FULL PAPER

Dalton
www.rsc.org/dalton

Exploring the coordination chemistry and reactivity of dialkylamino- and bis(dialkylamino)-phosphines in the coordination sphere of metals

Philip W. Dyer,* John Fawcett, Martin J. Hanton, Raymond D. W. Kemmitt,* Ranbir Padda and Narendra Singh

Department of Chemistry, University of Leicester, Leicester, UK LE1 7RH.
E-mail: p.dyer@le.ac.uk

Received 12th September 2002, Accepted 31st October 2002
First published as an Advance Article on the web 29th November 2002

The coordination chemistry of a range of dialkylamino- and bis(dialkylamino)-phosphines, $R_xP(NR'_2)_{3-x}$ (x = 1 or 2; R = Cl, Me, Ph, C_6F_5; R′ = Et, Pr^i), **1**–**7**, has been studied and the resulting Group 6 tetracarbonyl and platinum dichloride bis(phosphine) complexes fully characterised. Subsequently, the reactivity of the P–N bonds of the metal-bound phosphines was probed. Treatment of R″OH (R″ = Me, Et, allyl) solutions of the bis(dialkylaminodiphenylphosphine) complexes with anhydrous HCl gas led to substitution of NR'_2 by OR″; the resulting P-alkoxy complexes were isolated in excellent yields. Acidification of ethylene glycol solutions of the aminophosphine complexes afforded the corresponding bis(chlorodiphenylphosphine) derivatives. Following reaction of *trans*-$[W(CO)_4(P\{NEt_2\}Ph_2)_2]$ with either aqueous HCl or H_2SO_4, *trans*-$[W(CO)_4(P\{OH\}Ph_2)_2]$ could be isolated as its dichloromethane solvate in excellent yield (81%). Reactions of the bis(bis{dialkylamino}phenylphosphine) complexes under identical conditions yielded a range of unidentified products. Reactions of ligands **1**–**7** with $[\{RhCl(CO)_2\}_2]$ and elemental selenium have been undertaken and the products used to assess the phosphines' donor capabilities. Depending on the substituents at phosphorus, either *trans*-diphosphine or *cis*-dicarbonyl complexes result from reaction with $[\{RhCl(CO)_2\}_2]$. The sterically demanding phosphine $P(NPr^i_2)_2Ph$ (**5**) proved unreactive towards complexation with metals, although its selenide could be prepared and isolated. In order to probe the observed lack of oxidation or complexation the molecular structure $P(NPr^i_2)_2(C_6F_5)$ has been determined by X-ray crystallography.

Introduction

Since their discovery by Michaelis, amino-substituted phosphines have been the focus of considerable interest as potential precursors to P–N backbone polymeric materials and, more fundamentally, because of their potential to exhibit P–N multiple bonding.[1,2] In contrast, their coordination chemistry has been comparatively poorly studied, despite an initial flurry of activity[3–6] and the prevalence of many such phosphines in the literature; the amino group is often used as a convenient and versatile protecting/leaving group for phosphorus;[7–10] aminophosphines exhibit antimicrobial activity;[11] and sterically demanding variants have been used to protect reactive main group and organic moieties.[12] Some of the reluctance to use aminophosphine ligands can be attributed to their perceived susceptibility to protic reagents, in particular solvents. However, the advent of more robust heterocyclic systems **A** (Fig. 1) has led to a dramatic upturn in their application, especially in the asymmetric catalysis arena.[13,14]

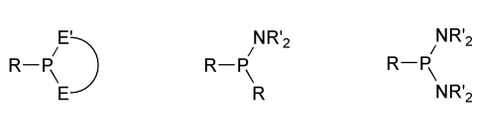


Fig. 1 Aminophosphine classification. E = E′ = NR″; E = O, E′ = NR″.

Recently, however, acyclic amino-functionalised phosphines **B** and **C** have seen somewhat of a renaissance as ligands.[15–20] In part, this can be attributed to the increasing demand for libraries of metal complexes for testing in a variety of catalytic applications and transformations.[21] Aminophosphines, $R_xP(NR'_2)_{3-x}$ (x = 0–2), are particularly attractive in this respect, as they are conveniently prepared through the reaction of halophosphines with amines, of which there is a structurally diverse range readily available. This obviously provides a simple method of tuning both the ligand's steric and electronic demands through variation of the amino substituents, R′, making them extremely versatile ligands.

Prior to the routine application of aminophosphines **B** and **C** in the catalysis arena however, it seems important that the fundamental behaviour of these relatively ill-explored ligands should be understood in the coordination spheres of metals, especially as they possess potentially reactive phosphorus–nitrogen linkages. Indeed, much of the early work on aminophosphines focussed on the reaction of this moiety with protic reagents rather than on coordination chemistry. It is noteworthy that one of the most studied aminophosphines is the readily prepared secondary phosphine, $(Pr^i_2N)_2PH$, which was investigated with a view to examining the reactivity associated with both the P–H and P–N bonds in the coordination sphere of metal carbonyl fragments.[22,23]

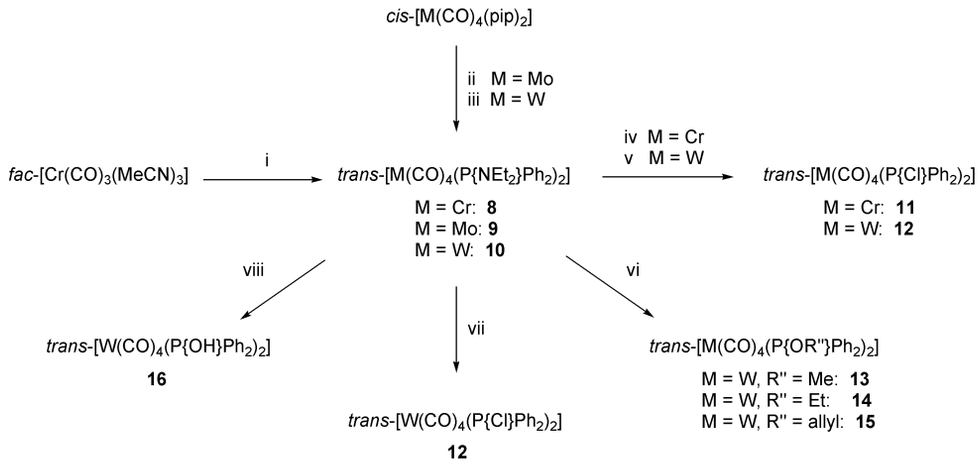
Here we describe the coordination chemistry of a number of monoamino-, diamino- and aminohalo-substituted phosphines of types **B** and **C**. In particular, the reactivity of the potentially labile P–N bond of the metal-bound ligands has been probed, in conjunction with a study of the relative donor properties of each of the ligands.

Results and discussion

Coordination chemistry and reactivity of aminophosphines

A range of simple amino-functionalised phosphines, $R_xP(NR'_2)_{3-x}$ (**1**–**7**), was chosen for this study (Table 1). Derivatives **1**–**5**, and **7** were prepared following literature procedures or slight modifications thereof. Where ligands were prepared through reaction of an organometallic reagent with a chlorophosphine, the organo-lithium derivatives were employed. In all cases, the use of the corresponding Grignards afforded mixtures of the desired product and the reductively-coupled diphosphines. In contrast, the previously unreported

DOI: 10.1039/b208886j



Scheme 1 Reagents and conditions: i 2 $P(NEt_2)Ph_2$, C_6H_6, rt, 12 h; ii 2 $P(NEt_2)Ph_2$, CH_2Cl_2, rt, 2 h; iii 2 $P(NEt_2)Ph_2$, C_6H_6, 80 °C, 3 h; iv HCl (g), CH_2Cl_2, rt, 15 min; v HCl (g), CH_2Cl_2, rt, 15 min; vi HCl (g), R″OH, rt, 30 min; vii HCl (g), $HOCH_2CH_2OH$, rt, 15 min; viii H_2SO_4 (10%), CH_2Cl_2, RT, 24 h, rt.

Table 1 $^{31}P\{^1H\}$ NMR data[a] for compounds **1**–**30**

Compound	$\delta(^{31}P)$/ppm	$^1J_{MP}$[g]/Hz
1 $P(NEt_2)Ph_2$	66.8	
2 $P(NPr^i_2)Ph_2$	36.7[i]	
3 $P(NEt_2)_2Ph$	99.0[f]	
4 $P(NPr^i_2)_2Me$	39.0[e]	
5 $P(NPr^i_2)_2Ph$	59.2[e]	
6 $P(NPr^i_2)_2(C_6F_5)$	48.7[f]	
7 $P(Cl)(NPr^i_2)_2$	140.6[f]	
8 *trans*-$[Cr(CO)_4(P\{NEt_2\}Ph_2)_2]$	132.5[d]	
9 *trans*-$[Mo(CO)_4(P\{NEt_2\}Ph_2)_2]$	97.2[d]	
10 *trans*-$[W(CO)_4(P\{NEt_2\}Ph_2)_2]$	85.1[d]	298
11 *trans*-$[Cr(CO)_4(P\{Cl\}Ph_2)_2]$	169.6[d]	
12 *trans*-$[W(CO)_4(P\{Cl\}Ph_2)_2]$	101.6[d]	323
13 *trans*-$[W(CO)_4(P\{OMe\}Ph_2)_2]$	129.5[d]	322
14 *trans*-$[W(CO)_4(P\{OEt\}Ph_2)_2]$	124.6[d]	317
15 *trans*-$[W(CO)_4(P\{OCH_2CHCH_2\}Ph_2)_2]$	126.8[d]	313
16 *trans*-$[W(CO)_4(P\{OH\}Ph_2)_2]\cdot CH_2Cl_2$	107.5[d]	269
17 *cis*-$[PtCl_2(P\{NEt_2\}Ph_2)_2]$	55.9[d]	3994
18 *trans*-$[PtCl_2(PNPr^i_2\{Ph\}_2)_2]$	60.3[d]	2759
19 *cis*-$[PtCl_2(P\{OMe\}Ph_2)_2]$	84.9[b,d]	4185
20 *cis*-$[PtCl_2(P\{OEt\}Ph_2)_2]$	81.1[b,d]	4185
21 *cis*-$[PtCl_2(P\{OCH_2CHCH_2\}Ph_2)_2]$	83.1[b,d]	4175
22 *cis*-$[PtCl_2(P\{Cl\}Ph_2)_2]$	71.2[b,d]	4116
23 *trans*-$[PtCl_2(P\{Cl\}Ph_2)_2]$	47.2[b,d]	3213
24 *trans*-$[PtCl_2(P\{NEt_2\}_2Ph)_2]$	88.0[f]	2926
25 *trans*-$[PtCl_2(P\{NPr^i_2\}_2Me)_2]$	86.0[f]	2755
26 *trans*-$[RhCl(CO)(P\{NEt_2\}Ph_2)_2]$	78.3[e]	131
27 *trans*-$[RhCl(CO)(P\{NPr^i_2\}Ph_2)_2]$	70.3[f]	131
28 *cis*-$[RhCl(CO)_2(P\{NEt_2\}_2Ph)]$	97.3[f]	147
29 *trans*-$[RhCl(CO)(P\{NPr^i_2\}_2Me)_2]$	110.0[f]	136
30 *cis*-$[RhCl(CO)_2(P\{NPr^i_2\}_2Ph)]$	107.2[e]	146

[a] $CDCl_3$. [b] CD_2Cl_2. [c] C_6D_6. [d] 24.0 MHz. [e] 101.3 MHz. [f] 121.9 MHz. [g] M = W, Pt, or Rh. [h] $^3J_{PF} = 47$ Hz. [i] See ref. 29.

phosphine **6** was prepared through reaction of $(Pr^i_2N)_2PCl$ with $(F_5C_6)MgBr$ and isolated in good yield (80%).[24] †

Tetracarbonyl complexes. In order to assess the reactivity of the P–N linkage of aminophosphines in the coordination sphere of a metal, it was desirable to study systems where potential reaction of the protic reagents with the metal centre was minimised. Hence, in the first instance, the Group 6 tetracarbonyl derivatives, *trans*-$[M(CO)_4(P\{NEt_2\}Ph_2)_2]$ {M = Cr (**8**), Mo (**9**), W (**10**)}, were prepared through simple ligand displacement from *fac*-$[Cr(CO)_3(MeCN)_3]$ (following CO scrambling) or from *cis*-$[M(CO)_4(pip)_2]$ (M = Mo, W; pip = piperidine) [Scheme 1]. The substitution reactions for both chromium and molybdenum proceeded cleanly in either benzene or CH_2Cl_2 at room temperature. In contrast, the tungsten bis(phosphine) analogue could only be prepared in refluxing benzene. All the tetracarbonyl derivatives are readily soluble in organic solvents and are air-stable.

