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Journal of Organometallic Chemistry 624 (2001) 110–113

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Synthesis and structure analysis of tricarbonyl[tetrakis(1′-methylcyclopropyl)cyclobutadiene]iron(0)

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Received 18 September 2000; accepted 27 November 2000

Abstract

Heating of bis(1′-methylcyclopropyl)ethyne with $Fe_3(CO)_{12}$ yielded yellow crystals of tricarbonyl[tetrakis(1′-methylcyclopropyl)cyclobutadiene]iron (**7**), which were characterized by X-ray structure analysis. The complex **7** constitutes the bulkiest metal-complexed peralkylated cyclobutadiene ever obtained. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyclobutadienes; Iron complexes; Alkynes; Cycloaddition; X-ray structure

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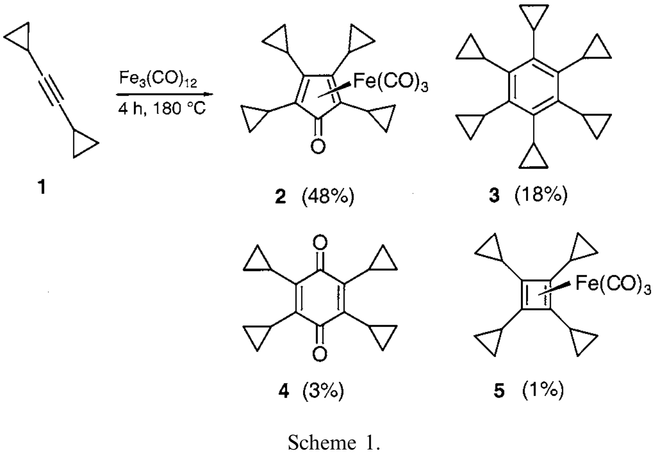
1. Introduction

The first cyclobutadienemetal complexes were reported more than forty years ago by Criegee et al. and six years later by Pettit et al. [1]. In the meantime, a variety of methods for the synthesis of an increasing number of such complexes has been established [2]. With sufficiently bulky substituents, the uncomplexed cyclobutadiene can be kinetically stabilized, as demonstrated by Maier et al. with the first preparation of the non-complexed tetra-*tert*-butylcyclobutadiene [3]. However, with increasing steric demand of the substituents, complexation of a cyclobutadiene becomes more difficult, thus no metal-complexed cyclobutadiene with four quaternary alkyl substituents has as yet been described. We now report the first formation and X-ray crystal structure analysis of tricarbonyl[tetrakis(1′-methylcyclopropyl)cyclobutadiene]iron(0) (**7**), the bulkiest metal-complexed persubstituted cyclobutadiene known so far.

2. Results and discussion

The reaction of dicyclopropylethyne (**1**) [4] with dodecacarbonyltriiron in a sealed tube at 180°C yielded a mixture of products from which, after flash column chromatography on silica gel, the previously described tricarbonyl(tetracyclopropylcyclopentadienone)iron (**2**) (48%) [5], hexacyclopropylbenzene (**3**) (18%) [5], tetracyclopropyl-*p*-benzoquinone (**4**) (3%) [6], and in addition the unknown tricarbonyl(tetracyclopropylcyclobutadiene)iron (**5**) (1%) were isolated (Scheme 1).

Under the same conditions, the reaction of bis(1′-methylcyclopropyl)ethyne (**6**) which was prepared by twofold methylation of dicyclopropylethyne, with $Fe_3(CO)_{12}$ yielded neither any of the peralkylated cyclopentadienone complex nor the corresponding benzene or benzoquinone derivatives. The sole low



Scheme 1.

