

REACTION OF (η^1, η^2 -BUT-3-EN-1-YL)TRICARBONYLIRON(0) ANION COMPLEXES WITH CARBON ELECTROPHILES⁽¹⁾

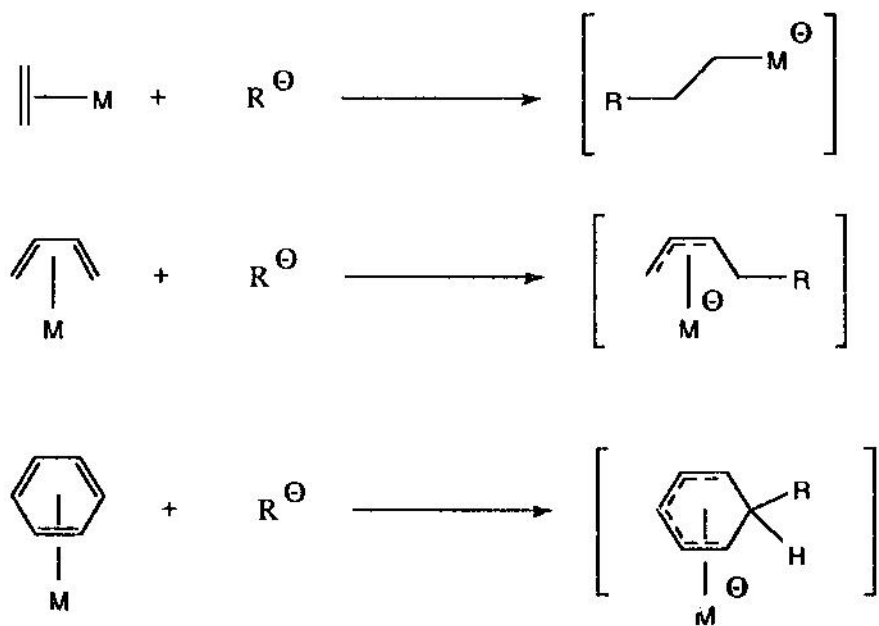
MING-CHANG P. YEH

*Institute of Chemistry, Academia Sinica,
Taipei 11529, Taiwan, ROC*

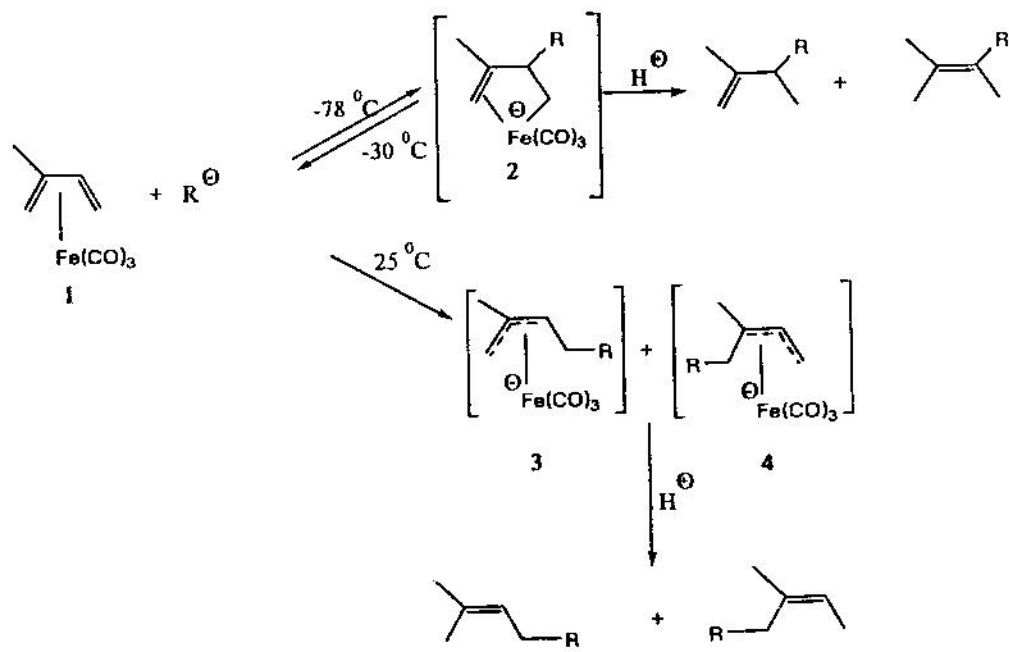
Abstract: Reaction of (η^1, η^2 -but-3-en-1-yl)tricarbonyliron(0) anion complexes with carbon electrophiles gives adduct incorporated with an additional CO. Different reaction pathways occur with functional groups at terminal positions of dienes.

