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STEREOCONTROLLED FUNCTIONALIZATION OF CYCLOOCTADIENE USING ORGANOIRON CHEMISTRY

Anthony J. Pearson,* Srinivasan Balasubramanian, and Kumar Srinivasan.

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.

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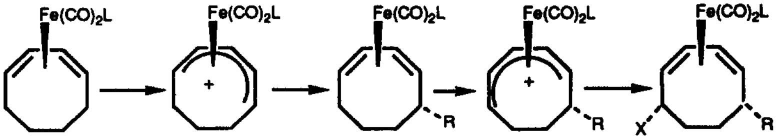
Abstract: Methods are described for controlling the reactivity of cyclooctadienyliron cations so as to give good yields during the stereocontrolled addition of carbon nucleophiles, thereby leading to efficient functionalization of eight membered carbocycles.

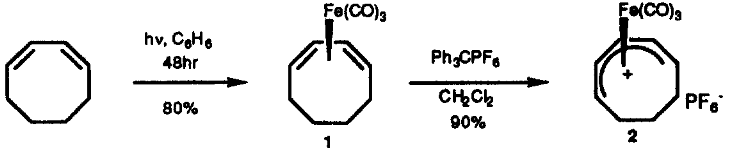
INTRODUCTION

Methods for stereocontrolled functionalization of carbocyclic diene-metal complexes have been investigated in our laboratories during the past ten years.[1] Similar to the 1,3 stereocontrol achieved from cyclohepta-1,3-diene iron complex, successive hydride abstraction followed by nucleophilic addition on the corresponding cycloocta-1,3-diene complex should give 1,4-stereocontrol (Scheme 1).



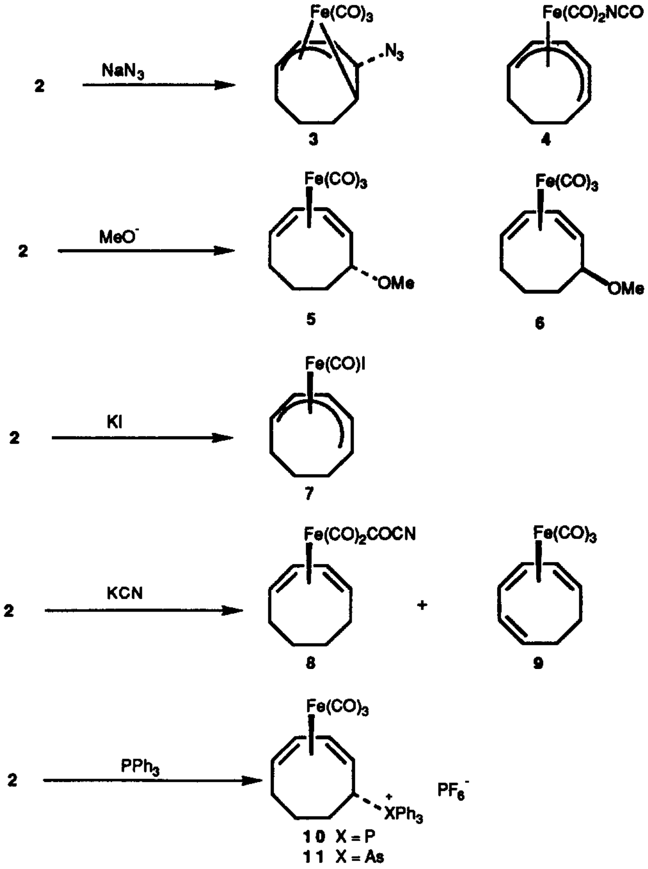
Scheme 1 1, 4-Functionalization using cyclocta-1,3-dieneiron complex

The literature reports on cyclooctadiene iron complexes, unlike cycloheptadiene complexes, are at best confusing and at worst positively discouraging. Another problem associated with tricarbonyl [(1-4-η)-cycloocta-1,3-diene]iron (**1**) is that it is rather unstable even at low temperature, which creates problems in handling and storage. Gustorf and co-workers[2] reported the preparation of complex **1** by photolysis of cyloocta-1,3-diene and $Fe(CO)_5$, from which **1** was obtained as a crystalline solid (Mp 90-91 °C). Lewis and co-workers reported[3] that this complex is a crystalline solid with a melting point of 36 °C, where as King *et al* [4] reported the complex as an oil. Treatment of the complex **1** with triphenylmethyl tetrafluoroborate gave the dienyl salt **2** in 90% yield.[4]



Scheme 2

Various nucleophilic additions to **2** have been reported.[4,5,6] Treatment of the dienyl salt **2** with sodium azide gave two products, the enediyl adduct **3** and an unstable product, presumed to be **4** on the basis of an IR absorption at 2173 cm^{-1} that indicates the presence of an isocyanate group. Addition of azide at the C.2 position of the dienyl salt is an unexpected result since with cyclohexadienyl- and cycloheptadienyl-$Fe(CO)_3$ complexes it adds to the terminus of the dienyl moiety.[1] Similarly, methoxide also has two modes of attack. The terminal



Scheme 3 Nucleophilic additions to the dienyl salt 2

adduct gave the *exo* substituted diene **5** and the *endo* substituted diene **6** via attack on the carbonyl ligand and an intermediate ester complex. Iodide reacted exclusively on the metal, displacing a carbonyl ligand to give the neutral iodo complex **7**. Treatment of **2** with KCN leads to two products **8** and **9**, the latter being formed reportedly by a base (CN$^-$) induced deprotonation during the migration of a cyano group from the carbonyl group to the organic entity with the elimination of HCN. Triphenylphosphine and triphenylarsine attacked exclusively at the terminus of the dienyl moiety giving the cationic diene compounds **10** and **11**.

