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Highly electron rich alkyl- and dialkyl-*N*-pyrrolidinyl phosphines: an evaluation of their electronic and structural properties

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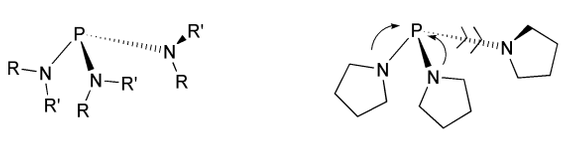
Received 19th September 2001, Accepted 3rd January 2002
First published as an Advance Article on the web 19th February 2002

Phosphines containing two N-bound pyrrolidine groups and one alkyl or aryl group have been prepared and shown to be unusually electron rich donor ligands when compared to either tris(*N*-pyrrolidinyl)phosphine or the trialkyl- or triaryl-phosphines. It is proposed that the electron donating ability of a pyrrolidine group towards phosphorus had been underestimated as only two pyrrolidinyl groups can donate towards the phosphine *via* the nitrogen lone pair. *trans*-$L_2Rh(CO)Cl$ complexes have been prepared from the phosphines and used to quantify the electron donor characteristics. Two of these complexes have been characterised by X-ray crystallography. The reaction of these phosphines with iron(II) complexes has also been studied. Platinum(II) complexes of the ligands have been prepared and also (in three examples) characterised by X-ray crystallography, which has enabled the steric and bonding properties to be evaluated. *tert*-Butyl(dipyrrolidinyl)phosphine is one of the most electron rich phosphines known. The dialkyl(pyrrolidinyl)phosphines have been found to contain less potent N⟶P donation, and are somewhat less good donor ligands.

Introduction

Phosphine ligands have many important applications in organometallic chemistry and catalysis. One of the many attractive features of these ligands is the widespread availability of ligands that possess significantly different electronic properties. Some phosphines have a π-acceptor character that approaches that of carbon monoxide, whereas other phosphines are very strong σ-donors.[1–4]

Consequently, a metal complex modified by a strong π-acceptor ligand will have entirely different properties to a metal complex of σ-donor ligands. Metal complexes of strongly electron donating alkylphosphines undergo many reactions which are not possible with arylphosphines.[5] This is often due to oxidative addition being a much easier process for an electron rich metal centre. In the last few years, there have been several new catalytic processes developed that rely on the increased reactivity of an electron rich metal complex. Important recent examples are catalytic C–H bond activation,[6] hydroformylation of alkenes to give commercially valuable alcohols instead of aldehydes,[7] and palladium catalysed Heck, Suzuki, and amination reactions of aryl chlorides, which do not normally react with most other phosphine based catalysts.[8–10] The synthesis of new electron donating ligands that offer different properties to those already existing has therefore become an important challenge. We were interested in using P–N bond formation to prepare ligands that might have a different combination of steric and electronic properties to that of existing ligands (see Fig. 1).



(1) (2)

Fig. 1 Proposed electronic properties of (**2**).

Tris(alkylamino)phosphines are known to be electron rich phosphine ligands. The high basicity (σ-donor strength) of the phosphorus atom is thought to arise from donation towards the phosphorus from the nitrogen lone pair. X-Ray crystal structures of tris(alkylamino)phosphines and their metal complexes[3,11] show these ligands to contain two short P–N bonds with planar nitrogens, and one long P–N bond with a non-planar nitrogen atom. This suggested to us that only two of the nitrogen lone pairs could donate electron density towards phosphorus, while the third nitrogen substituent acts merely as an electronegative atom bound to the phosphorus, and therefore reduces the overall basicity of the phosphine. If this were the case, a "hybrid" ligand that contains one electron donating alkyl group and two electron donating amino groups might be an extremely electron rich phosphine ligand, and have numerous applications in catalysis. In this paper we describe the synthesis of these new bis(*N*-pyrrolidinyl)alkylphosphines and metal complexes which shed light on their properties.[12]

Experimental

General

All manipulations were carried out under an atmosphere of nitrogen, unless stated otherwise. All solvents were either freshly distilled from an appropiate drying agent (THF, Et_2O, CH_2Cl_2) or obtained as anhydrous grade. ^1H, and ^{31}P NMR spectra were recorded using a "Varian 2000" 300 MHz spectrometer. IR spectra were recorded as KBr discs (prepared in air) on a Perkin Elmer PE1720 FTIR/RAMAN spectrometer. $Pt(COD)Cl_2$, $CpFe(CO)_2(I)$, $[CpFe(CO)_2(MeCN)]BF_4$ and (tripyrollidinyl)phosphine were prepared by literature methods.[3,13–15] All other materials used in this paper were obtained from Aldrich Chemical Company and used as received. All peaks above 700 cm^{-1} in the IR spectrum are reported to serve as a fingerprint.

General experimental procedure for synthesis of phosphines

Pyrrolidine (5 equiv. for (dipyrrolidinyl)phoshines, 2.5 equiv. for (monopyrrolidinyl)phosphines) was added dropwise to a solution of the appropriate chloro-phosphine in diethyl ether.

DOI: 10.1039/b108467d

This was stirred for a few hours (overnight in the case of $^{t}BuPCl_2$) prior to filtration under nitrogen and removal of solvent to give a colourless mobile liquid in essentially quantitative yields. The phosphines are air and moisture sensitive, but can be handled easily using standard Schlenk techniques. The purity and identity of these phosphines was determined spectroscopically.

Phenyl(dipyrrolidinyl)phosphine (3). IR(ν_{max}/cm^{-1}) 2971, 1638, 1459, 1291, 1163, 1061, 834, 720. ^{31}P NMR (121.4 MHz; C_6D_6) δ_P 64.46 (s). ^{1}H NMR (300 MHz; C_6D_6) δ_H 1.51 (8H, qn app. {app. = apparent}), 3.01 (4H, m, br), 3.16 (4H, m, br), 7.01–7.05 (5H, m, ArH). HRMS: Found: 248.1451 (M^+), $C_{14}H_{21}N_2P$ requires: 248.1442.

Methyl(dipyrrolidinyl)phosphine (4). IR(ν_{max}/cm^{-1}) 2962, 2841 1478, 1434, 1340, 1190, 1093, 1057, 997, 746, 702. ^{31}P NMR (121.4 MHz; C_6D_6) δ_P 74.07 (s). ^{1}H NMR (300 MHz; C_6D_6) δ_H 1.05 (3H, dd, 1.1, 6.6 Hz), 1.30 (8H, qn app.), 2,82 (8H, m). HRMS: Found: 186.1280 (M^+), $C_9H_{19}N_2P$ requires:186.1286.

***tert*-Butyl(dipyrrolidinyl)phosphine (5).** IR(ν_{max}/cm^{-1}) 2965, 1592, 1459, 1395, 1150, 1029, 910. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ_P 99.35. ^{1}H NMR (300 MHz; $CDCl_3$): δ_H 1.46 (9H, d, J = 12.9 Hz), 1.92 (8H, qn app.), 3.42 (8H, qn app.). HRMS (E.S.+): Found: 229.1832; $C_{12}H_{26}N_2P$ (MH^+) requires:229.1833.

Methyl(dipyrrolidinyl)phosphine selenide. Anal. Calcd for $C_9H_{19}N_2PSe$: C, 40.76; H, 7.22; N, 10.6. Found: C, 40.87; H, 7.41; N, 11.17%. ^{31}P NMR (121.4 MHz; CD_3) δ_P 65.95 ($J_{P–Se}$ = 735 Hz). ^{1}H NMR (300 MHz; CD_3) δ_H 1.7–1.95 (11H, m), 3.05 (8H, m).

Diisopropyl(pyrrolidinyl)phosphine (10). IR(ν_{max}/cm^{-1}) 2949, 1463, 1379, 1362, 1346, 1194, 1133, 1063, 1004, 876. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ_P 64.82. ^{1}H NMR (300 MHz; $CDCl_3$): δ_H 1.05 (12H, dd, J = 14.0, 7.1 Hz), 1.7 (4H, m), 1.93 (2H, m), 3.0 (4H, m). ^{13}C NMR (75.4 MHz; $CDCl_3$) δ 15.85 (d, J = 7.6 Hz), 22.15 (d, J = 11.9 Hz), 23.2 (d, J = 4.33 Hz), 47.2 (d, J = 10.82). Found: 187.1484: $C_{14}H_{19}NP$ requires: 187.1487.

Di-*tert*-butyl(pyrrolidinyl)phosphine (11). One equivalent of n-butyllithium was added to a cold (−60 °C) THF solution of pyrrolidine. This was allowed to warm to room temperature. The reaction was left stirring for 30 min prior to the addition of di-*tert*-butylchlorophosphine (*via* syringe). This solution was stirred overnight. THF was removed *in vacuo*, and the residue extracted with toluene, filtered under nitrogen (to remove LiCl) and pumped dry under vacuum to give the product as a colourless liquid. IR(ν_{max}/cm^{-1}) 2965, 2868, 1685, 1476, 1389, 1366, 1167, 1072, 1011, 981. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ_P 83.4. ^{1}H NMR (300 MHz; $CDCl_3$): δ_H 1.11 (18H, d, J = 11.8 Hz), 1.68 (4H, m), 3.16 (4H, m). HRMS: Found: 215.1810; $C_{12}H_{26}NP$ requires: 215.1803.

