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First Synthesis and Reactivity of Phosphinite and Phosphine Bridge Chelate Dicarbonyl (η^5-4-Methoxycyclohexadienyl)Iron Complexes

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Abstract : Chelated dicarbonyl (η^4-4-methoxycyclohexadiene) iron complexes **6** and **15** which possess a phosphinite and a phosphine bridge respectively form a new class of iron complexes. Their cations **5** and **16** reacted regioselectively with nucleophiles in good yields. The observed regioselectivities are unusual for carbonyl (η^5- 4-methoxycyclohexadienyl) iron compounds.
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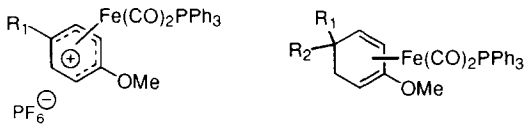
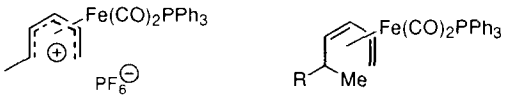
Over the past decade, tricarbonyl (η^5-cyclohexadienyl)iron cations have proved extremely useful as intermediates in organic synthesis.[1] The reactivity of such iron complexes depends upon the substituent attached to the dienyl system, and the ligand attached to iron. Of special interest to us is a peripheral ligand attached to iron that can influence the reactivity of the dienyl system. Recently it was shown that replacement of a carbonyl ligand by a triphenylphosphine improved the yield of quaternary carbon formation in the cyclohexadienyl[2,3] and pentadienyl series.[4] Thus, cations **1**[2,3] and **3**[4] reacted with nucleophiles to give complexes **2** and **4** respectively (Figure 1).



1 R_1= OMe; $(CH_2)_2OCH_3$; $(CH_2)_2NPht$ **2**



3 **4**

Figure 1

We now report the synthesis and the reactivity of (η^5-4-methoxycyclohexadienyl) chelate cations **5** and **16** which possess, respectively, a metal coordinated group $OPPh_2$ or PPh_2 in a side chain connected to the diene. These ligands create a bridge in the complex that may influence the regioselectivity of nucleophilic attack on the dienyl ligand. Nucleophilic attack on cations **5** and **16** were also examined. The literature contains only one example of an α,β-unsaturated ketone $Fe(CO)_2$ chelate complex with a phosphite group.[5]

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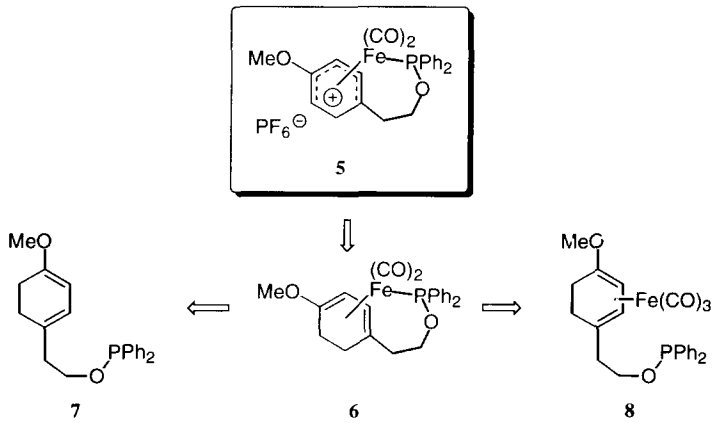
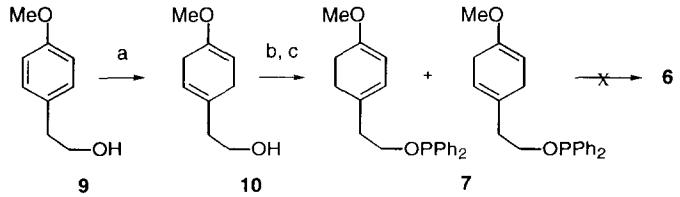
Synthesis of Chelate Dienylium complex 5

The new chelate cation **5** was obtained from the dicarbonyl (η^4-4-methoxycyclohexadiene)iron chelate complex **6**. Two methods of preparation of compound **6** were investigated starting either from the diene **7** or from the complex **8**. In the first route the $OPPh_2$ ligand was introduced before the complexation reaction, whereas in the second route its introduction was envisaged after the complexation of the diene (Scheme 1).



Scheme 1

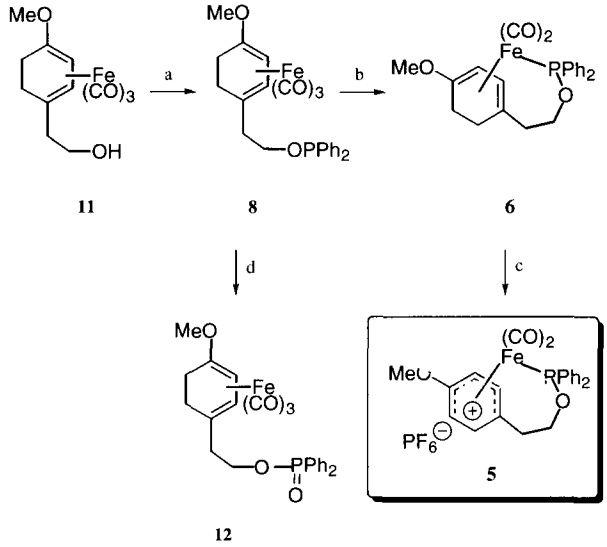
The new diene **7** was prepared from *p*-methoxyphenethyl alcohol **9**. The alcohol **9** was converted into its unconjugated dihydro derivative **10** by Birch reduction.[2] Reaction of the alcohol **10** with chlorodiphenylphosphine followed by diene isomerization in the presence of Wilkinson's catalyst gave **7** as an unseparable mixture of conjugated 1,3-diene (major) and unconjugated 1,4-diene (minor) isomers in a 60/40 ratio respectively. Complexation of the diene **7** under Heiquist's conditions[5] in the presence of dibenzylideneacetone tricarbonyl iron [η^4-(dba)$Fe(CO)_3$] did not lead to the expected complex **6**. No ligand exchange reaction between the "dba ligand" and the methoxycyclohexadiene occurred upon heating in tetrahydrofuran (Scheme 2).[6]



(a) : Li, NH_3, tBuOH, -78°C, 6h (100%)[2].
(b) : $ClPPh_2$, NEt_3, CH_2Cl_2, 25°C, 12h (100%).
(c) : $RhCl(PPh_3)_3$,$CHCl_3$ 60 °C, 10h (100%).
(d) : [η^4(dba)$Fe(CO)_2PPh_3$], THF, 67°C, 2h.

