–C(212)	95.6(3)	Pt–P(1)–C(111)	83.0(2)
Pt–P(1)–C(121)	122.1(3)	Pt–P(1)–C(131)	124.0(3)
Pt–P(2)–C(211)	81.6(3)	Pt–P(2)–C(221)	127.8(3)
Pt–P(2)–C(231)	122.5(3)		

Discussion

Although $C_6H_4(PPh_2)$-2 complexes of iridium(III) are readily obtainable by orthometallation of iridium(I)-triphenylphosphine complexes,[14,28] the transmetallation procedure allows access to the otherwise unobtainable complexes of platinum(II) and rhodium(III), **1** and **25**, respectively. The oxidative additions to complex **1** seem to occur more rapidly than those of comparable dimethyl- or diphenyl-platinum(II) complexes *cis*-$[PtR_2L_2]$ [R = Me or Ph; 2L = $2PMe_2Ph$, $2AsMe_2Ph$, or $C_6H_4(AsMe_2)_2$-1,2],[23,42] possibly as a consequence of the sterically more exposed metal centre. As in some of these cases, the kinetic products containing the added atoms in mutually *trans* positions rearrange to complexes in which they are mutually *cis*.

Complex **1** clearly differs from the *cis*-$[PtR_2L_2]$ complexes in the ease with which the phosphorus atoms of $C_6H_4(PPh_2)$-2 ligands are displaced successively from the co-ordination sphere. Other ligands of small bite angle, such as $Ph_2PCH_2PPh_2$, behave similarly.[43] The relatively long M–P bonds in complexes **1** and **25** and the small coupling constants to ^{195}Pt or ^{103}Rh suggest that the M–P bonds may be weaker or more strained than in a normal tertiary phosphine complex.

On the other hand, the compactness of the chelate $C_6H_4(PPh_2)$-2 groups combined with shielding of the metal centre by the phenyl groups must be responsible for the stability of the unusual six-co-ordinate tris(chelate) complex **25** containing three rhodium(III)–aryl bonds. Many arylrhodium(III) complexes containing moderately bulky ligands are five-co-ordinate, *e.g.* $[RhBr(1\text{-}C_{10}H_7)_2L_2]$ (L = PPr^n_3 or PEt_2Ph)[44] and $[RhCl_2(Ph)(PPh_3)_2]$,[35] and the only other tris(alkyl) or tris(aryl) derivatives of rhodium(III) appear to be three-co-ordinate $[Rh(C_6H_2Me_3\text{-}2,4,6)_3]$,[41] five-co-ordinate $[Rh(C_6F_5)_3L_2]$ (L = PEt_3 or $AsPh_3$),[45] and six-co-ordinate $[RhMe_3L_3]$ (L = PMe_3, PMe_2Ph).[46] A related compound is the six-co-ordinate iridium(III) complex containing five-membered chelate rings, $[Ir\{C_{10}H_6(PMe_2)\text{-}8\}_3]$, derived from dimethyl-1-naphthylphosphine.[47]

In conclusion, the reagent 2-$LiC_6H_4PPh_2$ provides access to a range of orthometallated complexes of the later 4d and 5d elements containing four-membered rings, thus enabling a more detailed study of their chemistry.

Table 3 Selected bond distances (Å) and angles (°) for $[Rh\{C_6H_4(PPh_2)\text{-}2\}_3]$ **25**

