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Homo- and Heterobimetallic Bis(fulvalene) Complexes from Bis(cyclopentadienyl)- and Bis(indenyl)-Substituted Ferrocenes[1,2]

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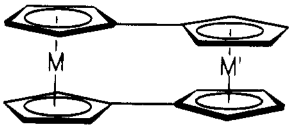
Reactions of dilithioferrocene with tetramethylcyclopentenone and with indan-1-one lead to bis(cyclopentadienyl)- and bis(indenyl)-substituted ferrocenes $Fc(C_5Me_4H)_2$ and $Fc(C_9H_7)_2$ (Fc = 1,1′-ferrocenediyl), respectively. From the dilithium salts of these compounds one obtains, by reactions with $Fe_2Cl_4(THF)_3$ and with $ZrCl_4(THF)_2$, the new ferrocenediyl-bridged complexes $Fc(\eta^5\text{-}C_5Me_4)_2Fe$, $Fc(\eta^5\text{-}C_5Me_4)ZrCl_2$, *rac*-$Fc(\eta^5\text{-}C_9H_6)_2ZrCl_2$, and *rac*-$Fc(\eta^5\text{-}C_9H_6)_2Fe$. The latter two complexes are formed as racemic isomers with a diastereomeric excess of at least 90%. The structures of all new compounds have been determined by X-ray diffraction. $Fc(C_5Me_4H)_2$, $Fc(C_9H_7)_2$, $Fc(\eta^5\text{-}C_5Me_4)_2Fe$, and *rac*-$Fc(\eta^5\text{-}C_9H_6)_2Fe$ display C_2-axial symmetry. $Fc(\eta^5\text{-}C_5Me_4)ZrCl_2$ and *rac*-$Fc(\eta^5\text{-}C_9H_6)_2ZrCl_2$ are fluxional in solution and are the first examples of a new class of ferrocenediyl-bridged *ansa*-zirconocenes.

Introduction

The physicochemical properties of homobimetallic bis(fulvalene)dimetal systems (M = M′ = V, Cr, Fe, Ni, etc.) have been extensively studied, especially in relation to metal–metal interactions,[4] but heterobimetallic compounds of this class have rarely been described.[5]

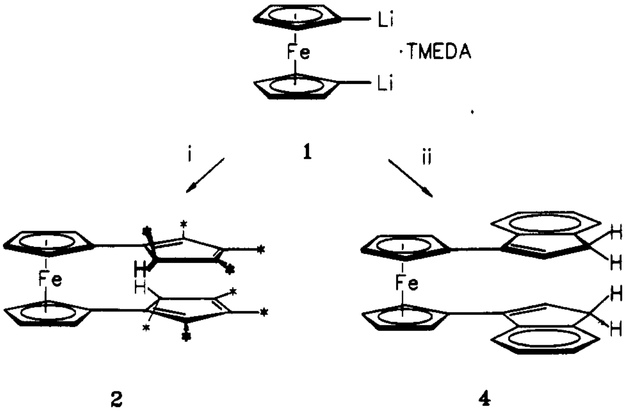


Here we describe the large-scale synthesis of a new, 1,1′-bis(cyclopentadienyl)ferrocene derivative, which allows a controlled synthesis of homo- and heterobimetallic bis(fulvalene)dimetal complexes, as well as a novel 1,1′-bis(indenyl)ferrocene which provides a highly stereoselective route to chiral compounds of this class.

Results and Discussion

Our approach to the preparation of 1,1′-bis(cyclopentadienyl)ferrocene derivatives was to react dilithioferrocene (1)[6] with suitable cyclopentenones. As a first, readily available source of C_5 rings we chose 2,3,4,5-tetramethylcyclopenten-1-one[7] since the methyl substituents make this ketone less susceptible to enolization by the strongly basic dilithioferrocene–TMEDA adduct.[8] Reaction of 1 in ether with 2,3,4,5-tetramethylcyclopentenone, followed by acidic workup and dehydration with *p*-toluenesulfonic acid (see Experimental Section) gave 1,1′-bis(2,3,4,5-tetramethylcyclopentadienyl)ferrocene (2) in ca. 90% yield (Scheme I). 2 was separated from side products such as ferrocene and (2,3,4,5-tetramethylcyclopentadienyl)ferrocene by chromatography in hexane on deactivated basic alumina or by crystallization from hexane.

Scheme I[a]



[a] Key: (i) 2,3,4,5-tetramethylcyclopentenone in diethyl ether, 0 °C, aqueous NH_4Cl, *p*-toluenesulfonic acid; (ii) indan-1-one in toluene, −80 °C, aqueous NH_4Cl, *p*-toluenesulfonic acid.

Compound 2 crystallizes in the monoclinic space group *C*2/*c*. Its molecular structure is shown in Figure 1; essential interatomic distances and angles are listed in Table I. The ferrocene unit is only slightly distorted ($Cp_{cent}\text{–}Fe\text{–}Cp_{cent}$ = 177.2°) to accommodate the cofacial arrangement of the tetramethylcyclopentadienyl rings. A similar orientation was recently reported for 1,1′-bis(3,4-dimethylcyclopentadienyl)ferrocene.[9] The dihedral angle between the mean planes of the ferrocene Cp rings and the attached tetramethyl Cp rings is 24.0°.

Carbon atoms 7 and 7a are chiral and related by C_2 symmetry. Thus compound 2 exists as the *rac* isomer in the solid state. ^1H and ^{13}C NMR spectra (see Experimental Section) are consistent with this structure being retained

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[1] *ansa*-Metallocene Derivatives. 28. For part 27 see ref 2.

[2] *ansa*-Metallocene Derivatives. 27. Chiral Zirconocene Complexes with Two Dimethylsilylene Bridges. Mengele, W.; Diebold, J.; Troll, C.; Röll, W.; Brintzinger, H. H. *Organometallics* **1993**, *12*, 1931.

[3] Present address: School of Chemical and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ.

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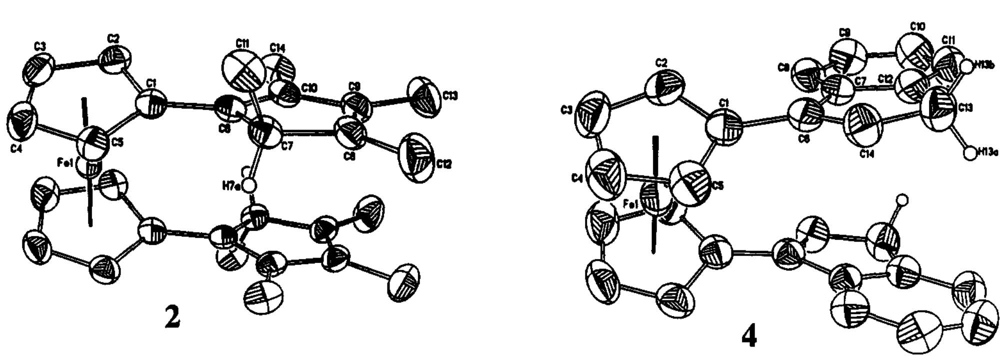


Figure 1. Molecular structures of ligands **2** (left) and **4** (right).

Table I. Selected Distances (pm) and Angles (deg) for Complexes 2 and 4

	2	**4**	**4A**
Fe(1)–C(1)	209.5(3)	206.7(2)	205.7(3)
Fe(1)–C(2)	205.4(3)	203.5(3)	203.9(2)
Fe(1)–C(3)	203.6(3)	203.5(3)	203.5(3)
Fe(1)–C(4)	204.5(4)	204.5(3)	203.5(4)
Fe(1)–C(5)	205.7(5)	205.8(3)	203.7(4)
CR(1)–Fe(1)–CR(1′)[b]	177.2	177.9	179.3
Cp(1)–Cp(2)[c]	24.0	30.5	10.4

[a] **4** and **4A** refer to the two independent molecules in the unit cell. [b] CR(1) and CR(1′) are the centroids of C(1) to C(5) and C(1A) to C(5A), respectively. [c] Cp(1) and Cp(2) are the mean planes of C(1) to C(5) and the C_5 moieties of the indenyl rings, respectively.