Scheme 2

Our current work on ligand exchange reactions,[2] inspired us to synthesize the chelate complex **6** via an intramolecular ligand exchange with the tricarbonyl iron complex **8**. This compound was prepared from the known alcohol **11**[7] by reaction with chlorodiphenylphosphine in the presence of triethylamine (Scheme 3). No ligand exchange was observed with trimethylamine-*N*-oxide dihydrate. The oxidized complex **12** was formed exclusively and isolated in 58% yield. However, selective irradiation of the phosphinite complex **8** at 254 nm[8] with a Hanau lamp (4W) under argon for 11h in a quartz apparatus gave a low yield of the chelate complex **6**, which underwent rapid hydride abstraction upon treatment with triphenylcarbenium hexafluorophosphate in dichloromethane to give cation **5**. The reaction proceeded to completion, as evidence by the disappearance of the diene carbonyl IR bands at 1970 and 1911 cm^{-1} and the growth of product peaks at 2043 and 2000 cm^{-1}, characteristic of the dienyl iron species. The cation **5** was not isolated and was used directly for further reactions since it could not be precipitated by addition of wet ether.



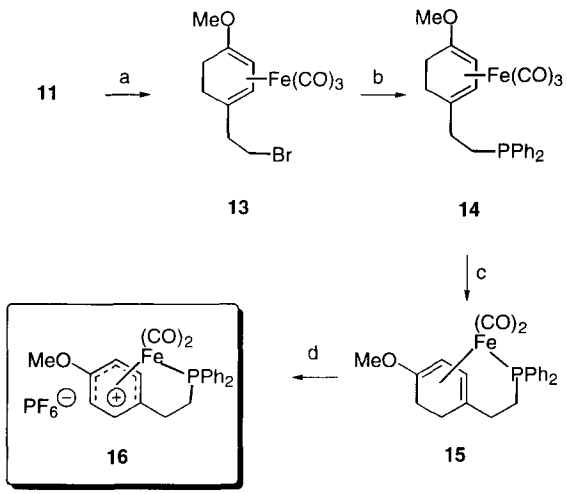
(a) : $ClPPh_2$, NEt_3, CH_2Cl_2, -78°C to 25°C, 12h (96%);
(b) : hv, heptane, 25°C, 11h (25%);
(c) : Ph_3CPF_6, CH_2Cl_2, 25°C, 5min;
(d) : Me_3NO, CH_3CN, 80°C, 15min. (58%).

Scheme 3

Synthesis of Chelate Dienylium complex 16

The new chelate cation **16** containing a 5-membered chelate ring was synthesized in order to observe the influence of the size of the chelate ring on the reactivity of the dienyl ligand. The chelate cation **16** was prepared from the alcohol **11**.[7] The synthesis of the new phosphine complex **14** was achieved by converting the alcohol complex **11** into the corresponding bromo derivative **13** which was subsequently reacted with lithium diphenylphosphide in *N*,*N*-dimethylformamide at 50°C to give the complex **14**. Selective irradiation at 254 nm with a Hanau lamp (4W) of a solution of **14** in heptane gave the chelate complex **15** in 45% yield. Subsequent

treatment of **15** with triphenylcarbenium hexafluorophosphate in methylene chloride provided cation **16**, isolated by precipitation with wet ether.

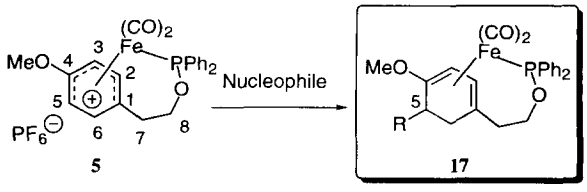


(a) : CBr_4, PPh_3, CH_2Cl_2, -20°C, 20 min. (78%).
(b) : $LiPPh_2$, THF, DMF, 50°C,45 min. (45%).
(c) : hv, heptane, 25°C, 1h40 (45%)
(d) : Ph_3CPF_6, CH_2Cl_2, 25°C, 5min (55%).

Scheme 4

Reactions of Chelate Dienylium Complexes 5 and 16 with Nucleophiles

The reactions of cation **5** with the sodium enolate of ethyl 2-cyclohexanonecarboxylate, sodium dimethyl malonate, sodium cyanide and methyl lithium proceeded *via* exclusive attack at the less substituted pentadienyl terminus (C5) to give the complexes **17 a-d** (Scheme 5) (Table 1). The cation **5** reacted with the first three nucleophiles in good yields, whereas the addition of methyl lithium was less efficient. However, the formation of compound **17d** was improved when the counter ion PF_6^- is replaced by BF_4^-. Interestingly, the sodium enolate of ethyl 2-cyclohexanonecarboxylate adds to **5** with significant diastereoselectivity (60%). Pearson and co-workers have previously reported that tin enolates add also to the tricarbonyl(4-methoxy-1-methylcyclohexadienyl)iron hexafluorophosphate with a moderate diastereoselectivity.[9]



