Metal-Mediated Transformations of Cyclooctatetraene to Novel Methylene-Bridged, Bicyclic Compounds

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The nucleophilic addition of Nu^1 to $[(\eta^5\text{-Cp})Fe(\eta^6\text{-cot})]PF_6$ (**1PF$_6$**) (cot = cyclooctatetraene) exclusively yields the neutral complex $[(\eta^5\text{-Cp})Fe(1,2,3,4,5\text{-}\eta\text{-}C_8H_8\text{-}Nu^1)]$ (**2**) [Nu^1 = $C(CO_2Et)_2CH_2CHCH_2$ (**2a**), $C(CO_2Et)_2(CH_2)_2CHCH_2$ (**2b**), $C(CO_2Et)_2(CH_2)_3CHCH_2$ (**2c**)], with the nucleophiles linked to the *cyclo*-C_8 ligand solely and stereoselectively in exo position with respect to the metal center. The protonation of the neutral complexes **2a**−**c** by addition of HBF_4 reveals the new ionic product $[(\eta^5\text{-Cp})Fe(\eta^6\text{-}C_8H_9\text{-}Nu^1)]BF_4$ (**3BF$_4$**) with a 1,2,3,4,5,6-η coordination mode of the *cyclo*-C_8 ligand. The cationic complexes **3a**−**c** 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 = $C(CO_2Et)_2CH_2CHCH_2/C(CO_2Et)_2CH_2CHCH_2$ (**4a**), $C(CO_2Et)_2CH_2CHCH_2/C(CO_2Et)_2(CH_2)_2CHCH_2$ (**4b**), $C(CO_2Et)_2CH_2CHCH_2/C(CO_2Et)_2(CH_2)_3CHCH_2$ (**4c**), $C(CO_2Et)_2(CH_2)_2CHCH_2/C(CO_2Et)_2(CH_2)_2CHCH_2$ (**4d**), $C(CO_2Et)_2(CH_2)_2CHCH_2/C(CO_2Et)_2(CH_2)_3CHCH_2$ (**4e**), $C(CO_2Et)_2(CH_2)_3CHCH_2/C(CO_2Et)_2(CH_2)_3CHCH_2$ (**4f**)]. The *cyclo*-C_8 ligand can be cleaved as *cis*-5,7-disubstituted cycloocta-1,3-diene (**5**) by protonation of the complexes **4a**−**f** with CF_3CO_2H in acetonitrile: Nu^1/Nu^2 = $C(CO_2Et)_2CH_2CHCH_2/C(CO_2Et)_2CH_2CHCH_2$ (**5a**), $C(CO_2Et)_2CH_2CHCH_2/C(CO_2Et)_2(CH_2)_2CHCH_2$ (**5b**), $C(CO_2Et)_2CH_2CHCH_2/C(CO_2Et)_2(CH_2)_3CHCH_2$ (**5c**), $C(CO_2Et)_2(CH_2)_2CHCH_2/C(CO_2Et)_2(CH_2)_2CHCH_2$ (**5d**), $C(CO_2Et)_2(CH_2)_2CHCH_2/C(CO_2Et)_2(CH_2)_3CHCH_2$ (**5e**), $C(CO_2Et)_2(CH_2)_3CHCH_2/C(CO_2Et)_2(CH_2)_3CHCH_2$ (**5f**). In an attempt to construct fused bicyclic ring systems with annelated 9- to 13-membered cycles employing the ring-closing metathesis (RCM), a novel ring opening−ring closing metathesis reaction was encountered to yield new methylene-bridged, bicyclic systems (**7**).

Introduction

The use of unsubstituted cyclooctatetraene[1] (cot) in effective stereoselective transformations is rather limited,[2] which among other things is due to the distinct symmetric structure of the D_{2d} point group of this "simple" hydrocarbon. However, stereoselectively functionalized *cyclo*-C_8 compounds developed from cot may be of great interest for the synthesis of, for example, *cyclo*-C_8 terpenoids,[3] some of which illustrate interesting biological activities.[4]

Our approach to transform cot stereoselectively is the coordination of cot to cationic metal atoms and to subject the cationic cot complex to nucleophilic additions.[5] Nucleophilic addition to coordinated unsaturated hydrocarbons is one of the most important reactions in synthetic organometallic chemistry[6] and is widely used even in the synthesis of natural products.[7] The present report summarizes the results which were obtained when we attempted the synthesis of fused ring systems

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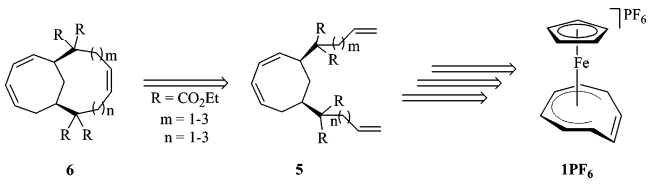
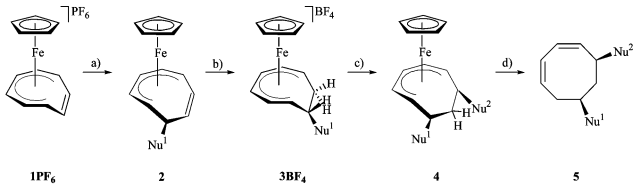
Scheme 1. Retrosynthesis of the Medium Sized Bicycles 6



6 **5** **1PF$_6$**

Scheme 2. Reaction Sequence for the Formation of *cis*-5,7-Disubstituted Cycloocta-1,3-diene Starting from Iron-Coordinated Cot[a]



1PF$_6$ **2** **3BF$_4$** **4** **5**

Nu^1	C(CO$_2$Et)$_2$CH$_2$CHCH$_2$	C(CO$_2$Et)$_2$(CH$_2$)$_2$CHCH$_2$	C(CO$_2$Et)$_2$(CH$_2$)$_3$CHCH$_2$
2	**a**	**b**	**c**

Nu^1	C(CO$_2$Et)$_2$CH$_2$CHCH$_2$	C(CO$_2$Et)$_2$(CH$_2$)$_2$CHCH$_2$	C(CO$_2$Et)$_2$(CH$_2$)$_3$CHCH$_2$
3BF$_4$	**a**	**b**	**c**
Nu^1/ Nu^2	C(CO$_2$Et)$_2$CH$_2$CHCH$_2$/ C(CO$_2$Et)$_2$CH$_2$CHCH$_2$	C(CO$_2$Et)$_2$CH$_2$CHCH$_2$/ C(CO$_2$Et)$_2$(CH$_2$)$_2$CHCH$_2$	C(CO$_2$Et)$_2$CH$_2$CHCH$_2$/ C(CO$_2$Et)$_2$(CH$_2$)$_3$CHCH$_2$
4	**a**	**b**	**c**

Nu^1/ Nu^2	C(CO$_2$Et)$_2$(CH$_2$)$_2$CHCH$_2$/ C(CO$_2$Et)$_2$(CH$_2$)$_2$CHCH$_2$	C(CO$_2$Et)$_2$(CH$_2$)$_2$CHCH$_2$/ C(CO$_2$Et)$_2$(CH$_2$)$_3$CHCH$_2$	C(CO$_2$Et)$_2$(CH$_2$)$_3$CHCH$_2$/ C(CO$_2$Et)$_2$(CH$_2$)$_3$CHCH$_2$
4	**d**	**e**	**f**

Nu^1/ Nu^2	C(CO$_2$Et)$_2$CH$_2$CHCH$_2$/ C(CO$_2$Et)$_2$CH$_2$CHCH$_2$	C(CO$_2$Et)$_2$CH$_2$CHCH$_2$/ C(CO$_2$Et)$_2$(CH$_2$)$_2$CHCH$_2$	C(CO$_2$Et)$_2$CH$_2$CHCH$_2$/ C(CO$_2$Et)$_2$(CH$_2$)$_3$CHCH$_2$
5	**a**	**b**	**c**

Nu^1/ Nu^2	C(CO$_2$Et)$_2$(CH$_2$)$_2$CHCH$_2$/ C(CO$_2$Et)$_2$(CH$_2$)$_2$CHCH$_2$	C(CO$_2$Et)$_2$(CH$_2$)$_2$CHCH$_2$/ C(CO$_2$Et)$_2$(CH$_2$)$_3$CHCH$_2$	C(CO$_2$Et)$_2$(CH$_2$)$_3$CHCH$_2$/ C(CO$_2$Et)$_2$(CH$_2$)$_3$CHCH$_2$
5	**d**	**e**	**f**

[a] (a) THF, NaNu^1; (b) Et$_2$O, HBF$_4$, −78 °C; (c) THF, NaNu^2; (d) MeCN, CF$_3$CO$_2$H.

composed of a *cyclo*-C$_8$ ring and an annelated medium-sized carbocycle (9−13-membered rings). This type of fused bicycles is a scarcely developed class of compounds, which thus far is only studied for homeomorphic isomerization reactions.[8]

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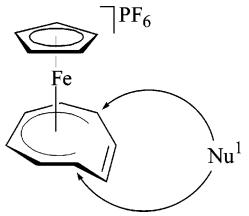

Figure 1. Nucleophilic attack on the enantiotopic sites generating a stereogenic center.

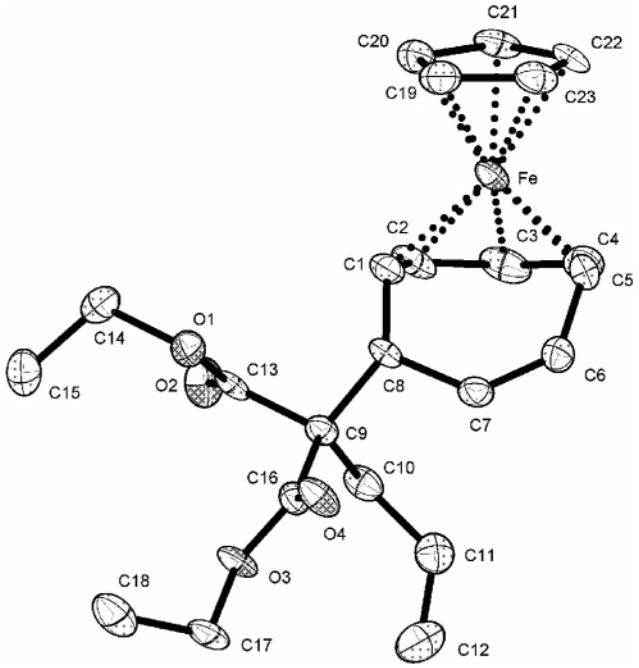

Figure 2. XSHELL style representation of the molecular structure of **2a** as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) for **2a**: Fe−C(1), 206.5(4); Fe−C(2), 201.4(4); Fe−C(3), 205.7(4); Fe−C(4), 200.9(4); Fe−C(5), 206.1(4); C(6)−C(7), 133.4(5); C(11)−C(12), 130.6(4).

