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Building a Lewis Acidic Phosphorus

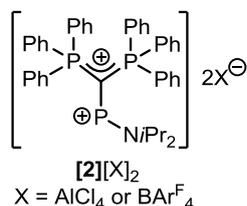
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Abstract



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

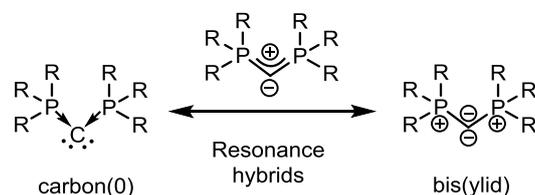
Phosphenium, Carbodiphosphoranes, Two-coordinate, Dication

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]

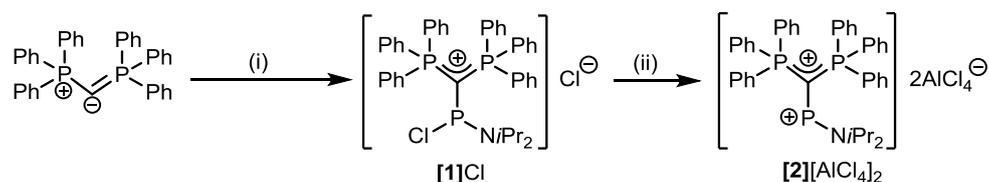
Results and Discussion

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



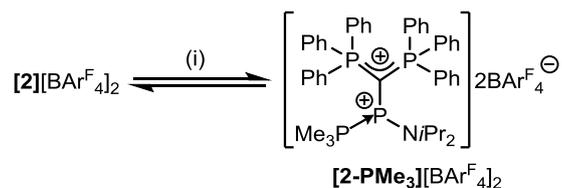
Scheme 1. Resonance structures of carbene ligands

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.



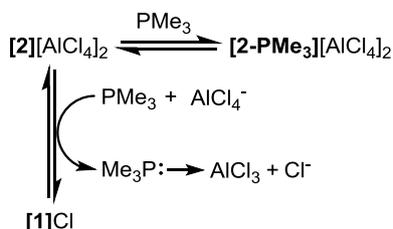
Scheme 2. Key reagents/conditions: i) $i\text{Pr}_2\text{NPCl}_2$ (excess), benzene; ii) 2.0 equiv of AlCl_3 in CH_2Cl_2 .

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.



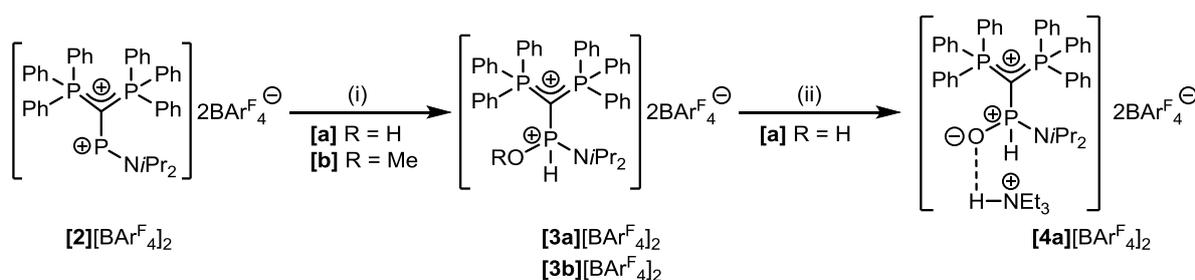
Scheme 3. Key reagents/conditions: i) 2.0 or 3.0 equiv of PMe_3 in CH_2Cl_2 , variable temperatures from 23 to -30°C .

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.

Acknowledgements

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References

- [1] Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2010**, 49, 46-76.
- [2] See, for example: a) Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, 100, 7784-7786; b) Gudat, D. *Coord. Chem. Rev.* **1997**, 163, 71-106; c) Gruetzmacher, H.; Pritzkow, H. *Angew. Chem. Int. Ed.* **1989**, 6, 740-741.
- [3] See, for example: a) Wanzlick, H. W. *Angew. Chem. Int. Ed.* **1962**, 1, 75-80; b) Arduengo, A. J. III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, 113, 361-363; c) Lavallo, V.; Canac, Y.; Prasang, C.; Donnadiu, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2005**, 44, 5705-5709.
- [4] See, for example: a) Inés, B.; Patil, M.; Carreras, J.; Goddard, R.; Thiel, W.; Alcarazo, M. *Angew. Chem. Int. Ed.* **2011**, 50, 8400-8403; b) Kuzu, I.; Kneusels, N.-J. H.; Bauer, M.; Neumueller, B.; Tonner, R. *Z. Anorg. Allg. Chem.* **2014**, 640, 417-422; c) Khan, S.; Gopakumar, G.; Thiel, W.; Alcarazo, M.; *Angew. Chem. Int. Ed.* **2013**, 52, 5644-5647.
- [5] Birum, G. H.; Matthews, C. N. *J. Am. Chem. Soc.* **1966**, 88, 4198-4203.
- [6] Schmidpeter, A.; Noeth, H.; Jochem, G.; Schroedel, H.-P.; Karaghiosoff, K. *Chem. Ber.* **1995**, 128, 379-393.
- [7] Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Vidovic, D. *Angew. Chem. Int. Ed.* **2013**, 52, 3132-3135.
- [8] Tay, M. Q. Y.; Lu, Y.; Ganguly, R.; Vidovic, D. *Chem. Eur. J.* **2014**, 20, 6628-6631.
- [9] See, for example: a) Tonner, R.; Oexler, F.; Neumueller, B.; Petz, W.; Frenking, G. *Angew. Chem. Int. Ed.* **2006**, 45, 8038-8042; b) Schmidbaur, H. *Angew. Chem. Int. Ed.* **2007**, 46, 2984-2985.