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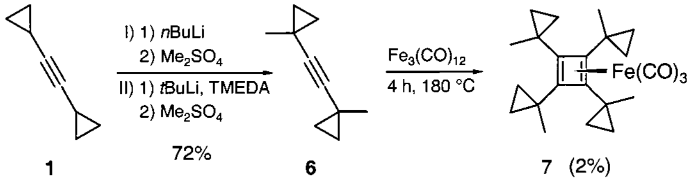
PII: S0022-328X(00)00917-7



Scheme 2.

molecular weight product isolated as a crystalline yellow material (1.7%), showed in its ^{1}H-NMR spectrum two multiplets at δ 0.45 and 0.97 (each 8 H) and one singlet at δ 1.18 (12 H). The ^{13}C-NMR spectrum displayed signals at δ 12.3 (C_{quat}), 16.5 (CH_2), 26.8 (CH_3), 93.6 (C_{quat}) and 216.3 (C_{quat}). The mass spectrum (EI, 70 eV) exhibited major peaks at *m*/*z* 408 (M^+, 100%), 380 ($M^+ - CO$, 19%), 352 ($M^+ - 2CO$, 39%), 324 ($M^+ - 3CO$, 61%), and 268 ($M^+ - Fe(CO)_3$, 98%). Both the NMR and the mass spectral data were consistent with the structure **7** of a tetrasubstituted tricarbonylcyclobutadieneiron complex. The IR spectrum showed prominent bands at 3004, 2961, 2928 (C–H) and 2023 and 1948 cm^{-1} (C=O) which are also in accord with **7** (Scheme 2). The structure was eventually confirmed by an X-ray analysis (Fig. 1).

The asymmetric unit cell contained two independent molecules which do not differ significantly. The central four-membered ring is planar (all four carbons are within 0.0054 Å of the plane) and, within the limits of errors, quadratic with an average bond length of 1.465(3) Å. In fact, the bond lengths in the central ring do differ slightly (Table 1) which agrees with theoretical results of Chinn and Hall who predicted that those bonds which are eclipsed with carbonyl groups should be longer [7]. The bond lengths in the cyclobutadiene ring of **7** are virtually the same as those reported for tricarbonyl-1,2,3,4-tetraphenylcyclobutadieneiron complex (average bond length 1.459 Å) [8].

The size of an unsubstituted cyclopropyl group is slightly larger than that of an ethyl group. Thus a 1-methylcyclopropyl substitutent is larger than an isopropyl but smaller than a *tert*-butyl group. The pairs of 1-methylcyclopropyl substituents opposing each other on the central ring take up the same conformation. Two are closer to a bisected (27.4 and 31.7°) and the other two are in a perpendicular orientation (89.6 and 89.5°) [9]. This must be due to crystal-packing forces, since in the ^{1}H- and ^{13}C-NMR spectra the chemical shifts of all methyl and all cyclopropylic methylene protons are equal. All four substituents are bent out of the plane of the cyclobutadiene ring away from the tricarbonyliron group. The two groups which are closer to a bisected orientation are bent by about 10° and the other two by about 15° out of the plane. This feature has also been observed in the crystal structure of tricarbonyl(tetraphenylcyclobutadiene)iron(0) [8].

3. Experimental

3.1. Reaction of dicyclopropylethyne (1) with $Fe_3(CO)_{12}$

In the literature [5,6] the compounds **2** and **4** were not fully characterized and the experimental sections

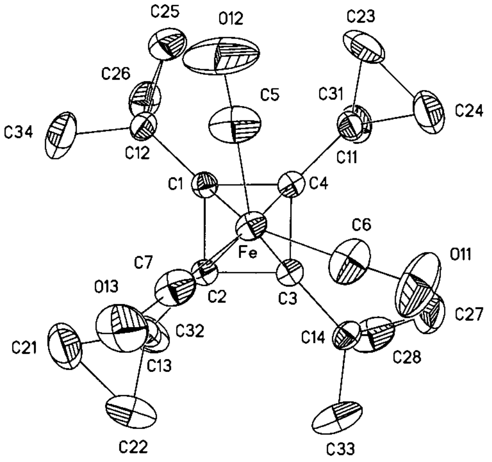


Fig. 1. Structure of tricarbonyl[tetrakis(1′-methylcyclopropyl)cyclobutadiene]iron (7) in the crystal.

