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Building a Lewis Acidic Phosphorus

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Abstract

Using the σ- and π-donating properties of carbodiphosphorane ligands, we recently synthesized a phosphorus (III)-containing dication. It is observed to undergo interesting reactivity with PMe₃, H₂O and MeOH.

Keywords

Phosphenium, Carbodiphosphoranes, Two-coordinate, Dication

Introduction

There has been recent interest in frustrated Lewis acid and base pairs.[1] Phosphenium salts potentially provide both acidic and basic sites on one atom and over the years, many crystallographically established phosphenium ions have been obtained.[2] Different types of ligands including N-heterocyclic carbenes[3a,b] and cyclic alkylamino carbenes[3c] have been used for the stabilization of a variety of main group compounds, including phosphenium ions. Such ligands act as strong 2- electron σ-donors but relatively poor π-acceptors. On the other hand, carbodiphosphorane ligands, also known as “carbones”, are quite different, in that they can act as strong 2- electron σ- and 2- electron π-donors. A number of research groups have utilized the electron donating properties of carbone ligands to stabilize electron deficient main group compounds[4] and Matthews[5] and Schmidpeter[6] have succeeded in using them to support phosphorus centers. We managed to utilize the strong donor properties of carbones to synthesize a carbone-stabilized two-coordinate phosphorus (III)-containing dication,[7] which exhibited interesting reactivity with PMe₃, H₂O and MeOH.[8]
Results and Discussion

Carbones can be represented using various different resonance structures as shown in Scheme 1.[9]

![Resonance structures of carbone ligands](image)

Scheme 1. Resonance structures of carbone ligands

The overall synthetic procedure for the preparation of the target dication is depicted in Scheme 2. Carbone was reacted with excess iPr₂NPCI₂ in benzene to give the monocationic chloride displacement product [1]Cl. Addition of 2.0 equiv of AlCl₃ resulted in the synthesis of a two-coordinate phosphorus (III)-containing dication via a halide abstraction reaction.

![Key reagents/conditions](image)

Scheme 2. Key reagents/conditions: i) iPr₂NPCI₂ (excess), benzene; ii) 2.0 equiv of AlCl₃ in CH₂Cl₂.

It was also possible to obtain 2 in the presence of BAr₄⁻ anions. When [2][BAr₄⁻]₂ was reacted with either 2.0 or 3.0 equiv of PMe₃, ³¹P NMR studies suggested an equilibrium between the dication and the dication-PMe₃ adduct (Scheme 3). As expected, the equilibrium could be shifted towards the adduct at low temperatures.

![Key reagents/conditions](image)

Scheme 3. Key reagents/conditions: i) 2.0 or 3.0 equiv of PMe₃ in CH₂Cl₂, variable temperatures from 23 to -30°C.
On the other hand, introducing 1.0 or 2.0 equiv of PMe₃ to a solution containing [2][AlCl₄]₂ showed anion interference and the establishment of an additional equilibrium between PMe₃ and the anion (Scheme 4). This could be rationalized by using the Hard-Soft Acid-Base (HSAB) concept, which has already been established for similar systems.[2b]

![Scheme 4. Proposed equilibria.](image)

A facile formal oxidative addition of water or methanol to [2][BARF₄]₂ was also possible at room temperature, in the absence of activators, using only 1.0 equiv of these substrates. Subsequently, it was possible to abstract a further proton from the water addition product [3a][BARF₄]₂ by introducing 1.0 equiv of NEt₃ (Scheme 5). Interestingly, the resulting compound [4a][BARF₄]₂ depicts a very rare example of H-bonding between two distinct cationic moieties.

![Scheme 5. Key reagents/conditions: i) 1.0 equiv of ROH (R = H or Me), CH₂Cl₂; ii) 1.0 equiv NEt₃, CH₂Cl₂.](image)

**Conclusion**

A carbone-stabilized two-coordinate phosphorus (III)-containing dication has been synthesized and its reactivity has been explored.

**Acknowledgements**

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References


