

Cobalt–Dinitrogen Complexes with Weakened N–N Bonds

Keying Ding,[†] Aaron W. Pierpont,[‡] William W. Brennessel,[†] Gudrun Lukat-Rodgers,[§]
Kenton R. Rodgers,^{*,§} Thomas R. Cundari,^{*,‡} Eckhard Bill,^{*,||} and Patrick L. Holland^{*,†}

Department of Chemistry, University of Rochester, Rochester, New York 14267, Department of Chemistry, University of North Texas, Denton, Texas 76203, Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105, and Max-Planck-Institut für Bioanorganische Chemie, Mülheim an der Ruhr, Germany

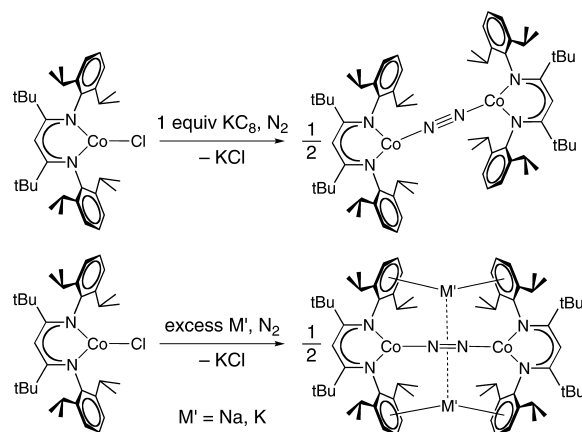
Received November 9, 2008; E-mail: holland@chem.rochester.edu

The binding of N₂ to transition metal complexes is a topic of great interest in the chemistry community.¹ While the reactivity of N₂ complexes does not always correlate with their ground-state properties, it has proven useful to estimate “activation” of N₂ using the N–N bond length and stretching frequency, quantities that are readily measurable. One trend that has emerged is that the “early” transition metals in groups 4–6 often give N₂ complexes with weaker, longer N–N bonds, whereas N₂ complexes of the “late” transition metals in groups 8–10 have shorter, stronger N–N bonds ($d_{\text{NN}} < 1.15 \text{ \AA}$, $\nu_{\text{NN}} > 1900 \text{ cm}^{-1}$).² For example, all N–N distances in satisfactory ($R < 10\%$) structures of metal–N₂ compounds of group 9 metals are less than 1.18 Å, suggesting relatively little activation.³ This trend is consistent with the importance of π -backbonding, where the low-energy d electrons of the electronegative “late” metals are not transferred effectively to the π^* orbitals of N₂. Paradoxically, biological (nitrogenase) and industrial (Haber–Bosch) catalysts for N₂ reduction use iron, a late metal whose isolated N₂ complexes typically have little N–N weakening. The α form of N₂ on elemental Fe surfaces has an N–N stretching frequency of 1415 cm⁻¹, indicating significant weakening that has never been achieved in a synthetic complex.⁴ It is not clear which properties of the catalysts enable them to achieve N–N weakening and cleavage.

Recently, we described a series of low-coordinate Fe–N₂–Fe complexes that have unprecedented weakening of the N–N bond (1.18–1.23 Å; 1583–1810 cm⁻¹) and explored their electronic structure in detail.⁵ Experimental and theoretical studies showed that the N₂ weakening in these complexes arises from the unusual low-coordinate geometry at iron, which gives high-energy, singly occupied d orbitals that transfer electron density into the π^* orbitals of N₂.⁶ Tetrahedral Fe–N₂–Fe complexes can also give long N–N bonds.^{3g,7} Therefore, it is of interest to learn whether low-coordinate geometries would also enable cobalt, which has lower-energy d orbitals than Fe, to weaken the N–N bond of N₂ as well. Here, we report that a dicobalt(I) complex has little N–N weakening ability but that a formally dicobalt(0) complex has significant weakening of the N–N bond from backbonding.

