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X-ray structural investigations and conformational particularities of ethyne-derived organometallics based on ferrocene and fluorene

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Abstract

The X-ray structures of eight different ethyne-based organometallic compounds, 1-trimethylsilylethynylferrocene [55997-95-0] (**I**), 1-iodoethynylferrocene [94598-10-4] (**II**), 1,1'-bis(2-hydroxy-2-methylbut-3-yn-4-yl)ferrocene [144975-44-0] (**III**), novel (5-hydroxy-5-methylhexa-1,3-diyne-1-yl)ferrocene-*co*-3-hydroxy-3-methyl-1-iodobut-1-yne (**IVb**), *endo*-1-hydroxy-1-ethynylferrocene-[2.3.a]indene (**V**), 9-ethynyl-9-hydroxyfluorenedicobalthexacarbonyl [148943-14-0] (**VI**), ethynylferrocene-derived (*Z*)-[2-(4-nitrophenyl)-1-chloroethenyl]ferrocene [151305-19-0] (**VII**) and (*Z*)-[2-(4-acetylphenyl)-1-chloroethenyl]ferrocene [151305-20-3] (**VIII**) are presented. Selected crystallographic data, particular structural features as well as the syntheses of **IVa**, **IVb** and **V** are reported. The importance of hydrogen bonding for the lattice formation of the ferrocenylpropargylalcohols **III** and **IV** as well as the relevance of hydrogen bonding and π -stacking in **VII** and **VIII** are discussed in detail. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: X-ray structure analysis; Ferrocene; Fluorene; Ethynyl

1. Introduction

Ethynyl spacers have attracted significant interest because of the intriguing physical and electro-optical properties [1] which they generate in materials containing one or more triple bonds [2–5]. Attached to phenylene spacers, ethyne groups provide a significantly reduced overlap of p_z -orbitals, yet generate more rigid systems which are of particular interest for luminescent, fluorescent [6–9] and photorefractive materials [10], respectively. The additional introduction of transition metals [11,12] or aromatic systems allows the design of two- and three-dimensional donor–acceptor systems which may show additional structure-related properties in the solid state [13–15].

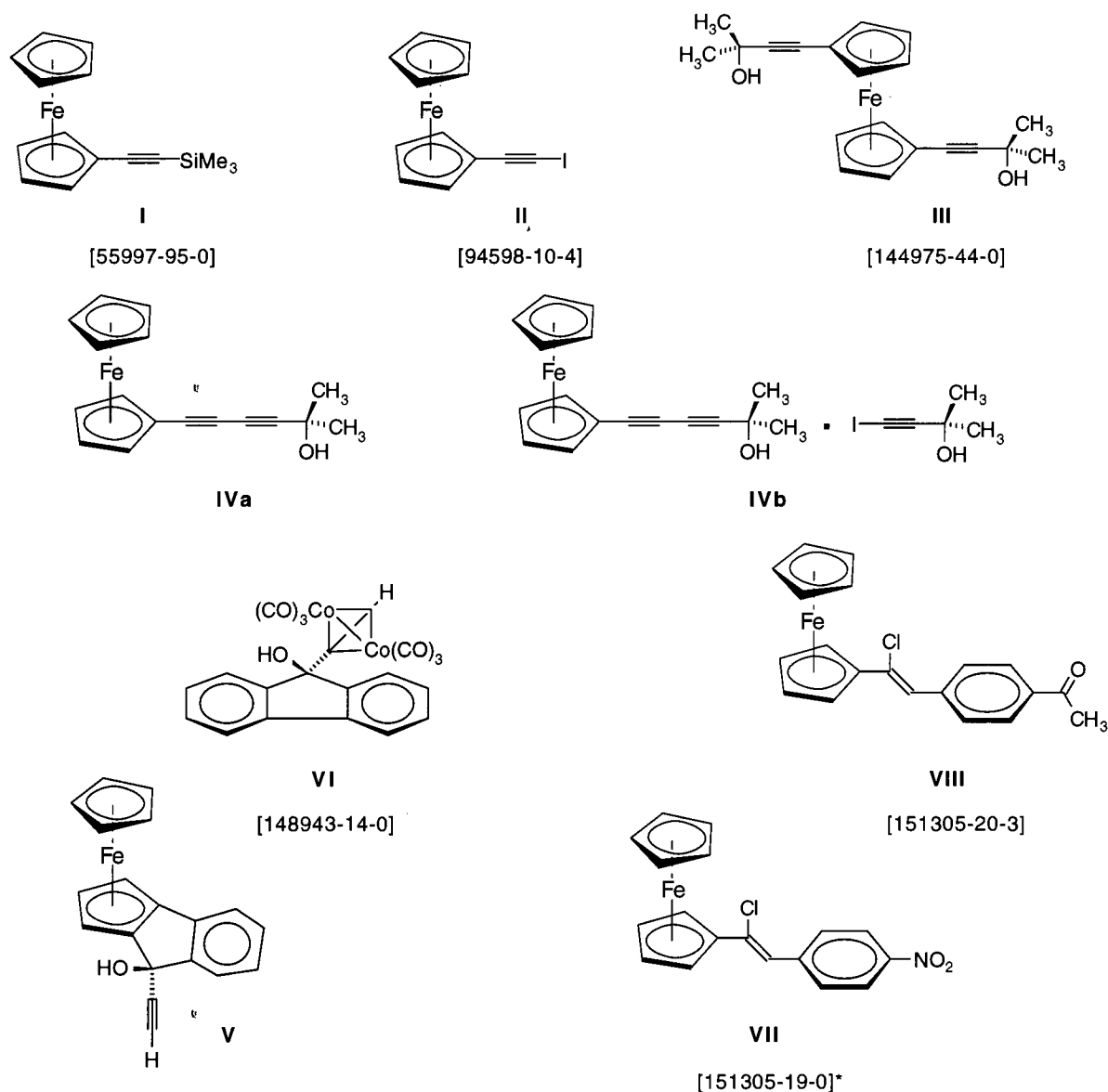
One of the most efficient synthetic approaches in the preparation of ethyne-based compounds is based on different coupling sequences. Among them, the Stephens–Castro [16], inverse Stephens–Castro [17,18], Sonogashira–Hagihara [19–22] reactions belong to the most important ones. In order to carry out these couplings in a satisfactory way, protecting groups based on the hydroxymethyl-, tri-*i*-propylsilyl-trimethylsilyl- and 2-hydroxy-*i*-propylmoieties [23] for terminal alkynes or the dicobalt hexacarbonyl group for internal and terminal carbon–carbon triple bonds have been used. In this contribution, we present some special structural features of such protected compounds, which have already successfully served as intermediates in ethyne chemistry [17,18,24–26] (Scheme 1).