General procedure for the synthesis of *trans*-$L_2Rh(CO)Cl$ complexes

$[Rh(CO)_2Cl]_2$ was added in one portion to a stirred solution of the appropriate phosphine (4.6 equiv.). The rhodium complex rapidly dissolves with evolution of carbon monoxide to give a solution of the desired rhodium complex. For L = phenyl-(dipyrrolidinyl)phosphine size exclusion chromatography was carried out to remove the excess ligand. For L = diethyl-(pyrrolidinyl)phosphine, the rhodium complex (described in ref. 22) proved difficult to isolate due to its sensitivity to air and extreme solubility. For all other ligands, the reaction solution was transferred *via* cannula to another Schlenk flask (this was a convenient method to remove traces of rhodium metal that are sometimes observed at the bottom of the reaction vessel), and had solvent reduced to about 0.2–1 mL *in vacuo*. Hexane or diethyl ether was then added dropwise to precipitate out/crystallise the product. This was collected on a frit in air, and washed with hexane (2 × 3 mL), and then dried *in vacuo* to yield pure product. On some occasions, a second crop of microcrystals could be obtained from the filtrate by repeating the above procedure. Typically yields were 60%.

***trans*-Carbonyl-chloro-bis(phenyl(dipyrrolidinyl)phosphine)-rhodium (7).** Anal. Calcd for $C_{29}H_{42}N_4P_2RhClO{\cdot}0.5\ CH_2Cl_2$: C, 50.23; H, 6.14; N, 7.94. Found: C, 50.35; H, 6.16; N, 7.99%. IR(ν_{max}/cm^{-1}) 2960, 2861, 1949, 1480,1435, 1191, 1100, 1064, 1010. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ_P 88.4 ($J_{P–Rh}$ = 136 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ_H 1.80 (8H, s, br,), 3.10 (8H, m), 7.30 (6H, m, ArH), 7.7 (4H, m, ArH).

***trans*-Carbonyl-chloro-bis(methyl(dipyrrolidinyl)phosphine)-rhodium (8).** Anal. Calcd for $C_{19}H_{38}N_4P_2RhClO{\cdot}0.5CH_2Cl_2$: C, 40.29; H, 6.76; N, 9.64. Found: C, 40.76; H, 7.20; N, 9.87%. IR(ν_{max}/cm^{-1}) 2965, 2857, 1947, 1457, 1349, 1324, 1281, 1261, 1197, 1080, 1014. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ_P 95.2 ($J_{P–Rh}$ = 130 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ_H 1.65 (6H, t, J = 7 Hz), 1.80 (16H, qn app.), 3.10 (16H, m). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 13.9 (t app., $J_{C–P}$ = 21.1 Hz, $J_{C–Rh}$ = 21 Hz,), 25.2 (CH_2), 47.1 (CH_2), CO too weak to observe. MS (E.S.+): Found: 539.1333; (MH^+) requires:539.1342.

***trans*-Carbonyl-chloro-bis(*tert*-butyl(dipyrrolidinyl)phosphine)-rhodium (9).** Anal. Calcd for $C_{25}H_{50}N_4P_2RhClO$: C, 48.20; H, 8.09; N, 9.00. Found: C, 48.24; H, 8.43; N, 8.96%. IR(ν_{max}/cm^{-1}) 2861, 1942, 1637, 1456, 1393, 1361, 1184, 1103, 1060. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ_P 114.1 ($J_{P–Rh}$ = 133 Hz). ^{1}H NMR (300 MHz; $CDCl_3$) δ_H 1.31 (9H, . app., J = 11 Hz), 1.82 (8H, m), 3.30 (8H, m). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ_C 25.2 (CH_2), 27.6 (CH_3), 37.8 (t app., $J_{C–P}$ = 20.1 Hz, $J_{C–Rh}$ = 20 Hz, R_4C), 48.7 (CH_2), 187.1 (dt, $J_{C–P}$ = 15.6, $J_{C–Rh}$ = 77 Hz (Rh–P–CO)). HRMS (E. S.+): Found: 587.2498; $C_{25}H_{50}N_4P_2ORh$ (M − Cl) requires:587.2515.

***trans*-Carbonyl-chloro-bis(diisopropyl(pyrrolidinyl)phosphine)-rhodium (12).** Anal. Calcd. for $C_{21}H_{44}N_2P_2OClRh$: C, 46.63; H, 8.20; N, 5.18. Found: C, 46.80; H, 8.96; N, 5.18%. IR(ν_{max}/cm^{-1}) 2967, 2864, 1954, 1455, 1382, 1361, 1347, 1240, 1118, 1066, 1021, 1009, 879. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ_P 89.4 (d, $J_{P–Rh}$ = 127.6 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ_H 1.3 (24H, m), 1.80 (4H, m), 2.72 (8H, m), 3.36 (8H, m) ^{13}C NMR (75.4 MHz; $CDCl_3$) δ_C 19.3 (d, $J_{C–P}$ = 19.6 Hz), 26.4, 27.2 (dd, $J_{C–P}$ = 13, 13 Hz), 51.0, CO too weak to observe. Found: 541.1748; $C_{21}H_{45}N_2P_2OClRh$ (MH^+) requires:541.1750.

***trans*-Carbonyl-chloro-bis(di-*tert*-butyl(pyrrolidinyl)phosphine)rhodium (13).** Anal. Calcd. for $C_{25}H_{52}P_2N_2OClRh$: C, 50.30; H, 8.78; N, 4.69; Found: C, 49.97; H, 8.78; N, 4.72%. IR(ν_{max}/cm^{-1}) 2952, 2870, 1995, 1956, 1480, 1457, 1388, 1363, 1179, 1119, 1066, 1010, 808. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ_P 103.3 (d, $J_{P–Rh}$ = 134 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ_H 1.55 (36H, dd, J = 6.7, 6.7 Hz), 1.74 (8H, m), 3.50 (8H, m). Found: 597.2363 $C_{25}H_{53}P_2N_2OClRh$ requires: 597.2377.

General procedure for the synthesis of platinum complexes

To a stirred solution of ligands **(3)**–**(5)** (two equiv.) in dichloromethane was added $(COD)PtCl_2$ (one equiv.) in one portion. The resultant solution was stirred for two hours, before the solvent was removed to near dryness. Diethyl ether was then added *via* a syringe to obtain a white precipitate that was collected on a frit and washed with diethyl ether (2 × 5 mL) and hexane (3 × 5 mL). Drying *in vacuo* gave the desired platinum complexes. Recrystallisation by slow diffusion of Et_2O into CH_2Cl_2 solutions of these compounds gave crystals suitable for X-ray analysis.

***cis*-Dichloro-bis(methyl(dipyrrolidinyl)phosphine)platinum(II) (17).** Anal. Calcd for $C_{18}H_{38}N_4P_2Cl_2Pt$: C, 33.86; H, 6.00; N, 8.78. Found: C, 34.23; H, 6.10; N, 8.49%. IR (ν_{max}/cm^{-1}) 2965, 2860, 1449, 1352, 1292, 1195, 1115, 1080, 1008, 876. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ_P 46.4 (J_{P-Pt} = 4232 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ_H 1.73 (6H, d, J = 7 Hz), 1.90 (16H, m), 3.30 (16H, m).

***cis*-Dichloro-bis(phenyl(dipyrrolidinyl)phosphine)platinum(II) (16).** Anal. Calcd for $C_{28}H_{42}P_2N_4PtCl_2$: C, 44.10; H, 5.55; N, 7.35. Found: C, 44.22; H, 5.68; N, 6.79%. IR (ν_{max}/cm^{-1}) 2965, 2870, 1483, 1434, 1349, 1331, 1246, 1190, 1105, 1070, 1009, 918, 866. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ_P 46.1 (J_{P-Pt} = 4358 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ_H 1.90 (16H, m), 3.30 (16H, m), 7.0–7.5 (10H, m).

***cis*-Dichloro-bis(tripyrrolidinylphosphine)platinum(II) (15).** ^{31}P NMR monitoring of a mixture of $(COD)PtCl_2$ and tripyrrolidinephosphine showed a major platinum containing species [δ_p: 40.7 ($^1J_{P-Pt}$ = 4950 Hz)] which we assign as the *cis* compound, (**15**). This formulation is further supported by mass spectrometry of the crude (isolated) product which shows peaks due to MH^+, M − Cl, M − 2Cl$^+$, (M − Cl − pyrrolidine), (M − 2Cl − pyrrolidine), (M − Cl − 2pyrrolidine), (M − 2Cl − 2pyrrolidine) *etc*. IR (ν_{max}/cm^{-1}) 2959, 2864, 1459, 1340, 1240, 1193, 1071, 1009, 916, 871. Recrystallisation only gave a few crystals that were analysed as being pure (**15**) by X-ray crystallography. There was not sufficient pure material for complete analytical characterisation. Fortunately, our primary interest in the synthesis of (**15**) was to determine its crystal structure.

***trans*-Dichloro-bis(*tert*-butyl(dipyrrolidinyl)phosphine)-platinum(II) (18).** A solution of *tert*-butyl(dipyrrolidinyl)-phosphine in CH_2Cl_2 was added dropwise to a solution of $K[PtCl_3(C_2H_4)]$ in acetone. After 30 min, the solvents were removed *in vacuo*, and the residue extracted with CH_2Cl_2 and centrifuged to remove KCl. Removal of solvent from this solution, followed by washing with diethyl ether gave the desired complex in quantitative yield. Anal. Calcd for $C_{24}H_{50}N_4P_2PtCl_2$: C, 39.89; H, 6.97; N, 7.75. Found: C, 40.15; H, 6.82; N, 7.65%. IR (ν_{max}/cm^{-1}) 2964, 2859, 1457, 1394, 1362, 1243, 1185, 1100, 1070, 1011, 994, ν_{Pt-Cl} = 341. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ_P 83.6 (J_{P-Pt} = 2702 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ_H 1.47 (18H, dd., J = 7.6, 7.6 Hz), 1.84 (16H, m), 3.40 (16H, m). HRMS (E. S.+): Found: 722.2608; $C_{24}H_{50}N_4P_2Pt_1Cl_2$ (MH^+) requires 722.2614.

