From Coordinated Cyclooctatetraene to *cis*-5,7-Disubstituted Cycloocta-1,3-diene by Iteratively Applied Nucleophilic and Electrophilic Addition

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The addition of various carbanionic nucleophiles Nu^1 to the cationic complex $[(\eta^5\text{-Cp})Fe(\eta^6\text{-Cot})]^+$ (**1**) exclusively yields the neutral complex $[(\eta^5\text{-Cp})Fe(1,2,3,4,5\text{-}\eta\text{-}C_8H_8Nu^1)]$ (**2**) with Nu^1 in *exo* position with respect to the metal center: $Nu^1 = CH(CO_2Me)_2$ (**2a**), $CEt(CO_2Me)_2$ (**2b**), CPh_2CN (**2c**), $CH(CN)_2$ (**2d**), $C(CO_2Et)_2(CH_2)_2CO_2Et$ (**2e**), $C(CO_2Et)_2(CH_2)_3CO_2Et$ (**2f**), $C(CO_2Me)_2(CH_2)_2CN$ (**2g**), $CH(COMe)CO_2Et$ (**2h**). Protonation of **2** by HBF_4 reveals the complexes $[(\eta^5\text{-Cp})Fe(\eta^6\text{-}C_8H_9Nu^1)]BF_4$ (**3**BF_4) with a 1,2,3,4,5,6-η coordination mode of the *cyclo*-C_8 ligand. The cationic complexes **3** are suitable for a second nucleophilic addition affording the *exo*-6,8-disubstituted cyclooctadienyl complex $[(\eta^5\text{-Cp})Fe(1,2,3,4,5\text{-}\eta\text{-}C_8H_9\text{-}6\text{-}Nu^1\text{-}8\text{-}Nu^2)]$ (**4**): $Nu^1/Nu^2 = CH(CO_2Me)_2/CH(CO_2Me)_2$ (**4a**), $CEt(CO_2Me)_2/CH(CO_2Me)_2$ (**4b**), CPh_2CN/CPh_2CN (**4c**). It can be shown that the nucleophilic addition occurs not only with the carbanionic nucleophiles, which must be prepared separately by deprotonation reactions with NaH, but also in-situ, when the cationic complex, the C,H acidic substrate, and the strong base tetramethyl guanidine (TMG) are present. The capability of facile deprotonation reaction by TMG enables a one-pot procedure of the synthesis of **4a** without isolation of the intermediates **2** and **3**. Attempts of intramolecular nucleophilic additions in **3d**BF_4 ($Nu^1 = C(CO_2Et)_2(CH_2)_2CO_2Et$) and **3e**$BF_4$ ($Nu^1 = C(CO_2Et)_2(CH_2)_3CO_2Et$) by application of TMG failed in the formation of *cyclo*-C_8-based bicycles but rather result in addition of TMG to the *cyclo*-C_8 ligand forming **4d** and **4e** with tetramethyl guanidinyl as Nu^2. The protonation of **4a**−**c** in acetonitrile by addition of CF_3CO_2H splits off the *cyclo*-C_8 ligand as a *cis*-5,7-disubstituted cycloocta-1,3-diene (**6**): $Nu^1/Nu^2 = CH(CO_2Me)_2/CH(CO_2Me)_2$ (**6a**), $CEt(CO_2Me)_2/CH(CO_2Me)_2$ (**6b**), CPh_2CN/CPh_2CN (**6c**). The protonation of **4d** and **4e** cleaves the guanidinyl substituent and recovers the starting complexes **3d** and **3e**. When the steric demand of Nu^1 and Nu^2 is different, as in **4b**, the isomer that bears the sterically most demanding nucleophile proximal to the endocyclic carbon−carbon double bond is preferentially formed.

Introduction

Nucleophilic addition to unsaturated organic ligands is pertinent to synthetic organometallic chemistry.[1] Since this type of reaction displays pronounced stereo- and regioselectivity, it is used in the synthesis of natural products.[2] More recent investigations demonstrate that this synthetic concept can be transferred to coordinated carbocycles such as cyclooctatetraene (Cot),[3,4] which generates an access to multiple stereo- and regioselectively functionalized *cyclo*-C_8 compounds. They may be of some importance in the synthesis of precursor compounds for *cyclo*-C_8 terpenoids,[5] which illustrate interesting biological activities.[6] Recently, we published the results of iterative nucleophilic and electrophilic additions to Ru-coordinated cyclooctatetraene resulting in regio- and stereoselectively functionalized *cyclo*-C_8 ligands, which demonstrate a remarkable coordination chemistry.[7] In this paper we present results obtained from the iteratively applied reaction sequence of nucleophilic and electrophilic additions on the corresponding cationic Fe complex $[(\eta^5\text{-Cp})Fe(\eta^6\text{-Cot})]^+$ which enables a facile access to regio- and stereoselectively modified cycloocta-1,3-dienes.

Results and Discussion

The initial nucleophilic addition to $[(\eta^5\text{-Cp})Fe(\eta^6\text{-Cot})]^+$ (**1**$^+$) occurs in good to excellent yields (63−96%) with the exception of $Nu^1 = HC(CN)_2$ (34%) and exclusively at the "terminal" carbon atom of the coordinated part of the Cot ligand as predicted from the Davis−Green−Mingos (DGM) rules (Scheme 1).[8] The use of the bifunctionalized nucleophiles, which yields the products **2e**−**h**, was intended to perform a second, but intramolecular nucleophilic addition gaining bicyclic compounds (vide infra). In contrast to the corresponding Ru complex[7] the reaction product displays only a 1,2,3,4,5-η coordination mode of the cyclooctatrienyl ligand in **2** (Scheme 1a), which has been shown for the malonate derivative **2a** ($Nu = CH(CO_2Me)_2$) by means of X-ray structure analysis[9] and which can easily be

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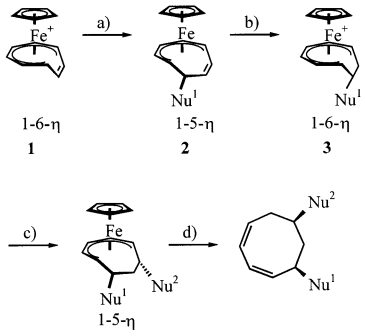
Scheme 1. Reaction Sequence for the Formation of 5,7-Disubstituted Cycloocta-1,3-dienes Starting from Iron-Coordinated Cot[a]



Nu^1	$CH(CO_2Me)_2$	$CEt(CO_2Me)_2$	CPh_2CN	$CH(CN)_2$	$C(CO_2Et_2)(CH_2)_2CO_2Et$
2	**a**	**b**	**c**	**d**	**e**

Nu^1	$C(CO_2Et)_2(CH_2)_3CO_2Et$	$C(CO_2Me)_2(CH_2)_2CN$	$CH(COMe)_2CO_2Et$
2	**f**	**g**	**h**

Nu^1	$CH(CO_2Me)_2$	$CEt(CO_2Me)_2$	CPh_2CN	$C(CO_2Et_2(CH_2)_2CO_2Et)$
3	**a**	**b**	**c**	**d**

Nu^1	$C(CO_2Et)_2(CH_2)_3CO_2Et$	$C(CO_2Me)_2(CH_2)_2C$ N	$CH(COMe)CO_2Et$
3	**e**	**f**	**g**

Nu^1/Nu^2	$CH(CO_2Me)_2/CH(CO_2Me)_2$	$CEt(CO_2Me)_2/CH(CO_2Me)_2$	CPh_2CN/CPh_2CN
4	**a**	**b**	**c**

Nu^1/Nu^2	$CH(CO_2Me)_2/CH(CO_2Me)_2$	$CEt(CO_2Me)_2/CH(CO_2Me)_2$	CPh_2CN/CPh_2CN
6	**a**	**b**	**c**

[a] (a) THF, $NaNu^1$; (b) Et_2O, HBF_4, −78 °C; (c) THF, $NaNu^2$, (d) MeCN, CF_3CO_2H.

proven by $^1H-^1H$ and $^1H-^{13}C$ correlation spectroscopy for the other products of **2**.[7]

Since the starting complex **1** contains a mirror plane, which includes the Fe atom and bisects the Cp and Cot ligands, the nucleophilic addition reveals chiral complexes in a racemic mixture (Figure 1). As a result, the two identical substituents on the Cot-linked carbon atom in **2a**−**g** (i.e., CO_2Me, Ph) are diastereotopic and thus display different NMR signals.

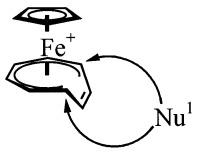


Figure 1. Nucleophilic attack on the two enantiotopic sites generating two stereogenic centers.

The addition of a second nucleophile requires a new cationic complex, which is gained by the protonation of **2** with HBF_4 in diethyl ether (Scheme 1b). The cationic product **3** is obtained in good to excellent yields (68−98%) and precipitates as a red crystalline material or forms a red oil, which can easily be separated from the reaction mixture. The product exclusively consists of 1,2,3,4,5,6-η haptomers, and no indication is found for the formation of the 1,2-η:4,5,6,7-η haptomers as in the case of the Ru congeners.[7] Again the coordination mode of the *cyclo*-C_8 ligand is demonstrated by $^1H-^1H$ and $^1H-^{13}C$ correlation spectra. It is noteworthy that one ^1H resonance signal of the endocyclic methylene group, which shows the characteristic ddd pattern due to the spin−spin coupling with three neighboring protons, is shifted below −1.7 ppm. It is suggested that the anisotropy cone of the diamagnetic sandwich complexes[7,10] induces the upfield shift of ^1H NMR signals for protons in *exo* position with respect to the metal center.

The second nucleophilic addition can in principle occur at two different terminal carbon atoms of the coordinated cyclooctatriene ligand (Figure 2), if this

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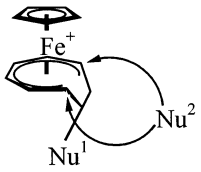
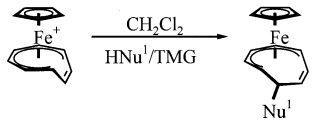


Figure 2. Possible target positions for the second nucleophilic addition.

Scheme 2. Nucleophilic Addition Supported by Tetramethyl Guanidine (TMG)



1 2

$HNu^1 = HCH(CO_2Me)_2$, $HCPh_2CN$

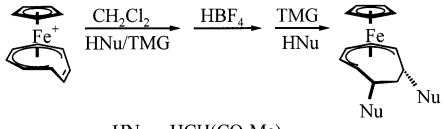
addition obeys the DGM rules as well. However, probably for steric reasons the addition exclusively occurs distal with respect to the first nucleophile Nu^1, forming the 6,8-disubstituted 1,2,3,4,5-η-cyclooctadienyl complexes **4** in good yields (60−87%), and additionally both nucleophiles are in *exo* position with respect to the metal center (Scheme 1c). The structural characterization can easily be carried out by taking into account the few signals of **4a** and **4c** due to the local C_s symmetry of the *cyclo*-C_8 ligand and the results of $^1H-^1H$ and $^1H-^{13}C$ correlation spectra.

According to previous descriptions, the nucleophiles used for the first and second nucleophilic addition have been prepared separately by deprotonation reactions of the C,H acidic precursor compounds with NaH; the solutions of the obtained carbanions were added to the cationic complexes **1** and **3**, respectively. To simplify this nucleophilic addition procedure, we attempted to generate the nucleophiles in-situ by adding the strong base (but weak nucleophile) tetramethyl guanidine (TMG) directly to a solution of the cationic starting complexes and the C,H acidic precursor compounds in dichloromethane. Due to its strong basicity, TMG[11] is often successfully used in Michael additions,[12] in combinatorial peptide synthesis,[13] and in esterification reactions of carboxylic acids with alkyl halides.[14]

The use of TMG as deprotonation reagent to form the nucleophiles in-situ is successfully demonstrated for dimethyl malonate and diphenyl acetonitrile (Scheme 2). The products **2a** and **2c** are obtained in very high yields, 89 and 96%, respectively.

