20: yield 85% (method B). IR: $\nu(C{\equiv}C)$ 2090 cm^{-1} (m). Anal. Calcd for $C_{47}H_{49}CoP_4$: C, 70.85; H, 6.20; Co, 7.40. Found: C, 70.62; H, 6.13; Co, 7.25.

21: yield 91% (method B). IR: $\nu(C{\equiv}C)$ 2092 cm^{-1} (m). Anal. Calcd for $C_{49}H_{53}CoP_4$: C, 71.36; H, 6.48; Co, 7.14. Found: C, 71.27; H, 6.43; Co, 6.99.

Protonation of the σ-Alkynyls 16–21. A stoichiometric amount of triflic acid (18 μL, 0.20 mmol) was syringed into stirred THF solutions (25 mL) of the σ-alkyne complexes **16–21** (ca. 0.2 mmol) in the temperature range 195–313 K. Regardless of the temperature, the starting yellow or orange solutions immediately turned deep red. Addition of solid $NaBPh_4$ (0.10 g, 0.29 mmol) and ethanol (25 mL) yielded red to purple crystals of vinylidene **4–6**, **9**, **10**, or **13**. The yields were ca. 85%.

Reaction of Vinylidenes 4–6, 9, 10, and 13 with CO. In a typical experiment, a THF solution (20 mL) of the appropriate vinylidene complex (**4–6**, **9**, **10**, or **13**) was saturated with CO and then heated for 12 h at 338 K. The solution was then cooled down to room temperature, and *n*-heptane was added until an orange microcrystalline solid precipitated. In all cases, $^{31}P\{^1H\}$ NMR analysis showed the crude products to contain the carbonyl complex $[(PP_3)Co(CO)]BPh_4$ (**22**) together with unreacted vinylidene complexes. The percentage concentration of **22** in the various preparations is as follows: **4** + CO, 49%; **5** + CO, 38%; **6** + CO, 35%; **9** + CO, 22%; **10** + CO, 7%; **13** + CO, 6%.

X-ray Diffraction Study. A summary of crystal and intensity data for the compound $[(PP_3)Co\{C{=}C(H)Ph\}]BPh_4$ (**10**) is reported in Table II. All X-ray measurements were performed at room temperature on a Philips PW1100 automated diffractometer using Cu Kα radiation monochromatized with a graphite crystal. The cell parameters were determined by least-squares refinement of the setting angles of 25 randomly selected reflections. Three standard reflections were collected every 2 h (the intensities were corrected for a decay of ca. 10%). The data were also corrected for Lorentz-polarization effects. An empirical absorption correction was made by using the program DIFABS.[32] Atomic scattering factors were those of Cromer and Waber[33] with anomalous dispersion corrections taken from ref 34. The structure was solved by the heavy-atom technique. Refinement was by full-matrix least-squares calculations; initially isotropic thermal parameters were generally applied, and later, anisotropic parameters were used for the Co and P atoms. The phenyl rings were treated as rigid hexagons (C–C distances 1.39 Å), and all of the hydrogen atoms were introduced at calculated positions. The final refinement cycles were performed with use of the weighting scheme $w = k/(\sigma^2(F) + pF^2)$ ($p = 0.0001$), which gave the smallest variations of the mean value of $w(F_o - F_c)^2$. The final Fourier map was practically featureless. Tables of atomic coordinates and temperature factors (including those of hydrogen atoms) are given as supplementary material.