2. Results and discussion

Besides the synthetic approaches involving the reaction of 1-monocuproethynylferrocene with chloro-

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Scheme 1. Overview of compounds I–VIII.

trimethylsilane [27], 1-trimethylsilylethynylferrocene (**I**) may either be prepared by reacting ethynylferrocene with one equivalent of base, preferably *n*-butyl lithium, followed by the reaction with one equivalent of chlorotrimethylsilane, or by the reaction of monocycloferrocene with one equivalent of 1-iodotrimethylsilylacetylene [17,28]. Compound **I** crystallizes in an orthorhombic space group, *Pna*2₁ (Fig. 1). Despite the fact that the TMS group possesses a significantly reduced electronegativity compared to iodine, the carbon–carbon triple bond distance for C11–C12 is practically identical (1.189(7) Å) to the one found in **II**, indicating a rather reduced influence of the terminal substituent on the carbon–carbon triple bond. 1-Iodoethynylferrocene (**II**) [17,28] is simply prepared by reaction of ethynylferrocene with one molequivalent of

base, preferably *n*-butyl lithium, followed by the reaction with one molequivalent of iodine [29,30]. Compound **II** crystallizes in the orthorhombic space group *Pnma* (Fig. 2). The carbon–carbon triple bond distance for C7–C8 is 1.190(7) Å.

1,1'-Bis(2-hydroxy-2-methylbut-3-yn-4-yl)ferrocene (**III**) [17] may be best prepared by the reaction of 1,1'-dicycloferrocenedimethylsulfide [144975-43-9] and two equivalents of 1-iodo-3-hydroxy-3-methylbut-1-yne [17]. Compound **III** crystallizes in the monoclinic space group *P*2₁/*c* (Fig. 3). The four oxygens of two molecules of **III** form a (slightly dwelled) eight-membered ring that is formed via hydrogen bonding, as can clearly be deduced from the average O–H distance of 206(5) pm. A similar arrangement has been observed in other ferrocenediols, e.g. 1,1'-bis(7-hydroxynorborn-2-

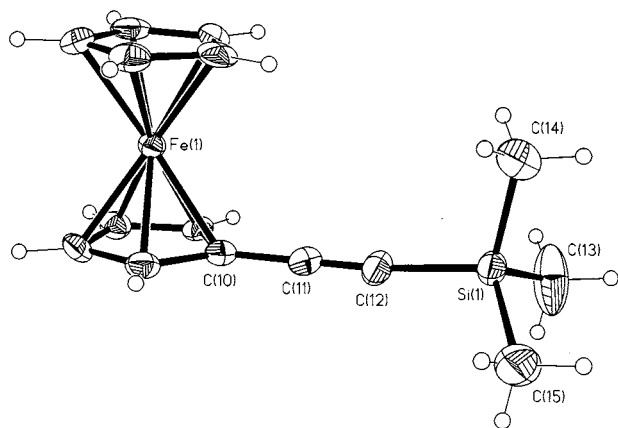


Fig. 1. X-ray structure of 1-trimethylsilylethynylferrocene (**I**).

ene-7-yl)ferrocene [31] and 1,1'-bis(2-hydroxymethyl)ferrocene [32], respectively. In order to provide an appropriate distance between O1 and O2 (2.801(4) Å), and as a consequence of the conformation of the two ethynyl-substituted cyclopentadienyl units, the dihedral angle defined by the two cyclopentadienyl units is 4.4(3)°. This results in an interatomic distance between C10 and C5 of 3.384(5) Å, while the distance between C3 and C8 is only 3.259 Å. The distance between O1 and O2a is 2.845(4) Å. The angles O2–O1–O2a and O1–O2–O1a are 92.6(1) and 87.4(1)°, respectively. The entire eight-membered ring is characterized by a center of inversion. The carbon–carbon triple bond distances for C11–C12 and C16–C17 are 1.189(5) and 1.179(5) Å, respectively, and may therefore be regarded as regular.

