Demetalation of Tricarbonyl(cyclopentadienone)iron Complexes Initiated by a Ligand Exchange Reaction with NaOH—X-Ray Analysis of a Complex with Nearly Square-Planar Coordinated Sodium[**]

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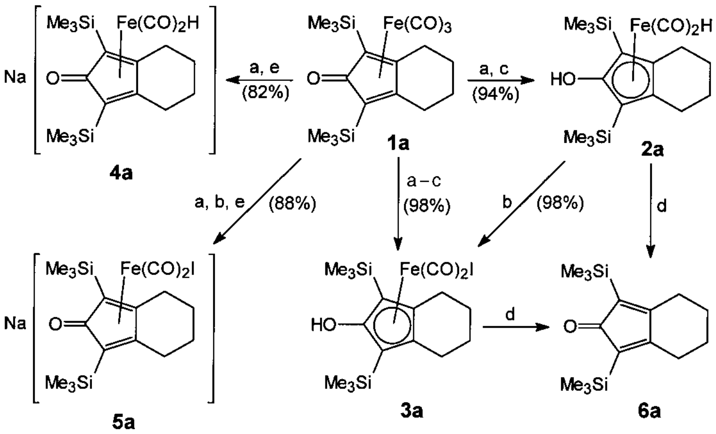
The [2+2+1] cycloaddition of two alkynes and carbon monoxide in the presence of pentacarbonyliron represents a useful method for the construction of five-membered ring systems.[1, 2] Applications of the resulting tricarbonyl(η^4-cyclopentadienone)iron complexes to organic synthesis are feasible by demetalation to the free cyclopentadienones. This transformation was achieved by oxidation with trimethylamine *N*-oxide.[1, 3] Recently we reported a novel method for the demetalation of tricarbonyl(diene)iron complexes by a photolytically induced exchange of the carbonyl ligands by acetonitrile.[4] Herein we describe an alternative procedure for the ligand exchange at tricarbonyl(η^4-cyclopentadienone)iron complexes and the subsequent demetalation in the air.

Tricarbonyl(η^4-cyclopentadienone)iron complexes undergo a transformation similar to the Hieber reaction.[5] Thus, reaction of complex **1a** with aqueous NaOH in THF leads to an equilibrium of the corresponding hydrido complexes **2a** and **4a** in a ratio of about 13:1 (Scheme 1). Tricarbonyl(cyclohexa-1,3-diene)iron complexes are inert under these conditions. Addition of H_3PO_4 affords **2a** in 94% yield, while reaction with NaH shifts the equilibrium towards the salt **4a** (82% yield). Reaction of the hydrido complex **2a** with 1-iodopentane provides the iodo complex **3a** in 98% yield. A related transformation is reported for the hydrido complex $[CpFe(CO)_2H]$.[6] The addition of 1-iodopentane after the reaction of **1a** with NaOH affords an equilibrium of the iodo complexes **3a** and **5a** that is shifted again by addition of H_3PO_4 or NaH, respectively. Preparation of the iodo complex **3a** without isolation of the intermediate hydrido complex **2a** increases the yield (98% based on complex **1a**).



Scheme 1. a) 1 M NaOH/THF (1/2); b) $C_5H_{11}I$; c) H_3PO_4; d) air, daylight, Et_2O/THF, $Na_2S_2O_3$, Celite, 3 h; e) NaH, Et_2O/THF.

The ^{13}C NMR and the IR data of the hydrido complex **2a** and the iodo complex **3a** suggest an η^5-coordinated hydroxycyclopentadienyl ligand for both compounds.[7] A characteristic structural feature of the hydrido complex **2a** is the unsymmetrical arrangement of the coligands, which is apparent from two CO signals in the ^{13}C NMR spectrum. This assignment was confirmed by an X-ray structure determination of complex **2a** (Figure 1),[8] which shows an η^5-coordinated hydroxycyclopentadienyl ligand and a C1–O1 bond length of 1.366 Å.[9] A loss of C_S symmetry was also found for the hydrido complex **4a** from the ^{13}C NMR spectrum, which exhibits the two signals for the carbonyl ligands and a peak at $\delta = 170.13$ for C1.[7]