There are two major concerns in organic synthesis, functional group interconversion and carbon-carbon bond formation. Carbon-carbon bond forming reactions can involve non-polar driving forces such as free radical coupling, electrocyclic processes such as the Diels-Alder reaction and the photochemically induced [2+2] cycloaddition reaction, or metal-induced reductive-elimination coupling reactions. Alternatively, polar driving forces can lead to coupling of an electrophilic carbon and a nucleophilic carbon. Examples of latter include the aldol condensation reaction and the Friedel-Crafts reaction. Simple unsaturated hydrocarbons such as ethylene, butadiene, and benzene are normally not susceptible to nucleophilic addition or substitution reactions. However, on coordination to electron-withdrawing transition metal centers, they are rendered susceptible to attack by a wide variety of nucleophiles, such as H^- , R^- , CN^- , RO^- , or amines.⁽²⁾ The metal-activated nucleophile addition to polyene ligands opens new strategies for organic synthesis and has been an area of high activity. A summary of possibilities is given in Scheme 1. The initial addition of nucleophile generates electron-rich intermediates which are not always easy to isolate. These reactive species are normally treated with strong oxidants, acid, or carbon electrophiles, and trapped *in situ*.

It has been well studied in the Semmelhack^(3,4,5) group that the reactive carbanion adds to (η^4 -1,3-diene)Fe(CO)₃ to produce the (η^1, η^2 -but-3-en-1-yl)Fe(CO)₃ anion complex at $-78^\circ C$ as exemplified by conversion of 1 to 2 in Scheme 2. Upon being warmed to $23^\circ C$, nucleophile R reverses and adds to the terminal position of the diene ligand to generate (η^3 -allyl)Fe(CO)₃ anion complexes, such as 3 and 4. The nucleophile is limited to carbanions more reactive than ketone enolates but not efficient with simple alkyllithium and Grignard reagents. Olefinic adducts are the major products when the reaction mixtures are quenched with trifluoroacetic acid. However, reaction of (η^1, η^2 -but-3-en-1-yl)Fe(CO)₃ anion complexes with carbon electrophiles remains unexplored. Nucleophilic addition followed by carbon electrophile quenching would result in two carbon-carbon bonds formation. We now wish to report that the reactive intermediate, such as 2 reacts with carbon electrophiles to produce γ, δ -unsaturated ketones.



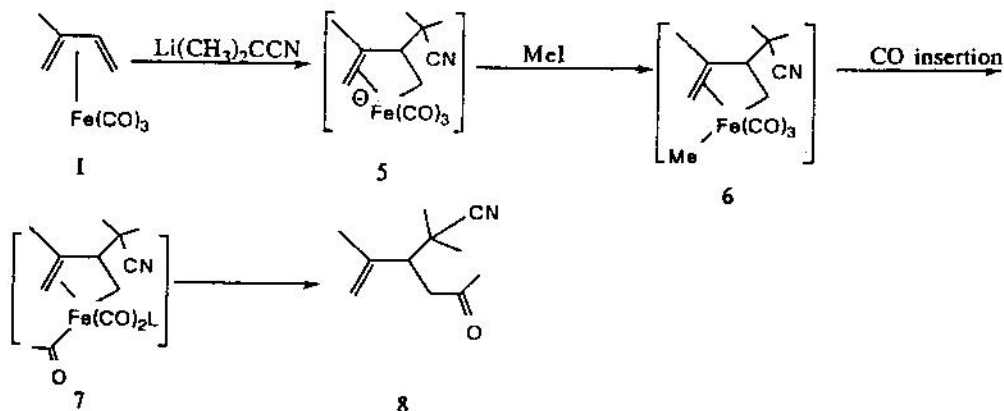
Scheme 2



Treatment of $(\eta^4\text{-isoprene})\text{Fe}(\text{CO})_3$ **1** with 2-lithio-2-methylpropionitrile at -78°C for 2 hr followed by quenching with excess iodomethane at -78°C gave the methyl ketone derivative **8** (43%) with an incorporated CO unit. The recovery of the starting complex **1** was 55%. This result suggested that the intermediate reacted with iodomethane in different ways:

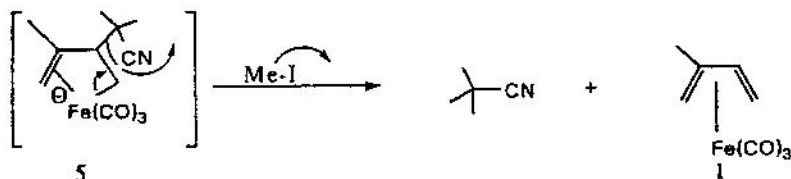
a) Methylation at metal center (**6**) followed by CO insertion (**7**) and finally reductive-elimination would give ketone **8** (Scheme 3).

Scheme 3



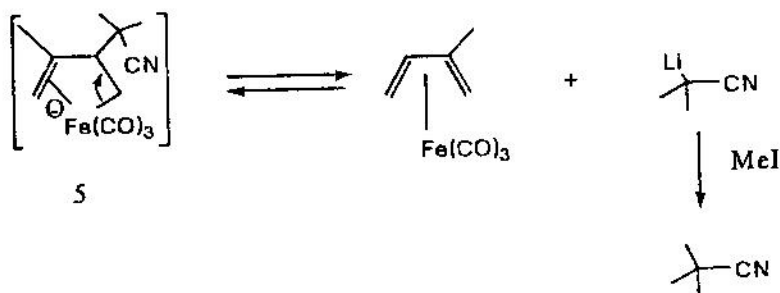
b). Direct transfer of the 2-methylpropionitrile anion to iodomethane accounted for the recovery of the starting complex **1** (Scheme 4).

