Protonation of CpCo(C_4Me_4): Ring-Opening with Formation of New σ,η^4-Butadienyl and η^5-Pentadienyl Cobalt Complexes

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Received March 3, 2003

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on April 11, 2003 on http://pubs.acs.org | doi: 10.1021/om030146h

Summary: Protonation of CpCoCb (Cb* = η^4-C_4Me_4) (**1**) produces the carbenoid complex [CpCo(σ,η^4-C_4HMe_4)]$^+$ (**2**$^+$). The structure of (**2**)BF_4 displays a σ,η^4-butadienyl-type ligand with Co−C(carbene) 1.792(6) Å and a terminal methyl group in anti position. DFT calculations on the protonation of the monomethyl complex CpCo(η^4-C_4H_3Me) show that protonation preferentially takes place from the endo side and is followed by a stereospecific ring-opening reaction to give the corresponding carbenoid complex [CpCo(σ,η^4-C_4H_4Me)]$^+$ with the same anti stereochemistry as found in **2**$^+$. Above −10 °C cation **2**$^+$ rearranges to produce the half-open cobaltocenium ion [CpCo(η^5-$C_5H_4Me_3$)] (**3**$^+$), which on addition of hydride from DIBALH gives CpCo(η^4-3,4-$Me_2C_6H_8$) (**4**).*

Addition of nucleophiles to electrophilic (cationic) cyclobutadiene complexes can lead either to η^3-cyclobutenyl complexes as in the nucleophilic addition to [CpNi(C_4R_4)]$^+$ (R = Me,[1a] Ph[1b]) or to ring-opening, afforting carbenoid σ,η^4(5e)-butadienyl complexes as in the case of hydride addition to [CpRu(NCMe)(η^4-C_4Ph_4)]$^+$.[2] It was shown that ruthenium complexes of this type behave as masked or latent, coordinatively unsaturated σ,η^2(3e)-butadienyl complexes.[2b,3] Analogous reaction paths can be envisaged for the reactions of nucleophilic (neutral) cyclobutadiene complexes with electrophiles. Here we describe the protonation of CpCoCb* (Cb* = η^4-C_4Me_4) (**1**)[4−6] and the formation of the novel cationic carbenoid complex **2**$^+$ and of the half-open cobaltocenium ion **3**$^+$ (Scheme 1).

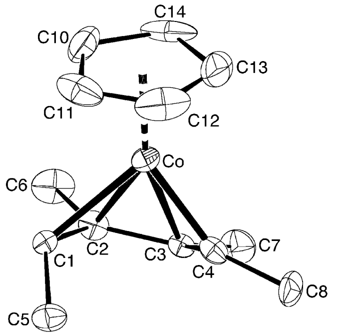

Figure 1. Platon plot[10] of the cation **2**$^+$ in (**2**)BF_4 (at the 30% probability level). Selected bond distances (in Å): Co−C1 2.076(5), Co−C2 2.006(5), Co−C3 2.079(6), Co−C4 1.792(6), Co−C(Cp) 2.030(7) av, C1−C2 1.405(8), C2−C3 1.415(8), C3−C4 1.390(7).

Treatment of a CD_2Cl_2 solution of **1** at −40 °C or up to ambient temperature with an excess of CF_3CO_2H or of HBF_4 in Et_2O results in an immediate color change from light yellow to dark red. The ^1H NMR spectrum of the reaction mixture shows the presence of a new species with four different methyl groups, three as singlets and the one at highest field as a doublet (δ = 0.55, J = 6.7 Hz), which is coupled to a single proton at rather low field (δ = 6.49, J = 6.7 Hz). A ^{13}C signal at 292.1 ppm indicates the presence of a carbenoid carbon atom. Hence the new cationic species **2**$^+$ is assigned a σ,η^4-butadienyl structure which may be viewed as a combination of coordinated η^3-allyl and carbene moieties.[7] The stereochemistry at C-4 with the hydrogen atom 4-H *syn* and the terminal methyl group (comprising C-5) *anti* follows from the chemical shifts observed.

Clean transformation from **1** to **2**$^+$ requires an at least 5-fold excess of acid. This observation suggests a primary protonation equilibrium **1** + $H^+ \rightleftharpoons$ (**1**H)$^+$. With

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(1) (a) Work by Criegee, R. et al., as reviewed in: Efraty, A. *Chem. Rev.* **1977**, *77*, 691. (b) Maitlis, P. M.; Efraty, A.; Games, M. L. *J. Am. Chem. Soc.* **1965**, *87*, 719.

