REACTION OF ZIRCONACYCLOPENTADIENES WITH ETHYNYLFERROCENES

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Various zirconacyclopentadienes fully substituted at the metallacycle react with ethynyl-ferrocene in the presence of $[NiBr_2(PPh_3)_2]$ or with methyl or ethyl 3-ferrocenylpropynoates in the presence of CuCl to give penta- and hexasubstituted phenylferrocenes, respectively. X-Ray diffraction analysis showed that the cyclopentadienyl and benzene rings in (5,8-di-phenyl-1,2,3,4-tetrahydronapthalen-6-yl)ferrocene are rotated by as much as 51°.
Keywords: Arenes; Zirconium; Zirconocene; Alkynes; Ferrocene; X-Ray diffraction; DFT calculations; Cyclotrimerizations; Cycloadditions.

Transition-metal induced cyclotrimerization of alkynes is one of the most powerful methods for the C–C bond formation because it allows to convert in one step three (different) alkynes into a single, aromatic molecule[1]. Formally, the cyclotrimerization can be carried out in a concerted or a step-wise manner using a catalytic or stoichiometric amount of a transition metal compound. Both approaches are suitable for the preparation of substituted benzene derivatives but suffer from some drawbacks: the former method is usually used in co-cyclotrimerization of diynes with alkynes to give benzofused compounds while the latter is the method of choice for the preparation of defined, unsymmetrically penta- and hexasubstituted

benzenes. Thus, highly substituted benzenes are conveniently obtained in good to high yields from a reaction of zirconacyclopentadienes[2] with alkynes in the presence of a stoichiometric amount of CuCl (ref.[3]) or $[NiCl_2(PPh_3)_2]$ (ref.[4]). This approach has been utilized in the synthesis of benzoheterocycles containing group-14 elements[5], haloterphenyls[6], haloterphenyls with a chiral backbone[7], perfluoroalkyl-substituted terphenyls[8], and polyacenes[9]. A number of substituted alkynes have been used as the reaction partner in the reaction of zirconacyclopentadienes; however, there is still a lack of general information on the relationship between the reactivity and structure of the alkyne, namely on the influence of steric effects of the substituents attached to the triple bond. In this regard, a study on steric and electronic effects in Dötz benzannulation involving aromatic alkynes may serve as a rather rare example[10]. A study of such effects has a direct implication for organic synthesis since a successful reaction of zirconacyclopentadienes with sterically hindered alkynes could provide an alternative route to potentially atropoisomeric biaryls and highly substituted arenes that have been recently targeted as potential models for molecular mechanics (nanotechnology)[11]. One of the interesting substrates for such a venture are ethynylferrocenes owing to the bulkiness and redox activity of the ferrocene unit. Reports on the use of ethynylferrocenes in cyclotrimerization are still scarce[12] and only the recent study on their catalytic cocyclotrimerization with diynes showed their unique properties[13]. The aim of this work is to study the scope of the Ni- and Cu-catalyzed reactions between zirconacyclopentadienes and various ethynylferrocenes with respect to the alkyne substitution pattern.

RESULTS AND DISCUSSION

The reactions of zirconacyclopentadienes[2] with ethynylferrocenes were carried out in the presence of $[NiCl_2(PPh_3)_2]$ and CuCl. The difference between Cu- and Ni-mediated reactions is that the former reaction proceeds only with alkynes bearing at least one electron-withdrawing group (CO_2R, CHO, CN, *etc.*) attached to the triple bond whereas the latter proceeds with any alkyne regardless of the nature of its substituents. In the former case, the reaction is likely initiated by conjugated addition of an organocopper intermediate onto the activated triple bond followed by a radical decomposition accompanied with ring closure[3b]. In the latter case, the arene formation begins with insertion of the alkyne into the Ni–C bond and is completed *via* reductive elimination[4]. In the view of the foregoing, we have carried out the reactions of zirconacyclopentadienes with ethynylferrocene in the pres-

ence of a Ni(II) complex and those with esters of (carboxyethynyl)ferrocene in the presence of CuCl (Scheme 1, Table I).