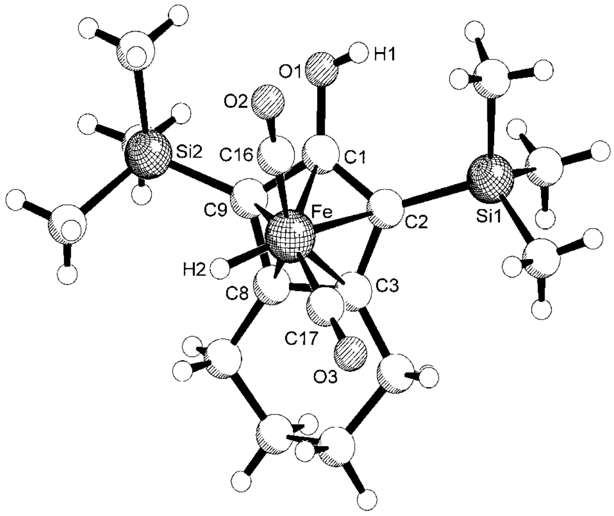


Figure 1. Molecular structure of **2a** in the crystal. Selected bond lengths [Å]: Fe–C1 2.1353(13), Fe–C2 2.1485(14), Fe–C3 2.0992(14), Fe–C8 2.0981(14), Fe–C9 2.1087(14), Fe–H2 1.38(2), Fe–C16 1.752(2), Fe–C17 1.741(2), C16–O2 1.143(2), C17–O3 1.153(2), C1–C2 1.437(2), C2–C3 1.452(2), C3–C8 1.430(2), C8–C9 1.445(2), C1–C9 1.445(2), C1–O1 1.366(2), O1–H1 0.75(2), C2–Si1 1.8876(14), C9–Si2 1.887(2).

The iodo complex **5a** was crystallized from pentane/THF (6/1). The X-ray analysis of **5a** shows a dimeric structure for the solid state (Figure 2a).[8] The oxygen atoms O1 and O1* are both coordinated to the sodium ions Na1 and Na1*. Each sodium ion is further coordinated with an iodine and one THF molecule. However, the sodium ions exhibit an extraordinary nearly square-planar arrangement of the ligands instead of the usual tetrahedral coordination. The bulky cyclopentadienone ligand with the trimethylsilyl (TMS) substituents and the $Fe(CO)_2I$ fragment forces the sodium ion into the unusual square-planar coordination geometry which is only slightly distorted. Each sodium ion and the three oxygen ligands are in one plane and the iodo ligand is only slightly out of this

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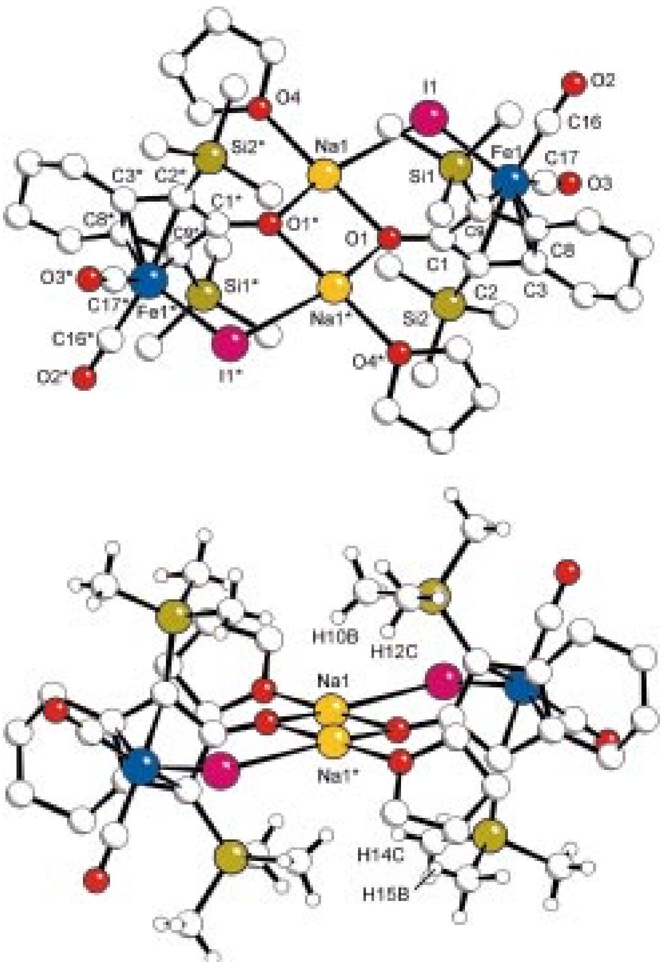


