Activation of P_4

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Bi–P Bond Homolysis as a Route to Reduced Bismuth Compounds and Reversible Activation of P_4

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Abstract: *Bismuth diphenylphosphanides* $Bi(NON^R)(PPh_2)$ *(*$NON^R = [O(SiMe_2NR)_2]$*, R = tBu, 2,6-iPr*$_2C_6H_3$*, Aryl) undergo facile decomposition via single-electron processes to form reduced Bi and P species. The corresponding derivatives* $Bi(NON^R)(PCy_2)$ *are stable. Reaction of the isolated* Bi^{II} *radical* $^{\bullet}Bi(NON^{Ar})$ *with white phosphorus (*P_4*) proceeds with the reversible and selective activation of a single P–P bond to afford the bimetallic* $\mu,\eta^{1:1}$*-bicyclo[1.1.0]-tetraphosphabutane compound.*

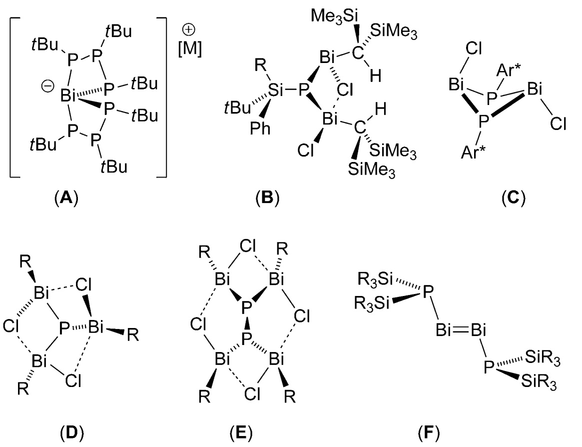


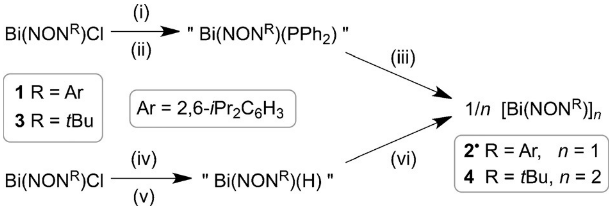
Figure 1. Structurally characterized compounds containing Bi–P bonds. **A**: $M^+ = [Li(THF)_4]^+$; **B**: R = *t*Bu, Ph; **C**: Ar* = 2,6-(Mes)$_2C_6H_3$; **D** and **E**: R = $CH(SiMe_3)_2$; **F**: $R_3 = Ph_2tBu$.

Until the 1990's[1] it was thought that bismuth forms no primary phosphides Bi_xP_y,[2] demonstrating an unusual reluctance for the elements to interact in the solid state.[3] Attempts to synthesize such compounds by dissolving phosphorus in molten bismuth resulted in segregation of the elements into their pure forms, a phenomenon exploited historically in the preparation of the black[4] and violet[5] allotropes of phosphorus. Work targeting molecular bismuth phosphanides containing $Bi{-}PR'_2$ groups also met with limited success. In 1999, "the first bismuth phosphanide complex" was reported, an anion consisting of two $\kappa^2P^{1,3}$-$[(PtBu)_3]^{2-}$ ligands and a Bi center (**A**, Figure 1).[6] Bismuth phosphinidenes containing $[PR']^{2-}$ ligands are restricted to bridging motifs (**B** and **C**).[7] When the reaction leading to formation of **B** was repeated with smaller silyl substituents on phosphorus (i.e., CMe_2iPr, Me), P–Si bond cleavage occurred to afford compounds containing $[P]^{3-}$ (**D**) or $[P_2]^{4-}$ (**E**) anions.[7a] The only structurally characterized terminal bismuth phosphanide is in the dibismuthene $[(tBuPh_2Si)_2PBi]_2$ (**F**).[8]

