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Hydrogen-Atom Abstraction from Ni(I) Phosphido and Amido Complexes Gives Phosphinidene and Imide Ligands

Vlad M. Iluc and Gregory L. Hillhouse*

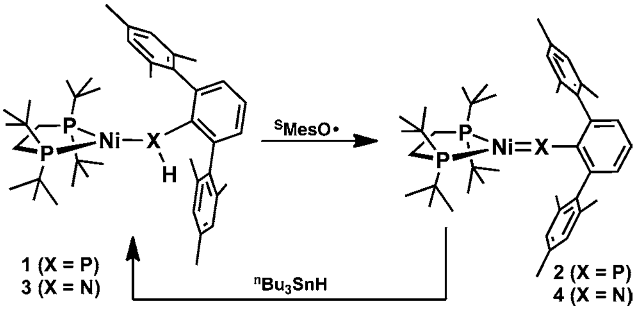
Gordon Center for Integrative Science, Department of Chemistry, The University of Chicago,
929 East 57th Street, Chicago, Illinois 60637

Received August 8, 2010; E-mail: g-hillhouse@uchicago.edu

Abstract: Hydrogen-atom abstraction from M−E(H) to generate M═E-containing complexes (E = PR, NR) is not well studied because only a few complexes are known to undergo such reactions. Hydrogen-atom abstraction from nickel(I) phosphide and amide complexes led to the corresponding phosphinidene and imide compounds. These reactions are unparalleled in the organometallic chemistry of nickel and feature an unusual example of a transition-metal phosphinidene synthesized by hydrogen-atom abstraction.

Hydrogen-atom transfer reactions are important in areas prominent in both chemistry and biology.[1] Of these, reactions with hydrogen-atom donors are common, especially when they involve reactive metal−element (M═X, X = O, N) multiple bonds.[2] The reverse process, hydrogen-atom abstraction to generate M═X-containing complexes, is not as well studied because examples of complexes known to undergo such reactions are rare.[3] Herein we report the successful conversion by hydrogen-atom abstraction of nickel(I) phosphide and amide complexes to the corresponding phosphinidene and imide derivatives. These reactions are unparalleled in the organometallic chemistry of nickel and include a unique example of a transition-metal phosphinidene synthesized by this hydrogen-atom abstraction route.

Scheme 1. Synthesis of (dtbpe)Ni═X(dmp) Complexes (X = P, N)



Our group has reported several three-coordinate nickel species, which include amides, imides, phosphides, and phosphinidenes.[4,5] The neutral amide/imide and phosphide/phosphinidene pairs differ by the nickel oxidation state and one hydrogen atom. The conversion from amide/phosphide to imide/phosphinidene was achieved previously in two steps: oxidation of the neutral Ni(I) center to cationic Ni(II), followed by deprotonation using a strong base.[4,5] We sought to determine whether an alternative route to nickel−ligand multiple bonds, hydrogen-atom abstraction directly from Ni(I) to Ni(II), is viable.

A new amide/imide pair that contains 2,6-dimesitylphenyl (dmp; mesityl = 2,4,6-trimethylphenyl) as a nitrogen substituent was targeted because it would parallel the phosphide/phosphinidene pair (dtbpe)Ni-PH(dmp) (**1**)/(dtbpe)Ni═P(dmp) (**2**) previously synthesized and characterized.[5] Although related nickel amide and imide complexes have been reported, (dtbpe)Ni═P(dmp) is the only nickel phosphinidene to have been successfully isolated. Consequently, the nickel amide (dtbpe)Ni−NH(dmp) (**3**) was synthesized in 80% yield by the reaction of the Ni(I) chloride dimer [(dtbpe)NiCl]$_2$ with (dmp)NHLi, analogous to the synthesis of the Ni(I) amide (dtbpe)Ni−NHAr (Ar = 2,6-di-*iso*-propylphenyl).[4] The new Ni(I) complex **3**, isolated as a bright-pink solid, is a one-electron paramagnet with $\mu_{\mathrm{eff}} = 1.9\ \mu_{\mathrm{B}}$ in CD$_2$Cl$_2$ solution measured by the Evans method. As with most Ni(I) paramagnetic species, its ^{1}H NMR spectrum is broad and **3** is silent in both ^{13}C and ^{31}P NMR spectra. The N−H stretch in the IR spectrum ($\nu_{\mathrm{NH}} = 3276$ cm^{-1}) was found at lower energy than that for (dtbpe)Ni-NHAr ($\nu_{\mathrm{NH}} = 3345$ cm^{-1}),[4] but it falls in the range of other reported amides.[6] The solid-state structure of **3**, determined by single-crystal X-ray diffraction (Figure 1), shows a slight pyramidalization at nickel (sum of angles = 349.66°) with the Ni−N bond displaced from the P(1)−Ni−P(2) plane by ∼29°. The amide hydrogen atom was located in the electron-density map at 0.79(3) Å from the nitrogen atom.