Rh–P(1)	2.400(4)	Rh–P(2)	2.418(3)	Rh–P(3)	2.393(3)
Rh–C(112)	2.06(1)	Rh–C(212)	2.06(1)	Rh–C(312)	2.03(1)
P(1)–C(111)	1.812(9)	P(1)–C(121)	1.83(1)	P(1)–C(131)	1.838(9)
P(2)–C(211)	1.80(1)	P(2)–C(221)	1.83(1)	P(2)–C(231)	1.82(1)
P(3)–C(311)	1.82(1)	P(3)–C(321)	1.83(1)	P(3)–C(331)	1.84(1)
P(1)–Rh–P(2)	109.3(1)	P(1)–Rh–P(3)	101.2(1)	P(2)–Rh–P(3)	106.7(1)
P(1)–Rh–C(112)	68.2(3)	P(2)–Rh–C(212)	68.0(3)	P(3)–Rh–C(312)	68.6(3)
P(1)–Rh–C(212)	162.8(3)	P(2)–Rh–C(312)	155.7(3)	P(3)–Rh–C(112)	158.3(2)
P(1)–Rh–C(312)	95.0(3)	P(2)–Rh–C(112)	94.8(2)	P(3)–Rh–C(212)	95.8(3)
C(112)–Rh–C(212)	94.9(4)	C(112)–Rh–C(312)	92.9(4)	C(212)–Rh–C(312)	88.4(4)
Rh–P(1)–C(111)	82.1(4)	Rh–P(2)–C(211)	82.1(3)	Rh–P(3)–C(311)	82.0(3)
Rh–P(1)–C(121)	124.9(4)	Rh–P(2)–C(221)	126.3(3)	Rh–P(3)–C(321)	115.0(4)
Rh–P(1)–C(131)	126.4(4)	Rh–P(2)–C(231)	125.2(3)	Rh–P(3)–C(331)	134.6(3)

Table 4 Elemental analyses and decomposition temperatures of M{$C_6H_4(PPh_2)$-2} complexes

Complex	Decomp. temp./°C	Analysis (%)[a] C	H	P	Other
1	220	59.8(60.25)	3.9(3.9)	8.8(8.6)	
3	215	66.5(66.2)	4.7(4.4)	9.1(9.5)	
4	172	63.4(63.1)	4.45(4.2)	8.6(9.0)	5.5(4.7) (O)
5	86	55.4(55.65)	4.55(4.4)	10.7(11.0)	6.8(5.7) (O)
6	138	61.2(61.5)	4.8(4.7)	7.7(7.7)	1.5(1.75) (N)
9	238	67.2(66.7)	4.8(4.7)	11.0(11.1)	
10	210	58.1(58.1)	5.3(5.1)	14.0(14.3)	
11	230	65.5(65.3)	6.8(6.7)	10.8(10.9)	
14	198	51.9(51.7)	3.4(3.6)	7.3(7.2)	14.9(14.8) (I)
15	202	52.2(51.7)	3.7(3.6)	7.15(7.2)	14.9(14.8) (I)
16[b]	210	51.4(52.2)	3.9(3.8)	6.6(7.1)	16.2(14.5) (I)
17[c]	188	57.9(58.0)	4.1(4.15)	8.1(7.6)	6.3(6.1) (Cl)
18[d]	220	57.2(58.1)	3.8(4.0)	7.0(7.0)	11.7(9.0) (Br)
19	132	44.9(44.5)	2.7(2.9)	6.15(6.4)	26.5(26.1) (I)
20	208	44.55(44.5)	2.7(2.9)	6.4(6.4)	26.1(26.1) (I)
22	216	48.6(48.4)	3.1(3.2)	6.7(6.9)	18.25(17.9) (Br)
25	240–243	73.3(73.1)	5.0(4.8)	10.05(10.5)	
28[e]	218–220	59.3(62.0)	4.4(4.2)	8.6(8.8)	6.7(6.7) (Cl)

[a] Calculated values in parentheses. [b] Sample contains small amount of complex **20** (^{31}P NMR) and CH_2Cl_2 (^{1}H NMR). [c] Sample contains 0.2 CH_2Cl_2 (^{1}H NMR). [d] Sample contains some [$PtBr_2(C_6H_4PPh_2$-2)$_2$] **21** (^{31}P NMR) and CH_2Cl_2 (^{1}H NMR). [e] Calc. figures refer to **28**·0.5 CH_2Cl_2.