The monosubstituted ferrocene(5-hydroxy-5-methylhexa-1,3-diyne-1-yl)ferrocene (**IVa**) shows similar structural features to **III**. It is prepared by the reaction of 1-monocuproethynylferrocene with 1-iodo-3-hydroxy-3-methylbut-1-yne (see Section 3). To achieve the necessary capability for hydrogen bonding, it cocrystallizes with one reactant of the synthetic sequence, 3-hydroxy-3-methyl-1-iodobut-1-yne, to form (2-hydroxy-2-methylpenta-3,5-diyne-6-yl)ferrocene-*co*-3-hydroxy-3-

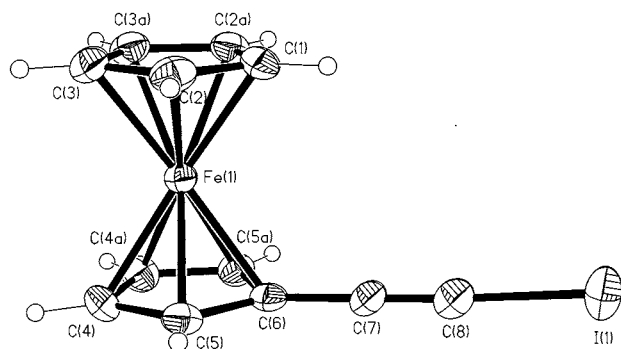


Fig. 2. X-ray structure of 1-iodoethynylferrocene (**II**).

methyl-1-iodobut-1-yne (**IVb**) (Fig. 4). The compound crystallizes in space group $P\bar{1}$ (no. 2). As in **III**, an eight-membered ring is formed with similar interatomic distances. The corresponding angles are practically similar to those found in **III**, thus the angle defined by O2–O1–O2a is 92.4(4)° and the one defined by O1–O2–O1a is 87.7(4)°, respectively. The O1–O2 distance is 2.79(1) Å, only the O1–O2a distance (2.77(1) Å) is comparably shorter than in **III**. The carbon–carbon triple bonds show a length of 1.16(2) Å (C11–C12), 1.20(2) Å (C13–C14) and 1.20(2) Å (C18–C19). Based on these data, the following conclusions can be drawn: (i) the formation of an eight-membered ring consisting of four different hydroxyl groups is highly favorable; and (ii) the gain of free energy during formation of such a system obviously easily compensates for the loss of free energy that results from the energetically unfavorable torsion of two substituted Cp systems as found in **III**. These conclusions are supported by previously reported quantum chemical calculations. Using an aug-cc-pVDZ basis set on a MP2 level, Xantheas et al. [33] demonstrated that a highly favored structure of water is the tetramer. O–O distances of 2.743 Å were calculated with a stabilizing energy of $-23.8 \text{ kcal mol}^{-1}$ [34] (aug-cc-pVDZ basis set on a MP4 level). Liedl et al. [35] predicted O–O distances in a water tetramer of 2.731 and 2.741 Å, using a 6-311++G(3df, 4pd)-basis set on a MP2 and B3LYP level, respectively. Far IR vibration–rotation tunneling (FIR-VRT) [36,37] spectroscopy revealed a quasicyclic planar minimum energy structure of the tetramer which is in good agreement for the O–O distances in ice (2.759 Å) [38,39]. As almost identical interatomic distances as for (H₂O)₄ are found in both compounds **III** and **IVb**, the formation of an eight-membered ring may also be considered as energetically highly favorable in alcohols. This is underlined by the fact that in **IVb**, two of the four hydroxyl groups stem from the cocrystallizing compound, which might be arranged more easily with more favorable sterics than those in a pure hypothetical tetramer of **IVa**. Finally, it should be noted that structures consisting of such eight-membered rings allow a coordinated proton-tunneling in the solid state. Such a tunneling has been found to play an important role in many chemical and biological processes [40].

1-Hydroxy-1-ethynylferroceno[2.3.a]indene (**V**) is prepared by an intramolecular Friedl–Crafts type cyclization of 2-ferrocenylbenzoyl chloride [41] and subsequent reaction of the intermediary ketone with lithium acetylide. Compound **V** crystallizes in the monoclinic space group $P2_1/c$ (Fig. 5). The absolute configuration at C-1 strongly depends on the ethynylation reagent. Thus, ethynylmagnesium bromide preferably forms the *exo* isomer with the hydroxyl group pointing in the opposite direction to the ferrocenyl group, while lithium acetylide-ethylenediamine preferably forms the

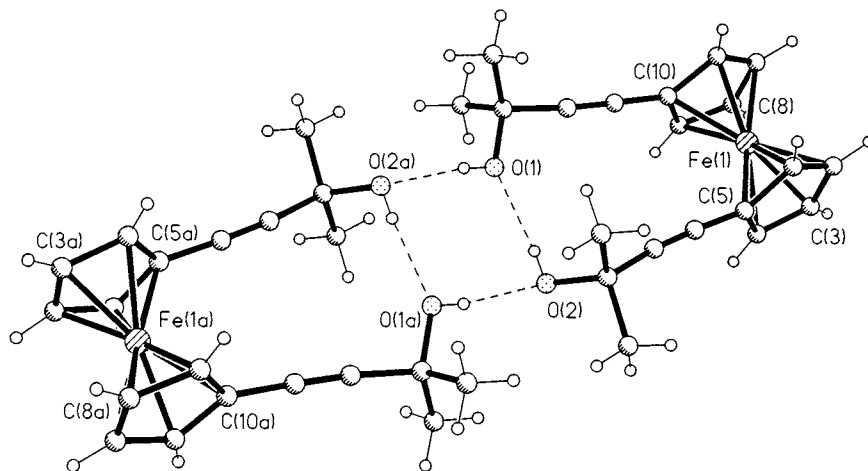


Fig. 3. X-ray structure of 1,1'-bis(2-hydroxy-2-methylbut-3-yn-4-yl)ferrocene (**III**).

