Synthesis and Structure of Mono(cyclopentadienyl)- and Bis(cyclopentadienyl)-Substituted Ferrocenes

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Received September 19, 1991

The reactions of the cyclopentenones 3,4-dimethylcyclopentenone, 1-indanone, and 2-indanone with mono- and dilithioferrocene lead to the synthesis of cyclopentadienyl-substituted ferrocenes: (3,4-dimethylcyclopenta-1,3-dienyl)ferrocene (**1**), (1-indenyl)ferrocene (**3**), (2-indenyl)ferrocene (**4**), and 1,1′-bis(3,4-dimethylcyclopenta-1,3-dienyl)ferrocene (**2**). The crystal structure of compound **2** was determined. The crystal data are as follows: $C_{24}H_{26}Fe$, triclinic, $P\bar{1}$, $a = 7.561$ (2) Å, $b = 10.738$ (2) Å, $c = 13.005$ (3) Å = 102.05 (3)°, $\beta = 104.29$ (3)°, $\gamma - 108.84$ (3)°, $V = 919.1$ (4) Å^3, $Z = 2$, $R = 0.0279$, and $R_w = 0.0398$ on the basis of 2336 reflections with $F \geq 4\sigma(F)$. It displays an unusual cofacial arrangement of the two 3,4-dimethylcyclopenta-1,3-dienyl rings. The lithium salt of **1** reacts with $FeCl_2$ to give the triferrocenyl bis(1-ferrocenyl-3,4-dimethylcyclopentadienyl)ferrocene (**5**). The reaction of the dilithium salt of **2** with $FeCl_2$ yields a mixture of polymeric ferrocenes.

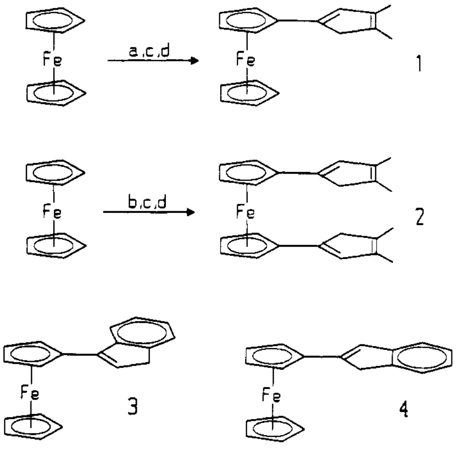
Introduction

Homo- and heteronuclear metal complexes, with the metals held in close proximity by bridging ligands, offer the chance to observe cooperative effects of the different metal centers.[1] This renders it possible to model multimetal catalysts[2] and to study the factors governing the mechanism of electron-transfer processes.[3] Metallocene complexes usually are of high thermal stability, and the strong bonding of the ligand backbone to most d- and f-block elements explains why the synthesis of linked cyclopentadienyls is receiving increased interest.[4] The simplest such system, fulvalenediyl, is part of the binuclear mixed-valence biferrocenium cations, whose intramolecular electron-transfer reactions have been the subject of numerous studies.[5] Other homo- and heteronuclear metal complexes with the fulvalene ligand have been described.[6] Here a synthetic route leading to mono(cyclopentadienyl)- and bis(cyclopentadienyl)-substituted ferrocenes, which contain up to four cyclopentadienyl units, will be reported.

Results and Discussion

Lithium and magnesium organyls react with cyclopentenones to give alcoholates, which, after hydrolysis and elimination of water, yield substituted cyclopentadienes.[7] It was interesting to find out if this type of reaction could also be applied to lithiated ferrocene. For this purpose the reaction of lithioferrocene with the easily available 3,4-dimethylcyclopentenone was investigated. Quenching of the alcoholate with aqueous NH_4Cl and elimination of water with *p*-toluenesulfonic acid yields the desired product (3,4-dimethylcyclopenta-1,3-dienyl)ferrocene (**1**) in 47% yield. The only other known compound of this type is the sodium salt of cyclopentadienylferrocene.[8] In its protonated, neutral form this compound is not stable; it dimerizes rapidly even at 0 °C.[8] The substitution of two hydrogen atoms by methyl groups, however, leads to a drastic increase in the stability of compound **1**; thus, it can be handled at room temperature for limited periods (several hours) but is best stored at −30 °C.