General procedure for the formation of monodentate iron complexes

A Schlenk flask containing a preweighed amount of the desired ligand (1.08 equiv.) was briefly opened under a stream of nitrogen to allow the introduction of $[CpFe(CO)_2]_2$ (3 mol%) and $CpFe(CO)_2I$ (1 equiv.). This flask was then sealed with a rubber septum, evacuated and flushed with nitrogen. Toluene (15 mL) was then added and the flask heated at 90 °C. The reactions were monitored for completion by removal of small aliquots by syringe and analysing by solution IR spectroscopy. The reactions are cooled and filtered through a sinter (briefly in air) to collect the ionic product (which is pure by NMR spectroscopy), and a dark green/brown solution. Solvent is reduced to dryness and the dark powder is dissolved in the minimum volume of dichloromethane and added to an alumina column that was then eluted with toluene until a green band containing the pure product is collected. We have found that it is acceptable to carry out this chromatography in air using normal solvents, despite the fact that the iron complexes do slowly decompose in solution when left exposed to the air for several hours. Yields are unoptimised.

Carbonyl-cyclopentadienyl-iodo-(tripyrrolidinylphosphine)iron (19). Yield: 120 mg, 0.232 mmol, 14.3%. Anal. Calcd for $C_{18}H_{29}N_3PFeIO$: C, 41.80; H, 5.65; N, 8.12. Found: C, 41.33; H, 5.85; N, 7.70%. IR (ν_{CO} = 1941 cm^{-1}). ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 136.7. ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.90 (12H, s, br), 3.1 (12H, m), 4.65 (5H, s, br). HRMS (E. S.+): Found: 518.0520; $C_{28}H_{30}N_3P_1O_1Fe_1I_1$ (MH^+) requires 518.0520.

The unpurified by-product separated from the reaction mixture can be identified as dicarbonyl-cyclopentadienyl-(tripyrrolidinylphosphine)iron iodide (**20**). Yield: 460 mg, 0.844 mmol, 52%. IR (ν_{CO} = 1991, 2036 cm^{-1}). ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 117.6. ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.96 (12H, s, br), 3.2 (12H, m), 5.53 (5H, s, br). HRMS (E. S.+): Found: 418.1353; $C_{19}H_{29}N_3P_1O_2Fe_1$ (M − I$^+$) requires 418.1347.

Carbonyl-cyclopentadienyl-iodo-(phenyl(dipyrrolidinyl)phosphine)iron (21). Yield: 250 mg, 0.477 mmol, 38.5%. Anal. Calcd for $C_{20}H_{26}N_2PFeIO$: C, 45.83; H, 5.00; N, 5.34. Found: C, 45.78; H, 4.96; N, 4.97%. IR (ν_{CO} = 1942 cm^{-1}). ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 125.1. ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.80 (8H, s, br), 2.8–3.4 (8H, m), 4.15 (5H, s, br), 7.3–7.8 (5H, m, ArH). HRMS (E. S.+): Found: 525.0246; $C_{20}H_{27}N_2POFeI$ (MH^+) requires 525.0255.

The unpurified by-product separated from the reaction mixture can be identified as dicarbonyl-cyclopentadienyl-(phenyl(dipyrrolidinyl)phosphine)iron iodide (**22**). Yield: 70 mg, 0.127 mmol, 10.2%. IR (ν_{CO} = 1992, 2037 cm^{-1}). ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 111.1. ^{1}H NMR (300 MHz; $CDCl_3$): δ 2.0 (8H, s, br), 2.9–3.3 (8H, m), 5.2 (5H, s, br), 7.5–7.7 (5H, m, ArH). HRMS (E. S.+): Found: 425.1080; $C_{21}H_{27}N_2P_1O_2Fe_1$ (M − I$^+$) requires 425.1081.

Iron complexes derived from $[CpFe(CO)_2(MeCN)]BF_4$

$[CpFe(CO)_2(MeCN)]BF_4$, (70.4 mg, 0.231 mmol, 1 equiv.) and phenyl(dipyrrolidinyl)phosphine (0.149 g, 0.600 mmol, 2.6 equiv.) were refluxed in dichloromethane for 2 hours. Solvent was then reduced to *ca*. 0.5 mL prior to the addition of diethyl ether (5 mL) which gave a beige precipitate. This was collected (in air) by filtration and washed with Et_2O (3 × 5 mL) and hexane (3 × 5 mL) which removed any traces of MeCN and free ligand. Yields are essentially quantitative.

Dicarbonyl-cyclopentadienyl-(tripyrrolidinylphosphine)iron tetrafluoroborate (23). Anal. Calcd for $C_{19}H_{29}N_3PFeO_2BF_4$ C, 45.18; H, 5.79; N, 8.32. Found: C, 45.26; H, 5.99; N, 8.82%. IR (ν_{CO} = 2071, 2027 cm^{-1}). ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 118.0. ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.8 (12H, s, br), 3.0 (12H, s, br), 5.4 (5H, s, br).

Dicarbonyl-cyclopentadienyl-(phenyl(dipyrrolidinyl)phosphine)iron tetrafluoroborate (24). Anal. Calcd for $C_{21}H_{26}N_2PFeO_2BF_4 \cdot 0.5CH_2Cl_2$ C, 49.42; H, 5.21; N, 5.36. Found: C, 49.19; H, 5.34; N, 5.54%. IR (ν_{CO} = 2042, 2011 cm^{-1}). ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 111.5. ^{1}H NMR (300 MHz; $CDCl_3$): δ 2.0 (8H, s, br), 3.0 (8H, s, br), 5.0 (5H, s,), 7.2–7.6 (5H, m).

X-Ray crystallography

The experimental details for (**15**) and (**17**) have already been reported (CCDC reference numbers 152757 and 152758).[12] Crystal structures were obtained using a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data were collected using 0.3 or 0.15° width ω steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures. All data were corrected for Lorentz, polarisation and long term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections. Structures were solved by direct methods and refined by full-matrix least squares against F^2 (SHELXTL).[16]

Table 1 Crystal data for compounds (**13**), (**14**), (**16**) and (**24**)

	(**13**)	(**14**)	(**16**)	(**24**)
Empirical formula	$C_{25}H_{52}ClN_2OP_2Rh$	$C_{37}H_{66}ClOP_2Rh$	$C_{28}H_{42}Cl_2N_4P_2Pt$	$C_{21}H_{26}BF_4FeN_2O_2P$
M	596.99	727.20	762.59	512.07
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P1$	$P\bar{1}$	$P2_1/n$
a/Å	26.7010(8)	9.9574(1)	9.8077(1)	11.6620(2)
b/Å	15.1617(5)	10.2575(1)	10.4935(3)	14.6306(1)
c/Å	24.5230(3)	10.8125(1)	16.7513(5)	13.7467(3)
α/°	90	113.782(1)	94.161(2)	90
β/°	116.033(1)	109.177(1)	101.821(2)	97.238(1)
γ/°	90	90.819(1)	116.604(1)	90
U/Å	8920.5(4)	940.65(2)	1481.95(6)	2326.80(7)
Z	12	1	2	4
μ/mm^{-1}	0.791	0.636	5.048	0.769
Reflections measured	22067	5922	6547	10002
Independent reflections	6403	5012	4236	3349
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0366 0.0752	0.0250 0.0582	0.0406 0.0842	0.0408 0.0969

The data for (**14**) were examined in some detail because of the possibility of space group ambiguity. There are no systematic absences to help distinguish between $P1$ and $P\bar{1}$ but the intensity statistics clearly indicate a non-centrosymmetric space group [mean $|E \times E^{-1}| = 0.741$, for centrosymmetric space groups 0.968 is expected, for non-centrosymmetric 0.736 is expected], refinements were also attempted in both $P1$ and $P\bar{1}$ to ascertain if a disordered centrosymmetric model could give a better fit. The refinement as reported gave the most satisfactory results. Details of data collection and crystal refinement are summarised in Table 1.

CCDC reference numbers 171245–171248.

See http://www.rsc.org/suppdata/dt/b1/b108467d/ for crystallographic data in CIF or other electronic format.

Molecular modelling/cone angle measurements

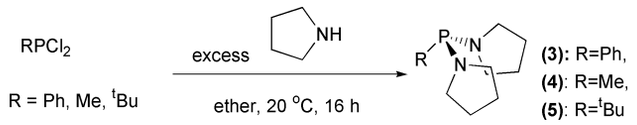
PC Spartan Pro (Wavefunction Inc., CA; www.wavefun.com) was used to calculate the cone angles using molecular mechanics minimisation of a phosphine. Then the half angles were measured using the program's measure angle function and selecting the three relevant angles (making sure the metal atom is set 2.28 Å from the P atom).

The Chemical Database Service search engine ConQuest was used to determine values of real angles. It was attempted, wherever possible, to measure the cone angle from a simple nickel complex or the sulfide of the phosphine, so as to avoid counter-ligand steric effects.

Results

a: Phosphine synthesis

The amino-phosphines described in this study were prepared by the addition of an excess of pyrrolidine to the appropriate phosphine dichloride (see Scheme 1, pyrrolidine was chosen as it is a very basic secondary amine).