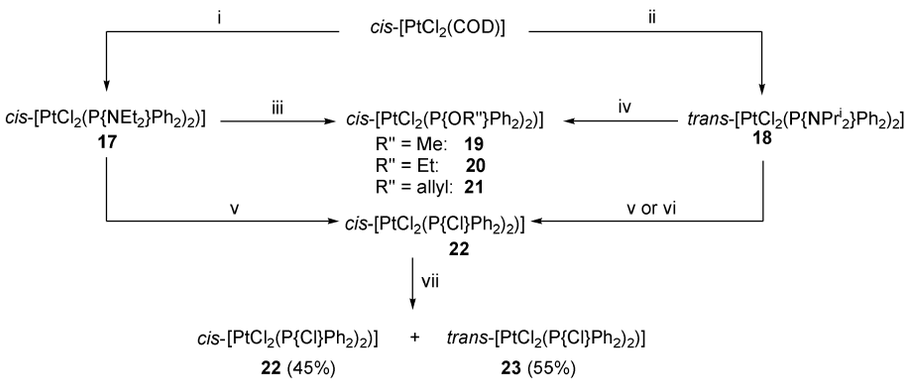
One of the reactions typically associated with compounds that possess P–N bonds is protolytic cleavage of this linkage with acids. Hence, the reaction of the simple carbonyl complexes **8**–**10** with a range of protic acids was investigated. Treatment of CH_2Cl_2 solutions of complexes **8** and **10** with anhydrous HCl gas afforded the complexes *trans*-$[M(CO)_4(P\{Cl\}Ph_2)_2]$ **11** (Cr, 84%)[25] and **12** (W, 77%) as bright yellow, crystalline, air stable species (Scheme 1). In contrast, an identical reaction with **9** afforded a complicated mixture of products which contained only trace amounts of *trans*-$[Mo(CO)_4(P\{Cl\}Ph_2)_2]$ according to ^{31}P NMR spectroscopy.[26] Clearly, this methodology provides a straightforward approach to the preparation of the potentially synthetically versatile complex **12**, for which no synthesis has previously been reported in the literature.

Another prototypical reaction associated with P–N bonds is their cleavage by alcohols. Thus, it was somewhat surprising to find that suspensions of complexes **8**–**10** could be stirred in methanol for 12 h at rt without reaction or decomposition, although similar resistance to alcoholysis has recently been reported for certain sterically demanding bis(dialkylamino)-phosphine complexes.[20]

In contrast, reaction at the P–N linkage could be induced by bubbling anhydrous HCl gas through suspensions of **10** in a range of alcohols. This afforded the corresponding alkyl diphenylphosphinite complexes, *trans*-$[W(CO)_4(P\{OR''\}Ph_2)_2]$ (**13**–**15**) in reasonable yields as air-sensitive solids; the complexes slowly darken and decompose over the period of a week in air. Treating a suspension of **10** in ethylene glycol with HCl gas resulted in only the formation of the chlorophosphine complex **12** (according to ^{31}P NMR spectroscopy), rather than the expected hydroxyethylphosphinite. In view of the ease and efficiency of these substitution reactions, it is surprising that there are only a few reports of this type of functional group interconversion in the literature.[27,28]

Conversely, it was found that treating suspensions of either the chromium (**8**) or the molybdenum (**9**) complexes in alcohols or ethylene glycol with gaseous HCl resulted in the formation of mixtures of species that included the *trans*-$[M(CO)_4(P\{Cl\}Ph_2)_2]$ complexes as only a minor component in each case, according to ^{31}P NMR spectroscopy.

† The Grignard is considerably safer to handle than the corresponding perfluoroaryl lithium which has a tendancy to eliminate lithium fluoride spontaneously at ambient temperatures.



Scheme 2 Reagents and conditions: i 2 $P(NEt_2)Ph_2$, CH_2Cl_2, rt, 2 h; ii 2 $P(NPr^i_2)Ph_2$, CH_2Cl_2, rt, 2 h; iii HCl (g), R″OH, rt, 30 min; iv HCl (g), R″OH, rt, 15 min; v HCl (g), $HOCH_2CH_2OH$, rt, 30 min; vi HCl (g), CH_2Cl_2, rt, 30 min; vii C_7H_8, 120 °C, 5 d.

Since complex **10** reacted cleanly with alcohols in the presence of HCl, it was of interest to try a similar reaction with water in the hope that a complex of diphenylphosphinous acid, $P(OH)Ph_2$, could be isolated, this hydroxy derivative being an attractive precursor for further functionalisation. Treatment of **10** with either excess aqueous HCl or aqueous H_2SO_4 afforded a single major product in both cases, according to $^{31}P\{^1H\}$ NMR spectroscopy (*ca.* +106 ppm, $^1J_{PW}$ 269 Hz). ‡ Following workup, *trans*-$[W(CO)_4(P\{OH\}Ph_2)_2].CH_2Cl_2$ (**16**) could be isolated as a purple solid in excellent yield (81%). Although the absence of the $-NEt_2$ moiety was clearly confirmed by ^1H NMR spectroscopy, no resonance attributable to the OH proton could be detected. However, its presence could be inferred through treatment of a sample of **16** with D_2O, which led to the appearance of a characteristic signal for HOD at *ca.* δ 4.20 ppm. Further evidence for the presence of the hydroxyl group comes from the observation of a broad, weak band at 2300 cm^{-1} in the IR spectrum of **16**.

Platinum dichloride complexes. The study of the Group 6 bis(aminophosphine) tetracarbonyl derivatives provided a comparatively inert framework in which to probe the reactivity of the P–N linkage, yet is of limited significance to many industrially relevant catalytic processes. With this in mind, similar investigations were undertaken for platinum(II) complexes of ligands **1** and **2**.

Reaction of *cis*-$[PtCl_2(COD)]$ with *ca.* 2 equivalents of either **1** or **2**, afforded the bis(phosphine) complexes *cis*-**17** (88%) and *trans*-**18** (81%), respectively, under identical reaction conditions (Scheme 2). The differences in geometry about platinum, were readily apparent from an examination of the magnitudes of the respective $^1J_{PPt}$ coupling constants (Table 1), and presumably reflect differences in the steric demands of phosphines **1** and **2**.[30] Treatment of alcoholic solutions of either *cis*-**17** or *trans*-**18** with HCl gas at room temperature led to the formation of the exclusively *cis*-bis(diphenylphosphinite) complexes **19**–**21** as white, air stable solids in excellent yields. The known bis(chlorodiphenylphosphine) complex *cis*-$[PtCl_2(P\{Cl\}Ph_2)_2]$ (**22**) was obtained by bubbling gaseous HCl through ethylene glycol solutions of **17** and **18** or through a CH_2Cl_2 solution of **18**.[31]

In contrast to the reactivity associated with the tungsten tetracarbonyl derivative **10**, complexes **17** and **18** proved inert towards an aqueous solution of H_2SO_4. However, the *cis*-chlorophosphine derivative **22** was formed in low yield following reaction of **17** with aqueous 1 M HCl, according to ^{31}P NMR spectroscopy.

Notably, for all the P–N bond cleavage reactions associated with **18**, the stereochemistry of the resultant products necessitates an efficient *trans*- to *cis*-isomerisation, presumably as a result of chloride ion catalysis.[32–34] An attempt to convert **22** into **23** by thermal methods resulted in only partial isomerisation (toluene, reflux, 5 d; **22** : **23** = 45 : 55 according to ^{31}P NMR spectroscopy). However, addition of a catalytic quantity of $[Pr^i_2NH_2]Cl$ to a toluene solution of **22** followed by thermolysis (toluene, reflux 5 d) resulted in an enhanced *cis*/*trans*-ratio, **22** : **23** = 25 : 75, something that supports the role of Cl^- in isomerisation of these $[PtCl_2(PR_3)_2]$ complexes.

To further probe the coordination chemistry and subsequent reactivity of the aminophosphine complexes, it was of interest to investigate some of the corresponding diamino derivatives. The complexes *trans*-$[PtCl_2(P\{NEt_2\}_2Ph)_2]$ (**24**) and *trans*-$[PtCl_2(P\{NPr^i_2\}_2Me)_2]$ (**25**) were readily prepared from $[PtCl_2(COD)]$ and the corresponding diaminophosphines $P(NEt_2)_2Ph$ (**3**) and $P(NPr^i_2)_2Me$ (**4**) in 81 and 74% yield, respectively. In contrast, no Group 6 or Pt(II) complexes of the bis(diisopropylamino) derivative $P(NPr^i_2)_2Ph$ (**5**) could be prepared despite either prolonged heating at reflux or sonication.

Since reaction at the P–N bonds of metal-bound aminophosphines proceed extremely smoothly, identical reactions were attempted with complexes **24** and **25** bearing bis(aminophosphine) ligands. Addition of anhydrous HCl to MeOH or CH_2Cl_2 solutions of **24** led to the formation of a variety of unidentified phosphorus-containing products in both cases, according to ^{31}P NMR spectroscopy. In contrast, complex **25** proved inert to HCl-induced P–N bond cleavage at room temperature, while decomposition occurred following prolonged heating at reflux in either MeOH or CH_2Cl_2; $O{=}P(H)(NPr^i_2)_2$ was identified as the major product.[35] It is interesting to note that no complexes could be prepared by direct reaction of $P(Cl)(NPr^i_2)_2$ (**7**) with labile Group 6 or Pt(II) precursors. It should be noted however that reaction of $[M(CO)_5(P\{NEt_2\}_2Ph)]$ (M = Cr, Mo) with HCl has been shown to afford the corresponding bis{$PCl(NEt_2)(Ph)$} complexes in reasonable yields.[36]

Mechanistic considerations

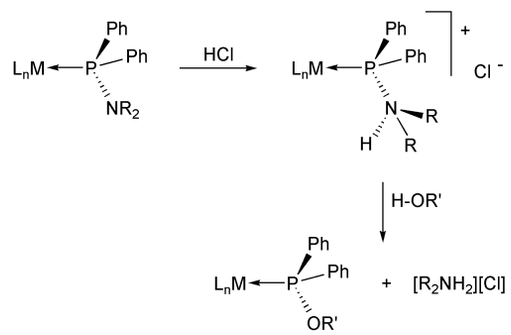
From the studies outlined above, it was deduced that in order to bring about P–N bond cleavage in the coordination sphere of metals, the presence of acid is essential. Previously it has been reported that $[M(CO)_5(P\{Cl\}\{NR_2\}\{R'\})]$ (M = Cr, Mo, W) can be prepared from reaction of the corresponding $\{P(NR_2)_2R'\}$ complexes by addition of HCl and elimination of $[R_2NH_2]Cl$.[6,36] This clearly accounts for the formation of **11**, **12** and **22**. Furthermore, it seems reasonable to suggest that the amino-alkoxy exchange process observed here (**13**–**15** and **19**–**21**) follows a similar pathway, whereby initial protonation at nitrogen occurs prior to formal nucleophilic substitution, resulting in elimination of ammonium chloride and formation of the corresponding phosphinite complex (Scheme 3). However, it remains unclear why attempts to instigate amino-alkoxy exchange for the Cr and Mo systems (**8** and **9**, respectively) were

‡ The exact value of the ^{31}P NMR chemical shift obtained from the crude reaction mixture varies slightly (±2 ppm) depending on the exact concentration of aqueous acid employed.

