

Trimethylchlorosilane-modified Clemmensen reduction of metallocenyl ketones: trapping and X-ray structures of aliphatic, olefinic, silylated pinacolic, and rearranged pinacolonic products

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Abstract

The Clemmensen reduction of a carbonyl group to give, in the simplest cases, a methylene unit, is one of the more familiar reactions in organic chemistry. Trimethylchlorosilane as a replacement for the proton allows controlled reductive deoxygenation of carbonyl compounds under formally anhydrous conditions as an alternative to the McMurry dicarbonyl coupling reaction. Aromatic carbonyl compounds with electron-donor substituents are preferred substrates for this reaction to yield symmetrical olefins in good yield. The high donor capacity of metallocenyl groups should especially favor the clean formation of olefins from the corresponding metallocenyl ketones. In this study, a number of ferrocenyl and ruthenocenyl aldehydes and ketones were treated with Zn and trimethylchlorosilane under controlled anhydrous reaction conditions with (a) catalytical and (b) low amounts of H⁺ present. The observed main products include alkanes, alkenes, silylated pinacols, and rearranged pinacolones, which have been characterized by spectroscopic methods and by X-ray analyses. The diverse outcome in these reactions indicates a reaction mechanism which involves electrophilic catalysis with different energetically similar pathways.

Keywords: Iron; Ferrocene; Clemmensen reduction; Trimethylchlorosilane

1. Introduction

Probably the most useful carbonyl coupling reactions to give symmetrical or unsymmetrical alkenes are the Wittig [1] and the McMurry [2] reactions. One of the more recent new synthetic alternatives is a modified Clemmensen reduction under anhydrous conditions with trimethylchlorosilane as a substitute for the proton [3]. We explored this route to prepare olefinic metallocenes for two reasons: first, the necessary metallocenyl phosphonium salts as precursors of the Wittig reagents are in most cases unknown and also in our experience not easily accessible; second, the McMurry reaction tends to give product mixtures with the olefinic target compounds as main products but contaminated with further reduced aliphatic side products, which are sometimes difficult to separate [4]. Olefin-forming reactions starting from metallocenyl ketones are of interest as a synthetic access to conjugatively bridged electrophores,

which serve as model compounds for molecular electronic devices [5]. In this study [6], a number of ferrocenyl and ruthenocenyl aldehydes and ketones were treated with Zn and trimethylchlorosilane under controlled reaction conditions. Despite our aim to prepare olefinic metallocenes in a straightforward fashion, we find an astonishing variety of products, which can be rationalized by a trapping of different intermediates at different stages of the mechanistic reaction course.

2. Results and discussion

2.1. Mechanism

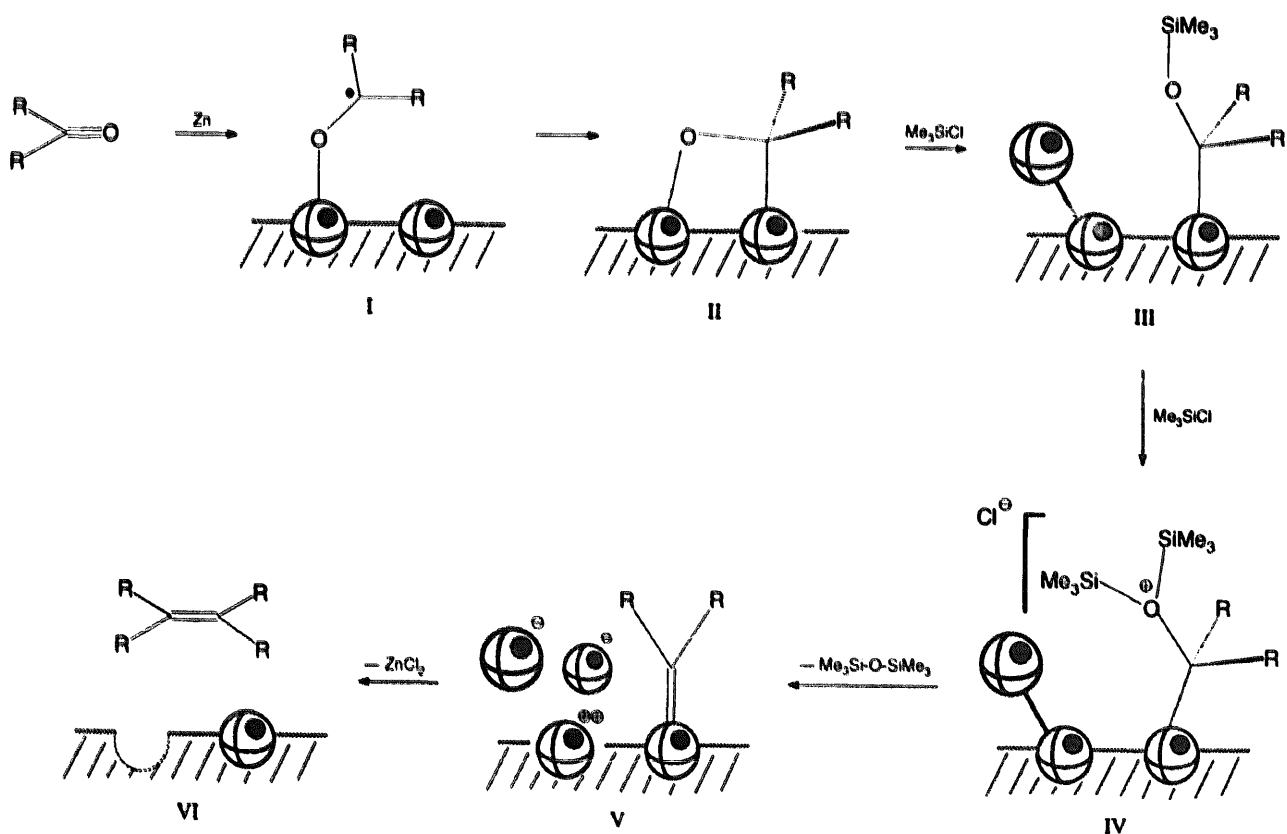
In a recent review by Motherwell and Nutley [3], covering the role of zinc carbenoids in organic synthesis, the direct deoxygenation of carbonyl compounds with Zn–chlorosilane to give alkenes has been proposed as a simple ‘one-pot’ method to achieve this reductive carbon–carbon bond forming process. Compared with

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the classical Clemmensen reduction, which converts ketones to methylene compounds (sometimes with pinacolic side products), the replacement of the proton by trimethylchlorosilane is believed to serve three purposes. First, using HCl-free chlorosilane should ensure essentially anhydrous reaction conditions, which are advantageous for acid-sensitive substrates; second, the formation of the strong silicon–oxygen bond promotes reduction of the ketone by facilitating removal of the carbonyl-oxygen in the form of hexamethylsiloxane; third, the increased activity of the chlorosilane–zinc–THF system allows performing the reaction at much lower temperature (-30 , 0 , or 20°C), thereby avoiding the sometimes thermally destructive Clemmensen conditions (aqueous HCl, cosolvent, reflux). A plausible mechanism [3] is outlined in Scheme 1: the carbonyl functionality is reduced by elemental zinc in a one-electron reduction to a ketyl radical species I, which is further reduced by zinc to the two-electron reduced oxometallacycle II; the first incoming trimethylchlorosilane opens this ring under formation of a siloxyalkyl-zinc intermediate III, which is silylated by a second equivalent trimethylchlorosilane to give an oxonium species IV and subsequent elimination of hexamethylsiloxane affords zinc carbenoid V, which dimerizes to afford the alkene. Since carbenoid V is stabilized by electron-donating substituents, electron-rich aromatic carbonyl

compounds give the best yields and are the preferred substrates for this reaction [3]. Therefore, it is to be expected that metallocenyl ketones, owing to the extraordinary donor capacity of the metallocene moiety [7], especially favor clean olefin formation. Although the mechanism depicted in Scheme 1 looks rather convincing, other intermediates, for example oxirans, pinacols [8] or carbonyl ylides [9], have been proposed to account for the observed products. In addition, trimethylchlorosilane has been replaced by other halogenosilanes (diiododimethylsilane [10] and 1,2-bis(chlorodimethylsilyl)ethane [11]) with beneficial effects in terms of selectivity and product yields. In general, all these mechanistic implications are more or less based on relative product composition considerations, but no direct proof of any of the proposed intermediates has been given, hence the question of the 'correct' mechanism is still open.

