Voyage in the Electronic Aspects of Phosphorus Chemistry

Gabriele Manca, Andrea Ienco, Maurizio Peruzzini, Carlo Mealli

Please leave one blank line

Consiglio Nazionale delle Ricerche Istituto di Chimica dei Composti Organometallici
Via Madonna del Piano 10, Sesto Fiorentino

Please leave one blank line

e-mail: gabriele.manca@iccom.cnr.it

Please leave two blank lines

Phosphorus shares with carbon the possibility of various allotropes with different stability and structure. Unlike white phosphorus, P_4, formed by discrete tetrahedral molecules, is highly reactive, the black allotrope (bP) one shows a layered extended structure and exhibits the most thermodynamic stability. Some years ago, the exfoliation the bP provides the mono-layer 2D material phosphorene (P_n),[1] which, due to its fast reactivity with oxygen, has to be protected or functionalized. Herein, we present a voyage in the structural/electronic underpinnings, which rules the reactivity of the phosphorus allotropes with small molecules, such as di-iodine, and transition metal fragments. In particular, we started with the P_4 for which a detailed analysis of the reaction between P_4 and I_2 highlighted multi-step concerted process with of 3 + 3 bond breakings/makings in each case.[2] On the gathered information on the simplest P_4, we explored the plausibility of some reaction pathway of P_n through solid state DFT calculations. The high density of the facial P atoms, with outpointing but not fully independent lone pairs, offers potential P_n reactivity with mono, bi- and three-functional acidic units, see Figure 1. In particular, we examined the reliability of the adducts between P_n and BH_3, I_2 or the ClAu(I) fragment.[3] Other unsaturated Transition Metal fragments of the L_2M and L_3M type were chosen on the basis of the *isolobal analogy* concept[4] for combining neighbor P_n atoms with a single metal that carries multiple vacant lobes.

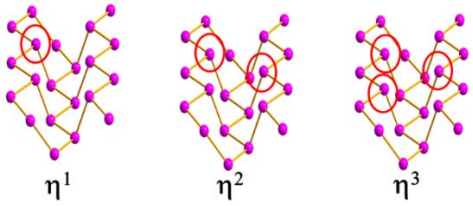

Fig.1. Different potential coordination of acids or metal fragments on the P_n surface.

---

[1] Kang, J.; Wood, J. D.; Wells, S. A.; Lee, J. -H.; Liu, X.; Chen, K.-S.; Hersam, M. C. *ACS Nano* **2015**, *94*, 3596-3604.
[2] Mealli, C.; Ienco, A.; Peruzzini, M.; Manca, G. *Dalton Trans.* **2018**, *47*, 394-408.
[3] Ienco, A.; Manca, G.; Peruzzini, M.; Mealli, C. *Dalton Trans.* **2018**, *47*, 17243-17256.
[4] Hoffmann R. Nobel Lecture *Angew. Chem., Int. Ed.* **1982**, *21*, 711-724.

Please leave one blank line

Acknowledgements: *The authors acknowledge the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant Agreement No.670173) for funding the project PHOSFUN "Phosphorene functionalization: a new platform for advanced multifunctional materials" through an ERC Advanced Grant.*