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 carbene 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 carbene-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]

Scheme 1. Resonance structures of carbene ligands

The overall synthetic procedure for the preparation of the target dication is depicted in Scheme 2. Carbone was reacted with excess $i\text{Pr}_2\text{NPCl}_2$ in benzene to give the monocationic chloride displacement product **[1]**Cl. Addition of 2.0 equiv of AlCl_3 resulted in the synthesis of a two-coordinate phosphorus (III)-containing dication via a halide abstraction reaction.

Scheme 2. Key reagents/conditions: i) $i\text{Pr}_2\text{NPCl}_2$ (excess), benzene; ii) 2.0 equiv of AlCl_3 in CH_2Cl_2 .

It was also possible to obtain **2** in the presence of BAR_4^{F} anions. When $[\mathbf{2}][\text{BAR}_4^{\text{F}}]_2$ was reacted with either 2.0 or 3.0 equiv of PMe_3 , ^{31}P NMR studies suggested an equilibrium between the dication and the dication- PMe_3 adduct (Scheme 3). As expected, the equilibrium could be shifted towards the adduct at low temperatures.

Scheme 3. Key reagents/conditions: i) 2.0 or 3.0 equiv of PMe_3 in CH_2Cl_2 , variable temperatures from 23 to -30°C .

On the other hand, introducing 1.0 or 2.0 equiv of PMe_3 to a solution containing $[\mathbf{2}][\text{AlCl}_4]_2$ showed anion interference and the establishment of an additional equilibrium between PMe_3 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.

A facile formal oxidative addition of water or methanol to $[\mathbf{2}][\text{BAR}^{\text{F}}_4]_2$ 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 $[\mathbf{3a}][\text{BAR}^{\text{F}}_4]_2$ by introducing 1.0 equiv of NEt_3 (Scheme 5). Interestingly, the resulting compound $[\mathbf{4a}][\text{BAR}^{\text{F}}_4]_2$ 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), CH_2Cl_2 ; ii) 1.0 equiv NEt_3 , CH_2Cl_2 .

Conclusion

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

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