Experimental

All experiments were carried out under an inert atmosphere with use of standard Schlenk techniques, though the metal complexes were usually stable to air after they had been isolated. Solvents were dried and degassed before use; ether was refluxed over and freshly distilled from sodium–benzophenone. The NMR spectra were measured on Varian XL-200 (^{1}H at 200 MHz, ^{31}P at 81.0 MHz) or Gemini 300 BB (^{1}H at 300 MHz, ^{13}C at 50.3 MHz) spectrometers. The ^{1}H chemical shifts (δ) were measured relative to the residual signals of CD_2Cl_2 (δ 5.32) or C_6D_6 (δ 7.15), ^{13}C relative to CD_2Cl_2 (δ 52.6), and ^{31}P recorded with 85% H_3PO_4 as external reference. Infrared spectra were measured as KBr discs on Perkin-Elmer 225 or 1800 FT instruments, mass spectra on a VG Micromass 7070 F operating in electron-impact (EI) or fast-atom bombardment (FAB) mode. Microanalyses were performed in-house on samples that had been dried *in vacuo* at 70–80 °C for 2 d. Melting points (uncorrected) were measured on a Gallenkamp melting point apparatus. The ^{31}P NMR and analytical data are collected in Tables 1 and 4, respectively. Aromatic protons appeared as complex multiplets in the region δ 6.2–8.2 for all compounds.

The compounds 2-$BrC_6H_4PPh_2$,[8,9,48] $R_2PCH_2CH_2PR_2$ (R = Me or Cy),[49] [$PtCl_2(SEt_2)_2$][50] and *mer*-[$RhCl_3(SEt_2)_3$][51] were prepared by literature methods.

The reported methods of preparation of *mer*-[$IrCl_3(SEt_2)_3$][51,52] were modified as follows. A solution of H_2IrCl_6·$6H_2O$ (38.5% Ir, 3.6 g, 7.0 mmol) in water (150 cm^3) and ethanol (20 cm^3) was treated with an excess of diethyl sulfide (5 cm^3). The dark red solution was heated under reflux for 20 h, changing slowly to orange-red. Solvents were removed by distillation until the volume of the solution was *ca.* 50 cm^3. The red solid that appeared when the solution was cooled in ice for 0.5 h was collected by filtration and re-dissolved in CH_2Cl_2 (*ca.* 20 cm^3). The solution was chromatographed on alumina (Grade III) and eluted with CH_2Cl_2. The eluate was evaporated to dryness and the residue recrystallised from CH_2Cl_2–hexane. The yellow solid was dried *in vacuo* at 70 °C for 2 d; it melted at 121–123 °C. The yield was 2.1 g (53%) (Found: C, 25.4; H, 5.6; Cl, 18.5; S, 16.2. $C_{12}H_{30}Cl_3IrS_3$ requires: C, 25.3; H, 5.3; Cl, 18.7; S, 16.9%) ^{1}H NMR (C_6D_6): δ 2.7–3.4 (br m, 6 H, CH_2), 1.38 (t, 3 H, Me, J_{HH} = 7.5 Hz) and 1.40 (t, 6 H, Me, J_{HH} = 7.5).

Preparations

***cis*-[Pt{C_6H_4(PPh_2)-2}$_2$] 1.** A stirred solution of 2-$BrC_6H_4PPh_2$ (1.4 g, 4.1 mmol) in ether (40 cm^3) was treated dropwise with a 1.6 M solution of Bu^nLi (2.8 cm^3, 4.5 mmol) in hexane at room temperature. A white precipitate began to form after *ca.* 10 min; the suspension of 2-$LiC_6H_4PPh_2$ was stirred for 2 h, cooled to −30 °C, and treated with [$PtCl_2(SEt_2)_2$] (*cis* or *trans*) (1.0 g, 2.2 mmol). The slurry was stirred for 0.5 h at −30 °C, allowed to warm to room temperature, and stirred overnight. The colourless solid was collected by filtration, washed with methanol (3 × 20 cm^3) and ether (2 × 10 cm^3), and recrystallised from CH_2Cl_2–methanol. The yield of complex **1** was 1.1 g (79%). The solid residue obtained after removal of solvents from the mother liquor contained some *trans* isomer **2** as well as **1**, as shown by its ^{31}P NMR spectrum.

***cis*-[Pt{C_6H_4(PPh_2)-2}{η^1-$C_6H_4(PPh_2)$}(PPh_3)] 3.** A solution of complex **1** (100 mg, 0.14 mmol) in benzene (10 cm^3) was treated with PPh_3 (50 mg, 0.19 mmol) and set aside at room temperature overnight. Addition of hexane (20 cm^3) gave the product **3** as a white solid, which was collected by filtration and washed with hexane (3 × 10 cm^3). The yield was 114 mg (83%).