Treatment of LCoCl (L = 2,2,6,6-tetramethyl-3,5-bis(2,6-triisopropylphenylimido)hept-4-yl)⁸ with 1 equiv of KC₈ gives the bimetallic dinitrogen complex LCoNNCoL⁹ and, with 2 equiv of reductant, gives K₂LCoNNCoL (Scheme 1). Reduction with metallic Na gives the analogous sodium salt Na₂LCoNNCoL. Each deep purple dinitrogen complex is obtained in a yield of 60–70%, and each has a 7-line ¹H NMR spectrum in C₆D₆ solution at room temperature that is consistent with averaged D_{2h} or D_{2d} symmetry on the NMR time scale. Solid-state magnetic susceptibility mea-

Scheme 1. Binding of Nitrogen by Low-Coordinate Cobalt



surements show that LCoNNCoL has a quintet ($S = 2$) ground state and K₂LCoNNCoL is a triplet ($S = 1$). Interestingly, in each case the CoNNCo group behaves as a single spin system (see Supporting Information for details).¹⁰

X-ray crystal structures were determined for each of the new cobalt–dinitrogen complexes. Table 1 compares the CoNNCo cores to the FeNNFe⁵ and NiNNNi¹¹ analogues. The Co–N bonds (1.8401(8) Å) are longer than the Fe–N bonds (1.771(5) Å), and the N–N bond is significantly shorter in the Co complex than in the Fe complex (1.1390(15) Å for Co vs 1.189(4) Å for Fe). In the nickel analogue LNiNNNiL, the N–N bond is even shorter (1.120(4) Å). Because of the exact correspondence of ligands, it is possible to conclude unambiguously that LCo and LNi are less effective at weakening the N–N bond than LFe at this oxidation level. We attribute this difference to the lower d orbital energies of Co and Ni, which give weaker backbonding into the π^* orbital of N₂.

Another difference between the LFeNNFeL and LCoNNCoL is the geometry at the metal. The iron atoms in LFeNNFeL have local C_{2v} symmetry (Y-shaped geometry), with the N₂ ligand on the C₂ axis of the diketiminate–iron unit. However, in the Co complex, the Co atoms have a significant distortion toward a T shape, with N_L–Co–N_{N2} angles of 101.01(3)° and 162.69(3)°. An independent crystal structure in a different space group, though poorly refining, showed a similar T distortion with N–Co–N angles of 108° and 156°, suggesting that the T distortion is not from crystal packing effects. There is a low barrier for interconversion of the T shapes in solution, because the two aryl groups of the diketiminate ligand are equivalent on the ¹H NMR time scale (apparent D_{2h}/D_{2d} symmetry) at temperatures from 205 to 355 K.

In contrast to these differences between formally cobalt(I) and iron(I) species, the formally cobalt(0) compounds with an [LCoNNCoL]²⁻ core have metrical parameters that are similar to

[†] University of Rochester.

[‡] University of North Texas.

[§] North Dakota State University.

^{||} Max-Planck-Institut für Bioanorganische Chemie.

Table 1. Metrical Parameters and Resonance Raman Frequencies for MNNM Cores

	N ₂	L ₂ Fe ₂ N ₂ ^a	L ₂ Co ₂ N ₂	L ₂ Ni ₂ N ₂ ^c	Na ₂ L ₂ Fe ₂ N ₂ ^b	Na ₂ L ₂ Co ₂ N ₂	K ₂ L ₂ Fe ₂ N ₂ ^b	K ₂ L ₂ Co ₂ N ₂	K ₂ L ₂ Ni ₂ N ₂ ^c
M–N (Å)	N/A	1.770(4), 1.772(4)	1.8401(8)	1.836(3), 1.830(3)	1.749(3), 1.746(3)	1.743(7), 1.735(6)	1.773(7), 1.761(7)	1.750(1)	1.747(4)
N–N (Å)	1.098	1.189(4)	1.139(2)	1.120(4)	1.213(4)	1.211(3)	1.241(7)	1.220(2)	1.185(8)
ν_{N-N} (cm ⁻¹) ^d	2331	1778 (1718)	<i>e</i>	2164 (2093)	1583	1598 (1542)	1589 (1536)	1599 (1545)	1696 (1642)

^a Rerefinement of the original data from ref 5a; see Supporting Information. ^b Reference 5a. ^c Reference 11. ^d Stretching frequencies of ¹⁵N₂ isotopomers given in parentheses. ^e No isotope-sensitive Raman bands were observed with 514.5, 413.1, or 406.7 nm excitation.

