Organometallics **1996,** *15,* 5428−5431

Preparation and Reactivity of $[(\eta^6\text{-CH}_3\text{-}\eta^5\text{-2-sil-C}_6\text{H}_4)\text{Fe(CO)}_3]\text{BF}_4$ (sil = $\text{Si(OCH}_2\text{CH}_2)_3\text{N}$)

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Summary: *$[(6\text{-CH}_3\text{-}\eta^5\text{-2-sil-C}_6\text{H}_4)\text{Fe(CO)}_3]\text{BF}_4$ (sil = $\text{Si(OCH}_2\text{CH}_2)_3\text{N}$) has been prepared and its reaction with stabilized carbanions studied. Carbanions such as $^-\text{CH}_2\text{CN}$, $^-\text{CH(Me)CN}$, $^-\text{CMe}_2\text{CN}$, and $^-\text{CH}_2\text{CO}_2{}^t\text{Bu}$ attack the carbonyl carbon to yield acyl derivatives, and $^-\text{C(H)PhCN}$ and $^-\text{CPh}_2\text{CN}$ add to the dienyl ring to give diene derivatives.*

Introduction

The structure and chemical properties of silatranes have been investigated by various methods.[1] Recently, we established the utility of (silatranylarene)$\text{Mn(CO)}_3{}^+$ cations in functionalizing silatranylcyclohexadiene derivatives by nucleophilic addition to coordinated silatranylarene.[2] This was apparently the first study on the synthesis of silatranylcyclohexadiene derivatives, since there have been no reports on silatranylcyclohexadiene transition metal complexes.

In the present paper, we describe the synthesis and chemistry of the (silatranylcyclohexadienyl)iron tricarbonyl cation (Scheme 1) and the liberation of substituted cyclohexadienes.

Experimental Section

All reactions were conducted under nitrogen using standard Schlenk type flasks. Workup procedures were performed in air.

Elemental analyses were carried out at the Korea Basic Science Center or at the Chemical Analytical Center, College of Engineering , Seoul National University. ^{1}H NMR spectra were obtained with a Varian XL-200 or a Bruker AMX-500 instrument. Infrared spectra were recorded on a Shimadzu IR-470 (spectra measured as films on NaCl by evaporation of solvent). Mass spectra were recorded with a VG ZAB-E double-focusing mass spectrometer. Compounds **1**−**5** were synthesized according to the published procedures.[2]

Synthesis of 6. Compound **5** (0.22 g, 0.8 mmol) and excess $\text{Fe}_2(\text{CO})_9$ were dissolved in 20 mL of diethyl ether. The reaction mixture was refluxed overnight. After cooling, the solution was concentrated to 5 mL and then applied to column chromatography, eluting with hexane and then with diethyl ether. A greenish band eluted first, followed by **6**. After evaporation of the solvent, **6** was obtained in 95% yield (0.32 g): IR ν (CO) 2040, 1955 cm^{-1}; ^{1}H NMR (CDCl_3) δ 5.71 (dd, J = 0.7, J = 4.2 Hz, 1 H, H^2), 5.29 (ddd, J = 0.1, 4.2, 6.3 Hz, 1 H, H^3), 3.75 (t, J = 5.9 Hz, 6 H, OCH_2), 2.80 (m, 1 H, H^4), 2.76 (t, J = 5.9 Hz, 6 H, CH_2N), 2.3 (m, 1 H, H^6), 2.15 (ddd, J = 2.9, 10.3, 13.6 Hz, 1 H, H$^{5-\text{exo}}$), 1.38 (dm, J = 13.6 Hz, 1 H, H$^{5-\text{endo}}$), 0.99 (d, J = 6.9 Hz, 3 H, CH_3) Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{FeNO}_6\text{Si}$: C, 47.19; H, 5.20; N, 3.44. Found: C, 47.12; H, 4.93; N, 3.11.

