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Co-Ordination Chemistry of a Novel Diphosphine Ligand Containing a P-N-Si-N-P Backbone

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A novel multifunctionalised diphosphine ligand containing a P-N-Si-N-P backbone has been prepared and studied. The ligand, Ph₂PN(Py)Si(Me)₂N(Py)PPh₂ from complexes with platinum and palladium containing six membered M-P-N-Si-N-P heterocycles. The structure, synthesis, and reactivity of these heterocycles is discussed.

Keywords: phosphine; bidentate; inorganic rings

Bidentate phosphine ligands are ubiquitous in co-ordination chemistry and catalysis. Whereas most bidentate phosphines consist of a carbon based backbone linking the two phosphine moieties, a smaller group of ligands consist of phosphorus atoms linked by an inorganic backbone containing main group and/or transition metals.

Bis-phosphino-amines, (1) and bis(phosphino)hydrazine ligands, (2), are well studied examples of inorganic backboned ligands. [1,2,3]
Reports of ligands, (3), which contain three main group atoms linking the phosphorus atoms are very scarce. [4,5,6,7]

We have begun an investigation into the co-ordination chemistry of this ligand class, as it might yield new applications in co-ordination chemistry and catalysis. We report here selected results from those presented at IRIS IX, concerning a PNSiNP backboned phosphine ligand and its metal complexes.

Ligand (5) can be prepared by deprotonation of (4) using lithium diisopropylamide (LDA) as base, followed by dropwise addition of Me₂SiCl₂.

Scheme 1

Ligand (5) reacts with the well known precursor M(COD)Cl₂ to generate (6) M=Pt, and (7) M=Pd, which contain the unusual PNSiNPPt heterocycle. Addition of two equivalents M(COD)Cl₂ to the ligand does not generate the bimetallic compound Cl₂M(5)MCl₂ as we might have expected given the strong preference that (4) shows for P,N chelation.^[8]

Scheme 2

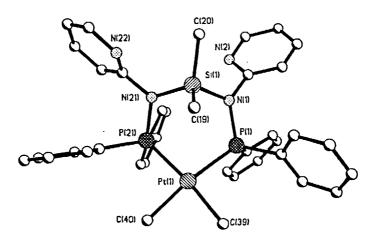
Attempts to obtain crystals of (6) or (7) suitable for X-ray diffraction by recrystallisation (dry CH₂Cl₂ / Et₂O, slow diffusion) yielded the hydrolysed product, Pt(Ph₂PNHPy)₂Cl₂.

Scheme 3

It was hoped that if we removed the possibility for P,N chelation, a metal complex with greater stability might result. This would enable us to structurally characterise a MPNSiNP ring system. We therefore decided to prepare the dimethylplatinum complex of ligand (5).

Scheme 4

This complex is significantly less susceptible to hydrolysis compared to the compounds described above, and could be recrystallised and characterised by X-ray crystallography. The X-ray structure is shown below.



References

- P. Bhattacharyya and J. D. Woolins, *Polyhedron*, 14, 3367, [1995].
 P. Bhattacharyya A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Inorg. Chem.*, 35, 3675, [1996].
 P. Bhattacharyya A. M. Z. Slawin, D. J. Williams, and J. D. Woollins *J. Chem. Soc. Dalton Trans.*, 3189, [1995].
- [2] V. Sreenivasa Reddy and Kattesh V. Katti, Inorg. Chem. 33, 2695, [1994]. V. Sreenivasa Reddy, K. V. Katti and C. L. Barnes, Inorg. Chem. 34, 5483, [1995].
- [3] M. Wainwright, A. M. Z. Slawin and J. D. Woollins, unpublished results.
- [4] For MPNPSiNP ring system: D. Gudat, L. M. Daniels and J. G. Verkade, Organometallics, 9, 1464, [1990].
- [5] For MPNSNP ring system: T. Chivers, C. Lensink, J. F. Richardson, J. Organomet. Chem., 325, 169, [1987].
- [6] For MPNPNP ring systems: J. Ellermann, J. Sutter, F. A. Knoch and M. Moll, Chem. Ber., 127, 1015, [1995]. K. K. Cheung, T. F. Lai, and S. Y. Yam, J. Chem. Soc. A, 3345, [1970]. R. Keat, W. Sim and D. S. Payne, J. Chem. Soc. A, , 2715, [1970]. A. P. Lane, D. A. Morton-Blake and D. S. Payne, J. Chem. Soc. A, 1492, [1967].
- [7] For MPNZrNP ring system: E. Hey and F. Weller, Chem. Ber., 121, 1207, [1988].
- [8] Stephen M. Aucott, PhD thesis, University of Loughborough, 1999.