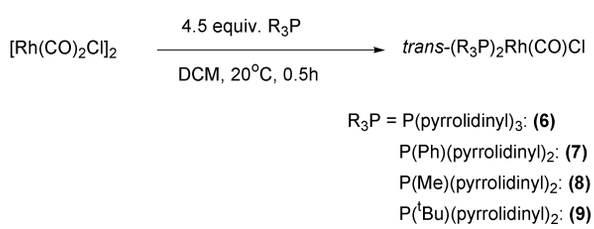


Scheme 1

P–N bond formation, which has been studied extensively in these laboratories[17] is generally facile, high yielding and gives products of high purity, providing air and moisture are absent during the reaction. ^{31}P and ^{1}H NMR of the air and moisture sensitive phosphine products showed them to be essentially pure, and they were therefore purified no further. The ligands are all liquids and stable for considerable periods of time if kept under an atmosphere of dry nitrogen. In an attempt to prepare a crystalline derivative of methyl(dipyrrolidinyl)phosphine, (**4**) was also characterised by its quantitative conversion to its selenide. This compound which is also a liquid, shows the expected selenium satellites in its phosphorus NMR spectrum. The magnitude of $^{1}J_{P=Se}$ (735 Hz) is significantly smaller than in tris(dialkylamino)phosphines. This is in line with previous studies which have shown that this coupling constant is smaller for alkylphosphines ($Me_3P{=}Se$, $^{1}J_{P=Se}$ = 648 Hz; $(Me_2N)_3P{=}Se$, $^{1}J_{P=Se}$ = 795 Hz) than in nitrogen substituted phosphines.[18]

b: Electronic properties of new phosphino-amines

Molloy and Petersen[3] prepared tris(*N*-pyrrolyl)phosphine which has exceptional π-acceptor character. This is due to the stabilisation of any negative charge accepted from the metal on nitrogen by an aromatic resonance structure in this ligand. They also prepared tris(*N*-pyrrolidinyl)phosphine as a comparison and showed this ligand to be a very electron rich phosphine. The method they used to gauge the electronic characteristics of their ligands was measurement of ν_{CO} in the infrared spectrum of the *trans*-$(R_3P)_2Rh(CO)Cl$ complexes. These are readily formed in high purity from $[Rh(CO)_2Cl]_2$ and an excess of ligand (Scheme 2).



Scheme 2

Vastag and co-workers have shown that a good correlation exists between the value of ν(CO) in $L_2Rh(CO)Cl$ and $Ni(CO)_3(L)$.[19] The position of ν_{CO} in the easily prepared rhodium complexes is known for a huge variety of phosphines, and is always in agreement with the expected donor strength of the phosphine. By way of ensuring the accuracy and validity of our values, we have reprepared *trans*-$(R_3P)_2Rh(CO)Cl$ complexes of tris(*N*-pyrrolidinyl)phosphine, Ph_3P, and Cy_3P. The values quoted in Table 2 are those found on our spectrometer (literature values are in parentheses). The rhodium complexes formed in the *in situ* IR experiments can be isolated by size exclusion chromatography (to remove the excess ligand) and/or by precipitation of very concentrated CH_2Cl_2 solutions with hexane. However, it was not possible to grow good quality crystals of (**6**) to (**9**) for X-ray analysis. The complexes all show

Table 2 Comparison of ν_{CO} of *trans*-$L_2Rh(CO)Cl$ complexes for pyrrolidine based ligands with other phosphines

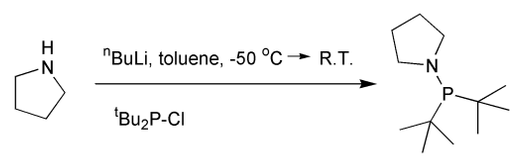
Entry	L	ν_{CO} [a] [$L_2Rh(CO)Cl$]	Ref.	Tolman cone angle [b]/°
1	$(PhO)_3P$	(2016)	3	128
2	$(p\text{-}CF_3C_6H_4)_3P$	(1990)	3	145
3	Ph_3P	1965 (1966)	3 [c]	145
4	$PhMe_2P$	(1965)	21	122
5	Me_3P	(1960)	3	118
6	Et_3P	(1956)	19	132
7	Cy_3P	1943 (1942)	22 [c]	170
8	$^tBu_3P$	— [e]	—	182
9	$P(N(CH_3)_2)_3$	(1959)	3	—
10	(**2**)	1951 (1952)	3 [c, d]	145
11	(**3**)	1949	[c, d]	145
12	(**4**)	1947	[c, d]	136
13	(**5**)	1942	[c, d]	157
14	(**12**)	1954	[c, d]	155
15	(**13**)	1955	[c, d]	170

[a] To ensure the accuracy and validity of our values, we have reprepared *trans*-$(R_3P)_2Rh(CO)Cl$ complexes of tris(*N*-pyrrolidinyl)phosphine, Ph_3P, and Cy_3P. The values quoted are those found on our spectrometer (literature values are in parentheses). [b] Cone angle taken from ref. 1 and 2, and in the case of the new ligands estimated assuming similar steric influence for phenyl and pyrollidinyl. [c] IR spectra recorded as KBr discs. [d] This work. [e] Tetrahedral rhodium complex, so cannot be compared

the expected doublets in their ^{31}P NMR spectra ($^1J_{P-Rh}$ between 128 and 136 Hz). The ^{13}C NMR spectra of these complexes generally did not show the (very weak) carbonyl resonance. However, in the case of complex (**9**), the spectrum was acquired overnight to reveal the expected doublet of triplets that arises by coupling of the carbonyl ligand to phosphorus and rhodium. As can be seen from Table 2, the position of ν_{CO} for $PhMe_2P$ is, as expected, in between electron rich Me_3P and the less basic Ph_3P. Phenylbis(*N*-pyrrolidinyl)phosphine, however, has ν_{CO} at lower wavenumber than tris(*N*-pyrrolidinyl)phosphine, and therefore can be assumed to be a more electron rich ligand. This is evidence (along with the properties of methylbis(*N*-pyrrolidinyl)phosphine and *tert*-butylbis(*N*-pyrrolidinyl)phosphine) that only two pyrrolidinyl groups can contribute towards the strong donor strength of (*N*-pyrrolidinyl)phosphines. The values of ν_{CO} for (**4**) and (**5**) are significantly lower than those of most other highly electron rich alkylphosphines (compare entries 12 and 13 to entries 5 and 6) which are often used in catalysis. Tri-*tert*-butylphosphine, which is generally thought of as the most electron donating phosphine actually forms a tetrahedral $(R_3P)_2Rh(CO)Cl$ complex and cannot be directly compared.[20]

The new ligands may be of particular use as they deliver a donor strength that is normally reserved for very bulky ligands (defined by their large cone angle). The cone angles of the three new ligands can readily be estimated as Molloy and Petersen have already shown that a pyrrolidinyl group has a similar steric effect to a phenyl group.[3] It follows that the cone angle of methyl(dipyrrolidinyl)phosphine is the same as (or similar to) $MePh_2P$ (136°). The cone angles of (**2**) and (**3**) are 145°. It can be seen from Table 2 that triethylphosphine and (**4**) have approximately similar steric properties, yet the new ligand is a considerably stronger donor ligand. It is known that a phosphine with a small cone angle and strong donating power will bind very tightly to a metal centre and stabilise organometallic compounds with respect to reductive elimination.[23] Ligand (**4**) can therefore be expected to be applied with success in organometallic chemistry and catalysis. Ligand (**5**) *tert*-butyl(dipyrrolidinyl)phosphine is actually a fairly bulky ligand, but given that is perhaps even more strongly electron donating than Cy_3P and somewhat smaller, it again delivers a different combination of steric and electronic effects to existing ligands, and promises to find application in transition metal chemistry and catalysis.

We have also prepared two dialkyl(pyrrolidinyl)phosphines. Ligand (**10**) is readily prepared by the addition of an excess of pyrrolidine to $^iPr_2PCl$. Pyrrolidine does not react with $^tBu_2PCl$ even at elevated temperatures or using stronger bases such as DMAP (4-dimethylaminopyridine) to promote the reaction. Since pyrrolidine is a particularly nucleophilic amine, it seems likely that it will prove impossible to prepare $^tBu_2P$ substituted amines under the standard mild conditions that are generally used throughout this work. The desired phosphine [(**11**)] could be prepared if pyrrolidine is first deprotonated with ^{n}BuLi prior to addition of $^tBu_2PCl$ (Scheme 3).



(**11**)

Scheme 3

Complexes of the type *trans*-$L_2Rh(CO)Cl$ could be readily prepared by standard methods. The electronic properties of these dialkyl(pyrrolidinyl)phosphines are also somewhat surprising. We expected ν(CO) for the rhodium complexes of diisopropyl(pyrrolidinyl)phosphine (**10**) and di-*tert*-butylpyrrolidinylphosphine (**11**) to be at around 1940–1947 cm^{-1}. This would represent a composite of the known electronic properties of each of the two groups. In actual fact, they represent significantly less strong donor ligands than could be expected (Table 2, entries 14 and 15). We propose that this may be due to the steric bulk of these phosphines preventing the nitrogen substituents from adopting an orientation that allows them to interact strongly with the phosphorus atom.[24] These results provide us with a useful lead in our ongoing work on catalysis of the Suzuki reaction of aryl chlorides.[25] We have at this stage prepared hemi-labile, weakly chelating ligands derived from $^iPr_2PCl$ and Cy_2PCl. The ligands do make effective catalysts, but were found to be less electron rich than we might have hoped. Given that a strongly electron donating phosphine is likely to be desirable in this reaction, our future work will utilise *tert*-butyldiaminophosphines as a hemilabile ligand. These investigations will be reported in due course.