Bulky *N,N'*-chelating diamido ligands have recently been used to support low-coordinate organometallic,[9] and cationic[10] bismuth complexes. The disilylamidoether ligand $[O(SiMe_2NAr)_2]^{2-}$ (abbreviated NON^{Ar}, Ar = 2,6-$iPr_2C_6H_3$) generates a sufficiently stable environment at bismuth to allow the first monomeric Bi^{II} radical, $^{\bullet}Bi(NON^{Ar})$ ($\mathbf{2^{\bullet}}$) to be isolated.[11] This compound is a metal-based radical in the solid state, confirmed through a combination of X-ray diffraction, EPR spectroscopy, and SQUID magnetic measurements. We report herein how the NON^R ligand (R = Ar, *t*Bu) has been used in the isolation of the first terminal bismuth(III) phosphanides, and its influence on the stability of Bi–P bonds.

The reaction of $Bi(NON^{Ar})Cl$ (**1**) with $LiPPh_2$ (Scheme 1) generated tetraphenyldiphosphane ($\delta_P = -15.0$[12]) and the Bi^{II} radical $^{\bullet}Bi(NON^{Ar})$ ($\mathbf{2^{\bullet}}$, characteristic $SiMe_2$ resonance $\delta_H = -1.56$). We reasoned that these products form through homolytic cleavage of the Bi–P bond in the intermediate species, "$Bi(NON^{Ar})(PPh_2)$".[13] To investigate whether a steric conflict between the $[NON^{Ar}]$ ligand and the phosphanide promotes decomposition, $Bi(NON^{tBu})Cl$ (**3**) was synthesized.[14] Reaction of **3** with $LiPPh_2$ also proceeded with formation of tetraphenyldiphosphane. However, the reduced size of the ancillary ligand allowed the Bi^{II} product to dimerize, affording dibismuthane $[Bi(NON^{tBu})]_2$ (**4**). The composition of **4** was verified through independent synthesis,[14] exploiting the spontaneous decomposition of the intermediate hydride "$Bi(NON^{tBu})(H)$" (Scheme 1).[15]

X-ray diffraction confirmed **4** as a dibismuthane supported by a chelating diamido framework (Figure 2).[16] The



Scheme 1. i) $LiPPh_2$; ii) $-LiCl$; iii) $-0.5\,Ph_2P{-}PPh_2$; iv) $LiBHEt_3$; v) $-LiCl$, $-BEt_3$; vi) $-0.5\,H_2$.

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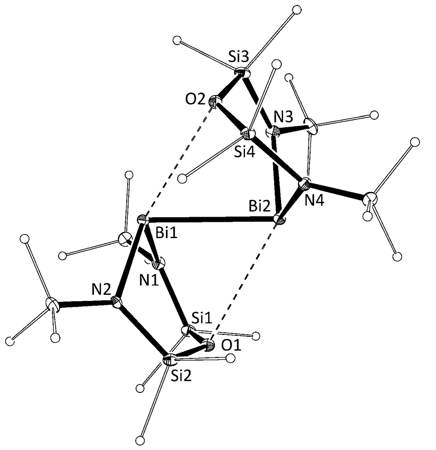


Figure 2. Thermal ellipsoid plot of **4** (120 K dataset, 30% probability and H-atoms omitted). Selected bond lengths [Å] and angles [°]: Bi1–Bi2 3.0201(2), Bi1–N1 2.199(3), Bi1–N2 2.194(3), Bi2–N3 2.188(3), Bi2–N4 2.191(3), O1⋯Bi2 3.274(2), O2⋯Bi1 3.330(2); N1-Bi1-N2 97.77(11), N1-Bi1-Bi2 85.43(8), N2-Bi1-Bi2 103.33(8), N3-Bi2-N4 96.46(11), N3-Bi2-Bi1 86.34(8), N4-Bi2-Bi1 104.96(8).

crystallographically distinct bismuth centers are pyramidal, with longer Bi–N bonds (2.194(3) Å and 2.199(3) Å) compared to those in **3** (2.153(3) Å and 2.130(3) Å), consistent with a reduced metal center. The Bi–Bi distance of 3.0201(2) Å is within the range recorded for dibismuthanes (2.990(2)–3.1821(3) Å),[17] and shows only minor variation over the temperature range 100–293 K (3.0201(2) Å–3.0393(2) Å, Figure S10 in the Supporting Information). Intramolecular bismuth⋯oxygen contacts to the ligand on the opposing metal center (3.274(2) Å and 3.330(2) Å) may contribute to the stability of the Bi–Bi core of this molecule.

