

P(TM_G)₃: Elusive or Synthetically Accessible Phosphane

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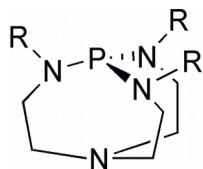


Figure 1. Verkade's base

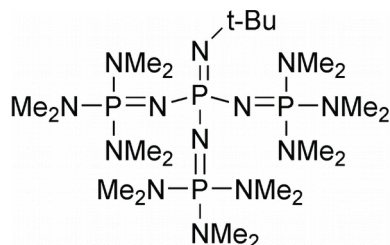


Figure 2. *t*-Bu-P₄ phosphazene

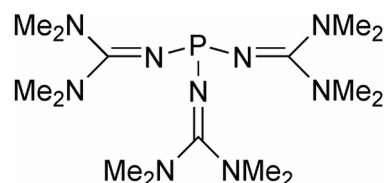


Figure 3. P(TM_G)₃

Phosphanes are commonly used as ligands to form transition metal complexes whose importance is prominent in organic catalysis. Due to predominantly low basicity of known phosphanes they are rarely utilized as a Brønsted bases in base-catalysed reactions. Notable exceptions are proazaphosphatranes also known as Verkade's bases (Fig. 1.). Verkade's bases have been successfully applied in a variety of organic reactions where deprotonation of reactant is the initial step of chemical reaction.^{1,2} Nevertheless, Verkade's bases with $pK_a = 33$ in acetonitrile are substantially weaker than the strongest organic (Schwesinger) base *t*-Bu-P₄ phosphazene with $pK_a = \sim 43$ (Fig. 2.).^{1,2} Meanwhile, it was computationally demonstrated that substitution of PH₃ with strong electron donating substituents like dimethylamino (NMe₂) or tetramethylguanidino (TMG) groups significantly increases the basicity of resulting phosphanes, opening the door for strong phosphane Brønsted base design. Further, it appears that tris-(tetramethylguanidiny) phosphane, P(TM_G)₃ (Fig. 3.), could be much stronger base than proazaphosphatranes.³ However, despite numerous synthetic attempts, the neutral P(TM_G)₃ has never been prepared. Only protonated form P(TM_G)₃H⁺ was isolated as a stable salt. Deprotonation attempts resulted in either compounds decomposition or no reaction at all.⁴ Using reliable DFT methods, we have investigated basicity, thermodynamics and kinetics of decomposition of P(TM_G)₃ phosphane to guide synthetic chemists in future attempts of P(TM_G)₃ preparation.

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