Tricarbonyl[(1−4-η)-2-Methoxy-5-methylenecyclohexa-1,3-diene]iron as a Synthetic Intermediate: Sequential Electrophilic and Nucleophilic Additions

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Summary: Tricarbonyl[(1−4-η)-2-methoxy-5-methylenecyclohexa-1,3-diene]iron reacts with electrophiles to give the cyclohexadienylium−Fe(CO)$_3$ cation, which either reacts with nucleophiles to form a new quaternary center or undergoes competitive loss of an acidic α-proton to give a new triene complex. This constitutes a new reaction sequence for the synthesis of 4,4-disubstituted cyclohexen-2-ones with the simultaneous introduction of two functional groups.

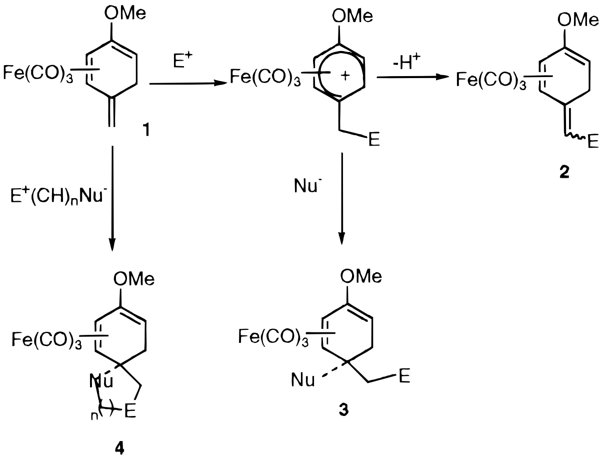
Introduction

The application of tricarbonyl[(1−4-η)-2-methoxy-5-methylenecyclohexa-1,3-diene]iron (**1**) as a valuable intermediate in organic synthesis has not been widely studied until our recent publication.[1] The Fe(CO)$_3$ group acts both as a protecting group for the diene by preventing aromatization and as an electron-releasing substituent for the exocyclic methylene group due to its polarizability. In general, complex **1** is protonated with strong acid to give the known tricarbonyl[(1−5-η)-2-methoxy-5-methylcyclohexadienyl]iron salt. It is thus extremely important that the reaction of electrophiles with complex **1** does not involve the use of strong acids. Electrophiles that can be generated from Lewis acids will be favored for these reactions. We herein report the bis-functionalization of the exocyclic methylene group in complex **1** through a sequential electrophilic−nucleophilic addition reaction. This reaction sequence proceeds with efficient regio- and stereocontrol and constitutes a rapid method for the construction of new compounds with increasing molecular complexity, which are useful in synthesis.

Results and Discussion

The complex **1** can be readily prepared from the reaction of tricarbonyl[(1−4-η)-2-methoxy-5-methylcyclohexadienyl]iron hexafluorophosphate with triethylamine in THF at room temperature.[1] Reaction of complex **1** with electrophiles provides a new tricarbonyl(η^5-cyclohexadienyl)iron intermediate which can be deprotonated to give **2** or undergo further nucleophilic addition to give **3** (Scheme 1). One of the most straightforward tests for the sequential electrophilic−nucleophilic addition at the exocyclic double bond is the hydroboration reaction.[2] Reaction of complex **1** with borane followed by oxidative workup (H$_2$O$_2$, NaOH) gave the alcohol complex **3a** in good yield. It was found that the hydroboration reaction had occurred endo to the Fe(CO)$_3$ group, as indicated by the low chemical shift for the endo-H(5) proton (δ 1.72) in **2**. Similarly, in **3a**, the endo-H(6) proton was found at δ 1.92 due to deshielding by the Fe(CO)$_3$ group, whereas exo-H(6) was found at δ 1.18. The COSY experiment confirmed the chemical shift for the endo-H(5) proton at δ 1.72, which showed a cross-peak with the hydroxymethyl group at δ 3.31. It has been reported that the ^{1}H NMR chemical shifts for cyclohexadiene-Fe(CO)$_3$ complexes are approximately δ 2.00 and 1.20 for the endo and exo protons, respectively. The product from the exo-hydroboration reaction places the hydroxymethyl group endo to the Fe(CO)$_3$ group, whereas the product from endo-hydroboration places a hydrogen endo to the Fe(CO)$_3$ group. In our experiment, endo attack predominates to give complex **3a** having an exo-methyl, which is the more stable product. As reported,[3] the stability of the product from the addition might outweigh the steric interaction between the nucleophile and the Fe(CO)$_3$ group in the transition structure. This phenomenon was also similar to the reported endo-borohydride for cyclohexadienyl−Fe(CO)$_3$ complexes having a substituent at the carbon center undergoing reduction to give the more stable exo-substituted product.[3,4]

