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Reactivity of Allenes towards Iron Carbonyl Complexes

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Abstract. A series of monosubstituted allenes was reacted with $\text{Fe}_2(\text{CO})_9$ to give dinuclear iron-carbonyl complexes containing organic ligands derived either from monomeric or dimerized allene. A mechanism of formation is proposed based on isolated intermediates. These intermediates point to an allene dimerization *via* addition of a reactive allene iron complex to free allene. Unusual chemical shifts were observed for many resonances in the ^1H - and ^{13}C -NMR spectra of the new compounds.

1. Introduction

Reactions of allenes with various types of iron-carbonyl complexes have been shown to yield either $(\eta^2\text{-allene})\text{Fe}(\text{CO})_4$ complexes [1][2], $(\eta^4\text{-diene})\text{Fe}(\text{CO})_3$ complexes by metal-induced H-shifts [1–3], dinuclear complexes of a monomeric [4], dimerized [5–7], or trimerized allenes [8], or substituted trimethylenemethane-ligand systems by reaction of allenes with a negatively charged iron-carbonyl species [9] or carbene complexes [10], by addition of lithiated allenes to $\text{Fe}(\text{CO})_5$ [11], or by photochemical complexation of allenes by $\text{Fe}(\text{CO})_5$ in the presence of aldehydes [12]. To investigate the influence of substituents on the type of products formed as well as the mechanism of formation, we initiated a study on the reactivity of a series of monosubstituted allenes towards complexation by iron-carbonyls.

2. Results and Discussion

The four monosubstituted allenes **1a–d** were reacted with $\text{Fe}_2(\text{CO})_9$ at room temperature in Et_2O . The resulting iron complexes were separated by column chro-

matography. The main components possess dinuclear structures of type **5** as shown by spectroscopic means. In the case of the allenes **1a–c**, these complexes were accompanied by mixtures of dinuclear complexes of dimerized allenes, whereas in the case of allene **1d** the diene complex **15** was isolated.

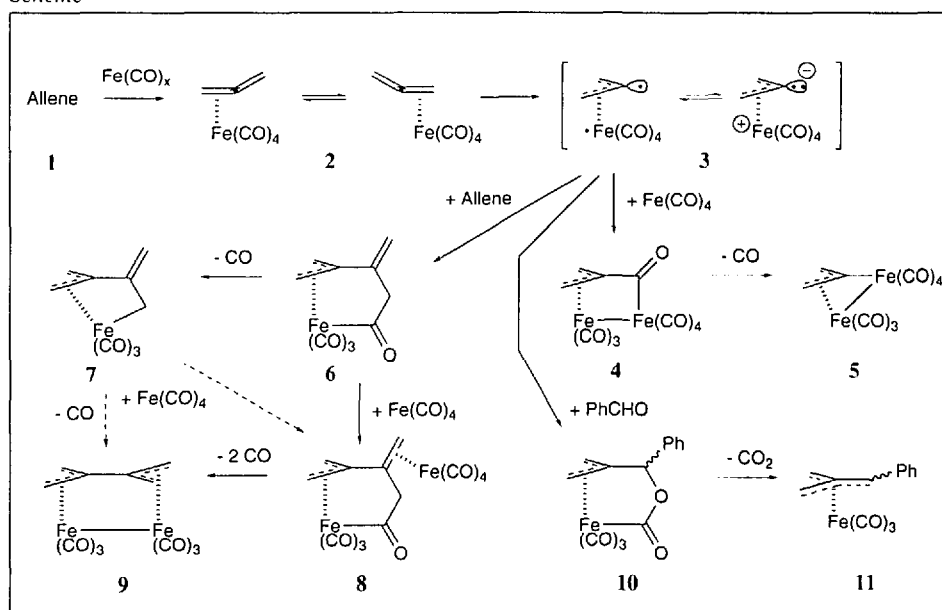
Products of the latter type had been found previously generally for substituted allenes exhibiting α -H-atoms, as diene complex **13** in the case of tetramethylallene [1]. Complexes exhibiting dimerized allenic ligands are absent in the product mixtures of these allenes except for a new product complex **14**, we found from the reaction of $\text{Fe}_2(\text{CO})_9$ with tetramethylallene. It is noteworthy that this dimeriza-

tion does not occur between the central C-atoms of two allenes as in the case of **1a–c**, its formation presumably involves the reaction of a primary intermediate of type **3** with already formed diene complex **13**.

