The Chemistry of Metallacyclic Alkenylcarbene Complexes, 3[◇]

C–C Bond Formation with Carbon Nucleophiles. Stereoselective Dienylation of Lithium Enolates and Cuprates and a Novel Cascade Synthesis of Highly Substituted Cyclopentenones from Lithium Acetylides

Jutta Böhmer, Walter Förtsch, Frank Hampel, and Rainer Schobert*

Institut für Organische Chemie der Universität Erlangen-Nürnberg,
Henkestraße 42, D-91054 Erlangen
Telefax: (internat.) +49(0)9131/856864. – E-mail: schobert@indigo8.organik.uni-erlangen.de

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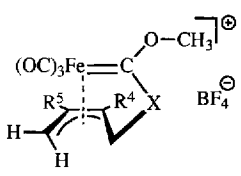
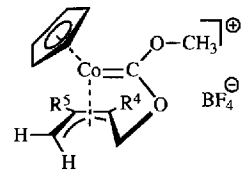
The cationic ferracyclic carbene complexes **1** react with carbon nucleophiles like lithium enolates and organocuprates to give the corresponding 4-substituted 1,(3*E*)-diene tricarbonyliron complexes **6** and **9**. The reaction is thought to proceed by initial attack on the allyl terminus and subsequent ferra Claisen-Ireland rearrangement of the intermediate (η^2-alkene)carbene complex **4**. This rationale is supported by the isolation and characterisation of analogous aminooxocarbene derivatives **8**. With sterically demanding enolates products **6** are formed in diastereomeric ratios of up to 90:10, thus demonstrating the inductive power of the chiral metallacycle in **1**. Lithium acetylides as carbon nucleophiles react with **1** according to a novel cascade to give regio- and stereospecifically 2,5,5-trisubstituted cyclopentenones **10** suggesting a concerted formation of four C–C bonds together with a CO insertion and a formal carbene transfer step.

We recently reported on the syntheses (starting from vinyl oxiranes), structures, and reactivity of novel metallacyclic dioxo- and aminooxocarbene complexes of iron **1**, **2**[1] and cobalt **3**[2] bearing a terminal η^3-allyl ligand. Although featuring similar structures as well as electron transfer behaviour, these types of complexes show a different reactivity towards nucleophiles. Whereas the cobalt complexes **3** display "typical carbene" reactivity to some extent, the ferracycles **1** react with a variety of heteroatom nucleophiles and bases either at the methoxy group or at the terminal carbon atom of the allyl ligand. Most interesting, with respect to possible synthetic applications, are those reactions which commence with an attack on the allyl terminus of **1**, thus leading to reactive intermediates with a shifted location and coordination number of the π-donor ligand. These intermediates in turn may give rise to concerted reactions involving the carbene moiety *and* the π-donor ligand. Examples we have already published[1] are intramolecular carbene transfer reactions leading to 2*H*-pyran complexes or the formation of heterosubstituted diene complexes by treatment of **1** with weak bases or with nucleophiles like phosphanes, respectively.

In the present paper we describe the extension of this reaction principle to carbon nucleophiles. We found that lithium enolates and lithium organocuprates smoothly react with C–C bond formation (the most important "organometallic" transformation) at the allyl ligand of **1** yielding 4-substituted 1,(3*E*)-diene complexes **6** and **9**. In general



	X	R^4	R^5
1a	O	Me	H
2a	N*i*Bu	H	Me
2b	NMe	H	Me
2c	NBzl	H	H



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tricarbonyliron complexes of acyclic dienes have found increasing application in organic synthesis over the last decade[3]. Furthermore, we provide some evidence for the proposed general mechanism of the underlying metalla Claisen rearrangement by isolating and characterising the corresponding "intermediates" **8** in the aminooxo series (X = NR). With **1** and lithium acetylides as carbon nucleophiles we observed an unexpected novel cascade reaction which regioselectively furnishes highly substituted cyclopentenones. In the course of this remarkable one-pot process no fewer than four new C–C bonds are formed with concomitant insertion of one CO group together with transfer of the carbene moiety as a methoxycarbonyl function to the former allyl terminus of **1**.

Results and Discussion

When carbene complexes **1** are treated with freshly prepared solutions of lithium enolates (derived from ketones or esters and lithium *N*-isopropylcyclohexylamide) in THF

[◇] Part 2: Ref.[2].

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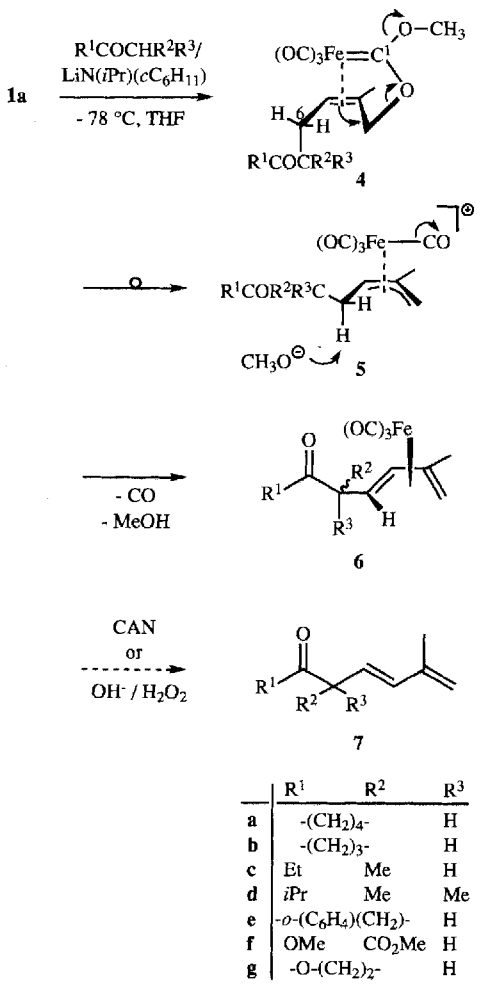
at −78 °C a swift C–C coupling reaction takes place at the allyl terminus. The resulting 4-substituted 1,(3*E*)-diene complexes **6** are formed within a couple of minutes in 70–80% yield without any (3*Z*) or other regioisomers. Compound **6** can then be demetalated with CAN to the "free" 3,5-bisunsaturated carbonyl system **7**, or – making use of the protective properties of the tricarbonyliron moiety – be first transformed into valuable derivatives like (methylene-separated) trienes[4a–c] (via Wittig olefination) or 3,5-diene-1-ols[4d] (by Grignard reagents) as occurring in vegetable material. With (pro)chiral enolates and (racemic) **1a** (R^4 = Me, R^5 = H), products **6** are formed as mixtures of diastereoisomers in a ratio depending mainly on the bulkiness of the nucleophile as can be inferred from Table 1. Ratios of up to 90:10 in the case of the enolates derived from indanone or cyclohexanone reveal a distinct inductive ability of the metallacycle which defines the chiral plane in **1**.

