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Photolysis and Thermolysis of Bis(imino)pyridine Cobalt Azides: C−H Activation from Putative Cobalt Nitrido Complexes

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Abstract: A series of planar aryl-substituted bis(imino)pyridine cobalt azide complexes were prepared and evaluated as synthetic precursors for the corresponding cobalt nitrido compounds. Thermolysis or photolysis of two examples resulted in intramolecular C−H activation of the benzylic positions of the aryl substituents. For the mesityl-substituted compound, C−H activation by the putative nitride resulted in formation of a neutral imine ligand and modification of the chelate by hydrogen transfer to the imine carbon.

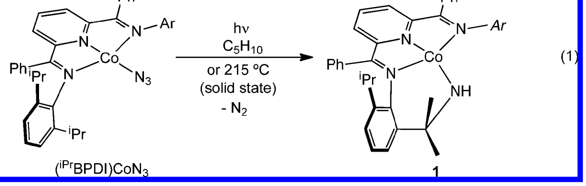
Terminal nitrido complexes, $L_nM{\equiv}N$, have been long-standing synthetic targets in first-row transition metal chemistry[1] due to their likely role in nitrogen fixation[2,3] and in N-atom-transfer chemistry.[4,5] Iron nitrides have received the most attention as a result of their intermediacy in both industrial Haber−Bosch N_2 hydrogenation catalysis[3] and in the function of nitrogenase enzymes.[2] In gas-phase chemistry, Schwarz and co-workers have generated an Fe(IV) nitride that promotes both C−H and N−H bond activation as well as [NH] group transfer to activated olefins.[6] Examples of four- and six-coordinate iron nitrido complexes with oxidation states ranging from +4 to +6 have been synthesized in condensed phases[7−14] and in some cases crystallographically characterized.[13,14] In each of these examples, the tetrahedral and octahedral ligand fields coupled with the high oxidation state of the metal center produce d-electron configurations where only bonding or nonbonding orbitals with respect to the $M{\equiv}N$ bond are populated. This results in high Fe−N bond orders, typically 3, and a relatively stable metal nitrido compound that can be characterized.

By contrast, metal nitrido compounds in square planar ligand fields with lower oxidation states have lower bond orders and hence likely weakened and more reactive $M{\equiv}N$ bonds that result from populating π^*-orbitals with respect to the M−N bond. To encourage this geometry, tridentate, meridional donors are attractive supporting ligands.[15,16] Caulton and co-workers have reported a rare group 8 example with the synthesis of $[N(SiMe_2CH_2P^tBu_2)_2]RuN$ from the corresponding azide compound.[17] Crystallographic characterization of the d^4 metal nitrido revealed a 25° distortion of the $Ru{\equiv}N$ vector from the idealized metal−chelate plane. This unusual geometric preference was rationalized by a Jahn−Teller distortion that obviates population of d-orbitals that are π^* with respect to the Ru−N bond and increases π-overlap with d_{z^2}. Burger and co-workers have since reported the synthesis of a planar, C_{2v}-symmetric iridium nitrido, $(^{iPr}PDI)IrN$ (^{iPr}PDI = 2,6-(2,6-$^iPr_2$-C_6H_3-N=CMe$)_2C_5H_3N$), by heating the corresponding azide compound to 40 °C in the solid state.[18] On the basis of a short $Ir{\equiv}N$ bond distance of 1.646(9) Å coupled with X-ray absorption data and DFT calculations, an Ir(III), d^6 formulation was proposed. The redox activity[19,20] of the bis(imino)pyridine-supporting ligand stabilizes higher oxidation states and suggests that an Ir(V), d^4 assignment for this compound is also plausible.

As part of our continuing interest in base metal chemistry with redox-active supporting ligands,[21] we sought to prepare the cobalt congener, $[(^{iPr}PDI)CoN]$, of Burger's iridium nitrido. Because cobalt is much less likely than iridium to adopt the +5 oxidation state, the putative metal nitrido would have a higher d-electron count and a lower Co−N bond order and likely be more reactive. Here we describe the photolysis and thermolysis of a family of bis(imino)pyridine cobalt azide complexes and the observation of C−H insertion into a putative cobalt nitride species. These results highlight potential differences in electronic structure and the consequences on reactivity between first- and third-row transition metal congeners.