The preparative access to this type of fused-ring compounds was assumed by the synthesis of the proper *cis*-5,7-disubstituted cycloocta-1,3-dienes (**5**). The substituents of the cyclo-octadienes bear terminal carbon−carbon double bonds, which are suggested to be prone for ring-closing metathesis reactions (RCM);[9] the *cis*-5,7-disubstituted cycloocta-1,3-dienes could be obtained after an iteratively conducted nucleophilic and electrophilic addition on coordinated cot (Scheme 1) and a successive ligand cleavage.

Results and Discussion

The reaction sequence of iterative nucleophilic and electrophilic additions on the complex [(η^5-Cp)Fe(η^6-cot)]PF$_6$ (**1PF$_6$**) affords a facile access to a variety of modified *cis*-5,7-disubstituted cycloocta-1,3-dienes (**5**). These cyclooctadiene derivates may be a suitable starting material for the synthesis of fused-ring systems of medium-sized carbocycles **6** by ring-closing metathesis reaction.

Substrate Synthesis. The nucleophiles used for the first and second nucleophilic addition were prepared by deprotonation

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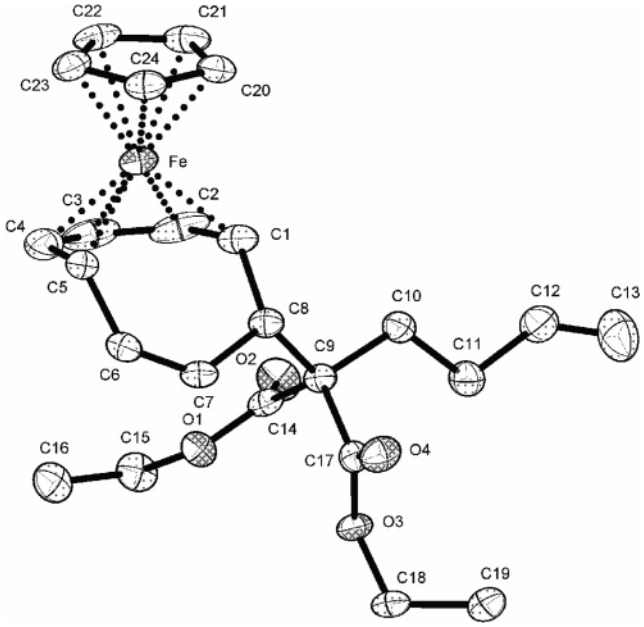

Figure 3. XSHELL style representation of the molecular structure of **2b** as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) for **2b**: Fe−C(1), 205.0(2); Fe−C(2), 201.5(2); Fe−C(3), 204.4(2); Fe−C(4), 200.2(2); Fe−C(5), 206.4(2); C(6)−C(7), 131.0(3); C(12)−C(13), 129.1(3).

reactions of the C,H acidic precursor compounds with NaH in accordance to previous works.[5a] The solutions of the obtained carbanions were added to the cationic complexes **1PF$_6$** and **3BF$_4$**, respectively. The first nucleophilic addition to [(η^5-Cp)-Fe(η^6-cot)]PF$_6$ (**1PF$_6$**) occurs in good to excellent yields (85−92%), resulting exclusively in the formation of neutral complex [(η^5-Cp)Fe(1,2,3,4,5-η-C$_8$H$_8$-Nu^1)] (**2**) (Scheme 2a).

Since the starting complex **1PF$_6$** contains a mirror plane, which bisects the Cp and cot ligands, the nucleophilic addition reveals chiral complexes in a racemic mixture (Figure 1).

The X-ray structure determinations of **2a**[10] (Nu^1 = C(CO$_2$Et)$_2$CH$_2$CHCH$_2$) (Figure 2) and **2b**[11] (Nu^1 = C(CO$_2$Et)$_2$(CH$_2$)$_2$CHCH$_2$) (Figure 3) reveal a 1,2,3,4,5-η coordination mode of the cyclooctatrienyl ligand. This coordination can easily be proven by ^{1}H-^{1}H and ^{1}H-^{13}C correlation spectroscopy for other products of **2** and differs from the 1,2-η:5,6,7-η coordination mode, which is found for corresponding Ru complexes.[12]

The nucleophiles are located in exo position with respect to the metal center and exclusively at the "terminal" carbon atom of the coordinated part of the cot ligand as predicted from the Davis−Green−Mingos (DGM) rules.[13]

The second nucleophilic addition also requires a cationic complex, which is obtained by protonation of **2** with HBF$_4$ in diethyl ether (Scheme 2b). The product **3BF$_4$** is obtained in excellent yields (97−99%) and can easily be separated from the reaction mixture because of its insolubility in diethyl ether. The product exclusively consists of 1−6-η haptomers, again in contrast to related Ru complexes, which adopt a 1,2-η:4,5,6,7-η coordination mode.[12] The *cyclo*-C$_8$ coordination mode of the iron complex can also be proven by ^{1}H-^{1}H and ^{1}H-^{13}C correlation spectroscopy of **3BF$_4$**. The ^{1}H resonance signal of proton 7*exo*-H of the endocyclic methylene group with an upfield shift up to −1.8 ppm is characteristic for this complex. Generally, protons in exo position with respect to the metal center of diamagnetic sandwich complexes are affected by an anisotropy cone and show upfield shifts.[14]

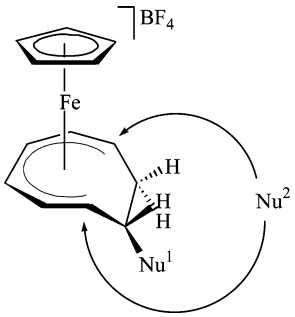

Figure 4. Possible target position for the second nucleophilic addition.

The addition of a second nucleophile can in principle ensue at two different terminal carbon atoms of the coordinated *cyclo*-C$_8$ ligand (Figure 4), in accordance with the DGM rules. Because of steric hindrance the addition happens instead exclusively distal with respect to the first nucleophile Nu,[1] forming 6,8-disubstituted 1,2,3,4,5-η-cyclooctadienyl complexes **4** (Scheme 2c) in moderate to good yields (60−91%).

The X-ray structure determination of **4a**[15] (Nu^1/Nu^2 = C(CO$_2$Et)$_2$CH$_2$CHCH$_2$) (Figure 5) once again reveals a 1,2,3,4,5-η coordination mode of the cyclooctadienyl ligand with both nucleophiles located in exo position with respect to the metal center. The coordination mode of the *cyclo*-C$_8$ ligand is easily confirmed by ^{1}H-^{1}H and ^{1}H-^{13}C correlation spectroscopy for other products of **4**. Because of the molecular C_s symmetry the spectroscopic data for **4a**, **4d** and **4f** result in only few signals.

The stereo- and regioselectively substituted *cyclo*-C$_8$ ligand is easily split off as a cycloocta-1,3-diene **5** by the addition of CF$_3$CO$_2$H in the presence of acetonitril (Scheme 2d). The assignment of the NMR signals can be performed by applying ^{1}H-^{1}H and ^{1}H-^{13}C correlation spectroscopy. During this reaction a portion of the desired product loses its nucleophile resulting in a dramatic reduction in yield (41−76%). The free nucleophiles however can be separated from the product by column chromatography and identified by ^{1}H NMR spectroscopy. The cleavage of an N-nucleophile upon protonation of an amino-substituted *cyclo*-C$_8$ ligand has been previously reported.[12] If two different compounds were used for the nucleophilic addition, after cleavage the preferred *cyclo*-C$_8$ regioisomer bears the sterically more demanding nucleophile directly next to one endocyclic double bond.

(10) Crystal data for **2a**: monoclinic, $P2_1/c$, orange plate, a = 1280.8(2) pm, b = 1196.22(19) pm, c = 1383.4(2) pm, α = 90°, β = 105.257(2)°, γ = 90°, V = 2.0449(6) nm^3, T = 153(2) K, Z = 4, R_1 = 0.0488 [$I > 2\sigma(I)$] and wR_2 = 0.0950.

(11) Crystal data for **2b**: triclinic, $P\bar{1}$, orange plate, a = 766.27(17) pm, b = 1204.4(3) pm, c = 1326.8(3) pm, α = 109.987(4)°, β = 98.118(4)°, γ = 106.197(4)°, V = 1.0665(4) nm^3, T = 153(2) K, Z = 2, R_1 = 0.0397 [$I > 2\sigma(I)$] and wR_2 = 0.0722.

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(15) Crystal data for **4a**: monoclinic, $P2_1/n$, orange plate, a = 1552.32(14) pm, b = 976.72(9) pm, c = 2060.31(19) pm, α = 90°, β = 91.152(2)°, γ = 90°, V = 3.1232(5) nm^3, T = 153(2) K, Z = 4, R_1 = 0.0434 [$I > 2\sigma(I)$] and wR_2 = 0.0605.

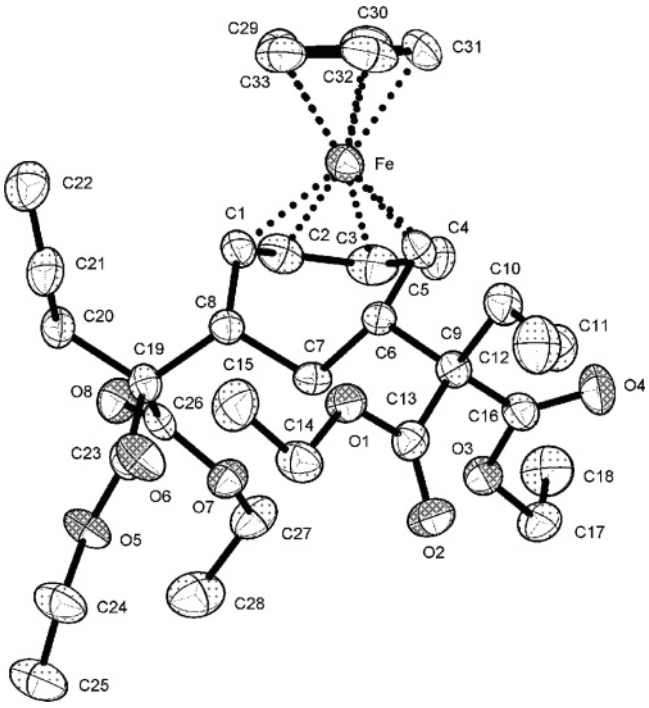


Figure 5. XSHELL style representation of the molecular structure of **4a** as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) for **4a**: Fe−C(1), 205.5(2); Fe−C(2), 200.0(3); Fe−C(3), 203.9(3); Fe−C(4), 200.6(3); Fe−C(5), 204.4(3); C(11)−C(12), 131.0(3); C(21)−C(22), 131.3(3).

