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Communications

Isolation of Bis(η^2-nitrato)(η^4-cyclobutadiene)cobalt(II) Complexes from the Oxidation of Sterically Hindered CpCo-Stabilized Cyclobutadiene Complexes

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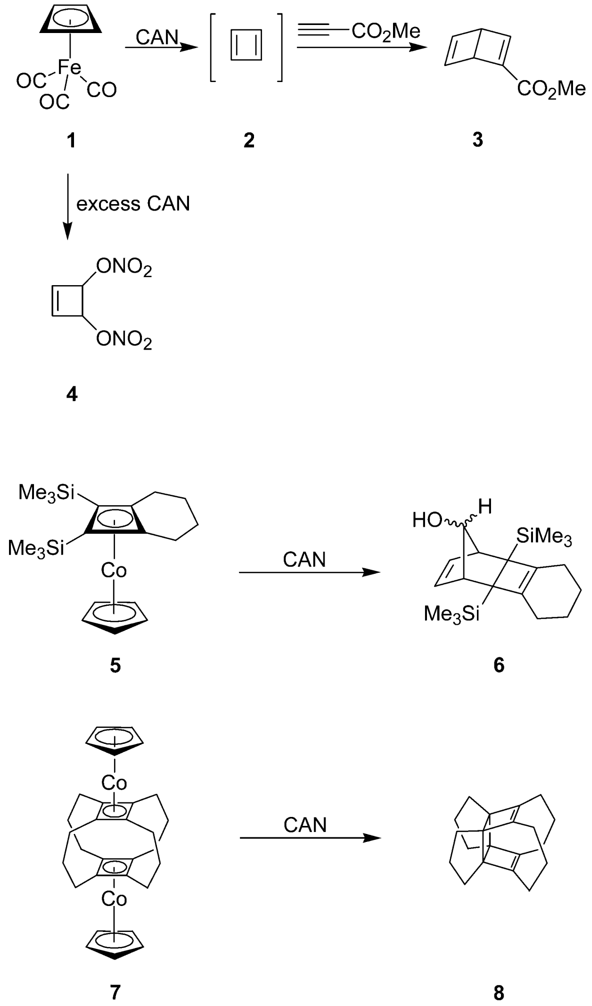
Summary: The oxidation of sterically hindered, CpCo-protected cyclobutadienes with ceric ammonium nitrate (CAN) yielded the paramagnetic Co(NO_3)$_2$-protected cyclobutadiene products. These half-sandwich complexes represent possible intermediates within the mechanism of the CAN decomplexation of CpCo−cyclobutadiene complexes.

The stabilization of cyclobutadiene and its derivatives by metal fragments[1] has been well-known ever since the discovery of the first metal-stabilized cyclobutadiene complexes.[2,3] The removal of metal fragments such as the Fe(CO)$_3$ and (η^5-cyclopentadienyl)cobalt (CpCo) units by mild oxidizing agents has been used in various protocols for the synthesis of hydrocarbons with cyclobutadienes as building blocks.[4,5] The most frequent method to remove the Fe(CO)$_3$ and CpCo units by oxidation is to use ceric ammonium nitrate, $(NH_4)_2[Ce(NO_3)_6]$ (CAN),[4−6] as shown for the cyclobutadiene complexes **1**, **5**, and **7** in Scheme 1.

For the Fe(CO)$_3$-stabilized cyclobutadiene **1**, a more detailed study of the CAN oxidation revealed that when CAN was added dropwise into a solution of **1** in the presence of a dienophile, the intermediate cyclobutadiene (**2**) can be trapped.[4] If, however, a surplus of CAN was used, the dinitrate **4** could be identified as the main product.[7] The formation of **4** in the presence of a dienophile suggested that the oxidation occurred when the cyclobutadiene was still complexed.

In this communication we present for the first time intermediates on the way to the complete removal of a CpCo unit by using CAN from sterically hindered CpCo-stabilized cyclobutadiene complexes.

Scheme 1



Recently we established a simple access to some sterically protected cyclic diynes such as **9a** and **9b**,[8] which could be converted into the CpCo-protected cyclobutadiene complexes **10a** and **10b** (Scheme 2) by refluxing **9** with CpCo(CO)$_2$ in decalin. Reacting **10** with CAN in acetonitrile afforded in high yields (90−95%) the corresponding dinitrato complexes **11a** and **11b**.

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[1] Reviews: (a) Efraty, A. *Chem. Rev.* **1977**, *77*, 691−744. (b) Seyferth, D. *Organometallics* **2003**, *22*, 2−20.

[2] Hübel, W.; Braye, E. H. *J. Inorg. Nucl. Chem.* **1959**, *10*, 250−268.

[3] Criegee, R.; Schröder, G. *Angew. Chem.* **1959**, *71*, 70−71.

