

Trapping of Tricarbonyl(η^1, η^2 -homoallyl)iron and Tricarbonyl(η^3 -allyl)iron Anion Intermediates with 2-(Phenylsulfonyl)-3-phenyloxaziridine

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The addition of reactive carbanions to (η^4 -1,3-diene)Fe(CO)₃ complexes at -78 °C and 25 °C produced putative homoallyl and allyl anion complexes, respectively. Reaction of the reactive intermediates with 2-(phenylsulfonyl)-3-phenyloxaziridine afforded nucleophilic substituted (η^4 -1,3-diene)Fe(CO)₃ complexes.

Keywords: Iron; Diene; Hydride; Davis reagent.

INTRODUCTION

Addition of reactive carbanions such as LiCHPh₂ to (η^4 -1,3-diene)Fe(CO)₃ complexes occurs at an unsubstituted, internal position of the diene ligands under kinetically controlled reaction conditions (-78 °C) to generate an unstable tricarbonyl(η^1, η^2 -homoallyl)iron anion intermediate. Reversal of the initial addition is rapid below 0 °C; nucleophilic addition recurs at a terminal position to provide a thermodynamically more stable tricarbonyl(η^3 -allyl)iron anion intermediate.¹ Trapping of acyclic homoallyl anions with a molecular of CO produces nucleophilic substituted cyclopentanone derivatives after acid quenching.² Reaction of homoallyl anions with bromine results in CO insertion to afford carboxylic acid derivatives after aqueous work-up.³ Treatment of η^3 -allyl anions with trifluoroacetic acid generates olefinic adducts with nucleophiles at the allylic position.⁴

The N-sulfonyloxaziridines are an important class of highly chemoselective oxidizing reagents and are finding increased utility in organic synthesis.⁵ These compounds are useful reagents for the oxidation of sulfides to sulfoxides,⁶ for the oxidation of organonitrogen compounds,⁷ for the epoxidation of alkenes,⁸ for the oxidation of organolithium and -Grignard reagents,⁹ and for the oxidation of enolates to α -hydroxy carbonyl compounds.¹⁰ Surprisingly, reports on the reaction of N-sulfonyloxaziridines such as 2-(phenylsulfonyl)-3-phenyloxaziridine (commonly known as the Davis reagent) with reactive anionic organoiron intermediates are not found. We now report that quenching of both tricarbonyl(η^1, η^2 -homoallyl)iron and tricarbonyl(η^3 -allyl)iron anion intermediates with the Davis reagent proceeds in abstracting a hydride from the anion intermediates to provide

nucleophilic-substituted (η^4 -1,3-diene)Fe(CO)₃ complexes.

RESULTS AND DISCUSSION

The starting (η^4 -1,3-diene)Fe(CO)₃ complexes were prepared by refluxing of the corresponding 1,3-dienes with Fe₂(CO)₉ in ether according to the literature procedure.¹¹ 2-Phenylsulfonyloxaziridine (Davis reagent) was synthesized starting from benzaldehyde and benzenesulfonamide followed by oxidation of the resulting N-benzylidenebenzenesulfonamide with *m*-chloroperbenzoic acid using the literature procedure.¹²

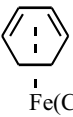
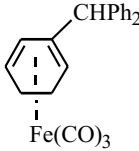

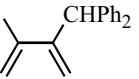
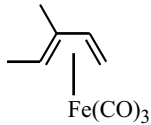
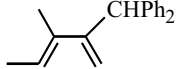
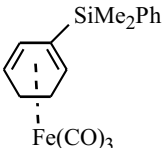
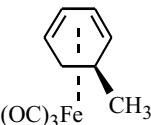
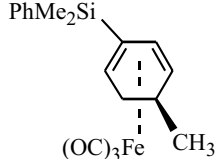
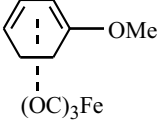
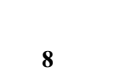
Quenching of Tricarbonyl(η^1, η^2 -homoallyl)iron Anion Intermediates with the Davis Reagent

Treatment of iron-diene complexes **1-3** with reactive carbanions (1.2 molar equiv, see experimental section) in THF/HMPA (3/1) at -78 °C for 4 h followed by trapping of the reactive intermediates with the Davis reagent (1.0 molar equiv, -78 °C, 2 h and 30 °C, 4 h) produced nucleophilic C-2-substituted iron complex **4** and 1,3-dienes **5** and **6** in low yields (entries 1-3, Table 1). Moreover, addition of a silyl anion, for example LiSiMe₂Ph, to iron-complexes **1** and **7** could only occur at 30 °C to produce C-2 silyl substituted iron-complexes **8** (48%, entry 4, Table 1) and **9** (40%, entry 5, Table 1), respectively. Results of the addition and quenching processes are summarized in Table 1.