SCHEME 1

1

2, R^1 = H
3, R^1 = COOEt
4, R^1 = COOMe

5, R^1 = H
6, R^1 = COOEt
7, R^1 = COOMe

CuCl
or
[NiCl$_2$(PPh$_3$)$_2$]
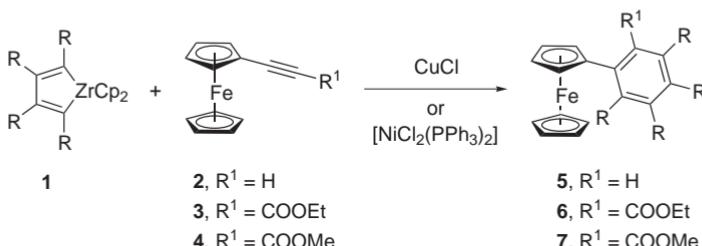
The reaction of tetraethylzirconacyclopentadiene (**1**; R = Et, Cp = η^5-cyclopentadienyl) and tetrapropylzirconacyclopentadiene (**1**; R = Pr) with ethynylferrocene (**2**) proceeded smoothly to give the desired products **5a** and **5b** as viscous liquids in 57 and 35% isolated yields, respectively. It is not clear why the yield of the product was substantially lower in the latter case; however, one cannot exclude that different steric requirements of Et and Pr groups may account for the difference in the yields of the respective arenes **5**. The reaction of tetraphenylzirconacyclopentadiene (**1**; R = Ph) afforded compound **5c** in only a low isolated yield albeit a NMR analysis of the crude reaction mixture revealed that the product was formed in at least 30% yield. The low isolated yield likely results from problems during separation of **5c** from side products: it was very difficult to obtain a reasonable amount of **5c** free of hexaphenylbenzene, which was clearly identified as a major side-product by ^{1}H and ^{13}C NMR spectra[14,15]. The reaction of 1-zircona-2,5-diphenylbicyclo[4.3.0]nona-2,4-diene with **2** gave 15% of compound **5d**. Again, the actual yield was *ca* 30% but the compound was difficult to separate from unindentified side products. The structure of **5d** (Fig. 1) was confirmed by X-ray diffraction analysis (*vide infra*).

A similar behaviour was observed also in the case of reaction of zirconacyclopentadienes with esters of carboxyethynylferrocene **3** and **4**. The reaction of tetramethylzirconacyclopentadiene (**1**; R = Me) with 3-ethoxy-3-oxo-1-propynylferrocene (**3**) resulted in the formation of **6** in 26% yield. On the other hand, the reaction of tetramethylzirconacyclopentadiene with 3-methoxy-3-oxo-1-propynylferrocene (**4**) gave **7a** in 17% isolated yield, though the ^{1}H NMR spectrum of the reaction mixture clearly indicated that it had been formed in 66% yield. Interestingly, product **7a** was rather unstable compared with other studied phenylferrocenes and slowly decomposed during isolation and upon standing. The reaction of tetraethylzirconacyclopentadiene with **4** gave benzoate **7b** in 32% yield while the reaction

T<small>ABLE</small> I
Reaction of zirconacyclopentadienes with ethynylferrocenes

Zirconacyclo-pentadiene	Ethynyl-ferrocene	Cu or Ni compound	Product		Isolated yield %
	2	[NiCl$_2$(PPh$_3$)$_2$]		**5a**	57
	2	[NiCl$_2$(PPh$_3$)$_2$]		**5b**	35
	2	[NiCl$_2$(PPh$_3$)$_2$]		**5c**	20
	2	[NiCl$_2$(PPh$_3$)$_2$]		**5d**	15
	3	CuCl		**6**	26
	4	CuCl		**7a**	17
	4	CuCl		**7b**	32
	4	CuCl		**7c**	10
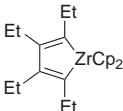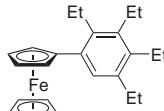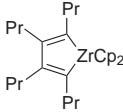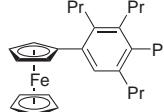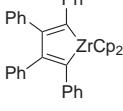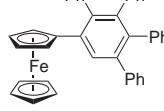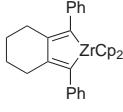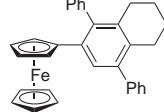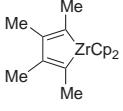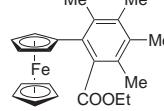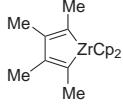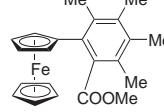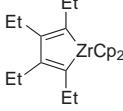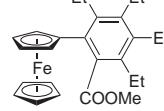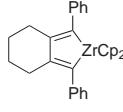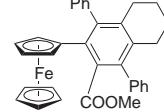
of 1-zircona-2,5-diphenylbicyclo[4.3.0]nona-2,4-diene with the same substrate furnished **7c** in only a low, 10% yield.

As to the reaction with other ethynylferrocenes, the obtained results were rather disappointing; no phenylferrocenes were formed in Ni-mediated reactions of tetraethylzirconacyclopentadiene with substituted ethynylferrocenes FcC≡CR (Fc = ferrocenyl and R = Me, SiMe$_3$, C(O)Me, and CO$_2$Et). It remains yet unclear whether this is a result of steric hindrance due to the two groups attached to the triple bond, which prevents the insertion into the Ni–C bond, or it is caused by other, possibly electronic, effects. The respective arene was not formed in the case of Cu-mediated reaction between tetraethylzirconacyclopentadiene and FcC≡CC(O)Me either[16]. This is rather surprising since no problems were observed in similar reactions with other alkynylketones[3b].

