4778 *Organometallics* **2010,** *29,* 4778–4780
DOI: 10.1021/om100335j

ORGANOMETALLICS
Communication

Carbene-Stabilized Parent Phosphinidene[†]

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Received April 22, 2010

*Summary: The lithiated N-heterocyclic carbene−phosphinidene adduct L′:P−H (**3**; L′: = :C{[N(2,6-*$Pr^i_2C_6H_3$*)]*$_2$*CHCLi(THF)*$_3$*}) unexpectedly resulted from the reaction of lithium metal with the carbene-stabilized diphosphorus species L:P−P:L (**2**; L: = :C{N(2,6-*$Pr^i_2C_6H_3$*)CH}*$_2$*). Compound **2** was previously prepared by the potassium graphite reduction of L:*PCl_3* (**1**).*

Free phosphinidenes (R-P), highly reactive group 15 analogues of carbenes,[1−5] typically have triplet ground states and are studied at low temperature.[6] Transition-metal complexation is an effective means to stabilize these short-lived species. The transition-metal complexes of phosphinidenes prefer singlet ground states,[7] where phosphinidenes may act as two- or four-electron donors.[1] However, the phosphorus valence shell in free phosphinidenes is unsaturated. This enables adduct formation with electron pair donors, in particular Lewis base ligands[2] such as phosphines[8] and N-heterocyclic carbenes (NHCs).[9,10]

In contrast to the diverse chemistry of substituted phosphinidenes,[2,3,5] studies of the parent H−P molecule have largely been computational.[7,11,12] With a triplet ground state and a 22 kcal/mol triplet−singlet energy gap, diatomic H−P is a highly reactive molecule.[13] The synthesis and characterization of its carbene complex $[(CH_3)_2N]_2C{=}P{-}H$ (**I**; Figure 1) were achieved more than two decades ago.[14−16] Consistent with an elongated carbon−phosphorus double bond (1.740(1) Å),[16] $[(CH_3)_2N]_2C{=}P{-}H$ may be regarded formally as an acyclic diaminocarbene (**I**)−parent phosphinidene adduct.[17] While such N-heterocyclic carbene (**II**)−PH complexes have been investigated theoretically,[11,12] experimental data have yet to be reported. We recently utilized N-heterocyclic carbenes[18−21] to stabilize a series of highly reactive low-oxidation-state main-group molecules, including the parent diborene(2) (H−B=B−H),[22,23] disilicon (Si_2),[24] diphosphorus (P_2),[25] diarsenic (As_2),[26] and a neutral Ga_6 octahedron.[27] We now report the syntheses,[28] structures,[28] and computations[29] of carbene-stabilized phosphorus trichloride, L:PCl_3 (**1**; L: = :C{N(2,6-$Pr^i_2C_6H_3$)CH}$_2$) and the first lithiated NHC (**III**) parent phosphinidene adduct, L′:P−H (**3**; L′: = :C{[N(2,6-$Pr^i_2C_6H_3$)]$_2$CH-CLi(THF)$_3$}). While both **I** and **II** are well-known and extensively investigated carbene ligands, **III**, in contrast, may be regarded as a new anionic N-heterocyclic dicarbene, an anionic C_3N_2 ring with two carbene centers: one is an anionic version of an "abnormal" carbene (*a*NHC) center,[30] while the other is a neutral carbene center.

The reaction of the carbene ligand (L:) with PCl_3 in hexane affords the hypervalent L:PCl_3 complex **1** in almost quantitative yield. Potassium graphite reduction of **1** gave the diphosphorus carbene complex L:P−P:L (**2**).[25] Phosphinidene **3** was isolated as yellow crystals from the reaction of **2** with lithium metal (Scheme 1). Although the mechanism is

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[†] Part of the Dietmar Seyferth Festschrift. This paper is dedicated to Professor Dietmar Seyferth for his dedicated service to Organometallics and to the field of organometallic chemistry.

