Iron-Mediated Conversions of Eucarvone-Derived Cationic Dienyl Complexes

Andreas Hirschfelder, Daniel Drost, Sven Meinhardt, and Peter Eilbracht*

Organische Chemie I (FB 3), Universität Dortmund,
Otto-Hahn-Straße 6, D-44221 Dortmund, Germany

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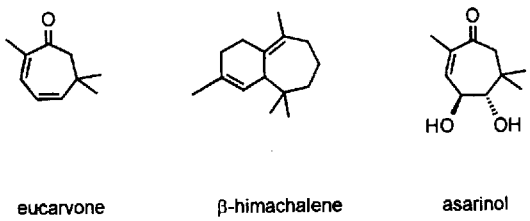
Cationic cycloheptadienyl iron complexes with new substitution patterns are generated by starting from the eucarvone complex **5** and the analogous triphenyl phosphite complex **6**. These complexes are converted with different nucleophiles. Regioselectivity of the nucleophilic attack depends on the substitution pattern of the seven-membered ring. A new type of cationic system **7b**, bearing an alkoxy substituent at C-1, was treated with nucleophiles leading to the *ipso* adducts of type **10**. Unexpected attack at the central C-3 of the dienyl moiety is observed during the conversion of cationic complexes of type **9** with nucleophiles. The diene iron complexes, obtained in these reactions, can be converted to substituted cycloheptadienes by oxidative decomplexation, as shown by a selected example.

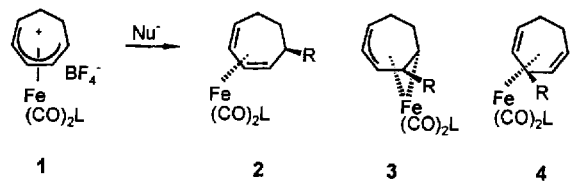
Numerous terpenoid natural products, such as β-himalachene[1] or asarinol[2], are containing the carbon skeleton of eucarvone. Although readily available from carvone[3], only a few examples of seven-membered ring natural product syntheses make use of eucarvone as starting material, presumably due to a lack of effective methods for a regio- and stereoselective introduction of further substituents and functionalities into the various positions of the seven-membered ring system.

Scheme 1



An attractive methodology meeting this goal is offered by the addition of carbon and heteroatom nucleophiles to cationic cycloheptadienyl iron complexes[4–8]. The regioselectivity of this reaction type, however, is very sensitive to changes in ring size, substitution pattern, ligands attached to the metal, the reaction conditions and the type of nucleophile[4–8]. Thus, treatment of cation **1** (L = CO) with hydride as nucleophile yields the diene complex **2** (L = CO) by attack at C-1 in competition with attack at C-2 leading to the σ-alkyl-π-allyl complex **3** (L = CO). Addition at C-3 is not observed here and only reported in a few cases with other dienyl complexes of various metals and ligand types[9–13]. The regioselectivity of nucleophilic attack to cycloheptadienyl ligands can be influenced by exchange of one CO ligand for a poorer π acceptor ligand like $P(OPh)_3$ or $P(Ph)_3$. Here, treatment of **1** [L = $P(OPh)_3$] with $NaBH_4$ leads to an enhanced formation of **3** [L = $P(OPh)_3$][5]. Similarly, the product selectivity can be affected by the choice of the nucleophile. Following a general rule[5–6], the attack of "soft" nucleophiles leads to η^4-diene complexes **2** [L = $P(OPh)_3$, $P(Ph)_3$] by addition at the terminal C-1 or C-5 (orbital control), whereas the attack of "hard" nucleophiles yields σ-alkyl-π-allyl complexes **3** [L = $P(OPh)_3$, $P(Ph)_3$] by addition at C-2 or C-4 (charge control)[5–6]. This is in line with rules earlier established for the nucleophilic attack to odd open ligands[14–15]. However, while for allyl ligands the terminal and internal attack can reliably be predicted, a similar rule allowing a decision between C-1/C-5 vs. C-3 attack is not available[14–15].

Scheme 2



L = CO, PPh_3, $P(OPh)_3$

R = H, alkyl, aryl, alkynyl, CN

These rules, however, cannot be generalized. For example, the conditions allowing selective attack at C-2/C-4 and formation of synthetically interesting alkyl-allyl complexes of type **3** cannot be applied to the corresponding six-membered ring systems[8]. Similarly, only few information is available for the nucleophilic attack to higher substituted cycloheptadienyl systems. Indeed, our investigations with eucarvone-derived complexes of this type show regioselectivities, which are not easily predicted and, in part, unusual for monocyclic cycloheptadienyl cation complexes.

We report on the synthesis and conversion of several cycloheptadienyl cation complexes with various substitution patterns starting from eucarvone and their reactivity towards nucleophiles. Complex **5**[16] is obtained by treatment of eucarvone with nonacarbonyldiiron. Exchange of

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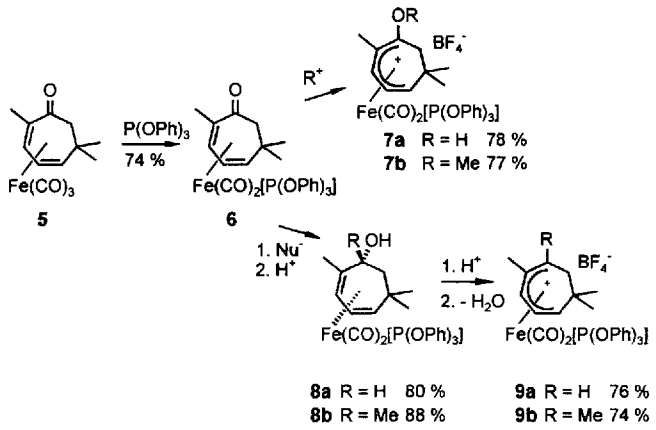
one CO ligand for $P(OPh)_3$ is achieved by treatment of complex **5** with triphenyl phosphite leading to complex **6**.

Selective transformation of the eucarvone carbonyl group within the complex leads to the required cationic systems. More effective than the reported conversion of **5**[16], reduction of complex **6** with $LiAlH_4$ gives the new complex **8a** in good yields. Similarly, the substituted complex **8b** can be obtained by treatment of **6** with methyllithium, whereas the tricarbonyliron complex **5** reacts unselectively. The complexes obtained are isolated as single diastereoisomers. Following the results of similar conversions[17], the stereochemistry at C-1 can be assigned as shown in Scheme 3. Complexes of type **8** are converted to cationic systems of type **9** by treatment with HBF_4. Using this procedure further examples of substituted complexes of type **8** and **9** (R = Ph) are obtained starting from compound **6**[18].

Scheme 3

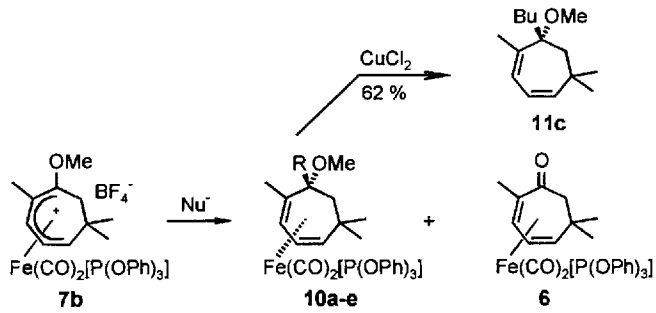


An alternative pathway to cationic cycloheptadienyl complexes of type **7** is achieved by addition of electrophiles to the oxygen atom of the carbonyl group of complex **6**. Cation **7a** is prepared by conversion of complex **6** with tetrafluoroboric acid, while treatment of **6** with the Meerwein salt $[(CH_3)_3O]BF_4$ leads to the *O*-alkylated complex **7b**.