Scheme 4



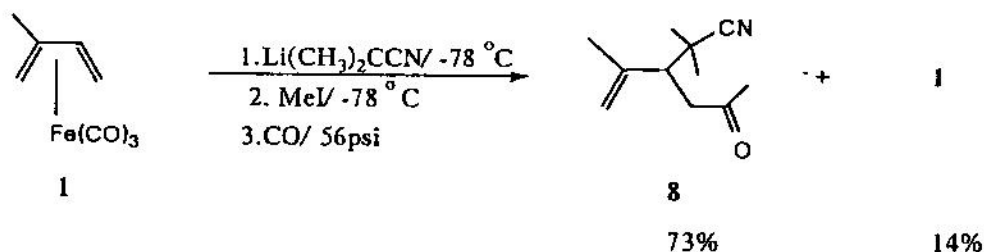
c). Alternatively, addition of 2-lithio-2-methylpropionitrile might be reversible. Iodomethane would react fast with a low equilibrium concentration of 2-lithio-2-methylpropionitrile, allowing recovery of the starting complex (Scheme 5).

Scheme 5



In an effort to inhibit reversible addition of the anion, triphenylphosphine was added in the expectation that it would react with intermediate **5** via displacement of the alkene ligand or induce migratory insertion of CO. However, there was no significant change in the yield of ketone **8** (48%). The yield of ketone **8** increased dramatically (73%) when CO (56 psi) was introduced into the reaction mixture immediately after quenching (Scheme 6).

Scheme 6



The reason for increasing the yield of **8** is not clear. A possible explanation is the facile CO insertion of proposed intermediate **6** under CO atmosphere to generate the acyliron Intermediate **7** ($\text{L}=\text{CO}$). Reductive elimination and loss of the $\text{Fe}(\text{CO})_3$ moiety would form ketone **8**. Treatment of complex **1** with the more reactive anion, such as diphenylmethyl lithium at -78°C for 2 hr, followed by quenching of the reaction mixture with carbon electrophiles also gives methyl ketone derivatives. Results of carbon electrophiles quenching are given in Tabel 1.

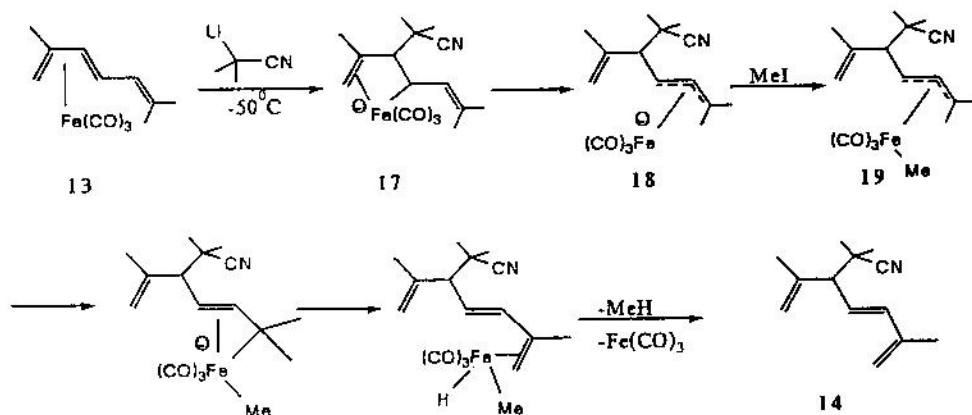
Nucleophilic addition followed by methylation of complexes **1** and **10** yields ketones **8** and **9** respectively. An atmosphere of CO affects the yields of ketones dramatically (entries 3 and 5), while triphenylphosphine does not influence CO migration (entry 2). The reactive (η^1, η^2 -but-3-en-1-yl)tricarbonyliron(0) anion also couples with benzyl bomide to generate ketone **12** (entry 7). The stereochemistry of ketones **11** and **12** are assigned as syn isomers, based on small constants of adjacent C-H bonds (see experimental). However, the reactive intermediate fails to react with secondary and tertiary halides. The starting complex **1** is isolated in high

Table 1. Reaction of (η^1, η^2 -But-3-en-1-yl)tricarbonyliron(0) Anion Complexes with Carbon Electrophiles