Scheme I[a]



[a] Legend: (a) *t*-BuLi; (b) 2 *n*-BuLi/tmeda; (c) 3,4-dimethylcyclopentenone; (d) aqueous NH_4Cl, *p*-TosOH.

An analogous reaction between dilithioferrocene and 2 equiv of 3,4-dimethylcyclopentenone affords 1,1′-bis(3,4-dimethylcyclopenta-1,3-dienyl)ferrocene (**2**) in 25% yield. The red compound is more stable than **1** and melts with decomposition at 150 °C.[9]

In addition to the expected product, an almost equal amount of **1** (23%) is produced. The formation of the

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[9] Moulton, R. D.; Bard, A. J. *Organometallics* **1988**, *7*, 351. This paper describes the attempted synthesis of 1,1′-dicyclopentadienylferrocene, but no stable product was isolated.

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Table I. Crystallographic Data for Compound 2

formula: $C_{24}H_{26}Fe$ (M_r 370.3)
space group: $P\bar{1}$
$Z = 2$
cell constants: $a = 7.561$ (2), $b = 10.738$ (2) Å, $c = 13.005$ (3) Å, $\alpha = 102.05$ (3)°, $\beta = 104.29$ (3)°, $\gamma = 108.84$ (3)°
volume: 919.2 (4) $Å^3$
$F(000) = 392$
cryst dimens: 0.5 × 0.3 × 0.2 mm^3
d(calcd): 1.338 g/cm^3
$T = 293$ K
abs coeff: 8.21 cm^{-1}
diffractometer: Enraf-Nonius CAD4
scan type: ω–2ϑ
2ϑ range: 7–45°
radiation: Mo Kα ($\lambda = 0.71073$ Å)
index range: $h \pm 8$, $k \pm 11$, $l \pm 14$
$T_{min/max}$: 0.91–0.84
no. of rflns collected, indep, obsd: 5108, 2554 ($R_{int} = 0.0085$), 2336 ($4\sigma F$)
no. of params: 226
data/param: 10.3/1
$R = 0.0279$, $R_w = 0.0398$, GOF = 1.99
largest and mean Δ/σ: 0.004, 0.001
min and max residual electron density: −0.23, +0.25 e $Å^{-3}$

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (10^{-1} pm^2)

	x	y	z	U(eq)[a]
Fe	3028 (1)	2939 (1)	2793 (1)	29 (1)
C(1)	3885 (3)	1450 (2)	3322 (2)	33 (1)
C(2)	4795 (3)	1889 (3)	2544 (2)	36 (1)
C(3)	5944 (3)	3337 (3)	2993 (2)	42 (1)
C(4)	5731 (3)	3819 (3)	4041 (2)	40 (1)
C(5)	4460 (3)	2670 (2)	4239 (2)	36 (1)
C(6)	−44 (3)	2150 (2)	2024 (2)	33 (1)
C(7)	968 (3)	2551 (2)	1276 (2)	37 (1)
C(8)	2215 (4)	3983 (3)	1743 (2)	42 (1)
C(9)	2007 (4)	4480 (2)	2791 (2)	41 (1)
C(10)	647 (3)	3359 (2)	2971 (2)	36 (1)
C(11)	2653 (3)	41 (2)	3207 (2)	32 (1)
C(12)	2303 (3)	−506 (2)	4023 (2)	37 (1)
C(13)	955 (3)	−1965 (2)	3532 (2)	37 (1)
C(14)	488 (3)	−2313 (2)	2415 (2)	37 (1)
C(15)	1515 (3)	−1085 (2)	2112 (2)	36 (1)
C(17)	−874 (4)	−3684 (3)	1547 (2)	53 (1)
C(16)	264 (4)	−2855 (3)	4220 (2)	50 (1)
C(18)	−1535 (3)	787 (2)	1831 (2)	32 (1)
C(19)	−1995 (3)	224 (2)	2739 (2)	34 (1)
C(20)	−3576 (3)	−1196 (2)	2125 (2)	35 (1)
C(21)	−4001 (3)	−1415 (2)	1019 (2)	38 (1)
C(22)	−2734 (3)	−185 (3)	839 (2)	37 (1)
C(24)	−5518 (4)	−2683 (3)	81 (2)	55 (1)
C(23)	−4435 (4)	−2155 (3)	2719 (2)	48 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Lengths (pm) and Angles (deg) for 2 with Esd's in Units of the Last Significant Figure in Parentheses[a]