It has been stressed [3,12], that the trimethylchlorosilane must be rigorously free of hydrogen chloride for a successful conversion of the ketone to the olefin. Unfortunately, there is no easy way to measure the presence or the amount of hydrogen chloride in a given sample of 'freshly distilled' trimethylchlorosilane. Curiously, and in contrast to the above statement, we find that our 'best' trimethylchlorosilane, which has been distilled twice under an atmosphere of argon prior to use, fails to



Scheme 1. Mechanism of the reaction of carbonyl compounds with trimethylchlorosilane and zinc (adapted from Ref. [3]).

Table 1
Product yield of metallocenyl carbonyl compounds upon reacting with zinc and trimethylchlorosilane in THF

	Methane	Ethane	Olefin	Siloxy pinacol	Pinacolone
Ferrocenecarboxaldehyde	—	—	1 (75%) ^a	—	—
Acetylferrocene	—	—	—	2 (66%) ^a	—
Benzoylferrocene	—	—	—	—	3 (62%) ^b
Diferrocenylketone	—	4 (5%) ^a	5 (73%) ^a	—	—
Ferroceny(ruthenocenyl)ketone	—	6 (18%) ^{a,c}	— ^c	—	—
Ferrocindenone	—	—	7 (76%) ^a	—	—
1,1'-Diacetylferrocene	8 (29%) ^{b,d}	—	—	—	—
1,1'-Diferrocenoylferrocene	9 (30%) ^{b,d}	—	—	—	—

^a Method (a). ^b Method (b). ^c Ethane and olefin are formed in approximately 60% combined yield, but only 18% ethane can be obtained in pure form due to decomposition of the olefin upon work-up. ^d Of the two carbonyl functionalities only *one* is reduced to the methylene unit (see text).

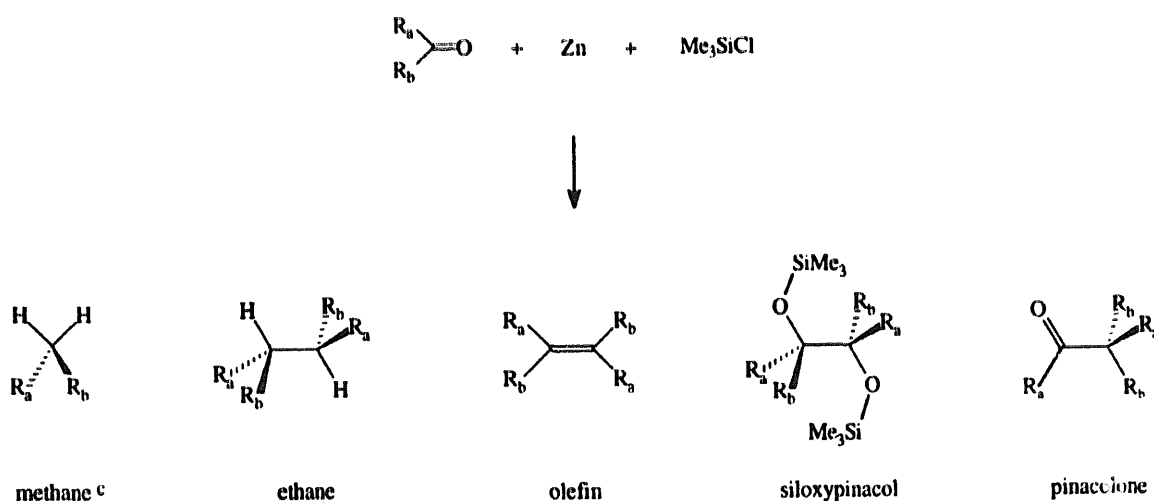
give any reaction! In contrast, using less carefully treated trimethylchlorosilane, for example 'fresh from an unopened bottle', induces reductive coupling of ketones satisfactorily. Therefore, we believe that a catalytic or very low concentration of hydrogen chloride is *necessary* for a successful reaction. Interestingly, it has been observed, that a low hydrogen chloride concentration under otherwise standard Clemmensen conditions (aqueous solvent mixture, no added trimethylchlorosilane) favors the formation of olefins rather than alkanes as the normal products under high acid concentration [13]. Further support for the occurrence of an electrophilic catalysis comes from the recently published very similar low-valent titanium-catalyzed McMurry reaction of oxamides [14].

For the purpose of this study, we therefore tried to perform the reaction of metallocenyl carbonyl substrates with trimethylchlorosilane and zinc at a hydrogen chloride concentration as low as possible. A two-way strategy with (a) catalytic and (b) low HCl concentration was applied: method (a) uses trimethylchlorosilane, which has been distilled once under an atmosphere of

argon prior to use; if no reaction was indicated according to TLC after 24 h, method (b) uses trimethylchlorosilane, to which one droplet of H₂O was added to supply a low HCl amount by partial hydrolysis of trimethylchlorosilane.

2.2. Results

Table 1 summarizes the product yield(s) of the reactions of different metallocenyl carbonyl compounds with trimethylchlorosilane and zinc in THF as solvent according to Scheme 2. As described above, the HCl concentration was kept as low as possible to maximize the yield of the desired olefinic products. Inspection of this table quickly reveals that there are no apparent trends correlating the type of products formed with (i) the steric bulk of the substituents attached to the carbonyl group, (ii) the electronic inductive effect of these substituents, and (iii) the hydrogen chloride concentration according to methods (a) and (b). This is quite unexpected in regard to the otherwise comparable reaction conditions. The desired olefinic products (1), (5),



Scheme 2. Products of trimethylchlorosilane-modified Clemmensen reduction of metallocenyl carbonyl compounds. Subscripts a, b denote different substituents according to Table 1. Subscript c denotes that of the two carbonyl functionalities of 1,1'-disubstituted ferrocenes only one is reduced to the methylene unit.

(7) are formed from ferrocenecarboxaldehyde, diferrocenylketone, ferrocenyl(ruthenocenyl)ketone (although not isolable, see Experimental part), and ferrocindone. The pinacolic products (2) from acetylferrocene and the pinacolone (3) from benzoylferrocene are somehow unexpected, but silylated pinacols have been observed as the sole products of aromatic ketones with Zn–trimethylchlorosilane under ultrasonic irradiation [15]. The facile quantitative conversion of silylated pinacols to rearranged pinacolones in the presence of Lewis acids is also known [15] and 2,2-diferrocenyl-1,2-diphenylethanone (3) has been observed as one of the main products in conventional Clemmensen reductions [16] of benzoylferrocene. Accordingly, in the case

of benzoylferrocene, the pinacolonic product (3) might be formed from an intermediate silylated pinacol by H⁺ promoted rearrangement. Strangely, for 1,1'-disubstituted ferrocenes, no carbon–carbon coupled products are formed. The reaction gives the mono-methylene products (8) and (9) in 30% yield with one of the two carbonyl groups fully reduced to the methylene unit, similar to the expected outcome of the reaction of simple ketones under standard Clemmensen conditions, with minor traces of bismethylene products which can be detected only spectroscopically (see Experimental part). Even under prolonged reaction times, no further reduction of the mono-methylene products could be achieved and unreacted starting material can be recov-