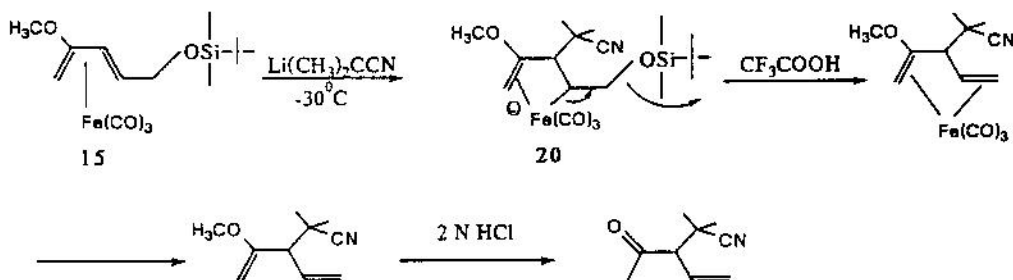
entry	complex	nucleophile	electrophile	product	yield
1		$\text{LiR}_1=$ 	MeI		(43%)
2	1	R_1	MeI/PPh ₃	8	(48%)
3	1	R_1	MeI/CO	8	(73%)
4	1	$\text{LiR}_2=$ LiCHPh_2	MeI		(64%)
5	1	R_2	MeI/CO	9	(86%)
6		R_2	MeI		(67%)
7	10	R_2	PhCH ₂ Br		(89%)
8		R_1	MeI		(60%)
9		R_1	MeI		(73%)

yields after aqueous work-up. Interestingly, complexes **13** and **15** (entries 8 and 9) operate very different reaction pathways. This difference might due to the functional groups at terminal positions of complexes **13** and **15**. It is rationalized beginning with isomerization of anionic homoallyl iron complex **17** to the more stable (η^3 -allyl)Fe(CO)₃ anionic complex **18**. Methylation of **18** gives **19**, which followed by successive β -hydride elimination, reductive elimination, and finally loss of the Fe(CO)₃ moiety to generate triene **14** (Scheme 7).⁽⁶⁾ Isobutyronitrile anion adds at the internal position of complex **15** at -30°C to give homoallyl anionic complex **20**.⁽⁷⁾ Complex **20** undergoes fac β -siloxy elimination, followed by loss of Fe(CO)₃ moiety to generate enol ether **21**. Treatment of **21** with 0.2N HCl produces β,γ -unsaturated ketone **22** with the nucleophile at α position (Scheme 8).

Scheme 7



Scheme 8



In conclusion, we have shown that reactive carbanions add at unsubstituted internal positions of (η^4 -1,3-diene)Fe(CO)₃ complexes to yield (η^1, η^2 -but-3-en-1-yl)Fe(CO)₃ anionic intermediates. Methylation of the reactive intermediates generates γ, δ -unsaturated ketones. Reaction undergoes different pathways with functional groups at terminal positions.

EXPERIMENTAL

Spectra. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded with a Bruker WM-250 Fourier transform spectrometer operating at 250 MHz or a Nicolet QE-300 Fourier transform spectrometer operating at 300 MHz. Peak positions are reported in parts per million relative to tetramethylsilane internal standard. Carbon nuclear magnetic resonance (¹³C 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. Peak positions are reported in parts per million relative to detueriochloroform (77.00). Spectra which were recorded with off-resonance decoupling have peaks reported as singlet(s), doublets(d), triplets(t), or quartets(q). Infraed (IR) spectra were recorded on a Perkin-Elmer Model 299 spectrometer and a Digilab FTS-20C spectrometer. Peaks 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 AEI MS-902 instrument and 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 biggest peak as 100%).

Chromatography. Flash column chromatography refers to separate components under positive argon pressure and eluted with gradient solvent (increasing polarity of solvent gradually). The material which was used to pack in the column is Badman 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 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. Acetyl

chloride (Aldrich Chemical Co.), 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 solution in hexane and the concentration was determined by using a literature procedure.⁽⁸⁾ (η^4 -*cis*-1-methoxy-1,3-butadiene)Fe(CO)₃, and (η^4 -*cis*-3-methyl-1,3-pentadiene)Fe(CO)₃ were obtained by treatment of free dienes with Fe₂(CO)₉ in anhydrous ether, flash column chromatography followed by flash distilled before use. Iodomethane was purchased from J.T. Baker Co., *n*-propyl iodide, isopropyl iodide, 2-methyl-2-iodopropane, diphenylmethane, and trifluoroacetic acid were purchased from Aldrich Chemical Co. and used without further purification.

General Information. The term "concentration" refers to removal of solvent at 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 were uncorrected.

Procedure for Generation of Anions

Diphenylmethane Anion:⁽⁹⁾ To 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 hr. This solution was used immediately in reaction with iron complexes (1 mmol in 1 ml THF, see below).

Lithium Isobutyronitrile Anion:⁽⁹⁾ To a solution of diisopropylamine (1.2 mmol) in THF (3 ml), under argon in a 100-ml pear shaped round bottom flask equipped with a rubber septum and a magnetic stirrer at -78°C was rapidly added via syringe a solution of *n*-butyllithium in hexane (1.04 mmol). The mixture was allowed to stir at -78°C for 20 min. To the solution prepared above was added rapidly neat via syringe isobutyronitrile (0.10 ml, 1.2 mmol), followed by addition of HMPA (1.00 ml). The mixture was allowed to stir 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: General Procedure for Addition of Anions to (η^4 -1,3 diene) Fe(CO)₃ at -78°C. The Formation of (η^1, η^2 -But-3-en-1-yl) tricarbonyliron(0) Anion Intermediates. To solution of the anion (1.3 mmol, see above) in 3:1 THE: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 hr.

