

Addition reactions of lithiodimethylphenylsilane to $(\eta^4\text{-}1,3\text{-diene})\text{-Fe}(\text{CO})_3$ and $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes

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Abstract

Treatments of $(\eta^4\text{-cyclohexa-}1,3\text{-diene})\text{Fe}(\text{CO})_3$ complex with 1.2 equivalents of PhMe_2SiLi , followed by quenching the reactive intermediate with CF_3COOH generated 1-dimethyl(phenyl)silylcyclohex-1-ene and with 2-(phenylsulfonyl)-3-phenyloxaziridine produced $[\eta^4\text{-}2\text{-dimethyl(phenyl)silylcyclohexa-}1,3\text{-diene}]\text{Fe}(\text{CO})_3$ complex as the major product. Additions of the silyl anion to $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-cyclohepta-}1,3,5\text{-triene})\text{Cr}(\text{CO})_3$ complexes produce dienyilsilanes after acid quenching.

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1. Introduction

Nucleophilic additions to conjugated dienes and arenes coordinated to a transition metal have attracted considerable interest in organic synthesis. Transition metals, such as molybdenum, palladium or iron, have been used to activate dienes toward nucleophilic addition reactions [1], and chromium, manganese, iron, or ruthenium have been utilized to activate arenes toward nucleophilic substitution and addition reactions [2]. Among them, nucleophilic additions to $(\eta^4\text{-}1,3\text{-diene})\text{Fe}(\text{CO})_3$ [3] and $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ [4] complexes have been studied intensively and used in the synthesis of a number of complex molecules. The disadvantage of the additions, however, is the relatively narrow range of stabilized carbon nucleophiles. For example, organomagnesium or -lithium reagents suffer competitive addition to the carbon monoxide ligand of diene- $\text{Fe}(\text{CO})_3$ complexes [5], and treatments of *n*-BuLi with

$(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes result in deprotonation at the arene ligand [6]. Carbon nucleophiles, such as ketone enolates, organocopper or -zinc reagents, fail to react with both complexes. Moreover, reports on the addition of silyl anions to $(\eta^4\text{-}1,4\text{-diene})\text{Fe}(\text{CO})_3$ and $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes are not found. Although the addition reactions of silicon–magnesium $[(\text{PhMe}_2\text{Si})_3\text{MnMgMe}]$ [7] and silicon–copper $[\text{PhMe}_2\text{Si-Cu}(\text{CN})\text{Li}]$ [8] reagents to 1,3-dienes were reported to give homoallyl- and allylsilanes after electrophilic quenching, both silylations were limited to acyclic 1,3-dienes bearing nonsubstituted terminal double bonds. It will be of great interest to extend the silylation reaction to cyclic 1,3-dienes. Here, we report, for the first time, on the addition of PhMe_2SiLi to both cyclic and acyclic dienes activated by $\text{Fe}(\text{CO})_3$. The intermediates obtained from the addition can be directly treated with CF_3COOH to produce vinyl- and allylsilanes or with 2-(phenylsulfonyl)-3-phenyloxaziridine (also known as Davis reagent) to afford nucleophilic substituted iron–diene complexes. Moreover, nucleophilic addition reactions of $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-cyclohepta-}$

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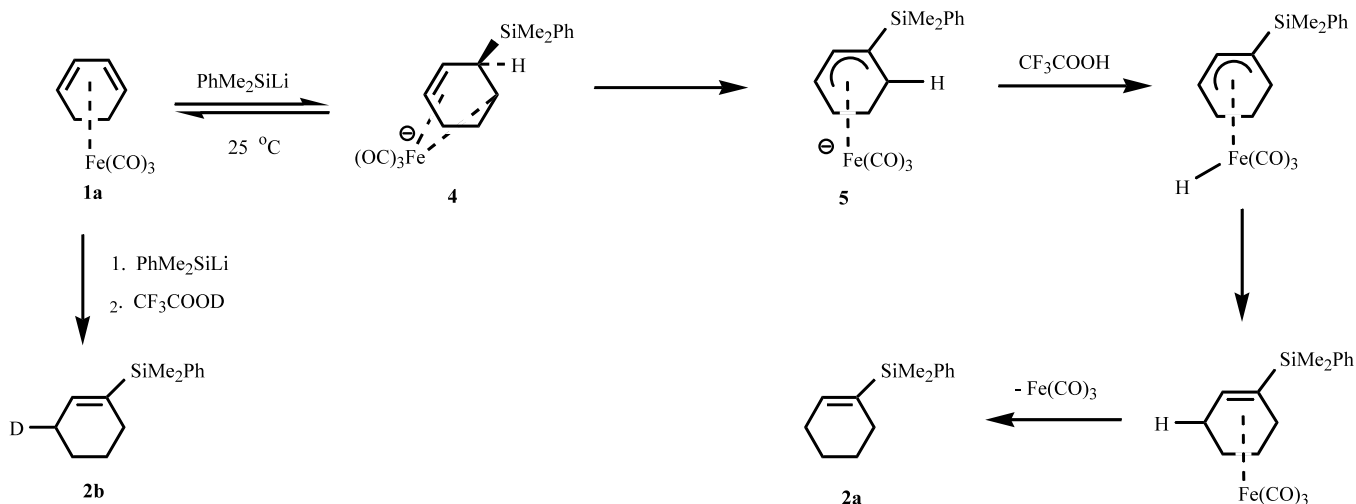
1,3,5-triene)-Cr(CO)₃ complexes with PhMe₂SiLi to give dienylsilanes after acid quenching will also be described.

