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Stereoselective Synthesis of 2-*exo*-Functionalized Bicyclo[3.2.1]oct-3-en-8-ones by Iron Mediated Carbonylation of Bicyclo[4.1.0]hept-2-enes

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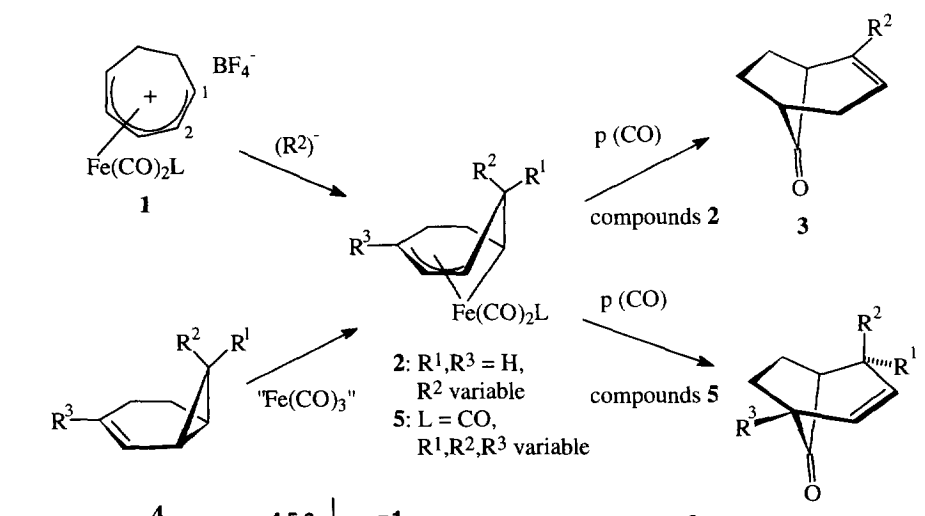
Abstract: Iron carbonyl complexes of type **5**, generated by the addition of tricarbonyl iron to the vinylcyclopropane subunit of bicyclo[4.1.0]hept-2-enes **4**, can be converted to bicyclo[3.2.1]octenones **6** via carbonylative decomplexation. Treatment of *syn*-substituted complexes **5** with CO (200 bar) at elevated temperatures (120 °C) yields functionalized ketones of type **6** with retention of the predetermined stereochemistry.

Recently we reported the synthesis of 2-substituted bicyclo[3.2.1]oct-2-en-8-ones **3** by carbonylative decomplexation of alkyl-allyl complexes of type **2** using CO pressure.[1] In these transformations the required starting material was generated by nucleophilic addition of various carbanion species to cationic cycloheptadienyl complex **1**.[1,2]



4,5,6	R1	R2	R3
a	H	H	H
b	CH_3	CH_3	CH_3
c	COOEt	H	H
d	COOEt	COOEt	H
e	CH_2OH	H	H
f	CH_2OSiMe_3	H	H
g	CH_2OAc	H	H

L = CO, $P(OPh)_3$

"$Fe(CO)_3$" = $Fe_2(CO)_9$; bis-(cyclooctene)$Fe(CO)_3$

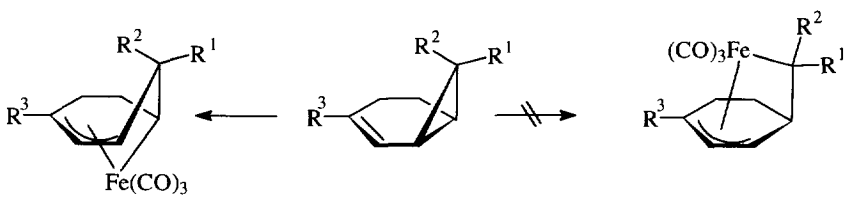
Scheme 1: Synthesis of Bicyclo[3.2.1]octenones of Type 3 and 6 via Alkyl-Allyl Complexes

According to these results, the carbonylation reaction is accompanied by a double bond migration. Thus, the stereochemical information, introduced during the carbanion attack *anti* to the iron carbonyl moiety, cannot be transferred to the decomplexation products. This disadvantage could be overcome by the use of copper(II) chloride as decomplexation agent.[1b]

Another access to alkyl-allyl complexes related to compounds of type **2** is reported via complexation and ring opening of bicyclo[4.1.0]hept-2-enes by treatment with iron carbonyls.[3,4,5] The ring opening product **5a** (R^1, R^2, R^3 = H) is obtained via regioselective cleavage of the C(1)-C(6)-bond in the strained vinylcyclopropane **4a** (R^1, R^2, R^3 = H).[3] Similarly, starting from enantiomerically pure (+)-2-carene **4b** (R^1, R^2, R^3 = CH_3), the corresponding alkyl-allyl complex **5b** was generated, which upon carbonylation gives the ketone **6b** in an overall stereospecific conversion.[4] An alternative synthetic pathway to optically pure bicyclo[4.1.0]hept-2-enes is opened by asymmetric cyclopropanation.[12,13] Following this synthetic concept, bicyclo[4.1.0]heptenes bearing variable substituents in different positions are obtainable. This includes heterofunctionalized substituents.

Since there are only few examples known for complexation and ring opening of heterosubstituted vinylcyclopropanes by iron carbonyls,[6,7] the chemical behaviour of heterosubstituted substrates in those transformations had to be investigated prior to use in stereoselective synthesis.

The vinycyclopropanes **4c**[8] and **4d**,[9] obtained via cyclopropanation of cyclohexa-1,3-diene with diazoesters, were chosen as model substrates. Starting from **4c** further heterofunctionalized vinylcyclopropanes with a bicyclo[4.1.0]heptene skeleton are generated. Thus, reduction of **4c** with $LiAlH_4$ yields the alcohol **4e**, which upon conversion with $ClSiMe_3$ or chloroacetic acid gives **4f** and **4g** in good yields.



5 **4** **7**

Scheme 2: Regioselectivity of C-C-Bond Cleavage in the Complexation of Vinylcyclopropanes of Type 4.

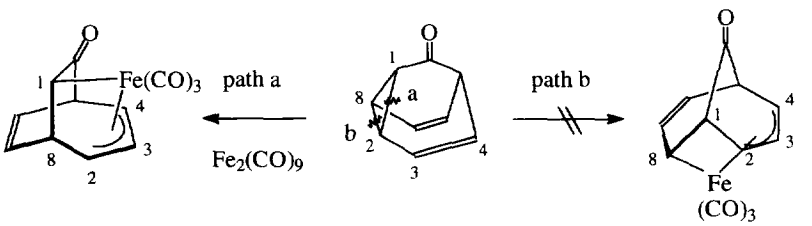
Treatment of compounds **4c-g** with $Fe_2(CO)_9$ in diethyl ether or with tricarbonyl-bis-(η^2-cyclooctene)iron[10] in petroleum ether leads to alkyl-allyl complexes of type **5** as the sole isolable products. The results are summarized in Table I.