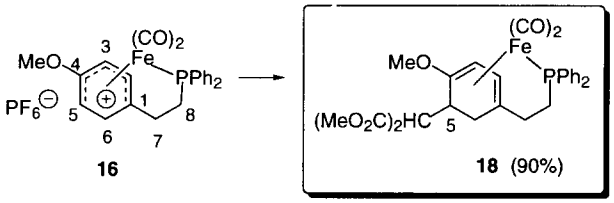
Scheme 5

starting compound	cation[a]	X-	Nucleophile	Product	Isolated Yields[b]
6	**5**	PF_6^-	$NaC(CO_2Et)(CH_2)_4C{=}O$	**17a** R = $C(CO_2Et)(CH_2)_4C{=}O$ mixture of two diastereoisomers (80/20)	(96%)
6	**5**	PF_6^-	$NaCH(CO_2Me)_2$	**17b** R = $CH(CO_2Me)_2$	(67%)
6	**5**	PF_6^-	NaCN	**17c** R = CN	(77%)
6	**5**	PF_6^-	CH_3Li	**17d** R = CH_3	(22%)
6	**5**	BF_4^-	CH_3Li	**17d** R = CH_3	(42%)

Table 1 : Nucleophilic Addition to cation **5**

[a] The cation **5** was not isolated. [b] The yields represent the overall yield two step process **6** to **5** to **17**

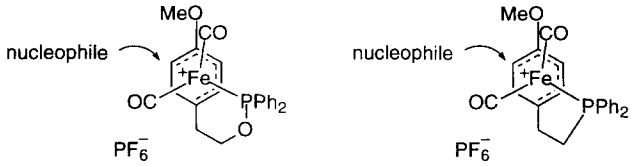
The cation **16** reacted also with $NaCH(CO_2Me)_2$ at the less substituted terminus to give the complex **18** in 90% yield (Scheme 6).The size of the chelate bridge had no influence on the regioselectivity of the nucleophilic attack on the dienyl ligand although the yield was improved in the 5-membered chelate complex series.



Scheme 6

The observed regioselectivities are unusual for the (η^5-4-methoxycyclohexadienyl) iron carbonyl series. The nucleophiles react with the less electrophilic and the less substituted terminus (C5) of the dienyl chelate complexes **5** and **16**. Thus, the steric hindrance at the C1 termini counterbalances the electron directing influence of the C4 methoxy group. Evidence of the regiochemistry came from by the chemical shifts and the multiplicities of the H_2 and H_3 protons in the ^1H NMR spectrum (J_{23} = 4.5 Hz). Additionally, the ^{13}C NMR spectra were consistent with the proposed structures of complexes **17a-d** and **18**.

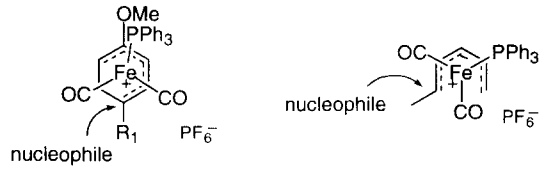
The P-CO coupling constants have been reported to provide a reliable aid to structure elucidation of simple $(diene)Fe(CO)_2L$ complexes (L = phosphine, phosphite) and have the values J (P axial - CO basal) $\simeq$ 5 Hz, J (P basal - CO axial) $\simeq$ 4 Hz and J (P basal - CO basal) $\simeq$ 25 Hz.[10] The ^{13}C NMR spectra of the chelate complexes **6**, **15, 17 a-d** and **18** present two CO chemical shifts at 220-218 (CO basal; J (Pbasal-CO basal) $\simeq$ 5 - 7 Hz) and 215 ppm (CO axial; J (Pbasal-CO axial) $\simeq$ 22-23 Hz). The values of these coupling constants are of the same order as those reported. Moreover, the tendency of phosphine ligands to occupy basal sites in $(dienyl)Fe(CO)_2L$ has been reported.[11] We propose that all the chelate complexes have the phosphorus ligand in the basal position. Thus, the cations **5** and **16** probably have the structures indicated in figure 2. Nucleophiles therefore attack the less substituted termini of the dienyl cations *trans* to the bulky phosphorus ligand.[12]



5 16

Figure 2

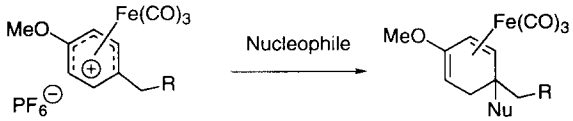
Previous work has also established that nucleophiles react *trans* to the PPh_3 ligand in the acyclic (dienylium)$Fe(CO)_2PPh_3$ series[4] and in the (methoxycyclohexadienylium)$Fe(CO)_2PPh_3$ series (Figure 3).[3] Thus, replacement of a carbonyl iron ligand by a triphenylphosphine increases the formation of quaternary carbon.



1 3

Figure 3

These results have to be compared with the known reactivities of complexes **19** and **21**. Complexes of general structure **19** were reported to react with nucleophile at the methyl-substituted dienyl terminus to give dienes of general structure **20** (Scheme 7).[13] For analogous complexes **21** where R = CH_2R_3 (longer alkyl side chain) the increased steric hindrance leads to a higher proportion (20%) of nucleophilic addition at the unsubstituted terminus.[7] Derivatives having an isopropoxy substituant instead of a methoxy undergo addition to the substituted terminus.[14]



19 : R = H
21 : R = CH_2R_3

20

Scheme 7

In summary, new chelate dicarbonyl(η^4-4-methoxy -1,3-cyclohexadiene)iron complexes **6** and **15** and their cations **5** and **16** have been prepared; they constitute the first examples of chelate complexes in the (diene)$Fe(CO)_2L$ series. It was showed for the first time that it is possible to direct nucleophilic attack exclusively at the less reactive C5 terminus of the 4-methoxycyclohexadienyl ligand. Nucleophiles reacted at the more reactive and the more substituted C1 termini of the dienylium ligand in the $Fe(CO)_2PPh_3$ series and with both termini of the dienylium ligand in the $Fe(CO)_3$ series. The ability to control the nucleophilic addition at the C5 terminus of the 4-methoxycyclohexadienyl ligand of chelate complexes could have interesting synthetic applications.

