Trinuclear Homo- and Heterometallic Complexes of a Doubly Bridged Cyclopentadienyl Ligand

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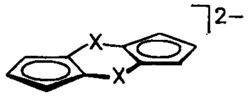
Received July 13, 1991

Key Words: Cyclopentadienyl ligand, doubly bridged / Cyclopentadienyl complexes, trinuclear / Polymers, organometallic

Metal complexes that are derived from the doubly bridged cyclopentadiene system 2,2,8,8-tetramethyl-2,8-disilatricyclo-[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraene (LH_2) are investigated. The dilithio salt of this compound (LLi_2) reacts with $(Me_3Si)_3$-C_5H_2FeCl to give, amongst other products, the trinuclear ferrocene $[(Me_3Si)_3C_5H_2FeL]_2Fe$ (**2**). A starting material well suited for the selective preparation of similar trinuclear complexes is the mononuclear ferrocene $(HL_2)Fe$ (**3**) which is formed by reaction of HLLi with iron(II) chloride. Reaction of dilithiated **3** with trimethyltin chloride yields $(Me_3SnL)_2Fe$ (**4**). Cocomplexation of dilithiated **3** and Cp*Li (Cp* = C_5Me_5) with iron(II) chloride leads to the trinuclear ferrocene $(Cp^*FeL)_2Fe$ (**5**). By reaction of **3** with octacarbonyldicobalt the heterometallic complex $[(CO)_2CoL]_2Fe$ (**6**) is obtained, which yields $[(CO)I_2CoL]_2Fe$ (**7**) by oxidative decarbonylation with iodine. The stereochemistry of the complexes presented is discussed. The trinuclear complexes **2**, **5**, **6**, and **7** are model systems for organometallic polymers with spatially directed structures, whose stability even in mixed-valence states is evidenced by the mass spectra of these complexes.

As part of an interdisciplinary search for "new materials" organometallic polymers that exhibit anisotropic properties (for example one-dimensional conductivity) have recently attracted a lot of attention[1]. We are currently investigating the synthesis, structure, and properties of molecular model systems for polymeric cyclopentadienyl complexes with spatially highly directed structures. Bifunctional Cp systems of type **A** are excellently suited for assembling metal centres in a stereochemically well-defined manner and thus are attractive building blocks for one-dimensional polymeric metal complexes.



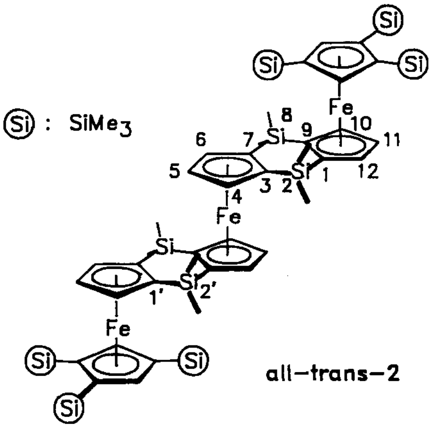
1a: X = $SiMe_2$
b: X = $(SiMe_2)_2$

A

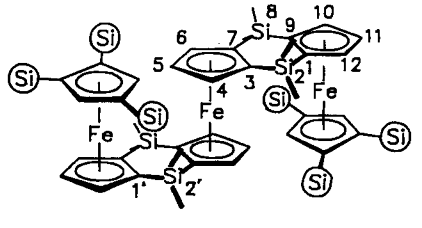
We have recently described the synthesis of dinuclear metal complexes of two silicon-bridged ligands of this type, namely **1a** (X = $SiMe_2$)[2] and **1b** [X = $(SiMe_2)_2$][2b,3]. Meanwhile, **1a** was also prepared by Köhler et al.[4a] and used for the preparation of a dinuclear chromocene[4b] and of mixtures of di-, tri-, and tetranuclear ferrocenes, which could be separated on a small scale by chromatography[4c]. We now report on the synthesis and properties of several trinuclear complexes of ligand **1a**.