2. Results and discussion

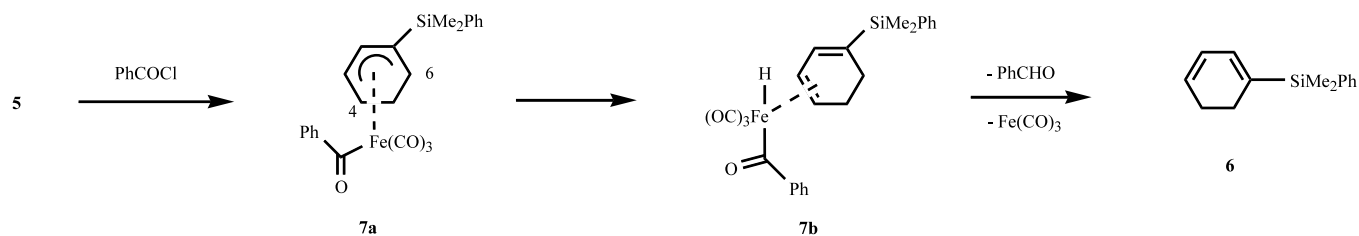
2.1. Addition of lithiodimethylphenylsilane to cyclic diene-irontricarbonyl complexes followed by electrophilic quenching

Lithiodimethylphenylsilane (PhMe₂SiLi) was prepared in tetrahydrofuran (THF) under argon according to a literature procedure [9]. Addition of a THF solution of PhMe₂SiLi (1.2 equivalents) to (η^4 -cyclohexa-1,3-diene)Fe(CO)₃ complex (**1a**) in THF for 20 h at 25 °C under argon followed by quenching the reaction mixture with CF₃COOH produced 1-dimethyl(phenyl)silylcyclohex-1-ene (**2a**) in 55% after purification by flash column chromatography on silica gel and short-path distillation under reduced pressure. Under the same reaction conditions, quenching the reactive intermediate with Davis reagent produced [η^4 -2-dimethyl(phenyl)silylcyclohexa-1,3-diene]Fe(CO)₃ complex (**3a**) in 40% yield and a trace of [η^4 -1-dimethyl(phenyl)silylcyclohexa-1,3-diene]Fe(CO)₃ complex (**3b**). A mechanism for the generation of **2a** is suggested in Scheme 1. The addition of the silyl anion to complex **1a** occurred at internal positions of the diene ligand to generate homoallyl anion intermediate **4**. Hydride migration may occur via β -hydride elimination and re-addition to give more stable η^3 -allyl anion intermediate **5**. Quenching of **5** with CF₃COOH led to the formation of vinylsilane **2a** after reductive elimination and detachment of the olefin ligand from the iron center. Moreover, quenching **5** with CF₃COOD gave **2b** with a deuterium at the allyl carbon. None of the decrease in integration on the vinyl or