(2) (a) Crocker, M.; Green, M.; Orpen, A. G.; Neumann, H.-P.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1351. (b) Crocker, M.; Green, M.; Nagle, K. R.; Orpen, A. G.; Neumann, H.-P.; Morton, C. E.; Schaverien, C. J. *Organometallics* **1990**, *9*, 1422.

(3) (a) Rüba, E.; Mereiter, K.; Schmid, R.; Kirchner, K.; Bustelo, E.; Puerta, M. C.; Valerga, P. *Organometallics* **2002**, *21*, 2912. (b) Brammer, L.; Crocker, M.; Dunne, B. J.; Green, M.; Morton, C. E.; Nagle, K. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1226.

(4) Complex **1** is prepared most efficiently from Cb*CoI$(CO)_2$[6] and TlCp in THF: Koelle, U. *Inorg. Chim. Acta* **1981**, *47*, 13. For an alternative that avoids the use of TlCp see ref 5.

(5) **1**: A solution of NaCp (888 mg, 10 mmol) in THF (20 mL) was added with stirring to [Cb*Co$(NCMe)_3$]PF_6 (4.38 g, 10 mmol).[6c] While stirring was continued for 1 h the starting complex dissolved completely and the color of the solution changed to yellow-orange. Removal of the volatiles, column chromatography on alumina (5% H_2O) with hexane as eluent, and crystallization from methanol at −80 °C afforded **1** (2.22 g, 95%) as a spectroscopically pure, brownish yellow, crystalline solid.

(6) (a) Cook, M. R.; Härter, P.; Pauson, P. L. Šraga, J. *J. Chem. Soc., Dalton Trans.* **1987**, 2757. (b) Bruce, R.; Maitlis, P. M. *Can. J. Chem.* **1967**, *45*, 2017. (c) Butovskii, M. V.; Englert, U.; Fil'chikov, A. A.; Herberich, G. E.; Koelle, U.; Kudinov, A. R. *Eur. J. Inorg. Chem.* **2002**, 2656.

(7) Data for (**2**)CF_3CO_2 (with assignment techniques): ^1H NMR (500 MHz, −20 °C, CD_2Cl_2): δ 0.55 [d, J = 6.7 Hz, Me(C-5)], 1.85 (s, 2-Me, HMBC), 2.51 (s, 3-Me, HMBC), 2.59 (s, 1-Me, HMBC), 5.39 (s, Cp), 6.49 (q, J = 6.7 Hz, 4-H_{syn}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 11.70 (2-Me, HMBC, HETCOR), 23.54 (3-Me, HMBC, HETCOR), 28.64 (C-5, HETCOR), 30.96 (1-Me, HMBC, HETCOR), 85.40 (C-4, HETCOR), 88.24 (Cp, HETCOR), 100.86 (C-2, HMBC), 119.45 (C-3, HMBC), 292.11 (C-1). The atom numbering is in accordance with the name (2*Z*,3*Z*)-1,2,3-trimethylpenta-1,3-dienyl of the open-chain ligand.

10.1021/om030146h CCC: $25.00 © 2003 American Chemical Society
Publication on Web 04/11/2003

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Published on April 11, 2003 on http://pubs.acs.org | doi: 10.1021/om030146h