Salt metathesis of the bis(imino)pyridine cobalt chloride compounds,[22−24] $(^{iPr}PDI)CoCl$ and $(^{Ar}BPDI)CoCl$ ($^{Ar}BPDI$ = 2,6-$(ArN{=}CPh)_2C_5H_3N$; Ar = 2,6-$^iPr_2$-C_6H_3; 2,4,6-Me_3-C_6H_2), with NaN_3 in THF furnished the corresponding azide complexes, $(^{iPr}PDI)CoN_3$ and $(^{Ar}BPDI)CoN_3$. The cobalt azide compounds are diamagnetic and exhibit NMR spectral features consistent with a low-spin cobalt(II) center antiferromagnetically coupled to a bis(imino)pyridine radical anion.[22,24] One example, $(^{iPr}BPDI)CoN_3$, was characterized by X-ray diffraction (see Supporting Information) and established an idealized planar compound with an essentially linear azide ligand ($N_\alpha{-}N_\beta{-}N_\gamma$ = 174.15(17)°) that is bent at N_α ($Co{-}N_\alpha{-}N_\beta$ = 139.07(12)°). The metrical parameters of the chelate are consistent with one-electron reduction and the $(^{iPr}BPDI^-)Co^{II}N_3$ assignment.[22,24]

The thermal and photochemical reactivity of each bis(imino)pyridine cobalt azide complex was examined in the context of synthesizing the corresponding cobalt nitrido compound. Both photolysis and thermolysis of $(^{iPr}PDI)CoN_3$ under a variety of conditions yielded free bis(imino)pyridine ligand and unidentified cobalt products. In contrast, photolysis of a cyclopentane solution of the phenyl-substituted cobalt azide, $(^{iPr}BPDI)CoN_3$, at 15 °C for 2 h followed by solvent removal and recrystallization cleanly furnished a bright green powder identified as the cyclometalated bis(imino)pyridine cobalt amide, **1**, in 90% yield (eq 1). The same product was obtained in >95% yield from solid-state thermolysis of $(^{iPr}BPDI)CoN_3$ at 215 °C for 1 h. A Toepler pump experiment was conducted in conjunction with the thermolysis procedure and 93% of the noncombustible gas expected for 1 equiv of N_2 was collected.

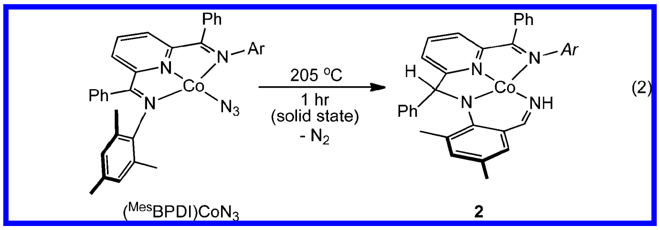


$(^{iPr}BPDI)CoN_3$ **1** (1)

The benzene-d_6 ^1H and ^{13}C NMR spectra of **1** exhibit the number of peaks consistent with a bis(imino)pyridine compound with C_1 molecular symmetry. Notable features in the ^1H NMR spectrum include singlets for the diastereotopic methyl groups that signal the cyclometalation of the methine carbon.[25] The N−H peak was located at 2.78 ppm in the ^1H NMR spectrum, and a diagnostic band was observed at 3307 cm^{-1} by IR spectroscopy. The identity of **1** was also established by X-ray diffraction (Figure 1). The Co−amide vector is lifted out of the metal−chelate plane by 21.78(12)° and has a short Co(1)−N(4) distance of 1.7826(19) Å. By comparison, the Co−N distance in the corresponding azide compound is 1.8582(13) Å. The structural data also confirm C−H activation of the methine position of the isopropyl aryl substituent, in agreement with the NMR and IR data. The metrical parameters of the bis(imino)pyridine chelate demonstrate one-electron reduction[18,19] and an electronic structure with a low-spin Co(II) d^7 ion antiferromagnetically coupled to a chelate radical anion similar to ($^{iPr}BPDI^-$)$Co^{II}N_3$ and previously reported monohalide and alkyl derivatives.[22−24]

Figure 1. Molecular structure of **1** at 30% probability of ellipsoids. Hydrogen atoms were located and are omitted, except H4N, for clarity.

