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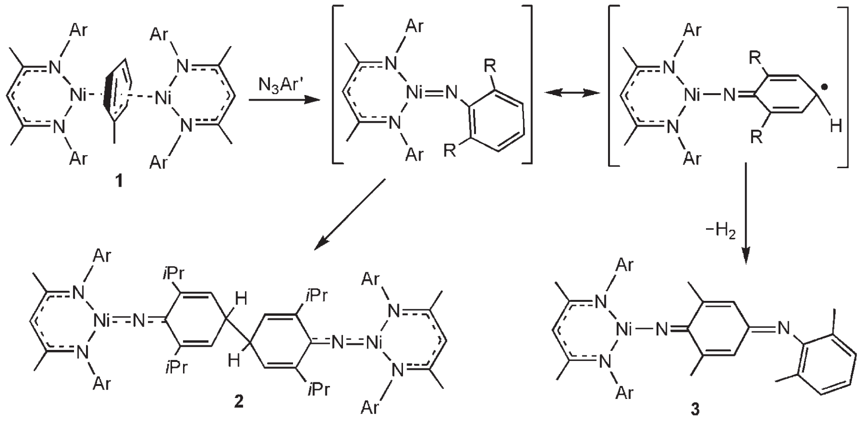
Formation of C–C and C–N Bonds in Ni^{II} Ketimide Complexes via Transient Ni^{III} Aryl Imides**

*Guangcai Bai and Douglas W. Stephan**

The formation of C–C and C–heteroatom bonds is an important general target of synthetic chemistry.[1–5] To these ends, the chemistry of early-metal amides[6–11] has been explored extensively. The corresponding chemistry of late-transition-metal imido ligands has drawn much less attention.[12–14] In fact, while McGlinchey and Stone[15] reported in 1970 the generation of [$(Ph_2MeP)_2M{=}NCF_2CFHCF_3$](M=Pd, Pt) incorporating an imido ligand, the number of subsequent reports was quite small until recently. In the late 1980s and 1990s Bergman and co-workers described the synthesis and reactivity of Ir[16,17] and Os imides[18,19] while Burrell and Steedman[20,21] reported the complex [(η^6-benzene)-Ru=NAr] (Ar = 2,6-iPr$_2$C$_6$H$_3$). In 2001, Mindiola and Hillhouse[22] showed the deprotonation of the corresponding amide to give the terminal Ni^{II} imide [(tBu$_2$PCH$_2$CH$_2$PtBu$_2$)Ni=NAr], which undergoes reactions with CO and benzyl isocyanide as well as ethylene to give the corresponding carbodiimide[22,23] and aziridines,[24] respectively. Low-valent metal centers have drawn attention recently as reactions of Co^{I} and Fe^{I} have been shown to give the corresponding double imido-bridged dimers or trivalent imido complexes.[25–33] Warren and co-workers[34] have applied a similar strategy most recently to prepare both imido-bridged and terminal Ni imides of the form [{(nacnac)Ni}$_2$(NAd)] and [(nacnac)Ni=NAd] (nacnac = CH{CMeN(2,6-iPr$_2$C$_6$H$_3$)}$_2$; Ad = 1-adamantyl). The latter species react with phosphine to produce the phosphinimide R$_3$P=NAd. In addition, Holland and co-workers have described the ability of Fe^{III} imides to abstract H atoms from the ligand or external reagents,[35] while the Warren group has described the reactivity of Cu aryl imides.[36] Herein, we report the oxidation a Ni^{I} synthon by aryl azides. In contrast to the alkyl azides, which give Ni^{III} imides, these reactions proceed to effect internal electron-transfer reactions affording the formation of new C–C or C–N bonds, thus resulting in products that are described as Ni^{II} ketimides.

We have previously reported the synthesis of [{(nacnac)-Ni}$_2$(μ-η^3:η^3-C$_6$H$_5$Me)] (**1**).[37] This species, although best formulated as a Ni^{II} dimer bridged by a reduced arene fragment, behaves as a convenient Ni^{I} synthon. The reaction of **1** with 2,6-iPr$_2$C$_6$H$_3$N$_3$ proceeded to generate a deep-green solution. The subsequent work up and isolation of the dark green solid gave **2** in 84 % yield (Scheme 1). The molecule **2** is paramagnetic with a molecular magnetic moment of 3.6 μ_B in C$_6$D$_6$ at 25 °C, consistent with the presence of unpaired spin. The IR data provides a fingerprint for this species but was not structurally informative. X-ray crystallography was performed on single crystals of **2** grown from toluene.