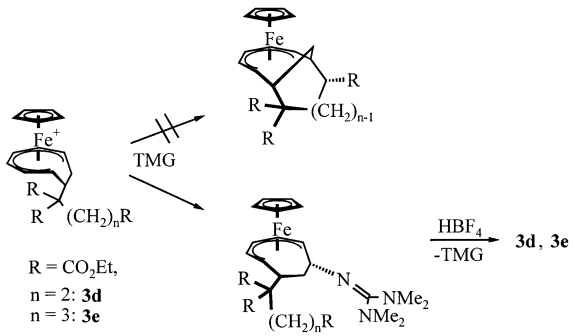
The successful application of TMG enables the nucleophilic addition twice without isolation of the products **2** and **3** and without changing the solvent. The first nucleophilic addition occurs when a 2-fold excess of TMG is added to a CH_2Cl_2 solution of **1** and a 4-fold excess of dimethyl malonate with respect to the amount of **1**. The reaction mixture is subsequently protonated by addition of HBF_4 at $T = -78$ °C, until the solution

Scheme 3. One-Pot Procedure to Synthesize Cyclooctadienyl Derivatives 4 without Isolation of the Intermediates 2 and 3 (see Scheme 1)



1 $HNu = HCH(CO_2Me)_2$ **4a**

Scheme 4. Attempts of an Intramolecular Nucleophilic Addition in the Presence of TMG Resulting in the Addition of TMG



$R = CO_2Et$,
n = 2: **3d**
n = 3: **3e**

$R = CO_2Et$,
n = 2: **4d**
n = 3: **4e**

is slightly acidic. After warming to room temperature, an excess of TMG is added again. After 18 h complex **4a** is isolated in a yield of 64% (Scheme 3), while a stepwise nucleophilic addition (Scheme 1) reveals a yield of 66%.

Attempts to perform an intramolecular second nucleophilic addition in **3d**,**e** fail although different non-nucleophilic bases such as lithium diisopropylamide (LDA), lithium tetramethyl piperidinide (LTMP), sodium bis(trimethylsilyl)amide (NaBTSA), and potassium *tert*-butoxide (K*t*BuO) are used. Product mixtures are formed, which are not yet analyzed. Only when the strong base TMG is applied, one definite product is isolated as a red oil, which is highly soluble in less polar solvents as diethyl ether and toluene. However, by means of FAB-MS, ^1H NMR, and IR spectroscopy it becomes evident that TMG is added to the *cyclo*-C_8 ligand even in the case of the longer chain in **3e**. The formation of **4d** and **4e** is also associated with the inclusion of varying amounts of $[HTMG]BF_4$ salt and TMG, which are very difficult to detach and thus make a reliable elemental analysis impossible. Attempts to separate the pure products by column chromatography result in the decomposition of **4d** and **4e** (Scheme 4).

The stereo- and regioselectively substituted *cyclo*-C_8 ligand is easily split off as a cycloocta-1,3-diene derivative **6** in the case of **4a**−**c** by addition of CF_3CO_2H in the presence of acetonitrile (Scheme 1d). For the guanidinyl derivatives **4d** and **4e** (Scheme 4) the guanidinyl substituent is cleaved upon protonation and the starting complexes **3d** and **3e** are recovered. The cleavage of a N nucleophile upon protonation was already reported from an amino-substituted *cyclo*-C_8 ligand.[7]

In the course of the protonation of **4b** a Fe hydride species **5** is formed (Scheme 5), which can be identified by means of low-temperature ^1H NMR spectroscopy at $T = -30$ °C. In Figure 3 the ^1H NMR spectra of a

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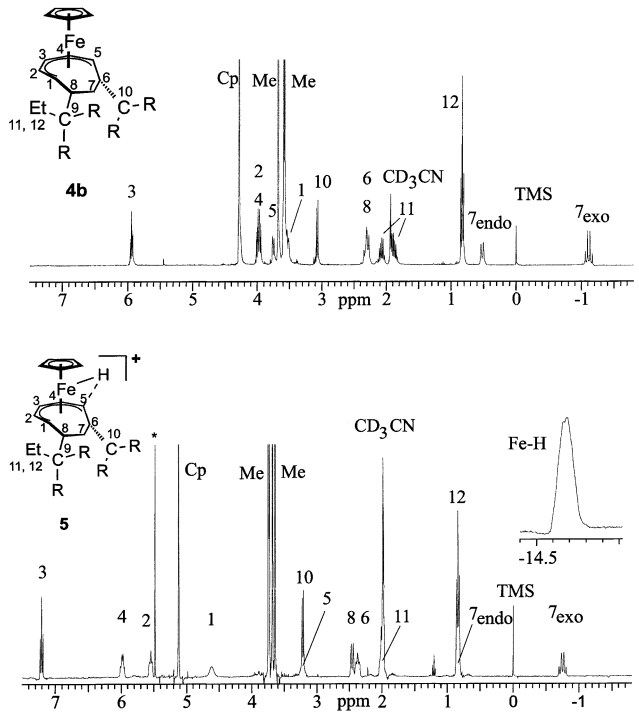
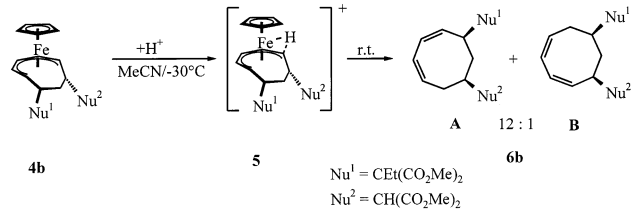


Figure 3. ^{1}H NMR spectra of complex **4b** ($Nu^1 = CEtR_2$, $Nu^2 = CHR_2$, R = CO_2Et) (top) and the result of the protonation of **4b** with CF_3CO_2H after 5 min at $T = -30$ °C (bottom) forming the hydride complex **5** (* = CH_2Cl_2).

Scheme 5. Protonation of Complex 4b Forming the Iron-Hydride Complex 5 and, Subsequently, the Free 1,3-Cyclooctadienes (r.t. = room temperature)



solution of **4b** in CD_3CN without CF_3CO_2H (top) and with an excess of CF_3CO_2H at −30 °C (bottom) measured 5 min after the sample preparation are shown.

Most indicative for the formation of the Fe hydride complex **5** is the presence of the distinctly upfield shifted signal of a single proton at $\delta = -14.6$ ppm. This shift range is typically found for classical iron hydride complexes.[15] Another important indication for the formation of a cationic species is the general low-field shift of the corresponding signals of the protons attached to the metal-bound carbon atoms on going from **4b** to **5**. An exception is the high-field shift of the proton signal 5, which is superimposed by the doublet of proton 10, but which can be assigned unequivocally by means of ^{1}H−^{1}H correlation spectra. In a ^{1}H−^{1}H COSY spectrum the signal at −14.6 ppm demonstrates cross-peaks with the proton signals at positions 5 and 4 of the *cyclo*-C_8 ligand, indicating a preferential agostic interaction with only one site of the eight-membered ring at $T = -30$ °C. The different interactions of the Fe hydride function with the two different sites of the *cyclo*-C_8 ligand (C1, C2, C8 vs C4, C5, C6) can also be identified by the shift variation of the corresponding proton signals of positions 1, 2, 4, 5, 6, and 8 in **4b** and **5**: in the ^{1}H NMR spectrum of **4b** the resonance signals are separated only about 0.22, 0.02, and 0.0 ppm for the protons in 1,5-, 2,4-, and 6,8-position, respectively; the difference increases distinctly upon protonation to 1.40, 0.43, and 0.08 ppm in **5**.

This site preference in the agostic interaction consecutively favors the formation of the regioisomer **A** of the 5,7-disubstituted cycloocta-1,3-diene (Scheme 5). The ratio of the two regioisomers **A** and **B** amounts to 12:1, which was calculated from the intensity of the ^{1}H NMR signals of the malonate proton H-10 in isomer **A** and H-9 in isomer **B**, respectively. One rationale behind this site preference of the agostic interaction may be the reduced steric demand of $Nu^2 = CH(CO_2Me)_2$ compared to $Nu^1 = CEt(CO_2Me)_2$, both of which are in *exo* position with respect to the metal center. The smaller nucleophile Nu^2 at carbon atom C6 allows carbon atom C5 to deflect from the metal center upon the agostic interaction rather than carbon atom C1, which is next to carbon atom C8 bearing the sterically more demanding nucleophile Nu^1.

Conclusions

The reaction sequence "first nucleophilic addition → protonation → second nucleophilic addition → second protonation → ligand decomplexation" applied on coordinated cyclooctatetraene in $[(\eta^5\text{-Cp})Fe(\eta^6\text{-Cot})]^+$ enables a facile access to *cis*-5,7-disubstituted cycloocta-1,3-dienes. The two nucleophilic additions strongly obey the DGM rules and are thus chemo-, regio-, and stereoselective. The nucleophilic addition can be conducted by the addition of the carbanionic nucleophiles, which have to be prepared separately, to the cationic sandwich complexes **1** and **3**, or in-situ by bringing together the cationic complexes, the C,H acidic compound as the nucleophile precursor, and tetramethyl guanidine (TMG) simultaneously. The addition of TMG as a deprotonating reagent allows a one-pot procedure for the synthesis of *exo*-6,8-disubstituted cyclooctadienyl ligands with the same nucleophiles. By adding different nucleophiles, apparently that regioisomer is preferentially formed, which bears one endocyclic double bond next to the sterically most demanding nucleophile, as shown for **6b**. This method opens a facile access to a very rarely investigated but remarkable class of compounds[16] that provides a great synthetic potential with regard to terpenoid *cyclo*-C_8 compounds.[6] The synthesis of *cis*-5,7-disubstituted cycloocta-1,3-dienes is a supplementation of the synthesis of *cis*-5,8-disubstituted cycloocta-1,3-dienes.[1f] Attempts of intramolecular nucleophilic additions in **3d** and **3e**, wherein the precursor function for Nu^2 is the end group of the bound nucleophile Nu^1, are unsuccessful in the presence of TMG, but instead result in the addition of a guanidinyl unit to the *cyclo*-C_8 ligand

(15) Jänicke, M.; Hund, H.-U.; Berke, H. *Chem. Ber.* **1991**, *124*, 719−724.

(16) According to our literature research only three (!) representatives of this type of compound have been reported (except ref 4), all of which show a *trans* configuration in the 5,7 position: (a) Zhang, H. *Hebei Shifan Daxue Xuebao, Ziran Kexueban* **1987**, *1*, 13−15. (b) Kroener, M. *Chem. Ber.* **1967**, *100*, 3162−3171.

Table 1. Preparative Details for the First Nucleophilic Addition

HNu^1	HNu^1 mg (mmol)	$\mathbf{1}PF_6$ mg (mmol)	method	reaction time (h)	product	yield mg (%)
$HCH(CO_2Me)_2$	289 (2.19)	809 (2.19)	A	4	**2a**	704 (91)
$HCH(CO_2Me)_2$	40 (0.30)	74 (0.20)	B	4	**2a**	63 (89)
$HCEt(CO_2Me)_2$	115 (0.72)	266 (0.72)	A	12	**2b**	228 (83)
$HCPh_2CN$	92 (0.47)	178 (0.48)	B	18	**2c**	193 (96)
$HCH(CN)_2$	41 (0.63)	234 (0.63)	A	3	**2d**	63 (34)
$HC(CO_2Et)_2(CH_2)_2CO_2Et$	244 (0.87)	320 (0.87)	A	18	**2e**	338 (62)
$HC(CO_2Et)_2(CH_2)_3CO_2Et$	327 (1.19)	438 (1.19)	A	3	**2f**	510 (86)
$HC(CO_2Me)_2(CH_2)_2CN$	188 (1.02)	377 (1.02)	A	3	**2g**	321 (77)
$HCH(COMe)CO_2Et$	47 (0.37)	142 (0.38)	A	18	**2h**	88 (65)

(**4d**,**e**). The protonation of the guanidinyl derivatives **4d** and **4e** recovers the starting complexes **3d** and **3c**.

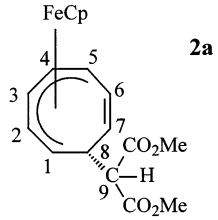
Experimental Section

All reactions were carried out under a nitrogen atmosphere, and all solvents were saturated with nitrogen. THF, Et_2O, hexane, and toluene were freshly distilled from the appropriate alkali metal or metal alloy. Dichloromethane was dried over CaH_2 and distilled under N_2. NMR: Bruker AM 360 and Varian Gemini 200. IR: Nujol mull, KBr cells, FT-IR 1720X (Perkin-Elmer). EI/FAB-MS: 70 eV, Finnigan MAT 311 A. Elemental analysis: CHN-O-Rapid, Institut für Anorganische und Angewandte Chemie, Universität Hamburg (the elemental analyses of the cationic products **3**BF_4 are often hampered by the inclusion of varying amounts of CH_2Cl_2, as indicated by ^{1}H NMR spectra). [(η^5-Cp)Fe(η^6-Cot)]PF_6 (**1**PF_6),[17] $CH(CO_2Et)_2$-$(CH_2)_2CO_2Et$, $CH(CO_2Me)_2(CH_2)_3CO_2Et$, $CH(CO_2Me)_2(CH_2)_2$-CN,[18] and the sodium salts of the malonester derivatives[19] were synthesized as described. HBF_4 was purchased as a 54% solution in diethyl ether from Fluka.