Photolysis and thermolysis of the mesityl-substituted cobalt azide complex, ($^{Mes}BPDI$)CoN_3, were also explored. While photolysis in cyclopentane solution resulted in decomposition, solid-state thermolysis at 205 °C for 1 h furnished a green powder, identified as the new cobalt complex, **2**, in >95% yield (eq 2). The benzene-d_6 ^1H NMR spectrum established formation of a C_1-symmetric molecule with features distinct from those of **1**. COSY, HSQC, and HMBC NMR experiments confirmed the presence of a neutral imine ($IR_{toluene}$: $\nu_{N-H} = 3293$ cm^{-1}) coordinated to cobalt arising from C−H activation of an *ortho*-methyl group of one of the mesityl rings. The multinuclear NMR experiments established six-bond coupling between H^8 and H^{25} (see Figure 2) and confirmed that the backbone of the chelate has also been modified with a new C−H bond formed at the carbon bonded to the *ortho* position of the central pyridine.



The identity of **2** was also established by X-ray diffraction (Figure 2), and the data were of sufficient quality that all of the hydrogens were located, including the imine N−H and the newly formed C−H bond on the modified chelate. One notable feature of the molecule is the near coplanarity of the functionalized mesityl ring with the cobalt−chelate plane, accounting for the coupling between H^8 and H^{25} (see Figure 2 for labeling). It is this conformation that accounts for the extended spin system observed by two-dimensional NMR spectroscopy.

Based on the observation of C−H activation of the benzylic positions of the imine substituents upon thermolysis or photolysis, bis(imino)pyridine cobalt azide complexes protected in these positions, *rac*/*meso*-($^{tBu}BPDI$)CoN_3 and ($^{Cl2}BPDI$)CoN_3 ($^{tBu}BPDI$ = 2,6-(2-$^tBuC_6H_4$-N=CPh)$_2C_5H_3N$); $^{Cl2}BPDI$ = 2,6-(2,6-Cl_2-C_6H_3-N=CPh)$_2C_5H_3N$), were prepared. Unfortunately, thermolysis (80−175 °C) or photolysis (cyclopentane solution or solid state) of these compounds resulted in decomposition to free bis(imino)pyridine ligand and other unidentified products.

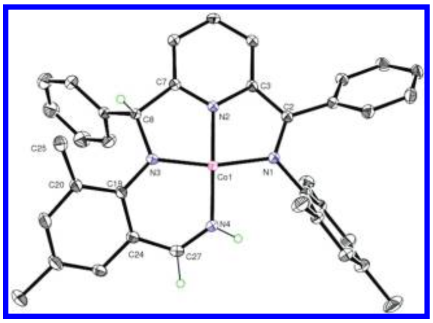


Figure 2. Molecular structure of **2** at 30% probability of ellipsoids. Hydrogen atoms, except for those on N(4), C(8), and C(27), omitted for clarity.

Deuterium labeling experiments were conducted to explore the source of the N−H bonds and understand the C−H activation pathways that yield **1** and **2**. Cyclopentane photolysis of ($^{iPr}BPDI$)CoN_3-d_{28} (where the isopropyl groups are deuterated) resulted in N−D formation in the isotopologues of **1**. Integration of the ^1H NMR spectrum following the reaction established approximately 30% incorporation of protons into the N−D from either the solvent or the glassware. In a related experiment, ($^{Mes}BPDI$)CoN_3-d_{18} (where the methyl groups of the mesityl ring are deuterated) was thermolyzed (205 °C) in the solid state. Analysis of the isotopologues and isotopomers of **2** by ^1H and ^2H NMR spectroscopy established deuterium incorporation into the expected imine and C−H backbone positions (Figure 3, inset). Significant hydrogen incorporation (20% (N−H) and 45% (C−H)) was also observed in both positions, again suggesting a more complicated isotopic exchange process. The excess proton incorporation in a solid-state reaction indicated that the glass reaction vessel was the hydrogen source. To test this possibility, the glassware was deuterated, and natural abundance ($^{Mes}BPDI$)CoN_3 was thermolyzed. Analysis at full conversion to **2** established deuterium incorporation into the methyl groups in the N-aryl rings and carbon backbone (C−H) of **2**.

A plausible mechanism for the formation of **1** and **2** from the corresponding cobalt azide likely involves initial formation of a