Scheme 1. Formation of **2** and **3** from **1**. Ar = 2,6-iPr$_2$C$_6$H$_3$; Ar' = 2,6-iPr$_2$C$_6$H$_3$ or 2,6-Me$_2$C$_6$H$_3$.

The X-ray crystallographic data[38] revealed that **2** is correctly formulated as the bimetallic species [{(nacnac)-Ni(NC$_6$H$_2$$iPr_2$)}$_2$] (Figure 1 a). This molecule is a centrosymmetric dimer; in each half the Ni center resides in an approximately trigonally planar coordination sphere composed of two N atoms of the nacnac ligand and a third N atom derived from the azide fragment. The Ni–N bond lengths to the nacnac ligand were found to be 1.8631(19) Å and 1.8646(19) Å. The bite angle for the nacnac chelate in **2** is 94.41(8)° while the metric parameters within the nacnac ligand are unexceptional. The Ni–N(3) bond length is 1.711(2) Å, with a Ni-N-C angle of 166.1(2)°. This bond length is markedly longer than that reported for [(nacnac)Ni=NAd] (1.662(2) Å),[34] similar to that reported for [(CH$_2$PtBu$_2$)$_2$Ni=NC$_6$H$_3$$iPr_2$] (1.702(2) Å),[39] and significantly shorter than reported for [(CH$_2$PtBu$_2$)$_2$NiNHC$_6$H$_3$$iPr_2$]

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[*] G. Bai, Prof. Dr. D. W. Stephan
Department of Chemistry and Biochemistry
University of Windsor
Windsor, ON, N9B 3P4 (Canada)
Fax: (+1) 519-973-7098
E-mail: stephan@uwindsor.ca

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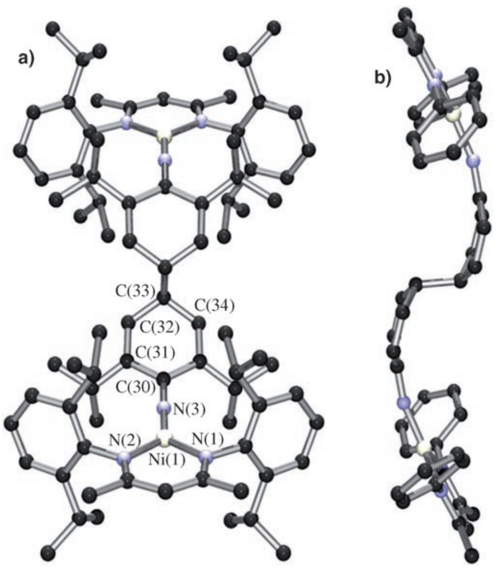
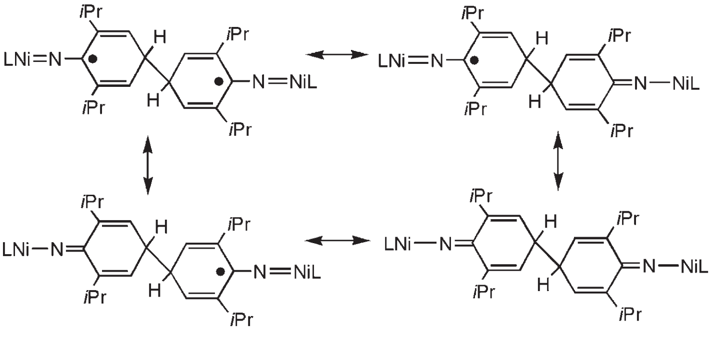


Figure 1. Pov-ray drawings of **2**; (a) and (b) are orthogonal views. Hydrogen atoms are omitted for clarity. In (b) the substituents on the arene groups have been removed for clarity. C black, N light blue, Ni white. Selected bond lengths [Å] and angles [°]: Ni(1)-N(3) 1.711(2), Ni(1)-N(2) 1.8631(19), Ni(1)-N(1) 1.8646(19), N(3)-C(30) 1.269(3), C(30)-C(31) 1.490(4), C(30)-C(35) 1.494(3), C(31)-C(32) 1.333(4), C(32)-C(33) 1.494(4), C(33)-C(34) 1.490(4), C(33)-C(33)′ 1.569(6), C(34)-C(35) 1.327(4); N(3)-Ni(1)-N(2) 132.36(9), N(3)-Ni(1)-N(1) 132.79(9), N(2)-Ni(1)-N(1) 94.41(8), C(30)-N(3)-Ni(1) 166.1(2), C(34)-C(33)-C(32) 111.4(2), C(34)-C(33)-C(33) 110.4(3), C(32)-C(33)-C(33)′ 111.2(3).