Figure 2. Dimeric structure of **5a** in the crystal. a) View perpendicular to the plane formed by the ligands coordinated at the sodium center; hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–C2 2.144(4), Fe1–C3 2.075(4), Fe1–C8 2.063(4), Fe1–C9 2.136(4), Fe1–I1 2.6409(8), Fe1–C16 1.766(6), Fe1–C17 1.763(5), C16–O2 1.151(6), C17–O3 1.148(6), C1–C2 1.468(6), C2–C3 1.453(6), C3–C8 1.419(6), C8–C9 1.442(6), C1–C9 1.466(6), C1–O1 1.268(5), Na1–O1 2.240(3), Na1–O1* 2.280(3), Na1–O4 2.298(4), Na1–I1 3.165(2); O1-Na1-O1* 83.13(12), O1-Na1-O4 179.02(14), O1*-Na1-O4 97.65(13), O1-Na1-I1 82.25(9), O1*-Na1-I1 162.86(10), O4-Na1-I1 96.88(10), Na1-O1-Na1* 96.87(12). b) Side view; only the hydrogen atoms of the TMS groups are shown. Selected atom distances [Å] and angles [°]: Na1–H10B 2.625, Na1*–H12C 3.014, Na1–H14C 3.249, Na1*–H15B 3.805; C10-H10B-Na1 118.32, C12-H12C-Na1* 148.62, C14-H14C-Na1 128.48, C15-H15B-Na1* 142.83.

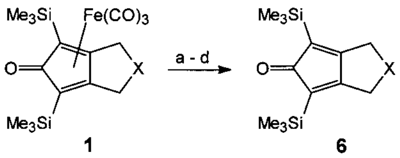
plane.[10] The corresponding bond angles O1-Na1-O4 and O1*-Na1-I1 are 179.02(14) and 162.86(10)°, respectively. Presumably, the shielding of the sodium ion by the TMS groups from both sides above and below the almost square-planar arranged ligands prevents the coordination of further ligands to the axial positions of the sodium ions, which would lead to octahedral coordination (Figure 2b). The cyclopentadienone ring consists of two planes, one is formed by the coordinated butadiene, and the second, defined by C2, C1, and C9, is bent away from the iron atom. The dihedral angle between these two planes is 13.9°, which is typical for cyclopentadienone-iron complexes (12–20°).[1a, 2a, 11] The IR spectrum of **5a** in KBr exhibits a carbonyl stretching frequency for the cyclopentadienone of 1492 cm^{-1}. The ^{13}C NMR spectrum of **5a** in CD_3OD shows a chemical shift of $\delta = 176.05$ for C1, which indicates a monomeric structure in solution.[7]

An X-ray crystal structure determination also confirmed that complex **4a** has a dimeric structure in the solid state. In this case a square-planar arrangement of the ligands at the sodium ions is realized by coordination of a carbonyl ligand. In solution complex **4a** is monomeric, as shown by the absence of the carbonyl bands in the IR spectrum at 1859, 1836, and 1819 cm^{-1}, which were present in the IR spectrum in KBr.[7]

