Inorganic Chemistry

Communication

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Cobalt(II) Complex of a Diazoalkane Radical Anion

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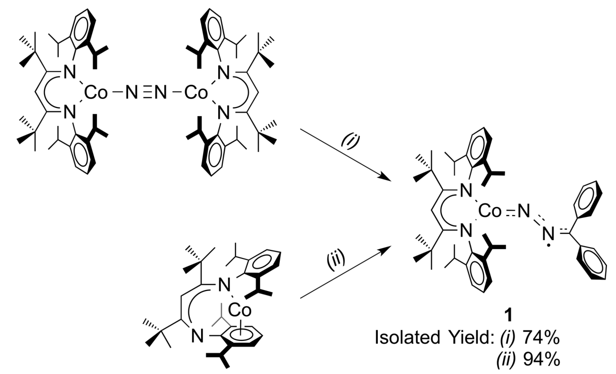
Supporting Information

ABSTRACT: β-Diketiminate cobalt(I) precursors react with diphenyldiazomethane to give a compound that is shown by computational studies to be a diazoalkane radical anion antiferromagnetically coupled to a high-spin cobalt(II) ion. Thermolysis of this complex results in formal N–N cleavage to give a cobalt(II) ketimide complex. Experimental evaluation of the potential steps in the mechanism suggests that free azine is a likely intermediate in this reaction.

Interest in diazoalkane complexes of first-row metals comes from the potential utility of these molecules as precursors to inexpensive carbene complexes for catalysis.[1,2] However, the diazoalkane complexes are also interesting in their own right,[3] particularly because of the potential for redox noninnocence. Coordinated diazoalkanes can bend at each nitrogen atom, which is most commonly ascribed to a two-electron reduction of the coordinated diazoalkane.[3,4] Single-electron reduction to form a radical anion of the diazoalkane is rarely invoked,[5] despite an early report of the one-electron reduction of diazofluorene with sodium metal[6] and a reductive coupling of two diazoalkanes proposed to go via a radical intermediate.[7] Because the charge movement within diazoalkanes is intimately connected with their reactions, including formal N–N[3,8] and C–N cleavage,[1,2] exploration of their electronic structure and reactivity is needed. Prior to this work, only three cobalt diazoalkane complexes had been structurally characterized.[9,10]

The new cobalt diazoalkane complex $L^{tBu}CoN_2CPh_2$ (**1**; L^{tBu} = $[\{(Dipp)NC(tBu)\}_2CH]^-$ where Dipp = 2,6-iPr$_2$C$_6$H$_3$) can be isolated in 74% yield by treating the cobalt(I) dinitrogen complex $L^{tBu}CoNNCoL^{tBu}$[11] with 2 equiv of diphenyldiazomethane under a nitrogen atmosphere (Scheme 1). The yield of **1** is 94% if the cobalt(I) synthon $L^{tBu}Co$[12] is treated with 1 equiv of diphenyldiazomethane, again under an atmosphere of nitrogen. The solid-state molecular structure of **1**, determined by X-ray crystallography (Figure 1), reveals η^1 coordination of the diazoalkane moiety to the trigonal-planar cobalt center (Σ_{Co} = 359.79°). The Co1–N14 bond length in **1** [1.719(2) Å] is shorter than Co–N single bonds [e.g., 1.796(2) Å in $L^{tBu}CoNCPh_2$ (**2**)], which suggests some Co–N multiple-bond character.[9b,13]

Scheme 1. Synthesis of 1[a]



[a]Reaction conditions: (i) 2 N_2CPh_2, pentane; (ii) 1 N_2CPh_2, pentane.

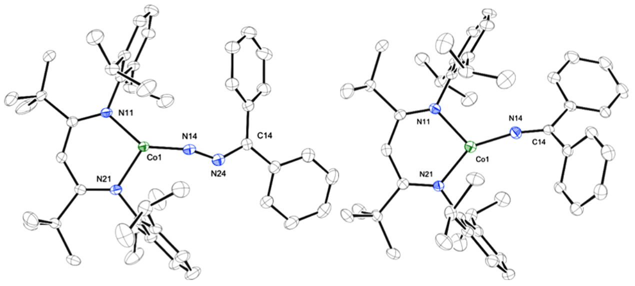


Figure 1. Molecular structures of **1** (left) and **2** (right). Thermal ellipsoids displayed at the 50% probability level. Hydrogen atoms omitted for clarity. See the SI for selected bond lengths and angles.