Table I. Conversion of Vinylcyclopropanes of Type 4 into Bicyclic Ketones of Type 6 via Alkyl-Allyl Complexes 5.

	R^1	R^2	R^3	Alkyl-Allyl Complex	Yield %	Ketone	Yield %
4a	H	H	H	**5a**	75[2]	**6a**	96[11]
4b	CH_3	CH_3	CH_3	**5b**	66[3]	**6b**	23[3]
4c	COOEt	H	H	**5c**	56	**6c**	64
4d	COOEt	COOEt	H	**5d**	87	**6d**	57
4e	CH_2OH	H	H	**5e**	73	**6e**	65
4f	CH_2OSiMe_3	H	H	**5f**	73	**6f**	85
4g	CH_2OAc	H	H	**5g**	56	**6g**	73

In all these cases, ring opening of the cyclopropane subunit occurs regioselectively at the C(1)-C(6) bond. The observed product selectivity is in line with the analogous conversions of non functionalized bicyclo[4.1.0]heptenes[3,4] as described above, and is obviously not influenced by the character of the substituent.

In the transformation of **4c** and **4d** the cleavage of the C-C-bond opposite to an electron withdrawing group takes place. In contrast to this, the conversion of barbaralone **9** with $Fe_2(CO)_9$ selectively leads to complex **8** via opening of the C(1)-C(2)-bond directly attached to the carbonyl-group (path a).[4] The formation of compound **10** following the alternative pathway b is not observed.



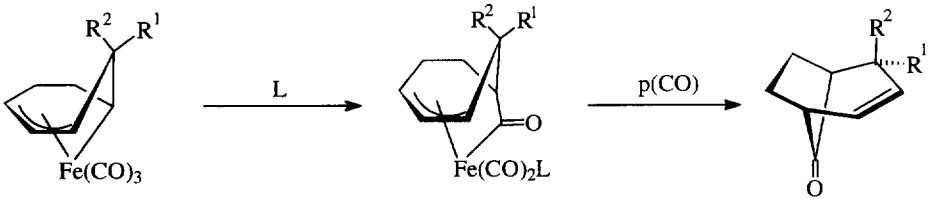
8 **9** **10**

Scheme 3: Regioselectivity of the Conversion of Barbaralone 9 with $Fe_2(CO)_9$.

Thus, the regioselectivity of ringopening and complexation of vinylcyclopropanes appears to be determined by the geometry of the organic substrate during the approach of the iron carbonyl group to the organic ligand. An influence of electronic effects of the substituents on the selectivity of C-C bond cleavage seems not to be effective here.

As described above, organic ligands, bound to an iron carbonyl unit in an alkyl-allyl fashion, can be converted to bicyclic ketones via carbonylative decomplexation.[1,4,11] Thus, heating a dioxane solution of the *syn*-substituted complexes **5c-g** to 120 °C under elevated CO pressure (200 bar) yields bicyclo[3.2.1]octenones of type **6** in medium up to good yields (57-85%). In these conversions, only *exo*-substituted bicyclic ketones were obtained; a double bond migration, as observed in analogous transformations of *anti*-substituted complexes of type **2**[1], does not occur. The results are integrated in Table I.

The carbonylative decomplexation described above is interpreted to proceed via CO insertion into the carbon-iron-σ-bond resulting the formation of acyl complexes of type **11** (L = CO).[11] As shown by conversions of **4a** and **4b**, this transformation can also be achieved upon treatment with PR_3 (R = Ph or OPh) or CO (1 bar).[3,4]



4 **11** L = CO; **12** L = $P(OPh)_3$; **13** L = PPh_3 **6**

Scheme 4: Carbonylation of Complexes 4 via Acyl Complexes of Type 12 and 13.

Similarly, starting from compounds **4c-g** the corresponding acyl complexes of type **12** or **13** are precipitated from petroleum ether. The air-stable solids can be stored, handled easily and transferred to ketones of type **6** in good yields as shown by carbonylation of **12c**. For synthetic use in the preparation of bicyclo[3.2.1]octenones, however, this stepwise conversion does not offer advantages over the one-pot carbonylative decomplexation as described above.

Table 2: Synthesis and Carbonylation of Acyl Complexes of Type 12 and 13.

	R^1	R^2	Acyl Complex	Yield %	Ketone	Yield %
5c	COOEt	H	**12c**	81	**6c**	64
5c	COOEt	H	**13c**	88		
5d	COOEt	COOEt	**12d**	20		
5e	CH_2OH	H	**13e**	79		
5f	CH_2OSiMe_3	H	**13f**	75		

The iron mediated carbonylation of the vinylcyclopropanes **4c-4g** to the corresponding bicyclooctenones **6c-6g** bearing additional heterosubstituents offers a new synthetic approach to these ketones. Starting from *exo*-substituted vinylcyclopropanes the stereochemical information can be transferred to the decomplexation products. Thus, the application of the elaborated methods to the conversions of substituted bicyclo[4.1.0]heptenes, obtained via asymmetric cyclopropanation of cyclohexadienes, should give an efficient pathway to enantiomerically pure bicyclic ketones of type **6**. The scope of this reaction sequence could be broadened evenmore either by starting from substituted cyclohexadienes or by employing alternative decomplexation methods leading to other functionalized seven-membered ring systems like bicyclic lactones or substituted cycloheptadienes.[4] Additionally, the functional groups, introduced during the synthesis of the vinylcyclopropanes of type **4**, can be transformed efficiently to various derivatives bearing a bicyclo[3.2.1]octane skeleton.

