Cobalt Complexes

DOI: 10.1002/anie.200701408

Transformation of Nitrile to Cyanide and Aldehyde Using a Cobalt(II) Complex and Dioxygen

*Jörg Müller, Christian Würtele, Olaf Walter, and Siegfried Schindler**

Dedicated to Professor Rudolf Hoppe on the occasion of his 85th birthday.

Activation of carbon–carbon bonds under mild conditions is of great interest in organometallic chemistry, and some transition-metal complexes have proven to be active in C–C bond cleavage.[1a] However, C(α)–CN bond cleavage in nitriles using transition-metal complexes has not been studied in detail (a few examples are given in the references), and usually the corresponding cyanide complexes and alkanes or alkenes were observed as products.[1] Furthermore, such a reaction was observed using a cobalt dinitrogen complex.[1f]

In this regard, the recent report by Lu et al. of the transformation of a nitrile into the corresponding alcohol and cyanide using a relative simple dinuclear copper(II) cryptate complex was quite interesting.[2] However, this result has been questioned by Nelson and co-workers, who could not reproduce the findings during their detailed investigations.[3] According to our own studies on related copper systems,[4] we believe that the reported formation of cyanide might occur, provided that the exact reaction conditions are met (although we disagree with the postulated reaction mechanism). Most recently, additional support for these findings was provided by Karlin and co-workers, who demonstrated that during oxidation with O_2, a dinuclear copper(I) complex with a phenol derivative of our previously reported ligand 1,3-bis[bis(2-pyridylmethyl)amino]benzene (1,3-tpbd)[5] caused hydroxylation of the nitrile substrate to cyanide and aldehyde.[6] Furthermore, heterolytic cleavage of the C–C bond of acetonitrile with simple monomeric copper(II) complexes has been described by Mascharak and co-workers.[7] We think that this C(α)–CN is a more general reaction that can occur with different transition-metal complexes, and we report herein such a reaction using a well-known cobalt complex.

The cobalt(II) complex of the dianion of bis[3-(salicylideneimino)propyl]methylamine (salmdptH_2), [Co(salmdpt)] (**1**), has been reported and is commercially available.[8] Reaction of **1** with dioxygen in benzene forms an end-on superoxo complex [Co(salmdpt)O_2] (**2**), which has been structurally characterized previously (1:1 cocrystallization with unreacted **1**).[9] Wanting to better understand the formation and reactivity of 1:1 dioxygen–metal adduct complexes,[10] we successfully repeated this oxidation reaction. Cini and Orioli claimed that the reaction can only occur in benzene,[9] but recent work with a silyl derivative of salmdptH_2 showed that such products can be obtained in nitrile solvents as well.[11] Therefore, we hoped that we might obtain a better yield of **2** using acetonitrile as solvent for the reaction with dioxygen. Reaction of **1** with air or dioxygen under reflux in acetonitrile for 10 min resulted in the unexpected formation of the cyanide Co^{III} complex [Co(salmdpt)CN] (**3**) in approximately 50 % yield. The molecular structure of **3** is shown in Figure 1. Crystallographic data of **3** are similar to other known Co–CN complexes described in the literature (only a few examples are given in the references).[12]

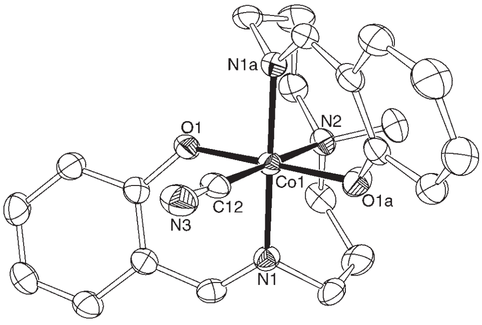
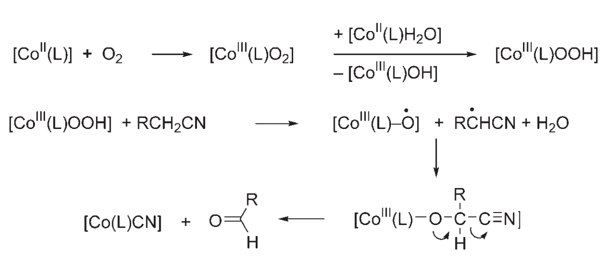


Figure 1. Molecular structure of [Co(salmdpt)CN] (**3**; thermal ellipsoids are set at 50 % probability; hydrogen atoms and acetonitrile solvent molecules present in the crystal lattice are not shown). Selected bond lengths [Å] and angles [°]: C12–N3 1.150(4), C12–Co1 1.890(3); N3-C12-Co1 180.0.

For this reaction, we propose the mechanism shown in Scheme 1, which is supported by several different findings. As discussed above, the existence of the end-on superoxo cobalt



Scheme 1. Postulated reaction mechanism (L = salmdpt).