Results and Discussion

We obtained the first example of such a trinuclear complex by serendipity: In an attempt to prepare a highly trimethylsilyl-substituted dinuclear ferrocene we treated two equivalents of $(Me_3Si)_3C_5H_2FeCl$[5] with the dilithio salt of **1a**[2] in THF at low temperatures. The reaction yielded a mixture of di-, tri-, and oligonuclear ferrocenes. Due to its surprisingly low solubility in hexane, the trinuclear species **2** could be isolated from this mixture in pure form as a bright red powder, which is air-stable. Recrystallization from benzene leads to very thin, raspberry-red platelets; these crystals include 0.5 solvent molecules per complex molecule. NMR spectroscopic data show that this compound has a highly symmetric structure which is either *all-cis* or *all-trans*. For steric reasons, the *all-trans* structure appears to be more likely.



all-trans-2

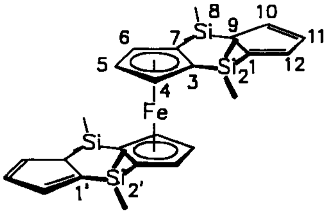


all-cis-2

0009–2940/92/0101–31 $ 3.50+.25/0

According to the NMR spectra, the two tris(trimethylsilyl)cyclopentadienyl rings are equivalent and are rotating rapidly on the NMR time scale. Only two signals are observed for their methyl groups in both the ^{1}H- and the ^{13}C-NMR spectra, and two resonances are obtained for the $SiMe_3$ units in the ^{29}Si-NMR spectrum; in each case, the two signals are observed with an intensity ratio of 2:1. Ring rotation is fast even at low temperatures: Apart from slightly broadened lines, a ^{1}H-NMR spectrum recorded at $-80\,^{\circ}C$ is virtually identical with a room-temperature spectrum. The bridging $SiMe_2$ units give rise to only two resonances in the ^{1}H- and ^{13}C-NMR spectra and to only one resonance in the ^{29}Si-NMR spectrum. For a *cis/trans* isomer one would expect to find twice the number of signals.

A much more controlled route to similar trinuclear complexes is their stepwise construction starting from the mononuclear ferrocene **3**. This species is formed in ca. 35% yield by treating 2,2,8,8-tetramethyl-2,8-disilatricyclo-[7.3.0.0^{3,7}]-dodeca-3,5,9,11-tetraene[6] with one equivalent of *n*-butyllithium and subsequent reaction of the metallated ligand with a stoicheiometric amount of iron(II) chloride in THF at low temperature[7].

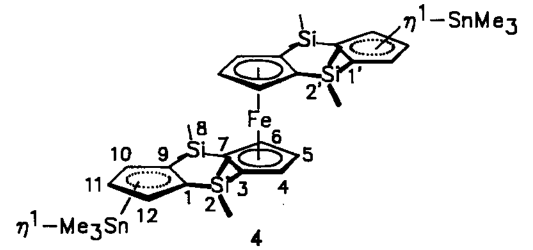


3

(mixture of isomers)

The compound is isolated as an orange microcrystalline powder, which is air-stable. Not unexpectedly, NMR spectroscopic data reveal that **3** forms a mixture of isomers. For example, at least ten signals are observed for the eight methyl groups in the ^{1}H-NMR spectrum. The ^{13}C- and ^{29}Si-NMR spectra appear to be less complex; they show, however, fairly broad signals which are probably due to superimposed resonances and dynamic phenomena. It is reasonable to assume that one of the two $SiMe_2$ units attached to each cyclopentadiene ring is in an allylic position. There are two possibilities for the stereochemical arrangement of the allylic sites in **3** with respect to each other: If the allylic site of one cyclopentadiene ring is held in a fixed position next to an $SiMe_2$ bridge, the allylic site of the other cyclopentadiene ring may be next to either of its two $SiMe_2$ bridges. Additionally, each allylic hydrogen atom may be oriented either *cis* or *trans* with respect to the coordinated iron centre. Altogether, six isomers are possible. It cannot be decided from the data available whether any of them is predominant in the mixture[8].