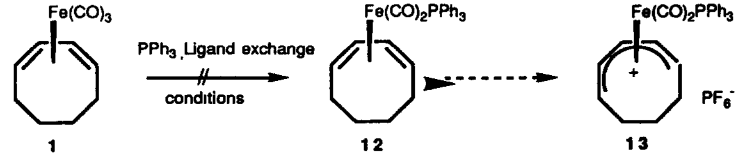
It is apparent from the literature reports that, unlike the corresponding cycloheptadienyliron complexes, no useful carbon-carbon bond forming reactions are known that use nucleophilic addition to the dienyl complex **2**. Our current interest in these compounds is primarily concerned with devising methods to introduce carbon substituents in a stereocontrolled manner in good yields, leading after demetallation to substituted cyclooctadienes that might be useful for synthetic purposes. To achieve this goal the reactivity of the dienyl salt has to be controlled. Previous work from our laboratory has indicated that dimethylcuprate and dimethyl malonate anion gave only very poor yields of products by addition to the dienyl terminus of complex **2**.[7] The major problem is that the dienyl salt **2** acts as an ambident electrophile, and nucleophiles can attack either at the dienyl terminus, at the C2 position or at a carbonyl ligand. Attack at the metal could be curtailed by replacing a CO ligand with a poorer π acceptor which would increase the electron density at the metal. This strategy was successfully employed with the cycloheptadiene complexes.[1] We expected a similar outcome for the cyclooctadiene complexes, but several early attempts to effect direct ligand exchange with complex **2** failed.[7]

RESULTS AND DISCUSSION

Synthesis of Dicarbonyl[(1-5-η)cycloocta-1,3-dienyl](triphenylphosphine)iron Hexafluorophosphate

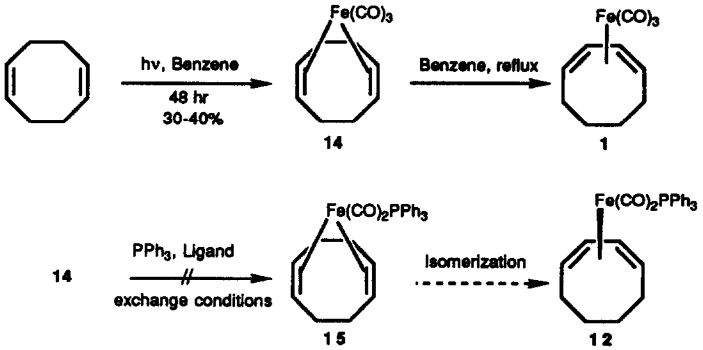
Dicarbonyl[(1-4-η)cycloocta-1,3-diene](triphenylphosphine)iron (**12**) has recently been prepared by photolyzing the 1,3- or 1,5-cyclooctadiene with $Fe(CO)_4PPh_3$ in a sealed tube at -10 °C.[8] Hydride abstraction using triphenylmethyl hexafluorophosphate should give the dienyl salt **13**, but to be synthetically useful a practical method that would lead to multigram quantities of **13** needs to be devised, because the sealed tube photochemical method will not be suitable for large scale preparations. Dicarbonyl[(1-5-η)cyclooctadienyl](triphenylphosphine)iron hexafluorophosphate (**13**) was reported to be obtained by treating the neutral iodo complex **7** with triphenylphosphine in the presence of silver hexafluorophosphate.[6] In our hands the iodo complex gave a very poor yield of the dienyl salt. This result, along with the high cost of silver hexafluorophosphate to be used in large scale reactions, led us to devise an alternate method for the preparation of **13**.

Tricarbonyl[(1-4-η)-cycloocta-1,3-diene]iron (**1**) was prepared according to the method of Deeming *et al.*.[4] Complex **1** was found to be highly unstable and decomposes appreciably even at low temperature. Attempts to introduce a poorer π acceptor ligand such as triphenylphosphine or triphenylphosphite into **1** failed completely. Direct thermal ligand exchange on **1** by refluxing in Bu_2O,[1] in benzene, or in acetone gave the decomplexed diene and $Fe(CO)_3(PPh_3)_2$. Photolysis of complex **1** with triphenylphosphine in benzene was not successful either. Partial decomplexation followed by ligand exchange by using trimethylamine-N-oxide[9] in the presence of triphenylphosphine also gave only the decomplexed diene and $Fe(CO)_3(PPh_3)_2$.



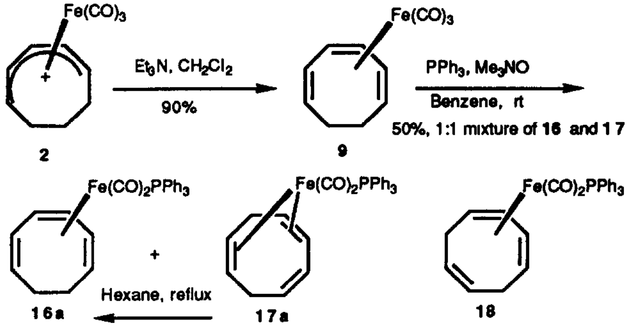
One explanation for this failure to effect the ligand exchange could be the inherent instability of the diene-$Fe(CO)_3$ complex. The uncomplexed diene has a dihedral angle of 41° between the C=C double bonds.[10] Complexation induces a planarity in the diene fragment of the molecule, which is essential for good overlap of the diene orbitals and the $Fe(CO)_3$ orbitals.[11] It is conceivable that this complexation-induced planarity introduces considerable strain in the diene ring of the cycloocta-1,3-dieneiron which makes this complex unstable. Therefore, we decided to try the ligand exchange on a more stable complex which could withstand the reaction conditions. The corresponding cycloocta-1,5-diene iron complex **14** seemed to be a better choice. It is reported to be inherently more stable, and it rearranges thermally to the 1,3-diene complex **1** in good yield.[3] Therefore it was envisaged that complex **15** could be prepared by, e.g., photoinduced ligand exchange with triphenylphosphine on **14**. Thermal rearrangement of the 1,5-diene complex **15** might then lead to the 1,3-diene complex **12**.