Experimental

NMR spectra were recorded on Bruker spectrometers AC 200, AM 300 and DRX 400 with TMS as internal standard. IR spectra were obtained on a Shimadzu 470, mass spectra on a Finnigan CH 5 and elemental analysis on a Carlo Erba Mod 1106. Column chromatography was carried out with silicagel 60 (70-230 mesh resp. 28-45 mesh for MPLC) or alumina (pH 10) from ICN, Eschwege, by using MTBE (methyl *t*-butyl ether) / PE (petroleum ether, bp. 60-90 °C) mixtures as eluent; gas chromatography with 25 m CP sil-5 capillaries. GC-MS spectra were obtained by using comparable capillaries and an Ion-Trap Mod. ITD 800. All reactions and operations were conducted under a dry and oxygen-free argon atmosphere. The vinylcyclopropanes **4c** and **4d** (reaction catalyzed by $Cu(acac)_2$ or $Rh(OAc)_2$) were prepared according to literature procedures.[8,9]

*7-exo-Hydroxymethyl-bicyclo[4.1.0]hept-2-ene (**4e**)*

A solution of **4c** (8.30 g, 50.0 mmol) in diethyl ether (20 mL) was added to a slurry of $LiAlH_4$ (1.20 g, 31.6 mmol) in diethyl ether (50 mL). The mixture was heated to reflux (2 h) and worked up. Distillation gave **4e** (5.02 g, 40.5 mmol, 81%) as a colourless liquid, b.p. 71 °C (3.0 mbar) (purity 97% GC).^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.00-2.36 (m, 7H, H-1, H-4, H-5, H-6, H-7), 2.20 (br s, 1H, OH), 3.38-3.52 (m, 2H, CH_2OH), 5.38-5.49 (m, 1H, H_{olef}), 5.99-6.08 (m, 1H, H_{olef}); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.1 (CH, C-6), 17.8 (CH_2, C-5), 19.1 (CH, C-7), 22.9 (CH_2, C-4), 25.5 (CH, C-1), 65.4 (CH_2, CH_2OH), 122.9 (CH, C_{olef}), 127.4 (CH, C_{olef}); IR (NaCl/film): ν/cm^{-1} = 3340, 3026, 2928, 2855, 1638; GC-MS (EI, 70 eV): m/z (%) = 124 (5, M^+), 107 (100, M^+-OH); $C_8H_{12}O$ (124.2) requires C: 77.38 H: 9.74; Found C: 77.10 H: 9.60.

*7-exo-Trimethylsiloxymethyl-bicyclo[4.1.0]hept-2-ene (**4f**)*

To a solution of **4e** (8.00 g, 64.5 mmol) in triethylamine (16.30 g, 161 mmol) and THF (95 mL), trimethylchlorsilane (8.39 g, 77.2 mmol) was added at r.t.. After stirring (8 h at r.t.) the solvent was removed

under reduced pressure. The residue was diluted with petroleum ether (60/90) (250 mL), filtered and dried over Na_2SO_4. Distillation yielded **4f** (12.10 g, 61.6 mmol, 96%), b.p. 60 °C (11 mbar). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.09 (s, 9H, $Si(C\underline{H}_3)_3$), 0.84-1.97 (m, 7H), 3.45 (dd, 2H, J = 3.6 Hz, J = 6.6 Hz), 5.38-5.43 (m, 1H, H_{olef}), 5.98-6.04 (m, 1H, H_{olef}); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -0.3 (3 x CH_3, $Si(\underline{C}H_3)_3$), 15.5 (CH, C-6), 18.1 (CH_2, C-5), 19.5 (CH, C-7), 21.2 (CH_2, C-4), 25.7 (CH, C-1), 65.8 (CH_2, $\underline{C}H_2OSi(CH_3)_3$), 123.0 (CH, C_{olef}), 127.7 (CH, C_{olef}); IR (NaCl/film): ν/cm^{-1} = 3030, 2960, 1636; MS (EI, 70 eV): m/z (%) = 196 (1, M^+), 107 (80, M^+-($OSi(CH_3)_3$)); $C_{11}H_{20}OSi$ (196.4) requires C: 67.28, H: 10.27; Found C: 66.90 H: 10.10.

*7-exo-Acetylmethyl-bicyclo[4.1.0]hept-2-ene (**4g**)*

To a solution of **4e** (7.10 g, 57.3 mmol) in pyridine (13.5 g, 172 mmol) chloroacetic acid (6.75 g, 85.9 mmol) was added. After 30 min the mixture was poured on ice (50 g) and 1 M HCl (100 mL). The mixture was extracted with ether, washed and dried over anhydrous $MgSO_4$. Distillation gave **4g** (5.40 g, 32.5 mmol, 57%), b.p. 85 °C (7.3 mbar).^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10-1.20 (m, 1H), 1.20-1.30 (m, 1H), 1.30-1.40 (m, 1H), 1.50-1.60 (m, 1H), 1.70-1.85 (m, 1H), 1.94-1.98 (m, 2H), 2.06 (s, 3H, $CH_2O(CO)C\underline{H}_3$), 3.87 (dd, 1H, $C\underline{H}_2O(CO)CH_3$, ^{2}J = 11.5 Hz, ^{3}J = 7.7 Hz), 3.99 (dd, 1H, $C\underline{H}_2O(CO)CH_3$, ^{2}J = 11.5 Hz, ^{3}J = 6.7 Hz), 5.46 (~dt, 1H, H_{olef}, J = 9 Hz, J = 2.7 Hz), 6.03 (m, 1H, H_{olef}); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.8 (CH, C-6 or C-7), 17.8 (CH_2, C-5), 19.6 (CH, C-6 or CH-7), 21.0 (CH_2, C-4), 21.1 (CH_3, $CH_2OOC\underline{C}H_3$), 22.0 (CH, C-1), 67.7 (CH_2, $\underline{C}H_2OOCCH_3$), 123.6 (CH, C_{olef}), 127.2 (CH, C_{olef}), 171.3 ($CH_2OO\underline{C}CH_3$); IR (NaCl/film): ν/cm^{-1} = 3028, 2928, 1740, 1640; GC-MS (EI 70 eV): m/z (%) = 166 (7, M^+), 107 (100, M^+-(CH_3COO)).

General procedures for complexation of compounds of type 4 with iron carbonyls

Method A: Complexation using $Fe_2(CO)_9$: 10 mmol bicyclo[4.1.0]hept-2-ene **4** and one equivalent $Fe_2(CO)_9$ in abs. ether (100 mL) were heated to reflux for 16 h. Then another half equivalent of $Fe_2(CO)_9$ was added and the mixture was heated for additional 4h, then allowed to cool to r.t., filtered over alumina and evaporated in vacuo. Purification of the raw material was carried out by column chromatography (silica gel).

Method B: Complexation using tricarbonyl-bis-(1,2-η-cyclooctene)iron[10]: Cyclooctene (27.90 g, 253 mmol), pentacarbonyliron (6.70 g, 34.3 mmol) and PE(60/90) (80 mL) were cooled to - 40 °C and irradiated for 14 h (Philips HPK 125 W, Duran). Compound **4** (25 mmol) was added and the mixture was allowed to warm up to r.t. (4-5 h). After filtration over alumina the solvent was evaporated. Separation of the residue by column chromatography (silica gel) gave in the first band tetracarbonyl-(1,2-η-cyclooctene)iron, in the second fraction green dodecacarbonyltriiron and then the yellow product **5**.