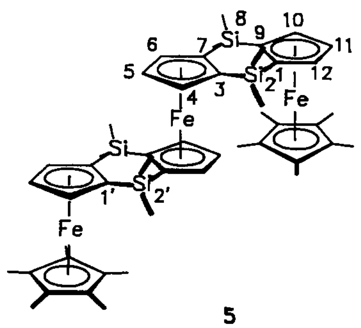
The two uncoordinated cyclopentadiene rings present in compound **3** can be utilized for the coordination of a variety of metal fragments. They can be metallated by treatment of **3** with two equivalents of *n*-butyllithium. The identity of the dilithio species formed in this reaction is proved by subsequent reaction with two equivalents of trimethyltin chloride which cleanly leads to the orange tin compound **4**, which is slightly air-sensitive. **4** is obtained as either the *all-cis* or the *all-trans* isomer exclusively according to NMR spectroscopic data. Not surprisingly, this compound exhibits fast stannatropic rearrangements; both $SnMe_3$ groups can be regarded as bound in a pseudo η^5 fashion. The protons on the cyclopentadienyl ring bound to the trimethyltin group give rise to a typical AX_2 pattern in the ^{1}H-NMR spectrum of **4**. The ^{13}C-NMR spectrum shows three resonances for this cyclopentadienyl ring: A sharp signal corresponding to the two tertiary carbon atoms C-10 and C-12 is observed at $\delta = 135.3$. A slightly broadened signal corresponding to the tertiary carbon atom C-11 is found at $\delta = 120.8$, and a broad signal is obtained at $\delta = 113.4$ for the two quaternary carbon atoms C-1 and C-9. The broadness of resonances for C-1, C-9, and C-11, together with their considerable high-field shift with respect to C-10 and C-12, indicates that these atoms participate in the migration of the trimethyltin group. It cannot be ruled out, however, that C-10 and C-12 also take part in this migration which can be explained as a series of [1, 2] shifts of the $SnMe_3$ group.



4

only the all–trans isomer is shown

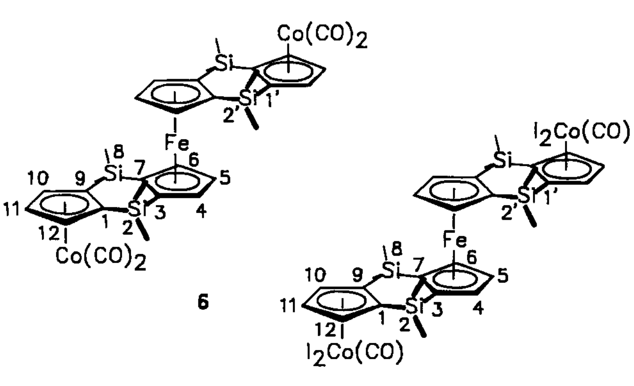
Cocomplexation of a mixture of dilithiated **3** (one part) and Cp*Li (20 parts) with a stoichiometric amount of iron(II) chloride in THF at low temperatures yields decamethylferrocene and the trinuclear ferrocene **5** as well as several per cent of higher nuclearity compounds. Purification of **5** is troublesome. After removal of decamethylferrocene by sublimation, an analytically pure sample is obtained only after four recrystallizations from hexane; the deep-orange, air-stable crystals have proved to be of the *cis/trans* isomer. The ^{1}H-NMR spectrum reveals the presence of two different Cp* rings (resonances at $\delta = 1.73$ and 1.90); four pairs of different methyl groups are observed for the bridging $SiMe_2$ units; as expected, four doublet/triplet sets



5

(AX_2 pattern) are obtained for the four groups of three protons on the chemically inequivalent cyclopentadienyl rings. The ^{13}C- and ^{29}Si-NMR spectra are also in accord with a *cis/trans* structure; especially, two silicon resonances of equal intensity are observed at $\delta = -5.9$ and -7.0. It is not yet clear whether the crude product contains considerable amounts of the symmetric isomers.