Table 2 Comparison of ν_{CO} for various *trans*-$[M(CO)_4(PR_3)_2]$ complexes

Entry	Complex	ν_{CO} [a, b]/cm^{-1}
1	**8**	1880
2	*trans*-$[Cr(CO)_4(PPh_3)_2]$ [c]	1878
3	**9**	1890
4	*trans*-$[Mo(CO)_4(PPh_3)_2]$ [c]	1892
5	**10**	1878
6	*trans*-$[W(CO)_4(PPh_3)_2]$ [c]	1880
7	**11**	1918
8	**12**	1918
9	**13**	1882
10	**14**	1890
11	**15**	1898
12	**16**	1895

[a] E_u symmetry band only. [b] KBr, Nujol. [c] Prepared as for **8** and **9** using PPh_3.



Scheme 3

unsuccessful, affording only trace quantities of *trans*-$[M(CO)_4(P\{Cl\}Ph_2)_2]$ (M = Cr, Mo), whereas **10** reacts cleanly as expected. Indeed, an examination of the heteropolar single bond energies (P–N: 293 kJ mol^{-1}; P–Cl: 331 kJ mol^{-1}; P–O: 360 kJ mol^{-1}) would suggest that the formation of the diphenylphosphinite derivatives would be thermodynamically more favourable.[37] Since the values of ν_{CO} for complexes **8**–**10** differ little from those of their corresponding PPh_3 complexes, it is reasonable to propose that $P(NEt_2)Ph_2$ exerts the same electronic influence in each of **8**–**10** (Table 2). Thus, it is unlikely that there is a significant variation in P–N bond strength (arising from variation in P–N multiple bonding) between complexes **8**–**10**.

The poor selectivity in the reactions of complex **24** (ligand **3**) and the lack of any reaction of complex **25** (ligand **4**) with HCl/ROH merits some comment. Since phosphine **3** possesses a phenyl substituent (−I) and **4** an Me group (+I), the latter is likely to exhibit a greater degree of P–N multiple bonding (and hence greater P–N bond strength). This combined with the greater steric bulk about the N atoms of **25** may account for its lack of reactivity compared with that of **24**. The origins of the low selectivity of reactions of complex **24** remain elusive.

Lewis basicity studies

The disparity in the reactivity observed for the various amino-phosphines clearly merits some further investigation. It is understandable that steric demands are likely to be significant, but it was intriguing to see if there was also any correlation with the electronic nature of the various phosphines. Indeed, the recent interest in amino-substituted phosphines has, in part, arisen from the potential variation in donor properties possible for such ligands.[15,16,19,42,43]

Although the energy associated with ν_{CO} of Group 6 tetra-carbonyl complexes is not generally used to quantify ligand basicity, a comparison of the IR spectroscopic data of the various complexes **8**–**16** was undertaken (Table 2). Somewhat surprisingly, little difference was observed between the values of ν_{CO} obtained for these aminophosphine derivatives and those possessing triphenylphosphine ligands (entries 2, 4, and 6). However, as expected, the chlorodiphenylphosphine complexes **11** and **12** exhibited higher frequency ν_{CO} bands as a result of the −I effect of chlorine.

Since this approach appeared relatively insensitive to variations in the framework of the phosphorus-based ligand, a more detailed investigation using the more widely employed approach, namely an examination of the CO stretching frequencies of *trans*-$[RhCl(CO)(PR_3)_2]$ complexes, was undertaken.[44–46]

Reactions with $[\{RhCl(CO)_2\}_2]$. The *trans*-$[RhCl(CO)\{PR^1{}_2R^2\}_2)]$ complexes **26**, **27** and **29** were prepared by treating $CDCl_3$ solutions of $[\{RhCl(CO)_2\}_2]$ with four equivalents of ligands **1**, **2** and **4**, respectively. After initial evolution of CO had ceased, the reaction vessel was sealed under 1 atmosphere of CO to prevent both ligand dissociation and decomposition in solution, as has been reported previously.[46]§ In solution ($CDCl_3$/1 atm CO) complexes **26**, **27** and **29** are stable for weeks, each exhibiting a single doublet resonance in their $^{31}P\{^1H\}$ NMR spectra, with both chemical shifts and $^1J_{PRh}$ coupling constants (*ca.* 133 Hz) being comparable to those previously reported in the literature for similar species (Table 1). The $^{13}C\{^1H\}$ NMR spectra of **26**, **27** and **29** showed a single carbonyl environment in each case.¶ At ambient probe temperatures, the CO resonance was a sharp singlet for **26** (which broadened significantly on lowering the temperature to −50 °C but was never completely resolved), was considerably broadened at rt for complexes **27** (suggesting rapid CO exchange), and appeared as a well-resolved doublet of triplets for **29** ($^1J_{RhC}$ 77.9 Hz, $^2J_{PC}$ 15.7 Hz).

An examination of the data for analogous Rh(I) carbonyl complexes of other phosphines indicates that ligands **1** and **2** are comparable donors to PPh_3 (Entry 16, Table 3), something that is entirely consistent with the results obtained for the tetra-carbonyl complexes **8**–**10** (*vide supra*). This suggests that N to P lone pair donation offsets any effect of the electron withdrawing amino substituents on the donor ability of **1** and **2**, however this does not take into account any differences in π-acceptor behaviour between the ligands. The extent of this latter component is hard to quantify with any certainty. Significantly, the carbonyl stretching frequency for the complex with ligand **4** (Entry 4) is consistent with it being a donor comparable to either $P(NMe_2)_3$ or $P(Npyrr)_2Ph$ (Entries 10 and 12, respectively), something that agrees with previous claims that for bis- or *tris*-aminophosphines, the third substituent is merely a spectator.[16]

Somewhat surprisingly, no reaction was observed to occur between $[\{RhCl(CO)_2\}_2]$ and **6** while an intractable mixture of products resulted when the same reaction was attempted with **7**. To probe this lack of coordination in greater detail, crystals of **6** were obtained and its structure investigated by X-ray crystallography. This revealed an essentially pyramidal phosphorus centre (Σ_{angles} 315.6°) with the plane of the C_6F_5 ring lying at an angle of 81.4° to the N_2P plane (Fig. 2, Table 4). The amino nitrogen atoms N(1) and N(2) are near trigonal planar (Σ_{angles} 359.1 and 359.6°, respectively) while the two P–N bond distances are near-equivalent [P(1)–N(1) 1.683(3) Å and P(1)–N(2) 1.669(4) Å]. These values are significantly shorter than those associated with true P–N single bonds, something

§ Each of the rhodium complexes was isolated as an orange solid that was stable for months under an atmosphere of nitrogen in the solid state.

¶ In order to facilitate obseravtion of the CO resonances, it was found essential to acquire ^{13}C NMR spectra with samples prepared under 1 atm CO.

Table 3 Comparison of ν_{CO} for *trans*-[RhCl(CO){$PR^1{}_2R^2$}$_2$] (**26**, **27**, **29**), *cis*-[RhCl(CO)$_2${$PR^1{}_2R^2$}] (**28**, **30**) and $^1J_{PSe}$ for Se=$PR^1{}_2R^2$ of various monodentate P-based ligands

	Ligand		Rh Complex	Se=$PR^1{}_2R^2$		
Entry	R^1	R^2	ν_{CO}/cm^{-1}	$\delta(^{31}P)$/ppm	$^1J_{PSe}$/Hz	Ref.
1	Ph	NEt_2 (**1**)	1974[a] (**26**)	67.1[b]	746	[f]
2	Ph	$NPr^i{}_2$ (**2**)	1973[a] (**27**)	59.7[b]	744	[f]
3	NEt_2	Ph (**3**)	2091, 2007[a] (**28**)	77.6[b]	761	[f]
4	$NPr^i{}_2$	Me (**4**)	1955[a] (**29**)	56.6[b]	761	[f]
5	$NPr^i{}_2$	Ph (**5**)	2089, 2004[a] (**30**)	70.2[b]	759	[f]
6	$NPr^i{}_2$	F_5C_6 (**6**)	[c]	[c]	[c]	[f]
7	$NPr^i{}_2$	Cl (**7**)	[c]	53.0[b]	884	38[f]
8	Me	NMe_2	—	59.0[b,f]	720	39
9	NMe_2	Me	—	80.5[b,f]	767	39
10	NMe_2	NMe_2	1959	81.2[b,f]	805	19, 40
11	NMe_2	Ph	—	84.0[b,f]	790	39
12	Npyrr[e]	Ph	1949	70.8[b,f]	759[f]	15
13	NEt_2	NEt_2	—	77.1	794	41
14	Npyrr[e]	Me	1947	66.0[a]	735	15
15	Me	Me	1966	8.0	684	19, 39
16	Ph	Ph	1978	34.1[b]	736	19, 39
17	OMe	OMe	1998	77.5	963	19, 39
18	OPh	OPh	2016	58.6	1027	19, 40

[a] $CDCl_3$. [b] $CDCl_3$, 101.3 MHz. [c] No reaction observed with either Se or {$Rh(CO)_2Cl$}$_2$. [d] No clean reaction observed with [{$Rh(CO)_2Cl$}$_2$]. [e] Npyrr = pyrrolydinyl. [f] This work.

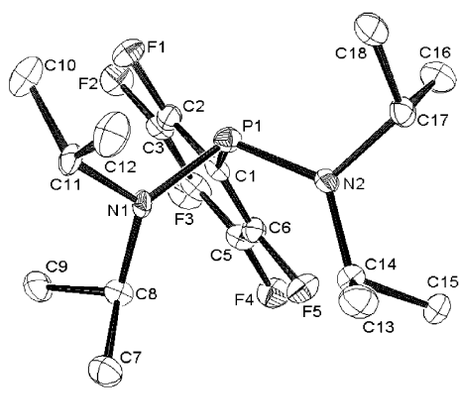


Fig. 2 Molecular structure of diaminophosphine **6** with the thermal ellipsoids set at the 30% probability level.