homoallyl protons was found (compared to the integral of phenyl and dimethyl groups at the silicon). Trapping of **5** with Davis reagent afforded the C-2 silyl-substituted complex **3a** as the major product and a trace of the C-1 silyl-substituted complex **3b** (Eq. (1)). Reaction of the allyl anion **5** with Davis reagent gave **3a** and **3b** together with isolation of PhSO₂NH₂ and PhCHO. Migration of β -hydrides from **5** occurred at both C-4 and C-6 position to Davis reagent afforded PhSO₂NH₂ and PhCHO after aqueous process. Moreover, quenching **5** with benzoyl chloride followed by aqueous process produced vinylsilane **2a** as the major product in 37% yield together with the C-1 substituted silyl diene **6** as the minor product in 15% yield (Eq. (2)). It was reasonable to view that quenching of **5** with benzoyl chloride was inefficient and vinylsilane **2a** was generated during aqueous work up. Reaction of **5** with benzoyl chloride may produce the postulate intermediate **7a** (Scheme 2). The intermediate **7a** may undergo β -hydride elimination at C-4 to give **7b**. Reductive elimination of **7b** (to release benzaldehyde) followed by detachment of the double bond from the iron center furnished silyl diene **6**. The reaction mechanism was proposed based upon isolation of benzaldehyde after flash column chromatography of the reaction mixture. It is important to mention that unlike stabilized carbanions attack at the internal position of the diene ligand of **1a** at -78 °C (kinetically controlled reaction conditions) to give homoallyl anion intermediates and at the terminal position of the diene ligand at 25 °C (thermodynamically controlled reaction conditions) to afford allyl anion intermediates [3], the silyllithium reagent (PhMe₂SiLi) does not add to **1a** at -78 °C and the addition occurs at internal positions of the cyclohexa-1,3-diene ligand at 25 °C to give **5**. Attempts to trap **5** with other electrophiles such as benzyl bromide and CO failed.



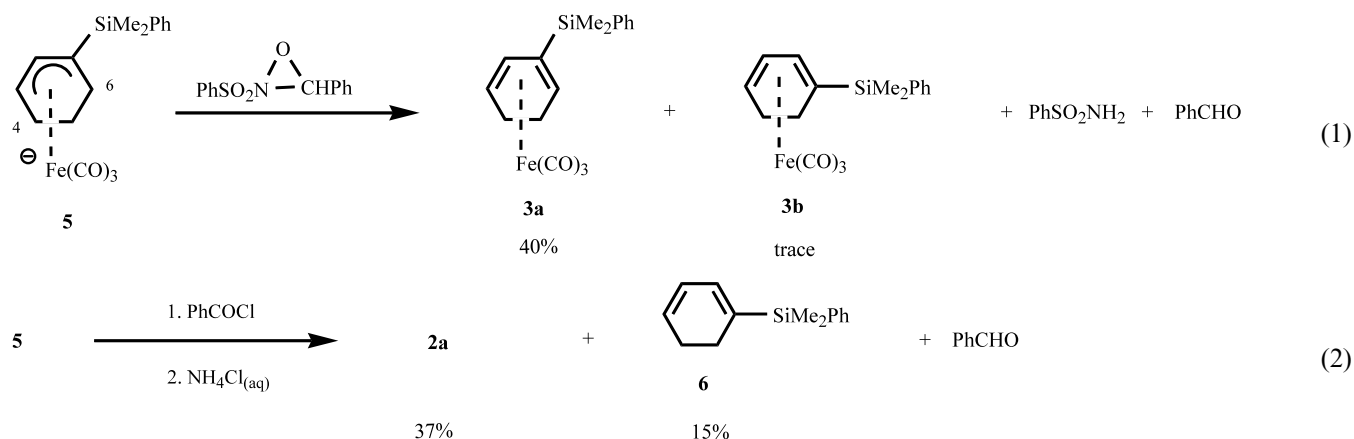
Scheme 1.



Scheme 2.

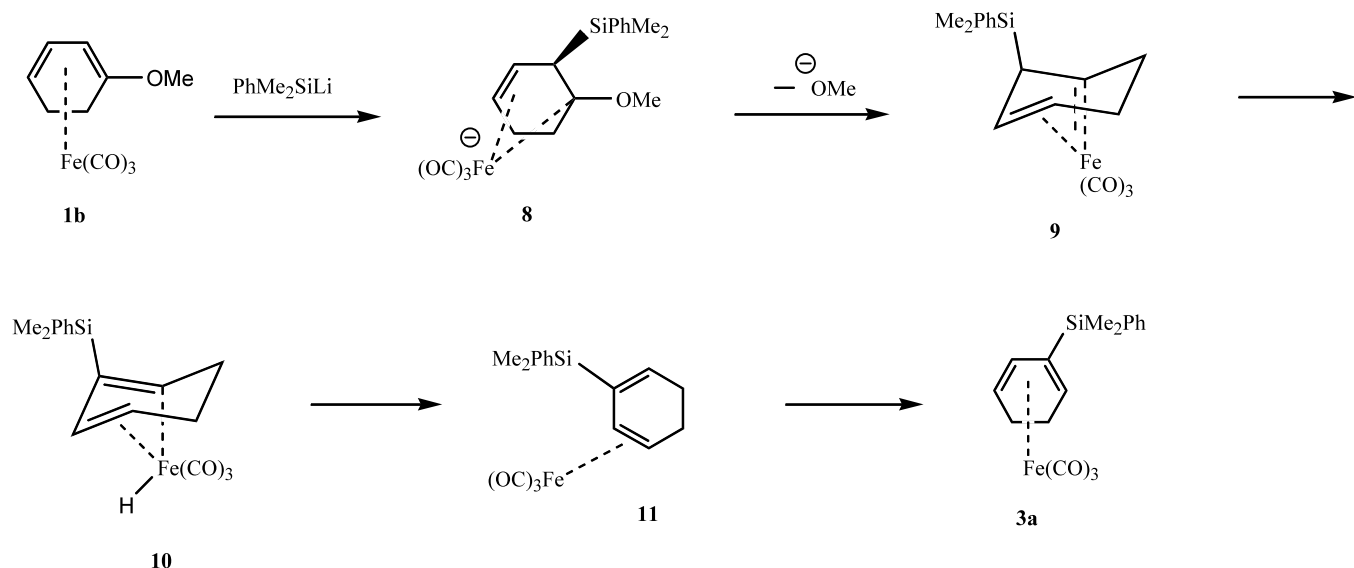
Vinylsilane **2a** was isolated as the major product in each case in 20–40% yield after aqueous work up and column chromatography of the crude mixture.

