475

Reaction of Tricarbonyl(η³-allyl)iron(0) Anions with Bromine

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The addition of reactive carbanions to tricarbonyl(η⁴-1,3-diene)iron(0) complexes proceeded at 23°C to give putative tricarbonyl(η³-allyl)iron(0) anion complexes. Trapping of the reactive intermediates with bromine produced nucleophilic-substituted tricarbonyl(η⁴-1,3-diene)iron(0) complexes.

INTRODUCTION

The metal-activated nucleophilic addition to polyene ligands opens new strategies for carbon-carbon bond-forming reactions. Unsaturated hydrocarbon ligands bound to neutral or cationic metal carbonyl moieties are normally activated toward addition of nucleophiles; examples include (arene)$Cr(CO)_3$,[1] (diene)$Fe(CO)_3$,[2] (olefin)Pd(II),[3] (olefin)$Fe(CO)_4$,[4] (arene)$Mn(CO)_3^+$,[5] (η^5-cylohexadienyl)$Fe(CO)_3^+$,[6] (η^3-allyl)$Fe(CO)_4^+$,[7] and (η^2-olefin)$FeCp(CO)_2^+$[8] complexes. Activation of unsaturated hydrocarbons toward electrophilic attack by complexation with anionic metal carbonyls has been reported.[9] Brookhard has shown that the tricarbonyl(η³-allyl)iron anionic complex, generated by reduction of (η^3-allyl)$Fe(CO)_3I$ complex with sodium-mercury amalgam, reacted with alkyl halides to give α,β-unsaturated ketone complexes.[10] It was presumed that the addition of alkyl halides occurred initially at the metal center followed by CO insertion and acyl migration to produce α,β-unsaturated ketone complexes. Alternatively, tricarbonyl(η³-allyl)iron anionic complexes are generated by addition of reactive carbanions to (η^4-1,3-diene)$Fe(CO)_3$ complexes under a thermodynamically controlled reaction.[2b] Trapping of the anionic complex 1 with benzoyl chloride gave a β,γ-unsaturated ketone 2 in 53% yield.[2c] However, the quenching process was limited to complexes derived from the reactive carbanions such as 2-lithio-2-phenyl-1,3-dithiane or 1-lithio-1,1-diphenyl-methane. For a stabilized anion such as 2-lithio-2-methyl-propionitrile, the primary process was detachment of the anion unit, allowing recovery of the starting complex 4. Nevertheless, quenching of the same reactive intermediates with strong acid produced olefins 5 and 6 in high yields (Scheme I). We report here that trapping of tricarbonyl(η³-allyl)iron anionic complexes with bromine produces nucleophilic-substituted (η^4-1,3-diene)$Fe(CO)_3$ complexes. This formal substitution for hydride promises a novel approach to coupling of carbon units with dienes and may have great potential in the synthesis of dienyl deriva-

tives.

Scheme I
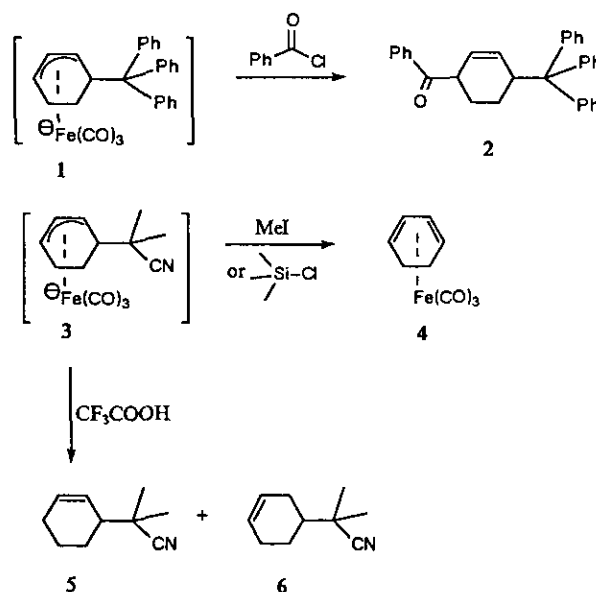
RESULTS AND DISCUSSION

Treatment of (η^4-1,3-diene)$Fe(CO)_3$ complexes with reactive carbanions (1.2 mol equiv, see experimental section) in THF/HMPA (3/1, 23°C, 2 h) followed by addition of bromine (1.0 equimolar, 23°C, 2 h) gave nucleophilic substituted (η^4-1,3-diene)$Fe(CO)_3$ complexes in 10-42% yields after flash column chromatography. Results of the addition and bromination are summarized in Table 1.

Based on the positions of nucleophiles, there are adducts of three different types in Table 1. (1) With complex 4, the addition/trapping sequences produced the C-5 substituted (η^4-cyclohexa-1,3-diene)$Fe(CO)_3$ derivatives 12 and 13 (entries 1, 2). (2) With a methoxy group at either C-1 or C-2 positions of cyclohexa-1,3-diene, the C-3 substituted (η^4-cyclohexa-1,3-diene)$Fe(CO)_3$ derivatives 14-17 were isolated (entries 3-6). (3) With acyclic complexes 9-