Table 2
Crystal data and structure refinement for 1, 2, 3, 4, 6, 7

	1	2	3	4	6	7
Molecular formula	C ₂₂ H ₂₀ Fe ₂	C ₃₀ H ₄₂ Fe ₂ O ₂ Si ₂	C ₃₄ H ₂₈ Fe ₂ O	C ₄₂ H ₃₈ Fe ₄	C ₄₂ H ₃₈ Fe ₂ Ru ₂	C ₃₄ H ₂₄ Fe ₂
Formula weight	396.08	602.52	564.26	766.12	856.56	544.23
Crystal system	monocline	monocline	monocline	orthorhombic	triclinic	tetragonal
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>Pbcn</i> (No. 60)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 4/ <i>ncc</i> (No. 130)
<i>a</i> (pm)	763.8(2)	1133.8(8)	1067.0(2)	1920.2(4)	1097.1(1)	1481.2(1)
<i>b</i> (pm)	1036.90(10)	1661.8(7)	1651.6(4)	942.6(2)	1132.4(1)	1481.2(1)
<i>c</i> (pm)	1091.7(3)	1587.0(4)	1447.7(2)	1786.2(4)	1535.3(1)	2192.8(6)
α (deg)	90	90	90	90	88.24(1)	90
β (deg)	105.35(2)	91.49(3)	98.84(1)	90	87.28(1)	90
γ (deg)	90	90	90	90	66.64(1)	90
Volume (nm ³)	0.8338(3)	2.989(3)	2.5209(8)	3.2330(12)	1.7489(2)	4.8109(14)
<i>Z</i>	2	4	4	4	2	8
Temperature (K)	293	193	213	293	293	223
Density, calc. (Mg m ⁻³)	1.578	1.339	1.487	1.574	1.627	1.503
Absorption coefficient (mm ⁻¹)	1.738	1.075	1.178	1.790	1.689	1.228
<i>F</i> (000)	408	1272	1168	1576	860	2240
Color, habit	orange platelet	orange prism	yellow prism	yellow prism	orange prism	black block
Crystal size (mm ³)	0.7 × 0.4 × 0.2	0.6 × 0.6 × 0.3	0.3 × 0.15 × 0.1	0.3 × 0.15 × 0.1	0.55 × 0.3 × 0.25	0.6 × 0.45 × 0.35
θ range for data collection (deg)	4.25 to 27.99	4.01 to 25.01	3.10 to 19.99	2.12 to 24.00	5.02 to 27.00	3.21 to 22.00
Index ranges	-1 ≤ <i>h</i> ≤ 9, -1 ≤ <i>k</i> ≤ 13, -14 ≤ <i>l</i> ≤ 14	-7 ≤ <i>h</i> ≤ 8, -17 ≤ <i>k</i> ≤ 19, -18 ≤ <i>l</i> ≤ 18	-6 ≤ <i>h</i> ≤ 10, -15 ≤ <i>k</i> ≤ 15, -13 ≤ <i>l</i> ≤ 13	-1 ≤ <i>h</i> ≤ 25, -1 ≤ <i>k</i> ≤ 13, -27 ≤ <i>l</i> ≤ 1	-1 ≤ <i>h</i> ≤ 13, -13 ≤ <i>k</i> ≤ 14, -19 ≤ <i>l</i> ≤ 19	0 ≤ <i>h</i> ≤ 15, -1 ≤ <i>k</i> ≤ 15, -1 ≤ <i>l</i> ≤ 23
Reflections collected	2429	5150	3081	3281	8735	3275
Independent reflections	1813 (<i>R</i> _{int} = 0.0204)	4000 (<i>R</i> _{int} = 0.0228)	2336 (<i>R</i> _{int} = 0.0454)	2541 (<i>R</i> _{int} = 0.0184)	7557 (<i>R</i> _{int} = 0.0184)	1477 (<i>R</i> _{int} = 0.0438)
Reflections with <i>I</i> > 2 σ (<i>I</i>)	1414	3189	1578	1377	5812	1111
Absorption correction	ψ -scan	ψ -scan	ψ -scan	none	ψ -scan	ψ -scan
Max. and min. transmission	0.840 and 0.685	0.961 and 0.699	0.886 and 0.843	-	0.916 and 0.770	0.924 and 0.793
Refinement method	Full-matrix least squares on <i>F</i> ²	Full-matrix least squares on <i>F</i> ²	Full-matrix least squares on <i>F</i> ²	Full-matrix least squares on <i>F</i> ²	Full-matrix least squares on <i>F</i> ²	Full-matrix least squares on <i>F</i> ²
Data/restraints/parameters	1701/0/109	3997/0/325	2335/0/284	2154/0/208	7557/0/415	1475/0/164
Goodness-of-fit on <i>F</i> ²	1.033	1.048	1.031	0.996	1.123	1.059
Final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0445, <i>wR</i> ₂ = 0.0891	<i>R</i> ₁ = 0.0435, <i>wR</i> ₂ = 0.1062	<i>R</i> ₁ = 0.0455, <i>wR</i> ₂ = 0.0793	<i>R</i> ₁ = 0.0576, <i>wR</i> ₂ = 0.1057	<i>R</i> ₁ = 0.0443, <i>wR</i> ₂ = 0.1270	<i>R</i> ₁ = 0.0347, <i>wR</i> ₂ = 0.0696
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0639, <i>wR</i> ₂ = 0.0996	<i>R</i> ₁ = 0.0611, <i>wR</i> ₂ = 0.1221	<i>R</i> ₁ = 0.0908, <i>wR</i> ₂ = 0.0934	<i>R</i> ₁ = 0.1345, <i>wR</i> ₂ = 0.1361	<i>R</i> ₁ = 0.0651, <i>wR</i> ₂ = 0.1382	<i>R</i> ₂ = 0.0550, <i>wR</i> ₂ = 0.0800
Largest diff. peak and hole (e nm ⁻³)	1170 and -906	445 and -321	363 and -278	365 and -359	1357 and -522	241 and -442

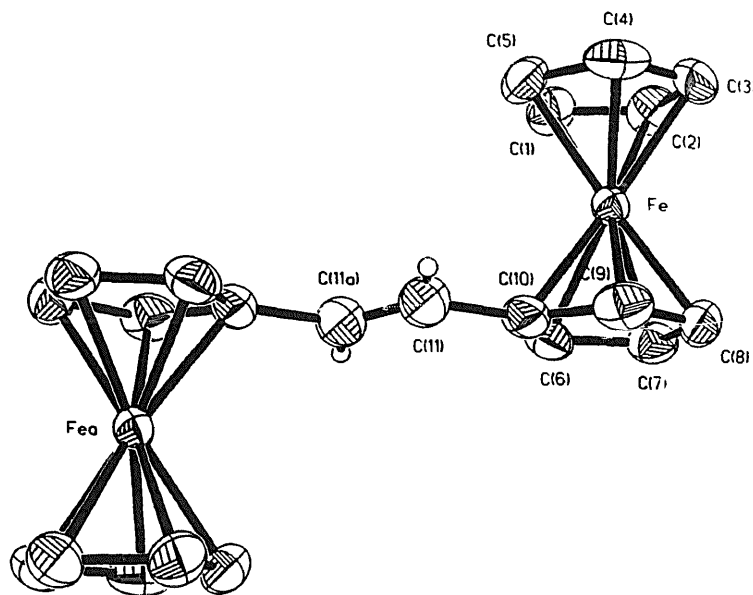


Fig. 1. Molecular structure of 1.

ered. Ethanes (4) and (6) are the often observed aliphatic by-products in reductive carbon–carbon coupling reactions.

Before we address the possible electronic reasons for this product composition in relation to different starting metallocenyl carbonyl substrates, X-ray crystallographic analyses were performed in an attempt to gain further insight into the sterical requirements of the different substituents on the carbon–carbon linkage of products (1)–(9) (Table 2).

trans-1,2-Diferrocenylethylene (1) (Table 2, Fig. 1) crystallizes in the monoclinic space group $P2_1/n$ with two molecules per unit cell and half a molecule in the

asymmetric unit. Each molecule will be produced from the half molecule by a center of symmetry. The cyclopentadienyl rings are planar but deviate slightly (by 2°) from a parallel arrangement. Bond lengths and angles in the ferrocene unit are quite normal; the average Fe–C bond length is 203.8(7) pm, the average C_{ar} – C_{ar} bond length is 141.0(6) pm. The distance between the ring and the ethylene atoms is 147(6) pm, only the length of the double bond with 117(1) pm seems to be unexpectedly short. The reason may be the thermal motion of the ethylene atoms parallel to the ring plane, represented by their anisotropic displacement parameters. The torsion angle between the cyclopentadi-