***cis*-[Pt{C_6H_4(PPh_2)-2}{η^1-$C_6H_4(PPh_2)$}{$P(OPh)_3$}] 4.** A benzene solution (10 cm^3) containing complex **1** (100 mg, 0.14 mmol) and $P(OPh)_3$ (38 μl, 0.15 mmol) was degassed by three freeze–pump–thaw cycles and stirred at room temperature for 7 d. The solvent was stripped and the solid residue dissolved in a small volume of toluene. Addition of hexane (20 cm^3) gave the product **4** as a white solid, which was collected by filtration and washed with hexane (3 × 5 cm^3). The yield was 75 mg (52%).

The trimethyl phosphite analogue **5** was obtained similarly from **1** (100 mg, 0.14 mmol) and $P(OMe)_3$ (20 μl, 0.17 mmol) in benzene (10 cm^3) for 15 h. The solid was purified by reprecipitation from toluene (1 cm^3) and hexane (10 cm^3) at solid CO_2 temperature. The yield was 45 mg (38%). ^{1}H NMR (C_6D_6): δ 3.22 (d, $^3J_{PH}$ = 12 Hz, OMe).

A solution of complex **1** (150 mg, 0.21 mmol) in benzene (3 cm^3) stirred for 3 d with an excess of $P(OMe)_3$ (0.10 cm^3, 0.85 mmol) was shown by ^{31}P NMR spectroscopy to contain

cis-[Pt{η¹-$C_6H_4(PPh_2)$}$_2${$P(OMe_3)$}$_2$] **7**, but attempted precipitation of this compound with hexane gave only **5**.

***cis*-[Pt{$C_6H_4(PPh_2)$-2}{η¹-$C_6H_4(PPh_2)$}(CNBu^t)] 6.** A solution of complex **1** (50 mg. 0.070 mmol) in benzene (5 cm^3) was treated with an equimolar amount of Bu^{t}NC (7.9 μl) and stirred for 1 h. The green-yellow solution was layered with hexane (10 cm^3) and set aside at 5 °C overnight. Complex **6** was separated by filtration. The yield was 30 mg (54%). ^{1}H NMR (C_6D_6): δ 0.76 (s, Bu^t). IR (KBr): 2160 cm^{-1} [s, ν(CN)].

A solution of complex **1** (105 mg, 0.15 mmol) in benzene (3 cm^3) to which an excess of Bu^{t}NC (50 μl, 0.44 mmol) had been added contained *cis*-[Pt{η¹-$C_6H_4(PPh_2)$-2}$_2$($CNBu^t$)$_2$] **8**, as shown by ^{31}P NMR spectroscopy, but on removal of solvent *in vacuo* a mixture of **6** and **8** was obtained.

cis-[Pt{η¹-$C_6H_4(PPh_2)$-2}$_2$(dppe)] **9** was prepared similarly to complex **3** from **1** (100 mg, 0.14 mmol) and dppe (80 mg, 0.20 mmol). The yield was 125 mg (80%). *cis*-[Pt{η¹-$C_6H_4(PPh_2)$-2}$_2$-(dmpe)] **10** was prepared similarly from **1** (50 mg, 0.070 mmol) and dmpe (0.2 cm^3, 1.2 mmol). The yield was 45 mg (74%). ^{1}H NMR (C_6D_6): δ 1.04 (d, 4H, $^2J_{PH}$ = 9.1, PCH_2CH_2P) and 0.34 (d, 12 H, $^2J_{PH}$ = 9.7 Hz, PMe). *cis*-[Pt{η¹-$C_6H_4(PPh_2)$-2}$_2$(dcpe)] **11** was prepared similarly from **1** (60 mg, 0.084 mmol) and dcpe (55 mg, 1.3 mmol). The yield was 57 mg (60%).

***trans*-[PtI(Me){$C_6H_4(PPh_2)$-2}$_2$] 14.** A sample of complex **1** (100 mg, 0.14 mmol) was treated with neat methyl iodide (3 cm^3) and the mixture stirred at room temperature for 4 h. The methyl iodide was removed under reduced pressure to give complex **14** quantitatively as a white solid. ^{1}H NMR (C_6D_6): δ 1.25 (t with ^{195}Pt satellites, $^3J_{PH}$ = 7.4, $^2J_{PH}$ = 70 Hz, PtMe). EI-MS: *m*/*z* 844, [*M* − Me]$^+$; 732, [*M* − I]$^+$; and 717 [*M* − MeI]$^+$.