All attempts at ligand exchange reactions on complex **14** were also very disappointing, none of the usual methods giving the desired product **15** or **12**. At this stage our attempts to synthesize the complex **12** on a large scale appeared to be destined to fail completely. We decided to attempt the ligand exchange on the tricarbonyl[(1–4–η) cycloocta-1,3,5-triene]iron (**9**), which was prepared in 70% yield by treating the dienyl salt **2** with triethylamine. The triene complex, unlike the diene complex **1** was quite stable and could be stored indefinitely under nitrogen at 0 °C without appreciable decomposition.

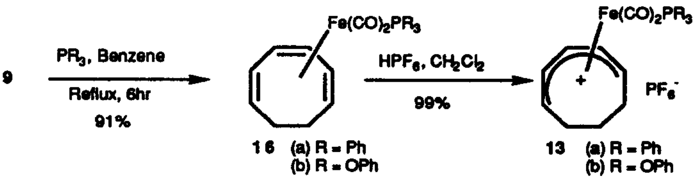


Treatment of complex **9** with PPh_3 and trimethylamine-N-oxide in benzene[9] at rt for 6 h gave two products . Both of these complexes decompose on silica gel during chromatography and showed very close R_f values on basic alumina in various solvents. These two products were separated by fractional recrystallization from CH_2Cl_2/ hexanes (-78 to -40 °C). The two products were obtained in almost 1:1 ratio and the overall yield for this reaction was 50%. One of the products was the ligand exchanged triene complex **16a**. The other product was apparently **17a** containing a rearranged triene ligand. The infrared spectrum of **17a** indicated the presence of two carbonyl ligands, while ten protons and eight ring carbons were shown in its ^1H and ^{13}C NMR spectra, respectively, indicating that this complex has no plane of symmetry, which rules out structure **18a**. In boiling hexanes, complex **17a** rearranges to give **16a**. Based on these observations **17a** was assigned the structure shown. The complex **16a** was obtained as orange crystals (Mp: 158-159 °C) and both **16a** and **17a** are quite stable even at room temperature. When the reaction was run in C_6D_6 and monitored by ^1H NMR, formation of complex **17a** was observed during the initial stages of the reaction, which suggests that complex **17a** is formed directly from the tricarbonyl complex **9**.

Having achieved the ligand exchange on the triene complex we turned our attention to solving the rearrangement problem and optimization of the yield. The fact that the triene complex **17a** rearranged at higher temperature to give the complex **16a** was encouraging since, even if we could not curtail the side reaction it would still be possible to isomerize the mixture to **16a** by refluxing in hexanes. Fortunately, thermal ligand exchange on **9** in refluxing benzene in the presence of 1.6 equivalents of PPh_3 proceeded smoothly to give the desired complex **16a** in excellent yield (91%). The product was isolated from the crude reaction mixture by recrystallization (CH_2Cl_2/hexanes) or on a small scale by chromatography on a basic alumina column. No trace of rearranged product was observed in the ^1H NMR spectrum of the crude product. Assignments for the ^1H NMR spectrum were made based on a COSY experiment. The triene complex **16a** was treated with 1.2



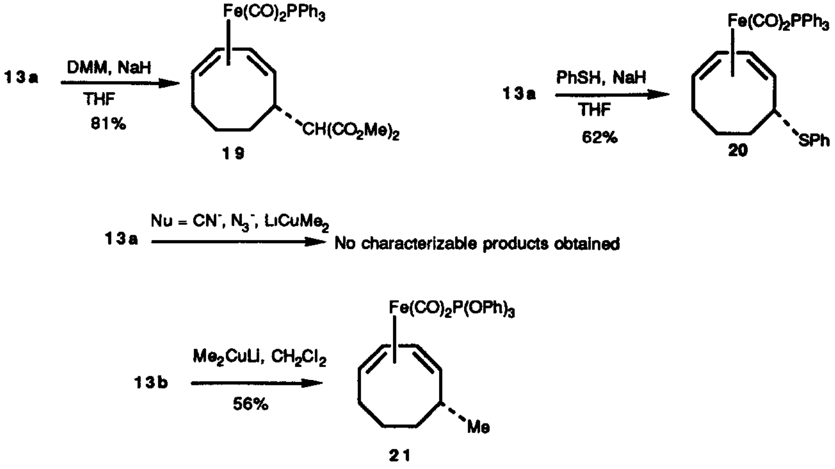
Scheme 4. Ligand exchange on triene complex **9** using PPh_3/Me_3NO



equivalents of 15% aqueous HPF_6 in CH_2Cl_2 to give the dienyl salt **13a** in near quantitative yield. The triphenylphosphite complexes (**b**) were prepared in an analogous fashion.

Reactions of Dienyl Complex 13 With Nucleophiles.

