DALTON COMMUNICATION

P–N bond formation as a route to a highly electron rich bidentate phosphine ligand and its application in homogenous catalysis

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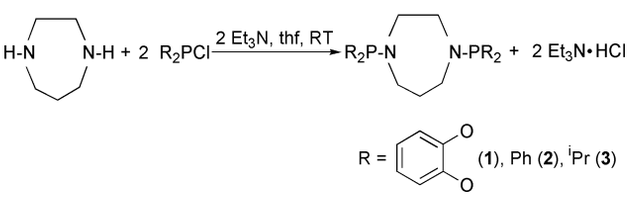
Received 20th February 2001, Accepted 20th February 2001
First published as an Advance Article on the web 15th March 2001

Bis-phosphines containing two electron donating alkyl groups linked by a diamine backbone are extremely electron rich σ-donor bidentate ligands and have been used, along with phenyl and catechol substituted bis-phosphinoamines, to study hydroformylation reactions.

Phosphine ligands have many important applications in organometallic chemistry and catalysis[1–4] We have recently demonstrated that phosphines derived from two N-bound pyrrolidine groups and one alkyl or aryl group are amongst the strongest σ-donor ligands, and surprisingly are even more electron rich than tris(*N*-pyrrolidinyl)phosphine.[5] The impetus behind our study was the many recent examples of electron rich metal complexes undergoing reactions which were not previously possible using metal complexes of aryl-phosphines.[6] Recent important applications are catalytic C–H bond activation,[7] hydroformylation of alkenes to give commercially valuable alcohols instead of aldehydes,[8] and palladium catalysed Heck, Suzuki, and amination reactions of aryl chlorides, which do not normally react with most other phosphine based catalysts.[9–12]

We now report a highly electron rich bidentate phosphine ligand, and two electronically different diphosphines that share the same homopiperazine backbone. The reaction of diamines with chlorophosphines in the presence of Et_3N gives P–N bond ligands easily due to the milder conditions required for this reaction compared to a P–C bond forming reaction.[13,14] The ligands **1** ($(C_6H_4O_2P)_2N^\frown N$), **2** ($(Ph_2P)_2N^\frown N$) and **3** ($(^iPr_2P)_2$-$N^\frown N$), where $N^\frown N$ = homopiperazinate, were obtained using the same general procedure, shown in Scheme 1, where one



Scheme 1 Synthesis of new bidentate phosphine ligands. In the case of ligand **3** Et_2O was used as the solvent.

equivalent of the starting amine (homopiperazine) was mixed with two equivalents of the starting chlorophosphine in the presence of two equivalents of triethylamine as a base in thf (or Et_2O for **3**).† The reactions were conducted under strictly anhydrous, anaerobic conditions and the ligands produced were essentially pure as determined by ^{31}P and ^1H NMR spectroscopy. So far we have not been able to prepare the $^tBu_2P$ substituted bis-phosphine even if ^nBuLi is used as base. Other workers in our group have previously found that a $^tBu_2P$–N linkage is difficult to form.

Ligand **3** was also characterised as its diselenide including by X-ray crystallography (Fig. 1).†‡

Generation of $Mo(CO)_4L$ complexes from *cis*-$(pip)_2$-$Mo(CO)_4$ (Hpip = piperidine) may be used as a rapid "spot test" for the donor properties of new ligands. This attribute has been recognised for many years and an extensive literature exists for these complexes, allowing ready comparison with a variety of other phosphorus(III) ligands. The value of ν_{CO} has been used to evaluate the ligand electronic properties and it has been found that for π-acceptor ligands, ν_{CO} is at higher wavenumber than for σ-donor ligands. A shift to lower frequency indicates a stronger donation of electron density from ligand to metal to carbonyl ligand and thereby indicates a stronger σ-donor ability for the P–N ligands.[3]

Table 1 Comparison of ν_{CO} of $Mo(CO)_4L$ compleces for bidentate phosphine ligands[a]

L	ν_{CO}[b]/cm^{-1}	Ref.
2 PF_3	2087	16
$F_2PCH_2CH_2PF_2$	2074	17
2 $EtNPF_2$	2066	18
$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$	2064	4
$Cl_2PCH_2CH_2PCl_2$	2061	19
$(pyrrole)_2PCH_2CH_2P(pyrrole)_2$	2043	3
$(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$	2041	19
$(MeO)_2PCH_2CH_2P(OMe)_2$	2033	20
dppe	**2021**	21, this work
$Cy_2PCH_2CH_2PCy_2$	2016	22
$Et_2PCH_2CH_2PEt_2$	2012	21
$(C_6H_4O_2P)_2N^\frown N^\frown N$[c]	2042, 1952, 1933	23
$(C_6H_4O_2P)_2N^\frown N$ (1)	**2055**	This work
$(Ph_2P)_2N^\frown N$ (2)	**2014**	This work
$(^iPr_2P)_2N^\frown N$ (3)	**2004**	This work

[a] Values in bold were recorded on our spectrometer. [b] Spectra recorded in DCM solution. [c] $N^\frown N^\frown N$ is $MeN(CH_2)_3NMe(CH_2)_3NMe$.