Table 1. Reaction of $(\eta^3$-allyl)Fe(CO)$_3$ Anionic Complexes with Bromine

Entry	Complexes	Nucleophiles[a]	Electrophiles	Products[b]
1	4	LiCHPh$_2$	Br$_2$	12 (21 %)
2	4	LiC(CH$_3$)$_2$CN	Br$_2$	13 (42 %)
3	7	LiCHPh$_2$	Br$_2$	14 (32 %)
4	7	LiC(CH$_3$)$_2$CN	Br$_2$	15 (29 %)
5	8	LiCHPh$_2$	Br$_2$	16 (10 %)
6	8	LiC(CH$_3$)$_2$CN	Br$_2$	17 (22 %)
7	9	LiCHPh$_2$	Br$_2$	18 (29 %)
8	10	LiCHPh$_2$	Br$_2$	19 (32 %)
9	11	LiCHPh$_2$	Br$_2$	20 (33 %)

[a] Nucleophiles (1.2 mol equiv) were added to iron complexes at -78°C. The reaction mixture was stirred at 23°C for 2 h.
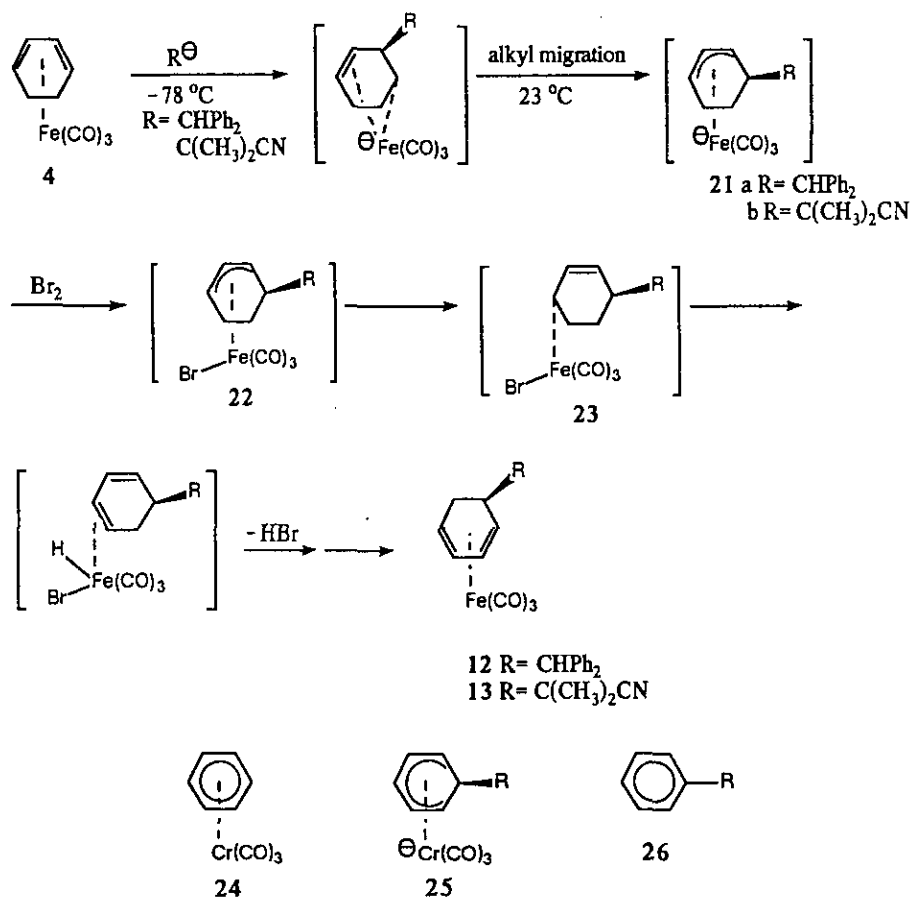
[b] All indicated yields are isolated yields of analytically pure compounds. Satisfactory spectral data (IR; ^{1}H; ^{13}C-NMR; and high resolution mass spectra) were obtained for all compounds.

10, the substituted diene complexes were obtained with nucleophiles at the terminal positions (entries 7, 8). This formal nucleophilic substitution for hydride is rare and may have special potential in the synthesis of dienyl derivatives.

It was presumed that the nucleophilic additions occur initially at the internal position of complex 4 at -78°C. Upon warming, nucleophiles reversed and added at the terminal position of the diene to form the tricarbonyl(η^3-allyl)iron(0) anion complex 21. Trapping of 21 with Br$_2$ could generate 22. Conversion of (η^3-allyl)Fe(CO)$_3$ anionic complex 22 to the unsaturated (η^1-allyl)Fe(CO)$_3$ anion 23 would allow β-hydride elimination to occur. Thus, complexes 12 or 13 could be formed after reductive elimination of HBr and the iron carbonyl moiety would re-coordinate to the pendant double bond (Scheme II). A similar process was also found in the iodination of the (η^5-alkylcyclohexadienyl)Cr(CO)$_3$ anion complex 25. The addition of reactive carbanions to (η^6-arene)Cr(CO)$_3$ complex 24 followed by trapping of the reactive intermediates with iodine gave the nucleophilic substituted free arenes 26.[11] Under our reaction conditions, bromination of (η^3-allyl)Fe(CO)$_3$ anionic complexes did not cause decomplexation of the iron carbonyl moiety. Furthermore, unlike methylation, bromination of 21b did not lead to recovery of the starting complex 4. The spectral evidence for complexes 12 and 13 is based on the chemical shifts of the internal protons in ^{1}H NMR spectra. (i) ^{1}H NMR spectra exhibiting lines due to two protons (multiplets) at 5.28 and 5.45 ppm respectively for 12 and 13 are consistent with those found in the starting complex 4 (5.30 ppm). (ii) The resonances (due to two protons) near 3.00 ppm for 12 and 13 also agree with lines of the external protons of complex 4 (3.3 ppm). (iii) The exo stereochemistry is assigned on the assumption that nucleophiles would likely add on the opposite side of the iron carbonyl moiety. Furthermore, the lines due to the C-5 protons appearing at 2.53 and 2.12 ppm respectively for 12 and 13 are near those of the endo proton (2.20 ppm) at the C-5 position of (5-exo-methyl-cyclohexa-1,3-diene)Fe(CO)$_3$ found in the literature.[12]