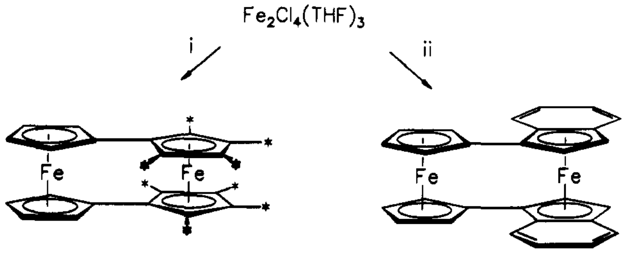
in solution. No cyclopentadienyl hydrogen shift reaction was detected even after weeks in $CDCl_3$ solution.

Treatment of crude **2** (prior to chromatography) in ethereal solution with a slight excess of *n*-butyllithium gave a fine orange precipitate; after filtration and thorough washing with pentane, pure $Li_2[1,1'\text{-}Fc(C_5Me_4)_2]$ (**3**) was obtained in 70% overall yield.[10] By this procedure, which circumvents the isolation of **2** by chromatography, **3** was prepared in 20-g quantities in 2 days from **1**. It can be stored in a glovebox at room temperature for extended periods.

The reaction of lithioferrocene with indan-1-one has been reported to give only a low yield of (3-indenyl)ferrocene.[9] Presumably, enolization of indan-1-one by the strongly basic lithioferrocene is the competing reaction. The presence of TMEDA in **1** is likely to further accentuate this problem. We have studied a variety of conditions and reagents designed to diminish the extent of enolization, including prior reaction of **1** with $CeCl_3$,[11] $TiCl_4$,[12] and $Ti(^iPrO)_3Cl$[13] and direct low-temperature reaction of **1** with indan-1-one. All reactions gave, after protolytic workup and dehydration with *p*-toluenesulfonic acid, clean mixtures of 1,1′-bis(3-indenyl)ferrocene (**4**), (3-indenyl)ferrocene, ferrocene, and indan-1-one in varying proportions. We have found that the highest yields (8–10% by ^{1}H NMR) of **4** are obtained by the latter two procedures (see Experimental Section). **4** was isolated, in ca. 8% yield, by chromatography on deactivated basic alumina in hexane.

Compound **4** crystallizes in the monoclinic space group *C*2/*c*. Figure 1 shows the structure of one of the two independent molecular units, while Table I contains the essential interatomic distances and angles. The dihedral angles between the planes of the ferrocene and indenyl C_5 rings are 30.5 and 10.4° for molecules **a** and **b**, respectively. Both independent molecular units are positioned on a crystallographic C_2 axis which passes through the Fe atom and renders the cofacial indenyl C_5 rings symmetric to each other.

Scheme II[a]



6 **rac–7**

[a] Key: (i) **3** in diethyl ether, 0 °C; (ii) **5** in THF.

The 3*H*-inden-1-yl structure of the indenyl fragments of **4** is retained in solution, as shown by its ^{1}H and ^{13}C NMR spectra. The appearance of only two ferrocenyl CH signals in the NMR spectra of **4** indicates that the indenyl fragments are free to rotate in solution on the NMR time scale and that the appearance of four ferrocenyl CH signals in the NMR spectra of **2** is most likely due to the presence of the chiral tetramethylcyclopentadiene substituents. Treatment of a solution of **4** in diethyl ether with 2 equiv of *n*-butyllithium gave a red microcrystalline precipitate which we presume to be the dilithium salt **5**, although this material was not further characterized.

Ether solutions of **3** and THF solutions of **5** react with $Fe_2Cl_4(THF)_3$ to give moderate yields of the monomeric bis(fulvalene)diiron derivatives $Fc(\eta^5\text{-}C_5Me_4)_2Fe$ (**6**) and *rac*-$Fc(\eta^5\text{-}C_9H_6)_2Fe$ (**7**), respectively (Scheme II).[14] The octamethyl complex **6** is considerably more soluble than the parent bis(fulvalene)diiron[4] and is quite air-stable. The chiral complex *rac*-**7** was formed together with very small amounts of the achiral meso isomer (de ca. 92% by ^{1}H NMR). Single crystals of **6** were obtained by slowly cooling a diethyl ether solution; those of *rac*-**7**, by slow evaporation of a dichloromethane solution in the glovebox.

The diiron complexes **6** and *rac*-**7** crystallize in the space groups $P2_1/c$ and $P2_1/n$, respectively. Their structures are represented in Figure 2; selected distances and angles are given in Table II. In both bases, the C_5 rings of the two ferrocene moieties deviate from coplanarity: The corresponding dihedral angles between adjacent C_5 rings

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(10) Careful hydrolysis of **3** gave a quantitative yield of pure **2**.

(11) Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4392.

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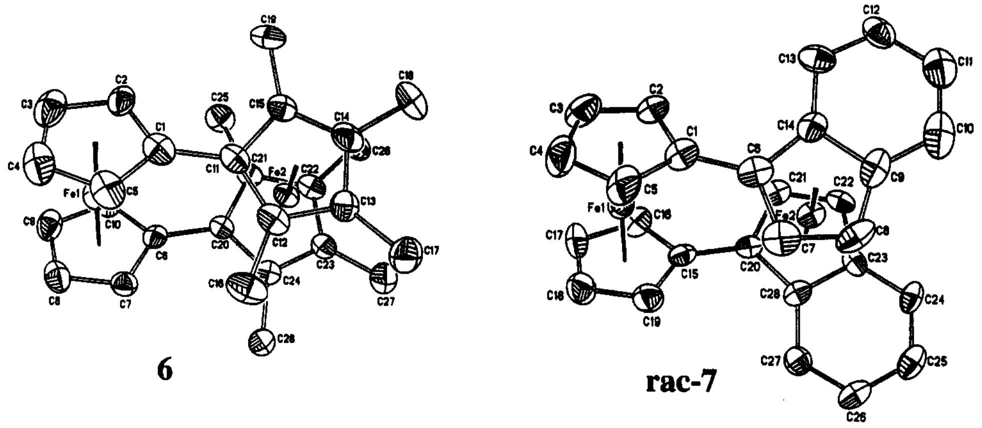
(13) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer-Verlag: Berlin, 1986.

(14) In contrast, the reaction of 1,1′-bis(3,4-dimethylcyclopentadienyl)ferrocene in THF with 2 equiv of lithium butyl followed by $FeCl_2$ is reported to give a mixture of polymeric ferrocenes.[9]



6

rac-7

Figure 2. Molecular structures of complexes 6 (left) and *rac*-7 (right).

