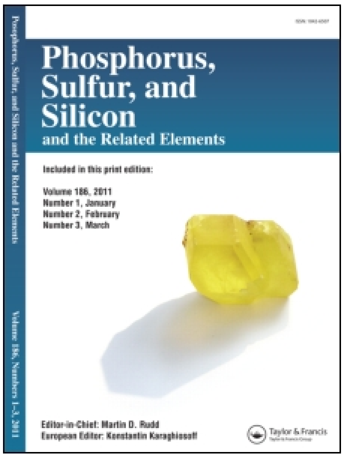

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Co-Ordination Chemistry of a Novel Diphosphine Ligand Containing a P-N-Si-N-P Backbone

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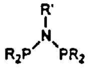
A novel multifunctionalised diphosphine ligand containing a P-N-Si-N-P backbone has been prepared and studied. The ligand, $Ph_2PN(Py)Si(Me)_2N(Py)PPh_2$ from complexes with platinum and palladium containing six membered M-P-N-Si-N-P heterocycles. The structure, synthesis, and reactivity of these heterocycles 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.



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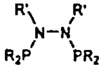

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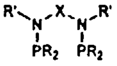
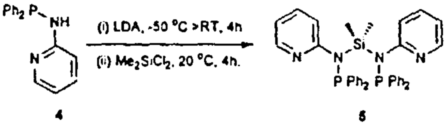


3

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]

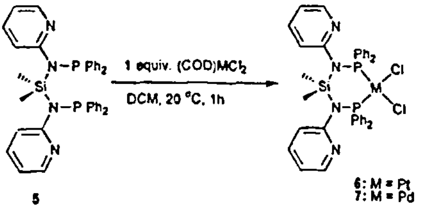
We have begun an investigation into the co-ordination chemistry of this ligand class, as it might yield new applications in co-ordination chemistry and catalysis. We report here selected results from those presented at IRIS IX, concerning a PNSiNP backboned phosphine ligand and its metal complexes.

Ligand (**5**) can be prepared by deprotonation of (**4**) using lithium diisopropylamide (LDA) as base, followed by dropwise addition of Me_2SiCl_2.



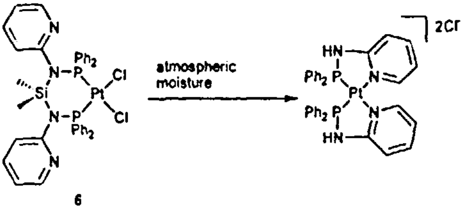
Scheme 1

Ligand (**5**) reacts with the well known precursor $M(COD)Cl_2$ to generate (**6**) M=Pt, and (**7**) M=Pd, which contain the unusual PNSiNPPt heterocycle. Addition of two equivalents $M(COD)Cl_2$ to the ligand does not generate the bimetallic compound $Cl_2M(5)MCl_2$ as we might have expected given the strong preference that (**4**) shows for P,N chelation.[8]



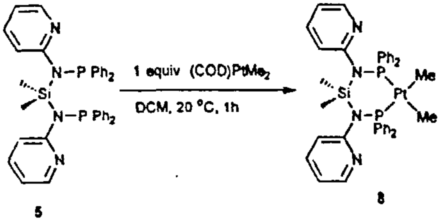
Scheme 2

Attempts to obtain crystals of (**6**) or (**7**) suitable for X-ray diffraction by recrystallisation (dry CH_2Cl_2 / Et_2O, slow diffusion) yielded the hydrolysed product, $Pt(Ph_2PNHPy)_2Cl_2$.



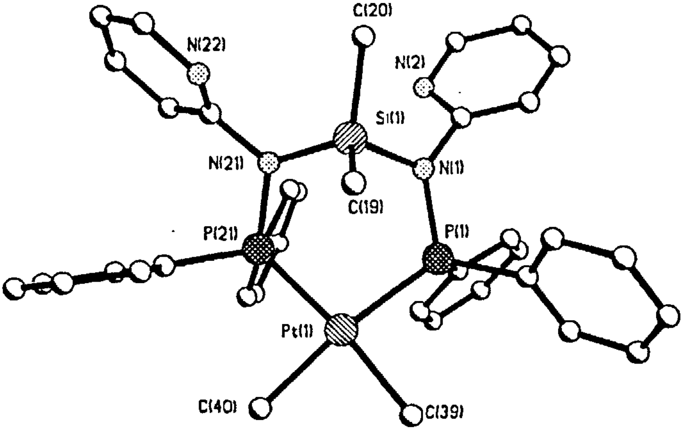
Scheme 3

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.



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