With a methoxy group at either the C-1 or C-2 positions of dienes, reactions follow varied pathways. It is well known that, upon warming to 23°C, complex 27 would likely undergo hydride migration to produce the allyl anion intermediate 28.[13] Bromination of 28 would yield complex 29. Complex 29 might undergo a series of β-hydride elimination, reductive elimination of HBr and re-coordination of the iron carbonyl moiety with the pendant double bond to yield complexes 14-17 (Scheme III). The identification of 14 and 15 is as follows: i) no resonance can be detected around 5.30 ppm in ^{1}H NMR spectra of 14 and 15 for the in-
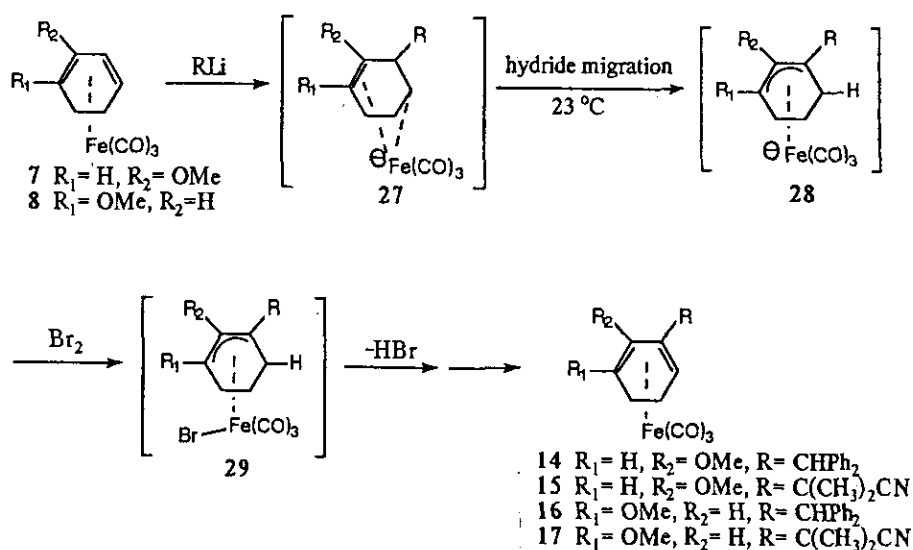
Scheme II

4   $R^\ominus$ $-78\,^\circ C$ R= CHPh$_2$ C(CH$_3$)$_2$CN   Fe(CO)$_3$

alkyl migration   23 °C $\ominus$Fe(CO)$_3$ 21 a R= CHPh$_2$ b R= C(CH$_3$)$_2$CN

Br$_2$ Br—Fe(CO)$_3$ 22   Br—Fe(CO)$_3$ 23

H—Br—Fe(CO)$_3$ − HBr   Fe(CO)$_3$

12 R= CHPh$_2$
13 R= C(CH$_3$)$_2$CN

Cr(CO)$_3$ 24 $\ominus$Cr(CO)$_3$ 25   26

ternal protons. ii) two multiplets are at 3.69 (C-1) and 2.94 (C-4) ppm for the external protons of 14 and two multiplets are at 3.47 (C-1) and 3.11 (C-4) ppm for the external protons of 15. The spectral evidence for complexes 16 and 17 is based on their ^{1}H NMR spectra. The resonances of a singlet at 4.81 and 5.29 ppm respectively for 16 and 17 are due to the internal protons at C-2. Resonances at 2.90 and 3.16 ppm respectively for 16 and 17 at C-4 are near those of the external proton of complex 4 (3.3 ppm).

Whereas the addition and bromination of complexes 9 and 10 proceeded under the same reaction routes, the nucleophilic additions of complexes 9 and 10 at the terminal positions gave tricarbonyl(η^3-allyl)iron anion complexes 30 and 31 respectively. Complexes 30 and 31 could undergo a sequence of β-hydride elimination, reductive elimination of HBr and re-coordination of the iron carbonyl moiety with the pendant double bond to give complexes 18 and 19. The structural assignment of complex 18 is based on comparison with the starting complex 9. The chemical shifts and patterns of C-4 endo (0.35 ppm) and exo (1.71 ppm) protons remain unchanged, and the endo proton of C-1 becomes a doublet and shifts down field (1.71

ppm), due to the adjacent diphenylmethyl group. Two singlets at 2.17 and 2.00 ppm (3 protons for each resonance) are due to the methyl groups at the C-2 and C-3 positions. The spectral data of 19 are consistent with the literature results.[14] The formation of complex 20 (entry 9) was unclear. We presume that the (η^3-allyl)Fe(CO)$_3$ anionic complex 32 was formed initially; rearrangement of the anionic intermediate 32 occurred, apparently via hydride transfer, to give the allyl complex 35 (Scheme IV). We viewed the hydride shift occurring via detachment of the alkene ligand, β-hydride elimination (33), readdition of the hydride (34), and then allyl syn and anti isomerization to form 35.[15] Bromination of 35 would produce complex 20 via a routes similar to those described above. The structural assignment of complex 20 is based on a doublet that appears at 4.69 ppm for the internal C-3 proton, for which the coupling parameter (J-H$_{3,4}$ = 8.4 Hz) indicates a trans orientation (for example, J-H$_{3,4}$ = 8.5 Hz for complex 10), and the endo proton of C-1 shows a doublet at 0.37 ppm, for which the exo proton of C-1 appears as a doublet at 1.67 ppm, although the endo proton at C-4 exhibits a multiplet at 1.08 ppm. All products (12-20) have characteristic car-