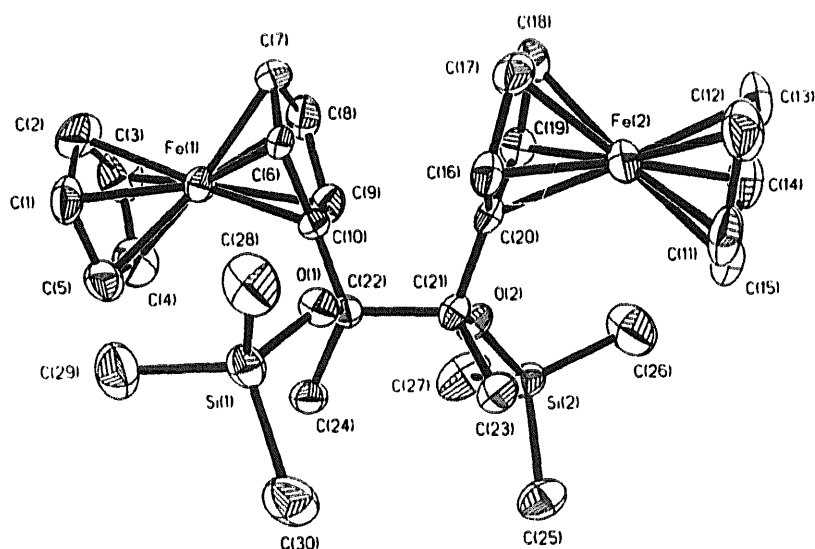


Fig. 2. Molecular structure of 2.

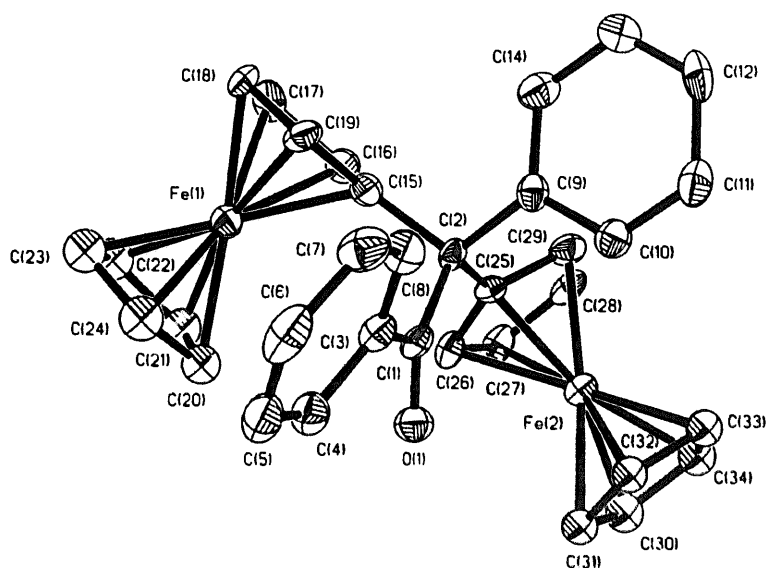


Fig. 3. Molecular structure of 3.

enyl plane and the double bond is 15.1° . Overall, the molecular structure of (1) is in accord with the expectations for a normal and undistorted olefin; the minor deviations from the ideal planarity of the conjugated cyclopentadienyl–ethylene–cyclopentadienyl framework are explicable by crystal forces.

The molecular structure of 2,3-diferrocenyl-2,3-bis(trimethylsiloxy)butane (2) (Table 2, Fig. 2) shows a staggered conformation of the two ferrocenyl and the two trimethylsiloxy substituents in this highly substituted ethane. Bond lengths and angles in the ferrocenyl units are in the normal range and similar to those of the ferrocenyl groups in compound (1). The trimethylsiloxy substituents are in an antiperiplanar arrangement with a torsion angle $O(1)-C(22)-C(21)-O(2)$ of $175.8(3)^\circ$, the ferrocenyl groups are in a synclinal arrangement with a torsion angle $C(10)-C(22)-C(21)-C(20)$ of $46.1(4)^\circ$, and the methyl groups are in an anticlinal arrangement with a torsion angle $C(23)-C(21)-C(22)-C(24)$ of $-66.5(4)^\circ$. The central bond in ethane (2) has a bond length $C(21)-C(22)$ of $158.2(6)$ pm, which is elongated compared with the standard $C(sp^3)-C(sp^3)$ bond length of 153 pm, due to the sterical requirements of the voluminous substituents. Similar values of bond lengths and torsion angles have been observed in other sterically congested 1,2-diferrocenylethanes [17].

2,2-Diferrocenyl-1,2-diphenylethan-1-one (3) adopts a conformation in the solid state (Table 2, Fig. 3) which allows the two ferrocenyl substituents on the quaternary carbon C(2) to be pointed away from each other as far as possible; the sterical hindrance of the substituents on this carbon can be seen in the minor deviations of the bond angles from the idealized tetrahedral angle: $C(1)-C(2)-C(15) = 107.0(5)^\circ$, $C(1)-C(2)-C(25) = 111.2(5)^\circ$,

$C(9)-C(2)-C(15) = 109.5(5)^\circ$, $C(9)-C(2)-C(25) = 108.2(5)^\circ$. In addition, one of the two bonds to the two ferrocenyl groups is slightly elongated ($C(2)-C(15) = 156.8(8)$ pm), whereas all other bond lengths in the molecule are quite unexceptional. The torsion angle of the phenyl plane $C(3)-C(8)$ with the plane of the carbonyl group is $-20.4(8)^\circ$, attributable to sterical hindrance by the neighboring ferrocenyl group of Fe(1).

Tetraferrocenylethane (4) (Table 2, Fig. 4) crystallizes in the orthorhombic space group *Pbcn* with four molecules per unit cell and half a molecule in the asymmetric unit. Each molecule will be produced from the half molecule by a C_2 axis. (4) represents a chiral

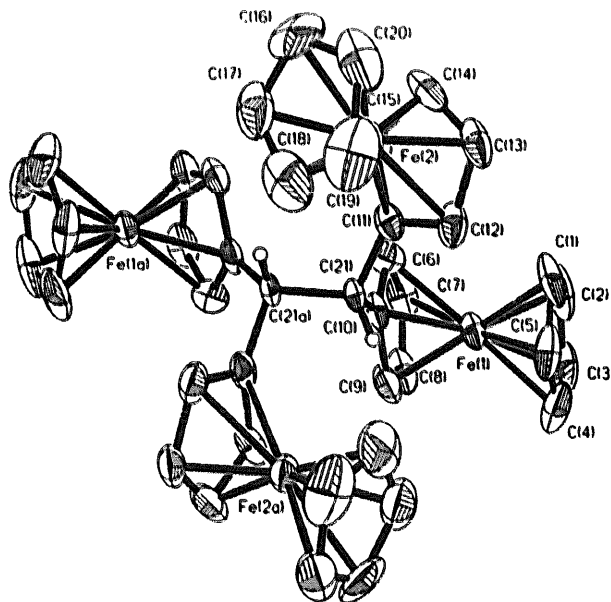


Fig. 4. Molecular structure of 4.

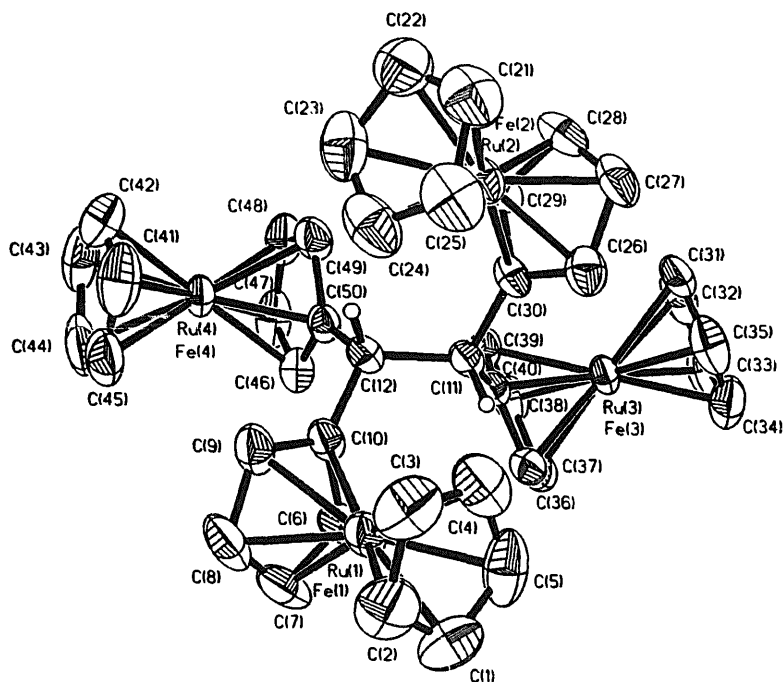


Fig. 5. Molecular structure of 6.

structure, as has been published with similar results [17], but we include our data for comparison with the isostructural 1,2-diferrocenyl-1,2-diruthenocyclohexane (6) (see in the following). The bond length C(21)–C(21a) of the ethane carbons in 4 is 151.6(10) pm, close to the expected value of a normal sp^3 – sp^3 bonding distance; the elongation of this bond to 158 pm [17] is not observed in our crystal structure analysis. The steric requirements of the four ferrocenyl substituents lead to a large torsion angle (H –C(21)–C(21a)– H =

89.6(9)°) of the two hydrogens of the ethane linkage. Otherwise the bonding distances and angles are in the expected range.