Based on data from literature and our own results, a mechanism of formation of the different products obtained is proposed (*Scheme*). The reaction sequence starts by η^2 -complexation of the allene by $\text{Fe}(\text{CO})_4$. Such a primary complex **2** has been observed so far only for sterically congested allenes [1][2]. A fluxional structure was deduced for $(\eta^2\text{-tetramethylallene})\text{Fe}(\text{CO})_4$ (**12**) from ^1H -NMR data [1]. We confirmed this finding by the observation of two very broad resonances for the Me groups (23 and 29 ppm) accompanied by a sharp peak (152 ppm) for the central allenic C-atom in the ^{13}C -NMR spectrum of **12**. The structure of the related cationic complex $[\text{Fe}(\text{CO})_2\text{Cp}(\text{tetramethylallene})]^+$ which shows a similar behavior [13] has been well established [14]. Monosubstitution on the allene lifts the degeneracy of this fluxionality, but it remains an open question which influence the substituent exerts on the position of the equilibrium.

The transformation of the primarily formed complex **2** to the highly reactive species **3** is assumed in a subsequent step. At this stage already, the nature of the substituent directs either to (*E*)- or (*Z*)-configured products. For the sake of simplicity, the substituents are omitted in the scheme. Strong electrophiles would react [15] with the zwitterionic limiting structure, other reagents like aldehydes, solvent-stabilized $\text{Fe}(\text{CO})_4$, or an allene rather with the diradicaloid form to yield intermediates **4** [16], **6**, **7**, **8** [16], or **10**.

Scheme



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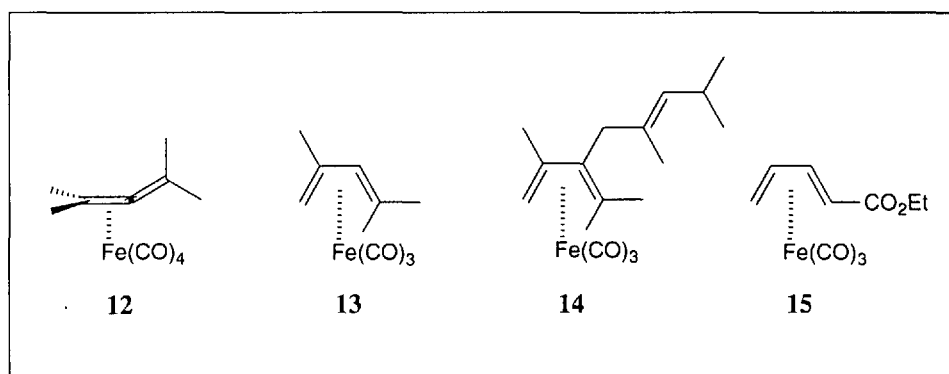
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The so far missing intermediates of type **6** and **7** have now been isolated and characterized in one case.

Complexes (*E*)-**6a** and (*E*)-**7a** were isolated as the main products from the reaction of *tert*-butylallene **1a** with $\text{Fe}_2(\text{CO})_9$ at room temperature in Et_2O for 3 h. Upon standing at room temperature the ratio of **6** to **7** shifted in favor of **7**. Higher temperatures or longer reaction times resulted in nearly complete conversion of these compounds into final products (mainly (*E*)-**5a**, (*E,E,E*)-**9a**, and (*E,Z,E*)-**9a**). Aumann *et al.* [16] isolated small amounts of a closely related complex (type **8**, $R = \text{H}$) after photolysis of $\text{Fe}(\text{CO})_5$ in the presence of propadiene at 0° .

The partition between products of type **5** and **9** varies from 3.7:1 to 1.5:1 for the series of the monosubstituted allenes **1a-c**. More important, the products differ in the orientation of the substituents: depending on the steric and electronic nature of this substituent, they either show exclusively ($R = t\text{-Bu}$) or predominantly (20:1, $R = \text{Ph}$ [17]) (*E*)-oriented, or exclusively ($R = \text{CO}_2\text{Me}$) or predominantly (20:1, $R = \text{OMe}$; 10:1, $R = \text{CH}_2\text{CO}_2\text{Et}$) (*Z*)-oriented substituents for the dinuclear complexes possessing a monomeric allene ligand. The (*Z*)-orientation is observed for those substituents which complex iron. This fact is reflected in the structures of (*Z*)-**5c** and (*Z*)-**5d** in which the ester carbonyl O-atom replaces a CO ligand at the σ -coordinated iron. The substitution pattern of the dimeric ligands follows this preference assuming an addition of the second allene in an (*E*)-oriented fashion in all cases.



Dinuclear complexes of type **4** or **5** ($R = \text{H}, \text{Ph}$) have been shown to insert in a much slower reaction (3–5 d) an additional allene to give complexes of type **9** [16]. This transformation cannot account, however, for the bulk of complexes of type **9** in our case, because their formation occurs within hours even in the presence of excess of $\text{Fe}_2(\text{CO})_9$. Furthermore, we observed in one case ($R = t\text{-Bu}$) the predominant formation of precursors (namely (*E*)-**6a** and (*E*)-**7a**) of complexes (*E,E,E*)-**9a** and (*E,Z,E*)-**9a** at a time where product (*E*)-**5a** was only present in trace amounts implying a much slower formation of the latter.