The methods described above provide a useful synthetic approach to cycloheptadienyl cation complexes of type **7** and **9** bearing various substituents (R = H, CH_3, OCH_3) directly attached to the cycloheptadienyl subunit. Since complex **7b**, bearing an alkoxy substituent in of the terminal position, has not been accessible up to now, the conversion of this compound with nucleophiles is of special interest. Using different nucleophiles, we studied the influence of the predetermined substitution pattern on the regioselectivity of the nucleophilic addition in the following reactions.

Conversion of the complex **7b** with organolithium compounds (MeLi, BuLi, PhLi) and $NaBH_4$ leads to the η^4-diene complexes of the type **10** as sole products resulting from nucleophilic attack at C-1. Treatment of complex **7b** with sodium cyanide unselectively gives a mixture of **10e** and **6** in a 2:1 ratio. In contrast to the reactions described above, here the cationic complex **7b** does not only undergo nucleophilic addition. It also reacts as a methylating agent regenerating the eucarvone complex **6**. Similarly, by the transformation of **7b** with lithium dimethylcuprate yields complex **6** as the sole isolable product. The results are compiled in Table 1. The observed *ipso*-directing effect of the methoxy subunit is also observed in conversions of related cationic complexes[19-22].

Scheme 4



	R	Reagent	10a-e	6
a	H	$NaBH_4$	86 %	--
b	Me	MeLi	73 %	--
c	Bu	*n*BuLi	74 %	--
d	Ph	PhLi	56 %	--
e	CN	NaCN	49 %	24 %
f	Me	Me_2CuLi	--	29 %

Various methods for the decomplexation of organic ligands from iron complexes are known[23-25]. As an example **10c** was chosen to liberate the organic ligand from the η^4-diene complex. In our hands the most successful method of degradation is the oxidative decomplexation using copper(II) chloride.

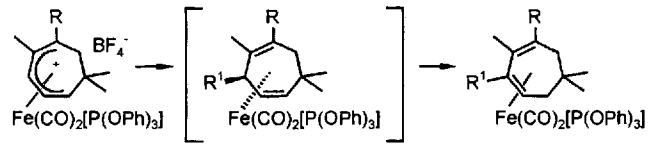
Treatment of cations of type **9** with nucleophiles shows different regioselectivities if compared with cations of type **7**. In contrast to the reactions described above, conversion of **9a** and **9b** with $NaBH_4$ and lithium dimethylcuprate unselectively results in a mixture of isomeric products which could not be separated by column chromatography.

On the other hand, treatment of **9a** with MeLi gives the symmetrical complex **13a** as the sole isolable product. The formation of this complex can be interpreted to proceed by an unusual attack at C-3, leading to **12a** as an intermediate compound, followed by regioselective hydrogen migration affording the η^4-diene complex **13a**. Similarly, the conversion of **9a** with PhLi and the reactions of **9b** with these organolithium compounds (MeLi and PhLi) proceed by addition at C-3 and hydrogen migration leading to the η^4-diene complexes **13b–c**.

Thus, these results give new insight into the behaviour of higher substituted cycloheptadienyl cationic complexes and offer new pathways to substituted seven-membered ring systems, which can be obtained from the corresponding carbonyliron complexes of type **13** by oxidative decomplexation.

As observed in our investigation, addition of appropriate nucleophiles to sterically loaded cationic systems like **7b** or **9** regioselectively occurs in different positions, depending on the substitution pattern. This either directly or by hydro-

Scheme 5



9a R = H
9b R = Me

12

13a R = H, R¹ = Me
13b R = H, R¹ = Ph
13c R = Me, R¹ = Me
13d R = Me, R¹ = Ph

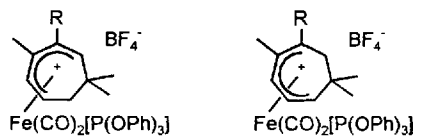
	Reagent	R	Product	R	Yield
9a	MeLi	H	**13a**	Me	55 %
9b	PhLi	H	**13b**	Ph	75 %
9c	MeLi	Me	**13c**	Me	59 %
9d	PhLi	Me	**13d**	Ph	61 %

gen migration leads to 1,3-diene complexes. The expected attack of "hard" nucleophiles at C-2 as observed in other cases[4–7] does not take place here. Thus, the regioselectivity of these transformations can not be easily predicted by general rules reflecting charge and orbital control within non-substituted and unstrained "open-odd" ligands[14,15].

The contradicting product selectivities as observed above can be explained with a change of the charge distribution in the cationic systems of type **1** [L = $P(OPh)_3$] and **9** due to the additional substituents. As shown by Pearson and coworkers ^{13}C-NMR spectroscopical investigations reveal[6] that the positive charge in compound **1** is mainly located at C-2 and C-4 of the dienyl system. The ^{13}C-NMR data of compound **9**, however, indicate that here C-3 carries the highest positive charge in the dienyl moiety. Thus, the conversion of cation **9** with "hard" nucleophiles such as MeLi or PhLi can be interpreted as a charge-controlled reaction. The observed change in charge distribution must be attributed to steric and/or electronic effects of the additional substituents.

In order to support this argumentation, analogous investigations of cationic systems of type **14**, bearing the dienyl moiety in the alternative position within the same carbon skeleton, are in progress.

Scheme 6



14
R = H, OMe

9
R = H, Me

Furthermore, the application of the methods described above to enantiomerically pure tricarbonyliron eucarvone complex **5** offers an access to optically active carbonyliron complexes of seven-membered ring systems (e.g. of type **9** and **13** and derivatives thereof). According to preliminary results[26] the enantiomerically enriched eucarvone tricarbonyliron complex is available in medium to good enantiomeric excess by enantioselective complexation or by kinetic resolution of racemic **5**. Thus, formation and decomplexation of the organic ligands of type **11** should lead to cycloheptadienes with defined stereochemistry at C-1.

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Experimental

All procedures were performed under dry argon, and anhydrous solvents were used – The (cycloheptadiene)iron complex **5** was prepared according to a literature procedure[16]. – NMR: Bruker AM 300 at 300 MHz and 75.5 MHz (^1H, ^{13}C, with TMS as standard in $CDCl_3$). – ^{13}C NMR: CH-decoupled, DEPT-135 pulse sequence. – CH analyses: Leco Elements Analyser CHNS-932. – IR: Shimadzu IR 470. – MS: Finnigan CA 5.