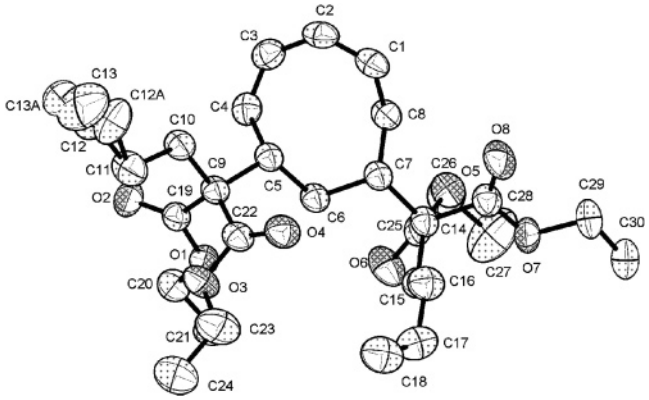
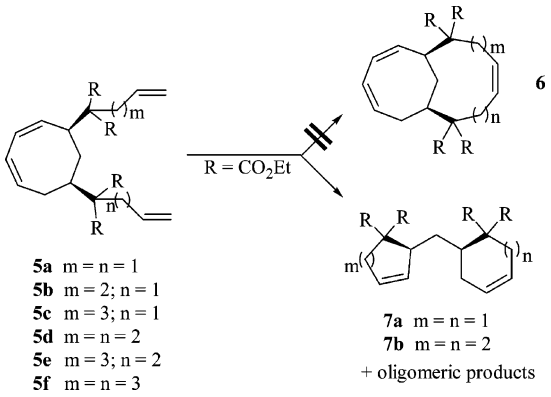


Figure 6. XSHELL style representation of the molecular structure of **5d** as determined by single-crystal X-ray crystallography. Thermal ellipsoids are given at a 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (pm) for **5d**: C(1)−C(2), 133.7(2); C(2)−C(3), 145.5(2); C(3)−C(4), 134.2(2); C(4)−C(5), 151.3(2); C(5)−C(6), 155.3(2); C(6)−C(7), 153.5(2); C(7)−C(8), 155.7(2); C(8)−C(1), 150.3(2); C(17)−C(18), 131.1-(2). Owing to a disorder the second double bond C(12)−C(13) has a fixed length.

The X-ray structure determination of **5d**[16] (Nu^1/Nu^2 = $C(CO_2Et)_2(CH_2)_2CHCH_2$) (Figure 6) shows both nucleophiles located in cis position beneath the highly tilted cyclooctadiene ring.

Grubbs Metathesis on 5. A ring-closing metathesis reaction on **5** using the first generation Grubbs' catalyst **G1** was attempted with the expectation of a reaction of the terminal olefins affording the fused bicyclic skeleton **6**. To the *cis*-5,7-disubstituted cycloocta-1,3-dienes **5a**−**f** were added 4−5 mol % **G1**, and the mixtures were allowed to react for few days at room temperature. After column chromatography of the reaction mixtures of **5a** and **5d**, the thin layer chromatography (tlc) and NMR spectra indicated a complete consumption of the starting material. One major product, along with small amounts of oligomeric byproducts, was detected. The symmetrically substituted cycloocta-1,3-dienes **5a** and **5d** had converted into **7a** and **7b** through a ring rearrangement metathesis. However, despite several attempts no clean product formation was observed for the metathesis reaction of **5b**, **5c**, **5e** and **5f**. After chromatographic workup the tlc and NMR spectral scrutiny indicated the formation of a complex mixture of oligomers or polymers presumably as a result of intermolecular cross-metathesis reaction after ring-opening metathesis (Scheme 3).

Scheme 3. Results of the Grubbs Metathesis on 5[a]



[a] Conditions: $[Ru(PCy_3)_2Cl_2CHPh]$, (4−5 mol %), CH_2Cl_2, room temp.

This tandem ring opening−ring closing metathesis or ring rearrangement metathesis is already known for bisalkenylated cyclomonoolefins,[17] but to the best of our knowledge no publications for doubly unsaturated bisalkenylated cycloolefins have been published thus far.

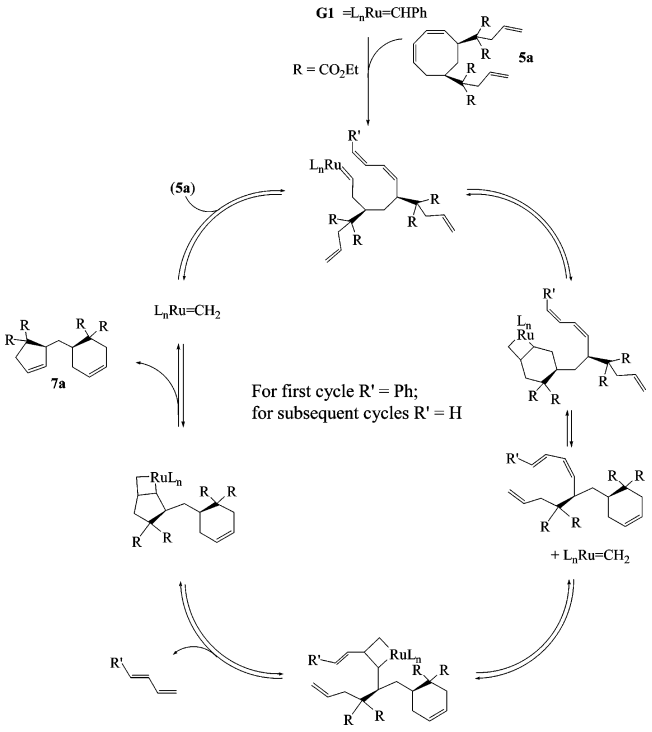
According to unpublished results, no metathesis reactions occur between substituents on coordinated bisalkenylated cyclooctadienyl ligands. Thus, the mechanism for the formation of **7a** and **7b** has to involve initial metathesis on an endocyclic olefin (Scheme 4). In analogy to the ring-opening metathesis polymerization (ROMP), this ring opening is enthalpically driven by the reduction of ring strain. Cleavage of the subsequently formed metallacyclobutane produces the first ring and a metal alkylidene. The final step is the closure of the second ring by an intramolecular ring-closing olefin metathesis under cleavage of 1-phenyl-1,3-butadiene or, depending on the cycle number, 1,3-butadiene, which could be confirmed by NMR spectroscopy.

Notable is the formation of the metathesis product **7b** from the unsymmetrically substituted cyclooctadiene **5e** as well as from the symmetrically substituted cyclooctadiene **5d**. Presumably a derivative **5e′** is formed (Scheme 5) by isomerization of the longer side chain in **5e** which undergoes a tandem ring

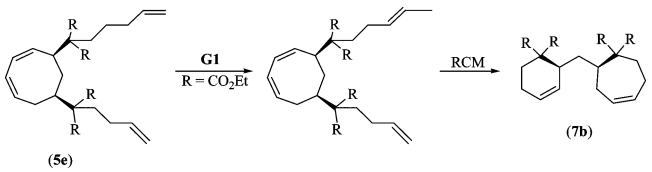
(16) Crystal data for **5d**: triclinic, $P\bar{1}$, colorless plate, a = 937.93(10) pm, b = 1325.27(14) pm, c = 1386.23(15) pm, α = 113.080(2)°, β = 93.004(2)°, γ = 100.126(2)°, V = 1.5464(3) nm^3, T = 213(2) K, Z = 2, R_1 = 0.0497 [$I > 2\sigma(I)$] and wR_2 = 0.1171.

(17) (a) Ma, S.; Ni, B.; Liang, Z. *J. Org. Chem.* **2004**, *69*, 6305−6309. (b) Schaudt, M.; Blechert, S. *J. Org. Chem.* **2003**, *68*, 2913−2920. (c) Zaminer, J.; Stapper, C.; Blechert, S. *Tetrahedron Lett.* **2002**, *43*, 6739−6741. (d) Stapper, C.; Blechert, S. *J. Org. Chem.* **2002**, *67*, 6456−6460. (e) Blechert, S.; Stapper, C. *Eur. J. Org. Chem.* **2002**, 2855−2858. (f) Zaminer, J.; Stapper, C.; Blechert, S. *Tetrahedron Lett.* **2002**, *43*, 6739−6741. (g) Nicolaou, K. C.; Vega, J. A.; Vassilikogiannakis, G. *Angew. Chem.* **2001**, *113*, 4573−4577. (h) Zuercher, W. J.; Hashimoto, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 6634−6640.

Scheme 4. Mechanism for a Tandem Ring Opening−Ring Closing Metathesis on 5a



Scheme 5. Probable Isomerization Leading to the Formation of 7b from 5e



opening−ring closing metathesis revealing the product **7b** in a yield of 9%. This type of metathesis isomerization is already known and applied for natural product synthesis.[18]

The ring opening−ring closing metathesis reaction takes place under stereochemical preservation of two stereogenic centers as verified by NOESY spectra and creates a possibility to obtain interesting products through deep-seated structural change.

Conclusion

Starting with the coordinated cyclooctatetraene in [(η^5-Cp)Fe(η^6-cot)]PF_6 (**1PF$_6$**), the reaction sequence "first nucleophilic addition/first protonation/second nucleophilic addition/second protonation = ligand cleavage" results in the formation of *cis*-5,7-disubstituted cycloocta-1,3-dienes (**5**). As shown by the crystal structures of **2a**, **2b** and **4a** both first and second nucleophilic additions obey the DGM rules and thus are chemo-, regio-, and stereoselective. When the steric demand of Nu^1 and Nu^2 differs, that regioisomer is apparently formed after cleavage of the *cyclo*-C_8 ligand, which bears the sterically more demanding nucleophile next to the endocyclic double bond. This reaction sequence opens a facile access to a very rarely investigated but remarkable class of compounds. The synthesis of *cis*-5,7-disubstituted cycloocta-1,3-dienes is a supplement to the syntheses of *cis*-3,7-disubstituted cycloocta-1,5-dienes,[19] *cis*-6,7-disubstituted cycloocta-1,3-dienes,[20] and *cis*-5,8-disubstituted cycloocta-1,3-dienes.[21] Grubbs metathesis on the cyclooctadiene derivatives **5** resulted only for **5a** and **5d** via tandem ring opening−ring closing metathesis to new methylene-bridged, bicyclic products **7a** and **7b**. The ring rearrangement metathesis takes place under stereochemical preservation (verified by NOESY spectra). No derivatives of **7a** and **7b** were formed from the metathesis reaction of **5b**, **5c** and **5f**.