It was presumed that nucleophilic additions occur at the internal position of iron-diene complexes, for example **1**, at -78 °C for reactive carbanions and at 30 °C for LiSiMe₂Ph to form tricarbonyl(η^1, η^2 -homoallyl)iron anion complex

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Table 1. Reaction of (η^1, η^2 -Homoallyl)Fe(CO)₃ Anion Intermediates with the Davis Reagent

Entry	Complex	Nucleophiles	Products
1		LiCHPh ₂	 35%
	1		4
2		LiCHPh ₂	 38%
	2		5
3		LiCHPh ₂	 9%
	3		6
4 ^a	1	LiSiMe ₂ Ph	 48%
			8
5 ^a		LiSiMe ₂ Ph	 40%
	7		9
6 ^a		LiSiMe ₂ Ph	 60%
	10		8

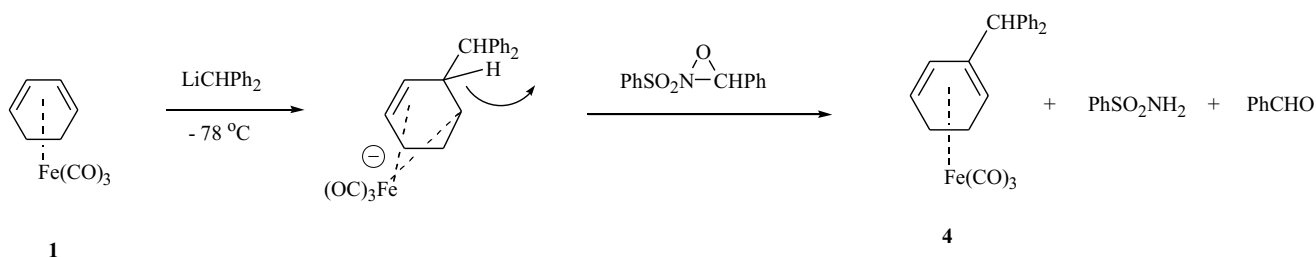
^a The addition of LiSiMe₂Ph was conducted at 30 °C for 16 h.

(Scheme I). Trapping of the postulated anion intermediate with the Davis reagent proceeded in migration of β -hydride to oxaziridine to give nucleophilic substituted diene-iron complexes **4** together with isolation of PhSO_2NH_2 and PhCHO after aqueous process (Scheme I). It must be mentioned that unlike reactive carbanions added at the internal position of the diene ligand at -78°C , the silyl anion (LiCH_2Ph_2) does not react with iron complexes at -78°C . The silyl anion could only attack at the internal position of the diene ligand at room temperature. Moreover, increasing a methyl group at C-5 with complex **7** the silylation added at the less hindered C-2 position of the diene ligand to give **9** in 40% yield after quenching the reactive intermediate with the Davis reagent. The spectral evidence for complex **4** is based on their ^1H NMR spectra. The resonances of a doublet at 5.00 ppm for **4** is due to the internal proton at C-2 and two resonances of multiplets at 3.02 and 3.2 ppm are due to two protons at C-1 and C-4. The spectral data of **8** are similar to those of **4**. Al-

though yields of the addition/quenching are low, this formal nucleophilic substitution for hydride at the C-2 position of dienes is rare and may have special potential in the synthesis of dienyl derivatives. Moreover, isolation of free dienes **5** and **6** indicated that decomplexation of the $\text{Fe}(\text{CO})_3$ moiety occurred during the aqueous workup and flash column chromatography.

Surprisingly, addition of PhMe_2SiLi to $(\eta^4\text{-1-methoxycyclohexa-1,3-diene})\text{Fe}(\text{CO})_3$ complex (**10**) also produced **8** in 60% yield (entry 6, Table 1). The formation of **8** from **10** is difficult to understand since it formally involves a kind of *cine*-substitution for methoxide. A possible reaction path involving α -methoxy elimination of the homoallyl anion intermediate **11** to generate the carbene intermediate **12** is proposed (Scheme II). The postulate carbene intermediate **12** may undergo β -hydride elimination (to give **13**) followed by reductive elimination to provide **14**. Reoordination of the pendant double bond to the iron center of **14** produced com-