Scheme 1



	R^1	R^2	R^3
a	-$(CH_2)_4$-		H
b	-$(CH_2)_3$-		H
c	Et	Me	H
d	*i*Pr	Me	Me
e	-*o*-$(C_6H_4)(CH_2)$-		H
f	OMe	CO_2Me	H
g	-O-$(CH_2)_2$-		H

Scheme 1 outlines a conceivable mechanism for the observed reaction. Initial attack of the nucleophile at the allylic terminus (C-6) should lead to a neutral, fairly unstable (η^2-alkene) ironcarbene complex **4** which is reminiscent of analogous tungsten complexes, thoroughly investigated by the groups of Casey[5] and Rudler[6]. These are either stable or undergo intramolecular cyclopropanation, depending on whether the η^2-olefin ligand and the W=C bond are oriented perpendicular or parallel to each other. Similar iron compounds, in which the carbene ligand is part of a $^{2+1}$L system (e.g. a ligand which is bound to the metal with three not entirely consecutive carbon atoms), are stable only if they are cationic and bear an additional electron-donating ligand like cyclopentadienyl (Cp) at the central metal[7]. The intermediate **4** obviously does not give cyclopropanation products but – as a formal ferravinyl allyl ether – can undergo an intramolecular Claisen-Ireland rearrangement[8] to the reactive cationic allyltetracarbonyliron compound **5**. Deprotonation by the methoxide anion from "underneath" (i.e. from the side opposite to the central metal fragment), loss of carbon monoxide and recomplexation of (the former) C-6 eventually lead to the formation of **6**.

Table 1. Diene complexes **6** from lithium enolates and carbene complex **1a** (R^4 = Me, R^5 = H)

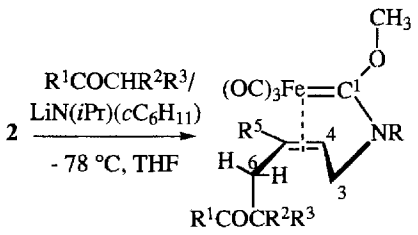
	R^1	R^2	R^3	diastereomeric ratio	yield in %
6a	-$(CH_2)_4$-		H	90 : 10	76
6b	-$(CH_2)_3$-		H	83 : 17	82
6c	C_2H_5	CH_3	H	55 : 45	67
6d	$(CH_3)_2CH$	CH_3	CH_3		78
6e	-*o*-$(C_6H_4)(CH_2)$-		H	85 : 15	70
6f	OCH_3	$COOCH_3$	H		40
6g	-O-$(CH_2)_2$-		H	60 : 40	40

Some aspects are worth mentioning. First, a sequence with a net increase in the coordination number ("hapticity") like η^3 (as in **1**) → η^2 (as in **4**) → η^4 (as in **6**) is quite untypical of cationic ironallyl complexes. They normally react with nucleophiles to yield (most often after spontaneous demetalation) substituted olefins[9]. Aumann[10] and Ley[11] reported on similar 1,2-shifts ($\eta^3 \rightarrow \eta^2 \rightarrow \eta^3$) with amines as nucleophiles in the ferralacton series from which our carbene complexes derive. A good deal of support for the proposed mechanism comes from the reaction of the corresponding aminooxocarbene complexes **2** with lithium enolates, which also starts with an attack on the allyl terminus. But here the resulting neutral (η^2-alkene)carbene complexes **8** are sufficiently stable to be isolated and characterised for two reasons. First, any rearrangement resembling **4** → **5** would create an isonitrile ligand at a zero-valent transition metal centre, which is quite unfavourable. As an X-ray structural analysis of **8a** (Figure 1) reveals, there is no good chance of a subsequent cyclopropanation either: the alkene ligand is oriented nearly perpendicular to the Fe=C bond.

Some other structural features of **8a** are remarkable. Despite the bis-donor substitution the bond distance between the carbene carbon and the iron atom is merely 1.96 Å. According to the C=C bond distance of 1.407 Å and its just "slightly disturbed planarity" the olefin seems to be coordinated in a somewhat loose manner. Two diastereoisomers of **8a** are formed, due to the newly created stereocen-

tre. As our first example in this class of compounds, **8a** exclusively features a *Z* configuration of the carbene–oxygen bond, presumably coerced by the bulky isobutyl residue at the adjacent nitrogen atom. Surprisingly **8b**, although lacking such an additional stereocentre, is formed as a mixture of two diastereoisomers as well. We ascribe this to a restricted rotation of the malonate moiety about the newly established C–C bond and not to a *Z*/*E* isomerism of the carbene carbon–oxygen bond. NMR studies show that the closer to this moiety given atoms lie, the more differ their shifts from those of their counterparts in the other diastereomer. When the methyl residue (R^5) at the olefin ligand is replaced by a hydrogen atom like in **8c**, no such restriction exists and only one species (the racemate) is observed in NMR!

Scheme 2



8

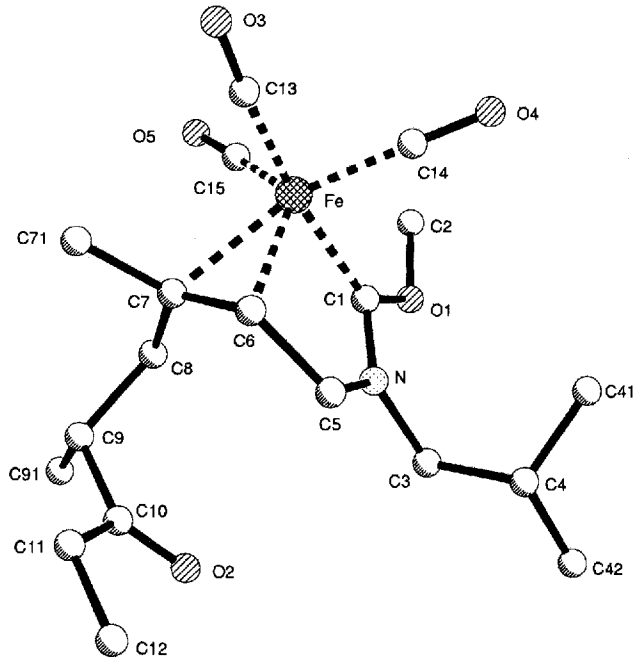
	R	R^1	R^2	R^3	R^5
8a	*i*Bu	Et	Me	H	Me
8b	Me	OMe	CO_2Me	H	Me
8c	Bzl	OMe	CO_2Me	H	H

Although we tried to use some other types of carbon nucleophiles, which in similar cases have proven quite useful, like enolates with potassium and sodium counterions[12], enamines[13], organomanganese[14], and organocadmium[15] compounds, only high-order lithium organocuprates reacted in as well-defined a manner as the lithium enolates did. Presumably according to the general mechanism shown in Scheme 1, 4-alkyl-substituted 1,(3*E*)-diene complexes **9** are formed, albeit as yet in moderate yields. As functionalised cuprates are also readily available, more complex structures featuring oligo-ene units or the like should be accessible in this way.