Another possibility of utilizing the free cyclopentadiene functionalities of the mononuclear ferrocene **3** for the construction of trinuclear complexes resides in reactions of **3** with metal carbonyls. For example, the trinuclear heterometallic complex **6** is obtained from **3** and octacarbonyldicobalt in boiling dichloromethane as a beige microcrystalline powder, which is slightly air-sensitive. As for compounds **2** and **4**, NMR spectroscopic data indicate that this species is highly symmetric (either *all-cis* or *all-trans*). For example, only two resonances are observed for the methyl groups of the bridging $SiMe_2$ units in both the ^1H- and ^{13}C-NMR spectra. Accordingly, the ^{29}Si-NMR spectrum shows one resonance. Owing to the electron-withdrawing effect of the $Co(CO)_2$ moiety, the resonances of the Cp rings coordinated to cobalt appear considerably more downfield than of those coordinated to the iron centre. The magnitude of this effect is ca. 0.5 ppm for the ^1H-NMR signals and ca. 10 ppm for the ^{13}C-NMR signals. The IR spectrum of **6** exhibits two bands at 2017 and 1950 cm^{-1} for the carbonyl stretching modes. These frequencies are similar to those observed for $CpCo(CO)_2$ [ref.[9] $\nu(CO) = 2028$ and 1967 cm^{-1}]. The carbonyl groups of **6** represent reactive centres, and a rich derivative chemistry of this compounds is to be expected. For example, by oxidative decarbonylation of **6** with iodine the respective iodo carbonyl complex **7** is obtained in quantitative yield as a black, air-stable, microcrystalline powder. Unlike the other trinuclear compounds, **7** is only sparingly soluble in all common organic solvents. The CO stretching mode is observed at 2057 cm^{-1} in the IR spectrum of this compound; this value is similar to the one observed for $CpCo(CO)I_2$ [ref.[9] $\nu(CO) = 2068$ cm^{-1}].



6

7

only the all–trans isomers are shown

6 and **7** are promising precursors for the construction of oligo- or polymeric complexes by decarbonylation processes.

Mass Spectra of the Trinuclear Compounds 2, 5, and 6: Occurence of Multiply Charged Ions

The ferrocenes **2** and **5** show very simple mass spectra with hardly any fragmentation taking place. The molecular ion gives rise to the highest intensity peak; M^{2+} is observed with 35–50% and M^{3+} with ca. 1% intensity. The cobalt carbonyl complex **6** does not show a very intense molecular ion peak due to facile loss of all four carbonyl ligands. Accordingly, the highest intensity peak is observed for the fragment $[M - 4\,CO]^+$; the respective doubly charged ion is detected with 28% intensity, and $[M - 4\,CO]^{3+}$ is present with very low intensity (0.3%). These results indicate the stability of extended mixed-valence structures based on the doubly bridged ligand **1a**.

This work was financially supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. U. S. thanks the *Studienstiftung des deutschen Volkes* for a dissertation grant.

Experimental

All reactions were carried out under purified argon by using standard Schlenk techniques. Solvents and reagents were appropriately dried and purified. – Melting points: Büchi 510 melting point apparatus. – NMR: Bruker AM 300 (300.133 MHz, ^1H, external TMS; 75.453 MHz, ^{13}C, external TMS; 59.595 MHz, ^{29}Si, external TMS; 70.859 MHz, ^{59}Co, external $K_3[Co(CN)_6]$; 111.817 MHz, ^{119}Sn, external Me_4Sn); where necessary, assignment of ^{13}C-NMR signals was made by using proton-coupled or *J*-modulated spectra. – MS: Varian 311 A (70 eV) or VG ZAB 3F (85 eV); only characteristic fragments are listed. – IR: CsI pellets, Mattson Polaris FTIR spectrophotometer. – Elemental analysis: Mikroanalytisches Laboratorium Beller (Göttingen, FRG), microanalytical laboratory of the Universität Bielefeld.

