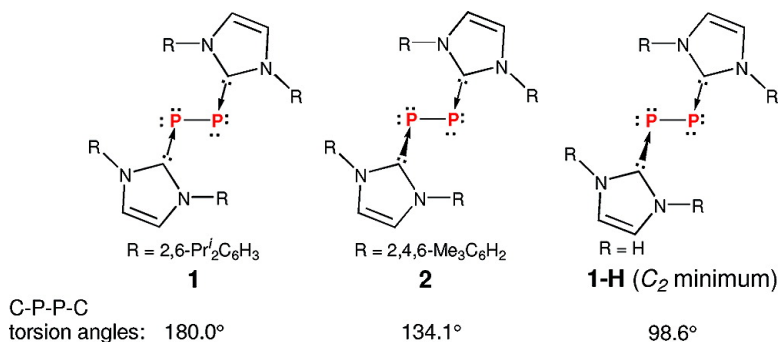


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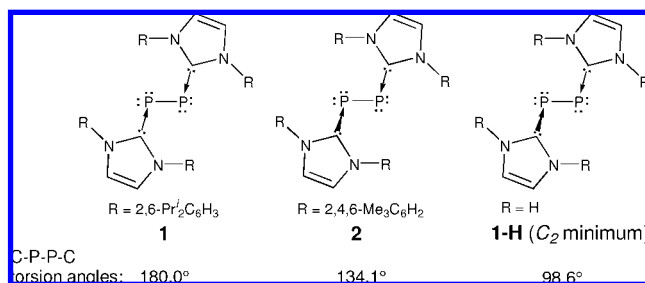
Carbene-Stabilized Diphosphorus

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Brand's quest for the "philosopher's stone," by distilling residual salts from evaporated urine, led instead to phosphorus, the only element originally derived from the human body.¹ The allotropy of phosphorus—white, red, and black—is well documented. Pyrolysis of white phosphorus, P₄, yields the high temperature diphosphorus allotrope, gaseous P₂.² In contrast to the legendary inert nature of its ubiquitous lighter congener N₂, P₂ is highly reactive and association-prone. Is it possible to stabilize the P₂ molecule to explore its expected versatility? Indeed, diphosphorus can function as four-, six-, and eight-electron donor ligands² in transition metal carbonyl complexes.³ Remarkably, Cummins and co-workers reported the "mild thermal extrusion" of P₂ from niobium diphosphazide complexes⁴ and that the Pt(0) species, (C₂H₄)Pt(PPh₃)₂, may serve as a trap for W(CO)₅-complexed P₂ molecules.⁵ In all these examples, P₂ behaves as a typical Lewis base (i.e., an electron pair donor). We now demonstrate the stabilization of P₂ by its serving as an electron pair acceptor and, thus, mimicking the behavior of a Lewis acid. Herein, we report the syntheses,⁶ structures,⁶ and computations⁷ of N-heterocyclic carbene (NHC, L:) stabilized P₂ molecules, L:P–P:L, **1** (L' = :C{N(2,6-Pr₂C₆H₃)CH₂})₂ and **2** (L'' = :C{N(2,4,6-Me₃C₆H₂)CH₂}). While the free P₂ molecule, :P≡P:, possesses a phosphorus–phosphorus triple bond, compounds **1** and **2** exhibit a unique bisphosphinidene structure: two phosphinidene units, each with two lone pairs of electrons, bridged by a phosphorus–phosphorus single bond.



Recently, Bertrand and co-workers reported P₄- and P₁₂-based carbene complexes.^{8–10} Our laboratory recently reported carbene-stabilized diborenes, L:(H)B=B(H):L,^{11,12} and diatomic silicon, L:Si=Si:L.¹³ Extending this strategy, we prepared L:PCl₃ by combining L: ligands with PCl₃. The potassium graphite reduction of L:PCl₃ (L:PCl₃/KC₈ ratio of 1:3.1) in THF affords the carbene-stabilized diphosphorus L:P–P:L compounds, **1** (L = L') and **2** (L = L''), respectively (Figure 1). Both **1** and **2** were isolated as moisture- and air-sensitive red crystals in moderate yields (**1**, 56.6%; **2**, 20.7%). The ¹H NMR imidazole resonances (C–H) of **1** and **2** are 5.98 and 5.71 ppm, respectively. The ¹H-coupled ³¹P NMR *singlet* resonances, –52.4 and –73.6 ppm for **1** and **2**, respectively, are comparable to those of other carbene-phosphinidene adducts,¹⁴

