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A Base-Stabilized Terminal Phosphinidene Complex

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Although terminal phosphinidene complexes, $RPML_n$, have been postulated as intermediates,[1] they have so far eluded isolation. Attempts to stabilize such compounds with use of the bulky group strategy have failed because of insertion of the phosphorus atom into peripheral C–H bonds.[2,3] The implied high electrophilicity of terminal phosphinidenes has been confirmed by molecular orbital calculations on model systems that reveal significant positive charge accumulation at phosphorus.[4] It occurred to us that terminal phosphinidenes might therefore be stabilized by Lewis base incorporation. Tris(pyrazolyl)borato ligands[5] seemed ideally suited for this purpose because of the chelate effect. The particular choice of the hydridotris(3,5-dimethyl-1-pyrazolyl)borato ligand, $[HB(pz^*)_3]^-$, is based on solubility and crystallizability considerations.

The halophosphine, $[HB(pz^*)_3]PCl_2$ (**1**), which to the best of our knowledge is the first tris(pyrazolyl)borato-substituted phosphorus compound, was prepared via the reaction of $[HB(pz^*)_3]K$ with PCl_3.[6] Compound **1** was characterized spectroscopically.[6] We have not yet determined the structure of **1**. It is likely, however, that the tris(pyrazolyl) borato moiety is bonded in a trihapto fashion, thus giving phosphorus a local five-coordinate geometry.

The reaction of equimolar quantities of **1** and $Na_2[Fe(CO)_4]$ in Et_2O at 25 °C afforded a small quantity of $[HB(pz^*)_3]_2Fe$[7] and a new compound of composition $[HB(pz^*)_3]PFe(CO)_4$ (**2**) in >70% yield after crystallization. The X-ray crystal structure of **2**[8] reveals that only two of the tris(pyrazolyl)borato nitrogens (N(11) and N(21)) are attached to phosphorus, the other nitrogen (N(31)) being uncoordinated (Figure 1). Within experimental error the P–N(11) and P–N(21) distances are identical and fall in the range anticipated for single bonds.[9] The geometry at phosphorus is approximately tetrahedral, the average bond angle being 103.7 (3)°. The Fe atom adopts an approximately trigonal-bipyramidal geometry in which the phosphorus atom occupies an axial site. NMR measurements[6] indicate that at 25 °C there is no exchange of free and coordinated nitrogens of the tris(pyrazolyl)borato group.

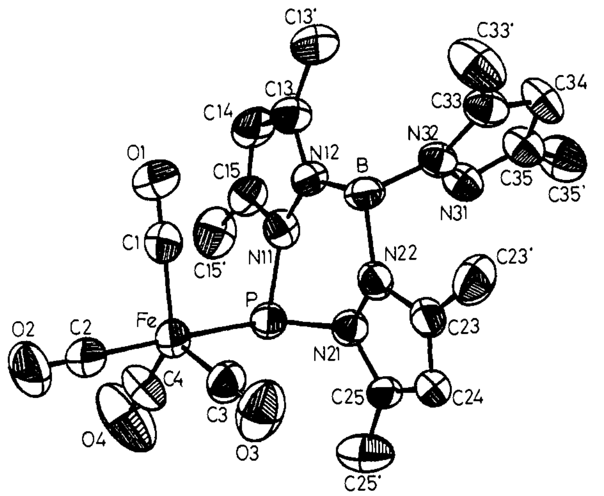
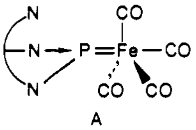
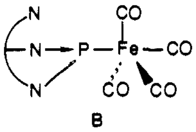


Figure 1. View (ORTEP) of $[HB(pz^*)_3]PFe(CO)_4$ (**2**) showing the atom numbering scheme. Important parameters: P–Fe 2.274 (2) Å, P–N(11) 1.777 (7) Å, P–N(21) 1.764 (7) Å, Fe–P–N(11) 109.7 (2)°, Fe–P–N(21) 110.1 (2)°, N(11)–P–N(21) 91.5 (3)°.