Fe–Cent	165.8 (5)	Fe–Cent′	165.9 (5)
C(1)–C(2)	143.3 (4)	C(11)–C(15)	149.5 (3)
C(1)–C(5)	143.2 (3)	C(12)–C(13)	146.0 (3)
C(1)–C(11)	145.1 (3)	C(13)–C(14)	134.5 (4)
C(2)–C(3)	141.9 (3)	C(13)–C(16)	150.0 (5)
C(3)–C(4)	142.1 (4)	C(14)–C(15)	148.5 (4)
C(4)–C(5)	141.5 (4)	C(14)–C(17)	150.1 (3)
C(6)–C(7)	142.9 (4)	C(18)–C(19)	149.9 (4)
C(6)–C(10)	143.3 (3)	C(18)–C(22)	135.0 (3)
C(6)–C(18)	145.5 (3)	C(19)–C(20)	149.5 (3)
C(7)–C(8)	141.9 (3)	C(20)–C(21)	134.4 (4)
C(8)–C(9)	142.3 (4)	C(20)–C(23)	149.3 (4)
C(9)–C(10)	141.3 (4)	C(21)–C(22)	146.3 (4)
C(11)–C(12)	135.5 (4)	C(21)–C(24)	150.5 (3)

C(1)–C(11)–C(12)	128.4 (2)	C(6)–C(18)–C(19)	124.4 (2)
C(1)–C(11)–C(15)	124.0 (2)	C(6)–C(18)–C(22)	127.6 (2)
C(12)–C(11)–C(15)	107.7 (2)	C(19)–C(18)–C(22)	108.0 (2)
C(11)–C(12)–C(13)	110.1 (2)	C(18)–C(19)–C(20)	104.0 (2)
C(12)–C(13)–C(14)	108.5 (2)	C(19)–C(20)–C(21)	109.1 (2)
C(12)–C(13)–C(16)	122.9 (2)	C(19)–C(20)–C(23)	122.1 (2)
C(14)–C(13)–C(16)	128.6 (2)	C(21)–C(20)–C(23)	128.8 (2)
C(13)–C(14)–C(15)	109.4 (2)	C(20)–C(21)–C(22)	108.8 (2)
C(13)–C(14)–C(17)	128.6 (3)	C(20)–C(21)–C(24)	127.9 (2)
C(15)–C(14)–C(17)	122.0 (2)	C(22)–C(21)–C(24)	123.3 (2)
C(11)–C(15)–C(14)	104.3 (2)	C(18)–C(22)–C(21)	110.0 (2)

[a] Cent and Cent′ denote the two centroids of the cyclopentadienyl rings.