A reasonable explanation for the puzzling fact that potassium enolates, normally forming and reacting with electrophiles much more cleanly than their lithium analogues[16], do not give any well-defined products with **1** could be provided by semiempirical calculations[2] (e.g. by SINDO[17]). These indicate a negligible positive charge on the organic ligand as a whole but a considerable orbital coefficient at C-6 in the LUMO of **1**, a fact that would favour the orbital-controlled attack of the weak and "more covalent" lithium enolates compared with that of the harder and "more ionic" ones of potassium.

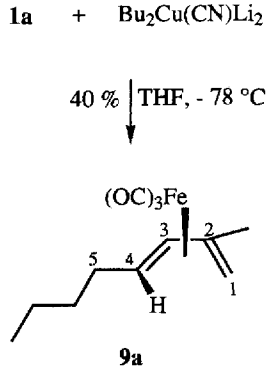
We finally tested lithium acetylides as carbon nucleophiles – with quite an unexpected result. When THF solutions of various derivatives (prepared by reaction of the corresponding 1-alkynes with *n*BuLi at −78°C) are added dropwise to slurries of **1a** (chosen to get information on the regiochemistry!) in THF at −78°C an almost instantaneous reaction takes place which gives after the usual aqueous workup the 2,5,5-trisubstituted cyclopentenones **10** exclusively, in yet unoptimised 20–40% yield. The structure of **10** was assigned unambiguously by NMR spectroscopy. Distinct NOE were observed between 3-H/4-H^{up}, 3-H/4-H^{down}, and 3-H/11-H whereas the H,H-COSY revealed ^3J(4-H^{up}/3-H), ^3J(4-H^{down}/3-H), and ^5J(4-H/11-H) couplings. Long-range ^1H-^{13}C connectivities (i.e. ^3J or ^4J) were detected by means of HMBC-NMR between 10-H/C-1 and 4-H/C-1, which rule out any alternative isomers.

Figure 1. Molecular structure of **8a**[a]



[a] Selected bond lengths [Å] and angles [°]: Fe–C1 1.964(7), Fe–C6 2.083(7), Fe–C7 2.158(7), Fe–C13 1.798(8), Fe–C14 1.774(8), Fe–C15 1.766(8), C1–O1 1.338(8), C1–N 1.305(8), C2–O1 1.434(8), C5–N 1.441(9), C5–C6 1.520(9), C6–C7 1.407(9), C5–C6–C7 125.4(6), C6–C7–C8 125.1(6), C1–Fe–C6 80.4(3), C6–Fe–C7 67.8(4), C1–Fe–C7 89.9(3), Fe–C1–O1 130.3(5)

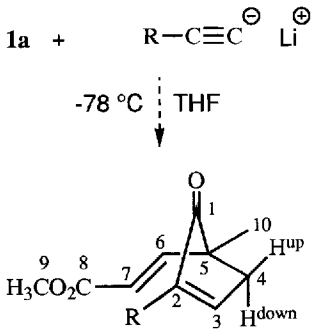
Scheme 3



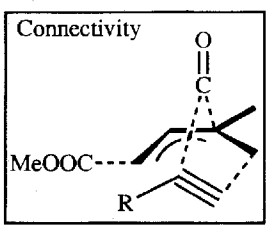
9a

Though the mechanistic details of this unprecedented reaction have not yet been elucidated some of its features deserve to be mentioned. In the course of this cascade process four new C–C bonds are formed with concomitant insertion of one CO unit and a formal transfer of the carbene function as a methoxycarbonyl group to the former allyl terminus (C-6). These processes proceed at −78 °C under argon. Predominantly (GC > 95%), the isomer with *E* configuration of the exocyclic double bond and with the alkyl residue of the starting acetylene next to the carbonyl group of the cyclopentenone ring is formed. Obvious mechanistic proposals like initial base-induced formation of the corresponding 2*H*-pyrantricarbonyliron complexes[1] followed by ring opening and subsequent cyclocarbonylation[18] of the diene complex thus formed could be excluded as these intermediate complexes proved unreactive towards 1-alkynes or acetylides. Keeping in mind the usefulness of similar reactions involving the formation of three new C–C bonds, one CO insertion and the same regiochemistry of the acetylene intake, like those of Pauson and Khand[19] or Dötz[20], synthetic application to the vast field of natural products with highly substituted cyclopentenone substructures seems promising, once the yield has been optimised. Interestingly, Eilbracht[21] recently reported that cationic tricarbonyl(cycloheptadienyl)iron complexes are readily attacked by lithiated alkynes also at a *non-terminal* (C-2) carbon atom of an η^5-ligand to give fairly air-stable allylalkyliron compounds which insert externally applied CO only under a pressure of 200 bar at about 120 °C! More detailed investigations are necessary to gain further insight into the mechanism of our novel cascade reaction.

Scheme 4



10a: R = C_5H_{11}
b: R = C_8H_{17}
c: R = *c*C_6H_{11}



In summary, metallacyclic ironcarbene complexes **1** have proven quite useful as a means of regio- and stereoselective C–C bond formation between carbon nucleophiles like enolates, cuprates, or acetylides with lithium as the counterion and allyl ligands where the particular properties of the metallacycle allow some special consecutive reactions like rearrangements to 4-substituted 1,(3*E*)-dienes **6** and **9** or even multistep cascades affording highly functionalised carbocycles like **10**.

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Experimental

All operations were carried out under Ar by using Schlenk equipment. The starting materials **1**, **2**[1] were prepared as published. Melting points are not corrected. – NMR: Jeol JNMX GX-400. – IR: Bruker IFS 48, Beckmann Acculab A1, A3. – MS: Varian MAT CH-4B (EFO-4B-source), Varian MAT 311A (EI/FD source). – MS: Heraeus Mikromat C–H–N. – Diastereomeric ratios are determined from the relative intensities of the pertaining ^{1}H-NMR signals.

1. Synthesis of **6** *and* **8**. – *General Procedure:* *n*BuLi (0.48 ml of a 2.5 M solution in hexane; 1.2 mmol) was added to a solution of *N*-isopropylcyclohexylamine (170 mg; 1.2 mmol) in THF (5 ml) at 0 °C. The mixture was stirred for 30 min, then cooled to −78 °C and treated with the carbonyl compound (1.2 mmol). After 1 h the resulting solution was transferred by means of a cannula to a slurry of **1a** (354 mg; 1.0 mmol) or **2** (1.0 mmol), respectively, in THF, chilled to −78 °C (or −40 °C in the case of cyclic ketones). Instantaneous deepening of the yellow shade indicated a swift reaction. Any volatile components were evaporated after another hour and the residue was repeatedly extracted with ether/hexane (2:1). The crude product thus obtained was subsequently purified by CC (silica; ether/petroleum ether, 1:1).