*Tricarbonyl-[1,3-5-η-(2-syn-ethoxycarbonyl-cyclohept-4-ene-1,3-diyl)]iron (**5c**)*

Method A: Column chromatography with PE(60/90) / MTBE 4:1 yielded 25% of **5c** as an orange oil.

Method B: Column chromatography with PE(60/90) / MTBE 10:1 gave **5c** (4.20 g, 56%) as an orange oil.

^{1}H NMR (300 MHz, C_6D_6): δ = 1.00 (t, 3H, $CH_2C\underline{H}_3$, ^3J = 7.0 Hz), 1.25 (br s, 1H, H-1), 1.31-1.35 (m, 1H, H-7), 1.54-1.60 (m, 1H, H-7), 1.75-1.95 (m, 2H, H-6), 2.91 (br s, 1H, H-2), 3.70 (~t, 1H, H-5, J = 7.5 Hz), 3.90-4.08 (m, 2H, $C\underline{H}_2CH_3$), 4.27 (d, 1H, H-3, J = 6.8 Hz), 4.39 (~t, 1H, H-4, J = 7.8 Hz); ^{13}C NMR (75 MHz, C_6D_6): δ = 14.2 (CH_3, $CH_2\underline{C}H_3$), 14.6 (CH, C-1), 24.8 (CH_2, C-7), 44.5 (CH_2, C-6), 49.6 (CH, C-2), 59.6 (CH, C-5), 60.0 (CH_2, $\underline{C}H_2CH_3$), 78.9 (CH, C-3), 94.9 (CH, C-4), 172.9 ($\underline{C}OOCH_2CH_3$), 203.3 (Fe(CO)), 214.0 (Fe(CO)), 214.6 (Fe(CO)); IR (NaCl/film): ν/cm^{-1} = 2055, 1975, 1730; MS (EI, 70 eV) m/z (%) = 306 (13, M^+), 278 (7, M^+-CO), 250 (78, M^+-2 CO), 222 (95, M^+-3 CO).

*Tricarbonyl[1,3-5-η-(2,2-bis(ethoxycarbonyl)-cyclohept-4-ene-1,3-diyl)]iron (**5d**)*

Method A: After crystallization from pentane **5d** (71%) was obtained as a yellow solid, m.p. 87-88 °C.
Method B: The crude product was recrystallized from pentane/ether to give **5d** (87%) as a yellow solid.

^{1}H NMR (300 MHz, C_6D_6): δ = 0.81 (t, 3H, $CH_2C\underline{H}_3$, ^3J = 7.1 Hz), 0.99 (t, 3H, $CH_2C\underline{H}_3$, ^3J = 7.1 Hz), 1.55-1.70 (m, 1H), 1.73-1.95 (m, 3H), 2.37 (br s, 1H, H-1), 3.79 (dq, 2H, $C\underline{H}_2CH_{3syn}$, ^3J = 7.1 Hz, ^2J = 9.5 Hz), 4.06 (q, 2H, $C\underline{H}_2CH_{3anti}$, ^3J = 7.1 Hz), 4.10-4.15 (m, 1H, H_{allyl}), 4.29-4.35 (m, 2H, H_{allyl}); ^{13}C NMR (75 MHz, C_6H_6): δ = 14.0 (CH_3, $CH_2\underline{C}H_3$), 14.1 (CH_3, $CH_2\underline{C}H_3$), 21.9 (CH, C-1), 26.3 (CH_2, C-7), 37.9 (CH_2, C-6), 60.0 (CH, C-5), 61.1 (CH_2, $\underline{C}H_2CH_3$), 62.0 (CH_2, $\underline{C}H_2CH_3$), 65.0 (C-2), 80.2 (CH, C-3), 97.1 (CH, C-4), 168.8 ($\underline{C}OOCH_2CH_3$), 169.5 ($\underline{C}OOCH_2CH_3$), 203.1 (Fe(CO)), 212.9 (Fe(CO)), 214.1 (Fe(CO)); IR (KBr/solid): ν/cm^{-1} = 2055, 1993, 1974, 1756, 1726; MS (FAB): m/z (%) = 350 (9, M^+-CO), 322 (100, M^+-2 CO); $C_{16}H_{18}FeO_7$ (378.2) requires C: 50.82 H: 4.80; Found C: 50.60 H: 4.60.

*Tricarbonyl[1,3-5-η-(2-syn-hydroxymethyl-cyclohept-4-ene-1,3-diyl)]iron (**5e**)*

Method A: Purification of the crude product on silica gel (PE(60/90) / MTBE 2:1) gave **5e** (73%) as a yellow solid: m.p. 61 °C (dec.).

Method B: 54% of **5e** were obtained as yellow-brown crystals, m.p. 59 °C (dec.).

^{1}H NMR (300 MHz, C_6D_6): δ = 0.52 (br s, 1H, H-1), 1.28-1.32 (m, 1H, H-6 or H-7), 1.60-2.00 (m, 3H, H-6 and H-7), 2.41 (~t, 1H, H-2, J = 7.0 Hz), 3.40 (br s, 1H, OH), 3.58 (d, 2H, $C\underline{H}_2OH$, J = 7.2 Hz), 3.84 (~t, 1H, H-5, J = 7.4 Hz), 3.94 (d, 1H, H-3, J = 6.6 Hz), 4.53 (~t, 1H, H-4, J = 7.3 Hz); ^{13}C NMR (75 MHz, C_6D_6): δ = 14.8 (CH, C-1), 25.3 (CH_2, C-7), 44.4 (CH_2, C-6), 47.4 (CH, C-2), 63.2 (CH, C-5), 65.1 (CH_2, $\underline{C}H_2OH$), 79.2 (CH, C-3), 94.9 (CH, C-4), 203.5 (Fe(CO)), 215.1 (Fe(CO)), 216.0 (Fe(CO)); IR (KBr/solid): ν/cm^{-1} = 3280, 3035, 2045, 1971, 1957; MS (EI, 70 eV): m/z (%) = 264 (6, M^+), 236 (24, M^+-CO), 208 (71, M^+-2 CO), 180 (62, M^+-3 CO); $C_{11}H_{12}FeO_4$ (264.1) requires C: 50.03 H: 4.58; Found C: 50.30 H: 4.70.

