

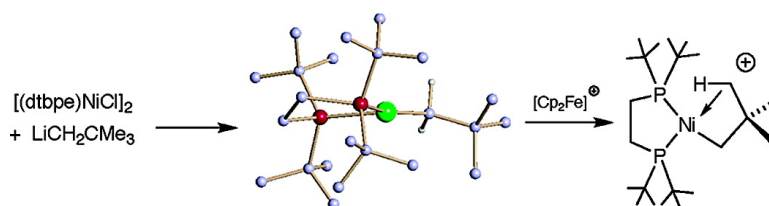
Communication

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Preparation of Stable Alkyl Complexes of Ni(I) and Their One-Electron Oxidation to Ni(II) Complex Cations

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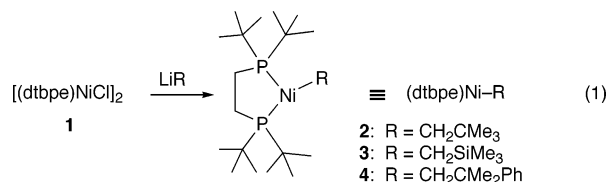
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The organometallic chemistry of nickel is rich and varied¹ and includes numerous significant industrial homogeneous catalytic processes,^{2–4} and organonickel intermediates are also implicated in the action of several enzymes.⁵ These transformations usually involve intermediates with nickel in the +2 or 0 oxidation state, with Ni(I) and Ni(III) intermediates occasionally observed or postulated. In this light, we note that there is a paucity of molecular complexes of Ni(I) possessing carbyl ligands. Several complexes of the type (C₅H₅)NiL₂ (L = neutral N- or P-donor ligands) featuring π -cyclopentadienyl ligands are known,⁶ but three-coordinate (PPh₃)Ni[(C,N: η^2 -C(SiMe₃)₂(SiMe₂-2-C₅H₄N)] is the lone example of a Ni(I) derivative containing a σ -bonded carbyl ligand.⁷

We have previously reported that the Ni(I) chloride [(dtbpe)-NiCl]₂ (**1**; dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane) is a good precursor to a family of three-coordinate, heteroatom-substituted Ni(I) derivatives via salt-metathesis reactions.⁸ Furthermore, the Ni(I) amido and phosphido complexes (dtbpe)Ni[NH(2,6-*i*-Pr₂C₆H₃)] and (dtbpe)Ni[PH(2,6-Me₂C₆H₃)] can be converted, by one-electron oxidation followed by deprotonation, to the corresponding nickel imido and phosphinidene complexes (dtbpe)Ni=NR and (dtbpe)Ni=PR.⁹ We were intrigued by the possibility of preparing related Ni(I) alkyl complexes and exploring their potential use as synthons to carbene complexes, (dtbpe)Ni=CR₂.

Reaction of cold (–35 °C) diethyl ether solutions of **1** with neopentyl lithium (1 equiv/Ni) affords the paramagnetic Ni(I) alkyl complex (dtbpe)Ni(CH₂CMe₃) (**2**) as orange crystals in 71% isolated yield (eq 1).¹⁰ Yellow (dtbpe)Ni(CH₂SiMe₃) (**3**) and orange (dtbpe)-Ni(CH₂CMe₂Ph) (**4**) were analogously prepared in 72 and 76% yields, respectively.¹⁰



Complexes **2–4** have been characterized by elemental analysis, magnetic moment measurements, and ¹H NMR and EPR spectroscopy.¹⁰ The solid-state structure of **2**, determined crystallographically, reveals a planar, three-coordinate nickel and a typical Ni–C single-bond distance (1.982(3) Å; Figure 1).¹¹ The neopentyl ligand is unsymmetrically disposed with respect to the dtbpe ligand, with the Ni–C(71) bond displaced 23.4° from the P(1)–Ni–P(2) bisector. Solutions of **2** (22 °C, C₆D₆) exhibit $\mu_{\text{eff}} = 2.18\mu_{\text{B}}$ consistent with a one-electron paramagnet.^{8,9} Although the ambient-temperature solution EPR spectrum of **2** shows an isotropic triplet due to coupling to the 2 ³¹P nuclei ($g_{\text{iso}} = 2.1196$, $A_{\text{iso}} = 70$ G),¹⁰