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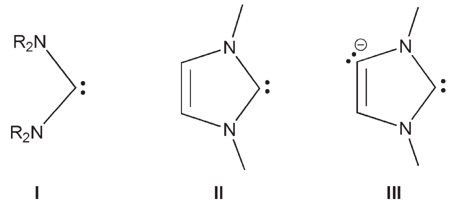
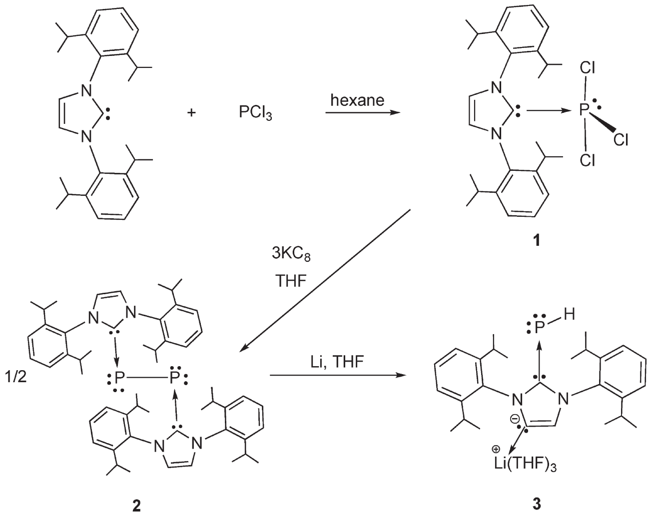


Figure 1. Examples of diaminocarbenes stabilizing the H−P molecule: (**I**) acyclic diaminocarbene; (**II**) N-heterocyclic carbene (NHC); (**III**) lithiated N-heterocyclic carbene (lithium omitted for clarity).

Scheme 1. Syntheses of Compounds 1, 2, and 3



unclear, the formation of **3** involves both the cleavage of the central P−P bond of **2** and the lithium-mediated C−H activation of the imidazole ring. While the selective activation of aromatic C−H bonds by lithium has been achieved,[31] the lithiation of NHC ligands has not been reported.

The imidazole ^{1}H NMR resonance of **1** resides at 6.51 ppm. The ^{31}P NMR resonance shifts from 219 ppm for PCl_3[32] to 16.9 ppm for **1** due to the electron donation from the NHC ligand (L:) to the phosphorus atom. In a manner similar to that for the arsenic atom in L:$AsCl_3$,[26] the four-coordinate phosphorus atom in **1** adopts a trigonal-bipyramidal geometry (Figure 2; only one set of structural data of the disordered PCl_3 core is shown[28]). While two Cl atoms occupy the axial positions, the ipso-C of the lithiated NHC ligand, one Cl atom, and one lone pair share the three equatorial sites. The 1.879 Å (average) P−C bond length is comparable to other phosphorus−carbon single bonds.[25] The P−Cl(2) bond distance (2.471 Å, average) is significantly longer than that of P−Cl(3) (2.238 Å, average) and of P−Cl(1) (2.032 Å, average).

The ^{1}H NMR of **3** shows the imidazole resonance at 6.24 ppm; the P−H doublet (δ 1.86 ppm, ^1J(PH) = 167 Hz) is shifted upfield compared to that reported for $[(CH_3)_2N]_2C{=}P{-}H$ (δ 3.10 ppm, ^1J(PH) = 159 Hz).[14] This is probably because the net electron-donating ability of the ligand **III** in **3** is stronger than that of **I** in $[(CH_3)_2N]_2C{=}P{-}H$. The presence of the P−H fragment in **3** also is confirmed unambiguously by the ^{1}H-coupled-^{31}P NMR spectrum. The ^{31}P doublet at −143.0 ppm (^1J = 171 Hz) is upfield when compared to that (δ −62.6 ppm, ^1J(PH) = 159 Hz) of $[(CH_3)_2N]_2C{=}P{-}H$[14] and those (δ 23.8 ppm, ^1J(PH) = 138 Hz; δ 34.3 ppm, ^1J(PH) = 174 Hz) of *P*-hydrogeno-*C*-phosphinophosphaalkenes.[33]

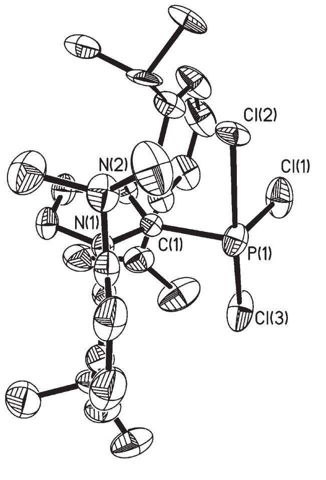
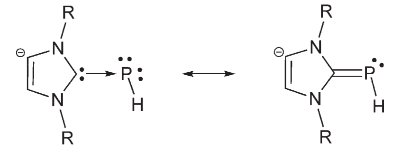