General Procedure for the First Nucleophilic Addition. Synthesis of 2a−h: Method A. One equivalent of the organic C,H acidic compound HNu^1 was added to a suspension of 1.3−1.5 equiv of NaH in THF at $T = -40$ °C. The reaction solution was allowed to warm to room temperature and was stirred until gas evolution (H_2) stopped. The THF solution was separated from unreacted NaH and was transferred by a cannula to a suspension of 1 equiv of **1**PF_6 in THF. The reaction mixture was stirred at room temperature and evaporated to dryness. The residue was extracted with toluene, and the extract was filtered through Celite. After removal of the solvent, the product was normally obtained as a red crystalline powder or red oil. For more preparative details see Table 1.

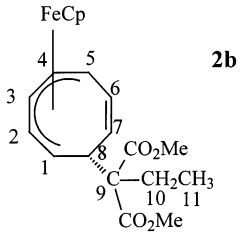
Method B. One equivalent of complex **1**PF_6, 1−1.5 equiv of HNu^1, and 1.5 equiv of TMG were dissolved in CH_2Cl_2 (20 mL) and stirred at room temperature. The workup procedure occurred as described in method A. For more preparative details see Table 1.

(η^5-Cyclopentadienyl)[1,2,3,4,5-η-8-*exo*-di(methoxycarbonyl)methylcyclooctatrien-6-yl]iron(II) (2a): red crystalline powder, soluble in Et_2O, more soluble in toluene. Fp: 83 °C. IR (KBr): $\tilde{\nu}$ 3092 (w) ν(C−H, aromat.), 2995 (m), 2951 (m) ν(C−H, aliph.), 1752 (s) ν(C=O), 1642 (w) ν(C=C), 1434 (m) d(CH_2/CH_3), 1290 (m), 1192 (s), 1156 (s) ν(C−O) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 5.79 (m, 1 H, 6-H), 5.41 (m, 2 H, 3-H, 7-H), 4.31 (dd, $^3J_{3,4}$ = 6.2 Hz, $^3J_{4,5}$ = 8.3 Hz, 1 H, 4-H), 4.07 (m, 2 H, 1-H, 2-H), 3.89 (s, 5 H, Cp), 3.82 (m, 1 H, 8-H), 3.51 (m, 1 H, 5-H), 3.42 (s, 3 H, Me), 3.25 (s, 3 H, Me), 3.10 (d, $^3J_{8,9}$ = 8.8 Hz, 1 H, 9-H) ppm. ^{13}C{^{1}H} NMR (50 MHz, C_6D_6): δ 169.2, 168.7 (C=O), 129.5 (C6), 125.6 (C7), 99.7 (C3), 78.4 (C4), 77.1 (s, Cp), 76.4 (C2), 60.4 (C9), 51.8, 51.6 (CO_2CH_3), 47.9 (C1), 44.5 (C5), 39.5 (C8) ppm. Anal. Calcd for $C_{18}H_{20}O_4Fe$ (356.20): C 60.70, H 5.66. Found: C 60.62, H 5.72.



2a

(η^5-Cyclopentadienyl)[1,2,3,4,5-η-8-*exo*-1,1-di(methoxycarbonyl)prop-1-ylcyclooctatrien-6-yl]iron(II) (2b): red crystalline powder, soluble in Et_2O, more soluble in toluene. Fp: 85 °C. IR (KBr): $\tilde{\nu}$ 3115 (w), 3085 (w) ν(C−H, aromat.), 3019 (w), 2979 (m), 2951 (m) ν(C−H, aliph.), 1724 (s), 1739 (s) ν(C=O), 1652 (w) ν(C=C), 1451 (m), 1432 (m) δ(CH_2/CH_3), 1332 (m), 1301 (m) δ(CH_3), 1227 (s), 1202 (s) ν(C−O) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 5.74 (ddd, $^3J_{5,6}$ = 6.4 Hz, $^3J_{6,7}$ = 10.8 Hz, 1 H, 6-H), 5.61 (dm, $^3J_{6,7}$ = 10.8 Hz, 1 H, 7-H), 5.42 (t′, $^3J_{2,3}$ = $^3J_{3,4}$ = 6.4 Hz, 1 H, 3-H), 4.30 (dd, $^3J_{3,4}$ = 6.3 Hz, $^3J_{4,5}$ = 8.8 Hz, 1 H, 4-H), 4.14 (dd, $^3J_{1,2}$ = 8.8 Hz, $^3J_{2,3}$ = 6.3 Hz, 1 H, 2-H), 3.93 (s, 5 H, Cp), 3.86 (dd, $^3J_{1,2}$ = 8.8 Hz, $^3J_{1,8}$ = 5.8 Hz, 1 H, 1-H), 3.76 (m, 1 H, 8-H), 3.50 (dd, $^3J_{4,5}$ = 8.8 Hz, $^3J_{5,6}$ = 6.4 Hz, 1 H, 5-H), 3.36 (s, 3 H, CO_2CH_3), 3.28 (s, 3 H, CO_2CH_3), 2.28 (m, 2 H, 10-H), 1.06 (t, ^3J = 7.5 Hz, 3 H, 11-H) ppm. ^{13}C{^{1}H} NMR (50 MHz, C_6D_6): δ 172.0, 170.9 (C=O), 127.4 (C6), 127.0 (C7), 99.0 (C3), 77.8 (C4), 77.5 (C2), 77.2 (s, Cp), 63.7 (C9), 51.6, 51.2 (CO_2CH_3), 44.6 (C8), 44.2 (C5), 43.1 (C1), 27.5 (C10), 10.3 (C11) ppm. EI-MS (70 eV): *m*/*z* (%) 384 (22) [M^+], 355 (2) [$M^+ - C_2H_5$], 325 (5) [$M^+ - COOCH_3$], 225 (41) [$CpFeC_8H_8^+$], 186 (31) [$CpFeC_5H_5^+$], 121 (35) [$CpFe^+$], 104 (100) [$C_8H_8^+$]. Anal. Calcd for $C_{20}H_{24}O_4Fe$ (384.26): C 62.41, H 6.30. Found: C 62.41, H 6.44.



2b

(η^5-Cyclopentadienyl)[1,2,3,4,5-η-8-*exo*-(diphenylcyano)-methylcyclooctatrien-6-yl]iron(II) (2c): red crystalline powder, sparingly soluble in Et_2O, soluble in toluene. Fp: 163 °C. IR (KBr): $\tilde{\nu}$ 3087 (w), 3057 (w), 3025 (w) ν(C−H, aromat.), 2973 (w), 2950 (m) ν(C−H, aliph.), 2237 (w) ν(C≡N), 1677 (m), 1599 (m), 1493 (m), 1450 (m) ν(C=C, aromat.), 750 (s), 705 (s) δ(C−H, aromat.) cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.62 (d, $^3J_{ortho,meta}$ = 7.7 Hz, 2 H, H_{ortho}), 7.46 (d, $^3J_{ortho,meta}$ = 7.7 Hz, 2 H, H_{ortho}), 7.02 (m, 6 H, $H_{meta,para}$), 5.67 (ddd, $^3J_{5,6}$ = 6.4 Hz, $^3J_{6,7}$ = 10.7 Hz, 1 H, 6-H), 5.47 (t′, $^3J_{2,3}$ = $^3J_{3,4}$ = 6.6 Hz, 1 H, 3-H), 5.18 (d, $^3J_{6,7}$ = 10.7 Hz, 1 H, 7-H), 4.34 (dd, $^3J_{3,4}$ = 6.6 Hz, $^3J_{4,5}$ = 9.0 Hz, 1 H, 4-H), 4.08 (m, 1 H, 1-H),

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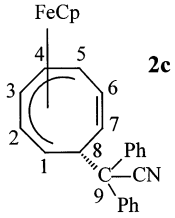
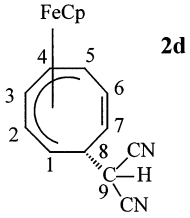
(18) Hörnfeld, K.; Antoni, G.; Långström, B. *Chem. Scand.* **1992**, *46*, 87−91.
(19) Pearson, A. J.; *J. Chem. Soc., Perkin Trans. 1* **1977**, 2069−2077.

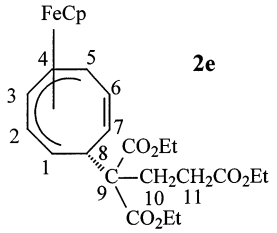
3.97 (dd, $^3J_{1,2}$ = 9.0 Hz, $^3J_{2,3}$ = 6.6 Hz, 1 H, 2-H), 3.83 (s, 5 H, Cp), 3.82 (m, 1 H, 8-H), 3.37 (dd, $^3J_{4,5}$ = 9.0 Hz, $^3J_{5,6}$ = 6.4 Hz, 1 H, H-5) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 141.5, 139.9 (s, C-phenyl), 131.8 (C6), 129.0, 128.9, 127.6 (s, C−phenyl), 123.5 (C7), 121.9 (s, CN), 99.9 (C3), 78.1 (C4), 77.7 (C2), 77.0 (s, Cp), 59.9 (C9), 47.8 (C1), 45.3 (C8), 43.5 (C5) ppm. FAB-MS (70 eV): *m/z* (%) 417 (9) [M^+], 391 (3) [M^+ − CN], 225 (100) [$CpFeC_8H_8^+$]. Anal. Calcd for $C_{27}H_{23}NFe$ (417.33): C 77.71, H 5.55, N 3.36. Found: C 77.31, H 5.71, N 3.18.



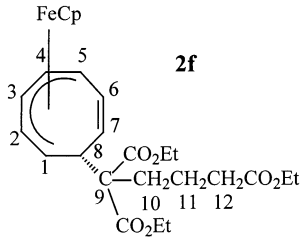
(η^5-Cyclopentadienyl)[1,2,3,4,5-η-8-*exo*-(dicyano)methylcyclooctatrien-6-yl]iron(II) (2d): red crystalline powder, sparingly soluble in Et_2O, soluble in toluene. Decomp: 118 °C. IR (KBr): $\tilde{\nu}$ 3085 (w) ν(C−H, aromat.), 2994 (s), 2947 (s), 2892 (s) ν(C−H, aliph.), 2248 (w) ν(C≡N), 1678 (m) ν(C═C), 1420 (m) $\delta(CH_3/CH_2)$ cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 5.66 (ddd, $^3J_{5,6}$ = 6.8 Hz, $^3J_{6,7}$ = 10.5 Hz, 1 H, 6-H), 5.40 (t′, $^3J_{2,3}$ = $^3J_{3,4}$ = 6.8 Hz, 1 H, 3-H), 4.79 (dm, $^3J_{6,7}$ = 10.5 Hz, 1 H, 7-H), 4.25 (dd, $^3J_{3,4}$ = 6.8 Hz, $^3J_{4,5}$ = 9.0 Hz, 1 H, 4-H), 3.99 (dd, $^3J_{1,2}$ = 9.0 Hz, $^3J_{2,3}$ = 6.8 Hz, 1 H, 2-H), 3.78 (s, 5 H, Cp), 3.60 (m, 1 H, 1-H), 3.31 (dd, $^3J_{4,5}$ = 9.0 Hz, $^3J_{5,6}$ = 6.8 Hz, 1 H, 5-H), 2.68 (m, 1 H, 8-H), 2.28 (d, $^3J_{8,9}$ = 6.4 Hz, 1 H, 9-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 133.3 (C6), 121.4 (C7), 113.3, 113.0 (s, CN), 100.7 (C3), 78.8 (C4), 77.3 (s, Cp), 75.8 (C2), 44.7 (C1), 44.2 (C5), 41.4 (C8), 30.4 (C9) ppm. EI-MS (70 eV): *m/z* (%) 290 (25) [M^+], 225 (64) [$CpFeC_8H_8^+$], 199 (23) [$CpFeC_6H_6^+$], 186 (38) [$CpFeC_5H_5^+$], 121 (100) [$CpFe^+$]. Anal. Calcd for $C_{16}H_{14}N_2Fe$ (290.15): C 66.23, H 4.86, N 9.65. Found: C 65.49, H 5.29, N 8.24.