Using the reported correlation between ν(CO) of $L_2Rh(CO)Cl$ and $Ni(CO)_3(L)$ complexes, a rough estimate of the values of ν(CO) in the extremely toxic nickel complexes can be made. These values clearly place *tert*-butyl(dipyrrolidine)phosphine as one of the most strongly electron donating phosphines known.[26] Tolman used the values of ν(CO) in $Ni(CO)_3(L)$ compounds to estimate a single substituent parameter χ, to describe the contribution of a substituent, R to the overall basicity of the phosphine $R^1R^2R^3P$.[1] It is obvious that a substituent

parameter cannot be assigned to a pyrrolidine group, as it will vary depending on the other substituents on phosphorus. We suspect that the variability in donor strength of pyrrolidine phosphines carries through to other phosphino-amines as other phosphino-amines show similar structural features to those reported and analysed here.

c: X-Ray crystal structures of rhodium complexes

Recrystallisation of complex (**13**), by cooling a hexane/CH_2Cl_2 solution overnight gave crystals suitable for an X-ray crystal structure determination. The molecular structure of (**13**) is shown in Fig. 2 with selected bond lengths and angles in Table

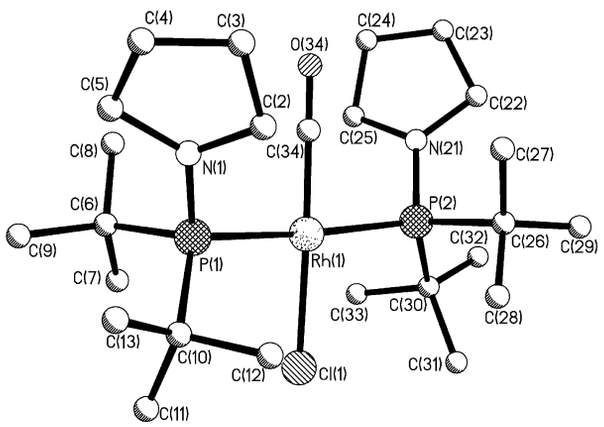


Fig. 2 Molecular structure of (**13**).

3. There are one and a half independent molecules in the unit cell, one of which lies about a crystallographic two-fold axis. The rhodium centre is square planar with little deviation from idealised geometry. A comparison of our data with that collated by Molloy and Petersen [Rh–C bond lengths in the range 1.77(1)–1.845(15) Å, Rh–P bonds in the range 2.282(4)–2.428(1) Å, and Rh–Cl bond lengths in the range 2.350(4)–2.479(1) Å] is perhaps of interest. They found that the very electron poor phosphine, tripyrollylphosphine gave very short Rh–P and Rh–Cl distances, with an elongated Rh–C bond. This is readily rationalised by considering back bonding within the π-acceptor and π-donor ligands. Ligand (**11**) behaves as a bulky, moderately electron rich ligand. The Rh–P bond lengths are amongst the longest reported for these types of complex (av. 2.374(1) Å), whereas the Rh–C bonds are relatively short (av. 1.791(7) Å). It is to be expected that a weaker Rh–P interaction should strengthen the metal–carbonyl bond. The Rh–Cl bond lengths are fairly typical for these types of complex. The P–N bonds within the structure are planar, but are completely asymmetrical with respect to the geometry about the N atom. In particular, the carbon nearest the bulky *tert*-butyl groups is severely bent away to minimise repulsive interaction between these groups (mean C–N–P angle = 129.2(3)°). This effect is not seen in the other three structures reported in this paper, and we tentatively suggest that it is the inability of the nitrogen atom to adopt a more symmetrical geometry that weakens the N⟶P donor interaction and therefore reduces the donor strength of this ligand. The P–N bond lengths are not exceptional, but are, nevertheless longer than those found on planar nitrogens in the other three structures reported here (Tables 4, 5, and 6).

It was mentioned in the discussion of the IR data that tri-*tert*-butylphosphine forms a tetrahedral rhodium complex of type $Rh(L)_2(CO)Cl$, as verified by X-ray crystallography.[20] Tricyclohexylphosphine is thought to be nearly as bulky as tri-*tert*-butylphosphine, so it was not clear whether the complex *trans*-$(Cy_3P)_2Rh(CO)Cl$ (**14**) contained some distortion away from the square planar geometry expected. It was therefore of interest to determine its structure by X-ray crystallography.

Table 3 Selected bond lengths (Å) and angles (°) for (**13**), the values for the second independent molecule are not significantly different

Rh(1)–P(1)	2.370(1)	P(1)–N(1)	1.681(4)
Rh(1)–P(2)	2.375(1)	P(2)–N(41)	1.691(4)
Rh(1)–Cl(1)	2.378(1)	P(2)–N(21)	1.684(3)
Rh(1)–C(34)	1.793(5)	C(34)–O(34)	1.111(5)
Rh(2)–C(54)	1.789(7)		
P(1)–Rh(1)–Cl(1)	92.62(4)	P(2)–Rh(1)–Cl(1)	92.43(4)
P(2)–Rh(1)–Cl(1)	92.43(4)	P(1)–Rh(1)–Cl(1)	92.62(4)
P(1)–Rh(1)–P(2)	173.43(4)	C(2)–N(1)–C(5)	106.8(4)
C(34)–Rh(1)–P(1)	87.9(1)	C(5)–N(1)–P(1)	128.6(3)
C(34)–Rh(1)–P(2)	87.3(1)	C(2)–N(1)–P(1)	121.6(3)
C(25)–N(21)–P(2)	121.4(3)	C(25)–N(21)–C(22)	106.6(3)
C(22)–N(21)–P(2)	129.9(3)		

Table 4 Selected bond lengths (Å) and angles (°) for (**14**)

Rh(1)–P(1)	2.352(3)	Rh(1)–Cl(1)	2.422(4)
Rh(1)–P(2)	2.358(3)	Rh(1)–C(37)	1.93(1)
P(1)–Rh(1)–Cl(1)	91.0(1)	C(37)–Rh(1)–P(1)	89.1(3)
P(2)–Rh(1)–Cl(1)	88.6(1)	C(37)–Rh(1)–P(2)	91.2(3)

Table 5 Selected bond lengths (Å) and angles (°) for (**15**)

Pt(1)–P(1)	2.270(3)	P(1)–N(6)	1.72(1)
Pt(1)–P(2)	2.246(3)	P(1)–N(11)	1.64(1)
Pt(1)–Cl(1)	2.398(3)	P(2)–N(16)	1.66(1)
Pt(1)–Cl(2)	2.371(3)	P(2)–N(21)	1.68(1)
P(1)–N(1)	1.63(1)	P(2)–N(26)	1.678(9)
P(1)–Pt(1)–Cl(1)	86.3(1)	C(15)–N(11)–C(12)	110(1)
P(2)–Pt(1)–Cl(2)	90.4(1)	C(12)–N(11)–P(1)	124.4(9)
Cl(2)–Pt(1)–Cl(1)	85.1(1)	C(15)–N(11)–P(1)	123(1)
P(1)–Pt(1)–P(2)	98.2(1)	C(20)–N(16)–C(17)	110(1)
P(1)–Pt(1)–Cl(2)	170.9(1)	C(17)–N(16)–P(2)	123(1)
P(2)–Pt(1)–Cl(1)	175.4(1)	C(20)–N(16)–P(2)	123.9(8)
C(2)–N(1)–C(5)	107(1)	C(25)–N(21)–C(22)	110(1)
C(5)–N(1)–P(1)	126.4(8)	C(25)–N(21)–P(2)	126(1)
C(2)–N(1)–P(1)	125.5(9)	C(22)–N(21)–P(2)	119(1)
C(7)–N(6)–P(1)	124.7(10)	C(27)–N(26)–P(2)	124.4(8)
C(7)–N(6)–C(10)	111.9(10)	C(27)–N(26)–C(30)	110.7(7)
C(10)–N(6)–P(1)	121.6(10)	C(30)–N(26)–P(2)	122.6(7)

Crystals were grown easily by slow diffusion of Et_2O into a CH_2Cl_2 solution of *trans*-$(Cy_3P)_2Rh(CO)Cl$. The molecular structure (shown in Fig. 3) shows the rhodium centre to be

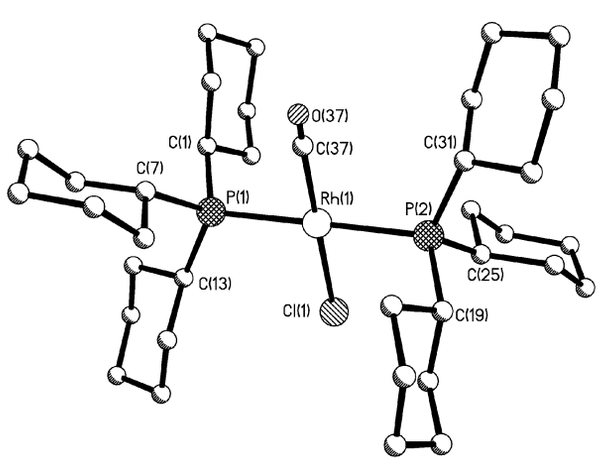


Fig. 3 Molecular structure of $Cy_3P_2Rh(CO)Cl$ (**14**).

square planar with little deviation from square planar geometry. The bond lengths around the metal centre are somewhat anomalous, with very long Rh–P, Rh–Cl and Rh–C bond lengths (Table 4). The Rh–C bond (1.93(1) Å) is especially surprising, as it would be expected that an electron rich ligand that does not form a particularly strong Rh–P bond would lead to strong π-back bonding to the carbonyl ligand. We interpret

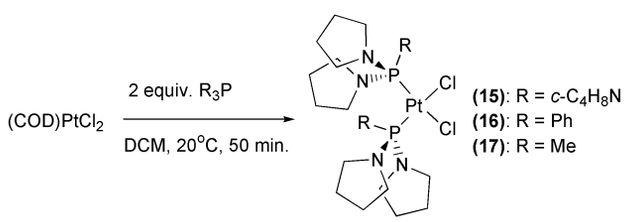
Table 6 Selected bond lengths (Å) and angles (°) for (**17**). There are two independent molecules. The related values for the second independent molecule are given in square brackets

