

STUDY ON THE NUCLEOPHILIC ADDITION TO (η^4 -CIS-1-METHOXY-1,3-BUTADIENE)IRON TRICARBONYL COMPLEX

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Reaction of the reactive carbanion with (η^4 -cis-1-methoxy-1,3-butadiene)Fe(CO)₃, followed by acid quenching, generates the C-1 substitution product (27%) together with the regular C-2 adduct (71%). A very stable ferracyclopentanone was isolated and its x-ray diffraction analysis determined.

INTRODUCTION

Transition metal complexes of organic substrates are becoming increasingly popular tools for the construction of pharmacologically active natural products.¹ Among the characteristic reactions of these complexes, one of the most useful is the addition of carbon, nitrogen, and oxygen nucleophiles to otherwise unreactive carbon-carbon double bonds.² In contrast, tricarbonyliron(0) diene complexes are better known for their Friedel-Crafts reactivity with electrophiles (Scheme 1).³

Nonetheless, Semmelhack and coworkers have demonstrated that kinetically controlled addition (-78°C) of nucleophiles is generally preferred at an unsubstituted internal position.⁴ Upon warming to 23°C the addition reverses and the nucleophile adds predominantly at a terminal position. Olefinic adducts are the major products when reaction mixtures are quenched with trifluoroacetic acid (Scheme 2).

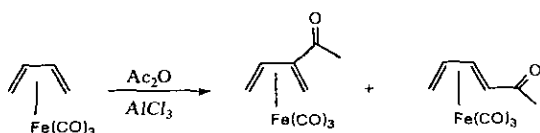
However, very little information is available concern-

ing the nucleophilic addition to (η^4 -diene)Fe(CO)₃ complexes carrying electron-withdrawing or donating groups. Functional groups, such as esters, nitriles, halides at C-1 position of dienes might alter the regioselectivity of nucleophilic additions under kinetically controlled conditions (-78°C). The electron deficiency at C-1 might direct nucleophilic addition toward C-1 rather than at regular internal positions (C-2 or C-3). We report here that the nucleophilic addition to (η^4 -cis-1-methoxy-1,3-butadiene)Fe(CO)₃, **4** follows an uncommon pathway. Coupling of the reactive anionic intermediate, derived from the nucleophilic addition, with various electrophiles will also be discussed.

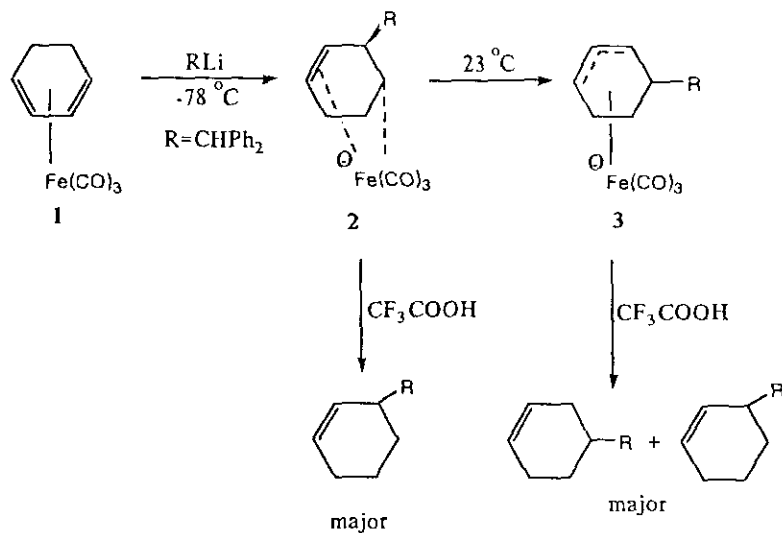
RESULTS AND DISCUSSION

(η^4 -cis-1-Methoxy-1,3-butadiene)Fe(CO)₃, **4** is prepared from cis-1-Methoxy-1,3-butadiene and iron pentacarbonyl in the presence of ultra-violet irradiation, according to the procedure of Koerner von Gustorf.⁵ Reaction of complex **4** with diphenylmethyl lithium at -78°C for two h followed by quenching of the anionic intermediate with excess trifluoroacetic acid (10 mol-eq), gives cyclobutanone **8** (7%), cyclopentanone **9** (36%), ferracyclopentanone **10** (9%), complex **7** (20%), and a trace of cyclopentanone **11**. Complex **7** is apparently derived from