Table 4 Selected bond lengths (Å) and angles (°) for **6**

P(1)–N(1)	1.683(3)	C(2)–C(3)	1.375(6)
P(1)–N(2)	1.669(4)	C(3)–C(4)	1.379(7)
P(1)–C(1)	1.896(5)	C(4)–C(5)	1.366(7)
C(1)–C(2)	1.385(6)	C(5)–C(6)	1.379(6)
C(1)–C(6)	1.387(6)		
N(2)–P(1)–N(1)	109.17(19)	C(11)–N(1)–P(1)	117.3(3)
N(2)–P(1)–C(1)	108.0(2)	C(14)–N(2)–C(17)	114.4(4)
N(1)–P(1)–C(1)	98.41(18)	C(14)–N(2)–P(1)	128.3(3)
C(8)–N(1)–C(11)	116.3(3)	C(17)–N(2)–P(1)	116.9(3)
C(8)–N(1)–P(1)	125.5(3)		

indicative of a degree of P–N multiple bond character.[47] The P(1)–C(1) bond distance of 1.896(5) Å that is relatively long compared to a typical P–C single bond, lying between the distances observed in $P(C_6F_5)_3$, $Ph_2PC_6F_5$ (P–CAr^F distances 1.834 and 1.846 Å, respectively) and $(Pr^i{}_2N)_2P$–fluorenyl [1.99(7) Å].[48–50] Together these data suggest that the elongation of the P–C bond in **6** must largely be ascribed to a negative hyperconjugation effect through N(nσ) → P(1)–C(1)σ* donation.[51]

The metric parameters about phosphorus are consistent with other examples of metal-bound $P(NPr^i{}_2)_2$-derived phosphines that have been reported in the literature.[20] Thus it appears that steric constraints imposed by the two amino groups and *ortho*-fluorine atoms are the major factor in preventing coordination of phosphine **6** to metals.

Surprisingly, rather than the desired bis(phosphine) complexes, the reaction of four equivalents of either ligand **3** or **5** with [{$RhCl(CO)_2$}$_2$] led to the formation of *cis*-[RhCl-$(CO)_2$(P{NR_2}$_2$Ph)] {R = Et (**28**), Pr^i (**30**)}. Complexes with identical analytical data can be prepared through direct reaction of [{$RhCl(CO)_2$}$_2$] with two equivalents of **3** or **5**. The coordination of **5** to rhodium(I) contrasts with the lack of reactivity observed towards the Group 6 carbonyls and $PtCl_2(L_2)$, something that reflects the lability of the Rh(I) complex.

Despite a number of attempts, neither crystals of **28** or **30** suitable for a molecular structure determination could be obtained. The presence of only one phosphorus-containing ligand is however evident from elemental analysis and IR spectroscopy, the latter exhibiting two intense carbonyl bands at *ca.* 2090 and 2006 cm^{-1}. Furthermore, two resonances are observed in the carbonyl region of the ^{13}C NMR spectrum of **30** (δ 184.4 {br}, 182.4 {dd, $^1J_{RhC}$ 143.0 Hz, $^2J_{PC}$ 57.0 Hz}), although only a severely broadened CO resonance was detected for **28** (δ 183.1). These data are in good agreement with those reported for an analogous complex *cis*-[$RhCl(CO)_2(PPh_3)$] characterised *in situ*.[52] Notably, the ^{31}P NMR chemical shifts for complexes **28** and **30** are comparable to those for the bis(phosphine) complexes **26**, **27** and **29**, while the associated $^1J_{PRh}$ coupling constants are only slightly greater at *ca.* 147 Hz.

Generally, rhodium(I) dicarbonyl phosphine complexes, *cis*-[$RhCl(CO)_2(L)$] (L = PR_3), can only be identified in solution as they are unstable towards loss of CO, evolving to dimeric $[Rh(\mu\text{-}Cl)(CO)(L)]_2$.[52–54] In contrast, complexes in which ligand L is an amine, phosphine oxide, or enamine, are stable and can be isolated, presumably as a consequence of their lower π-acceptor and greater σ-donor character, relative to tertiary phosphines.[55–57] Hence, the fact that complexes **28** and **30** are isolable, is in good accord with the elevated basicity and poor π-acceptance expected for bis(dialkylamino)-phosphines.[15,19] However, why bridge splitting reactions of [{$RhCl(CO)_2$}$_2$] should lead to monophosphine complexes for ligands **2** and **5** remains unclear.

Interestingly, complex **29** (ligand **4**, entry 4, Table 3) exhibits a value of ν_{CO} (1955 cm^{-1}) that lies in the zone typical of a tris(amino)phosphine, but is also remarkably similar to that

determined for the rhodium complex of di-*tert*-butylpyrrolidinylphosphine.[16] The value of ν_{CO} for the latter (1955 cm^{-1}), consistent with unexpectedly poor donor character, was believed to arise from steric constraints upon the interaction of the nitrogen with the phosphorus centre.

Since not all the ligands discussed here afforded *trans*-[RhCl(CO){PR_3}$_2$)] complexes suitable for comparison by IR spectroscopy and because it is difficult to separate σ-donor/π-acceptor contributions using this approach, an alternative strategy was sought in order to probe variations in the electronic nature of the various phosphine ligands.

Phosphine selenides. There exists a well established correlation between the magnitude of $^1J_{PSe}$ coupling constants and the basicity of phosphines.[58–62] It has been demonstrated that the greater the $^1J_{PSe}$ coupling constant the greater the s-character of the P lone pair, meaning that poorly donating phosphines will exhibit values of $^1J_{PSe}$ that are larger than those for electron-rich phosphines.

The selenium derivatives of phosphines **1**–**5** and **7** were prepared as solutions in $CDCl_3$ by addition of a slight excess of 'grey' selenium followed by sonication, then subsequently characterised *in situ* by multinuclear NMR spectroscopy. In each case a single new resonance was observed by ^{31}P NMR spectroscopy that exhibited coupling to ^{77}Se (Table 3), except with phosphine **6** where, despite both prolonged heating and sonication, no reaction was observed to occur. This lack of reactivity is presumed to reflect an inaccessibility of the phosphorus lone pair on steric grounds combined with the electron withdrawing effect of the pentafluorophenyl substituent (*vide supra*).

Thus, using the criteria outlined above, the aminophosphines **1**–**5** and **7** can be ordered in terms of decreasing donor capability: **1**, **2** ($^1J_{PSe}$ ≈ 745 Hz) > **3**–**5** ($^1J_{PSe}$ ≈ 760 Hz) > **7** ($^1J_{PSe}$ = 884 Hz). For the series Se=$PR'_{3-x}(NR''_2)_x$ (x = 0–3; R′ = Me, Ph; R″ = alkyl), as the number of amino groups (−I effect) increase, so the magnitude of $^1J_{PSe}$ increases, making these phosphines progressively less electron-rich, as expected. This agrees with donor strength predications made from an examination of ν_{CO} for the rather limited set of rhodium complexes possible **26** (1974 cm^{-1}), **27** (1973 cm^{-1}) and **29** (1955 cm^{-1}), **1** ≈ **2** > **4**.

There is no significant difference in the magnitudes of the $^1J_{PSe}$ coupling constants between phosphine **4**, the related $P(Npyrr)_2Ph$ (Entry 12, Table 3), **3** and **5** (all *ca*. 760 Hz), suggesting that the potential donor capability of each system is comparable. Since only the latter two phosphines afford *cis*-[$RhCl(CO)_2$(L)] it suggests that steric rather than electronic factors are most significant in determining the outcome of their reactions with [{$RhCl(CO)_2$}$_2$].

A significantly smaller magnitude of $^1J_{PSe}$ coupling constant (735 Hz) is observed for the known phosphine selenide Se=$P(Npyrr)_2Me$ compared with that of its phenyl counterpart (759 Hz) as would be expected from the relative inductive effects of Me *versus* Ph, +I and −I, respectively (Entries 14 and 12, Table 3). However, the values of ν_{CO} for the rhodium carbonyl complexes of these two phosphines are comparable (1949 and 1947 cm^{-1}, respectively).

Together these observations emphasise that measurement of either ν_{CO} or $^1J_{PSe}$ alone, are not sufficient to predict the behaviour of aminophsophines. Somewhat unsurprisingly, trends in the reactivity of the P–N linkages of bound aminophosphines are thus subject to both steric and electronic effects.

Conclusion

Historically, the envisaged susceptibility of aminophosphine ligands to air, moisture and protic solvents such as alcohols has long been regarded as a limitation to their potential use. However, by and large, complexes of the simple acyclic amino-functionalised phosphines described here, show considerable stability. Selective substitution reactions of the amino group of Pt- or W-bound dialkylaminophosphines can only be induced, albeit cleanly, in the presence of gaseous HCl, affording a simple route for the preparation of either the analogous phosphinite or the synthetically versatile chlorophosphine complexes. These observations open the way to the use of the extremely diverse range of acyclic aminophosphines **B** and **C** in catalysis.

It has been demonstrated that the ^{31}P NMR spectroscopic data for related *trans*-[$RhCl(CO)_2(PR_3)$] and *trans*-[$RhCl(CO)(PR_3)_2$] complexes are extremely similar and can not be used to distinguish between the two structures. Since there has been considerable recent interest in the use of these types of Rh(I) chloro-monocarbonyl complex as probes to measure ligand basicity, it should be noted that it is essential that either elemental analyses or ^{13}C NMR data consistent with the formulation of the bis(phosphine) complex, have been obtained before any meaningful comparison of ν_{CO} frequencies can be made. The preparation of selenium adducts of phosphines and examination of the attendant $^1J_{PSe}$ coupling constants provides a simple, yet complementary technique for estimating the σ-donor ability of phosphines, especially where the desired rhodium(I) carbonyl complexes are inaccessible.

Experimental

General considerations

All manipulations of air and/or water sensitive materials were performed under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove box (unless stated otherwise). Solvents were freshly distilled under nitrogen from sodium–benzophenone (tetrahydrofuran, diethyl ether, toluene, dme), from calcium hydride (dichloromethane), from sodium (hexane, pentane, 40–60 PE) or from P_2O_5 (C_6D_6 and $CDCl_3$) and degassed prior to use. Elemental analyses were performed by C.H.N. Analyses Ltd., Butterworth Laboratories Ltd., or by S. Boyer at the University of North London. NMR spectra were recorded on a Bruker AM 250, AMX 300, AMX 400, Varian EM 390 or JEOL JNM-FX 90Q; chemical shifts were referenced to residual protio impurities in the deuterated solvent (^{1}H), to the deuterated solvent (^{13}C), external $CFCl_3$ (^{19}F), or to external aqueous 85% H_3PO_4 (^{31}P). All spectra were obtained at ambient probe temperatures unless stated otherwise. Infrared spectra were recorded (Nujol mulls [KBr windows], KBr discs, or in solution [KBr windows]) on a Perkin-Elmer 1600 spectrophotometer; Nujol was dried over sodium wire. Mass spectra were recorded on a Kratos Concept 1H instrument and are reported in *m*/*z*. Sonication was achieved by suspending the desired reaction vessel in a water-filled Grant Ultrasonic Bath XB2.

cis-[$Mo(CO)_4$(pip)$_2$], *fac*-[$Cr(CO)_3(NCCH_3)_3$], (F_5C_6)MgBr,[63] $PNPr^i_2(Ph)_2$ (**2**),[29] P{NEt_2}$_2$Me,[8] $P(NPr^i_2)_2$Me (**4**),[64] and P{NPr^i_2}$_2$Ph (**5**)[8] were prepared according to literature procedures. $PNEt_2(Ph)_2$ was prepared by treating Ph_2PCl with 2 equivalents of diethylamine in refluxing toluene for 3 h. The desired phosphine was obtained, sufficiently pure for further reaction following removal of volatiles *in vacuo*, extraction with dme and subsequent removal of solvent under vacuum: δ_H (301.2 MHz, $CDCl_3$) 7.28–7.45 (10H, m, P*Ph*$_2$), 3.08 (4H, dq, $^3J_{PH}$ 9.7 Hz, $^3J_{HH}$ 7.0 Hz, NC*H*$_2$CH$_3$), 0.92 (6H, t, $^3J_{HH}$ 7.0 Hz, NCH$_2$C*H*$_3$); δ_P {^{1}H} (122.0 MHz, $CDCl_3$) +66.8 (s). P{NEt_2}$_2$Ph was prepared by a modification of the literature procedure through reaction of $PCl(NEt_2)_2$ with PhLi: δ_P {^{1}H} (122.0 MHz, $CDCl_3$) +99.0 (s).[65,66] All other chemicals were obtained commercially and used as received. Melting points were obtained in sealed glass tubes under nitrogen, using a Gallenkamp Melting Point apparatus and are uncorrected.