Figure 2. Molecular structure of **1** (thermal ellipsoids represent 30% probability; hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): P(1)−C(1) = 1.871(11), P(1)−Cl(1) = 2.018(8), P(1)−Cl(2) = 2.492(10), P(1)−Cl(3) = 2.235(10); C(1)−P(1)−Cl(1) = 102.5(4), C(1)−P(1)−Cl(2) = 86.5(4), C(1)−P(1)−Cl(3) = 91.6(5), Cl(1)−P(1)−Cl(2) = 90.0(5), Cl(1)−P(1)−Cl(3) = 76.9(4), Cl(2)−P(1)−Cl(3) = 166.1(5).

The tetrahedrally solvated $Li^+\cdot(THF)_3$ cation completes the trigonal-planar geometry around atom C(3) in **3** (Figure 3). The natural charge distribution at Li^+ (+0.84) and P−H (−0.21) supports the in-plane anionic character of the NHC fragment in **3**,[29] but this does not appear to significantly influence the nature of the P−C bond.

While being shorter than the P−C single bond distances (1.879 Å (average) for **1**; 1.828(2) and 1.856(2) Å for $L''P(BH_3)_2Ph$, L'' = :C{N(2,4,6-$Me_3C_6H_2$)CH}$_2$),[10] the P−C bond in **3** (1.763(2) Å) compares well to that computed for $[CH(CH_3)N]_2CP{-}H$ (1.770 Å)[12] and is slightly longer than the experimental value for $[(CH_3)_2N]_2C{=}P{-}H$ (1.740(1) Å).[15] Perhaps expectedly, the P−C bond distance in **3** is much longer than the P=C double bonds in *P*-hydrogeno-*C*-phosphinophosphaalkenes (1.713(2) Å)[33] and in $H_2C{=}P{-}H$ (1.675 Å, computed).[34]

Much like the case for N-heterocyclic carbene stabilized phosphinidenes[9,10] and bisphosphinidenes,[25] two extreme P−C bonding modes of lithiated **3** may be considered: a carbene−phosphinidene adduct (**3A**) and a phosphaalkene (**3B**). The pronounced high-field ^{31}P chemical shift of **3** (−143.0 ppm), coupled with the elongated P−C bond (1.763(2) Å; see above) also favor **3A** as the predominant formulation. The 102° (average) C−P−H bond angle in **3** is comparable to the 103(1)° in $[(CH_3)_2N]_2C{=}P{-}H$[15] and to the computed 94.0° in $[CH(CH_3)N]_2CP{-}H$.[12]



Density functional theory (DFT) computations at the B3LYP/DZP level on the simplified L″:P−H model (**3-H**;

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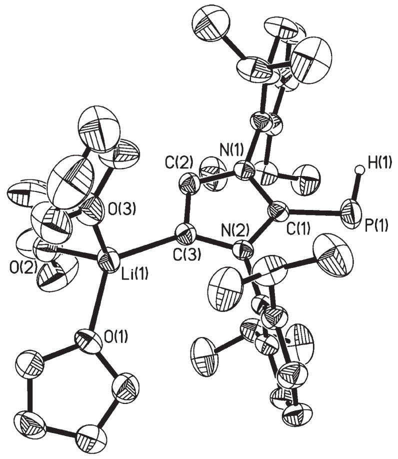

Figure 3. Molecular structure of **3** (thermal ellipsoids represent 30% probability; hydrogen atoms on carbons omitted for clarity). Selected bond distances (Å) and angles (deg): P(1)−C(1) = 1.763(2), P(1)−H(1) = 1.232(19), Li(1)−C(3) = 2.116(5); C(1)−P(1)−H(1) = 102(2), N(1)−C(1)−P(1) = 127.19(16), N(2)−C(1)−P(1) = 129.14(17), C(2)−C(3)−N(2) = 101.27(18), C(2)−C(3)−Li(1) = 120.7(2), N(2)−C(3)−Li(1) = 135.68(19).

