

P–N bond formation as a route to highly electron rich phosphine ligands

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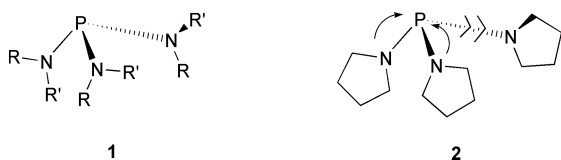
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Phosphines containing two N-bound pyrrolidine groups and one alkyl or aryl group are unusually electron rich σ -donor ligands when compared to either tris(*N*-pyrrolidinyl)phosphine or trialkyl- and triaryl-phosphines.

One of the many attractive features of phosphine ligands is their wide range of electronic properties.^{1,2} Metal complexes of strongly electron donating alkyl phosphines undergo many reactions which are not possible with aryl phosphines,³ and these types of metal complexes have recently found important applications in homogenous catalysis.^{4–6} Tris(alkylamino)-phosphines are strongly electron donating phosphine ligands. The high basicity (σ -donor strength) of the P atom is thought to arise from donation towards the P from the N lone pair. X-Ray crystal structures of tris(alkylamino)phosphines and their metal complexes^{2,7} show these ligands to contain two short P–N bonds with planar N, and one long P–N bond with a non-planar N atom (**1** and **2**). This suggested to us that only two of the N lone pairs could donate electron density towards P, while the third N substituent acts merely as an electronegative atom bound to the P, 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. Here, we describe the preparation of these new di(*N*-pyrrolidinyl)alkylphosphines and preliminary experiments which suggest that the new phosphine ligands are amongst the most electron rich phosphines known.

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

³¹P and ¹H NMR spectra of the air and moisture sensitive phosphine products showed them to be 90–98% pure, and they were therefore purified no further. They were further characterised by their conversion to the metal complexes described below. Molloy and Petersen have previously prepared tris(*N*-pyrrolidinyl)phosphine and shown it to be a highly electron rich ligand, in contrast to tris(*N*-pyrrolyl)phosphine which has exceptional π -acceptor character. The method they used to gauge the electronic characteristics of their ligands was measurement of ν_{CO} in the IR spectrum of the *trans*-(R₃P)₂Rh(CO)Cl complexes. These are readily formed in high purity from [Rh(CO)₂Cl]₂ and an excess of ligand.⁸ As the position of ν_{CO} in these complexes is known for a huge variety

of phosphines (and is always in agreement with the expected σ -donor strength of the phosphine) this does seem to be an excellent spot test to gauge the donor characteristics of a particular phosphine.

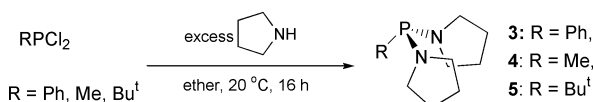
As can be seen from Table 1, the position of ν_{CO} for PhMe₂P is, as expected, in between electron rich Me₃P and the less basic Ph₃P. PhP(*N*-pyrr)₂, however, has ν_{CO} at lower wavenumber than P(*N*-pyrr)₃, and therefore can be assumed to be a more electron rich ligand. This is evidence [along with the properties of MeP(*N*-pyrr)₂ and Bu^tP(*N*-pyrr)₂] that only two pyrrolidinyl groups can contribute towards the strong donor strength of *N*-pyrrolidinyl phosphines. The values of ν_{CO} for MeP(*N*-pyrr)₂ and Bu^tP(*N*-pyrr)₂ are significantly lower than those of most other highly electron rich alkylphosphines (compare entries 11 and 12 to 5 and 6) which are often applied in catalysis. Tri-*tert*-butylphosphine, which is generally thought of as the most electron donating phosphine, actually forms a tetrahedral (R₃P)₂Rh(CO)Cl complex and cannot be directly compared.¹³ The new ligands may be of particular use as they deliver a donor strength that is normally reserved for very bulky ligands, as defined by their large cone angle. It is expected that the ligands **3–5** (especially **4**) will have relatively small cone angles. We also note here that iron(II) complexes of type CpFe(CO)I(PR₃) can also be prepared from the four *N*-pyrrolidinyl phosphines by the method of Colville *et al.*¹⁴ The position of ν_{CO} in the IR spectrum of these four compounds is less informative than the Rh compounds, but is at significantly lower wavenumber than the iron complexes of Ph₃P, PhMe₂P or Bz₃P.

