2-(Dimethylamino)phosphinine: A Phosphorus Containing Aniline Derivative

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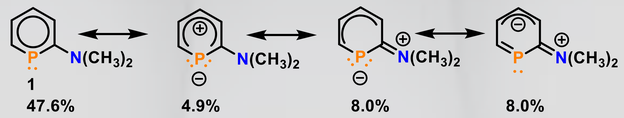
Introduction: Since the discovery of phosphinines by Märkl in 1966 a broad spectrum of associated coordination compounds became accessible and a variety of complexes with unusual features and exciting new properties have been presented in recent years[1,2]. A donor substituent at the 2-position of the heterocycle has a substantial impact on the coordination chemistry of phosphinines rendering them as either μ_2-bridging 2-electron or 4-electron ligands (μ_2-P-2e or μ_2-P-4e) as was shown in the case of phosphinin-2-ol and its anionic form[3].
The corresponding phosphorus containing aniline derivative was still unknown, however, with nitrogen being less electronegative than oxygen we expected a significant electronic interaction of its lone pair with the π-accepting system of the heterocycle. We therefore started an in-depth investigation on the theoretical properties, the synthesis and the coordination chemistry of hitherto unknown 2-aminophosphinines (**1**)[4].

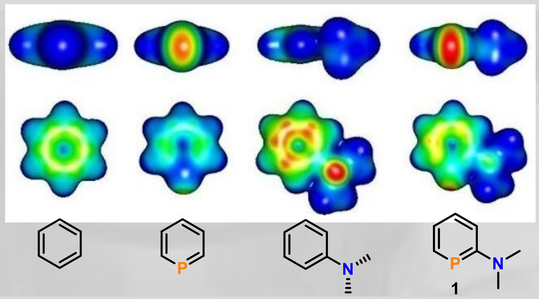
Natural Resonance Theory and Electrostatic-Potential-Maps (EP) of 1



Calculations were carried out at B3LYP/cc-pVTZ level of theory

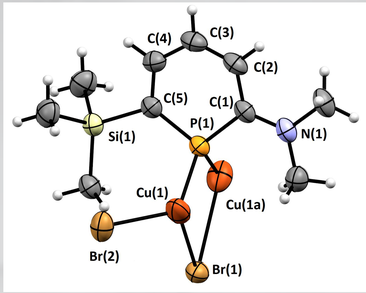
- Relevant contribution of **P-4e** zwitterionic structure of about 12.9% to electronic ground state
- Indication of an electronic interaction of the nitrogen lone pair with the π-system

The EP (in a.u.) colour-coded from -0.025 (red) to 0.050 (blue) is mapped on electron density isosurfaces of 0.02 e/au³.

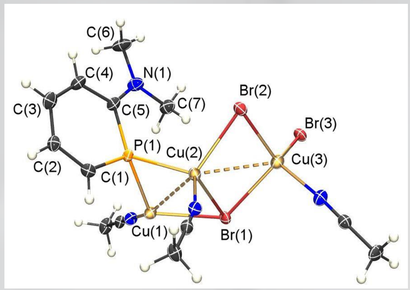


- Amino substitution increases negative charge (red) accumulation in the ring π-system
- In *N,N*-dimethylaniline, the nitrogen lone pair shows the most negative EP
- π-accepting phosphinine **1** compensates for rendering the ring more negative than the nitrogen lone pair
- **Pronounced impact of –NMe$_2$ on phosphinine π-system**

Coordination Chemistry of 1 and 2 with CuBr·SMe$_2$



Selected bond lengths (Å):
Cu(1)-Br(1): 2.488(11), Cu(1)-Br(2): 2.623(9)
P(1)-Cu(1): 2.226(11),
C(1)-P(1): 1.803(4),
P(1)-C(5): 1.769(4),
C(1)-N(1): 1.331(5),
C(5)-Si(1): 1.897(4),
C(1)-C(2): 1.422(6), C(2)-C(3): 1.358(6),
C(3)-C(4): 1.397(6), C(4)-C(5): 1.374(5)

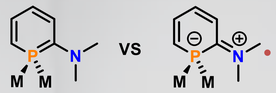


Selected bond lengths (Å):
P(1)-Cu(1): 2.2778(17), P(1)-Cu(2): 2.3028(17),
Cu(2)-Cu(1): 2.6077(10),
P(1)-C(1): 1.775(6),
C(5)-P(1): 1.729(6),
C(1)-N(1): 1.359(8),
C(1)-C(2): 1.411(8), C(2)-C(3): 1.388(9),
C(3)-C(4): 1.407(9), C(4)-C(5): 1.372(8)

Conclusion

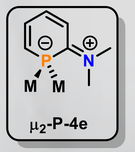
- Unprecedented 2-aminophosphinines are powerful neutral π-donating P,N-hybrid-ligands
- First example of neutral phosphinine acting as rare **μ_2-P-4e** bridging donor ligand
- Closing the gap of known 2-donor functionalized phosphinines

Ligand Classification: μ_2-P-2e or μ_2-P-4e?



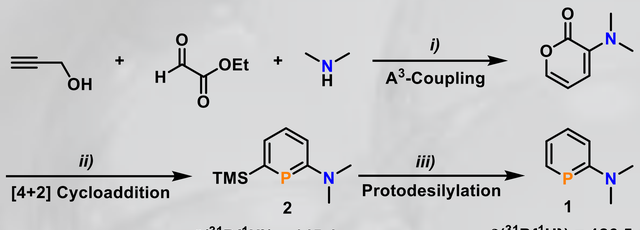
Structural features in the solid state:

- Elongation of P-C-bond (P-C-single bond in free phosphinines: ~ 1.70-1.73 Å)
- Partial double bond character of C-N-bond (C-N-single bond: ~ 1.47 Å)
- Planar nitrogen atom ($\Sigma_{C\text{-}N\text{-}C}$ = 360°)
- Alternating C-C bonds



μ_2-P-4e bridging phosphinine in the solid state matching theoretical investigations

Ligand Synthesis via Pyrone-Route[5]



i): a) CuBr (0.2 eq.), 3Å MS, THF, 18 h, b) silica, toluene, 18 h; ii) $(CH_3)_3Si$-CP (1.0 eq.), toluene, reflux, 12 h; iii): a) HCl·Et$_2$O (2M, 4.7 eq.), r.t., 12 h; b) triethylamine (xc.), r.t. 1 h.

References:
1) G. Märkl, *Angew. Chem.* **1966**, *78*, 907–908; 2) N. T. Coles, A. S. Abels, J. Leitl, R. Wolf, H. Grützmacher, C. Müller, *Coord. Chem. Rev.* **2021**, *433*, 213729–213755; 3) Y. Hou, Z. Li, Y. Li, P. Liu, C. Y. Su, F. Puschmann, H. Grützmacher, *Chem. Sci.* **2019**, *10*, 3168–3180; 4) S. Giese, K. Klimov, A. Mikeházi, Z. Kelemen, D. S. Frost, S. Steinhauer, P. Müller, L. Nyulászi, C. Müller, *Angew. Chem. Int. Ed.* **2021**, *60*, 3581–3586; 5) W. Fan, S. Ma, *Angew. Chem. Int. Ed.* **2014**, *53*, 14542–14545.

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