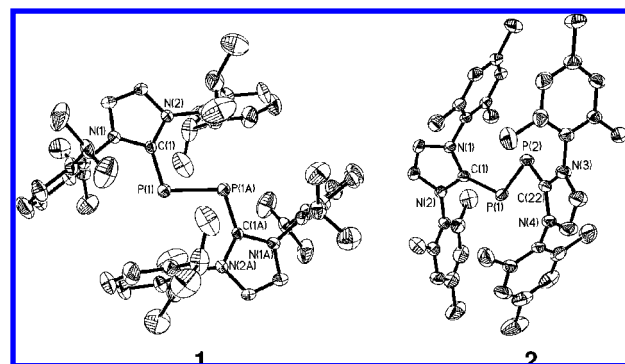


Figure 1. Molecular structures of **1** and **2** (thermal ellipsoids represent 30% probability; hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): For **1**, P(1)–P(1A) 2.2052(10), P(1)–C(1) 1.7504(17); C(1)–P(1)–P(1A) 103.19(6). For **2**, P(1)–P(2) 2.1897(11), P(1)–C(1) 1.754(3), P(2)–C(22) 1.754(3); C(1)–P(1)–P(2) 102.57(10), C(22)–P(2)–P(1) 103.01(10).

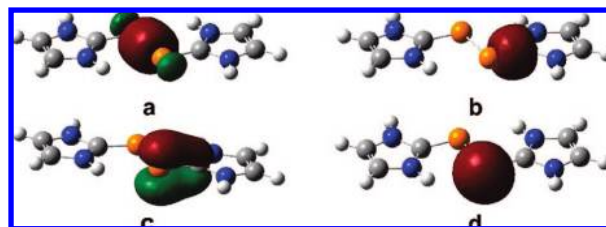


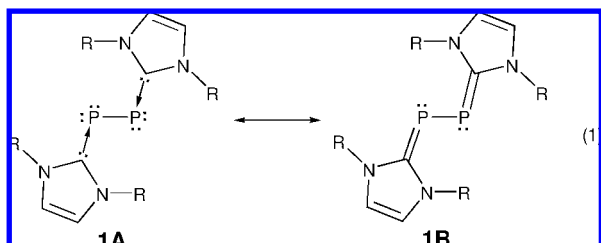
Figure 2. Localized molecular orbitals (LMOs) of **1-H** with C_{2h} symmetry. (a) P–P σ-bonding orbital; (b) P–C σ-bonding orbital; (c) lone pair orbital (mainly p-character) with pπ back-donation to the empty p orbital of CNHC; (d) lone pair orbital (mainly s-character).

L:P(Ph), –53.5 ppm (L = tetramethylimidazol-2-ylidene) (**3a**) and –23.0 ppm (L = :C{N(2,4,6-Me₃C₆H₂)CH₂})₂ (**3b**), but are quite different from those (34 to 54 ppm) of diphosphabutadienes, (R₂N)₂C=P–P=C(NR₂)₂ (R = Me, Et).¹⁵ The lack of detectable ³¹P–¹H coupling in **1** and **2** also supports the assigned structures.

Compound **1** has C_i symmetry and a trans-bent geometry with a 180.0° C(1)–P(1)–P(1A)–C(1A) torsion angle about the central P–P bond. The P–P bond distance, 2.205 Å, compares well to the 2.21 Å P–P single bond distance in T_d P₄.² The C(1)–P(1)–P(1A) bond angle (103.2°) corresponds to the 110° C–P–P angle (av) in the L:[P=P–P]:L carbene adduct, **4**,⁸ and the computed C–P–P angles in both H₂C=P–P=CH₂ (**5**, C_{2h}) (101.2°) and H₃CP=PCH₃ (**6**, C_{2h}) (99.9°).⁷ Hence, the C–P–P angle does not help delineate the nature of the P–C_{NHC} bonding. Notably, the two imidazole rings and the P–P bond of **1** are almost coplanar (the N(2)–C(1)–P(1)–P(1A) torsion angle is 2.3°; this value is 8.2° (av) in **2**). The P–C bond length (1.750 Å) in **1**, similar to those (1.75–1.79 Å) in **2–4**, is between the 1.65–1.67 Å P=C double bond lengths of the nonconjugated phosphalkenes¹⁶ and the normal