Pt(1)–P(1)	2.226(2) [2.246(2)]	P(1)–N(1)	1.652(7) [1.690(7)]
Pt(1)–P(2)	2.255(2) [2.229(2)]	P(1)–N(6)	1.675(7) [1.627(7)]
Pt(1)–Cl(1)	2.372(2) [2.375(2)]	P(2)–N(11)	1.643(6) [1.692(7)]
Pt(1)–Cl(2)	2.391(2) [2.370(2)]	P(2)–N(16)	1.676(6) [1.651(7)]
P(1)–Pt(1)–Cl(1)	91.32(8)8 [88.49(8)]	C(15)–N(11)–C(12)	109.9(7) [110.3(7)]
P(2)–Pt(1)–Cl(2)	89.32(8) [91.00(9)]	C(12)–N(11)–P(2)	124.3(5) [120.6(6)]
Cl(2)–Pt(1)–Cl(1)	86.14(8) [91.00(9)]	C(15)–N(11)–P(2)	125.3(6) [120.9(6)]
P(1)–Pt(1)–P(2)	93.37(7) [93.90(8)]	C(20)–N(16)–C(17)	110.9(6) [110.0(8)]
C(2)–N(1)–C(5)	109.8(6) [110.3(7)]	C(17)–N(16)–P(2)	118.3(5) [121.2(6)]
C(5)–N(1)–P(1)	124.4 (5) [120.3(6)]	C(20)–N(16)–P(2)	124.3(6) [125.2(7)]
C(7)–N(6)–C(10)	110.7(7) [109.7(6)]	C(2)–N(1)–P(1)	122.4(5) [123.4(6)]
C(10)–N(6)–P(1)	122.3 (6) [123.9(6)]	C(7)–N(6)–P(1)	120.3(5) [125.9(5)]

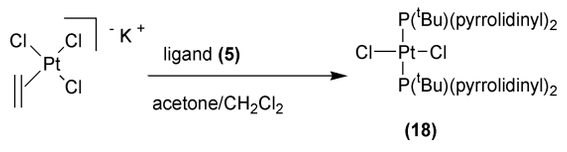
this data with caution as chloride and carbonyl ligands have been found to be disordered in these types of complexes.[27]

d: Platinum complexes of pyrrolidinylphosphines

We have also characterised the dichloroplatinum complexes, $(R_3P)_2PtCl_2$, of the four *N*-pyrrolidinylphosphines (**15**) to (**18**). These are formed quantitatively from $(COD)PtCl_2$ and two equivalents of phosphines (**3**) and (**4**) (Scheme 4). These compounds all show the expected singlets with platinum satellites typical of these compounds. The sizes of $^1J_{P-Pt}$ reflect the smaller coupling constants observed when phenyl groups are compared to alkyl groups, and the larger constants typical of compounds that contain either P–N or P–O bonds. Tris-(pyrrolidinyl)phosphine (**2**), does not react so cleanly with $(COD)PtCl_2$. However, (**15**) is the major Pt complex formed (^{31}P NMR monitoring), and a few good quality crystals of this compound could be obtained from CH_2Cl_2/Et_2O (slow diffusion). Bulky electron rich ligands do not react with $(COD)PtCl_2$ in such a straightforward way as smaller or less basic ligands. Ligand (**2**) appears to be an intermediate case. *tert*-Butyl(dipyrrolidine)phosphine does not react with $(COD)PtCl_2$ to give the desired product. (An unidentified, unstable mixture of products is formed.) A complex, (**18**) of *trans* geometry can be readily obtained from Zeises salt (Scheme 5).



Scheme 4



Scheme 5

We have been successful in obtaining the crystal structure of three of the complexes by X-ray diffraction. The molecular structures of tris(*N*-pyrrolidinyl)phosphine- (**15**), methylbis(*N*-pyrrolidinyl)phosphine- (**17**) and phenylbis(*N*-pyrrolidinyl)-phosphine-dichloroplatinum(II) (**16**) are shown in Figs 4, 5 and 6 respectively. Selected bond lengths and angles can be found in Tables 5, 6 and 7. The crystal structures of (**15**) and (**17**) have been described in our preliminary communication,[12] so are only briefly discussed here.

A feature observed in all three solid state structures is an asymmetry regarding the Pt–P and Pt–Cl bond lengths. Thus

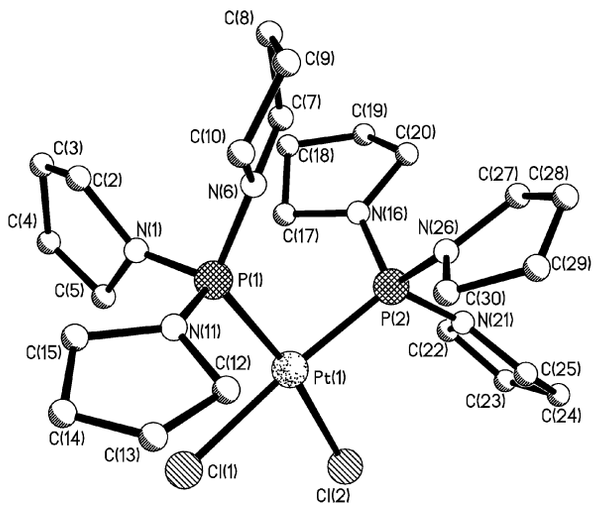


Fig. 4 Molecular structure of (**15**).

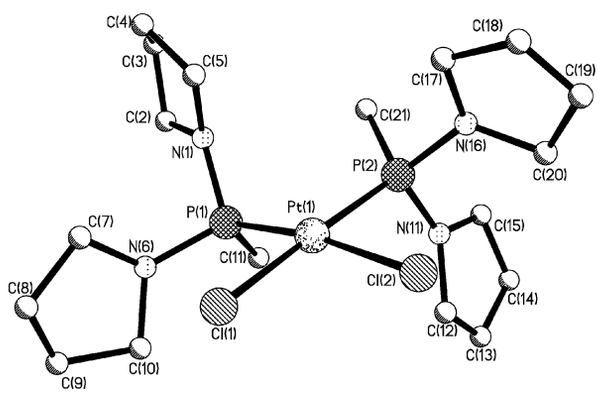


Fig. 5 Molecular structure of (**17**).

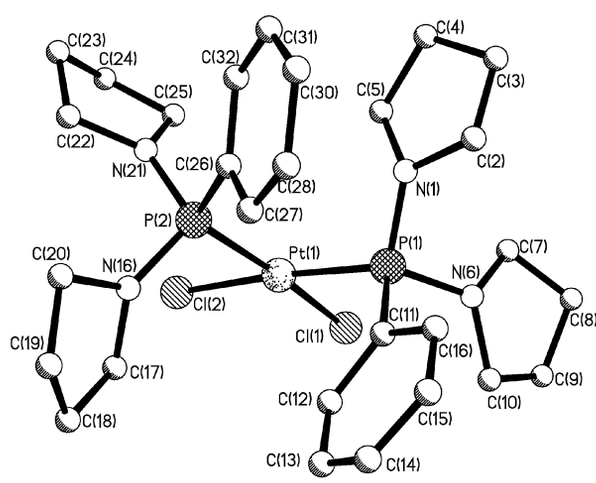


Fig. 6 Molecular structure of (**16**).

Table 7 Selected bond lengths (Å) and angles (°) for (**16**)

Pt(1)–P(1)	2.252(2)	P(1)–N(1)	1.667(6)
Pt(1)–P(2)	2.268(2)	P(1)–N(6)	1.678(7)
Pt(1)–Cl(1)	2.351(2)	P(2)–N(16)	1.652(7)
Pt(1)–Cl(2)	2.393(2)	P(2)–N(21)	1.673(7)
P(1)–Pt(1)–Cl(1)	90.40(8)	C(20)–N(16)–C(17)	106.6(7)
P(2)–Pt(1)–Cl(2)	87.44(8)	C(17)–N(16)–P(2)	126.6(6)
Cl(2)–Pt(1)–Cl(1)	85.77(8)	C(20)–N(16)–P(2)	126.3(6)
P(1)–Pt(1)–P(2)	96.39(8)	C(25)–N(21)–C(22)	110.9(6)
P(1)–Pt(1)–Cl(2)	175.41(8)	C(25)–N(21)–P(2)	125.9(6)
P(2)–Pt(1)–Cl(1)	173.21(8)	C(22)–N(21)–P(2)	123.2(6)
C(2)–N(1)–C(5)	109.7(6)	C(7)–N(6)–P(1)	120.9(5)
C(5)–N(1)–P(1)	119.8(5)	C(7)–N(6)–C(10)	109.6(6)
C(2)–N(1)–P(1)	125.5(5)	C(10)–N(6)–P(1)	122.0(5)

one of the phosphorus–platinum bonds is *ca*.0.02 Å longer than the other [*e.g*. Pt(1)–P(1) = 2.270(3)Å, Pt(1)–P(2) = 2.246(3) Å in (**15**)]. The elongation of one of the Pt–P bonds also results (in all three structures) in a shortening of the Pt–Cl bond *trans* to it, undoubtedly due to the *trans* influence [*e.g*. Pt(1)–Cl(1) = 2.398(3) Å, Pt(1)–Cl(2) = 2.371(3) Å in (**15**)]. This type of solid state effect has been observed in the crystal structures of some other $(R_3P)_2PtCl_2$ complexes. A study by Nelson and co-workers showed that this difference in bond length is reflected in the solid state ^{31}P NMR spectra of such molecules.[28]