Table II. Selected Distances (pm) and Angles (deg) for Complexes 6 and 7

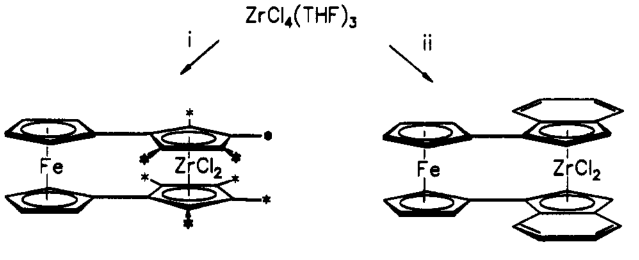
	6		7	7A[a]
Fe(1)–C(1)	206.6(6)	Fe(1)–C(1)	205.8(8)	205.3(8)
Fe(1)–C(2)	203.0(6)	Fe(1)–C(2)	203.6(8)	205.9(8)
Fe(1)–C(3)	205.2(6)	Fe(1)–C(3)	203.7(9)	204.3(9)
Fe(1)–C(4)	204.5(6)	Fe(1)–C(4)	206.2(10)	205.3(10)
Fe(1)–C(5)	205.1(6)	Fe(1)–C(5)	204.0(9)	206.0(9)
Fe(1)–C(6)	204.4(5)	Fe(1)–C(15)	204.4(8)	206.3(8)
Fe(1)–C(7)	202.6(5)	Fe(1)–C(19)	203.7(8)	203.3(8)
Fe(1)–C(8)	204.8(6)	Fe(1)–C(18)	204.3(9)	203.0(8)
Fe(1)–C(9)	205.2(6)	Fe(1)–C(17)	206.3(9)	204.7(8)
Fe(1)–C(10)	206.0(5)	Fe(1)–C(16)	202.9(8)	204.8(7)
Fe(2)–C(11)	204.3(5)	Fe(2)–C(6)	203.8(8)	204.5(8)
Fe(2)–C(12)	205.7(5)	Fe(2)–C(7)	204.0(8)	203.5(7)
Fe(2)–C(13)	206.3(5)	Fe(2)–C(8)	204.2(8)	204.3(7)
Fe(2)–C(14)	207.5(6)	Fe(2)–C(9)	210.9(9)	209.1(7)
Fe(2)–C(15)	205.9(5)	Fe(2)–C(14)	208.9(8)	207.9(8)
Fe(2)–C(20)	204.8(5)	Fe(2)–C(20)	203.8(7)	203.5(7)
Fe(2)–C(21)	205.9(5)	Fe(2)–C(21)	204.3(7)	204.8(7)
Fe(2)–C(22)	206.3(5)	Fe(2)–C(22)	204.6(8)	206.0(8)
Fe(2)–C(23)	207.6(5)	Fe(2)–C(23)	207.2(8)	208.5(8)
Fe(2)–C(24)	206.4(5)	Fe(2)–C(28)	208.3(7)	206.7(7)
Fe(1)–Fe(2)	395.9	Fe(1)–Fe(2)	391.8	390
CR(1)–Fe(1)–CR(1′)[b]	177.3		177.4	177.1
CR(2)–Fe(2)–CR(2′)[c]	178.5		177.5	177.5
Cp(1)–Cp(2)	19.1		29.9	29.2
Cp(1′)–Cp(2′)	21.1		28.6	27.9
Cp(1)–Cp(1′)	3.3		3.3	2.5
Cp(2)–Cp(2′)	3.2		4.7	4.7

[a] 7 and 7A refer to the two independent molecules in the unit cell. [b] CR(*n*) and R(*n*′) are the centroids of the lower and higher numbered C_5 rings, respectively, bonded to Fe(*n*). [c] Cp(*n*) and Cp(*n*′) are the mean planes of the lower and higher numbered C_5 rings, respectively, bonded to Fe(*n*).

are 20° for 6 and 29° for 7, compared to 2.5° in the parent bis(fulvalene)diiron.[15] This is probably due to substantial steric interactions between adjacent C_5 rings. The Fe–Fe distances of 3.96 Å in 6 and 3.91 Å in 7 are just marginally shorter than that of 3.98 Å in bis(fulvalene)diiron, as expected from the twisted geometries of 6 and 7.

The dilithium salts 3 and 5 were further reacted with 1 equival of $ZrCl_4(THF)_2$ in THF solution to give, after purification, $[Fc(\eta^5\text{-}C_5Me_4)ZrCl_2]$ (8) and *rac*-$Fc(\eta^5\text{-}C_9H_6)_2\text{-}ZrCl_2$ (9) in yields of ca. 50% and 42%, respectively (Scheme III). The octamethyl complex 8 is quite air-stable and slightly soluble in pentane; this allows its efficient isolation by Soxhlet extraction. The chiral complex *rac*-9 was formed with high stereospecificity; no achiral *meso*-9 was detected by ^1H NMR spectroscopy. Single crystals of 8 were grown by diffusion of pentane into a THF/toluene solution at 4 °C; those of *rac*-9, by diffusion of ether into a THF solution at 25 °C.

Scheme III[a]



8

rac-9

[a] Key: (i) 3 in THF; (ii) 5 in THF, −80 °C.

Complexes 8 and *rac*-9 crystallize in space groups $P2_12_12_1$ and $P2_1/n$, respectively. Their crystal structures (Figure 3, Table III) show distinct deviations from C_2-axial symmetry. The wedge-shaped geometry of the zirconocene units, with ring centroid–Zr–centroid angles of 138.5 and 129.7°, respectively, requires that the $ZrCl_2$ groups point to one side of the ferrocene-bridged ligand framework; the Cl–Zr–Cl bisector axis thus deviates from the Fe–Zr vector by 39.5° in 8 and by 64.2° in *rac*-9.

The ^1H and ^{13}C NMR spectra of 8 and *rac*-9 are similar to those of 6 and *rac*-7, respectively, indicating that these molecules are averaged to a C_2-axial symmetry on the NMR time scale. The libration of the $ZrCl_2$ groups from one side of these molecules to the other, which renders both sides equivalent in the time average in solution (Figure 4), appears to be fast even at lower temperatures; no significant change was recorded in the ^1H NMR spectrum when toluene-d_8 solutions of 8 and *rac*-9 were cooled to −80 °C.

Conclusions

We have described the efficient syntheses of the ferrocenediyl-bridged $(Cp^*)_2$-type ligand 2 and its dilithium salt 3 and have shown that both parallel (6) and bent (8) metallocene derivatives may be formed. This opens the possibility to prepare, in a controlled manner, additional heterobimetallic derivatives of the bis(fulvalene) type, which are more soluble than the unsubstituted parent complexes, due to their octamethyl substitution.

We have further found that the dilithium salt 5 of the ferrocenediyl-bridged bis(indenyl) ligand 4 forms the chiral complexes *rac*-7 and *rac*-9 with more than 90% de. In this diastereoselectivity, 5 is quite unlike other achiral

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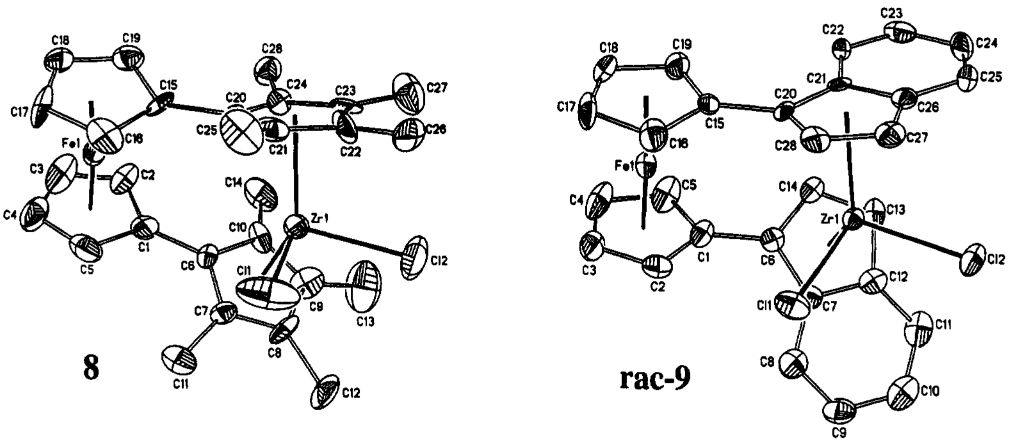

8 **rac-9**

Figure 3. Molecular structures of complexes 8 (left) and *rac*-9 (right).