(η^5-Cyclopentadienyl)[1,2,3,4,5-η-8-*exo*-(1,1,3-triethoxycarbonyl)prop-1-ylcyclooctatrien-6-yl]iron(II) (2e): red oil, highly soluble in Et_2O, toluene. IR (KBr): $\tilde{\nu}$ 3084 (w) ν(C−H, aromat.), 2981 (m), 2952 (m), 2904 (m) ν(C−H, aliph.), 1732 (s) ν(C═O), 1631 (w) ν(C═C), 1445 (m) $\delta(CH_3/CH_2)$, 1368 (m), 1300 (m) $\delta(CH_3)$, 1243−1181 (s) ν(C−O) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 5.71 (ddd, $^3J_{5,6}$ = 6.5 Hz, $^3J_{6,7}$ = 10.8 Hz, 1 H, 6-H), 5.55 (dm, $^3J_{6,7}$ = 10.8 Hz, 1 H, 7-H), 5.44 (t′, $^3J_{2,3}$ = $^3J_{3,4}$ = 6.5 Hz, 1 H, 3-H), 4.30 (dd, $^3J_{3,4}$ = 6.5 Hz, $^3J_{4,5}$ = 9.0 Hz, 1 H, 4-H), 4.15 (dd, $^3J_{1,2}$ = 8.3 Hz, $^3J_{2,3}$ = 6.5 Hz, 1 H, 2-H), 4.08−3.80 (m, 8 H, $CO_2CH_2CH_3$, 8-H, 1-H), 3.90 (s, 5 H, Cp), 3.47 (dd, $^3J_{4,5}$ = 9.0 Hz, $^3J_{5,6}$ = 6.5 Hz, 1 H, 5-H), 2.69 (m, 4 H, 10-H, 11-H), 0.92 (m, 9 H, $CO_2CH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 173.0, 171.4, 170.3 (C═O), 128.0 (C6), 126.6 (C7), 99.3 (C3), 77.7 (C4), 77.6 (C2), 77.2 (Cp), 62.1 (C9), 61.0, 60.7, 60.2 ($CO_2CH_2CH_3$) 45.2 (C1), 44.0 (C8), 43.1 (C5), 30.8 (C10), 28.6 (C11), 14.2, 14.1, 13.9 ($CO_2CH_2CH_3$) ppm. EI-MS (70 eV): *m/z* (%) 484 (29) [M^+], 439 (7) [$M^+ - C_2H_5O$], 315 (24) [$M^+ - \{(C_2H_5O)_2(COOC_2H_5)\}$], 225 (67) [$CpFeC_8H_8^+$], 199 (36) [$CpFeC_6H_6^+$], 186 (68) [$CpFeC_5H_5^+$], 121 (100) [$CpFe^+$]. Anal. Calcd for $C_{25}H_{32}O_6Fe$ (484.37): C 61.96, H 6.66. Found: C 60.71, H 7.03.

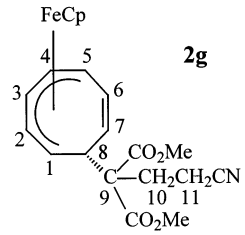


(η^5-Cyclopentadienyl)[1,2,3,4,5-η-8-*exo*-(1,1,4-triethoxycarbonyl)but-1-ylcyclooctatrien-6-yl]iron(II) (2f): red oil, highly soluble in Et_2O, toluene. IR (KBr): $\tilde{\nu}$ 3106 (w) ν(C−H, aromat.), 2980 (s) ν(C−H, aliph.), 1732 (s) ν(C═O), 1630 (w) ν(C═C), 1446 (m), 1422 (m) $\delta(CH_3/CH_2)$, 1367 (m) $\delta(CH_3)$, 1238−1158 (s) ν(C−O) cm^{-1}. ^1H NMR (360 MHz, C_6D_6): δ 5.70 (ddd, $^3J_{5,6}$ = 6.4 Hz, $^3J_{6,7}$ = 10.8 Hz, 1 H, 6-H), 5.64 (dm, $^3J_{6,7}$ = 10.8 Hz, 1 H, 7-H), 5.49 (t′, $^3J_{2,3}$ = $^3J_{3,4}$ = 6.4 Hz, 1 H, 3-H), 4.35 (dd, $^3J_{3,4}$ = 6.4 Hz, $^3J_{4,5}$ = 9.0 Hz, 1 H, 4-H), 4.19 (dd, $^3J_{2,3}$ = 6.4 Hz, 1 H, 2-H), 4.00 (m, 1 H, 1-H), 3.99 (s, 5 H, Cp), 3.86−4.10 (m, 6 H, $CO_2CH_2CH_3$), 3.83 (m, 1 H, 8-H), 3.51 (dd, $^3J_{4,5}$ = 9.0 Hz, $^3J_{5,6}$ = 6.4 Hz, 1 H, 5-H), 2.36 (m, 2 H, 12-H), 2.21 (t, ^3J = 7.4 Hz, 2 H, 10-H), 1.87 (m, 2 H, 11-H), 0.99, 0.95, 0.91 (t, ^3J = 7.4 Hz, 9 H, $CO_2CH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 172.6, 171.4, 170.4 (C═O), 127.3 (C6), 127.1 (C7), 99.2 (C3), 77.6 (C2), 77.5 (C4), 77.2 (Cp), 62.8 (C9), 60.8, 60.5, 60.0 ($CO_2CH_2CH_3$), 44.5 (C1), 44.0 (s, C8), 43.3 (s, C5), 34.7 (s, C10), 33.5 (s, C12), 21.2 (s, C11), 14.3, 14.2, 14.0 (s, $CO_2CH_2CH_3$) ppm. EI-MS (70 eV): *m/z* (%) 498 (74) [M^+], 453 (15) [$M^+ - C_2H_5O$], 225 (100) [$CpFeC_8H_8^+$], 186 (45) [$CpFeC_5H_5^+$], 121 (81) [$CpFe^+$]. Anal. Calcd for $C_{26}H_{34}O_6Fe$ (498.40): C 62.66, H 6.88. Found: C 62.76, H 6.88.



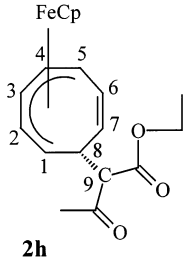
(η^5-Cyclopentadienyl)[1,2,3,4,5-η-8-*exo*-(3-*cyano*-1,1-dimethoxycarbonyl)prop-1-ylcyclooctatrien-6-yl]iron-(II) (2g): orange red crystalline powder. Decomp: > 95 °C. IR (KBr): $\tilde{\nu}$ 3083 (w), 3015 (m) ν(C−H, aromat.), 2953 (m) ν(C−H, aliph.), 2247 (w) ν(C≡N), 1732 (s) ν(C═O), 1438 (m) δ(CH3/CH2), 1296 (s) δ(CH3), 1246 (m), 1226 (m), 1195 (m) ν(C−O) cm^{-1}. ^1H NMR (360 MHz, C6D6): δ 5.68 (ddd, $^3J_{6,7}$ = 10.8 Hz, $^3J_{5,6}$ = 6.8 Hz, 1 H, 6-H), 5.35 (t′, $^3J_{2,3}$ = $^3J_{3,4}$ = 6.4 Hz, 1 H, 3-H), 5.28 (dm, $^3J_{6,7}$ = 10.8 Hz, 1 H, 7-H), 4.24 (dd, $^3J_{3,4}$ = 6.4 Hz, $^3J_{4,5}$ = 9.0 Hz, 1 H, 4-H), 3.99 (dd, $^3J_{2,3}$ = 6.4 Hz, $^3J_{1,2}$ = 9.2 Hz, 1 H, 2-H), 3.89 (s, 5 H, Cp), 3.78 (m, 1 H, 8-H), 3.58 (ddd, $^3J_{1,2}$ = 9.2 Hz, $^3J_{1,8}$ = 5.8 Hz, 1 H, 1-H), 3.43 (dd, $^3J_{4,5}$ = 9.0 Hz, $^3J_{5,6}$ = 6.8 Hz, 1 H, 5-H), 3.34 (s, 3 H, CH_3), 3.23 (s, 3 H, CH_3), 2.11 (m, 4 H, 10-H, 11-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 170.9, 170.1 (C═O), 129.0 (C6), 125.4 (C7), 119.6 (CN), 99.3 (C3), 78.1 (C4), 77.3 (Cp), 77.2 (C2), 61.4 (C9), 52.1, 51.7 (CH_3), 45.2 (C8), 44.0 (C5), 42.5 (C1), 28.8, 13.7 (C10, C11) ppm. EI-MS (70 eV): *m/z* (%) 409 (18) [M^+], 343 (36), 225 (44) [$CpFeC_8H_8^+$], 199 (28) [$CpFeC_6H_6^+$], 186 (42) [$CpFeC_5H_5^+$], 121 (79) [$CpFe^+$], 104 (85) [$C_8H_8^+$]. Anal. Calcd for $C_{21}H_{23}N_1O_4Fe$ (409.26): C 61.63, H 5.66, N 3.42. Found: C 60.80, H 5.75, N 3.46.

(η^5-Cyclopentadienyl)[1,2,3,4,5-η-*8-exo*-(1,3-dioxo-1-ethoxy)but-2-ylcyclooctatrien-6-yl]iron (II) (2h): red oil,



2g

very soluble in Et_2O, toluene. IR (KBr): $\tilde{\nu}$ 3092 (w) ν(C−H, aromat.), 2983 (m), 2952 (m) ν(C−H, aliph.), 1739 (s), 1712 (s) ν(C═O), 1638 (w) ν(C═C), 1421 (m) $\delta(CH_3/CH_2)$, 1356 (m) $\delta(CH_3)$, 1243(m), 1155(m) ν(C−O) cm^{-1}. ^1H NMR (360 MHz, C_6D_6): δ 5.81, 5.76 (ddd, $^3J_{5,6} = 7.3$ Hz, $^3J_{6,7} = 10.6$ Hz, 1 H, 6-H), 5.42, 5.39 (t′, $^3J_{2,3} = {}^3J_{3,4} = 6.2$ Hz, 1 H, 3-H), 5.35, 5.25 (dm, $^3J_{6,7} = 10.6$ Hz, 1 H, 7-H), 4.31, 4.29 (dd, $^3J_{3,4} = 6.2$ Hz, $^3J_{4,5} = 8.9$ Hz, 1 H, 4-H), 4.08−3.90 (m, 6 H, CH_2, 2-H), 3.89, 3.88 (s, 5 H, Cp), 3.85 (dd, $^3J_{1,2} = 7.3$ Hz, 1 H, 1-H), 3.79 (m, 3 H, 1-H, 8-H), 3.54, 3.49 (dd, $^3J_{4,5} = 8.9$ Hz, $^3J_{5,6} = 7.3$ Hz, 1 H, 5-H), 3.10, 2.95 (d, $^3J_{8,9} = 8.9$ Hz, 1 H, 9-H), 2.07, 1.84 (s, 3 H, CH_3), 0.95, 0.84 (t, $^3J = 7.1$ Hz, 3 H, $CO_2CH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 169.4, 168.9 (C═O), 129.7, 129.6 (C6), 126.2, 125.5 (C7), 99.8, 99.7 (C3), 78.4, 78.2 (C4), 77.1 (Cp), 76.3, 76.1 (C2), 68.5 (C9), 60.9, 60.8 (C8), 48.6, 48.0 ($CO_2CH_2CH_3$), 44.7, 44.3 (C5), 39.4, 39.1 (C1), 29.8, 29.4 (CH_3), 14.2, 14.0 ($CO_2CH_2CH_3$) ppm. EI-MS (70 eV): *m*/*z* (%) 354 (22) [M^+], 311 (12) [$M^+ - CH_3CO$], 225 (40) [$CpFeC_8H_8^+$], 186 (77) [$CpFeC_5H_5^+$], 121 (96) [$CpFe^+$], 104 (89) [$C_8H_8^+$]. Anal. Calcd for $C_{19}H_{22}O_3Fe$ (354.23): C 64.42, H 6.26. Found: C 64.16, H 6.66.



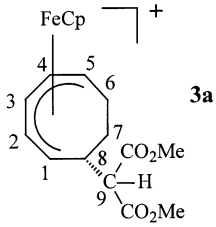
2h

General Procedure for the First Protonation (Synthesis of 3aBF$_4$−3gBF$_4$). Compound **2** was dissolved in Et_2O (50 mL). If a derivative of **2** was only sparingly soluble in Et_2O, a minimum amount of CH_2Cl_2 was added until a clear solution was obtained. At $T = -78$ °C an equimolar amount of HBF_4 dissolved in Et_2O was added. After 30 min stirring the reaction mixture was allowed to warm to room temperature. The product was obtained as a light red crystalline material or red oil. The upper layer was decanted, and the remaining oily or solid product was washed several times with Et_2O and dried under high vacuum. For more details see Table 2.