Although the presented isolated yields of the phenylferrocenes were occasionally low, they can be accounted for difficulties during their separation from side products. Unfortunately, it was not generally possible to check the conversions of the starting product by NMR spectra because of the presence of some paramagnetic species.
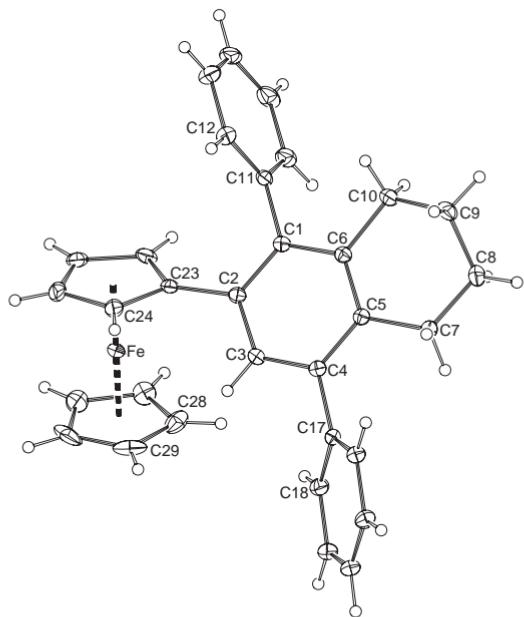

FIG. 1
The molecular structure of **5d** showing the atom labelling scheme. Thermal motion ellipsoids are drawn at the 30% probability level

X-Ray Crystallography

Compound **5d** crystallizes with the symmetry of the monoclinic $P2_1/c$ space group with one molecule in the asymmetric unit. The crystal packing is essentially molecular, showing intermolecular contacts only at the van der Waals level and without significant C–H···π-ring and π···π stacking interactions. Geometric parameters of the molecule of **5d** and its individual parts are rather unexceptional (Table II). However, the overall arran-

TABLE II
The selected geometric parameters for **5d** (in Å and °)

Bond lengths and angles			
C1–C2	1.405(2)	C6–C1–C2	120.1(1)
C2–C3	1.395(2)	C1–C2–C3	118.2(1)
C3–C4	1.391(2)	C2–C3–C4	122.7(1)
C4–C5	1.411(2)	C3–C4–C5	119.1(1)
C5–C6	1.403(2)	C4–C5–C6	119.1(1)
C1–C6	1.409(2)	C5–C6–C1	120.8(1)
C5–C7	1.518(2)	C6–C5–C7	120.9(1)
C7–C8	1.519(2)	C5–C7–C8	113.1(1)
C8–C9	1.515(2)	C7–C8–C9	109.1(1)
C9–C10	1.519(2)	C8–C9–C10	109.8(1)
C6–C10	1.518(2)	C9–C10–C6	113.6(1)
C1–C11	1.501(2)	C2–C1–C11	119.9(1)
C2–C23	1.484(2)	C6–C1–C11	120.0(1)
C4–C17	1.493(2)	C3–C4–C17	117.2(1)
		C5–C4–C17	123.7(1)
		C1–C6–C10	118.2(1)
		C4–C5–C7	119.9(1)
Fe–Cg1	1.6458(7)	Cg1–Fe–Cg1	178.84(4)
Fe–Cg1	1.6488(9)		
Dihedral angles			
Ar1,Cp1	51.25(8)	Ar1,Ph1	80.93(7)
Cp1,Cp2	1.1(1)	Ar1,Ph2	49.91(7)
Cp1,Ph1	59.82(9)	Ph1,Ph2	49.83(8)
Cp1,Ph2	80.14(8)		

[a] Definition of the ring planes: aryl rings: Ar1, C(1–6); Ph1, C(11–16); Ph2, C(17–22); cyclopentadienyl rings: Cp1, C(23–27); Cp2, C(28–32); Cg(1) and Cg(2) are the respective centroids.

gement, particularly the mutual arrangement of the molecular parts, is worth discussing.

The six-membered saturated ring in the central tetrahydronaphthalene unit adopts a half-chair conformation as evidenced by the ring puckering parameters[17]: Q = 0.526(2) Å, ϕ = 127.4(2)°, and θ = 33.5(2)°. The conformation reflect that the saturated ring is *ortho*-fused to an aromatic ring since only the C(8) and C(9) carbon atoms can be disposed from the parent aromatic plane without bending the aromatic ring (C(8) and C(9) atoms are displaced from the aromatic least-squares plane by 0.496(2) and 0.332(2) Å, respectively, in the opposite directions).