The molecular structure of tetraferrocenylethylene (5) is quite unusual. (5) is a helically chiral, strongly twisted, and sterically congested olefin. Structural, spectroscopical and chemical properties have recently been published by us [4] and independently by others [18].

As noted above, the solid state molecular structure of 1,2-diferrocenyl-1,2-diruthenocyclohexane (6) is very

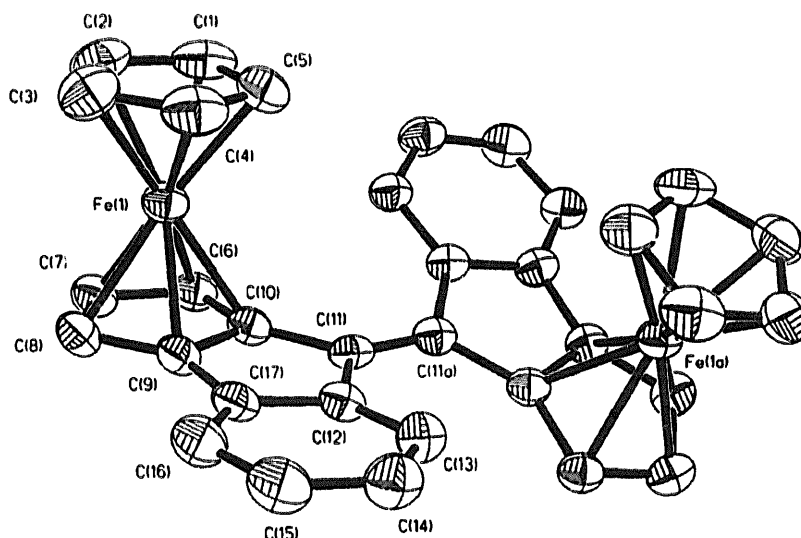


Fig. 6. Molecular structure of 7.

similar to the structure of 1,1,2,2-tetraferrocenylethane (4). In solution, the complex ^1H and ^{13}C NMR spectra suggest the existence of at least three isomers, as can be most easily seen by the observation of six intense singlets in the ^1H NMR spectrum, corresponding to six different unsubstituted cyclopentadienyl rings. From this mixture, suitable single crystals of a mixture of two isomers (Table 2, Fig. 5) could be obtained. The bond length C(11)–C(12) of the ethane carbons is 157.9(6) pm, corresponding to a stretched carbon–carbon single bond. The torsion angle (H–C(11)–C(12)–H) of the ethane hydrogens is 89.4(5)°, identical in value to that observed in tetraferrocenylethane (4). Also, the four metallocenyl substituents are arranged in an analogous manner as in (4) with similar bond and torsion angles, resulting in a chiral molecule in the asymmetric unit. (6) crystallizes as the racemate with one pair of both enantiomers in the unit cell. The ferrocenyl and ruthenocenyl substituents of the former (ferrocenyl)ruthenocenylketone are positionally disordered with a site occupation ratio of 2:1; therefore, in the solid state a mixture of two isomers, which differ only in the metals, but not in the conformation of the ligand spheres of the metallocenes, are observed in the asymmetric unit.

Bis(ferrocoindenylidene) (7) exists in solution as a mixture of cis–trans–syn–anti isomers according to the very complex ^1H and ^{13}C NMR spectra (see Experimental part). From this mixture, single crystals of the trans–syn isomer (Table 2, Fig. 6) could be obtained. (7) crystallizes as the racemate in the tetragonal space group $P4/ncc$ with eight molecules (four pairs of enantiomers) per unit cell and half a chiral molecule per asymmetric unit. Each molecule will be produced from the half molecule by a C_2 axis. The central double bond is elongated (C(11)–C(11a) = 137.4(6) pm) and twisted (angle of plane C(10)–C(11)–C(11a) to plane C(11)–C(11a)–C(10a) is 21.54(46)°), similar in value to other highly strained olefins [4,19]. The two ferrocene systems (ferrocene annealed with indenylidene) are planar with normal bond lengths and angles in the ferrocene part and in the annelated aromatic indenylidene unit.

2.2. Discussion

The crystal structure analyses of compounds (1)–(7) prove the existence of olefins or ethanes which are highly distorted and sterically congested. Therefore, it seems unlikely that steric stress prevents the formation of the desired olefins, because ethanes (4) and (6) were obtained only as by-products (in the case of ferrocenyl-(ruthenocenyl)ketone the corresponding olefin is the main product but, due to the easy oxidation of the ruthenocenyl substituents, only the by-product ethane (6) could be isolated and characterized). Therefore, electronic reasons might be responsible for the diverse outcome of this silicon-mediated reductive coupling

reaction. The metallocenyl substrates in Table 1 are listed approximately in the order of increasing donor strength of the substituents of the carbonyl group (with the exception of 1,1'-disubstituted compounds) and one would expect that the reduction of the carbonyl functionality by elemental zinc to a ketyl radical according to Scheme 1 is facilitated by donor substituents. At the same time, the carbenium-stabilizing properties of metallocenes [7,20] makes the formation of a trimethylsiloxy-substituted carbenium ion by silylation of the carbonyl oxygen likely, similar to the known relatively easy protonation of metallocenyl ketones [7,21], which could be an alternative first step in activation of the carbonyl group. In summary, the electronic influence of the donor substituents should favor initiation of the reaction and therefore product formation. The type of products formed depends obviously on an intermediate later in the mechanistic pathway (see Scheme 1), and the isolation of aliphatic, olefinic, pinacolic, and pinacolonic products suggest that these intermediates are very close in energy, allowing the minor electronic differences of the substrates to direct the reaction to these varying products. The isolation of siloxypinacol (2) and pinacolone (3), which is formed most likely from a precursor siloxypinacol, is a strong argument for the existence of an intermediate III in Scheme 1. However, we have no real explanation for the fact that only for the substrates acetylferrocene and benzoylferrocene are pinacolic products observed, whereas for the other substrates (with the exception of 1,1'-disubstituted compounds) the expected reductive deoxygenation occurs. A possible explanation would be a facilitated extrusion of hexamethyldisiloxane owing to the increased donor capacity of the substituents attached to the former carbonyl group in these substrates. The successful olefin formation from ferrocenecarboxaldehyde, the least substituted substrate, is in contrast with this argument; however, the known higher reactivity of aldehydes compared with ketones might be responsible in this case. 1,1'-Disubstituted ferrocenes behave completely differently; only reduction and no reductive coupling is observed. The role of the proton in either catalytic or low amounts needs further investigation, but it is clear that at some stage in the mechanistic pathway, either according to Scheme 1 or with other intermediates (oxirans, pinacols, carbonyl ylides, etc.), electrophilic catalysis by H^+ is in operation. From a preparative point of view this reaction is useful as an alternative to the McMurry reaction, because the experimental conditions are very simple, although no definite prediction of the outcome can be made and sometimes undesired or unexpected products are formed. Detailed mechanistic investigations are necessary to clarify the (probably) complex mechanism, but this study shows qualitatively that electrophilic catalysis is a necessary requirement for this reaction.

