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Reaction of a Redox-Active Ligand Complex of Nickel with Dioxygen Probes Ligand-Radical Character

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Redox-active ligands profoundly influence the electronic properties of transition metal complexes and may participate in their multielectron redox chemistry. For example, such ligands are capable of enabling oxidative addition chemistry at formal d^0 metal centers and the activation of molecular hydrogen and oxygen.[1,2] Bis(imino)pyridines constitute a particularly versatile group of redox-active ligands as they have afforded 3d metal complexes that promote a variety of bond-forming and bond-breaking transformations.[3] The ligands were shown to accept up to three electrons,[4,5] and as suggested by spectroscopic and structural data, the reduction of complexes of these ligands often places the electron density into molecular orbitals of predominantly ligand character.[5−8] An intriguing aspect of these compounds is that, even though the reducing equivalents are not stored directly at the metal center, small-molecule reactivity such as N_2 activation still occurs at the metal center.[3b,9−11]

We have investigated the reactivity of bis(arylimino)pyridine complexes with dioxygen to gain further insights into the small-molecule reactivity involving this class of ligands. In the present report, we describe a one-electron reduced Ni complex that activates O_2 to cause the cleavage of a ligand C−C bond. The ligand oxygenation points to a mechanism that entails direct electron transfer from the ligand to O_2. In contrast, the O_2 reaction of a redox-active ligand complex of an early transition metal resulted in the formation of metal-bound peroxo groups while leaving the redox-active ligands intact.[2b] Furthermore, metal-centered reduction of O_2 by genuine Ni$^{\mathrm{I}}$ complexes of redox-inactive ligands is evident from the observation of Ni−O_x species.[12]

Scheme 1. Synthesis of Compounds **2** and **3**[a]

[a] Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; (*i*) 1 equiv of Na(Hg), N_2; (*ii*) O_2, 60 °C.

Reduction of [Ni{2,6-(ArN=CMe)$_2$C$_5$H$_3$N}Cl$_2$], **1** (where Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$),[13] with a sodium amalgam under an inert gas atmosphere afforded the new complex [Ni{2,6-(ArN=CMe)$_2$-C$_5$H$_3$N}Cl], **2** (Scheme 1). Insights into the molecular and electronic structure of **2** were obtained by X-ray crystallography and EPR spectroscopy. The crystallographic analysis on a black single crystal of **2**·2C$_7$H$_8$ confirmed that the Ni center is coordinated by the three nitrogen atoms of the tridentate bis(imino)pyridine and a chloride ligand in a distorted square-planar geometry (Figure 1 and Supporting Information). Notable parameters in the ligand framework are the C−C distances adjacent to the pyridine ring, i.e., 1.451(4) Å for C1−C6 and 1.446(4) Å for C5−C8, which are shorter, and the imine C−N distances, which are slightly longer than the corresponding distances in **1** and the free ligand.[13,14] Distances similar to those in **2** were found in related complexes of other first-row transition metals (i.e., Cr,[15] Fe,[16] and Co[9]) and were attributed to localization of the added electron in a ligand-based orbital.[5,8,15] Consistent with the crystallographic data, the EPR spectrum of **2** in frozen toluene solution displays an isotropic resonance signal centered at $g = 2.016$ (peak-to-peak separation ≈ 25 G). Thus, complex **2** may be best described as a ligand radical anion complex of Ni$^{\mathrm{II}}$ (Scheme 1, depicting only one resonance structure). It is of note that other one-electron reduced Ni complexes of bis(arylimino)pyridine ligands were described as Ni$^{\mathrm{I}}$ complexes of the unreduced ligand on the basis of their EPR parameters.[6,17]

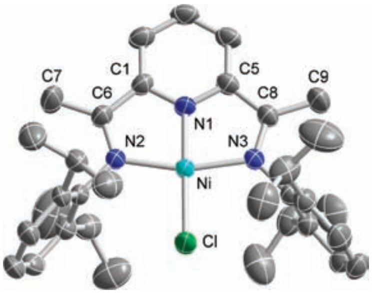

Figure 1. Molecular structure of **2**. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Color key: turquoise = Ni, blue = N, gray = C, green = Cl.