Acknowledgements : One of us (N. M) thanks the Ministère de l'Enseignement Supérieur et de la Recherche for a grant.

General : IR spectra were recorded on a Nicolet FT-IR spectrometer. ^1H NMR spectra were recorded at 200, 250 and 300 MHz and ^{13}C NMR spectra at 50.32, 62.96 and 72.5 MHz. All separations were carried out under flash chromatographic conditions on Merck silica gel 60 (70-230 mesh) at medium pressure (200 mbar). TLC was done on Merck silica gel plates ($60F_{254}$) with a fluorescent indicator. Elemental analyses were performed by the "Service de microanalyses" (ICSN, CNRS, Gif-sur-Yvette). HRMS spectra were recorded at CRMP (University of Rennes I). Chemical ionisation mas spectra were recorded in presence of isobutane gas. THF and heptane were distilled from sodium/benzophenone complex. CH_3CN was distilled from CaH_2, CH_2Cl_2 from P_2O_5 and NEt_3 from KOH. Organic layers were washed with brine and dried with anhydrous $MgSO_4$. Mass spectra were recorded with a KRATOS MS-80 (FAB), or AEI MS-9 (CI) or AEI MS-50 (EI) instruments.

Dicarbonyl[1-η^1-diphenylphosphinite-2-(1-5-η^5-4-methoxycyclohexa-2,4-dienylium)ethane]iron hexafluorophosphate **5**

To a solution of chelate complex **6** (102 mg, 0.226 mmol) in CH_2Cl_2 (2 mL) was added triphenylcarbenium hexafluorophosphate (112 mg, 0.29 mmol) at room temperature. The mixture was left at this temperature. After 5 min., the reaction had proceeded to completion, as evidence by the disappearance of the diene carbonyl IR bands at 1970 and 1911 cm^{-1} and the growth of the product peaks at 2043 and 2000 cm^{-1} characteristic of the dienyl iron species. The cation **5** was not isolated since it could not be precipitated by addition of anhydrous ether. After its generation *in situ*, the cation **5** was used directly.

Dicarbonyl[1-η^1-diphenylphosphinite-2-(1-4-η^4-4-methoxycyclohexa-1,3-dienyl)ethane]iron **6**

A pale yellow solution of **8** (410 mg; 0.9 mmol) in heptane (105 mL) was irradiated with a HANÄU NK 6/20 (4 Watt) (254 nm) lamp under argon for 11h in a quartz apparatus. The resulting orange mixture was filtered through celite and eluted with ether. The filtrate was evaporated *in vacuo*. Flash chromatography (elution with toluene) of the residue afforded the chelate complex **6** (100.9 mg, 25%) as a yellow oil. IR ($CHCl_3$) ν : 1970; 1911; 1620; 1455; 1330; 1210; 810 cm^{-1}. ^1H NMR (C_6D_6; 200 MHz) δ : 7.68 (4H, dd; J = 10.2 Hz; J = 15.6 Hz); 7.12-6.98 (6H, m); 5.20 (1H, d; J = 4.4 Hz); 4.24 (1H, t; J = 4.4 Hz; J = 5.3 Hz); 3.65-3.28 (2H; m); 3.17 (3H, s); 2.43-2.24 (1H, m); 1.75-1.50 (4H, m); 1.38-1.31 (1H; m). ^{13}C NMR (C_6D_6; 50 MHz) δ: 220.6 (d; J = 7.0 Hz); 215.5 (d; J = 21.0 Hz); 141.2 (d; J = 38.2 Hz); 131.6 (d; J = 13.9 Hz); 130.7; 130.0; 128.6; 129.7 (d; J = 11.8 Hz); 113.1 (d; J = 11.7 Hz); 78.4; 76.1; 66.5 (d; J = 9.3 Hz); 57.0; 31.3; 25.6. CIMS m / z : 451 $(MH)^+$; 450; 449; 421; 392; 237. Anal. calcd for $C_{23}H_{23}FeO_4P$: C, 61.36; H, 5.15 ; P, 6.88 Found C, 61.11; H, 5.13; P, 7.11.

Tricarbonyl[1-diphenylphosphinite-2-(1-4-η^4-4-methoxycyclohexa-1,3-dienyl)ethane]iron **8**

To a solution of the alcohol **11** (930 mg, 3.16 mmol) in CH_2Cl_2 (19 mL) was added dropwise chlorodiphenylphosphine (0.57 mL, 3.17 mmol) and triethylamine (0.45 mL, 3.22 mmol) at -78°C. The reaction mixture was stirred at -78°C for 1h and evaporated *in vacuo*. The residue was triturated with pentane (40 mL). The white precipitate was removed by filtration and washed with pentane. The yellow filtrate was diluted with water and extracted with pentane. The combined organic layers were washed with brine and dried ($MgSO_4$). Solvent evaporation afforded **8** (1.45 g, 96%) as a yellow oil spectroscopically pure. IR ($CHCl_3$) ν : 2037; 1966; 1480; 1461; 1435; 997 cm^{-1}.^1H NMR ($CDCl_3$; 200 MHz) δ : 7.52-7.45 (4H, m); 7.40-7.35 (6H,

m); 5.13 (1H, d; J = 4.6 Hz); 4.95 (1H, d ; J = 4.6 Hz); 3.9-3.85 (2H, m); 3.43 (3H, s); 2.32-2.06 and 1.82-1.63 (6H, m). ^{13}C NMR ($CDCl_3$; 50 MHz) δ: 213.5; 131.2 (d; J = 32.0 Hz); 131.2; 130.8; 130.1 (d; J = 7.0 Hz); 129.0 (d; J = 10.0 Hz); 81.9; 76.2; 74.8; 69.3 (d ; J = 29.0 Hz); 57.4; 42.3 (d; J = 11.1 Hz); 27.3; 26.6. CIMS m/z : 479 $(MH)^+$; 451; 423; 339; 137.