(1'E)-Tricarbonyl[(1'-4'-η⁴)-2-{(3'-methyl)buta-1',3'-dien-1'-yl}cyclohexan-1-one]iron(0) (**6a**): 231 mg (0.76 mmol; 76%) as a 90:10 mixture of diastereoisomers; yellow oil from 118 mg of cyclohexanone. – IR (neat): $\tilde{\nu}$ = 2945 cm^{-1}, 2870 [ν(C–H)], 2010, 1940, 1725 [ν(C=O)], 1685, 1630, 1430. – Major diastereoisomer (90%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.41 [d, ^2J(4'-H^{en}/4'-H^{ex}) = 1.50 Hz, 1H, 4'-H^{en}], 0.45 [dd, ^3J(1'-H/2'-H) = 8.30 Hz, ^3J(2-H/1'-H) = 9.52 Hz, 1H, 1'-H], 1.60–1.82 [m, 4H, 4-H, 5-H], 1.83 [d, ^2J(4'-H^{en}/4'-H^{ex}) = 1.50 Hz, 1H, 4'-H^{ex}], 1.84–2.47 [m, 5H, 2-H, 3-H, 6-H], 2.16 [s, 3H, CH_3], 5.08 [d, ^3J(1'-H/2'-H) = 8.30 Hz, 1H, 2'-H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 22.75 (C-4), 24.70 (CH_3), 27.59 (C-3), 36.41 (C-5), 41.53 (C-6), 43.72 (C-4'), 55.78 (C-1'), 59.41 (C-2), 88.19 (C-2'), 100.16 (C-3'), 211.26 (Fe=CO), 218.64 (C-1). – MS (70 eV); *m/z* (%): 304 (1) [M$^+$], 276 (30) [M$^+$ − CO], 248 (52) [M$^+$ − 2 CO], 220 (100) [M$^+$ − 3 CO], 150 (38) [M$^+$ − Fe(CO)$_3$], 56 (38) [Fe]. – $C_{14}H_{16}FeO_4$ (304.1): calcd. C 55.29, H 5.30; found C 55.20, H 5.14.

(1'E)-Tricarbonyl[(1'-4'-η⁴)-2-{(3'-methyl)buta-1',3'-dien-1'-yl}cyclopentan-1-one]iron(0) (**6b**): 238 mg (0.82 mmol; 82%) as a 83:17 mixture of diastereoisomers; yellow oil from 101 mg of cyclopentanone. – IR (neat): $\tilde{\nu}$ = 2940 cm^{-1}, 2860 [ν(C–H)], 2005, 1965, 1945, 1720 [ν(C=O)], 1690, 1625, 1435. – Major diastereoisomer (83%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.35 [d, ^2J(4'-H^{en}/4'-H^{ex}) = 1.50 Hz, 1H, 4'-H^{en}], 0.45 [dd, ^3J(1'-H/2'-H) = 8.30 Hz, ^3J(2-H/1'-H) = 9.30 Hz, 1H, 1'-H], 1.65–1.80 [m, 2H, 3-H],

1.81 [d, ^2J(4'-H^{en}/4'-H^{ex}) = 1.50 Hz, 1H, 4'-H^{ex}], 1.85–2.70 [m, 5H, 2-H, 4-H, 5-H], 2.18 [s, 3H, CH_3], 5.34 [d, ^3J(1'-H/2'-H) = 8.30 Hz, 1H, 2'-H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 20.66 (C-3), 22.82 (CH_3), 32.58 (C-4), 38.33 (C-5), 43.61 (C-4'), 54.43 (C-1'), 58.00 (C-2), 88.10 (C-2'), 100.59 (C-3'), 211.64 (Fe=CO), 218.11 (C-1). – MS (70 eV); *m/z* (%): 290 (2) [M$^+$], 262 (28) [M$^+$ – CO], 234 (49) [M$^+$ – 2 CO], 206 (100) [M$^+$ – 3 CO], 150 (45) [M$^+$ – Fe(CO)$_3$], 134 (23), 56 (33) [Fe]. – $C_{13}H_{14}FeO_4$ (290.1): calcd. C 53.82, H 4.86; found C 54.02, H 4.98.

(5E)-Tricarbonyl[(5-8-η^4)-4,7-dimethyl-5,7-octadien-3-one]iron(0) (**6c**): 195 mg (0.67 mmol; 67%) as a 55:45 mixture of diastereoisomers; yellow oil from 86 mg of diethyl ketone. – IR (neat): ṽ = 3070 cm^{-1} [ν(=C–H)], 2990, 2970, 2890 [ν(C–H)], 2045, 1990, 1970, 1720 [ν(C=O)], 1455. – Major diastereoisomer (55%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.43 [d, ^2J(8-H^{en}/8-H^{ex}) = 1.42 Hz, 1H, 8-H^{en}], 0.86 [dd, ^3J(5-H/6-H) = 8.55 Hz, ^3J(4-H/5-H) = 9.55 Hz, 1H, 5-H], 1.07 [m, 3H, 1-H], 1.26 [d, ^3J(4-H/CH_3) = 4.88 Hz, 3H, 4-CH_3], 1.78 [d, ^2J(8-H^{en}/8-H^{ex}) = 1.42 Hz, 1H, 8-H^{ex}], 2.16 [s, 3H, 7-CH_3], 2.33 [dd, ^3J(4-H/5-H) = 9.55 Hz, ^3J(CH_3/4-H) = 4.88 Hz, 1H, 4-H], 2.54 [m, 2H, 2-H], 5.12 [d, ^3J(5-H/6-H) = 8.55 Hz, 1H, 6-H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 7.77 (C-1), 19.44 (7-CH_3), 21.76 (4-CH_3), 34.68 (C-2), 43.68 (C-8), 51.32 (C-5), 62.21 (C-4), 86.34 (C-6), 100.30 (C-7), 211.47 (Fe=CO), 211.89 (C-3). – Minor diastereoisomer (45%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.40 [d, ^2J(8-H^{en}/8-H^{ex}) = 1.42 Hz, 1H, 8-H^{en}], 0.72 [dd, ^3J(5-H/6-H) = 8.55 Hz, ^3J(4-H/5-H) = 9.55 Hz, 1H, 5-H], 1.07 [m, 3H, 1-H], 1.24 [d, ^3J(4-H/CH_3) = 6.35 Hz, 3H, 4-CH_3], 1.82 [d, ^2J(8-H^{en}/8-H^{ex}) = 1.42 Hz, 1H, 8-H^{ex}], 2.17 [s, 3H, 7-CH_3], 2.31 [dd, ^3J(4-H/5-H) = 9.55 Hz, ^3J(CH_3/4-H) = 6.35 Hz, 1H, 4-H], 2.54 [m, 2H, 2-H], 5.18 [d, ^3J(5-H/6-H) = 8.55 Hz, 1H, 6-H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 7.55 (C-1), 19.44 (7-CH_3), 21.36 (4-CH_3), 33.73 (C-2), 43.52 (C-8), 50.79 (C-5), 62.31 (C-4), 86.84 (C-6), 100.03 (C-7), 211.47 (Fe=CO), 211.53 (C-3). – MS (70 eV); *m/z* (%): 264 (15) [M$^+$ – CO], 236 (42) [M$^+$ – 2 CO], 208 (94) [M$^+$ – 3 CO], 152 (57) [{208} – CH_3CH_2CO], 57 (64) [$CH_3CH_2CO^+$]. – $C_{13}H_{16}FeO_4$ (292.1): calcd. C 53.45, H 5.52; found 53.22, H 5.60.