Table 1. Preparative Details for the First Nucleophilic Addition

product	**1PF$_6$** mg (mmol)	HNu^1	HNu^1 mg (mmol)	yield mg (%)
2a	482 (1.30)	$CH(CO_2Et)_2CH_2CHCH_2$	294 (1.47)	496 (90)
2b	303 (0.819)	$CH(CO_2Et)_2(CH_2)_2CHCH_2$	314 (1.46)	327 (92)
2c[a]	249 (0.672)	$CH(CO_2Et)_2(CH_2)_3CHCH_2$	169 (0.740)	258 (85)

[a] Spectroscopic data is given in the Supporting Information

Experimental Section

General Methods. All reactions were carried out under a nitrogen atmosphere; all solvents were saturated with nitrogen and freshly distilled from appropriate alkali metal or metal alloy. The following instrumentation was used: NMR, AVANCE 400 (Bruker); IR, KBr plates, NaCl plates, FT-IR 1720 (Perkin-Elmer); EI-MS, 70 eV, Finnigan MAT 311 A; FAB-MS, Xenon, VG Analytical 70−250 S. For elemental analyses the following instrumentation was used: air stable, EA 1108 CHNS-O (Carlo Erba Instruments); air sensitive, Vario EL III (Elementar) (some elemental analyses of a few products are hampered by small amounts of solvents or nucleophiles, as indicated by ^{1}H NMR spectra). X-ray crystal structure analyses was performed using SMART CCD (Bruker). [(η^5-Cp)Fe(η^6-cot)]PF_6 (**1PF$_6$**),[22] $CH(CO_2Et)_2CH_2CHCH_2$,[23] $CH(CO_2Et)_2(CH_2)_2CHCH_2$,[24] and $CH(CO_2Et)_2(CH_2)_3CHCH_2$[23] were synthesized as described.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-620935 (**2a**), CCDC-620936 (**2b**), CCDC-620937 (**4a**), CCDC-638599 (**5d**).

General Procedure for the First Nucleophilic Addition. Synthesis of 2a−c. One equivalent of the organic C−H acidic compound HNu^1 was slowly added to a suspension of 2−3 equiv of NaH in THF at room temperature and stirred overnight. The THF solution was separated from unreacted NaH and transferred to a suspension of 1 equiv of **1PF$_6$** in THF. The reaction mixture was stirred overnight at room temperature and evaporated to dryness. The residue was extracted with toluene. After removal of the solvent the product was recrystallized from hexane to obtain the product as orange oil or crystalline powder. For more preparative details see Table 1.

(η^5-Cyclopentadienyl)[1,2,3,4,5-η-8-*exo*-(1′,1′-diethoxycarbonyl-3′-buten-1′-yl)-cyclo-octatrien-6-yl]iron(II) (2a): orange crystalline powder, soluble in hexane, more soluble in toluene; fp 57 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 6.16 (m, $^3J_{11,10}$ = 7.3 Hz, $^3J_{11,12}$ = 10.1 Hz, 1 H, 11-H), 5.73 (d, 2 H, 6-H, 7-H), 5.42 (t′, $^3J_{3,2}$ = 6.7 Hz, $^3J_{3,4}$ = 6.2 Hz, 1 H, 3-H), 5.09 (m, $^3J_{12,11}$ = 10.1

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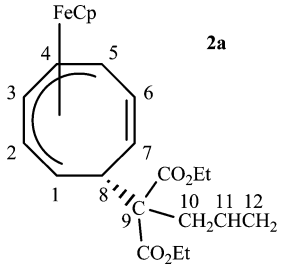
(24) Deleris, G.; Dunogues, J.; Gadras, A. *Tetrahedron* **1988**, *44*, 4243−4258.

Table 2. Preparative Details for the First Protonation

product	starting complex	**2** mg (mmol)	Nu[1]	yield mg (%)
3a	**2a**	361 (0.850)	$C(CO_2Et)_2CH_2CHCH_2$	429 (99)
3b	**2b**	264 (0.560)	$C(CO_2Et)_2(CH_2)_2CHCH_2$	292 (99)
3c[a]	**2c**	232 (0.512)	$C(CO_2Et)_2(CH_2)_3CHCH_2$	268 (97)

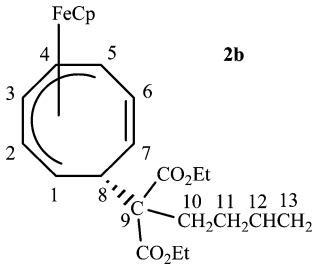
[a] Spectroscopic data is given in the Supporting Information.

Hz, 2 H, 12-H), 4.28 (dd, $^3J_{4,3}$ = 6.2 Hz, 1 H, 4-H), 4.15 (dd, $^3J_{2,3}$ = 6.7 Hz, 1 H, 2-H), 4.02 (dq, $^3J_{CH2,CH3}$ = 7.1 Hz, 4 H, CH_2), 3.95 (m, 1 H, 1-H), 3.92 (s, 5 H, Cp), 3.86 (m, 1 H, 8-H), 3.50 (m, 1 H, 5-H), 3.04 (d, $^3J_{10,11}$ = 7.3 Hz, 2 H, 10-H), 0.95 (t′, $^3J_{CH3,CH2}$ = 7.1 Hz, 3 H, CH_3), 0.89 (t, $^3J_{CH3,CH2}$ = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR {1H} (100 MHz, C_6D_6): δ 171.1, 170.2 (s, C═O), 135.3 (s, C-11), 127.3, 127.2 (s, C-6, C-7), 117.7 (s, C-12), 99.3 (s, C-3), 77.6 (s, C-4), 77.5 (s, C-2), 77.1 (s, Cp), 63.0 (s, C-9), 60.8, 60.6 (s, CH_2), 44.3, 44.3 (s, C-5, C-8), 43.1 (s, C-1), 38.7 (s, C-10), 14.2, 14.0 (s, CH_3) ppm. IR (KBr): 3079 (w) ν(C−H, aromatic), 2980 (m), 2954 (m), 2935 (m) ν(C−H, aliphatic), 1727 (ss) ν(C═O), 1634 (m) ν(C═C), 1460 (w) δ(CH_2/CH_3), 1366 (w) δ(CH_3), 1213 (s), 1194 (s) ν(C−O) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) 424 (100) [M^+], 358 (6) [M−Cp^+], 317 (42) [M−Cp-$CH_2CHCH_2^+$], 225 (44) [$CpFeC_8H_8^+$], 199 (22) [$C(CO_2Et)_2CH_2CHCH_2^+$], 121 (37) [$CpFe^+$], 56 (4) [Fe^+], 41 (3) [$CH_2CHCH_2^+$]. Anal. Calcd for $C_{23}H_{28}FeO_4 \cdot 1/14(NaPF_6)$ (436.32): C, 63.31; H, 6.47. Found: C, 63.34; H, 6.38.



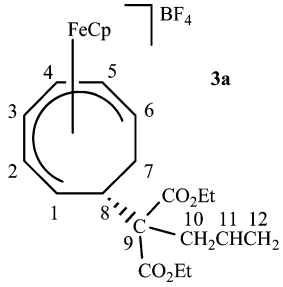
(η⁵-Cyclopentadienyl)[1,2,3,4,5-η-8-*exo*-(1′,1′-diethoxycarbonyl-4′-penten-1′-yl)-cyclooctatrien-6-yl]iron(II) (2b): orange crystalline powder, soluble in hexane, more soluble in toluene; fp 43 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 5.89 (m, $^3J_{12,11}$ = 10.7 Hz, $^3J_{12,13}$ = 10.2 Hz, 1 H, 12-H), 5.69 (m, 2 H, 6-H, 7-H), 5.42 (t′, $^3J_{3,2}$ = $^3J_{3,4}$ = 6.4 Hz, 1 H, 3-H), 5.06 (m, $^3J_{13,12}$ = 10.2 Hz, 2 H, 13-H), 4.29 (dd, $^3J_{4,3}$ = 6.4 Hz, 1 H, 4-H), 4.15 (dd, $^3J_{2,3}$ = 6.4 Hz, 1 H, 2-H), 4.01 (dq, $^3J_{CH2,CH3}$ = 7.1 Hz, 4 H, CH_2), 3.93 (m, 1 H, 1-H), 3.91 (s, 5 H, Cp), 3.86 (m, 1 H, 8-H), 3.49 (dd, 1 H, 5-H), 2.49−2.19 (m, $^3J_{11,12}$ = 10.7 Hz, 4 H, 10-H, 11-H), 0.94 (t, $^3J_{CH3,CH2}$ = 7.1 Hz, 3 H, CH_3), 0.90 (t, $^3J_{CH3,CH2}$ = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR {1H} (100 MHz, C_6D_6): δ 171.6, 170.4 (s, C═O), 138.9 (s, C-12), 127.4 (s, C-6), 127.1 (s, C-7), 114.9 (s, C-13), 99.2 (s, C-3), 77.7 (s, C-2), 77.6 (s, C-4), 77.1 (s, Cp), 62.7 (s, C-9), 60.9, 60.5 (s, CH_2), 45.0 (s, C-1), 44.1 (s, C-5), 43.4 (s, C-8), 33.6 (s, C-10), 30.3 (s, C-11), 14.1, 14.0 (s, CH_3) ppm. IR (KBr): 3078 (w) ν(C−H, aromatic), 2979 (m), 2952 (m) ν(C−H, aliphatic), 1732 (ss) ν(C═O), 1640 (m) ν(C═C), 1445 (m) δ(CH_2/CH_3), 1366 (m) δ(CH_3), 1298 (m), 1243 (s), 1208 (s), 1111 (s) ν(C−O) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) 438 (82) [M^+], 393 (1) [M−OEt^+], 293 (100) [$CpFeC_8H_9CCH_2CH_2CHCH_2^+$], 225 (63) [$CpFeC_8H_8^+$], 199 (29) [$CpFeC_6H_6^+$], 160 (20) [$FeC_8H_8^+$], 121 (55) [$CpFe^+$], 55 (8) [$CH_2CH_2CHCH_2^+$]. Anal. Calcd for $C_{24}H_{30}FeO_4$ (438.35): C, 65.76; H, 6.90. Found: C, 65.45; H 6.87.