[(η^5-Cyclopentadienyl){(1,2,3,4,5,6-η-8-*exo*-di(methoxycarbonyl)methylcycloocta-1,3,5-triene}iron(II)] Tetrafluoroborate (3aBF$_4$): red oil, highly soluble in acetone and dichloromethane. IR (KBr): $\tilde{\nu}$ 3099 (w) ν(C−H, aromat.), 2953 (w) ν(C−H, aliph.), 1732 (s) ν(C═O), 1436 (m) (m) $\delta(CH_3/CH_2)$, 1260 (m), 1198 (m), 1155 (s) ν(C−O), 1084−1056 (s) $\nu(BF_4^-)$ cm^{-1}. ^1H NMR (200 MHz, $CD_3C(O)CD_3$): δ 7.20 (dd, $^3J_{3,4} = 9.0$ Hz, $^3J_{4,5} = 6.8$ Hz, 1 H, 4-H), 6.98 (dd,$^3J_{2,3} = 9.8$ Hz, $^3J_{3,4} = 9.0$ Hz, 1 H, 3-H), 6.90 (m, 1 H, 1-H), 6.71 (dd, $^3J_{4,5} = 6.8$ Hz, $^3J_{5,6} = 7.3$ Hz, 1 H, 5-H), 5.85 (dd, $^3J_{5,6} = 7.3$ Hz, $^3J_{6,7} = 10.5$ Hz, 1 H, 6-H), 5.73 (t′, $^3J_{1,2} = {}^3J_{2,3} = 9.8$ Hz, 1 H, 2-H), 5.32 (s, 5 H, Cp), 4.21 (m, 1 H, 8-H), 3.74 (s, 3 H, CH_3), 3.62 (s, 3 H, CH_3), 3.33 (d,$^3J_{8,9} = 7.1$ Hz, 1 H, 9-H), 1.33 (m, 1 H, 7_{endo}-H), −1.75 (m, 1 H, 7_{exo}-H) ppm.- $^{13}C\{^1H\}$NMR (50 MHz, C_6D_6): δ = 168.9 (C═O), 105.4 (C3), 97.6 (C4), 95.1 (C5), 93.9 (C1), 89.5 (C2), 88.0 (C6), 82.9 (Cp), 58.2 (C9), 52.7, 52.6 (CH_3), 51.2 (C8), 27.6 (C7) ppm. Anal. Calcd for $C_{18}H_{21}BF_4FeO_4 \cdot 1/5(CH_2Cl_2)$ (461.0): C 47.42, H 4.68. Found: C 47.63, H 4.58.

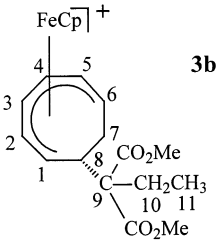
Table 2. Preparative Details of the First Protonation

starting complex	Nu[1]	mg (mmol)	product	yield mg (%)
2a	$CH(CO_2Me)_2$	211 (0.59)	**3a**BF_4	176 (67)
2b	$CEt(CO_2Me)_2$	274 (0.71)	**3b**BF_4	333 (98)
2c	CPh_2CN	128 (0.31)	**3c**BF_4	107 (68)
2e	$C(CO_2Et)_2(CH_2)_2CO_2Et$	238 (0.49)	**3d**BF_4	230 (83)
2f	$C(CO_2Et)_2(CH_2)_3CO_2Et$	337 (0.68)	**3e**BF_4	272 (68)
2g	$C(CO_2Me)_2(CH_2)_2CN$	300 (0.73)	**3f**BF_4	357 (98)
2h	$CH(COMe)CO_2Et$	122 (0.34)	**3g**BF_4	121 (80)



3a

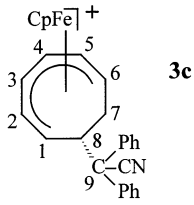
[(η^5-Cyclopentadienyl){1,2,3,4,5,6-η-8-*exo*-di(methoxycarbonyl)prop-1-ylcycloocta-1,3,5-triene}iron(II)] Tetrafluoroborate (3bBF$_4$): red crystalline powder, soluble in acetone and dichloromethane. Fp: 48 °C. IR (KBr): $\tilde{\nu}$ 3116 (w) ν(C−H, aromat.), 2953 (w), 2884 (w) ν(C−H, aliph.), 1725 (s) ν(C═O), 1457 (m), 1433 (m) $\delta(CH_3/CH_2)$, 1241 (s) ν(C−O), 1154−1058 (s) $\nu(BF_4^-)$ cm^{-1}. ^1H NMR (200 MHz, $CD_3C(O)CD_3$): δ 7.14 (dd, $^3J_{3,4} = 8.7$ Hz, $^3J_{4,5} = 7.0$ Hz, 1 H, 4-H), 6.98 (dm, $^3J_{1,2} = 10.4$ Hz, 1 H, 1-H), 6.92 (t′, $^3J_{2,3} = {}^3J_{3,4} = 8.9$ Hz, 1 H, 3-H), 6.70 (dd, $^3J_{4,5} = 7.0$ Hz, $^3J_{5,6} = 7.3$ Hz, 1 H, 5-H), 5.73 (m, 2 H, 6-H, 2-H), 5.32 (s, 5 H, Cp), 4.25 (ddd, $^3J_{1,8} = 5.5$ Hz, $^3J_{7exo,8} = 13.7$ Hz, $^3J_{7endo,8} = 8.8$ Hz, 1 H, 8-H), 3.69 (s, 3 H, CO_2CH_3), 3.67 (s, 3 H, CO_2CH_3), 1.81 (m, 2 H, 10-H), 1.42 (m, 1 H, 7_{endo}-H), 0.92 (t, $^3J = 7.6$ Hz, 3 H, 11-H), −1.84 (ddd, $^3J_{6,7exo} = 10.5$ Hz, $^3J_{7exo,7endo} = 12.2$ Hz, $^3J_{7exo,8} = 13.7$ Hz, 1 H, 7_{exo}-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CD_3C(O)CD_3$): δ 170.1 (C═O), 104.1 (C3), 97.0 (C4), 94.3 (C5), 92.4 (C1), 89.4 (C2), 85.5 (C6), 82.4 (Cp), 63.7 (C9), 52.8 (C8), 51.8 (CO_2CH_3), 26.9 (C10), 25.2 (C7), 8.4 (C11) ppm. FAB-MS: *m*/*z* (%) 385 (100) [$M^+ - BF_4$]. Anal. Calcd for $C_{20}H_{25}BF_4FeO_4$ (472.07): C 50.89, H 5.34. Found: C 49.42, H 5.45.



3b

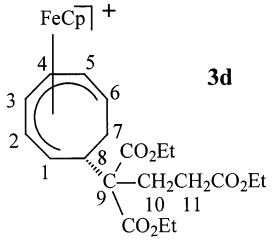
[(η^5-Cyclopentadienyl){1,2,3,4,5,6-η-8-*exo*-{(diphenylcyano)methylcycloocta-1,3,5-triene}iron(II)] Tetrafluoroborate (3cBF$_4$): light red crystalline powder, soluble in acetone and dichloromethane. Decomp. > 115 °C. IR (KBr): $\tilde{\nu}$ 3109 (w), 3059 (w) ν(C−H, aromat.), 2946 (w) ν(C−H, aliph.), 2239 (w) ν(C≡N), 1696 (w), 1600 (w), 1492 (m), 1449 ν(C═C, aromat.), 1084−1001 (s) $\nu(BF_4^-)$, 750 (m), 701 (m) δ(C−H, aromat.) cm^{-1}. ^1H NMR (360 MHz, $CD_3C(O)CD_3$): δ 7.93 (d, $^3J_{ortho,meta} = 7.9$ Hz, 2 H, $phenyl_{ortho}$), 7.54 (m, 4 H, $phenyl_{ortho,meta}$), 7.44 (t, $^3J_{meta,para} = 7.2$ Hz, 1 H, $phenyl_{para}$), 7.34 (dd, $^3J_{ortho,\ meta} = 7.9$ Hz, $^3J_{meta,para} = 7.2$ Hz, 2 H, $phenyl_{meta}$), 7.25 (t, $^3J_{meta,para} = 7.2$ Hz, 1 H, $phenyl_{para}$), 7.20 (dd, $^3J_{3,4} = 8.9$ Hz, $^3J_{4,5} = 7.6$ Hz, 1 H, 4-H), 7.02 (dd, $^3J_{2,3} = 9.2$ Hz, $^3J_{3,4} = 8.9$ Hz, 1 H, 3-H), 6.70 (dd, $^3J_{4,5} = 7.6$ Hz, $^3J_{5,6} = 7.2$ Hz, 1 H, 5-H), 6.56 (ddd, $^3J_{1,2} = 10.2$ Hz, $^3J_{1,8} = 6.9$ Hz,

1 H, 1-H), 5.84 (m, 2 H, 2-H, 6-H), 5.31 (s, 5 H, Cp), 5.27 (m, 1 H, 8-H), 1.12 (m, 1 H, 7_{endo}-H), −1.60 (m, 1 H, 7_{exo}-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CD_3C(O)CD_3$): δ 141.8, 139.6 (C_q-phenyl), 131.1, 130.6 (C_{meta}-phenyl), 129.8, 129.6 (C_{para}-phenyl), 128.5, 127.2 (C_{ortho}-phenyl), 122.1 (CN), 105.8 (C3), 98.5 (C4), 95.9 (C5), 91.3 (C2), 90.9 (C1), 86.2 (C6), 83.8 (Cp), 61.5 (C9), 56.8 (C8), 27.4 (C7) ppm. FAB-MS: *m*/*z* (%) 418 (100) [$M^+ - BF_4$], 313 (32) [$M^+ - BF_4 - C_8H_9$], 226 (57) [$CpFeC_8H_8^+$]. Anal. Calcd for $C_{27}H_{24}BF_4FeN \cdot 1/5(CH_2Cl_2)$ (522.13): C 62.57, H 4.71, N 2.68 for $C_{27}H_{24}BF_4FeN$. Found: C 62.63, H 4.87, N 2.69.



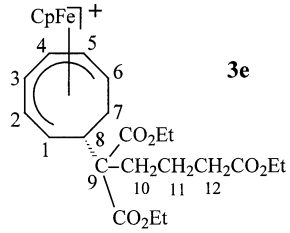
3c

[(η^5-Cyclopentadienyl){1,2,3,4,5,6-η-8-*exo*-{(1,1,3-triethoxycarbonyl)prop-1-ylcycloocta-1,3,5-triene}iron-(II)] Tetrafluoroborate (3dBF_4): red oil, very soluble in acetone and dichloromethane. IR (KBr): $\tilde{\nu}$ 3107 (w) ν(C−H, aromat.), 2985 (w) ν(C−H, aliph.), 1726 (s) ν(C═O), 1635 (w) ν(C═C), 1447 (m), 1419 (m) $\delta(CH_3/CH_2)$, 1370 (m) $\delta(CH_3)$, 1227 (s), 1163 (s) ν(C−O), 1083−1030 (s) $\nu(BF_4^-)$ cm^{-1}. ^1H NMR (200 MHz, $CD_3C(O)CD_3$): δ 7.15 (dd, $^3J_{3,4} = 8.9$ Hz, $^3J_{4,5} = 6.8$ Hz, 1 H, 4-H), 6.98 (dm, $^3J_{1,2} = 10.6$ Hz, 1 H, 1-H), 6.92 (t′, $^3J_{2,3} = {}^3J_{3,4} = 8.9$ Hz, 1 H, 3-H), 6.69 (dd, $^3J_{4,5} = 6.8$ Hz, $^3J_{5,6} = 7.6$ Hz, 1 H, 5-H), 5.75 (m, 2 H, 2-H, 6-H), 5.32 (s, 5 H, Cp), 4.26 (m, 1 H, 8-H), 4.17 (t, $^3J = 7.3$ Hz, 4 H, 2 × $CO_2CH_2CH_3$), 4.09 (t, $^3J = 7.3$ Hz, 2 H, $CO_2CH_2CH_3$), 2.29 (m, 4 H, 10-H, 11-H), 1.43 (m, 1 H, 7_{endo}-H), 1.22 (m, 9 H, $CO_2CH_2CH_3$), −1.77 (m, 1 H, 7_{exo}-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CD_3C(O)CD_3$): δ 173.1, 170.0, 169.9 (C═O), 104.9 (C3), 97.8 (C4), 95.1 (C5), 92.7 (C1), 90.4 (C2), 86.4 (C6), 83.2 (Cp), 62.6 (C9), 62.1, 62.0, 60.9 ($CO_2CH_2CH_3$), 54.2 (s, C8), 30.5, 29.0 (s, C10, C11), 26.0 (s, C7), 14.5, 14.3, 14.2 (s, $CO_2CH_2CH_3$) ppm. FAB-MS: *m*/*z* (%) 485 (100) [$M^+ - BF_4$]. Anal. Calcd for $C_{25}H_{33}BF_4FeO_6 \cdot (CH_2Cl_2)$ (657.12): C 47.52, H 5.37. Found: C 47.76, H 5.99.