(5E)-Tricarbonyl[(5-8-η^4)-2,4,4,7-tetramethyl-5,7-octadien-3-one]iron(0) (**6d**): 250 mg (0.78 mmol; 78%) as yellow oil from 138 mg of diisopropyl ketone. – IR (neat): ṽ = 2975 cm^{-1}, 2930, 2875 [ν(C–H)], 2040, 1975, 1960, 1705 [ν(C=O)], 1465. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.32 [d, ^2J(8-H^{en}/8-H^{ex}) = 1.65 Hz, 1H, 8-H^{en}], 0.91 [d, ^3J(5-H/6-H) = 9.35 Hz, 1H, 5-H], 1.01 [d, ^3J(1-H/2-H) = 6.6 Hz, 3H, 1-H], 1.03 [d, ^3J(2-H/CH_3) = 6.6 Hz, 3H, 2-CH_3], 1.15 [s, 3H, 4-CH_3], 1.29 [s, 3H, 4-CH_3], 1.80 [d, ^2J(8-H^{en}/8-H^{ex}) = 1.65 Hz, 1H, 8-H^{ex}], 3.13 [qq, ^3J(1-H/2-H) = 6.6 Hz, 1H, 2-H], 5.34 [d, ^3J(5-H/6-H) = 9.35 Hz, 1H, 6-H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 20.65 (C-1, 2-CH_3), 21.30 (7-CH_3), 22.98 (4-CH_3), 27.66 (4-CH_3), 34.55 (C-2), 43.39 (C-8), 49.89 (C-4), 69.00 (C-5), 85.61 (C-6), 96.83 (C-7), 211.77 (Fe=CO), 216.43 (C-3). – MS (70 eV); *m/z* (%): 292 (10) [M$^+$ – CO], 264 (38) [M$^+$ – 2 CO], 236 (100) [M$^+$ – 3 CO], 166 (73), 109 (48), 43 (64). – $C_{15}H_{20}FeO_4$ (320.2): calcd. C 56.27, H 6.29; found C 55.98, H 6.39.

(1'E)-Tricarbonyl[(1'-4'-η^4)-2-{(3'-methyl)buta-1',3'-dien-1'-yl}indan-1-one]iron(0) (**6e**): 237 mg (0.70 mmol; 70%) as a 85:15 mixture of diastereoisomers; yellow oil from 159 mg of 1-indanone. – IR (neat): ṽ = 3040 cm^{-1} [ν(=C–H)], 2965, 2930 [ν(C–H)], 2050, 1945, 1910, 1700 [ν(C=O)], 1460. – Major diastereoisomer (85%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.35 [d, ^2J(4'-H^{en}/4'-H^{ex}) = 1.10 Hz, 1H, 4'-H^{en}], 0.62 [dd, ^3J(1'-H/2'-H) = 8.29 Hz, ^3J(2-H/1'-H) = 7.70 Hz, 1H, 1'-H], 1.84 [d, ^2J(4'-H^{en}/4'-H^{ex}) = 1.10 Hz, 1H, 4'-H^{ex}], 2.23 [s, 3H, 3'-CH_3], 2.48 [dd, ^2J(2-H/3-H) = 3.85 Hz, ^2J(3-H/3-H') = 12.65 Hz, 1H, 3-H], 2.97 [dd, ^3J(2-H/3-H') = 4.40 Hz, ^2J(3-H/3-H') = 12.65 Hz, 1H, 3-H'], 3.50 [ddd, ^3J(2-H/3-H) = 3.85 Hz, ^3J(2-H/3-H') = 3.85 Hz, ^3J(1'-H/2-H) = 7.70 Hz, 1H, 2-H], 5.60 [d, ^3J(1'-H/2'-H) = 8.29 Hz, 1H, 2'-H], 7.37–7.7 [m, 4H, aromat. H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 22.80 (3'-CH_3), 35.18 (C-4'), 43.68 (C-3), 52.64 (C-1'), 58.79 (C-2), 88.19 (C-2'), 101.09 (C-3'), 124.36, 124.48, 127.64, 135.08 (aromat. C), 135.99, 153.27 (aromat. quart. C), 205.66 (C-1), 210.17 (Fe=CO). – MS (70 eV); *m/z* (%): 310 (8) [M$^+$ – CO], 282 (28) [M$^+$ – 2 CO], 254 (100) [M$^+$ – 3 CO], 184 (41), 56 (28) [Fe]. – $C_{17}H_{14}FeO_4$ (338.1): calcd. C 60.39, H 4.17; found C 60.20, H 4.02.

(3E)-Tricarbonyl{η-[methyl (2-methoxycarbonyl-5-methyl)-3,5-hexadienoate]}iron(0) (**6f**): 135 mg (0.40 mmol; 40%) as yellow oil from 158 mg of dimethyl malonate. – IR (neat): ṽ = 3020 cm^{-1} [ν(=C–H)], 2870 [ν(C–H)], 2050, 1995, 1970, 1805, 1790 [ν(C=O)], 1490, 1230. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.53 [dd, ^2J(6-H^{en}/6-H^{ex}) = 1.22 Hz, 1H, 6-H^{en}], 0.93 [dd, ^3J(2-H/3-H) = 10.61 Hz, ^3J(3-H/4-H) = 7.95 Hz, 1H, 3-H], 1.87 [d, ^2J(6-H^{en}/6-H^{ex}) = 1.22 Hz, 1H, 6-H^{ex}], 2.17 [s, 3H, 5-CH_3], 3.21 [d, ^3J(2-H/3-H) = 10.61 Hz, 1H, 2-H], 3.75 [s, 3H, CO_2CH_3], 3.81 [s, 3H, CO_2CH_3], 5.27 [d, ^3J(4-H/3-H) = 7.95 Hz, 1H, 4-H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 22.66 (5-CH_3), 43.88 (C-6), 51.69 (C-3), 52.65 ($COOCH_3$), 52.91 ($COOCH_3$), 56.44 (C-2), 86.89 (C-4), 101.22 (C-5), 168.23 (COO), 168.67 (COO), 210.70 (Fe=CO). – MS (70 eV); *m/z* (%): 310 (11) [M$^+$ – CO], 282 (42) [M$^+$ – 2 CO], 254 (100) [M$^+$ – 3 CO], 196 (83), 138 (26) [Fe(CO)$_3$], 80 (31). – $C_{13}H_{14}FeO_7$ (338.1): calcd. C 46.18, H 4.17; found C 46.10, H 4.22.