Scheme 1



The Perrier complexes were the second group of electrophiles that were studied. The Friedel−Crafts

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[1] Ong, C. W.; Chien, T. L. *Organometallics* **1996**, *15*, 1323.

[2] Evans, G.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1975**, *102*, 507.

[3] Ong, C. W.; Liou, W. T. *J. Chin. Chem. Soc.* **1991**, *38*, 239.

[4] Birch, A. J.; Kimberlain, K. B.; Haan, M. A.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1882.

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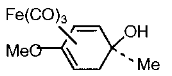
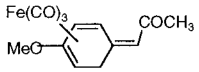
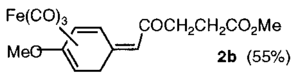
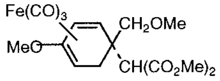
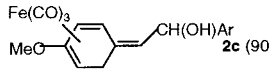
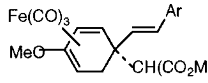
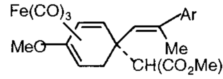
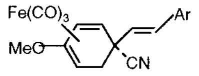
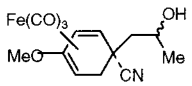
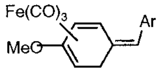
acylation of polyene–$Fe(CO)_3$ complexes has been shown to proceed selectively at the uncomplexed double bond.[5,6] It was hoped that the reaction of complex **1** with a Perrier complex would proceed to give a cyclohexadienylium–$Fe(CO)_3$ cation intermediate, which could be converted into the stable hexafluorophosphate salt by anion exchange with ammonium hexafluorophosphate, followed by a subsequent nucleophilic addition reaction. The reaction of complex **1** with $CH_3COCl/AlCl_3$ was found to give efficiently the new acetylated triene complex **2a**. Attempts to isolate the acetyl–cyclohexadienylium–$Fe(CO)_3$ cation intermediate or to carry out an in situ reaction with the potassium enolate of dimethyl malonate failed, and **2a** was obtained as the sole product due to deprotonation of the salt. We subsequently obtained the hexafluorophosphate salt by treating complex **2a** with HPF_6; this did not give an addition product with the potassium enolate of dimethyl malonate but, rather, resulted in deprotonation to give complex **2a**. This suggests that the α-proton of the salt is very acidic and undergoes spontaneous deprotonation during the reaction with the Perrier complex. We hoped to remedy this limitation by using an electrophile with a "built-in" enolizable center to act as a nucleophile that might participate in an intramolecular cyclization reaction in the cyclohexadienylium–$Fe(CO)_3$ cation intermediate. Thus, we reacted complex **1** with succinyl chloride monoester in the presence of $AlCl_3$ with the hope of obtaining product **4** (Scheme 1, $n = 1$). Disappointingly, only the deprotonated product **2b** was obtained (Table 1).