Syntheses and reactions

$P(NPr^i_2)_2(C_6F_5)$ 6. To a stirred, cooled (−78 °C) suspension of $PCl(Pr^i_2N)_2$ (0.53 g, 2.00 mmol) in Et_2O (25 cm^3) was added

(F_5C_6)MgBr (0.8 M, Et_2O, 3.2 mL, 2.50 mmol). The reaction mixture was stirred at −78 °C for 2 h and the vessel was then left to warm to rt and stirred at rt for 18 h. Extraction of the product with hexane (20 cm^3), followed by removal of solvent *in vacuo* gave **6** as a white solid (0.64 g, 80%), (Found: C, 54.4; H, 7.0; N, 7.0. $C_{18}H_{28}N_2F_5P$ requires: C, 54.3; H, 7.1; N, 7.1%); δ_H (250.1 MHz; $CDCl_3$) 3.48 [4H, sept, $^3J_{HH}$ 6.6 Hz, PNC*H*$(CH_3)_2$], 1.27 [12H, d, $^3J_{HH}$ 6.7 Hz, PNCH(C*H*$_3)_2$], 1.04 [12H, d, $^3J_{HH}$ 6.7 Hz, PNCH(C*H*$_3)_2$]; $\delta_C\{^1H\}$ (75.8 MHz; $CDCl_3$) C_6F_5 not observed,‖ 49.17 [d, $^2J_{PC}$ 13.8, PN*C*H$(CH_3)_2$], 23.85 [d, $^3J_{PC}$ 7.2, PNCH(*C*H$_3)_2$], 23.48 [d, $^3J_{PC}$ 7.8, PNCH(*C*H$_3)_2$].

***trans*-[Cr(CO)$_4$(P{NEt$_2$}Ph$_2$)$_2$] 8.** A solution of $PNEt_2(Ph)_2$ (1.2 g, 4.67 mmol) in benzene (10 cm^3) was added to a stirred suspension of $[Cr(CO)_3(MeCN)_3]$ (0.4 g, 1.54 mmol) in benzene (25 cm^3). The reaction mixture was stirred overnight, filtered and the solvent removed *in vacuo*. Addition of excess Et_2O precipitated a yellow crystalline solid from the oily residue. This was filtered, washed with light petroleum and dried *in vacuo* to afford **8** (0.49 g, 70% based on CO groups), mp 135–137 °C, (Found: C, 63.5; H, 6.0; N, 4.1. $C_{36}H_{40}N_2O_4P_2Cr$ requires C, 63.7; H, 5.9; N, 4.1%); δ_H (90.0 MHz, $CDCl_3$) 7.42–7.28 (20H, m, PNEt$_2$*Ph*$_2$), 3.15 (8H, m, C*H*$_2$CH$_3$), 0.73 (12H, t, $^3J_{HH}$ 6.1 Hz, CH$_2$C*H*$_3$); $\delta_C\{^1H\}$ (75.5 MHz, $CDCl_3$) 223.0 (t, CO, $^2J_{CP}$ 13.4 Hz).

***trans*-[Mo(CO)$_4$(P{NEt$_2$}Ph$_2$)$_2$] 9.** A solution of $P(NEt_2)Ph_2$ (0.40 g, 1.60 mmol) in CH_2Cl_2 (10 cm^3) was added to a stirred suspension of $[Mo(CO)_4(pip)_2]$ (0.30 g, 0.79 mmol) in CH_2Cl_2 (20 cm^3) and the reaction mixture was stirred for 2 h. The solution was concentrated to *ca.* 10 cm^3. Addition of Et_2O gave a creamy white precipitate of **9** that was dried *in vacuo* (0.45 g, 79%), mp 156–158 °C, (Found: C, 59.9; H, 5.60; N, 3.9. $C_{36}H_{40}N_2O_4P_2Mo$ requires C, 59.8; H, 5.5; N, 3.9%); δ_H (90.0 MHz, $CDCl_3$) 7.40–7.29 (20H, m, PNEt$_2$*Ph*$_2$), 2.85 (8H, m, C*H*$_2$CH$_3$), 0.65 (12H, t, $^3J_{HH}$ 6.3 Hz, CH$_2$C*H*$_3$); $\delta_C\{^1H\}$ (75.5 MHz, $CDCl_3$) 216.0 (t, CO, $^2J_{CP}$ 12.0 Hz).

***trans*-[W(CO)$_4$(P{NEt$_2$}Ph$_2$)$_2$] 10.** A solution of $P(NEt_2)Ph_2$ (0.34 g, 1.32 mmol) in benzene (10 cm^3) was added to a stirred suspension of of $[W(CO)_4(pip)_2]$ (0.30 g, 0.64 mmol) in benzene (20 cm^3) and the reaction mixture was heated at reflux for 3 h to afford a dirty yellow solution, which was filtered and all volatiles removed *in vacuo*. Recrystallisation from CH_2Cl_2–Et_2O afforded yellow microcrystals of **10** that were dried *in vacuo* (0.43 g, 64%), mp 162–165 °C, (Found: C, 53.3; H, 5.0; N, 3.4. $C_{36}H_{40}N_2O_4P_2W$ requires C, 53.1; H, 4.9; N, 3.5%); δ_H (90.0 MHz, $CDCl_3$) 7.5–7.28 (20H, m, PNEt$_2$*Ph*$_2$), 3.23 (8H, m, C*H*$_2$CH$_3$), 0.85 (12H, t, $^3J_{HH}$ 6.3 Hz, CH$_2$C*H*$_3$); $\delta_C\{^1H\}$ (75.5 MHz, $CDCl_3$) 203.5 (t, CO, $^2J_{CP}$ 6.3 Hz).

***trans*-[Cr(CO)$_4$(P{Cl}Ph$_2$)$_2$] 11.** Anhydrous HCl gas was bubbled through a CH_2Cl_2 solution (20 cm^3) of **8** (0.20 g, 0.77 mmol) for 15 min during which time the colour changed from pale yellow to bright yellow. Volatile components were removed *in vacuo* and the residue extracted with Et_2O (30 cm^3). The resulting solution was concentrated and afforded bright yellow crystals of **11** on standing (0.15 g, 84%), mp 155–157 °C, (Found: C, 55.0; H, 3.4; N, 0.0. $C_{28}H_{20}Cl_2O_4P_2Cr$ requires C, 55.5; H, 3.3; N, 0.0%); δ_H (90.0 MHz, $CDCl_3$) 7.52–7.30 (20H, m, P*Ph*$_2$); $\delta_C\{^1H\}$ (75.5 MHz, $CDCl_3$) 218.7 (t, CO, $^2J_{CP}$ 13.9 Hz).

Reaction of 9 with anhydrous HCl gas. A similar procedure was employed to that used for the preparation of **11** and bubbling HCl through a solution of **9** (0.20 g, 0.28 mmol) for 20 min. The $^{31}P\{^1H\}$ NMR spectrum of the crude, bright yellow reaction mixture displayed numerous signals, one of which could be attributed to the desired complex *trans*-[Mo(CO)$_4$(P{Cl}Ph$_2$)$_2$], present as a minor component and identified by comparison with the chemical shift of an authentic sample prepared according to literature procedures.

***trans*-[W(CO)$_4$(P{Cl}Ph$_2$)$_2$] 12.** Anhydrous HCl gas was bubbled through a CH_2Cl_2 solution (20 cm^3) of **10** (0.20 g, 0.25 mmol) for 30 min to give a lemon yellow solution. Volatile components were removed *in vacuo* and the residue extracted with Et_2O (60 cm^3). The resulting solution was concentrated and afforded bright yellow crystals of **12** on standing (0.14 g, 77%), mp 148–150 °C, (Found: C, 45.5; H, 2.8; N, 0.0. $C_{28}H_{20}Cl_2O_4P_2W$ requires C, 45.6; H, 2.7; N, 0.0%); δ_H (90.0 MHz, $CDCl_3$) 7.50–7.30 (20H, m, P*Ph*$_2$); $\delta_C\{^1H\}$ (75.5 MHz, $CDCl_3$) 200.1 (t, CO, $^2J_{CP}$ 6.8 Hz).

***trans*-[W(CO)$_4$(P{OMe}Ph$_2$)$_2$] 13.** Anhydrous HCl gas was bubbled through a stirred suspension of **10** (0.40 g, 0.50 mmol) in MeOH (15 cm^3) for 30 min. A cream coloured material was formed. Following removal of volatile components *in vacuo*, the residue was extracted with Et_2O (60 cm^3). The resulting solution was concentrated and afforded an off-white solid **13** on standing (0.23 g, 64%), mp 156–157 °C, (Found: C, 48.8; H, 3.6; N, 0.0. $C_{30}H_{26}O_6P_2W$ requires C, 49.5; H, 3.6; N, 0.0%); ν/cm^{-1}, 1882 (vs, CO); δ_H (300.0 MHz, $CDCl_3$) 7.45–7.26 (20H, m, P*Ph*$_2$), 3.45 (6H, second order d, $^3J_{PH}$ + $^5J_{PH}$ 13.2 Hz, O*Me*); $\delta_C\{^1H\}$ (75.5 MHz, $CDCl_3$) 201.6 (t, CO, $^2J_{CP}$ 7.1 Hz).

***trans*-[W(CO)$_4$(P{OEt}Ph$_2$)$_2$] 14.** A similar procedure to that used for the preparation of **13** was adopted, passing HCl gas through a suspension of **10** (0.40 g, 0.50 mmol) in EtOH (10 cm^3) for 30 min. Complex **14** was isolated as a yellow solid (0.21 g, 56%), mp 156–157 °C, (Found: C, 50.5; H, 3.9; N, 0.0. $C_{32}H_{30}O_6P_2W$ requires C, 50.8; H, 4.0; N, 0.0%); δ_H (90.0 MHz, $CDCl_3$) 7.65–7.32 (20H, m, P*Ph*$_2$), 4.02 (4H, m, C*H*$_2$CH$_3$), 1.58 (6H, t, $^3J_{HH}$ 6.1 Hz, CH$_2$C*H*$_3$); $\delta_C\{^1H\}$ (75.5 MHz, $CDCl_3$) 200.9 (t, CO, $^2J_{CP}$ 7.9 Hz).

***trans*-[W(CO)$_4$(P{OCH$_2$CHCH$_2$}Ph$_2$)$_2$] 15.** A similar procedure to that used for the preparation of **13** was adopted, passing HCl gas through a suspension of **10** (0.40 g, 0.50 mmol) in allyl alcohol (6 cm^3) for 30 min. Complex **15** was isolated as a bright yellow solid (0.27 g, 70%), mp 121–122 °C, (Found: C, 51.1; H, 3.8; N, 0.0. $C_{32}H_{30}O_6P_2W$ requires C, 52.2; H, 3.8; N, 0.0%); δ_H (90.0 MHz, $CDCl_3$) 7.60–7.28 (20H, m, P*Ph*$_2$), 5.70 (2H, m, OCH$_2$*C*HCH$_2$), 5.18 (4H, m, OCH$_2$*C*HC*H*$_2$), 4.02 (4H, d, $^3J_{HH}$ 6.1 Hz, OC*H*$_2$CHCH$_2$); $\delta_C\{^1H\}$ (75.5 MHz, $CDCl_3$) 201.5 (t, CO, $^2J_{CP}$ 7.3 Hz).