***cis*-[PtI(Me){$C_6H_4(PPh_2)$-2}$_2$] 15.** A solution of complex **14** (50 mg, 0.058 mmol) in CH_2Cl_2 (5 cm^3) that had been set aside at room temperature for 30 h changed from colourless to orange. Complex **15** was obtained quantitatively as a yellow solid. ^{1}H NMR (C_6D_6): δ 2.31 (t with ^{195}Pt satellites, $^3J_{PH}$ = 7.6, $^2J_{PtH}$ = 65 Hz, PtMe). ^{13}C NMR (CD_2Cl_2): δ 0.36 (d with ^{195}Pt satellites, $^2J_{PC}$ = 107, $^1J_{PtC}$ = 506 Hz, PtMe). X-Ray quality crystals were obtained from benzene at room temperature.

***cis*-[PtI(Et){$C_6H_4(PPh_2)$-2}$_2$] 16.** A solution of complex **1** (81 mg, 0.11 mmol) in CH_2Cl_2 (4 cm^3) was treated with ethyl iodide (2 cm^3) and the mixture stirred at 55 °C for 2 d. Solvent was removed *in vacuo*. The residue was re-dissolved in CH_2Cl_2 and the orange solid product **16** precipitated with ether. The yield was 35 mg (35%). ^{1}H NMR (CD_2Cl_2): δ 2.93 (m, 1 H, Pt C*H*H), 2.37 (m, 1 H, Pt CH*H*) and 0.64 (dt with ^{195}Pt satellites, 3 H, J_{HH} = 7.2, $^4J_{PH}$ = 14, $^3J_{PtH}$ = 67 Hz, $PtCH_2CH_3$). ^{13}C NMR (CD_2Cl_2): δ 14.32 (d with ^{195}Pt satellites, $^2J_{PC}$ = 104, $^1J_{PtC}$ = 504, $PtCH_2$) and 19.70 (d with ^{195}Pt satellites, $^3J_{PC}$ = 6, $^2J_{PtC}$ = 12 Hz, $PtCH_2CH_3$).

***cis*-[PtCl(η¹-C_3H_5){$C_6H_4(PPh_2)$-2}$_2$] 17.** A solution of complex **1** (100 mg, 0.14 mmol) in CH_2Cl_2 (10 cm^3) was treated with allyl chloride (0.3 cm^3). The mixture was stirred at room temperature for 30 h, becoming pale yellow. The solution was evaporated under reduced pressure to *ca*. 2 cm^3 volume, layered carefully with hexane (5 cm^3) and set aside overnight at −5 °C. The pale yellow, crystalline solid **17** was collected by filtration and washed with hexane (2 × 4 cm^3). The yield was 91 mg (81%). ^{1}H NMR (CD_2Cl_2): δ 5.68 (m, 1 H, CH_2CHCH_2), 4.36 (m, 2 H, $PtCH_2CHCH_2$), 3.36 (m, 1 H, PtC*H*H) and 3.18 (m, 1 H, PtCH*H*). ^{13}C NMR (CD_2Cl_2): δ 25.92 (d with ^{195}Pt satellites, $^2J_{PC}$ = 104, $^1J_{PtC}$ = 484, $PtCH_2$), 110.21 (d with ^{195}Pt satellites, $^4J_{PC}$ = 12, $^3J_{PtC}$ = 53, $PtCH_2CHCH_2$) and 144.12 (d with ^{195}Pt satellites, $^3J_{PC}$ = 8.3, $^2J_{PtC}$ = 35 Hz, $PtCH_2$).