The Co1–N11/N21 bond lengths [1.902(2) and 1.916(2) Å, respectively] are within the range of those previously reported for three-coordinate cobalt(I) complexes $L^{tBu}CoL'$ [1.881(3)–1.998(2) Å; L′ = THF, PPh$_3$, Py],[12,14] and cobalt(II) complexes $L^{tBu}CoR$ [1.902(2)–1.960(2) Å; R = Cl, alkyl].[12,15] The diazoalkane NNC unit is not linear and indicates that reduction of the diazoalkane occurred upon coordination. The doubly bent geometry compares well with the only definitively assigned example of a first-row transition-metal complex bound to a diphenyldiazomethanyl radical anion, $[tpeFeN_2CPh_2][Li(THF)]$ [tpe = tris(5-mesitylpyrrolyl)ethane; Figure 2].[5a] The N14=N24 double bond [1.216(2) Å] and the long N24=C14 double bond [1.322(3) Å] are similar to those in $[tpeFeN_2CPh_2][Li(THF)]$ [1.12(1) and 1.31(1) Å, respectively]. The Co–N14–N24 [159.4(2)°] and N14–N24–C14

Received: March 24, 2015
Published: May 19, 2015

DOI: 10.1021/acs.inorgchem.5b00673
Inorg. Chem. 2015, 54, 5148–5150

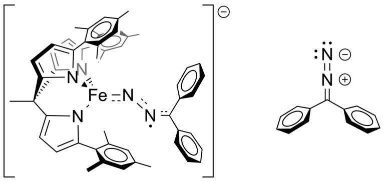


Figure 2. [tpeFeN$_2$CPh$_2$][Li(THF)],[5a] (left) and uncoordinated diphenyldiazomethane (right).

[134.2(2)°] angles and planar C14 atom ($\Sigma_{C14} = 360.0°$) are also consistent with those of [tpeFeN$_2$CPh$_2$][Li(THF)] [160.3(8) and 149(1)°, respectively; $\Sigma_{C14} = 358.9°$]. A search of the CCSD revealed that the N−N−C angles in transition-metal diazo complexes tend to either 120° or 180°.[16] Although there are examples of intermediate N−N−C angles (130−170°), there are only three others in which the N$_2$C unit does not form part of a chelate and the M−N−N angle is less than 170°.[17]

The ^{1}H NMR spectrum of **1** is constant with rotation around the Co−N bond that is fast on the NMR time scale. A band corresponding to an N−N stretching mode could not be definitively assigned in the IR spectrum because it presumably lies in the same region as the L^{tBu} aromatic and C−N stretching modes. The solution magnetic susceptibility [$\mu_{eff} = 3.0(1)\ \mu_B$] indicated an $S = 1$ ground state, and the complex was electron paramagnetic resonance (EPR) silent at 7.6 K. This is consistent with either high-spin cobalt(I) or high-spin cobalt(II) antiferromagnetically coupled to a diazoalkane radical.

Computational studies shed light on the electronic struture of **1**. The geometry of the triplet ($S = 1$) state was optimized using several functionals, and we chose the M06L functional because it gave a geometry (which we refer to as **1a**) that agreed best with the crystallographically determined structure of **1** (see the Supporting Information, SI).[18] The electronic structure of **1a** was determined using M06,[19] with the pseudopotential valence SDD basis set on cobalt and the triple-ζ all-electron basis set 6-311++G(d,p) on all other atoms. Maximal alignment of the α- and β-spins of the molecular orbital (MO) diagram indicated significant spin polarization, where one electron pair has an orbital overlap of 67% (Figure 3), a relatively low value that is characteristic of diradicals having strong antiferromagnetic coupling.[20] The β-spin orbital lies on the diazoalkane, indicating the presence of a ligand-based radical that is delocalized within the N$_2$C unit.

Natural bond order (NBO) analysis correlates canonical MOs with a localized valence bond or Lewis structure model.[21] Using the different Lewis structures for different spins approach,[22] the α- and β-spin densities were represented by resonance forms **A** and **B**, respectively (Figure 4). Resonance structure **A** indicates that there are more α spins on the metal, whereas resonance structure **B** indicates more β spins on the ligand. These resonance structures, along with the Wiberg bond indices (WBIs), are again consistent with the overall description of a radical on the diazoalkane unit, which derives from one-electron reduction of the ligand in the ground state.

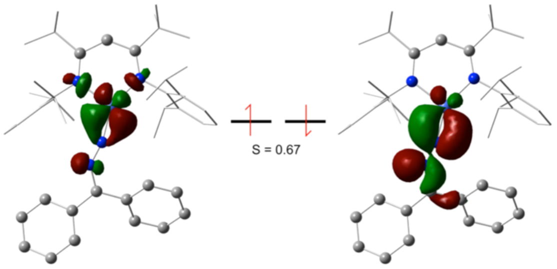


Figure 3. Spin-polarized orbitals in the qualitative MO diagram of **1a** (the computational model of **1**) that come from maximal alignment of the α- and β-spin orbitals. Surfaces depicted with an isovalue of 0.04 au sulfur represent the overlap integral between the correlated α- and β-spin electrons; all other overlaps were greater than 0.97. Other orbitals are shown in the SI.

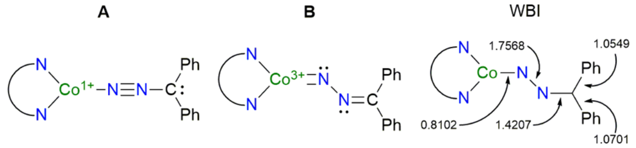


Figure 4. Resonance structures that correspond to the NBO-determined *single electron* α-spin (**A**) and β-spin (**B**) orbitals for **1a**. Two-electron Lewis structures are depicted for clarity, although these are meant to indicate the locations of single electrons. WBIs in **1a** are also presented on the right.