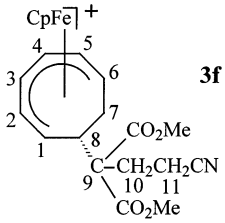
3d

[(η^5-Cyclopentadienyl){1,2,3,4,5,6-η-8-*exo*-(1,1,4-triethoxycarbonyl)but-1-ylcycloocta-1,3,5-triene)iron(II)] Tetrafluoroborate (3eBF_4): red oil, only sparingly soluble in Et_2O, but very soluble in dichloromethane and acetone. IR (KBr): $\tilde{\nu}$ 3115 (w) ν(C−H, aromat.), 2983 (w), 2939 (w) ν(C−H, aliphat.), 1723 (s) ν(C═O), 1431 (m) u, 1420 (m) $\delta(CH_3/CH_2)$, 1370 (m) $\delta(CH_3)$, 1212 (s) u, 1177 (s) ν(C−O), 1083 (s) u, 1053 (s) $\nu(BF_4^-)$ cm^{-1}. ^1H NMR (200 MHz, $CD_3C(O)CD_3$): δ 7.13 (dd, $^3J_{3,4} = 9.0$ Hz, $^3J_{4,5} = 7.0$ Hz, 1 H, 4-H), 7.03 (dm, $^3J_{1,2} = 10.3$ Hz, 1 H, 1-H), 6.90 (t′, $^3J_{2,3} = {}^3J_{3,4} = 9.0$ Hz, 1 H, 3-H), 6.69 (dd, $^3J_{4,5} = 7.0$ Hz, $^3J_{5,6} = 7.6$ Hz, 1 H, 5-H), 5.75 (m, 2 H, 2-H, 6-H), 5.30 (s, 5 H, Cp), 4.28 (m, 1 H, 8-H), 4.13 (m, 6 H, 3 × $CO_2CH_2CH_3$), 2.36 (t′, $^3J = 6.7$ Hz, 2 H, 12-H), 1.72 (m, 4 H, 10-H, 11-H), 1.49 (m, 1 H, 7_{endo}-H), 1.23 (dt, $^3J = 7.1$ Hz, 3 H, $CO_2CH_2CH_3$), 1.21 (t, $^3J = 7.1$ Hz, 3 H, $CO_2CH_2CH_3$), 1.12 (t, $^3J = 7.1$ Hz, 3 H, $CO_2CH_2CH_3$), −1.80 (ddd, $^2J_{7exo,7endo} = 12.5$ Hz, $^3J_{6,7exo} = {}^3J_{7exo,8} = 10.5$ Hz, 1 H, 7_{exo}-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CD_3C(O)CD_3$): δ 173.3, 170.2, 170.1 (C═O), 104.9 (C3), 97.7 (C4), 95.0 (C5), 93.6 (C1), 90.3 (C2), 86.5 (C6), 83.1 (Cp), 63.5 (C9), 62.0, 61.9, 60.7 ($CO_2CH_2CH_3$), 53.5 (C8), 34.2 (C12), 33.7 (C11), 25.9 (C7), 20.2 (C10), 14.6, 14.3, 14.2 ($CO_2CH_2CH_3$) ppm. FAB-MS: *m*/*z*, (%) 499 (100) [$M^+ - BF_4$], 385 (2) [$M^+ - BF_4 - CH_2CH_2CH_2CO_2C_2H_5$], 274 (3) [$HC(CO_2Et)_2(CH_2)_3CO_2Et^+$]. Anal. Calcd for $C_{26}H_{35}BF_4FeO_6 \cdot 1/3(CH_2Cl_2)$ (614.52): C 51.47, H 5.85. Found: C 51.64, H 5.87.



3e

[(η^5-Cyclopentadienyl){1,2,3,4,5,6-η-8-*exo*-(3-cyano-1,1-dimethoxycarbonyl)-prop-1-ylcycloocta-1,3,5-triene}iron-(II)] Tetrafluoroborate (3fBF_4): orange powder, sparingly soluble in acetone, very soluble in acetonitrile. Fp: 85 °C. IR (KBr): $\tilde{\nu}$ 3107 (w) ν(C−H, aromat.), 2954 (w) ν(C−H, aliphat.), 2248 (m) ν(C≡N), 1726 (s) ν(C═O), 1432 (m) $\delta(CH_3/CH_2)$, 1240 (s) ν(C−O), 1084−1037 (s) $\nu(BF_4^-)$ cm^{-1}. ^1H NMR (360 MHz, $CD_3C(O)CD_3$): δ 7.17 (dd, $^3J_{3,4} = 8.8$ Hz, $^3J_{4,5} = 7.0$ Hz, 1 H, 4-H), 6.99 (ddd, $^3J_{1,2} = 10.3$ Hz, $^3J_{1,8} = 5.9$ Hz, 1 H, 1-H), 6.95 (dd, $^3J_{2,3} = 9.2$ Hz, $^3J_{3,4} = 8.8$ Hz, 1 H, 3-H), 6.73 (t′, $^3J_{4,5} = {}^3J_{5,6} = 7.0$ Hz, 1 H, 5-H), 5.79 (m, 1 H, 2-H) 5.76 (m, 1 H, 6-H), 5.31 (s, 5 H, Cp), 4.29 (ddd, $^3J_{1,8} = 5.9$ Hz, $^3J_{7exo,8} = 10.5$ Hz, 1 H, 8-H), 3.73 (s, 3 H, Me), 3.70 (s, 3 H, Me), 2.65 (t′, $^3J = 7.4$ Hz, 2 H, 11-H), 2.43 (ddd, $^3J = 7.4$ Hz, 1 H, 10-H), 2.23 (ddd, $^3J = 7.4$ Hz, 1 H, 10-H), 1.45 (m, 1 H, 7_{endo}-H), −1.78 (ddd, $^2J_{7exo,7endo} = 12.5$ Hz, $^3J_{7exo,8} = {}^3J_{6,7exo} = 10.5$ Hz, 1 H, 7_{exo}-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CD_3C(O)CD_3$): δ 169.9, 169.8 (C═O), 133.1 (CN), 105.2 (C3), 97.9 (C4), 95.2 (C5), 91.6 (C1), 90.3 (C2), 86.2 (C6), 83.3 (Cp), 62.6 (C9), 54.2 (C8), 53.1, 53.0 (CH_3), 39.9 (C11, C12), 26.0 (C7) ppm. FAB-MS: *m*/*z* (%) 410 (100) [$M^+ - BF_4$]. Anal. Calcd for $C_{21}H_{24}BF_4FeNO_4$ (497.08): C 50.74, H 4.87, N 2.82. Found: C 50.03, H 5.07, N 2.47.



3f

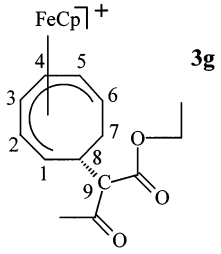
[(η^5-Cyclopentadienyl){1,2,3,4,5,6-η-8-*exo*-(1,3-dioxo-1-ethoxy)but-2-ylcycloocta-1,3,5-triene}iron(II)] Tetrafluoroborate (3gBF_4): orange oil, very soluble in acetone and dichloromethane. IR (KBr): $\tilde{\nu}$ 3109 (w) ν(C−H, aromat.), 2986 (w), 2939 (w) ν(C−H, aliph.), 1731 (s), 1710 (s) ν(C═O), 1454 (w), 1419 (w) $\delta(CH_3/CH_2)$, 1367 (w) $\delta(CH_3)$, 1248 (m) ν(C−O), 1118−1051 (s) ν (BF_4^-) cm^{-1}. ^1H NMR (360 MHz, $CD_3C(O)CD_3$): δ 7.20 (m, 2 H, 4-H), 6.97, 6.95 (dd, $^3J_{2,3} = 9.2$ Hz, $^3J_{3,4} = 8.9$ Hz, 1 H, 3-H), 6.85, 6.84 (dd, $^3J_{1,2} = 10.2$ Hz, $^3J_{1,8} = 4.3$ Hz, 1 H, 1-H), 6.68 (t′, $^3J_{4,5} = {}^3J_{5,6} = 7.2$ Hz, 1 H, 5-H), 5.83 (m, 2 H, 6-H), 5.71 (dd, $^3J_{1,2} = 10.2$ Hz, $^3J_{2,3} = 9.2$ Hz, 1 H, 2-H), 5.30 (s, 10 H, Cp), 4.25, 4.06 (q, $^3J = 7.2$ Hz, 2 H, $CO_2CH_2CH_3$), 4.20 (m, 2 H, 8-H), 3.49, 3.34 (d, $^3J_{8,9} = 7.9$ Hz, 1 H, 9-H), 2.25, 2.11 (s, 3 H, CH_3), 1.29, 1.17 (t, $^3J = 7.2$ Hz, 3 H, $CO_2CH_2CH_3$), 1.27 (m, 2 H, 7_{endo}-H), −1.82 (m, 2 H, 7_{exo}-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CD_3C(O)CD_3$): δ 167.2 (s, C═O), 104.9, 104.6 (C3), 96.9 (C4), 94.4 (C5), 94.2 (C1), 88.8, 88.7 (C2), 88.1, 88.0 (C6), 82.3, 82.2 (Cp), 66.0 (C9), 61.5, 61.2 ($CO_2CH_2CH_3$), 50.3 (s, C-8), 27.5, 26.6 (s, C-7), 29.0 (s, CH_3), 27.5, 26.6 (s, C-7), 13.6, 13.5 (s, $CO_2CH_2CH_3$) ppm. FAB-MS: *m*/*z* (%) 356 (100) [$M^+ - BF_4$], 225 (25) [$CpFeC_8H_8^+$]. Anal.

Table 3. Preparative Details of the Second Nucleophilic Addition

starting complex	Nu[1]	mg (mmol)	HNu[2]	mg (mmol)	base	reaction time (h)	product	yield mg (%)
3aBF_4	$CH(CO_2Me)_2$	1831 (4.52)	$HCH(CO_2Me)_2$	704 (4.57)	NaH	2	**4a**	1943 (87)
3aBF_4	$CH(CO_2Me)_2$	52 (0.13)	$HCH(CO_2Me)_2$	26 (0.20)	TMG	23	**4a**	56 (86)
3bBF_4	$CEt(CO_2Me)_2$	201 (0.43)	$HCH(CO_2Me)_2$	54 (0.41)	NaH	18	**4b**	174 (79)
3cBF_4	CPh_2CN	274 (0.54)	CPh_2CN	100 (0.52)	NaH	24	**4c**	261 (79)
3dBF_4	$C(CO_2Et)_2$-$(CH_2)_2CO_2Et$	200 (0.35)			TMG[a]	3	**4d**	n.d.[b]
3eBF_4	$C(CO_2Et)_2$-$(CH_2)_3CO_2Et$	260 (0.52)			TMG[a]	3	**4e**	n.d.[b]

[a] Attempts of an intramolecular nucleophilic addition. [b] n.d. = not determined since varying amounts of $[HTMG]BF_4$ and TMG were present in the product.

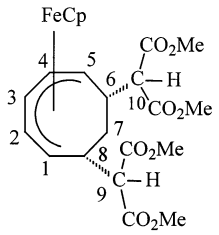
Calcd for $C_{19}H_{23}BF_4FeO_3 \cdot 1/6(CH_2Cl_2)$ (456.10): C 50.47, H 5.52. Found: C 50.68, H 5.42.



3g

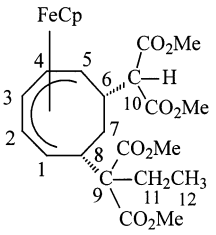
Second Nucleophilic Addition (Synthesis of 4a−d). The second nucleophilic addition was performed in close analogy with the first one (vide supra). For more preparative details see Table 3. Attempts of the intramolecular second nucleophilic addition: 1 equiv of **3d**BF_4 (200 mg, 0.35 mmol) and **3e**BF_4 (260 mg, 0.52 mmol), respectively, were dissolved in CH_2Cl_2 (20 and 30 mL, respectively), and 8 equiv of TMG was added slowly. After stirring for 3 h the solvent was removed in vacuo. The residue was too soluble in Et_2O and hydrocarbon solvents, and attempts of chromatography led to decomposition of the product. Hence, the products were characterized by means of ^1H, ^{13}C NMR, and IR spectroscopy and FAB-MS.