formation of **3a** is difficult to understand since it formally involves a kind of *cine*-substitution for methoxide. A possible reaction path involving α -methoxy



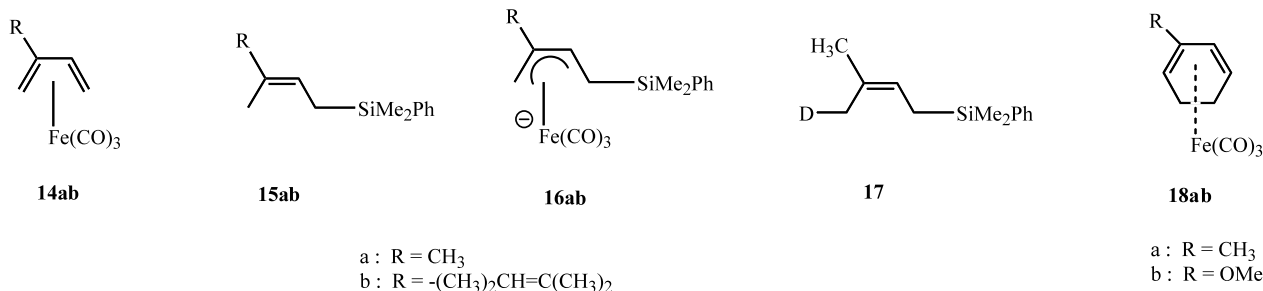
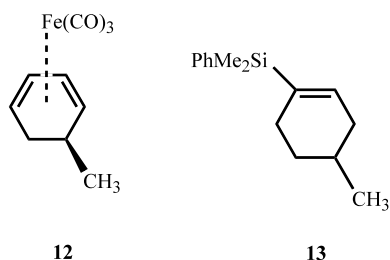
Surprisingly, addition of PhMe_2SiLi to $(\eta^4\text{-1-methoxycyclohexa-1,3-diene})\text{Fe(CO)}_3$ complex (**1b**) also produced **3a** in 60% yield after acid quenching. The

elimination of the homoallyl anion intermediate **8** to generate the carbene intermediate **9** is proposed (Scheme 3). The postulate carbene intermediate **9** may undergo β -



Scheme 3.

hydride elimination (to give **10**) followed by reductive elimination to provide **11**. Reoordination of the pendant double bond to the iron center of **11** produced complex **3a**. An additional methyl group at the C-5 position of the ring, for example, with complex **12** [10], the silylation occurred only at the less hindered C-2 position of the diene ligand to produce vinylsilane **13** in 41% yield after acid quenching. None of vinylsilane derived from silyl anion addition at hindered terminal C-1 or C-4 positions was found.



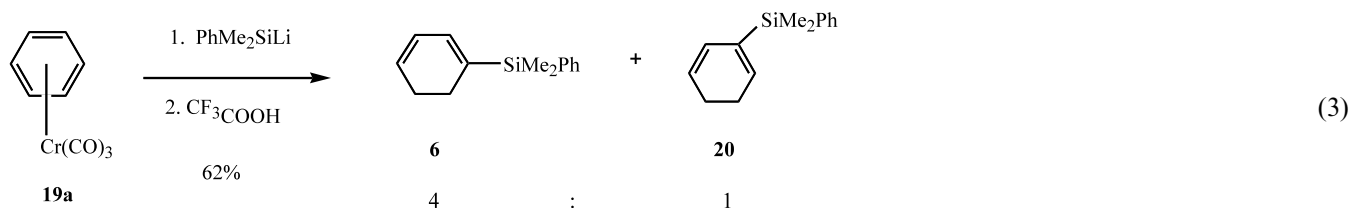
2.2. Addition of lithiodimethylphenylsilane to acyclic diene-irontricarbonyl complexes followed by electrophilic quenching