Reaction of 10 with ethylene glycol in the presence of HCl gas. Using a procedure analogous to that used above, HCl gas was bubbled through a suspension of **10** (0.40 g, 0.44 mmol) in ethylene glycol (6 cm^3) for 30 min. The ^{31}P NMR spectrum of the resulting yellow solution revealed only the presence of **12**.

***trans*-[W(CO)$_4$(P{OH}Ph$_2$)$_2$]·CH$_2$Cl$_2$ 16.** H_2SO_4 (10%, 5 cm^3) was added to a solution of **10** (0.5 g, 0.62 mmol) in CH_2Cl_2 (5 cm^3). The emulsion was stirred for 24 h. The CH_2Cl_2 layer was separated, washed with several portions of degassed water, and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo*, the residue washed with Et_2O (20 cm^3), and the product dried *in vacuo*. Complex **16** was isolated as a purple, microcrystalline solid (0.35 g, 81%), mp 97–102 °C, (Found: C, 44.5; H, 3.1; N, 0.0. $C_{29}H_{24}Cl_2O_6P_2W$ requires C, 45.2; H, 3.0; N, 0.0%); δ_H (90.0 MHz, $CDCl_3$) 7.50–7.31 (20H, m, P*Ph*$_2$), 5.30 (2H, s, CH_2Cl_2); OH not observed, but addition of D_2O led to appearance of a signal due to HOD at δ 4.20 ppm; $\delta_C\{^1H\}$ (75.5 MHz, $CDCl_3$) 200.8 (t, CO, $^2J_{CP}$ 16.9 Hz).

‖ The aromatic carbon signals could not be observed, presumably due to extensive coupling with both fluorine and phosphorus.

***cis*-[PtCl$_2$(P{NEt$_2$}Ph$_2$)$_2$] 17.** A solution of PNEt$_2$(Ph)$_2$ (0.4 g, 1.56 mmol) in CH_2Cl_2 (10 cm^3) was added to a solution of [PtCl$_2$(cod)] (0.25 g, 0.67 mmol) in CH_2Cl_2 (20 cm^3). A clear, pale yellow solution was obtained after stirring for 2 h at rt. The solvent was removed *in vacuo* and the residue washed with hexane. Recrystallisation from CH_2Cl_2 and hexane afforded **17** as a white crystalline material (0.46 g, 88%), mp 113–114 °C (Found: C, 50.1; H, 5.6; N, 3.4. $C_{32}H_{40}N_2Cl_2P_2Pt$ requires C, 49.2; H, 5.1; N, 3.6%); δ_H (90.0 MHz, $CDCl_3$) 7.38–7.26 (20H, m, P*Ph*$_2$NEt$_2$), 3.37 (8H, m, C*H*$_2$CH$_3$), 0.93 (12H, t, $^3J_{HH}$ 6.1 Hz, CH$_2$C*H*$_3$).

***trans*-[PtCl$_2$(P{NPr$^i_2$}Ph$_2$)$_2$] 18.** In a similar procedure to that used above, reaction of Ph$_2$PNPr$^i_2$ (0.4 g, 1.4 mmol) with [PtCl$_2$(cod)] (0.25 g, 0.7 mmol) in CH_2Cl_2 (25 cm^3) gave **18** as yellow crystals (0.45 g, 81%), mp 149–150 °C (Found: C, 51.7; H, 5.8; N, 3.3. $C_{36}H_{48}N_2Cl_2P_2Pt$ requires C, 51.7; H, 5.7; N, 3.4%); δ_H (90.0 MHz, $CDCl_3$) 7.49–7.29 (20H,m, P*Ph*$_2$), 4.18 (4H, m, C*H*Me$_2$), 1.25 (24H, d, $^3J_{HH}$ 6.6 Hz, CH$_2$*Me*$_2$).

Reaction of 13 with HCl gas. HCl gas was bubbled through a stirred CH_2Cl_2 solution (20 cm^3) of **17** (0.2 g, 0.26 mmol) for 15 min. The solvent was removed *in vacuo* and the white residue extracted with THF (20 cm^3). The solution was concentrated and addition of Et$_2$O afforded a white microcrystalline compound identified as *cis*-[PtCl$_2$(PPh$_2$Cl)$_2$] (**22**) by comparison with data obtained from an authentic sample.

Reaction of 18 with HCl gas. HCl gas was bubbled through a stirred CH_2Cl_2 solution (20 cm^3) of **18** (0.25 g, 0.3 mmol) for 30 min. Using the same procedure as before a white microcrystalline compound identified as the *cis*-complex **22** by comparison with data obtained from an authentic sample.

Reaction of 17 with MeOH in the presence of HCl. HCl gas was bubbled through a stirred MeOH suspension (15 cm^3) of **17** (0.2 g, 0.26 mmol) for 30 min. During which time the white suspension changed to a clear solution. The solvent was removed *in vacuo* and the white residue washed with H_2O (10 cm^3). The residue was redissolved in CH_2Cl_2 (15 cm^3) and dried over $MgSO_4$. The solution was concentrated and addition of hexane afforded a white microcrystalline compound identified as *cis*-[PtCl$_2$(P{OMe}Ph$_2$)$_2$] (**19**) (0.14 g, 78%), mp >230 °C (Found: C, 45.0; H, 3.8. $C_{26}H_{26}O_2Cl_2P_2Pt$ requires C, 44.7; H, 3.8%); δ_H (90.0 MHz, CD_2Cl_2) 7.55–7.30 (20H, m, P*Ph*$_2$), 3.36 (6H, d, $^3J_{HP}$ 12.4, C*H*$_3$).

Reaction of 17 with EtOH in the presence of HCl. HCl gas was bubbled through a stirred EtOH suspension (15 cm^3) of **17** (0.2 g, 0.26 mmol) for 30 min. The solvent was removed *in vacuo* and the white residue extracted with THF (20 cm^3). The solution was concentrated and addition of Et$_2$O afforded a white microcrystalline compound identified as *cis*-[PtCl$_2$(P{OEt}Ph$_2$)$_2$] (**20**) (0.15 g, 81%), mp >230 °C (Found: C, 46.2; H, 4.2. $C_{28}H_{30}O_2Cl_2P_2Pt$ requires C, 46.3; H, 4.2%); δ_H (90.0 MHz, CD_2Cl_2) 7.6–7.29 (20H, m, P*Ph*$_2$), 3.8 (4H, m, C*H*$_2$CH$_3$), 1.08 (6H, t, $^3J_{HH}$ 6.1 Hz, CH$_2$C*H*$_3$).

Reaction of 17 with CH$_2$CHCH$_2$OH in the presence of HCl. As above, HCl gas was bubbled through a suspension of **17** (0.2 g, 0.26 mmol) in allyl alcohol (15 cm^3) for 30 min. Recrystallisation from CH_2Cl_2–hexane yielded a crystalline compound identified as *cis*-[PtCl$_2$(P{OCH$_2$CHCH$_2$}Ph$_2$)$_2$] (**21**) (0.14 g, 73%), mp 157–158 °C (Found: C, 47.6; H, 4.0. $C_{30}H_{30}O_2Cl_2P_2Pt$ requires C, 48.0; H, 4.0%); δ_H (90.0 MHz, $CDCl_3$) 7.50–7.29 (20H, m, P*Ph*$_2$), 5.50 (2H, m, CH$_2$C*H*CH$_2$), 5.05 (4H, m, CH$_2$CHC*H*$_2$), 4.20 (4H, m, POC*H*$_2$).

Reaction of 17 with HOCH$_2$CH$_2$OH in the presence of HCl. As above, HCl gas was bubbled through a suspension of **17** (0.2 g, 0.26 mmol) in ethylene glycol (6 cm^3) for 30 min. ^{31}P NMR spectroscopy revealed only the formation of the *cis*-chlorophosphine derivative **22**.

Reaction of 18 with MeOH in the presence of HCl gas. HCl gas was bubbled through a stirred MeOH solution (15 cm^3) of **18** (0.15 g, 0.18 mmol) for 15 min. Using the same procedure as before a white microcrystalline compound identified as *cis*-**19**.

Reaction of 18 with EtOH in the presence of HCl gas. HCl gas was bubbled through a stirred EtOH solution (15 cm^3) of **18** (0.15 g, 0.18 mmol) for 15 min. Using the same procedure as before a white microcrystalline compound identified as *cis*-**20**.

Reaction of 14 with CH$_2$CHCH$_2$OH in the presence of HCl gas. HCl gas was bubbled through a stirred CH$_2$CHCH$_2$OH solution (10 cm^3) of **18** (0.15 g, 0.18 mmol) for 15 min. Using the same procedure as before a white microcrystalline compound identified as *cis*-**21**.

Reaction of 18 with HOCH$_2$CH$_2$OH in the presence of HCl. As above, HCl gas was bubbled through a suspension of **18** (0.15 g, 0.18 mmol) in ethylene glycol (6 cm^3) for 15 min. ^{31}P NMR spectroscopy revealed only the formation of the *cis*-chlorophosphine derivative **22**.

Attempted isomerisation of *cis*-[PtCl$_2$(PPh$_2$Cl)$_2$] (22). A toluene solution of **22** (0.1 g, 0.14 mmol) was heated at reflux for 5 d and afforded a mixture of *cis*-(**22**) and *trans*-(**23**) isomers, in a ratio of 45 : 55%, respectively, deduced from the integration of the ^{31}P{^{1}H} NMR spectrum of the crude reaction mixture.

Attempted Cl-ion-catalysed isomerisation of *cis*-[PtCl$_2$(PPh$_2$Cl)$_2$] (22). A toluene solution of **22** (0.1 g, 0.14 mmol) containing a catalytic quantity of [Pr$^i_2$NH$_2$]Cl (2 mg, 0.01 mmol) was heated at reflux for 5 d. The ^{31}P{^{1}H} NMR spectrum of the crude reaction mixture revealed a *cis*/*trans*-ratio, **22** : **23**, of 25 : 75%.

Attempted reaction of 17 with H$_2$SO$_4$ (aq.). Complex **17** (0.2 g, 0.78 mmol) was dissolved in CH_2Cl_2 (8 cm^3) and stirred with H_2SO_4 (aq.) (8 cm^3) of varying concentrations (10–50% v/v) for 3 h. Only unreacted starting material was isolated in each case, as shown by ^{31}P{^{1}H} NMR spectroscopy.

Attempted reaction of 17 with 1.0 M HCl. Treatment of **13** (0.2 g, 0.78 mmol) in water (10 cm^3) with HCl (1.0 M, 10 cm^3) afforded only unreacted starting material according to ^{31}P{^{1}H} NMR spectroscopy.

Attempted reaction of 18 with H$_2$SO$_4$ (aq.) and HBF$_4$ (50% in H$_2$O). Complex **18**, under identical conditions to those used for **17**, did not react with either acid according to ^{31}P{^{1}H} NMR spectroscopy.

Reaction of 18 with 1.0 M HCl. Treatment of **18** (0.2 g, 0.16 mmol) in water (10 cm^3) with HCl (1.0 M, 10 cm^3) afforded the *cis*-chlorophosphine complex **22** (*ca.* 10%) in addition to unreacted **18** and a number of unidentifiable phosphorus-containing products according to ^{31}P{^{1}H} NMR spectroscopy.