The proposed mechanism (*Scheme*) which hinges on the formation of a highly reactive diradicaloid intermediate is corroborated by the poor stereoselectivity observed for the products of this putative species:

i) complexation of the optically active menthyl ester of buta-2,3-dienoic acid, either with $\text{Fe}_2(\text{CO})_9$ in Et_2O at room temperature, or with $\text{Fe}(\text{CO})_5$ in pentane under irradiation at -78° , leads only to a

very small chiral induction (d.e. 11%) in the product (menthyl derivative of (*Z*)-**5c**), very different from the notable chiral induction (d.e. 55–76%) of the same compound in the *Lewis*-acid-catalyzed *Diels-Alder* reaction of the substituted allenic C=C bond and cyclopentadiene [18];

ii) complexation of *tert*-butylallene with $\text{Fe}_2(\text{CO})_9$ in Et_2O at room temperature in the presence of benzaldehyde led to the expected [12] trimethylenemethane complexes (*Z*)-**11a** and (*E*)-**11a** in a 57:43 ratio implying essentially no selection during the stereogenic primary coupling step **3** \rightarrow **10** (*Scheme*). Thermal isomerization between (*Z*)-**11a** and (*E*)-**11a** was not observed below 100° , in accordance with observations on a closely related compound (Me instead of *t*-Bu) [12].

3. Structure Assignments

The structures of the new iron complexes were deduced from spectroscopic data. Dinuclear complexes possessing covalently linked Fe-atoms are character-

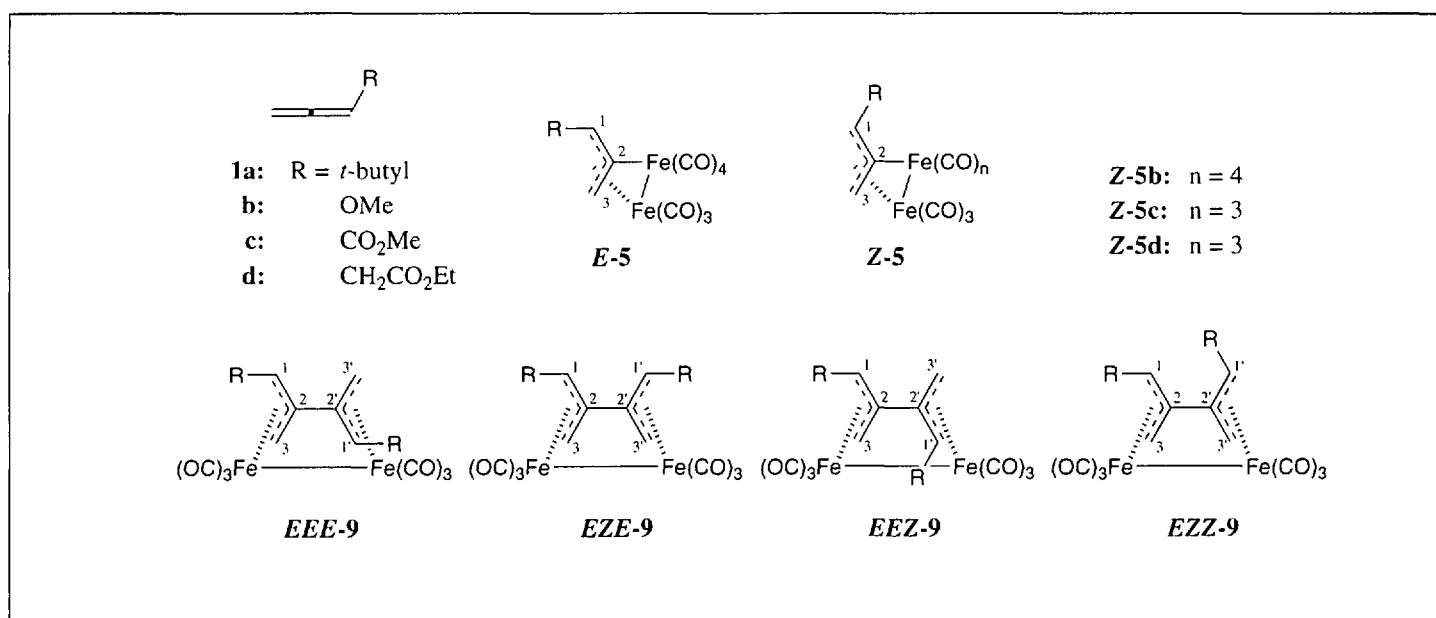


Table. $^1\text{H-NMR}$ Data of Complexes of Type **5** and **9** [$\delta(\text{TMS})$ (multiplicity, J in Hz, % NOE (irradiated signal))]