The $Mo(CO)_4L$ complexes of **1**, **2** and **3** were obtained using the same procedure where one equivalent of the ligand was mixed with one equivalent of the metal starting material under reflux using dichloromethane (DCM) as solvent (Scheme 2).[15] The new complexes gave satisfactory microanalyses and the appropriate parent ion in their mass spectra.

The position of ν_{CO} for these molybdenum complexes is shown in Table 1 and can be compared with ligands from the literature. We have also reprepared $Mo(CO)_4$(dppe) and recorded its IR spectra to calibrate our values. It was found that in the molybdenum complex [$Mo(CO)_4$(**3**)] the CO stretching frequency (2004 cm^{-1}) is significantly lower than in the $Mo(CO)_4L$ complexes of depe (2012 cm^{-1}) and dcype (2016 cm^{-1}). Hence **3** is, to the best of our knowledge, the most electron rich bidentate phosphine ligand yet prepared.

Given that the ligands depe and dcype often show completely altered chemistry compared with other diphosphines (dppe, *etc.*), the new very electron rich ligand prepared here should, given its ease of preparation, be a useful tool in organometallic chemistry and catalysis. It is also useful to compare **3**, $(^iPr_2P)_2N^\frown N$, with the phenyl, (**2**), and catechol, (**1**), substituted phosphines that share the same backbone. Ligand **1** is quite electron poor (2055 cm^{-1}) and seems to share similar electronic properties to 1,2-bis(dichlorophosphino)ethane, (2061 cm^{-1}),

DOI: 10.1039/b101656n

Table 2 Hydroformylation of 1-hexene catalysed by rhodium complexes of the new bidentate phosphines[a]

Ligand	Time/h	Conversion (%)	Selectivity to aldehyde (%)	l : b[b]	Initial rate/ mol dm^{-3} s^{-1}
1	2.5	76.0	64.0	3.7	7.7×10^{-4}
2	24	100	80.2	1.3	8.6×10^{-5}
3	1	98.9	95.5	1.2	2.5×10^{-3}

[a] [Rh(acac)(CO)$_2$] (0.01 mol dm^{-3}), phosphine (0.023 mol dm^{-3}), 1-hexene (1 cm^3) in toluene (4 cm^3) at 100 °C and 20 bar CO/H$_2$ (1 : 1) for time stated in table. The rhodium complex, phosphine and toluene were heated at 100 °C and 14 bar CO/H$_2$ (1 : 1) for 45 min, to allow the active catalyst to form before injection of the 1-hexene and pressurising to 20 bar. [b] Linear : branched ratio.

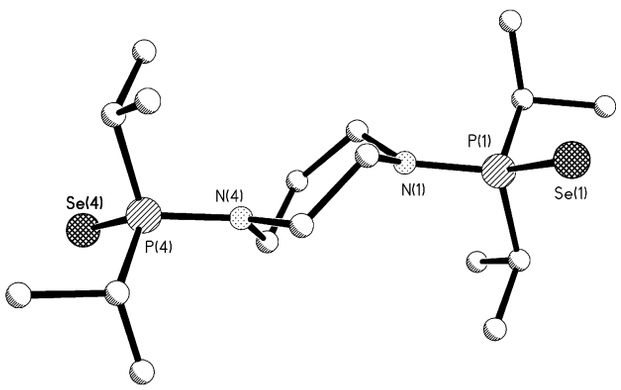
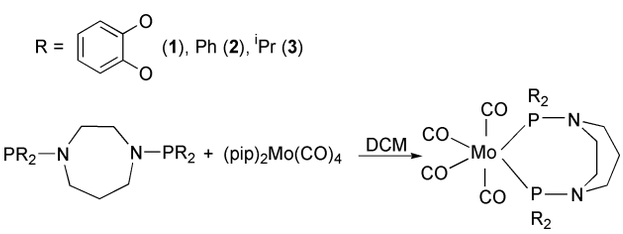


Fig. 1 X-Ray crystal structure of bis(*N*,*N*′-diisopropylhomopiperazinate)diselenide **3Se$_2$**. Selected bond lengths (Å) P(1)–Se(1) 2.115(5), P(4)–Se(4) 2.118(5), P(1)–N(1) 1.655(13), P(4)–N(4) 1.688(14).



Scheme 2 Preparation of Mo(CO)$_4$L complexes from *cis*-(pip)$_2$-Mo(CO)$_4$.

and 1,2-bis(dipyrrollylphosphino)ethane, (2043 cm^{-1}). The ligand **2** shows an intermediate value, (2014 cm^{-1}), between dcype (2016 cm^{-1}) and depe (2012 cm^{-1}).