*Tricarbonyl[1,3-5-η-(2-syn-trimethylsiloxymethyl-cyclohept-4-ene-1,3-diyl)]iron (**5f**)*

Method A: The raw material was purified by column chromatography on alumina (PE(60/90) / MTBE 5:1). To remove traces of **4f** the product was heated (50 °C) in vacuo yielding **5f** (29%) as a yellow oil.

Method B: Column chromatography on alumina with PE(60/90) / MTBE 10:1 gave **5f** (73%) as a yellow oil. ^{1}H-NMR (300 MHz, C_6D_6, 25 °C): δ = 0.21 (s, 9H, Si($C\underline{H}_3$)$_3$), 0.58 (br s, 1H, H-1), 1.20-1.50 (m, 1H, H-7), 1.50-2.10 (m, 3H, H-6 and H-7), 2.54 (~t, ^{3}J = 7.7 Hz, 1H, H-2), 3.65 (d, 2H, $C\underline{H}_2$OSi(CH_3)$_3$, ^{3}J = 7.7 Hz), 3.77 (~t, 1H, H-5, J = 7.3 Hz), 4.06 (d, 1H, H-3, J = 6.5 Hz), 4.50 (~t, 1H, H-4, J = 7.6 Hz); ^{13}C-NMR (75 MHz, C_6D_6): δ = -0.4 (3 x CH_3, $CH_2OSi(\underline{C}H_3)_3$), 14.6 (CH, C-1), 25.2 (CH_2, C-7), 44.3 (CH_2, C-6), 47.1 (CH, C-2), 63.7 (CH, C-5), 64.8 (CH_2, $C\underline{H}_2OSi(CH_3)_3$), 79.0 (CH, C-3), 94.7 (CH, C-4), 203.7 (Fe(CO)), 215.2 (Fe(CO)), 216.0 (Fe(CO)); IR (NaCl/film): ν/cm^{-1} = 2075, 2045, 1966, 1251, 1107, 1086.

*Tricarbonyl[1,3-5-η-(2-syn-acetylmethyl-cyclohept-4-ene-1,3-diyl)]iron (**5g**)*

Method B: Column chromatography on silica gel with PE(60/90) / MTBE 10:1 yielded **5g** (56%) as a yellow, viscous oil. ^{1}H-NMR (400 MHz, C_6D_6): δ = 0.44 (br s, 1H, H-1), 1.17 (dd, 1H, J = 11.8 Hz, J = 7.1 Hz), 1.61-1.68 (m, 1H), 1.76 (s, 3H, $COC\underline{H}_3$), 1.77-1.85 (m, 1H), 1.88-1.95 (m, 1H), 2.42 (~t, 1H, H-2, J = 7.8 Hz), 3.60 (d, 1H, H-3 , J = 6.4 Hz), 3.71 (~t, 1H, H-5, J = 7.5 Hz), 4.09 (m, 2H, $C\underline{H}_2O(CO)CH_3$), 4.48 (~t, 1H, H-4, J = 8.2 Hz); ^{13}C NMR (100 MHz, C_6D_6): δ = 13.7 (CH, C-1), 20.4 (CH_3, $CH_2O(CO)\underline{C}H_3$), 25.0 ($CH_2$, C-7), 43.9 (CH, C-2), 44.0 (CH_2, C-6), 61.7 (CH, C-5), 66.1 (CH_2, C-8), 79.3 (CH, C-3), 94.9 (CH, C-4), 170.0 ($CH_3\underline{C}OO$), 203.5 (Fe(CO)), other Fe(CO) not detected; IR (NaCl/film): ν/cm^{-1} = 2940, 2045, 1968, 1741; MS (EI, 70 eV): m/z (%) = 306 (12, M$^+$), 278 (4, M$^+$-CO), 250 (91, M$^+$-2 CO), 222 (92, M$^+$-3 CO), 134 (100).

General procedure for the carbonylation of complexes of type 5

A solution of 5.0 g alkyl-allyl complex **5** (or acyl-allyl complex **12c**) in dioxane (10 mL) (and dichloromethane (5 mL) with **12c**) was heated (120 °C) in an autoclave (steel, volume 75 mL) under CO pressure (200 bar) for 75 h. The reaction mixture was filtered over alumina and the solvent removed in vacuo.

*2-exo-Ethoxycarbonyl-bicyclo[3.2.1]oct-3-en-8-one (**6c**)*

Carbonylation of **5c**: The crude product was distilled in a *kugelrohr-oven* to yield **6c** (64%) as a colourless liquid (purity > 97% (GC)).

Carbonylation of **12c**: The crude product was purified by MPLC (PE(60/90) / MTBE 10:1) to yield **6c** (64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, 3H, $CH_2C\underline{H}_3$, ^{3}J = 7.2 Hz), 1.75-2.35 (m, 4H, H-6 and H-7), 2.53 (~t, 1H, H-1, J = 5.7 Hz), 2.70 (br d, 1H, H-2, J = 7.9 Hz), 3.59-3.62 (m, 1H, H-5), 4.16 (q, 2H, $C\underline{H}_2CH_3$, ^{3}J = 7.2 Hz), 5.67 (ddd, 1H, H-4, ^{3}J = 9.2 Hz, J = 3.9 Hz, J = 1.0 Hz), 6.06 (ddd, 1H, H-3, ^{3}J = 9.2 Hz, J = 7.0 Hz, J = 1.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3, $CH_2\underline{C}H_3$), 24.2 (CH_2, C-6 or C-7), 28.3 (CH_2, C-6 or C-7), 43.2 (CH, C-1 or C-2), 44.3 (CH, C-1 or C-2), 58.5 (CH, C-5), 61.0 (CH_2, $\underline{C}H_2CH_3$), 123.3 (CH,

C_{olef}), 134.9 (CH, C_{olef}), 170.8 ($\underline{C}OOCH_2CH_3$), 213.8 ($\underline{C}O$); IR (NaCl/film): ν/cm^{-1} = 1759, 1730, 1637; GC MS (EI, 70 eV): m/z (%) = 195 (100, M^++H), 166 (25, M^+-CO); $C_{11}H_{14}O_3$ (194.2) requires C: 68.02 H: 7.27; Found C: 67.80 H: 7.50.