***cis*-[PtBr(CH$_2$Ph){$C_6H_4(PPh_2)$-2}$_2$] 18.** A solution of complex **1** (104 mg, 0.14 mmol) in CH_2Cl_2 (5 cm^3) was treated with benzyl bromide (0.5 cm^3) and stirred at room temperature for 5 d. The pale yellow solution was concentrated *in vacuo* to *ca*. 2 cm^3 volume and the product **18** precipitated by addition of hexane, collected by filtration and washed with hexane (2 × 3 cm^3). The yield was 68 mg (53%). ^{1}H NMR (CD_2Cl_2): δ 4.25 (ddd with ^{195}Pt satellites, 1 H, J_{HH} = 11.5, $^3J_{PH}$ = 5.8, 8.5, $^2J_{PtH}$ = 95, C*H*HPh) and 3.78 (dt with ^{195}Pt satellites, 1 H, J_{HH} = 11.5, $^3J_{PH}$ = 8.2, $^2J_{PtH}$ = 83 Hz, CH*H*Ph). ^{13}C NMR (CD_2Cl_2): δ 27.60 (d with ^{195}Pt satellites, $^2J_{PC}$ = 103, J_{PtC} = 474 Hz, CH_2Ph). The ^{31}P-{^{1}H} NMR spectrum showed that a small amount of [$PtBr_2${$C_6H_4(PPh_2)$-2}$_2$] **21** was also present.

***trans*-[PtI$_2${$C_6H_4(PPh_2)$-2}$_2$] 19.** A solution of complex **1** (59 mg, 0.082 mmol) in CH_2Cl_2 (5 cm^3) was treated with a solution of iodine (22 mg, 0.087 mmol) in CH_2Cl_2 (5 cm^3). After 10 min the solvent was stripped to give the product **19** quantitatively.

***cis*-[PtI$_2${$C_6H_4(PPh_2)$-2}$_2$] 20.** A mixture of complex **1** (100 mg, 0.14 mmol) and iodine (50 mg, 0.20 mmol) in toluene (10 cm^3) was stirred for 2 d; a yellow precipitate formed slowly. The solid product **20** was collected by filtration and washed with benzene (2 × 2 cm^3) to remove remaining **19** and hexane (3 × 5 cm^3). The yield was 80 mg (59%).

***cis*-[PtBr$_2${$C_6H_4(PPh_2)$-2}{$C_6H_4[P(O)Ph_2]$-2}] 22.** Two drops of bromine (*ca*. 0.1 cm^3) were added to a solution of complex **1** (180 mg, 0.25 mmol) in CH_2Cl_2 (10 cm^3) and the red solution was stirred overnight at room temperature. Addition of hexane (20 cm^3) precipitated the product **22** as a pale yellow solid, which was collected by filtration and washed with benzene (3 × 5 cm^3). The yield was 150 mg (67%). IR(KBr): 1062s cm^{-1} [ν(P=O)]. FAB-MS: *m*/*z* 734 [*M* + H − 2Br]$^+$.

When the supernatant benzene–hexane solution and benzene washings were concentrated *in vacuo* and more hexane was added more yellow solid precipitated. After being washed with hexane, the solid was redissolved in benzene and the solution chromatographed on alumina. The yellow band that eluted with benzene–ethanol (4:1 v/v) was evaporated to dryness to give a solid (10 mg) identified tentatively as *trans*-[$PtBr_2${$C_6H_4[P(O)Ph_2]$-2}$_2$-2}] **23**. IR (KBr): 1060s cm^{-1} [ν(P=O)]. FAB-MS: *m*/*z* 829, [*M* − Br]$^+$; 813, [*M* − O, Br]$^+$; and 749, [*M* − 2Br]$^+$.

***trans*-[Pt(OH)$_2${$C_6H_4(PPh_2)$-2}$_2$] 24.** A two-phase mixture of a solution of complex **1** (100 mg, 0.14 mmol) in CH_2Cl_2 (50 cm^3) and 30 vol. aq. hydrogen peroxide (2 cm^3) was stirred at room temperature for 20 h. The organic phase was separated and washed with water (3 × 10 cm^3). The residue obtained after solvents had been removed was dissolved in CH_2Cl_2 and re-precipitated with hexane. The yield of crude **24** was 85 mg (81%). The product decomposed on attempted chromatography. IR (KBr) 3590m and 1662m cm^{-1}. EI-MS: *m*/*z* 749, [*M* − 2H]$^+$; and 734, [*M* − OH]$^+$. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 1.1 (br, OH or H_2O).