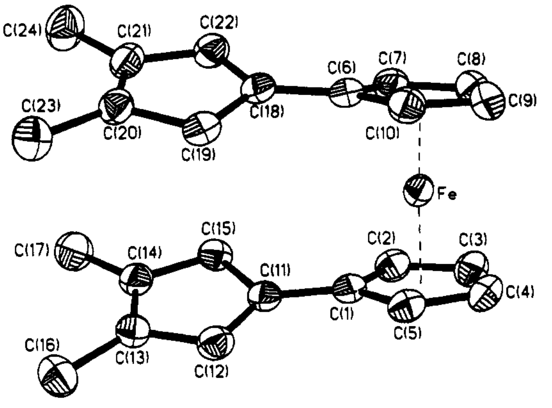


Figure 1. Molecular geometry and atom-labeling scheme for 2.

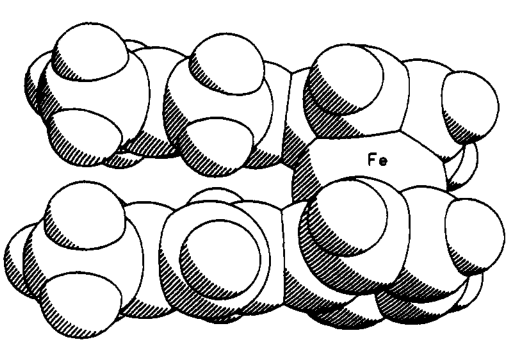
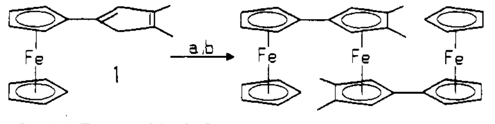


Figure 2. van der Waals presentation of compound 2.

monosubstituted product 1 cannot be explained by incomplete metalation of ferrocene, as BuLi/tmeda is known to produce a greater than 90% yield of dilithioferrocene. It is therefore suggested that the cyclopentenone itself serves as a source of protons. Its deprotonation to form the corresponding enolate regenerates lithioferrocene. This leads to a mixture of ferrocene, 1, and 2 that must be separated chromatographically. 1-Indanone and 2-indanone can be reacted in the same manner to give the corresponding products (1-indenyl)ferrocene (3) and (2-indenyl)ferrocene (4). Whereas compound 3 is produced in a satisfactory yield (40%), the low yield of compound 4 (12%) probably is due to the fact that the keto group of 2-indanone is not conjugated with the double bonds of the aromatic ring. In this case enolate formation seems to be the preferred process.

Single crystals of 2 were grown by slowly cooling a diethyl ether solution. Compound 2 crystallizes in the triclinic space group $P\bar{1}$ (Table I). Bond lengths and angles display no unusual features (Tables II and III). The most surprising aspect of the solid-state structure lies in the fact that the two $C_5H_3(CH_3)_2$ rings attached to ferrocene adopt an eclipsed 1,1′-geometry (Figure 1). This cofacial arrangement of the two $C_5H_3(CH_3)_2$ rings appears to be less favorable from a steric point of view (Figure 2). A comparison of structural data for 1,1′-substituted ferrocenes shows that a 1,1′-orientation of the two substituents is usually only observed for ring-bridged ansa species.[10] The

Scheme II[a]



[a] Legend: (a) BuLi; (b) $FeCl_2$.

typical 1,3′-orientation of 1,1′-bis(*N*-methylcarbamyl)ferrocene was explained on the grounds of minimization of steric repulsion and an efficient packing within the crystal.[11] In compound **2** the stacking of the two π-systems[12] seems to compensate for the sterically less favorable cofacial 1,1′-orientation of the substituents. It is unlikely that this conformation persists in solution, but one fact is worth noting. The ^1H NMR shifts ($CDCl_3$, 300 K) of the CH_2 and the CH units in the $C_5H_3(CH_3)_2$ rings of the mono- (**1**) and the bis(cyclopentadienyl) compound (**2**) differ significantly (3.10, 6.25 in **1**; 2.85, 6.16 in **2**). To minimize contact between the opposing $C_5H_3(CH_3)_2$ units, the C_5H_4 rings are tilted against each other by 4.4°. This opening up of the rings increases the distance between the carbon atoms from 342.7 pm (C1–C6) to 364.6 pm (C11–C18). The planes of the $C_5H_3(CH_3)_2$ rings are close to parallel with a tilt of 7.5°. In contrast, the planes of the two pairs of C_5H_4 and $C_5H_3(CH_3)_2$ rings are tilted against each other by 23.5 and 26.1°.

