

Renaissance of Imino Phosphorane and Phosphorimidate Chemistry

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The emergence of phosphorimidate (NPR_3^-) complexes used as ethylene polymerization catalysts and imino phosphorane ($\text{R}'\text{NPR}_3$) based proton sponges has resulted in an increased interest in the use of imino phosphorane and phosphorimidates as ligands.

Main group phosphorimidate complexes have doubly bridging phosphorimidates, which yield the structure shown in Figure 1.¹ Phosphorimidate complexes involving metals with high oxidation states result in terminally bound phosphorimidate complexes, such as $\text{Os}(\text{NPR}_3)(\text{PPh}_3)_2\text{Cl}_2$.² Phosphorimidate complexes involving metals in low oxidation states result in phosphorimidate complexes which feature phosphorimidate ligands that are triply bridging to three metals, this is shown in Figure 2.²

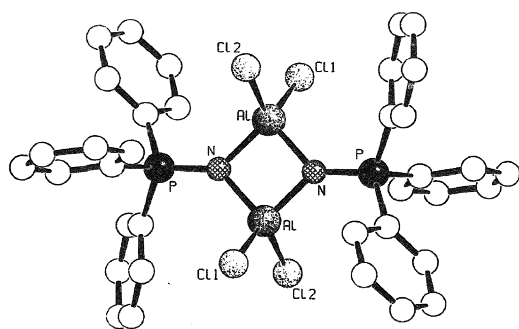


Figure 1: $[\text{Cl}_2\text{Al}(\text{NPPH}_3)]_2$ structure.

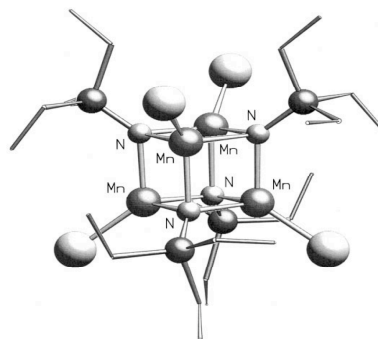


Figure 2: $[\text{Mn}_4(\text{NPEt}_3)_4]\text{Cl}_4$ structure.

The most active phosphorimidate catalyst was found to be a monosubstituted $\text{CpZr}(\text{NP}(t\text{-Bu})_3)\text{Me}_2$ catalyst, which had high activity, and analogous reactivity to the metallocene catalyst, Cp_2ZrMe_2 .³⁻⁵ Stephan demonstrated that a zirconium complex with a cyclopentadienyl group and only one phosphorimidate ligand resulted in higher activity than for a zirconium catalyst containing two phosphorimidate ligands and no cyclopentadienyl ligand.⁶ Stephan showed that phosphorimidate complexes exhibit both the electron donating and steric bulk properties of cyclopentadienyl groups. The steric properties of the phosphorimidate catalysts were found to dominate over the effect of electronics in catalytic activity.⁷ Other groups such as Bochmann and Zhang have begun to explore more complex phosphorimidate and imino phosphorane complexes and their effect on polymerization of olefins.^{8,9}

The discovery of the super basicity of 1,8-bis(dimethylamino)naphthalene (DMAN) has led to increased interest in the chemistry of "proton sponges."¹⁰ Recently, investigation in the basicity of imino phosphoranones has led to the synthesis of Verkade's Super Base, which was found to have a pK_a of 29.0 in acetonitrile and can be seen in Figure 3.^{11,12} Also, in an attempt to create analogs of DMAN, the characterization of 1,8-bis(hexamethyltriaminophosphazanyl)naphthalene (HMPN) was carried out, which was found to have a pK_a of 29.9 in acetonitrile,

nearly 12 orders of magnitude more basic than DMAN.^{12,13} Though Verkade's Super Base and HMPN have large pK_a values, the values are still small in comparison with the imino phosphorane bases developed by Schwesinger, where an increase of pK_a with the increase in the number of imino phosphorane units present was observed. Schwesinger's best imino phosphorane base, P_4 -*t*-Bu, which is shown in Figure 4, has been found to have a pK_a of 42.7 in acetonitrile.

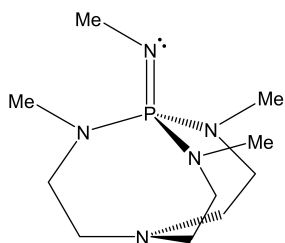


Figure 3: Verkade's Super Base

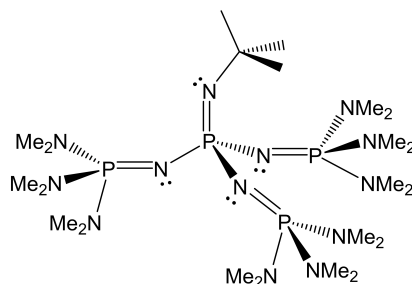


Figure 4: Schwesinger's P_4 -*t*-Bu

Future applications of imino phosphorane and phosphorimidate complexes involve further investigation of the basicity of imino phosphoranes in the search of stronger super bases and whether the basicity will reach a maximum as the number of imino phosphorane subunits are increased beyond Schwesinger's P_4 -*t*-Bu. Also, the future use of phosphorimidate complexes, as possible radiopharmaceutical agents, is being examined due to their stability in both hydrophobic and hydrophilic environments.^{14,15}

References

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