Heating solutions of **1** to 80 °C in benzene or cyclohexane over 42 h led to the gradual formation of a compound with an ^{1}H NMR spectrum having 10 paramagnetically shifted resonances that grew at the expense of those assigned to **1**. An internal integration standard showed a maximum yield of only 27%. Despite this difficulty, crystals suitable for single-crystal X-ray diffraction were grown from concentrated pentane solutions of the crude reaction mixture and isolated in 15% yield.

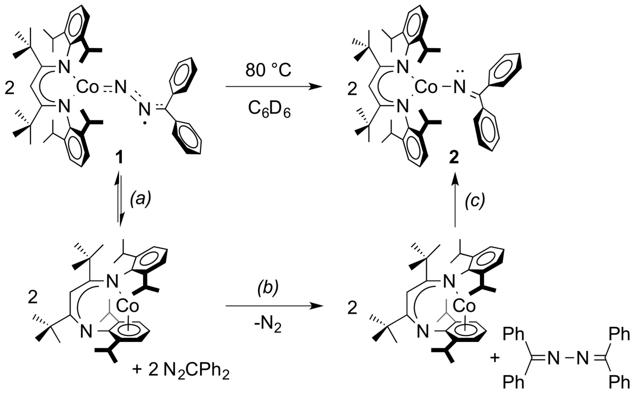
X-ray diffraction analysis revealed that the product is the ketimide complex **2** (Figure 1). The trigonal-planar ($\Sigma_{Co} = 358.92°$) cobalt(II) center features a fairly short Co1−N14 single bond [1.796(2) Å] to the ketimide moiety, which contains an imine N═C double bond [1.263(3) Å]. The Co−N−C angle is only slightly bent in the solid state [160.7(2)°], which in combination with the short Co−N distance suggests π-bonding interactions between nitrogen and cobalt.

Compound **2** can also be isolated in higher yield (50%) by treating L^{tBu}CoCl with LiNCPh$_2$ in THF. The Co−N and/or N−C bonds are rapidly rotating on the NMR time scale because compound **2** displays averaged C_{2v} symmetry in its ^{1}H NMR spectrum. An N═C double-bond stretching mode is readily identifiable in the IR spectrum (1630 cm^{-1}), which is within the range of the N═C stretching frequencies reported for the terminal cobalt(II) ketimide complex Co(N═C*t*Bu$_2$)$_3$·Li(12-crown-4) (1600−1640 cm^{-1}).[23]

The transformation of **1** to **2** is remarkable because of the apparent loss of a single nitrogen atom from the diazoalkane complex, in contrast to the loss of dinitrogen to form a carbene complex. This is presumably due to the large degree of steric protection afforded by the ligand L^{tBu} at the cobalt center, which prevents Co−C bond formation.

In our system, mechanistic studies were hampered by the low yield of the transformation and the presence of one or more alternate pathways at the reaction temperature (unidentified products were observed by ^{1}H NMR spectroscopy). Nevertheless, we tentatively propose a mechanism (Scheme 2) in which compound **1** dissociates in solution (step a), the microscopic reverse of the observed diazoalkane coordination (Scheme 1). (We were unsuccessful in finding a suitable trap for free L^{tBu}Co during the thermolysis reaction; see the SI.) Coupling of diazoalkanes to form azines (step b) can occur under our thermolysis conditions in 5 h at 80 °C, in the absence of metal.[24] The azine formed here could subsequently react with L^{tBu}Co, the byproduct from the initial dissociation step, via a

Scheme 2. Proposed Mechanism for the Formation of 2 from Heating Solutions of 1



reductive N–N bond cleavage to form **2** (step c). A related cleavage of benzophenone azine with a cobalt(I) complex has been reported previously.[25] In order to test step c independently, we added benzophenone azine to 2 mol equiv of isolated $L^{tBu}Co$ under argon in C_6D_{12} at 80 °C for 85 min, which gave **2** in 82% yield, as judged by ^1H NMR spectroscopy with an internal integration standard. Thus, step c is also kinetically competent to be part of the mechanism in Scheme 2 for forming **2** from **1**. Overall, this proposed mechanism is reasonable because it consists of experimentally verified steps.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, spectroscopic data, and X-ray crystallographic data in CIF format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00673.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Thomas Cundari and Daniel DeRosha for helpful discussions and David Vinyard for collecting the EPR data. Funding was provided by the American Australian Association (to S.J.B.) and the U.S. Department of Energy, Office of Basic Energy Sciences, through Grant DE-FG02-09ER16089 (to P.L.H.). Analytical data were from the CENTC Elemental Analysis Facility at the University of Rochester, funded by the NSF (Grant CHE-0650456). This work was supported in part by the facilities and staff of the Yale High Performance Computing Center, which was partially funded by the NSF (Grant CNS 08-21132).

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