(5-Methyl-5-hexen-2-on-4-yl)-2-methylpropionitrile (8). The mixture from the General Procedure I (2-lithio-2-methylpropionitrile, 1.30 mmol, and complex 1, 1.00 mmol) was quenched with excess iodomethane (0.5 ml) at -78°C . The reaction mixture was allowed to stir at 25°C for 14 hr. The solution was poured into hexane (120 ml) in a separatory funnel, the hexane layer was washed three 100 ml portions of water, three 100 ml portions of saturated aqueous sodium chloride solution, dried over magnesium sulfate, filtered through Celite, and finally concentrated on a rotary evaporator. Flash column chromatography of the residue (0.20 g, 18 g of silica gel) afforded a fraction containing the starting complex 1 (0.11 g, 0.55 mmol, 55% recovery) eluted with 30:1 hexane: ethyl acetate and a fraction containing ketone 8 eluted with 4:1 hexane: ethyl acetate, 75 mg, 0.43 mmol, 43% yield from 0.21 g (1.00 mmol) of $(\eta^4\text{-isoprene})\text{Fe}(\text{CO})_3$ 1. Short-path distillation (0.03 mmHg, $70\text{-}90^\circ\text{C}$) gave a colorless liquid 65 mg, 0.36 mmol, 36% yield. ^1H NMR (CDCl_3 , 300 MHz): δ 4.96 (s, 1 H), 4.92 (s, 1 H), 2.92 (dd, 1 H, $J=16.8, 10.2$ Hz), 2.72 (dd, 1 H, $J=16.8, 3.7$ Hz), 2.61 (dd, 1 H, $J=10.2, 3.7$ Hz), 2.16 (s, 3 H), 1.85 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 206.3 (s), 124.8 (s), 143.5 (s), 115.7 (t), 49.8 (d), 44.8 (t), 35.2 (s), 31.3 (q), 26.5 (q), 22.5 (q), 21.7 (q). IR (neat): 3090 (s), 2990 (m), 2980 (w), 2215 (s), 1720 (s), 1645 (s), 1450 (w), 1370 (m), 1160 (m) cm^{-1} . Mass spec (EI): 179 (M^+ , 7), 164 (M- CH_3 , 2), 136 (17), 122 (22), 95 (20) 69 (100). Anal. (distillation). Calcd. for $\text{C}_{11}\text{H}_{17}\text{NO}$: C, 73.63; H, 9.56; N, 7.81; O, 8.92. Found: C, 73.26; H, 9.42; N, 8.05.

Reaction of the mixture, Derived from 2-Lithio-2-methylpropionitrile and Complex 1, with Iodomethane in the Presence of Triphenylphosphine. The reaction mixture from the General Procedure I (2-lithio-2-methylpropionitrile, 2.00 mmol, and complex 1, 1.63 mmol) was added of a solution of PPh_3 (0.43 g, 1.63 mmol) in 2 ml of THF. The reaction mixture was allowed to stirred at -78°C for 2 hr before quenched with 1 ml of iodomethane. The reaction mixture was allowed to stir at 25°C for 14 hr. After aqueous processing (*via supra*), the solution was concentrated on a rotary evaporatory. Flash distillation of the residue afforded the starting complex 1 (0.14 g, 0.65 mmol, 40% recovery). Short-path distillation of the remaining residue gave compound 8 (0.14 g, 0.78 mmol, 48%). The proton NMR spectrum of 8 was identical to the previous results.

Reaction of the mixture, Derived from 2-Lithio-2-methylpropionitrile and Complex 1, with Iodomethane in the Presence of CO Pressure. In this experiment the reaction apparatus was a medium-pressure glass bomb equipped with a septum adapter, magnetic stirrer, and pressure gauge. The reaction mixture from the General Procedure I (2-lithio-2-methylpropionitrile, 0.94 mmol, and complex 1, 0.72 mmol) in a pressure bottle was pressurized under CO (56 psi) immediately after the reaction was quenched with excess iodomethane (1.0 ml), at -78°C . The reaction mixture was allowed to stirred at 25°C for 14 hr. After aqueous processing (*via supra*), the solution was concentrated on a rotary evaporator. Flash column chromatography of the residue (0.13 g, 18 g of silica gel) afforded a fraction containing the starting complex 1 (25 mg, 0.12 mmol, 16% recovery) eluted with 30:1 hexane:ethyl acetate, 0.10 g, 0.58 mmol, 81% yield from 0.15 g (0.72 mmol) of

complex 1. Short-path distillation (0.03 mmHg, 70-90°C) gave a colorless liquid, 94 mg, 0.52 mmol, 73% yield. The proton NMR spectrum of 1 was identical to the previous result.