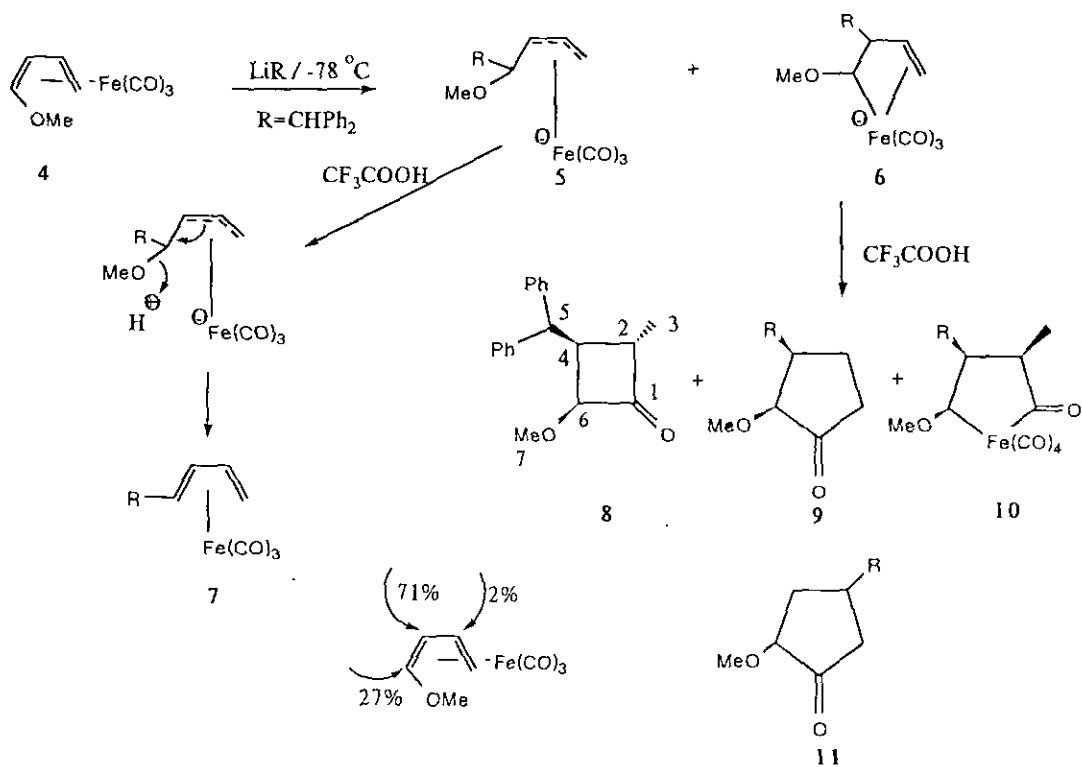
Scheme 1



Scheme 2



Scheme 3



the C-1 addition (terminal adduct), while compounds **8**, **9**, and **10** are obtained from the usual internal addition (C-2) under a kinetically controlled reaction (-78°C). The methoxy group at C-1 does influence the regioselectivity of the nucleophilic addition. The formation of **7** could involve the initial addition of the diphenylmethyl anion at the C-1 position of complex **4** followed by β -methoxy elimination during the protonation to give complex **7** as shown in Scheme 3. This is the first example of the dienyl nucleophilic substitution.

The product distribution shows that the internal adduct (C-2 addition) is still the major product at -78°C . However, the significant amount of C-1 addition (27%) and the lack of C-3 adduct (only 2%) indicate the methoxy group might direct the nucleophilic addition toward C-1 and C-2.

A possible mechanism for the formation of cyclobutanone **8**, cyclopentanone **9**, and ferracyclopentanone **10** is outlined in Scheme 4. The initial addition of the diphenylmethyl anion at the internal (C-2) position of complex **4** would give the $(\eta^1, \eta^2\text{-but-3-en-1-yl})\text{Fe}(\text{CO})_3$ anion intermediate **12**, which after acid quenching, generates intermediate **13**. Double bond insertion into the iron-hydride bond of **13** leads to the formation of ferracyclopentane **14** and ferracyclobutane **15**. Carbonyl insertions into the iron-carbon bonds of **14** and **15** generate acyliron intermediates **16**, and **17**. Reductive elimination of **16** gives cyclopentanone **9**, and reductive eliminations of **17** lead to cyclobutanone **8** (after epimerization at C-2). Complex **17** could also absorb an additional molecule of CO to form complex **10**. Complex **10** is very stable and isolated as a yellow crystalline compound.