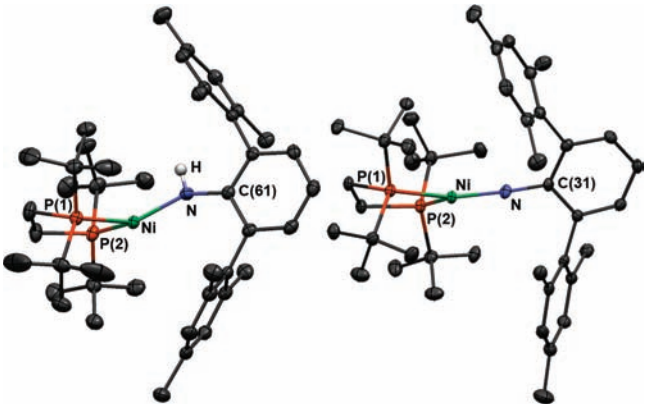


Figure 1. Thermal-ellipsoid (50% probability) representation of (dtbpe)Ni−NH(dmp) (**3**, left) and (dtbpe)Ni═N(dmp) (**4**, right). H atoms, except on N, were omitted for clarity. Selected metrical parameters for **3**: Ni−N = 1.881(2), Ni−P(1) = 2.2167(7), Ni−P(2) = 2.2192(7), N−C(61) = 1.364(3), N−H = 0.79(3) Å; Ni−N−C(61) = 147.1(2), P(1) −Ni−P(2) = 92.27(3), P(1)−Ni−N = 132.69(8), P(2)−Ni−N = 124.70(8), Ni−N−H = 104(2), C(61)−N−H = 106(2)°. For **4**: Ni−N = 1.697(2), Ni−P(1) = 2.1717(6), Ni−P(2) = 2.1397(6), N−C(31) = 1.345(2) Å; Ni−N−C(31) = 168.98(12), P(1)−Ni−P(2) = 91.56(2), P(1)−Ni−N = 142.46(5), P(2)−Ni−N = 125.29(5)°.

The bulky 2,4,6-tris-*tert*-butylphenoxyl radical (^{S}MesO$^{•}$)[8] is the simplest of stable phenoxyl radicals, and it was used by Mayer[9] for hydrogen-atom abstraction from N-H bonds in transition-metal complexes and by Smith for the conversion of

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[L]Co−N(H)^{t}Bu to [L]Co═N^{t}Bu (L = phenyltris(1-*tert*-butylimidazol-2-ylidene)borato).[3a] The reaction of **3** with ^{S}MesO$^•$ generated the Ni(II) imide (dtbpe)Ni═N(dmp) (**4**, Scheme 1) under mild conditions (ambient temperature, 12 h) and in high yield (90%). The same reactivity was observed for (dtbpe)Ni−NHAr.[10] ^{1}H, ^{31}P, and ^{13}C NMR spectra of **4** confirmed the presence of a pseudo-C_{2v} symmetric complex in solution, with magnetically equivalent phosphorus nuclei (^{31}P δ 119.23). The solid-state structure of **4**, determined by single-crystal X-ray diffraction (Figure 1), revealed a trigonal-planar geometry at the metal center with the sum of angles around Ni at 359.31°. The Ni−N bond deviates from the P(1)−Ni−P(2) bisector by ~9°, and the Ni−N distance of 1.697(2) Å is, within error, equal to the distance found for other Ni(II) aryl imides.[4,11] The Ni−N−C(31) angle at 168.98(12)° deviates slightly from linearity, with the complex (dtbpe)Ni═NMes being the only imide with collinear Ni, N, and C atoms.[11] Steric requirements of the dmp substituent force its central aryl ring to lie perpendicular to the Ni coordination plane, in contrast to the coplanar geometry found in other arylimides in this (dtbpe)Ni system.[4,11]

We also became interested in studying the analogous hydrogen-abstraction process with the nickel phosphide complex **1** since no such syntheses have been reported for phosphinidenes. The preparation of such complexes usually employs halogen abstraction,[12a,b] hydrogen-atom migration,[12c−e] methatesis,[12f] or dehydrohalogenation,[13] in addition to the oxidation/deprotonation protocol detailed above.[5] Reaction of ^{S}MesO$^•$ with **1** led to **2** in 75% isolated yield (Scheme 1). Interestingly, the phosphinidene (**2**) and imide (**4**) complexes can be reconverted to the corresponding Ni(I) phosphide (**1**) and amide (**3**) compounds in 87% and 75% yield, respectively, by reaction with the H$^•$ donor ^{n}Bu$_3$SnH (Scheme 1).