A particularly interesting part of structure (**15**) concerns the P–N bond lengths and angles. The sum of angles around each nitrogen was similar (356–360°) and planar. The P–N bond lengths do not show any particular pattern. This was unexpected as the X-ray structure of *trans*-carbonyl-chlorobis(tripyrrolidinylphosphine)rhodium shows two of the pyrrolidine rings to have planar N atoms (sum of angles around nitrogen = 354 to 360°), and one tetragronally distorted N atom (sum of angles around nitrogen = 347, 350°) with a 0.02 Å longer P–N bond length (av. 1.667(3) Å *vs*. 1.688(3) Å). There have been several other crystal structure studies of tris(dialkylamino)phosphines such as tris(*N*-piperidinyl)phosphine, tris(*N*-morpholino)phosphine and the selenides, sulfides, and transition metal complexes of related phosphines.[11] Each of these structures shows two planar nitrogens and one more tetrahedral nitrogen. We were therefore surprised to find the crystal structure of (**15**) not showing this phenomenon. Husebye and co-workers have alerted us to a similar structural effect observed in their tellurium complexes derived from tris(dimethylamino)phosphine selenides.[29]

The crystal structure of (**17**) shows a similar co-ordination environment to complex (**15**), but with some differences that may reflect the smaller size (and stronger donor power) that we anticipated for ligand (**4**). The Pt–P bond lengths are *ca*. 0.02 Å shorter in complex (**17**) (average 2.239(2) Å *vs*. 2.258(3) Å). This is an indication that this phosphine may be binding to the platinum more strongly than tripyrrolidinylphosphine. In the crystal structures of other *cis*-bisphosphine platinum dichloride complexes, it appears that the Pt–P bond length is dominated by the steric bulk of the phosphine ligands. Hence, in $(Cy_3P)_2PtCl_2$, particularly long (av. 2.294(4) Å) Pt–P bonds are observed,[30] whereas the complexes of the small cone angle ligands, Me_3P and PF_3 show particularly short bond lengths (2.243(10) and 2.142(3) Å respectively).[31] It is therefore likely that the smaller size of methyl(dipyrrolidinyl)phosphine with respect to tripyrrolidinylphosphine is responsible for the shorter bond lengths observed. The angle P(1)–Pt(1)–P(2) between the phosphines is considerably smaller than in complex (**15**) (93.90(8)°, 93.37(7)° *vs*. 98.2(1)°), and is also consistent with ligand (**4**) being less sterically demanding than (**2**).

The crystal structure of (**16**) is broadly similar to (**15**). The angle between the phosphine ligands (P(1)–Pt(1)–P(2) = 96.39(8) Å, see Table 7) is slightly smaller than that found in the tripyrrolidinylphosphine structure. This may be a result of the phenyl groups within the structure adopting an eclipsed confirmation in which repulsive interactions are kept to a minimum. (It is probably easier to pack two rigid hexagons in an eclipsed face/edge conformation than a non planar ring with sp^3 hybridised carbon atoms.) The nitrogen atoms within this structure are all approximately planar (355, 352.5, 359.5, 360°).

Table 8 Data used for Fig. 7

Phosphine	Tolman angle/°	Spartan calculated angle/°	Actual crystallographic angle/°
PH_3	87	51.76	45.43
PH_2Ph	101	69.55	61.88
PF_3	104	55.74	49.73
$P(OMe)_3$	107	115.20	98.27
$P(OEt)_3$	109	112.11	96.57
PMe_3	118	84.16	88.12
PMe_2Ph	122	96.75	109.38
PCl_3	124	61.70	52.73
$PHPh_2$	128	103.39	87.03
$P(OMe)Ph_2$	132	126.17	120.73
PEt_3	132	124.30	104.10
$P(OEt)Ph_2$	133	135.12	114.75
PEt_2Ph	136	124.19	132.67
$P(CF_3)_3$	137	87.86	83.49
$PEtPh_2$	140	113.34	124.30
$P(O\text{-}o\text{-}Tol)_3$	141	164.00	135.20
$PPh_2{}^tBu$	142	130.89	127.62
PPh_3	145	130.25	130.87
$P(NMe_2)_3$	154	131.30	129.17

The crystal structure of (**15**) reveals different structural features to the other crystal structure studies of tris(dialkylamino)phosphines. This may suggest that the bonding observed in these compounds is slightly subtler than we originally supposed, and could also be related to the exact co-ordination environment of the ligand. The co-ordination environment provided by the platinum complex is also likely to have an effect on the structural features observed within the phosphines of complex (**17**), especially considering the genuine but relatively small distortions observed. In the crystal structure of complex (**16**), there is a variation between P–N bond lengths, but with no particular trend with regard to the bond angles. There is considerable X-ray (and photoelectronic spectral) data on tris(dialkylamino)phosphines which supports the idea that one of the P–N bonds is different in character (less N–P π-donation) than the other two, our structural data suggest that conclusions can only be drawn when certain structural phenomena reappear time after time.

e: Crystallographic cone angles *versus* Tolman cone angles

The Tolman cone angle of a phosphine $R^1R^2R^3P$ is defined as 2/3 of the sum of half-angles, where half-angles can be measured from simple molecular models. M–P bond lengths are set at 2.28 Å and the phosphine substituent bond lengths and orientation are set using intuition and perhaps known crystallographic data. The substituents are arranged to give a minimum cone angle. The half-angle is that between metal, phosphorus, and the *outer edge* of the outermost atom on a phosphorus substituent. It is a useful *estimate* of the steric bulk of a ligand.[1] It is perhaps unwise to use this method to evaluate very small differences between ligands. It is an attractive idea to suggest crystallographic cone angles (calculated by measuring M–P–X, where X is the *middle* of the outermost atom on each substituent) as a replacement for the Tolman value. This has the advantage of being a real value that is not subject to the accuracy and/or bias of a model. However, Muller and Mingos showed that while the mean average of a large number of crystal structures has a good correlation with the Tolman value, there is a considerable range throughout the series.[32] We have found that the correlation between Tolman, crystallographic and molecular modelled (PC Spartan) cone angles (see Table 8)

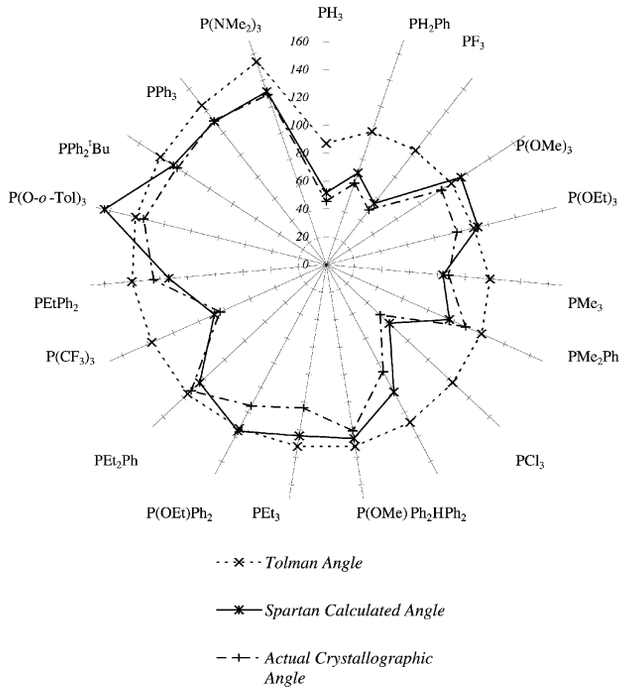


Fig. 7 Differences (in °) between the Tolman, PC Spartan Pro and crystallographic (CDS) cone angles.

Table 9 Comparison of ν_{CO} of (Cp)Fe(CO)(I)L complexes for pyrrolidine based ligands with iron complexes of other phosphines

Entry	L	ν_{CO} [a]/cm^{-1}	Ref.	Cone angle [b]/°
1	$(PhO)_3P$	(1984)	34	128
2	$(EtO)_3P$	(1961)	34	109
3	$(^iPrO)_3P$	(1960)	34	130
3	$(C_6H_5)_3P$	(1957)	34	145
4	$PhMe_2P$	(1950)	34	122
5	Bz_3P	(1949)	34	165
6	(**2**)	1941		145
7	(**3**)	1942		145

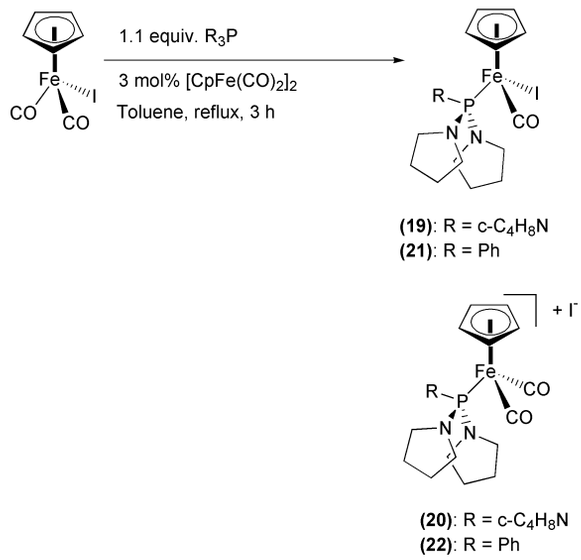
[a] Chloroform or toluene solution. [b] Cone angle data are taken from ref. 1. [c] This work.

is reasonable for trialkylphosphines but less good for those containing P–F, P–Cl or P–H groups (Fig. 7).