The substituents attached to the tetrahydronaphthalene unit, two phenyl and ferrocenyl groups, are all rotated with respect to the aromatic plane (see dihedral angles in Table II). The rotation prevents an extensive conjugation of these aromatic groups and, accordingly, the lengths of the substituent-linking bonds [C(1)–C(11), C(2)–C(23), and C(4)–C(17)] are not shortened, not differing much from 1.50 Å.

In order to obtain an insight into energy variations resulting from changing the conformation in a similar system, we have chosen phenylferrocene as a model and attempted to estimate the height of the rotational barrier for the rotation of the phenyl ring along the pivotal C–C bond using DFT calculations. The results are shown in Fig. 2. The estimated position of the minimum is at the dihedral angle of the phenyl and its adjacent cyclopentadienyl planes (θ) 30° and the height of the rotational barrier is *ca*
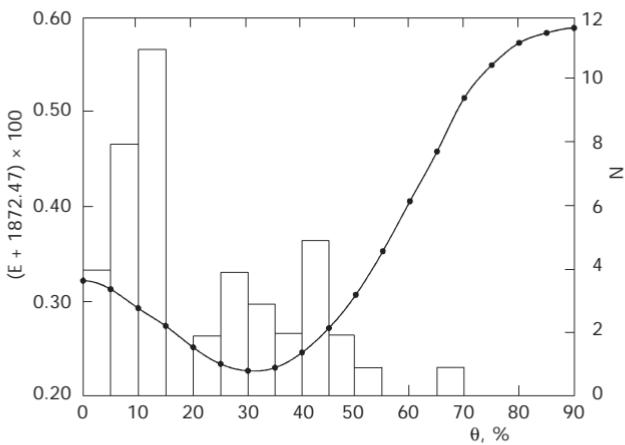

FIG. 2
A plot of the calculated total energy (E, a.u.) and the number of structures (N) *vs* the torsion angle θ. The calculated points are shown as full circles

6.9 kJ mol^{-1}. This energy difference is roughly comparable with the energy of intermolecular interactions frequently encountered in non-polar ferrocene derivatives such as C–H···π-ring hydrogen bonding and π–π stacking of aromatic rings[18], indicating that intermolecular forces may easily change the conformation of such compounds. Likewise, the conformation with θ ≠ 0° seems to be a compromise between energy increase resulting from a steric congestion at low θ and a loss of conjugation at high θ values. This is supported by a distribution of the torsion angles θ observed for various ferrocene derivatives in the solid state as obtained by X-ray crystallographic studies (Fig. 2)[19] and by the fact that phenylferrocene in the solid state has θ = 11.4°, which is by *ca* 20° different from the value calculated for an isolated molecule.

CONCLUSIONS

We may conclude that the reaction of fully substituted zirconacyclopentadienes with ethynylferrocenes represents a new and attractive approach towards the preparation of highly substituted phenylferrocenes that cannot be prepared by other methods. X-Ray structure analysis of **5d** showed that steric hindrance due to an *ortho*-substituent or intermolecular interactions may force ferrocene cyclopentadienyl and the directly attached aromatic ring out of a coplanar arrangement – though, as indicated by DFT calculations for phenylferrocene – without a significant energy increase.

EXPERIMENTAL

Materials and Methods

All reactions were carried out under argon. THF was distilled prior to use from sodium and benzophenone under argon. Ferrocenylethyne[20] and [NiCl$_2$(PPh$_3$)$_2$] (ref.[21]) were synthesized according to the published procedures. 1,8-Diphenylocta-1,7-diyne was synthesized from octa-1,7-diyne and iodobenzene by using the modified Sonogashira conditions[22]. 3-Methoxy- and 3-ethoxy-3-oxo-1-propynylferrocene were synthesized by lithiation of ethynylferrocene with BuLi followed by reaction with methyl and ethyl chloroformate as described previously[16]. But-2-yne, hex-3-yne, oct-4-yne, diphenylethyne, and octa-1,7-diyne were purchased from Aldrich and used as received.

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra (δ, ppm; *J*, Hz) were recorded on a Varian Unity Inova 400 spectrometer using tetramethylsilane as an internal standard. Infrared spectra (ν, cm^{-1}) were recorded on a PE-640 Perkin–Elmer spectrometer. Mass spectra were obtained on a ZAB-SEQ VG Analytical spectrometer. Elemental analyses were obtained on a Perkin–Elmer 2400 elemental analyser. TLC was performed on Merck Silica Gel 60 F$_{254}$ aluminium sheets and column chromatography was carried out on Merck Silica Gel 60. Melting points were determined on a Kofler block and are uncorrected.

