

Low oxidation state diphosphorus and diarsenic compounds stabilized by N-heterocyclic carbenes

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Literature Seminar

November 10, 2014

Although the allotropes of phosphorus and arsenic have been extensively studied, the chemistry of their diatomic forms has remained elusive. The free diphosphorus molecule P_2 forms only at temperatures above 800 °C, and the free diarsenic molecule As_2 has never been directly observed.¹ Triply bonded dipnictogen units, however, are known to exist as 4-, 6-, or 8-electron donor ligands in certain transition metal carbonyl complexes.²

In recent years, reactive diboron and disilicon molecules have been stabilized by forming adducts with N-heterocyclic carbenes (NHCs).² With these successes, the use of NHCs has been extended to the stabilization of group 15 diatomics. Specifically, Robinson and coworkers have demonstrated that zero valent dipnictogen units can be stabilized by forming adducts with bulky, aromatic NHCs.² The NHCs, which serve as neutral two electron donors, convert the triply bonded dipnictogen core into a singly bonded dipnictinidene structure with four lone pairs (two on each pnictogen atom). The P_2 and As_2 units convert into the singly-bonded form in order to create the empty p-orbitals necessary for adduct formation with the NHCs.

To synthesize a stable compound with a diphosphorus core, the adduct $L:PCl_3$ (**1-P**) was first synthesized in almost quantitative yield (Figure 1)³ by treatment of phosphorus trichloride with the desired bulky NHC.⁴ In this phosphorus(III) compound, the phosphorus center has a trigonal bipyramidal geometry in which one equatorial site is occupied by a lone pair (the four atoms coordinated to phosphorus thus form a see-saw structure). The phosphorus-carbon bond length for **1b-P** is 1.879 Å, which is indicative of a two-electron phosphorus-carbon single bond.³ For comparison, P-C single bond lengths of 1.828 and 1.803 Å are seen in triphenylphosphine⁵ and triphenylphosphine oxide⁶, respectively.

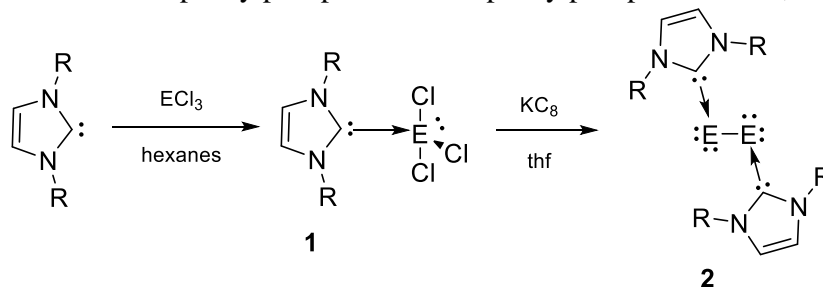


Figure 1. General synthesis of NHC stabilized bis-pnictinidene molecules, where E= As or P; and R = 2,4,6-trimethylphenyl (**a**), 2,6-diisopropylphenyl (**b**), or H (**c**).

Reduction of **1-P** with potassium graphite in THF affords the bis-phosphinidenes, $L:P-P:L$ (**2-P**), which form air- and moisture-sensitive red crystals in moderate yields (**2a-P**, 57%; **2b-P**, 21%).³ The ^{31}P NMR shift of δ -52.4 is suggestive of a bis-phosphinidine structure of phosphorus(I) and not a 2,3-phosphabutadiene structure of phosphorus(III); the latter typically have ^{31}P NMR shifts of 34-54 ppm.⁷ The crystal structure of the bis-phosphinidine compound reveals a trans bent geometry with a C-P-P-C torsion angle of 180.0° for **2a-P** and 134.1° for **2b-P**.³ The phosphorus-phosphorus bond length is ca. 2.20 Å is identical to the distance of 2.199 Å in white phosphorus.⁸ The phosphorus-carbon bond length of 1.75 Å for both **2a-P** and **2b-P**, which is slightly longer than the 1.72 Å distances typically seen for the P-C double bonds in 2,3-phosphabutadienes,⁹ suggests that there is partial double bond character.

DFT studies at the B3LYP/DZP level on a simplified model (**2c-P**) gave an energy-minimized structure with a C-P-P-C torsion angle of 98.6°. This result attests that the C-P-P-C torsion angle increases with increased steric bulk of the R-group of the NHC. A natural bond order (NBO) analysis, performed on **2c-P** with a constrained C_{2h} symmetry, showed that one phosphorus lone pair has mostly s character

(68.8% s, 31.2% p, 0.0 % d), the other is almost pure p (0.0% s, 99.8% p, 0.2 % d) and is involved in modest interaction with the p-orbital of the ipso carbon of the NHC. The Wiberg bond indices of the P-P bond (1.004) and the P-C bond (1.397) suggest that the P-P bond is single whereas the P-C bond has partial double bond character.