Finally, we have also characterised the dichloroplatinum complexes, (R₃P)₂PtCl₂, of the four *N*-pyrrolidinyl phosphines [(pyrr)₃P]₂PtCl₂ **6**, [(pyrr)₂PhP]₂PtCl₂ **7**, [(pyrr)₂MeP]₂PtCl₂ **8** and [(pyrr)₂Bu^tP]₂PtCl₂ **9**. These are formed quantitatively from Pt(cod)Cl₂ and 2 equivalents of phosphine. The sizes of ¹J_{Pt} reflect the reduction in coupling constant observed when a phenyl group is replaced by an alkyl group, and the increased size of ¹J_{Pt} observed for compounds containing P–N or P–O bonds.⁸ The molecular structures¹⁵ (determined by X-ray crystallography) of [P(*N*-pyrr)₃]₂PtCl₂ and [MeP(*N*-pyrr)₂]₂PtCl₂ are shown in Fig. 1 and 2, respectively.

Table 1 Comparison of ν_{CO} of *trans*-L₂Rh(CO)Cl complexes for pyrrolidine based ligands with other phosphines

Entry	L	ν_{CO}^a [L ₂ Rh(CO)Cl]	Ref.
1	(PhO) ₃ P	(2016)	9
2	(<i>p</i> -CF ₃ C ₆ H ₄) ₃ P	(1990)	2
3	Ph ₃ P	1965 (1966)	2 ^b
4	PhMe ₂ P	(1965)	10
5	Me ₃ P	(1960)	2
6	Et ₃ P	(1956)	11
7	Cy ₃ P	1943 (1942)	12 ^b
8	P(NMe ₂) ₃	(1959)	2
9	P(<i>N</i> -pyrr) ₃ ^c	1951 (1952)	<i>b,d</i> ₂
10	PhP(<i>N</i> -pyrr) ₂	1949	<i>b,d</i>
11	MeP(<i>N</i> -pyrr) ₂	1947	<i>b,d</i>
12	Bu ^t P(<i>N</i> -pyrr) ₂	1942	<i>b,d</i>

^a To ensure the accuracy and validity of our values, we have reprepared *trans*-(R₃P)₂Rh(CO)Cl complexes of (*N*-pyrr)₃P, Ph₃P and Cy₃P. The values quoted above are those found on our spectrometer (lit. values in parentheses). ^b IR spectra recorded as KBr discs. ^c pyrr = pyrrolidinyl. ^d This work.



Scheme 1

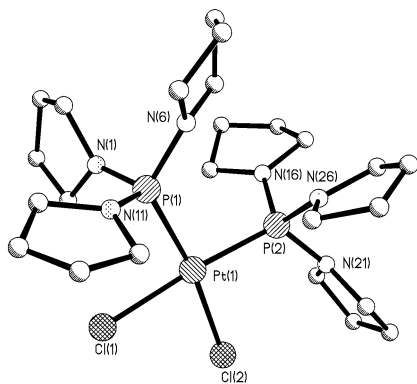


Fig. 1 Ball and stick representation of $[P(N\text{-pyrr})_3]_2PtCl_2$ **6**. Selected bond lengths (Å) and angles (°): Pt–P(1) 2.246(3), Pt–P(2) 2.270(3), Pt–Cl(1) 2.398(3), Pt–Cl(2) 2.371(3); P(2)–Pt–P(1) 98.24(10), Cl(2)–Pt–Cl(1) 85.08(11).