It is possible to deprotonate the cyclopentadienylferrocenes **1**–**4** with BuLi in THF. The reaction of the lithium salt of **2** with $FeCl_2$ at 0 °C in THF affords the expected triferrocenyl compound bis(1-ferrocenyl-3,4-dimethylcyclopentadienyl)ferrocene (**5**) in a 38% yield.

The dilithium salt of compound **2** can be prepared with 2 equiv of BuLi. Addition of $FeCl_2$ to this solution produces a mixture of polymeric ferrocenes.

The reactions of the lithiated indenylferrocenes **3** and **4** with electrophiles, however, are less clear-cut. The D_2O quench of the lithium salt of compound **3** gives an excellent yield of the monodeuterated (1-indenyl)ferrocene (**3a**), but the reaction with $FeCl_2$ is not well-understood. Hydrogenation of the green product of this reaction with Pd/C to prepare (tetrahydroindenyl)ferrocene gives an orange material of unknown composition.

The cyclopentadienyl-substituted ferrocenes described here should be versatile ligands for a large number of metals. Future research will be directed to synthesizing heteronuclear metal complexes, with a view to possible metal–metal interactions.

Experimental Section

All reactions were carried out under dry argon using standard Schlenk techniques. Commercially available solvents and reagents were purified according to literature procedures.[13] Chromatography was carried out with silica MN 60 or alumina activity V. NMR spectra were recorded at 300 K on Bruker AC 200 F (^1H NMR 200 MHz, ^{13}C NMR 50 MHz) or Varian Unity 300 spectrometers (^1H NMR 300 MHz, ^{13}C NMR 75 MHz), referenced to $CHCl_3$ (7.26 ppm) or C_6D_5H (7.15 ppm). Elemental analyses were performed at the Mikroanalytisches Laboratorium der Chemischen Laboratorien Universität Freiburg. Melting points were determined on a Meltemp melting point apparatus in sealed capillaries. Starting materials were commercially available or were prepared according to literature procedures: lithioferrocene,[14] dilithioferrocene,[15] 3,4-dimethylcyclopentenone,[16] 2-indanone.[17]

Synthesis of (3,4-Dimethylcyclopenta-1,3-dienyl)ferrocene (1). To a stirred solution of lithioferrocene (prepared from ferrocene (2.23 g, 12 mmol) and *t*-BuLi (5.9 mL, 1.7 M in pentane)) in 25 mL of THF at 0 °C was added 3,4-dimethylcyclopentenone (1.09 g, 10 mmol). The reaction mixture was stirred at room temperature for 1 h and quenched with 25 mL of aqueous NH_4Cl and 25 mL of Et_2O. The organic layer was separated, 1 g *p*-toluenesulfonic acid was added, and the mixture was stirred for 30 min. The organic phase was extracted with water, separated, dried over $MgSO_4$, and filtered, and the solvent was evaporated. The remaining orange-red solid was kept under high vacuum (10^{-5} Torr) for 6 h to remove most of the ferrocene. The remaining solid was rapidly chromatographed (basic alumina/*n*-hexane) to separate residual ferrocene: yield 1.3 g (47%); dec pt >60 °C. Anal. Calcd for $C_{17}H_{18}Fe$ (M_r 278.18): C, 73.40; H, 6.52. Found: C, 73.54; H, 6.30. ^1H NMR ($CDCl_3$): δ 1.86 (s, CH_3) 1.92 (s, CH_3), 3.10 (s, CH_2), 4.06 (s, C_5H_5), 4.20 ("t", J = 1.8 Hz, C_5H_4), 4.37 ("t", J = 1.8 Hz, C_5H_4), 6.25 (s, CH). ^{13}C NMR ($CDCl_3$): δ 12.56 (CH_3), 13.37 (CH_3), 46.14 (CH_2), 65.40 (C_5H_4), 68.05 (C_5H_4), 69.21 (C_5H_5), 82.40 (C-CpMe$_2$), 129.24 (CH), 133.19, 135.24, 141.20 (sp^2 in CpMe$_2$).