Synthesis of 7. Compound **6** (0.32 g, 0.78 mmol) was added to a methylene dichloride solution (20 mL) of Ph_3CBF_4 (0.28 g, 0.85 mmol). The resulting solution was stirred at room temperature for 1 h. The solution was then concentrated to 10 mL by evaporation of the solvent, and a few drops of water were added to quench the remaining Ph_3CBF_4. The resulting solution was dried over anhydrous MgSO_4, concentrated to 5 mL, and treated with excess diethyl ether to precipitate the products. The yield was 93% (0.34 g): IR ν (CO) 2100, 2045 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 7.17 (t, J = 4.9 Hz, 1 H, H^3), 5.96 (t, J = 5.9 Hz, 1 H, H^4), 5.77 (d, J = 4.9 Hz, 1 H, H^2), 4.50 (td, J = 0.7, 5.9 Hz, H^5), 3.86 (t, J = 5.6 Hz, 6 H, OCH_2), 3.12 (t, J = 5.6 Hz, 6 H, CH_2N), 0.63 (d, J = 6.6 Hz, 3 H, CH_3). Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{BF}_4\text{FeNO}_6\text{Si}$: C, 38.97; H, 4.09; N, 2.84. Found: C, 39.28; H, 4.02; N, 2.67.

Synthesis of 8(CH_2CN). Compound **7** (0.17 g, 0.34 mmol): was suspended in 20 mL of THF. The solution was cooled to −78 °C, and LiCH_2CN (generated *in situ* from CH_3CN (0.05 mL, 1.0 mmol) in 10 mL of THF) was added dropwise via syringe to the above solution at −78 °C. After being stirred for 10 min, the reaction mixture was allowed to warm to room temperature. The crude product was extracted using excess diethyl ether. The ether extracts were concentrated and then column chromatographed on silica gel, eluting with diethyl ether. After evaporation of the solvent, the product was obtained in 32% yield (0.05 g, 0.11 mmol): IR ν (CN) 2236 cm^{-1}, ν (CO) 2004, 1948 cm^{-1}, ν (C═O) 1612 cm^{-1}; ^{1}H NMR (CDCl_3) δ 6.29 (dd, J = 1.2, 5.1 Hz, 1 H, H^3), 4.8 (br d, 1 H, H^2), 4.65 (dd, J = 5.6, 6.1 Hz, 1 H, H^4), 3.76 (t, J = 5.8 Hz, 6 H, OCH_2), 3.56 (br, 1 H, H^5), 3.54 (d, J = 18.5 Hz, 1 H, CH_2CN), 3.45 (d, J = 18.5 Hz, 1 H, CH_2CN), 2.85 (t, J = 5.8 Hz, 6 H, CH_2N), 2.73 (q, J = 6.1 Hz, 1 H, H^6), 0.46 (d, J = 6.6 Hz, 3 H, CH_3). Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{FeN}_2\text{O}_6\text{Si}$: C, 48.45; H, 4.93; N, 6.28. Found: C, 48.09; H, 5.07; N, 6.04.

Synthesis of 8($\text{CH(CH}_3)\text{CN}$). The typical procedure was almost the same as that employed in the synthesis of **8**-**(CH_2CN)**, except that $\text{LiCH(CH}_3)\text{CN}$ was used instead of LiCH_2CN, yielding 46%: IR ν (CN) 2232 cm^{-1}, ν (CO) 2016, 1952 cm^{-1}, ν (C═O) 1624 cm^{-1}; ^{1}H NMR (CDCl_3) δ 6.36 (br t, J = 4.6 Hz, 1 H, H^3), 6.28 (t, J = 5.1 Hz, 1 H, H^{3*}), 4.87 (br, 2 H, H^2), 4.69 (t, J = 4.5 Hz, 1 H, H^4), 4.66 (t, J = 7.3 Hz, 1 H, H^{4*}), 3.79 (t, J = 5.7 Hz, 14 H, OCH_2, H^5, and H^8), 3.59 (br, 1 H, H^{10}), 2.85 (t, J = 5.4 Hz, 12 H, NCH_2 and H^9), 2.79 (m, 1 H, H^6), 1.21 (d, J = 7.3 Hz, CH_3), 0.47 (d, J = 5.6 Hz, 3 H, CH_3), 0.46 (d, J = 5.6 Hz, 3 H, $\text{CH}_3{}^*$). Compound **8($\text{C(H)(CH}_3)\text{CN}$)** is a diastereomeric mixture. The peaks due to the diastereomer are marked with asterisks. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{FeN}_2\text{O}_6\text{Si}$: C, 49.57; H, 5.26; N, 6.09. Found: 49.74; H, 5.52; N, 6.08.