(1'E)-Tricarbonyl[(1'-4'-η^4)-3-{(3'-methyl)buta-1',3'-dien-1'-yl}tetrahydrofuran-2-one]iron(0) (**6g**): 117 mg (0.40 mmol; 40%) as a 60:40 mixture of diastereoisomers; yellow oil from 103 mg of butyrolactone. – IR (neat): ṽ = 3040 cm^{-1} [ν(=C–H)], 2980, 2930 [ν(C–H)], 2025, 1980, 1960, 1770 [ν(C=O)], 1440 [ν(C=C)], 1280. – Major diastereoisomer (60%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.44 [d, ^2J(4'-H^{en}/4'-H^{ex}) = 1.65 Hz, 1H, 4'-H^{en}], 0.53 [dd, ^3J(1'-H/2'-H) = 7.70 Hz, ^3J(3-H/1'-H) = 9.90 Hz, 1H, 1'-H], 1.89 [d, ^2J(4'-H^{en}/4'-H^{ex}) = 1.65 Hz, 1H, 4'-H^{ex}], 2.19 [s, 3H, 3'-CH_3], 2.12–2.33 [m, 1H, 3-H], 2.46–2.57 [m, 2H, 4-H], 4.29–4.42 [m, 2H, 5-H], 5.44 [d, ^3J(1'-H/2'-H) = 7.70 Hz, 1H, 2'-H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 22.67 (3'-CH_3), 31.89 (C-4'), 44.11 (C-4), 44.84 (C-1'), 55.81 (C-2'), 66.25 (C-5), 87.70 (C-3), 101.47 (C-3'), 177.21 (C-2), 211.01 (Fe=CO). – Minor diastereoisomer (40%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.35 [d, ^2J(4'-H^{en}/4'-H^{ex}) = 1.65 Hz, 1H, 4'-H^{en}], 0.63 [dd, ^3J(1'-H/2'-H) = 8.00 Hz, ^3J(3-H/1'-H) = 10.45 Hz, 1H, 1'-H], 1.82 [d, ^2J(4'-H^{en}/4'-H^{ex}) = 1.65 Hz, 1H, 4'-H^{ex}], 2.18 [s, 3H, 3'-CH_3], 2.33–2.40 [m, 1H, 3-H], 2.46–2.57 [m, 2H, 4-H], 4.11–4.22 [m, 2H, 5-H], 5.26 [d, ^2J(1'-H/2'-H) = 8.30 Hz, 1H, 2'-H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 22.74 (3'-CH_3), 31.31 (C-4'), 43.26 (C-1'), 44.86 (C-4), 54.85 (C-3), 66.56 (C-5), 85.56 (C-2'), 100.48 (C-3'), 176.59 (C-2), 211.01 (Fe=CO). – MS (70 eV); *m/z* (%): 264 (8) [M$^+$ – CO], 236 (25) [M$^+$ – 2 CO], 208 (100) [M$^+$ – 3 CO], 150 (45), 56 (30) [Fe]. – $C_{12}H_{12}FeO_5$ (292.1): calcd.C 49.35, H 4.14; found C 49.76, H 4.26.

Tricarbonyl[(4-5-η^2)-2-aza-5,7-dimethyl-2-isobutyl-1-methoxy-4-decen-8-on-1-ylidene]iron(0) (**8a**): 326 mg (0.80 mmol; 80%) as a 55:45 mixture of diastereoisomers from 409 mg of **2a** (R = *i*Bu, R^4 = H, R^5 = Me) and 86 mg of diethylketone; yellow crystals, m.p. 74 °C (hexane). – IR (KBr, solid): ṽ = 2940, 2910, 2850 [ν(C–H)], 2000, 1930, 1900, 1700 [ν(C=O)], 1530, 1445, 1250. – ^{1}H NMR ($CDCl_3$, 400 MHz) of the mixture: δ = 0.80 [d, ^3J = 6.05 Hz, 3H, CH(CH_3)(CH_3)], 0.87 [d, ^3J = 6.05 Hz, 3H, CH(CH_3)(CH_3)], 1.04–1.10 [m, 6H, 7-CH_3, 10-H], 1.21–1.26 [m,

1 H, 4-H], 1.43–1.45 [m, 1 H, 4-H], 1.60 [s, 3 H, 5-CH_3], 1.92–1.95 [m, 1 H, $CH(CH_3)_2$], 2.08–2.13 [m, 1 H, 6-H], 2.51–2.61 [m, 3 H, 9-H, 6-H'], 2.79–2.92 [m, 2 H, CH_2CMe_2], 3.49–3.59 [m, 2 H, 3-H, 3-H'], 3.75–3.83 [m, 1 H, 7-H], 4.09 and 4.11 [s, 3 H, OCH_3]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 16.57 (C-10), 19.44/19.74 (7-CH_3), 20.33/20.37 [$CH(CH_3)_2$], 26.36/26.46 [$CH(CH_3)_2$], 30.16/30.70 (5-CH_3), 34.44/36.01 (C-9), 39.08/41.25 (C-6), 45.19/45.72 (C-7), 53.16/53.26 (NCH_2), 56.05/56.25 (C-3), 56.05/56.25 (C-4), 62.34/62.38 ($COCH_3$), 69.38/70.69 (C-5), 214.71/216.27 (C-8), 216.43 (Fe=CO), 238.32/238.86 (C-1). – MS (70 eV); *m/z* (%): 379 (14) [M^+ – CO], 323 (100) [M^+ – 3 CO], 239 (53), 197 (58), 57 (46). – $C_{19}H_{29}FeNO_5$ (407.3): calcd. C 56.03, H 7.18, N 3.44; found C 56.11, H 7.31, N 3.17.

Tricarbonyl[(4-5-η²)-2-aza-7-bis(methoxycarbonyl)-2,5-dimethyl-1-methoxy-4-hepten-1-ylidene]iron(0) (**8b**): 164 mg (0.40 mmol; 40%) as a 55:45 mixture of diastereoisomers; yellow oil from 367 mg of **2b** (R = Me, R^4 = H, R^5 = Me) and 158 mg of dimethyl malonate. – IR (neat): $\tilde{\nu}$ = 3020 cm^{-1}, 2940, 2840 [ν(C–H)], 2000, 1935, 1900, 1750, 1730 [ν(C=O)], 1545, 1460, 1260, 1220. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.85–0.89 [m, 1 H, 4-H], 1.56/1.75 [s, 3 H, 5-CH_3], 2.00–2.06 [m, 1 H, 3-H of 1st diastereoisomer], 2.18 [dd, ^3J(3-H/3-H') = 14.60 Hz, ^3J(3-H/4-H) = 6.04 Hz, 1 H, 3-H of 2nd diastereoisomer], 2.26–2.30 [m, 1 H, 3-H' of 1st diastereoisomer], 2.55–2.60 [dd, ^2J(3-H/3-H') = 14.60 Hz, ^3J(3-H/4-H) = 6.04 Hz, 1 H, 3-H' of 1st diastereoisomer], 2.48–2.49 [m, 1 H, 6-H' of 1st diastereoisomer], 2.85/2.86 [s, 3 H, NCH_3], 3.47–3.48 [m, 1 H, 7-H of 1st diastereoisomer], 3.52–3.58 [m, 1 H, 6-H' of 2nd diastereoisomer], 3.73–3.85 [m, 3 H, 6-H of both and 7-H of 2nd diastereoisomer], 3.73/3.74 [s, 6 H, CO_2CH_3], 4.12 [s, 3 H, $COCH_3$]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 32.98/45.69 (5-CH_3), 31.91/36.42 (C-6), 32.25/32.35 (NCH_3), 51.93/53.94 (C-7), 52.37/52.49/52.53 (CO_2CH_3), 54.97/55.23 (C-4), 57.02/61.02 (C-3), 62.24/67.03 (C-5), 62.46/62.55 ($COCH_3$), 169.48/170.15/170.23/170.75 (CO_2CH_3), 215.80 (Fe=CO), 237.88/238.24 (C-1). – MS (70 eV); *m/z* (%): 383 (8) [M^+ – CO], 355 (28) [M^+ – 2 CO], 327 (100) [M^+ – 3 CO], 227 (36), 212 (23), 140 (75), 108 (32). – $C_{16}H_{21}FeNO_8$ (411.2): calcd. C 46.74, H 5.15, N 3.41; found C 47.10, H 4.96, N 3.42.