(5-Methyl-hex-5-en-2-on-4-yl)-1,1-diphenylmethane (9). The mixture from the General Procedure I (diphenylmethane anion) was quenched with excess iodomethane (0.6 ml) at -78°C. The reaction was allowed to stir at 25°C for 14 hr. The solution was poured into hexane (120 ml), the hexane layer was washed three 120 ml portions of water, three 120 ml portions of saturated aqueous sodium chloride solution, dried over magnesium sulfate, filtered through Celite, and finally concentrated on a rotary evaporator. Flash column chromatography of the residue 280 mg (18.0 g of silica gel) afforded a fraction containing the starting complex 1 (62 mg, 0.30 mmol, 30% recovery) and a major fraction containing ketone 9 (192 mg, 0.69 mmol, 69% yield from 208 mg, 1.00 mmol, of the starting complex 1) eluted with 9:1 (hexane: ethyl acetate). The compound was recrystallized from pentane: 178 mg, 0.64 mmol, 64% yield. mp 105.5-106°C. ¹H NMR (CDCl₃, 300 MHz): δ 7.10-7.37 (m, 10 H), 4.78 (s, 1 H), 4.74 (s, 1 H), 3.84 (d, 1 H, J=11.9 Hz), 3.70 (m, 1 H), 2.53 (dd, 1 H, J=15.7, 10.2 Hz), 2.38 (dd, 1 H, J=15.7, 3.7 Hz), 1.96 (s, 3 H), 1.58 (s, 3 H). ¹³C NMR (CDCl₃, 75.5 MHz): δ 207.8, (s), 145.2 (s), 143.1 (s), 142.9 (s), 129.9 (d), 129.3 (d), 125.6 (d), 114.1 (t), 55.87 (d), 47.01 (q), 46.68 (d), 30.50 (q), 20.25 (q). IR (CDCl₃): 3060 (s), 3020 (s), 2970 (w), 2240 (s, CDCl₃), 1775 (m), 1490 (s), 1450 (w), 1360 (m), 1260 (s), 1160 (m), 1060 (s) cm⁻¹. Mass spec (EI): 278 (M⁺, 1), 220 (2), 167 (100), 152 (9), 43 (43). Mass spectral mol. wt: 278.1662. Calcd. for C₂₀H₂₂O: 278.1671.

Reaction of the Mixture Derived from Diphenylmethyl Lithium and Complex 1, with Iodomethane in the Presence of CO Pressure. In this experiment the reaction apparatus was a medium pressure glass bomb equipped with a septum adapter, magnetic stirrer, and pressure gauge. The reaction mixture from the General Procedure I (diphenylmethyl anion, 1.10 mmol, and complex 1, 1.00 mmol) was pressurized under CO (18 psi) immediately after the reaction was quenched with iodomethane (0.6 ml) at -78°C. The reaction was allowed to stir at 25°C for 14 hr under CO. After aqueous processing (*via supra*), the solution was concentrated on a rotary evaporator. Flash column chromatography of the residue (289 mg, 18.0 g of silica gel) afforded a major fraction containing ketone 9 (240 mg, 0.86 mmol, 86% yield from 1.00 mmol of the starting complex 1) eluted with 9:1 (hexane: ethyl acetate). The compound was recrystallized from pentane: 219 mg, 0.79 mmol, 79% yield. The proton NMR of ketone 9 was consistent with the previous result.

Reaction of the Mixture Derived from Diphenylmethyl Lithium and Complex 1, with 1-Iodopropane, 2-Iodopropane, or 2-Iodo-2-methylpropane. The reaction mixture from the General Procedure I (diphenylmethyl lithium, 1.10 mmol, and complex 1, 1.00 ml) was quenched with 1-iodopropane, 2-iodopropane, or 2-iodo-2-methylpropane (1 ml) at -78°C, and stirred at 25°C for 14 hr. After aqueous processing (*via supra*), the solution was concentrated on a rotary evaporator. Flash distillation of the residue gave the starting complex 1 in high yield (175 mg, 0.84 mmol, 84%; 162 mg, 0.78 mmol, 78%; 187 mg, 0.90 mmol, 90% respectively).

4-Diphenylmethyl-3-methoxy-1-hexen-2-one (11). The reaction from the General Procedure I was quenched with excess methyl iodide (2 ml) at -78°C . The reaction mixture was allowed to stir at room temperature for 14 hr before 300 ml of hexane was poured to the reaction mixture. The hexane solution was washed three 300 ml portions of water, three 300 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 (931 mg from 896 mg, 4.00 mmol, of the starting complex 10, 50.0 g of silica gel), gave a major fraction containing 785 mg (67%) of ketone 11 as a colorless oil. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 7.2-7.5 (m, 10 H), 5.69 (ddd, 1 H, $J=17.3, 10.3, 10.0$ Hz), 4.97 (dd, 1 H, $J=10.3, 1.3$ Hz), 4.92 (dd, 1 H, $J=17.3, 1.3$ Hz), 4.27 (d, 1 H, $J=11.7$ Hz), 3.47 (d, 1 H, $J=2.4$ Hz), 3.36 (ddd, 1 H, $J=11.7, 10.0, .4$ Hz), 3.23 (s, 3 H), 2.13 (s, 3 H). $^{13}\text{C NMR}$ (CDCl_3 , 75.5 Hz): δ 212.13, 143.1, 142.8, 135.4, 129.1, 128.61, 128.53, 128.3, 126.8, 126.4., 119.1, 88.2, 59.4, 53.1, 51.8, 27.3. IR (neat): 3078 (w), 3059 (w), 3024 (m), 2931 (m), 2927 (m), 1715 (s), 1597 (m), 1493 (m), 1450 (m), 1420 (w), 1390 (m). Mass spec. (EI): 215 ($\text{M}^+\text{-COCH}_3$, 1), 206 (3), 167 (100), 129 (3). Mass spectral mol. wt.: (distillation, 130-150°C 0.02 mmHg). 251.1434. Calcd. for $\text{C}_{18}\text{H}_{19}\text{O}$ (M-COCH₃) 251.1436.