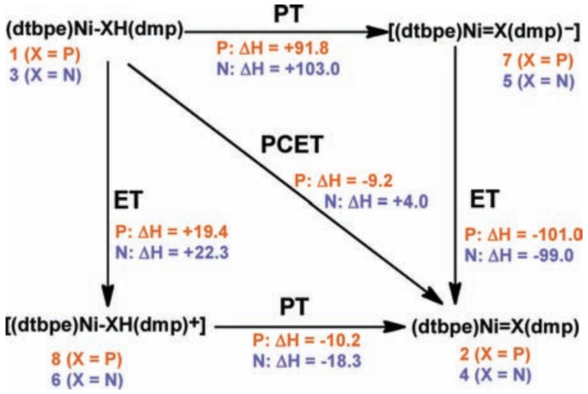

Figure 2. Possible reaction pathways and calculated energies (kcal/mol; solvent-corrected for benzene) for the conversion of **1** to **2** (X = P) and **3** to **4** (X = N); the organic reactants and products were omitted for clarity.

The conversion of **1**/**3** to **2**/**4** by ^{S}MesO$^•$ may follow three pathways (Figure 2): (A) deprotonation (PT = proton transfer) followed by oxidation (ET = electron transfer), (B) oxidation followed by deprotonation, and (C) proton-coupled-electron transfer (PCET). We disfavor path A since all our attempts to isolate the anionic species [(dtbpe)Ni═N(dmp)$^-$] (**5**) from the reduction of **4** led to decomposition, indicating that **5** is not stable. This observation is supported by DFT calculations that show that the conversion of **2**/**4** to **7**/**5** is highly endothermic (101.0/99.0 kcal/mol, Figure 2). In addition, **3** is inert toward either ^{n}BuLi or (Me$_3$Si)$_2$NNa, bases stronger than ^{S}MesO$^•$ (for ^{S}MesOH$^{•+}$: p$K_a \approx 3$),[13] further supporting that A is not a viable pathway in the transformation of **3** to **4** mediated by ^{S}MesO$^•$.

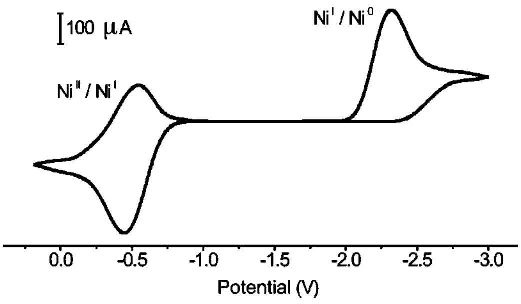

Figure 3. Cyclic voltammogram for (dtbpe)Ni-NH(dmp) (**3**) at 100 mV/s, 10 mM in 1 M [^{n}Bu$_4$N]PF$_6$ in THF, Cp$_2$Fe/Cp$_2$Fe$^+$ corrected.

Next, we probed the feasibility of pathway B. As mentioned, **4** can be independently synthesized from **3** by [Cp$_2$Fe]$^+$ oxidation to give the cationic Ni(II) complex [(dtbpe)Ni−NH(dmp][B(Ar^F)$_4$] (**6**), followed by deprotonation using NaN(SiMe$_3$)$_2$. Based on the Ni(I)/Ni(II) redox potential ($E_{1/2} = -0.55$ V; Figure 3) and E(^{S}MesOH/^{S}MesO$^•$) = −0.5 V,[14] it is uncertain, however, whether ^{S}MesO$^•$ is thermodynamically competent to oxidize **3**. We also explored the second step, deprotonation, by employing ^{S}MesOK as a base to convert **6** to **4**. By monitoring this reaction by ^{1}H NMR spectroscopy, the *reduction* of **6** to **3** was observed initially and not its deprotonation, a fact that seems to invalidate this mechanistic pathway. Therefore, we propose that the transformations of **1**/**3** to **2**/**4** in the presence of ^{S}MesO$^•$ occur by PCET (path C, Figure 2). This proposal is in agreement with the PCET mechanism proposed by Smith for the conversion of [L]Co−N(H)^{t}Bu to [L]Co═N^{t}Bu.[3a]

DFT calculations are consistent with the experimental data. DFT calculations also support C as a viable, low-barrier mechanism since the calculated reaction energies are −9.2/4.0 kcal/mol for the conversion of **1**/**3** to **2**/**4** (Figure 2). The formation of the anionic intermediate **5** and the cationic complex **6** are both energetically uphill (103.0 and 22.3 kcal/mol, Figure 2), and the base and oxidant energetics are included in the thermodynamic analysis.

In conclusion, we have described two examples of hydrogen-atom abstraction from nickel phosphide and amide complexes to form the corresponding phosphinidene and imide derivatives. These processes were enabled by the synthesis of the dmp-substituted imide and phosphinidene complexes, and their mechanism was discussed on the basis of experimental and computational results. In both cases, proton-coupled-electron transfer was found to be the most viable reaction pathway. These transformations open an avenue for the synthesis of late-transition-metal−element multiply bonded species and contribute to the understanding of hydrogen-atom abstraction processes in metal complexes.

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Supporting Information Available: Crystallographic data for **3** and **4** (CIF). Synthetic and spectroscopic characterization of all complexes and computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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