Reaction of **1** and **3** with $LiPCy_2$ afforded the terminal phosphanides $Bi(NON^{R})(PCy_2)$ (**5**, R = Ar; **6**, R = *t*Bu) as crystalline materials.[14] The ^{31}P NMR spectra show a sharp singlet (**5**, $\delta_P = 53.5$; **6**, $\delta_P = 18.4$), indicating a single phosphorus environment. X-ray diffraction data confirmed **5** and **6** as the first bismuth(III) phosphanides with terminal $Bi{-}PR'_2$ bonds (Figure 3). The Bi–P bond lengths (**5**: 2.6490(4) Å; **6**: 2.6465(7) Å) are equal within 3σ, and consistent with calculated values for $\Sigma r_{cov}(Bi{-}P) = 2.62$ Å.[18] The BiN_2Si_2O metallacycles in **5** and **6** approximate to a "boat" conformation, although their positions relative to the phosphanide ligand are different. In **5**, the bismuth atom lies "above" the least-squares plane defined by the silicon and nitrogen atoms by 0.97 Å, whereas it lies "below" this plane in **6** by 0.83 Å. These conformers are designated **5**(*exo*) and **6**(*endo*), respectively, based on the definition of Fulton et al. for pyramidally coordinated metal centers in β-diketiminate compounds (Figure S11).[19]

To avoid the use of chlorinated intermediates, the activation of white phosphorus (P_4) is of continued interest as an entry into organophosphorus compounds.[20] This reactivity has been observed for a few p-block elements,[21] including group-13 (Al, Ga, In, Tl) and -14 (Sn) metals that form M–P bonds when reacted with P_4 under mild conditions. There have been no recorded examples of group-15 metalloids/metals (As, Sb, Bi) active in this area.[22] Inspired by the research of Lappert et al. on the reaction of phosphinyl radicals with P_4,[23] we examined the reaction of the Bi^{II} radical with P_4.

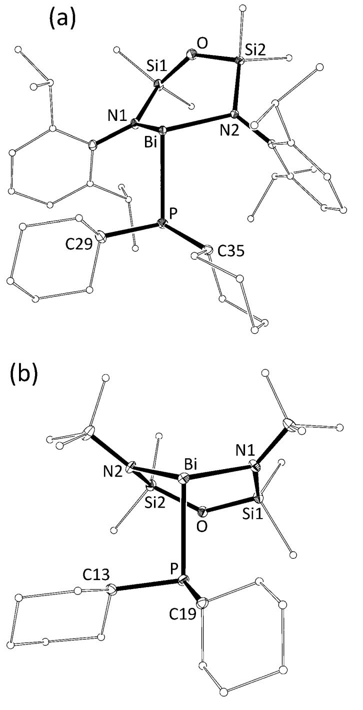
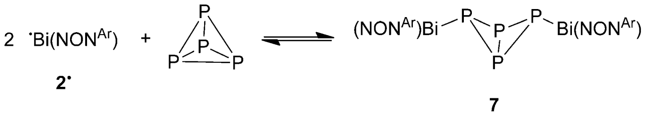


Figure 3. Molecular structures of a) **5** and b) **6** (ellipsoids at 30% probability, ligand substituents reduced, H-atoms omitted). Selected bond lengths [Å] and angles [°]: **5**: Bi–P 2.6490(4), Bi–N1 2.2043(12), Bi–N2 2.1853(12); N1-Bi-N2 95.24(5), N1-Bi-P 91.30(3), N2-Bi-P 101.32(3), Bi-P-C29 98.60(5), Bi-P-C35 107.01(5), C29-P-C35 109.66(7). **6**: Bi–P 2.6465(7), Bi–N1 2.183(2), Bi–N2 2.181(2); N1-Bi-N2 100.02(9), N1-Bi-P 96.69(6), N2-Bi-P 94.53(6), Bi-P-C13 97.97(9), Bi-P-C19 99.38(9), C13-P-C19 104.62(12).