*2,2-Bis(ethoxycarbonyl)-bicyclo[3.2.1]oct-3-en-8-one (**6d**)*

The crude product from carbonylation of **5d** was purified by MPLC (PE(60/90) / MTBE 1:1). First a mixture of **6d** and **4d** was eluated. Evaporation of the second fraction yielded **6d** (yield 57%) as a colourless oil (99% (GC)). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.24 (t, 3H, $CH_2C\underline{H}_3$, ^3J = 7.2 Hz), 1.28 (t, 3H, $CH_2C\underline{H}_3$, ^3J = 7.1 Hz), 1.70-2.18 (m, 4H, H-6, H-7), 2.58 (m, 1H, H-1), 3.08 (br d, 1H, H-5, J = 7.7 Hz), 4.22 (q, 2H; $C\underline{H}_2CH_3$, ^3J = 7.2 Hz), 4.26 (q, 2H; $C\underline{H}_2CH_3$, ^3J = 7.1 Hz), 5.91 (~dt, 1H, H_{olef}, ^3J = 9.4 Hz, J = 1.5 Hz), 6.18 (ddd, 1H, H_{olef}, ^3J = 9.4 Hz, J = 6.8 Hz, J = 1.2 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.6 (CH_3, $CH_2\underline{C}H_3$), 13.7 (CH_3, $CH_2\underline{C}H_3$), 20.5 (CH_2, C-6 or C-7), 26.4 (CH_2, C-6 or C-7), 43.9 (CH, C-1), 45.4 (CH, C-5), 61.7 (CH_2, $\underline{C}H_2CH_3$), 61.8 (CH_2, $\underline{C}H_2CH_3$), 69.0 (C-2), 123.6 (CH, C_{olef}), 134.9 (CH, C_{olef}), 167.5 ($\underline{C}OOCH_2CH_3$), 168.0 ($\underline{C}OOCH_2CH_3$), 210.1 (CO); IR (NaCl/film): ν/cm^{-1} = 2987, 1772, 1753; MS (EI, 70 eV): m/z (%) = 267 (20, M^++H), 91 (100); $C_{14}H_{18}O_5$ (266.3) requires C: 63.15 H: 6.81; Found C: 63.30 H: 6.70.

*4-exo-Hydroxymethyl-bicyclo[3.2.1]oct-2-en-8-one (**6e**)*

The raw material from carbonylation of **5e** was distilled in a *kugelrohr-oven* to yield **6e** (65%) as a yellow liquid (purity > 89% (GC)). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.80-3.00 (m, 8H), 3.52 (br s, 2H, $C\underline{H}_2OH$), 5.52 (d, 1H, H_{olef}, J = 7.2 Hz), 5.93 (~t, 1H, H_{olef}, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.6 (CH_2), 28.7 (CH_2), 43.3 (CH,), 45.2 (CH,), 57.6 (CH), 62.5 (CH_2, $\underline{C}H_2OH$), 126.6 (CH_{olef}), 133.5 (CH_{olef}), 218.1 (CO); IR (NaCl/film): ν/cm^{-1} = 3495, 1963, 1744, 1636; GC MS (EI, 70 eV): m/z (%) = 153 (65, M^++H).

*4-exo-Trimethylsiloxymethyl-bicyclo[3.2.1]oct-2-en-8-one (**6f**)*

Carbonylation of **5f** yielded **6f** (85%) as a pale yellow liquid (purity > 95% (GC)). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 9H, $Si(C\underline{H}_3)_3$), 1.82 (d, 1H, J = 11 Hz), 1.93 (d, 1H, J = 4.8 Hz), 2.04 (~t, 1H, J = 11 Hz), 2.15 (~t, 1H, J = 9.8 Hz), 2.34-2.40 (m, 2H), 2.84 (br s, 1H), 3.45 (d, 2H, $C\underline{H}_2OSi(CH_3)_3$, J = 6.0 Hz), 5.47 (d, 1H, H_{olef}, J = 6.0 Hz), 5.89 (~t, 1H, H_{olef}, J = 7.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = -0.6 (3 x CH_3, $Si(\underline{C}H_3)_3$), 24.8 (CH_2, C-6 or C-7), 29.0 (CH_2, C-6 or C-7), 43.3 (CH, C-4 or C-5), 45.4 (CH, C-4 or C-5), 57.6 (CH, C-1), 63.0 ($\underline{C}H_2OSi(CH_3)_3$), 126.9 ($CH_{olef}$), 133.8 ($CH_{olef}$), 216.8 (CO); IR (NaCl/film): ν/cm^{-1} = 2958, 2853, 1751, 1253, 1123, 875; MS (EI, 70 eV): m/z (%) = 224 (35, M^+), 209 (7, M^+-CH_3), 166 (47); $C_{12}H_{20}O_2Si$(224.4) requires C: 64.24, H: 8.98; Found C: 64.53 H: 8.83.

*2-exo-Acetylmethyl-bicyclo[3.2.1]oct-3-en-8-one (**6g**)*

Carbonylation of **5g** yielded a mixture of **4g** and **6g** (15:85). Purification by MPLC (PE(60/90) / MTBE 8:1) gave **6g** (73%) as a colourless liquid (purity > 96% (GC)). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.82-1.94 (m, 1H), 1.95-2.03 (m, 1H), 2.05 (s, 3H, $CH_2O(CO)C\underline{H}_3$), 2.08-2.14 (m, 1H), 2.18-2.28 (m, 1H), 2.35 (d, 1H, J = 7.8 Hz), 2.48 (~t, 1H, J = 6.0 Hz), 3.03 (br s, 1H), 3.91 (~t, 1H, $C\underline{H}_2O(CO)CH_3$, J = 10 Hz), 4.12 (dd, 1H, $C\underline{H}_2OOCCH_3$, ^{2}J = 11.2 Hz, ^{3}J = 5.0 Hz), 5.51 (dd, 1H, H_{olef}, J = 9.0 Hz, J = 3.2 Hz), 6.01 (~t, 1H, H_{olef}, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.5 (CH_3, $CH_2O(CO)\underline{C}H_3$), 24.5 ($CH_2$, C-6 or C-7), 28.7 ($CH_2$, C-6 or C-7), 43.6 (CH, C-1 or C-2), 44.8 (CH, C-1 or C-2), 53.7 (CH, C-5), 64.1 (CH_2, $\underline{C}H_2O(CO)CH_3$), 125.4 ($CH_{olef}$), 134.6 ($CH_{olef}$), 170.4 ($CH_2O(\underline{C}O)CH_3$), 215.7 (CO); IR (NaCl/film): ν/cm^{-1} = 2957, 2914, 1740, 1633, 1447; GC-MS (EI, 70 eV): m/z (%) = 195 (100, M^++H), 135 (50, M^+-(CH_3COO)); $C_{11}H_{14}O_3$ (194.2) requires C: 68.02 H: 7.27; Found C: 67.90 H: 7.30.