Dicarbonyl[2-5-η-(2,6,6-trimethyl-2,4-cycloheptadien-1-one)]-(triphenyl phosphite)iron (**6**): To a solution of 20.4 g (70.0 mmol) of **5** in 150 ml of di-*n*-butyl ether a solution of 24.0 g (77.0 mmol) of triphenyl phosphite in 50 ml of di-*n*-butyl ether was added dropwise at 140 °C. The resulting mixture was heated at reflux for 4 h, filtered through alumina and washed with dichloromethane. Removal of the solvent under reduced pressure gave 29.8 g (74%) of **6** as orange crystals, m.p. 124–126 °C. – IR (KBr/solid): $\tilde{\nu}$ = 1655 cm^{-1} [ν(CO)], 1928, 1965 [ν(Fe(CO)$_2$)]. – ^1H NMR ($CDCl_3$): δ = 0.84 (s, 3H, 6-CH_3), 0.93 (s, 3H, 6-CH_3), 1.45 (d, J = 4.4 Hz, 3H, 2-CH_3), 1.58 (dd, ^2J = 11.4, J = 1.4 Hz, 1H, 7-H), 1.71 (d, ^2J = 11.4 Hz, 1H, 7-H), 2.72 (dd, J = 13.5, 8.1 Hz, 1H, 5-H), 4.49 (m_c, 1H, 4-H), 5.12 (d, J = 5.3 Hz, 1H, 3-H), 7.15–7.38 (m, 15H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 22.9 (s, CH_3), 28.3 (s, CH_3), 36.8 (s, CH_3), 47.3 (d, J_{C-P} = 6.0 Hz, C_q, C-6), 52.1 (s, CH_2, C-7), 67.4 (d, J_{C-P} = 12.0 Hz, C_q, C-2), 72.8 (d, J_{C-P} = 11.5 Hz, CH, C-5), 82.2 (s, CH), 96.2 (s, CH), 120.7 (d, J_{C-P} = 4.5 Hz, CH, Ph-C-*o*), 125.1 (s, CH, Ph-C-*p*), 129.8 (s, CH, Ph-C-*m*), 151.1 (d, J_{C-P} = 8.0 Hz, C_q, P–O–C), 207.5 (d, J_{C-P} = 3.4 Hz, C_q, C-1), 209.3 (d, J_{C-P} = 33.9 Hz, CO), 217.4 (d, J_{C-P} = 14.9 Hz, CO). – MS (EI, 70 eV), *m/z* (%): 572 (12) [M^+], 543 (100) [M^+ – CO – 1], 366 (4) [Fe[P(OPh)$_3$]$^+$], 310 (42) [P(OPh)$_3^+$], 150 (12) [M^+ – Fe(CO)$_2$-P[(OPh)]$_3$], 77 (33) [Ph^+]. – $C_{30}H_{29}FeO_6P$ (572.4): calcd. C 62.95, H 5.11; found C 63.00, H 5.11.

Dicarbonyl[2-5-η-(2,6,6-trimethyl-2,4-cycloheptadien-1-ol)](triphenyl phosphite)iron (**8a**): A solution of 13.0 g (22.7 mmol) of **6** in 50 ml of diethyl ether was cooled to –78 °C. To this solution 2.6 g (68.5 mmol) of $LiAlH_4$ in 20 ml of diethyl ether was added dropwise. After stirring for 1.5 h at –78 °C, the mixture was treated with ethyl acetate and hydrogen chloride (10%), extracted with diethyl ether and dried with Na_2SO_4. The solvent was removed under reduced pressure to afford the crude product, which after recrystallization from pentane/dichloromethane (5:1) gave 10.5 g (80%) of **8a** as yellow crystals (m.p. 135–136 °C). – IR (KBr/solid): $\tilde{\nu}$ = 1915 cm^{-1}, 1996 [ν(Fe(CO)$_2$)], 3625 [ν(OH)]. – ^1H NMR ($CDCl_3$): δ = 0.76 (s, 3H, 6-CH_3), 0.88 (s, 3H, 6-CH_3), 1.01 (dd, ^2J = 14.6, ^3J = 3.6 Hz, 1H, 7-H), 1.23 (dd, ^2J = 14.6, ^3J = 3.6 Hz, 1H, 7-H), 1.52 (d, J = 3.6 Hz, 3H, 2-CH_3), 1.56 (s, 1H, OH), 2.52 (dd, J = 14.9, 7.8 Hz, 1H, 5-H), 3.68 (br s, 1H, 1-H), 4.38–4.44 (m, 2H, 3, 4-H), 7.14–7.37 (m, 15H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 30.3 (s, CH_3), 30.6 (s, CH_3), 32.7 (s, C_q, C-6), 38.3 (s, CH_3), 44.1 (s, CH_2, C-7), 72.4 (d, J_{C-P} = 10.7 Hz, CH, C-1 or C-5), 73.6 (s, CH, C-1 or C-5), 75.9 (d, J_{C-P} = 19.7 Hz, C_q, C-2), 81.9 (s, CH), 92.6 (s, CH), 120.9 (d, J_{C-P} = 4.4 Hz, CH, Ph-C-*o*), 124.7 (s, CH,

Ph-C-*p*), 129.7 (s, CH, Ph-C-*m*), 151.4 (d, J_{C-P} = 7.5 Hz, C_q, P–O–C), 211.9 (d, J_{C-P} = 32.3 Hz, CO), 219.7 (d, J_{C-P} = 10.4 Hz, CO). – MS (EI, 70 eV), *m/z* (%): 518 (16) [M^+ – 2 CO], 500 (25) [M^+ – 2 CO – H_2O – 1], 366 (18) [FeP[(OPh)$_3$]$^+$], 310 (45) [P(OPh)$_3^+$], 152 (15) [M^+ – Fe(CO)$_2$[P(OPh)$_3$]], 77 (42) [Ph^+]. – $C_{30}H_{31}FeO_6P$ (574.4): calcd. C 62.73, H 5.44; found C 62.60, H 5.50.

Dicarbonyl[1-5-η-(2,6,6-trimethylcycloheptadienyl)](triphenyl phosphite)iron Tetrafluoroborate (**9a**): To a mixture of 10.5 g (18.3 mmol) of **8a**, 5 ml of propionic anhydride, and 125 ml of dichloromethane a solution of 3 ml of tetrafluoroboric acid (54% in ether) in 3 ml of diethyl ether was added. After 40 ml of ice had been added, the solution was stirred for 1.5 h at room temp. The yellow precipitate was filtered and dried in vacuo to afford 9.0 g (76%) of **9a** as a white solid, m.p. 149–151°C. – IR (KBr/solid): $\tilde{\nu}$ = 2010 cm^{-1}, 2060 [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.69 (s, 3H, 6-CH_3), 1.16 (s, 3H, 6-CH_3), 1.95 (s, 3H, 2-CH_3), 2.07 (dd, ^2J = 16.6, ^3J = 4.5 Hz, 1H, 7-H), 2.69 (dd, ^2J = 16.6, ^3J = 4.5 Hz, 1H, 7-H), 3.97 (d, ^3J = 7.9 Hz, 1H, 5-H), 4.34 (br s, 1H, 1-H), 5.68 (d, ^3J = 5.7 Hz, 1H, 3-H), 5.83 (m, 1H, 4-H), 7.25–7.50 (m, 15H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 26.2 (s, CH_3), 32.2 (s, CH_3), 33.3 (s, CH_3), 40.4 (d, J_{C-P} = 4.0 Hz, C_q, C-6), 50.0 (s, CH_2, C-7), 85.1 (d, J_{C-P} = 9.8 Hz, CH, C-1), 97.2 (s, CH, C-4), 98.4 (s, CH, C-5), 99.0 (s, CH, C-3), 117.2 (C_q, C-2), 120.4 (d, J_{C-P} = 3.9 Hz, CH, Ph-C-*o*), 126.5 (CH, Ph-C-*p*), 130.4 (CH, Ph-C-*m*), 149.7 (d, J_{C-P} = 9.5 Hz, P–O–C), 203.3 (d, J_{C-P} = 41.5 Hz, CO), 211.9 (d, J_{C-P} = 23.5 Hz, CO). – MS (FAB), *m/z* (%): 557 (72) [M^+ – BF_4^-], 501 (100) [M^+ – BF_4^- – 2 CO], 366 (14) [Fe[P(OPh)$_3$]$^+$], 77 (11) [Ph^+]. – $C_{30}H_{30}BF_4FeO_5P$ (644.2): calcd. C 55.94, H 4.69; found C 55.80, H 4.80.