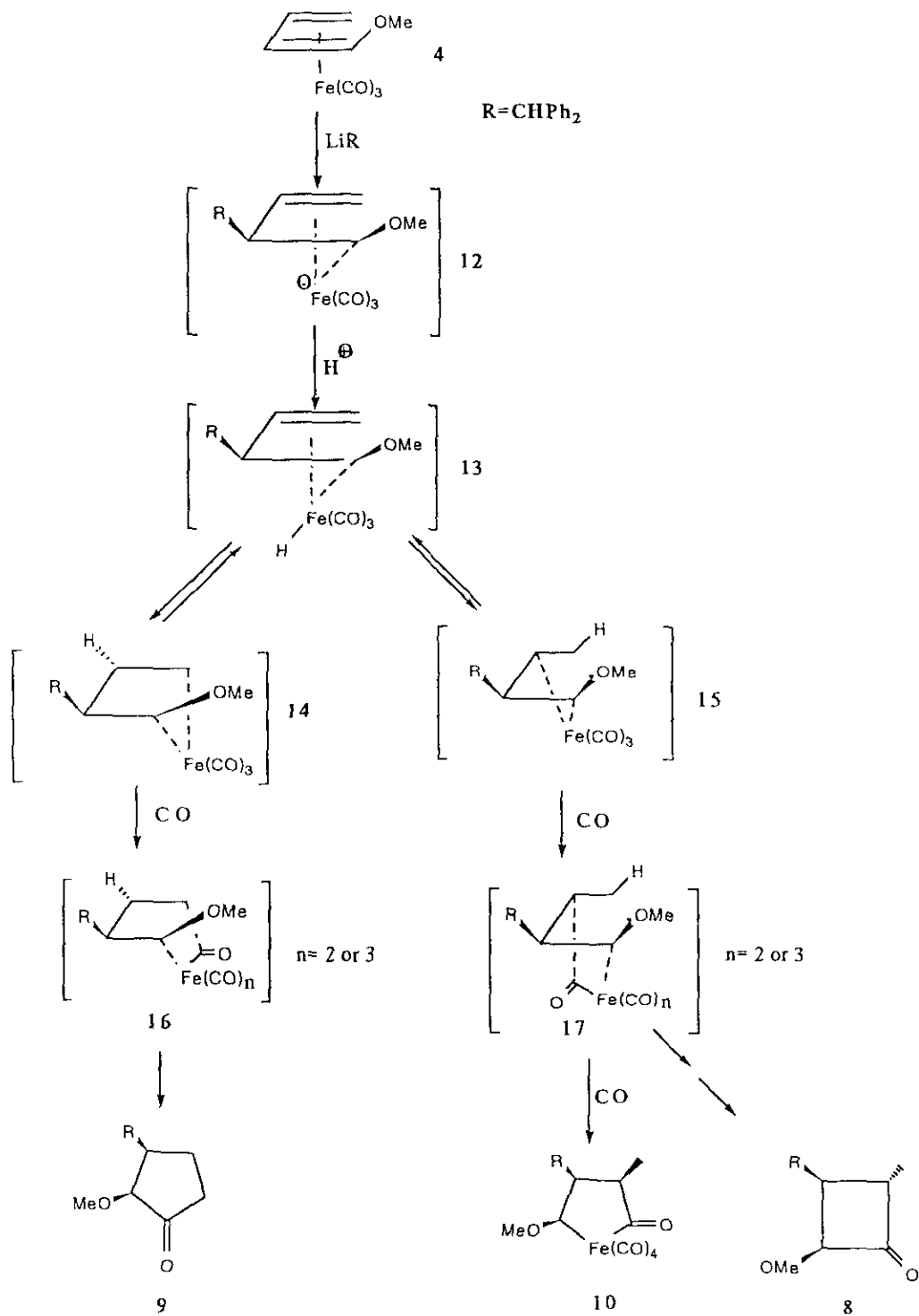
There is considerable evidence to support this mechanism: I). The yield of ferracyclopentanone **10** (incorporating two additional CO) increases (43%) when CO is introduced immediately after the protonation of **12** (Scheme 5). II). The all cis relationship of 3 substituents of complex **10** proves the reaction pathway. III). Cyclobutanone **8** is first isolated as all syn isomer (major) which epimerizes to cis (MeO, R) and trans (R, Me) after a long time (14 h) standing in trifluoroacetic acid.

The spectroscopic evidence for the cyclobutanone **8** is based on the frequency of the CO stretching band. The infrared spectrum absorption is at 1767cm^{-1} for the stretching vibration of CO in the cyclobutanone ring. This absorption is consistent with those found in most cyclobutanone derivatives ($1780\text{-}1760\text{ cm}^{-1}$).⁶ The relative configurations are determined based on an NOE experiment. The signal assigned to the proton at C-4 is enhanced when the proton at C-3 is irradiated, and the signal assigned to the proton at C-7 (MeO) is enhanced when the proton at C-5 (diphenylmethyl) is irradiated. These results indicate a trans configuration for the methyl and the diphenylmethyl group and a cis configuration for the methoxy and the diphenylmethyl group. The spectroscopic evidence for ferracyclopentanone **10** follows: (1). The infrared spectrum exhibits a peak at 1685 cm^{-1} for the stretching vibration of C=O (acyliron);⁷ two peaks at 2098 and 2014 cm^{-1} for the CO of $\text{Fe}(\text{CO})_4$, no peak appears at 1770 cm^{-1} . The carbon-13 NMR spectrum exhibits a peak at δ 261 ppm for acyl ligand peak and three peaks at δ 206, 203, and 199 for $\text{Fe}(\text{CO})_4$. The structure of complex **10** was further confirmed by x-ray diffraction analysis. The all cis orientation for the three substituents on the five membered ring supports the pathway of Scheme 4.