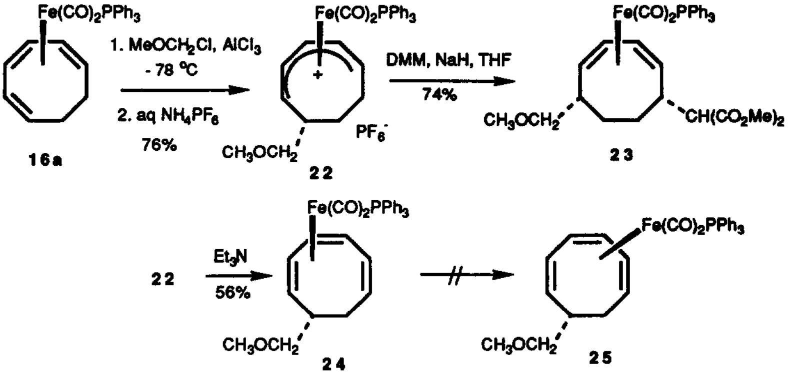
The reactions of **13a** with nucleophiles was first studied. Dimethyl malonate anion and thiophenoxide added exclusively at the terminus of the dienyl ligand giving the diene complexes **19** and **20** in 81 and 62% yield, respectively. These results show again a remarkable tuning of reactivity of the dienyl system since the corresponding tricarbonyl salt gave a poor yield of the terminal adduct with dimethyl malonate anion. Furthermore, in contrast to the cycloocta-1,3-diene-$Fe(CO)_3$ complex, which decomposes during handling and storage, complexes **19** and **20** are quite stable and easy to handle. Unlike the tricarbonyl salt **2** the triphenylphosphine substituted salt **13a** did not give any characterizable products with cyanide or azide. Most disappointingly alkylation with dimethyl cuprate led to complete decomposition. An unusually subtle ligand effect was noted at this point: the triphenyl*phosphite* complex **13b** reacted with Me_2CuLi to give the nucleophile addition product **21**. This result contrasts with those obtained for cycloheptadienyliron complexes, where no difference is observed between PPh_3 and $P(OPh)_3$ complexes.[1]



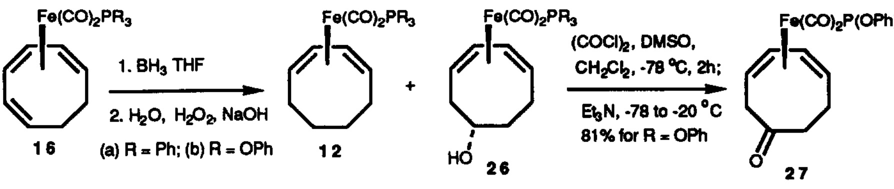
Electrophilic Alkylation of Cyclooctatriene Complex 16a.

There are many examples of carbon carbon bond forming reactions with unsaturated hydrocarbon ligands bound to electrophilic transition metal complexes *via* their reactions with nucleophiles. Apart from the dienyl-$Fe(CO)_2L$ complexes [L = PPh_3, $P(OPh)_3$] discussed in this paper, π-allyl palladium complexes and arene(tricarbonyl)chromium complexes represent a few examples that have been thoroughly studied. On the other hand, the alternative approach to carbon-carbon bond formation *via* the addition of electrophiles to η^4-triene or tetraene complexes has received little attention.[10]

While there are many examples for electrophilic acylation on the η^4-triene and tetraene complexes there are hardly any reports on electrophilic alkylations. We envisioned that a Friedel-Crafts type alkylation on the triene complex **16a** would directly yield a substituted cyclooctadienyl salt **22** which could lead to 1,4-functionalized **23** by subsequent nucleophilic addition. Deprotonation of the dienyl salt **22** would give monosubstituted triene **24**, and this can in principle be functionalized in a manner analogous to **16**. The electrophile chosen for this study was the methoxymethyl cation. This could be easily generated from the readily available chloromethyl methyl ether (MOMCl) and $AlCl_3$. Treatment of triene complex **16a** with excess of $AlCl_3$ and MOMCl in CH_2Cl_2 at -78 °C followed by anion exchange with aqueous ammonium hexafluorophosphate gave the stable methoxymethyl substituted dienyl salt **22** in 76% yield, the stereochemistry of which was assigned by analogy with the known acylations of cycloheptatrieneiron tricarbonyl.[11] The product in this reaction was invariably contaminated with the dienyl salt **13a** formed by protonation of the triene with traces of acid that are present in the reaction mixture. Treatment of dienyl salt **22** with dimethyl sodiomalonate gave the 1,4- disubstituted cyclooctadiene complex **23** in 74% yield. Deprotonation of the dienyl salt **22** by treatment with triethylamine proceeded smoothly to give the methoxymethyl substituted triene **24** in 56% yield. The triene **24** is configurationally stable at room temperature (from ^{1}H NMR) and no haptotropic equilibration to **25** is observed.



Scheme 5



Hydroboration of the Trienes 16.

Future work on the cyclooctadiene system is expected to focus on alkylations of enolates derived from ketones. Unlike cycloheptadiene complexes[12] the cyclooctadiene-$Fe(CO)_3$ complexes are quite unstable to hydroboration conditions. The initial addition of borane to the uncomplexed double bond of **9** proceeds without any problem (by TLC analysis), but during the oxidative hydrolysis the complex is completely destroyed. Unlike **9**, the triene complexes **16a** and **16b** are quite stable to hydroboration conditions and gave the alcohol complexes **26** in good yield along with small amounts of the diene complexes **12**, probably formed by hydrolysis of the intermediate alkylborane during the oxidative step. This type of hydrolysis has been observed previously during the hydroboration of π-allyl molybdenum complexes.[13] The stereochemical outcome of the reaction was assigned by analogy with results obtained during the hydroboration of corresponding cycloheptatriene complexes.[12] Oxidation of the alcohol complex **26** under Corey-Kim conditions[14] gave the ketone complexes **27** in modest yields; again, the triphenylphosphite complex was better behaved. Even more striking is the observation that the triphenylphosphite complex **26b** underwent Swern oxidation to give **27** in 81% yield, while **26a** afforded *none* of the desired ketone under identical conditions.