Dicarbonyl[1-4-η-(2,3,6,6-tetramethyl-1,3-cycloheptadiene)](triphenyl phosphite)iron (**13a**): A solution of 1.5 g (2.3 mmol) of **9a** in 15 ml of dichloromethane was cooled to –78°C. Then 2.7 ml of methyllithium (*c* = 1.6 mol/l, in diethyl ether, 4.3 mmol) was added, and the mixture was stirred for 20 min at room temp. The mixture was then diluted with 1 ml of methanol and 20 ml of dichloromethane. The organic layer was separated and washed three times with water. The solution was dried with Na_2SO_4 and the solvent removed under reduced pressure. Purification of the resulting residue by column chromatography on silica gel using dichloromethane as eluent gave 0.7 g (53%) of **13a** as yellow crystals, m.p. 109–110°C. – IR (KBr/solid): $\tilde{\nu}$ = 1927 cm^{-1}, 1984 [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.62 (s, 3H, 6-CH_3), 0.71 (s, 3H, 6-CH_3), 1.67–1.69 (m, 4H, 5,7-H), 1.97 (s, 6H, 2-CH_3, 3-CH_3), 2.43 (m, 2H, 1,4-H), 7.10–7.32 (m, 15H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 21.0 (s, CH_3), 27.0 (s, CH_3), 31.6 (s, C_q, C-6), 33.8 (s, 2 CH_3), 40.7 (s, CH_2, C-5,7), 55.6 (s, CH, C-1,4), 100.1 (s, C_q, C-2,3), 121.4 (d, J_{C-P} = 3.8 Hz, CH, Ph-C-*o*), 124.4 (s, CH, Ph-C-*p*), 129.5 (s, CH, Ph-C-*m*), 151.6 (d, J_{C-P} = 8.3 Hz, P–O–C), 215.3 (d, J_{C-P} = 15.1 Hz, CO). – MS (EI, 70 eV), *m/z* (%): 544 (18) [M^+ – CO], 516 (27) [M^+ – 2 CO], 366 (100) [Fe[P(OPh)$_3$]$^+$], 77 (6) [Ph^+]. – High resolution MS: (572.42 – 2 CO) 516.1516, calculated for $C_{29}H_{33}FeO_3P$: 516.1517.

Dicarbonyl[1-4-η-(3,6,6-trimethyl-2-phenyl-1,3-cycloheptadiene)](triphenyl phosphite)iron (**13b**): Conversion of 1.5 g (2.3 mmol) of **9a** in 15 ml of dichloromethane with 2.7 ml of phenyllithium (*c* = 1.6 mol/l, in diethyl ether, 4.3 mmol) as described above and chromatography (silica gel, PE/MTBE, 10:1) gave 1.1 g (75%) of **13b** as yellow crystals, m.p. 116–118°C. – IR (KBr/solid): $\tilde{\nu}$ = 1931 cm^{-1}, 1991 [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.68 (s, 3H, 6-CH_3), 0.90 (s, 3H, 6-CH_3), 1.50–1.86 (m, 4H, 5,7-H), 2.10 (s, 3H, 3-CH_3), 2.48 (m_c, 2H, 1,4-H), 7.02–7.57 (m, 20H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 21.3 (s, CH_3), 27.4 (s, CH_3), 31.8 (s, C_q, C-6), 34.0 (s, CH_3), 40.4 (s, CH_2), 41.0 (s, CH_2), 53.0 (d, J_{C-P} = 12.4 Hz, CH, C-1 or C-4), 54.1 (d, J_{C-P} = 6.6 Hz, CH, C-4 or C-1), 102.5 and 104.8 (s, 2 C_q, C-2,3), 121.2 (d, J_{C-P} = 4.5 Hz, CH, Ph-C-*o*), 124.5 (s, CH, Ph-C-*p*), 126.9 (s, CH, 2-Ph-*o*), 127.4 (s, CH, 2-Ph-*p*), 129.6 (s, CH, Ph-C-*m*), 130.8 (s, CH, 2-Ph-*m*), 140.6 (s, C_q, P–O–C), 151.6 (d, J_{C-P} = 4.7 Hz, C_q, P–O–C), 212.5 (s, CO). – MS (EI, 70 eV), *m/z* (%): 634 (2) [M^+], 606 (20) [M^+ – CO], 578 (13) [M^+ – 2 CO], 366 (100) [Fe[P(OPh)$_3$]$^+$], 77 (6) [Ph^+]. – $C_{36}H_{35}FeO_5P$ (634.5): calcd. C 68.15, H 5.81; found C 68.10, H 5.60.

Dicarbonyl[2-5-η-(1,2,6,6-tetramethyl-2,4-cycloheptadien-1-ol)](triphenyl phosphite)iron (**8b**): Conversion of 10.0 g (17.4 mmol) of **6** in 30 ml of dichloromethane and 110 ml of diethyl ether with 12.5 ml of methyllithium (*c* = 1.6 mol/l, in diethyl ether, 20.0 mmol) as described above gave 9.1 g (88%) of **8b** as yellow crystals, m.p. 115–117°C. – IR (KBr/solid): $\tilde{\nu}$ = 1919 cm^{-1}, 1935 [ν(Fe(CO)$_2$)], 3615 [ν(OH)]. – ^{1}H NMR ($CDCl_3$): δ = 0.81 (s, 3H, 6-CH_3), 0.82 (s, 3H, 6-CH_3), 1.12 (d, ^2J = 14.1 Hz, 1H, 7-H), 1.18 (s, 3H, CH_3), 1.20 (d, ^2J = 14.1 Hz, 1H, 7-H), 1.55 (s, 3H, CH_3), 1.56 (m, 1H, OH), 2.60 (dd, *J* = 14.6, 7.5 Hz, 1H, 5-H), 4.38–4.41 (m, 2H, 3,4-H), 7.16–7.36 (m, 15H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 27.7 (s, CH_3), 31.7 (s, CH_3), 33.1 (d, J_{C-P} = 3.5 Hz, C_q, C-6), 33.4 (s, CH_3), 37.0 (s, CH_3), 54.5 (s, CH_2, C-7), 73.9 (s, CH, C-5), 81.8 (s, C_q, C-1 or C-2), 82.1 (s, C_q, C-1 or C-2), 83.1 (s, CH), 92.6 (s, CH), 120.4 (d, J_{C-P} = 3.9 Hz, CH, Ph-C-*o*), 126.5 (s, CH, Ph-C-*p*), 130.4 (s, CH, Ph-C-*m*), 151.5 (d, J_{C-P} = 7.6 Hz, C_q, P–O–C), 211.9 (d, J_{C-P} = 32.7 Hz, CO), 219.9 (d, J_{C-P} = 10.0 Hz, CO). – MS (EI, 70 eV), *m/z* (%): 570 (2) [M^+ – H_2O], 542 (14) [M^+ – H_2O – CO], 514 (100) [M^+ – H_2O – 2 CO], 366 (48) [Fc[P(OPh)$_3$]$^+$], 310 (38) [P(OPh)$_3$], 94 (53) [PhOH]. – $C_{31}H_{33}FeO_6P$ (588.4): calcd. C 63.28, H 5.65; found C 63.10, H 5.70.