Application of the above reaction was somewhat limited because of the difficulty in performing the subsequent nucleophilic addition reaction. The use of Friedel–Crafts alkylation should give a more stable cyclohexadienylium–$Fe(CO)_3$ intermediate with a less acidic α-proton. This would disfavor deprotonation and increase the chances for the isolation of the cyclohexadienylium–$Fe(CO)_3$ cation intermediate for the subsequent nucleophilic addition reaction. Complex **1** was reacted with $CH_3OCH_2Cl/AlCl_3$ to give the cyclohexadienyl–$Fe(CO)_3$ cation intermediate, which was converted into the stable hexafluorophosphate salt by anion exchange with aqueous ammonium hexafluorophosphate. As was postulated, this salt was less prone to deprotonation and was stable enough for further manipulations. The reaction of the salt with the potassium enolate of dimethyl malonate took place stereoselectively to give complex **3b** in high yield. Reaction of this salt with the potassium enolate of dimethyl malonate has been reported to give both C-1 (major) and C-5 (minor) addition products.[7,8] In this case, the minor C-5 adduct may have been lost during the workup and purification processes. The overall sequence of electrophilic–nucleophilic addition reactions should lead to a useful methodology for organic synthesis (Table 1).

Table 1. Reaction of Complex 1 according to Scheme 1

Electrophile	Nucleophile (base)	Product / compd. no. (yield)
1. BH_3/Et_2O		 **3a** (80%)
2. $CH_3COCl/AlCl_3$		 **2a** (60%)
3. CH_2COCl CH_2CO_2Me $AlCl_3$		 **2b** (55%)
4. CH_3OCH_2Cl $AlCl_3$	$KCH(CO_2Me)_2$	 **3b** (76%)
5. C_6H_5CHO/BF_3	Et_3N	 **2c** (90%)
6. C_6H_5CHO/BF_3	$KCH(CO_2Me)_2$	 **3c** (82%)
7. $C_6H_5COCH_3/BF_3$	$KCH(CO_2Me)_2$	 **3d** (50%)
8. C_6H_5CHO/BF_3	TMS-CN	 **3e** (75%)
9. CH_3CHO/BF_3	TMS-CN	 **3f** (65%)
10. $C_6H_5N_2^+PF_6^-$		 **2d** (60%)

Treatment of an aldehyde or ketone with boron trifluoride is another common method used to generate a transient cation for reaction with alkenes. Our immediate goal was to prove that this reaction sequence could be successfully carried out with complex **1**. A preliminary experiment involved the reaction of complex **1** with benzaldehyde in the presence of BF_3, followed by quenching with triethylamine to give **2c** in high yield. The feasibility of this reaction sequence tempted us to isolate the requisite intermediate cyclohexadienylium–$Fe(CO)_3$ salt by treatment with HPF_6 in acetic anhydride after the reaction of complex **1** with benzaldehyde–BF_3. This salt was found to undergo regio- and stereoselective reaction with the potassium enolate of dimethyl malonate to give a high yield of the desired complex **3c**, indicating that dehydration of the alcohol took place during the reactions to give a trans exocyclic double bond. The ^1H NMR of **3c** shows a doublet exhibiting a trans coupling constant of 16 Hz for the vicinal hydrogens in the double bond. In a similar manner the reaction sequence was carried out with acetophenone, which also gave the dehydrated product **3d**, which has a trans exocyclic double bond. The stereochemistry of **3d** was assigned on the basis of the trans coupling constant of 1.2 Hz ($HC{=}CCH_3$) and the

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(5) Johnson, B. F. G.; Lewis, J.; McArdle, P.; Randall, G. L. P. *J. Chem. Soc., Dalton Trans.* **1972**, 456.

(6) Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Chem. Commun.* **1976**, 6601.

(7) Pearson, A. J.; Chandler, M. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2238.

(8) Ong, C. W. *J. Chin. Chem. Soc.* **1985**, *32*, 89.

lack of NOE between the vicinal H and CH_3 group. Instead, we observed a NOE between the exocyclic olefinic H and the 2-H proton of cyclohexadienyl−Fe-$(CO)_3$. Reaction of acetaldehyde with **1** gave decomposition products on treatment with HPF_6 in acetic anhydride.

