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Monomeric Phosphido and Phosphinidene Complexes of Nickel

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Received December 17, 2001

Examples of transition-metal and actinide complexes with terminal-phosphinidene (PR^{2-}) ligands are rare, limited to Group 8 and earlier metals.[1] These species can exhibit either electrophilic[2] or nucleophilic[1f] reactivity at phosphorus. Later metals, particularly those of Group 10, have received less attention in this regard as evidenced by the limited number of nickel[3] and platinum[4,5] terminal phosphido compounds. Our recent report of the synthesis of a three-coordinate nickel imido complex stimulated the pursuit of an analogous nickel phosphinidene.[6] Herein we report the preparation of stable Ni(I) and Ni(II) phosphido derivatives containing the bulky 1,2-bis(di-*tert*-butylphosphino)ethane (dtbpe) ligand and the conversion of the phosphido ligand of one such complex to a terminal, multiply bonded phosphinidene ligand.

Reaction of lithium di-*tert*-butylphosphide[7] with the Ni(I) chloro dimer $\{(dtbpe)Ni(\mu\text{-}Cl)\}_2$ (**1**)[6] affords the paramagnetic Ni(I) phosphide (dtbpe)Ni{P(*t*-Bu)$_2$} (**2**) as turquoise crystals in 71% isolated yield (Scheme 1). **2** has been characterized by ^1H NMR and IR spectroscopy, its magnetic moment, elemental analysis, and single-crystal X-ray diffraction.[8] Oxidation of **2** in diethyl ether by ferrocenium hexafluorophosphate gives the diamagnetic salt $[(dtbpe)Ni\{P(t\text{-}Bu)_2\}^+][PF_6^-]$ (**3**) as green crystals in 91% yield (Scheme 1). Compound **3** was fully characterized by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy, elemental analysis, and a single-crystal X-ray diffraction study.[8] The most distinctive spectroscopic signature of the phosphido ligand of **3** is its resonance as a triplet at δ 348 in the ^{31}P NMR spectrum. There are a few well-characterized terminal phosphido complexes of nickel, such as $(C_5H_5)(PPh_3)Ni\{P(SiMe_3)_2\}$ and $(Cy_2PCH_2CH_2PCy_2)Ni\{P(SiMe_3)_2\}$, and the latter has been shown to possess a pyramidal phosphido ligand with Ni−P = 2.225(2) Å.[3b,c]

The solid-state structures of **2** and **3**, shown in Figure 1, exhibit interesting features associated with the $Ni-PR_2$ moieties (summarized in Table 1). Both complexes are planar at Ni. In the d^9 complex **2**, the phosphido P(1) is substantially pyramidalized with a Ni−P(1) bond length of 2.2077(12) Å. The structure of the cationic d^8 complex **3** reveals a significantly shorter Ni−P(1) bond length of 2.098(2) Å (Δ = 0.11 Å) and a planar P(1). These values can be compared to Pauling's predicted bond lengths of 2.23 and 2.13 Å for Ni−P single and double bonds, respectively, based on their covalent radii corrected for electronegativity differences.[9] While these bond lengths may be partially explained by charge effects, we interpret the structural data as providing strong evidence of double-bond character for the $Ni-PR_2$ bond in **3**, with the p-bond arising from overlap of a P(1) electron-pair with the empty d-orbital of π symmetry in the Ni-coordination plane (which could have p-character as p−d mixing is allowed).

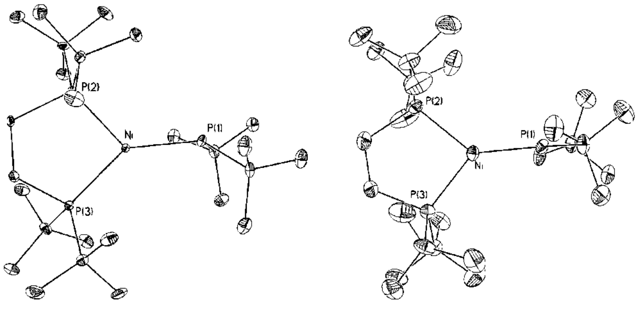

Figure 1. Perspective views of the molecular structures of **2** (left) and the complex cation of **3** (right). H-atoms have been omitted for clarity. See the text and Table 1 for selected metrical parameters.

Scheme 1

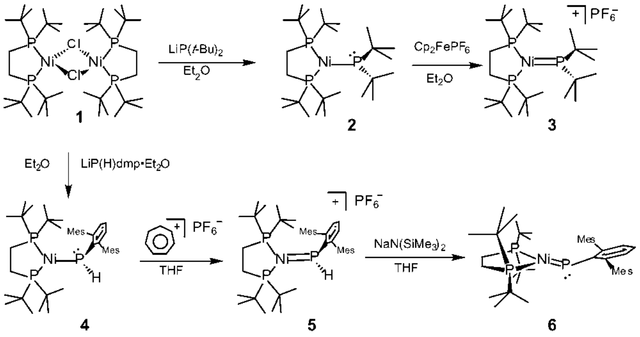

Table 1. Selected Spectroscopic and Structural Data[a]

compd	δ ^{31}P (J_{PP})[b]	Ni–P(1) (Å)	Ni–P(1)–C (deg)	Σ P $\angle$ (deg)
2	*c*	2.2077(12)	116.7(1)[d]	344
3	348 (175)	2.098(2)	124.1(2)[d]	360
5	125 (182)[e]	2.0540(11)	147.9(1)	360
6	970 (134)	2.0772(9)	130.78(11)	

[a] Data for nonchelate P. [b] In Hz. [c] Not observed. [d] Average value. [e] Non-first-order spin system, value from simulation.