Bis[μ-{(1)9—12-η:3—7-η}-2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraen-1,7-diyl]bis[η^5-1,2,4-tris(trimethylsilyl)-2,4-cyclopentadien-1-yl]triiron(II,II,II) (**2**): A solution of 15.9 mmol of 1,2,4-tris(trimethylsilyl)cyclopentadienyl*lithium*, prepared in 120 ml of THF from 4.49 g (15.9 mmol) of tris(trimethylsilyl)cyclopentadiene and 10.0 ml of a 1.59 M solution of *n*-butyllithium in hexane (15.9 mmol), is added dropwise with stirring to a suspension of 2.03 g (16.0 mmol) of iron(II) chloride in 80 ml of THF at −100°C. The mixture is allowed to warm to −80°C over a period of 40 min. Subsequently, a suspension of 7.95 mmol of the dilithio salt of **1a**, prepared in 100 ml of THF from 1.95 g (7.98 mmol) of 2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraene[6] and 10.0 ml of a 1.59 M solution of *n*-butyllithium in hexane (15.9 mmol), is added dropwise with stirring at −100°C. The mixture is allowed to warm to room temp. overnight, volatile components are removed in vacuo, and the solid residue is extracted with 120 ml of *n*-hexane. Insoluble material is removed by filtration through a 3-cm layer of Florisil, and the filtrate is reduced to ca. 40 ml. The raspberry-red precipitate is collected by filtration, washed with *n*-hexane (2 × 5 ml) and dried in vacuo. Yield 376 mg [5.8% with respect to iron(II) chloride], m.p. 292–295°C. An analytical sample is obtained by one recrystallization from benzene; the crystals include 0.5 solvent molecules per complex molecule. – ^1H NMR ([D$_8$]toluene): $\delta = 0.23$ (s; 18H, $SiMe_3$), 0.36 (s; 36H, $SiMe_3$), 0.56 (s; 12H, $SiMe_2$), 0.66 (s; 12H, $SiMe_2$), 3.67 (t, $^3J = 2.1$ Hz, 2H, 11-, 11′-H), 4.11 (d, $^3J = 2.1$ Hz; 4H, 10-, 10′-, 12-, 12′-H), 4.34 [s; 4H, $C_5H_2(SiMe_3)_3$], 4.47 (d, $^3J = 2.1$ Hz; 4H, 4-, 4′-, 6-, 6′-H), 4.57 (t, $^3J = 2.1$ Hz; 2H, 5-, 5′-H). –

^{13}C{^{1}H} NMR (C_6D_6): δ = 0.6 (SiMe$_2$), 0.7 (SiMe$_3$), 2.0 (SiMe$_3$), 4.5 (SiMe$_2$), 72.0 (CH), 75.2 (CH), 76.3 (CH), 76.4 (CH), 77.4 (quat. C), 79.7 (quat. C), 80.2 (quat. C), 83.7 (CH). — ^{29}Si NMR (C_6D_6): δ = −6.9 (SiMe$_2$), −3.4 (SiMe$_3$), −3.0 (SiMe$_3$). — IR: $\tilde{\nu}$ = 3107 cm^{-1} vw, 3075 w, 2954 m, 2900 w, 2856 vw, 828 s, 809 s, 756 m, 425 m, 411 m, 403 m. — MS: *m/z* (%) = 1215.5 (100) [M$^+$], 607.3 (48) [M^{2+}], 405.2 (1) [M^{3+}].

$C_{56}H_{94}Fe_3Si_{10} \cdot 0.5\ C_6H_6$ (1254.8) Calcd. C 56.47 H 7.79
Found C 56.52 H 7.88

Bis[(3—7-η)-2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraen-7-yl]iron(II) (**3**): 7.73 g (31.6 mmol) of 2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraene[6] in 300 ml of THF is metallated with 20.0 ml of a 1.58 M solution of *n*-butyllithium in hexane (31.6 mmol). A suspension of 2.01 g (15.9 mmol) of iron(II) chloride in 40 ml of THF is added through a syringe at −110°C, and the mixture is allowed to warm to room temp. overnight. Volatile components are removed in vacuo, and the resultant orange solid is extracted with 200 ml of *n*-hexane. Insoluble material is separated off by filtration through a 2-cm layer of Florisil and is subsequently washed with 20 ml of *n*-hexane. The solvent is removed in vacuo, and 1.72 g of 2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraene can be recovered by sublimation at 10^{-3} mbar. The remaining orange powder is washed with 10 ml of *n*-hexane and dried in vacuo. Yield 2.15—2.40 g (32—36% with respect to 2,2,8,8-tetramethyl-2,8-disilatricyclo-[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraene), m.p. 189—191°C. Similar results are obtained by using FeBr$_2$ · DME or Fe(acac)$_2$ as a source of iron(II). — ^{1}H NMR ([D$_8$]toluene): δ = −0.49, −0.47, 0.36, 0.38, 0.45, 0.46, 0.50, 0.52, 0.56, 0.58 (all s; together 24H, SiMe$_2$), 4.13—4.52 (several m; together 8H, 4-, 4′-, 5-, 5′-, 6-, 6′-H, and two allylic H), 6.90—7.07 (m; 6H, vinylic H). — ^{13}C{^{1}H} NMR (C_6D_6): δ = −5.8 (br.; SiMe$_2$), −0.7 (br.; SiMe$_2$), 1.0 (br.; SiMe$_2$), 57.6 (br.; allylic C), 75.7 (C-4, -4′, -6, -6′), 76.6 (C-5, -5′), 79.2 (br.; C-3, -3′, -7, -7′), 132.5 (vinylic CH), 137.6 (vinylic CH), 140.8 (vinylic CH), 142.9 (vinylic C). — ^{29}Si NMR (C_6D_6): δ = −13.9, −0.5. — MS: *m/z (%)* = 542 (100) [M$^+$].