L'': = :C[(NH)$_2$CHCLi(THF)$_3$]) support the bonding analysis of **3**.[29] The computed bond distances (P−C = 1.775 Å, C−Li = 2.095 Å) and 180° H−P−C−N torsion angle match the experimental values of **3** (P−C = 1.763(2) Å, C−Li = 2.116(5) Å) and 180° H(1)−P(1)−C(1)−N(2) torsion angle. The steric repulsion between one of the bulky 2,6-diisopropylphenyl groups in **3** and the P−H hydrogen atom is responsible for the C−P−H bond angle in **3** (102°, average) being larger than that computed for **3-H** (93.2°).

Localized molecular orbitals (LMOs) (Figure 4) and natural bond orbital (NBO) analysis support the bonding description of **3A**. The C−Li σ bond is strongly polarized to carbon, which has 40.5% s and 59.5% p character (LMO **a**). The localized phosphorus MOs include a P−C σ bond (LMO **b**), a P−H σ bond (LMO **d**), and two lone pairs (LMOs **c** and **e**). LMO **e** has mainly s character (68.1% s, 31.9% p), whereas LMO **c** is essentially pure p character (0.0% s, 99.8% p, 0.2% d). Notably, the latter involves modest pπ back-donation to the p orbital of ipso-C of the lithiated NHC ligand (71.2% P and 28.8% C components). This back-donation interaction is weaker than that reported for **2** (64.8% P and 35.2% C components).[25]

In addition, the P−C σ-bond polarization of 65.7% toward carbon and 34.3% toward phosphorus in **3-H** is very similar to that in **2** (64.8% C and 35.2% P). Notably, the Wiberg bond index (WBI) of the P−C bond of **3-H** (1.332) is even less than that of **2** (1.397). These computational results reveal that the pπ-bonding interaction between the ipso-carbon of the lithiated NHC ligand and phosphorus is not developed effectively, further supporting **3A** as the predominant depiction of **3**.

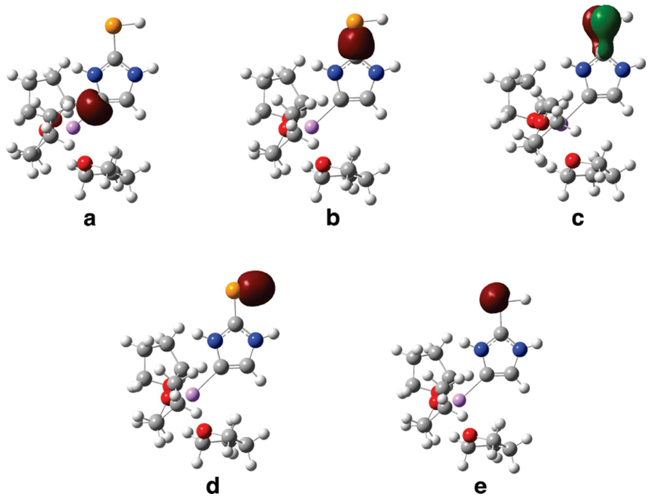

Figure 4. Localized molecular orbitals (LMOs) of **3-H**: (a) C−Li σ-bonding orbital; (b) P−C σ-bonding orbital; (c) lone pair orbital (mainly p character) with some pπ back-donation to the C_{ipso} p orbital of the lithiated NHC ligand; (d) P−H σ-bonding orbital; (e) lone pair orbital (mainly P s character).

Acknowledgment. We are grateful to the National Science Foundation for support of this work: Grant Nos. CHE-0608142 (G.H.R.), CHE-0953484 (G.H.R., Y.W.), CHE-0749868 (H.F.S.), and CHE-0716718 (P.v.R.S.). Either as a Harvard graduate student contemporary (P.v.R.S.), freshman chemistry professor at MIT (H.F.S.), or valued mentor (G.H.R.), Professor Seyferth has touched us all in various capacities. We, much like the entire organometallics community, will forever remain indebted to our dear friend Dietmar.

Supporting Information Available: Text, tables, and CIF files giving full details of the syntheses, computations, and X-ray crystal determinations. This material is available free of charge via the Internet at http://pubs.acs.org.