(1.881(2) Å).[39] The angles at the nickel center between the nacnac N atoms and the third N atom [N(3)-Ni(1)-N(2) and N(3)-Ni(1)-N(1)] average 132.6(2)°. Notably the N(3)–C(30) bond length is markedly short (1.269(3) Å), as are the C(31)–C(32) (1.333(4) Å) and C(34)–C(35) (1.327(4) Å) bonds in the ligand ring. These lengths are indicative of double bonds, while the remaining bonds within the ring are substantially longer (av 1.495(5) Å). The two halves of the dimer are linked through the C atom *para* to the N atom, C(33), with a C(33)–C(33)′ bond length of 1.569(6) Å. Saturation at the *para* C atom of this ring gives rise to a displacement of the C atom from the plane of the C_6 ring and results in a gradual S curve of the dimerized ligand linkage between the metal centers (Figure 1b). These data clearly show the reduction of the arene ring of the precursor azide, resulting in the dimerization by coupling of the *para* carbon atoms of two such fragments. Related back-to-back coupling of imido ligands has been previously observed in the oxidation of μ-imido Rh dimers.[40] While the structural data suggest a Ni^{II} ketimide formulation for **2**, the observed paramagnetism of **2** suggests that a Ni^{III} imido radical formulation is at least an accessible state (Scheme 2).

The analogous reaction of **1** with 2,6-$Me_2C_6H_3N_3$ was performed. The liberation of N_2 was evident immediately as the solution became dark green. Subsequent work up of the reaction afforded dark green crystals of **3** (Scheme 1). The ^{1}H NMR data for **3** are consistent with the presence of two fragments derived from the azide reagent in addition to the {(nacnac)Ni} fragment. Yields of **3** were increased to 74% upon adjustment of the stoichiometry of Ni/azide to 1:2. The X-ray crystallographic data[38] for **3** established the formulation as the monometallic species [(nacnac)$NiNC_6H_2Me_2$-($NC_6H_3Me_2$)] (Figure 2). The geometry about the Ni center as well as the metric parameters of the nacnac ligand are similar to those observed in **2**, and **3** is thus formulated in a similar fashion as a Ni^{II} ketimide species. The Ni–N bond length for the ketimide ligand (1.699(3) Å) is slightly shorter than that observed in **1**, consistent with the presence of less sterically demanding substituents. The resulting C(30)-N(3)-Ni(1) angle is approximately linear at 175.0(3)°. The ketimide N–C bond length (1.289(4) Å) is consistent with double-bond character. Similarly to **2**, the bond lengths within the C_6 ring between N(3) and N(4) alternate in length. Thus, the C(31)–C(32) and C(34)–C(35) bond lengths (1.339(5) Å) are shorter than the remaining C–C bonds, which average 1.459(6) Å. The substituent on the C atom *para* to N(3) is N(4), which is derived from addition of a second equivalent of 2,6-$Me_2C_6H_3N_3$. The C(33)–N(4) bond length is 1.299(5) Å. The geometry at this remote N atom is bent with a C-N-C angle of 120.9(3)° and an N–C bond length to the terminal ring of 1.414(5) Å. These structural data support the description of the {$NC_6H_2Me_2(NC_6H_3Me_2)$} unit as a *para* diketimine diene fragment.

The formation of **2** and **3** is proposed to take place via transient Ni^{III} imide intermediates. Repeated attempts to intercept a formal Ni^{III} imide using other aryl azides such as 2,4,6-$Me_3C_6H_3N_3$ ($MesN_3$) led only to unresolved, uncharacterized products. Nonetheless, cyclic voltammetric experiments for **1** and the azides 2,6-$Me_2C_6H_3N_3$ and 2,6-$i$$Pr_2C_6H_3N_3$ showed redox potentials consistent with the notion that the Ni^{I} synthon is indeed a thermodynamically competent reductant for the azides, which supports the notion of a transient Ni^{III} species.[41] In addition, literature precedent supports this view; the groups of Holland[35] and Warren[34] have shown that {(nacnac)Fe^{I}} and {(nacnac)Ni^{I}} are oxidized by alkyl azides to give isolable M^{III} imides. In the case of **2** and **3**, the electron-rich character of the aryl imide intermediates prompt further reactivity. Formally, one can view the aryl imide intermediates as Ni^{II} radicals which either dimerize or



Scheme 2. Resonance forms of **3**. L = nacnac.