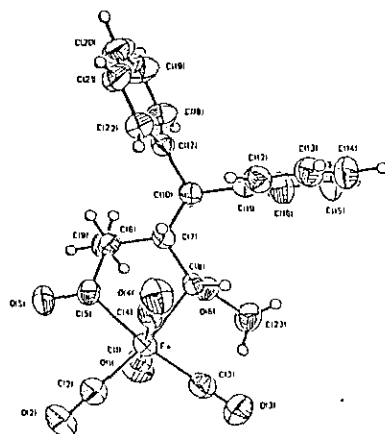
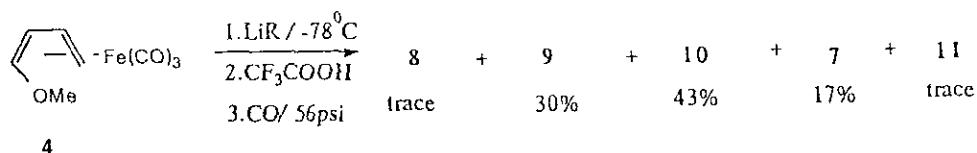
Interestingly, a different pathway follows when the anionic intermediate is quenched with carbon electrophiles. Addition of the diphenylmethyl anion to complex **4** is carried out at -78°C for 4 h. The reaction mixture reacts with methyl vinyl ketone, benzil, and chlorotrimethylsilane respectively to give complexes **7** and **20** in moderate yields (Scheme 6).

The formation of complex **20** is difficult to understand since it formally involves a kind of cine-substitution for methoxide. A possible pathway involving α -methoxy elimination (induced by certain carbon electrophiles) to generate the carbene complex **21** is proposed. Carbene **21** would undergo successive β -hydride elimination followed by reductive elimination, and finally re-coordination of the pendent double bond to produce complex **20** (Scheme 7). The formation of complex **7** might be similar to that involved in the protonation process.

Scheme 4



Scheme 5

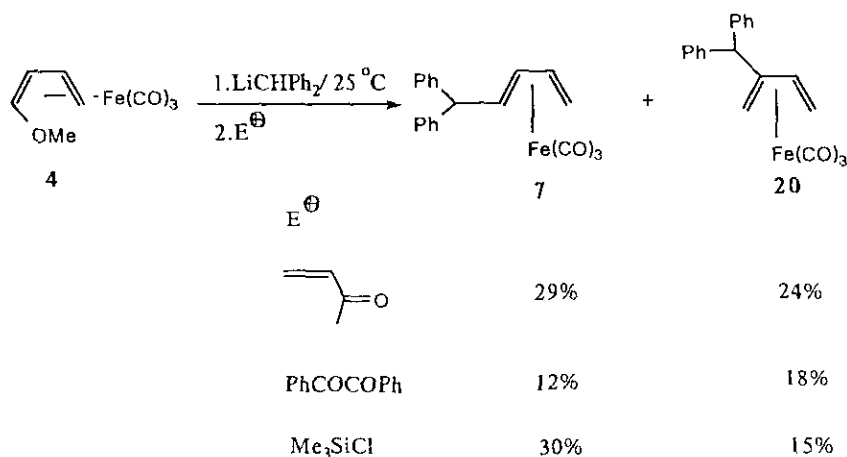


The ORTEP presentation of complex 10

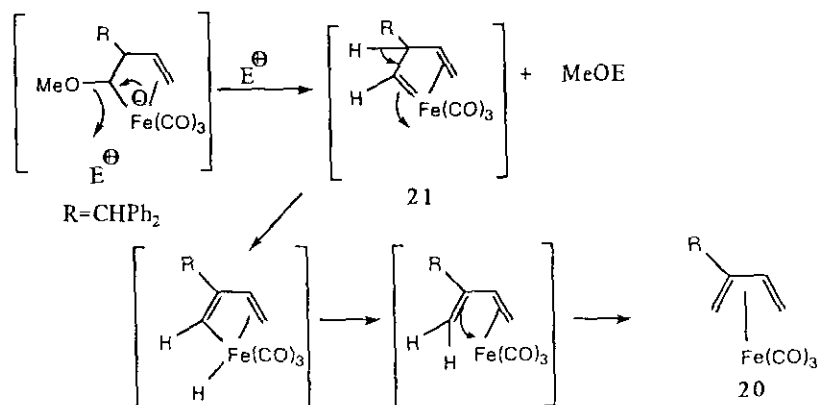
However, $(\eta^4\text{-1-methoxy-1,3-cyclohexadiene})\text{Fe}(\text{CO})_3$, **22** does not behave in the same way as the acyclic complex **4**. Reaction of diphenylmethyl anion with complex **22** at -78°C , followed by acid quenching, gives ketone **23**. No C-1 and C-2 adduct can be detected on the ^1H NMR scale (<

5%). The steric congestion of C-1 might prevent C-1 and C-2 addition. Thus, the anion adds at the C-3 position at -78°C . Intermediate **24**, derived from the anion addition, reacts with acid to yield enol ether **25**. Enol ether **25** produces ketone **23** after an aqueous process.