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Supplementary Material Available: Tables of atomic parameters (including coordinates of hydrogen atoms) for the structure of $[(PP_3)\{C{=}C(H)Ph\}]BPh_4$ (**10**) (6 pages); a list of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of (Phenylsilatrane)manganese Tricarbonyl Perchlorate: Molecular Structure of $[\{\eta^5\text{-}1\text{-}N(CH_2CH_2O)_3Si\text{-}6\text{-}PhC_6H_5\}Mn(CO)_3]$

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$[\{N(CH_2CH_2O)_3SiC_6H_5\}Mn(CO)_3]ClO_4$ (**1**) undergoes regioselective reaction with RMgBr (R = Ph, Me, Et) in CH_2Cl_2 to give $[\eta^5\text{-}1\text{-}(N(CH_2CH_2O)_3Si)\text{-}6\text{-}(R)C_6H_5]Mn(CO)_3$ (**2a**, R = Ph; **2b**, R = Me; **2c**, R = Et), with EtLi in THF to yield $[\eta^5\text{-}2\text{-}(N(CH_2CH_2O)_3Si)\text{-}6\text{-}(R)C_6H_5]Mn(CO)_3$ (**3c**, R = Et), and with RMgBr (R = Ph, Me, Et), $LiCH_2CO_2CMe_3$, $LiCH_2CN$, and $Li\overline{CHS(CH_2)_3S}$ in THF to yield $[\eta^5\text{-}3\text{-}(N(CH_2CH_2O)_3Si)\text{-}6\text{-}(R)C_6H_5]Mn(CO)_3$ (**4a**, R = Ph; **4b**, R = Me; **4c**, R = Et; **4e**, R = $CH_2CO_2CMe_3$; **4j**, R = CH_2CN; **4k**, R = $\overline{CHS(CH_2)_3S}$). However, **1** does not react regioselectively with the carbanions from isobutyronitrile, acetone, or *tert*-butyllithium or with sodium cyanide. The selectivity of the nucleophilic addition to **1** is strongly dependent on the nucleophile and reaction medium. The structure of **2a** has been confirmed by X-ray diffraction: space group $P\bar{1}$; $a = 9.169$ (2) Å, $b = 9.905$ (2) Å, $c = 12.353$ Å, $\alpha = 110.25$ (2)°, $\beta = 97.33$ (1)°, $\gamma = 97.70$ (2)°; final error indices $R = 0.042$, $R_G = 0.043$ for 2856 unique data with $I > 3\sigma(I)$.

Introduction

The structure and the chemical properties of silatranes have been investigated by various methods.[1] Although atrane compounds have been much studied recently,[2] silatrane derivatives have received little attention as π-coordinating ligands for transition metals until we reported the $Cr(CO)_3$ and $Mn(CO)_3^+$ derivatives of phenylsilatrane[3]

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Table I. IR[a] and Analytical[b] Data for 2–4

complex	ν_{CO}, cm^{-1}	ν_{CN}, cm^{-1}	ν_{CO_2}, cm^{-1}	anal., %
2a	2010, 1930, 1908			C, 53.97 (53.96); H, 5.00 (4.74); N, 3.09 (3.00)
2b	2000, 1927, 1902			C, 46.85 (47.40); H, 5.30 (4.97); N, 2.96 (3.45)
2c	1998, 1920, 1900			C, 48.65 (58.69); H, 5.14 (5.28); N, 2.73 (3.34)
4b	2000, 1912			C, 48.15 (47.40); H, 5.48 (4.97); N, 3.60 (3.45)
4e	2012, 1920		1716	C, 49.67 (49.90); H, 5.65 (5.58); N, 2.65 (2.77)
4f	2000, 1914		1705	C, 48.20 (48.32); H, 5.24 (4.96); N, 2.93 (3.13)
4g	2000, 1908	2226		C, 49.73 (49.78); H, 5.14 (5.06); N, 6.01 (6.11)
4i	2000, 1912			C, 46.67 (46.04); H, 4.59 (4.64); N, 3.63 (3.58)
4j	2012, 1921	2245		C, 47.16 (47.44); H, 4.31 (4.45); N, 6.28 (6.50)
2d + 4d	2018, 1929	2220		C, 46.16 (46.04); H, 4.12 (3.71); N, 6.73 (6.21)

[a] In CH_2Cl_2. [b] Calculated values in parentheses.

and the molecular structure of the former. We also studied nucleophilic addition reactions to $[(\text{phenylsilatrane})Mn(CO)_3]^+$ (cation of **1**). Our previous communications revealed that compound **1** undergoes regioselective nucleophilic reaction with the carbanion of *tert*-butyl acetate and $NaBH_4$ to give the C-4 adduct **4** and with RMgBr (R = Me, Ph) to give the C-2 adduct **2**. In this report we describe in detail the reaction of compound **1** with several nucleophiles and the medium effect of such reactions. The molecular structure of $[\{\eta^5\text{-}1\text{-}(N(CH_2CH_2O)_3Si)\text{-}6\text{-}PhC_6H_5\}Mn(CO)_3]$ is also discussed.