Acyclic iron–diene complexes **14a** and **14b** also underwent silylation, however, at the less hindered terminal position (C-4) of the diene ligand to produce allylsilanes **15a** [8] (37%) and **15b** [8] (32%), respectively, as a single olefinic regioisomer in each case. None of the addition at the other terminus (C-1) and the internal position (C-3) of the diene ligand was found. Although the yields of the silyl addition to acyclic iron–diene complexes are low, the addition provides only a single allylsilane [8]. Thus, the steric hindrance imposed by an adjacent alkyl group at the C-2 position of acyclic diene ligands may impede the silyl anion attack at C-1 and C-3 positions of the diene ligands. Addition of the silyl anion at the less hindered terminal position (C-4) of the diene ligand generated allyl anions **16a** and **16b**. Protonation

of **16a** and **16b** with CF₃COOH gave allylsilanes **15a** and **15b**. To further prove the proposed allyl anion intermediate **16a**, the anion intermediate **16a** was quenched with CF₃COOD. Allylsilane **17** was isolated in 40% yield. ¹H-NMR of **17** shows that only two protons appear at the allylic carbon *cis* to the dimethyl(phenyl)silyl group. Moreover, the silylation failed to cyclic iron–diene complexes bearing an additional substituent at the C-2 position of the diene ligand. For example, addition of PhMe₂SiLi to [η⁴-2-methylcyclohexa-1,3-diene]Fe(CO)₃ complex (**18a**) and [η⁴-2-methoxycyclohexa-1,3-diene]Fe(CO)₃ complex (**18b**) failed to give any additional product. The starting complexes **18a** and **18b** were recovered quantitatively in both cases. This result further indicated that the silylation was limited to the diene ligand containing a substituent at the C-2 position, especially for C-2 substituted cyclic 1,3-diene iron complexes.

2.3. Addition of lithiodimethylphenylsilane to arene-chromiumtricarbonyl complexes followed by electrophilic quenching

The above reaction patterns were also observed for (η⁶-arene)Cr(CO)₃ complexes. For example, addition of PhMe₂SiLi to (η⁶-benzene)Cr(CO)₃ (**19a**) at 25 °C followed by acid quenching afforded dienyilsilanes **6** and **20** (**6:20** = 4:1) in 62% yield (Eq. (3)). The initial nucleophilic addition generated the (η⁵-cyclohexadienyl)Cr(CO)₃ anion intermediate **21**. Protonation of **21** followed by hydride transfer (via *supra*) afforded **6** and **20**. Quenching **21** with Davis reagent also resulted in hydride abstraction to generate [η⁶-dimethyl(phenyl)silylbenzene]Cr(CO)₃ complex (**19e**) in 30% yield together with the isolation of PhSO₂NH₂ and PhCHO. Moreover, addition of PhMe₂SiLi to arene–chromium complex containing a fluorine (**19b**), a chlorine (**19c**) or a methoxy (**19d**) group proceeded in an addition/elimina-

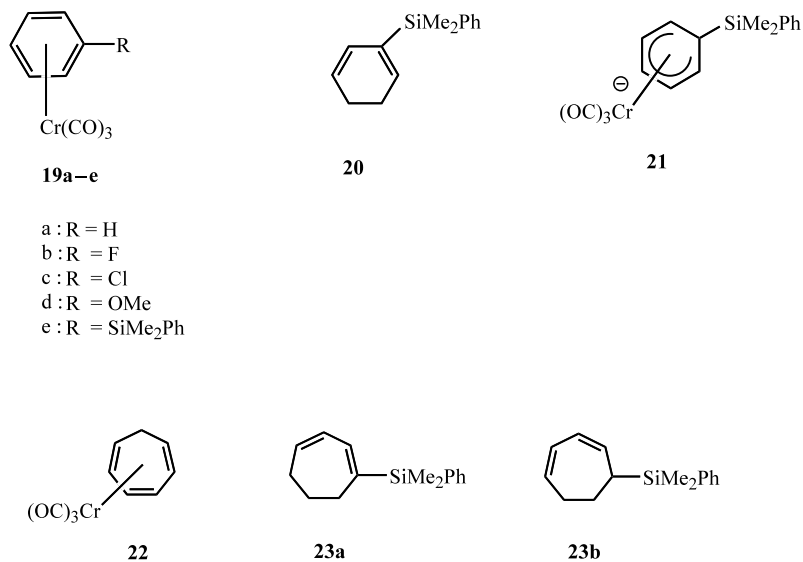


tion process to afford complex **19e** in fair to good yields (**19b**, 70%; **19c**, 36%; **19d**, 56%). Changing to the seven-membered ring with (η^6 -cyclohepta-1,3,5-triene)-Cr(CO)₃ complex (**22**) also allowed the silyl anion addition to give silylated cyclohepta-1,3-diene derivatives **23a** and **23b** (**23a**:**23b** = 3:1) in 68% yield after acid quenching.