We next investigated the demetalation behavior of the complexes **2a** and **3a**. The crystals of complex **2a** can be handled in air for a short period of time and can be stored in an inert gas atmosphere at −30 °C. Stirring a solution of **2a** in diethyl ether for 5 h in the air leads to demetalation and provides the free ligand **6a** in 80 % yield based on **1a** (Scheme 1). A related demetalation of a tricarbonyl(η^4-cyclopentadienone)iron complex with concomitant oxidation of the ligand was achieved on treatment of an aqueous alkaline solution with molecular oxygen.[11d] However, these conditions are too harsh in the present case since bases cause an isomerization and subsequent desilylation.[1b]

The iodo complex **3a** remains nearly unchanged after stirring a solution of **3a** in the air for 42 h in the dark. However, stirring a solution of **3a** in the air with exposure to daylight leads to a highly selective demetalation within 3 h and provides the free cyclopentadienone **6a** in 95 % yield based on complex **1a**. In the optimized procedure some Celite is added to remove iron particles and photochemically generated iodine is reduced with sodium thiosulfate (see experimental procedure). A photolytically induced exchange of the carbon monoxide ligands was found for the related complex $[CpFe(CO)_2I]$.[12] The removal of the carbon monoxide ligand in the air is irreversible and leads to demetalation.

The application of the novel one-pot demetalation procedure to a series of bicyclic tricarbonyl(η^4-cyclopentadienone)iron complexes **1**[1a,b] provided the corresponding free ligands **6a–d** in excellent yields (Scheme 2, Table 1). Thus, the results for demetalation of the complexes **1** obtained by our previous photolytically induced ligand exchange were improved once again.[4] Only the demetalation of complex **1e** to **6e** afforded a poor yield, which is a consequence of concomitant ester cleavage.



Scheme 2. a) 1 M NaOH/THF (1/2); b) $C_5H_{11}I$; c) H_3PO_4; d) air, daylight, Et_2O/THF, $Na_2S_2O_3$, Celite, 3 h.

Table 1. Demetalation of the tricarbonyl(η^4-cyclopentadienone)iron complexes **1** via the intermediate iodo complexes **3**.

1	X	Yield (**6**) [%]
a	$(CH_2)_2$	95
b	CH_2	93
c	O	89
d	S	87
e	$C(COOMe)_2$	12

In conclusion, we have developed a novel procedure for the demetalation of tricarbonyl(η^4-cyclopentadienone)iron complexes, which proceeds by a ligand exchange initiated by sodium hydroxide. The X-ray analysis of an intermediate dimeric complex revealed an extraordinary nearly square-planar coordinated sodium ion.

Experimental Section

General procedure for the demetalation of the bicyclic tricarbonyl(η^4-cyclopentadienone)iron complexes **1** by NaOH-initiated ligand exchange: A solution of complex **1** (0.478 mmol) in THF (8 mL) and aqueous 1M NaOH (4 mL) was stirred for 2.5 h under an argon atmosphere. Then 1-iodopentane was added (0.15 mL, 228 mg, 1.15 mmol) and the yellow solution turned brown. After stirring the mixture for an additional 15 min under argon, H_3PO_4 (0.15 mL) was added, the organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over Na_2SO_4 and filtered through a short path of silica gel. After addition of $Na_2S_2O_3$ (200 mg) and Celite (200 mg) the filtrate was stirred slowly in the air for 3 h in the presence of daylight. Filtration through a short path of Celite, evaporation of the solvent, and flash chromatography (pentane/diethyl ether) of the residue on silica gel provided the free ligand **6**.

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[1] a) H.-J. Knölker, J. Heber, C. H. Mahler, *Synlett* **1992**, 1002; b) H.-J. Knölker, J. Heber, *Synlett* **1993**, 924; c) H.-J. Knölker, E. Baum, J. Heber, *Tetrahedron Lett.* **1995**, *36*, 7647.

[2] a) A. J. Pearson, R. J. Shively, R. A. Dubbert, *Organometallics* **1992**, *11*, 4096; b) A. J. Pearson, R. J. Shively, *Organometallics* **1994**, *13*, 578; c) A. J. Pearson, X. Yao, *Synlett* **1997**, 1281.

[3] Y. Shvo, E. Hazum, *J. Chem. Soc. Chem. Commun.* **1974**, 336; H.-J. Knölker, *J. Prakt. Chem.* **1996**, *338*, 190.