4-Diphenylmethyl-3-Methoxy-1-phenyl-5-hexen-2-one (12). The reaction mixture obtained from the General Procedure I was quenched with excess benzyl bromide (1 ml) at -78°C . The reaction mixture was allowed to stir at 25°C for 14 hr before 100 ml of hexane was poured into the reaction mixture. The hexane solution was washed three 100 ml portions of water, three 100 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 (553 mg, from 224 mg of starting complex 10, 12.0 g of silica gel), gave a major fraction containing the ketone 12 (331 mg, 89%) with a trace of impurity. Further purification by Prep TLC was not successful. $^1\text{H NMR}$ (CDCl_3 , 250 MHz): δ 7.1-7.4 (m, 15 H), 5.67 (ddd, 1 H, $J=17.2, 11.2, 10.3$ Hz), 4.97 (dd, 1 H, $J=10.3, 1.6$ Hz), 4.93 (dd, 1 H, $J=17.2, 1.6$ Hz), 4.21 (d, $J=11.6$ Hz), 3.73 (s, 1 H), 3.71 (s, 1 H), 3.58 (d, 1 H, $J=1.2$ Hz), 3.43 (ddd, 1 H, $J=11.6, 11.2, 2.3$ Hz), 3.11 (s, 3 H). $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): 210.0, 135.38, 119.31, 87.36, 59.53, 53.16, 51.67, 46.65, and many peaks in the aromatic region between 120 and 150. IR (neat): 3060 (w), 3025 (m), 2940 (w), 1718 (s), 1600 (m), 1490 (s), 1450 (s), 1120 (m) cm^{-1} . Mass spec. (EI): 338 (M- MeOH, 1), 251 (2), 205 (5), 167 (100, 152 (7). Mass spectral mol. wt.: (distillation, 150-160°C, 0.03 mmHg). 338.1670. Calcd. for $\text{C}_{25}\text{H}_{22}\text{O}$ (M- MeOH): 338.1665.

(2,6-Dimethyl-1,4,6-heptatriene-3-yl)-2-methylpropionitrile (14). The mixture from the General Procedure I (2-lithio-2-methylpropionitrile, 1.10 mmol, and complex 13 1.00 mmol) at -52°C . The reaction mixture was quenched with excess iodomethane (0.50 ml). The reaction mixture was poured into hexane (120 ml) after stirred at 25°C for 14 hr. The hexane solution was washed with three 120-ml portions of water, three 120-ml portions of saturated aqueous sodium chloride solution, dried over magnesium sulfate, filtered through Celite and finally concentrated on a rotary evaporator. Flash distillation of the residue afforded a

mixture of the starting complex 13 and triene 14 (0.18 g). The ratio of 13 to 14 was 1 to 9. Flash column chromatography (12 g of silica gel) afforded triend 14 (0.12 g, 63%) from 0.26 g of the starting complex 13. Compound 14 is a colorless liquid. ^1H NMR (CDCl_3 , 250 MHz): δ 6.20 (d, 1 H, $J=15.4$ Hz), 5.83 (dd, 1 H, $J=15.4, 9.5$ Hz), 4.98-4.90 (m, 4 H), 2.56 (d, 1 H, $J=9.5$ Hz), 1.89 (s, 3 H), .87 (s, 3 H), 1.34 (s, 3 H), 1.33 (s, 3 H). ^{13}C NMR (CDCl_3 , 75.5 Hz): δ 144.3, 141.6, 136.5, 127.1, 124.6, 116.9, 114.7, 59.7, 34.6, 25.7, 21.1, 18.8. IR (neat): 3078 (m), 3020 (w), 2974 (s), 2935 (s), 2873 (w), 2290 (m), 1643 (m), 1608 (m), 1465 (m), 1450 (s), 1377 (m), 1307 (m), 1030 (w), 968 (s), 895 (s) cm^{-1} . Mass spectral mol. wt.: 189.1516. Calcd. for $\text{C}_{13}\text{H}_{19}\text{N}$: 189.1519.