Scheme I



Scheme II

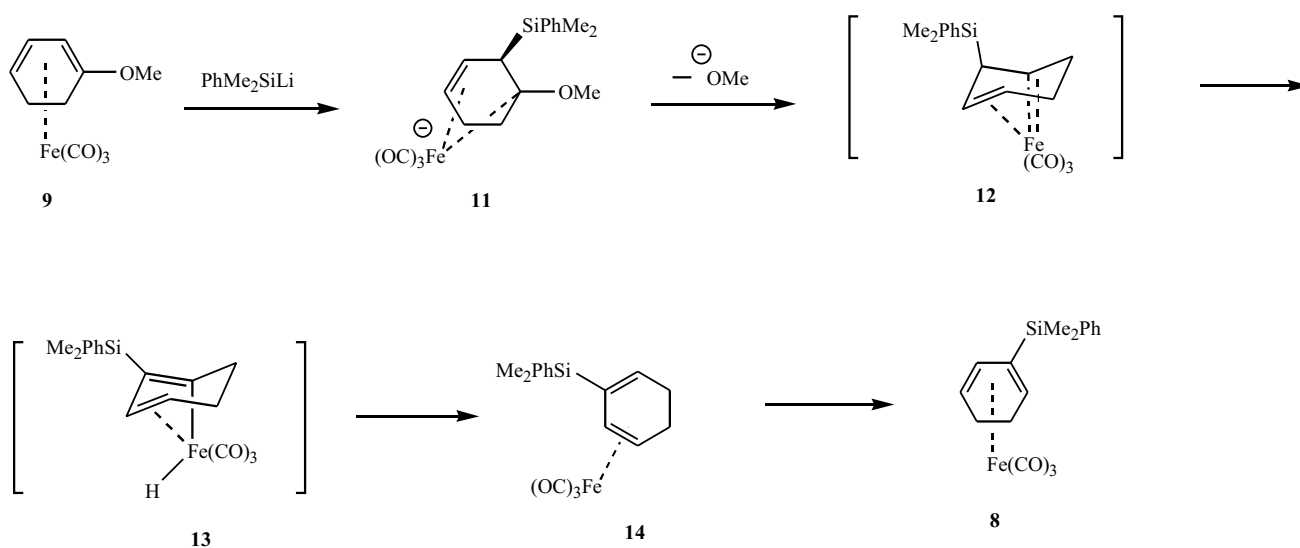
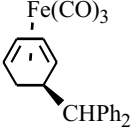
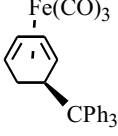
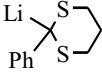
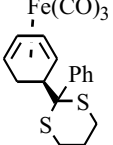
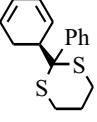
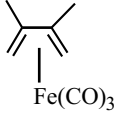
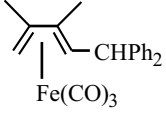
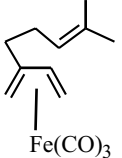
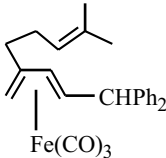
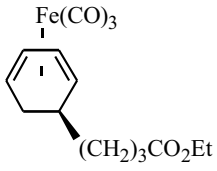
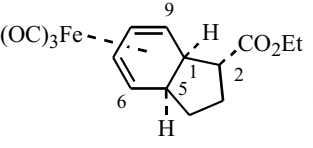


Table 2. Reaction of (η^3 -allyl)Fe(CO)₃ Anion Intermediates with the Davis Reagent

Entry	Complex	Nucleophiles (25 °C)	Products	
1	1	LiCHPh ₂	 15 27%	
2	1	LiCPh ₃	 16 52%	
3	1		 17 28%	 18 40%
4	 19	LiCHPh ₂	 20 39%	
5	 21	LiCHPh ₂	 22 35%	
6	 24	LDA	 25 30%	

plex **8**.

Quenching of Tricarbonyl(η^3 -allyl)iron Anion Intermediates with the Davis Reagent