	H-C(1); H-C(1')	H _E -C(3); H _E -C(3')	H _Z -C(3); H _Z -C(3')	R; R'
(<i>E</i>)- 5a	4.56 (<i>dd</i> , 2.2, 0.7, 2% [0.81])	3.04 (<i>dd</i> , 1.2, 0.7, 20% [3.44])	3.44 (<i>dd</i> , 2.2, 1.2, 30% [3.04])	0.81 (<i>s</i> , 13% [3.04], 9 H, <i>t</i> -Bu)
(<i>E</i>)- 5b	5.98 (<i>d</i> , 2.0, 16% [2.75])	3.45 (<i>s</i> , 31% [3.54])	3.54 (<i>d</i> , 2.0, 29% [3.45])	2.75 (<i>s</i> , 11% [5.98], 3 H, OCH ₃)
(<i>E</i>)- 5d	4.65 (<i>ddd</i> , 8.0, 6.3, 2.0)	2.51 (<i>d</i> , 1.2)	3.45 (<i>dd</i> , 2.0, 1.2)	2.21 (<i>dd</i> , 17.0, 6.3), 1.92 (<i>dd</i> , 17.0, 8.0, CH ₂), 3.90, 0.94 (OEt)
(<i>Z</i>)- 5b	4.93 (<i>s</i> , 4% [2.97], 15% [1.35])	1.35 (<i>d</i> , 0.4, 10% [4.93], 32% [3.07])	3.07 (<i>d</i> , 0.4, 34% [1.35])	2.97 (<i>s</i> , 8% [4.93], 3 H, OCH ₃)
(<i>Z</i>)- 5c	2.60 (<i>s</i> , 6% [3.15])	3.15 (<i>s</i> , 23% [3.90])	3.90 (<i>s</i> , 23% [3.15])	2.83 (<i>s</i> , 3 H, OCH ₃)
(<i>Z</i>)- 5d	2.58 (<i>t</i> , 3.4, 13% [2.26])	2.26 (<i>s</i> , 25% [3.48], 13% [2.58])	3.48 (<i>s</i> , 25% [2.26])	2.41 (<i>d</i> , 3.4, CH ₂), 3.29, 3.07 (<i>dq</i> each, 10.5, 7.1, OCH ₂), 2.10 (<i>t</i> , 7.1, CH ₃)
(<i>E,E,E</i>)- 9a	2.04 (<i>dd</i> , 2.2, 1.9, 16% [2.77], 11% [1.88])	2.77 (<i>d</i> , 2.2, 20% [2.04])	1.88 (<i>d</i> , 1.9, 14% [2.04])	0.74 (<i>s</i> , 7% [2.77], 6% [1.88], 18 H, <i>t</i> -Bu)
(<i>E,Z,E</i>)- 9a	2.78 (<i>d</i> , 2.7)	2.16 (<i>d</i> , 3.1, 18% [1.27])	1.27 (<i>dd</i> , 3.1, 2.7, 8% [2.16])	0.85 (<i>s</i> , 8% [1.27], 3% [2.78], 18 H, <i>t</i> -Bu)
(<i>E,E,Z</i>)- 9b	3.34 (<i>d</i> , 2.5); 4.75 (<i>d</i> , 2.5, 14% [0.76], 1% [2.71])	2.01 (<i>d</i> , 2.1, 18% [0.46]); 0.76 (<i>d</i> , 3.4, 11% [4.75], 25% [0.07])	0.46 (<i>d</i> , 2.1, 18% [2.01]); 0.07 (<i>d</i> , 3.4, 22% [0.76])	2.71 (<i>s</i> , 6 H, 8% [4.75])
(<i>E,Z,Z</i>)- 9b	6.42 (<i>d</i> , 2.5); 3.68 (<i>s</i> , 2% [2.60], 13% [-0.09])	2.68 (<i>d</i> , 2.5, 29% [1.69]); -0.09 (<i>d</i> , 3.2, 7% [3.68], 28% [0.52])	1.69 (<i>t</i> , 2.5, 10% [2.68], 12% [0.52]); 0.52 (<i>d</i> , 3.2, 9% [1.69], 32% [-0.09])	2.86 (<i>s</i> , 3 H, 6% [6.42]); 2.60 (<i>s</i> , 3 H, 9% [3.68])
(<i>E,E,Z</i>)- 9c	4.00 (<i>dd</i> , 2.0, 1.2); 2.37 (<i>d</i> , 1.2)	2.71 (<i>d</i> , 2.8); 0.36 (<i>d</i> , 2.5)	1.99 (<i>dd</i> , 2.8, 2.0); 0.23 (<i>d</i> , 2.5)	3.15, 3.20 (<i>s</i> each, 3 H each, 2 OCH ₃)
(<i>E,Z,Z</i>)- 9c	4.21 (<i>dd</i> , 1.5, 1.3); 1.67 (<i>s</i>)	1.05 (<i>dd</i> , 2.8, 0.4); 3.62 (<i>dd</i> , 2.8, 1.5)	0.78 (<i>dd</i> , 2.8, 1.3); 1.92 (<i>dd</i> , 2.8, 0.4)	3.15, 3.20 (<i>s</i> each, 3 H each, 2 OCH ₃)

ized in their mass spectra by a prominent peak at m/z 112, accompanied by the appropriate satellites for the iron isotopes.