$C_{28}H_{38}FeSi_4$ (542.8) Calcd. C 61.96 H 7.06
Found C 62.08 H 7.10

Bis[(3—7-η)-2,2,8,8-tetramethyl-1-(trimethylstannyl)-2,8-disilatricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraen-7-yl]iron(II)(**4**): 868 mg (1.60 mmol) of **3** in 30 ml of THF is metallated with 2.00 ml of a 1.60 M solution of *n*-butyllithium in hexane (3.20 mmol). After 1 h at room temp., a solution of 657 mg (3.30 mmol) of trimethyltin chloride in 5 ml of THF is added. After stirring the resultant dark red solution at room temp. for 1 h, volatile components are removed in vacuo, and the remaining orange solid is extracted with 20 ml of dichloromethane. Insoluble material is separated off by filtration through a 2-cm layer of Florisil and is subsequently washed with 10 ml of dichloromethane. The filtrate is reduced to ca. 10 ml and stored at −60°C to yield deep orange needles, which are collected by filtration and dried in vacuo, whereupon they lose included solvent to form an orange powder. Yield 1.12 g (81%), m.p. 187—190°C. — ^{1}H NMR (C_6D_6): δ = −0.18 (s; 18H, SnMe$_3$; tin satellites are observed with ^2J(^{119}Sn, ^{1}H) = 53 Hz), 0.34 (s; 12H, SiMe$_2$), 0.41 (s; 12H, SiMe$_2$), 4.36 (d, ^3J = 2.2 Hz; 4H, 4-, 4′-, 6-, 6′-H), 4.42 (t, ^3J = 2.2 Hz; 2H, 5-, 5′-H), 6.71 (t, ^3J = 2.9 Hz; 2H, 11-, 11′-H), 6.94 (d, ^3J = 2.9 Hz, 4H, 10-, 10′-, 12-, 12′-H). — ^{13}C{^{1}H} NMR (C_6D_6): δ = −7.4 (SnMe$_3$; tin satellites are observed with ^1J(^{119}Sn, ^{13}C) = 341 Hz), −0.1 (SiMe$_2$), 1.9 (SiMe$_2$), 74.8 (C-5, -5′), 76.2 (C-4, -4′, -6, -6′), 77.7 (C-3, -3′, -7, -7′), 113.4 (br.; C-1, -1′, -9, -9′), 120.8 (C-11, -11′), 135.3 (C-10, -10′, -12, -12′). — ^{29}Si NMR (C_6D_6): δ = −10.5. — ^{119}Sn NMR (C_6D_6): δ = 16.5 ($\nu_{1/2}$ = 24 Hz). — MS: *m/z* (%) = 870 (17) [M$^+$(2 × ^{120}Sn)], 705 (0.6) [M$^+$(2 × ^{120}Sn) − ^{120}SnMe$_3$], 540 (10) [M$^+$(2 × ^{120}Sn) − 2 ^{120}SnMe$_3$], 525 (26) ([M$^+$(2 × ^{120}Sn) − 2 ^{120}SnMe$_3$ − Me], 165 (83) [^{120}SnMe$_3$].