[4] Watts, L.; Fitzpatrick, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3253−3254.

[5] Gesing, E. F.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1981**, *217*, 105−118.

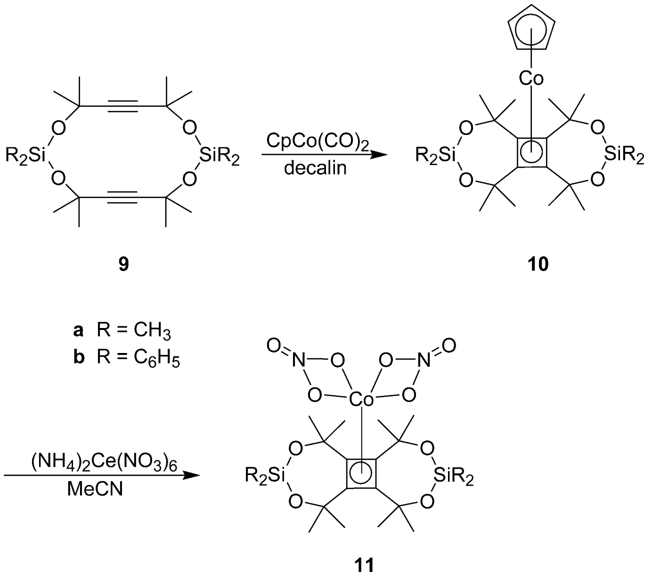
[6] Gleiter, R.; Karcher, M. *Angew. Chem.* **1998**, *100*, 851−852; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 840−841.

[7] Schmidt, E. K. G. *Chem. Ber.* **1975**, *108*, 1598−1608.

[8] Schaefer, C.; Gleiter, R.; Rominger, F. *Eur. J. Org. Chem.* **2003**, 3051−3059.

10.1021/om049907m CCC: $27.50

Scheme 2



This unprecedented result can be rationalized by assuming that the CAN oxidation yields first a Co(II) complex in which the Cp ligand is replaced by the nitrate anions. The resulting 19-valence-electron species **11a** and **11b** are stable at room temperature and in the presence of air in the solid state. We ascribe this stability to the fact that the metal is perfectly shielded by the ligands.

We were able to grow single crystals from **11a** and **11b** which allowed an X-ray study.[9] Both species adopt approximately C_2 symmetry in the solid state. This is due to a twisting of the N···N axis of the $Co(NO_3)_2$ fragment by about 45° toward the Si···Si axis (Figure 1). The seven-membered rings of the dioxasilacycloheptene units adopt a twist-boat-like conformation.

Both complexes exhibit a violet color (λ_{max} 546 nm). The powder ESR spectrum taken at room temperature reveals two g values ($g_{\|}$, $g_{\perp}$), indicating a symmetry axis for **11**. The hyperfine structure of the ESR spectrum is compatible with the assumption that the unpaired electron couples with the cobalt center ($I = {}^7/_2$) only. The g values ($g_{\perp} = 2.10$, $g_{\|} = 2.45$) and the magnetic moment determined for **11a** ($\mu_{eff} = 1.58 \pm 0.16\ \mu_B$) point to the fact that only the unpaired spin of the electron in the $3d_{x^2-y^2}$ orbital contributes to the magnetism. Heating of **11a** in toluene at 145 °C under pressure and under exclusion of oxygen yielded the tricyclic cyclopropene derivative **13a** (Scheme 3).

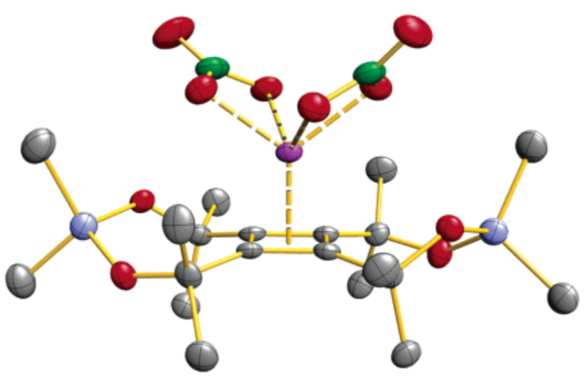
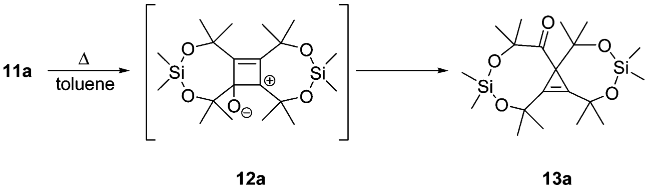
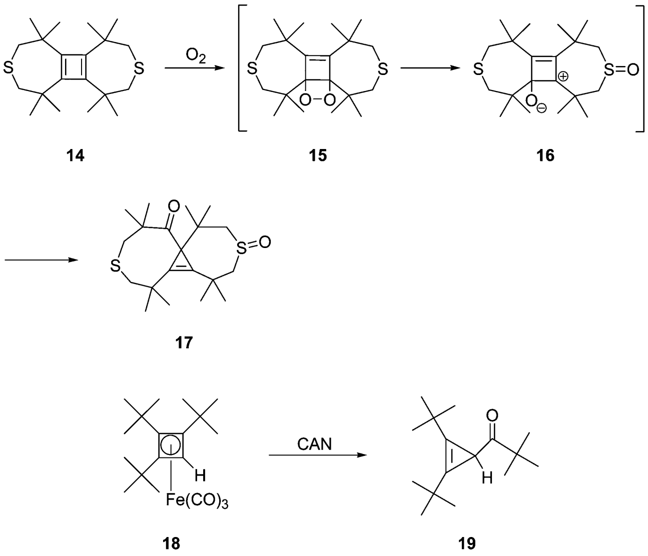