On the basis of these successes, we investigated the possibility of achieving the electrophilic−nucleophilic reaction sequences using a "one-pot" reaction system. All attempts in using the potassium enolate of dimethyl malonate failed. We then decided to use TMS−CN as the nucleophile for the one-pot reaction sequence, and this was successful.[9] The complete consumption of complex **1** upon reaction with benzaldehyde−BF_3 could be monitored by TLC, and this was followed by the addition of TMS−CN, which gave the dehydrated product **3e**. We again tested the reaction sequence with acetaldehyde−BF_3 followed by addition of TMS−CN in one pot, and this successfully afforded a diastereoisomeric mixture of alcohol complex **3f** without dehydration (Table 1). This can be rationalized from the fact that alkyl alcohols are less prone to dehydration compared to benzylic alcohols. At this stage no attempt has been made to separate the diastereoisomers. The one-pot reaction sequence for the Friedel−Crafts reactions with **1** followed by TMS−CN were unsuccessful.

Finally, we examined the use of diazonium salts as electrophiles. Diazonium is one of the best leaving groups known and undergoes nucleophilic displacement readily.[10] Benzenediazonium hexafluorophosphate[11] was prepared by treating aniline with nitrous acid generated from sodium nitrite and HPF_6. The hexafluorophosphate salt was prepared because this gave rise directly to a stable salt. Reaction of complex **1** with benzenediazonium hexafluorophosphate at −78 °C did not give the expected salt. The deprotonated triene complex **2d** was obtained as the sole product. This result was in accordance with that of the acylation reaction, which solely formed the deprotonated product due to the increasing acidity of the α-proton. To attempt this reaction with TMS−CN, the benzenediazonium perchlorate salt was prepared using $HClO_4$. We have previously reported that perchlorate salts of $Fe(CO)_3$ complexes[12] react smoothly with TMS−CN without any side reactions. Disappointingly, reaction of benzenediazonium perchlorate with **1** followed by TMS−CN also gave triene complex **2d** (Table 1).

Conclusions

We have shown that there are two types of reaction pathways that dominate the chemistry of electrophilic−nucleophilic addition to complex **1**. Reactions with electrophiles that consequently increase the acidity of the α-proton in the cyclohexadienylium−$Fe(CO)_3$ intermediate lead to rapid deprotonation with the formation of a new triene complex. When appropriate electrophiles are used, the cyclohexadienyl−$Fe(CO)_3$ intermediate can be isolated as the hexafluorophosphate salt for further nucleophilic addition reactions. A one-pot reaction sequence can be carried out with TMS−CN. This work describes the first electrophilic−nucleophilic adddition reaction to complex **1** and provides a new strategy for the functionalization of two adjacent centers, one of which is quaternary. The reactions should be useful in organic synthesis.

Experimental Section

All the reactions were performed under an atmosphere of dry nitrogen. Infrared spectra were recorded on a BioRad FTS-40 instrument, and NMR spectra were recorded on a Varian VXR-300 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal standard. High-resolution mass spectra were obtained using a JEOL-JMS-HX 100 mass spectrometer. The products are unstable oils and did not give satisfactory microanalysis.

Tricarbonyl[(1−4-η)-2-methoxy-5-hydroxy-5-methylcyclohexa-1,3-diene]iron (3a). Borane in THF (5.0 mL, 1.0 M) was added to an ice-cooled solution of complex **1** (524 mg, 2mM) in THF (20 mL). The reaction mixture was stirred at 0 °C for 6 h and worked up oxidatively by adding water and sodium hydroxide and hydrogen peroxide solutions. The reaction mixture was extracted twice with ether; the ether layers were combined, washed with water, dried ($MgSO_4$), and evaporated to give the product (448 mg, 80% yield after purification by preparative chromatography using ethyl acetate: hexane, 1:3 as eluent). IR: υ_{max} ($CHCl_3$) 3600, 3460, 2040, 1970 cm^{-1}. ^1H NMR: δ 5.11(dd, 1H), 3.60 (s, 3H), 3.43 (m, 1H), 3.22 (d, 2H), 2.77 (d, 1H), 1.87 (dq, 1H), 1.72 (m, 1H), 1.22 (dq, 1H). Mass: *m/z* 280 (M^+), 252, 224, 196. Exact mass: found *m/z* 280.0032 (M^+), calcd for $C_{11}H_{12}O_5Fe$ 280.0034.