Scheme III

7 $R_1 = H, R_2 = OMe$
8 $R_1 = OMe, R_2 = H$

14 $R_1 = H, R_2 = OMe, R = CHPh_2$
15 $R_1 = H, R_2 = OMe, R = C(CH_3)_2CN$
16 $R_1 = OMe, R_2 = H, R = CHPh_2$
17 $R_1 = OMe, R_2 = H, R = C(CH_3)_2CN$

bonyl absorptions at 2050 and 1980 cm^{-1} for the typical tricarbonyl(η^4-1,3-diene)iron complexes in their infrared spectra. Resonances are near 210 ppm in their ^{13}C NMR spectra for the carbonyl signals of tricarbonyl(η^4-1,3-diene)iron complexes.

In conclusion, we have shown that the addition and bromination of (η^4-1,3-diene)Fe(CO)$_3$ complexes gave nucleophilic-substituted (η^4-1,3-diene)Fe(CO)$_3$ complexes. The position of the nucleophiles varies with various starting complexes.
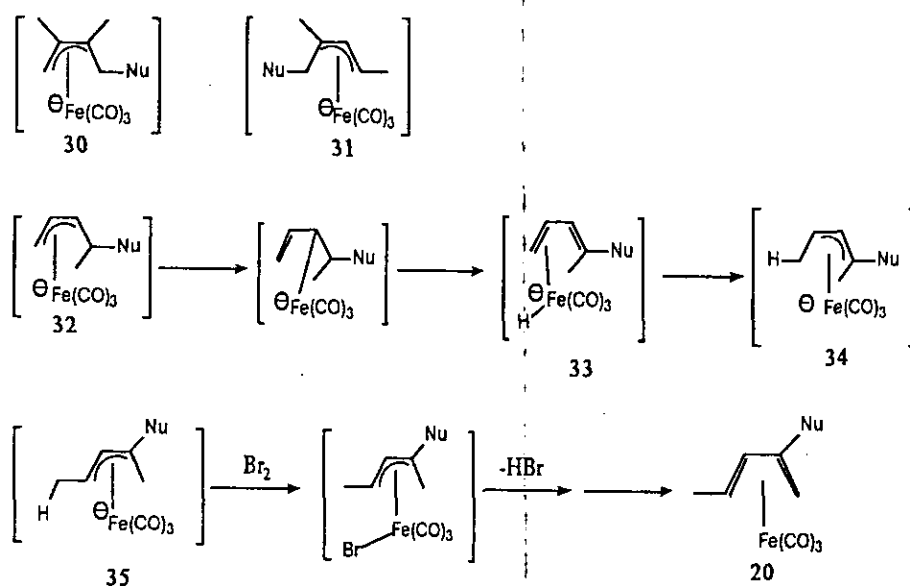
EXPERIMENTAL SECTION

Spectra

^{1}H NMR spectra were recorded with a Bruker AC-200 spectrometer operating at 200 MHz and are quoted in ppm down field from TMS. ^{13}C NMR spectra were recorded with a Bruker AC-200 spectrometer operating at 50.5 MHz and are quoted relative to chloroform-d (77.00). Infrared spectra (4000-800 cm^{-1}) were recorded with a Perkin-Elmer Model 597 double-beam spectrophotometer

Scheme IV

30   31

32   33   34

35   20

Reaction of Tricarbonyl(η^3-allyl)iron(0) Anions

J. Chin. Chem. Soc., Vol. 38, No. 5, 1991 · 479

calibrated with polystyrene film (1602 cm^{-1}). All spectra were recorded for neat liquids between KBr plates or as dichloromethane solutions in KBr cells. Peaks intensities are indicated as strong (s), medium (m), or weak (w). Mass spectra were recorded on the AEI MS-902 instrument and the Kratos MS-50 at the Institute of Chemistry, Academia Sinica, Taipei. Only the parent ion in the mass spectra is generally reported to establish the molecular mass. The data are expressed with the nominal fragment mass followed in parentheses by the percent intensity (taking the most intense peak as 100 %). High-resolution mass spectra (HRMS) data were obtained on an AEI MS-9 double focusing mass spectrometer in the Institute of Chemistry, Academia Sinica, Taipei. Standard Schlenk techniques were used for all manipulations involving oxygen or moisture-sensitive experiments.

Chromatography

Flash column chromatography was used to separate components under positive nitrogen pressure, with elution under a solvent gradient (increasing the polarity of the solvent gradually). The material used to pack 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 0.25-mm thickness. Developed plates were visualized under UV light and by charring with 1% sufuric acid and 1 % of 4-anisaldehyde in ethanol solution.

