Reactions of Organoazides with Nickel Alkyls. Syntheses and Reactions of Nickel(II) Amido Complexes

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Amido complexes ($L_nM{-}NR_2$) of late transition metals are rare, but they are interesting because the M–N bonds in these complexes are relatively weak in comparison with other late-metal M–X bonds (halide, alkyl, hydrido, etc.) and thus exhibit unusual reactivities.[1] Stable amido complexes of nickel are limited to the (trialkylsilyl)amido derivatives $(PPh_3)_2Ni\{N(SiMe_3)_2\}$ and $Ni(Cl)\{N(SiMe_2)(CH_2PPh_2)_2\}$[2,3] and the interesting homoleptic arylamido complexes $Ni(NPh_2)_2$,[4] $\{Ni(NPh_2)_2\}_2$,[4] $[Ni(NPh_2)_3^-][Li(thf)_4^+]$,[4] and $Ni\{N(Mes)(BMes_2)\}_2$.[5] Herein we report that reaction of arylazides with several nickel alkyls provides a new synthetic route to Ni(II) complexes containing arylamido ligands, and we describe the facile reactions of these complexes with carbon monoxide to yield organic amides.

Tetrahydrofuran solutions of $(bipy)Ni(R)_2$ (**1a**, R = Me; **1b**, R = Et; bipy ≡ 2,2′-bipyridine)[6] react cleanly with *p*-tolylazide (N_3Tol) to give N_2 and the nickel(II) amido complexes (bipy)Ni{N(Tol)(R)}(R) (**2a**, R = Me; **2b**, R = Et) in excellent yield (Scheme 1).[7] Addition of 2 equiv of N_3Tol does not give bis(amido) products. The ^1H NMR spectra of **2a** and **2b** indicate the eight protons of the bipyridine ligands are chemically inequivalent, consistent with the formulation of these compounds as rigid, square-planar, d^8 complexes. Reaction of **1b** with $N{=}N{=}^{15}NPh$ gives only $(bipy)Ni\{^{15}N(Ph)(Et)\}(Et)$ ($[^{15}N]$**2c**) and no unlabeled (bipy)Ni{N(Ph)(Et)}(Et) (**2c**, prepared independently from **1b** and N_3Ph), demonstrating that the N—C bond of the azide is maintained during the formal insertion into the Ni—alkyl bond to give the $Ni{-}NR_2$ product.

Examination of variable-temperature ^1H NMR spectra (−90 to +60 °C; C_7D_8 solution; 500 MHz) of **2b** reveals two interesting dynamic processes involving the (*p*-tolylethyl)amido ligand. The low-temperature limiting spectrum for the aromatic protons of the tolyl group exhibits an ABCD spin pattern (i.e., four chemically inequivalent aryl protons) indicative of hindered rotation about the N–C(ipso) bond. Warming the sample results in (reversible) spectral changes for these resonances, first to an AA′BC pattern and then to a classic AA′BB′ tolyl pattern. Analysis of the coalescence parameters (T, $\Delta\nu$) gives an activation barrier of 11.7 kcal/mol for this N–C rotation.[8] This relatively large rotational barrier suggests substantial double-bond character in the N–C linkage due to delocalization of the nitrogen lone pair into the aryl π^* system.[9] Variable-temperature ^1H NMR data also give insight on rotation about the Ni–N bond of the amido ligand. The methylene protons of the ethyl group of the amido ligand of **2b** are diastereotopic at ambient temperature, but rotation about the Ni–N bond gives access to a transition state in which the amido methylene protons are related by mirror symmetry and are therefore chemically equivalent (see Figure 1). There is a surprisingly large activation barrier to rotation about this Ni–N bond ($\Delta G^\ddagger = 16.1$ kcal/mol), and it is probably primarily of steric origin, since no empty Ni-based orbitals of proper symmetry are available for N(pπ)-to-Ni(dπ) multiple bonding.[10]