4. Experimental

4.1. General

All reactions were run under an argon atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via



3. Conclusion

The reaction outlined herein demonstrates that the addition of PhMe₂SiLi to diene-Fe(CO)₃ complexes produces vinyl- or allylsilanes after acid quenching. Treatments of the same reaction intermediate with Davis reagent proceeded in hydride abstraction to afford silyl-substituted diene-Fe(CO)₃ complexes. Nucleophilic addition reactions of (η^6 -arene)Cr(CO)₃ and (η^6 -cyclohepta-1,3,5-triene)Cr(CO)₃ complexes with PhMe₂SiLi generate dienylsilanes after acid quenching.

an oven-dried syringe or cannula. THF was distilled under nitrogen from a deep blue sodium benzophenone ketyl solution. Complexes **1a** and **1b** and **14a** and **14b** were prepared by heating Fe₂(CO)₉ and the corresponding dienes in ether. Complexes **19a–19d** were obtained by refluxing the corresponding arenes with Cr(CO)₆ in *n*-butyl ether. Complex **22** was synthesized by refluxing cyclohepta-1,3,5-triene with Cr(CH₃CN)₃(CO)₃ in THF [11]. 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 [12]. $^1\text{H-NMR}$ 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. $^{13}\text{C-NMR}$ 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.

4.1.1. General procedure for addition of PhMe_2SiLi to $(\eta^4\text{-}1,3\text{-diene})\text{Fe}(\text{CO})_3$, $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-cyclohepta-}1,3,5\text{-triene})\text{Cr}(\text{CO})_3$ complexes

In a typical procedure, to a solution of complex **1a** (0.22 g, 5.0 mmol) in 9 ml of THF under argon at 0°C was added rapidly, neat, via cannula, a solution of PhMe_2SiLi [9] (6.0 mmol) in 15 ml of THF and via syringe 3 ml of hexamethylphosphoramide (HMPA). The reaction was stirred at 25°C for 20 h. The reaction mixture was quenched with 0.5 ml of trifluoroacetic acid via syringe needle at 0°C and stirred at 25°C for 1 h, after which time the reaction mixture was diluted with hexane (30 ml). The resultant solution was washed with water (3×50 ml) and brine (3×50 ml), dried over anhydrous magnesium sulfate (5.0 g) and concentrated to give the crude mixture.

4.1.2. 1-Dimethyl(phenyl)silylcyclohex-1-ene (**2a**)

The crude mixture from the addition of PhMe_2SiLi (6.0 mmol) to complex **1a** (1.10 g, 5.0 mmol) followed by quenching the reaction mixture with trifluoroacetic acid (0.5 ml) was purified via flash column chromatography (silica gel, hexanes) to give **2a** (0.60 g, 2.75 mmol, 55%) as a colorless liquid: IR (CH_2Cl_2) 3373, 3057, 1622, 1421, 1075 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.67 (m, 2H), 7.48 (m, 3H), 6.25 (m, 1H), 2.22 (m, 4H), 1.76 (m, 4H) and 0.49 (s, 6H); $^{13}\text{C-NMR}$ (100.4 MHz, CDCl_3) δ 138.8, 137.9, 136.7, 134.0, 128, 127, 26.8, 26.7, 22.9, 22.4, -3.7 ; MS (20 eV) m/e 216 [M^+ , 56], 215 (23), 202 (62), 156 (12), 137 (16), 136 (13), 135 (100), 121 (20); HRMS (EI) m/e Calc. for $\text{C}_{14}\text{H}_{20}\text{Si}$: 216.1334; Found, 216.1334. The reaction mixture was also quenched with CF_3COOD to give **2b** with a deuterium at the allyl carbon. None of the decrease in integration on the vinyl or homoallyl protons was found (compared to the integral of phenyl and dimethyl groups at silicon).

4.1.3. $[\eta^4\text{-}2\text{-Dimethyl(phenyl)silylcyclohexa-}1,3\text{-diene}]\text{Fe}(\text{CO})_3$ complex (**3a**)

Addition of PhMe_2SiLi (6.0 mmol) to complex **1a** (1.10 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g) gave **3a** (0.71 g, 2.0 mmol, 40%) as a colorless liquid and a trace of **3b** (less than 20 mg). Only complex **3a** can be isolated as a pure compound. 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 Calc. for $\text{C}_{17}\text{H}_{18}\text{FeO}_3\text{Si}$: 354.0375; Found, 354.0360.