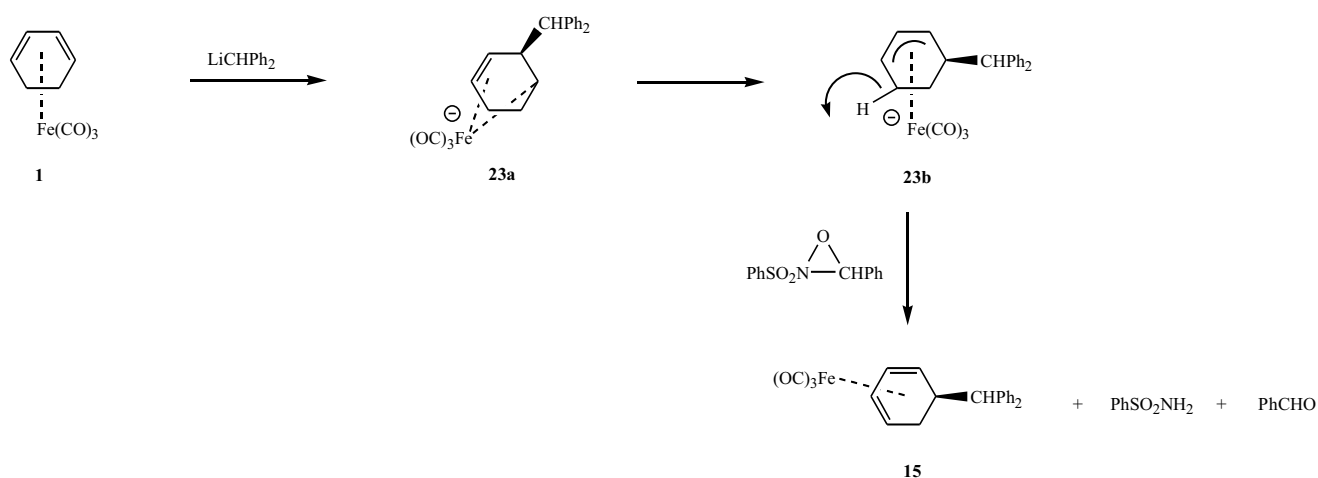
Treatment of (η^4 -1,3-diene)Fe(CO)₃ complexes with reactive carbanions (1.2 molar equiv, see experimental section) in THF/HMPA (3/1, -78 °C, 0.5 h and 30 °C, 4 h) followed by addition of the Davis reagent (1.0 molar equiv, -78 °C, 2 h and 30 °C, 4 h) provided nucleophilic substituted (η^4 -1,3-diene)Fe(CO)₃ complexes in 30-50% yields. Results of the addition and quenching processes are summarized in Table 2.

Based on the positions of nucleophiles, there are adducts of two different types in Table 2. (1) With cyclic complex **1**, the addition/trapping sequences produced the C-5 nucleophilic substituted (η^4 -cyclohexa-1,3-diene)Fe(CO)₃ derivatives **15-17** and free diene **18** (entries 1-3, Table 2). (2) With acyclic complexes **19** and **21**, the reaction sequence provided the terminal nucleophilic substituted diene complexes **20** (39%) and **22** (35%), respectively (entries 4 and 5, Table 2). The path leading to isolation of nucleophilic C-5 substituted diene iron complex **15** is suggested in Scheme III. The initial formed homoallyl anion intermediate **23a** may rearrange to **23b** upon warming the reaction mixture above 0 °C. Quenching **23b** with Davis reagent resulted in β -hydride elimination at the methylene carbon to furnish **15**. It must be mentioned that free cyclohexa-1,3-diene derivative **18** (40%) was isolated as the major product and the corresponding iron-diene complex **17** (28%) was obtained as the minor product (entry 3, Table 2). The result showed that some of **17** may be decomplexed due to coordination of a lone pair electrons of the sulfur atom to the iron center.

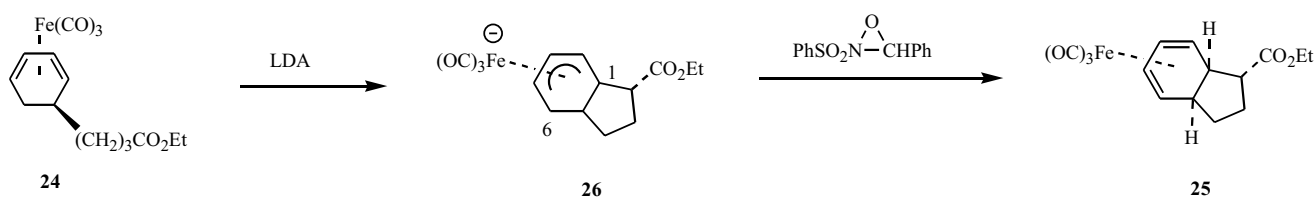
Moreover, this formal nucleophilic substitution for hydride of dienes can also be applied for the intramolecular variant. For example, intramolecular cyclization of the ester functionalized diene-iron complex **24** using LDA at 30 °C provided fused bicyclic complex **25** as the only diastereomer isolated in 30% yield after quenching of the reaction intermediate with the Davis reagent (entry 6, Table 2). The relative stereochemistry of **25** is assigned as depicted based upon coupling constant of 9.0 Hz observed for H₁-H₂ and cis relationship between H₁-H₅ which is fixed by anti-addition of the ester enolate at the β -face of the diene ligand. The assignment is consistent with those of fused bicyclic compounds obtained from intramolecular cyclization of **24** using LDA under an atmosphere of CO.¹¹ It was explained that anti addition of the ester stabilized carbanion occurred at the internal position of iron complexes at -78 °C. Upon warming, the carbanion reversed and added at the terminal position of the diene to form the bicyclic tricarbonyl(η^3 -allyl)iron anion intermediate **26** (Scheme IV). Trapping of the postulated anion intermediate with the Davis reagent resulted in hydride migration from the less steric hindered C-6 position to the Davis reagent to afford bicyclic iron-diene complex **25**. It is important to note that three contiguous stereogenic centers of the fused bicyclic compound **25** are created with extreme diastereoselectivity.