General procedure for the synthesis of acyl complexes of type 12 and 13

Complexes of type **5** (5.00 g) were dissolved in pentane (10 mL) at r.t.. To this mixture a solution of one equivalent PR_3 (R = Ph or OPh) in ether (10 mL) was added dropwise. A fine yellow solid precipitated, which was recrystallized from pentane/dichloromethane.

*Dicarbonyl-[1',3-5-η-(1-carbonyl-2-syn-ethoxycarbonyl-cyclohept-4-ene-1',3-diyl)]triphenyl phosphiteiron (**12c**)*

Yield 78%, m.p. 115 °C (dec.).^{1}H NMR (300 MHz, C_6D_6): δ = 0.44-0.50 (m, 1H), 0.98 (t, 3H, $CH_2C\underline{H}_3$, ^{3}J = 7.0 Hz), 1.53-1.59 (m, 1H), 1.74-1.81 (m, 1H), 1.98-2.04 (m, 1H), 2.27 (br s, 1H, H-1), 2.69 (br d, 1H, H-2, J = 9.5 Hz), 3.80-3.92 (m, 1H, H-5), 3.96 (q, 2H, $C\underline{H}_2CH_3$, ^{3}J = 7.0 Hz), 4.70-4.78 (m, 2H, H-3 and H-4), 6.85-7.12 (m, 15H, H_{arom}); ^{13}C NMR (75 MHz C_6D_6): δ = 14.1 (CH_3, $CH_2\underline{C}H_3$), 26.5 (CH_2, C-6 or C-7), 27.9 (CH_2, C-6 or C-7), 52.1 (CH, C-2), 58.3 (d, CH, C-1, $J_{C,P}$ = 27 Hz), 60.9 (CH_2, $\underline{C}H_2CH_3$), 72.7 (CH, C-5), 81.6 (CH, C-3), 88.1 (CH, C-4), 11.5 (CH, C_{ortho}), 125.4 (CH, C_{para}), 130.1 (CH, C_{meta}), 151.3 (d, C_{ipso}, $J_{C,P}$ = 8 Hz), 171.5 ($\underline{C}OOCH_2CH_3$), 213.2 (d, Fe(CO), $J_{C,P}$ = 21 Hz), 215.1 (d, Fe(CO), $J_{C,P}$ = 20 Hz), 264.4 (d, CO_{acyl}, $J_{C,P}$ = 59.8 Hz); IR (KBr/solid): ν/cm^{-1} = 2940, 2015, 1956, 1729, 1642, 1592; MS (FAB): m/z (%) = 617 (10, M^++H), 561 (20, M^++H-2 CO), 560 (10, M^+-2 CO), 366 (100, $FeP(OPh)_3$); $C_{31}H_{29}FeO_8P$ (616.4) requires C: 60.41 H: 4.74; Found C: 60.20 H: 4.70.

*Dicarbonyl-[1',3-5-η-(1-carbonyl-2-syn-ethoxycarbonyl-cyclohept-4-ene-1',3-diyl)]triphenyl-phosphineiron (**13c**)*

Yield: 88% of **13c** as a fine yellow solid, m.p. 133 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.12 (t, 3H, $CH_2C\underline{H}_3$, ^{3}J = 7.1 Hz), 1.40-1.50 (m, 1H), 1.70-1.85 (m, 1H), 1.85-2.00 (m, 1H), 2.15-2.35 (m, 1H), 2.50 (br s, 1H, H-1), 3.04 (br d, 1H, H-2, J = 10 Hz), 3.68-3.75 (m, 1H, H-3 or H-5), 3.95-4.00 (m, 1H, H-3 or H-5), 4.10-

4.24 (m, 2H, C$\underline{H}_2$CH$_3$), 5.01 (d, 1H, H-4, J = 8.3 Hz), 7.00-7.57 (m, 15H, H$_{arom}$); ^{13}C NMR (75 MHz, C_6D_6): δ = 14.1 (CH$_3$, CH$_2\underline{C}$H$_3$), 27.0 (CH$_2$, C-6 or C-7), 27.9 (CH$_2$, C-6 or C-7), 52.5 (CH, C-2), 59.4 (d, CH, C-1, $J_{C,P}$ = 14.6 Hz), 60.9 (CH$_2$, $\underline{C}$H$_2$CH$_3$), 72.5 (CH, C-5), 82.2 (CH, C-3), 90.5 (CH, C-4), 128.8 (d, CH, C$_{meta}$, $J_{C,P}$ = 9 Hz), 130.1 (CH, C$_{para}$), 133.1 (d, CH, C$_{ortho}$, $J_{C,P}$ = 10 Hz), 133.5 (d, C$_{ipso}$, $J_{C,P}$ = 32 Hz), 171.8 ($\underline{C}$OOCH$_2$CH$_3$), 216.6 (d, Fe(CO), $J_{C,P}$ = 16 Hz), 218.1 (d, Fe(CO) , $J_{C,P}$ = 15.7 Hz), 266.8 (CO$_{acyl}$); IR (KBr/solid): ν/cm^{-1} = 2920, 2850, 2045, 1987, 1723; MS (EI, 70 eV): m/z (%) = 512 (5, M$^+$-2 CO), 484 (30, M$^+$-3 CO), 262 (100, PPh$_3$); $C_{31}H_{29}FeO_5P$ (568.4) requires C: 65.51 H: 5.14; Found C: 65.40 H: 5.10.

*Dicarbonyl[1',3-5-η-(1-carbonyl-2,2-bis(ethoxycarbonyl)-cyclohept-4-ene-1',3-diyl]triphenyl-phosphiteiron (**12d**)*