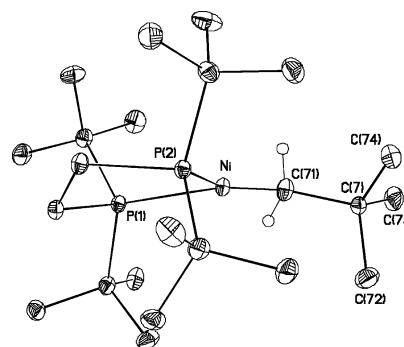
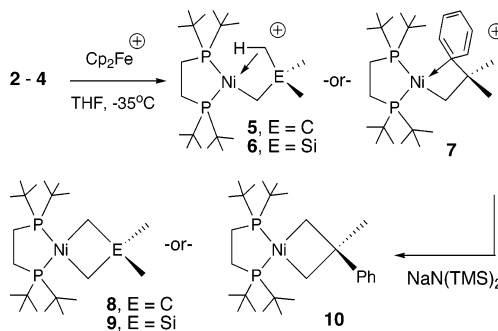


Figure 1. Perspective view of the molecular structure of **2** (only the H-atoms on C(71) are shown). Selected metrical parameters: Ni–C(71) = 1.982(3) Å, Ni–P(1) = 2.2101(11) Å, Ni–P(2) = 2.2080(11) Å, P(1)–Ni–P(2) = 91.02(3)°, P(1)–Ni–C(71) = 110.97(8)°, P(2)–Ni–C(71) = 157.82(8)°, Ni–C(71)–C(7) = 118.43(17)°.

Scheme 1



K data in glassy toluene reveal a well-resolved rhombic spectrum and indicate that the inequivalency of the ³¹P nuclei in the crystal is maintained in solution.¹⁰

A cyclic voltammogram of **2** (THF/TBAH) shows a reversible Ni(I)/Ni(II) couple at $E_{1/2} = -1.25$ V (vs Fc/Fc⁺), and as suggested by this potential, ferrocenium salts effect the oxidation of **2–4** to give the corresponding complex cations [(dtbpe)Ni(CH₂CMe₃)⁺] (**5**), [(dtbpe)Ni(CH₂SiMe₃)⁺] (**6**), and [(dtbpe)Ni(CH₂CMe₂Ph)⁺] (**7**) as red-brown [PF₆[–]] or [BARF₄[–]] salts in 52–82% isolated yield (Scheme 1). Characterization of these unusual cationic d⁸ alkyl derivatives followed from ¹H, ¹³C, and ³¹P NMR and IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction.¹⁰

The electron-deficient alkyl cations **5–7** (formally 14-e species) are stabilized by secondary interactions between the alkyl ligands and Ni. The structures of **5**[PF₆[–]] and **6**[PF₆[–]] show square-planar Ni engaged in γ -C–H agostic interactions with a methyl group of the alkyl (for **6**[PF₆[–]], Ni–C(71) = 2.150(8), Ni–C(73) = 2.300(8) Å; Figure 2).¹² The structure of **7** exhibits an interaction between Ni and the *ipso*-C of the phenyl group of the neophyl ligand (Ni–C(71) = 1.954(3), Ni–C(751) = 2.478(4) Å; Figure 2). There are no significant cation–anion interactions. Similar *ipso*-C interactions