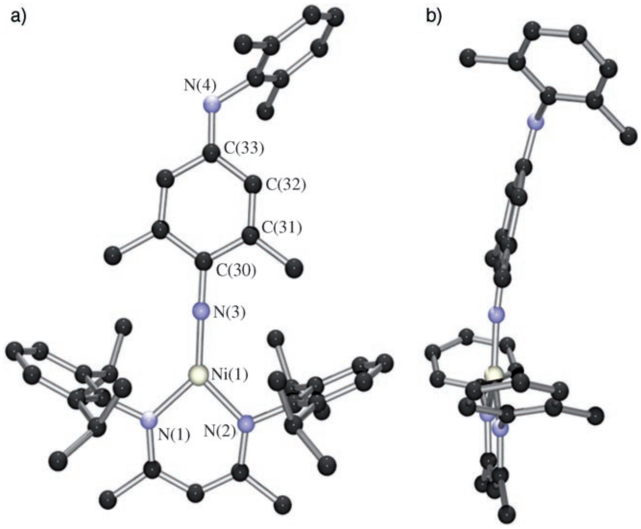


Figure 2. Pov-ray drawing of **3**; (a) and (b) are orthogonal views. Hydrogen atoms are omitted for clarity. C black, N light blue, Ni white. Selected bond lengths [Å] and angles [°]: Ni(1)-N(3) 1.699(3), Ni(1)-N(1) 1.860(3), Ni(1)-N(2) 1.863(3), N(3)-C(30) 1.289(4), N(4)-C(33) 1.299(5); N(3)-Ni(1)-N(1) 133.46(13), N(3)-Ni(1)-N(2) 132.05(12), N(1)-Ni(1)-N(2) 94.44(12), C(30)-N(3)-Ni(1) 175.0(3), C(33)-N(4)-C(38) 120.9(3).

react further with azide to give **2** and **3** (Scheme 1). The preferential formation of the C–C bond in **2** and the C–N bond in **3** is attributed to the impact of steric effects. Large *ortho* substituents on the azide preclude reaction of the transient intermediate with excess azide, thus favoring back-to-back C–C bond coupling (dimerization). In the case of **3**, the smaller *ortho* substitutents allow radical attack of azide with loss of H_2 and C–N bond formation.

Preliminary DFT calculations using the models [CH-(CMeNMe)$_2$NiN(C$_6$H$_6$)] (**4**), derived from the crystallographic data for **2**, were performed with the B3LYP-311 g(d,p) basis set. The HOMO of **4** is composed primarily of a Ni–N π bond while the LUMO has considerable N–C π-bond character. In contrast, analogous calculations for [CH-(CMeNMe)$_2$NiN(C$_6$H$_4$NMe)] (**5**) showed a more diffuse HOMO with contributions from the π bonds of the nacnac ligand, the C–N bond, and a metal-based d orbital, whereas the corresponding LUMO is clearly the π* orbital of the NC_6H_4N fragment. These findings suggest that the extended $\{NC_6H_4N\}$ π system stabilizes the Ni^{II} ketimide nature of **3**. On the other hand, these results also suggest that facile access of a triplet state of **2** accounts for the paramagnetism. Further, more detailed computational studies of these features are continuing.

In summary, reduction of the transient Ni^{III} imido species results in the formation of a C–C or C–N bond. The utility of such internal redox chemistry in the formation of extended ring assemblies continues to be probed in our laboratories.

Experimental Section

All preparations were done under an atmosphere of dry, O_2-free N_2 by employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert-atmosphere glove box. Solvents were purified by employing a Grubbs' column system. ^{1}H NMR spectra were recorded on a Bruker Avance 300 and/or 500 spectrometer and referenced to $SiMe_4$. Magnetic susceptibility was determined by the Evan's method. Combustion analyses were performed in house. Compound **1** was prepared as previously described in the literature.[37]

2: A solution of **1** (0.208 g, 0.2 mmol) in toluene (10 mL) was added to a solution of 2,6-iPr$_2$C$_6$H$_3$N$_3$ (0.081 g, 0.4 mmol). Liberation of N_2 was immediately observed, and the solution became dark green. The resulting mixture was stirred overnight. After concentration (to 3 mL) in vacuo, the resulting deep-green solution was kept at −35 °C for one week to isolate dark green crystals of **2** (0.22 g, 84 %). IR (nujol): $\tilde{\nu} = 1924$ (w), 1860 (w), 1704 (w), 1651 (w), 1623 (w), 1583 (w), 1548 (s), 1531 (s), 1494 (m), 1462 (s), 1396 (s), 1379 (s), 1319 (s), 1295 (m), 1250 (s), 1203 (m), 1179 (m), 1157 (m), 1121 (m), 1107 (m), 1054 (m), 1024 (m), 962 (m), 943 (m), 889 (m), 861 (m), 847 (m), 797 (s), 758 (m), 749 (m), 722 (m), 649 (w), 528 (m), 516 (w), 448 cm^{-1} (m); magnetic susceptibility (χ, C_6D_6, 25 °C): $\mu = 3.61\,\mu_B$. Elemental analysis (%) calcd for $C_{82}H_{116}N_6Ni_2$ (1303.30): C 75.6, H 9.0, N 6.5; found: C 75.9, H 8.7, N 6.4.