***trans*-[PtCl$_2$(P{NEt$_2$}$_2$Ph)$_2$] 24.** Using a procedure analogous to that for the preparation of **18**, reaction of P(NEt$_2$)$_2$Ph (0.25 g, 1.0 mmol) with [PtCl$_2$(cod)] (0.17 g, 0.5 mmol) in CH_2Cl_2 (15 cm^3) gave **24** as yellow crystals (0.45 g, 81%), mp 148–150 °C (Found: C, 43.9; H, 6.6; N, 7.1 $C_{28}H_{50}N_4Cl_2P_2Pt$ requires C, 43.6; H, 6.5; N, 7.3%); δ_H (301.2 MHz, $CDCl_3$) 7.39–7.23 (10H, m, P*Ph*), 3.40 (16H, m, C*H*$_2$CH$_3$), 0.96 (24H, t, $^3J_{HH}$ 6.1 Hz, CH$_2$C*H*$_3$).

***trans*-[PtCl$_2$(P{NPr$^i_2$}$_2$Me)$_2$] 25.** An NMR tube fitted with a J. Young's valve was charged under nitrogen with [PtCl$_2$(cod)] (18.8 mg, 0.05 mmol) and a solution of MeP{NPr$^i_2$}$_2$ (25 mg, 0.10 mmol) in $CDCl_3$ (0.5 cm^3) added. On standing at rt for 2 h, the sample was transferred under nitrogen to a Schlenk line, all volatiles removed *in vacuo* to give an off white solid. Washing with 40–60 PE (3 × 2 cm^3) gave **25** as a white solid (28 mg, 74%), mp 155–157 °C, (Found: C, 41.5; H, 8.3; N, 7.3 $C_{26}H_{62}N_4Cl_2P_2Pt$ requires C, 41.2; H, 8.2; N, 7.4%); δ_H (250.1 MHz, $CDCl_3$) 4.23 [8H, sept., $^3J_{HH}$ 6.9 Hz, C*H*(CH$_3$)$_2$], 1.78 (6H, pseudo t, PC*H*$_3$), 1.42 [24H, t, $^3J_{HH}$ 6.9 Hz, CH(C*H*$_3$)$_2$], 1.30 [24H, t, $^3J_{HH}$ 6.9 Hz, CH(C*H*$_3$)$_2$]; $\delta_C\{^1H\}$ (62.9 MHz, $CDCl_3$) 47.7 [pseudo t, $^2J_{CP}$ 4.4 Hz, *C*H(CH$_3$)$_2$], 25.5 [s, CH(*C*H$_3$)$_2$], 24.9 [s, CH(*C*H$_3$)$_2$], 19.0 (pseudo t, $^2J_{CP}$ 22.4 Hz, P*C*H$_3$).

***trans*-[RhCl(CO)(P{NEt$_2$}Ph$_2$)$_2$] 26.** An NMR tube fitted with a J. Young's valve was charged under nitrogen with [{RhCl(CO)$_2$}$_2$] (12.5 mg, 0.03 mmol) and a solution of PNEt$_2$(Ph)$_2$ (33.0 mg, 0.19 mmol) in $CDCl_3$ (0.5 cm^3) added. An immediate change in colour and evolution of gas was observed to occur. After 30 minutes, when gas evolution had finished, the tube was transferred to a Schlenk line, the solution was freeze/thaw degassed, let down to a CO atmosphere and sealed. Complex **26** formed as the only product according to IR and ^{31}P NMR spectroscopies and was isolated after removal of all volatile components *in vacuo* as an orange solid, 38 mg, 87%. (Found: C, 58.28; H, 6.02; N, 4.05. $C_{33}H_{40}ON_2ClPRh$ requires C, 58.20; H, 5.92; N, 4.11%); δ_H (250.1 MHz, $CDCl_3$) 7.58 (8H, br, *o*-Ph), 7.24 (12H, m, *m*-/*p*-Ph), 3.28 (8H, br, C*H*$_2$CH$_3$), 0.90 (12H, t, $^3J_{HH}$ 7.0 Hz, CH$_2$C*H*$_3$); $\delta_C\{^1H\}$ (75.8 MHz, $CDCl_3$) 187.3 (s, CO), 136.1 (pseudo t, $^1J_{PC}$ 24.0 Hz, *ipso*-Ph), 132.9 (br, *o*-Ph), 129.7 (s, *p*-Ph), 127.9 (br, *m*-Ph), 44.1 (s, *C*H$_2$CH$_3$), 14.1 (s, CH$_2$*C*H$_3$).

***trans*-[RhCl(CO)(P{NPr$^i_2$}Ph$_2$)$_2$] 27.** An analogous procedure to that employed for the preparation of **26** was followed using [{RhCl(CO)$_2$}$_2$] (13 mg, 0.03 mmol) and a solution of PNPr$^i_2$(Ph)$_2$ (38 mg, 1.34 mmol) in $CDCl_3$ (0.5 cm^3). Complex **27** formed as the only product according to IR and ^{31}P NMR spectroscopies and was subsequently isolated as an orange solid, 42 mg, 86%. δ_H (250.1 MHz, $CDCl_3$) 7.75–7.69 (8H, m, *o*-Ph), 7.35–7.18 (12H, m, *m*-/*p*-Ph), 3.99 [4H, br, NC*H*(CH$_3$)$_2$], 1.15 [24H, d, $^3J_{HH}$ 6.7 Hz, NCH(C*H*$_3$)$_2$]; $\delta_C\{^1H\}$ (75.8 MHz, $CDCl_3$) 184.1 (br, CO), 136.8 (pseudo t, J_{PC} 23.4 Hz, *ipso*-Ph), 133.4 (s, *o*-Ph), 129.5 (m, *m*-Ph), 127.6 (s, *p*-Ph), 52.2 [s, N*C*H(CH$_3$)$_2$], 24.9 [s, NCH(*C*H$_3$)$_2$].

Attempted synthesis of *trans*-[RhCl(CO)(P{NEt$_2$}$_2$Ph)$_2$]. An analogous procedure to that employed for the preparation of **26** was followed using [{RhCl(CO)$_2$}$_2$] (8 mg, 0.02 mmol) and a solution of P(NEt$_2$)$_2$Ph (20 mg, 0.08 mmol) in $CDCl_3$ (0.5 cm^3). Following removal of volatile components and washing with hexane (3 × 2 cm^3) the monophosphine complex *cis*-[RhCl(CO)$_2$(P{NEt$_2$}$_2$Ph)] (**28**) was isolated as an orange solid, 16 mg, 87%; (Found: C, 42.9; H, 5.6; N, 6.2. $C_{16}H_{25}N_2O_2ClPRh$ requires C, 43.0; H, 5.6; N, 6.3%); δ_H (301.2 MHz, $CDCl_3$) 7.70–7.61 (4H, m, *o*-Ph), 7.47–7.42 (6H, m, *m*-/*p*-Ph), 3.30 (16H, dq, $^3J_{HH}$ 7.0 Hz, $^3J_{PH}$ 10.2 Hz, NC*H*$_2$CH$_3$), 1.15 (24H, t, $^3J_{HH}$ 7.0 Hz, NCH$_2$C*H*$_3$); $\delta_C\{^1H\}$ (75.8 MHz, $CDCl_3$) 183.1 (br, CO), 136.3 (d, J_{PC} 67.1 Hz, *ipso*-Ph), 133.4 (d, $^2J_{PC}$ 12.5 Hz, *o*-Ph), 130.8 (s, *p*-Ph), 128.6 (d, $^3J_{PC}$ 21.5 Hz, *m*-Ph), 42.8 (d, $^2J_{PC}$ 6.2 Hz, N*C*H$_2$), 14.5 (d, $^3J_{PC}$ 3.5 Hz, NCH$_2$*C*H$_3$); IR (ν_{max}/cm^{-1}, $CDCl_3$) 2091, 2007.

***trans*-[RhCl(CO)(P{NPr$^i_2$}$_2$Me)$_2$] 29.** An analogous procedure to that employed for the preparation of **26** was followed using [{RhCl(CO)$_2$}$_2$] (42 mg, 0.11 mmol) and a solution of P(NPr$^i_2$)Me (106 mg, 0.43 mmol) in $CDCl_3$ (0.5 cm^3). Complex **29** formed as the only product according to IR and ^{31}P NMR spectroscopies and was subsequently isolated as an orange solid, 118 mg, 83%. (Found: C, 49.7; H, 9.3; N, 8.3. $C_{27}H_{62}Cl_1N_4O_1P_2Rh$ requires C, 49.2; H, 9.5; N, 8.5%); δ_H (250.1 MHz, $CDCl_3$) 4.16 [8H, sept, $^3J_{HH}$ 6.9 Hz, NC*H*(CH$_3$)$_2$], 1.94 (6H, t, $^2J_{PH}$ 2.3 Hz, PC*H*$_3$), 1.40 [24H, d, $^3J_{HH}$ 6.9 Hz, NCH(C*H*$_3$)$_2$], 1.22 [24H, d, $^3J_{HH}$ 6.9 Hz, NCH(C*H*$_3$)$_2$]; $\delta_C\{^1H\}$ (75.8 MHz, $CDCl_3$) 189.9 (dt, $^1J_{RhC}$ 77.9 Hz, $^2J_{PC}$ 15.7 Hz, CO), 48.1 [t, $^2J_{PC}$ 5.1 Hz, N*C*H(CH$_3$)$_2$], 25.8 [s, NCH(*C*H$_3$)$_2$], 25.0 [s, NCH(*C*H$_3$)$_2$], 23.6 (m, P*C*H$_3$).

Attempted synthesis of *trans*-[RhCl(CO)(P{NPr$^i_2$}$_2$Ph)$_2$]. An analogous procedure to that employed for the preparation of **26** was followed using [{RhCl(CO)$_2$}$_2$] (12.0 mg, 0.03 mmol) and a solution of PhP(NPr$^i_2$)$_2$ (38 mg, 1.23 mmol) in $CDCl_3$ (0.5 cm^3). Removal of all volatile components under reduced pressure followed by washing with hexane (3 × 2 cm^3) afforded the monophosphine complex *cis*-[RhCl(CO)$_2$(P{NPr$^i_2$}$_2$Ph)] (**30**) as an orange solid, 23 mg, 77%. (Found: C, 46.49; H, 6.69; N, 5.73. $C_{19}H_{33}O_2N_2ClPRh$ requires C, 46.50; H, 6.78; N, 5.71%); δ_H (250.1 MHz, $CDCl_3$) 7.75–7.66 (2H, m, *o*-Ph), 7.30–7.24 (3H, m, *m*-/*p*-Ph), 4.03 [4H, d sept., $^3J_{HH}$ 7.0 Hz, $^3J_{PH}$ 2.5 Hz, NC*H*(CH$_3$)$_2$], 1.33 [12H, d, $^3J_{HH}$ 7.0 Hz, NCH(C*H*$_3$)$_2$], 1.24 [12H, d, $^3J_{HH}$ 7.0 Hz, NCH(C*H*$_3$)$_2$]; $\delta_C\{^1H\}$ (75.8 MHz, $CDCl_3$) 184.1 (br, CO), 182.4 (dd, $^1J_{RhC}$ 143.0 Hz, $^2J_{PC}$ 57.0 Hz, CO), 139.1 (dd, $^1J_{PC}$ 54.5 Hz, $^2J_{PC}$ 4.0 Hz, *ipso*-Ph), 131.4 (d, $^2J_{PC}$ 14.0 Hz, *o*-Ph), 130.6 (d, $^4J_{PC}$ 1.0 Hz, *p*-Ph), 128.1 (d, $^3J_{PC}$ 11.0 Hz, *m*-Ph), 50.8 [d, $^2J_{PC}$ 10.0 Hz, N*C*H(CH$_3$)$_2$], 25.9 [d, $^3J_{PC}$ 3.0 Hz, NCH(*C*H$_3$)$_2$], 25.6 [d, $^3J_{PC}$ 3.0 Hz, NCH(*C*H$_3$)$_2$]; IR (ν_{max}/cm^{-1}, $CDCl_3$) 2089, 2004.