Synthesis of 1,1′-Bis(3,4-dimethylcyclopenta-1,3-dienyl)ferrocene (2). To a stirred suspension of dilithioferrocene (prepared from ferrocene (1.86 g, 10 mmol), BuLi (8 mL, 2.5 M in hexane), and tmeda (1.76 g, 20 mmol)) in 50 mL of hexane at 0 °C was added 3,4-dimethylcyclopentenone (2.18 g, 20 mmol) in 50 mL of Et_2O. Workup was as described for (3,4-dimethylcyclopenta-1,3-dienyl)ferrocene: dec pt >150 °C; yield 0.49 g (23%) of 3,4-dimethylcyclopenta-1,3-dienyl-ferrocene and 0.63 g (25%) of 1,1′-bis(3,4-dimethylcyclopenta-1,3-dienyl)ferrocene, eluted in the order ferrocene, **1**, and **2**. Anal. Calcd for $C_{24}H_{26}Fe$ (M_r 370.32): C, 77.84; H, 7.08. Found: C, 77.35; H, 7.06. ^1H NMR ($CDCl_3$): δ 1.83 (s, CH_3), 1.86 (s, CH_3), 2.85 (s, CH_2), 4.11 ("t", J = 1.7 Hz, C_5H_4), 4.26 ("t", J = 1.7 Hz, C_5H_4), 6.16 (s, CH). ^{13}C NMR ($CDCl_3$): δ 12.55 (CH_3), 13.26 (CH_3), 45.88 (s, CH_2), 66.29 (C_5H_4), 68.78 (C_5H_4), 83.80 (C-CpMe$_2$), 129.53 (CH), 133.75, 134.99, 140.37 (sp^2 in CpMe$_2$).

The reactions of 1-indanone and 2-indanone with lithioferrocene are carried out according to the procedure described for 3,4-dimethylcyclopentenone.

(1-Indenyl)ferrocene (3): yield 1.2 g (40%); mp 86 °C. Anal. Calcd for $C_{19}H_{16}Fe$ (M_r 300.18): C, 76.02; H, 5.37. Found: C, 76.09; H, 5.45. ^1H NMR ($CDCl_3$): δ 3.39 (d, CH_2 ^3J = 2.3 Hz), 4.13 (s, C_5H_5), 4.33 ("t", C_5H_4, J = 1.9 Hz), 4.64 ("t", C_5H_4, J = 1.9 Hz), 6.52 (t, C_5H_4, ^3J = 2.3 Hz), 7.26 (t, ArH, ^3J = 7.3 Hz), 7.40 (t, ArH, ^3J = 7.5 Hz), 7.51 (d, ArH, ^3J = 7.3 Hz), 7.91 (d, ArH, ^3J = 7.6 Hz). ^{13}C NMR ($CDCl_3$): δ 38.03 (CH_2), 67.06 (C_5H_4), 68.40 (C_5H_4), 69.15 (C_5H_5), 80.67 (C_5H_4-indenyl), 120.90, 123.84, 124.53, 125.99, 128.60 (sp^2 indenyl-CH), 141.44, 144.12, 144.89 (sp^2 indenyl-C).