(2-Methoxy-1,4-pentadien-3-yl)-2-methylpropionitrile (22). The mixture from the General Procedure I (isobutyronitrile anion) was stirred at -30°C for 22 hr. The reaction was quenched with excess trifluoroacetic acid (0.7 ml) at -30°C . The mixture was allowed to stir at 25°C for 30 min. The solution was poured into hexane (120 ml) in a separatory funnel, the hexane layer was washed three 120 ml portions of water, three 120 ml portions of saturated aqueous sodium chloride solution, dried over magnesium sulfate, filtered through Celite, and finally concentrated on a rotary evaporator. Flash distillation of the residue (0.01 mmHg) afforded 0.10 g (0.82 mmol, 100%) of enol ether 22 (from 0.24 g, 0.65 mmol, of complex 15). ^1H NMR (CDCl_3 , 250 MHz): δ 6.05 (ddd, 1 H, $J=16, 9.5, 8.6$ Hz), 5.25 (dd, 1 H, $J=9.5, 8.6$ Hz), 4.04 (s, 2H), 3.57 (s, 3H), 2.61 (d, 1 H, $J=9.5$ Hz), 1.35 (s, 3 H), 1.33 (s, 3H). The enol ether 22 was used for hydrolysis without further purification.

(4-Penten-2-on-3-yl)-2-Methylpropionitrile (23). To a solution of 10 ml of 2N HCl solution in 10 ml methanol at 25°C was added via syringe a solution of 0.10 g (0.6 mmol) of enol ether 22 in 10 ml of methanol. The reaction was allowed to stir at 25°C for 18 hr. The solution was poured into water (50 ml) in a separatory funnel, the aqueous layer was extracted three times with 100 ml of ether, the combined ethereal layers was washed three 300 ml portions of water, three 300 ml portions of 10% aqueous sodium carbonate solution, three 300 ml portions of water, three 300 ml portions of saturated aqueous sodium chloride solution, dried over magnesium sulfate, and finally concentrated on a rotary evaporator. Flash column chromatography (3.0 g of silica gel) of the residue (81 mg), eluted with 10:1 hexane:ethyl acetate, followed by flash distillation afforded 67 mg (0.44 mmol, 73%) of compound 23 from 0.24 g (0.65 mmol) of the complex 22. ^1H NMR (CDCl_3 , 250 MHz): δ 5.42 (ddd, 1 H, $J=16.9, 9.7, 9.0$ Hz), 5.44 (dd, 1 H, $J=9.0, 1.1$ Hz), 5.36 (dd, 1 H, $J=16.9, 1.1$ Hz), 3.10 (d, 1 H, $J=9.7, 9.0$ Hz), 5.44 (dd, 1 H, $J=9.0, 1.1$ Hz), 5.36 (dd, 1 H, $J=16.9, 1.1$ Hz), 3.10 (d, 1 H, $J=9.7$ Hz), 2.23 (s, 3 H), 1.38 (s, 3 H), 1.37 (s, 3 H). ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 206.6, 132.6, 124.9, 124.4, 66.4, 34.7, 31.4, 26.7, 26.3. IR (neat): 3090 (s), 3060 (s), 2980 (s), 2225 (s), 1740 (m), 1641 (s), 1451 (m), 1418 (m), 1377 (s), 1354 (s), 1340 (m), 1210 (s), 1170 (s), 1148 (s) cm^{-1} . Mass spec (EI): 151 (M^+ , 3), 136 ($\text{M}-\text{CH}_3$, 1), 124 (1), 109 (11), 82 (100, 67 (32), 43 (97). Mass spectral mol. wt.: 151.0985. Calcd. for $\text{C}_9\text{H}_{13}\text{NO}$: 151.0997.

ACKNOWLEDGEMENTS

We would like to thank Professor Martin Semmelhack for his valuable discussion on the project.

REFERENCES

- (1) This work is taken in part from M.C.P. Yeh Ph.D. Dissertation, Princeton University, 1987, Princeton, NJ 08544 U.S.A.
- (2) For a review of nucleophilic addition to polyene-metal complexes, see: S. G. Davis, M. L. H. Greene and D. M. P. Mingos, *Tetrahedron*, **34**, 3047-3077 (1978).
- (3) J. W. Herndon, Ph.D. thesis 1983, Princeton University, Princeton NJ 08544 U.S.A.
- (4) M.F. Semmelhack and J.W. Herndon, *Organometallics* **2**, 363-372, (1983).
- (5) M.F. Semmelhack, J.W. Herndon and J.P. Springer, *J. Am. Chem. Soc.* **104**, 2497-2499 (1982).
- (6) Reaction of (η^3 -allyl)Fe(CO)₃ complexes with iodomethane at 25°C also gives diene complexes or free dienes. M.C.P. Yeh Ph.D. thesis. Princeton University, 1987, Princeton, NJ 08544 U.S.A.
- (7) Lithium isobutyronitrile does not react with complex **15** at 78°C nor 50°C.
- (8) G. G. Emerson, J. E. Mahler, R. Koehbar and R. Pettit, *J. Org. Chem.*, **29**, 3620-3623 (1964).
- (9) Hahn M.T. Le, Ph.D. thesis. Princeton University, 1987, Princeton, NJ 08544 U.S.A.
- (10) G. Wittig and A. Hesse, *Org. Syn.*, **50**, 66-70 (1970).

高丙烯三羰鐵與親電子試劑之反應

葉 名 倉

摘 要

高丙烯三羰鐵與親電子試劑反應產生不飽和酮類，當官能基在第一位置時，有不同的反應方式。