Synthesis of 8($\text{C(CH}_3)_2$ CN). The typical procedure was almost the same as that employed in the synthesis of **8**-**(CH_2CN)**, except that $\text{LiC(CH}_3)_2\text{CN}$ was used instead of LiCH_2CN, yielding 38%: IR ν (CN) 2240 cm^{-1}, ν (CO) 2008, 1952

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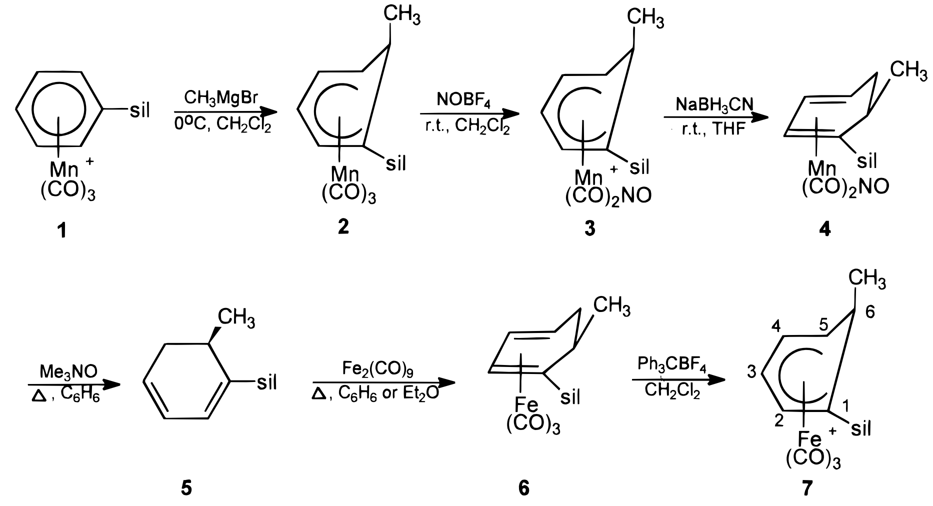
Scheme 1



sil = Si(OCH$_2$CH$_2$)$_3$N

cm^{-1}, ν (C=O) 1612 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.41 (dd, J = 4.5, 5.53 Hz, 1 H, H^3), 4.97 (d, J = 4.6 Hz, 1 H, H^2), 4.64 (t, J = 6.6 Hz, 1 H, H^4), 3.79 (t, J = 5.8 Hz, 6 H, OCH$_2$), 3.53 (dd, J = 6.4, 6.8 Hz, 1 H, H^5), 2.83 (t, J = 5.8 Hz, 6 H, CH$_2$N), 1.19 (s, 3 H, C(CH$_3$)$_2$CN), 1.18 (s, 3 H, C(CH$_3$)$_2$CN), 0.46 (d, 6.6 Hz, 3 H, CH$_3$). Anal. Calcd for C$_{18}$H$_{26}$FeN$_2$O$_6$Si: C, 50.64; H, 5.53; N, 5.91. Found: C, 51.16; H, 5.69; N, 5.87.

Reaction of 7 with LiCH(Ph)CN. The typical procedure was almost the same as that employed in the synthesis of **8-(CH$_2$CN)**, except that LiC(H)PhCN was used instead of LiCH$_2$CN. After workup, a mixture of free (2-methylphenyl)silatrane, **9(CH(Ph)CN)**, and an unidentified compound was obtained in the ratio 1:1:1. The ratio was calculated from the integration of ^{1}H NMR of the characteristic peaks of each compound. We only succeeded in obtaining the IR and ^{1}H NMR spectra of **9(CH(Ph)CN)**: IR ν (CN) 2232 cm^{-1}, ν (CO) 2030, 1954 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.30 (m, Ph), 5.87 (d, J = 4.1 Hz, 1H, H^2), 5.78 (d, J = 4.1 Hz, 1 H, H^{2*}) 5.43 (dd, J = 6.1, 4.1 Hz, 1 H, H^3), 5.25 (dd, J = 6.1, 4.1 Hz, 1 H, H^{3*}), 3.71 (m, J = OCH$_2$, H^{4,4*}, and C*H*CN), 2.74 (m, J = NCH$_2$, H^{5,5*}, and H^{6,6*}), 1.02 (d, J = 6.6 Hz, 3 H, CH$_3$), 0.87 (d, J = 5.6 Hz, 3 H, CH$_3{}^*$) ppm. Compound **9(CH(Ph)CN)** is a diastereomeric mixture. The peaks due to the diastereomer are marked with asterisks.