General Procedure for the First Protonation. Synthesis of 3a−c. Compound **2** was dissolved in Et_2O. At T = −78 °C an equimolar amount of HBF_4 dissolved in Et_2O was added. After 30 min of stirring, the reaction mixture was allowed to warm to room temperature. The product precipitates as an oil. The clear upper layer was decanted, and the remaining product was washed several

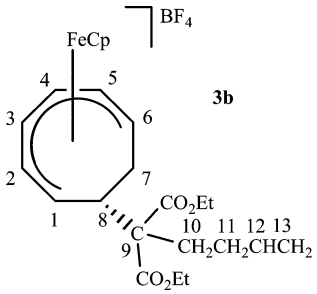


times with Et_2O and dried in vacuo to obtain the product as a dark red oil or crystalline powder. For more preparative details see Table 2.

[(η⁵-Cyclopentadienyl)(1,2,3,4,5,6-η-8-*exo*-{1′,1′-diethoxycarbonyl-3′-buten-1′-yl}cycloocta-1,3,5-triene)iron(II)] Tetrafluoroborate (3a): red crystalline powder, soluble in THF, more soluble in acetone; fp 107 °C. ^{1}H NMR (400 MHz, $CD_3C(O)CD_3$): δ 7.14 (dd, $^3J_{4,5}$ = 7.8 Hz, 1 H, 4-H), 7.02 (m, 1 H, 3-H), 6.92 (dd, 1 H, 1-H), 6.70 (dd, $^3J_{5,4}$ = 7.8 Hz, $^3J_{5,6}$ = 7.1 Hz, 1 H, 5-H), 5.88−5.70 (m, $^3J_{6,5}$ = 7.1 Hz, $^3J_{11,10}$ = 7.3 Hz, 3 H, 2-H, 6-H, 11-H), 5.32 (s, 5 H, Cp), 5.21 (dd, 2 H, 12-H), 4.20−4.08 (m, $^3J_{8,7exo}$ = 11.8 Hz, $^3J_{CH2,CH3}$ = 7.1 Hz, 5 H, 8-H, CH_2), 2.85−2.49 (m, $^3J_{10,11}$ = 7.3 Hz, 2 H, 10-H), 1.48 (m, 1 H, 7_{endo}-H), 1.21 (dt, $^3J_{CH3,CH2}$ = 7.1 Hz, 6 H, CH_3), −1.78 (ddd, $^3J_{7exo,8}$ = 11.8 Hz, 1 H, 7_{exo}-H) ppm. ^{13}C NMR {1H} (100 MHz, $CD_3C(O)CD_3$): δ 169.9, 169.8 (s, C═O), 133.3 (s, C-11), 119.8 (s, C-12), 105.0 (s, C-3), 97.8 (s, C-4), 95.1 (s, C-5), 93.2 (s, C-1), 90.4 (s, C-2), 86.5 (s, C-6), 83.1 (s, Cp), 63.4 (s, C-9), 62.0, 61.9 (s, CH_2), 53.7 (s, C-8), 38.7 (s, C-10), 26.0 (s, C-7), 14.4, 14.3 (s, CH_3) ppm. IR (KBr): 3115 (w) ν(C−H, aromatic), 2976 (w), 2940 (w) ν(C−H, aliphatic), 1743 (m), 1722 (s) ν(C═O), 1639 (w) ν(C═C), 1460 (w), 1430 (w), 1420 (w) δ(CH_2/CH_3), 1270 (m), 1226 (m) ν(C−O), 1050 (ss, br) ν(BF_4^-) cm^{-1}. FAB-MS: *m*/*z* (%) 425 (100) [M^+ -BF_4^-], 937 (2) [$2M^+$-BF_4^-]. Anal. Calcd for $C_{23}H_{29}BF_4FeO_4$ (512.13): C, 53.89; H, 5.71. Found: C, 53.80; H, 5.69.



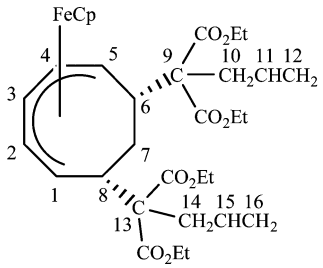
[(η⁵-Cyclopentadienyl)(1,2,3,4,5,6-η-8-*exo*-{1′,1′-diethoxycarbonyl-4′-penten-1′-yl}cycloocta-1,3,5-triene]iron(II)] Tetrafluoroborate (3b): dark red oil, soluble in THF, more soluble in acetone. ^{1}H NMR (400 MHz, $CD_3C(O)CD_3$): δ 7.14 (m, 1 H, 4-H), 7.01 (m, 1 H, 1-H), 6.92 (t′, 1 H, 3-H), 6.70 (m, 1 H, 5-H), 5.83 (m, 1 H, 12-H), 5.76 (m, $^3J_{6,7exo}$ = 10.6 Hz, 2 H, 2-H, 6-H), 5.32 (s, 5 H, Cp), 5.02 (m, 2 H, 13-H), 4.26 (m, 1 H, 8-H), 4.14 (m, $^3J_{CH2,CH3}$ = 7.1 Hz, 4 H, CH_2), 1.97 (m, 4 H, 10-H, 11-H), 1.44 (m, 1 H, 7_{endo}-H), 1.22 (dt, $^3J_{CH3,CH2}$ = 7.1 Hz, 6 H, CH_3), −1.78 (m, $^3J_{7exo,6}$ = 10.6 Hz, 1 H, 7_{exo}-H) ppm. ^{13}C NMR {1H} (100 MHz, $CD_3C(O)CD_3$): δ = 170.2 (s, C═O), 138.4 (s, C-12), 115.6 (s, C-13), 104.9 (s, C-3), 97.8 (s, C-4), 95.0 (s, C-5), 93.4 (s, C-1), 90.3 (s, C-2), 86.4 (s, C-6), 83.1 (s, Cp), 63.4 (s, C-9), 62.0, 61.9 (s, CH_2), 54.0 (s, C-8), 33.8 (s, C-10, C-11), 26.0 (s, C-7), 14.3 (s, CH_3) ppm. IR (KBr): 3115 (w) ν(C−H, aromatic), 2981 (w), 2940 (w) ν(C−H, aliphatic), 1721 (s) ν(C═O), 1641 (w) ν(C═C), 1449 (w), 1431 (w), 1419 (w) δ(CH_2/CH_3), 1272 (m), 1219 (m) ν(C−O), 1054 (ss, br) ν(BF_4^-) cm^{-1}. FAB-MS: *m*/*z* (%) 439 (100) [M^+ -BF_4^-]. Anal. Calcd for $C_{24}H_{31}BF_4FeO_4 \cdot 1/5(CH_2Cl_2)$ (543.15): C, 53.52; H, 5.83. Found: C, 53.54; H, 5.93.



3b

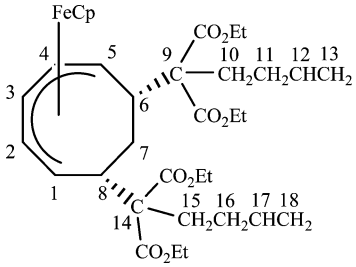
General Procedure for the Second Nucleophilic Addition. Synthesis of 4a−f. The second nucleophilic addition was performed in close analogy with the first one (vide supra). For more preparative details see Table 3.

(η^5-Cyclopentadienyl)[1,2,3,4,5-η-6,8-*exo,exo*-bis(1′,1′-diethoxycarbonyl-3′-buten-1′-yl)cyclooctadienyl)]iron(II) (4a): orange crystalline powder, soluble in hexane, more soluble in toluene; fp 86 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 6.20 (m, $^3J_{11,10} = {}^3J_{15,14} =$ 8.1 Hz, $^3J_{11,12} = {}^3J_{15,16} =$ 10.1 Hz, 2 H, 11-H, 15-H), 5.59 (t′, 1 H, 3-H), 5.14 (m, $^3J_{12,11} = {}^3J_{16,15} =$ 10.1 Hz, 4 H, 12-H, 16-H), 4.07 (q, $^3J_{CH2,CH3} =$ 7.1 Hz, 8 H, CH_2), 3.98 (s, 5 H, Cp), 3.86−4.06 (m, 4 H, 1-H, 2-H, 4-H, 5-H), 3.06 (m, $^3J_{10,11} = {}^3J_{14,15} =$ 8.1 Hz, 4 H, 10-H, 14-H), 2.82 (dt, $^3J_{6,7endo} = {}^3J_{8,7endo} =$ 2.0 Hz, 2 H, 6-H, 8-H), 1.33 (m, $^2J_{7exo,7endo} =$ 12.7 Hz, $^3J_{7endo,6} = {}^3J_{7endo,8} =$ 2.0 Hz, 1 H, 7_{endo}-H), 1.03 (dt, $^3J_{CH3,CH2} =$ 7.1 Hz, 12 H, CH_3), −0.71 (m, $^2J_{7exo,7endo} =$ 12.7 Hz, 1 H, 7_{exo}-H) ppm. ^{13}C NMR {1H} (100 MHz, C_6D_6): δ 170.8, 170.6 (s, C═O), 135.1 (s, C-11, C-15), 117.9 (s, C-12, C-16), 102.6 (s, C-3), 77.4 (s, Cp), 75.0 (s, C-2, C-4), 64.5 (s, C-9, C-13), 60.7, 60.6 (s, CH_2), 48.0 (s, C-6, C-8), 45.8 (s, C-1, C-5), 39.0 (s, C-10, C-14), 23.3 (s, C-7), 14.3 (s, CH_3) ppm. IR (KBr): 3075 (w) ν(C−H, aromatic), 2980 (m), 2932 (w) ν(C−H, aliphatic), 1730 (ss), 1718 (ss) ν(C═O), 1638 (w) ν(C═C), 1451 (w) δ(CH_2/CH_3), 1234 (s), 1214 (s) ν(C−O) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) 624 (40) [M$^+$], 583 (2) [M−$CH_2CHCH_2^+$], 559 (56) [M−Cp$^+$], 454 (100) [M−CH_2CCH_2−$CH_2CCH_2^+$], 425 (51) [M−C(CO_2Et)$_2CH_2CHCH_2^+$], 320 (47) [$FeC_8H_9CH(CO_2Et)_2$], 105 (83) [$C_8H_9^+$], 41 (6) [$CH_2CHCH_2^+$]. Anal. Calcd for $C_{33}H_{44}FeO_8$ (624.55): C, 63.46; H, 7.10. Found: C, 63.53, H 7.17.