An orange/red crystalline solid that was analyzed as being the bimetallic compound $(Bi\{NON^{Ar}\})_2(P_4)$ (**7**) was obtained from the reaction between P_4 and two equivalents of $\mathbf{2}^{\bullet}$.[14] No reaction between P_4 and **4** was observed. The ^{1}H NMR spectrum of an isolated sample of crystalline **7** indicated a diamagnetic species with a pyramidally coordinated bismuth center and a chelating NON^{Ar} ligand ($\delta_H = 0.47$ and 0.26, Si*Me₂*); the presence of radical $\mathbf{2}^{\bullet}$ was also noted in the ^{1}H NMR spectrum from its paramagnetically shifted resonances (Figure S14). The ^{31}P NMR spectrum showed two mutually coupled triplets of an A_2X_2 system at $\delta_P = -107.2$ and -350.3 ($J_{PP} = 164$ Hz), in addition to a singlet at $\delta_P = 521.2$ corresponding to P_4. The relative ratio of **7** and P_4 varied with temperature, indicating an equilibrium mixture in solution ($K_{eq} = 1.5 \times 10^{3}\,M^{-2}$ at 293 K). These data are interpreted as the selective and reversible activation of a single P–P bond in the P_4 tetrahedron, to afford the tetraphosphabicyclo[1.1.0]butane-bridged bimetallic compound **7** [Eq. (1)]. A van 't Hoff plot (Figure S13) obtained from ^{31}P NMR data of **7** over the range −40 °C to 20 °C gives $\Delta H^{\ominus} = -64.8\,kJ\,mol^{-1}$ and $\Delta S^{\ominus} = -154.8\,J\,K^{-1}\,mol^{-1}$. These data show that, as expected, the activation is exothermic, with a reduction in the entropy at low temperature as the bimetallic complex **7** is formed.



X-ray diffraction analysis confirmed the bridging $\mu,\eta^{1:1}$-P_4 unit in **7** (Figure 4). This is an unusual structural motif that has been crystallographically characterized in only seven other metal systems, dominated by transition metals (Fe × 2,[24] Ni × 2,[25] Cr,[26] Mn[27]). A single example involving tin has also been documented.[28] The Bi–P distance in **7** is slightly larger than in **5** and **6**, indicative of a weaker bond and consistent with a reversible bond-cleavage/formation process.

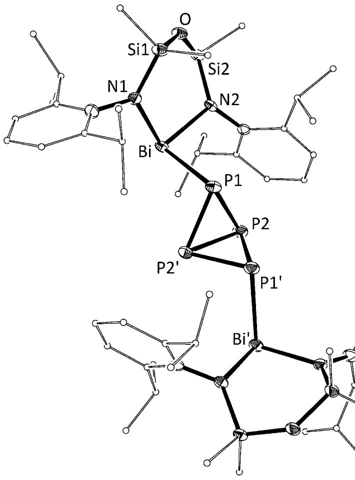


Figure 4. Molecular structure of **7** (ellipsoids at 30% probability, ligand substituents reduced, H-atoms omitted, ′=1−x, y, 3/2−z). Selected bond lengths [Å] and angles [°]: Bi–P1 2.6749(13), P1–P2 2.2094(17), P1–P2′ 2.2229(17), P2–P2′ 2.178(2), Bi–N1 2.169(4), Bi–N2 2.192(3); N1-Bi-N2 95.19(13), N1-Bi-P1 98.10(10), N2-Bi-P1 95.35(9), P2-P1-P2′ 58.88(7), Bi-P1-P2 96.70(6), Bi-P1-P2′ 96.88(6), P1-P2-P1′ 77.56(7), P1-P2-P2′ 60.87(6), P2′-P2′-P1′ 60.25(5).