Two canonical forms can be written for **2**. Structure A involves a P=Fe double bond, hence phosphorus and iron are in +3 and −2 oxidation states, respectively. By contrast, the P–Fe bond order is unity in B and the oxidation states of P and Fe are +1 and 0, respectively. From a structural standpoint the major differentiating feature of structures A and B is the P–Fe bond length. Since the observed distance of 2.274 (2) Å falls in the range anticipated for a single bond,[9] it is clear that B is the preferred structure.



A



B

Although previous workers[1,2a] have implied a formal metal–phosphorus double bond for base-free terminal phosphinidene complexes, $RP{=}ML_n$, the present study suggests that the phosphorus(I)/metal (0) description, $RP \rightarrow ML_n$, might be more appropriate. Indeed, an analogous representation, $R_2E \rightarrow ML_n$, has been suggested[10] for terminal germylene and stannylene complexes. The reaction chemistry of transient terminal phosphinidene complexes can, in fact, be accounted for more satisfactorily by a $RP \rightarrow ML_n$ formalism. In this canonical form, the terminal phosphinidene moiety features both a lone pair and a vacant orbital at phosphorus,[11] thus accounting for the observed $n + 2$ cyclization and oxidative addition reactions, respectively.[1a,b,2]

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(1) See, for example: (a) Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.* **1982**, *104*, 4484. (b) Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* **1985**, *4*, 2134. See also: (c) Borm, J.; Huttner, G.; Orama, O. *J. Organomet.* Chem. **1986**, *306*, 29.

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(3) An attempt at resonance stabilization of the phosphinidene moiety via aryl substitution resulted in a metal–oxygen interaction in $[Os(P{=}C[O]\text{-}CF_3)(CO)_2(PPh_3)_2]$. Bohle, D. S.; Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1985**, *1594*.

(4) Gonbeau, D.; Pfister-Guillouzo, G.; Marinetti, A.; Mathey, F. *Inorg. Chem.* **1985**, *24*, 4133. See also: Lee, J.-G.; Boggs, J. E.; Cowley, A. H. *Polyhedron* **1986**, *5*, 1027.

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(6) Compound **1** was prepared by treatment of equimolar quantities of PCl_3 and $[HB(pz^*)_3]K$ in THF (−78 °C). The resulting colorless, air-sensitive solid was purified by dissolution in CH_2Cl_2 followed by filtration and solvent removal. Decomposition of **1** to an insoluble yellow powder occurs after standing a few hours at ambient temperature. EI–MS data for **1** (70 eV): m/e 398 (M^+), 303 ($M^+ - pz^*$). ^{31}P NMR data for **1** (121.5 MHz, CH_2Cl_2, 25 °C): s, δ −26.7. ^1H NMR data for **1** (300.15 MHz, C_6D_6, 25 °C): δ 1.93 (s, 9 H, pz*–Me), 2.26 (s, 9 H, pz*–Me), 5.37 (s, 3 H, C–H) ^{31}P NMR data for **2** (121.5 MHz, C_6D_6, 25 °C): s, δ 281.5. ^1H NMR data for **2** (300.15 MHz, C_6D_6, 25 °C) δ 1.40 (s, 6 H, pz*–Me), 1.92 (s, 6 H, pz*–Me), 2.15 (s, 3 H, pz*–Me), 2.22 (s, 3 H, pz*–Me), 5.26 (s, 2 H, C–H), 5.72 (s, 1 H, C–H).

(7) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288.