Experimental Section

General Methods. All solvents were purified by standard methods and all synthetic procedures were done under a nitrogen atmosphere. THF was freshly distilled from sodium benzophenone ketyl prior to use, and other solvents were purified and dried according to standard methods. Reagent grades chemicals were used without further purification.

Elemental analyses were performed with a Yanaco MT-2 elemental analyzer at the Chemical Center of the College of Engineering, Seoul National University. ^1H NMR spectra were obtained with either a Bruker AC 80 or Varian XL-200 instrument. Infrared spectra were recorded on a Perkin-Elmer 782 spectrometer, and mass spectra were recorded on a VG ZAB-E double-focusing mass spectrometer.

Compound **1** was synthesized as previously described.[3] Following published procedures, nucleophilic addition of $NaBH_4$, NaCN, MeLi, EtLi, RMgBr (R = Me, Et, Ph), $LiCH_2CN$, $LiCH_2CO_2CMe_3$, $LiCMe_2CN$, $LiCMe_3$, $LiCH_2C(O)CH_3$, and $Li\overline{CHS(CH_2)_3S}$ to **1** gave the corresponding cyclohexadienyl complexes, **2**–**4**. Several of these are new or have not been completely characterized in the past, and accordingly some selected spectroscopic data are given in Tables I and II.

Reaction between 1 and RMgBr (R = Me, Et, Ph). In CH_2Cl_2. Typical procedure: Compound **1** (245 mg, 0.50 mmol) was stirred in dry methylene chloride (50 mL) under N_2 at 0 °C while the Grignard reagent (2 molar equiv) was added dropwise. After 40 min the excess carbanion was quenched by dropwise addition of 0.1 N HCl solution, and the mixture was allowed to warm to room temperature. The solution was dried ($MgSO_4$) and evaporated to dryness, yielding a brown residue. Extraction into diethyl ether and chromatography on a silica gel column with diethyl ether as eluent gave a yellow solution. Evaporation to dryness gave the product **2** as a yellow crystalline solid.

In THF. Under conditions identical with those above except for the reaction medium (THF), a 57.2% isolated yield of a mixture of **3a** and **4a** was obtained for PhMgBr addition. The isomer ratio of **3a** and **4a** was determined to be 1:4.3 by comparing the integration of H^3 of **3a** with that of $H^{2,4}$ of **4a** of the ^1H NMR spectrum. A 72% isolated yield of **4b** was obtained for MeMgBr addition. A 42% isolated yield of **3c** and **4c** was obtained for EtMgBr addition. The isomer ratio of **3c** and **4c** was determined to be 1:7.3 by comparing the integration of H^3 of **3c** with that of $H^{2,4}$ of **4c** of the ^1H NMR spectrum.

Reaction between 1 and RLi (R = Me, Et, *t*-Bu). In THF. Typical procedure: To a stirred suspension of **1** (245 mg, 0.50 mmol) in 30 mL of THF at −78 °C was added 4 equiv of RLi. The reaction mixture was stirred for 1 h at −78 °C and warmed to room temperature. The reaction mixture was poured into water and extracted three times with diethyl ether (100 mL). The ether extracts were dried ($MgSO_4$) and evaporated to dryness, yielding a yellow crystalline solid.

In CH_2Cl_2. The reaction was carried out under conditions identical with those above except for the reaction medium (CH_2Cl_2) and the reaction temperature (0 °C).