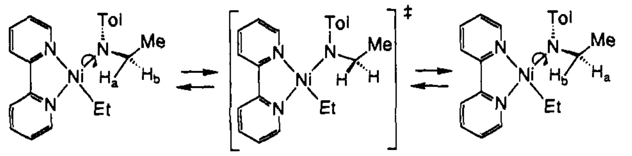
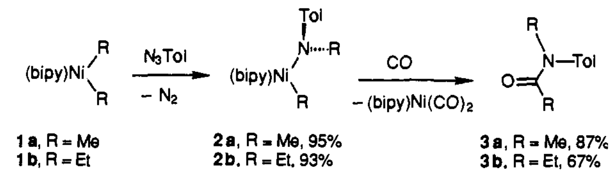
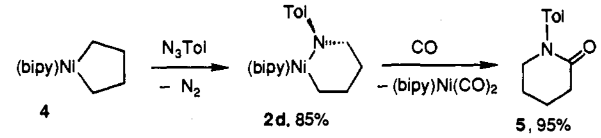


Figure 1. Illustration of rotation (or oscillation) about the Ni–N bond of **2b**. Assuming facile rotation about the N–Et bond, a transition state can be accessed in which the methylene carbon of the amido ligand is contained in a mirror plane that equilibrates the otherwise diastereotopic methylene protons of the (*p*-tolylethyl)amido group. From ^1H NMR coalescence data, $\Delta G^\ddagger = 16.1$ kcal/mol for the Ni–N rotation (or oscillation).

Scheme 1



Scheme 2



Carbon monoxide (1 atm) reacts with **2a** and **2b** to give $(bipy)Ni(CO)_2$ and the corresponding organic amides RC(O)N(R)(Tol) (**3a**, R = Me; **3b**, R = Et) in good yields, as shown in Scheme 1. We have no mechanistic basis for differentiation between initial CO insertion into the $Ni{-}NR_2$ or Ni–R bonds of **2a** and **2b** (no intermediates were spectroscopically detected) prior to reductive elimination of the organic amide. The carbonylations are analogous to the reactions of CO with (bipy)Ni(R)(OR) that give $(bipy)Ni(CO)_2$ and esters.[11] It is noteworthy that while the **1** → **3** transformations formally proceed by sequential addition of "Tol–N" and "CO" to the dialkylnickel complexes, neither **3a** nor **3b** can be prepared by reaction of the dialkyl complexes with *p*-tolyl isocyanate.

The reaction of nickel alkyls with arylazides is not limited to acyclic dialkyls. As shown in Scheme 2, the nickelacyclopentane

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complex (bipy)$Ni(CH_2)_4$ (**4**)[6c] undergoes reaction with N_3Tol to yield the corresponding cyclic nickel amide (bipy)$Ni\{N(Tol)(CH_2)_4\}$ (**2d**), which in turn reacts with carbon monoxide (1 atm) to afford the tolyl lactam **5** in 95% yield.

In considering possible mechanisms for these nickel–arylazide interactions, it is noteworthy that only two examples of reactions of arylazides with transition-metal alkyls have been previously reported, and in both cases very stable 1,3-disubstituted triazenido complexes ($L_nM—NR—N=NR'$) result which do not lose N_2 to yield the corresponding metal amides ($L_nM—NRR'$).[12] Many transition-metal hydrides, however, are known to react with arylazides to give either 1,3-triazenido ($L_nM—NH—N=NR$) or arylamido ($L_nM—NHR$) complexes,[13] and in one instance the conversion of the former to the latter (with N_2 extrusion) has been observed.[14]

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Supplementary Material Available: Text describing experimental details and spectroscopic and analytical data for new compounds (5 pages). This material is contained in many libraries on mircofiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(12) $Cp_2Zr(Me)(MeN_3Ph)$ and $Co(Me)_2(PMe_3)_2(MeN_3Tol)$ result from the reactions of arylazides with $Cp_2Zr(Me)_2$ and $Co(Me)_3(PMe_3)_3$, respectively. Chiu, K. W.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. *Polyhedron* **1984**, *3*, 79.

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