3: 2,6-Me$_2$C$_6$H$_3$N$_3$ (0.118 g, 0.8 mmol) was added to a solution of **1** (0.208 g, 0.2 mmol) in toluene (10 mL). Liberation of N_2 was immediately observed, and the solution became dark green. The resulting mixture was stirred overnight. Upon removal of toluene in vacuo, hexane (5 mL) was added, and the resulting deep-green solution was kept at −35 °C for two days to isolate dark green crystals of **3** (0.12 g). After concentration of the filtrate to 3 mL, the solution was kept at −35 °C for three days. An additional crop of **2** (0.09 g) was formed. Yield: 0.21 g (74 %). ^{1}H NMR (C_6D_6): $\delta = 7.01$–6.88 (m, 9 H, Ar and 2,6-Me$_2$C$_6$$H_3$), 6.20 (brs, 1 H, MeCC$H$), 5.36 (brs, 1 H, MeCC$H$), 4.73 (s, 1 H, γ-CH), 4.10 (sept, $^3J_{HH} = 6.8$ Hz, 4 H, CHMe$_2$), 1.90 (s, 2,6-Me_2C$_6$H$_3$; and d, $^3J_{HH} = 6.8$ Hz, CHMe$_2$, 18 H), 1.40 (s, 6 H, CMe), 1.25 (d, $^3J_{HH} = 6.9$ Hz, 12 H, CHMe_2), 0.61 (s, 3 H, MeCCH), 0.20 (s, 3 H, MeCCH); ^{13}C NMR (C_6D_6): 159.1, 159.0 (NC), 150.6 (CN(2,6-Me$_2$$C_6H_3$)), 150.0, 142.9 (Ar), 140.9 (NC(Me)CH)), 131.6, 130.1, 126.9, 126.5, 124.1 (Ar and 2,6-Me$_2$$C_6H_3$), 123.4 (MeC$C$H), 120.6 (Me$C$CH), 97.7 (γ-C), 29.1 ($CHMe_2$), 24.8, 23.8 (CH$Me_2$), 21.9 (NC$Me$), 18.79 (2,6-$Me_2C_6H_3$), 17.5, 17.4 ppm ($Me$CCH); IR (nujol): $\tilde{\nu} = 2141$(w), 2106 (w) 2051 (w), 1934 (w), 1901 (w), 1869 (w), 1836 (w), 1802 (w), 1706 (w), 1629 (m), 1587 (m), 1568 (m), 1548 (m), 1533 (s), 1513 (s), 1459 (s), 1438 (s), 1399 (s), 1320 (s), 1253 (s), 1218 (m), 1180 (m), 1162 (m), 1145 (w), 1101 (m), 1090 (m), 1056 (m), 1029 (s), 953 (m), 936 (m), 879 (m), 866 (w), 822 (m), 800 (m), 762 (s), 748 (m), 724 (m), 712 (m), 634 (w), 528 (m), 448 cm^{-1} (m). Elemental analysis (%) calcd for $C_{45}H_{58}N_4Ni$ (713.70): C 75.7, H 8.2, N 7.9; found: C 75.5, H 8.4, N 7.7.

ORTEP figures of **2** and **3** can be found in the Supporting Information. CCDC-626524 and 626525 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[38] X-ray data: **2**: monoclinic, space group $P2_1/n$, $a = 10.4112(13)$, $b = 25.123(3)$, $c = 15.3140(19)$ Å, $\beta = 95.6460(10)°$, $V = 3986.1(9)$ Å^3, 7019 variables, 406 parameters, $R = 0.0431$, $R_w = 0.1098$, GOF = 1.022. **3**: triclinic, space group $P\bar{1}$, $a = 8.735(2)$, $b = 15.091(3)$, $c = 15.875(4)$ Å, $\alpha = 89.290(2)$, $\beta = 84.792(2)$, $\gamma = 83.995(2)°$, $V = 2072.7(8)$ Å^3, 7271 variables, 451 parameters, $R = 0.0572$, $R_w = 0.1382$, GOF = 1.020.

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