Typical Experimental Procedure

An ethynylferrocene (1 mmol) and [NiCl$_2$(PPh$_3$)$_2$] (654 mg, 1 mmol) or CuCl (198 mg, 2 mmol) were added to a solution of zirconacyclopentadiene (1 mmol) in THF (5 ml) (prepared as described in refs[3,4] from zirconocene dichloride (292 mg, 1 mmol), BuLi (1.25 ml of 1.6 M solution in hexanes, 2 mmol), and the respective alkyne (2 mmol) or diyne (1 mmol)). The reaction mixture was stirred at 20 °C or heated to 50 °C for an appropriate period of time and then quenched by addition of 3 M HCl. The organic phase was separated, washed with brine, dried over anhydrous MgSO$_4$, and evaporated. The residue was purified by column chromatography on silica gel and recrystallized (usually from hexane) to give the corresponding ferrocenylarenes.

(2,3,4,5-Tetraethylphenyl)ferrocene (**5a**). Reaction time 3 h at 20 °C. Column chromatography on silica gel (hexane/EtOAc 20:1) afforded 220 mg (57%) as an orange liquid. ^{1}H NMR (CDCl$_3$): 1.02 t, 3 H, J = 7.2 (CH$_3$); 1.19 m, 6 H (2 CH$_3$); 1.32 t, 3 H, J = 7.2 (CH$_3$); 2.60–2.75 m, 8 H (4 CH$_2$); 4.18 s, 5 H (C$_5$H$_5$); 4.22–4.28 m, 2 H (C$_5$H$_4$); 4.38–4.42 m, 2 H (C$_5$H$_4$); 7.60 s, 1 H (C$_6$Et$_4$**H**). ^{13}C NMR (CDCl$_3$): 15.35, 15.72, 15.91, 21.82, 21.99, 22.15, 22.39, 25.44, 67.14, 69.25, 70.42, 90.72, 130.09, 134.57, 138.50, 138.54, 138.58, 139.59. IR (neat): 2965, 2930, 2871, 1451, 1106, 1056, 816, 494. HR-MS, for C$_{24}$H$_{30}$Fe calculated: 374.16969; found: 374.16607. For C$_{24}$H$_{30}$Fe (373.6) calculated: 77.00% C, 8.08% H; found: 76.70% C, 8.47% H. R_f (hexane/EtOAc 9:1) 0.55.

(2,3,4,5-Tetrapropylphenyl)ferrocene (**5b**). Reaction time 48 h at 20 °C. Column chromatography on silica gel (hexane/ether 97:3) afforded 149 mg (35%) of the title compound as a red oily liquid. ^{1}H NMR (CDCl$_3$): 0.87 t, 3 H, J = 7.2 (CH$_3$); 1.04 t, 3 H, J = 7.2 (CH$_3$); 1.06 t, 3 H, J = 7.2 (CH$_3$); 1.08 t, 3 H, J = 7.2 (CH$_3$); 1.32–1.38 m, 2 H (CH$_3$**CH$_2$**CH$_2$); 1.48–1.57 m, 4 H (2 CH$_3$**CH$_2$**CH$_2$); 1.70–1.75 m, 2 H (CH$_3$**CH$_2$**CH$_2$); 2.53–2.62 m, 8 H (CH$_3$CH$_2$**CH$_2$**); 4.20 s, 5 H (C$_5$H$_5$); 4.23–4.27 m, 2 H (C$_5$H$_4$); 4.35–4.38 m, 2 H (C$_5$H$_4$); 7.50 s, 1 H (C$_6$Pr$_4$**H**). ^{13}C NMR (CDCl$_3$): 14.65, 15.08, 15.14, 24.42, 24.56, 24.82, 25.03, 31.67, 31.97, 32.05, 35.15, 67.17, 69.26, 70.35, 90.67, 130.67, 134.44, 137.29, 137.32, 137.53, 138.73. IR (CDCl$_3$): 3024, 2961, 2933, 2873, 1468, 1456, 1378, 1106. HR-MS, for C$_{28}$H$_{38}$Fe calculated: 430.23229; found: 430.23065. For C$_{28}$H$_{38}$Fe (429.7) calculated: 78.13% C, 8.90% H; found: 78.54% C, 9.10% H. R_f (hexane/ether 97:3) 0.42.