Tricarbonyl[(2−5-η)-1-(4-methoxycyclohexa-2,4-dien-1-ylidene)acetone]iron (2a). $AlCl_3$ (320 mg, 2.4 mM) was added portionwise to a mixture of **1** (524 mg, 2 mM) and CH_3-COCl (0.17 mL, 2.4 mM) in CH_2Cl_2 (20 mL) at −78 °C. After 4 h, a saturated solution of ammonium hexaflurorophosphate was added and the mixture stirred for an additional 1 h at room temperature. Addition of dry ether did not give rise to precipitation of the PF_6^- salt. The ether layer was separated, washed with water and brine, dried ($MgSO_4$), and evaporated to give an oily product. Purification by preparative layer chromatography (silica gel; benzene/ethyl acetate, 5:1) afforded the triene **2a** (365 mg, 60%, oil). IR: υ_{max} ($CHCl_3$) 2035, 1978, 1668 cm^{-1}. ^1H NMR: δ 5.36 (dd, 1H), 5.14 (s, 1H), 4.75 (d, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.46 (m, 1H), 2.52 (br. d, 2H). Mass: *m/z* 320 (M^+). Exact mass: found *m/z* 319.9991, calcd for $C_{13}H_{12}O_6Fe$ 319.9983.

Tricarbonyl[methyl(2−5-η)-5-(4-methoxycyclohexa-2,4-dien-1-ylidene)-4-oxo-pentanoate]iron (2b). The same procedure as above was used, expect CH_3COCl was replaced with methyl 3-(chlorocarbonyl)propionate. Purification by preparative layer chromatography (silica gel; ethyl acetate/hexane, 1:4) afforded the triene **2b** (414 mg, 55%, oil). IR: υ_{max} ($CHCl_3$) 2051, 1971, 1723, 1665 cm^{-1}. ^1H NMR: δ 6.01 (s, 1H), 5.38 (dd, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 3.50 (m, 1H), 3.20 (dd, 1H), 3.05 (d, 1H), 2.68 (dd, 1H), 2.80−2.51 (m, 4H). Mass: *m/z* 376 (M^+). Exact mass: found *m/z* 376.0243, calcd for $C_{16}H_{16}O_7Fe$ 376.0245.

Tricarbonyl{dimethyl 2-[(2−5-η)-1-(2-methoxyethyl)-4-methoxycyclohexa-2,4-dien-1-yl]malonate}iron (3b). $AlCl_3$ (320 mg, 2.4 mM) was added portionwise to a mixture of **1** (524 mg, 2 mM) and CH_3OCH_2Cl (0.20 mL, 2.4 mM) in CH_2Cl_2 (20 mL) at −78 °C. After 5 h, a saturated solution of ammonium hexafluorophosphate was added and the mixture stirred for an additional 1 h at room temperature. Addition of dry ether gave rise to a yellow precipitate. The product was obtained by filtration and dried under vacuum (866 mg).

Enolate Addition. THF (20 mL) was added to potassium *tert*-butoxide (210 mg, 1.6 mM) followed by addition of dimethyl

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(9) Alexander, R. P.; James, T. D.; Stephenson, G. R. *J. Chem. Soc., Dalton Trans.* **1987**, 2031.

(10) Collins, C. J. *Acc. Chem. Res.* **1971**, *4*, 315.

(11) Hegarty, A. J. In *The Chemistry of Diazonium amd Diazo Groups;* Patai, S., Ed.; Wiley: New York, 1978; Part 2, pp 511−591.

(12) Ong, C. W.; Chao, Y. K.; Chang, Y. A. *Tetrahedron Lett.* **1994**, *35*, 6303.

malonate (200 mg, 1.8 mM), and the reaction mixture was strirred at room temperature for 1 h. This was then cooled in an ice bath and the yellow precipitate obtained above added and reacted for 2 h. The THF was removed and the product extracted with ether. Purification by preparative layer chromatography (silica gel; benzene/hexane, 5:1) afforded **3b**[7,8] (666 mg, 76%, oil). IR: $\upsilon_{\max}$ ($CHCl_3$) 2047, 1967, 1727 cm^{-1}. ^{1}H NMR: δ 4.98 (dd, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.69 (s, 3H), 3.60 (s, H), 3.38 (t, 2H), 3.32 (m, 1H), 3.26 (s, 3H), 2.83 (d, 1H), 2.57 (dd, 1H), 1.82 (t, 2H), 1.60 (dd, 1H). Mass: *m/z* 438 (M^+). Exact mass: found *m/z* 438.0617, calcd for $C_{18}H_{22}O_9Fe$ 483.0613.