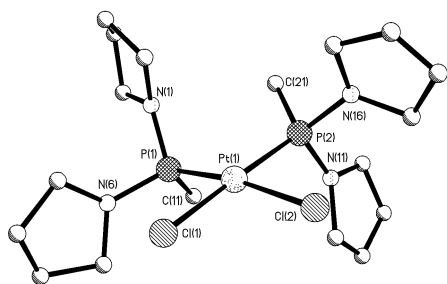


Fig. 2 Ball and stick representation of $[MeP(N\text{-pyrr})_2]_2PtCl_2$ **8**. Selected bond lengths (Å) and angles (°): Pt–P(1) 2.226(2), Pt–P(2) 2.255(2), Pt–Cl(1) 2.372(2), Pt–Cl(2) 2.391(2); P(2)–Pt–P(1) 93.37(7), Cl(1)–Pt–Cl(2) 86.14(8).

The X-ray structure of *trans*- $[P(N\text{-pyrr})_3]_2Rh(CO)Cl$ **2** shows two of the pyridine rings in a given $P(N\text{-pyrr})_3$ fragment to have planar N atoms (sum of angles around N = 354–360°) and one tetrahedral N atom (sum of angles around N = 347, 350°) with a 0.02 Å longer P–N bond length [av. 1.667(3) vs. 1.688(3) Å]. We therefore expected the crystal structure of $[P(N\text{-pyrr})_3]_2PtCl_2$ to show this phenomenon. The crystal structure of $[P(N\text{-pyrr})_3]_2PtCl_2$ shows the expected *cis* square planar Pt complex, but to our surprise, the sum of angles around each N was similar (356–360°) and planar. The P–N bond lengths [1.628(10), 1.721(11), 1.642(11), 1.659(10), 1.678(12) and 1.678(9) Å] do not show any particular pattern.

The crystal structure of $[MeP(N\text{-pyrr})_2]_2PtCl_2$ **8** has two independent molecules in each unit cell, but there are no drastic differences between the two molecules. Complex **8** shows a similar coordination environment to complex **6**, with fairly similar Pt–Cl and Pt–P bond lengths. The angle P(1)–Pt(1)–P(2) between the phosphines is considerably smaller than in complex **6** [93.90(8), 93.37(7) vs. 98.24(10)°], and indicates that $MeP(N\text{-pyrr})_2$ is less sterically demanding than $P(N\text{-pyrr})_3$. As a result of this, the angle between the Cl ligands is slightly larger in complex **8** [87.01(9), 86.14(8) vs. 85.08(11)°]. The bond lengths and angles about the N atoms are again somewhat surprising. Each phosphine has one planar N (sum of angles from the four phosphine ligands in the two independent molecules: 356.6, 359.5, 359.5, 356.4°), and in each of the four phosphine molecules present, the other N atom shows a slight tetragonal distortion (sum of angles: 353.3, 353.5, 354.0, 351.8°), and slightly longer P–N bond length [average bond lengths: 1.683(6) vs. 1.643(7) Å].

The crystallographically determined cone angles of $P(pyrr)_3$ and $MeP(pyrr)_2$ are 122 and 110°, respectively. These values refer to 2/3 of the sum of the largest possible angle observed between the Pt centre and the centre H atoms on the phosphine

substituents. This value differs from the Tolman cone angle (determined by molecular modelling) by using the centre of the H atom and the real Pt–P bond length. It is also likely to differ due to the volume of space occupied by the phosphine being partly determined by the coordination environment provided by the Pt. The values obtained clearly confirm the smaller size of ligand **4** with respect to ligand **2**. It has been estimated that the Tolman cone angle of **2** is 145°.²

The crystal structure of **6** 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 more subtle than we originally supposed, and could also be related to the exact coordination environment of the ligand. The coordination environment provided by the Pt complex is also likely to have an effect on the ligand structure observed within that of complex **8**. In conclusion, we have prepared three new phosphine ligands and shown them to be especially strong donor ligands. Studies to evaluate the potential uses of these ligands in catalysis are now underway.

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