Scheme 6



Scheme 7



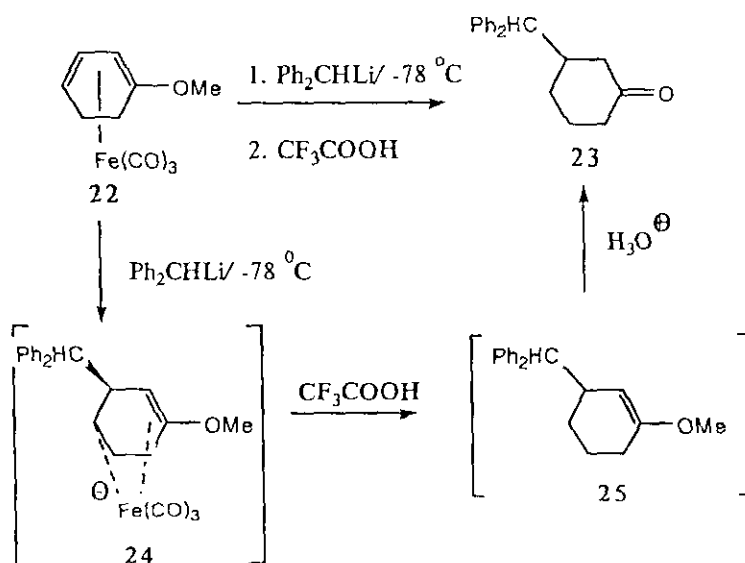
In conclusion, we have demonstrated nucleophilic additions to $(\eta^4\text{-1-methoxy-1,3-butadiene})\text{Fe}(\text{CO})_3$, **4** mainly at the C-1 and C-2 positions under kinetically controlled conditions. The air stable ferracyclopentanone **10** has been isolated and its structure confirmed by x-ray diffraction analysis. We have further shown that direct nucleophilic substitution and cine substitution occur with certain carbon electrophiles. Further extensions of these studies are underway in our laboratories.

EXPERIMENTAL

Spectra

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a Bruker WM-250 and WM-200 Fourier transform spectrometer operating at 250 MHz and 200 MHz or a Nicolet QE-300 Fourier transform spectrometer operating at 300 MHz. Peak positions are reported in parts per million relative to tetramethylsilane

Scheme 8



internal standard. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a JEOL FX-90Q Fourier transform spectrometer operating at 22.5 MHz or a Nicolet QE-300 Fourier transform spectrometer operating at 75.5 MHz or a Bruker WM-200 Fourier transform spectrometer operating at 50.0 MHz. Peak positions are reported in parts per million relative to deuteriochloroform (77.00). Spectra which were recorded with off-resonance decoupling have peaks reported as singlet(s), doublets(d), triplets(t), or quartets(q). Infrared (IR) spectra were recorded on a Perkin-Elmer Model 299 spectrometer and a Digilab FTS-20C spectrometer. Peak intensities were recorded as strong(s), medium(m) or weak(w). The 1602 cm^{-1} signal of polystyrene was used for calibration. Mass spectra were recorded on the AEI MS-902 instrument and the Kratos MS-50 at the Department of Chemistry, Princeton University. Microanalyses were obtained from Scandinavian Microanalytical Laboratories, Herlev, Denmark. High resolution mass spectra data were obtained on an AEI MS-9 double focusing mass spectrometer in the Department of Chemistry, Cornell University, Ithaca, NY and a Kratos MF-50 at Midwest center for Mass Spectrometry at the Department of Chemistry, University of Nebraska. Only the parent ion in the mass spectra is generally reported to establish molecular weight. In cases where the spectra have been analyzed, the data are expressed with the nominal fragment weight followed in parentheses by the percent intensity (taking the biggest peak as 100%).

Chromatography

Flash column chromatography refers to separate components under positive argon pressure and eluted with gradient solvent (increasing the polarity of the solvent gradually). The material which was used to pack in the column is Bodman silica gel 60 (230-400 Mesh). Analytical thin-layer chromatography (TLC) was done with Macherey-Nagel silica gel-backed plates with a 0.25 mm thickness. Developed plates were visualized under UV light and by charring with 1% sulfuric acid and 1% of p-anisaldehyde in ethanol solution. The preparative TLC (prep TLC) was done with Analtech Reagents silica gel GF

Uniplate Taper plate (1000 microns) or Analtech silica gel GF 20 cm x 20 cm 1000 microns or 2000 microns. The analytical GLPC column is a 12-ft x 0.125-in a column packed with 3% 1:1 FFAP/PPE on Chromosorb W (AW), and separated on a Perkin-Elmer 3920 Gas Chromatograph.

Reagents and Solvents

Diethyl ether (ether), and tetrahydrofuran (THF) were distilled under argon from benzophenone ketyl immediately before use. Chlorotrimethylsilane (Aldrich Chemical Co.), hexamethylphosphoramide (HMPA, Aldrich Chemical Co.), and diisopropylamine (Aldrich Chemical Co.) were distilled from calcium hydride (under reduced pressure as necessary) and stored under argon. n-Butyllithium was used as a solution in hexane and the concentration was determined by using a literature procedure.⁸ $(\eta^4\text{-cis-1-Methoxy-1,3-butadiene})\text{Fe}(\text{CO})_3$, **4** and $(\eta^4\text{-cis-1-Methoxy-1,3-cyclohexadiene})\text{Fe}(\text{CO})_3$, **22** were obtained by treatment of free dienes with $\text{Fe}_2(\text{CO})_9$ in anhydrous ether, purified by flash column chromatography followed by flash distillation before use. Iodomethane was purchased from J.T. Baker Co., diphenylmethane, and trifluoroacetic acid was purchased from Aldrich Chemical Co. and used without further purification.