Tricarbonyl[1-diphenylphosphinite-2-(1-4-η⁴-4-methoxycyclohexa-1,3-dienyl)ethane]iron **12**

To a solution of the phosphinite complex **8** (44.5 mg, 0.093 mmol) in refluxing acetonitrile (4 mL) was added trimethylamine *N*-oxide dihydrate (13 mg, 0.118 mmol). After 15 min., the reaction mixture was filtered through celite and eluted with ether. The filtrate was evaporated under reduced pressure. Purification by preparative T.L.C. (elution with ether) of the residue provided 26.5 mg (58%) of **12** as a yellow oil. IR ($CHCl_3$) ν : 2038; 1967; 1440; 1220; 1024 cm^{-1}. ^1H NMR ($CDCl_3$; 250 MHz) δ : 7.87-7.78 (4H, m); 7.54-7.45 (6H, m); 5.18 (1H, d; J = 4.6 Hz); 5.01 (1H, d; J = 4.6 Hz); 4.20-3.98 (2H, m); 3.43 (3H, s); 2.32-2.10 (3H, m); 1.79-1.58 (3H, m). ^{13}C NMR ($CDCl_3$; 62.5 MHz) δ : 213.6; 134.0; 133.4 (d; J = 9.8 Hz); 133.3 (d; J = 9.4 Hz); 130.4 (d; J = 3.7 Hz); 130.3 (d; J = 3.7 Hz); 130.2 (d; J = 3.7 Hz); 130.1 (d; J = 3.7 Hz); 116.9; 81.8; 76.6; 73.7; 64.2 (d; J = 5.7 Hz); 57.6; 41.0 (d; J = 7.6 Hz); 27.3; 26.9. CIMS m / z : 495 $(MH)^+$; 439; 355.

Tricarbonyl[1-bromo-2-(1-4-η⁴-4-methoxycyclohexa-1,3-dienyl)ethane]iron **13**

To a solution of the alcohol **11** (2.32 g, 7.89 mmol) and PPh_3 (2.69 g, 10.26 mmol) in CH_2Cl_2 (50 mL) was added portionwise with ice-salt cooling CBr_4 (2.88 g, 8.68 mmol). After the addition was complete, the mixture was stirred for an additional 20 min., and filtered through celite (elution with CH_2Cl_2). Evaporation of the filtrate left an orange oil, which was dissolved in hot AcOEt (35 mL). Pentane (70 mL) was added, and the mixture was left at room temperature for 1.5h. The triphenylphosphine oxide was removed by filtration and washed with pentane. The filtrate was evaporated until triphenylphosphine oxide precipitated. The new precipitate was removed by filtration and the filtrate was reduced by evaporation until triphenylphosphine oxide precipitated. This procedure was repeated four times. Complete evaporation of the filtrate *in vacuo* left a yellow oily residue. Flash chromatography (elution with petroleum ether / Et_2O 100/0; 95/5) afforded **13** (2.20 g, 78%) as a yellow light sensitive oil. IR ($CHCl_3$) ν : 2039; 1964; 1464; 1220; 679; 652 cm^{-1}. ^1H NMR ($CDCl_3$; 300 MHz) δ : 5.21 (1H, d; J = 4.7 Hz); 5.06 (1H, d; J = 4.7 Hz); 3.46 (3H, s; OCH_3); 3.46 (2H, m); 2.43-2.20 (3H, m); 1.87-1.62 (3H, m).^{13}C NMR ($CDCl_3$; 72.5 MHz) δ : 212.7; 116.1; 80.9; 75.7; 74.0; 56.8; 43.1; 31.0; 26.1; 25.9. CIMS m / z : 359 and 357 $(MH)^+$; 275; 273; 278; 193; 137. Anal. calcd for $C_{12}H_{13}BrFeO_4$: C, 40.37; H, 3.67; Br, 22.38. Found C, 40.53; H, 3.68; Br, 22.14.

Tricarbonyl[1-diphenylphosphine-2-(1-4-η⁴-4-methoxycyclohexa-1,3-dienyl)ethane]iron ***14***

To a solution of chlorodiphenylphosphine (0.736 mL, 4.1 mmol) in THF (2 mL) was added lithium (68 mg, 9.81 mmol) at 0°C. The reaction mixture was stirred at room temperature during 2h., and turned to red. This $LiPPh_2$ solution was added dropwise to a solution of the bromo complex **13** (940 mg, 3.40 mmol) in DMF (10 mL) at 50°C. After being stirred for 30 min., the mixture was filtered through celite (elution with Et_2O). Evaporation of the filtrate under reduce pressure (bath temperature < 40°C) gave a residue which was diluted with water and extracted with ether. The combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography (elution with petroleum ether/Et_2O 100/0; 95/5; 90/10) to give **14** (982 mg, 45%) as a yellow oil. IR ($CHCl_3$) ν : 2036; 1965; 1434; 1220 cm^{-1}. ^1H NMR ($CDCl_3$; 300 MHz) δ : 7.43-7.34 (10H, m); 5.14 (1H, d; J = 4.7 Hz); 4.87 (1H, d; J = 4.7 Hz); 3.44

(3H, s); 2.33-2.29 (1H, m); 2.27-2.18 (2H, m); 1.93-1.74 (4H, m); 1.66-1.59 (1H, m). ^{13}C NMR ($CDCl_3$; 72.5 MHz) δ: 213.1; 129.1; 128.4; 128.2; 115.8; 80.4; 79.5; 75.3; 56.9; 29.6; 26.4; 25.8. CIMS m / z : 463 $(MH)^+$; 435; 406; 378; 323. Anal. calcd for $C_{24}H_{23}FeO_4P$: C, 62.36; H, 5.01; P, 6.70. Found C, 62.33; H, 5.25; P, 6.66.