CONCLUSIONS

This paper demonstrates the feasibilty of controlling nucleophile additions to cyclooctadiene complexes by judicious choice of spectator ligands. There is a significant difference in the reactivity of cyclooctadienyl-$Fe(CO)_3$ and $-Fe(CO)_2PPh_3$ complexes, and a more subtle effect of ligand was noted when comparing $-Fe(CO)_2PPh_3$ complexes with $-Fe(CO)_2P(OPh)_3$ systems. We have also shown the possibility of using controlled electrophile addition to the uncomplexed double bond of η^4-cyclooctatrieneiron complexes to effect stereo- and regiocontrolled functionalization of the eight-membered ring. While there are still a number of unanswered questions, this work reveals the potential utility of organoiron systems for controlling substitution in traditionally awkward ring sizes, and demonstrates some of the tactics and strategies that can be used to encourage reticent or hyperactive molecules to "behave".

ACKNOWLEDGEMENTS

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EXPERIMENTAL SECTION

For a description of general experimental techniques and methods used for the characterization of new compounds, see reference 12. Procedures are described for the triphenylphosphine compounds only (series **a**); triphenylphosphite complexes were prepared in an identical fashion. All new compounds that were not subjected to combustion analysis were judged to be at least 95% pure by ^2H and ^{13}C NMR spectroscopy.

Tricarbonyl[(1-4-η)-cycloocta-1,3,5-triene]iron (9). To a suspension of 4.6 g (11.73 mmol) of dienyl complex **2** in 60 mL of CH_2Cl_2 was added dropwise 60 μL of freshly distilled triethylamine over 15 min. The suspension turned clear and the solution was stirred at rt for 30 min, then filtered through celite and concentrated under reduced pressure. The last traces of triethylamine were removed by evacuation through a cold trap to give 2.6 g (90%) of triene **9** as a yellow oil . R_f: 0.56 (hexanes). IR: 3028, 2043, 1968, 1446 cm^{-1}. ^1H NMR (200 MHz) δ 5.92 (ddd, J = 11.0, 8.0, 2.1 Hz, 1H, H-5), 5.65 (dd, J = 8.0, 6.1 Hz, H-6), 5.31-5.10 (m, 2H, H-2, H-3), 3.54 (t, J = 8.2 Hz, H-1), 3.17 (t, J = 8.2 Hz, 1H, H-4), 1.83-2.08 (m, 2H), 1.68 (dt, J = 14.0, 6.0 Hz, 1H), 1.50-1.45 (m, 1H). ^{13}C NMR (75 MHz) δ 211.3, 132.0, 122.2, 89.1, 88.7, 60.2, 59.2, 24.9, 22.2. HRMS calcd for $C_9H_{10}OFe$ (M^+ - 2CO): 190.0081. Found: 190.0088.

Dicarbonyl[(1-4-η)-cycloocta-1,3-diene](triphenylphosphine)iron (12a). This complex was obtained as a side product during hydroboration of **16a**. R_f: 0.52 (10% EtOAc-hexanes). ^1H NMR (200 MHz) δ 7.51-7.27 (m, 15H, phosphine-H), 4.56-4.50 (m, 2H, H-2, H-3), 2.70-2.66 (m, 2H, H-1, H-4), 2.06-1.96 (m, 4H, H-5, H-8), 1.36-1.09 (m, 4H, H-6, H-7), ^{13}C NMR (75 MHz), δ 219.4, 136.4 (d, J_{C-P} = 37 Hz), 133.5, (d, J_{C-P} = 10.3 Hz), 129.7, 92.7, 60.23, 29.45, 25.82. HRMS calcd for $C_{26}H_{27}FeP$ (M^+ - 2CO): 426.1200. Found: 426.1981.

Dicarbonyl[(1-5-η)-cyclohepta-1,3-dienyl](triphenylphosphine)iron Hexafluorophosphate (13a). To an ice cooled solution of 500mg (1.04 mmol) of triene **16a** in 10 mL of CH_2Cl_2 was added 3 mL of HPF_6 solution (15% by weight in water). The reaction mixture was stirred at rt for 10 min, then diluted with ether and centrifuged to remove the precipitated dienyl salt **12a**. The dienyl salt was further washed with 10 mL of ether and centrifuged again to remove ether. The last traces of solvent were removed by evacuation through a cold trap to give 650 mg of **13a** (94%). IR 2039, 1998 cm^{-1}. ^1H NMR (300 MHz, CD_3COCD_3, 50 °C) δ 7.66-7.33 (m, 15H, Ar-H), 7.34 (t, J = 7.0 Hz, H-3), 5.4 (br, 2H, H-2, H-4), 2.82, (br, 2H, H-1, H-5), 2.19 (br, 2H, *endo* H-6, *endo* H-8), 1.88 (br, 2H, *exo* H-6, *exo* H-8), 1.28, (d, J = 14 Hz, 1H, *exo* H-7), 0.23 (q, J = 14.0 Hz, 1H, *endo* H-7) ^{13}C NMR (75 MHz, acetone d_6) δ 133.9 (d, $J_{C\text{-}P}$ = 10 Hz), 132.8, 130.1 (d, $J_{C\text{-}P}$ = 10.3 Hz), 129.4, 109.8, 96.0, 92.3, 74.5, 73.4, 25.9, 17.3.