endo isomer. The absolute configuration at C-1 may be deduced from the IR data of the corresponding compounds and is in accordance with their crystallographic data. As for the 1-hydroxyferroceno[2.3.a]indenes, which may be prepared by reduction of the cyclic ketone with borohydrides, significant differences for the ν_{OH} signal of the *endo* and *exo* isomers are observed [42]. Due to the coordination of the hydroxyl group in the *endo* isomer with the iron, the OH-bond itself is weakened and the ν_{OH} -signal shifts from 3540 to 3525 cm^{-1} . As a direct consequence of the interaction of the hydroxyl group with the iron and because of the sterically demanding nature of the ferrocenoindene moiety, no hydrogen bond-mediated aggregation as found for the other ferrocenylpropargyl alcohols **III** and **IVb**, is observed. As a consequence of the incorporation of C-1 into an annelated five-membered ring, **V** shows a distorted tetrahedral geometry at this carbon.

As another relevant example of an organometallic derivative of a propargylic alcohol, the structure of 9-ethynyl-9-hydroxyfluorene-dicobalthexacarbonyl (**VI**) is presented (Fig. 6). The parent 9-ethynyl-9-fluoreno¹ [13461-74-0] is synthesized by the reaction of lithium acetylide-ethylenediamine with fluorenone [13461-74-0]. Subsequent protection of the parent alkyne with dicobaltoctacarbonyl [43] yields **VI** which crystallizes in the triclinic space group $P\bar{1}$ (no. 2) (Fig. 6). As might be expected from similar systems [44], the C2–C1 distance is 1.329(4) Å. The alkyne dicobalthexacarbonyl-system itself possesses a distorted tetrahedral geometry. While the angles found for Co1–C1–Co2 and Co1–C2–Co2 are 77.79 and 78.10°, respectively, somewhat smaller ones are found in C1–Co1–C2 and C1–Co2–C2 (39.51 and 39.71°). The angles defined by C2–C1–Co1 and C2–C1–Co2 are 70.7(2) and 69.2(2)°.

A combination of different driving forces for the formation of two conformationally divergent types of compounds within one single unit cell can be observed in (Z)-[2-(4-nitrophenyl)-1-chloroethenyl]ferrocene (**VII**). Compound **VII** is prepared [45] via an autocatalytic Meerwein reaction of 4-nitrobenzenediazonium chloride with ethynylferrocene [46] [1271-47-2]. X-ray structure determination of this compound as well as for its derivative **VII** have been filed previously without any discussion enclosed [45]. Compound **VII** crystallizes in the monoclinic space group $P2_1/n$ (Fig. 7). Two molecules are oriented in a way that each nitro-group forms weak, yet observable hydrogen bonds with the 1'-hydrogen of the second ferrocene.

The observed O1–H and O4–H distances are 2.58 and 2.65 Å, respectively. Nevertheless, another driving force for this type of packing lies in a highly favorable orientation of the two phenylene groups of these two molecules. They show an almost perfect parallel orientation with a mean distance of 3.45–3.58 Å, typical distances found in Π -stacks [47–49]. The gain of free energy from this orientation obviously compensates for at least one unfavorable dihedral angle. One vinylene group (the angle of the corresponding plane is defined by C12–C31–C32) in the first molecule is almost coplanar and therefore in conjugation with the Cp ring ($2.9 \pm 2.5^\circ$). The second vinylene group (the angle of the corresponding plane is defined by C11–C11–C12) is twisted out of the plane of conjugation with the Cp ring, resulting in a dihedral angle of $25.0 \pm 2^\circ$. The carbon–carbon double bond itself seems to be governed by the influence of the adjacent chlorine atom. Irrespective of the type of conjugation, both possess almost the same length (C11–C12 = 1.31(2), C31–C32 = 1.33(2) Å).

As for **VII**, (Z)-[2-(4-acetylphenyl)-1-chloroethenyl]ferrocene (**VIII**) is prepared [45] via an autocatalytic Meerwein reaction of 4-acetylbenzenediazonium chlo-

¹ Commercially available from Lancaster Ltd.

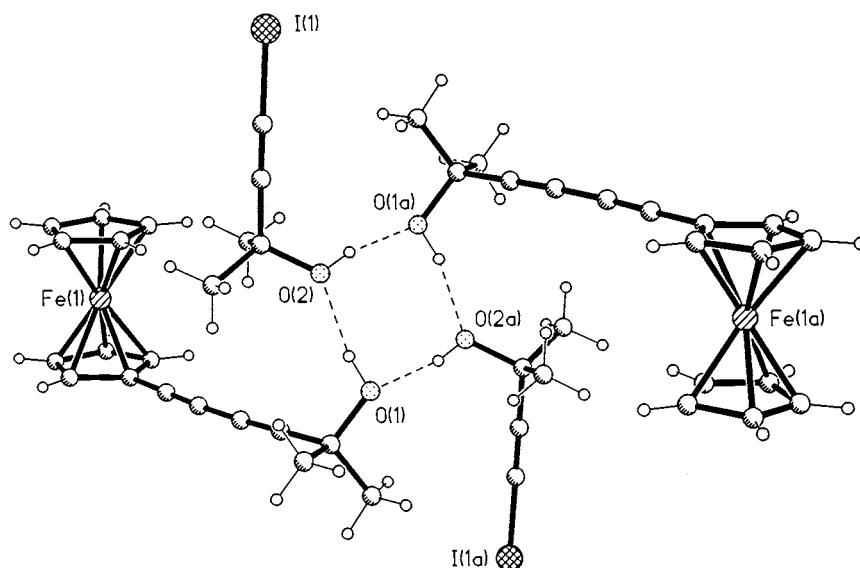


Fig. 4. X-ray structure of (2-hydroxy-2-methylpenta-3,5-dien-6-yl)ferrocene-co-3-hydroxy-3-methyl-1-iodobut-1-yne (**IVb**).