The electronic structure of the Bi–P bond has been examined by density functional calculations. Results for *endo*- and *exo*-Bi(NON^R)(PR′$_2$) (**I**, R = *t*Bu, **II**, R = Ar; **a**, R′ = Ph, **b**, R′ = Cy show the constitution of the "Bi–P" fragment is as predicted from Lewis structure models (Table S3). NBO analyses indicate approximate 40:60 contributions from Bi and P, respectively, with Wiberg Bond Indices (WBI) lower for the diphenyl phosphanides (R′ = Ph, WBI = 0.79 to 0.82) than for the dicyclohexyl derivatives (R′ = Cy, WBI = 0.85 to 0.88). In agreement with the isolated structures, the *endo* conformers are more stable for the [NON^{tBu}] ligand (*exo*-**Ia**: $+12.3\ \text{kcal mol}^{-1}$, *exo*-**Ib**: $+14.3\ \text{kcal mol}^{-1}$), whilst the *exo*-[NON^{Ar}] derivatives are lower in energy, although the energy difference is considerably less (*endo*-**IIa**: $+2.5\ \text{kcal mol}^{-1}$, *endo*-**IIb**: $+3.1\ \text{kcal mol}^{-1}$). The Bi–P bond in **7** most closely resembles that of the diphenylphosphanide derivatives, with 35:65 contributions from Bi and P, respectively, and a WBI of 0.79 (Table S4).

Previous work has shown that P_4 activation by GeAr*$_2$ is reversible under exposure to UV light, caused by a transition from the HOMO (Ge–P bonding) to the LUMO (Ge···P antibonding).[29] The UV/Vis spectrum of **7** (−40 °C) shows a peak at 405 nm, in addition to absorptions from radical **2˙** (Figure S4). Time-dependent DFT calculations show that three electronic transitions contribute to this absorption, each associated with excitation from the HOMO (Bi–P bonding, P1···P1′ antibonding) to the LUMO + 1 (Bi···P antibonding, P1-P1′ bonding; Figure 5). Related calculations performed on *endo*- and *exo*-Bi(NON^R)(PR′$_2$) show an average bathochromic shift of about 70 nm for transitions representing excitation from Bi–P bonding to Bi···P antibonding orbitals when R′ = Ph (Tables S6, S15). These data are consistent with the experimentally observed higher lability of the Bi–PPh$_2$ bond, and indicate that photolysis may play an important role in the stability of Bi–P bonds.

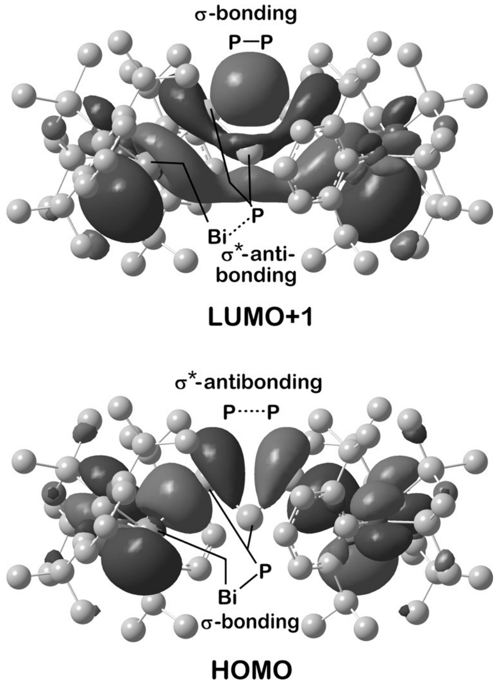


Figure 5. Orbitals associated with the electronic transitions observed in **7**.

Keywords: bismuth · bond homolysis · main-group radicals · P_4 activation · phosphanides

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