The reactions of homoallyliron and allyliron anion intermediates with 2-(phenylsulfonyl)-3-phenyloxaziridine resulted in β -hydride abstraction from the anion intermediates to produce nucleophilic substituted (η^4 -diene)Fe(CO)₃ complexes. This nucleophilic addition and quenching process can also be applied to intramolecular fashion to give a fused bicyclic iron-diene complex.

Scheme III



Scheme IV



EXPERIMENTAL

All reactions were run under an argon atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Tetrahydrofuran (THF) was predried by molecular sieves and then by passing through an Al_2O_3 column. Lithiodiphenylmethane, 2-lithio-2-phenyl-1,3-dithiane and lithiodimethylphenylsilane were prepared in THF/HMPA (3/1) according to literature procedures.³⁻⁴ All starting iron complexes were prepared by heating $\text{Fe}_2(\text{CO})_9$ and the corresponding dienes in ether. Flash column chromatography, following the method of Still, was carried out with E. Merck silica gel (Kieselgel 60, 230-400 mesh) using the indicated solvents.¹³ ^1H nuclear magnetic resonance (NMR) spectra were obtained with JEOL-EX 400 (400 MHz), and Varian G-200 (200 MHz) spectrometers. The chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or CHCl_3 (7.26 ppm) as internal standard. ^{13}C NMR spectra were recorded with JEOL-EX 400 (100.4 MHz) and Varian G-200 (50 MHz) spectrometers with CDCl_3 (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge (m/e) with percent relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Central Instrument Center, Taichung, Taiwan.

General Procedure I: Quenching of Tricarbonyl(η^1, η^2 -homoallyl)iron Anion Intermediates with 2-(Phenylsulfonyl)-3-phenyloxaziridine

To a solution of an anion (1.5 mmol) at -78°C under argon was added rapidly via syringe a (η^4 -diene) $\text{Fe}(\text{CO})_3$ complex (1.00 mmol) in 1.00 mL of THF. The temperature was maintained at -78°C for 4 h. The reaction mixture was quenched with the Davis reagent (1.2 mmol) at -78°C under argon and stirred at 30°C for 14 h, after which time the reac-

tion mixture was diluted with hexane (30 mL). The resultant solution was washed with water (50 mL \times 3) and brine (50 mL \times 3), dried over anhydrous magnesium sulfate (5.0 g), and concentrated to give the crude mixture.

General Procedure II: Quenching of Tricarbonyl(η^3 -allyl)iron Anion Intermediates with 2-(Phenylsulfonyl)-3-phenyloxaziridine

To a solution of an anion (1.5 mmol) at -78°C under argon was added rapidly via syringe a (η^4 -diene) $\text{Fe}(\text{CO})_3$ complex (1.00 mmol) in 1.00 mL of THF. The reaction temperature was raised to 30°C and stirred for 4 h. The reaction mixture was then quenched with the Davis reagent (1.2 mmol) at -78°C under argon and stirred at 30°C for 14 h, after which time the reaction mixture was diluted with hexane (30 mL). The resultant solution was washed with water (50 mL \times 3) and brine (50 mL \times 3), dried over anhydrous magnesium sulfate (5.0 g), and concentrated to give the crude mixture.

[(1-4- η)-2-Diphenylmethylcyclohexa-1,3-diene]tricarbonyliron Complex (4)

The crude mixture from addition of LiCHPh_2 (6.0 mmol) to complex 1 (1.10 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g, 6.0 mmol) was purified via flash column chromatography (silica gel, hexanes) to give 4 (0.68 g, 1.76 mmol, 35%). ^1H -NMR (CDCl_3 , 200 MHz): δ 7.29 (m, 10H), 4.75 (m, 2H), 3.11 (m, 2H), 1.73 (m, 4H); ^{13}C -NMR (CDCl_3 , 50 MHz): δ 212.2, 144.3, 140.5, 129.4, 128.9, 128.5, 128.2, 126.9, 126.6, 108.9, 86.7, 64.0, 59.8, 56.3, 25.4, 23.9; MS (20 eV) m/e (rel intensity): 386 (M^+ , 2), 358 (8), 330 (36), 302 (92), 300 (100); HRMS (EI) m/e calcd for $\text{C}_{22}\text{H}_{18}\text{FeO}_3$ 386.0605, found 386.0604.