ride with ethynylferrocene. In contrast to **VII**, **VIII** crystallizes in the orthorhombic space group *Pbca* with only one type of molecule in the unit cell (Fig. 8). The 4-acetyl-*p*-phenylenevinylene system may roughly be regarded as conjugated. Thus, both the vinylene (the angle of the corresponding plane is defined by C11–C11–C12) as well as the acetyl group (the angle of the corresponding plane is defined by O1–C19–C20) are almost in conjugation with the *p* phenylene ring (5.3 ± 0.2 and $10.0 \pm 0.2^\circ$, respectively). The Cp-ring is significantly twisted out of the plane of conjugation ($18.2 \pm 0.3^\circ$) with the vinylene group. The entire crystal lattice is formed in a way that the distance between two adjacent *p*-phenylene groups is 3.53–3.55 Å. Nevertheless, despite this highly favorable distance, π -stacking is believed to be of minor relevance as the aromatic six-membered rings are organized stepwise instead of being perpendicularly eclipsed. Similarly, the O–H distances found between the acetyl- and the neighboring ferrocene group are too large (2.932 Å) in order to be regarded as significant hydrogen bondings.

3. Experimental

The synthesis, spectroscopic data as well as the synthetic potential of compounds 1-trimethylsilylethynylferrocene [55997-95-0] (**I**), 1-iodoethynylferrocene [94598-10-4] (**II**), 1,1'-bis(2-hydroxy-2-methylbut-3-yn-4-yl)ferrocene [144975-44-0] (**III**), 9-ethynyl-9-hydroxyfluorenedicobalthexacarbonyl [1489-43-14-0] (**VI**), (*Z*)-[2-(4-nitrophenyl)-1-chloro-ethenyl]ferrocene [151305-19-0] (**VII**), and (*Z*)-[2-(4-acetylphenyl)-1-chloroethenyl]ferrocene (**VIII**) are described elsewhere [17,43,45]. Elemental analyses for compounds **I–VIII** were in the expected ranges.

3.1. (5-Hydroxy-5-methylhexa-1,3-dien-1-yl)ferrocene-co-3-hydroxy-3-methyl-1-iodobut-1-yne (**IVb**)

Novel (5-hydroxy-5-methylhexa-1,3-dien-1-yl)ferrocene (**IVa**) was prepared by a modified Cadiot–Chodkiewicz-coupling [50] employing in situ generated 1-monocuproethynylferrocene-dimethylsulfide and 1-iodo-3-hydroxy-3-methylbut-1-yne and purified by flash-chromatography of an aliquot of the mother liquor on silica G-60. The cocrystallite **IVb** was obtained by harvesting single crystals which separated from the crude reaction mixture. Compound **IVa**: IR (KBr): 3350b,w; 3090w; 2980m; 2240m; 1380m; 1365w; 1300w; 1265w; 1220m; 1160b,s; 1110m; 1030m; 1005m;

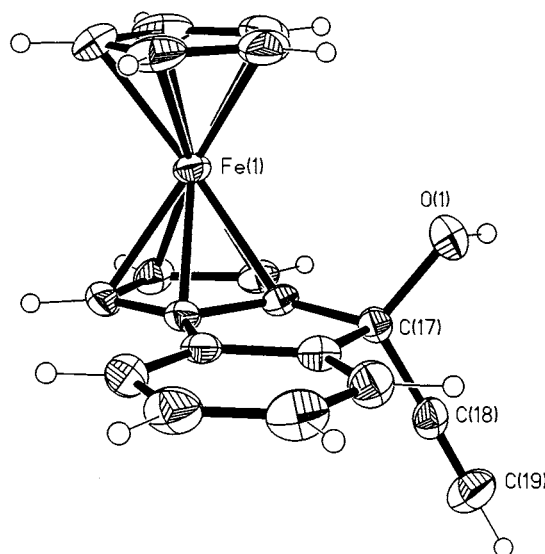


Fig. 5. X-ray structure of 1-hydroxy-1-ethynylferroceno[2.3.a] indene (**5**).

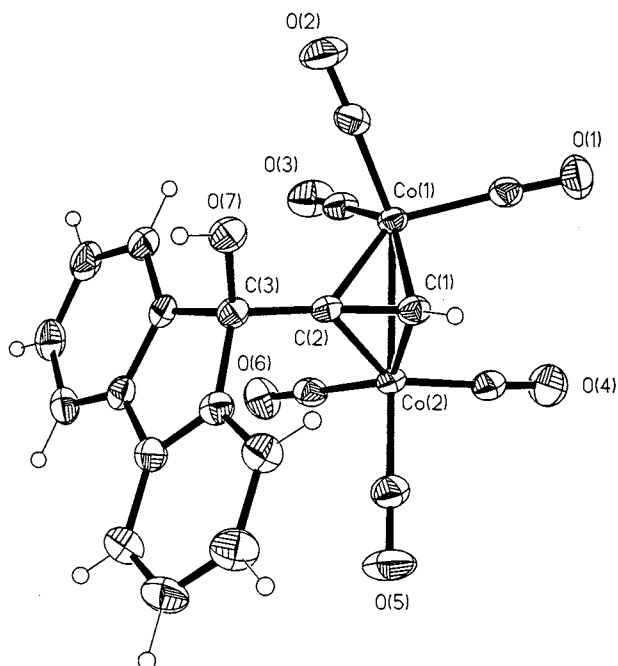


Fig. 6. X-ray structure of 9-ethynyl-9-hydroxyfluorene-dicobalthexacarbonyl (VI).