3. Experimental section

All of the reactions were carried out in the absence of air using standard Schlenk techniques and vacuum-line manipulations. Solvents were deoxygenated, purified and dried prior to use. Trimethylchlorosilane was carefully distilled under an atmosphere of argon.

Instrumentation: Bruker AC 200 (^1H and ^{13}C NMR); Nicolet 510 FT-IR (IR); Bruins Instruments Omega 20 (UV-vis); Varian CH-7, Finnigan MAT 95 (MS); Siemens P4 (X-ray). Melting points were determined on a Kofler hot-plate apparatus. Microanalyses were obtained from the Department for Microanalysis, University of Vienna, Austria.

Formylferrocene [22], acetylferrocene [22], 1,1'-diacetylferrocene [22], benzoylferrocene [23], diferrocenylketone [24], 1,1'-bis(ferrocenyl)ferrocene [25], ferrocenyl(ruthenocenyl)ketone [24b], and *rac*-ferrocindenone [26] were either obtained commercially or prepared according to literature procedures.

3.1. Reaction of metallocene carbonyls with trimethylchlorosilane and zinc: general procedure, method (a)

A Schlenk vessel was charged with 100 mg (1.53 mmol) Zn powder, 1.0 ml (8.1 mmol) freshly distilled trimethylchlorosilane, and 30 ml THF. To this stirred suspension was added dropwise a solution of 0.25 mmol metallocenyl carbonyl, dissolved in 15 ml THF. After stirring at 0°C for 2 h, the mixture was poured into water, the organic materials were extracted with three portions of ether, the combined organic layers were washed with water, and dried with CaCl_2 . After removing of all volatile materials in vacuo the product was purified by chromatography on silica. For yields, physical and spectroscopic properties, see below.

3.2. Reaction of metallocene carbonyls with trimethylchlorosilane and zinc: general procedure, method (b)

A round bottom flask was charged with 100 mg (1.53 mmol) Zn powder, 1.00 ml (8.1 mmol) trimethylchlorosilane, 30 ml THF, and 0.25 mmol metallocenyl carbonyl. To this stirred suspension was added one drop of water, to supply a low concentration of HCl by partial hydrolysis of trimethylchlorosilane. The mixture was stirred at ambient temperature. Darkening of the solution indicated start of the reaction, and stirring was continued (1–12 h) until no further change in relative product composition occurred according to TLC analysis. Work-up and purification in an analogous manner as described above yielded the product. For yields, physical and spectroscopic properties, see below.

3.3. X-ray structure determinations of 1, 2, 3, 4, 6, 7

A Siemens P4 diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 71.073$ pm) was

Table 3

Atomic coordinates (10^{-4}) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for 1

	x	y	z	U_{eq}
Fe	283(1)	1704(1)	7895(1)	29(1)
C(1)	-635(6)	3493(4)	7245(4)	45(1)
C(2)	-172(6)	3484(4)	8581(4)	48(1)
C(3)	-1207(7)	2540(5)	8972(4)	52(1)
C(4)	-2362(6)	1959(4)	7878(5)	52(1)
C(5)	-1990(6)	2558(4)	6806(4)	47(1)
C(6)	2396(6)	1263(5)	7168(4)	50(1)
C(7)	2976(5)	1277(4)	8514(4)	44(1)
C(8)	1952(6)	353(4)	8960(4)	43(1)
C(9)	747(6)	-231(4)	7897(4)	46(1)
C(10)	1007(6)	316(4)	6786(4)	47(1)
C(11)	-82(8)	-81(7)	5512(4)	83(2)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. Symmetry transformations used to generate equivalent atoms: $-x, -y, 1-z$.

used for data collection. Crystal data, data collection, and refinement parameters of are summarized in Table 2. The unit cells were determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Data were measured via ω -scan and corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* [27] and an empirical absorption correction [28] was made. The structures were solved by direct methods, SHELXS-86 [29] and refined by a full matrix least squares procedure using SHELXL-93 [30]. All non-hydrogen atoms were refined with anisotropic displacement parameters (Tables 2–8). Hydrogen atoms were placed in calculated positions. The metal atoms in 6 are positionally disordered. They were refined with site occupation 0.666 for Ru(1), Ru(2), Fe(3), Fe(4) and 0.333 for Fe(1), Fe(2), Ru(3), Ru(4) and with equal anisotropic displacement parameters for the metal atoms on the same position. The authors have deposited atomic coordinates for structures 1, 2, 3, 4, 6, 7 with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge, CB2 1EW, UK.

3.4. Data for *trans*-1,2-diferrocenylethylene (1)

Red crystals, 75% yield (method (a)). Spectral and physical properties concur with published data [31]. X-ray structure (Tables 2, 3, Fig. 1): single crystals were obtained from THF.

3.5. Data for 2,3-diferrocenyl-2,3-bis(trimethylsiloxy)butane (2)

Orange crystals, m.p. 162–163°C, 66% yield (method (a)). Anal. Found: C, 59.46; H, 7.40; O, 5.22.

$C_{30}H_{42}Fe_2O_2Si_3$. Calc.: C, 59.80; H, 7.03; O, 5.31%. IR (KBr): cm^{-1} 3095w, 3002w, 2953m, 2900w, 1635w, 1449w, 1412w, 1386w, 1363m, 1260m, 1247s, 1106m, 1082m, 1030m, 1000m, 984m, 836s, 814s, 753m, 709m, 681m, 476s. MS (EI, 70 eV): m/z (%) 602(48) (M^+), 600(1) ($M^+ - 2H$), 587(1) ($M^+ - CH_3$), 511(2) ($M^+ - OSi(CH_3)_3$, $-2H$), 496(4) ($M^+ - OSi(CH_3)_3$, $-2H$, $-CH_3$), 422(19) ($M^+ - 2(OSi(CH_3)_3)$, $-2H$), 300(100) ($M^+ / 2 - H$). 1H NMR ($CDCl_3$) δ 0.23 (s, 18H, $-Si(CH_3)_3$), 1.47 (s, 6H, $-CH_3$), 3.97 (brs, 4H, Cp_{subst}), 4.07 (brs, 14H, Cp_{subst} and $Cp_{unsubst}$). ^{13}C NMR ($CDCl_3$) δ 3.7 ($-Si(CH_3)_3$); 26.4 (CH_3); 65.1, 65.9, 67.6, 68.2, 69.6, 97.9 (ferrocenyl); 82.0 (C–C). X-ray structure (Tables 2, 4, Fig. 2): single crystals were obtained from dichloromethane–*n*-hexane.

Table 4
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for 2

	x	y	z	U_{eq}
Fe(1)	6525(1)	4215(1)	2236(1)	28(1)
Fe(2)	1463(1)	6069(1)	1128(1)	31(1)
Si(1)	3323(1)	2661(1)	966(1)	31(1)
Si(2)	2079(1)	5054(1)	3980(1)	31(1)
O(1)	3405(3)	3562(2)	1371(2)	27(1)
O(2)	2715(3)	4898(2)	3086(2)	28(1)
C(1)	7447(5)	3239(3)	1822(3)	41(1)
C(2)	8213(5)	3879(3)	2020(3)	49(1)
C(3)	8085(5)	4084(3)	2878(3)	53(2)
C(4)	7240(5)	3561(3)	3214(3)	51(2)
C(5)	6840(5)	3041(3)	2557(3)	41(1)
C(6)	5328(4)	4618(2)	1329(2)	26(1)
C(7)	6213(5)	5203(3)	1497(3)	39(1)
C(8)	6170(5)	5409(3)	2361(3)	40(1)
C(9)	5271(4)	4939(3)	2726(3)	33(1)
C(10)	4744(4)	4447(2)	2088(2)	24(1)
C(11)	–273(5)	5827(3)	882(3)	49(1)
C(12)	120(5)	6456(3)	362(3)	54(2)
C(13)	507(5)	7096(3)	889(4)	52(2)
C(14)	373(5)	6844(3)	1736(3)	49(1)
C(15)	–117(5)	6067(3)	1723(3)	44(1)
C(16)	2463(4)	5120(3)	734(2)	30(1)
C(17)	2815(5)	5842(3)	344(3)	38(1)
C(18)	3181(4)	6394(3)	976(3)	37(1)
C(19)	3064(4)	6002(2)	1763(2)	31(1)
C(20)	2643(4)	5216(2)	1622(2)	24(1)
C(21)	2545(4)	4549(2)	2270(2)	23(1)
C(22)	3625(4)	3958(2)	2163(2)	24(1)
C(23)	1356(5)	4116(3)	2185(3)	33(1)
C(24)	3704(4)	3356(2)	2887(2)	30(1)
C(25)	999(5)	4268(3)	4270(3)	48(1)
C(26)	1368(7)	6053(3)	3964(4)	72(2)
C(27)	3293(5)	5034(4)	4787(3)	59(2)
C(28)	3134(5)	2852(3)	–183(3)	51(2)
C(29)	4683(5)	2057(3)	1155(3)	49(1)
C(30)	2037(5)	2092(3)	1351(3)	49(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for 3