$C_{34}H_{54}FeSi_4Sn_2$ (868.4) Calcd. C 47.03 H 6.27
Found C 46.43 H 6.03

Bis(η^5-1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)[cis-μ-{(1)9—12-η:3—7-η)}-2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraen-1,7-diyl][trans-μ-{(1)9—12-η:3—7-η)}-2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,1-tetraen-1,7-diyl]triiron(II,II,II) (**5**): A mixture of 10.9 g (80.0 mmol) of 1,2,3,4,5-pentamethylcyclopentadiene and 2.15 g (3.96 mmol) of **3** in 300 ml of THF is metallated with 55.0 ml of a 1.60 M solution of *n*-butyllithium in hexane (88.0 mmol). Subsequently, a suspension of 5.70 g (45.0 mmol) of iron(II) chloride in 80 ml of THF is added through a syringe at −110°C. The reaction mixture is allowed to warm to room temp. overnight. Volatile components are removed in vacuo, and the resultant solid is extracted with 200 ml of *n*-hexane. Insoluble material is separated off by filtration through a 2-cm layer of Florisil, and the orange filtrate is reduced to dryness in vacuo. Decamethylferrocene is removed by sublimation at 10^{-3} mbar. According to mass spectrometry, the remaining orange powder (2.80 g) contains at least 80% of the desired trinuclear ferrocene. Higher nuclearity by-products can be removed only by four recrystallisations from *n*-hexane. Yield 195 mg (5.3%), m.p. 280°C (dec.). — ^{1}H NMR ([D$_8$]toluene): δ = 0.21 (s; 6H, SiMe$_2$), 0.62 (s; 6H, SiMe$_2$), 0.68 (s; 6H, SiMe$_2$), 0.95 (s; 6H, SiMe$_2$), 1.73 (s; 15H, Cp*),1.90 (s; 15H, Cp*), 3.83 (d, ^3J = 2.2 Hz; 2H, CH), 3.86 (d, ^3J = 2.2 Hz; 2H, CH), 3.94 (t, ^3J = 2.2 Hz; 1H, CH), 3.97 (t, ^3J = 2.2 Hz; 1H, CH), 4.15 (t, ^3J = 2.2 Hz; 1H, CH), 4.28 (d, ^3J = 2.2 Hz; 2H, CH), 4.67 (d, ^3J = 2.1 Hz; 2H, CH), 4.98 (t, ^3J = 2.1 Hz; 1H, CH). — ^{13}C{^{1}H} NMR (C_6D_6): δ = 0.9 (SiMe$_2$), 2.8 (SiMe$_2$), 2.9 (SiMe$_2$), 3.9 (SiMe$_2$), 11.9 (C$_5$*Me*$_5$), 12.3 (C$_5$*Me*$_5$), 72.8 (CH), 74.6 (CH), 75.4 (CH), 76.3 (CH), 76.8 (two superimposed signals; CH), 77.9 (quart. C), 78.0 (quart. C), 78.6 (quart. C), 79.1 (CH), 79.7 (quart. C), 79.87 (*C*$_5$Me$_5$), 79.93 (*C*$_5$Me$_5$). — ^{29}Si NMR (C_6D_6): δ = −7.0, −5.9. — IR: $\tilde{\nu}$ = 3097 cm^{-1} vw, 3082 w, 3070 w, 2965 m, 2904 m, 2860 w, 824 s, 808 s, 774 s, 447 m, 426 m, 403 s, 380 m. — MS: *m/z* (%) = 922 (100) [M$^+$], 461 (35) [M^{2+}], 307.4 (1) [M^{3+}].