Tricarbonyl[(4-5-η²)-2-aza-2-benzyl-7-bis(methoxycarbonyl)-1-methoxy-4-hepten-1-ylidene]iron(0) (**8c**): 236 mg (0.50 mmol; 50%) as a yellow oil from 429 mg of **2c** (R = Bzl, R^4 = R^5 = H) and 158 mg of dimethyl malonate. – IR (neat): $\tilde{\nu}$ = 3015 cm^{-1}, 2940, 2860 [ν(C–H)], 2005, 1940, 1910, 1745/1730 [ν(C=O)], 1520, 1450/1430, 1220. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.03 [ddd, ^2J(6-H/6-H') = 12.00 Hz, ^3J(6-H/7-H) = 4.80 Hz, ^3J(6-H/5-H) = 10.70 Hz, 1 H, 6-H], 2.30 [ddd, ^2J(6-H/6-H') = 12.00 Hz, ^3J(6-H'/5-H) = 6.00 Hz, ^3J(6-H'/7-H) = 5.60 Hz, 1 H, 6-H'], 2.50 [dd, ^2J(3-H/3-H') = 13.70 Hz, ^3J(4-H/3-H') = 4.90 Hz, 1 H, 3-H'], 3.43 [m, 1 H, 3-H], 3.51 [mc, 1 H, 7-H], 3.73 [s, 6 H, CO_2CH_3], 3.81 [mc, 3 H, 3-H, 4-H, 5-H], 4.20 [s, 3 H, $COCH_3$], 4.28 [d, ^2J = 14.29 Hz, 1 H, NCH_2], 4.71 [d, ^2J = 14.29 Hz, 1 H, NCH_2], 7.13 [m, 2 H, aromat. H], 7.31 [m, 3 H, aromat. H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 31.02 (C-3), 46.78 (C-4 or C-5), 49.40 (C-6), 50.65 (C-4 or C-5), 52.40 (CO_2CH_3), 53.86 (C-7), 54.34 (NCH_2), 62.81 ($COCH_3$), 127.67, 127.83, 128.77, 134.79 (aromat. C), 169.40/169.88 (CO_2CH_3), 215.78 (Fe=CO), 238.97 (C-1). – MS (70 eV); *m/z* (%): 455 (11) [M^+ – CO], 389 (100) [M^+ – 3 CO], 152 (74) [{389} – $C_6H_5CH_2^+$], 278 (40), 198 (66), 148 (29), 91 (83) [$C_6H_5CH_2^+$]. – $C_{21}H_{23}FeNO_8$ (473.3): calcd. C 53.30, H 4.90, N 2.96; found C 53.24, H 4.90, N 3.08.

2. (3E)-Tricarbonyl(η-2-methyl-1,3-octadiene)iron(0) (**9a**): A solution of $nBu_2Cu(CN)Li_2$ in THF was first prepared as described in ref.[22] from CuCN (75 mg; 0.85 mmol) and *n*BuLi (0.61 ml of a 2.5 M solution in hexane; 1.5 mmol). It was then slowly added by means of a cannula to a slurry of **1a** (200 mg; 0.57 mmol) in 5 ml of THF at –78 °C. After 20 min the reaction was quenched by the addition of an excess of 0.05 M HCl. The mixture was allowed to warm up to ambient temp. and then repeatedly extracted with ether. The combined organic extracts were dried and filtered. The solvent was evaporated and the residue purified by CC (silica; petroleum ether); yield 58 mg (0.21 mmol, 40%) of **9a**. – IR (neat): $\tilde{\nu}$ = 3010 cm^{-1}, 2940, 2900, 2840 [ν(C–H)], 2010, 1970, 1955 [ν(C=O)], 1430, 1250. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.30 [dd, ^2J(1-H^{en}/1-H^{ex}) = 1.68 Hz, 1 H, 1-H^{en}], 0.79–0.91 [m, 4 H, 4-H, 8-H], 1.25–1.56 [m, 4 H, 6-H, 7-H], 1.62–1.69 [m, 2 H, 5-H], 1.72 [d, ^2J(1-H^{en}/1-H^{ex}) = 1.68 Hz, 1 H, 1-H^{ex}], 2.15 [s, 3 H, 2-CH_3], 5.10 [d, ^3J(4-H/3-H) = 8.55 Hz, 1 H, 3-H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 13.92 (C-8), 22.86 (2-CH_3), 29.75 (C-5), 33.95 (C-7), 34.20 (C-6), 42.86 (C-1), 62.52 (C-4), 88.30 (C-3), 98.93 (C-2), 212.12 (CO). – MS (70 eV); *m/z* (%): 264 (12) [M^+], 236 (26) [M^+ – CO], 208 (22) [M^+ – 2 CO], 180 (100) [M^+ – 3 CO], 138 (86), 96 (37). – $C_{12}H_{16}FeO_3$ (264.1): calcd. C 54.57, H 6.11; found C 54.42, H 6.14.

3. Synthesis of **10**. – *General Procedure:* A solution of the 1-alkyne (1.20 mmol) in 2 ml of THF was cooled to –78 °C and then treated with *n*BuLi (0.48 ml of a 2.5 M solution in hexane; 1.20 mmol). The resulting mixture was stirred at this temperature for 15 min and finally at room temp. for a further 60 min. After recooling to –78 °C it was slowly transferred with a cannula to a slurry of **1a** (350 mg; 1.00 mmol) in 5 ml of THF at –78 °C. The reaction was stopped by the addition of one equivalent of a saturated aqueous solution of NH_4Cl after another hour at –78 °C. The mixture was then repeatedly extracted with ether and the combined organic extracts were dried. The solvent was evaporated and the residue purified by CC (silica; petroleum ether/ether, 5:1).