[Rh{$C_6H_4(PPh_2)$-2}$_3$] 25. A stirred suspension of 2-LiC_6-H_4PPh_2, prepared as described above from 2-$BrC_6H_4PPh_2$ (1.4 g, 4.1 mmol) in ether (30 cm^3) and Bu^{n}Li (3.0 cm^3 of 1.6 M solution in hexane, 4.5 mmol), was treated with [$RhCl_3(SEt_2)_3$] (0.59 g. 1.2 mmol) in small portions at room temperature. The suspension initially cleared but later a precipitate (presumably of LiCl and LiBr) formed. The ether was removed *in vacuo* and the residual solid extracted with benzene (100 cm^3). The solution was chromatographed twice on alumina (grade 1). On

Table 5 Crystal and structure refinement data for *cis*-[PtI(Me){C_6H_4(PPh_2)-2}$_2$]·C_6H_6 **15** and [Rh{C_6H_4(PPh_2)-2}$_3$]·CH_2Cl_2 **25**

	15	**25**
Chemical formula	$C_{37}H_{31}IP_2Pt·C_6H_6$	$C_{54}H_{42}P_3Rh·CH_2Cl_2$
M	937.70	971.69
Crystal system	Monoclinic	Monoclinic
Space group	Pn	$P2_1/c$
a/Å	13.494(1)	23.145(22)
b/Å	9.409(2)	9.425(3)
c/Å	14.991(2)	21.756(10)
β/°	95.27(1)	104.75(2)
U/Å^3	1895.3(9)	4589(5)
Z	2	4
T/K	298(1)	293(1)
μ(Cu-Kα)/cm^{-1}	144.8	54.6
Unique reflections	3148	7601
Used reflections	3056 [$I > 3\sigma(I)$]	5327 [$I > 3\sigma(I)$]
R (used reflections)	0.030	0.085
R_w (used reflections)	0.038	0.096

evaporation to dryness the benzene eluate gave complex **25** as a colourless oily solid, which was purified by recrystallisation from CH_2Cl_2–ethanol. The yield was 0.25 g (23%). Crystals suitable for X-ray structural analysis were obtained from CH_2Cl_2–hexane at −5 °C. IR (KBr): 1552m and 724s cm^{-1}. EI-MS: m/z 810, $[M - Ph]^+$; 701, $[M - PPh_2]^+$; and 625, $[M - C_6H_4PPh_2]^+$.

[IrCl{C_6H_4(PPh_2)-2}$_2$(PPh_3)] 28. A stirred suspension of 2-Li$C_6H_4PPh_2$, prepared as above from 2-Br$C_6H_4PPh_2$ (1.0 g, 2.9 mmol) in ether (30 cm^3) and Bu^{n}Li (2.2 cm^3 of 1.6 M solution in hexane), was treated with [$IrCl_3(SEt_2)_3$] (450 mg, 0.79 mmol) in small portions at room temperature and the mixture stirred overnight. The ether was stripped and the solid residue extracted with benzene (3 × 50 cm^3). The extract was concentrated under reduced pressure to *ca*. 30 cm^3 volume and the crude product **28** precipitated as a yellow solid, which was purified by chromatography [CH_2Cl_2, alumina (grade 1)] and recrystallisation from CH_2Cl_2–hexane. The yield was 0.28 g (35%). FAB-MS: m/z 1012, $[M]^+$; 977, $[M - Cl]^+$; 750, $[M - PPh_3]^+$; and 715, $[M - Cl - PPh_3]^+$.

X-Ray crystallography of *cis*-[PtI(Me){C_6H_4(PPh_2)-2}$_2$]·C_6H_6 **15** and [Rh{C_6H_4(PPh_2)-2}$_3$]·CH_2Cl_2 **25**

Selected crystal data and details of data collection and processing are in Table 5. Crystals of complex **25** were generally of poor quality and readily lost solvent, which probably accounts for the 24–50% decrease in intensity during data collection of three check reflections measured at 90 min intervals. For **15** there was a 5% decrease in intensity under the same conditions. Its absolute structure was clearly established with a Flack[53] parameter of 0.018(8). Data reduction and refinement computations were performed with XTAL 3.0.[54]

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