[(η^5-Cyclopentadienyl)(1,2,3,4,5-η-6,8-*exo*,*exo*-bis{di(methoxycarbonyl)methyl}cyclooctadienyl]iron(II) (4a): orange powder, soluble in diethyl ether, very soluble in toluene. Fp: 142 °C. IR (KBr): $\tilde{\nu}$ 3002 (w) ν(C−H, aromat.), 2980 (w), 2950 (m) ν(C−H, aliph.), 1729 (s) ν(C═O), 1631 (w) ν(C═C), 1439 (m), 1423 (m) $\delta(CH_2/CH_3)$, 1343 (m) $\delta(CH_3)$, 1256 (m), 1229 (m), 1191 (m), 1163 (m), 1154 (m) ν(C−O) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 5.55 (t′, $^3J_{2,3} = {}^3J_{3,4} = 5.3$ Hz, 1 H, 3-H), 3.89 (s, 5 H, Cp), 3.78 (m, 4 H, 1-H, 2-H, 4-H, 5-H), 3.39 (s, 3 H, CH_3), 3.34 (s, 9 H, CH_3), 3.32 (m, 2 H, 9-H, 10-H), 2.83 (m, 2 H, 6-H, 8-H), 1.03 (d, $^2J_{7exo,7endo} = 12.8$ Hz, 1H, 7_{endo}-H), −0.63 (m, 1 H, 7_{exo}-H). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 169.1, 168.7 (C═O), 103.6 (C3), 77.5 (Cp), 73.0 (C2, C4), 61.3 (C9, C10), 51.7, 51.6 (CH_3), 48.8 (C1, C5), 42.4 (C6, C8), 26.3 (C7) ppm. Anal. Calcd for $C_{23}H_{28}FeO_8$ (488.32): C 56.57, H 5.78. Found: C 56.61, H 5.68.



4a

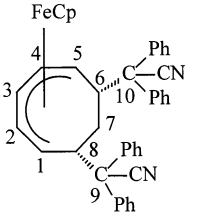
(η^5-Cyclopentadienyl)[1,2,3,4,5-η-6-*exo*-di(methoxycarbonyl)methyl-8-*exo*-di(methoxycarbonyl)prop-1-yl-cyclooctadienyl]iron(II) (4b): orange powder, soluble in diethyl ether, very soluble in toluene. IR (KBr): $\tilde{\nu}$ 3090 (w) ν(C−H, aromat.), 2952 (m) ν(C−H, aliph.), 1732 (s) ν(C═O), 1436 (m) $\delta(CH_2/CH_3)$, 1238 (s), 1156 (s), 1132 (s) ν(C−O) cm^{-1}. ^1H NMR (360 MHz, C_6D_6): δ 5.59 (t′, $^3J_{2,3} = {}^3J_{3,4} = 6.5$ Hz, 1 H, 3-H), 3.94 (s, 5 H, Cp), 3.92 (m, 1 H, 1-H), 3.83 (dd, $^3J_{3,4} = 6.5$ Hz, $^3J_{4,5} = 8.4$ Hz, 1 H, 4-H), 3.82 (dd, $^3J_{1,2} = 8.4$ Hz, $^3J_{2,3} = 6.5$ Hz, 1 H, 2-H), 3.66 (dm, $^3J_{4,5} = 8.4$ Hz, 1 H, 5-H), 3.45, 3.43, 3.41, 3.33 (s, 3 H, CO_2CH_3), 3.34 (d, $^3J_{6,12} = 9.2$ Hz, 1 H, 10-H), 2.83 (m, 1 H, 6-H), 2.72 (dm, $^3J_{7,8} = 12.2$ Hz, 1 H, 8-H), 2.34 (m, 1 H, 11-H), 2.12 (m, 1 H, 11-H), 1.08 (m, 1 H, 7_{endo}-H), 1.05 (t, $^3J = 7.5$ Hz, 3 H, 12-H), −0.76 (m, 1 H, 7_{exo}-H) ppm. ^1H NMR (360 MHz, CD_3CN): δ 5.94 (t′, $^3J_{2,3} = {}^3J_{3,4} = 6.6$ Hz, 1 H, 3-H), 4.28 (s, 5 H, Cp), 3.99 (dd, $^3J_{3,4} = 6.6$ Hz, $^3J_{4,5} = 8.4$ Hz, 1 H, 4-H), 3.97 (dd, $^3J_{1,2} = 8.4$ Hz, $^3J_{2,3} = 6.6$ Hz, 1 H, 2-H), 3.75 (dm, $^3J_{1,2} = 8.4$ Hz, 1 H, 1-H), 3.68 (s, 3 H, CO_2CH_3), 3.59 (s, 6 H, CO_2CH_3), 3.58 (s, 3 H, CO_2CH_3), 3.53 (dm, $^3J_{4,5} = 8.4$ Hz, 1 H, 5-H), 3.07 (d, $^3J_{6,12} = 7.6$ Hz, 1 H, 10-H), 2.30 (m, 2 H, 6-H, 8-H), 2.08 (m, 1 H, 11-H), 1.90 (m, 1 H, 11-H), 0.83 (t, $^3J = 7.5$ Hz, 3 H, 12-H), 0.52 (m, 1 H, 7_{endo}-H), −1.11 (m, 1 H, 7_{exo}-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 171.5, 171.4, 169.1, 168.6 (C═O), 103.2 (C3), 77.5 (Cp), 74.6 (C4), 72.8 (C2), 65.0 (C9), 61.8 (C10), 51.7, 51.6, 51.4 (CO_2CH_3), 48.2 (C5), 46.9 (C6), 46.8 (C1), 43.6 (C8), 27.5 (C11), 24.4 (C7), 9.8 (C12) ppm. FAB-MS: *m*/*z*, (%) 516 (62) [M^+], 484 (18) [$M^+ - CH_4O$], 450 (68) 385 (56) [$M^+ - (CH(COOCH_3)_2)$], 357 (92) [$M^+ - C(COOCH_3)_2Et$]. Anal. Calcd for $C_{25}H_{32}O_8Fe \cdot 1/3(C_7H_8)$ (547.09): C 59.98, H 6.39. Found: C 59.88, H 6.65.



4b

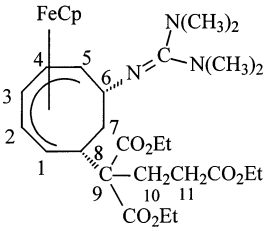
(η^5-Cyclopentadienyl)[1,2,3,4,5-η-6,8-*exo*,*exo*-bis-{(diphenylcyano)methyl}cyclooctadienyl]iron(II) (4c): orange-red powder, sparingly soluble in diethyl ether, very soluble in dichloromethane and toluene. IR (KBr): $\tilde{\nu}$ 3086 (w), 3058 (w), 3022 (w) ν(C−H, aromat.), 2961 (w), 2930 (w) ν(C−H, aliph.), 2237 (w) ν(C≡N), 1657 (w), 1599 (m), 1493 (s), 1450 (s) ν(C═C, aromat.), 746 (s), 703 (s) δ(C−H, aromat.) cm^{-1}. ^1H NMR (360 MHz, C_6D_6): δ 7.66 (d, $^3J_{ortho,meta} = 7.6$ Hz, 4 H, $phenyl_{ortho}$), 7.15−6.92 (m, 10 H, phenyl), 6.75 (m, 6 H, $phenyl_{meta,para}$), 5.70 (t′, 3J2,3 = $^3J_{3,4} = 6.8$ Hz, 1 H, 3-H), 4.05 (dd, $^3J_{1,2} = {}^3J_{4,5} = 8.6$ Hz, $^3J_{2,3} = {}^3J_{3,4} = 6.8$ Hz, 2 H, 2-H, 4-H), 3.73 (s, 5 H, Cp), 3.69 (dm, $^3J_{1,2} = {}^3J_{4,5} = 8.6$ Hz, 2 H, 1-H, 5-H), 2.89 (dm, $^3J_{6,7exo} = {}^3J_{7exo,8} = 11.9$ Hz, 2 H, 6-H, 8-H), 0.77 (dm, $^2J = 12.8$ Hz, 7_{endo}-H), −0.42 (m, 1 H, 7_{exo}-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 141.3, 139.8 (C_q-phenyl), 129.1, 128.9 (C_{meta}-phenyl), 127.6 (C_{ortho}-phenyl), 127.1, 126.7 (C_{para}-phenyl), 121.3 (CN), 103.1 (C3), 77.1 (Cp), 75.9 (C2, C4), 61.1 (C9, C10), 50.5 (C6, C8), 45.7 (C1, C5), 42.5 (C7) ppm.

FAB-MS: *m/z* (%) 532 (7) [$M^+ - C_6H_6$], 418 (92) [$M^+ - CPh_2CN$], 313 (62) [$M^+ - \{(CPh_2CN)(C_8H_9)\}$], 226 (100) [$CpFeC_8H_8^+$]. Anal. Calcd for $C_{41}H_{34}FeN_2$ (610.58): C 80.65, H 5.61, N 4.59. Found: C 79.24, H 5.64, N 4.68.



4c

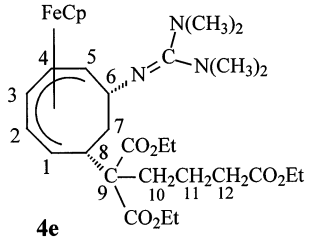
(η^5-Cyclopentadienyl)[1,2,3,4,5-η-6-*exo*-tetramethylguanidinyl-8-*exo*-[1,1,3-triethoxycarbonyl)prop-1-ylcyclooctadienyl]iron(II) (4d): red oil, light and moisture sensitive, highly soluble in diethyl ether and toluene. IR (KBr): $\tilde{\nu}$ 3083 (w) ν(C−H, aromat.), 2981 (w), 2938 (m) ν(C−H, aliph.), 1732 (s) ν(C═O), 1608 (s) ν(C═N), 1449 (w), 1367 (m) δ(CH_3/CH_2), 1240 (s), 1181 (s), 1036 (s) ν(C−O) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 5.70 (t′, $^3J_{2,3} = {}^3J_{3,4}$ = 6.2 Hz, 1 H, 3-H), 4.15−3.83 (m, 10 H, 4-H, 2-H, 6-H, 1-H, $CO_2CH_2CH_3$), 3.97 (s, 5 H, Cp), 3.65 (dm, $^3J_{4,5}$ = 6.3 Hz, 1 H, 5-H), 3.00 (dm, $^3J_{7exo,8}$ = 12.4 Hz, 1 H, 8-H), 2.88−2.65 (m, 4 H, 10-H, 11-H), 2.66 (m, 12 H, NCH_3), 1.15 (m, 1 H, 7_{endo}-H), 0.95, 0.92, 0.91 (t, ^3J = 7.0 Hz, 3 H, $CO_2CH_2CH_3$), −0.23 (m, 1 H, 7_{exo}-H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 172.9, 171.2, 170.8 (s, C═O), 103.0 (s, C-3), 77.1 (s, Cp), 74.8 (s, C-2), 74.4 (s, C-4), 63.5 (s, C-9), 62.0 (C-6), 60.7, 60.2 (s, $CO_2CH_2CH_3$), 55.0 (C5), 47.7 (C8), 45.8 (C1), 40.3 (NCH_3), 31.0 (C10), 28.9 (C11), 29.6 (C7), 14.3, 14.2, 14.1 ($CO_2CH_2CH_3$) ppm. FAB-MS: *m/z*, (%) 599 (3) [M^+], 485 (100) [$M^+ - NC(N(CH_3)_2)_2$], 315 (22) [$M^+ - \{(C_2H_5O)_2(COOC_2H_5)\}$]. $C_{30}H_{45}FeN_3O_6$ (599.55).



4d

(η^5-Cyclopentadienyl)[1,2,3,4,5-η-6-*exo*-tetramethylguanidinyl-8-*exo*-{1,1,4-triethoxycarbonyl)butylcyclooctadienyl]iron(II) (4e): red oil, light and moisture sensitive, highly soluble in diethyl ether and toluene. IR (KBr): $\tilde{\nu}$ 3109 (w) ν(C−H, aromat.), 2981 (w) ν(C−H, aliph.), 1728 (s) ν(C═O), 1456 (m), 1413 (m) δ(CH_3/CH_2), 1649 (m), 1611 (s), 1567 (m) ν(C═N), 1234 (s), 1160 (s) ν(C−O) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 5.94 (t′, $^3J_{2,3} = {}^3J_{3,4}$ = 6.3 Hz, 1 H, 3-H), 4.46 (dd, $^3J_{3,4}$ = 6.3 Hz, 1 H, 4-H), 4.21 (s, 5 H, Cp), 4.16−3.99 (m, 6 H, 2-H, 1-H, 2 × $CO_2CH_2CH_3$), 3.95 (q, ^3J = 7.3 Hz, 2 H, $CO_2CH_2CH_3$), 3.78 (m, 1 H, 5-H), 3.66 (dm, $^3J_{6,7}$ = 12.0 Hz, 1 H, 6-H), 2.83 (m, 1 H, 8-H), 2.60 (m, 12 H, N-CH_3), 2.42 (m, 1 H, 10-H), 2.22 (m, 3 H, 10-H,12-H), 1.93 (m, 1 H, 11-H), 1.75 (m, 1 H, 11-H), 1.16 (m, 1 H, 7_{endo}-H), 1.12, 1.05, 0.98 (t, ^3J = 7.3 Hz, 3 H, $CO_2CH_2CH_3$), −0.52 (m, 1 H, 7_{exo}-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 172.7, 171.2, 170.5 (C═O), 160.0 (TMG), 104.4 (C3), 77.8 (Cp), 75.4 (C2), 73.4 (C4), 63.7 (C9), 61.3 (C6), 61.0, 60.2 ($CO_2CH_2CH_3$), 48.3 (C5), 46.6 (C1), 45.9 (C8), 39.3 (NCH_3), 34.3 (C10), 33.3 (C12), 27.6 (C7), 20.6 (C11), 14.3, 14.2 ($CO_2CH_2CH_3$) ppm. FAB-MS: *m/z* (%) 614 (3) [M^+], 499 (100) [$M^+ - NC(N(CH_3)_2)_2$], 225 (9) [$CpFeC_8H_8^+$]. $C_{26}H_{34}FeO_6$ (613.58).