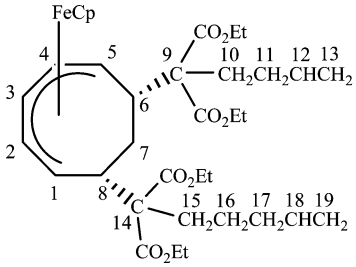
4a

(η^5-Cyclopentadienyl)[1,2,3,4,5-η-6,8-*exo,exo*-bis(1′,1′-diethoxycarbonyl-4′-penten-1′-yl)cyclooctadienyl]iron(II) (4d): orange oil, soluble in hexane, more soluble in toluene. ^{1}H NMR (400 MHz, C_6D_6): δ 5.92 (m, $^3J_{12,13} = {}^3J_{17,18} =$ 10.1 Hz, 2 H, 12-H, 17-H), 5.58 (m, 1 H, 3-H), 5.11 (m, $^3J_{13,12} = {}^3J_{18,17} =$ 10.1 Hz, 4 H, 13-H, 18-H), 4.06 (mq, $^3J_{CH2,CH3} =$ 7.1 Hz, 8 H, CH_2), 3.96 (s, 5 H, Cp), 3.95−3.91 (m, 4 H, 1-H, 2-H, 4-H, 5-H), 2.82 (m, 2 H, 6-H, 8-H), 2.56−2.23 (m, 8 H, 10-H, 11-H, 15-H, 16-H), 1.27 (m, $^2J_{7endo,7exo} =$ 12.6 Hz, 1 H, 7_{endo}-H), 1.03 (dt, $^3J_{CH3,CH2} =$ 7.1 Hz, 12 H, CH_3), −0.72 (m, $^2J_{7exo,7endo} =$ 12.6 Hz, 1 H, 7_{exo}-H) ppm. ^{13}C NMR {1H} (100 MHz, C_6D_6): δ 171.2, 171.0 (s, C═O), 138.8 (s, C-12, C-17), 115.0 (s, C-13, C-18), 102.6 (s, C-3), 77.4 (s, Cp), 74.9 (s, C-2, C-4), 64.2 (s, C-9, C-14), 60.7, 60.6 (s, CH_2), 48.3 (s, C-6, C-8), 46.1 (s, C-1, C-5), 33.9 (s, C-11, C-16), 30.0 (s, C-10, C-15), 23.0 (s, C-7), 14.2, 14.2 (s, CH_3) ppm. IR (NaCl): 3078 (w) ν(C−H, aromatic), 2979 (s), 2937 (m), 2904 (m) ν(C−H, aliphatic), 1723 (ss) ν(C═O), 1641 (m) ν(C═C), 1446 (m), 1367 (m) δ(CH_2/CH_3), 1244 (s), 1216 (s) ν(C−O) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) 652 (29) [M$^+$], 587 (26) [M−Cp$^+$], 441 (86) [M−CpFe−OEt−OEt$^+$], 273 (100) [$C_8H_9C(CO_2Et)(CO)CH_2CH_2CHCH_2^+$], 186 (32) [C($CO_2$-Et)$_2CH_2CH_2^+$], 173 (14) [$HC(CO_2Et)_2CH_2^+$], 105 (54) [$C_8H_9^+$], 41 (4) [$CH_2CHCH_2^+$]. Anal. Calcd for $C_{35}H_{48}FeO_8$ (652.61): C, 64.42; H, 7.41. Found: C, 64.38; H, 7.52.



4d

(η^5-Cyclopentadienyl)[1,2,3,4,5-η-6-*exo*-(1′,1′-diethoxycarbonyl-4′-penten-1′-yl)-8-*exo*-(1″,1″-diethoxycarbonyl-5″-hexen-1″-yl)cyclo-octadienyl]iron(II) (4e): orange oil, soluble in hexane, more soluble in toluene. ^{1}H NMR (400 MHz, C_6D_6): δ 5.98−5.80 (m, $^3J_{12,13} = {}^3J_{18,19} =$ 10.1 Hz, 2 H, 12-H, 18-H), 5.59 (m, 1 H, 3-H), 5.24−4.96 (m, $^3J_{13,12} = {}^3J_{19,18} =$ 10.1 Hz, 4 H, 13-H, 19-H), 4.15−4.01 (m, $^3J_{CH2,CH3} =$ 7.1 Hz, 8 H, CH_2), 3.98 (s, 5 H, Cp), 4.01−3.90 (m, 4 H, 1-H, 2-H, 4-H, 5-H), 2.83 (m, 2 H, 6-H, 8-H), 2.47 (m, 2 H, 10-H), 2.42−2.20 (m, 4 H, 11-H, 15-H), 2.12 (m, 2 H, 17-H), 1.86−1.53 (m, 2 H, 16-H), 1.28 (m, $^2J_{7endo,7exo} =$ 12.5 Hz, 1 H, 7_{endo}-H), 1.04 (m, $^3J_{CH3,CH2} =$ 7.1 Hz, 12 H, CH_3), −0.74 (m, $^2J_{7exo,7endo} =$ 12.5 Hz, 1 H, 7_{exo}-H) ppm. ^{13}C NMR {1H} (100 MHz, C_6D_6): δ 171.3, 171.2, 171.0 (s, C═O), 138.8, 138.7 (s, C-12, C-18), 115.0, 115.0 (s, C-13, C-19), 102.5 (s, C-3), 77.4 (s, Cp), 74.9, 74.9 (s, C-2, C-4), 64.4, 64.2 (s, C-9, C-14), 60.6, 60.6, 60.6 (s, CH_2), 48.2, 48.1 (s, C-6, C-8), 46.3, 46.1 (s, C-1, C-5), 34.7 (s, C-17), 34.0, 33.9 (s, C-11, C-15), 29.9 (s, C-10), 24.7 (s, C-16), 23.0 (s, C-7), 14.3 (s, CH_3) ppm. IR (KBr): 3077 (w) ν(C−H, aromatic), 2979 (s), 2935 (m), 2904 (m) ν(C−H, aliphatic), 1723 (ss) ν(C═O), 1641 (m) ν(C═C), 1463 (w), 1446 (m) 1384 (w), 1367 (m) δ(CH_2/CH_3), 1239 (ss), 1216 (ss) ν(C−O) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) 666 (13) [M$^+$], 651 (5) [M−CH_3^+], 601 (23) [M−Cp$^+$], 453 (25) [M−C(CO_2Et)$_2CH_2CH_2CHCH_2^+$], 439 (28) [M−C(CO_2Et)$_2(CH_2)_3CHCH_2^+$], 293 (45) [M− C(CO_2Et)$_2(CH_2)_3$-$CHCH_2$−CO_2Et−CO_2Et^+], 225 (6) [$CpFeC_8H_8^+$], 186 (76) [CH(CO_2-Et)$_2CH_2CH_2^+$], 160 (100) [$FeC_8H_8^+$], 105 (69) [$C_8H_9^+$], 55 (34) [$CH_2CH_2CHCH_2^+$], 41 (29) [$CH_2CHCH_2^+$]. Anal. Calcd for $C_{36}H_{50}$-FeO_8 (666.64): C, 64.86; H, 7.56. Found: C, 64.81; H, 7.30.



4e

General Procedure for Cleavage of the Cyclooctadiene Ligand. Synthesis of 5a−f. A 1 equiv portion of **4a−f** was dissolved in MeCN, and 10 equiv of CF_3CO_2H was added at room temperature. The reaction mixture changed from red to violet and finally to orange. After 3 h stirring at room temperature, the reaction mixture was evaporated to dryness. The residual brownish oil was chromatographed on silica (70−230 mesh) with petrolether/ethyl acetate (10/1) as eluent. The fractions of the column chromatography were monitored by tlc. For more preparative details see Table 4.

Table 3. Preparative Details for the Second Nucleophilic Addition

product	starting complex	**3BF$_4$** mg (mmol)	HNu^2	HNu^2 mg (mmol)	yield mg (%)
4a	**3a**	337 (0.657)	$CH(CO_2Et)_2CH_2CHCH_2$	132 (0.657)	369 (90)
4b[a]	**3a**	429 (0.838)	$CH(CO_2Et)_2(CH_2)_2CHCH_2$	214 (1.00)	451 (84)
4c[a]	**3a**	440 (0.860)	$CH(CO_2Et)_2(CH_2)_3CHCH_2$	217 (0.951)	470 (84)
4d	**3b**	254 (0.483)	$CH(CO_2Et)_2(CH_2)_2CHCH_2$	134 (0.625)	188 (60)
4e	**3b**	469 (0.892)	$CH(CO_2Et)_2(CH_2)_3CHCH_2$	202 (0.884)	541 (91)
4f[a]	**3c**	656 (1.22)	$CH(CO_2Et)_2(CH_2)_3CHCH_2$	269 (1.18)	726 (88)

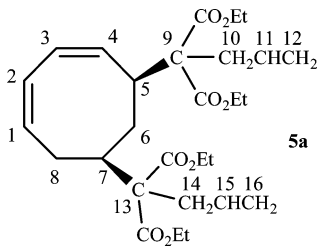
[a] Spectroscopic data is given in the Supporting Information.

Table 4. Preparative Details for the Cleavage of the Cyclooctadiene Ligands

product	starting complex	**4** mg (mmol)	Nu^1/Nu^2	yield mg (%)
5a	**4a**	130 (0.208)	$C(CO_2Et)_2CH_2CHCH_2$/ $C(CO_2Et)_2CH_2CHCH_2$	79.9 (76)
5b[a]	**4b**	451 (0.706)	$C(CO_2Et)_2CH_2CHCH_2$/ $C(CO_2Et)_2(CH_2)_2CHCH_2$	182 (50)
5c[a]	**4c**	470 (0.720)	$C(CO_2Et)_2CH_2CHCH_2$/ $C(CO_2Et)_2(CH_2)_3CHCH_2$	264 (69)
5d	**4d**	174 (0.272)	$C(CO_2Et)_2(CH_2)_2CHCH_2$/ $C(CO_2Et)_2(CH_2)_2CHCH_2$	100 (69)
5e	**4e**	413 (0.619)	$C(CO_2Et)_2(CH_2)_2CHCH_2$/ $C(CO_2Et)_2(CH_2)_3CHCH_2$	182 (54)
5f[a]	**4f**	375 (0.551)	$C(CO_2Et)_2(CH_2)_3CHCH_2$/ $C(CO_2Et)_2(CH_2)_3CHCH_2$	126 (41)

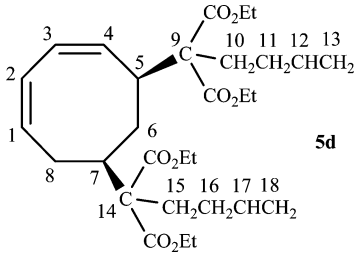
[a] Spectroscopic data is given in the Supporting Information.