---

[*] Dipl.-Chem. J. Müller, Dipl.-Chem. C. Würtele, Prof. Dr. S. Schindler
Institut für Anorganische und Analytische Chemie
Justus-Liebig-Universität Gießen
Heinrich-Buff-Ring 58, 35392 Gießen (Germany)
Fax: (+49) 641-993-41-49
E-mail: siegfried.schindler@chemie.uni-giessen.de

Dr. O. Walter
ITC-CPV
Forschungszentrum Karlsruhe GmbH
Postfach3640, 76021 Karlsruhe (Germany)

complex has been confirmed by X-ray crystallography.[9] Furthermore, a detailed kinetic study of the formation of **2** in acetone has been reported by Busch and co-workers.[13] So far, we do not have proof of the occurrence of a hydroperoxo complex [Co^{III}(salmdpt)OOH] (**4**) as an intermediate, but such compounds are known, and the first full characterization of such a species with a macrocyclic ligand has been reported by Guzei and Bakac.[14]

Furthermore, Karlin and co-workers observed a dinuclear copper hydroperoxo complex (characterized by UV/Vis and resonance Raman spectroscopy).[6] The presence of dioxygen and water is necessary, because under inert conditions **1** could be recrystallized from acetonitrile solutions. However, when a solution of **1** in toluene was heated in the presence of water and air, the cobalt hydroxo complex [Co^{III}(salmdpt)OH] (**5**; shown in Scheme 1) was formed, again in line with the proposed mechanism (unfortunately, we were not yet able to isolate **5** from the reaction in acetonitrile). The molecular structure of **5** is shown in Figure 2. A similar reaction pathway has been proposed for the oxidation of a related cobalt Schiff base complex in methanol.[15]

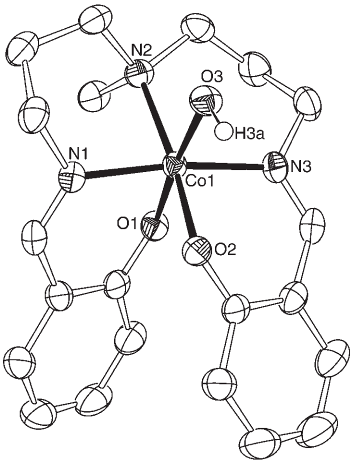


Figure 2. Molecular structure of [Co(salmdpt)OH] (**5**; thermal ellipsoids are set at 50% probability; hydrogen atoms except H of OH and water and methanol molecules present in the crystal lattice are not shown). Selected bond lengths [Å] and angles [°]: O1–Co1 1.901(2), O2–Co1 1.903(2), O3–Co1 1.897(2), N1–Co1 1.933(2), N2–Co1 1.965(2), N3–Co1 2.065(2); O3-Co1-O1 175.01(8).

To date we have support neither for the interaction between **4** and the nitrile molecule nor for the O–O cleavage and can only suggest the mechanism in Scheme 1 as a possible pathway. In general, the reaction could be performed in acetonitrile, propionitrile, and butyronitrile. While it was not possible to unambiguously detect formaldehyde or acetaldehyde under our reaction conditions, we could clearly detect **3**, and we observed the formation of propionaldehyde in ^{1}H NMR spectra and by GC–MS analysis if butyronitrile was used as a solvent. Karlin and co-workers detected benzaldehyde by GC–MS analysis in their experiments using a mixture of benzylcyanide and CH_2Cl_2.[6a]

In the future, complexes of the type discussed herein might be useful in organic synthesis if these reactions can be further optimized. Specifically, such a reaction could be performed in a solvent such as toluene (using an excess of the cobalt complex) with a nitrile compound as a substrate to obtain the corresponding aldehyde shortened by one carbon atom.

Experimental Section

H_2Salmdpt and **1** were prepared according to the literature.[8]

3: Complex **1** (1.0 g, 2.437 mmol) was heated at reflux in acetonitrile (approximately 25 mL) while O_2 was passed through the solution for 10 min. Subsequently, the solution was filtered while hot. The resulting brown solution was allowed to cool very slowly from 80 °C to room temperature in a Dewar flask filled with hot water. After two days, dark brown crystals suitable for structural characterization formed.

5: Similar to the preparation of **3**, complex **1** (1.0 g, 2.437 mmol) was heated at reflux in toluene (25 mol) for one hour after bubbling dioxygen through the hot solution for 10 min. A brown solution was obtained after the reaction mixture was filtered while hot. The filtrate was allowed to cool very slowly from 80 °C to room temperature in a Dewar flask filled with hot water. After two days, dark brown crystals suitable for structural characterization formed.

CCDC-642243 (**3**) and 642244 (**5**) 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.