Complex **2** is stable in solution but is air-sensitive. Upon addition of O_2 to a toluene solution of **2** at 60 °C, the characteristic absorption bands of **2** in the visible and near-IR region disappeared under concomitant formation of new bands at ca. 400, 480, and 515 nm and appearance of isosbestic points at 375 and 430 nm (Figure 2). These observations suggest that a new compound, **3**, was produced from **2**. On a preparative scale, **3** was isolated as an orange-red solid and recrystallized from nitromethane at −25 °C

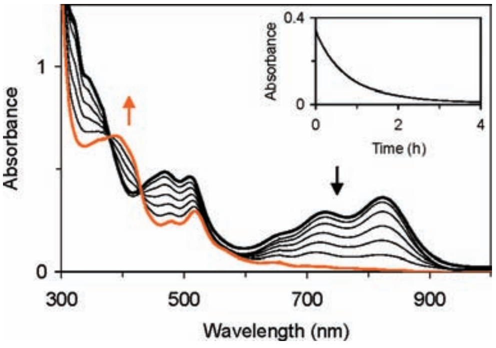

Figure 2. Reaction of 1 mM **2** (black) in toluene with O_2 at 60 °C (product solution containing **3**, orange), as monitored by electronic absorption spectroscopy (path length, 0.5 cm). Inset: Time course of the reaction (λ = 820 nm).

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to afford single crystals of **3**•$2CH_3NO_2$. The structure determination unveiled an unexpected modification of the tridentate supporting ligand. Akin to **2**, the Ni center in **3** is situated in a distorted square-planar environment consisting of three nitrogen donor atoms and a chloride ligand (Figure 3). However, one of the two acetimino groups of the tridentate ligand in **2** was transformed into an amidato group with a C−O distance of 1.236(2) Å and a C−N distance of 1.348(2) Å. Furthermore, the C1−C6 and C5−C8 distances of 1.472(3) and 1.506(3) Å are longer than those in **2** and consistent with $C(sp^2)-C(sp^2)$ single bonds, suggesting that the newly formed iminoethylpyridylcarboxamidato ligand is in its closed-shell form. Consequently, the Ni center remains in the +II oxidation state (Scheme 1). While the Ni−N and Ni−Cl distances in **3** are slightly shorter than those in **2**, the most significant contraction is observed for the Ni−N3 distance (1.892(2) Å in **3** vs 1.942(2) Å for the average of the Ni−N2 and Ni−N3 distances in **2**) due to the conversion of the imino donor into the anionic amidato donor.

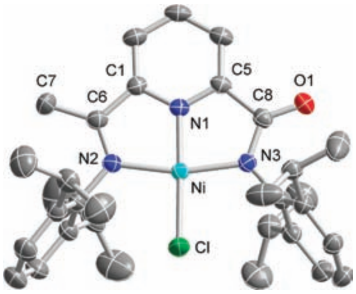

Figure 3. Molecular structure of **3**. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Color key: turquoise = Ni, blue = N, gray = C, red = O, green = Cl.

Compound **3** was further characterized by ESI-MS of the reaction solution and the isolated product. In both cases, the mass spectra exhibit peaks at $m/z = 540$ and 576, whose masses and isotope distribution patterns are consistent with $\{\mathbf{3} - Cl\}^+$ and $\{\mathbf{3} + H\}^+$, respectively. The presence of the amidato group was affirmed by a band at 1635 cm^{-1} (attributable to ν_{CO}) in the IR spectrum of **3**. Upon removal of the new carboxamidato ligand from the Ni center, the corresponding carboxamide, **4**, was isolated as a colorless solid in nearly quantitative yield. The ^1H NMR spectrum of **4** exhibits the expected resonance signals of an asymmetrically disubstituted pyridine ring and of two sets of isopropyl substituents. The presence of only one acetimino group is evidenced by the intensity ratio of the peaks arising from the $N{=}CCH_3$ and $ArCH(CH_3)_2$ protons of 1:4:4 (cf. Supporting Information).

The facile oxidative C−C bond cleavage in **2** is remarkable and differs from the chemistry of reactive $Ni-O_x$ intermediates, which rather react with ligand C−H bonds that are disposed in close proximity to the Ni center or oxidize external substrates.[12,18,19] The exact mechanism by which **2** is oxidized, including the fate of the CH_3 group and the second O atom of O_2, is not known. Given the radical character of **2**, however, its oxidation could be initiated by direct attack of the O_2 diradical on an imino carbon atom (C6 or C8 in Figure 1) that perhaps is assisted by coordination to the Ni center. Aspects of the mechanism of this reaction may be related to that of catechol oxygenation, which involves binding of the redox-active substrate to a metal center.[2a]

To explore the generality of the ligand-based oxygenation observed here, we tested the reactivity of the Co analogue of **2**, $[Co\{2,6\text{-}(ArN{=}CMe)_2C_5H_3N\}Cl]$.[9] Under the same conditions as those used for **2**, this complex was readily oxidized to a Co^{II} complex of the unmodified bis(imino)pyridine ligand by apparent one-electron oxidation. Thus, the O_2 reactivity of these ligand-radical complexes varies significantly with the nature of the metal center. Further investigations of the mechanisms and the factors influencing this reactivity are warranted.