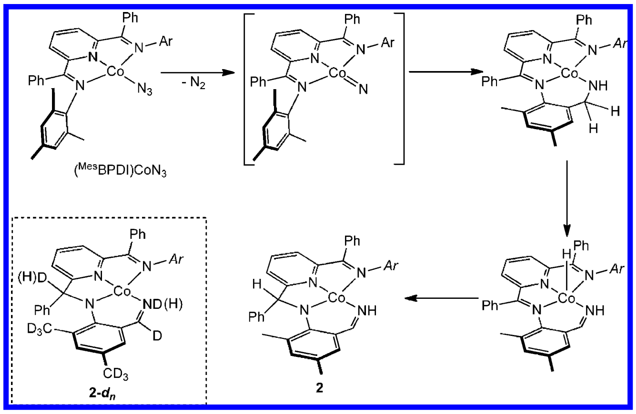
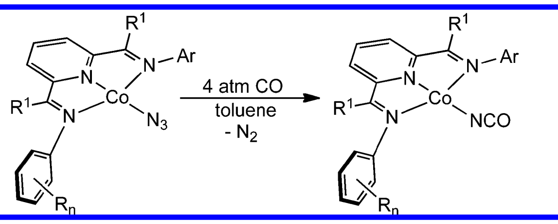


Figure 3. Proposed mechanism for the formation of **2**. Inset: Sites of proton incorporation from the solid state thermolysis of ($^{Mes}BPDI$)CoN_3-d_{18}.

transient cobalt nitride followed by C−H insertion. It is also possible that the C−H bond activation event occurs prior to N_2 loss from the azide and avoids nitrido formation.[25] We are currently unable to distinguish between these two possibilities. Intramolecular C−H bond activation following photolysis of bis(cyclopentadienyl)uranium(IV) azide complexes has recently been postulated to proceed through a terminal uranium(VI) nitride,[26] and Berry and workers have recently observed aryl C−H bond activation from a putative terminal Ru nitride.[27] If formed, the bis(imino)pyridine cobalt nitrides, [(^{Ar}BPDI)CoN], are likely Co(III) compounds with unpaired spin density on the nitrogen atom which promotes the C−H bond activation event, possibly via H-atom abstraction. Such a postulate is supported by Theopold's observation of intramolecular C−H activation by open-shell and likely isoeletronic Co(III) imido complexes.[28,29] In the case of isopropyl-substituted **1**, the site of C−H activation is the weak benzylic C−H bond of the methine rather than the terminal methyl groups that are known in related iron compounds to participate in oxidative addition[28] and 1,2-addition chemistry.[31]

A possible mechanism to account for the formation of **2** is shown in Figure 3. Following C−H bond activation by the putative cobalt nitrido, the resulting cyclometalated cobalt amide complex undergoes β-hydrogen elimination to form the coordinated imine and a cobalt hydride. The lability of the metal hydride likely accounts for the isotopic exchange with the glassware. Hydrogen migration to the phenylated imine carbon position yields **2**.

Attempts to trap the cobalt nitrides with hydrogen gas,[18] phosphines, 1,4-cyclohexadiene, 9,10-dihydroanthracene, or $ONMe_3$[18] were unsuccessful and yielded only the cyclometalated compounds **1** and **2**. Performing the thermolysis of (^{iPr}BPDI)CoN$_3$ in toluene solution at 100 °C for 4 h in the presence of 4 atm of carbon monoxide cleanly furnished the bis(imino)pyridine cobalt isocyanate complex, (^{iPr}BPDI)CoNCO (eq 3). Similarly, (^{Mes}BPDI)CoNCO was obtained following stirring a toluene solution of the azide complex at 23 °C for 2 h in the presence of 4 atm of CO. Notably, photolysis of (^{iPr}PDI)CoN$_3$ in the presence of 4 atm of CO cleanly yielded the cobalt isocyanate complex, (^{iPr}PDI)CoNCO, even though clean cyclometalation chemistry was not observed in the absence of CO. Each of the bis(imino)pyridine cobalt isocyanate complexes was independently synthesized from treatment of the cobalt chloride compounds with either KOCN or AgOCN.



(3)

Although carbonylation of both terminal[32,33] and bridging[34] metal nitrides has precedent, it is more likely that the formation of the bis(imino)pyridine cobalt isocyanate complexes proceeds through direct insertion of CO into the azide[35] rather than nitride carbonylation. Experimental support for this hypothesis is derived from the significantly lower temperatures (e.g., 23 °C versus 205 °C for (^{Mes}BPDI)CoN$_3$) needed to promote the carbonylation versus the intramolecular C−H activation reaction.

In summary, thermolysis and photolysis of bis(imino)pyridine cobalt azide complexes resulted in intramolecular C−H activation chemistry to furnish cyclometalated amide complexes. These products are in stark contrast to the previously reported isolable bis(imino)pyridine iridium nitride[18] and suggest formation of a more reactive, likely open-shell first-row congener.

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Supporting Information Available: Complete experimental procedures, electronic absorption spectra, and crystallographic data (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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