965b,s; 905s; 825b,s; 535m; 500b,s. $^1\text{H-NMR}$ (CDCl_3 , TMS): 1.50 (s, 6H), 2.22 (bs, 1H), 4.18 (s, 7H), 4.41 (t, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , TMS): 31.1 (methyl), 65.8, 69.3, 70.1, 72.2 (ferrocenyl), 78.9 (alkyne), 83.8 (alkyne). EI MS (70 eV): $m/z = 292$ (M^+ , 100%), 277 ($\text{M}^+ - 15$, 20%).

3.2. Endo-1-hydroxy-1-ethynylferroceno[2.3.a]indene (V) [51,52]

Lithium acetylide-ethylenediamine (0.38 g, 4.30 mmol) is added to 40 ml of NH_3 (l). Ferroceno[2.3.a]indene-1-one (1.03 g, 3.56 mmol) dissolved in diethyl ether (40 ml) is added over a period of 2 h. The reaction mixture is brought to room temperature and the solution is poured on water. Extraction is performed with diethyl ether (3×100 ml), and the combined organic extracts are dried over sodium sulfate.

LC (aluminum oxide, 4×100 cm; diethyl ether:petroleum ether = 25:75) allows the separation of V. Yield: 898 mg (83.2%). IR (KBr): 3394m, 3054w, 1607s, 1499m, 1465m, 1171s, 1154s, 1105vs, 1042s, 1019s, 1004s, 818vs, 758vs, 719vs, 700s, 563vs, 524vs. $^1\text{H-NMR}$ (CDCl_3 , TMS): 2.85 (s, 1H, HCC-), 4.00 (s, 5H, Cp), 4.0 bs (1H, OH), 4.22 (t, 1H, $J = 1.5$), 4.37 (t, 1H, $J = 1.5$), 4.46 (t, 1H, $J = 1.5$), 7.1–7.4 (m, 4H, Ar); $^{13}\text{C-NMR}$ (CDCl_3 , TMS): 60.1, 62.4, 67.9 (C_{ipso}), 69.7, 69.9 (C_{ipso}), 70.3, 83.0, 89.5, 100.5, 120.3, 124.3, 126.3, 128.8, 138.5 (C_{ipso}), 151.7 (C_{ipso}). EI MS (70 eV): $m/z = 314$ (M^+ , 40%), 288 ($\text{M}^+ - 26$ (HCCH), 100%).

3.3. X-ray structure determination of I–VIII

X-ray crystallographic data (Table 1) were collected by a Siemens P4 diffractometer with graphite-monochromatized Mo- K_α radiation ($\lambda = 71.073$ pm). The unit cell parameters were determined and refined from 23 to 29 randomly selected reflections in the θ range of 5.4–12.5°, obtained by P4 automatic routines. Data were measured via ω -scan and corrected for Lorentz and polarization effects, an empirical absorption correction, based on ψ -scans [53], was applied for I, II, III, V, VI and VIII. The structures were solved by direct methods (SHELXS-86) [54] and refined by a full-matrix least-squares procedure using F^2 (SHELXL-93) [55]. The function minimized was $\Sigma[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters, except for compound VII, where carbon atoms were refined isotropically, because of poor crystal quality. Hydrogen atoms were located by differential Fourier methods, but in the refinement they were included in calculated positions and refined with isotropic displacement parameters 1.2 and 1.5 times (for methyl hydrogen atoms) higher than U_{eq} of the attached carbon atoms, except for the hydrogen atoms at C1 and O7 of VI and O1 and O2 of I and IVb, which were refined isotropically.

The crystal of III, with a monoclinic angle β of $90.08(2)^\circ$, was pseudo-merohedrally twinned and the structure was solved by introduction of a twinning

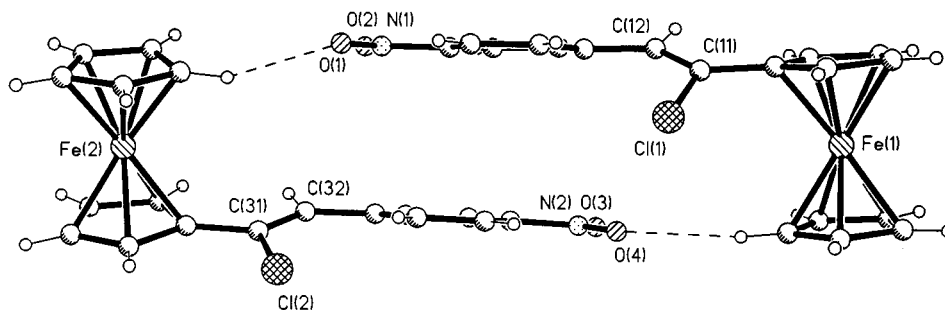


Fig. 7. X-ray structure of (Z)-[2-(4-nitrophenyl)-1-chloroethenylferrocene] (VII).