Monodeuterated (1-Indenyl)ferrocene (3a). To a solution of (1-indenyl)ferrocene (150 mg, 0.5 mmol) in THF at 0 °C was added dropwise BuLi (0.2 mL, 2.5 M in hexane). After 30 min the mixture was quenched with excess D_2O. The volatiles were removed under vacuum, and the product was extracted with *n*-hexane. Evaporation of the solvent gave 135 mg (90%) of the monodeuterated product. ^1H NMR ($CDCl_3$): δ 3.39 (m, CHD), 4.14 (s, C_5H_5), 4.34 ("t", C_5H_4, J = 1.9 Hz), 4.64 ("t", C_5H_4, J = 1.9 Hz), 6.53 (d, CH, ^3J = 2.2 Hz), 7.26 (t, ArH, J = 7.3 Hz), 7.40 (t, ArH, ^3J = 7.5 Hz), 7.51 (d, ArH, ^3J = 7.3 Hz), 7.92 (d, ArH, ^3J = 7.5 Hz).

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(2-Indenyl)ferrocene (4): yield 0.36 g (12%). Anal. Calcd for $C_{19}H_{16}Fe$ (M_r 300.18): C, 76.02; H, 5.37. Found: C, 76.37; H, 5.21. ^1H NMR ($CDCl_3$): δ 3.62 (s, CH_2), 4.06 (s, C_5H_5), 4.28 ("t", J = 1.8 Hz, C_5H_4), 4.52 ("t", J = 1.8 Hz, C_5H_4), 6.79 (s, CH), 7.08–7.30 (m, 3 ArH), 7.39 (d, ^3J = 7.2 Hz, 1 ArH). ^{13}C NMR ($CDCl_3$): δ 39.80 (CH_2), 66.40 (C_5H_4), 68.99 (C_5H_4), 69.39 (C_5H_5), 80.88 (C_5H_4-indenyl), 119.88, 123.44, 123.68, 123.86, 126.54 (sp^2 indenyl-CH), 142.53, 145.96, 146.41 (sp^2 indenyl-C).

Synthesis of Bis(1-ferrocenyl-3,4-dimethylcyclopentadienyl)ferrocene (5). To a stirred solution of (3,4-dimethylcyclopenta-1,3-dienyl)ferrocene (278 mg, 1 mmol) in THF at 0 °C was added dropwise BuLi (0.4 mL, 2.5 M in hexane), followed after 30 min by $FeCl_2$ (63 mg, 0.5 mmol). After 12 h at room temperature the volatiles were removed in vacuo, the solid was washed with 25 mL of *n*-hexane, and the product was extracted with CH_2Cl_2. The CH_2Cl_2 was stripped in vacuo and the remaining orange solid recrystallized from toluene/*n*-hexane: yield 230 mg (38%). Anal. Calcd for $C_{34}H_{34}Fe_3$ (M_r 610.2): C, 66.93; H, 5.62. Found: C, 66.94; H, 5.66. ^1H NMR (C_6D_6): δ 1.71 (s, CH_3), 3.71 (s, CH in $C_5H_2(CH_3)_2$), 3.94 (s, C_5H_5), 4.13 ("t", J = 1.7 Hz, CH in C_5H_4), 4.22 ("t", J = 1.7 Hz, CH in C_5H_4). ^{13}C NMR (C_6D_6): δ 12.13 (CH_3), 65.85 (CH in Cp), 67.82 (CH in Cp), 69.21 (CH in Cp), 69.55 (C_5H_5), 81.72 (C in Cp), 82.92 (C in Cp), 84.11 (C in Cp).

Reaction of the Dilithio Salt of 2 with $FeCl_2$. To a stirred solution of 1,1′-bis(3,4-dimethylcyclopenta-1,3-dienyl)ferrocene (200 mg, 0.54 mmol) in THF at 0 °C was added dropwise BuLi (0.43 mL, 2.5 M in hexane), followed after 30 min by $FeCl_2$ (68 mg, 0.54 mmol). After 12 h at room temperature the volatiles were removed in vacuo, the solids were washed with 25 mL of *n*-hexane, and the product was extracted with CH_2Cl_2. After evaporation of the solvent an orange powder stayed behind. Anal. Calcd for the polymer $(C_{24}H_{26}Fe_2)_x$: C, 67.46; H, 6.15. Found: C, 66.20; H, 5.86. ^1H NMR ($CDCl_3$): δ 1.45 (bs, 6 H), 3.64 (bs, 2 H), 5.00 (b, 2 H), 5.08 (b, 2 H).