The orientation of the substituents on the ligands and the attribution of the peaks in the $^1\text{H-NMR}$ spectra were mainly deduced from homonuclear decoupling or differential NOE experiments (Table). Chemical-shift information from both ^1H - and $^{13}\text{C-NMR}$ spectra could only be used to a very limited extent for the structure determination because of the very large spread of the values, e.g. the chemical shift of the central allenic C-atom in complexes of type **9** varies from 128.7 for (*E*)-**5a** to 190.2 for (*Z*)-**5c**. Unusual chemical shifts were found in many cases, e.g. -17 ppm for the ^{13}C -resonance of the saturated CH₂ group bridging to iron in compound **7a**. Most likely, these unusual values are due to the shielding anisotropy of the metal centers, because even protons at uncomplexed C-atoms appear outside the normal range (e.g. the Me signal at 2.83 ppm of the methyl ester in complex (*Z*)-**5c** or the Me signal at 2.10 ppm of the EtO group in complex (*Z*)-**5d**), but a sound interpretation will need more data from related compounds.

The structures of the diene complexes **14** and **15** were easily deduced from their $^1\text{H-NMR}$ spectra by comparison with known compounds.

Experimental Part

General. All reactions involving iron complexes were carried out under N₂ using dried and deoxygenated solvents. IR: Perkin-Elmer IR-599 and FTIR: Mattson 5020 spectrometers; $\tilde{\nu}$ in cm⁻¹. ^1H - and $^{13}\text{C-NMR}$: (360.13 and 90.56 MHz, resp.) Bruker AM-360 spectrometer; chemical shifts in ppm rel. to int. TMS, coupling constants J in Hz; NOE's: % enhancement on observed signal {irradiation frequency}. MS: Carried out on Vacuum Generators Micromass VG 7070E and Hewlett Packard HP 5988A instruments, m/z (rel. int.).

Heptacarbonyl(η^3, η^1 -4,4-dimethylpent-2-ene-1,2-diyl)diiron ((*E*)-5a**).** 4,4-Dimethylpent-1,2-diene (**1a**) [19] (0.3 g, 3 mmol) was reacted with Fe₂(CO)₉ (1.14 g, 3 mmol) in Et₂O (10 ml) at r.t. for 15 h. Chromatography with pentane on silica gel of the crude residue (245 mg), obtained by filtration of the reaction mixture through Al₂O₃ and evaporation of the solvent, yields two major fractions consisting of red (*E*)-**5a** (R_f 0.57; 98 mg, 16.2%) and an inseparable orange 5:2 mixture (R_f 0.46; 40 mg, 5.6%) of (*E,E,E*)-**9a** and (*E,Z,E*)-**9a**.

Data of (*E*)-5a**.** IR (CCl₄): 2090w, 2060m, 2005s, 1990s, 1850m. $^1\text{H-NMR}$ (Table). $^{13}\text{C-NMR}$ (C₆D₆): 207.4 (*s*, CO); 128.7 (*s*, C(2)); 112.7 (*d*, C(3)); 69.5 (*t*, C(1)); 39.3 (*s*, C(4)); 31.6 (*q*, Me). EI-MS: 404 (1, *M*⁺, C₁₄H₁₂Fe₂O₇), 376 (22), 348 (40), 320 (25), 292 (54), 264 (67), 236 (80), 208 (98), 112 (100), 96 (55).

Data of (*E,E,E*)-9a** and (*E,Z,E*)-**9a**.** IR (CCl₄): 2060s, 2018s, 1990s, 1979s, 1963s. $^1\text{H-NMR}$ (Table). $^{13}\text{C-NMR}$ (C₆D₆): (*E,E,E*)-**9a** 216.5 (*s*, CO); 81.5 (*s*, C(4, 5)); 77.7 (*d*, C(3, 6)); 39.5 (*t*, C(4', 5')); 39.3 (*s*, C(2, 7)); 31.6 (*q*, CH₃); (*E,Z,E*)-**9a** 212.5 (*s*, CO); 84.4 (*s*, C(4, 5)); 73.6 (*d*, C(3, 6)); 35.8 (*t*, C(4', 5')); 35.3 (*s*, C(2, 7)); 31.4 (*q*, Me). EI-MS: 472 (4, *M*⁺, C₂₀H₂₄Fe₂O₆), 444 (32), 416 (15), 388 (17), 360 (76), 332 (72), 304 (100), 112 (40), 56 (35).

After 3 h of reaction time following the same workup the mixture was shown by $^1\text{H-NMR}$ to contain products (*E*)-**5a**, (*E,E,E*)-**9a**, and (*E,Z,E*)-**9a** in trace amounts. The complexes (*E*)-**6a** and (*E*)-**7a** were isolated as the main components from the mixture by column chromatography.