their Fe analogues, with N–N distances of 1.21–1.22 Å (Table 1). These N–N distances are similar to the N–N double bond in azobenzene of 1.24(2) Å.¹² These are the longest N–N distances in any cobalt dinitrogen complex, including tetrahedral examples.³ They are also significantly longer than the N–N bond in the nickel analogue K₂LNiNNNiL (1.185(8) Å).¹¹ Resonance Raman spectra ($\lambda_{\text{ex}} = 406.7$ nm) of the [LCoNNCoL]²⁻ complexes in toluene solution show bands below 1600 cm⁻¹ that shift 50–60 cm⁻¹ lower in the ¹⁵N₂ isotopomer. The very low N–N stretching frequency confirms the crystallographically observed weakening of the N–N bond. Thus, even though Co is less activating than Fe in LMNNML species, it is as effective as Fe at weakening N₂ in [LMNNML]²⁻ compounds. The short Co–N bonds of 1.73–1.75 Å suggest some multiple bond character from π -backbonding.¹³

Is the N–N weakening in the Co₂ dianions due to the additional electron density at cobalt or from the influence of the alkali metal cations? Because the alkali-metal-free dianions have not been isolable, DFT calculations are used to elucidate the reasons for the exceptional N–N bond weakening. Calculations use a simplified β -diketiminato ligand (L' = C₃N₂H₅⁻) with a pure functional and an extended all-electron basis set, BPW91/6-311+G(d). The triplet dianion [L'CoNNCoL']²⁻ optimizes to a Y-shape minimum with Co–N = 1.76 Å, N–N = 1.19 Å, and $\nu_{\text{NN}} = 1742$ cm⁻¹. This shows that reduction alone gives significant N–N stretching, but not as much as the observed compounds. Interestingly, geometry optimization of triplet K₂L'CoNNCoL' gives a model that has excellent agreement with the experimental metrical data, with Co–N = 1.74 Å (expt 1.75), N–N = 1.22 Å (expt 1.22), and $\nu_{\text{NN}} = 1603$ cm⁻¹ (expt 1599). The presence of the potassium ions heightens the electron transfer from Co to N₂; Natural Bond Order (NBO) analyses show that the N–N bond order changes from 2.05 to 1.82 upon incorporation of the K⁺ ions. Clearly, both reduction and alkali metal binding work in concert to weaken N₂, whereby the positively charged alkali metal pulls electrons into N₂.

Thus, iron and cobalt have different abilities to weaken N₂ in formally monovalent compounds and similar abilities in formally

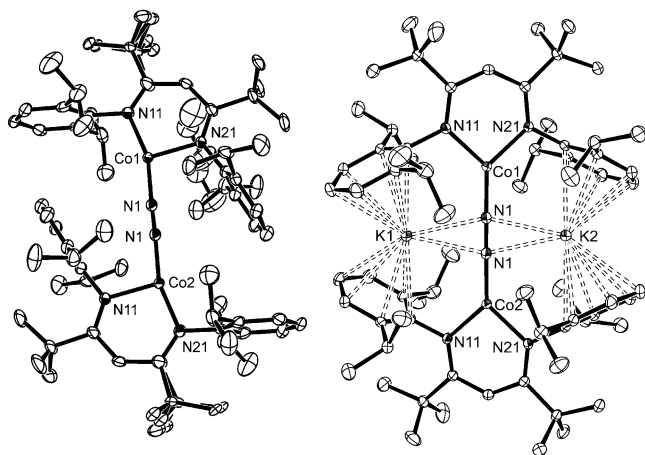


Figure 1. Solid state structures of (a) LCoNNCoL and (b) K₂LCoNNCoL (right), using 50% thermal ellipsoids. Metrical parameters are in Table 1.

zerovalent compounds. In neutral LMNNML, Fe is significantly better than Co at backbonding into the π^* orbitals of N₂. Reduction of LCoNNCoL by two more electrons gives the first Co complex with a significantly weakened N₂ ligand, and this N–N bond weakening is similar between the formally zerovalent complexes (alkali)₂[LMNNML] with Fe and Co. These results demonstrate that the coordination geometry and presence of alkali metals can have a major impact on the reduction level of bound N₂, even with a more poorly backbonding metal like cobalt.

Acknowledgment. The authors acknowledge a gift of ¹⁵N₂ from Cambridge Isotopes and financial support from the NIH (GM065313 to P.L.H., AI072719 to K.R.R.) and the NSF (CHE-0112658 to P.L.H., CHE-0701247 to T.R.C.).