Dicarbonyl[1-η^1-diphenylphosphine-2-(1-4-η^4-4-methoxycyclohexa-1,3-dienyl)ethane]iron **15**

A pale yellow solution of **14** (152 mg; 0.329 mmol) in heptane (57 mL) was irradiated with a HANÄU NK 6/20 (4 Watt) (254 nm) lamp under argon for 4h in a quartz apparatus. The resulting orange mixture was filtered through celite and eluted with ether. The filtrate was evaporated *in vacuo*. Flash chromatography (elution with toluene/AcOEt 100/0; 95/5) afforded the chelate complex **15** (48.3mg, 45%) as a yellow oil and the starting complex **14** (36 mg; 24%). IR ($CHCl_3$) ν : 1974; 1921; 1470; 1330; 1215 cm^{-1}. ^1H NMR (C_6D_6; 200 MHz) δ : 7.50 (4H, m); 7.16-7.01 (6H, m); 5.15 (1H, d; J = 4.5 Hz); 3.98 (1H, t; J= 4.5 Hz; J_{H3P} = 4.4 Hz); 3.49 (3H, s); 2.59 (1H, m); 2.39-2.12 (1H, m); 2.02-1.85 (2H; m); 1.78-1.62 (2H, m); 1.59-1.47 (2H, m). ^{13}C NMR (C_6D_6; 50 MHz) δ: 221.0 (d; J = 7.0 Hz); 216.3 (d; J = 21.0 Hz); 138.3 (d; J = 36.4 Hz); 132.7 (d; J = 12.1 Hz); 130.6 (d; J = 10.4 Hz); 130.1-129.4; 128.9-128.7; 128.3; 127.9; 119.2; 92.8; 76.2; 72.8; 57.0; 33.8 (d; J = 10.4 Hz); 32.5 (d; J = 26.2 Hz); 27.7; 27.5. HRMS calcd for $C_{23}H_{23}FeO_3P$ (M^+) : 434.0754 Found 434.0752. Anal. calcd for $C_{23}H_{23}FeO_3P$: C, 63.62; H, 5.34. Found C, 64.09; H, 5.63.

Dicarbonyl[1-η^1-diphenylphosphine-2-(1-5-η^5-4-methoxycyclohexa-2,4-dienylium)ethane]iron hexafluorophosphate **16**

To a solution of chelate complex **15** (112 mg, 0.29 mmol) in CH_2Cl_2 (1 mL) was added triphenylcarbenium hexafluorophosphate (31 mg, 0.08 mmol) at room temperature. The mixture was left at this temperature. After 5 min., the reaction had proceeded to completion, as evidence by the disappearance of the diene carbonyl IR bands at 1976 and 1921 cm^{-1} and the growth of the product peaks at 2038 and 1995 cm^{-1} characteristic of the dienyl iron species. The reaction mixture was filtered through celite (elution with CH_2Cl_2). Evaporation of the filtrate under reduce pressure gave a residue which was diluted with 0.5 mL of CH_2Cl_2. Then ether was added dropwise and the product was collected by filtration and washed with ether to afford pure **16** (23 mg, 55%) as a yellow powder. IR ($CHCl_3$) ν : 2038; 1995;1422 ;1210 cm^{-1}. ^1H NMR (CD_3CN; 200 MHz) δ : 7.70-7.51 (10H, m); 6.83 (1H, dd; J = 5.4 Hz; J = 1.9 Hz); 4.43 (1H, dd; J = 5.4 Hz; J = 1.1 Hz); 4.00 (1H, m); 3.63 (3H, s); 3.21-2.45 (6H, m). HRMS calcd for $C_{23}H_{22}FeO_3P$ (M^+) : 433.0656 Found 433.0654.

Dicarbonyl[1-η^1-diphenylphosphinite-2-{1-4-η^4-4-methoxy-5-(1-(ethyl 2-oxocyclohexanecarboxylate))cyclohexa-1,3-dienyl}ethane]iron **17a**

To a suspension of sodium hydride (4 mg; 0,14 mmol) in THF (1.4 mL) was added 2-carboethoxycyclohexanone (25 mg; 0,15 mmol) at room temperature. After 5 min., a clear yellow solution of its sodium salt was obtained. This solution was added dropwise to a solution of cation **5** (prepared as described previously from **6** (22 mg; 0.05 mmol)) in CH_2Cl_2 at 0°C. After being stirred for 30 min., the red reaction mixture was diluted with water and extracted with ether. After general work-up, the combined organic layers were evaporated. Flash chromatography (elution with petroleum ether/Et_2O 6/4) of the residue afforded two diastereoisomers. One diastereoisomer was obtained as a yellow powder (24 mg; 79%); whereas the other diastereoisomer (more polar) was isolated as a yellow oil (6 mg; 16%). IR ($CHCl_3$) ν : 1974; 1916; 1730; 1707; 1455; 1436; 1197; 810 cm^{-1}. ^1H NMR (C_6D_6; 200 MHz) major diastereoisomer δ : 7.85-7.58 (4H, m); 7.12-6.97 (6H, m); 5.37 (1H, dd; J = 4.3 Hz; J = 1.0 Hz); 4.19 (1H, t; J = 4.3 Hz; J = 5.4 Hz); 3.93 and 3.87 (2H, 2dq; J = 10.6 Hz; J = 7.1 Hz); 3.8-3.9 (1H, m); 3.62-3.30 (2H, m); 3.45 (3H, s); 3.00 (1H, m); 2.45-2.21 (3H, m); 1.76 (1H, d; J = 15.7 Hz); 1.69 (1H, m); 1.68-1.45 (6H, m); 1.31 (1H, dd; J = 15.5 Hz;