5,7-Bis[(1′,1′-diethoxycarbonyl-)but-3′-enyl]-cycloocta-1,3-dien (5a): colorless oil, soluble in hexane, more soluble in benzene. ^{1}H NMR (400 MHz, C_6D_6): δ 6.28, 5.83 (m, $^3J_{11,12} = {}^3J_{15,16} =$ 10.1 Hz, 2 H, 11-H, 15-H), 6.05 (m, 1 H, 1-H), 5.95−5.86 (m, 3 H, 2-H, 3-H, 4-H), 5.16−4.99 (m, $^3J_{12,11} = {}^3J_{16,15} =$ 10.1 Hz, 4 H, 12-H, 16-H), 4.17−3.88 (m, $^3J_{CH2,CH3} =$ 7.1 Hz, 8 H, CH_2), 3.11−2.89 (m, $^3J_{5,6trans} =$ 9.6 Hz, 5 H, 5-H, 10-H, 14-H), 2.72 (m, $^2J_{8cis,8trans} =$ 13.0 Hz, 1 H, 8_{cis}-H), 2.41 (m, $^2J_{6cis,6trans} =$ 12.6 Hz, $^3J_{7,8trans} =$ 9.1 Hz, 2 H, 6_{cis}-H, 7-H), 2.10 (dt, $^3J_{8trans,7} =$ 9.1 Hz, $^2J_{8trans,8cis} =$ 13.0 Hz, 1 H, 8_{trans}-H), 1.20 (m, $^3J_{6trans,5} =$ 9.6 Hz, $^2J_{6trans,6cis} =$ 12.6 Hz, 1 H, 6_{trans}-H), 1.04, 0.96, 0.94, 0.91 (4t, $^3J_{CH3,CH2} =$ 7.1 Hz, 12 H, CH_3) ppm. ^{13}C NMR {1H} (100 MHz, C_6D_6): δ 170.8, 170.7, 170.6, 170.4 (s, C═O), 134.6, 133.3 (s, C-11, C-15), 133.3 (s, C-1), 132.2 (s, C-4), 127.4, 127.0 (s, C-2, C-3), 118.8, 118.3 (s, C-12, C-16), 63.2, 62.4 (s, C-9, C-13), 61.2, 61.1, 61.0, 60.9 (s, CH_2), 41.6 (s, C-5), 40.2 (s, C-7), 39.5, 39.1 (s, C-10, C-14), 33.3 (s, C-8), 29.7 (s, C-6), 14.2, 14.1, 14.1 (s, CH_3) ppm. IR (NaCl): 2981 (m), 2936 (w) ν(C−H, aliphatic), 1727 (ss) ν(C═O), 1640 (w) ν(C═C), 1446 (m) δ(CH_2/CH_3), 1368 (m) δ(CH_3), 1276 (m), 1224 (s), 1200 (s) ν(C−O) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) 504 (29) [M$^+$], 459 (43) [M−OEt$^+$], 431 (13) [M−CO_2Et^+], 305 (65) [M−$C(CO_2Et)_2CH_2CHCH_2^+$], 200 (100) [$HC(CO_2Et)_2CH_2CHCH_2^+$], 154 (28) [$C(CO_2Et)_2CH_2CHCH_2$−OEt$^+$], 105 (46) [$C_8H_9^+$]. Anal. Calcd for $C_{28}H_{40}O_8$ (504.62): C, 66.65; H, 7.99. Found: C, 66.52, H, 8.24.



5a

5,7-Bis[(1′,1′-diethoxycarbonyl-)pent-4′-enyl]-cycloocta-1,3-dien (5d): colorless oil, soluble in hexane, more soluble in benzene. ^{1}H NMR (400 MHz, C_6D_6): δ 6.10 (m, 1 H, 1-H), 5.97−5.88 (m, 3 H, 2-H, 3-H, 4-H), 5.88, 5.75 (m, $^3J_{12,13} = {}^3J_{17,18} =$ 10.1 Hz, 2 H, 12-H, 17-H), 5.23−4.90 (m, $^3J_{13,12} = {}^3J_{18,17} =$ 10.1 Hz, 4 H, 13-H, 18-H), 4.17−3.88 (m, $^3J_{CH2,CH3} =$ 7.1 Hz, 8 H, CH_2), 3.11 (m, $^3J_{5,6trans} =$ 8.6 Hz, 1 H, 5-H), 2.78 (m, $^2J_{8cis,8trans} =$ 12.6 Hz, 1 H, 8_{cis}-H), 2.63−1.99 (m, $^2J_{6cis,6trans} =$ 12.3 Hz, $^2J_{8trans,8cis} =$ 12.6 Hz, 11 H, 6_{cis}-H, 7-H, 8_{trans}-H, 10-H, 11-H, 15-H, 16-H), 1.15 (m, $^3J_{6trans,5} =$ 8.6 Hz, $^2J_{6trans,6cis} =$ 12.3 Hz, 1 H, 6_{trans}-H), 1.05, 0.95, 0.92 (t, $^3J_{CH3,CH2} =$ 7.1 Hz, 12 H, CH_3) ppm. ^{13}C NMR {1H} (100 MHz, C_6D_6): δ 171.4, 171.2, 170.8, 170.7 (s, C═O), 138.6, 138.1 (s, C-12, C-17), 133.7 (s, C-1), 132.1 (s, C-4), 127.3, 126.8 (s, C-2, C-3), 115.0, 115.0 (s, C-13, C-18), 62.4, 61.8 (s, C-9, C-14), 61.1, 61.0, 60.9, 60.8 (s, CH_2), 41.3 (s, C-5), 39.5 (s, C-7), 34.3, 33.9 (s, C-10, C-15), 33.5 (s, C-8), 29.4 (s, C-6), 29.3, 28.8 (s, C-11, C-16), 14.2, 14.1 (s, CH_3) ppm. IR (KBr): 2980 (s), 2938 (m) ν(C−H, aliphatic), 1723 (ss) ν(C═O), 1641 (m) ν(C═C), 1464 (m), 1446 (m) δ(CH_2/CH_3), 1367 (m) δ(CH_3), 1298 (s), 1221 (s), 1197 (s) ν(C−O) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) 532 (8) [M$^+$], 487 (13) [M−OEt$^+$], 459 (9) [M−CO_2Et^+], 319 (54) [M−$C(CO_2Et)_2(CH_2)_2CHCH_2^+$], 173 (96) [$HC(CO_2Et)_2CH_2^+$], 105 (100) [$C_8H_9^+$]. Anal. Calcd for $C_{30}H_{44}O_8 \cdot 1/2(C_{11}H_{18}O_8)$ (671.80): C, 66.64; H, 8.35. Found: C, 66.69; H, 8.17.



5d

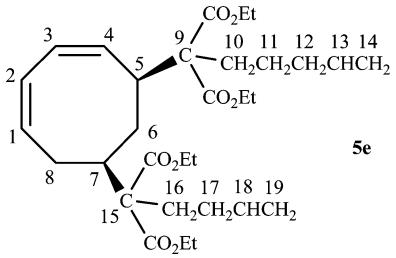
5-[(1′,1′-Diethoxycarbonyl-)hex-5′-enyl]-7-[(1′,1′-diethoxycarbonyl-)pent-4′-enyl]-cycloocta-1,3-dien (5e): colorless oil, soluble in hexane, more soluble in benzene. ^{1}H NMR (400 MHz, C_6D_6): δ 6.11 (m, 1 H, 1-H), 5.99−5.87 (m, 3 H, 2-H, 3-H, 4-H), 5.86 (m, $^3J_{18,19} =$ 10.1 Hz, 1 H, 18-H), 5.73 (m, $^3J_{13,14} =$ 10.1 Hz, 1 H, 13-H), 5.23−4.90 (m, $^3J_{14,13} = {}^3J_{19,18} =$ 10.1 Hz, 4 H, 14-H, 19-H), 4.19−3.88 (m, $^3J_{CH2,CH3} =$ 7.1 Hz, 8H, CH_2), 3.11 (m, 1 H, 5-H), 2.79 (m, $^2J_{8cis,8trans} =$ 12.6 Hz, 1 H, 8_{cis}-H), 2.64−2.12 (m, $^2J_{6cis,6trans} =$ 12.6 Hz, 6 H, 6_{cis}-H, 7-H, 10-H, 16-H), 2.12−1.52 (m, $^2J_{8trans,8cis} =$ 12.6 Hz, 4 H, 8_{trans}-H, 12-H, 17-H), 1.35 (m, 2 H, 11-H), 1.13 (m, $^2J_{6trans,6cis} =$ 12.6 Hz, 1 H, 6_{trans}-H), 1.09−0.89 (m, $^3J_{CH3,CH2} =$ 7.1 Hz, 12 H, CH_3) ppm. ^{13}C NMR {1H} (100 MHz,

Table 5. Preparative Details for the Grubbs-Metathesis on *cis*-5,7-Disubstituted Cycloocta-1,3-diene 5a−f

starting complex	**5** mg (mmol)	Nu^1 (*n*)/Nu^2 (*n*) $C(CO_2Et)_2(CH_2)_n$ $CHCH_2$	**G1** mg (mol %)	product	yield mg (%)
5a	166 (0.328)	1/1	11.8 (4)	**7a**	86 (58)
5b	206 (0.386)	1/2	15.5 (5)	*a*	
5c	232 (0.436)	1/3	13.0 (5)	*a*	
5d	164 (0.307)	2/2	13.0 (5)	**7b**	90 (60)
5e	315 (0.577)	2/3	23.2 (5)	**7b**	24 (9)
5f	262 (0.467)	3/3	18.0 (5)	*a*	

[a] No clear product formation.