Dicarbonyl[1-5-η-(1,2,6,6-tetramethylcycloheptadienyl)](triphenyl phosphite)iron Tetrafluoroborate (**9b**): To a mixture of 8.6 g (14.6 mmol) of **8b**, 5 ml of propionic anhydride and 100 ml of dichloromethane a solution of 3 ml of tetrafluoroboric acid (54% in ether) in 3 ml of diethyl ether was added. After 40 ml of ice had been added, the solution was stirred for 1.5 h at room temp. The precipitated yellow crystals were filtered and dried in vacuo to afford 8.0 g (74%) of **9b** as a yellow solid, m.p. 115–117°C. – IR (KBr/solid): $\tilde{\nu}$ = 2059 cm^{-1}, 1999 [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.81 (s, 3H, 6-CH_3), 1.33 (s, 3H, 6-CH_3), 1.78 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.06–2.19 (m, 2H, 7-H), 4.04 (s, 1H, 5-H), 5.5–5.7 (m, 2H, 4,3-H), 7.25–7.47 (m, 15H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 22.0 (s, CH_3), 27.4 (s, CH_3), 31.9 (s, CH_3), 34.1 (s, CH_3), 46.6 (s, C_q, C-6), 52.3 (s, CH_2, C-7), 96.2 (s, CH), 97.8 (s, CH), 98.1 (s, CH), 104.6 (d, J_{C-P} = 11.4 Hz, C_q, C-1), 115.7 (s, C_q, C-2), 120.4 (d, J_{C-P} = 4.0 Hz, CH, Ph-C-*o*), 126.5 (s, CH, Ph-C-*p*), 130.5 (s, CH, Ph-C-*m*), 149.8 (d, J_{C-P} = 9.6 Hz, C_q, P–O–C), 204.8 (d, J_{C-P} = 41.6 Hz, CO), 213.3 (d, J_{C-P} = 21.9 Hz, CO). – MS (FAB), *m/z* (%): 571 (100) [M^+ – BF_4^-], 515 (46) [M^+ – 2 CO – BF_4^-], 366 (46) [Fe[OPh)$_3$]$^+$], 77 (16) [Ph^+]. – $C_{31}H_{32}BF_4FeO_5P$ (658.2): calcd. C 56.57, H 4.90; found C 56.50, H 4.90.

Dicarbonyl[1-4-η-(1,2,3,6,6-pentamethyl-1,3-cycloheptadiene)](triphenyl phosphite)iron (**13c**): At –78°C a solution of 2.8 ml of methyllithium (*c* = 1.6 mol/l, in diethyl ether, 4.5 mmol) was added dropwise to a solution of 2.0 g (3.0 mmol) **9b** in 15 ml of dichloromethane, and the mixture was stirred for 20 min at room temp. It was then diluted with 1 ml of methanol and 20 ml of dichloromethane, the organic layer was separated and washed three times with water. The solution was dried with Na_2SO_4, and the solvent

was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, dichloromethane) gave as the second fraction 1.1 g (59%) of **13c** as a yellow oil. IR (NaCl/film): $\tilde{\nu}$ = 1982 cm^{-1}, 1924 [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.65 (s, 3H, 6-CH_3), 0.68 (s, 3H, 6-CH_3), 1.43–1.47 (m, 1H), 1.45 (d, J = 4.2 Hz, 3H, CH_3), 1.59 (m, 2H), 1.97–1.99 (m, 1H), 1.98 (s, 3H, CH_3), 2.05 (d, J = 2.4 Hz, 3H, CH_3), 2.49 (dt, J = 14.8, 4.2 Hz, 1H, 4-H), 7.11–7.33 (m, 15H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 16.7 (s, CH_3), 22.7 (s, CH_3), 26.8 (s, CH_3), 30.8 (s, CH_3), 33.9 (s, CH_3), 40.7 (s, C_q, C-6), 49.7 (s, 2 CH_2, C-5,7), 55.6 (d, J_{C-P} = 10.5 Hz, CH, C-4), 64.2 (d, J_{C-P} = 14.1 Hz, C-1), 97.8 (s, C_q), 101.3 (s, C_q), 120.9 (d, J_{C-P} = 4.5 Hz, CH, Ph-C-*o*), 124.3 (CH, Ph-C-*p*), 129.5 (s, CH, Ph-C-*m*), 151.7 (d, J_{C-P} = 8.9 Hz, Cq, P–O–C), 212.5 (d, J_{C-P} = 27.5 Hz, CO). – MS (EI, 70 eV), *m/z* (%): 559 (22) [M^+ – CO – 1], 531 (8) [M^+ – 2 CO – 1], 366 (100) [Fe[P(OPh)$_3$]$^+$], 77 (13) [PH^+].

Dicarbonyl[1-4-η-(1,2,6,6-tetramethyl-3-phenyl-1,3-cycloheptadiene)](triphenyl phosphite)iron (**13d**): Conversion of 2.0 g (3.0 mmol) of **9b** in 15 ml of dichloromethane with 2.4 ml of phenyllithium (c = 1.6 mol/l, in diethyl ether, 4.5 mmol) as described above and chromatography (silica gel, PE/MTBE, 5:1) afforded as the second fraction 1.2 g (61%) of **13d** as yellow crystals, m.p. 130–131 °C. – IR (KBr/solid): $\tilde{\nu}$ = 1991 cm^{-1}, 1934 [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.95 (s, 3H, 6-CH_3), 1.12 (s, 3H, 6-CH_3), 1.73 (m, 1H), 1.75 (s, 3H, CH_3), 1.99 (br s, 2H), 2.32 (s, 3H, CH_3), 2.47 (br d, J = 15.9 Hz, 1H), 2.79 (m, 1H), 7.22–7.74 (m, 20H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 17.2 (s, CH_3), 27.1 (s, CH_3), 31.3 (s, CH_3), 34.2 (s, CH_3), 40.9 (s, C_q, C-6), 48.9 (s, 2 CH_2, C-5,7), 52.5 (d, J_{C-P} = 10.5 Hz, CH, C-4), 63.1 (d, J_{C-P} = 6.3 Hz, C_q, C-1), 101.9 (s, C_q, C-2 or C-3), 104.3 (s,C_q, C-3 or C-2), 121.2 (d, J_{C-P} = 3.9 Hz, CH, Ph-C-*o*), 124.3 (s, CH, Ph-C-*p*), 126.9 (s, CH, 2-Ph-C-*o*), 127.1 (s, CH, 2-Ph-C-*p*), 129.4 (s, CH, Ph-C-*m*), 131.9 (s, CH, 2-Ph-C-*m*), 141.5 (s, C_q, Ph-C-*ipso*), 151.9 (d, J_{C-P} = 10.5 Hz, C_q, P–O–C), 212.0 (d, J_{C-P} = 20.6 Hz, CO). – MS (EI, 70 eV), *m/z* (%): 620 (13) [M^+ – CO], 592 (8) [M^+ – 2 CO], 514 (9) [M^+ – 2 CO – C_6H_5], 366 (100) [Fe[P(OPh)$_3$]$^+$], 77 (10) [Ph^+]. – $C_{37}H_{37}FeO_5P$ (648.5): calcd. C 68.53, H 5.75; found C 68.60, H 5.70.