Tricarbonyl[(2−5-η)-2-(4-methoxycyclohexa-2,4-dien-1-ylidene)-1-phenylethanol]iron (2c). Benzaldehyde (0.265 mL, 2.5 mM) was stirred in CH_2Cl_2 (10 mL) and boron trifluoride etherate (0.5 mL, 2 mM) added. The solution was stirred for 30 min, after which a solution of complex **1** (564 mg, 2 mM) was added. The progress of the reaction was monitored by TLC, and after the disappearance of **1**, triethylamine was added; the reaction mixture was then stirred for a further 30 min. The reaction mixture was poured into water and the product extracted with CH_2Cl_2 in the usual way, followed by purification by preparative layer chromatography (silica gel; ethyl acetate/hexane, 1:4) to afford **2c** (662 mg, 90%). IR: $\upsilon_{\max}$ ($CHCl_3$) 3471, 2043, 1965, 1600 cm^{-1}. ^{1}H NMR: δ 7.34 (m, 5H), 5.55 (dd, 1H), 5.20 (dd, 1H), 5.04 (d, d), 3.67 (s, 3H), 3.56 (d, 1H), 3.50 (m, 1H), 2.40 (m, 2H), 1.79 (d, 1H). Mass: *m/z* 340 ($M^+ - CO$). Exact mass: found *m/z* 340.0408, calcd for $C_{18}H_{16}O_5Fe$ 340.0398 ($M^+ - CO$).

Tricarbonyl{dimethyl 2-[(2−5-η)-4-methoxy-1-(2-phenyl-1-ethenyl)cyclohexa-2,4-dien-1-yl]malonate}iron (3c). The experiment was carried out as above, but instead of triethylamine, acetic anhydride (1.5 mL) and 60% aqueous HPF_6 (0.3 mL) were added and reacted for 1 h. Partial removal of the solvent and acetic anhydride followed by addition of dried ether gave a yellow salt, which was filtered and dried under vacuum. This was used immediately for the nucleophilic addition reaction without further purification.

Enolate Addition. THF (20 mL) was added to potassium *tert*-butoxide (224 mg, 2.0 mM) followed by addition of dimethyl malonate (0.23 mL, 2.2 mM), and the reaction mixture was stirred at room temperature for 1 h. This mixture was then cooled in an ice bath and the yellow precipitate above added and reacted for 1 h. The THF was removed and the product extracted with ether. Purification by preparative layer chromatography (silica gel; ethyl acetate/hexane, 1:4) afforded **3c** (790 mg, 82%, oil). IR: $\upsilon_{\max}$ ($CHCl_3$) 2047, 1975, 1600 cm^{-1}. ^{1}H NMR: δ 7.28 (m, 5H), 6.40 (d, 1H), 6.30 (d, 1H), 5.06 (dd, 1H), 3.83 (s, 1H), 3.68 (s, 6H), 3.64 (3, 3H), 3.36 (m, 1H), 2.80 (d, 1H), 2.60 (dd, 1H), 2.11 (dd, 1H). Mass: *m/z* 454 ($M^+ -$ CO). Exact mass: found *m/z* 454.0708, calcd for $C_{22}H_{22}O_7Fe$ 454.0715 ($M^+ - CO$). Yield: 80%.