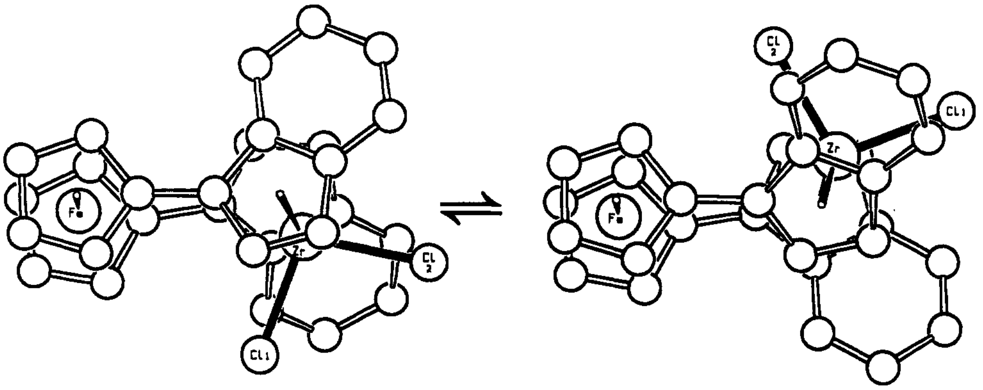

Figure 4. Conformational interchange for complex *rac*-9 in solution.

Table III. Selected Distances (pm) and Angles (deg) for Complexes 8 and 9

	8		9
Fe(1)–C(1)	209.5(15)	Fe(1)–C(1)	205.5(10)
Fe(1)–C(2)	204.4(15)	Fe(1)–C(2)	204.7(11)
Fe(1)–C(3)	204.2(19)	Fe(1)–C(3)	205.2(12)
Fe(1)–C(4)	203.5(19)	Fe(1)–C(4)	204.5(10)
Fe(1)–C(5)	200.1(18)	Fe(1)–C(5)	204.0(9)
Fe(1)–C(15)	205.9(17)	Fe(1)–C(15)	207.5(9)
Fe(1)–C(16)	200.2(18)	Fe(1)–C(16)	203.6(9)
Fe(1)–C(17)	202.7(13)	Fe(1)–C(17)	203.9(10)
Fe(1)–C(18)	203.5(17)	Fe(1)–C(18)	204.3(11)
Fe(1)–C(19)	205.4(17)	Fe(1)–C(19)	204.7(11)
Zr(1)–C(6)	256.3(15)	Zr(1)–C(6)	256.3(8)
Zr(1)–C(7)	257.8(15)	Zr(1)–C(7)	268.6(9)
Zr(1)–C(8)	257.1(16)	Zr(1)–C(12)	264.4(9)
Zr(1)–C(9)	257.5(17)	Zr(1)–C(13)	245.3(7)
Zr(1)–C(10)	260.2(16)	Zr(1)–C(14)	248.8(7)
Zr(1)–C(20)	256.0(14)	Zr(1)–C(20)	252.3(9)
Zr(1)–C(21)	256.6(16)	Zr(1)–C(28)	249.6(9)
Zr(1)–C(22)	253.6(15)	Zr(1)–C(27)	246.4(9)
Zr(1)–C(23)	258.2(16)	Zr(1)–C(26)	255.1(10)
Zr(1)–C(24)	255.5(15)	Zr(1)–C(21)	260.5(9)
Zr(1)–Cl(1)	242.7(6)		241.3(2)
Zr(1)–Cl(2)	242.7(7)		243.2(3)
Fe(1)–Zr(1)	444.8		429.5
Cl(1)–Zr(1)–Cl(2)	94.8		98.6
CR(1)–Fe(1)–CR(1′)[a]	179.2		177.6
CR(2)–Zr(1)–CR(2′)	138.5		129.7
Cp(1)–Cp(2)[b]	15.0		41.3
Cp(1)–Cp(1′)	3.8		3.3
Cp(1′)–Cp(2′)	31.7		12.6
Cp(2)–Cp(2′)	41.5		53.2

[a] CR(*n*) and CR(*n*′) are the centroids of the C_5 rings bonded to Fe (*n* = 1) and Zr (*n* = 2). [b] Cp(*n*) and Cp(*n*′) are the mean planes of the lower and higher numbered C_5 rings, respectively, bonded to Fe (*n* = 1) and Zr (*n* = 2).

bridged bis(indenyl)ligands,[16] resembling more some chiral bis(indenyl)ligand systems which were recently found to be similarly diastereoselective in their complexation reactions.[17] The free ligand 4 was found to adopt a C_2-symmetric, cofacial arrangement of its indenyl fragments in the solid state. A related, ferrocenediyl-bridged ligand system has recently been shown to exist in solution as a $[Cp_2Li]^-Li^+$ sandwich unit.[18] The question thus arises as to whether the unusually stereospecific complex formations with 5 are due to a *chiral* sandwich structure of this dilithium precursor. This is currently under investigation.

Experimental Section

General Comments. Reactions were carried out by standard Schlenk procedures or in a glovebox unless otherwise stated. Solvents were dried by refluxing over CaH_2 (pentane), sodium benzophenone ketyl (ether, THF), or sodium (toluene) and distilled under argon. Dilithioferrocene (TMEDA),[6] 2,3,4,5-tetramethylcyclopent-2-en-1-one,[7] and $ZrCl_4(THF)_2$[19] were prepared by published procedures; $Fe_2Cl_4(THF)_3$ was prepared by Soxhlet extraction of commercial $FeCl_2$ into THF. Indan-1-one (Aldrich) was recrystallized from ether before use. Chlorotriisopropoxytitanium was purchased from Fluka Chemicals and used without purification. Lithium butyl (1.55 M in hexanes) was supplied by Chemetall AG. Basic alumina (pH = 9.5) was deactivated by addition of 6% water. Elemental microanalyses were performed by the microanalysis service of this laboratory. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250 FT

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[16] Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965.

[17] Attachment of chiral groups to bis(indenyl) ligands has been shown to increase the forces favoring one diastereomer: Burk, M. J.; Colletti, S. L.; Halterman, R. L. *Organometallics* **1991**, *10*, 2998. Chen, Z.; Halterman, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 2276. Erickson, M. S.; Fronczek, F. R.; McLaughlin, M. L. *J. Organomet. Chem.* **1991**, *415*, 75. Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11*, 1869.

[18] Eiermann, M.; Hafner, K. *J. Am. Chem. Soc.* **1992**, *114*, 135.