2-Methyl-3-diphenylmethylbuta-1,3-diene (5)

The crude mixture from addition of LiCHPh_2 (6.0 mmol) to complex 2 (1.04 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g, 6.0 mmol) was purified via flash column chromatography (silica gel, hexanes) to give 5 (0.44 g, 1.88

mmol, 38%) as a yellow liquid. $^1\text{H-NMR}$ (CDCl_3 , 200 MHz): δ 7.27 (m, 10H), 6.11 (m, 2H), 4.91 (m, 2H), 4.79 (t, 1H), 1.89 (s, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz): δ 143.8, 134.4, 132.5, 128.6, 128.4, 128.3, 126.4, 115.9, 54.0, 18.7; MS (20 eV) m/e (rel intensity): 234 (M^+ , 60), 319 (38), 205 (13), 180 (40), 167 (100), 156 (19), 143 (68); HRMS (EI) m/e caclcd for $\text{C}_{18}\text{H}_{18}$ 234.1409, found 234.1408.

***trans*-3-Methyl-2-diphenylmethylpenta-1,3-diene (6)**

The crude mixture from addition of LiCHPh_2 (6.0 mmol) to complex **3** (1.10 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g, 6.0 mmol) was purified via flash column chromatography (silica gel, hexanes) to give **6** (0.10 g, 9%). Efforts to purify **6** using various analytical methods were not successful. $^1\text{H-NMR}$ (CDCl_3 , 200 MHz): δ 7.28 (m, 10H), 5.44 (s, 1H), 2.02 (s, 3H), 1.68 (d, $J = 3.0$ Hz, 1H), 1.50 (s, $J = 6.2$ Hz, 3H), 0.97 (m, 1H), 0.29 (d, $J = 3.0$ Hz, 1H).

$[\eta^4\text{-2-Dimethyl(phenyl)silylcyclohexa-1,3-diene}]\text{Fe}(\text{CO})_3$ Complex (8)

The crude mixture from addition of PhMe_2SiLi (6.0 mmol) to complex **1** (1.10 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g) using general procedure I was purified via flash column chromatography (silica gel, hexanes) to give **8** (0.71 g, 2.0 mmol, 40%) as a colorless liquid. IR (CH_2Cl_2) 3688, 3100, 2900, 1968, 1607, 1079, 918 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 (m, 2H), 7.41 (m, 3H), 5.11 (d, $J = 8.0$ Hz, 1H), 3.44 (m, 1H), 3.30 (m, 1H), 1.70 (m, 4H), 0.50 (s, 3H) and 0.49 (s, 3H); $^{13}\text{C NMR}$ (100.4 MHz, CDCl_3) δ 212.5, 137.9, 133.9, 129.4, 127.9, 90.6, 89.8, 67.4, 65.9, 24.2, 23.9, -3.3, -4.0; MS (20 eV) m/e 354 (M^+ , 1), 326 (4), 298 (12), 270 (100), 271 (18), 268 (30); HRMS (EI) m/e caclcd for $\text{C}_{17}\text{H}_{18}\text{FeO}_3\text{Si}$ 354.0375, found 354.0360.

$[\text{exo}-(\eta^4\text{-Cyclohexa-1,3-diene-5-yl})\text{-diphenylmethyl}]\text{Fe}(\text{CO})_3$ Complex (15)

The crude mixture from addition of LiCHPh_2 (6.0 mmol) to complex **1** (1.10 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g, 6.0 mmol) was purified via flash column chromatography (silica gel, hexanes) to give **15** (0.86 g, 2.23 mmol, 45%) as a yellow liquid. mp 112 °C; $^1\text{H-NMR}$ (CDCl_3 , 200 MHz): δ 7.19 (m, 10H), 5.31 (m, 2H), 3.26 (d, 1H, $J = 11.2$), 2.92 (m, 3H), 1.95 (m, 1H), 1.25 (m, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz): δ 212.1, 144.7, 144.0, 128.7, 128.5, 128.1, 127.5, 126.3, 126.2, 85.9, 84.5, 65.0, 62.2, 59.7, 41.6, 30.9; MS (20 eV) m/e (rel intensity): 386 (M^+ , 1), 358 (7), 330 (16),

303 (15), 302 (100); HRMS (EI) m/e caclcd for $\text{C}_{22}\text{H}_{18}\text{FeO}_3$ 386.0605, found 386.0607.