Table 1
Crystal data and structure refinement for compounds I–VIII

| Largest difference peak | least-squares on I | least-squares on II | Full-matrix least- III | $R_1 = 0.0000$, $wR_2 =$ IVb | $R_1 = 0.0000$, $wR_2 =$ V | $R_1 = 0.0000$, $wR_2 =$ VI | $R_1 = 0.0000$, $wR_2 =$ VII ^a | $R_1 = 0.0000$, $wR_2 =$ VIII |
|---|--|--|--|--|--|--|---|---|
| Empirical formula | C ₁₅ H ₁₈ FeSi | C ₁₂ H ₉ FeI | C ₂₀ H ₂₂ FeO ₂ | C ₂₂ H ₂₃ FeIO ₂ | C ₁₉ H ₁₄ FeO | C ₂₁ H ₁₀ Co ₂ O ₇ | C ₁₈ H ₁₄ ClFeNO ₂ | C ₂₀ H ₁₇ ClFeO |
| M_r | 282.23 | 335.94 | 350.23 | 505.15 | 314.15 | 492.15 | 367.6 | 364.64 |
| Crystal system | Orthorhombic | Orthorhombic | Monoclinic | Triclinic | Monoclinic | Triclinic | Monoclinic | Orthorhombic |
| Space group | <i>Pna</i> 2 ₁ | <i>Pnma</i> | <i>P2</i> ₁ / <i>c</i> | <i>P</i> $\bar{1}$ (no. 2) | <i>P2</i> ₁ / <i>c</i> | <i>P</i> $\bar{1}$ (no. 2) | <i>P2</i> ₁ / <i>n</i> | <i>Pbca</i> |
| <i>a</i> (pm) | 3160.7(5) | 1673.5(5) | 1426.2(7) | 1015.4(4) | 2037.5(2) | 907.3(1) | 1185.5(2) | 775.7(2) |
| <i>b</i> (pm) | 601.5(3) | 888.9(2) | 1101.0(5) | 1072.6(4) | 762.40(10) | 1033.1(2) | 992.7(2) | 1068.3(2) |
| <i>c</i> (pm) | 751.0(2) | 736.9(2) | 1070.5(4) | 1161.9(4) | 1831.5(3) | 1112.9(2) | 2720.2(5) | 3847.0(8) |
| α (°) | 90 | 90 | 90 | 67.27(2) | 90 | 107.59(2) | 90 | 90 |
| β (°) | 90 | 90 | 90.08(2) | 70.98(3) | 90.98(1) | 96.61(3) | 100.36(3) | 90 |
| γ (°) | 90 | 90 | 90 | 89.81(2) | 90 | 96.98(1) | 90 | 90 |
| <i>V</i> (nm ³) | 1.4278(8) | 1.0962(5) | 1.6809(13) | 1.0925(7) | 2.8446(7) | 0.9783(3) | 3.1491(10) | 3.1879(12) |
| <i>Z</i> | 4 | 4 | 4 | 2 | 8 | 2 | 8 | 8 |
| <i>T</i> (K) | 213(2) | 213(2) | 208(2) | 293(2) | 223.(2) | 213(2) | 293.(2) | 218(2) |
| D_{calc} (g cm ⁻³) | 1.313 | 2.036 | 1.384 | 1.527 | 1.467 | 1.671 | 1.551 | 1.519 |
| Absorption coefficient (mm ⁻¹) | 1.116 | 4.147 | 0.904 | 2.115 | 1.055 | 1.737 | 1.135 | 1.114 |
| <i>F</i> (000) | 592 | 640 | 736 | 500 | 1296 | 492 | 1504 | 1504 |
| Color, habit | Yellow plate | Orange prism | Orange prism | Yellow prism | Brown plate | Red prism | Purple prism | Dark red prism |
| Crystal size (mm) | 0.5 × 0.2 × 0.07 | 0.21 × 0.19 × 0.16 | 0.5 × 0.45 × 0.11 | 0.25 × 0.11 × 0.1 | 0.85 × 0.45 × 0.25 | 0.59 × 0.26 × 0.19 | 0.25 × 0.15 × 0.07 | 0.6 × 0.3 × 0.25 |
| θ Range for data collection (°) | 3–23 | 3.02–22.47 | 3.01–22.99 | 3.19–20.99 | 5–21.99 | 3.22–24.00 | 1.52–19.50 | 3.61–23.49 |
| Index ranges | –1 ≤ <i>h</i> ≤ 36, –1 ≤ <i>k</i> ≤ 6, –5 ≤ <i>l</i> ≤ 8 | –1 ≤ <i>h</i> ≤ 18, –1 ≤ <i>k</i> ≤ 9, –7 ≤ <i>l</i> ≤ 4 | –1 ≤ <i>h</i> ≤ 16, –12 ≤ <i>k</i> ≤ 1, –1 ≤ <i>l</i> ≤ 11 | –1 ≤ <i>h</i> ≤ 10, –10 ≤ <i>k</i> ≤ 10, –11 ≤ <i>l</i> ≤ 11 | –23 ≤ <i>h</i> ≤ 23, –1 ≤ <i>k</i> ≤ 8, –1 ≤ <i>l</i> ≤ 20 | –10 ≤ <i>h</i> ≤ 0, –11 ≤ <i>k</i> ≤ 11, –12 ≤ <i>l</i> ≤ 12 | –1 ≤ <i>h</i> ≤ 16, –1 ≤ <i>k</i> ≤ 13, –38 ≤ <i>l</i> ≤ 38 | –1 ≤ <i>h</i> ≤ 7, –1 ≤ <i>k</i> ≤ 12, –1 ≤ <i>l</i> ≤ 44 |
| Reflections collected | 2314 | 2011 | 1810 | 2786 | 4436 | 3120 | 3758 | 2614 |
| Independent reflections | 1825 [$R_{\text{int}} = 0.0253$] | 752 [$R_{\text{int}} = 0.0224$] | 1499 [$R_{\text{int}} = 0.0255$] | 1190 [$R_{\text{int}} = 0.0296$] | 3426 [$R_{\text{int}} = 0.0442$] | 3017 [$R_{\text{int}} = 0.0104$] | 2732 [$R_{\text{int}} = 0.0999$] | 1891 [$R_{\text{int}} = 0.0417$] |
| Reflections observed [$I > 2\sigma(I)$] | 1544 | 656 | 1401 | 1678 | 2261 | 2582 | 1142 | 1397 |
| Absorption correction | ψ -scan | ψ -scan | ψ -scan | None | ψ -scan | ψ -scan | None | ψ -scan |
| Max./min. transmission | 0.902, 0.833 | 0.935, 0.787 | 1.000, 0.785 | – | 0.969, 0.771 | 0.816, 0.568 | – | 0.964, 0.858 |
| Refinement method | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 | Full-matrix least- squares on F^2 | Full-matrix least- squares on F^2 | Full-matrix least- squares on F^2 | Full-matrix least- squares on F^2 | Full-matrix least- squares on F^2 | Full-matrix least- squares on F^2 |
| Data/restraints/ parameters | 1754/1/155 | 730/0/74 | 1477/0/218 | 2120/2/244 | 3262/0/379 | 3012/0/279 | 2208/0/235 | 1714/0/209 |
| Goodness-of-fit on F^2 | 1.050 | 1.101 | 1.069 | 1.066 | 1.051 | 1.032 | 1.017 | 1.054 |
| Final <i>R</i> indices [$I > 2\sigma(I)$] | $R_1 = 0.0343$, $wR_2 = 0.0768$ | $R_1 = 0.0221$, $wR_2 = 0.0404$ | $R_1 = 0.0249$, $wR_2 = 0.0597$ | $R_1 = 0.0622$, $wR_2 =$ 0.1496 | $R_1 = 0.0399$, $wR_2 =$ 0.1051 | $R_1 = 0.0310$, $wR_2 =$ 0.0777 | $R_1 = 0.0861$, $wR_2 =$ 0.1480 | $R_1 = 0.0411$, $wR_2 =$ 0.0851 |
| <i>R</i> indices (all data) | $R_1 = 0.0499$, $wR_2 = 0.0879$ | $R_1 = 0.0289$, $wR_2 = 0.0422$ | $R_1 = 0.0287$, $wR_2 = 0.0617$ | $R_1 = 0.0943$, $wR_2 =$ 0.1820 | $R_1 = 0.0527$, $wR_2 =$ 0.1286 | $R_1 = 0.0406$, $wR_2 =$ 0.0863 | $R_1 = 0.2283$, $wR_2 =$ 0.2266 | $R_1 = 0.0707$, $wR_2 =$ 0.1213 |
| Largest difference peak and hole (e nm ⁻³) | 283 and –365 | 647 and –581 | 193 and –199 | 3174 and –385 | 268 and –477 | 373 and –523 | 514 and –349 | 230 and –229 |