Ether solutions of lithium 2,6-dimesitylphenylphosphide (LiP(H)(dmp))[10] react cleanly with **1** at −35 °C to give green blocks of the primary phosphide (dtbpe)Ni{P(H)(dmp)} (**4**) in 93% yield (Scheme 1).[8] Paramagnetic **4** has been characterized by ^1H NMR and IR spectroscopy, its magnetic moment, and elemental analysis. Oxidation of **4** with tropylium hexafluorophosphate (THF, −35 °C) gives dark green crystals of $[(dtbpe)Ni\{P(H)(dmp)\}^+][PF_6^-]$ (**5**) in 63% yield (Scheme 1).[8] Complex **5** has been characterized by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. Its characteristic P*H* resonance appears as a doublet-of-triplets at δ 8.06 ($^1J_{PH}$ = 280 Hz, $^3J_{PH}$ = 8 Hz) in the ^1H NMR spectrum. As observed for **3**, the structure of **5** (Figure 2; Table 1) exhibits a short Ni−P(1) bond (2.0540(11) Å) and a phosphido ligand planar at P(1), oriented in the geometry required for in-plane Ni−P π-bonding. The Ni−P(1)−C(11) angle is opened considerably from the idealized 120° of an sp^2 hybrid, perhaps in part as a consequence of the steric demands

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10.1021/ja017787t CCC: $22.00

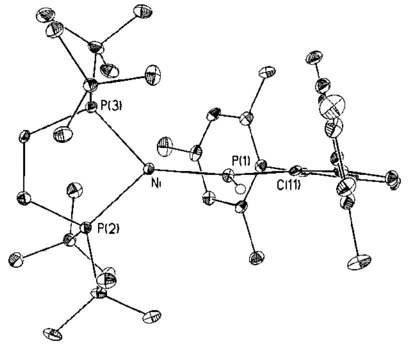

Figure 2. A perspective view of the complex cation of **5**. H-atoms, except that on P(1), have been omitted for clarity. See the text and Table 1 for selected metrical parameters.

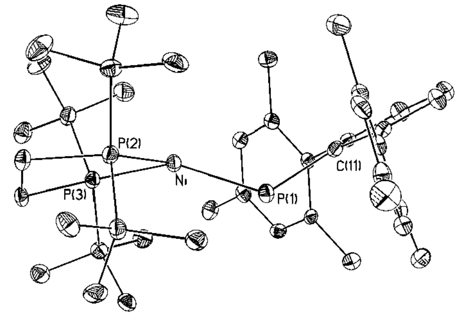

Figure 3. A perspective view of the molecular structure of **6**. H-atoms have been omitted for clarity. See the text and Table 1 for selected metrical parameters.

of the bulky 2,6-dimesitylphenyl substituent. (The hydrogen atom attached to P(1) was located in a difference map and refined isotropically.) A distortion from planarity is observed at Ni, where the sum of the P−Ni−P angles is 352°.

Reaction of cationic **5** with $NaN(SiMe_3)_2$ (THF, −35 °C) effects deprotonation of the phosphide to afford bright green crystals of (dtbpe)Ni{P(dmp)} (**6**) in 86% isolated yield (Scheme 1). Characterization of **6** as a terminal Ni(II) phosphinidene complex followed from ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopy, elemental analysis, and crystallography. The phosphinidene ligand of **6** resonates as a triplet at δ 970 ($^{2}J_{PP} = 134$ Hz) in the ^{31}P NMR spectrum (Table 1).[8]

The solid-state structure of **6** boasts several interesting features (see Figure 3). A distortion from planarity is also observed for the Ni in **6**, where the sum of the P−Ni−P angles is 353°. The Ni−P(1) bond length (2.0772(9) Å) is similar to those found in **3** and **5** and is consistent with the expected Ni−P(1) double bond (Table 1). The Ni−P(1)−C(11) angle is significantly bent at 130.8(1)°, which is in contrast to the more linear imido ligand found in the related complex (dtbpe)Ni{N(2,6-di-*iso*-Pr-C_6H_3)} (**7**; Ni−N−C = 162.8(2)°).[6] The direction of the bending, out of the Ni-coordination plane, gives the geometry required for in-plane Ni−P(1) π overlap. The aryl ring attached to P(1) in **6** is rotated ~90° from its orientation in **5**; similar changes in ring orientations were observed in the structures of **7** and its cationic amido precursor [(dtbpe)Ni{NH(2,6-di-*iso*-Pr-C_6H_3)}$^+$][PF_6^-].[6] It is noteworthy that the solution ^{1}H NMR spectrum of **6** shows equivalent *tert*-butyl groups in the temperature range of +23 to −83 °C (THF-d_8), although in the solid state they are clearly pairwise inequivalent.

In summary, we have prepared a family of three-coordinate, d^{8} and d^{9} nickel phosphido and phosphinidene complexes, and have structurally characterized several of them. As was found for related amido and imido complexes,[6] the three-coordinate d^{8} species participate in symmetry-allowed π bonding involving ligand p-electrons and an empty in-plane metal orbital of π symmetry. We are currently exploring the reactivity of these unusual phosphido and phosphinidene species, and examining their electronic structures through calculations.

Acknowledgment. G.L.H. thanks the National Science Foundation for financial support of this research and Prof. John Protasiewicz for a generous gift of 2,6-dimesitylphenyl phosphine. Helpful insight was provided by Prof. Protasiewicz and Prof. David Glueck. R.M. is grateful to the Department of Education for a GAANN Fellowship, and D.J.M. acknowledges postdoctoral fellowship support from the Ford Foundation.

Supporting Information Available: Experimental, spectroscopic, and analytical details; crystallographic details; atomic coordinates; bond angles and distances; anisotropic thermal parameters; hydrogen atom coordinates; least-squares planes; torsion angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA017787T