Data of (*E*)-6a**.** $^1\text{H-NMR}$ (C₆D₆): 5.66 (*t*, $^4J = 2.3$, H-C(6)); 1.99 (*d*, apparent splitting 3.3, CH₂-C(5)); 1.82 (*s*, H-C(3)); 1.13 (*d*, $^2J = 0.8$, H_{amr}-C(4')); 1.02, 0.81 (*s* each, *t*-Bu); 0.41 (*d*, $^2J = 0.8$, H_{syn}-C(4')). $^{13}\text{C-NMR}$ (C₆D₆): 228.7 (*td*, $^1J(\text{C,H}) = 13$, $^4J(\text{C,H}) = 5$, bridging CO); 209.9, 209.2, 208.6 (*s*, 3 CO); 146.9 (*s*, C(5)); 134.1 (*dm*, $^1J(\text{C,H}) = 158$, C(6)); 86.4 (*dm*, $^1J(\text{C,H}) = 152$, C(3)); 37.3 (*s*, C(4)); 36.2, 35.0 (*br. s*, C(2, 7)); 34.8 (*td*, $^1J(\text{C,H}) = 165$, $^3J(\text{C,H}) = 9$, C(5')); 30.9,

30.1 (qm, $^1J(\text{C},\text{H}) = 126$, *t*-Bu); 11.9 (*td*, $^1J(\text{C},\text{H}) = 164$, $^3J(\text{C},\text{H}) = 7$, C(4¹)).

Data of (E)-7a. $^{13}\text{C-NMR}$ (C_6D_6): 215.1, 214.5, 208.6 (*s*, 3 CO); 139.6 (*dm*, $^1J(\text{C},\text{H}) = 148$, C(6)); 131.7 (*s*, C(5)); 91.7 (*dm*, $^1J(\text{C},\text{H}) = 149$, C(3)); 82.6 (*d*, $^3J(\text{C},\text{H}) = 7$, C(4)); 46.3 (*td*, $^1J(\text{C},\text{H}) = 160$, $^3J(\text{C},\text{H}) = 5$, C(4¹)); 34.6, 34.0 (*br.s*, C(2, 7)); 31.3, 30.4 (*qm*, $^1J(\text{C},\text{H}) = 126$, *t*-Bu); -17.3 (*td*, $^1J(\text{C},\text{H}) = 149$, $^3J(\text{C},\text{H}) = 11$, C(5¹)).

Heptacarbonyl(η^3, η^1 -1-methoxyprop-2-ene-1,2-diyl)diiron (Z)-5b. **Methoxypropadiene (1b)** [20] (1.05 g, 15 mmol) was reacted with $\text{Fe}_2(\text{CO})_9$ (5.48 g, 15 mmol) in Et_2O (30 ml) at r.t. for 15 h to obtain a dark-red soln. Addition of hexane (20 ml) and concentration of the soln. yields very dark crystals (160 mg) which were filtered off but not investigated further. MPLC of the crude residue (1.19 g after evaporation of the solvent) with pentane/ Et_2O (10:1) on Al_2O_3 yields two major fractions (R_f 0.57 and 0.12), each consisting of two isomers. The first fraction was further separated on a silica-gel HPTLC plate using pentane to yield red (Z)-5b (R_f 0.3; 418 mg, 14.7%) and red (E)-5b (R_f 0.2; 21 mg, 0.7%). The second fraction contains an orange 10:7 mixture (325 mg, 10.3%) of (E,E,Z)-9b and (E,Z,Z)-9b.

Data of (Z)-5b. FT-IR (C_6D_6): 2092.1m, 2024.2vs, 1967.0s. $^1\text{H-NMR}$: Table. $^{13}\text{C-NMR}$ (C_6D_6): 213.5 and 207.8 (*s*, CO); 167.2 (*s*, C(2)); 125.6 (*d*, C(1)); 59.8 (*t*, C(3)); 57.4 (*q*, MeO). EI-MS: 378 (1, M^+ , $\text{C}_{11}\text{H}_6\text{Fe}_2\text{O}_8$), 350 (14), 322 (20), 294 (15), 266 (15), 238 (43), 210 (47), 182 (94), 152 (47), 128 (19), 112 (100), 84 (28), 56 (68).

Data of (E)-5b. FT-IR (C_6D_6): 2090.4m, 2030.8vs, 2008.3vs, 2000.3s, 1972.9m. $^1\text{H-NMR}$: Table. $^{13}\text{C-NMR}$ (C_6D_6): 207.8 (*s*, CO); 159.2 (*s*, C(2)); 122.4 (*d*, C(1)); 65.5 (*q*, MeO); 58.1 (*t*, C(3)). EI-MS: 378 (1, M^+ , $\text{C}_{11}\text{H}_6\text{Fe}_2\text{O}_8$), 350 (9), 322 (11), 294 (9), 266 (9), 238 (26), 210 (27), 182 (53), 152 (23), 128 (11), 112 (56), 84 (15), 56 (41).