Table 1
Selected bond distances (Å) and bond angles (°) for tricarbonyl[tetrakis(1′-methylcyclopropyl)cyclobutadiene]iron (7)

C1–C2	1.460(3)	C2–C3	1.450(3)
C3–C4	1.476(3)	C4–C1	1.473(3)
Fe–C1	2.062(2)	Fe–C2	2.079(3)
Fe–C3	2.076(2)	Fe–C4	2.044(2)
Fe–C5	1.778(3)	Fe–C6	1.784(3)
Fe–C7	1.778(3)	O13–C7	1.149(3)
O12–C5	1.148(4)	O11–C6	1.147(4)
C4–C11	1.482(4)	C1–C12	1.481(4)
C11–C24	1.497(4)	C11–C23	1.505(4)
C11–C31	1.513(4)	C24–C23	1.526(5)
C12–C25	1.495(4)	C12–C34	1.504(4)
C12–C26	1.512(4)	C26–C25	1.522(5)
Fe–centroid	1.787(3)		
C1–C4–C3	88.93(19)	C3–C2–C1	90.46(19)
C2–C1–C4	90.18(19)	C2–C3–C4	90.42(19)
C2–C1–C12	133.1(2)	C4–C1–C12	135.0(2)
C25–C12–C34	115.4(3)	C25–C12–C26	60.8(2)
C34–C12–C26	115.7(2)	C12–C26–C25	59.05(19)
C12–C25–C26	60.16(19)	C24–C11–C23	61.1(2)
C1–C4–C11	134.0(2)	C3–C4–C11	133.4(2)
C24–C11–C31	114.7(2)	C23–C11–C31	116.1(2)
C11–C24–C23	59.70(19)	C11–C23–C24	59.19(19)

are incomplete. A mixture of $Fe_3(CO)_{12}$ (300 mg, 0.596 mmol) and dicyclopropylethyne (**1**) (1.60 g, 15.1 mmol) was heated for 2 h at 180°C in a 10 ml sealed tube. After cooling to room temperature, $Fe_3(CO)_{12}$ (300 mg, 0.596 mmol) was added, and the mixture was heated for an additional 2 h. The mixture was taken up in dichloromethane and filtered through 10 g of Celite. After evaporation of the solvent in vacuo and chromatography on silica gel (column 3.0×40 cm, pentane–diethyl ether = 10:1 to 2:1), gave a mixture of **3** (288 mg, 18%, based on **1**) and **5** (18 mg, 1%, based on $1/3Fe_3(CO)_{12}$), which could be separated by sublimation under reduced pressure, **4** (62 mg, 3%, based on **1**) and **2** (656 mg, 48%, based on $1/3Fe_3(CO)_{12}$). The adding of the $Fe_3(CO)_{12}$ in two portions turned out to be necessary to prevent the glass tube from bursting.

Selected data for **2**. IR (KBr, cm^{-1}): $\nu = 3012$, 2049, 1979, 1635, 1437, 1027, 623, 592. ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 0.62$ (m, 10 H, *c*Pr), 0.81 (m, 2 H, *c*Pr), 1.03 (m, 2 H, *c*Pr), 1.36 (m, 2 H, *c*Pr), 1.59 (m, 2 H, *c*Pr), 1.92 (m, 2 H, *c*Pr). ^{13}C-NMR (62.9 MHz, C_6D_6, DEPT): $\delta = 6.81$ (CH_2, *c*Pr), 7.17 (CH_2, *c*Pr), 7.60 (CH_2, *c*Pr), 8.08 (CH, *c*Pr), 8.58 (CH_2, *c*Pr), 9.40 (CH, *c*Pr), 85.68 [C_{quat}, C-2(5)], 104.09 [C_{quat}, C-3(4)], 170.81 (C_{quat}, C-1), 210.27 [C_{quat}, CO]. MS (EI, 70 eV): m/z (I_{rel}): 380 (16, M^+), 352 (52, $M^+ - CO$), 324 (19, $M^+ - 2CO$), 296 (64, $M^+ - 3CO$), 240 [100, $M^+ - Fe(CO)_3$], 56 (12, Fe^+). Anal. Calc. for $C_{20}H_{20}FeO_4$ (380.2): C 63.18, H 5.30. Found: C 63.42, H 5.32%. Calc. 380.0710 (correct HRMS).

Selected data for **4**. IR (KBr, cm^{-1}): $\nu = 3084$, 3007, 1646, 1576, 1382, 1253, 1059, 928, 667. ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 0.77$ (m, 8 H, *c*Pr), 1.00 (m, 8 H, *c*Pr), 1.58 (m, 4 H, *c*Pr). ^{13}C-NMR (62.9 MHz, C_6D_6, DEPT): $\delta = 8.79$ (CH_2, *c*Pr), 11.15 (CH, *c*Pr), 145.60 [C_{quat}, C-2(3,5,6)], 187.39 [C_{quat}, C-1(4)]. MS (EI, 70 eV): m/z (I_{rel}): 268 (35, M^+), 213 (48), 206 (65), 138 (100). Anal. Calc. for $C_{18}H_{20}O_2$ (268.4): C 80.56, H 7.51. Found: C 80.50, H 7.51%. Calc. 268.1463 (correct HRMS).