Figure 1. ORTEP representation as a MOLEK-9000 plot of complex **11a**. The CH_2Cl_2 molecule present in the unit cell is omitted for clarity. Color scheme: green, N; gray, C; red, O; light blue, Si; red-purple, Co.

Scheme 3



Scheme 4



To rationalize this product, we assume an oxidation of **11a** by the NO_3 ligands to the intermediate **12a**, which then rearranges to **13a**.[10] Similar products have been reported when **14** was oxidized with oxygen to yield **17**,[11] or when the cyclobutadiene−$Fe(CO)_3$ complex **18** was oxidized with CAN (Scheme 4).[12]

In conclusion, we found that the hitherto unknown $Co^{II}(NO_3)_2$ group is able to stabilize a cyclobutadiene moiety. In this paper we present for the first time a possible intermediate within the mechanism of the CAN

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(9) Crystal data for complex **11a**: $C_{20}H_{36}CoN_2O_{10}Si_2{\cdot}CH_2Cl_2$: $M_r = 664.54$, red crystal (lamina), dimensions 0.38 × 0.28 × 0.03 mm^3, monoclinic crystal system, space group $P2_1/c$, $Z = 4$, $a = 11.3438(2)$ Å, $b = 15.0766(4)$ Å, $c = 17.6375(4)$ Å, $\alpha = 90°$, $\beta = 94.560(1)°$, $\gamma = 90°$, $V = 3006.92(12)$ Å^3, $\rho = 1.468$ g/cm^3, $T = 200(2)$ K, $\theta_{max} = 21.99°$, Mo Kα radiation, $\lambda = 0.710\ 73$ Å, 0.3° ω scans with CCD area detector, covering a whole sphere in reciprocal space, 19 335 reflections measured, with 3668 unique ($R(\text{int}) = 0.0768$) and 2632 observed ($I > 2\sigma(I)$), intensities corrected for Lorentz and polarization effects, empirical absorption correction applied using SADABS[13] based on the Laue symmetry of the reciprocal space, $\mu = 0.88$ mm^{-1}, $T_{min} = 0.73$, $T_{max} = 0.97$, structure solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL-PLUS (5.10)[14] software package, 355 parameters refined, hydrogen atoms treated using appropriate riding models, goodness of fit 1.02 for observed reflections, final residual values $R1(F) = 0.044$, $wR(F^2) = 0.101$ for observed reflections, residual electron density −0.54 to 0.67 e Å^{-3}, CCDC file number 225445. The ORTEP view was created with MOLEK-9000.[15]

(10) Alternative intermediates for this reaction are derivatives of **4** that can be isolated in some CAN oxidations of (Cbd)Fe(CO)$_3$ derivatives.[7]

(11) Krebs, A.; Kemper, R.; Kimling, H. *Liebigs Ann. Chem.* **1979**, 473−483.

(12) Ciabattoni, J.; Feiring, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 5113−5115.

(13) Sheldrick, G. M. Bruker Analytical X-ray Division, Madison, WI, 2001.

decomplexation of CpCo−cyclobutadiene complexes. These dinitrato complexes can be generated by CAN oxidation of CpCo-stabilized, sterically hindered cyclobutadienes. The thermal decomposition of **11a** yielded the cyclopropene derivative **13a**. Its formation was explained by an oxidation/rearrangement mechanism.

Experimental Section. General Remarks. All melting points are uncorrected. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. UV light absorption data were recorded using a Hewlett-Packard 8452A spectrometer. IR spectra were recorded with a Bruker Vector 22 instrument. The NMR spectra were measured with a Bruker Avance 500 spectrometer (^{1}H NMR at 500 MHz; ^{13}C NMR at 125.77 MHz) using the solvent as internal standard (δ). FAB mass spectra refer to data from a JEOL JMS-700 instrument; ESI mass spectra were obtained on an ESI-Q-TOF Ultima API instrument. All reactions were carried out in dried glassware under an argon atmosphere using dried and oxygen-free solvents.