Synthesis of 9(CPh$_2$CN). The typical procedure was almost the same as that employed in the synthesis of **8-(CH$_2$CN)**, except that LiCPh$_2$CN was used instead of LiCH$_2$CN, yielding 67%: IR ν (CN) 2228 cm^{-1}, ν (CO) 2024, 1958 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.26 (m, 10 H, Ph), 5.84 (d, J = 3.7 Hz, 1 H, H^2), 5.37 (dd, J = J = 3.9, 6.2 Hz, 1 H, H^3), 3.72 (t, J = 5.8 Hz, 7 H, OCH$_2$ + H^4), 2.80 (t, J = 5.8 Hz, 6 H, NCH$_2$), 2.50 (m, 1 H, H^5), 0.95 (d, J = 7.1 Hz, 3 H, CH$_3$). Anal. Calcd for C$_{27}$H$_{30}$FeN$_2$O$_6$Si: C, 60.20; H, 5.05; N, 4.68. Found: 59.91; H, 5.49; N, 4.95.

Synthesis of 11. To synthesize **8(CH$_2$CO$_2{}^t$Bu)**, we used 0.15 g (0.30 mmol) of **7** and applied the same procedure as that employed in the synthesis of **8(CH$_2$CN)**, except that LiCH$_2$CO$_2$C(CH$_3$)$_3$ was used instead of LiCH$_2$CN. Selected IR spectral data of **8(CH$_2$CO$_2{}^t$Bu)**: IR ν(CO) 2012, 1949 cm^{-1}, ν(CO$_2$) 1718 cm^{-1}, ν(C=O) 1620 cm^{-1}. Compound **8(CH$_2$CO$_2{}^t$Bu)** was used for further reaction.

Compound **8(CH$_2$CO$_2{}^t$Bu)** was suspended in THF and then kept in the freezer for several days. The suspended compound was then dissolved in 10 mL of CH$_2$Cl$_2$ and the solution stirred at room temperature for 1 day. The solution was filtered and column chromatographed on silica gel, eluting with diethyl ether. After evaporation of the solvent, **11** (0.03 g, 0.07 mmol) was isolated: ^{1}H NMR (CDCl$_3$) δ 6.10 (t, J = 3.6 Hz, 1 H, H^3), 4.84 (d, J = 2.0 Hz, 1 H, H^2), 4.62 (t, J = 6.2 Hz, 1 H, H^4), 3.78 (t, J = 5.7 Hz, 6 H, OCH$_2$), 3.62 (2 H, CH$_2$CO), 3.57 (br, 1 H, H^5), 2.83 (t, J = 5.4 Hz, 6 H, NCH$_2$), 2.70 (m, 1 H, H^6), 1.40 (s, 9 H, -CMe$_3$), 0.45 (d, J = 6.6 Hz, 3 H, CH$_3$).

Mercuration of 5. To a solution of **5** (0.10 g, 0.4 mmol) in 10 mL of EtOH and H$_2$O (2:1 v/v) was added dropwise a solution of HgCl$_2$ (0.14 g, 0.5 mmol), NH$_4$Cl (0.07 g, 1.3 mmol), and NH$_4$F (0.05 g, 1.4 mmol) in 5 mL of EtOH and H$_2$O (2:1 v/v). Immediately, white solids were precipitated out of the solution. After the solution was stirred for 3 h, the white solids were filtered and washed with Et$_2$O (30 mL × 3) and H$_2$O (20 mL × 2). The yield of **12** was 90%: ^{1}H NMR (CDCl$_3$) δ 5.81 (m, 3 H, H^{2,3,4}), 2.43 (m, 1 H, H^6), 2.29 (dddd, J = 17.3, 7.8, 4.9, 1.1 Hz, 1 H, H$^{5-\mathrm{endo}}$), 1.97 (dddd, J = 17.3, 13.2, 4.0, 2.1 Hz, 1 H, H$^{5-\mathrm{exo}}$), 1.07 (d, J = 7.2 Hz, 3 H, CH$_3$); HRMS M$^+$ calcd 330.0099, obsd 330.0164.

Demercuration of 12. To a solution of **12** (0.050 g, 0.15 mmol) in 10 mL of THF and H$_2$O (1:1 v/v) was added NaBH$_4$ (8.7 mg, 0.23 mmol). Immediately, white solids precipitated out of the solution. After the solution was stirred for 1 h, all solids were filtered off. The filtrate was analyzed by GC/MS to confirm the liberation of 5-methylcyclohexadiene (mass number 94).