Reagents and Solvents

Diethyl ether (ether) and tetrahydrofuran (THF) were distilled under nitrogen from benzophenone ketyl immediately before use. Chlorotrimethylsilane (Aldrich), hexamethylphosphoramide (HMPA, Aldrich), and diisopropylamine (Aldrich) were distilled from calcium hydride (under reduced pressure as necessary) and stored under nitrogen. Butyllithium was used as a solution in hexane. Iodomethane was (J. T. Baker), diphenylmethane and trifluroacetic acid (Aldrich) were used without further purification.

General Information

The term "concentration" refers to the removal of solvent with an Aspirator pump (Cole-Parmer, Model 7049-00) with a Buchi Rotovapor-R. The term "under nitrogen" implied that the apparatus was evacuated (oil pump) and then filled with nitrogen 3 times. The term "flash distillation" refers to 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 are uncorrected.

Synthesis of (η^4-2-Methoxy-1,3-cyclohexadiene)Fe(CO)$_3$ (7)[12]

. ' To a solution of triethylamine (16 mL) was added via spatula of zinc chloride (1.5 g). The reaction mixture was stirred at 23°C untill a suspension formed (*ca.* 1 h). With the solution at 23°C, a solution of 2-cyclohexen-1-one (5 mL, 0.05 mol) in benzene (16 mL) was added via syringe followed by addition of chlorotrimethylsilane (13 mL). The reaction mixture was diluted with anhydrous ethyl ether (200 mL) after being stirred at 70°C for 19 h. The solid suspension was filtered through Celite and the Celite was fully washed with ether (100 mL). The solvent was concentrated on a rotary evaporator. Flash distillation under vacuum gave desired diene (7.6 g). ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.78 (*m*, 1H), 5.57 (*m*, 1H), 4.75 (*m*, 1H), 1.95-2.05 (*m*, 4H), 0.07 (*s*, 9H). The crude diene was used without further purification. To a solution of the diene (7.4 g, 44 mmol) obtained above in anhydrous ethyl ether (60 mL) was added slowly via spatula Fe$_2$(CO)$_9$ (19 g). The reaction mixture was stirred at reflux for 16 h. The reaction mixture was then filtered through a bed of Celite and the Celite was washed with ether (50 mL). The solvent was concentrated on a rotary evaporator. Flash column chromatography of the residue on silca gel with hexane-ethyl acetate (20/1) afforded a crude oil. The crude oil was used in the next step without purification. To a solution of sodium hydride (1.0 g, 33 mmol) in N,N-dimethylformamide (5 mL) at 0°C under nitrogen was added slowly via syringe a solution of the crude complex (6.0 g, 25 mmol) in N,N-dimethylformamide (30 mL). The reaction mixture was stirred at 0°C for 40 min. Iodomethane (3.0 mL, 48 mmol) was added to the solution via syringe. The reaction mixture was then diluted with hexane-ethyl acetate (300 mL, 1/1) after being stirred at 23°C for 5 h. The solution was washed with water (three 200-mL portions), saturated aqueous sodium chloride solution (three 200-ml portions), dried over magnesium sulfate and finally concentrated on a rotary evaporator. Flash-column chromatography of the residue on silica gel with hexane-ethyl acetate (10/1) as eluent followed by a short-path distillation (50-60°C, 0.08 Torr) produced complex (7) (4.8 g, 19 mmol, 77 %) of. ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.09 (*dd*, J = 6.6, 2.3 Hz, 1H), 3.61 (*s*, 3H), 3.45 (*m*, 1H), 2.76 (*m*, 1H), 1.72 (*m*, 2H), 1.52 (*m*, 2H).

General Method for the Synthesis of Complexes 4,8-11

Complexes **4, 8-11** were generated by refluxing the corresponding free dienes (1 equimolar) with of $Fe_2(CO)_9$ (2 eqiumolar) in anhydrous ethyl ether for 14 h. The resulting solution was filtered through a bed of Celite and the solvent was concentrated on a rotary evaporator. Flash column chromatography of the residue on silica gel with hexane as eluent followed by flash distillation generated complexes **4,8-11**. Complex (**4**) (56 %):[2c] ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.3 (d, J = 5.2 Hz, 2H), 3.3 (m, 2H), 1.7 (m, 4H). Complex **8** (41 %):[16] ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.31 (d, 1H), 5.02 (m, 1H), 3.46 (s, 3H), 2.95 (m, 1H), 2.24 (m, 1H), 1.81-1.66 (m, 3H). Complex (**9**) (49 %):[17] ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.18 (s, 6H), 1.72 (d, 2H), 0.10 (d, 2H) Complex (**10**) (48 %):[18] ^{1}H NMR (CDCl$_3$, 200MHz) δ 5.10 (d, 1H), 2.14 (s, 3H), 1.71 (d, 1H), 1.39 (d, 3H), 0.86 (m, 1H), 0.3 (d, 1H). Complex (**11**) (53 %):[18] ^{1}H NMR (CDCl$_3$, 200MHz) trans: δ 5.17 (m, 2H), 1.64 (dd, 1H), 1.5 (d, 3H), 1.08 (m, 1H), 0.22 (dd, 1H). cis: δ 5.30 (m, 2H), 2.67 (m, 1H), 1.75 (dd, 1H), 1.47 (dd, 1H), 1.10 (d, 3H).