Dicarbonyl[(1-4-η)-cycloocta-1,3,5-triene](triphenylphosphine)iron (16a). To a solution of 1.04 g (4.22 mmol) of triene complex **9** in 20 mL of CH_2Cl_2 was added 1.66 g (6.33 mmol) of PPh_3. The resulting solution was stirred at rt for 15 min under a vigorous stream of nitrogen and then refluxed for 6 h, cooled to rt and diluted with 200 mL of hexane. The hexane solution was filtered through celite and the celite pad was washed with 20 mL of hexane. The combined hexane solutions were concentrated under reduced pressure to give the crude product as a yellow oil that was purified by recrystallization from hexanes to give the the title compound as orange crystals; yield 1.83 g (90%). Mp: 156-157 °C. IR 1971, 1912, 1521, 1477 cm^{-1}. ^{1}H NMR (300 MHz,) δ 7.60-7.47 (m, 6H, phosphine-H), 7.00-6.93 (m, 9H, phosphine-H), 6.25 (m, dd, J = 11.0, 7.8 Hz, 1H, H-5), 5.29 (dt, J = 11.1, 7.1 Hz, 1H, H-6), 4.90-4.88 (m, 1H, H-2), 4.33-4.31 (m, 1H, H-3), 3.05 (q, J = 6.5 Hz, 1H, H-4), 2.77 (q, J = 7.8 Hz, 1H, H-1), 1.77-1.64 (m, 4H, H-7, H-8). ^{13}C NMR (75 MHz) δ 218.8, 217.8, 135.8 (d, $J_{C\text{-}P}$ = 37.0 HZ), 133.6 , 133.1 (d, $J_{C\text{-}P}$ = 10.3 Hz), 129.4, 128.9 (d, $J_{C\text{-}P}$ = 6.7 Hz), 119.6, 90.3, 88.7, 57.3, 56.2, 25.2, 22.3. HRMS calcd for $C_{26}H_{25}FeP$ (M - 2CO): 424.1043. Found: 424.1045.

Dicarbonyl[(1,2-η^2),(7,8-η^2)-cycloocta-1,3,7-triene](triphenylphosphine)iron (17a). This complex was obtained as side product in the ligand exchange reaction of **9**, using Me_3NO. Mp: 158-159 °C (CH_2Cl_2/hexanes). IR($CHCl_3$): 1980, 1920, 1472, 1435 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6) δ 7.57-7.49 (m, 6H, Phosphine-H), 6.98-6.92 (m, 9H, Phosphine-H), 5.61-5.59 (m, 1H), 5.50-5.49 (m, 1H), 4.67 (dd, J = 14.0 Hz, 9.0Hz 1H), 4.30-4.28 (m, 1H), 3.93 (dt, J = 18.0 Hz, 9.0 Hz, 1H), 3.25 (m, 1H), 2.99-2.95 (m, 1H), 2.17-2.16 (m, 1H), 1.96-1.93 (m, 1H), 1.71-1.68 (m, 1H). HRMS calcd for $C_{26}H_{25}FeP$ (M^+ - 2CO): 424.1043. Found: 424.1037.

Dicarbonyl[(1-4-η)-5-*exo*-(dicarbomethoxymethyl)-cycloocta-1,3-diene](triphenylphosphine) iron (19). To a stirred suspension of 9.6 mg (0.2 mmol) of NaH in THF at rt was added dropwise a solution of 25 μL (0.2 mmol) of dimethyl malonate in 1.0 mL of THF. After stirring the reaction mixture for 15 min, 60 mg (0.1 mmol) of dienyl salt **13a** was added in one portion. The resulting mixture was stirred at rt for 30 min and then diluted with 20 mL of ether. The ether solution was subjected to standard workup to give a crude product that was purified by flash chromatography (1:3-EtOAc:hexanes) to give 53 mg of product as a yellow oil (86%). Rf 0.3 (20% EtOAc-hexanes). ^{1}H NMR (200 MHz) δ 7.56-7.46 (m, 6H, phosphine-H), 7.00-6.97 (m 9H, phosphine-H), 4.82-4.74 (m, 1H, H-2 or H-3), 4.56-4.48 (m, 1H, H-3 or H-2), 3.51 (d, J = 6.4 Hz, 1H, malonate-H), 3.37 (s, 3H, COO$\underline{CH_3}$), 3.35 (s, 3H, COO$\underline{CH_3}$), 3.21-3.12 (m, 1H), 2.94-2.87 (m 1H), 2.79-2.69 (m, 1H), 2.13-2.01 (m, 2H), 1.50-1.19 (m, 4H). ^{13}C NMR (75 MHz) δ 168.6, 135.5 (d, $J_{C\text{-}P}$ = 37 Hz), 133.1 (d, $J_{C\text{-}P}$ = 10 Hz), 129.4, 93.5, 90.1, 61.2, 60.8, 59.8, 51.4, 51.3, 40.3, 29.7, 29.0, 24.4, (metal carbonyl not observed). HRMS calcd for $C_{31}H_{33}O_4FeP$ (M^+ - 2CO): 556.1466. Found: 556.1460