Data of (E,E,Z)-9b and (E,Z,Z)-9b. $^1\text{H-NMR}$: Table. EI-MS: 420 (2, M^+ , $\text{C}_{14}\text{H}_{12}\text{Fe}_2\text{O}_8$), 392 (32), 364 (14), 336 (16), 308 (9), 280 (23), 252 (100), 168 (58), 112 (60), 84 (74), 56 (72).

Hexacarbonyl(η^3, η^1 -1-carbomethoxyprop-2-ene-1,2-diyl)diiron (Z)-5c. **Methyl buta-2,3-dienoate (1c)** [21] (0.98 g, 10 mmol) was reacted with $\text{Fe}_2(\text{CO})_9$ (3.64 g, 10 mmol) in Et_2O (50 ml) at r.t. for 2 h to obtain a dark brown soln. Chromatography with Et_2O on silica gel of the crude residue (1.17 g), obtained by filtration of the reaction mixture through Al_2O_3 and evaporation of the solvent, yields two major fractions consisting of red (Z)-5c (R_f 0.8; 624 mg, 33%) and an inseparable orange 5:4 mixture (R_f 0.5; 214 mg, 9%) of (E,E,Z)-9c and (E,Z,Z)-9c.

Data of (Z)-5c. IR (CCl_4): 2080m, 2035s, 1990s, 1970m. $^1\text{H-NMR}$ (Table). $^{13}\text{C-NMR}$ (C_6D_6): 210.0 (*s*, CO); 198.4 (*s*, C(1)); 190.2 (*s*, C(3)); 66.8 (*t*, C(4)); 59.7 (*d*, C(2)); 55.1 (*q*, MeO). EI-MS: 378 (18, M^+ , $\text{C}_{11}\text{H}_6\text{Fe}_2\text{O}_8$), 350 (50), 322 (24), 294 (55), 266 (6), 238 (98), 210 (100), 112 (79).

Data of (E,E,Z)-9c and (E,Z,Z)-9c. $^1\text{H-NMR}$: Table.

Hexacarbonyl(η^3, η^1 -1-(ethoxycarbonyl)-methylprop-2-ene-1,2-diyl)diiron (Z)-5d. **Ethyl penta-3,4-dienoate (1d)** [22] (1.65 g, 13 mmol) was reacted with $\text{Fe}_2(\text{CO})_9$ (4.75 g, 13 mmol) in Et_2O (35 ml) at r.t. for 24 h to obtain a red soln. MPLC with pentane/ Et_2O (13:3) on silica gel of

the crude oil (3.0 g), obtained by filtration of the reaction mixture through Al_2O_3 and evaporation of the solvent, yields two major fractions consisting of red (Z)-5d (R_f 0.42; 930 mg, 35%) and an inseparable mixture (R_f 0.31; 780 mg) of (E)-5d (4%) and 15 (19%).

Data of (Z)-5d. FT-IR (CCl_4): 2101.2m, 2093.6w, 2034.8m, 2014.5s, 1987.0m, 1976.0m. $^1\text{H-NMR}$ (Table). EI-MS: 406 (1, M^+ , $\text{C}_{13}\text{H}_{10}\text{Fe}_2\text{O}_8$), 378 (6), 350 (9), 322 (8), 294 (14), 266 (31), 238 (100), 182 (42), 137 (23), 112 (69), 84 (36), 56 (63).

Data of (E)-5d and 15. $^1\text{H-NMR}$ (C_6D_6): (E)-5d: Table; 15: 5.57 (*dd*, $^3J = 8.2$, $^3J = 5.0$, H-C(3)); 4.46 (*dm*, $^3J = 8.2$, H-C(4)); 3.91 (*q*), 0.89 (*t*, $J = 7.1$, Et); 0.83 (*d*, $^3J = 5.0$, H-C(2)); -0.04 (*dd*, $^3J = 9.3$, $^2J = 2.6$, $\text{H}_E\text{-C}(5)$). EI-MS: 378 (3, $M^+ - 2\text{CO}$, $\text{C}_{14}\text{H}_{10}\text{Fe}_2\text{O}_9$), 350 (4), 322 (8), 294 (7), 266 (21, M^+ , $\text{C}_{10}\text{H}_{10}\text{FeO}_5$), 238 (57), 221 (6), 210 (26), 182 (47), 165 (5), 154 (17), 138 (15), 137 (13), 112 (34), 110 (100), 84 (33), 56 (63).