We have found that our three ligands possess a wide range of electronic properties with the same ligand backbone. We elected to study ligand electronic effects on the rate of rhodium catalysed hydroformylation of 1-hexene which is one of the most important homogeneously catalysed reactions in industry. Two different products can be obtained, the linear or the branched aldehyde. The linear aldehydes are more useful products, and it is therefore desirable to have a high n/i ratio. It has recently been found that the selectivity increases when the bite angle of the ligand becomes larger (it seems that the optimum is near 112–120° in the ligands named 9,9-dimethyl-4,6-bis(diphenylphosphino)xanthene, (Xantphos) and 2,2'-bis((diphenylphosphino)methyl)-1,1′-biphenyl (BISBI)).[24] The rigidity of the ligand backbone is also important for obtaining high selectivity.[1,25–27]

The ligands **1**, **2** and **3** were tested in rhodium catalysed hydroformylation and the results are shown in Table 2 and Fig. 2.

The initial rate of hydroformylation does not correlate with either the steric or electronic properties of the ligands, varing in the order **3** > **1** > **2** with **3** giving a rate 50× that of **1**. The complexes derived from ligands **1** and **3** show first order reactions leading to complete conversion to products, suggesting that the P–N interaction is stable under the reaction conditions. Ligand **2** on the other hand gives relatively low conversion and selectivity to aldehyde before the reaction stops. This is a result of catalyst decomposition (brown precipitate formed) and the

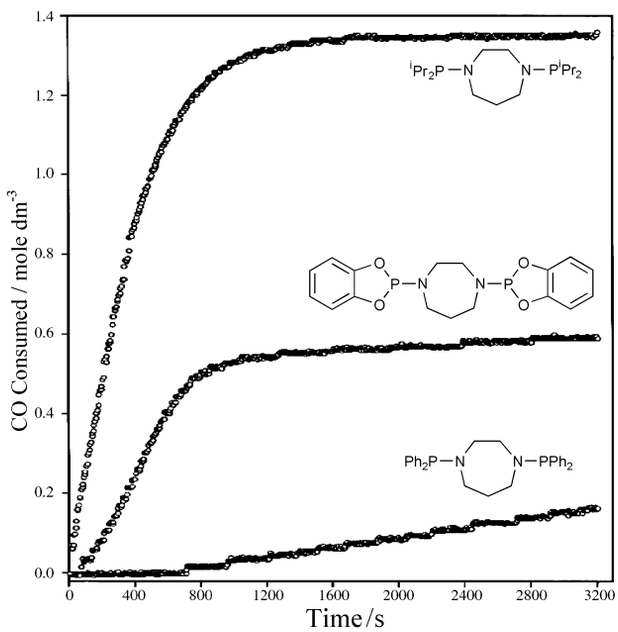


Fig. 2 Kinetics of 1-hexene hydroformylation with bidentate phosphine ligands, upper trace ligand **3**, middle trace **1**, lower trace **2**.

presence of 1,2-dihydroxybenzene in the product suggests the P–O bonds are hydrolytically unstable. Water can be produced in these reactions from aldol condensation of the aldehyde product. The linear selectivity of these catalysts is, at best, modest, but better for **1**. It appears that **1** is acting like other phosphite ligands, which often give higher l : b ratios and more isomerisation than phosphines.[28]

In this work we have synthesised three new ligands with significantly different electronic properties containing the same ligand backbone. We have studied their effect on the rate of rhodium catalysed hydroformylation and observed considerable difference between the three ligands. These results should aid future ligand design for this reaction.

Acknowledgements

We would like to thank the EPSRC for funding, to the JREI for an equipment grant and to Dr Matthew Wainwright and Dr J. Nicholas B. Smith (University of Loughborough) for preliminary work on the homopiperazine ligands.

Notes and references

† All new compounds gave satisfactory CHN analyses. (NMR, 300 MHz, $CDCl_3$) **1** δ_P = 147.9, ν(CN) = 1450 cm^{-1}, ν(PN) = 931 cm^{-1}. **2** δ_P = 71.1, ν(CN) = 1431 cm^{-1}, ν(PN) = 921 cm^{-1}. **3** δ_P = 96.0. **3Se$_2$** δ_P = 101.5 ($^2J_{PSe}$ = 735 Hz), ν(CN) = 1435 cm^{-1}, ν(PN) = 909 cm^{-1}.

‡ Single crystal X-ray diffraction studies on crystals were performed using a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods, the non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were fixed (C–H 0.95 Å). Structural refinements were by the full-matrix least-squares method on F^2 using the program SHELXTL-PC.[29] **3Se$_2$** $C_{17}H_{38}N_2P_2Se_2$, M =

490.35, triclinic, $a = 6.959(3)$ Å, $b = 11.700(5)$ Å, $c = 14.974(7)$ Å, $\alpha = 108.22(1)°$, $\beta = 98.72(1)°$, $\gamma = 93.16(1)°$, $U = 1138$ Å^3, $T = 293$ K, space group $P\bar{1}$, $Z = 2$, μ(Mo-Kα) = 3.39 mm^{-1}. Of 6629 measured data, 3281 were unique, to give $R1[I > 2\sigma(I)] = 0.113$. CCDC reference number 154470. See http://www.rsc.org/suppdata/dt/b1/b101656n/ for crystallographic data in CIF or other electronic format.

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