J = 6.1 Hz); 0.91 (3H, t; J = 7.1 Hz). ^{13}C NMR (C_6D_6; 50 MHz) major diastereoisomer δ : 220.6 (sl); 214.7 (d; J = 22.5 Hz); 205.8; 171.2; 140.6 (d; J = 36.3 Hz); 131.6 (d; J = 13.8 Hz); 130.7; 130.1; 130.0 (d; J = 11.1 Hz); 128.4 (d; J = 12.1 Hz); 111.5 (d; J = 12.1 Hz); 79.3; 78.5; 65.5 (d ; J = 27.6 Hz); 64.7; 61.0; 58.8; 42.0; 41.4; 38.7; 35.5 (d; J = 5.6 Hz); 33.7; 26.9; 23.1; 14.0. CIMS m / z : 619 $(MH)^+$; 591; 562; 450; 422; 393. Anal. calcd for $C_{32}H_{35}FeO_7P$: C, 62.15; H, 5.70 ; Found C, 62.58 ; H, 5.55. ^1H NMR (C_6D_6; 200 MHz) minor diastereoisomer δ : 7.71–7.58 (4H, m); 7.10–7.04 (6H, m); 5.22 (1H, d; J = 4.2 Hz); 4.22 (1H, dm; J = 10.7 Hz); 3.98 (1H, t; J = 4.2 Hz; J_{H3P} = 5.4 Hz); 4.06 and 3.78 (1H, dq; J = 10.7 Hz; J = 7.1 Hz); 3.38 (3H, s); 3.60-3.20 (2H, m); 2.72 -2.59 (2H, m); 1.55 and 1.20 (6H, m).^{13}C NMR (C_6D_6; 50 MHz) minor diastereoisomer δ : 234.6; 226.9 (d; J = 34.0 Hz); 197.3; 170.3; 131.6; 130.7; 130.1; 129.8; 129.1; 110.6 (d; J = 12.1 Hz); 78.6; 76.0; 65.0 (d; J = 55.0 Hz) 64.9; 61.1; 58.12; 42.0; 41.3; 40.5; 35.5; 30.2; 26.6; 22.9; 13.9. FABMS m / z : 618 $(M)^+$; 617; 590; 562; 483; 449; 421; 392.

Dicarbonyl{dimethyl [2-5-η^4-2-methoxy-5-(2-η^1-diphenylphosphinitethyl)cyclohexa-2,4-dienyl]malonate}iron **17b**

To a suspension of sodium hydride (5 mg; 0.20 mmol) in THF (1.5 mL) was added dimethyl malonate (0.025 mL; 0.21 mmol) at room temperature. After stirring for 5 min., this solution was added dropwise to a solution of the cation **5** (prepared as described previously from **6** (24 mg; 0.053 mmol)) in CH_2Cl_2 (1 mL) at 0°C. After 10 min., the mixture was diluted with water and extracted with ether. After general work-up, the combined organic layers were evaporated. Flash chromatography (elution with petroleum ether/Et_2O 6/4) of the residue afforded **17b** (21 mg; 67%) as a yellow oil. IR ($CHCl_3$) ν : 1977; 1919 ; 1747; 1730; 1455; 1436; 1231; 793 cm^{-1}. ^1H NMR (C_6D_6; 200 MHz) δ : 7.61 (4H, qm; J = 8.0 Hz); 7.08-6.97 (6H, m); 5.22 (1H, d; J = 4.3 Hz); 4.21 (1H, t ; J = 4.3 Hz ; J_{H3P} = 5.4 Hz); 3.77-3.68 (1H, m); 3.60 (1H, d; J = 7.3 Hz); 3.57-3.44 and 3.32-3.19 (2H, m); 3.40 (3H, s); 3.36 (3H, s); 3.33 (3H, s); 2.28 (1H, dd; J = 15.1 Hz; J = 4.2 Hz); 1.76 (1H, d; J = 15.1 Hz; 1.62 (1H, ddd; J = 15.8 Hz; J = 8.9 Hz; J = 3.1 Hz); 1.30 (1H; dd; J = 15.8 Hz; J = 5.9 Hz). ^{13}C NMR (C_6D_6; 50 MHz) δ: 220.3 (d; J = 8.7 Hz); 214.5 (d; J = 22.5 Hz); 169.4; 169.0; 140.4 (d; J = 36.4 Hz); 131.6 (d; J = 13.8 Hz); 130.8; 130.1; 129.7 (d; J = 12.1 Hz); 128.5 (d; J = 13.8 Hz); 111.2 (d; J = 13.9 Hz); 79.6; 76.5; 64.7 (d; J = 8.9 Hz); 64.5; 57.8; 56.4; 56.3; 51.9; 38.3; 37.7; 35.2 (d; J = 5.0 Hz). MS (FAB) m / z : 580 $(M)^+$; 579; 552; 521; 449; 421; 392; 337. HRMS calcd for $C_{28}H_{29}FeO_8P$ (M^+) : 580.0933 Found 580.0950.

Dicarbonyl[1-η^1-diphenylphosphinite-2-(1-4-η^4-5-cyano-4-methoxycyclohexa-1,3-dienyl)ethane]iron **17c**

To a solution of cation **5** (prepared as previously described from **6** (21 mg; 0.046 mmol) followed by evaporation of CH_2Cl_2) in acetone (2 mL) was added sodium cyanide (15 mg; 0.316 mmol). The reaction mixture was stirred for 2h at room temperature, then diluted with water and extracted with ether. After general work-up, the combined organic layers were evaporated. Flash chromatography (elution with petroleum ether/Et_2O 6/4) of the residue afforded **17c** (17 mg; 77%) as a white powder. IR ($CHCl_3$) ν : 2236; 1984; 1927; 1455; 1436; 1231; 793 cm^{-1}. ^1H NMR (C_6D_6; 200 MHz) δ : 7.49 (4H, qm; J = 8.0 Hz); 7.07-7.02 (6H, m); 5.13 (1H, d; J = 4.5 Hz); 4.13 (1H, t; J = 4.3 Hz; J_{H3P} = 5.6 Hz); 3.50-3.34 (1H, m); 3.27 (3H, s); 3.23-3.08 (1H, qm; J = 12.0 Hz); 3.03 (1H, dt ; J = 10.0 Hz; J = 4.0 Hz); 1.57 (2H, m); 1.50-1.40 (1H, m); 1.17 (1H, sl). ^{13}C NMR (C_6D_6; 50 MHz) δ: 219.0 (d; J = 8.7 Hz); 213.3 (d; J = 21.7 Hz); 141.6 (d; J = 56.7 Hz); 139.3 (d; J = 36.7 Hz); 131.7 (d; J = 13.8 Hz); 131.2; 130.2; 129.4 (d; J = 12.1 Hz); 128.8; 128.3; 107.8 (d; J = 13.6 Hz); 80.3; 75.8; 63.9; 63.6 (d; J = 8.6 Hz); 57.2; 37.0; 34.0 (d; J = 4.1 Hz); 27.3. CIMS m / z : 476 $(MH)^+$; 450; 449; 447. HRMS calcd for $C_{24}H_{22}FeNO_4P$ (M^+) : 475.0636 Found 475.0626.