Tricarbonyl(η^4 -4,4-dimethyl-2-methylidene-1-phenylpenta-1,3-diyl)iron (11a). A mixture of 4,4-dimethylpenta-1,2-diene (1a) (0.48 g, 5 mmol), $\text{Fe}(\text{CO})_5$ (3.92 g, 20 mmol), and benzaldehyde (1.28 g, 12 mmol) in Et_2O (50 ml) are irradiated under Ar at -78° for 2 h with a high-pressure Hg lamp (125 W). The first fraction from column chromatography with pentane on silica gel of the crude residue (1.23 g), obtained by filtration of the reaction mixture through Al_2O_3 and evaporation of the solvent, consists of red (E)-5a (R_f 0.57; 27 mg, 1.3%). The second fraction (R_f 0.42; 183 mg, 11.2%) contains 57:43 mixture (Z)-11a/(E)-11a.

Data of (Z)-11a and (E)-11a. IR (C_6D_6): 2050m, 2011m, 1981s. $^1\text{H-NMR}$ (C_6D_6): (Z)-11a 7.13-6.91 (*m*, Ph), 3.68 (*d*, $^4J = 2.5$, $\text{H}_Z\text{-C}(3)$), NOE 3% {0.90}; 3.50 (*s*, $\text{H}_E\text{-C}(1)$); NOE 17% {1.51}; 2.56 (*s*, $\text{H}_E\text{-C}(2^1)$), NOE 28% {1.51}, 2% {0.90}; 1.51 (*d*, $^4J = 2.5$, $\text{H}_Z\text{-C}(2^1)$), NOE 10% {3.50}, 24% {2.56}; 0.90 (*s*, *t*-Bu); (E)-11a: 7.13-6.91 (*m*, Ph); 3.53 (*d*, $^4J = 2.8$, $\text{H}_E\text{-C}(1)$), NOE 26% {2.51}, 2.99 (*dd*, $^4J = 2.8$, $^2J = 1.2$, $\text{H}_E\text{-C}(2^1)$), NOE 30% {2.80}, 3% {0.96}; 2.80 (*dd*, $^4J = 2.6$, $^2J = 1.2$, $\text{H}_Z\text{-C}(2^1)$), NOE 25% {2.99}; 2.51 (*d*, $^4J = 2.6$, $\text{H}_E\text{-C}(3)$), NOE 20% {3.53}, 3% {0.96}; 0.90 (*s*, *t*-Bu). $^{13}\text{C-NMR}$ (C_6D_6): (Z)-11a: 212.3 (3 CO); 138.4, 130.4, 126.4 (Ph); 98.1 (C(2)); 94.0 (C(2¹)); 75.1 (C(1)); 52.1 (C(3)); 34.8 (C(4)); 31.4 (C(5)); 2 C(4¹); (E)-11a: 212.6 (3 CO); 138.1, 129.7, 126.3 (Ph); 98.3 (C(2)); 93.0 (C(2¹)); 76.4 (C(1)); 54.3 (C(3)); 34.6 (C(4)); 31.7 (C(5), 2 C(4¹)). EI-MS: 326 (8, M^+ , $\text{C}_{17}\text{H}_{18}\text{FeO}_3$), 298 (20), 270 (15), 242 (100), 200 (11), 186 (7), 184 (9), 172 (9), 160 (47), 148 (20), 128 (15), 115 (27), 112 (11), 96 (11), 91 (16), 84 (23), 71 (8), 56 (67).

Tricarbonyl(η^4 -2,5,7-trimethyl-3-(1-methyl-ethylidene)octa-1,5-diene)iron (14). 2,4-Dimethylpenta-2,3-diene [23] (0.96 g, 10 mmol) and $\text{Fe}_2(\text{CO})_9$ (3.63 g, 10 mmol) in THF (40 ml) were stirred at 0° for 24 h. After filtration and evaporation of the solvent below 0° , the residue is dissolved in pentane and purified by passing through a short column of silica gel to yield 12 (0.52 g, 20%). If the reaction is carried out in Et_2O at r.t. for 2 h, two other products are obtained after filtration through Al_2O_3 and column chromatography on silica gel using pentane. The first band (R_f 0.78) contains complex 14 (723 mg, 44%), whereas the second band (R_f 0.65) was identified as the known 13 (666 mg, 28%).

Data of 14. $^1\text{H-NMR}$ (C_6D_6): 5.02 (*dm*, $^3J = 9.7$, H-C(6)); 3.44 (*dd*, $^2J = 15.2$, $^4J = 0.9$, $\text{H}_A\text{-C}(4)$); 3.08 (*d*, $^2J = 15.2$, $\text{H}_B\text{-C}(4)$); 2.50 (*dsept.*, $^3J = 9.7$, $^3J = 6.6$, H-C(7)); 1.81 (*s*, Me-C(2)); 1.47 (*d*, $^2J = 3.1$, $\text{H}_E\text{-C}(1)$); 1.45 (*d*, $^4J = 1.1$, Me-C(5)); 1.42 (*s*, Me_E-C(3¹)); 1.38 (*d*, $^2J = 3.1$, $\text{H}_Z\text{-C}(1)$); 0.91 (*d*, $^3J = 6.6$, (Me)₂-C(7)); 0.79 (*s*, $\text{CH}_3\text{-C}(3^1)$).

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