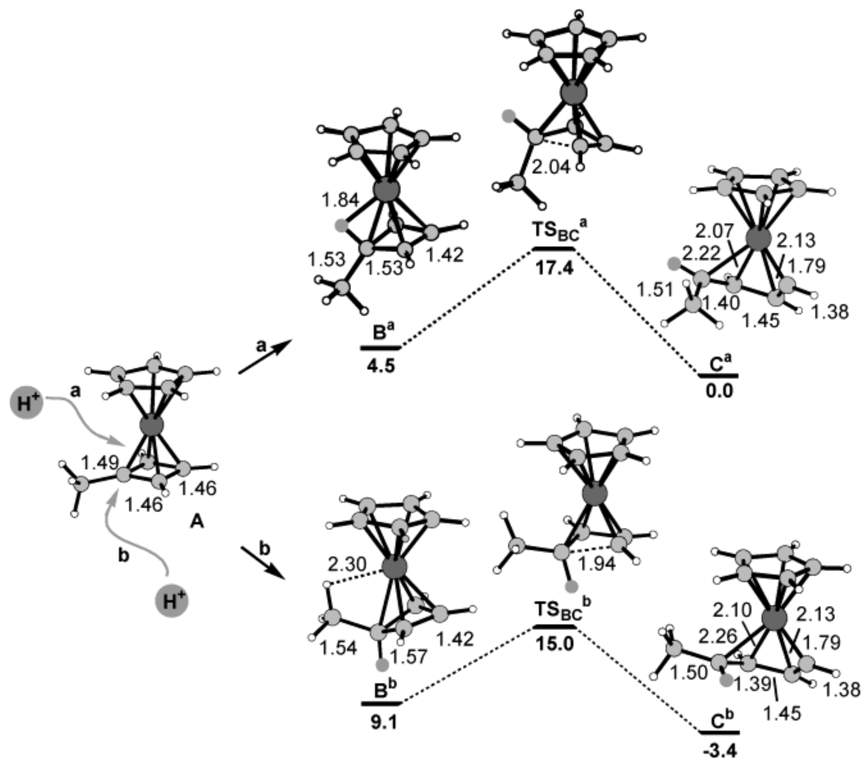
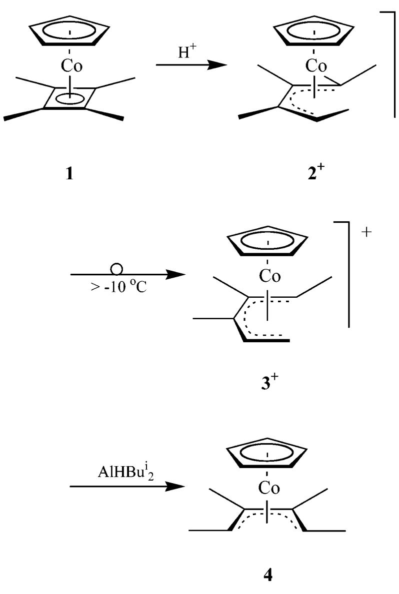


Figure 2. Optimized geometries (bond lengths are in Å) for **A**, **B^a**, **C^a**, **TS$_{BC}$^{a}**, **B^b**, **C^b**, and **TS$_{BC}$^{b}**, and relative energies (kcal/mol), calculated at the B3LYP (Co sdd; C, H, 6-31g**) level of theory.

Scheme 1



HBF$_4$ in Et$_2$O the salt (**2**)BF$_4$ could be obtained free of excess acid and in high yield.[8] The structure of **2**$^+$ [9] (Figure 1) exhibits a four-carbon chain bound to Co with three similar C−C distances. The chain subtends a dihedral angle of −22°, resulting in a particularly short interatomic distance between Co and the terminal atom C4 (1.792(6) Å); this interaction is assigned the carbenoid Co=C bond. The structure determination also confirmed the *anti* position of the methyl group at C-4 of the 1,3-butadienyl chain.

The protonation/ring-opening reaction sequence was further investigated by means of a DFT/B3LYP study, using the monomethyl compound CpCo(η^4-C$_4$H$_3$Me) (**A**) as model complex (Figure 2). Protonation from the *endo* side of the cyclobutadiene ligand (route **a**) produces a cyclobutenyl intermediate **B^a** with a stabilizing agostic C−H$_{endo}$··Co interaction. Ring-opening via the transition state **TS$_{BC}$^{a}** gives the σ,η^4-butadienyl complex **C^a** with the terminal methyl group in *anti* position. A transition state that would lead to the thermodynamically more stable isomer **C^b** with the methyl group in *syn* position could not be found. Protonation from the *exo* side of the cyclobutadiene ligand (route **b**, reaction sequence **A** → **B^b** → **C^b**) would proceed via the energetically less favorable intermediate **B^b**, which, in contrast to **B^a**, features only a weak agostic CH$_2$−H$_{endo}$··Co bond. In any case, protonation of **A** requires concomitant bending of the methyl group out of the cyclobutadiene plane.

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(8) (**2**)BF$_4$: An excess of HBF$_4$ (2.5 mL, 54%, $d = 1.18$ g/mol, 18 mmol) in Et$_2$O was added to **1** (465 mg, 2.00 mmol) in CH$_2$Cl$_2$ (15 mL) at −50 °C. The mixture was stirred for 10 min. Then the product was precipitated by addition of Et$_2$O and was purified by several reprecipitations from CH$_2$Cl$_2$/THF and finally from CH$_2$Cl$_2$/Et$_2$O to give (**2**)-BF$_4$ (620 mg, 97%) as a brown powder. The product can be stored at −30 °C and may be handled at ambient temperature for short times. Crystals of (**2**)BF$_4$ that were suitable for a structural study were obtained as black cubes by crystallization from a CH$_2$Cl$_2$/Et$_2$O mixture.