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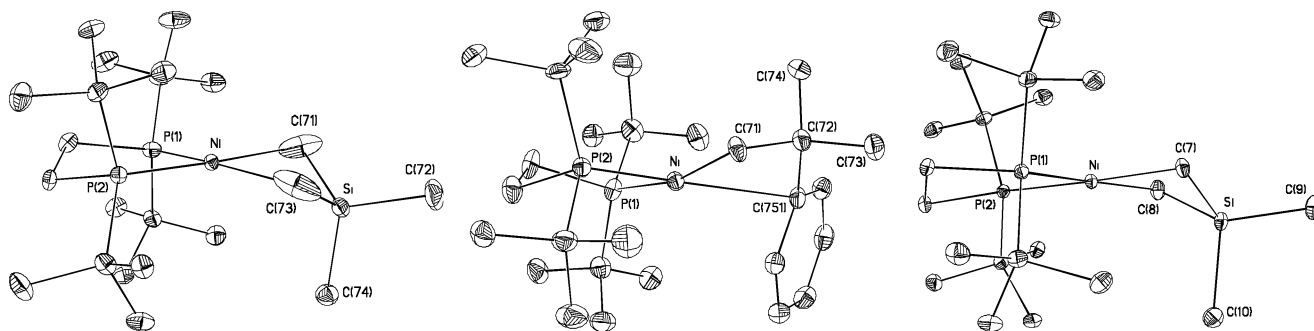
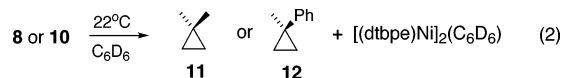


Figure 2. Views (left to right) of the molecular structures of the complex cations of **6**[PF₆⁻], **7**[BARF₄⁻], and neutral **9** (H-atoms omitted for clarity).

with Pd have been characterized by Carmona,¹³ and Spencer has reported the structure of [(dtbpe)Ni(CH₂CH₃)] [BF₄⁻] to have a β-C–H agostic interaction involving Ni and the ethyl ligand.^{11c}

Cations **5–7** are highly fluxional on the NMR time scale. Even at –90 °C (CD₂Cl₂), all nine CH₃ protons of the neopentyl ligand of **5** appear equivalent (singlet), suggesting that the γ-agostic interaction is weak and the rotation of the *tert*-Bu group rapid.¹⁴ The barrier to a higher-energy dynamic process that equates the P'Bu₂ substituents of the dtbpe ligand (e.g., the windshield-wiper movement of the alkyl group across the pseudo C₂-axis) has been determined for **5** and **7** by VT NMR methods and is ~13.0 kcal/mol for both complexes.¹⁵

Reaction of **5–7** with NaN(TMS)₂ results in deprotonation of a γ-CH₃ group to give the metallacyclobutane complexes **8–10** (Scheme 1) as yellow crystalline solids in good yields. The solid-state structure of **9** (Figure 2) features square-planar Ni(II) and a puckered (138.6°) metallacyclobutane moiety. NMR data indicate analogous structures for **8** and **10**. Whitesides has reported that related Pt metallacyclobutanes, (PR₃)₂Pt(CH₂CMe₂CH₂) (R = Cy, ⁱPr), undergo reductive elimination to give 1,1-dimethylcyclopropane.¹⁶ While solutions of **9** are stable at 140 °C with respect to cyclopropane elimination, benzene solutions of **8** and **10** quantitatively eliminate the cyclopropanes **11** and **12** at ambient temperature, as determined by NMR and GS-MS analysis, with formation of [(dtbpe)Ni]₂(C₆D₆) (eq 2).^{10,17}



In summary, we have prepared several three-coordinate, monomeric Ni(I) alkyl complexes (**2–4**). While thermally robust, they undergo mild one-electron oxidation to give the corresponding Ni(II) complex cations (**5–7**). In contrast to cationic amido and phosphido analogues that undergo α-deprotonation to afford imido and phosphinidene derivatives, deprotonation of **5–7** occurs at a γ-CH₃ group to give metallacyclobutane products (**8–10**), not (dtbpe)Ni=CHR. Reactivity studies of these unusual complexes are underway.

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Supporting Information Available: Experimental and spectroscopic details (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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