[19] Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

Table IV. Crystallographic and Experimental Data for Complexes 2, 4, and 6–9[a]

	2	**4**	**6**	**7**	**8**	**9**
formula	$C_{28}H_{34}Fe$	$C_{28}H_{22}Fe$	$C_{28}H_{32}Fe_2$	$C_{28}H_{20}Fe_2$	$C_{28}H_{32}Cl_2FeZr$	$C_{28}H_{20}Cl_2FeZr$
fw	426.4	414.3	480.2	468.1	586.5	574.4
cryst col. form	red octahedron	orange rhomb	orange plate	red quader	red rhomb	red cube
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$C2/c$	$C2/c$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
a, pm	1801.9(4)	1398.8(5)	1203.2(5)	1809.7(5)	8623(3)	1286.1(5)
b, pm	1115.0(3)	2043.9(8)	1008.3(4)	1104.8(3)	1359.9(5)	1087.8(4)
c, pm	1356.2(3)	1457.9(5)	1793.1(8)	1965.2(5)	2049.9(8)	1614.7(6)
β, deg	125.61(2)	109.08(3)	90.53(3)	91.55(2)		105.86(3)
V, 10^6 pm^3	2215.2(10)	3939(2)	2175.2(16)	3928(2)	2403.6(17)	2173.1(15)
d_{calcd}, g/cm^3	1.279	1.397	1.466	1.583	1.621	1.756
Z	4	8	4	8	4	4
cryst dimens, mm	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.3	0.4 × 0.2 × 0.1	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.3	0.1 × 0.1 × 0.1
abs coeff (μ), cm^{-1}	6.90	7.74	13.46	14.89	12.69	14.03
T, K	227	296	237	245	296	241
scan range, deg	0.60	0.60	0.60	0.60	0.60	0.90
2θ range, deg	4.0–54.0	4.0–54.0	4.0–54.0	4.0–54.0	4.0–54.0	4.0–54.0
weighting parameter, χ[b]	0.0008	0.0006	0.0004	0.0002	0.0010	0.0002
scan speed, deg/min	2.30–29.30	2.30–29.30	2.30–29.30	2.30–29.30	2.30–29.30	2.30–29.30
no. of data collcd	5280	9119	5262	9313	3002	5226
no. of data obsd	2033	3136	2810	4063	1946	2765
observn criterion	$F > 4.0\sigma(F)$	$F > 4.0\sigma(F)$	$F > 4.0\sigma(F)$	$F > 4.0\sigma(F)$	$F > 4.0\sigma(F)$	$F > 4.0\sigma(F)$
no. of params	132	263	271	541	289	289
R_F[c]	0.040	0.043	0.055	0.062	0.073	0.062
R_{wF}[d]	0.066	0.051	0.056	0.051	0.083	0.056
residual density, 10^{-6} e pm^{-3}	0.40	0.26	0.57	0.54	0.91	0.85

[a] Conditions: Syntex/Siemens P3 four-cycle diffractometer, Mo Kα radiation, λ 71.073 pm, graphite monochromator′ Wyckoff scan mode. [b] $w^1 = \sigma^2(F) + \chi F^2$. [c] $R_F = \sum\|F_o| - |F_c\|/\sum|F_c\delta|$. [d] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum F_o{}^2]^{1/2}$.

Table V. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (pm^2 × 10^{-1}) for Compound 2

	x	y	z	U(eq)[a]
Fe(1)	0	1045(1)	2500	27(1)
C(1)	1071(2)	−23(3)	2801(2)	29(1)
C(2)	1353(2)	709(3)	3831(3)	36(1)
C(3)	1212(2)	1938(3)	3470(3)	42(2)
C(4)	834(2)	1989(3)	2217(3)	40(2)
C(5)	744(2)	790(3)	1805(3)	33(1)
C(6)	1130(2)	−1319(3)	2724(2)	27(1)
C(7)	1205(2)	−1893(3)	1772(3)	31(1)
C(8)	1212(2)	−3210(3)	1996(3)	35(1)
C(9)	1222(2)	−3370(3)	2995(3)	34(1)
C(10)	1173(2)	−2196(3)	3453(3)	31(1)
C(11)	2073(2)	−1495(3)	1898(3)	43(2)
C(12)	1243(3)	−4125(3)	1212(4)	55(2)
C(13)	1261(3)	−4537(3)	3577(4)	51(2)
C(14)	1160(2)	−2065(3)	4544(3)	41(2)

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

Table VI. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (pm^2 × 10^{-1}) for Compound 4

	x	y	z	U(eq)[a]
Fe(1)	0	896(1)	2500	44(1)
C(1)	1103(2)	1475(1)	3440(2)	44(1)
C(2)	1527(2)	1019(1)	2936(2)	54(1)
C(3)	1281(2)	376(1)	3161(3)	64(1)
C(4)	708(3)	432(1)	3786(2)	62(1)
C(5)	588(2)	1103(1)	3959(2)	52(1)
C(6)	1222(2)	2190(1)	3486(2)	41(1)
C(7)	1341(2)	2619(1)	2718(2)	41(1)
C(8)	1358(2)	2487(1)	1793(2)	47(1)
C(9)	1473(2)	2998(2)	1217(2)	57(1)
C(10)	1566(2)	3634(2)	1550(2)	60(1)
C(11)	1540(2)	3774(1)	2470(2)	56(1)
C(12)	1428(2)	3265(1)	3057(2)	46(1)
C(13)	1358(3)	3269(1)	4063(2)	55(1)
C(14)	1245(2)	2560(1)	4248(2)	50(1)
Fe(2)	0	1877(1)	7500	40(1)
C(21)	4(2)	2467(1)	6359(2)	41(1)
C(22)	−880(2)	2067(1)	6107(2)	49(1)
C(23)	−577(3)	1400(1)	6211(2)	58(1)
C(24)	495(3)	1384(1)	6528(2)	60(1)
C(25)	854(2)	2033(1)	6626(2)	52(1)
C(26)	81(2)	3184(1)	6329(2)	40(1)
C(27)	−742(2)	3667(1)	6178(2)	41(1)
C(28)	−1765(2)	3604(1)	6049(2)	51(1)
C(29)	−2366(3)	4164(2)	5858(2)	63(1)
C(30)	−1951(3)	4773(2)	5826(2)	73(1)
C(31)	−931(3)	4840(2)	5985(2)	65(1)
C(32)	−325(2)	4290(1)	6164(2)	50(1)
C(33)	787(3)	4227(2)	6343(2)	61(1)
C(34)	936(2)	3506(1)	6402(2)	50(1)

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

spectrometer operating at 250.16 and 62.90 MHz, respectively. Signal notations: vt, virtual triplet; qm, quartet of unresolved multiplets.

1,1′-Bis(2,3,4,5-tetramethylcyclopentadienyl)ferrocene (2). To a stirred suspension of the TMEDA adduct of dilithioferrocene (20.0 g, 64 mmol) in ether (400 mL) at 0 °C was added 2,3,4,5-tetramethylcyclopenten-1-one (20 mL, 133 mmol) dropwise over ca. 30 min. The suspension slowly dissolved to give a clear orange solution, which was allowed to stir at ambient temperature overnight. It was then hydrolyzed carefully with 5% HCl (2 × 400 mL). The ether layer was separated from the mixture, and *p*-toluenesulfonic acid hydrate (*ca.* 2 g) was added with stirring, which was continued for 2 h. The red ether solution was shaken carefully with saturated aqueous $NaHCO_3$ (2 × 400 mL) and water before drying over $MgSO_4$. Filtration and evaporation gave a red oil which slowly crystallized *in vacuo*. Chromatography of a small portion (*ca.* 1 g) on basic alumina with hexane gave pure 2. Total yield: *ca.* 90% by ^{1}H NMR. ^{1}H NMR ($CDCl_3$): δ 4.36 (m, 2H), 4.15 (m, 4H), 4.08 (m, 2H), 2.67 (qm, 7.6, 1.5 Hz, 2H), 1.96 (d, 1.6 Hz, 6H), 1.82 (br m, 6H), 1.78 (m, 6H), 1.02 (d, 7.6 Hz, 6H). $^{13}C\{^1H\}_{sel}$ NMR ($CDCl_3$): δ 139.7 (s), 138.2 (s), 135.9 (s), 135.0 (s), 83.0 (s), 68.92 (d), 68.87 (d), 68.4 (d), 67.7 (d), 50.2 (d), 16.3 (q), 13.1 (q), 11.9 (q), 11.1 (q). MS (EI): *m/z* 426.6 (M^+, 100%), 306.4 ($M^+ - C_5Me_4H$, 8%), 213.1 (M^{2+}, 7%). Anal. Calcd for $C_{28}H_{34}Fe$: C, 78.85; H, 8.05. Found: C, 78.73; H, 8.01.