General Information

The term "concentration" refers to the removal of solvent with an Aspirator pump (Cole-Parmer Instrument Company Model 7049-00) with a Buchi Rotovapor-R. The term "under argon" implies that the apparatus was evacuated (oil pump) and then filled with argon 3 times. The term "flash distillation" refers to a vacuum distillation at 25°C with a receiver at -78°C . The term "short-path distillation" refers to the process in which the entire distillation apparatus (a tube closed at one end, held horizontally), with the exception of the collection bulb was slowly heated in an air bath from 25 to 150°C under vacuum; the distillate was collected at -78°C , and boiling points for fractions refer to the bath temperature range. All boiling points and melting points was uncorrected.

Procedure for Generation of Anions**Diphenylmethane Anion⁹**

To a solution of diphenylmethane (0.22 mL, 1.3 mmol) in THF (3 mL), in a 100-mL pear shaped round bottom flask equipped with a rubber septum and a magnetic stirrer, under argon at -78°C was added rapidly via syringe a solution of *n*-butyllithium in hexane (1.28 mmol), followed by addition of HMPA (1 mL). The mixture was allowed to stir at 0°C for 1.5 h. This solution was used immediately in reaction with iron complexes (1 mmol in 1 mL THF, see below).

General Procedure I: General Procedure for Addition of Anions to (η^4 -1,3 diene)Fe(CO)₃ at -78°C . The Formation of ($\eta^1\eta^2$ -But-3-en-1-yl) tricarbonyliron(0) Anion Intermediates

To a solution of the anion (1.3 mmol, see above) in 3:1 THF:HMPA (4 mL) at -78°C under argon was added rapidly via syringe the (η^4 -1,3 diene)Fe(CO)₃ (1.0 mmol) in 1.0 mL of THF. The cooling bath was maintained at -78°C for 1 h.

(η^4 -5,5-Diphenyl-1,3-pentadiene)Fe(CO)₃ (7)

The reaction mixture from the General Procedure I (diphenylmethyl lithium, 5.2 mmol, and complex 4, 4.0 mmol) was quenched with trifluoroacetic acid (1 mL) at -78°C . The reaction mixture was stirred at 25°C for 14 h. After aqueous processing, the solution was concentrated on a rotary evaporator. Flash column chromatography (0.98 g of the residue, 60 g of silica gel) afforded a fraction containing the complex 7 ($R_f = 0.80$, 0.28 g, 20%, from 0.90 g, 4.00 mmol, of the starting complex 4) eluted with 20:1 hexane:ethyl acetate, a fraction containing ferracyclopentanone 10 ($R_f = 0.64$, 0.16 g) eluted with 15:1 hexane:ethyl acetate, a fraction containing cyclopentanone 9 ($R_f = 0.42$, 0.40 g, 36%) eluted with 10:1 hexane:ethyl acetate, a fraction containing cyclobutanone 8 ($R_f = 0.31$, 78 mg, 7%) eluted with 5:1 hexane:ethyl acetate and a trace of cyclopentanone 11 ($R_f = 0.15$, 10 mg, 0.9%) eluted with 3:1 hexane:ethyl acetate. The R_f numbers were based upon one analytical TLC development with 10:1 hexane:ethyl acetate as the eluent. The complex 7 was recrystallized from pentane:0.21

g, 15% yield from 0.90 g, 4.0 mmol, of the starting complex 4. mp 72.5 – 73°C . $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 7.35–7.14 (*m*, 10 H), 5.36 (*dd*, 1 H, $J = 8.5, 4.9$ Hz), 5.24 (*m*, 1 H), 3.81 (*d*, 1 H, $J = 10.3$ Hz), 1.75 (*ddd*, 1 H, $J = 9.4, 1.2, 1.0$ Hz), 1.55 (*dd*, 1 H, $J = 10.3, 8.5$ Hz), 0.42 (*dd*, 1 H, $J = 9.6, 2.5$ Hz). Irradiation at δ 1.55 caused δ 5.36 to collapse to a doublet and δ 3.81 collapse to a singlet; irradiation at 0.42 caused δ 1.75 (*exo* H at C-1) to collapse to a broad doublet and δ 5.24 collapse to a doublet of a doublet. $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): δ 212.5 (*s*), 146.7 (*s*), 144.92 (*s*), 128.68, 128.54, 127.74, 127.6, 126.72, 126.67, 126.43, 87.83 (*d*), 81.87 (*d*), 68.16 (*d*), 55.75 (*d*), 40.03 (*t*). IR (neat): 3080 (*s*), 3060 (*s*), 3035 (*s*), 3010 (*s*), 2980 (*m*), 2023 (*s*), 1970 (*m*), 1601 (*s*), 1583 (*s*), 1490 (*s*), 1450 (*s*), 1260 (*m*), 1240 (*m*), 1070 (*s*), 1030 (*m*), 780 (*m*), 700 (*s*) cm^{-1} . Mass spec (EI): 360 (M^+ , 3), 332 (*M-CO*, 12), 304 (*M-2CO*, 19), 276 (*M-3CO*, 100), 224 (5), 165 (6). Anal. (recrystallization from pentane). Calcd. for $\text{C}_{20}\text{H}_{16}\text{FeO}_3$: C, 66.73; H, 4.48; Fe, 15.50; O, 13.32. Found: C, 66.36; H, 4.59.