4.1.4. 4-Dimethyl(phenyl)silylcyclohexa-1,3-diene (**6**)

Addition of PhMe_2SiLi (3.75 mmol) to complex **1a** (0.41 g, 1.88 mmol) followed by quenching the reaction mixture with benzoyl chloride (0.54 g, 3.75 mmol) afforded **2** (0.15 g, 0.69 mmol, 37%) and **6** (0.06 g, 0.28 mmol, 15%) both as colorless liquid. Compound **6**: IR (CH_2Cl_2) 3364, 3070, 2986, 2306, 1624, 1282, 1247 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.54 (m, 2H), 7.36 (m, 3H), 6.24 (m, 1H), 5.98 (m, 1H), 5.91 (m, 1H), 2.10 (m, 4H), 0.36 (s, 6H); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) δ 138.36, 137.02, 134.06, 133.76, 128.97, 128.24, 127.78, 124.76, 24.14, 22.05, -3.72 ; MS (20 eV) m/e 214 [M^+ , 22], 197 (20), 135 (100), 121 (26); HRMS (EI) m/e Calc. for $\text{C}_{14}\text{H}_{18}\text{Si}$: 214.1178; Found, 214.1179.

4.1.5. 5-Methyl-1-dimethyl(phenyl)silylcyclohex-1-ene (**13**)

Addition of PhMe_2SiLi (6.0 mmol) to complex **12** [10] (1.17 g, 5.0 mmol) followed by quenching the reaction mixture with trifluoroacetic acid (0.5 ml) produced **13** (0.47 g, 2.05 mmol, 41%) as a colorless liquid. IR (CH_2Cl_2) 3369, 2986, 1617, 1429, 1078 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.52 (m, 2H), 7.36 (m, 3H), 6.06 (m, 1H), 2.10 (m, 3H), 1.68 (m, 3H), 1.14 (m, 1H), 0.94 (d, $J = 6.0$ Hz, 3H) and 0.32 (s, 6H); $^{13}\text{C-NMR}$ (100.4 MHz, CDCl_3) δ 138.9, 137.6, 136.3, 134.0, 128.8, 127.7, 35.5, 31.1, 28.2, 27.1, 22.0, -3.6 ; MS (20 eV) m/e 230 [M^+ , 49], 229 (100), 216 (27), 215 (28), 202 (64), 201 (34), 187 (31), 168 (51), 167 (43), 153 (28); HRMS (EI) m/e Calc. for $\text{C}_{15}\text{H}_{22}\text{Si}$: 230.1491; Found, 230.1473.

4.1.6. 2-Methyl-4-dimethyl(phenyl)silylbut-1-ene (**15a**) [8]

Addition of PhMe_2SiLi (6.0 mmol) to complex **14a** (1.04 g, 5.0 mmol) followed by quenching the reaction mixture with trifluoroacetic acid (0.5 ml) produced **15a** (0.38 g, 1.86 mmol, 37%) as a colorless liquid. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.53 (m, 2H), 7.36 (m, 3H), 5.17

(t, $J = 8.6$ Hz, 1H), 1.68 (s, 3H), 1.63 (d, $J = 8.6$ Hz, 2H), 1.50 (s, 3H), 0.26 (s, 6H); $^{13}\text{C-NMR}$ (100.4 MHz, CDCl_3) δ 133.6, 128.8, 127.7, 119.3, 25.8, 17.7, 17.6, -3.2.

4.1.7. 2,6-Dimethyl-8-dimethyl(phenyl)silylocta-2,6-diene (**15b**) [8]

Addition of PhMe_2SiLi (6.0 mmol) to complex **14b** (1.38 g, 5.0 mmol) followed by quenching the reaction mixture with trifluoroacetic acid (0.5 ml) gave **15b** (0.44 g, 1.62 mmol, 32%) as a colorless liquid. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.52 (m, 2H), 7.31 (m, 3H), 5.11 (m, 2H), 2.00 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H), 1.62 (m, 5H), 0.30 (s, 6H); $^{13}\text{C-NMR}$ (100.4 MHz, CDCl_3) δ 133.6, 128.9, 127.7, 124.6, 119.6, 39.9, 27.3, 26.8, 25.6, 17.6, 15.7, -3.4.