Generation of 1-Lithio-1,1-diphenylmethane

To a solution of diphenylmethane (0.25 mL, 1.50 mmol) in THF (3 mL), in a Schlenk flask equipped with a rubber septum and a magnetic stirrer, under nitrogen at -78°C, was added rapidly via syringe a solution of butyl-lithium (0.9 mL, 1.35 mmol, 1.50 M in hexane), followed by addition of hexamethylphosphoramide (HMPA, 1 mL). The resulting orange-red solution was stirred 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).

Generation of 2-Lithio-2-methylpropionitrile

To a solution of diisopropylamine (0.21 mL, 1.50 mmol) in THF (3 mL), in a Schlenk flask equipped with a rubber septum and a magnetic stirrer, under nitrogen at -78°C, was added rapidly via syringe a solution of butyl-lithium in hexane (0.9 mL, 1.35 mmol, 1.50 M in hexane). The reaction mixture was stirred at -78°C for 20 min. To the solution prepared aboved was added rapidly neat via syringe 2-methylpropionitrile (0.13 mL, 1.40 mmol), followed by addition of hexamethylphosphoramide (HMPA, 1.00 mL). The resultant light yellow solution was stirred at -78°C for 20 min, and was used immediately in reaction with iron complexes (1.00 mmol in 1.00 mL THF, see below).

General Procedure I: Addition of Anions to (η^4-1,3-dienes)Fe(CO)$_3$ Complexes at 23°C Followed by Trapping of the Reactive Intermediates with Bromine

To a solution of an anion (1.5 mmol, see above) at -78°C under nitrogen was added rapidly via syringe a (η^4-1,3-diene)Fe(CO)$_3$ complex (1.00 mmol) in THF (1.00 mL). The reaction mixture was stirred at 23°C for 2 h. Bromine (1.0 mmole) was added neat via syrange at -78°C to the reaction mixture. The reaction was then stirred at 23°C for 2hr. The resultant reaction mixture was diluted with water (10 mL). The solution was then extracted with ethyl acetate (2 x 100 mL). The combined extracts were washed with water (three 100-mL portions), saturated sodium chloride solution (three 100-mL portions), dried over magnesium sulfate, filtered through Celite, and finally concentrated on a rotary evaporator.

Formation of Tricarbonyl[(η^4-1,3-cyclohexadiene-5-yl)-diphenylmethyl]iron (12)

The reaction mixture derived using General Procedure I (1-lithio-1,1-diphenylmethane, 6.0 mmol, complex **4**, 4.0 mmol, bromine, 4.0 mmol) was separated by flash-column chromatography (hexane as eluent) to provide complex (**12**) (0.33 g, 0.85 mmol, 21 %) as a yellow liquid. IR (CH$_2$Cl$_2$) 3064(m), 3029(m), 2912(m), 2853(m), 2044(s), 1977(s), 1602(m), 1492(m), 1445(s), 1261(m), 1077(m), 972(m), 862(s), 780(s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.34-7.14 (m, 10 H, aryl), 5.28 (m, 2H, C$_2$ and C$_3$), 3.69 (d, J = 10.4Hz, 1H, C$_7$), 3.24 (m, 1H, C$_1$), 2.89 (m, 1H, C$_4$), 2.53 (m, 1H, C$_5$), 1.75 (m, 1H, C$_6$), 1.36 (m, 1H, C$_6$); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 212.3, 143.1, 142.9, 128.6, 128.4, 128.0, 126.3, 86.6, 83.8, 65.6, 63.2, 58.4, 37.2, 34.1; MS (m/z) 386 (M$^+$, 1), 338(8), 330(12), 302(75), 224(100), 190(1), 167(5); HRMS Calcd for C$_{22}$H$_{18}$FeO$_3$: 386.0598, Found: 386.0605.

Formation of Tricarbonyl[(η^4-1,3-cyclohexadiene-5yl)-2-methylpropionitrile]iron (13)

The reaction mixture derived using General Procedure I (2-lithio-2-methylpropionitrile, 3.0 mmol, complex **4**, 2.0 mmol, bromine, 2.0 mmol) was separated by flash-column chromatography (hexane as eluent) to provide complex 13 (0.24 g, 0.84 mmol, 42 %) as a yellow liquid. IR (CH$_2$Cl$_2$) 3070(m), 2985(s), 2943(s), 2901(s), 2859(s), 2235(s), 2051(s), 1992(s), 1603(m), 1446(s), 1367(s), 1220(s), 1183(s), 987(s), 913(s), 864(s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.45 (m, 2H, C$_2$ and C$_3$), 3.05 (m, 2H, C$_1$ and C$_4$), 2.12 (m, 1H, C$_5$), 1.56 (m, 2H, C$_6$), 1.27 (s, 3H, C$_8$ or C$_9$), 1.18 (s, 3H, C$_8$ or C$_9$); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 211.3, 124.3, 85.8, 85.6, 58.8, 58.3, 47.2, 37.8, 27.5, 25.4, 25.0; MS (m/z) 287 (M$^+$, 20), 259(100), 231(70), 203(52), 176(5), 134(7); HRMS Calcd for C$_{13}$H$_{13}$FeNO$_3$: 287.0245, Found: 287.0301.