In conclusion, a reduced bis(imino)pyridine nickel complex (**2**) was synthesized and characterized as a Ni^{II}-ligand-radical species. The ligand-centered oxygenation observed in the reaction of this complex with O_2 contrasts with the prevailing metal-centered chemistry of redox-active bis(imino)pyridine ligands and demonstrates that they can be directly involved in the activation and conversion of a small molecule.

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Supporting Information Available: Experimental procedures, characterization data of all compounds, details of the crystal structure determinations (Tables S1−S4, PDF), and crystallographic information files of **2** and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Blackmore, K. J.; Sly, M. B.; Haneline, M. R.; Ziller, J. W.; Heyduk, A. F. *Inorg. Chem.* **2008**, *47*, 10522. (b) Nguyen, A. I.; Blackmore, K. J.; Carter, S. M.; Zarkesh, R. A.; Heyduk, A. F. *J. Am. Chem. Soc.* **2009**, *131*, 3307. (c) Ringenberg, M. R.; Kokatam, S. L.; Heiden, Z. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2008**, *130*, 788.

(2) (a) Yin, C.-X.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 13988. (b) Stanciu, C.; Jones, M. E.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 12400.

(3) (a) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745. (b) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13794. (c) Trovitch, R. J.; Lobkovsky, E.; Bouwkamp, M. W.; Chirik, P. J. *Organometallics* **2008**, *27*, 6264. (d) Russell, S. K.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 36.

(4) Enright, D.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3873.

(5) Knijnenburg, Q.; Gambarotta, S.; Budzelaar, P. H. M. *Dalton Trans.* **2006**, 5442.

(6) de Bruin, B.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 2936.

(7) Knijnenburg, Q.; Hetterscheid, D.; Kooistra, T. M.; Budzelaar, P. H. M. *Eur. J. Inorg. Chem.* **2004**, 1204.

(8) Bart, S. C.; Chlopek, K.; Bill, E.; Bouwkamp, M. W.; Lobkovsky, E.; Neese, F.; Wieghardt, K.; Chirik, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 13901.

(9) Gibson, V. C.; Humphries, M. J.; Tellmann, K. P.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 2252.

(10) (a) Vidyaratne, I.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M. *Inorg. Chem.* **2005**, *44*, 1187. (b) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Budzelaar, P. H. M. *Inorg. Chem.* **2007**, *46*, 7040. (c) Scott, J.; Vidyaratne, I.; Korobkov, I.; Gambarotta, S.; Budzelaar, P. H. M. *Inorg. Chem.* **2008**, *47*, 896.

(11) In principle, the ligands are amenable to chemical modification (cf. refs 3a and 5).

(12) (a) Kieber-Emmons, M. T.; Riordan, C. G. *Acc. Chem. Res.* **2007**, *40*, 618. (b) Yao, S.; Bill, E.; Milsmann, C.; Wieghardt, K.; Driess, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7110.

(13) Fan, R.-q.; Zhu, D.-s.; Mu, Y.; Li, G.-h.; Su, Q.; Ni, J.-g.; Feng, S.-h. *Chem. Res. Chin. Univ.* **2005**, *21*, 496.

(14) Yap, G. P. A.; Gambarotta, S. Private communication to the Cambridge Structural Database, 1999, deposition number CCDC 116252.

(15) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Duchateau, R. *Organometallics* **2007**, *26*, 3201.

(16) Bouwkamp, M. W.; Bart, S. C.; Hawrelak, E. J.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2005**, 3406.

(17) (a) Baidya, N.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 9666. (b) Marganian, C. A.; Vazir, H.; Baidya, N.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **1995**, *117*, 1584.

(18) (a) Chen, D.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1991**, *30*, 1396. (b) Hikichi, S.; Yoshizawa, M.; Sasakura, Y.; Komatsuzaki, H.; Moro-oka, Y.; Akita, M. *Chem.−Eur. J.* **2001**, *7*, 5011. (c) Suzuki, M. *Acc. Chem. Res.* **2007**, *40*, 609.

(19) The methine C−H bonds in **2** are nearby an open coordination site of the Ni center but remain unaltered. Furthermore, the presence of more easily oxidizable substrates (e.g., PPh_3, Me_2S, *cis*-cyclooctene, or 9,10-dihydroanthracene) does not affect the oxidation of **2** to **3**.

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