(9) (a) Crystal data for (**2**)BF$_4$: C$_{13}$H$_{18}$BCoF$_4$, black crystals, 0.40 × 0.35 × 0.05 mm, monoclinic, space group $P2_1/c$ (No. 14), $a = 7.4834(12)$ Å, $b = 13.920(3)$ Å, $c = 13.978(7)$ Å, $\beta = 102.98(3)°$, $V = 1418.9(8)$ Å^3, $Z = 4$, $d_{calc} = 1.498$ g cm^{-3}, $\mu = 1.236$ mm^{-1}, $F(000) = 656$. Data collection: Enraf-Nonius CAD4, Mo Kα radiation, graphite monochromator, $\omega-2\theta$ scans at 213 K in the range 2.1° < θ < 27.0°. 15 200 reflections measured, 3098 unique reflections, numerical absorption correction by Gaussian integration.[9b] The structure was solved by direct methods[9c] and refined on F^2:[9d] 176 parameters, $R = 0.0658$ for 1316 observed data with $I > 2\sigma(I)$, $R_w = 0.1186$ for all 3098 data, $w^{-1} = \sigma^2 F_o^2 + (0.03P)^2$, $P = (F_o^2 + 2F_c^2)/3$; non-hydrogen atoms were refined anisotropically, all hydrogen atoms were included as riding in idealized geometry. Further details of the crystal structure determinations are available on request from the Cambridge Crystallographic Data Centre, on quoting the depository number CCDC-204444. (b) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035. (c) Sheldrick, G. M. *SHELXS97*, Program for Crystal Structure Solution; University of Göttingen, 1997. (d) Sheldrick, G. M. *SHELXL97*, Program for Crystal Structure Refinement; University of Göttingen, 1997.

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Bending toward the *endo* side was calculated to require almost twice as much energy than bending away from the metal. In a highly acidic medium deprotonation of **B**$^{\mathbf{a}}$ is suppressed, and product formation takes place via $\mathbf{TS_{BC}}^{\mathbf{a}}$, although the transition state $\mathbf{TS_{BC}}^{\mathbf{b}}$ is lower in energy. Thus the experimentally observed formation of **2**$^+$ as contrathermodynamic stereoisomer and with 100% stereoselectivity can be understood as the consequence of three features: (i) the preferential protonation from the *endo* side, (ii) the high proton activity in the reaction mixture, and (iii) the stereocontrol of the ring-opening step.

Above −10 °C the cation **2**$^+$ slowly rearranges to the half-open cobaltocenium ion **3**$^+$.[11] Characteristic features in the ^{1}H NMR spectrum of **3**$^+$ are a methyl region similar to that of **2**$^+$ and an AMX pattern indicating the presence of a vinyl group $CH_2{=}CH$. Note the shift of the quartet due to the C*H*Me hydrogen atom from 6.49 ppm in **2**$^+$ to 1.43 ppm in **3**$^+$, indicating that this proton is now in an *anti* position.

Deuteration experiments generating **2**$^+$-d_1 from **1** and CF_3CO_2D show a singlet for what was the doublet of **2**$^+$ at 0.55 ppm and only residual intensity for the quartet at 6.49 ppm. The rearrangement product of **2**$^+$-d_1 is now **3**$^+$-d_1; this species lacks the H_X signal at 5.43 ppm and consequently possesses a deutero-vinyl group $CH_2{=}CD$. This experiment unequivocally substantiates the rearrangement mechanism for the conversion **2**$^+$ → **3**$^+$ (Scheme 1), i.e., C−H bond cleavage at the *anti* methyl group (comprising C-5) and transfer of the cleaved hydrogen to the carbenoid carbon atom which becomes C-5 in the product **3**$^+$.

For this rearrangement reaction first-order kinetics was found (^{1}H NMR, CD_2D_2) with $k_1 = 1.6 \times 10^{-4}\ s^{-1}$ at 22.5 °C, corresponding to $\Delta G^{\ddagger} = 94$ kJ/mol at this temperature. In neat CF_3CO_2D as solvent a similar value, $k_1 = 1.4 \times 10^{-4}\ s^{-1}$, was measured. The 1,5-hydrogen shift leading from **2**$^+$ to **3**$^+$ is in essence a C−H activation at a methyl group. The moderate free enthalpy of activation for this process indicates strong metal assistance for the cleavage of the C−H bond, which is then followed by transfer of the metal-bound hydrogen to the carbenic carbon atom. This rearrangement can be viewed in analogy with the known 1,2-shift of Fischer-type carbene complexes to yield olefin complexes.[12] In the present case, a 1,5-shift rather than a 1,2-shift brings about partial saturation of the carbenic carbon atom with concomitant extension of the olefinic carbon chain.