[4] H.-J. Knölker, H. Goesmann, R. Klauss, *Angew. Chem.* **1999**, *111*, 727; *Angew. Chem. Int. Ed.* **1999**, *38*, 702.

[5] a) W. Hieber, F. Leutert, *Z. Anorg. Allg. Chem.* **1932**, *204*, 145; b) W. Reppe, H. Vetter, *Liebigs Ann. Chem.* **1953**, *582*, 133.

[6] R. J. Kazlauskas, M. S. Wrighton, *Organometallics* **1982**, *1*, 602.

[7] Spectroscopic data: **2a**: IR (KBr): $\tilde{\nu} = 3581, 1991, 1932\ \text{cm}^{-1}$; ^1H NMR (400 MHz, C_6D_6): $\delta = -11.62$ (s, 1H), 0.30 (s, 18H), 1.23 (m, 2H), 1.45 (m, 2H), 2.01 (m, 2H), 2.36 (m, 2H), 3.75 (s, 1H); ^{13}C NMR and DEPT (100 MHz, C_6D_6): $\delta = 1.48$ ($6\,CH_3$), 23.65 ($2\,CH_2$), 26.09 ($2\,CH_2$), 70.73 (2C), 103.61 (2C), 146.18 (C), 217.57 (CO), 217.64 (CO); elemental analysis calcd for $C_{17}H_{28}FeO_3Si_2$: C 52.03, H 7.19; found: C 51.97, H 7.21. **3a**: IR (KBr): $\tilde{\nu} = 3584, 2011, 1968\ \text{cm}^{-1}$; ^1H NMR (400 MHz, C_6D_6): $\delta = 0.35$ (s, 18H), 1.03 (m, 2H), 1.13 (m, 2H), 1.87 (m, 2H), 2.14 (m, 2H), 4.34 (s, 1H); ^{13}C NMR and DEPT (125 MHz, C_6D_6): $\delta = 1.34$ ($6\,CH_3$), 22.81 ($2\,CH_2$), 24.92 ($2\,CH_2$), 75.65 (2C), 102.15 (2C), 147.74 (C), 216.57 (2CO); elemental analysis calcd for $C_{17}H_{27}FeIO_3Si_2$: C 39.39, H 5.25; found: C 39.54, H 5.10. **4a**: IR (KBr): $\tilde{\nu} = 2000, 1967, 1943, 1859, 1836, 1819\ \text{cm}^{-1}$; IR ($CH_3OH$): $\tilde{\nu} = 1997, 1970, 1937, 1904\ \text{cm}^{-1}$; ^1H NMR (500 MHz, CD_3OD): $\delta = -13.05$ (s, 1H), 0.25 (s, 18H), 1.56 (m, 2H), 1.72 (m, 2H), 2.30 (m, 2H), 2.52 (m, 2H); ^{13}C NMR and DEPT (125 MHz, CD_3OD): $\delta = 1.56$ ($6\,CH_3$), 24.60 ($2\,CH_2$), 27.49 ($2\,CH_2$), 68.47 (2C), 102.53 (2C), 170.13 (C=O), 221.06 (CO), 221.18 (CO). **5a**: IR (KBr): $\tilde{\nu} = 1993, 1957, 1911, 1492\ \text{cm}^{-1}$; IR ($CH_3OH$): $\tilde{\nu} = 1992, 1937\ \text{cm}^{-1}$; ^{13}C NMR and DEPT (125 MHz, CD_3OD): $\delta = 1.11$ ($6\,CH_3$), 23.93 ($2\,CH_2$), 26.67 ($2\,CH_2$), 65.41 (2C), 106.29 (2C), 176.05 (C=O), 219.17 (2CO); elemental analysis calcd for $C_{21}H_{34}FeINaO_4Si_2$: C 41.19, H 5.60; found: C 41.14, H 5.52.