General Procedure for the Synthesis of the Bis(nitrato)cobalt Complexes. A solution of ceric ammonium nitrate in acetonitrile was cooled to −40 °C. The cyclobutadiene complex (dissolved or suspended in pentane) was added dropwise with stirring. The pentane layer slowly lost its yellow color, and the acetonitrile solution turned dark green immediately. The stirring was continued for 1 h, during which time the reaction mixture was warmed to room temperature. The acetonitrile solution turned deep red, and a yellow precipitate was formed. Then the solvents were removed in vacuo. The residue was treated with dichloromethane, and the solution was filtered over Celite. Removal of solvent from the obtained solution in vacuo yielded the bis(nitrato)cobalt complexes as purple solids.

11a. Reaction mixture: ceric ammonium nitrate (1.41 g, 2.57 mmol) in acetonitrile (20 mL), **9a** (334 mg, 0.642 mmol) dissolved in pentane (20 mL). Yield: 329 mg (89%) of a purple solid. Mp: 144 °C dec. UV−vis (CH_2Cl_2; λ_{max}/nm (log ϵ)): 248 (4.08), 306 (3.40), 368 (2.65), 440 (2.52), 546 (2.54). IR (KBr): 2984, 2936, 1628, 1544, 1384, 1297, 1190, 1117, 1083, 1020 cm^{-1}. HR-MS (ESI+): calcd for $C_{20}H_{36}CoNO_7Si_2$ ($M^+ - NO_3$) 517.1335, found 517.1362. Anal. Calcd for $C_{20}H_{36}CoN_2O_{10}Si_2 \cdot 0.25CH_3CN$: C, 41.74; H, 6.28; N, 5.34. Found: C, 41.50, H, 5.92; N, 5.67.

11b. Reaction mixture: ceric ammonium nitrate (237 mg, 0.432 mmol) in acetonitrile (4 mL), **9b** (83 mg, 0.108 mmol) dissolved in pentane (4 mL). Yield: 85 mg (95%) of a purple solid. Mp: 80 °C dec. UV−vis (CH_2Cl_2; λ_{max}/nm (log ϵ)): 252 (4.03), 272 (3.85), 300 (3.44), 366 (2.68), 546 (2.42). IR (KBr): 3070, 1640, 1525, 1462, 1429, 1384, 1280, 1182, 1119, 1063, 1025 cm^{-1}. HR-MS (ESI+): calcd for $C_{40}H_{44}CoNO_7Si_2$ ($M^+ - NO_3$) 765.1964, found 765.1988.

Synthesis of Cyclopropenyl Ketone 13a. Complex **11a** (295 mg, 0.509 mmol) was dissolved in degassed toluene (10 mL) in a pressurized Schlenk tube (50 mL capacity) fitted with a Teflon tap. The tube was evacuated and sealed. The reaction mixture was heated to 145 °C with stirring for 12 h. After it was cooled to room temperature, the solvent was removed in vacuo. Column chromatography (SiO_2, petroleum ether/diethyl ether 20:1) of the residue yielded the ketone **13a** as a colorless solid (48 mg, 23%). Mp: 82 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.13 (s, 3H, CH_3), 0.13 (s, 3H, CH_3), 0.15 (s. 6H, CH_3), 1.33 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.77 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 0.90 (CH_3), 1.64 (CH_3), 2.23 (CH_3), 2.49 (CH_3), 29.25 (CH_3), 29.30 (CH_3), 29.35 (CH_3), 30.11 (CH_3), 30.65 (CH_3), 30.68 (CH_3), 31.27 (CH_3), 31.40 (CH_3), 48.89 (C), 69.91 (C), 71.99 (C), 77.27 (C), 80.79 (C), 116.30 (C), 120.74 (C), 214.00 (CO). UV−vis (CH_2Cl_2; λ_{max}/nm (log ϵ)): 324 (2.19). IR (KBr): 2974, 2938, 1678, 1377, 1361, 1257, 1176, 1120, 1050, 1032, 1015 cm^{-1}. MS (FAB+): *m*/*z* 413 [$(M + H)^+$, 52%], 412 (M^+, 22%), 397 [$(M - CH_3)^+$, 34%], 356 (46%), 355 (100%). Anal. Calcd for $C_{20}H_{36}O_5Si_2$: C, 58.21; H, 8.79. Found: C, 57.95; H, 8.85.

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Supporting Information Available: Tables giving crystal data for **11a**; these data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049907M

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(14) Sheldrick, G. M. Bruker Analytical X-ray Division, Madison, WI, 1997.

(15) Bischof, P. MOLEK-9000, Universität Heidelberg, personal communication.