Tricarbonyl{dimethyl 2-[(2−5-η)-4-methoxy-1-(2-phenylpropen-1-yl)cyclohexa-2,4-dienyl]malonate}iron (3d). This was carried out as for **3c** with acetophenone. IR: $\upsilon_{\max}$ ($CHCl_3$) 2046, 1979, 1600 cm^{-1}; ^{1}H NMR: δ 7.28 (m, 5H), 5.77 (s, 1H), 5.06 (dd, 1H), 3.98 (s, 1H), 3.75 (s, 3H), 3.63 (s, 3H), 3.62 (s, 3H), 3.30 (m, 1H), 3.26 (d, 1H), 2.74 (dd, 1H), 2.35 (dd, 1H), 2.00 (s, 3H). Mass (FAB): *m/z* 468 ($M^+ - CO$). Exact mass (FAB): found *m/z* 468.0869, calcd for $C_{23}H_{24}O_7Fe$ 454.0715 ($M^+ - CO$). Yield: 50%.

Tricarbonyl{(1−4-η)-[2-methoxy-5-(2-phenyl-1-ethenyl)-5-cyanocyclohexa-1,3-diene}iron (3e). In the one-pot reaction sequence, TMS−CN was added after the disappearance of **1** (monitored by TLC) as for **2c** and the reaction mixture refluxed overnight. The reaction mixture was cooled to room temperature and water added. The aqueous layer was further extracted with CH_2Cl_2 and the combined extract washed with brine, dried (Na_2SO_4), and evaporated to afford the product (560 mg, 75%). IR: $\upsilon_{\max}$ ($CHCl_3$) 2043, 1963 cm^{-1}. ^{1}H NMR: δ 7.35 (m, 5H), 6.77 (d, 1H), 5.98 (d, 1H), 5.20 (dd, 1H), 3.70 (s, 3H), 3.51 (m, 1H), 2.64 (d, 1H), 2.52 (dd, 1H), 2.07 (dd, 1H). Mass: *m/z* 377 (M^+). Exact mass: found *m/z* 377.0351, calcd for $C_{19}H_{15}O_4NFe$ 377.0357 (M^+).

Tricarbonyl[(2−5-η)-1-(2-(hydroxypropyl)-4-methoxy-1-cyanocyclohexa-2,4-diene)]iron (3f). This was carried out as for **3e** using acetaldehyde. IR: $\upsilon_{\max}$ ($CHCl_3$) 2050, 1972 cm^{-1}. ^{1}H NMR: δ 5.17 (dd, 1H), 4.12 (m, 1H), 3.68 (s, 3H), 3.47 (m, 1H), 3.05 (d, 1H), 2.44 (dd, 1H), 1.77 (dd, 1H), 1.61 (m, 2H), 1.27 (d, 3H); diastereomer δ 2.12 (dd, 1H) and 1.26 (d, 3H). Mass: *m/z* 333 (M^+). Exact mass: found *m/z* 333.029 96, calcd for $C_{14}H_{15}O_5NFe$ 333.0301 (M^+). Yield: 65%.

Tricarbonyl[([1−4-η)-2-methoxy-5-(1-phenylmethylidene)cyclohexa-1,3-diene]iron (2d). The diazonium salt (250 mg, 1 mM) was dissolved in CH_2Cl_2 (10 mL) and cooled to −78 °C, after which a solution of complex **1** (262 mg, 1 mM) in CH_2Cl_2 (5 mL) was added slowly. The reaction mixture was warmed to room temperature. In an attempt to isolate the intermediate salt, the solvent was evaporated and dried ether was added. In this case, the salt did not precipitate. The ether layer was washed with water, dried over Na_2SO_4, and evaporated to afford the product. Purification by preparative layer chromatography (silica gel; ethyl acetate/hexane, 1:4) afforded **2d** (203 mg, 60%, oil). IR: $\upsilon_{\max}$ ($CHCl_3$) 2048, 1977, 1600 cm^{-1}. ^{1}H NMR: δ 7.22 (m, 5H), 6.23 (s, 1H), 5.20 (dd, 1H), 3.69 (d, 1H), 3.59 (s, 3H), 3.39 (m, H), 2.65 (m, 2H). Mass: *m/z* 338 (M^+). Exact mass: found *m/z* 338.0243, calcd for $C_{17}H_{14}O_4Fe$ 338.0241.

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Supporting Information Available: Figures giving proton NMR spectra for all the compounds (9 pages). Ordering information is given on any current masthead page.

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