(5′,6′-Diphenyl-[1,1′:2,1″-terphenyl]-3′-yl)ferrocene (**5c**). Reaction time 148 h at 20 °C. Column chromatography on silica gel (hexane/EtOAc 20:1) afforded 90 mg (20%) of the title compound as an orange solid. M.p. 243–244 °C (toluene). ^{1}H NMR (CDCl$_3$): 3.93–3.97 m, 2 H (C$_5$H$_4$); 4.03–4.05 m, 2 H (C$_5$H$_4$); 4.15 s, 5 H (C$_5$H$_5$); 6.30–6.60 m, 2 H (Ph); 6.80–6.90 m, 10 H (Ph); 6.95–7.15 m, 4 H (Ph); 7.18–7.23 m, 4 H (Ph); 8.03 s, 1 H (C$_6$Ph$_4$**H**). ^{13}C NMR (CDCl$_3$): 67.71. 69.53, 70.45, 86.65, 125.16, 125.43, 125.78, 126.21, 126.50, 126.83, 127.07, 127.72, 129.87, 131.17, 131.40, 131.47, 131.74, 137.04, 137.93, 139.24, 140.07, 140.17, 140.34, 140.61, 141.23, 142.13. IR (KBr): 3081, 3055, 3022, 2924, 1600, 1495, 1442, 1425, 1106, 1028, 763, 698. HR-MS, for C$_{40}$H$_{30}$Fe calculated: 566.16969; found: 566.16910. R_f (hexane/EtOAc 9:1) 0.55.

(5,8-Diphenyl-1,2,3,4-tetrahydronapthalen-6-yl)ferrocene (**5d**). Reaction time 48 h at 20 °C. Column chromatography on silica gel (hexane/ether 97:3) afforded 72 mg (15%) of the title compound as a red solid. M.p. 232–235 °C (hexane). ^{1}H NMR (CDCl$_3$): 1.65–1.72 m, 4 H (2 CH$_2$); 2.39–2.46 m, 2 H (CH$_2$); 2.62–2.68 m, 2 H (CH$_2$); 3.88–3.92 m, 2 H (C$_5$H$_4$); 3.98–4.02 m, 2 H (C$_5$H$_4$); 4.04 s, 5 H (C$_5$H$_5$); 7.12–7.13 m, 2 H (Ph); 7.30–7.47 m, 8 H (Ph); 7.63 s, 1 H (C$_6$R$_4$**H**). ^{13}C NMR (CDCl$_3$): 22.86, 23.19, 28.82, 29.43, 67.67, 69.49, 70.01,

86.60, 126.52, 126.77, 128.10, 128.16, 129.06, 129.35, 130.14, 132.85, 134.42, 135.46, 139.43, 140.91, 141.24, 142.30. IR ($CDCl_3$): 2924, 2856, 1438, 1107, 1024, 1003, 830, 815, 771, 755, 719, 703. HR-MS, for $C_{32}H_{28}Fe$ calculated: 468.15404; found: 468.15184. R_f (hexane/ether 97:3) 0.41.

(2-Ethoxycarbonyl-3,4,5,6-tetramethylphenyl)ferrocene (**6**). Reaction time 148 h at 20 °C. Column chromatography on silica gel (hexane/EtOAc 20:1) afforded 40 mg (26%) as an orange solid. M.p. 156–157 °C (MeOH). ^1H NMR ($CDCl_3$): 1.09 t, 3 H, $J = 7.2$ (C**H**$_3$CH$_2$O); 2.19 s, 3 H (CH$_3$); 2.22 s, 3 H (CH$_3$); 2.28 s, 3 H (CH$_3$); 2.87 s, 3 H (CH$_3$); 4.04 q, 2 H, $J = 7.2$ (CH$_3$C**H**$_2$O); 4.17 s, 5 H (C$_5$H$_5$); 4.26 m, 2 H (C$_5$H$_4$); 4.37 m, 2 H (C$_5$H$_4$). ^{13}C NMR ($CDCl_3$): 13.97, 16.44, 16.93, 17.42, 18.26, 60.72, 67.75, 69.49, 70.27, 87.78, 129.99, 130.20, 133.08, 134.14, 134.65, 137.34, 171.70. IR ($CDCl_3$): 2977, 2898, 1717, 1385, 1307, 1280, 1186, 1045, 832, 810. HR-MS, for $C_{23}H_{26}FeO_2$ calculated: 390.12822; found: 390.12942. For $C_{23}H_{26}FeO_2$ (389.5) calculated: 70.78% C, 6.71% H; found: 70.60% C, 6.81% H. R_f (hexane/EtOAc 9:1) 0.32.

(2-Methoxycarbonyl-3,4,5,6-tetramethylphenyl)ferrocene (**7a**). Reaction time 148 h at 20 °C. Column chromatography on silica gel (hexane/EtOAc 20:1) afforded 32 mg (17%) as an orange solid. M.p. 109–110 °C (MeOH). ^1H NMR ($CDCl_3$): 2.18 s, 3 H (CH$_3$); 2.22 s, 3 H (CH$_3$); 2.28 s, 3 H (CH$_3$); 2.86 s, 3 H (CH$_3$); 3.59 s, 3 H (CH$_3$O); 4.17 s, 5 H (C$_5$H$_5$); 4.32–4.34 m, 2 H (C$_5$H$_4$); 4.35–4.38 m, 2 H (C$_5$H$_4$). ^{13}C NMR ($CDCl_3$): 16.41, 16.92, 17.48, 18.23, 51.61, 67.84 (2 C), 69.54 (2 C), 70.38, 87.73, 130.00, 130.25, 133.05, 134.08, 134.37, 137.40, 172.10. IR ($CDCl_3$): 2924, 1698, 1456, 1430, 1291, 1211, 1045, 820. HR-MS, for $C_{22}H_{24}O_2Fe$ calculated: 376.11257; found: 376.11161. R_f (hexane/EtOAc 9:1) 0.30.