Reaction of Tricarbonyl(η^3-allyl)iron(0) Anions

J. Chin. Chem. Soc., Vol. 38, No. 5, 1991 **481**

Formation of Tricarbonyl[(η^4-1,3-cyclohexadiene-2-methoxy-3yl)-diphenylmethyl]iron (14)

The reaction mixture derived using General Procedure I (1-lithio-1,1-diphenylmethane, 3.0 mmol; complex **7**, 2.0 mmol; bromine, 2.0 mmol) was separated by flash-column chromatography (hexane as eluent) to give complex **14** (0.21 g, 0.50 mmol, 32 %) as a yellow solid. mp 88-90°C; IR (CH$_2$Cl$_2$) 3058 (w), 3026 (w), 2944 (w), 2850 (w), 2038 (w), 1964 (s), 1602 (w), 1493 (w), 1462 (m), 1419 (w), 1237 (m), 1210 (m), 1127 (w), 1033 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.31-7.08 (*m*, 10H, aryl), 5.49 (*s*, 1H, C$_8$), 3.69 (*brs*, 1H, C$_4$), 3.44 (*s*, 3H, C$_7$), 2.94 (*s*, 1H, C$_1$), 1.75-1.56 (*m*, 4H, C$_5$ and C$_6$); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 210.9, 145.3, 141.1, 139.1, 130.5, 129.4, 128.3, 128.1, 127.9, 127.7, 126.8, 126.1, 95.7, 55.4, 52.1, 47.1, 29.7, 24.9, 24.7; MS (m/z) 416 (M$^+$, 7), 388(7), 360(100), 322(75), 300(15), 284(80), 167(20). HRMS Calcd for C$_{23}$H$_{20}$FeO$_4$: 416.0710, Found: 416.0698.

Formation of Tricarbonyl[(η^4-1,3-cyclohexadiene-2-methoxy-3yl)-2-methylpropionitrile]iron (15)

The reaction mixture derived using General Procedure I (2-lithio-2-methylpropionitnle, 3.0 mmol; complex **7**, 2.0 mmol; bromine, 2.0 mmol) was separated by flash-column chromatography (hexane/EtOAc = 10/1 as eluent) to afford complex **15** (0.18 g, 0.58 mmol, 29 %) as a yellow liquid. IR (CH$_2$Cl$_2$) 3076(m), 3034(m), 2986(m), 2942(m), 2860(m), 2236(m), 2042(s), 1970(s), 1060(m), 1467(s), 1418(m), 1276(m), 1256(m), 1210(m), 1178(m), 1106(m), 1066(m), 1031(m), 921(m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 3.62 (*s*, 3H, C$_7$), 3.47 (*brs*, 1H, C$_4$), 3.11 (*brs*, 1H, C$_1$), 1.75 (*s*, 3H, C$_9$ or C$_{10}$), 1.67 (*s*, 3H, C$_9$ or C$_{10}$), 1.69-1.39 (*m*, 4H, C$_5$ and C$_6$); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 210.4, 138.6, 123.5, 92.6, 55.2, 51.7, 47.1, 35.1, 27.2, 26.3, 25.1, 24.0; MS (m/z) 317 (M$^+$, 9), 289(32), 261(100), 233(70), 206(25); HRMS Calcd for C$_{14}$H$_{15}$FeNO$_4$: 317.0350, Found: 317.0360.

Formation of Tricarbonyl[(η^4-1,3-cyclohexadiene-1-methoxy-3yl)-diphenylmethyl]iron (16)

The reaction mixture derived using General Procedure I (1-lithio-1,1-diphenylmethane, 6.0 mmol; complex **8**, 4.0 mmol; bromine, 4.0 mmol) was separated by flash-column chromatography (hexane as eluent) to provide complex **16** (0.16 g, 0.38 mmol, 10 %) as a yellow liquid. IR (CH$_2$Cl$_2$) 3030(m), 2954(s), 2856(s), 2034(s), 1967(s), 1600(m), 1491(s), 1455(s), 1380(s), 1073(s), 1030(s), 1005(s), 920(s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.33-7.08 (*m*, 10 H, aryl), 4.81 (*s*, 1H, C$_2$), 4.77 (*s*, 1H, C$_8$), 3.48 (*s*, 3H, C$_7$), 2.90 (*m*, 1H, C$_4$), 1.76 (*m*, 4H, C$_5$ and C$_6$); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 212.5, 144.5, 140.1, 129.3, 128.8, 128.5,

128.2, 129.6, 126.6, 115.5, 101.5, 80.2, 60.0, 56.6, 55.8, 25.4, 24.6; MS (m/z) 416 (M$^+$, 1), 388(8), 360(48), 330(78), 300(100), 274(13), 224(10), 197(8), 167(52), 152(14), 133(8), 111(24), 84(12), 55(9); HRMS Calcd for C$_{23}$H$_{20}$FeO$_4$: 416.0710, Found: 416.0703.

Formation of Tricarbonyl[(η^4-1,3-cyclohexadiene-1-methoxy-3yl)-2-methylpropionitrile]iron (17)

The reaction mixture derived using General Procedure I (2-lithio-2-methylpropionitrile, 3.0 mmol; complex **8**, 2.0 mmol; bromine, 2.0 mmol) was separated by flash-column chromatography (hexane/EtOAc = 10/1 as eluent) to produce complex **17** (0.14 g, 0.44 mmol, 22 %) as a yellow solid. mp 58-60°C; IR (CH$_2$Cl$_2$) 3078(m), 2996(m), 2944(m), 2902(m), 2860(m), 2238(m), 2040(s), 1970(s), 1606(s), 1491(m), 1461(m), 1418(m), 1413(m), 1371(m), 1335(m), 1276(m), 1238(m), 1204(m), 1178(m), 1154(m), 1113(m), 1058(m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.29 (*brs*, 1H, C$_2$), 3.46 (*s*, 3H, C$_7$), 3.16 (*t*, J = 1.8Hz, 1H, C$_4$), 2.26 (*m*, 1H, C$_6$), 1.81 (*m*, 1H, C$_6$), 1.68 (*m*, 2H, C$_5$), 1.65 (*brs*, 6H, C$_9$ and C$_{10}$); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 211.4, 122.5, 115.8, 99.9, 75.8, 56.7, 54.6, 36.6, 29.1, 27.5, 25.3, 24.0; MS (m/z) 317 (M$^+$, 8), 289(48), 261(100), 233(48), 206(36), 135(28); HRMS Calcd for C$_{14}$H$_{15}$FeNO$_4$: 317.0350, Found: 317.0347.