Dicarbonyl[(1-4-η)-5-*exo*-phenylthiocycloocta-1,3-diene](triphenylphosphine)iron (20). To a solution of 13 μL (0.12 mmol) of thiophenol in 1 mL of THF was added 3 mg (0.12 mmol) of NaH. The reaction mixture was allowed to stir for 10 min then cooled to 0 °C and 63 mg (0.1 mmol) of dienyl salt **13a** was added in one portion. The yellow solution was stirred at 0 °C for 1 h then diluted with 20 mL of ether and the ether solution was subjected to the usual workup to give 38 mg of crude product (62%). This compound was not stable to silica gel and was not further purified. NMR showed the crude product to be approximately 95% pure. ^{1}H NMR (200 MHz) δ 7.65 (dd, 2H, J = 8.1Hz, 2H), 7.54-7.31 (m, 18H, phosphine-H, S-Ph), 4.69-4.57 (m, 1H), 4.50-4.38 (m, 1H), 3.95-3.83 (m, 1H), 2.88-2.64 (m, 1H), 2.23, 2.09 (m, 1H) 1.85-1.66 (m, 1H), 1.38-1.12 (m, 4H), 0.90-0.80 (m,1H).

Dicarbonyl[(1-4-η)-5-*exo*-methylcycloocta-1,3-diene](triphenylphosphite)iron (21). A suspension of CuI (56.4 mg, 0.297 mmol) was stirred in ether under N_2 at 0 °C while MeLi (435 μL of 1.4 M solution in ether, 0.608 mmol) was added dropwise. After stirring for 2 min at 0 °C, a solution of complex **12b** (100 mg, 0.148 mmol) in CH_2Cl_2 (1 mL) was added. After stirring for 1 h at 0 °C, the reaction mixture was quenched with saturated aq. NH_4Cl (2 mL), the mixture was stirred in air for 30 min, and extracted with ether in the usual way. The crude product was purified by flash chromatography (3% EtOAc in hexane) to give **21** (45 mg, 56%) as a yellow oil. IR: 1989, 1935, 1590, 1489 cm^{-1}. ^{1}H NMR (benzene-d_6) δ 7.25 (d, J = 7.7 Hz), 7.12 - 6.98 (m), 6.84 (t, J = 7.4 Hz), 4.66 -4.54 (m, 2H), 3.21 - 3.17 (m, 1H), 2.82 - 2.78 (m, 1H), 1.93 - 1.88 (m, 2H), 1.81 - 1.77 (m, 1H), 1.19 - 1.16 (m, 1H), 1.06 - 0.98 (m, 2H), 0.88 (d, J = 7 Hz, 3H). ^{13}C NMR δ 216.6 (d, $J_{C\text{-}P}$ = 6 Hz), 216.4 (d, $J_{C\text{-}P}$ = 6 Hz), 152.1 (d, $J_{C\text{-}P}$ = 6.7 Hz), 130, 125, 121.6 ($J_{C\text{-}P}$ = 4 Hz), 90.3, 89.9, 69.6 (d, $J_{C\text{-}P}$ = 5 Hz), 62.1 (d, $J_{C\text{-}P}$ = 5.6 Hz), 35, 34.4, 28.9, 27.1, 25.1.

Dicarbonyl[(1-5-η)-5-*exo*-(methoxymethyl)-cycloocta-1,3-dienyl](triphenylphosphine)iron Hexafluorophosphate (22). A solution of 250 mg (0.52 mmol) of triene **16a** in 5.0 mL of CH_2Cl_2 was cooled to -78 °C and 200 µL (2.6 mmol) of MOMCl was added. The reaction mixture was stirred for 2 min and then 346 mg of anhydrous $AlCl_3$ was added in small portions. After completion of the addition of $AlCl_3$ the reaction mixture was stirred for 30 min and then 10 mL of 10% NH_4PF_6 solution was added. The temperature was raised to rt and the mixture was stirred for 1 h, the layers were separated and the dienyl salt was precipitated by adding the CH_2Cl_2 layer to large excess of ether to give 296 mg (75% yield) of **22** contaminated with 5-10% of **12** formed by protonation of triene **16a**. Compound **22** was used in the next steps without further characterization or purification.

Dicarbonyl[(1-4-η)-5-*exo*-(dicarbomethoxymethyl)-8-*exo*-(methoxymethyl)cycloocta-1,3-diene](triphenylphosphine)iron (23). A solution of dimethyl sodiomalonate in THF was generated and to this solution was added 63 mg (90 % pure, 0.08 mmol) of crude dienyl salt **22**. The reaction mixture wasstirred for 1 h, then diluted with 30 mL of ether and the ether solution was subjected to the usual workup to give the crude product that was purified by flash chromatography to afford **23** (39 mg, 74%). IR ($CHCl_3$): 1972, 1917, 1756, 1735 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$)) δ 7.46-7.20 (m, 15H, phosphine-H), 4.79-4.78 (m 1H, H-3), 4.54-4.53 (m, 1H, H-2), 3.66 (s, 3H, $COOCH_3$), 3.63 (s, 3H, $COOCH_3$), 3.27 (d, J = 4.3 Hz, 1H, malonate-H), 3.17 (s, 3H, $-OCH_3$), 2.96 (d, J = 6.4 Hz, 2H), 2.75-2.74, (m, 1H, H-5), 2.48-3.47 (m, 1H, H-8), 2.24-2.12 (m, 2H, H-1, H-4), 1.54-1.52 (m, 2H), 1.23-1.19, (m, 2H). ^{13}C NMR (75 MHz) δ 169.1, 134.5 (d, J_{C-P} = 37.5Hz), 133.3 (d, J_{C-P} = 10.6), 129.7, 128.2 (J_{C-P} = 7.1 Hz), 92.9, 89.6, 79.6, 77.3, 76.3, 63.8, 59.8, 58.6, 52.3, 52.2, 40.3, 39.5, 28.7, 27.6. HRMS cacld for $C_{15}H_{22}O_5$ (M^+ - $Fe(CO)_2PPh_3$): 282.1467. Found: 282.1461.