General Procedure to Cleave the Cyclooctadiene Ligand. Ten equivalents of CF_3COOH was added to a solution



4e

of 1 equiv of **4a**−**c** in MeCN. The reaction mixture changed from red to violet and finally became colorless after 30 min. After 2 h stirring at room temperature, the reaction mixture was evaporated to dryness. The residual brownish oil was chromatographed on silica gel 60, with hexane−ethyl acetate, 2:7, as eluent. The fractions of the column chromatography were monitored by TLC. For more details see Table 4.

***cis*-5,7-Bis[(dimethoxycarbonyl)methyl]cycloocta-1,3-diene (6a):** colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ 6.01 (dd, $^3J_{1,2}$ = 10.5 Hz, $^3J_{2,3}$ = 3.4 Hz, 1 H, 2-H), 5.91 (m, 1 H, 3-H), 5.80 (dd, $^3J_{1,2}$ = 10.5 Hz, $^3J_{1,8cis}$ = 8.1 Hz, 1 H, 1-H), 5.58 (dd, $^3J_{3,4}$ = 10.8 Hz, $^3J_{4,5}$ = 7.8 Hz, 1 H, 4-H), 3.75, 3.74, 3.73, 3.72 (s, 3 H, CH_3), 3.46 (d, $^3J_{5,10}$ = 8.3 Hz, 1 H, 10-H), 3.31 (d, $^3J_{7,9}$ = 7.6 Hz, 1 H, 9-H), 2.86 (m, 1 H, 5-H), 2.26 (dd, $^3J_{1,8}$ = 8.1 Hz, $^2J_{8,8}$ = 12.7 Hz, 1 H, 8_{cis}-H), 2.11 (m, 1 H, 7-H), 1.86 (ddd, $^3J_{7,8}$ = 8.6 Hz, $^2J_{8,8}$ = 12.7 Hz, 1 H, 8_{trans}-H), 1.46 (dd, $^2J_{6,6}$ = 13.2 Hz, $^3J_{6,7}$ = 3.7 Hz, 1 H, 6_{cis}-H), 1.25 (m, 1 H, 6_{trans}-H) ppm. $^{13}C\{^1H\}$ NMR (50 MHz $CDCl_3$): δ 169.0, 168.2 (C═O), 132.0, 130.6, 127.8. 126.8 (C1−C4), 57.9, 57.2, (C9, C10), 52.4 (CH_3), 38.2, 35.5, 31.7, 31.4, (C5−C8). MS (70 eV): *m/z* (%) 368 (4) [M^+], 336 (5), 305 (8), 276 (13), 236 (17), 189 (20), 176 (49), 133 (21), 117 (89), 105 (100). Anal. Calcd for $C_{18}H_{24}O_8$ (368.38): C 58.69, H 6.57. Found: C 58.87, H 6.91.

***cis*-5-[1′,1′,-Di(methoxycarbonyl)prop-1-yl]-7-di(methoxycarbonyl)methylcycloocta-1,3-diene (6b):** colorless oil. IR (KBr): $\tilde{\nu}$ 2953 (m) ν(C−H, aliph.), 1735 (s) ν(C═O), 1627 (w) ν(C═C), 1436 (m) δ(CH_3/CH_2), 1295−1156 (s) ν(C−O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.98 (m, 2 H, 2-H, 3-H), 5.86 (ddd, $^3J_{1,2}$ = 10.2 Hz, $^3J_{1,8cis}$ = 7.9 Hz, $^3J_{1,8trans}$ = 7.9 Hz, 1 H, 1-H), 5.59 (dd, $^3J_{3,4}$ = 10.2 Hz, $^3J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.73 (s, 6 H, CH_3), 3.72, 3.71 (s, 3 H, CH_3), 3.31 (d, $^3J_{7,9}$ = 7.6 Hz, 1 H, 9-H), 2.76 (t′, $^3J_{4,5} = {}^3J_{5,6trans}$ = 9.2 Hz, 1 H, 5-H), 2.20 (dd, $^3J_{1,8}$ = 7.9 Hz, $^2J_{8,8}$ = 12.7 Hz, 1 H, 8_{cis}-H), 2.10 (m, 1 H, 7-H), 1.95−1.78 (m, 3 H, 11-H, 8_{trans}-H), 1.71 (dd, $^2J_{6,6}$ = 13.2 Hz, $^3J_{6,7}$ = 3.6 Hz, 1 H, 6_{cis}-H), 0.98 (ddd, $^3J_{5,6}$ = 9.2 Hz, $^2J_{6,6}$ = 13.2 Hz, $^3J_{6,7}$ = 12.2 Hz, 1 H, 6_{trans}-H), 0.71 (t, ^3J = 7.6 Hz, 3 H, 12-H) ppm. $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ 171.9, 171.8, 169.5, 169.4 (C═O), 132.0 (C2), 131.7 (C3), 127.8 (C4), 127.2 (C1), 62.9 (C10), 57.8 (C9), 52.8, 52.7, 52.5, 52.4 (CO_2CH_3), 41.1 (C5), 35.9 (C7), 32.5 (C6), 32.1 (C8), 27.6 (C11), 9.1 (C12) ppm. EI-MS (70 eV): *m/z* (%) 396 (6) [M^+], 365 (6) [$M^+ - CH_3O$], 304 (10) [$M^+ - \{(CO_2CH_3)(CH_4O)\}$], 337 (24) [$M^+ - CO_2CH_3$], 276 (8) [$M^+ - \{(CO_2CH_3)(CH_3O)_2\}$], 237 (12) [$M^+ - (C(CO_2CH_3)_2Et)$], 205 (29) [$M^+ - \{(CO_2CH_3)_2(CH_2COOCH_3)\}$], 160 (85) [$M^+ - (CO_2CH_3)_4$], 145 (59) [$M^+ - \{(CO_2CH_3)_4(CH_3)\}$], 105 (100) [$C_8H_9^+$]. Anal. Calcd for $C_{20}H_{28}O_8$ (396.44): C 60.59, H 7.12. Found: C 60.76, H 6.98.

***cis*-5,7-Bis[(diphenylcyano)methyl]cycloocta-1,3-diene (6c):** light yellow powder. IR (KBr): $\tilde{\nu}$ 3062 (w), 3011 (w) ν(C−H, aromat.), 2928 (m), 2853 (w) ν(C−H, aliph.), 2237 (w) ν(C≡N), 1599 (w), 1494 (m), 1451 (s) ν(C═C, aromat.), 745 (s), 700 (s) δ(C−H, aromat.) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, $^3J_{ortho,meta}$ = 7.6 Hz, 2 H, $phenyl_{ortho}$), 7.33 (t, $^3J_{ortho,meta}$ = 7.6 Hz, 2 H, $phenyl_{meta}$), 7.25 (m, 7 H, phenyl), 7.19 (m, 4 H, phenyl), 7.00 (m, 5 H, phenyl), 6.17 (dd, $^3J_{1,2}$ = 10.2 Hz, $^3J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 5.99 (dd, $^3J_{2,3}$ = 10.7 Hz, $^3J_{3,4}$ = 11.2 Hz, 1 H, 3-H), 5.92 (ddd, $^3J_{1,2}$ = 10.2 Hz, $^3J_{1,8trans}$ = 8.1 Hz, 1 H, 1-H), 5.77 (dd, $^3J_{3,4}$ = 11.2 Hz, $^3J_{4,5}$ = 8.7 Hz, 1 H, 4-H), 3.37 (t′, $^3J_{4,5} = {}^3J_{5,6trans}$ = 8.7 Hz, 1 H, 5-H), 2.36 (dd, $^3J_{7,8cis}$ = 8.1 Hz, $^2J_{8,8}$ = 12.7 Hz, 1 H, 8_{cis}-H), 2.26 (ddd, $^3J_{6trans,7}$ = 11.7 Hz, $^3J_{6cis,7}$ = 3.1 Hz, $^3J_{7,8trans}$ = 9.2 Hz, 1 H, 7-H), 2.13 (dd, $^3J_{7,8trans}$

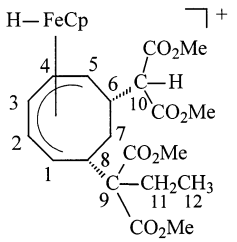
Table 4. Preparative Details Concerning the Cleavage of the Cyclooctadiene Ligands in 4a−c

starting complex	mg (mmol)	MeCN (mL)	product	R_f[a]	yield mg (%)
4a	300 (0.35)	80	**6a**	0.24	129 (57)
4b	200 (0.39)	25	**6b**	0.22	95 (62)
4c	261 (0.43)	30	**6c**	0.39	125 (60)

[a] R_f from TLC.

= 9.2 Hz, $^2J_{8,8}$ = 12.7 Hz, 1 H, 8_{trans}-H), 1.57 (dd, $^2J_{6,6}$ = 13.7 Hz, $^3J_{6cis,7}$ = 3.1 Hz, 1 H, 6_{cis}-H), 1.46 (m, 1 H, 6_{trans}-H) ppm. $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ 139.6, 139.2, 139.0, 138.9 (C_q-phenyl), 125.4, 126.2, 126.6, 127.1, 127.3, 127.5, 127.6, 128.7, 129.0, 129.1 (C-phenyl), 133.3 (C4), 131.4 (C1), 127.8 (C2), 128.4 (C3), 120.8, 120.3 (CN), 58.3, 58.0 (C9, C10), 44.6 (C5), 41.7 (C7), 31.4 (C8), 28.9 (C6) ppm. EI-MS (70 eV): *m*/*z* (%) 490 (2) [M^+], 298 (100) [$M^+ - CPh_2CN$], 192 (90) [CPh_2CN^+], 165 (99) [CPh_2H], 105 (45) [$C_8H_9^+$]. Anal. Calcd for $C_{36}H_{30}N_2(CH_2Cl_2)$ (575.58): C 77.21, H 5.60, N 4.87. Found: C 77.73, H 5.99, N 4.50.

[(η^5-Cyclopentadienyl){1,2,3,4,5-η-6-*exo*-di(methoxycarbonyl)methyl-8-*exo*-di(methoxycarbonyl)prop-1-ylcyclooctadienyl}hydridoiron(II)] Trifluoroacetate ($5CF_3CO_2$). ^1H NMR (360 MHz, CD_3CN, T = −30 °C): δ 7.21 (dd, $^3J_{2,3}$ = 7.6 Hz, $^3J_{3,4}$ = 6.9 Hz, 1 H, 3-H), 5.98 (dd, $^3J_{1,2}$ = 6.9 Hz, $^3J_{2,3}$ = 7.6 Hz, 1 H, 4-H), 5.55 (t′, $^3J_{3,4} = {}^3J_{4,5}$ = 6.9 Hz, 1 H, 2-H), 5.12 (s, 5 H, Cp), 4.61 (brs, 1 H, 1-H), 3.75, 3.74, 3.68, 3.65 (s, 3 H, CO_2CH_3), 3.22 (d, $^3J_{6,12}$ = 8.4 Hz, 1 H, 10-H), 3.21 (m, 1 H, 1-H), 2.46 (d, $^3J_{7,8}$ = 11.4 Hz, 1 H, 8-H), 2.38 (m, 1 H, 6-H), 2.00 (m, 1 H, 11-H), 0.85 (m, 1 H, 7_{endo}-H), 0.84 (t, ^3J = 7.6 Hz, 3 H, 12-H), −0.75 (m, 1 H, 7_{exo}-H), −14.64 (brd, ^3J = 3.1 Hz, 1 H, Fe−H) ppm.



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