	x	y	z	U_{eq}
Fe(1)	2052(1)	6805(1)	5059(1)	24(1)
Fe(2)	1747(1)	5496(1)	8758(1)	23(1)
C(1)	3941(7)	6317(4)	7202(5)	24(2)
C(2)	3104(6)	5584(4)	6836(4)	19(2)
C(3)	5202(7)	6511(5)	6871(4)	24(2)
C(4)	5603(7)	7306(5)	6982(4)	30(2)
C(5)	6738(8)	7546(5)	6727(4)	33(2)
C(6)	7509(7)	6990(6)	6374(5)	37(2)
C(7)	7146(7)	6190(5)	6282(4)	33(2)
C(8)	5988(7)	5960(5)	6514(4)	28(2)
C(9)	3842(7)	4784(4)	6924(5)	22(2)
C(10)	4705(7)	4613(4)	7726(4)	25(2)
C(11)	5350(7)	3888(5)	7848(5)	30(2)
C(12)	5121(7)	3297(4)	7159(5)	31(2)
C(13)	4270(7)	3444(5)	6377(5)	34(2)
C(14)	3614(7)	4173(5)	6255(4)	30(2)
C(15)	2586(7)	7753(4)	5780(4)	23(2)
C(16)	1257(7)	5724(4)	5397(4)	26(2)
C(17)	1191(7)	5810(4)	4409(5)	32(2)
C(18)	2410(7)	5892(4)	4195(4)	29(2)
C(19)	3274(6)	5862(4)	5028(4)	25(2)
C(20)	2287(7)	7793(4)	5922(4)	31(2)
C(21)	1029(7)	7750(4)	5481(4)	34(2)
C(22)	1028(7)	7780(4)	4489(5)	38(2)
C(23)	2289(7)	7851(4)	4345(5)	37(2)
C(24)	3090(7)	7861(4)	5240(5)	38(2)
C(25)	1967(6)	5497(4)	7366(4)	20(2)
C(26)	1089(7)	6107(4)	7554(4)	28(2)
C(27)	65(7)	5733(5)	7910(4)	32(2)
C(28)	303(7)	4887(5)	7954(4)	27(2)
C(29)	1466(7)	4733(4)	7614(4)	27(2)
C(30)	1528(7)	5937(5)	10037(4)	34(2)
C(31)	2544(6)	6331(4)	9708(4)	27(2)
C(32)	3468(6)	5735(4)	9577(4)	25(2)
C(33)	2987(7)	4968(4)	9815(4)	28(2)
C(34)	1813(7)	5114(4)	10107(5)	33(2)
O(1)	3597(4)	6790(3)	7758(3)	29(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3.6. Data for 2,2-diferrocenyl-1,2-diphenylethane-1-one (3)

Red crystals, 62% yield (method (b)). Spectral and physical properties concur with published data [16]. X-ray structure (Tables 2, 5, Fig. 3): single crystals were obtained from dichloromethane–*n*-hexane.

3.7. Data for 1,1,2,2-tetraferrocenylethane (4)

Yellow crystals, 5% yield (method (a)). Spectral and physical properties concur with published data [17]. X-ray structure (Tables 2, 6, Fig. 4): single crystals were obtained from *n*-hexane.

Table 6

Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for 4

	x	y	z	U_{eq}
Fe(1)	6152(1)	9368(1)	8941(1)	36(1)
Fe(2)	3848(1)	5343(1)	8479(1)	37(1)
C(1)	5920(5)	8282(10)	9831(4)	65(3)
C(2)	6196(7)	9637(11)	9989(4)	78(3)
C(3)	6918(6)	9737(11)	9710(5)	69(3)
C(4)	7074(5)	8462(11)	9381(5)	68(3)
C(5)	6451(5)	7568(9)	9445(4)	59(3)
C(6)	5199(4)	9979(8)	8442(4)	43(2)
C(7)	5701(5)	11145(8)	8490(4)	47(2)
C(8)	6357(5)	10736(9)	3142(4)	53(3)
C(9)	6256(4)	9327(9)	7887(4)	49(2)
C(10)	5532(4)	8857(7)	8075(3)	32(2)
C(11)	4671(4)	6902(7)	8447(3)	32(2)
C(12)	4853(4)	5795(8)	8924(4)	44(2)
C(13)	4288(5)	5696(9)	9427(4)	53(2)
C(14)	3743(5)	6724(9)	9276(4)	52(2)
C(15)	3971(4)	7476(8)	8675(3)	42(2)
C(16)	2800(5)	4719(13)	8224(6)	79(3)
C(17)	3220(6)	5001(11)	7622(5)	68(3)
C(18)	3827(6)	4141(11)	7607(5)	76(3)
C(19)	3804(7)	3270(9)	8185(7)	81(3)
C(20)	3165(7)	3602(12)	8587(5)	77(3)
C(21)	5188(3)	7457(7)	7873(3)	30(2)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. Symmetry transformations used to generate equivalent atoms: 1 - x, y, 3/2 - z.

3.8. Data for tetraferrocenylethylene (5)

Red crystals, 73% yield (method (a)). The synthesis, structure, and spectroscopic properties of 5 have recently been published [4,18].

3.9. Data for 1,2-diferrocenyl-1,2-diruthenocyleneethane (6)

Orange crystals, m.p. 235°C, 18% yield (method (a)). In this case, the reaction yields a mixture of orange ethane and purple ethylene in approximately 60% yield, but the attempted separation by chromatography is unsuccessful and only ethane (6) can be isolated in 18% yield by fractionated crystallization from THF-H₂O; the corresponding ethylene is destroyed oxidatively in solution. Anal. Found: C, 58.64; H, 4.49. C₄₂H₃₈Fe₂Ru₂. Calc.: C, 58.89; H, 4.47%. IR (KBr): cm⁻¹ 3085w, 2923w, 1634m, 1457m, 1410m, 1392m, 1299s, 1266s, 1225m, 1102s, 1040s, 1025s, 996s, 936s, 807s, 751m. MS (EI, 70 eV): m/z(%) 856(7) (M⁺), 670(2) (M⁺ - 2Cp - Fe), 612(2) (M⁺ - 2Cp - 2Fe - 2H), 428(100) (M⁺/2), 363(40) (M⁺/2 - Cp), 307(31) (M⁺/2 - Cp - Fe), 242(8) (M⁺/2 - 2Cp - Fe). ¹H NMR (CDCl₃) δ 3.20 (s, 2H, CH-CH); 3.73–4.73 (complex m, 36H, ferrocenyl and ruthenocenyl). ¹³C NMR (CDCl₃) δ 45.2 (CH-CH); 64.8, 65.7, 66.6, 67.1, 68.0, 68.4, 68.5, 68.6, 69.2, 69.6, 69.9, 70.3, 70.6, 70.8, 71.0, 71.7, 72.3, 72.7,

74.0, 74.5, 90.9, 93.0 (Cp_{subst} and Cp_{unsubst} of ferrocenyl and ruthenocenyl). X-ray structure (Tables 2, 7, Fig. 5): single crystals were obtained from THF-H₂O.