Received: April 1, 2007

Keywords: cobalt · coordination chemistry · cyanides · oxygen · peroxo ligands

---

[1] a) "Activation of unreactive bonds and organic synthesis": *Top. Organomet. Chem.* **1999**, *3* (Ed.: S. Murai); b) J. J. Garcia, A. Arevalo, N. M. Brunkan, W. D. Jones, *Organometallics* **2004**, *23*, 3997; c) M. Tobisu, Y. Kita, N. Chatani, *J. Am. Chem. Soc.* **2006**, *128*, 8152; d) G. W. Parshall, *J. Am. Chem. Soc.* **1974**, *96*, 2360; e) Q. X. Liu, F. B. Xu, Q. S. Li, H. B. Song, Z. Z. Zhang, *Organometallics* **2004**, *23*, 610; f) F. Ozawa, K. Iri, A. Yamamoto, *Chem. Lett.* **1982**, 1707.

[2] T. Lu, X. Zhuang, Y. Li, S. Chen, *J. Am. Chem. Soc.* **2004**, *126*, 4760.

[3] a) A. D. Bond, S. Derossi, F. Jensen, F. B. Larsen, C. J. McKenzie, J. Nelson, *Inorg. Chem.* **2005**, *44*, 5987; b) A. D. Bond, S. Derossi, C. J. Harding, E. J. L. McInnes, V. McKee, C. J. McKenzie, J. Nelson, J. Wolowska, *Dalton Trans.* **2005**, 2403.

[4] M. Schatz, M. Becker, O. Walter, G. Liehr, S. Schindler, *Inorg. Chim. Acta* **2001**, *324*, 173.

[5] a) S. Schindler, D. J. Szalda, C. Creutz, *Inorg. Chem.* **1992**, *31*, 2255; b) S. Foxon, J.-Y. Xu, S. Turba, M. Leibold, F. Hampel, F. W. Heinemann, O. Walter, C. Würtele, M. Holthausen, S. Schindler, *Eur. J. Inorg. Chem.* **2007**, 429.

[6] a) L. Li, A. A. N. Sarjeant, M. A. Vance, L. N. Zakharov, A. L. Rheingold, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2005**, *127*, 15360; b) S. Thyagarajan, N. N. Murthy, A. A. N. Sarjeant, K. D. Karlin, S. E. Rokita, *J. Am. Chem. Soc.* **2006**, *128*, 7003; c) L. Li, N. N. Murthy, J. Telser, L. N. Zakharov, G. P. A. Yap, A. L. Rheingold, K. D. Karlin, S. E. Rokita, *Inorg. Chem.* **2006**, *45*, 7144; d) L. Li, A. A. Narducci Sarjeant, K. D. Karlin, *Inorg. Chem.* **2006**, *45*, 7160.

[7] D. S. Marlin, M. M. Olmstead, P. K. Mascharak, *Angew. Chem.* **2001**, *113*, 4888; *Angew. Chem. Int. Ed.* **2001**, *40*, 4752.

[8] a) R. H. Bailes, M. Calvin, *J. Am. Chem. Soc.* **1947**, *69*, 1886; b) L. Sacconi, I. Bertini, *J. Am. Chem. Soc.* **1966**, *88*, 5180.

[9] a) R. Cini, P. Orioli, *J. Chem. Soc. Chem. Commun.* **1981**, 196; b) R. Cini, P. Orioli, *J. Chem. Soc. Dalton Trans.* **1983**, 2563.

[10] a) M. Schatz, V. Raab, S. P. Foxon, G. Brehm, S. Schneider, M. Reiher, M. C. Holthausen, J. Sundermeyer, S. Schindler, *Angew. Chem.* **2004**, *116*, 4460; *Angew. Chem. Int. Ed.* **2004**, *43*, 4360; b) C. Würtele, E. Gaoutchenova, K. Harms, M. C. Holthausen, J. Sundermeyer, S. Schindler, *Angew. Chem.* **2006**, *118*, 3951; *Angew. Chem. Int. Ed.* **2006**, *45*, 3867.

[11] F. Carré, R. J. P. Corriu, E. Lancelle-Beltran, A. Mehdi, C. Reyé, R. Guillard, J. Sýkora, A. van der Lee, *Dalton Trans.* **2003**, 3211.

[12] a) O. Rotthaus, S. LeRoy, A. Tomas, K. M. Barkigia, I. Artaud, *Eur. J. Inorg. Chem.* **2004**, 1545; b) A. L. Reiff, E. M. Garcia-Frutos, J. M. Gil, O. P. Anderson, L. S. Hegedus, *Inorg. Chem.* **2005**, *44*, 9162; c) M. Zabel, A. L. Poznyak, V. I. Pawlowski, *J. Struct. Chem.* **2005**, *46*, 556.

[13] E. V. Rybak-Akimova, W. Otto, P. Deardorf, R. Roesner, D. H. Busch, *Inorg. Chem.* **1997**, *36*, 2746.

[14] I. A. Guzei, A. Bakac, *Inorg. Chem.* **2001**, *40*, 2390.

[15] A. Nishinaga, T. Kondo, T. Matsuura, *Chem. Lett.* **1985**, 905.