Dilithio-1,1′-bis(2,3,4,5-tetramethylcyclopentadienyl)ferrocene (3). The crude reaction product above (ca. 26.5 g) was dissolved in dry ether (400 mL); *n*-butyllithium (90 mL, 1.6 M in hexanes, 144 mmol) was added dropwise over *ca.* 2 h. Approximately halfway through the addition, precipitation of

Table VII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (pm^2 $\times$ 10^{-1}) for Compound 6

	x	*y*	*z*	*U*(eq)[a]
Fe(1)	3714(1)	390(1)	1278(1)	31(1)
Fe(2)	2143(1)	−362(1)	3162(1)	26(1)
C(1)	4008(5)	−1141(6)	2020(3)	35(2)
C(2)	3571(5)	−1615(6)	1323(3)	36(2)
C(3)	4297(6)	−1259(6)	736(4)	50(2)
C(4)	5183(5)	−540(6)	1051(4)	49(2)
C(5)	5025(4)	−466(6)	1837(3)	41(2)
C(6)	2439(4)	1447(5)	1734(3)	27(2)
C(7)	3458(4)	2176(5)	1765(3)	31(2)
C(8)	3859(5)	2366(6)	1035(3)	40(2)
C(9)	3092(5)	1753(6)	535(3)	41(2)
C(10)	2213(4)	1206(5)	961(3)	33(2)
C(11)	3534(4)	−1293(5)	2780(3)	29(2)
C(12)	3806(4)	−508(5)	3426(3)	33(2)
C(13)	3148(5)	−984(6)	4032(3)	34(2)
C(14)	2501(5)	−2069(5)	3764(3)	36(2)
C(15)	2719(4)	−2260(5)	2993(3)	29(2)
C(16)	4656(4)	575(5)	3503(3)	43(2)
C(17)	3186(5)	−483(6)	4820(3)	49(2)
C(18)	1730(5)	−2923(6)	4231(3)	50(2)
C(19)	2259(5)	−3391(5)	2537(3)	42(2)
C(20)	1729(4)	1029(5)	2375(3)	25(2)
C(21)	912(4)	−14(5)	2381(3)	28(2)
C(22)	450(4)	−47(5)	3113(3)	32(2)
C(23)	960(4)	960(5)	3552(3)	30(2)
C(24)	1749(4)	1628(5)	3101(3)	26(2)
C(25)	552(5)	−870(6)	1739(3)	39(2)
C(26)	−448(5)	−982(6)	3376(3)	44(2)
C(27)	677(5)	1308(6)	4338(3)	47(2)
C(28)	2375(4)	2843(5)	3351(3)	33(2)

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

an orange solid began to occur. The mixture was stirred overnight. The solid was isolated by cannula filtration, washed with pentane (2 × 100 mL), and dried *in vacuo*. Yield: 20.0 g, 72% from 1.

1,1′-Bis(3-indenyl)ferrocene (4). Method A. An orange suspension of 1 (4.40 g, 14 mmol) in ether (100 mL) was cooled to −80 °C, and a solution of Ti(^{i}PrO)$_3$Cl (8.0 g, 31 mmol) in ether (100 mL) was added dropwise over 1 h to give a deep red suspension. A solution of indan-1-one (3.7 g, 28 mmol) in ether (50 mL) was added dropwise over 0.5 h and the mixture stirred at −80 °C for 5 h before it was allowed to warm slowly to ambient temperature and stirred overnight. The mixture was hydrolyzed with aqueous KF (which reduces the problem of TiO_2 colloid formation), and the yellow ether layer was filtered and washed with 5% HCl (2 × 100 mL) before stirring with *p*-toluenesulfonic acid (*ca.* 1 g) for 2 h. Washing with saturated $NaHCO_3$ and water, drying over $MgSO_4$, filtration, and evaporation gave an orange-yellow crystalline solid. This was rapidly chromatographed on basic alumina in hexane to give clear bands of ferrocene, (3-indenyl)ferrocene[9] (1.34 g, 32%), and a third orange band, which was recrystallized from hexane to give clear orange plates of 4 (520 mg, 9%).

Method B. Compound 2 (10 g, 32 mmol) was suspended in toluene (200 mL) at −80 °C. A solution of indan-1-one (8.50 g, 64 mmol) in toluene (50 mL) was added dropwise to the stirred suspension. The mixture was stirred at −80 °C for a further 2 h and allowed to warm slowly in the cold bath to room temperature overnight. Deionized water (5 mL) was added to the resultant orange solution and the toluene removed *in vacuo*. Ether (400 mL) and 5% aqueous HCl (200 mL) were added, and the clear orange ether layer was separated from the mixture and stirred with *p*-toluenesulfonic acid (1 g) for 1 h. After most of the ferrocene byproduct had been removed at high vacuum onto a cold finger, the mixture was chromatographed as in method A. Yield: 1.14 g (8.5%). ^{1}H NMR ($CDCl_3$): δ 7.78 (d, 7.3 Hz, 2H), 7.43 (d, 7.0 Hz, 2H), 7.2–7.4 (m, 4H), 6.34 (t, 2.3 Hz, 2H), 4.59 (vt, 3.4 Hz, 4H), 4.29 (vt, 3.4 Hz, 4H), 3.20 (d, 2.2 Hz, 4H). ^{13}C-{^{1}H}$_{sel}$ NMR ($CDCl_3$): δ 144.8 (s), 143.9 (s), 140.5 (s), 129.1 (d), 125.8 (d), 124.4 (d), 123.7 (d), 121.0 (d), 81.5 (s), 69.7 (d), 68.0 (d), 37.9 (t). MS (EI): *m/z* 414.2 (M$^+$, 100%). Anal. Calcd for $C_{28}H_{22}Fe$: C, 81.16; H, 5.36. Found: C, 81.34; H, 5.43.

Table VIII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (pm^2 $\times$ 10^{-1}) for Compound *rac*-7