In spite of all this, it is perhaps still useful to glance at crystallographic cone angles of similar metal complexes as these do represent what a given phosphine will 'look like' when complexed to that metal fragment (see Table 9). This may be a more useful measure when a series of metal complexes (*e.g. trans*-$L_2Rh(CO)Cl$) have been used to catalyse or undergo a reaction. The crystallographic data in this case are likely to be valid sets of information that may shed light on the reactivity patterns involved. The crystallographic cone angles in complexes of type *trans*-$L_2Rh(CO)Cl$ are: L = PPh_3, 111.9°; L = *p*-Tol_3P, 106.4°; L = Me_3P, 80.3°; L = Ph_2MeP, 97.6°. This can be compared with that found in the two structures reported here, which give crystallographic cone angles of 125° and 124° for (**13**) L = di-*tert*-butylpyrrolidine and (**14**), L = Cy_3P respectively. The Tolman cone angle predicted for these two phosphines is 170°.

f: Iron carbonyl complexes of pyrrolidinyl phosphines

It is well known that iron complexes of type CpFe(CO)(L)I and $[CpFe(CO)_2(L)]I$ can be prepared from phosphines and $[CpFe(CO)_2]_2$.[33] The proportion of ionic and neutral complexes varies depending on the nature of the phosphines and reaction conditions. In 1987, Coville and co-workers demonstrated that $[CpFe(CO)_2]_2$ can efficiently catalyse this reaction, and hence give a greater proportion of the neutral products.[34] (The ionic compounds are most likely intermediates in the synthesis of the neutral compounds.) It has been noted that reaction of $CpFe(CO)_2I$ with more electron rich phosphines such as Cy_3P and Bz_3P often gives some ionic products in which iodide is substituted from the co-ordination sphere of the iron centre. In contrast, the reaction of triphenylphosphine with $CpFe(CO)_2I$ gives an 80% yield of the neutral compound within 1 hour in refluxing benzene (using ≈3 mol% $[CpFe(CO)_2]_2$, see Scheme 6).

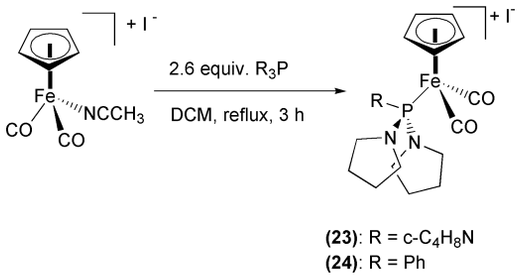


Scheme 6

We have prepared iron(II) complexes of type CpFe(CO)I(PR_3) from two of the *N*-pyrrolidinylphosphines by the method of Colville *et. al.*[34] The reaction of these phosphines with $CpFe(CO)_2I$ yields a mixture of insoluble ionic compounds, $[CpFe(CO)_2(L)]I$, which can be filtered off, and the soluble CpFeCO(L)I complexes which are readily purified by chromatography using an alumina column.

Tripyrrolidinylphosphine reacts with $CpFe(CO)_2I$ under $[CpFe(CO)_2]_2$ catalysis to give, after 90 min at 90 °C in toluene, a 3.6 : 1 mixture of ionic to neutral compounds (**19**) and (**20**). In order to obtain a larger yield of neutral compound, phenyl(dipyrrolidinyl)phosphine was reacted for three hours at 90 °C in toluene. This gave a 1 : 3.8 mixture of ionic to neutral compounds. In both cases, it is more difficult to prepare the neutral species than if less electron rich ligands were used. The FAB mass spectrum of the iron complexes is especially informative in confirming the formulation. The CpFeCO(L)I compounds show similar fragmentation patterns in which MH^+, $(M - CO)^+$, $(M - I)^+$, $(M - I - CO)^+$ and $(M - CpFe(CO)I)$ are detected. These compounds were additionally characterised by showing good agreement with calculated values in their high resolution electrospray mass spectra. The ionic complexes, $[CpFe(CO)_2(L)]I$, show $(M - I)^+$ and $(M - CO - I)^+$ peaks in their FAB mass spectrum, and were also characterised by giving acceptable high resolution electrospray mass spectra. All the iron complexes were additionally characterised by ^1H and ^{31}P NMR, and IR spectroscopy, and the purity of the neutral complexes was further confirmed by acceptable chemical analyses. Although the position of ν_{CO} in the IR spectrum is not generally used as a quantitative measure of phosphine basicity, both neutral complexes show ν(CO) at significantly lower wavenumber than in the iron complexes of Ph_3P, $PhMe_2P$ or Bz_3P. The co-ordination chemical shift is greater in the neutral complexes, [for L = (**2**), $\Delta\delta$ = 31.8 in (**19**), 12.7 in (**20**); L = **3**, $\Delta\delta$ = 60.5 in (**21**), 46.6 in (**22**)].

Another method to prepare cationic iron complexes of type $[CpFe(CO)_2(L)]X$ is the reaction of a phosphine with the labile precursor $[CpFe(CO)_2(MeCN)]BF_4$ (Scheme 7).[15]



(23): R = c-C_4H_8N
(24): R = Ph

Scheme 7

This type of synthesis is more straightforward for cationic compounds as there is no possibility for neutral iron dicarbonyl complexes being formed. Refluxing either tripyrrolidinylphosphine or phenyl(dipyrrolidinyl)phosphine with $(CpFe(CO)_2(MeCN)]BF_4$ in dichloromethane rapidly gave the desired complexes [(**23**) and (**24**) respectively] in high purity.

A few brown crystals of (**24**) could be grown by layering a CH_2Cl_2 solution with diethyl ether. The molecular structure of (**24**) is shown in Fig. 8 and consists of discrete cations and

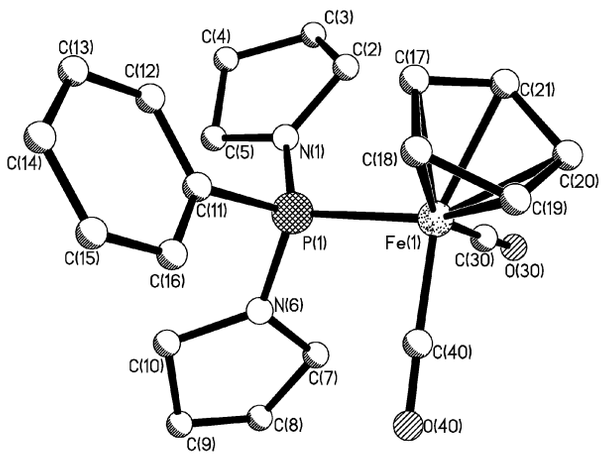


Fig. 8 Molecular structure of (**24**).

anions. The cationic iron centre displays octahedral piano stool geometry, with the Cp ligand occupying three faces of this octahedron. Two of the carbons within the Cp ligand show slightly elongated bonds lengths, which reflects their positions *trans* to carbon monoxide ligands which have a higher *trans* effect relative to the phosphine ligand. The carbon monoxide ligands are linear and show similar Fe–C bond lengths to that found in the crystal structure of $[CpFe(CO)_2PPh_3]^+$ (1.773(4) Å in (**24**), *vs*. 1.776 Å).[35] The iron–phosphorus bond length [2.226(1) Å, see Table 10] is somewhat shorter than that found in the analogous triphenylphosphine complex [2.242(1) Å]. Since PPh_3 and phenyl(dipyrrolidinyl)phoshpine are thought to have a similar cone angle, it is likely that the shorter P–Fe bond arises from stronger bonding from the more electron rich ligand. The P–N bonds within the structure are fairly typical for this type of ligand, and have planar nitrogen atoms (sum of angles at N = 360(3) and 356.6(3)°).

Summary and conclusions

In this work, we have shown the consequences of an esoteric structural phenomenon on the donor strength of phosphino-amines. It is hoped that two of the phosphines prepared in the course of this study [(**4**) and (**5**)], will find applications in organometallic chemistry and catalysis. These phosphines have a different combination of electronic and steric properties from those reported before, with *tert*-butyl(dipyrrolidinyl)phosphine being amongst the most electron donating phosphines known. As tri-*tert*-butylphosphine (the most electron rich tri-alkylphosphine) is often reluctant to behave in a similar fashion to 'normal' phosphines, the somewhat smaller cone angles of (**4**) and (**5**) should broaden their applications further. In any case these studies have led us to a greater understanding of the donor strength of phosphino-amines which we are now applying to functionalised phosphines which are showing considerable promise in catalysis.[25]

Table 10 Selected bond lengths (Å) and angles (°) for (**24**)

Fe(1)–P(1)	2.226(1)	Fe(1)–C(40)	1.773(4)
Fe(1)–C(17)	2.085(4)	Fe(1)–C(30)	1.772(4)
Fe(1)–C(18)	2.086(4)	Fe(1)–C(21)	2.095(4)
Fe(1)–C(19)	2.101(4)	Fe(1)–C(20)	2.108(4)
P(1)–N(1)	1.650(3)	P(1)–N(6)	1.655(3)
C(30)–O(30)	1.130(5)	C(40)–O(40)	1.135(5)
C(30)–Fe(1)–C(40)	96.7(2)	C(30)–Fe(1)–P(1)	93.0(1)
C(40)–Fe(1)–P(1)	89.9(1)	O(40)–C(40)–Fe(1)	177.6(4)
O(30)–C(30)–Fe(1)	178.2(4)	C(7)–N(6)–P(1)	120.8(3)
C(10)–N(6)–P(1)	126.4(3)	C(10)–N(6)–C(7)	109.4(3)
C(2)–N(1)–C(5)	109.6(3)	C(5)–N(1)–P(1)	122.0(3)
C(2)–N(1)–P(1)	128.4(3)		

Acknowledgements

We are grateful to the EPRSC for financial support and the use of the EPRSC National Mass Spectrometry Service (Swansea). We would also like to thank the JREI for equipment grants.

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