Reaction of PCl(NPr$^i_2$)$_2$ with {RhCl(CO)$_2$}$_2$. An analogous procedure to that employed for the preparation of **26** was followed using [{RhCl(CO)$_2$}$_2$] (12 mg, 0.03 mmol) and a solution of PCl(NPr$^i_2$)$_2$ (33 mg, 1.23 mmol) in $CDCl_3$ (0.5 cm^3). The ^{31}P NMR spectrum of the crude reaction mixture displayed three sets of signals in a 2 : 1 : 1 ratio: δ 144.8 (d, $^1J_{PRh}$ 186 Hz), 136.2 (s, PCl{NPr$^i_2$}$_2$), and 130.5 (d, $^1J_{PRh}$ 192 Hz). No further evolution was observed after 3 d at rt. Heating the mixture to 40 °C led to the formation an unidentifiable mixture of products according to ^{31}P NMR spectroscopy.

Representative preparation of Se=PMe(NPr$^i_2$)$_2$. An NMR tube fitted with a J. Young's valve was charged with grey Se (26 mg, 0.28 mmol), PMe(NPr$^i_2$)$_2$ (66 mg, 2.66 × 10^{-4} mol) and $CDCl_3$ (0.5 mL) under nitrogen. The reaction mixture was subject to sonication until complete reaction had occurred according to ^{31}P NMR spectroscopy.

Crystallography

Single crystals of phosphine **6** were obtained as colourless plates following prolonged cooling (−30 °C) of a saturated hexane solution. $C_{18}H_{28}N_2F_5P$, M = 398.39, orthorhombic, space group *Pbca*, a = 12.9383(15), b = 10.3076(19), c = 29.874(3) Å, V = 3984.1(10) Å^3, Z = 8, D_c = 1.328 Mg m^{-3}, μ(Mo-Kα) = 0.143 mm^{-1}, F(000) = 1680, T = 183(2) K; 0.12 × 0.40 × 0.42 mm, Bruker SMART 1000 diffractometer with CCD area detector, ϕ- and ω-scans, 1688 measured, 1092 independent reflections (R_{int} = 0.0336). The structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically using full matrix least-squares based on F^2 to give R_1 = 0.0316, wR_2 = 0.0668 (all data) for 783 independent observed reflections [$I > 2\sigma(I)$, $2\theta \leq 52.62°$] and 243 parameters. The data : parameter ratio is poor (4.49), while the ratio of unique/expected reflections was only 27% as a result of particularly weak data.

CCDC reference number 193475.

See http://www.rsc.org/suppdata/dt/b2/b208886j/ for crystallographic data in CIF or other electronic format.

Acknowledgements

The Royal Society and The Nuffield Foundation are thanked for grants to P. W. D. Johnson Matthey Plc. is thanked for the loan of platinum salts. Financial support from the EPSRC, Lubrizol Ltd. (CASE award M. J. H.), and The University of Leicester is gratefully acknowledged.

References

1 A. Michaelis, *Ann. Chem.*, 1903, **326**, 129.
2 C. Rømming and J. Songstad, *Acta Chem. Scand., Ser. A*, 1978, **32**, 689.
3 See for example: J. G. Verkade and K. J. Coskram, in *Organophosphorus Compounds*, eds. G. M. Kosolapoff and L. Maier, Wiley, New York, 1972, vol. 2, p. 1; A. H. Cowley, R. E. Davies and K. Remadna, *Inorg. Chem.*, 1981, **20**, 2146; R. B. King, *Inorg. Chem.*, 1963, **2**, 936; S. A. Katz, V. S. Allured and A. D. Norman, *Inorg. Chem.*, 1994, **33**, 1762.
4 G. Ewart, D. S. Payne, A. L. Porte and A. P. Lane, *J. Chem. Soc.*, 1962, 3984.
5 D. S. Payne and A. P. Walker, *J. Chem. Soc. C*, 1966, 498.
6 M. Höfler and W. Marre, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 187.
7 S. Singh and K. M. Nicholas, *Chem. Commun.*, 1998, 149.
8 Y. Hayakawa, M. Hirose, M. Hayakawa and R. Noyori, *J. Org. Chem.*, 1995, **60**, 925.
9 J.-J. Brunet, R. Chauvin, J. Chiffre, S. Huguet and P. Leglaye, *J. Organomet. Chem.*, 1998, **566**, 117.
10 S. Juge, M. Stephan, J. A. Laffitte and J. P. Genet, *Tetrahedron Lett.*, 1990, **31**, 6357.
11 N. R. Price and J. Chambers, in *The Chemistry of Organophosphorus Compounds*, ed. F. R. Hartley, Wiley, Chichester, 1990, vol. 1, p. 649.
12 Y. L. Bennani and S. Hanessian, *Chem. Rev.*, 1997, **97**, 3161.
13 H. Tye, D. Smyth, C. Eldred and M. Wills, *Chem. Commun.*, 1997, 1053.
14 J. Ansell and M. Wills, *Chem. Soc. Rev.*, 2002, **31**, 259.
15 M. L. Clarke, D. J. Cole-Hamilton, A. M. Z. Slawin and J. D. Woollins, *Chem. Commun.*, 2000, 2065.
16 M. L. Clarke, G. L. Holliday, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 2002, 1093.
17 J. M. Brunel, A. Heumann and G. Buono, *Angew. Chem., Int. Ed.*, 2000, **39**, 1946.
18 M. P. Magee, W. Luo and W. H. Hersh, *Organometallics*, 2002, **21**, 362.
19 K. G. Moloy and J. L. Petersen, *J. Am. Chem. Soc.*, 1995, **117**, 7696.
20 F. Dahan, P. W. Dyer, M. J. Hanton, M. Jones, D. M. P. Mingos, A. J. P. White, D. J. Williams and A.-M. Williamson, *Eur. J. Inorg. Chem.*, 2002, 737.
21 R. Kranich, K. Eis, O. Geis, S. Mühle, J. W. Bats and H. G. Schmalz, *Chem. Eur. J.*, 2000, **6**, 2874.
22 R. B. King and P. M. Sundaram, *J. Org. Chem.*, 1984, **49**, 1784.
23 See for example: R. B. King and W.-K. Fu, *Inorg. Chem.*, 1986, **25**, 2384.
24 W. E. Piers and T. Chivers, *Chem. Soc. Rev.*, 1997, **26**, 345.
25 W.-K. Wong and F.-W. Lee, *Polyhedron*, 1992, **11**, 863.
26 E. H. Wong and F. C. Bradley, *Inorg. Chem.*, 1981, **20**, 2333.
27 F. Mercier and F. Mathey, *J. Chem. Soc., Chem. Commun.*, 1984, 782.
28 K. Diemert, A. Hinz, W. Kuchen and D. Lorenzen, *J. Organomet. Chem.*, 1990, **393**, 379.
29 H.-J. Cristau, A. Chêne and H. Christol, *Synthesis*, 1980, **7**, 551.
30 P. S. Pregosin and R. W. Kunz, in *31P, 13C NMR of Transition Metal Phosphine Complexes*, eds. P. Diehl, E. Fluck and R. Kosfeld, Springer-Verlag, Berlin, 1979.
31 P. Braunstein, Pierre, D. Matt, O. Bars, M. Louër, D. Grandjean, J. Fischer and A. Mitschler, *J. Organomet. Chem.*, 1981, **213**, 79.
32 M. K. Cooper and J. M. Downes, *Inorg. Chem.*, 1978, **17**, 880.
33 R. Roulet and C. Barbey, *Helv. Chim. Acta*, 1973, **56**, 2179.
34 W. J. Louw, *Inorg. Chem.*, 1977, **16**, 2147.
35 E. H. Wong, M. M. Turnbull, K. D. Hutshinson, C. Valdez, E. J. Gabe, F. L. Lee and Y. Le Page, *J. Am. Chem. Soc.*, 1988, **110**, 8422.
36 K. Diemert, W. Kuchen and D. Lorenzen, *J. Organomet. Chem.*, 1989, **378**, 17.
37 D. E. C. Corbridge, *Phosphorus: An Outline of its Chemistry and Biochemistry*, 5th edn., Elsevier, Amsterdam, 1995, p. 51.
38 N. Burford, R. E. v. H. Spence and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1990, 3611.
39 W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Dalton Trans.*, 1973, 2162.
40 E. Krawczyk, A. Skowronska and J. Michalski, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1135.
41 S. M. Godfrey, S. L. Jackson, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1998, 4201.
42 S. Serron, S. P. Nolan and K. G. Moloy, *Organometallics*, 1996, **15**, 4301.
43 A. Huang, J. E. Marcone, K. L. Mason, W. J. Marshall, K. G. Moloy, S. Seron and S. P. Nolan, *Organometallics*, 1997, **16**, 3377.
44 D. De Montauzon and R. Poilblanc, *J. Organomet. Chem.*, 1975, **93**, 397.
45 T. Sakakura, T. Sodeyama, K. Sasaki, K. Wada and M. Tanaka, *J. Am. Chem. Soc.*, 1990, **112**, 7221.
46 S. Vastag, B. Heil and L. Markó, *J. Mol. Catal.*, 1979, **5**, 189.
47 P–N single bond = 1.8 Å: L. Pauling, *Nature of the Chemical Bond*, Cornell University Press, New York, 1960.
48 A. Karipides and C. M. Cosio, *Acta Crystallogr., Sect. C*, 1989, **45**, 1743.
49 O. B. Shawkataly, M.-L. Chong, H.-K. Fun and K. Sivakumar, *Acta Crystallogr., Sect. C*, 1996, **52**, 1725.
50 N. Burford, J. A. C. Clyburne, S. V. Sereda, T. S. Cameron, J. A. Pincock and M. Lumsden, *Organometallics*, 1995, **14**, 3762.
51 N. Poetschke, M. Nieger, M. A. Khan, E. Niecke and M. T. Ashby, *Inorg. Chem.*, 1997, **36**, 4087.
52 E. Rotondo, G. Battaglia, G. Giordano and F. P. Cusmano, *J. Organomet. Chem.*, 1993, **450**, 245.
53 P. Uguagliati, G. Deganello and U. Belluco, *Inorg. Chim. Acta*, 1974, **9**, 203.
54 D. F. Steele and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1972, 2161.
55 D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1965, 1900.
56 G. Bandoli, D. Clemente, G. Deganello, G. Carturan, P. Uguagliati and U. Belluco, *J. Organomet. Chem.*, 1974, **71**, 125.
57 J. W. Kang and P. M. Maitlis, *Can. J. Chem.*, 1968, **46**, 897.
58 N. G. Anderson and B. A. Keay, *Chem. Rev.*, 2001, **101**, 997.
59 C. Glidewell and E. J. Leslie, *J. Chem. Soc., Dalton Trans.*, 1977, 527.
60 D. W. Allen and B. F. Taylor, *J. Chem. Res. (S)*, 1981, 220.
61 R. D. Kroshefsky, R. Weiss and J. G. Verkade, *Inorg. Chem.*, 1979, **18**, 469.
62 D. W. Allen and B. R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 51.
63 E. Nield, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, 1959, 166.
64 Y. Hayakawa, M. Hirose, M. Hayakawa and R. Noyori, *J. Org. Chem.*, 1995, **60**, 925.
65 R. M. Moriarty, J. Hiratake and K. Liu, *J. Am. Chem. Soc.*, 1990, **112**, 8575.
66 W. Hawes and S. Trippett, *J. Chem. Soc. C*, 1969, 1465.