	x	*y*	*z*	*U*(eq)[a]
Fe(1)	2285(1)	1853(1)	59(1)	34(1)
Fe(2)	2628(1)	−1648(1)	106(1)	29(1)
C(1)	3144(4)	921(8)	−363(4)	34(3)
C(2)	3392(4)	1605(8)	210(4)	40(3)
G(3)	3238(5)	2835(9)	92(5)	52(4)
C(4)	2895(5)	2969(9)	−552(5)	54(4)
C(5)	2830(5)	1774(8)	−836(4)	49(3)
C(6)	3165(4)	−409(8)	−469(4)	34(3)
C(7)	2636(5)	−1061(9)	−879(4)	41(3)
C(8)	2821(5)	−2307(9)	−844(4)	42(3)
C(9)	3479(5)	−2458(8)	−447(4)	39(3)
C(10)	3926(5)	−3477(8)	−244(5)	51(4)
C(11)	4547(5)	−3309(9)	148(5)	53(4)
C(12)	4754(5)	−2127(9)	376(4)	45(3)
C(13)	4341(4)	−1126(9)	219(4)	41(3)
C(14)	3696(4)	−1255(7)	−205(4)	31(3)
C(15)	1651(4)	559(7)	503(4)	31(3)
C(16)	1777(4)	1563(7)	952(4)	38(3)
C(17)	1490(5)	2642(8)	647(5)	44(3)
C(18)	1190(5)	2302(8)	−2(5)	44(3)
C(19)	1287(4)	1027(8)	−86(4)	40(3)
C(20)	1877(4)	−702(7)	648(3)	26(3)
C(21)	2489(4)	−1052(7)	1078(3)	30(3)
C(22)	2555(4)	−2340(8)	1067(4)	31(3)
C(23)	1963(4)	−2806(7)	649(4)	28(3)
C(24)	1763(5)	−4007(7)	448(4)	36(3)
C(25)	1156(5)	−4173(8)	23(4)	43(3)
C(26)	719(4)	−3176(8)	−215(4)	39(3)
C(27)	901(4)	−2006(8)	−48(4)	36(3)
C(28)	1531(4)	−1796(7)	392(3)	28(3)
Fe(1A)	4718(1)	4668(1)	2442(1)	32(1)
Fe(2A)	5110(1)	1206(1)	2592(1)	25(1)
C(1A)	5514(4)	3858(8)	3051(4)	34(3)
C(2A)	5848(4)	4454(9)	2500(5)	51(4)
C(3A)	5645(5)	5716(9)	2541(6)	58(4)
C(4A)	5201(6)	5872(9)	3114(6)	64(4)
C(5A)	5118(5)	4718(9)	3433(5)	50(4)
C(6A)	5533(4)	2542(7)	3209(4)	30(3)
C(7A)	4970(4)	1888(8)	3542(3)	31(3)
C(8A)	5168(4)	663(7)	3586(4)	33(3)
C(9A)	5881(4)	515(8)	3302(4)	33(3)
C(10A)	6352(5)	−509(9)	3205(4)	53(4)
C(11A)	6993(5)	−347(10)	2892(5)	62(4)
C(12A)	7217(5)	808(11)	2668(5)	62(4)
C(13A)	6802(4)	1810(9)	2743(4)	41(3)
C(14A)	6107(4)	1700(8)	3066(4)	33(3)
C(15A)	4166(4)	3277(7)	1946(3)	26(2)
C(16A)	4347(4)	4214(7)	1482(4)	32(3)
C(17A)	4018(4)	5313(8)	1691(4)	36(3)
C(18A)	3632(4)	5080(8)	2292(5)	43(3)
C(19A)	3721(4)	3821(8)	2453(4)	38(3)
C(20A)	4421(4)	2033(7)	1901(3)	24(3)
C(21A)	5085(4)	1656(7)	1581(3)	29(3)
C(22A)	5181(5)	377(8)	1657(4)	36(3)
C(23A)	4546(4)	−65(7)	1991(4)	30(3)
C(24A)	4363(5)	−1242(8)	2207(4)	41(3)
C(25A)	3745(5)	−1428(8)	2569(4)	44(3)
C(26A)	3276(4)	−429(8)	2733(4)	37(3)
C(27A)	3423(4)	731(8)	2535(3)	31(3)
C(28A)	4072(4)	945(7)	2152(3)	25(2)

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

1,1′-Ferrocenediylbis(η^5-2,3,4,5-tetramethylcyclopentadienyl)iron (6). A suspension of 3 (2 g, 4.6 mmol) in ether (50 mL) at 0 °C was stirred while a suspension of $Fe_2Cl_4(THF)_3$ (1.08 g, 2.3 mmol) in ether (50 mL) was added dropwise over 0.5 h. Stirring was continued at ambient temperature overnight. The mixture was then hydrolyzed with water to give a red ether layer. This layer was filtered to remove an insoluble red solid before washing thoroughly with water and drying with $MgSO_4$. The solution

Table IX. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (pm^2 × 10^{-1}) for Compound 8

	x	*y*	*z*	*U*(eq)[a]
Zr(1)	7760(2)	9469(1)	1575(1)	27(1)
Fe(1)	11148(3)	11135(2)	369(1)	28(1)
Cl(1)	5553(6)	10338(5)	1119(3)	76(2)
Cl(2)	6219(9)	8447(5)	2298(3)	89(3)
C(1)	10430(22)	9686(11)	200(8)	36(6)
C(2)	12090(21)	9767(10)	251(8)	34(5)
C(3)	12626(22)	10390(13)	−233(10)	49(7)
C(4)	11403(29)	10789(15)	−591(9)	66(9)
C(5)	10009(24)	10388(13)	−322(9)	45(6)
C(6)	9303(18)	9057(10)	542(7)	23(5)
C(7)	7768(18)	8878(11)	380(7)	28(4)
C(8)	7209(20)	8107(10)	737(8)	33(5)
C(9)	8408(21)	7738(12)	1144(10)	43(6)
C(10)	9775(20)	8302(11)	1034(7)	29(5)
C(11)	6832(22)	9369(14)	−156(8)	47(7)
C(12)	5592(24)	7649(13)	731(10)	56(8)
C(13)	8363(31)	6809(15)	1548(12)	94(11)
C(14)	11364(22)	8001(14)	1240(9)	52(7)
C(15)	10312(18)	11539(10)	1270(8)	25(5)
C(16)	9641(23)	12099(12)	746(8)	37(6)
C(17)	10803(21)	12608(10)	412(8)	36(6)
C(18)	12152(22)	12388(12)	709(8)	38(5)
C(19)	11895(19)	11738(13)	1232(8)	36(6)
C(20)	9456(16)	10983(10)	1782(7)	20(4)
C(21)	8000(19)	11212(12)	2043(7)	32(5)
C(22)	7680(20)	10566(13)	2576(6)	35(5)
C(23)	9024(21)	9969(13)	2668(8)	39(6)
C(24)	10122(18)	10194(11)	2154(7)	26(5)
C(25)	7052(21)	12125(12)	1892(8)	45(6)
C(26)	6031(19)	10627(16)	3012(8)	50(7)
C(27)	9182(28)	9249(13)	3211(9)	61(8)
C(28)	11760(18)	9857(12)	2192(9)	37(6)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table X. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (pm^2 × 10^{-1}) for Compound *rac*-9

	x	*y*	*z*	*U*(eq)[a]
Zr(1)	3001(1)	351(1)	1429(1)	18(1)
Fe(1)	2668(1)	−3473(1)	745(1)	24(1)
Cl(1)	3666(2)	−697(2)	2788(1)	35(1)
Cl(2)	3221(2)	2457(2)	1953(2)	34(1)
C(1)	1507(7)	−2474(8)	1104(6)	27(3)
C(2)	2095(8)	−3229(9)	1798(6)	35(4)
C(3)	1974(9)	−4475(9)	1530(7)	45(4)
C(4)	1320(8)	−4515(9)	664(7)	47(4)
C(5)	1031(7)	−3255(9)	400(7)	41(4)
C(6)	1383(6)	−1121(8)	1084(5)	23(3)
C(7)	1149(6)	−367(9)	1746(5)	26(3)
C(8)	1012(7)	−642(9)	2564(6)	35(4)
C(9)	728(7)	270(10)	3023(6)	40(4)
C(10)	550(7)	1505(10)	2698(7)	40(4)
C(11)	719(7)	1789(9)	1932(7)	40(4)
C(12)	988(6)	862(9)	1419(6)	27(3)
C(13)	1165(6)	854(8)	566(6)	26(3)
C(14)	1331(6)	−390(8)	367(5)	23(3)
C(15)	3810(7)	−2305(8)	476(6)	24(3)
C(16)	4293(7)	−3178(8)	1117(6)	34(4)
C(17)	4062(7)	−4379(8)	763(7)	36(4)
C(18)	3411(8)	−4250(8)	−95(6)	35(4)
C(19)	3252(8)	−2972(8)	−265(6)	32(3)
C(20)	3966(6)	−970(7)	588(5)	21(3)
C(21)	3510(6)	3(7)	−9(5)	20(3)
C(22)	2787(7)	36(7)	−838(5)	23(3)
C(23)	2523(8)	1150(9)	−1255(6)	35(4)
C(24)	3005(8)	2261(9)	−846(6)	37(4)
C(25)	3730(8)	2264(8)	−58(6)	33(4)
C(26)	4021(7)	1127(8)	381(5)	23(3)
C(27)	4764(7)	831(8)	1179(6)	27(3)
C(28)	4772(6)	−423(9)	1289(5)	24(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

