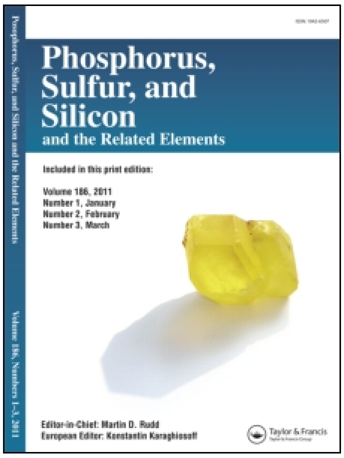

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Synthesis of New Phosphino-Amines, their Metal Complexes and their Application in Catalysis

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The compounds $(C_6H_4O_2P)_2N^\frown N$, $(Ph_2P)_2N^\frown N$ and $({}^iPr_2P)_2N^\frown N$ (where $N^\frown N$ = homopiperazine) prepared by the condensation reaction of diamines with chlorophosphines in presence of Et_3N have been tested in Rhodium catalysed hydroformylation and Palladium allylic alkylation. Also a variety of late transition metal complexes with Pt(II), Pd(II), Au(I) and Mo(0) were prepared.

Keywords: Phosphorus-Nitrogen bond containing ligands and complexes; Selenium; Catalysis

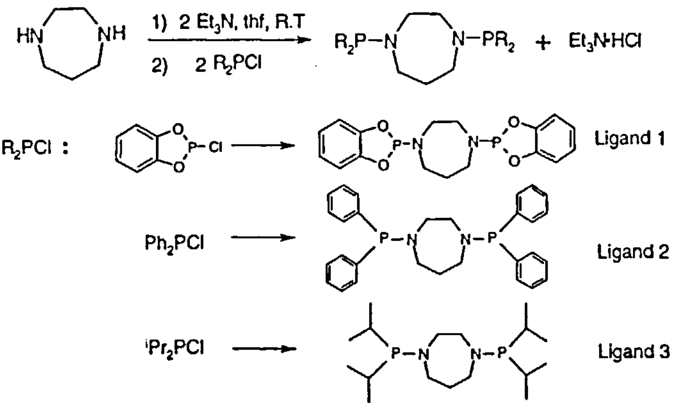
Introduction

Throughout inorganic and organometallic chemistry ligands containing P-N bonds are now becoming more important. Surprisingly, little advantage has been taken of the ease of P-N bond-forming reactions in the synthesis of the new phosphines, in part perhaps because of assumptions about the lability of the P-N bonds. This work demonstrates:

- Simple accessible reaction chemistry based on P-N bond formation and complexation
- Facile synthesis of new types of neutral and anionic ligands
- Potential applications in coordination chemistry and catalysis.

Results and Discussion

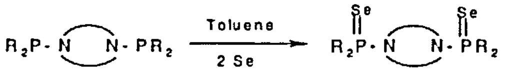
The condensation reaction of diamines with chlorophosphines in presence of Et_3N gives P-N bond ligands.



Generation of $Mo(CO)_4L$ complexes (from 1 equivalent of $(pip)_2Mo(CO)_4$ with 1 equivalent of the ligand starting material) may be used as a rapid "spot test" of the donor properties of the new ligands. This proves an important point because, compare to the data shown in Table 1, the three ligands present a wide range of electron properties and Ligand 3 is the most electron rich bidentate ligand.

Mo-COMPLEX	ν_{CO}
2 PF_3	2087
$F_2PCH_2CH_2PF_2$	2074
2 $EtNPF_2$	2066
$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$	2064
$Cl_2PCH_2CH_2PCl_2$	2061
$(pyrole)_2PCH_2CH_2P(pyrole)_2$	2043
$(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$	2041
$(MeO)_2PCH_2CH_2P(OMe)_2$	2033
dppe	2020
$Cy_2PCH_2CH_2PCy_2$	2016
$Me_2PCH_2CH_2PMe_2$	2012
$(C_6H_4O_2P)_2N^\frown N$ (L^1)	**2055**
$(Ph_2P)_2N^\frown N$ (L^2)	**2014**
$(^iPr_2P)_2N^\frown N$ (L^3)	**2004**

The X-ray crystallographic analysis have finally confirmed the structure of the three P-N bond containing ligands binding with late transition metals. We also characterised the ligands as their selenides, below is shown an X-ray structure (Fig.1).



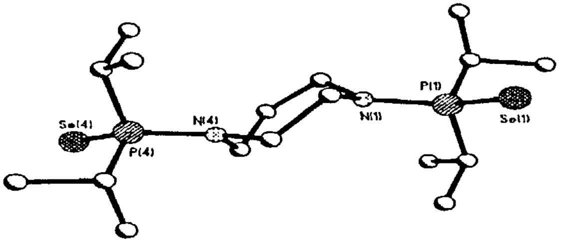
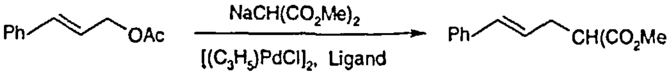


Figure 1 X-Ray crystal structure of $({}^{i}Pr_2PSe)_2N^{\frown}N$

The development of new ligands systems for catalysis is an important challenge and the ability of the reactions proposed here to be used for the development of ligands with readily manipulated steric and electronic properties is technologically important in the mid-term. Some use has been made of P-N bond containing ligands in catalysis.

Rhodium catalysed hydroformylation: Selectivity in the hydroformylation reaction increases when the bite angle of the ligand becomes larger and increases the rigidity of the ligand backbone - the results are shown below.

Palladium allylic alkylation: The ligands were tested in this reaction and the rate of reaction was estimated by T.L.C and the times taken for 100% conversion can be found in Table.



LIGAND	TIME
$(C_6H_4O_2P)_2N^\frown N$ (L^1)	> 6 hours
$(Ph_2P)_2N^\frown N$ (L^2)	45 min
$(^iPr_2P)_2N^\frown N$ (L^3)	> 60 hours

Conclusions

These compounds demonstrate the ability of the ligands to act as a bidentate chelating ligand and bridging ligands between two metal centres.

As the Pd-P and Pt-P IR results show, the diphosphinoamine ligands bind in *cis* configuration with the metal. As Mo-P IR results show, the L^3 is the most electron rich bidentate ligand.

The wide range of electronic properties provided by the three ligands, L^1, L^2 and L^3 has allowed us to study electronic effects in homogenous catalysis. These results should influence future ligand design.

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