Discussion and Results

A silatranylcyclohexadiene derivative **5** was obtained from **4** in 82% yield (Scheme 1). To prepare the (silatranylcyclohexadienyl)iron derivative **6**, **5** was treated with Fe$_2$(CO)$_9$ in refluxing benzene or diethyl ether. At first, Fe$_2$(CO)$_9$ was not soluble and was suspended in benzene or diethyl ether. However, as the reaction proceeded, Fe$_2$(CO)$_9$ disappeared slowly. After workup, **6** was obtained in 95% yield. Since the 1,3-cyclohexadiene moiety in **6** necessarily has the cisoid geometry, its conversion to the cyclohexadienyliron derivative **7** is readily achieved by treatment with trityl tetrafluoroborate (Scheme 1).[3] In contrast to the expected difficulty in synthesizing a cyclohexadienyliron cation with a substituent at the C(6) carbon,[4] **7** was obtained as the 6-methyl salt in a single stereoisomer. The conformation of **7** was confirmed by ^{1}H NMR. If **7** has the methyl group in an *endo* configuration, the coupling between H-5 and H-6 (exo) is negligible, and the peak

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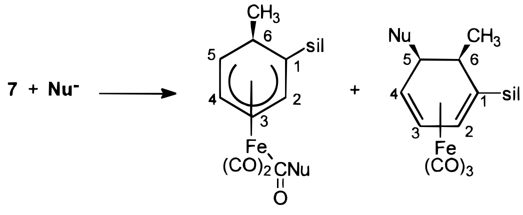
Scheme 2



8 **9**

Nu$^-$	**8**	**9**
$^-CH_2CN$	**8**(CH_2CN)	
$^-CH(CH_3)CN$	**8**($CH(CH_3)CN$)	
$^-C(CH_3)_2CN$	**8**($C(CH_3)_2CN$)	
$^-CH(Ph)CN$		**9**($CH(Ph)CN$)
$^-CPh_2CN$		**9**(CPh_2CN)
-$CH_2CO_2{}^tBu$	**8**($CH_2CO_2{}^tBu$)	

of H-5 should appear as a doublet due to the coupling with only H-4. However, the peak of H-5 appears as a triplet due to the coupling with H-4 and H-6 by 5.9 Hz. In addition, due to the long-range coupling with H-3 by 0.7 Hz, we could see the doublet splitting of the triplet. Thus, according to the ^1H NMR spectrum of **7**, the methyl group is situated at the *exo* position.

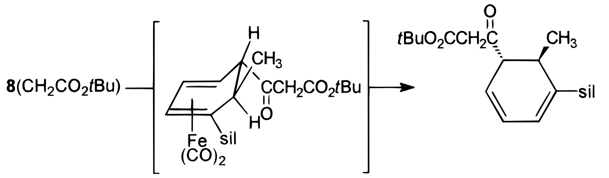
Nucleophilic addition of various nucleophiles to **7** was studied (Scheme 2). When $LiCH_2CN$ was used as a nucleophile, the acyl complex **8(CH_2CN)** was obtained in 32% yield, as evidenced by the ν (C=O) stretching feature at 1612 cm^{-1} and the methylene protons at δ 3.54 and 3.45 ppm, respectively. The peaks were doublets with geminal coupling (J = 18.5 Hz). When $LiC(CH_3)_2CN$ and $LiCH(CH_3)CN$ were used as nucleophiles, the acyl complexes **8($C(CH_3)_2CN$)** and **8($CH(CH_3)CN$)** were obtained in 46% and 37% yields, respectively. In the latter case, a mixture of two diastereomers was obtained. The low yields of **8** were due to the demetalation of **8** during purification. Thus, we usually obtained **8** with (2-methylphenyl)silatrane. While reactions with nucleophiles prepared from acetonitrile having aliphatic substitution provided **8** as a major product, those prepared from aryl-substituted acetonitrile furnished a different outcome. Thus, when LiCH(Ph)CN was used as a nucleophile, a mixture of free (2-methylphenyl)silatrane, **9(CH(Ph)CN)**, and an unidentified compound was obtained. The estimated yield of **9(CH(Ph)CN)** was ~20%. When $LiCPh_2CN$ was used as a nucleophile, the cyclohexadiene complex **9(CPh_2CN)** was obtained in 67% yield.