(2-Methoxycarbonyl-3,4,5,6-tetraethylphenyl)ferrocene (**7b**). Reaction time 148 h at 20 °C. Column chromatography on silica gel (hexane/EtOAc 20:1) afforded 69 mg (32%) as an orange solid. M.p. 133–134 °C (MeOH). ^1H NMR ($CDCl_3$): 1.15–1.25 m, 9 H (3 CH$_3$); 1.29 t, 3 H, $J = 7.5$ (CH$_3$); 2.52 q, 2 H, $J = 7.5$ (CH$_2$); 2.69 q, 2 H, $J = 7.5$ (CH$_2$); 2.79 q, 2 H, $J = 7.5$ (CH$_2$); 3.54 s, 3 H (CH$_3$O); 3.60–3.80 m, 2 H (CH$_2$); 4.12 s, 5 H (C$_5$H$_5$); 4.29–4.31 m, 2 H (C$_5$H$_4$); 4.37–4.39 m, 2 H (C$_5$H$_4$). ^{13}C NMR ($CDCl_3$): 15.56, 16.02, 16.08, 17.36, 21.87, 22.47, 24.12, 51.40, 67.69, 69.57, 69.94, 131.02, 136.29, 139.34, 139.56, 142.48, 172.10. IR ($CDCl_3$): 2971, 1719, 1452, 1294, 1272, 1217, 1198, 1173. HR-MS, for $C_{26}H_{32}O_2Fe$ calculated: 432.17517; found: 432.17387. For $C_{26}H_{32}FeO_2$ (431.6) calculated: 72.22% C, 7.46% H; found: 71.75% C, 7.46% H. R_f (hexane/EtOAc 9:1) 0.43.

(7-Methoxycarbonyl-5,8-diphenyl-1,2,3,4-tetrahydronapthalen-6-yl)ferrocene (**7c**). Reaction time 48 h at 20 °C. Column chromatography on silica gel (hexane/ether/chloroform 9:1:1) afforded 55 mg (10%) of the title compound as a red solid. M.p. 186–189 °C. ^1H NMR ($CDCl_3$): 1.50–1.62 m, 4 H (2 CH$_2$); 2.28–2.40 m, 4 H (2 CH$_2$); 3.32 s, 3 H (CH$_3$O); 3.95–4.05 m, 9 H (C$_5$H$_4$ and C$_5$H$_4$); 7.03–7.08 m, 2 H (Ph); 7.23–7.33 m, 6 H (Ph); 7.40–7.45 m, 2 H (Ph). ^{13}C NMR ($CDCl_3$): 22.56, 22.94, 28.96, 29.93, 51.07, 67.01, 69.20, 71.21, 85.28, 126.43, 126.97, 127.85, 127.87, 129.52, 130.55, 130.59, 132.65, 134.06, 137.36, 139.47, 139.62, 141.55, 142.03, 169.85. IR ($CDCl_3$): 3015, 2945, 1726, 1434, 1292, 1228. HR-MS, for $C_{34}H_{30}FeO_2$ calculated: 526.15952; found: 526.160237. R_f (hexane/ether/chloroform 9:1:1) 0.31.

X-Ray Crystallography

X-Ray quality crystals were obtained by crystallization from hexane. Full-set diffraction data (±h±k±l) were collected on a Nonius KappaCCD diffractometer equipped with Cryostream

Cooler (Oxford Cryosystems) at 150 K using graphite monochromatized MoKα radiation (λ = 0.71073 Å) and analyzed with HKL program package[23]. The structures were solved by direct methods (SIR92)[24] and refined by weighted full-matrix least squares procedure on F^2 (SHELXL97)[25]. All non-hydrogen atoms were refined with anisotropic thermal motion parameters while the hydrogen atoms were included in the calculated positons (C–H bond lengths 0.97 (methylene), and 0.93 (aromatic) Å) and assigned $U_{iso}(H) = 1.2\ U_{eq}(C)$. The final geometric calculations were carried out with Platon program[26]. The relevant crystallographic data and structure refinement parameters are given in Table III.