(±)-{5-[(E)-2-methoxycarbonylethen-1-yl]-5-methyl-2-pentylcyclopent-2-en-1-one} (**10a**): 77 mg (0.31 mmol, 31%); colourless liquid from 0.16 ml of 1-heptyne. – IR (neat): $\tilde{\nu}$ = 2940 cm^{-1}, 2910, 2840 [ν(C–H)], 1710 [ν(C=O)], 1640, 1620 [ν(C=C)], 1430, 1310, 1270, 1190. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.85 [t, ^3J(15-H/14-H) = 6.90 Hz, 3 H, 15-H], 1.27–1.34 [m, 7 H, 10-H, 13-H, 14-H], 1.43–1.52 [m, 2 H, 12-H], 2.17 [dt, ^3J(11-H/12-H) = 7.7 Hz, ^4J(11-H/3-H) = 1.5 Hz, 2 H, 11-H], 2.52 [dq, ^4J(4-H^{up}/10-CH_3) = 2.3 Hz, ^2J(4-H^{up}/4-H^{down}) = 18.8 Hz, 1 H, 4-H^{up}], 2.77 [dq, ^4J(4-H^{down}/10-CH_3) = 2.3 Hz, ^2J(4-H^{up}/4-H^{down}) = 18.8 Hz, 1 H, 4-H^{down}], 3.72 [s, 3 H, 9-H], 5.89 [d, ^3J(6-H/7-H) = 15.9 Hz, 1 H, 7-H], 6.87 [d, ^3J(6-H/7-H) = 15.9 Hz, 1 H, 6-H], 7.27 [m, 1 H, 3-H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 14.05 (C-15), 22.38 (C-14), 22.87 (C-10), 25.07 (C-11), 27.28 (C-12), 31.53 (C-13), 41.66 (C-4), 49.71 (C-5), 51.59 (C-9), 120.16 (C-7), 144.37 (C-2), 150.33 (C-6), 154.23 (C-3), 166.86 (C-8), 208.64 (C-1). – MS (70 eV); *m/z* (%): 250 (50) [M^+], 235 (10) [M^+ – CH_3], 219 (18) [M^+ – OCH_3], 191 (100) [M^+ – $COOCH_3$], 175 (8) [{191} – CH_4], 161 (38), 133 (22), 112 (18), 105 (21), 80 (38). – $C_{15}H_{22}O_3$ (250.3): calcd. C 71.97, H 8.86; found C 71.90, H 8.82.

(±)-{5-[(E)-2-methoxycarbonylethen-1-yl]-5-methyl-2-octylcyclopent-2-en-1-one} (**10b**): 70 mg (0.24 mmol, 24%); colourless liquid from 0.21 ml of 1-decyne. – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2920, 2860 [ν(C–H)], 1730, 1710 [ν(C=O)], 1650, 1630 [ν(C=C)], 1440, 1320, 1270, 1170. – ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.88 [t, ^3J(18-H/17-H) = 6.5 Hz, 3 H, 18-H], 1.19–1.29 [m, 13 H, 10-H, 13-H, 14-H, 15-H, 16-H, 17-H], 1.42–1.50 [m, 2 H, 12-H], 2.17 [t, ^3J(12-H/11-H) = 7.2 Hz, 2 H, 11-H], 2.51 [d, ^2J(4-H^{up}/4-H^{down}) = 18.7 Hz, 1 H, 4-H^{up}], 2.76 [d, ^2J(4-H^{up}/4-H^{down}) = 18.7 Hz, 1 H, 4-

H^{down}], 3.72 [s, 3H, 9-H], 5.89 [d, ^3J(6-H/7-H) = 15.9 Hz, 1H, 7-H], 6.87 [d, ^3J(6H/7-H) = 15.9 Hz, 1H, 6-H], 7.27 [m, 1H, 3-H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 14.1 (C-18), 22.7 (C-17), 22.9 (C-10), 25.1 (C-11), 27.6 (C-12), 29.2, 29.3, 29.4, 31.9, 41.7 (C-4), 49.7 (C-5), 51.6 (C-9), 120.2 (C-7), 144.4 (C-2), 150.3 (C-6), 154.3 (C-3), 166.9 (C-8), 208.6 (C-1). – MS (70 eV); *m/z* (%): 292 (82) [M^+], 261 (38) [$M^+ - OCH_3$], 233 (100) [$M^+ - COOCH_3$], 193 (45), 161 (43), 133 (32), 112 (22), 105 (27), 80 (45). – $C_{18}H_{28}O_3$ (292.4): calcd. C 73.93, H 9.65; found C 74.04, H 9.68.

(±)-{5-[(E)-2-methoxycarbonylethen-1-yl]-5-methyl-2-cyclohexyl-cyclopent-2-en-1-one} (**10c**): 78 mg (0.30 mmol, 30%); colourless liquid from 130 mg of cyclohexylethyne. – IR (neat): $\tilde{\nu}$ = 2900 cm^{-1}, 2840 [ν(C–H)], 1720, 1700 [ν(C=O)], 1640, 1610 [ν(C=C)], 1440, 1260, 1160. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.12–1.35 and 1.69–1.83 [m, 13H, cyclohexyl-H, 10-H], 2.25–2.32 [m, 1H, 11-H], 2.50 [d, ^2J(4-H^{up}/4-H^{down}) = 18.8 Hz, 1H, 4-H^{up}], 2.74 [d, ^2J(4-H^{up}/4-H^{down}) = 18.8 Hz, 1H, 4-H^{down}], 3.72 [s, 3H, 9-H], 5.88 [d, ^3J(6-H/7-H) = 15.7 Hz, 1H, 7-H], 6.86 [d, ^3J(6-H/7-H) = 15.7 Hz, 1H, 6-H], 7.15–7.20 [m, 1H, 3-H]. – ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ = 22.8 (C-10), 26.2, 26.3, 31.7, 31.8, 34.5 (C-11), 41.6 (C-4), 50.0 (C-5), 51.6 (C-9), 120.1 (C-7), 149.3 (C-2), 150.4 (C-6), 152.6 (C-3), 166.9 (C-8), 208.2 (C-1). – MS (70 eV); *m/z* (%): 262 (64) [M^+], 231 (29) [$M^+ - OCH_3$], 220 (45), 203 (84). – $C_{16}H_{22}O_3$ (262.4): calcd. C 73.25, H 8.45; found C 73.06, H 8.40.

X-ray Structure Determination of **8a**[23]: Clear, bright yellow single crystals were obtained by slowly cooling a solution of **8a** in pentane to 0°C; formula $C_{19}H_{29}FeNO_5$, molar mass 407.29 g mol^{-1}, crystal size 0.40 × 0.30 × 0.30 mm, a = 9.245(49, b = 10.888(7), c = 11.449(5) Å, α = 80.25(4)°, β = 87.29(3)°, γ = 66.18(4)°, V = 1038.8(9) Å^3, T = 293 K, d_{calc} = 1.303 g cm^{-3}, μ = 7.53 cm^{-1}, Z = 2, triclinic, space group P-1, Nicolet R3mV diffractometer, λ = 0.71073 Å, Θ range 3.61° to 22.57°; ω2Θ scans, index ranges $0 \leq h \leq 9$, $-10 \leq k \leq 11$, $-12 \leq l \leq 12$, 2695 collected reflections, 2695 independent reflections [$I > 2\sigma(I)$], 236 refined parameters, no absorption correction. Structure solution: direct methods (SHELXTL PLUS V4.11), structure refinement: full-matrix least-squares on F^2 (SHELXL93), H atoms calculated and not included into least-squares refinement, $R1$ = 0.0835 [$w = 1/\sigma^2(F_o)$], $wR2$ = 0.2348 (all data), largest diff. peak and hole 1.442 and −1.025 eÅ^{-3}.

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