4.1.8. 1-Deutero-2-methyl-4-dimethyl(phenyl)silylbut-1-ene (**17**)

Addition of PhMe_2SiLi (3.75 mmol) to complex **14a** (0.39 g, 1.88 mmol) followed by quenching the reaction mixture with CF_3COOD (0.29 ml) produced **17** (0.15 g, 0.75 mmol, 40%) as a colorless liquid. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.53 (m, 2H), 7.36 (m, 3H), 5.17 (t, $J = 8.6$ Hz, 1H), 1.68 (s, 3H), 1.63 (d, $J = 8.6$ Hz, 2H), 1.50 (s, 2H), 0.26 (s, 6H).

4.1.9. Addition of PhMe_2SiLi to complex **19a** followed by acid quenching generated dienylsilanes **6** and **20**

Addition of PhMe_2SiLi (6.0 mmol) to complex **19a** (1.07 g, 5.0 mmol) followed by quenching the reaction mixture with trifluoroacetic acid (0.5 ml) gave **6** (0.54 g, 2.5 mmol, 50%) liquid and **20** (0.13 g, 0.60 mmol, 12%) both as colorless liquid. The analytical data of **6** obtained from this addition is identical to that of the previous result obtained from quenching the anion intermediate **4b** with benzoyl chloride. Attempts to obtain pure compound **20** were not successful. Complexation of the impure material with $\text{Fe}_2(\text{CO})_9$ in refluxing ether produced complex **3a** (0.04 g) after flash column chromatography of the crude mixture. The analytical data are consistent with that of complex **3a** obtained from addition/quenching process as mentioned in Eq. (1).

4.1.10. (η^6 -Dimethyl(phenyl)silylbenzene)tricarbonylchromium complex (**19e**)

Addition of PhMe_2SiLi (6.0 mmol) to complex **16a** (1.16 g, 5.0 mmol) followed by quenching the reaction mixture with 2-(phenylsulfonyl)-3-phenyloxaziridine (1.57 g) or trifluoroacetic acid (0.5 ml) gave **19e** (0.52 g, 1.5 mmol, 30%) as a yellow liquid. IR (CH_2Cl_2) 3688, 3367, 1968, 1890, 1606, 1427, 1083 cm^{-1} ; $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 7.52 (m, 2H), 7.40 (m, 3H), 5.50 (t, $J = 6.4$ Hz, 1H), 5.41 (d, $J = 6.6$ Hz, 2H), 5.13 (dd, $J = 6.6$, 6.4 Hz, 2H), 0.60 (s, 6H); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) δ

135.90, 134.06, 129.89, 128.15, 99.97, 97.92, 95.65, 90.26, -2.96; MS (20 eV) m/e 348 [M^+ , 24], 331 (33), 266 (28), 265 (89), 264 (80); HRMS (EI) m/e Calc. for $\text{C}_{17}\text{H}_{16}\text{CrO}_3\text{Si}$: 348.0274; Found, 348.0270.

4.1.11. 1-Dimethyl(phenyl)silylcyclohepta-1,3-diene (**23a**)

Addition of PhMe_2SiLi (6.0 mmol) to complex **22** (1.14 g, 5.0 mmol) followed by quenching the reaction mixture with trifluoroacetic acid (0.5 ml) produced **23a** (0.58 g, 2.55 mmol, 51%) and **23b** (0.19 g, 0.85 mmol, 17%) as a colorless liquid. Compound **23b** rearranged to an unidentified mixture of silyl compounds upon standing at room temperature for ca. 20 h, and only $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ data could be obtained immediately after column separation. Only **23a** could be isolated as a pure compound. Compound **23a**: IR (CH_2Cl_2) 3676, 3376, 2989, 1607, 1427, 1083 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.51 (m, 2H), 7.33 (m, 3H), 6.14 (m, 1H), 5.88 (m, 2H), 2.35 (m, 4H), 1.79 (m, 2H), 0.35 (s, 6H); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) δ 145.68, 138.55, 135.53, 134.78, 134.11, 128.90, 127.74, 126.04, 32.93, 32.58, 27.27, -3.43; MS (20 eV) m/e 228 [M^+ , 60], 213 (96), 185 (31), 168 (50), 145 (34), 137 (97), 135 (49); HRMS (EI) m/e Calc. for $\text{C}_{15}\text{H}_{20}\text{Si}$: 228.1334; Found, 228.1323.

4.1.12. 1-Dimethyl(phenyl)silylcyclohepta-1,3-diene (**23b**)

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.44 (m, 5H), 5.76 (m, 4H), 2.33 (m, 3H), 1.94 (m, 1H), 1.83 (m, 1H), 0.30 (s, 6H); $^{13}\text{C-NMR}$ (100.4 MHz, CDCl_3) δ 138.06, 135.22, 133.87, 133.05, 128.99, 127.73, 125.62, 123.25, 35.19, 31.86, 27.88, -3.78, -4.54.

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