Crystal Structure Determination of Compound 2. Crystals of compound 2 were grown by slowly cooling a diethyl ether solution. Crystallographic data, positional and thermal parameters, and bond distances and angles of 2 are collected in Tables I–III. All software used is included in the SHELXTL PLUS (PC-Version) package.[18] The lack of systematic absences determined the triclinic crystal system. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. An absorption correction was applied (ψ scans[19]). The structure was solved by direct methods and refined by full-matrix least squares. The distribution of the E statistics seemed to indicate the acentric space group $P1$, in which the structure was initially solved and refined. Choosing the centrosymmetric alternative $P\bar{1}$, however, gave chemically more reasonable results and was therefore considered the correct solution. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were localized on the final Fourier map and fixed isotropic.

Acknowledgment. I wish to thank Prof. H. Vahrenkamp for generous support and a reviewer for valuable comments on the X-ray structure.

Registry No. 1, 140175-32-2; 2, 140175-33-3; 3, 140175-34-4; 3a, 140175-36-6; 4, 140175-35-5; 5, 140201-41-8; dilithioferrocene, 33272-09-2; 3,4-dimethylcyclopentenone, 84627-96-3; 1-indanone, 83-33-0; 2-indanone, 615-13-4.

Supplementary Material Available: A table giving the structure determination summary and complete lists of bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (7 pages). Ordering information is given on any current masthead page.

OM9105942

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Cluster-Bound Ketenylidenes as Precursors to Dicarbide Ligands: Synthesis and Characterization of $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$

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Received October 4, 1991

The triiron acetylide cluster compound $[PPN][Fe_3(CO)_9CCOAc]$ (1) [PPN = bis(triphenylphosphine)nitrogen(1+), $(Ph_3P)_2N^+$] reacts with $[Fe(CO)_4]^{2-}$ to produce the metalated acetylide cluster $[PPN]_2[Fe_3(CO)_9CCFe(CO)_4]$ (2). Further metalation of 2 with excess $Co_2(CO)_8$ produces a hexametallic dicarbido cluster $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$ (5). The reaction proceeds by formation of two intermediate compounds, the dicarbide-containing cluster compound $[PPN]_2[Fe_4Co_2(C_2)(CO)_{18}]$ (3) and the acetylide $[PPN][Fe_2Co(CO)_9CCFe(CO)_4]$ (4). Compound 4 also forms in moderate yield directly from 1, and the reaction of 5 with $[Fe_2(CO)_8]^{2-}$ regenerates 3. $[PPN][Fe_3Co_3(C_2)(CO)_{18}]$ (5) was the subject of a single-crystal X-ray structure determination. The compound crystallizes in the space group $P2_1/c$ (No. 14), with a = 15.878 (2) Å, b = 29.774 (4) Å, c = 11.930 (1) Å, β = 90.32 (1)°, V = 5640 (2) Å^3, and Z = 4. Refinement of 568 variables on 5217 observed [$I > 3\sigma(I)$] reflections converged to R = 4.4% and R_w = 5.6%. The structure of the cluster anion 5 consists of two metal triangles at either end of the dicarbide bond, with the metal triangles in a nonparallel configuration. Extended Hückel MO calculations indicate that the nonparallel configuration of the metal triangles in solution gives rise to the observed diamagnetic ground state.

Introduction

Carbido clusters have been intensively investigated as models for adsorbed surface carbides that occur in heterogeneous chemistry such as the Fischer–Tropsch process.[1] Carbides have been incorporated into a wide range

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0276-7333/92/2311-1859$03.00/0