(8) Crystal data for **2**: $C_{19}H_{22}BFeN_6O_4P$, monoclinic, $P2_1$ (No. 4), a = 9.590 (1) Å, b = 11.611 (3) Å, c = 10.694 (1) Å, β = 93.41 (1)°, V = 1188.5 Å^3, Z = 2, D(calcd) = 1.386 g cm^{-3}, μ(Mo Kα) = 7.34 cm^{-1}. A total of 2200 unique reflections was collected on an Enraf-Nonius CAD-4 diffractometer over the range $3.0 \leq 2\theta \leq 50.0°$ at 25 °C using the $\theta/2\theta$ scan mode. Of these, 2199 were considered observed ($I > 3.0\sigma(I)$). The data were corrected for Lorentz, polarization, decay, and absorption. The structure was solved by direct methods. Refinement (full matrix least squares) afforded the final residuals R = 0.0579 and R_w = 0.0692.

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(11) In **2** the vacant orbital is utilized for intramolecular donor–acceptor bonding to nitrogen.

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Acknowledgment. We are grateful to the National Science Foundation and the Robert A. Welch Foundation for financial support. We also thank Dr. Andrew R. Barron for helpful discussion.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for **2** (9 pages); listing of observed and calculated structure factors for **2** (11 pages). Ordering information is given on any current masthead page.

Triple Ion Formation in Ethereal Solutions of Lithium *N*-Isopropylanilide Induced by Hexamethylphosphoric Triamide

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It is well known that the addition of small quantities (~4 equiv/cation) of certain cosolvents of high Lewis basicity, such as hexamethylphosphoric triamide (HMPT)[1,2] and *N*,*N*′-dimethyl-*N*,*N*′-propylene urea,[2] to solutions of alkali metal salts of carbon acids in weakly polar solvents (e.g., ethers) can dramatically enhance the nucleophilicity of the anion as well as changing its regiochemistry. In the absence of the cosolvent, lithium salts of very weak organic acids are usually aggregated contact ion pairs, and the role of the cosolvent is presumably concerned with inducing some degree of dissociation of the aggregates. For example, ^{13}C chemical shift data[3,4] for lithium enolates in HMPT/ether solvents strongly indicate such a dissociative process although the nature of the resulting species is unknown. We now show that the addition of 2–4 equiv of HMPT to lithium *N*-isopropylanilide (a model for lithium enamides) in diethyl ether results in the conversion of a dimer to a mixture of a monomer and a triple ion salt(ate complex[5]).

Lithium *N*-isopropylanilide in diethyl ether exists as a dimer characterized by its ^{13}C chemical shifts ($\delta_{c(4)}$, 110.4 ppm at −100 °C).[6] The addition of 4.1 equiv of HMPT completely converts the dimer to a mixture of two new species, **1** ($\delta_{c(4)}$, 101.9 ppm) and **2** ($\delta_{c(4)}$, 103.1 ppm) in a 6:1 ratio. The same system, however, exhibits *three* ^{6}Li and ^{7}Li resonances (Figure 1). The identities of the two new species are established by the low-temperature ^{15}N and ^{6}Li spectra (Figures 2 and 3)[7] of the fully labeled ^{15}N,^{6}Li isotopomer. The ^{15}N and ^{6}Li resonances of **2** are a 1:1:1 triplet and a 1:1 doublet, respectively, proving that it is the monomeric ion pair. $J_{6\text{Li},15\text{N}}$ and $\delta_{15\text{N}}$ are similar to those (7.5 Hz and 152.5 ppm, respectively) observed for the same salt in THF at −100 °C.[5] The ^{15}N resonance of the major species is also a 1:1:1 triplet showing that each nitrogen is attached to only *one* lithium atom. The corresponding ^{6}Li resonance, however, is a 1:2:1 triplet thus establishing the presence of the structural element, $(-\text{NLiN}-)^-$. The remaining peak (δ 2.3 ppm) in the ^{6}Li spectrum is a singlet with the same area of the triplet and is assigned to the Li(HMPT)$_4^+$ counterion. The line widths of the corresponding ^{7}Li resonances (Figure 1) are in accord with these assignments. Thus, that of the δ 2.3 ppm peak is very narrow (~7 Hz) as expected for ^{7}Li in a tetrahedral environment. The other two peaks are broad (~51 and ~25 Hz for δ 4.6 and 3.7 ppm, respectively).[8] The two species exchange rapidly on the ^{6}Li NMR time scale at room temperature (Figure 1a). The addition of HMPT causes