Yield: 20% **12d** as a fine yellow solid, m.p. 104 °C (dec.). ^{1}H NMR (300 MHz, C_6H_6): δ = 0.84 (t, 3H, CH$_2$C$\underline{H}_3$, ^{3}J = 7.2 Hz), 1.01 (t, 3H, CH$_2$C$\underline{H}_3$, ^{3}J = 7.2 Hz), 1.52 (m, 1H, H-7), 1.83 (m, 1H, H-7), 2.05 (m, 1H, H-6), 3.18 (d, 1H, H-6, J = 8.9 Hz), 3.8-4.2 (m, 2H, H$_{allyl}$ and H-1), 3.90 (q, 2H, C$\underline{H}_2$CH$_3$, ^{3}J = 7.2 Hz), 4.06 (q, 2H, C$\underline{H}_2$CH$_3$, ^{3}J = 7.2 Hz), 4.93 (d, 1H, H$_{allyl}$, J = 7.8 Hz), 5.16 (m, 1H, H$_{allyl}$), 6.88-7.17 (m, 15H, H$_{arom}$); ^{13}C NMR (75 MHz, C_6D_6): δ = 13.9 (CH$_3$, CH$_2\underline{C}$H$_3$), 14.0 (CH$_3$, CH$_2\underline{C}$H$_3$), 23.1 (CH$_2$, C-7), 25.8 (CH$_2$, C-6), 59.2 (d, CH, C-1, $J_{C,P}$ = 26.1 Hz), 61.7 (CH$_2$, $\underline{C}$H$_2$CH$_3$), 61.9 (CH$_2$, $\underline{C}$H$_2$CH$_3$), 64.9 (C-2), 74.5 (CH, C-3 or C-5), 79.7 (CH, C-3 or C-5), 89.9 (CH, C-4), 121.4 (CH, C$_{ortho}$), 125.4 (CH, C$_{para}$), 130.1 (CH, C$_{meta}$), 151.1 (d, C$_{ipso}$, $J_{C,P}$ = 8.5 Hz), 169.5 ($\underline{C}$OOCH$_2$CH$_3$), 169.7 ($\underline{C}$OOCH$_2$CH$_3$), 213.5 (d, Fe(CO) , $J_{C,P}$ = 22.0 Hz), 214.4 (d, Fe(CO) , $J_{C,P}$ = 19.5 Hz), 259.7 (d, CO$_{acyl}$, $J_{C,P}$ = 59.6 Hz); IR (KBr/solid): ν/cm^{-1} = 2990, 2025, 1966, 1741, 1720, 1652; MS (FAB): m/z (%) = 689 (8, M$^+$+H), 604 (16, M$^+$-3 CO), 366 (100); $C_{34}H_{33}FeO_{10}P$ (688.5) requires C: 59.32 H: 4.83; Found C: 59.20 H: 4.70.

*Dicarbonyl[1',3-5-η-(1-carbonyl-2-syn-hydroxymethyl-cyclohept-4-ene-1',3-diyl)]triphenyl-phosphineiron (**13e**)*

Yield: 79% **13e** as a yellow solid, m.p. 111 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.76 (m, 1H), 1.60-1.96 (m, 3H), 2.10-2.25 (m, 1H, H-1), 2.29 (d, 1H, H-2, J = 7.2 Hz), 3.43 (~t, 1H, H-5, J = 6.5 Hz), 3.63 (d, 2H, C$\underline{H}_2$OH, J = 6.4 Hz), 3.85-4.05 (m, 1H, H-3), 4.74 (d, 1H, H-4, J = 7.3 Hz), 6.96-7.15 (m, 15H, H$_{arom}$), O$\underline{H}$ not detected; ^{13}C NMR (75 MHz, C_6D_6): δ = 27.5 (CH$_2$, C-6 or C-7), 28.8 (CH$_2$, C-6 or C-7), 49.9 (CH, C-2), 61.8 (d, CH, C-1, $J_{C,P}$ = 15.3 Hz), 66.8 (CH$_2$, $\underline{C}$H$_2$OH), 72.6 (CH, C-5), 86.0 (CH, C-3), 90.7 (CH, C-4), 128.8 (d, CH, C$_{meta}$, $J_{C,P}$ = 8.3 Hz), 130.1 (CH, C$_{para}$), 133.1 (d, CH, C$_{ortho}$, $J_{C,P}$ = 10.4 Hz), 133.4 (d, C$_{ipso}$, $J_{C,P}$ = 32 Hz), 216.3 (d, Fe(CO) , $J_{C,P}$ = 16.3 Hz), 222.5 (d, Fe(CO), $J_{C,P}$ = 21.5 Hz), CO$_{acyl}$ not detected; IR (KBr/solid): ν/cm^{-1} = 3415, 2975 1994, 1936; MS (EI, 70 eV): m/z (%) = 526 (8, M$^+$), 498 (2, M$^+$-CO), 470 (8, M$^+$-2 CO), 442 (45, M$^+$-3 CO); $C_{29}H_{27}FePO_4$ (526.4) requires C: 66.18 H: 5.17; Found C: 66.15 H: 5.10.

Dicarbonyl[1',3-5-η-(1-carbonyl-2-syn-trimethylsiloxymethyl-cyclohept-4-ene-1',3-diyl)]-triphenylphosphineiron (13f)

Yield: 75% **13f** as a fine yellow solid, m.p. 128 °C (dec.). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.20 (s, 9H, $Si(C\underline{H}_3)_3$), 0.47 (br s, 1H, H-1), 1.85-2.27 (m, 4H, H-6 and H-7), 2.17 (d, 1H, H-2, J = 9.6 Hz), 3.45-3.72 (m, 2H, $C\underline{H}_2OSi(CH_3)_3$), 4.00-4.15 (m, 1H, H_{allyl}), 4.56-4.68 (m, 1H, H_{allyl}), 5.05 (d, 1H, H_{allyl}, J = 7.5 Hz), 7.0-7.5 (m, 15H, H_{arom}); ^{13}C NMR (75 MHz, C_6D_6): δ = -0.4 (CH_3, $Si(\underline{C}H_3)_3$), 27.4 (CH_2, C-6 or C-7), 28.9 (CH_2, C-6 or C-7), 49.7 (CH, C-2), 61.6 (d, CH, C-1, $J_{C,P}$ = 17 Hz), 66.5 (CH_2, $\underline{C}H_2OSi$), 72.5 (CH, C_{allyl}), 86.3 (CH, C_{allyl}), 90.6 (CH, C_{allyl}), 128.7 (d, CH, C_{meta}, $J_{C,P}$ = 9 Hz), 130.1 (CH, C_{para}), 133.1 (d, CH, C_{ortho}, $J_{C,P}$ = 10 Hz), 133.5 (d, C_{ipso}, $J_{C,P}$ = 32 Hz), 216.7 (Fe(CO)), 218.9 (Fe(CO)), CO_{acyl} not detected; IR (KBr/solid): ν/cm^{-1} = 1994, 1938, 1632; MS (EI, 16 eV): m/z (%) = 570 (1, M^+-CO), 542 (8, M^+-2 CO), 514 (51, M^+-3 CO), 262 (100, PPh_3^+); $C_{32}H_{35}FeO_4PSi$ (598.5) requires C: 64.22 H: 5.89; Found C: 63.95 H: 5.80.

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