Selected data for **5**. IR (KBr, cm^{-1}): $\nu = 3004$, 2022, 1948, 1425, 1025, 922, 629, 597, 570. ^{1}H-NMR (250 MHz, $CDCl_3$): $\delta = 0.53$ (m, 16 H, *c*Pr), 0.97 (m, 4 H, *c*Pr). ^{13}C-NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 7.00$ (CH, *c*Pr), 7.94 (CH_2, *c*Pr), 87.65 [C_{quat}, C-1(2,3,4)], 215.96 [C_{quat}, CO]. MS (EI, 70 eV): m/z (I_{rel}): 352 (40, M^+), 324 (46, $M^+ - CO$), 296 (4, $M^+ - 2CO$), 268 (46, $M^+ - 3CO$), 212 (100, $M^+ - Fe(CO)_3$], 56 (24, Fe^+). $C_{19}H_{20}FeO_3$ (352.2): Calc. 352.0761 (correct HRMS).

3.2. Preparation of **6**

To a stirred solution of **1** [4] (5.00 g, 47.1 mmol) in Et_2O (100 ml) was added dropwise at 0°C *n*BuLi in hexane (42.4 ml, 2.36 M, 100 mmol), and the mixture was stirred for 16 h at ambient temperature. After cooling to 0°C, the solution was treated with Me_2SO_4 (15.1 g, 120 mmol) and was stirred for an additional 1 h at room temperature. To the mixture was added an ammonia solution (30% in water, 100 ml), and the aqueous phase was extracted with Et_2O (3×50 ml). The combined organic layers were washed with 2 M HCl (20 ml), $NaHCO_3$ solution (5%, 20 ml) and water (20 ml), and were dried over $MgSO_4$. Trap-to-trap distillation (53–55°C/16 mbar) yielded the monoalkylated alkyne (4.85 g, 86%) as a colorless liquid. This alkyne (4.36 g, 36.3 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (6.32 g, 54.4 mmol) were dissolved in 100 ml of dry hexane, and the solution was treated dropwise with *t*BuLi in pentane (37.0 ml, 1.47 M, 54.4 mmol). After the solution had been stirred for an additional 2 h at ambient temperature, Me_2SO_4 (8.83 g, 70.0 mmol) was added. After complete conversion (1 h, room temperature) the solution was washed with an ammonia solution (30% in water, 100 ml). The layers were separated, the aqueous layer was extracted with Et_2O (3×50 ml), and the combined organic layers were washed with 2 M HCl (50 ml), $NaHCO_3$ solution (5%, 20 ml) and water (3×20 ml) and dried over $MgSO_4$. Distillation (45°C/8 mbar) yielded **6** (4.11 g, 84%, 72% from **1** overall) as a colorless liquid. IR (neat, cm^{-1}): $\nu = 3086$, 3007, 2964, 2933, 2904, 2870, 1464, 1424, 1379, 1357, 1090, 1019, 992, 717. ^{1}H-NMR ($CDCl_3$): $\delta = 0.49$ (AA′ part of an AA′BB′ system, $^3J = 6.3$, $^3J = 3.9$ Hz, 4 H, CH_2), 0.78 (BB′ part of an AA′BB′ system, $^3J = 6.3$, $^3J = 3.9$ Hz, 4 H, CH_2), 1.21 (s, 6 H, CH_3). ^{13}C-NMR ($CDCl_3$, DEPT): $\delta = 6.58$ (C_{quat}, *c*Pr), 16.22 (CH_2, *c*Pr), 24.72 (CH_3), 81.45 (C_{quat}, C≡C). MS (EI, 70 eV): m/z (I_{rel}): 134 (61, M^+), 119 (59) ($M^+ - CH_3$), 91 (100, $M^+ - CH_3 - C_2H_4$). Anal. Calc. for $C_{10}H_{14}$ (134.2): C 89.49, H 10.51. Found: C 89.49, H 10.63%.