$[\text{exo}-(\eta^4\text{-Cyclohexa-1,3-diene-5-yl})\text{-triphenylmethyl}]\text{Fe}(\text{CO})_3$ Complex (16)

The crude mixture from addition of LiCPh_3 (6.0 mmol) to complex **1** (1.10 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g, 6.0 mmol) was purified via flash column chromatography (silica gel, EA/Hexanes = 1/30) to give **16** (1.20 g, 2.59 mmol, 52%) as a yellow liquid. Mp 199 °C; $^1\text{H-NMR}$ (CDCl_3 , 200 MHz): δ 7.27-7.20 (m, 15H), 4.75 (m, 1H), 4.63 (m, 1H), 4.19 (dt, $J = 6.8$; 3.6 Hz, 1H), 3.14 (m, 1H), 2.84 (m, 1H), 2.16 (m, 1H), 1.44 (m, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz): δ 212.5, 142-124, 86.8, 82.9, 62.5, 61.7, 59.6, 43.8, 27.6; IR (CH_2Cl_2): 3875, 3688, 3100, 2900, 2700, 2515, 2415, 2310, 2080, 1900 cm^{-1} ; MS (20 eV) m/e (rel intensity): 378 ($\text{M}^+ - 3\text{CO}$, 28), 300 (40), 243 (25), 218 (100), 191 (28); HRMS (EI) m/e caclcd for $\text{C}_{25}\text{H}_{22}\text{Fe}$ ($\text{M}^+ - 3\text{CO}$) 378.1071, found 378.1063.

$[\text{exo}-(\eta^4\text{-1,3-Cyclohexadiene-5-yl})\text{-2-phenyl-1,3-dithiyl}]\text{-tricarboxyliron (17)}$

The crude mixture from addition of 2-Lithio-2-phenyl-1,3-dithiane (6.0 mmol) to complex **1** (1.10 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g, 6.0 mmol) was purified via flash column chromatography (silica gel, EA/Hexanes = 1/40) to give **17** (0.58 g, 1.40 mmol, 28%) as a yellow solid and **18** (0.55 g, 2.00 mmol, 40%) as a yellow liquid. Complex **17**: mp 146-148 °C; $^1\text{H-NMR}$ (CDCl_3 , 200 MHz): δ 7.92-7.88 (m, 2H), 7.43-7.23 (m, 3H), 5.36 (m, 1H), 5.24 (m, 1H), 2.98 (m, 1H), 2.77 (m, 1H), 2.74-2.53 (m, 5H), 2.04-1.74 (m, 4H); $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz): δ 211.9, 140.5, 129.5, 127.0, 86.3, 85.1, 65.6, 59.3, 58.8, 51.6, 27.24, 27.2, 27.1; IR (CH_2Cl_2): 3875, 3688, 3100, 2900, 2700, 2515, 2415, 2310, 2080, 1900 cm^{-1} ; MS (20 eV) m/e (rel intensity): 414 (M^+ , 0.03), 386 (1), 358 (10), 330 (19), 254 (10), 252 (42), 224 (78), 195 (100), 178 (19); HRMS (EI) m/e caclcd for $\text{C}_{19}\text{H}_{18}\text{FeO}_3\text{S}_2$ 414.0046, found 414.0042.

$[\text{exo}-(\eta^4\text{-Cyclohexa-1,3-diene-5-yl})\text{-2-phenyl-1,3-dithiyl}]\text{-tricarboxyliron (18)}$

mp: 146-148 °C; $^1\text{H-NMR}$ (CDCl_3 , 200 MHz): δ 7.92-7.88 (m, 2H), 7.43-7.23 (m, 3H), 5.36 (m, 1H), 5.24 (m, 1H), 2.98 (m, 1H), 2.77 (m, 1H), 2.74-2.53 (m, 5H), 2.04-1.74 (m, 4H); $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz): δ 211.9, 140.5, 129.5, 127.0, 86.3, 85.1, 65.6, 59.3, 58.8, 51.6, 27.24, 27.2, 27.1; IR (CH_2Cl_2): 3875, 3688, 3100, 2900, 2700, 2515, 2415, 2310, 2080, 1900 cm^{-1} ; MS (20 eV) m/e (rel intensity): 414 (M^+ ,

0.03), 386 (1), 358 (10), 330 (19), 254 (10), 252 (42), 224 (78), 195 (100), 178 (19); HRMS (EI) *m/e* cacl'd for C₁₉H₁₈FeO₃S₂ 414.0046, found 414.0042.