Formation of Tricarbonyl[(η^4-1,3-butadiene-2,3-dimethyl-1-yl)-diphenylmethyl]iron (18)

The reaction mixture derived using General Procedure I (1-lithio-1,1-diphenylmethane, 3.6 mmol; complex **9**, 3.0 mmol; bromine, 3.0 mmol) was separated by flash-column chromatography (hexane as eluent) to obtain complex **18** (0.34 g, 0.89 mmol, 29 %) as a yellow liquid. IR (CH$_2$Cl$_2$) 3064(s), 3029(s), 2921(s), 2044(s), 1982(s), 1798(m), 1601(s), 1488(s), 1445(s), 1377(s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.31-7.14 (*m*, 10 H, aryl), 4.06 (*d*, J = 10.5, 1H, C$_5$), 2.17 (*s*, 3H, C$_6$ or C$_7$), 2.00 (*s*, 3H, C$_6$ or C$_7$), 1.71 (*d*, J = 2.5Hz, 1H, C$_1$, exo), 1.25 (*d*, J = 10.5Hz, 1H, C$_4$, endo), 0.35 (*d*, J = 2.5Hz, 1H, C$_1$, endo); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 211.3, 146.1, 144.5, 128.6, 128.2, 127.4, 127.0, 126.2, 126.0, 100.1, 97.4, 66.4, 53.4, 42.4, 20.6, 15.1; MS (m/z) 388 (M$^+$, 2), 360(9), 332(5), 304(100), 250(3), 224(15), 167(6), 91(6); HRMS Calcd for C$_{22}$H$_{20}$FeO$_3$: 388.0761, Found: 388.0757.

Formation of Tricarbonyl[(η^4-1,3-pentadiene-2-methyl-1-yl)-diphenylmethyl]iron (19)

The reaction mixture derived using General Procedure I (1-lithio-1,1-diphenylmethane, 3.0 mmol; complex **10**, 2.0 mmol; bromine, 2.0 mmol) was separated by flash-

column chromatography (hexane as eluent) to give complex 19 (0.25 g, 0.64 mmol, 32 %) as a yellow liquid. IR (CH_2Cl_2) 3060(w), 3040(m), 2980(m), 2960(m), 2040(s), 1980(s), 1620(m), 1510(m), 1480(m), 1360(m), 1180(s) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.4-7.2 (*m*, 10 H, aryl), 5.02 (*d*, J = 8.5, 1H, C_3), 4.08 (*d*, J = 10.5, 1H, C_6), 2.03 (*s*, 3H, C_7), 1.47 (*d*, J = 10.5Hz, 1H, C_5), 1.41 (*d*, J = 6.1Hz, 3H, C_1), 1.14 (*m*, 1H, C_2); MS (m/z) 388 (M^+, 1), 360(3), 332(6), 304(100), 262(3), 224(9), 200(5), 167(9), 152(6); HRMS Calcd for $C_{22}H_{20}FeO_3$: 388.0761, Found: 388.0757.

Formation of Tricarbonyl[(η^4-1,3-pentadiene-2-yl)-diphenylmethyl]iron (20)

The reaction mixture derived using General Procedure I (1-lithio-1,1-diphenylmethane, 3.0 mmol; complex 11, 2.0 mmol; bromine, 2.0 mmol) was separated by flash-column chromatography (hexane as eluent) to form complex 20 (0.25 g, 0.67 mmol, 33 %) as a yellow liquid. IR (CH_2Cl_2) 3086(s), 3064(s), 3031(s), 2962(s), 2925(s), 2865(s), 2044(s), 1982(s), 1569(m), 1490(s), 1449(s), 1378(m), 1259(w), 1199(m), 1076(s), 1025(s), 969(s) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.26-7.07 (*m*, 10 H, aryl), 4.69 (*s*, 1H, C_6), 4.56 (*d*, J = 8.4Hz, 1H, C_3), 1.67 (*d*, J = 1.4Hz, 1H, C_1), 1.25 (*d*, J = 6.1Hz, 3H, C_5), 1.08 (*m*, 1H, C_4), 0.37 (*d*, J = 2.7Hz, C_1); ^{13}C NMR ($CDCl_3$, 50.5 MHz) δ 211.9, 144.2, 141.1, 129.5, 129.2, 128.3, 128.2, 126.9, 126.6, 104.9, 90.1, 56.7, 56.9, 41.9, 19.7; MS (m/z) 374 (M^+, 1), 346(3), 318(25), 290(100), 224(30), 167(100), 143(12), 91(10); HRMS Calcd for $C_{21}H_{18}FeO_3$: 374.0605, Found: 374.0593.

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