3.10. Data for bis(ferrocindenylidene) (7)

Purple crystals, m.p. 155–158°C (dec.), 76% yield (method (a)). Anal. C, 75.03; H, 4.44%. Found: C,

Table 7

Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for 6

	x	y	z	U_{eq}
Ru(1)	2221(1)	2507(1)	7388(1)	43(1)
Fe(1)	2221(1)	2507(1)	7388(1)	43(1)
C(1)	3213(8)	3783(8)	7395(6)	78(2)
C(2)	3646(7)	2891(8)	8089(6)	76(2)
C(3)	2560(8)	3045(8)	8634(5)	74(2)
C(4)	1453(7)	4019(8)	8298(5)	71(2)
C(5)	1854(8)	4472(6)	7531(6)	75(2)
C(6)	1335(5)	2129(6)	6256(4)	50(1)
C(7)	2730(6)	1367(7)	6239(5)	64(2)
C(8)	3014(6)	549(6)	6985(6)	69(2)
C(9)	1808(5)	820(5)	7474(4)	51(1)
C(10)	747(5)	1803(5)	7016(4)	40(1)
Ru(2)	-2345(1)	3715(1)	9347(1)	44(1)
Fe(2)	-2345(1)	3715(1)	9347(1)	44(1)
C(21)	-1975(8)	3391(8)	10706(4)	72(2)
C(22)	-2385(8)	2464(8)	10413(5)	73(2)
C(23)	-1441(8)	1756(6)	9756(5)	72(2)
C(24)	-452(7)	2242(7)	9659(4)	70(2)
C(25)	-782(8)	3266(8)	10244(5)	71(2)
C(26)	-2472(6)	5336(5)	8545(4)	48(1)
C(27)	-3609(7)	5670(6)	9124(4)	57(2)
C(28)	-4287(6)	4888(6)	8934(4)	57(2)
C(29)	-3582(5)	4062(6)	8239(3)	46(1)
C(30)	-2445(5)	4324(5)	7991(3)	37(1)
Ru(3)	-3501(1)	6097(1)	6022(1)	36(1)
Fe(3)	-3501(1)	6097(1)	6022(1)	36(1)
C(31)	-4910(8)	7060(6)	6985(6)	79(3)
C(32)	-5526(6)	7286(7)	6148(7)	78(3)
C(33)	-4888(7)	7876(6)	5619(5)	68(2)
C(34)	-3931(7)	8057(6)	6083(5)	64(2)
C(35)	-3941(7)	7564(6)	6912(5)	65(2)
C(36)	-1484(5)	4948(5)	5759(4)	43(1)
C(37)	-2202(6)	5210(6)	4978(4)	50(1)
C(38)	-3184(6)	4692(5)	5100(4)	47(1)
C(39)	-3087(5)	4144(5)	5949(3)	39(1)
C(40)	-2021(5)	4290(4)	6362(3)	33(1)
Ru(4)	-937(1)	-439(1)	6741(1)	37(1)
Fe(4)	-937(1)	-439(1)	6741(1)	37(1)
C(41)	306(10)	-1488(7)	7708(6)	82(2)
C(42)	-641(9)	-1933(7)	7637(6)	80(2)
C(43)	-596(8)	-2381(6)	6807(6)	76(2)
C(44)	504(10)	-2226(6)	6360(5)	86(3)
C(45)	1035(7)	-1671(6)	6955(7)	76(2)
C(46)	-1150(6)	1146(5)	5935(4)	44(1)
C(47)	-2084(7)	635(5)	5727(5)	59(2)
C(48)	-2908(6)	714(6)	6490(5)	59(2)
C(49)	-2462(5)	1259(5)	7162(4)	49(1)
C(50)	-1383(5)	1554(4)	6811(3)	35(1)
C(12)	-700(4)	2257(4)	7291(3)	33(1)
C(11)	-1439(5)	3770(4)	7245(3)	33(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 8

Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for h7

	x	y	z	U_{eq}
Fe(1)	306(1)	8274(1)	3910(1)	34(1)
C(1)	-1013(3)	8306(3)	3641(2)	53(1)
C(2)	-958(3)	8280(3)	4286(2)	53(1)
C(3)	-472(3)	9043(3)	4482(2)	52(1)
C(4)	-225(3)	9545(2)	3958(2)	49(1)
C(5)	-558(3)	9090(3)	3439(2)	49(1)
C(6)	924(2)	7162(2)	3528(2)	33(1)
C(7)	961(2)	7121(2)	4172(2)	37(1)
C(8)	1423(2)	7899(2)	4401(2)	37(1)
C(9)	1679(2)	8415(2)	3886(2)	33(1)
C(10)	1363(2)	7980(2)	3343(2)	31(1)
C(11)	1672(2)	8496(2)	2803(2)	30(1)
C(12)	2190(2)	9270(2)	3068(2)	31(1)
C(13)	2571(3)	10027(2)	2795(2)	36(1)
C(14)	2961(2)	10693(3)	3150(2)	43(1)
C(15)	2962(3)	10633(3)	3781(2)	45(1)
C(16)	2552(3)	9907(2)	4068(2)	40(1)
C(17)	2174(2)	9235(2)	3713(2)	33(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. Symmetry transformations used to generate equivalent atoms: $-x+1$, $-y+1$, $-z+1/2$.

74.62; H, 4.46. $\text{C}_{34}\text{H}_{24}\text{Fe}_2$. Calc.: UV-vis (THF): $\lambda_{\text{max}}/\log \epsilon$ 275/4.3, 395/4.1, 579/3.7 nm/ $\log \epsilon$. IR (KBr): cm^{-1} 3091w, 3050w, 1692w, 1605m, 1497w, 1462m, 1261m, 1105m, 1053m, 1020m, 1001m, 820m, 804m, 762s, 683w, 559w, 515m, 497m, 463m. MS (EI, 70 eV): $m/z(\%)$ 560(39) (M^+ + oxygen), 544(100) (M^+), 476(13) (M^+ - Cp = 3H), 423(30) (M^+ - Cp - Fe), 301(60) (M^+ - 2Cp = 2Fe - H), 300(62) (M^+ - 2Cp = 2Fe = 2H), 272(63) ($\text{M}^+/2$), 363(40) ($\text{M}^+/2$ - Cp). ^1H NMR (CDCl_3) δ 3.84, 3.91, 4.04 (each signal: s, 5H, $\text{Cp}_{\text{unsubst}}$); 3.76–5.25 (m, Cp_{subst}); 7.01–8.45 (m, aryl). ^{13}C NMR (CDCl_3) δ 70.9, 71.1, 71.7 ($\text{Cp}_{\text{unsubst}}$ of ferrocenyl); 61.4, 61.5, 63.4, 63.9, 66.1, 70.5, 70.9, 71.5, 71.9, 72.1, 72.4, 90.9 (Cp_{subst}); 120.1–144.0 (aryl). X-ray structure (Tables 2, 8, Fig. 6): single crystals were obtained from toluene.

3.11. Data for 1-acetyl-1'-ethyl-ferrocene (8)

Orange oil, 29% yield (method (b)). Spectral and physical properties concur with published data [32]. Besides (8) as the main product, 1,1'-diethylferrocene is obtained in 14% yield with properties in agreement with published data [33].

3.12. Data for 1-ferrocenylmethyl-1'-ferrocenyl-ferrocene (9)

Red crystals, m.p. 142–145°C, 30% yield (method (b)). Anal. Found: C, 64.06; H, 4.76; O, 2.66. $\text{C}_{32}\text{H}_{28}\text{Fe}_3\text{O}$. Calc.: C, 64.48; H, 4.73; O, 2.68%. IR (KBr): cm^{-1} 3091m, 2956m, 2925m, 2856m, 1620s,

1459s, 1291s, 1046m, 820s. MS (EI, 70 eV): $m/z(\%)$ 596.5(100) (M^+), 530.5(100) (M^+ - Cp), 383(46) (M^+ - COFec). ^1H NMR (C_6D_6): δ 3.21 (s, 2H, CH_2), 3.91–3.99 (m, 18H, Cp_{subst} and $\text{Cp}_{\text{unsubst}}$), 4.16–4.21 (m, 4H, Cp_{subst}), 5.00–5.01 (m, 4H, Cp_{subst}). ^{13}C NMR (C_6D_6): δ 29.1 (CH_2), 67.7–72.2 (Cp), C=O: not observed. Besides (9) as the main product, chromatography also yields traces of 1,1'-bis(ferrocenylmethyl)ferrocene, identified by mass spectroscopy.

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