The chemoselectivity of the nucleophilic addition to **7** and the stability of the nucleophilic addition products were quite dependent on the nature of the nucleophiles. In the case of the carbanions derived from alkyl-substituted acetonitrile, the nucleophilic addition to the carbonyl carbon is quite general for **7**. As the substitution of the aryl group in the carbanion increased, the yield of the ring addition product increased.

Generally, attack at an unsaturated hydrocarbon ligand is preferred when the choice is between an unsaturated ligand and CO. Thus, the addition of carbon nucleophiles to the carbonyl carbon of (cyclohexadienyl)$Fe(CO)_3{}^+$ was very unusual.[5] Recently, Stephenson *et al.* reported the formation of acyl compounds from the addition of 2-substituted nucleophiles on (η^5-1-Me-4-MeO-C_6H_5)$Fe(CO)_3{}^+$.[6] They reported that solvent effects could be used to switch between formation of acyl products and direct addition to the dienyl ligand in aryllithium addition to (η^5-cyclohexadienyl)tricarbonyliron complexes: the yield of acyl complex could be improved to 30% by changing the solvent from THF to DME. However, when the reaction of **7** with $LiC(CH_3)_2CN$ was carried out in THF or CH_2Cl_2, the acyl complex **8($C(CH_3)_2CN$)** was obtained in 46% and 38% yeilds, respectively. Thus, in our cases, solvent effects do not seem to alter the chemoselectivity of nucleophilic addition. Instead of solvent effects, the steric bulk of the carbanion seems to play an important role in the nucleophilic addition. Why is it so common for **7** to attack a CO ligand? Generally, attack at a carbonyl carbon is not common for cyclohexadienyliron tricarbonyl cations containing a trimethylsilyl group as a substituent.[7] We expect that the electronic and steric effects of trimethylsilyl and silatranyl groups are not very different from each other. However, the chemoselectivities of nucleophilic additions are quite different from each other. While answering the question requires further investigation, at the present we suspect that the silatranyl group may play a role in the chemoselectivity of the nucleophilic addition.

When the nucleophiles were $NaBH_4$, NaCN, and RMgBr (R = Me and Et), the formation of **8** could be confirmed by ^1H NMR or/and IR spectra. However, compounds **8** were not stable enough to be characterized completely.

The addition of $LiCH_2CO_2C(CH_3)_3$ to **7** gave acyl compound **8($CH_2CO_2{}^tBu$)** (eq 1). This acyl complex rearranged very slowly to a diene compound, presumably **10**. Compound **10** ultimately decomposed to afford the *trans*-disubstituted cyclohexadiene derivative of silatrane, **11**. Thus, the preparation of *trans*-disubstituted cyclohexadienes was accomplished via nucleophilic attack at the CO, followed by rearrangement. Similar rearrangements have been observed in the reaction of [(η^5-1-sil-6-CH_3-C_6H_5)$Mn(CO)_2NO$]$^+$ with carbanions such as $^-CH_2CN$, $^-CHCO_2{}^iPr$, and $^-CHCO_2{}^tBu$.[2]



(1)

10 **11**

Desilylation from the disubstituted cyclohexadiene derivative of silatrane (**5**) was performed by treating with $HgCl_2$, NH_4Cl, and NH_4F in aqueous solution (eq 2).[8] After reaction, the formation of HgCl derivative **12** was confirmed by ^1H NMR analysis and high-resolution mass spectrometry. Liberation of HgCl gave 5-methyl cyclohexadiene.[9] It is expected that the HgCl group can

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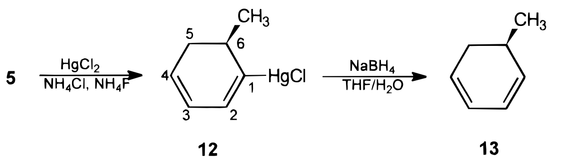

(2)

be easily converted to other functional groups. This could open up new routes for *cis*-disubstituted cyclohexadiene derivatives.

In conclusion, we have demonstrated that nucleophilic attack to the carbonyl carbon on the (6-methyl-1-silcyclohexadienyl)Fe(CO)$_3^+$ was due not to a solvent effect but rather to the chemoselectivity of carbanion addition governed by the nature of the carbanions. We have also demonstrated that *trans*-disubstituted cyclohexadiene derivatives of silatrane and 5-methylcyclohexadiene can be obtained from **8($CH_2CO_2{}^tBu$)** and **5**, respectively.

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