P–C single bond distance (i.e., the 1.839 Å P–C lengths in **3b** and the computed 1.87 Å in **6**). Two interpretations of the bonding in **1**, **1A** (bis-phosphinidene), and **1B** (bis-phosphaalkene) (eq 1) are akin to two resonance forms of carbene–phosphinidene adducts.¹⁷ Donation of the two carbene electron lone pairs to P decreases the phosphorus–phosphorus bond order from three in :P≡P: to one in **1A** or **1B**.

The P=C double bond character implied by **1B** inhibits, however, the imidazole π -delocalization and should be consistent with the ³¹P NMR chemical shifts (34 to 54 ppm) of the diphosphabutadienes.¹⁵ Instead, the high-field ³¹P NMR chemical shift (–52.4 ppm) of **1** favors **1A** as the predominate formulation.^{14,17,18}



Our DFT computations on the simplified L:P–P:L model, **1-H**, support this interpretation.⁷ Optimization of **1-H** (C_{2h} symmetry) affords the same trans-bent conformation as that for **1**, but with one imaginary frequency corresponding to a rotational transition state. Notably, the ca. 7 kcal/mol more stable gauche minimum of **1-H** (C_2 symmetry) (C–P–P–C torsion angle = 98.6°) resembles that of the isolobal H₂S₂ (H–S–S–H torsion angle = 90.6°).¹⁹ The sensitivity of the conformation about the P–P bond to the steric effects of the nearby carbene ligands (shown clearly by inspecting space-filling models) was confirmed by preparing **2**, which has a smaller carbene ligand than **1**. Although having bond distances similar to those for **1**, compound **2** adopts a gauche conformation. The C(1)–P(1)–P(2)–C(22) torsion angle (134.1°) of **2** lies between the 180° of **1** and the 98.6° of **1-H** (C_2 minimum).

The localized molecular orbitals (LMOs) of the simplified models (with L = :C(NHCH)₂) **1-H** (optimized in both C_{2h} (Figure 2) and C_2 symmetries) and **2-H** (employing the X-ray coordinates of **2**) are quite similar.⁷ All LMOs have one P–P σ -bond (**a**), one P–C σ -bond (**b**), and two lone-pair orbitals on each P atom (**c** and **d**). As exemplified in the **1-H** model (C_{2h}), (**d**) has mainly s-character (68.8% s, 31.2% p, 0.0% d) according to natural bond orbital (NBO) analysis, while (**c**) is essentially pure p (0.0% s, 99.8% p, 0.2% d), but involving modest interaction with the p orbital of C_{NHC} as implied by **1B**. This $p\pi$ back-donation, involving 64.8% P and 35.2% C components, results in modest P=C double bond character and is consistent with the structural data of **1** (i.e., the coplanarity of the imidazole rings and the P₂ unit, the 1.750 Å P–C bond distance, and the 1.397 P–C Wiberg bond index (WBI)).⁷ The P–C

σ bond polarization is 64.8% toward carbon and 35.2% toward phosphorus that has 20.7% s-, 78.6% p-, and 0.7% d-character. The P–P bond is single (WBI = 1.004) with 11.5% s-, 87.9% p-, and 0.6% d-character. Thus, like the silicon atoms in L:Si=Si:L¹³ and third-period elements generally, the phosphorus atoms in **1** and **2** do not hybridize extensively. Notably, the P₂ unit in the L:P–P:L molecules is demonstrated to serve as electron pair acceptors, thereby mimicking the behavior of a Lewis acid.

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Supporting Information Available: Complete ref 7, full details of the syntheses, computations, and X-ray crystal determination, including cif files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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