[(1,4- η)-Diphenylmethyl-4-methoxy-2-methyl-1-oxo]Fe(CO)₄ (10)

Complex 10 obtained as a light yellow crystalline compound was recrystallized from hexane and ethyl acetate at -10°C . Compound 10 decomposed upon heating above 130°C . $^1\text{H NMR}$ (C_6D_6 , 250 MHz): δ 7.34–6.93 (*m*, 10 H), 5.22 (*dd*, 1 H, $J = 4.20, 1.72$ Hz), 4.46 (*d*, 1 H, $J = 11.48$ Hz), 3.17 (*m*, 1 H), 2.97 (*m*, 1 H), 2.86 (*s*, 3 H), 1.26 (*d*, 3 H, $J = 8.5$ Hz). $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): δ 260.95, 205.85, 202.68, 198.79, 143.74, 143.64, 128.68, 128.04, 127.88, 127.44, 126.53, 126.31, 100.40, 64.41, 59.67, 56.87, 50.53, 12.78. IR (CDCl_3): 3080 (*w*), 3060 (*w*), 2980 (*m*), 2300 (*w*, CDCl_3), 2098 (*s*), 2014 (*b*), 1685 (*s*), 1350 (*m*), 1100 (*m*), 920 (*m*) cm^{-1} . Mass Spec. (FAB): 448 (M^+ , 1), 393 (15), 365 (14), 336 (14), 309 (100), 277 (25), 209 (80), 119 (95). Anal. (recrystallization). Calcd. for $\text{C}_{23}\text{H}_{20}\text{FeO}_6$: C, 61.63; H, 4.50; O, 21.42; Fe, 12.46. Found: C, 61.68; H, 4.66. The structure of 10 is further confirmed by x-ray diffraction analysis (see supplementary material for the complete crystallographic data).

3-Diphenylmethyl-2-methoxycyclopentanone (9)

$^1\text{H NMR}$ (CDCl_3 , 250 MHz): δ 7.42–7.05 (*m*, 10 H),

4.20 (*d*, 1 H, $J = 11.3$ Hz), 3.20 (*s*, 3 H), 2.98 (*d*, 1 H, $J = 4.6$ Hz), 2.80 (*m*, 1 H), 2.41 (*ddd*, 1 H, $J = 19.3, 4.9, 4.9$ Hz), 2.10 (*m*, 1 H), 1.80 (*m*, 2 H). NOE experiment shows enhancement at 3.20 when irradiates at 2.80, which suggests a *cis* orientation for diphenyl and methoxy unit. ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 214.87, 143.98, 142.84, 128.75, 128.62, 128.49, 128.38, 128.26, 127.82, 126.61, 126.49, 81.26, 57.82, 50.77, 47.07, 36.44, 25.44. IR (neat): 3082 (*w*), 3055 (*w*), 3024 (*w*), 2930 (*s*), 2824 (*m*), 1740 (*s*), 1597 (*m*), 1493 (*m*), 1450 (*m*), 1404 (*w*) cm^{-1} . Mass Spec. (EI): 280 (M^+ , 3), 262 (5), 223 (6), 204 (7), 193 (23), 167 (100), 152 (11), 115 (11). Anal. (distillation, 80-100°C, 0.03 mmHg). Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_2$: C, 81.40; H, 7.19; O, 11.41. Found: C, 81.29; H, 7.20.

3-Diphenylmethyl-4-methoxy-2-methyl-cyclobutanone (8)

Cyclobutanone **8** obtained as a white crystalline compound was recrystallized from hexane/ethyl acetate. mp 134-136°C. ^1H NMR (C_6D_6 , 250 MHz): δ 7.37-7.02 (*m*, 10 H), 3.90 (*dd*, 1 H, $J = 7.14, 2.78$ Hz), 3.71 (*d*, 1 H, $J = 9.6$ Hz), 3.19 (*s*, 3 H), 2.62 (*ddd*, 1 H, $J = 9.6, 7.2, 7.14$ Hz), 2.30 (*m*, 1 H), 0.80 (*d*, 3 H, $J = 7.1$ Hz). NOE experiment shows enhancement at 2.62 (H at C-4) when irradiates at 0.80 (H at C-3), and enhancement at 3.19, when irradiates at 3.71. These results suggest a *trans* orientation for methyl and diphenylmethyl group, and a *cis* orientation for diphenylmethyl and methoxy group. ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 208.5, 143.5, 142.0, 128.79, 128.43, 128.15, 126.97, 92.36, 58.79, 57.84, 51.95, 46.07, 13.02. IR (CDCl_3): δ 3059 (*w*), 3024 (*w*), 2928 (*m*), 2874 (*w*), 2250 (*s*, CDCl_3), 1767 (*s*), 1617 (*m*), 1601 (*m*), 1450 (*s*), 1327 (*s*) cm^{-1} . Mass Spec. (EI): 280 (M^+ , 1), 224 (72), 192 (43), 167 (68), 115 (19), 85 (100). Mass spectral mol. wt: 280.1474. Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_2$: 280.1464.