^a X-ray data deposited with the Cambridge file.

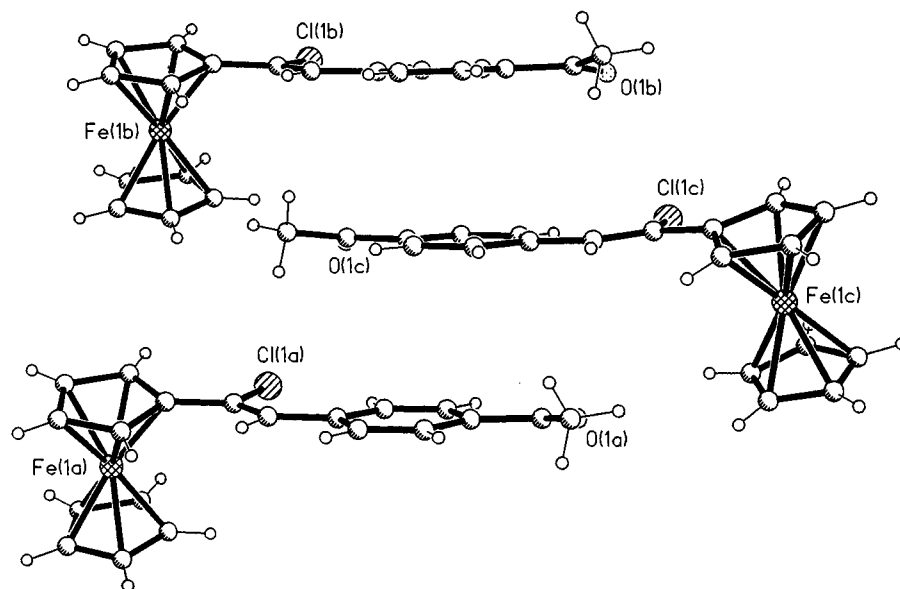


Fig. 8. X-ray structure of (Z)-[2-(4-acetylphenyl)-1-chloroethenylferrocene] (VIII).

element. The twinning element can either be a mirror plane in (100) or (001) or a twofold rotation axis along [100] or [001]. In the refinement, a twofold rotation around the a^* -axis was chosen with the instruction card: TWIN 1 0 0 0-1 0 0 0-1. The volume ratio of the twins refined nearly to 1:1.

4. Supplementary material

Further details of the crystal structure investigation for compound VII are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the depository numbers CCDC 121726–121733, the names of authors, and the journal citations.

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