The half-open cobaltocenium complex (**3**)BF_4 reacts with DIBALH ($AlHBu^i_2$) to produce the symmetrical complex CpCo(η^4-3,4-dimethylhexa-2,4-diene) (**4**)[13,14] with both terminal methyl groups in *syn* position. We are presently investigating the reaction of the complex (**2**)BF_4 with bases. The sterically hindered base NEt_3 effects deprotonation at the carbenic methyl group to give a neutral complex CpCo(η^4-$CH_2CCMeCMeCHMe$) with a 1,2,4-pentatriene-type ligand, while pyridine effects *anti*/*syn* isomerization of the terminal methyl group and formation of a pyridinio derivative [CpCo{η^4-C(NC_5H_5)MeCMeCMeCHMe}]BF_4. These aspects will be described in a later full paper.

Acknowledgment. This work was generously supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

Supporting Information Available: X-ray crystallographic file for the structure determination of (**2**)BF_4 and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(11) (**3**)BF_4: A solution of HBF_4 in Et_2O (5.5 mL, 40 mmol) was added dropwise to a solution of complex **1** (919 mg, 3.96 mmol) in CH_2Cl_2 (40 mL) at −40 °C. The dark red reaction mixture was allowed slowly to warm to 0 °C; it was then kept at 0 °C for 1 day and at ambient temperature for 0.5 day. The then light red solution was concentrated to 10 mL, and the raw product was precipitated by addition of Et_2O. It was then dissolved in acetone and the solution was passed through a 5 cm layer of alumina. Crystallization from Et_2O/acetone gave (**3**)BF_4 (1.01 g, 80%) as brick red crystals; dec 155−165 °C. Anal. Calcd for $C_{13}H_{18}CoBF_4$: C, 48.79; H, 5.67. Found: C, 48.78; H, 5.65. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.43 (q, $J = 6.4$ Hz, 5-H_{anti}), 1.69 [d, $J = 6.4$ Hz, Me (C-6)], 2.17 (dd, $^3J_{1anti,\,2} = 12.1$ Hz, $^2J_{1syn,\,1anti} = 3.66$ Hz, 1-H_{anti}), 2.28 (s, 4-Me, HMBC), 2.51 (s, 3-Me, HMBC), 3.93 (dd, $^3J_{1syn,\,2} = 10.1$ Hz, $^2J_{1syn,1anti} = 3.66$ Hz, 1-H_{syn}), 5.35 (s, Cp), 5.43 (dd, $^3J_{1anti,2} = 12.1$ Hz, $^3J_{1syn,2} = 10.1$ Hz, 2-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 17.31 (4-Me, HMBC, HETCOR), 19.60 [Me(C-6), HETCOR], 22.38 (3-Me, HMBC, HETCOR), 58.53 (C-1, HETCOR), 81.47 (C-5, HETCOR), 88.63 (Cp, HETCOR), 93.40 (C-2, HETCOR), 109.53 (C-4, HMBC), 113.75 (C-3, HMBC). The atom numbering is in accordance with the name (2*Z*,3*Z*,4*E*)-3,4-dimethylhexa-2,4-dienyl for the open-chain ligand.

(12) For carbene to olefin conversions see: (a) Casey, C. P.; Miles, W. H.; Tukada, H. *J. Am. Chem. Soc.* **1985**, *107*, 2924. (b) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C13. (c) Fischer, E. O.; Held, W. *J. Organomet. Chem.* **1976**, *112*, C59.

(13) **4**: DIBALH ($AlHBu^i_2$, 1 M in toluene, 2.89 mL) was added with stirring to a slurry of (**3**)BF_4 (308 mg, 0.96 mmol) in hexane (10 mL). Stirring was continued until all solid material had dissolved (24 h). The product was chromatographed on alumina (5% H_2O, 15 cm column) using hexane as eluent. Removal of the volatiles and short way vacuum distillation gave **4** (0.11 g, 50%) as a red crystalline solid, mp 49 °C, bp 244 °C (dec). Anal. Calcd for $C_{13}H_{19}Co$: C, 66.66; H, 8.17. Found: C, 66.76; H, 7.90. ^{1}H NMR (500 MHz, CD_2Cl_2): δ −0.21 (q, $J = 6.35$ Hz, 2-/5-H_{anti}), 1.12 [d, $J = 6.35$ Hz, 2 Me_{syn} (C-1,6)], 2.06 (s, 3-/4-Me), 4.44 (s, Cp). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 14.80 (3-/4-Me, HETCOR), 19.10 (C-1,6, HETCOR), 45.75 (C-2,5, HETCOR), 81.83 (Cp, HETCOR), 88.98 (C-3,4, HETCOR).

(14) The use of $NaBH_4$ as hydride source produces a mixture of isomers and is also accompanied by reductive decomposition.