3-Diphenylmethyl-4-methoxycyclopentanone (11)

Cyclopentanone **11** was isolated as a white crystalline compound, and further crystallized from hexane and ethyl acetate. mp 138-139 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 7.38-7.17 (*m*, 10 H), 3.82 (*dd*, 1 H, $J = 11.3, 7.8$ Hz), 3.70 (*d*, 1 H, $J = 11.0$ Hz), 3.47 (*s*, 3 H), 2.93 (*m*, 1 H), 2.30-2.50 (*m*, 2 H), 1.95 (*dd*, 1 H, $J = 19.10, 10.6$ Hz), 1.48 (*dd*, 1 H, $J = 19.4, 11.8$ Hz). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 214.27, 142.47,

142.14, 128.06, 128.05, 126.37, 126.06, 125.90, 83.66, 58.89, 58.39, 42.29, 35.06, 35.01. IR (neat): 3020 (*m*), 2940 (*m*), 1751 (*s*), 1490 (*m*), 1450 (*m*), 1120 (*m*) cm^{-1} . Mass Spec. (EI): 280 (M^+ , 3), 262 (3), 248 (6), 193 (17), 167 (100), 115 (9). Mass spectral mol. wt.: 280.1468. Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_2$: 280.1463.

$(\eta^4\text{-2-Phenylmethyl-1,3-butadiene})\text{Fe}(\text{CO})_3$ (20)

The reaction mixture from the General Procedure II was quenched with excess methyl vinyl ketone (1 mL) at -78°C. The reaction mixture was stirred at 25°C for 14 h before 200 mL of hexane was poured into the reaction mixture. The hexane solution was washed with three 200 mL portions of water, three 200 mL portions of saturated aqueous sodium chloride solution, dried over magnesium sulfate, and finally concentrated on a rotary evaporator. Flash column chromatography of the residue (406 mg, from 448 mg, 2.00 mmol of the starting complex **4**, 22.0 g of silica gel), gave a fraction containing the complex **20** (215 mg, 29%), and a fraction containing the complex **7** (187 mg, 24%) eluted with hexane. Complex **7** was identical to the previous result. Complex **20** was recrystallized from hexane. mp 94-95°C. ^1H NMR (CDCl_3 , 300 MHz): δ 7.38-7.28 (*m*, 10H), 4.90-4.85 (*m*, 2 H), 1.89 (*brs*, 1 H), 1.74 (*dd*, 1 H, $J = 6.8, 1.2$), 0.48 (*d*, 1 H, $J = 2.5$ Hz), 0.32 (*dd*, 1 H, $J = 9.1, 1.4$ Hz). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 211.40, 144.28, 141.00, 129.56, 129.24, 128.70, 128.50, 128.32, 127.77, 126.78, 109.05, 57.01, 43.00, 39.00. IR (neat): 3080 (*w*), 3040 (*m*), 3020 (*m*), 2980 (*w*), 2060 (*s*), 1980 (*s*), 1610 (*m*), 1540 (*s*), 1520 (*s*) cm^{-1} . Mass spec. (EI): 332 (M-CO , 3), 304 (7), 276 (100), 224 (25), 167 (3). Anal. (recrystallization hexane). Calcd. for $\text{C}_{20}\text{H}_{16}\text{FeO}_3$: C, 66.69; H, 4.48; Fe, 15.50; O, 13.32. Found: C, 67.13; H, 4.69.

3-Diphenylmethylcyclohexanone (23)

The reaction mixture derived using General Procedure I was quenched with 1 mL of trifluoroacetic acid. The reaction mixture was poured into a 250 mL separatory funnel containing 100 mL of ether. The ethereal solution was washed three times with water (100 mL), three times with saturated sodium chloride aqueous solution (100 mL) and finally dried over sodium sulfate. Concentration fol-

lowed by column chromatography of the residue, gave 0.14 g (0.51 mmol, 72%) of ketone **23** from 0.18 g (0.72 mmol) of complex **22**. $^1\text{H NMR}$ (CDCl_3 , 200 MHz): δ 7.29-7.14 (*m*, 10 H), 3.62 (*d*, 1 H, $J = 10.8$ Hz), 2.63 (*m*, 1 H), 2.34 (*m*, 2 H), 2.03 (*m*, 1 H), 1.83 (*m*, 1 H), 1.65 (*m*, 1 H), 1.28 (*m*, 2 H). $^{13}\text{C NMR}$ (CDCl_3 , 50.5 MHz): δ 211.4, 142.5, 128.7, 127.8, 126.4, 58.9, 46.9, 42.5, 41.4, 30.2, 24.9. IR (neat): 2925.0 (*s*), 2823.0 (*m*), 1701.0 (*m*), 1460.0 (*w*) cm^{-1} . Mass spec (EI): 264 (M^+ , 18), 178 (2), 167 (100), 152 (13), 128 (4), 115 (5), 97 (7), 69 (11). Mass spectral mol. wt.: 264.1491. Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}$ 264.1514.

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Key Word Index-

Cine substitution; α -methoxy elimination; β -hydride elimination; CO insertion; Reductive elimination.

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