Dicarbonyl[(2-6-η)-7-*exo*-(methoxymethyl)cycloocta-1,3,5-triene](triphenylphosphine)iron (24). To a solution of 150 mg (90% pure, 0.2 mmol) of dienyl salt **22** in 1 mL of CH_2Cl_2 was added 10 µL of Et_3N. The reaction mixture was stirred at rt for 30 min, then diluted with ether and the ether solution was filtered through celite. The filtrate was concentrated at reduced pressure to give crude product that was purified by column chromatography (basic alumina, 5% EtOAc-hexanes) to give 59 mg of the title compound (58%) and 10 mg of parent triene **16a**. ^1H NMR (300 MHz, $CDCl_3$) for **24**: δ 7.57-7.41 (m, 15H, phosphine-H), 6.06 (ddd, J = 10.5, 8.1, 1.7 Hz, 1H, H-2), 5.26-5.20 (m, 1H, H-1), 5.00-4.98 (m, 1H, H-3 or H-4), 4.54-4.53 (m, 1H, H-4 or H-3), 3.29 (s, 3H, $-OCH_3$), 3.06 (d, J = 7.1 Hz, 2H, CH_2OCH_3), 2.73-2.63 (m, 2H, H-2, H-6), 1.82 (dd, J = 13.5, 9.1 Hz, 1H, H-8), 1.73-1.67 (m, 1H, H-7), 1.42-1.34 (m, 1H, H-8). HRMS calcd for $C_{28}H_{29}FeOP$ (M^+ - 2CO): 468.1305. Found: 468.1306.

Dicarbonyl[(1-4-η)-6-*exo*-hydroxycycloocta-1,3-diene](triphenylphosphine)iron (26). A solution of 100 mg (0.2 mmol) of triene complex **16a** in 2.0 mL of THF was cooled to 0 °C and 600 µL of 1.0 M solution of BH_3-THF complex in THF was added. The temperature of the reaction mixture was gradually raised to rt and stirring aws continued for 2 h. It was then cooled back to 0 °C and 1.0 mL of water was added followed by 0.4 mL of 15% NaOH solution and 30% H_2O_2. The resulting mixture was stirred for 1.5 h, diluted with ether (100 mL) and subjected to the usual workup to give a mixture of two products **26** and **12** that were separated by flash chromatography (40% EtOAc-hexanes) to give 84 mg (81%) of alcohol **26** and 12 mg of diene complex **12**. R_f: 0.59 (1:1 EtOAc-hexanes). Mp: 120-121 °C (CH_2Cl_2-hexanes) IR: 3628, 1967, 1906 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.46-7.38 (m, 15H, Phosphine-H), 4.82-4.80 (m, 1H, H-3), 4.63-4.59 (m, 1H, H-2), 3.74-3.68 (m, 1H, H-6), 2.85-2.81 (m, 1H), 2.43-2.23 (m, 3H), 2.14-1.85 (m, 2H), 1.78-1.1-64 (m, 1H), 1.31-1.28 (m, 1H), 1.01-0.88 (m,1H). ^{13}C NMR (75 MHz) δ 135.5 (d, J_{C-P} = 37.8 Hz), 133.15 (d, J_{C-P} = 10.3 Hz), 129.7, 128.2, 94.9, 89.9, 70.2, 58.5, 52.5, 38.8, 36.0, 27.2. HRMS cacld for $C_{26}H_{27}OFeP$ (M^+ - 2CO): 442.1149. Found: 442.1171.

Dicarbonyl[(1-4-η)-6-oxo-cycloocta-1,3-diene](triphenylphosphite)iron (27). To a solution of oxalyl chloride (51 µL, 0.584 mmol) in 2 mL CH_2Cl_2 cooled to -78 °C was added dimethyl sulfoxide (108 µL, 1.169 mmol) and the mixture was stirred for 5 min.. To this was added a solution of the alcohol **26b** (290 mg, 0.531 mmol) in methylene chloride (3 mL) and stirring was continued at -78 °C for 2 h. To the mixture was added triethylamine (0.37 mL, 2.656 mmol) and the temperature was allowed to rise gradually to -20 °C. Water was added, the product was extracted with CH_2Cl_2 and worked up in the usual way. Purification using flash chromatografy (20% EtOAc in hexane) afforded the ketone **27** as a yellow solid (235 mg, 81%) which decomposed without melting at 125 - 130 °C. IR: 1997, 1942, 1703, 1589, 1488 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.34 - 7.16 (m, aromatic), 4.71 - 4.68 (m, 1H), 3.09 - 3.07 (m, 1H), 2.96 (d, J = 13.3 Hz, 1H), 2.76 - 2.73 (m, 1H), 2.45 (t, J = 12 Hz, 1H), 2.13 - 2.04 (m, 2H), 1.99 - 1.89 (m, 2H). ^{13}C NMR (CD_2Cl_2) δ 212, 151 (d, J_{C-P} = 7 Hz), 130 (d, J_{C-P} = 4 Hz), 125, 121 (d, J_{C-P} = 5 Hz), 91, 90, 59, 43, 42, 25.

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