Supporting Information Available: Synthetic, computational, spectroscopic, and crystallographic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- MacKay, B. A.; Fryzuk, M. D. *Chem. Rev.* **2004**, *104*, 385–401.
- Tuczek, F.; Lehnert, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 2636–2638. Note that geometric “activation” and reactivity do not necessarily correlate. We emphasize ground-state weakening here because it is more readily quantified. See also: Leigh, G. J. *Acc. Chem. Res.* **1992**, *25*, 177–181.
- Selected cobalt complexes: (a) Davis, B. R.; Payne, N. C.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2719–2728. (b) Hammer, R.; Klein, H. F.; Schubert, U.; Frank, A.; Huttner, G. *Angew. Chem.* **1976**, *88*, 648–649. (c) Yamamoto, A.; Miura, Y.; Ito, T.; Chen, H. L.; Iri, K.; Ozawa, F.; Miki, K.; Sei, T.; Tanaka, N.; Kasai, N. *Organometallics* **1983**, *2*, 1429–1436. (d) Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1437–1441. (e) Bianchini, C.; Peruzzini, M.; Zanolini, F. *Organometallics* **1991**, *10*, 3415–3417. (f) Detrich, J. L.; Konecny, R.; Vetter, W. M.; Doren, D.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1996**, *118*, 1703–1712. (g) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 10782–10783. (h) Scott, J.; Gamarotta, S.; Korobkov, I. *Can. J. Chem.* **2005**, *83*, 279–285. (i) Fout, A. R.; Basuli, F.; Fan, H.; Tomaszewski, J.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 3291–3295.
- Freund, H. J.; Bartos, B.; Messmer, R. P.; Grunze, M.; Kuhlenbeck, H.; Neumann, M. *Surf. Sci.* **1987**, *185*, 187–202.
- (a) Smith, J. M.; Lachicotte, R. J.; Pittard, K. A.; Cundari, T. R.; Lukat-Rodgers, G.; Rodgers, K. R.; Holland, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 9222–9223. (b) Smith, J. M.; Sadique, A. R.; Cundari, T. R.; Rodgers, K. R.; Lukat-Rodgers, G.; Lachicotte, R. J.; Flaschenriem, C. J.; Vela, J.; Holland, P. L. *J. Am. Chem. Soc.* **2006**, *128*, 756–769. (c) Stoian, S. A.; Vela, J.; Smith, J. M.; Sadique, A. R.; Holland, P. L.; Münck, E.; Bominaar, E. L. *J. Am. Chem. Soc.* **2006**, *128*, 10181–10192.
- Holland, P. L. *Acc. Chem. Res.* **2008**, *41*, 905–914.
- Chomitz, W. A.; Arnold, J. *Chem. Commun.* **2007**, 4797–4799.
- Holland, P. L.; Cundari, T. R.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 14416–14424.
- An iron–cobalt heterobimetallic dinitrogen complex LFeNNCoL is also accessible, though it has not been crystallographically characterized. Its ¹H NMR spectrum is consistent with two inequivalent diketiminato environments. An N–N stretching vibration is present in the IR spectrum at 1806 cm⁻¹ (1743 cm⁻¹ with ¹⁵N₂). The N–N stretching mode is not observed in infrared spectra of LFeNNFeL or LCoNNCoL, and the observation of an infrared-active N–N band is strong evidence for the heterobimetallic complex LFeNNCoL. See the Supporting Information for characterization of this and other compounds.
- Related magnetism of an MNNM core: Curley, J. J.; Cook, T. R.; Reece, S. Y.; Muller, P.; Cummins, C. C. *J. Am. Chem. Soc.* **2008**, *130*, 9394–9405.
- Pfiffmann, S.; Limberg, C.; Herwig, C.; Stösser, R.; Ziemer, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 3357–3361.
- Harada, J.; Ogawa, K. *J. Am. Chem. Soc.* **2004**, *126*, 3539–3544.
- The Co–N single bonds in LCoNNCoL are 1.83 Å, and a Co–N triple bond in a three-coordinate diketiminato complex is 1.62 Å. See: Dai, X.; Kapoor, P.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 4798–4799.

JA808783U