Dicarbonyl[1-5-η-(2,6,6-trimethylcycloheptadien-1-ol)](triphenyl phosphite)iron Tetrafluoroborate (**7a**): To a solution of 1.0 g (1.7 mmol) of **6** in 5 ml of dichloromethane 1 ml of tetrafluoroboric acid (54% in ether) was added at 0 °C. After 15 min 5 ml of dicthyl ether was added and the yellow precipitate was filtered. Recrystallization from diethyl ether and dichloromethane gave 0.8 g (71%) of **7a** as yellow crystals, m.p. 140–141 °C. – IR (KBr/solid): $\tilde{\nu}$ = 2045 cm^{-1}, 1998 [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.83 (s, 3H, 6-CH_3), 1.24 (s, 3H, 6-CH_3), 1.79 (s, 3H, 2-CH_3), 2.12 (d, ^2J = 15.5 Hz, 1H, 7-H), 2.82 (d, ^2J = 15.5 Hz, 1H, 7-H), 3.48 (br s, 1H, 5-H), 5.20 (br s, 1H, 4-H), 5.30 (br s, 1H, 3-H), 7.19–7.59 (m, 15H, Ph). OH proton not detected. – ^{13}C NMR ($CDCl_3$): δ = 20.6 (s, CH_3), 31.4 (s, CH_3), 34.8 (s, CH_3), 44.5 (s, C_q, C-6), 50.2 (s, CH_2, C-7), 85.6 (s, CH, C-5), 86.8 (s, C_q, C-2), 90.6 (s, CH, C-3 or C-4), 94.6 (s, CH, C-3 or C-4), 120.5 (d, J_{C-P} = 3.8 Hz, CH, Ph-C-*o*), 126.4 (s, CH, Ph-C-*p*), 130.4 (s, CH, Ph-C-*m*), 150.1 (d, J_{C-P} = 9.0 Hz, C_q, P–O–C), 163.3 (s, C_q, C-1), 205.3 (d, J_{C-P} = 41.0 Hz, CO), 213.4 (d, J_{C-P} = 20.2 Hz, CO). – MS (FAB), *m/z* (%): 573 (77) [M^+ – BF_4^-], 517 (100) [M^+ – 2 CO – BF_4^-], 366 (40) [Fe[P(OPh)$_3$]$^+$].

Dicarbonyl[1-5-η-(1-methoxy-2,6,6-trimethylcycloheptadienyl)](triphenyl phosphite)iron Tetrafluoroborate (**7b**): To a solution of 5.0 g (8.7 mmol) of **6** in 25 ml of dichloromethane 2.7 g (0.02 mol) of trimethyloxonium tetrafluoroborate was added at room temp. The suspension was stirred for 60 h at room temp. and washed with water. The organic layer was separated, dried with $MgSO_4$ and the solvent removed under reduced pressure. The product was precipitated by pouring the resulting brown oil into diethyl ether to afford 4.5 g (77%) of **7b** as a yellow powder, m.p. 148–149 °C. – IR (KBr/solid): $\tilde{\nu}$ = 2061 cm^{-1}, 1999 [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.85 (s, 3H, 6-CH_3), 1.35 (s, 3H, 6-CH_3), 1.84 (s, 3H, 2-CH_3), 2.03 (d, ^2J = 15.7 Hz, 1H, 7-H), 2.90 (d, ^2J = 15.7 Hz, 1H, 7-H), 3.67 (dd, J = 8.5, 3.7 Hz, 1H, 5-H), 3.85 (s, 3H, OCH_3), 5.58 (m, 2H, 3,4-H), 7.21–7.53 (m, 15H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 20.6 (s, CH_3), 32.1 (s, CH_3), 34.1 (s, CH_3), 43.0 (d, J_{C-P} = 5.0 Hz, C_q, C-6), 46.1 (s, CH_2, C-7), 57.9 (s, CH_3, OCH_3), 90.8 (d, J_{C-P} = 4.0 Hz, CH, C-5), 92.9 (s, CH), 95.3 (s, CH), 98.1 (s, C_q, C-2), 120.6 (d, J_{C-P} = 4.1 Hz, CH, Ph-C-*o*), 126.6 (s, CH, Ph-C-*p*), 130.5 (s, CH, Ph-C-*m*), 148.8 (d, J_{C-P} = 7.5 Hz, C_q, C-1), 150.1 (d, J_{C-P} = 9.2 Hz, C_q, P–O–C), 205.0 (d, J_{C-P} = 9.1 Hz, CO), 214.4 (d, J_{C-P} = 29.9 Hz, CO). – MS (FAB), *m/z* (%): 587 (100) [M^+ – BF_4^-], 531 (49) [M^+ – 2 CO – BF_4^-], 366 (47) [Fe[P(OPh)$_3$]$^+$], 77 (8) [Ph^+]. – $C_{31}H_{32}BF_4FeO_6P$ (674.2): calcd. C 55.23, H 4.78; found C 55.30, H 4.60.