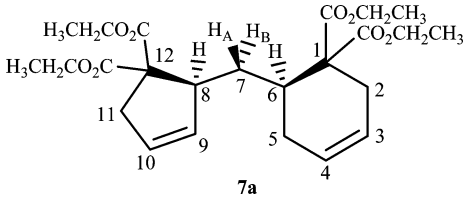
C_6D_6): δ 171.4, 171.4, 171.2, 170.8 (s, C═O), 138.6 (s, C-18), 138.4 (s, C-13), 133.7, 133.7 (s, C-1, C-4), 132.2, 132.2 (s, C-2, C-3), 115.0, 115.0 (s, C-14, C-19), 62.6, 62.4 (s, C-9, C-15), 61.1, 61.0, 60.9, 60.8 (s, CH_2), 41.3 (s, C-5), 39.5 (s, C-7), 34.6, 33.9 (s, C-12, C-17), 33.5 (s, C-8), 29.3 (s, C-6), 29.2, 28.8 (s, C-10, C-16), 23.5 (s, C-11), 14.2, 14.1, 14.1 (s, CH_3) ppm. IR (KBr): 2979 (m), 2932 (m) ν(C−H, aliphatic), 1724 (ss) ν(C═O), 1641 (w) ν(C═C), 1446 (m) $\delta(CH_2/CH_3)$, 1368 (w) $\delta(CH_3)$, 1254 (s), 1221 (s), 1201 (s) ν(C−O) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) 546 (4) [M^+], 501 (7) [$M-OEt^+$], 473 (6) [$M-CO_2Et^+$], 427 (2) [$M-CO_2Et-OEt-H^+$], 399 (1) [$M-CO_2Et-CO_2Et-H^+$], 333 (19) [$M-C(CO_2Et)_2(CH_2)_2CHCH_2^+$], 319 (15) [$M-C(CO_2Et)_2(CH_2)_3CHCH_2^+$], 228 (8) [$HC(CO_2Et)_2(CH_2)_3CHCH_2^+$], 173 (65) [$HC(CO_2Et)_2CH_2^+$], 105 (100) [$C_8H_9^+$]. Anal. Calcd for $C_{31}H_{46}O_8$ (546.70): C, 68.11; H, 8.48. Found: C, 68.11; H, 8.22.



5e

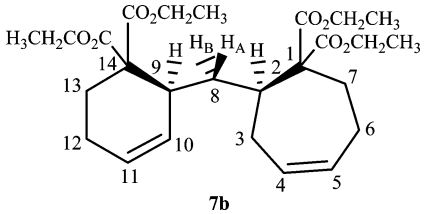
General Procedure for Grubbs-Metathesis on *cis*-5,7-Disubstituted cycloocta-1,3-dienes 5a−f. One equivalent of **5a−f** was dissolved in dichloromethane, and 4−5 mol % of **G1** was added at room temperature. The reaction mixture changed during 1 h from violet to brown. After 7 d stirring at room temperature, the reaction mixture was evaporated to dryness. The residual brownish oil was chromatographed on silica (70−230 mesh) with petrolether/ethyl acetate as eluent. The fractions of the column chromatography were monitored by tlc. For more preparative details see Table 5.

1,1-Diethoxycarbonyl-6-(5′,5′-diethoxycarbonylcyclopent-2′-enylmethyl)cyclohex-3-ene (7a): Eluent, PE/EE 7/2; R_f = 0.50, colorless oil, soluble in hexane, more soluble in toluene. ^{1}H NMR (400 MHz, C_6D_6): δ 5.65 (m, $^3J_{9,10}$ = 6.0 Hz, 1 H, 9-H), 5.59 (m, $^3J_{3,4}$ = 10.1 Hz, 1 H, 3-H), 5.51 (m, $^3J_{4,3}$ = 10.1 Hz, 1 H, 4-H), 5.41 (m, $^3J_{10,9}$ = 6.0 Hz, 1 H, 10-H), 4.19−3.84 (m, $^3J_{CH2,CH3}$ = 7.1 Hz, 8 H, CH_2), 3.94 (m, 1 H, 8-H), 3.49 (m, $^2J_{11B,11A}$ = 17.4 Hz, 1 H, 11B-H), 2.85 (m, $^2J_{11A,11B}$ = 17.4 Hz, 3 H, 2-H, 11A-H), 2.72 (m, $^3J_{6,7A}$ = 7.6 Hz, $^3J_{6,7B}$ = 3.3 Hz, 1 H, 6-H), 2.60 (m, $^2J_{5A,5B}$ = 18.4 Hz, 1 H, 5A-H), 2.16 (m, $^2J_{5B,5A}$ = 18.4 Hz, 1 H, 5B-H), 1.99 (ddd, $^3J_{7B,6}$ = 3.3 Hz, $^2J_{7B,7A}$ = 13.9 Hz, 1 H, 7B-H), 1.54 (ddd, $^3J_{7A,6}$ = 7.6 Hz, $^2J_{7A,7B}$ = 13.9 Hz, 1 H, 7A-H), 1.06 (dt, $^3J_{CH3,CH2}$ = 7.1 Hz, 6 H, CH_3), 0.98 (t, $^3J_{CH3,CH2}$ = 7.1 Hz, 3 H, CH_3), 0.91 (t, $^3J_{CH3,CH2}$ = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR {1H} (100 MHz, C_6D_6): δ 172.0, 171.4, 170.3, 170.2 (s, C═O), 133.7 (s, C-9), 127.3 (s, C-10), 126.1 (s, C-4), 124.1 (s, C-3), 64.1 (s, C-1), 61.4, 61.2 (s, CH_2), 57.8 (s, C-12), 50.3 (s, C-8), 40.3 (s, C-11), 36.7 (s, C-6), 33.5 (s, C-7), 30.5 (s, C-5), 30.1 (s, C-2), 14.1, 14.1, 14.0, 14.0 (s, CH_3) ppm. IR (KBr): 2982 (m), 2938 (w) ν(C−H, aliphatic), 1731 (ss) ν(C═O), 1660 (w) ν(C═C), 1465 (w), 1447 (w) $\delta(CH_2/CH_3)$, 1367 (w) $\delta(CH_3)$, 1253 (s), 1227 (m), 1180 (s) 1095 (m), 1075 (m), 1049 (m) ν(C−O) cm−1. EI-MS (70 eV): *m*/*z* (%) 450 (100) [M^+], 405 (46) [$M-OEt^+$], 330 (60) [$M-CO_2Et-OEt-H_2^+$], 285 (26) [$M-CO_2Et-OEt-OEt-H_2^+$], 257 (31) [$M-CO_2Et-OEt-OEt-H_2-C_2H_6^+$], 239 (20) [$C_7H_9(CO_2Et)_2^+$], 211 (19) [$C_5H_5(CO_2Et)_2^+$], 183 (34) [$C(CO_2Et)_2CCH^+$], 152 (28) [$C_6H_7(CO_2Et)^+$], 79 (38) [$C_6H_7^+$]. Anal. Calcd for $C_{24}H_{34}O_8$ (450.23): C, 63.98; H, 7.61. Found: C, 64.03; H, 7.72.



7a

1,1-Diethoxycarbonyl-2-(6′,6′-diethoxycarbonylcyclohex-2′-enylmethyl)cyclohept-4-ene (7b): Eluent, PE/EE 10/3; R_f = 0.30 (PE/EE 10/1), colorless oil, soluble in hexane, more soluble in toluene. ^{1}H NMR (400 MHz, C_6D_6): δ 5.95 (m, $^3J_{10,9}$ = 5.0 Hz, $^3J_{10,11}$ = 10.1 Hz, 1 H, 10-H), 5.67 (m, 2 H, 4-H, 5-H), 5.52 (m, $^3J_{11,10}$ = 10.1 Hz, 1 H, 11-H), 4.27−3.92 (m, $^3J_{CH2,CH3}$ = 7.1 Hz, 8 H, CH_2), 3.42 (m, $^3J_{9,8A}$ = 8.9 Hz, $^3J_{9,8B}$ = 5.5 Hz, $^3J_{9,10}$ = 5.0 Hz, 1 H, 9-H), 2.88 (ddt, $^3J_{2,8A}$ = 8.9 Hz, $^3J_{2,8B}$ = 2.6 Hz, 1 H, 2-H), 2.68 (m, 2 H, 3-H), 2.43 (m, $^2J_{13B,13A}$ = 13.8 Hz, 3 H, 7-H, 13B-H), 2.18 (ddd, $^2J_{13A,13B}$ = 13.8 Hz, 1 H, 13A-H), 2.08 (m, 2 H, 6-H), 1.91 (m, 2 H, 12-H), 1.75 (ddd, $^3J_{8B,2}$ = 2.6 Hz, $^2J_{8B,8A}$ = 13.9 Hz, $^3J_{8B,9}$ = 5.5 Hz, 1 H, 8B-H), 1.57 (ddd, $^3J_{8A,2}$ = 8.9 Hz, $^2J_{8A,8B}$ = 13.9 Hz, $^3J_{8A,9}$ = 8.9 Hz, 1 H, 8A-H), 1.10 (t, $^3J_{CH3,CH2}$ = 7.1 Hz, 3 H, CH_3), 1.08 (t, $^3J_{CH3,CH2}$ = 7.1 Hz, 3 H, CH_3), 0.95 (t, $^3J_{CH3,CH2}$ = 7.1 Hz, 3 H, CH_3), 0.91 (t, $^3J_{CH3,CH2}$ = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR {1H} (100 MHz, C_6D_6): δ 171.7, 171.1, 171.0, 170.6 (s, C═O), 132.3 (s, C-5), 130.7 (s, C-10), 129.9 (s, C-4), 125.1 (s, C-11), 63.3 (s, C-1), 61.3, 61.3, 61.0 (s, CH_2), 57.6 (s, C-14), 39.2 (s, C-2), 37.8 (s, C-9), 34.1 (s, C-8), 30.1, 29.9 (s, C-7, C-13), 24.9 (s, C-6), 24.3 (s, C-3), 23.0 (s, C-12), 14.1 (s, CH_3) ppm. IR (NaCl): 2926 (ss), 2873 (m), 2850 (m) ν(C−H, aliphatic), 1731 (s) ν(C═O), 1654 (w) ν(C═C), 1464 (s), 1447 (s) $\delta(CH_2/CH_3)$, 1390 (m), 1367 (s) $\delta(CH_3)$, 1263 (s), 1240 (s), 1161 (s), 1095 (s), 1066 (s), 1049 (s) ν(C−O) cm^{-1}. EI-MS (70 eV): *m*/*z* (%) 478 (9) [M^+], 411 (16) [$M-CH_2CHCHCH_2CH^+$], 306 (53) [$M-CH_2C(CO_2Et)_2^+$], 173 (100) [$H_3CC(CO_2Et)_2^+$], 127 (26) [$CHCHCH_2CH_2CO_2Et^+$], 99 (8) [$CHCHCO_2Et^+$], 79 (14) [$C_6H_7^+$]. Anal. Calcd for $C_{26}H_{38}O_8$ (478.58): C, 65.24; H, 8.01. Found: C, 65.31; H, 8.01.



7b

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Supporting Information Available: CIF files giving crystal data for **2a**,**b**, **4a**, **5d** and text giving spectroscopic data for **2c**, **3c**, **4b**,**c**,**f**, and **5b**,**c**,**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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