[8] X-ray crystal structure analyses: **2a**: yellow needles, $C_{17}H_{28}FeO_3Si_2$; $M_r = 392.42\ \text{g mol}^{-1}$, triclinic, space group $P\bar{1}$, $\lambda = 0.71073$ Å, $a = 6.7797(4)$, $b = 11.2561(8)$, $c = 13.9334(12)$ Å, $\alpha = 104.343(5)$, $\beta = 92.265(5)$, $\gamma = 97.624(4)^\circ$, $V = 1018.14(13)$ Å^3, $Z = 2$, $\mu = 0.868\ \text{mm}^{-1}$, $\rho_{\text{calcd}} = 1.280\ \text{g cm}^{-3}$, $T = 200(2)$ K, θ range: 2.70–27.50°; 4598 independent reflections; full-matrix least squares on F^2; $R_1 = 0.0272$, $wR_2 = 0.0710$ $[I > 2\sigma(I)]$; maximal residual electron density 0.620 e Å^{-3}. All hydrogen atoms were determined by Fourier difference calculation and refined isotropically. **5a**: brown cubes, $C_{17}H_{26}FeINaO_3Si_2 \cdot C_4H_8O$; $M_r = 612.40\ \text{g mol}^{-1}$, monoclinic, space group $P2_1/n$, $\lambda = 0.71073$ Å, $a = 11.254(2)$, $b = 15.508(3)$, $c = 15.254(3)$ Å, $\beta = 93.52(3)^\circ$, $V = 2657.2(9)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.531\ \text{g cm}^{-3}$, $\mu = 1.859\ \text{mm}^{-1}$, $T = 200(2)$ K, θ range: 1.87–25.50°; 4950 independent reflections; full-matrix least squares on F^2; $R_1 = 0.0390$, $wR_2 = 0.0712$ $[I > 2\sigma(I)]$; maximal residual electron density 0.565 e Å^{-3}. Programs: G. M. Sheldrick, SHELXS-86 (Göttingen, **1986**), SHELXL-93 (Göttingen, **1993**); E. Keller, SCHAKAL-97 (Freiburg im Breisgau, **1997**). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114303 (**5a**) and CCDC-114304 (**2a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] Compare: a) E. Weiss, W. Hübel, R. Merényi, *Chem. Ber.* **1962**, *95*, 1155; b) E. Weiss, R. Merényi, W. Hübel, *Chem. Ber.* **1962**, *95*, 1170.

[10] For distorted tetrahedral or square-pyramidal coordinations at sodium centers, see for example S. G. Bott, A. W. Coleman, J. L. Atwood, *J. Am. Chem. Soc.* **1986**, *108*, 1709; M. Veith, J. Böhnlein, V. Huch, *Chem. Ber.* **1989**, *122*, 841; M. Hong, F. Jiang, X. Huang, W. Su, W. Li, R. Cao, H. Liu, *Inorg. Chim. Acta* **1997**, *256*, 137; E. Gallo, E. Solari, N. Re, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *J. Am. Chem. Soc.* **1997**, *119*, 5144.

[11] a) N. A. Bailey, R. Mason, *Acta Crystallogr.* **1966**, *21*, 652; b) K. Hoffmann, E. Weiss, *J. Organomet. Chem.* **1977**, *128*, 237; c) G. G. Cash, R. C. Pettersen, *Inorg. Chem.* **1978**, *17*, 650; d) D. Fornals, M. A. Pericàs, F. Serratosa, J. Vinaixa, M. Font-Altaba, X. Solans, *J. Chem. Soc. Perkin Trans. 1* **1987**, 2749.

[12] D. G. Alway, K. W. Barnett, *Inorg. Chem.* **1978**, *17*, 2826; X. Pan, C. E. Philbin, M. P. Castellani, D. R. Tyler, *Inorg. Chem.* **1988**, *27*, 671.

A Molybdenum–Iron–Sulfur Cluster Containing Structural Elements Relevant to the P-Cluster of Nitrogenase[**]

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The commonly occurring iron–sulfur cluster cores—rhomboidal Fe_2S_2, cuboidal Fe_3S_4, and cubane-type Fe_4S_4—have been synthesized in research directed toward an understand-

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