[(η^4 -1,3-Butadiene-2,3-dimethyl-1-yl)-diphenylmethyl]-tricarbyliron (20)

The crude mixture from addition of LiCHPh₂ (6.0 mmol) to complex **19** (1.10 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g, 6.0 mmol) was purified via flash column chromatography (silica gel, EA/Hexanes = 1/30) to give **20** (0.75 g, 1.94 mmol, 39%) as a yellow liquid. ¹H-NMR (CDCl₃, 200 MHz): δ 7.31-7.14 (m, 10H), 4.06 (d, *J* = 10.5 Hz, 1H), 2.17 (s, 3H), 2.00 (s, 3H), 1.71 (d, *J* = 2.5 Hz, 1H), 1.25 (d, *J* = 10.5 Hz, 1H), 0.35 (d, *J* = 2.5 Hz, 1H); ¹³C-NMR (CDCl₃, 50 MHz): δ 211.3, 141.1, 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; IR (CH₂Cl₂): 3064, 3029, 3921, 2044, 1982, 1798, 1601, 1488, 1445, 1377 cm⁻¹; MS (20 eV) *m/e* (rel intensity): 388 (M⁺, 2), 369 (9), 332 (5), 304 (100), 250 (3), 224 (15), 167 (6), 191 (6); HRMS (EI) *m/e* cacl'd for C₂₂H₂₀FeO₃ 388.0761, found 388.0757.

[(η^4 -2-(4-Methyl-3-penten-1-yl)-4-dimethylohenyl-1,3-butadiene)tricarbyliron (22)

The crude mixture from addition of LiCHPh₂ (6.0 mmol) to complex **21** (1.38 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g, 6.0 mmol) was purified via flash column chromatography (silica gel, hexanes) to give **22** (0.78 g, 1.76 mmol, 35%) as a yellow liquid. ¹H-NMR (CDCl₃, 200 MHz): δ 7.35-7.13 (m, 10H), 5.27-5.17 (m, 2H), 3.80 (d, *J* = 10.4 Hz, 1H), 2.36-2.28 (m, 4H), 1.77-1.73 (m, 1H), 1.67 (s, 3H), 1.60 (s, 3H), 1.35 (m, 1H), 0.41 (m, 1H); ¹³C-NMR (CDCl₃, 50 MHz): δ 211.6, 146.1, 145.1, 132.9, 128.5, 128.4, 127.7, 127.5, 126.5, 126.2, 122.8, 103.2, 87.3, 65.7, 55.6, 42.3, 37.4, 29.9, 25.6, 17.7; IR (CH₂Cl₂): 3900, 3725, 3100, 2900, 2875, 2650, 2550, 2420, 2300, 2100, 1900 cm⁻¹; MS (20 eV) *m/e* (rel intensity): 442 (M⁺, 0.1), 414 (0.5), 386 (6.02), 359 (8), 358 (36), 290 (12), 84 (100); HRMS (EI) *m/e* cacl'd for (M⁺ - CO) C₂₅H₂₆FeO₂ 414.1282, found 414.1280.

(1R*,2R*,5R*,6S*,7S*,8S*,9R*)-[(6-9- η)-2-Carboxy-bicyclo[4.3.0]nona-6,8-diene]tricarbyliron (25)

The crude mixture from addition of LDA (6.0 mmol) to complex **24** (1.67 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g, 6.0 mmol) was purified via flash column chromatography (silica gel, hexanes) to give **25** (0.59 g, 1.8 mmol,

36%). ¹H-NMR (CDCl₃, 200 MHz): δ 5.4 (m, 2H), 4.17 (m, 2H), 3.08 (td, *J* = 9.0, 5.2 Hz, 1H, H₁), 2.93 (m, 1H), 2.76 (m, 2H), 2.60 (m, 1H), 1.88-1.32 (m, 4H), 1.28 (t, 3H); ¹³C-NMR (CDCl₃, 50 MHz): δ 212.1, 173.4, 86.4, 85.1, 66.5, 60.8, 60.2, 50.2, 45.2, 43.2, 33.0, 25.8, 14.3; MS (20 eV) *m/e* (rel intensity): 332 (M⁺, 2), 304 (6), 276 (12), 249 (13), 248 (100); HRMS (EI) *m/e* cacl'd for (M⁺ - CO) C₁₅H₁₆FeO₅ 332.0347, found 332.0346.

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