$C_{48}H_{66}Fe_3Si_4$ (922.9) Calcd. C 62.47 H 7.21
Found C 62.14 H 7.18

Bis[dicarbonylcobalt(I)]bis[μ-{(1)9—12-η:3—7-η}-2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraen-1,7-diyl]iron(II) (**6**): A solution of 3.36 g (9.83 mmol) of octacarbonyldicobalt, 4.98 g (9.17 mmol) of **3**, and 1.4 ml of 1,3-cyclohexadiene in 40 ml of dichlormethane is refluxed for 12 h. After cooling to room temp., the mixture is filtered through a 1-cm layer of Florisil, which is subsequently washed with 10 ml of dichloromethane. The filtrate is reduced to 10 ml in vacuo, 30 ml of *n*-hexane is added, and the volume is again reduced to 10 ml in vacuo. The solution is allowed to stand at room temp. for 24 h, during which time the product precipitates as a beige microcrystalline powder, which is collected by filtration, washed with cold *n*-hexane (2 × 3 ml), and dried in vacuo. Yield 1.58 g (22%), dec. above ca. 140°C. — ^{1}H NMR (CDCl$_3$): δ = 0.13 (s; 12H, SiMe$_2$), 0.62 (s; 12H, SiMe$_2$), 4.45 (d, ^3J = 2.1 Hz; 4H, 4-, 4′-, 6-, 6′-H), 5.06 (d, ^3J = 2.4 Hz; 4H, 10-, 10′-, 12-, 12′-H), 5.15 (t, ^3J = 2.1 Hz; 2H, 5-, 5′-H), 5.62 (t, ^3J = 2.4 Hz; 2H, 11-, 11′-H). — ^{13}C{^{1}H} NMR (C_6D_6): δ = 0.0 (SiMe$_2$), 3.2 (SiMe$_2$), 75.0 (C-3, -3′, -7, -7′), 75.8 (C-4, -4′, -6, -6′), 78.5 (C-5, -5′), 89.8 (C-10, -10′, -12, -12′), 91.3 (C-11, -11′), 99.8 (C-1, -1′, -9, -9′), 205.6 (CO). — ^{29}Si NMR (C_6D_6): δ = −11.3. — ^{59}Co NMR (C_6D_6): δ = −2154 ($\nu_{1/2}$ = 12000 Hz). — IR: $\tilde{\nu}$ = 3100 cm^{-1}

vw, 3090 vw, 3082 vw, 3073 vw, 2952 w, 2017 s, 1950 (sh) s, 829 m, 809 m, 772 m. – MS: *m/z* (%) = 770 (13) [M^+], 752 (1) [M^+ – CO], 714 (9) [M^+ – 2 CO], 686 (1) [M^+ – 3 CO], 658 (100) [M^+ – 4 CO], 599 (25) [M^+ – 4 CO – Co], 329 (28) [M^{2+} – 4 CO], 219.3 (0.3) [M^{3+} – 4 CO].

$C_{32}H_{36}Co_2FeO_4Si_4$ (770.7) Calcd. C 49.87 H 4.71
Found C 49.29 H 4.62

Bis[carbonyldiiodocobalt(III)bis[μ-{(1)9–12-η:3–7-η}-2,2,8,8-tetramethyl-2,8-disilatricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraen-1,7-diyl]iron(II) (**7**): A solution of 140 mg (1.10 mmol) of iodine in 10 ml of diethyl ether is added dropwise with stirring to a solution of 210 mg (272 μmol) of **6** in 30 ml of diethyl ether. After stirring overnight, the violet-grey precipitate is collected by filtration, washed with diethyl ether (3 × 5 ml), and dried in vacuo. Yield 325 mg (98%), dec. above ca. 200°C. – ^{1}H NMR ([D$_8$]THF): δ = 0.27 (br. s; 12H, SiMe$_2$), 1.03 (br. s; 12H, SiMe$_2$), 4.76 (br. s; 4H, 4-, 4′-, 6-, 6′-H). 5.26 (br. s; 2H, 5-, 5′-H), 6.29 (br. s; 4H, 10-, 10′-, 12-, 12′-H), 6.74 (br. s; 2H, 11-, 11′-H). – IR: $\tilde{\nu}$ = 3080 cm^{-1} vw, 2951 w, 2047 (sh) s, 834 m, 812 s, 776 m, 470 m. – No interpretable mass spectrum could be obtained.

$C_{30}H_{36}Co_2FeI_4O_2Si_4$ (1222.3) Calcd. C 29.48 H 2.97
Found C 30.14 H 3.16

CAS Registry Numbers

2: 136721-11-4 / **3**: 136721-12-5 / **4**: 136721-13-6 / **5**: 136721-14-7 / **6**: 136721-15-8 / **7**: 136749-06-9 / LH$_2$: 78921-94-5 / LLi$_2$: 134153-32-5 / 1,2,4-$(Me_3Si)_3C_5H_3$: 41991-86-0 / $FeCl_2$: 7758-94-3 / $FeBr_2$ · DME: 99611-53-7 / Fe(acac)$_2$: 14024-17-0 / Me_3SnCl: 1066-45-1 / Me_5C_5H: 4045-44-7 / $Co_2(CO)_8$: 10210-68-1

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