Dicarbonyl[1-η^1-diphenylphosphinite-2-(1-4-η^4-5-methyl-4-methoxycyclohexa-1,3-dienyl)ethane]iron **17d**

To a solution of chelate complex **6** (77 mg; 0.17 mmol) in CH_2Cl_2 (4 mL) was added triphenylcarbenium tetrafluoroborate (63 mg; 0.19 mmol) at room temperature. The mixture was heated to reflux for 40 min., and cooled at -78°C. A methyllithium solution in ether (1.4M; 0.36 mL; 0.51 mmol) was then added dropwise. The reaction mixture was stirred for 5 min., diluted with water and extracted with ether. After general work-up, the combined organic layers were evaporated. Flash chromatography (elution with heptane /AcOEt 99/1) of the residue afforded **17d** (33 mg; 42%) as a white powder. IR ($CHCl_3$), ν : 1970; 1911; 1455; 1436; 1234; 793 cm^{-1}. ^1H NMR ($CDCl_3$; 250 MHz) δ : 7.72-7.23 (10H, m); 5.24 (1H, d; J = 4.2 Hz); 4.64 (1H, t; J = 4.2 Hz; J_{H3P} = 5.4 Hz); 4.05-3.87 (2H, m); 3.62 (3H, s); 2.94-2.86 (1H, m); 2.21-2.06 (2H, m); 1.96-1.88 (1H, m); 1.92 (1H, dm; J = 13.8 Hz); 1.12 (3H, d; J = 6.6 Hz). ^{13}C NMR (C_6D_6; 62.5 MHz) δ: 218.3 (d; J = 6.4 Hz); 212.3 (d; J = 21.6 Hz); 139.9 (d; J = 54.0 Hz); 138.0 (d; J = 34.9 Hz); 129.3; 123.3; 114.5 (d; J = 10.4 Hz); 75.9; 72.9; 61.7; 60.8 (d; J = 8.8 Hz); 53.9; 38.6; 32.9; 28.2; 18.6. CIMS m / z : 465 $(MH)^+$; 436. HRMS calcd for $C_{24}H_{25}FeO_4P$ (M^+) : 464.0840 Found 464.0837.

To a solution of cation **5** (prepared as previously described from **6** (98 mg; 0.22mmol) in CH_2Cl_2 (2 mL) was added dropwise 0.47 mL of a methyllithium solution in ether (1.4M; 0.66 mmol) at -100°C. The reaction mixture was stirred for 20 min. at -100°C then diluted with water and extracted with ether. After general work-up, the combined organic layers were evaporated. Flash chromatography (elution with petroleum ether/Et_2O 6/4) of the residue afforded **17d** (28 mg; 23%) as a white powder.

Dicarbonyl{dimethyl[2-5-η^4-2-methoxy-5-(2-η^1-diphenylphosphinethyl)cyclohexa-2,4-dienyl]malonate}iron **18**

To a suspension of sodium hydride (7 mg; 0.28 mmol) in THF (2 mL) was added dimethyl malonate (0.032 mL; 0.28 mmol) at room temperature. After stirring for 5 min., this solution was added dropwise to a solution of the cation **16** (21 mg; 0.035 mmol) in CH_2Cl_2 (1 mL) at 0°C. The reaction mixture was stirred for 5h, then diluted with water and extracted with ether. After general work-up, the combined organic layers were evaporated. Flash chromatography (elution with petroleum ether/Et_2O 6/4) of the residue afforded **18** (18 mg; 90%) as a yellow oil. IR ($CHCl_3$) ν : 1972; 1912; 1729; 1455; 1436; 1220 cm^{-1}.^1H NMR (C_6D_6; 200 MHz) δ : 7.46-7.26 (4H, m); 7.09-7.00 (6H; m); 5.12 (1H; d; J = 4.4 Hz); 4.10 (1H, t; J = 4.4 Hz; J_{H3P}= 5.5 Hz); 3.57 (1H, d; $J_{5\text{-}CH}$ = 4.6 Hz); 3.40 (3H, s); 3.34 (3H, s); 3.31 (1H, m); 3.27 (3H, s); 3.19-3.08 (2H, m); 2.53 (1H, dm; J = 14.0 Hz); 2.36-1.95 (3H, m). ^{13}C NMR (C_6D_6; 50 MHz) δ : 221.1 (d; J = 5.3 Hz); 216.2 (d; J = 20.8 Hz); 169.1; 168.7; 138.7 and 137.7 (d; J = 39.8 Hz); 132.6 (d; J = 12.2 Hz); 130.5 (d; J = 9.5 Hz); 128.8 (d; J = 10.6 Hz); 129.7 (d; J = 12.1 Hz); 130.1; 129.4; 128.3; 127.9; 127.0; 110.1 (d; J = 10.4 Hz); 76.4; 76.3; 73.1; 56.8; 55.4; 51.9; 51.7; 42.7 (d; J = 3.3 Hz); 34.4 ; 32.7 (d; J = 26.9 Hz); 32.0 (d; J = 10.2 Hz). MS (FAB) m / z : 563 $(M\text{-}H)^+$; 535; 508; 433; 405; 376; 321. HRMS calcd for $C_{28}H_{29}FeO_7P$ (M^+) : 564.1001 Found 564.1002.

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