3.3. Reaction of **6** with $Fe_3(CO)_{12}$

A mixture of $Fe_3(CO)_{12}$ (300 mg, 0.596 mmol) and **6** (1.70 g, 12.7 mmol) was heated for 2 h at 180°C in a 10 ml sealed tube. After cooling down, $Fe_3(CO)_{12}$ (300 mg, 0.596 mmol) was added and the mixture was heated for an additional 2 h. The mixture was dissolved in dichloromethane (100 ml), the solution was filtered through 10 g of Celite. After evaporation of the solvent, the residue was subjected to chromatography on silica gel (column 3.0×40 cm, pentane–diethyl ether = 10:1 to 2:1) to yield **7** (25 mg, 2%, based on $1/3Fe_3(CO)_{12}$) as yellow crystals. IR (KBr, cm^{-1}): $\nu = 3004$, 2961, 2928, 2023, 1948, 1667, 1455, 1380, 1021, 638, 602. ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 0.45$ (m, 8 H, *c*Pr), 0.97 (m, 8 H, *c*Pr), 1.18 (s, 12 H, CH_3). ^{13}C-NMR (62.9 MHz, C_6D_6, DEPT): $\delta = 12.25$ (C_{quat}, *c*Pr), 16.49 (CH_2, *c*Pr), 26.82 (CH_3), 93.59 [C_{quat}, C-1(2,3,4)], 216.29 [C_{quat}, $Fe(CO)_3$].

MS (EI, 70 eV): m/z (I_{rel}): 408 (100, M^+), 380 (19, $M^+ - CO$), 352 (39, $M^+ - 2CO$), 324 (61, $M^+ - 3CO$), 268 [98, $M^+ - Fe(CO)_3$], 250 (35), 240 (54), 211 (34), 197 (33), 183 (50), 165 (51), 153 (32), 141 (36), 128 (36), 115 (31), 91 (30), 56 (56, Fe^+). $C_{23}H_{28}FeO_3$ (408.3): Calc. 408.1387 (correct HRMS).

3.4. *X-ray structure analysis of complex* **7**

A suitable specimen of **7** was grown from dichloromethane by slow evaporation of the solvent. One of the yellow crystals (crystal size $0.50 \times 0.40 \times 0.30$ mm^3) was mounted on a Stoe-Siemens-Huber diffractometer, and the data were collected at 133 K, using Mo–K_α radiation (graphite monochromator). Crystal data and structure solution of **7**: $2 \times C_{23}H_{28}FeO_3$, $M_r = 408.30$, monoclinic, $P2_1/c$, $a = 929.80(19)$, $b = 1825.3(4)$, $c = 2503.0(5)$ pm, $\alpha = 90$, $\beta = 99.78(3)$, $\gamma = 90°$, $\lambda(\text{Mo–K}_\alpha) = 71.073$ pm, $V = 4186.3(15)$ nm^3, $Z = 4$, $d_{calc} = 1.296$ g cm^{-3}, $F(000) = 1728$, $\mu = 0.739$ mm^{-1}, ω–2θ scans ($1.99 < \theta < 23.26$). Out of 45117 collected reflections, 6010 were independent ($R_{int} = 0.0271$). The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-square calculations using all measured F^2 data. All non-hydrogen atoms were refined anisotropically. The refinement with 6010 reflections and 495 parameters converged to the final values $R_1 = 0.0382$ for $I > 2\sigma(I)$ and $R_1 = 0.0407$ for all data, $wR_2 = 0.0879$ for $I > 2\sigma(I)$ and $wR_2 = 0.0894$ for all data. The maximum and minimum residual electron densities were 708 and -292 e nm^{-3}. The molecular structure is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1.

4. Supplementary material

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, CCDC no. 149148. Copies and information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cm.ac.uk).

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie. The authors are grateful to Dr B. Knieriem for his careful proofreading of the manuscript.

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[9] The interplanar (dihedral) angles in each case were calculated for the following four points: [center of the cyclobutadiene ring]–[cyclobutadienylic carbon]–[quaternary cyclopropylic carbon]–[calculated middle of the cyclopropylic CH_2–CH_2 bond].