was reduced in volume until the onset of crystallization and was then heated slightly before filtration. The solution was cooled to −20 °C to give thick red plates. Yield: 0.45 g, 20%. ^{1}H NMR (CDCl$_3$): δ 5.46 (vt, 3.7 Hz, 4H), 3.93 (vt, 3.7 Hz, 4H), 2.62 (s, 12H), 1.58 (s, 12H). ^{13}C{^{1}H}$_{sel}$ NMR (CDCl$_3$): δ 95.4 (s), 86.8 (s), 82.1 (s), 79.1 (s), 71.1 (d), 65.6 (d), 12.0 (q), 9.5 (q). MS (EI): *m/z* 480.3 (M$^+$, 100%), 240.1 (M^{2+}, 38%). Anal. Calcd for $C_{28}H_{32}Fe_2$: C, 70.02; H, 6.73. Found: C, 69.78; H, 6.86.

***rac*-[1,1′-Ferrocenediylbis(1-η^5-indenyl)]iron (7).** A solution of 4 (160 mg, 0.39 mmol) in diethyl ether (10 mL) was stirred while lithium butyl (0.5 mL, 0.8 mol) was added over 5 min. The orange solution turned red overnight and deposited a red precipitate. The volatiles were removed *in vacuo*, and the pyrophoric residue (largely 5) was dissolved in THF (20 mL). This solution was transferred onto solid $Fe_2Cl_4(THF)_3$ (180 mg, 0.38 mmol) and the mixture stirred overnight to give a dark purple solution. After removal of volatiles, the residue was extracted with toluene (50 mL), the extract was filtered, and the volume was slowly reduced to *ca.* 3 mL to yield a microcrystalline purple solid, which was isolated by filtration and dried *in vacuo* (88 mg, *ca.* 50%). Slow evaporation of a dichloromethane solution in the glovebox gave analytically pure purple rhombohedra. ^{1}H NMR (CDCl$_3$): δ 8.13 (d, 8.9 Hz, 2H), 7.45 (d, 8.7 Hz, 2H), 7.27 (dd, 7.8, 8.0 Hz, 2H), 6.97 (dd, 8.1, 7.8 Hz, 2H), 6.10 (m, 2H), 5.27 (m, 2H), 4.88 (d, 2.5 Hz, 2H), 4.50 (m, 2H), 3.96 (m, 2H), 3.63 (d, 2.5 Hz, 2H). ^{13}C{^{1}H}$_{sel}$ NMR (CDCl$_3$): δ 130.1 (d), 128.7 (d), 124.9 (d), 122.9 (d), 92.7 (s), 85.53 (s), 85.45 (s), 83.7 (s), 77.2 (d), 72.5 (d), 70.5 (d), 69.2 (d), 65.9 (d), 65.2 (d). MS (EI): *m/z* 468.3 (M$^+$, 100%), 234.1 (M^{2+}, 45%). Anal. Calcd for $C_{28}H_{20}Fe_2$: C, 71.83; H, 4.31. Found: C, 71.00; H, 4.11.[20]

1,1′-Ferrocenediylbis(η^5-2,3,4,5-tetramethylcyclopentadienyl)zirconium Dichloride (8). A suspension of $ZrCl_4(THF)_2$ (4.3 g, 11.4 mmol) in THF (50 mL) was added dropwise over 1 h to a solution of 3 (5 g, 11.4 mmol) in THF (150 mL) at ambient temperature. The mixture was stirred overnight and then transferred onto dry Kieselguhr (3 g) before evaporation of volatiles. The red solid thus obtained was transferred into the thimble of a Soxhlet apparatus and extracted with pentane (300 mL) over 3 days. The red pentane extract was cooled to −80 °C to complete precipitation of the analytically pure, air-stable red solid. Yield: 3.1 g, 46%. Further crystallization from toluene at −20 °C gave red needles. ^{1}H NMR (CDCl$_3$): δ 4.89 (vt, 3.8 Hz, 4H), 4.20 (vt, 3.8 Hz, 4H), 2.45 (s, 12H), 2.01 (s, 12H). ^{13}C{^{1}H}$_{sel}$ NMR (CDCl$_3$): δ 130.7 (s), 126.8 (s), 122.3 (s), 84.7 (s), 70.7 (d), 68.3 (d), 14.3 (q), 13.0 (q). MS (EI): *m/z* 586.1 (M$^+$, 100%). Anal. Calcd for $C_{28}H_{32}Cl_2FeZr$: C, 57.33; H, 5.51. Found: C, 57.51; H, 5.62.

***rac*-[1,1′-Ferrocenediylbis(1-η^5-indenyl)]zirconium Dichloride (9).** The dilithium salt 5 was prepared as above from 4 (650 mg, 1.57 mmol) and dissolved in THF (40 mL). The solution was cooled to −80 °C and stirred while $ZrCl_4(THF)_2$ (590 mg, 1.56 mmol) in THF (20 mL) was added dropwise over 15 min. The mixture was allowed to warm slowly and was stirred at ambient temperature overnight to give a purple solution and a small amount of purple precipitate. The volatiles were removed *in vacuo*, the residue was extracted with diethyl ether (100 mL), and the extract was filtered and reduced in volume to 20 mL. Cooling to −20 °C overnight gave a flocculant precipitate which was removed by filtration. The filtrate was cooled slowly to −80 °C to give purple cubes (340 mg, 42%). ^{1}H NMR (C_6D_6): δ 7.85 (d, 8.2 Hz, 2H), 7.55 (d, 8.3 Hz, 2H), 7.07 (dd, 8.0, 7.8 Hz, 2H), 6.90 (dd, 8.1, 7.8 Hz, 2H), 6.66 (d, 2.5 Hz, 2H), 5.67 (br d, 2.5 Hz, 2H), 5.18 (m, 2H), 4.74 (m, 2H), 4.02 (m, 2H), 3.94 (m, 2H). ^{13}C{^{1}H}$_{sel}$ NMR (C_6H_6): δ 127.2 (d), 126.5 (s), 126.4 (d), 126.1 (s), 124.9 (d), 124.2 (d), 123.5 (d), 116.2 (s), 106.4 (d), 83.9 (s), 69.9 (d), 69.0 (d), 67.9 (d), 67.7 (d). MS (EI): *m/z* 574.2 (M$^+$, 100%). Anal. Calcd for $C_{28}H_{20}Cl_2FeZr$: C, 58.54; H, 3.51. Found: C, 57.45; H, 3.59.[20]

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(20) The low carbon value of these elemental analyses is ascribed to the partial formation of metal carbides in the combustion process, which is occasionally observed with organometallic complexes of this type.

Crystal Structure Determinations. Diffraction data collection and solution and refinement of the structures were conducted as summarized in Table IV. Atom coordinates and thermal parameters obtained are listed in Tables V–IX.

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Supplementary Material Available: Additional structural diagrams and tables of structure determination details, bond lengths, bond angles, anisotropic displacement coefficients, and hydrogen coordinates and isotropic displacement coefficients (53 pages). Ordering information is given on any current masthead page. Additional crystallographic data for these six compounds are available on request from Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2, Germany, upon quotation of Deposit Nos. CSD-56823 and CSD-56863, the authors, and the journal reference for this article.

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