TABLE III
Crystallographic data, data collection and refinement parameters for **5d**

Formula	$C_{32}H_{28}Fe$
M, g mol^{-1}	468.39
Crystal size, mm^3	$0.13 \times 0.28 \times 0.35$
Crystal description	rusty orange block
T, K	150(2)
Crystal system	monoclinic
Space group	$P2_1/c$ (No.14)
a, Å	11.2960(2)
b, Å	9.7246(1)
c, Å	21.3207(3)
β, °	98.0870(8)
V, Å^3	2318.77(6)
Z, D_c, g ml^{-1}	4, 1.342
μ(MoKα), mm^{-1}	0.669
$θ_{max}$, °; data completeness, %	27.5; 99.6
No. of collected diffractions	40039
No. of unique diffractions	5321
No. of observed diffractions[a]	4578
No. of parameters	398
R, wR observed diffractions[b], %	3.17, 7.80
R, wR all data[b], %	4.02, 8.28
S all data[c]	1.04
Residual electron density, e Å^{-3}	0.27, –0.42

[a] Diffractions with $I_o > 4σ(I_o)$. [b] $R(F) = Σ||F_o| - |F_c||/Σ|F_o|$, $wR(F^2) = [Σ(w(F_o^2 - F_c^2)^2)/(Σw(F_o^2)^2)]^{1/2}$. [c] $S = [Σ(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$.

CCDC 216066 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Theoretical Calculations

The method used was a hybrid of the Hartree–Fock exchange part and Becke's three-parameter functional exchange-correlation part (B3LYP) with standard 3-21G basis set as implemented in the Gaussian program package[27]. This method is known to produce accurate thermochemical data. For selected fixed values of torsion angles θ, we carried out otherwise full optimization of the molecular geometry. The solid-state structure of phenylferrocene from the Cambridge structral database (refcode: DICBIA) was used as the inital geometry.

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19. A list of reference compounds retrieved from the Cambridge structral database [refcode, θ (°)]: 1,8-diferrocenylnaphthalene (CUKKUO, 40.2, 42.2), phenylferrocene (DICBIA, 11.4), (4-nitrophenyl)ferrocene (GEJVUM01, 12.7), 3-[4-(4-methoxyphenoxycarbonyl)phenoxy-carbonyl]propyl 4-ferrocenylbenzoate (GEXQAB, 9.9), (pentaphenylphenyl)ferrocene (HOPQIM, 50.9), 2,2′-diferrocenyl-1,1′-binaphthyl (LEDJIN, 44.2, 6.8), 4-ferrocenyl-phenyl 4-[4′-(methoxycarbonyloxy)phenyl]benzoate (MAYVEN, 2.2), 3′-fluoro-4′-(octyloxy)biphenyl-1-yl 4-ferrocenylbenzoate (MAYVIR, 7.7), 4-(4-ferrocenylphenyl)pyri-dine (NAGDUU, 10.7), 1,3,5-triferrocenylbenzene (NUDCUK, 13.6, 27.5, 7.3), 4,4-diferro-cenyl-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (QANZEK, 32.2, 37.4), 1,2-diferrocenylbenzene (ROQCEF, 68.6, 32.4), 3,5-diferrocenylchlorobenzene (ROQCIJ, 14.7, 12.3), 3,5-diferrocenyl-benzonitrile (ROQCOP, 10.0, 6.8, 14.6, 25.7), 15-ferrocenyl-2,3,5,6,8,9,10,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine (SIJFOG, 23.3), 2-(ethynylphenyl)ferrocene (SOBQEF, 25.6, 30.2), 1,1-bis(8-ferrocenylnaphthyl)ferrocene (SOKMOU, 45.8, 44.9), 4-ferrocenyl-2′-methyl-4′-nitroazobenzene (TAZYAU, 27.9), 1,5-diferrocenylnaphthalene (TEJXAH, 47.0), 2′-ferrocenyl-2,5′-dimethyl-4-nitroazobenzene (XAQJUU, 36.9, 41.3), 2′,3′-difluoro-4′-octyloxybiphenyl 4-ferrocenylbenzoate (YARHEE, 9.5), 1-[4-(ferro-cenyl)phenyl]-2-(4-pyridyl)ethene (ZETTUN, 11.1, 5.0), 4-ferrocenyl-4′-formylbiphenyl (OFOGUL, 10.8), 1-{4-[(1,4-benzoquinonyl)carbonylamino]phenyl}ferrocene (UFULIQ, 20.2), ethyl 4-ferrocenylbenzoate (LUPSOE, 6.9), isopropyl 4-ferrocenylbenzoate (LUPSUK, 10.5), methyl 4-ferrocenylbenzoate (XUPDAN, 9.4), *N*-(4-ferrocenylbenzoyl)-L-alanine methyl ester (XUPDER, 4.9), and (4-ferrocenylphenyl) 4-[4-(methoxy-carbonyloxy)phenyl]benzoate (MAYVEN01, 1.4).
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