Dicarbonyl[2-5-η-(1-methoxy-2,6,6-trimethyl-2,4-cycloheptadiene)](triphenyl phosphite)iron (**10a**): To a mixture of 20 ml of ice, 20 ml of water, and 40 ml of diethyl ether 0.24 g (6.4 mmol) of $NaBH_4$ was added. To the obtained mixture was then given 2.2 g (3.3 mmol) of **7b**. After 1.5 h 10 g ice was added, and the solution was extracted with diethyl ether. The organic layer was washed with water, dried with $MgSO_4$, and the solvent was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, dichloromethane) gave 1.6 g (86%) of **10a** as yellow crystals, m.p. 106–107 °C. – IR (KBr/solid): $\tilde{\nu}$ = 1994 cm^{-1}, 1934 [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.69 (dd, ^2J = 14.8, ^3J = 2.7 Hz, 1H, 7-H), 0.74 (s, 3H, 6-CH_3), 0.82 (s, 3H, 6-CH_3), 1.41 (d, ^2J = 14.8 Hz, 1H, 7-H), 1.50 (d, J = 4.7 Hz, 3H, 2-CH_3), 2.44 (dd, J = 15.8, 7.7 Hz, 1H, 5-H), 3.11 (m, 1H, 1-H), 3.25 (s, 3H, OCH_3), 4.30 (m, 1H, 4-H), 4.34 (m, 1H, 3-H), 7.11–7.34 (m, 15H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 28.6 (s, CH_3), 30.7 (s, CH_3), 33.2 (s, C_q, C-6), 36.9 (s, CH_2, C-7), 38.6 (s, CH_3), 56.5 (s, CH_3, OCH_3), 71.4 (d, J_{C-P} = 11.7 Hz, CH, C-5), 72.5 (d, J_{C-P} = 19.3 Hz, C_q, C-2), 80.6 (s, CH), 83.2 (s, CH), 92.3 (s, CH), 120.9 (d, J_{C-P} = 3.6 Hz, CH, Ph-C-*o*), 124.5 (s, CH, Ph-C-*p*), 129.6 (s, CH, Ph-C-*m*), 151.6 (d, J_{C-P} = 7.4 Hz, C_q, P–O–C), 212.1 (d, J_{C-P} = 32.5 Hz, CO), 218.9 (d, J_{C-P} = 8.3 Hz, CO). – MS (EI, 70 eV), *m/z* (%): 588 (5) [M^+], 560 (5) [M^+ – CO], 532 (42) [M^+ – 2 CO], 500 (51) [M^+ – 2 CO – OCH_3 – 1], 366 (6) [Fe[P(OPh)$_3$]$^+$], 77 (25) [Ph^+]. – $C_{31}H_{33}FeO_6P$ (588.4): calcd. C 63.28, H 5.65; found C 63.30, H 5.70.

Dicarbonyl[2-5-η-(1-methoxy-1,2,6,6-tetramethyl-2,4-cycloheptadiene)](triphenyl phosphite)iron (**10b**): To a solution of 2.0 g (3.0 mmol) of **7b** in 15 ml of dichloromethane 3.2 ml of methyllithium (c = 1.6 mol/l, in diethyl ether, 5.1 mmol) was added dropwise at –78 °C. The mixture was stirred for 20 min at room temp. It was then diluted with 1 ml of methanol and 20 ml of dichloromethane. The organic layer was separated, washed three times with water and dried with Na_2SO_4. The solvent removed under reduced pressure. Purification of the resulting residue by column chromatography (silica gel, dichloromethane) gave as the second fraction 1.3 g (73%) of **10b** as yellow crystals, m.p. 83–84 °C. – IR (KBr/solid): $\tilde{\nu}$ = 1994 cm^{-1}, 1931 [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.69 (d, ^2J = 14.5 Hz, 1H, 7-H), 0.78 (s, 3H, 6-CH_3), 0.79 (s, 3H, 6-CH_3), 1.10 (s, 3H, CH_3), 1.39 (d, ^2J = 14.5 Hz, 1H, 7-H), 1.49 (d, J = 5.2 Hz, 3H, CH_3), 2.51 (m, 1H, 5-H), 3.14 (s, 3H, OCH_3), 4.33 (m, 2H, 4,3-H), 7.13–7.36 (m, 15H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 27.7 (s, CH_3), 30.0 (s, CH_3), 30.6 (s, CH_3), 33.2 (s,

C_q, C-6), 37.6 (s, CH_3), 45.4 (s, CH_2, C-7), 49.5 (s, CH_3, OCH_3), 72.8 (d, J_{C-P} = 11.7 Hz, CH, C-5), 79.8 (s, C_q), 80.1 (s, C_q), 82.1 (s, CH), 92.5 (s, CH), 120.9 (d, J_{C-P} = 4.3 Hz, CH, Ph-C-*o*), 124.5 (s, CH, Ph-C-*p*), 129.6 (s, CH, Ph-C-*m*), 151.6 (d, J_{C-P} = 7.3 Hz, C_q, P–O–C), 212.1 (d, J_{C-P} = 33.1 Hz, CO), 218.9 (d, J_{C-P} = 8.1 Hz, CO). – MS (EI, 70 eV), *m/z* (%): 546 (16) [M^+ – 2 CO], 514 (71) [M^+ – 2 CO – OCH_3 – 1], 366 (39) [Fe[P(OPh)$_3$]$^+$], 236 (100) [M^+ – 2 CO – P(OPh)$_3$], 77 (67) [Ph^+]. – $C_{32}H_{35}FeO_6P$ (602.5): calcd. C 63.80, H 5.86; found C 64.20, H 6.00.

Dicarbonyl[2-5-η-(1-butyl-1-methoxy-2,6,6-trimethyl-2,5-cycloheptadiene)](triphenyl phosphite)iron (**10c**): Treatment of a solution of 2.0 g (3.0 mmol) of **7b** in 15 ml of dichloromethane with 3.7 ml of butyllithium (*c* = 1.22 mol/l, in hexane, 4.5 mmol) as described above and chromatography (silica gel, dichloromethane) afforded as the second fraction 1.5 g (74%) of **10c** as yellow crystals, m.p. 130–131°C. – IR (KBr/solid): $\tilde{\nu}$ = 1936 cm^{-1}, 2000 [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.71 (s, 3H, 6-CH_3), 0.72 (s, 3H, 6-CH_3), 0.77 (t, ^3J = 7.2 Hz, 3H, CH_2CH_3), 0.93–0.99 (m, 2H, CH_2), 1.13–1.14 (m, 2H, CH_2), 1.15–1.16 (m, 2H, CH_2), 1.26–1.32 (m_c, 2H, CH_2), 1.35 (d, *J* = 5.2 Hz, 3H, CH_3), 2.41 (dd, *J* = 15.5, 8.0 Hz, 1H, 5-H), 3.08 (s, 3H, OCH_3), 4.19 (m, 1H, CH, 3-H or 4-H), 4.36 (s, 1H, CH, 3-H or 4-H), 7.06–7.29 (m, 15H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (s, CH_3), 23.2 (s, CH_2), 27.1 (s, CH_2), 27.8 (s, CH_3), 30.3 (s, CH_3), 33.0 (d, $^2J_{C-P}$ = 3.7 Hz, C_q, C-6), 37.1 (s, CH_3, 2-CH_3), 40.7 (s, CH_2), 40.8 (s, CH_2), 49.2 (s, CH_3, OCH_3), 73.0 (d, J_{C-P} = 12.7 Hz, CH, C-5), 78.6 (d, J_{C-P} = 21.6 Hz, C_q), 79.8 (s, C_q), 81.2 (s, CH), 93.7 (s, CH), 120.9 (d, J_{C-P} = 5.1 Hz, CH, Ph-C-*o*), 124.4 (s, CH, Ph-C-*p*), 129.6 (s, CH, Ph-C-*m*), 151.4 (d, J_{C-P} = 7.6 Hz, C_q, P–O–C), Fe(CO) not detected. – MS (EI, 70 eV), *m/z* (%): 584 (10) [M^+ – $MCH_2CH_2CH_2CH_3$], 556 (59) [M^+ – C_4H_9 – CO], 366 (58) [Fe[P(OPh$_3$)]$^+$].