Further reduction of the bis-phosphinidene with lithium metal cleaves the P-P bond. The product is not a phosphide but is rather a C-deprotonated phosphinidene, **3a** (Figure 2).⁴ The ³¹P NMR shift (δ -143.0) for **3a** and the elongated P-C bond (1.763 Å) are consistent with a carbene-stabilized phosphinidene structure.

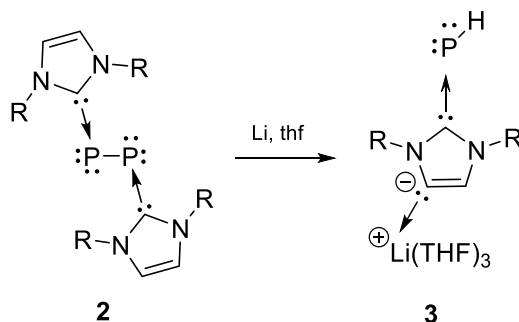


Figure 2: Reduction of bis-phosphinidene (**2a-P**).

In 2010, Bertrand and coworkers demonstrated that one-electron oxidation **2b-P** with triphenylmethyl tetrakis(pentafluorophenyl)borate occurs readily and forms green crystals of the corresponding bis-phosphinidene cation **2d-P⁺**.¹⁰ The crystal structure of this cation shows that its structure is very similar to that of **2d-P**, except that the P-P bond distance of 2.094 Å is significantly shorter than that of 2.184 Å in the neutral compound, and is mid-way between a P-P double bond and a P-P single bond. Two-electron oxidation of **2d-P** with two equivalents of ferrocenium triflate gives the dication **2d-P²⁺**. A single crystal X-ray diffraction shows that the P-P bond length has shortened even further (2.083 Å). The NBO analysis on this series of compounds revealed a clear increase in the amount of π -bonding between the two phosphorus atoms upon oxidation.

The bis-arsenidene analogue L-As-As-L, **2d-As**, was synthesized by means of a similar procedure.¹¹ The As-As bond distance of 2.442 Å is comparable to the As-As single bond length in As₄ (2.44 Å) and the sum of the As single-bonded covalent radii (2.424 Å). The As-C bond distance of 1.881 Å is slightly shorter than the As-C bond in NHC-arsenic trichloride adducts (1.900-1.902 Å). Wiberg bond indices for the As-As bond (1.009) and the As-C bond (1.341) were determined by DFT calculation on the simplified model (**2c-As**) with the symmetry constrained to the X-ray coordinates for **2d-As**. These results suggest that this compound, much like **2a-P**, is a bis-arsenidene and not a 2,3-diarsenobutadiene. This compound is the first example of a NHC-stabilized zero-valent diatomic molecule in the fourth period or higher.

One- and two-electron oxidation of **2d-As** was achieved by treatment with two and four equivalents of gallium trichloride, respectively.¹² X-ray diffraction data for both **2a-As⁺** and **2a-As²⁺** show that the As-As bond distance shortens, whereas the As-C distance increases, upon oxidation. NBO analysis on simplified models of these two cations gave clear evidence of π -bonding between the two arsenic atoms.

Attempts to extend this chemistry by stabilizing a diantimony or dibismuth core with NHCs have been unsuccessful.¹³ Although NHC-antimony trichloride and NHC-bismuth trichloride adducts have been synthesized, attempted reduction with potassium graphite resulted in decomposition with formation of the free NHC ligand and elemental antimony or bismuth. In order to stabilize heavier main group diatomics, other carbene ligands have been utilized, the most successful being cycloalkyl(amino)carbenes (CAACs).¹⁴ In 2014, Bertrand and coworkers successfully isolated the first bis-stibinidene (Figure 3).² The success of this synthesis has mainly been attributed to the increased electrophilicity of CAAC as compared to an NHC. The increased donor ability helps to stabilize the diantimony unit.¹⁴

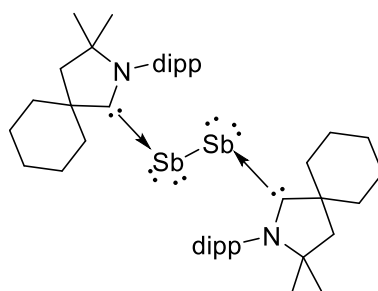


Figure 3. Structure of the first bis-stibinidene.

In conclusion, NHCs can be used to stabilize main group diatomics P_2 and As_2 , whereas the stronger donor CAAC is necessary to stabilize the heavier main-group diatomic Sb_2 . These interesting analogues of dinitrogen have provided insights into the reactivity of unstable allotropes and the fundamentals of main group pi-bonding.

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