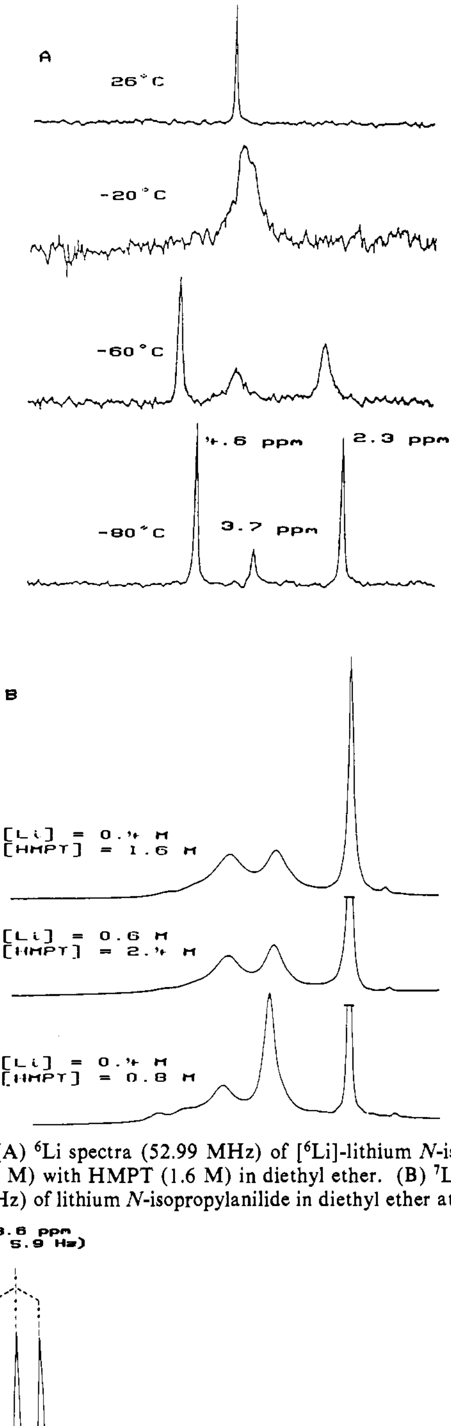

Figure 1. (A) ^{6}Li spectra (52.99 MHz) of [^{6}Li]-lithium *N*-isopropylanilide (0.4 M) with HMPT (1.6 M) in diethyl ether. (B) ^{7}Li spectra (139.95 MHz) of lithium *N*-isopropylanilide in diethyl ether at −60 °C.

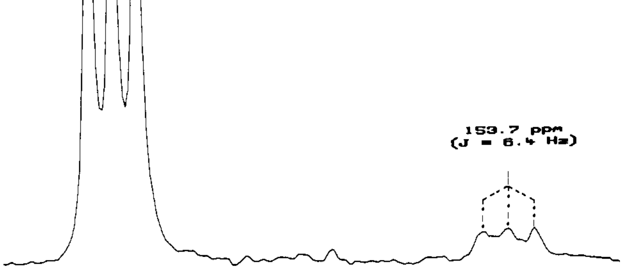

Figure 2. ^{15}N spectrum (20.2 MHz) of [^{6}Li,^{15}N]-lithium *N*-isopropylanilide (0.5 M) with HMPT (2.0 M) in diethyl ether at −85 °C.

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(7) ^{15}N spectra are referenced to external 0.5 M *N*-methylaniline (52.8 ppm) in diethyl ether. ^{6}Li and ^{7}Li chemical shifts are relative to external 0.1 M LiOH (aqueous) (0.00 ppm).

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