Dicarbonyl[2-5-η-(1-methoxy-2,6,6-trimethyl-1-phenyl-2,4-cycloheptadiene)](triphenyl phosphite)iron (**10d**): Treatment of a solution of 2.0 g (3.0 mmol) **7b** in 15 ml of dichloromethane with 2.7 ml of phenyllithium (*c* = 1.6 mol/l, in diethyl ether, 4.3 mmol) as described above and chromatography (silica gel, dichloromethane) furnished as the second fraction 1.1 g (56%) of **10d** as yellow crystals, m.p. 105–106°C. – IR (KBr/solid): $\tilde{\nu}$ = 1994, 1935 cm^{-1} [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.69 (s, 3H, 6-CH_3), 0.90 (m_c, 1H, 7-H), 0.92 (s, 3H, 6-CH_3), 1.18 (d, *J* = 4.8 Hz, 3H, CH_3), 1.37 (d, ^2J = 14.8 Hz, 1H, 7-H), 2.58 (dd, *J* = 15.8, 7.5 Hz, 1H, 5-H), 3.40 (s, 3H, OCH_3), 4.44 (m, 1H), 4.53 (br s, 1H), 7.12–7.38 (m, 20H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 29.3 (s, CH_3), 31.3 (s, CH_3), 33.9 (s, C_q, C-6), 38.8 (s, CH_3), 47.9 (s, CH_2, C-7), 52.5 (s, CH_3, OCH_3), 72.5 (d, J_{C-P} = 11.9 Hz, CH, C-5), 75.2 (d, J_{C-P} = 21.6 Hz, C_q), 81.7 (s, CH), 85.0 (s, C_q), 95.3 (s, CH), 120.9 (d, J_{C-P} = 4.3 Hz, CH, Ph-C-*o*), 124.7 (s, CH, Ph-C-*p*), 127.4 (s, CH, 2-Ph-C-*o*), 127.7 (s, CH, 2-Ph-C-*p*), 129.5 (s, CH, 2-Ph-C-*m*), 133.1 (s, CH, Ph-C-*m*), 147.4 (s, C_q, Ph-C-*ipso*), 151.6 (d, J_{C-P} = 7.5 Hz, C_q, P–O–C), 211.7 (d, J_{C-P} = 34.2 Hz, CO), 219.8 (d, J_{C-P} = 9.1 Hz, CO). – MS (EI, 70 eV), *m/z* (%): 576 (9) [M^+ – $HOCH_3$ – 2 CO], 366 (18) [Fe[P(OPh$_3$)]$^+$], 310 (40) [P(OPh)$_3^+$], 77 (100) [Ph^+]. – $C_{37}H_{37}FeO_6P$ (664.9): calcd. C 66.88, H 5.61; found C 66.80, H 5.60.

Dicarbonyl[2-5-η-(1-cyano-1-methoxy-2,6,6-trimethyl-2,4-cycloheptadiene)](triphenyl phosphite)iron (**10e**): To a solution of 0.2 g (4.1 mmol) of sodium cyanide in 100 ml of tetrahydrofuran and 15 ml of water cooled to 0°C 2.0 g (3.0 mmol) of **7b** was added. After 15 min, 20 ml of water was added, and the solution was extracted with diethyl ether. The organic layer was dried with $MgSO_4$, and the solvent was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, dichloromethane) gave 1.3 g (73%) of **10e** as yellow crystals, m.p. 83–84°C. – IR (KBr/solid): $\tilde{\nu}$ = 2004 cm^{-1}, 1941 [ν(Fe(CO)$_2$)]. – ^{1}H NMR ($CDCl_3$): δ = 0.77 (s, 3H, 6-CH_3), 0.80 (s, 3H, 6-CH_3), 1.07 (d, ^2J = 14.9 Hz, 1H, 7-H), 1.69 (d, *J* = 4.6 Hz, 3H, 2-CH_3), 1.72 (m_c, 1H, 7-H), 2.50 (dd, *J* = 16.1, 7.8 Hz, 1H, 5-H), 3.37 (s, 3H, OCH_3), 4.35 (m, 1H, 4-H), 4.49 (d, *J* = 4.6 Hz, 1H, 3-H), 7.17–7.40 (m, 15H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 28.1 (s, CH_3), 29.1 (s, CH_3), 33.3 (d, J_{C-P} = 5.1 Hz, C_q, C-6), 38.0 (s, 2-CH_3), 41.5 (s, CH_2, C-7), 53.5 (s, CH_3, OCH_3), 68.2 (d, J_{C-P} = 21.6 Hz, C_q, C-2), 70.5 (d, J_{C-P} = 12.1 Hz, CH, C-5), 81.1 (d, J_{C-P} = 2.6 Hz, C_q, C-1), 82.9 (s, CH), 92.3 (d, J_{C-P} = 2.1 Hz, CH), 120.1 (d, J_{C-P} = 4.6 Hz, C_q, CN), 120.8 (d, J_{C-P} = 4.6 Hz, CH, Ph-C-*o*), 124.9 (s, CH, Ph-C-*p*), 129.8 (s, CH, Ph-C-*m*), 151.3 (d, J_{C-P} = 7.8 Hz, C_q, P–O–C), 210.7 (d, J_{C-P} = 34.5 Hz, CO), 218.0 (d, J_{C-P} = 11.5 Hz, CO). – MS (EI, 70 eV), *m/z* (%): 585 (4) [M^+ – CO], 559 (3) [M^+ – 2 CO – CN], 366 (91) [FeP(OPh)$_3^+$], 77 (67) [Ph^+]. – $C_{32}H_{32}FeNO_6P$ (613.4): calcd. C 62.66, H 5.26, N 2.28; found C 62.70, H 5.30, N 2.30.

1-Butyl-1-methoxy-2,6,6-trimethyl-2,4-cycloheptadiene (**11c**): To a solution of 0.3 g (0.5 mmol) of **10c** in 10 ml of methanol and 2 ml of dichloromethane 0.4 g (2.9 mmol) of copper(II) chloride was added and the mixture stirred for 80 h at room temp. It was subsequently diluted with 30 ml of water and extracted three times with 25 ml of dichloromethane. The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. Purification of the residue by column chromatography (silica gel, PE/MTBE, 10:1) gave as the first fraction 0.07 g (62%) of **11c** as a yellow oil. – ^{1}H NMR ($CDCl_3$): δ = 0.87 (d, *J* = 6.0 Hz, 3H, CH_3), 1.04 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.59 (d, *J* = 12.9 Hz, 2H, CH_2), 1.70 (s, 3H, CH_3), 1.84–1.97 (m, 2H, CH_2), 2.00–2.17 (m, 2H, CH_2), 2.35–2.32 (m, 2H, CH_2), 3.21 (s, 3H, OCH_3), 5.94–5.89 (m, 3H, 3,4,5-H). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (s, CH_3), 17.3 (s, CH_3), 22.7 (s, CH_2), 22.8 (s, CH_3), 25.6 (s, CH_3), 30.6 (s, CH_2), 35.3 (s, CH_2), 38.7 (s, C_q, C-6), 45.8 (s, CH_2, C-7), 54.4 (s, C_q, C-1), 58.5 (s, CH_3, OCH_3), 129.6 (s, CH), 133.6 (s, CH), 133.9 (s, CH), 139.5 (s, C_q, C-2). – GC-MS, *m/z* (%): 222 (100) [M^+], 191 (32) [M^+ – OCH_3], 133 (72) [M^+ – OCH_3 – C_4H_9].

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