Tables III and IV show the yield and the product distribution for alkyllithium reagent additions in both solvents.

Reaction between 1 and NaCN. To a stirred suspension of **1** (245 mg, 0.50 mmol) and a slight excess of NaCN in 30 mL of THF at room temperature was added 2 mL of water. After being stirred for 30 min, the solution was concentrated and extracted with diethyl ether (100 mL). The ether extracts were dried ($MgSO_4$) and evaporated to give a yellow solid (56%), as a 1:1.7 mixture of **2d** and **4d**. The isomer ratio was determined by comparing the integration of H^3 of the **2d** with that of $H^{2,4}$ of **4d** of the ^1H NMR spectrum. The mixture has the following properties: mp 156 °C; IR (CH_2Cl_2) ν_{CO} 2018, 1929 cm^{-1}, ν_{CN} 2220 cm^{-1}.

Reaction between 1 and $NaBH_4$. In THF. To a stirred suspension of **1** (245 mg, 0.50 mmol) in 30 mL of THF at −5 °C was added a slight excess of $NaBH_4$. After being stirred for 1 h, the solution was evaporated to dryness and extracted with diethyl ether (100 mL). Evaporation of the ether gave a yellow crystalline solid of a mixture of **3i** and **4i** (76%). The ratio of **3i** and **4i** was determined to be 1:16 by comparing the integration of H^3 of **3i** with that of $H^{2,4}$ of **4i** of the ^1H NMR spectrum. The mixture has the following properties: mp 184–186 °C; EI-MS *m/z* 391 (M^+), 335 ($M^+ - 2CO$), 307 ($M^+ - 3CO$), 251 ($M^+ - Mn(CO)_3 - H$).

In CH_2Cl_2. Under identical conditions except for the reaction medium (CH_2Cl_2) and reaction temperature (0 °C), a 74% isolated yield of a mixture **3i** and **4i** was obtained in the ratio of 1:16. The isomer ratio was determined by the same way as above.

Preparation of Carbon Nucleophiles. Freshly prepared solutions of the carbon nucleophiles were used in all experiments. The nucleophiles were generated as follows:

$LiCMe_2CN$. A solution of lithium diisopropylamide was prepared by dropwise addition via syringe of *n*-BuLi (1.2 mL of a 2.5 M solution in hexane, 3.0 mmol) to diisopropylamine (0.4 mL, 3.0 mmol) in THF (15 mL) at −78 °C. After 30 min, 2-methylpropionitrile (0.27 mL, 3.0 mmol) was added dropwise. After being stirred for 30 min, the reagent solution was used in the addition reactions described below. The same procedure was used in the preparation of $LiCH_2CN$, $LiCH_2CO_2CMe_3$, and $LiCH_2C(O)CH_3$. $Li\overline{CHS(CH_2)_3S}$ was prepared by following the procedure of Corey and Seebach.[4]

General Procedure for Carbon Nucleophile Addition to 1. To the suspension of **1** (245 mg, 0.50 mmol) in THF (50 mL) at −78 °C was added the carbon nucleophile (3.0 mmol) in 15 mL of THF. The reaction mixture was stirred for 1 h at −78 °C. Then

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Table II. ^{1}H NMR Spectral Data[a] (δ) for 2–4

complex	H-1	H-2	H-3	H-4	H-5	H-6	OCH_2	NCH_2	other
2a		5.17 (d, J = 5 Hz)	5.72 (td, J = 5 Hz)	4.84 (tt, J = 5.6 Hz)	3.24 (t, J = 6)	4.03 (d, J = 6 Hz)	3.70 (t, J = 5.9 Hz)	2.76 (t, J = 5.9 Hz)	7.2–6.9 (m, Ph)
2b		4.95 (d, J = 5.3 Hz)	5.72 (t, J = 5.3 Hz)	4.69 (t)[b]	3.04 (t)[b]	2.59 (m)	3.78 (t, J = 5.6 Hz)	2.80 (t, J = 5.6 Hz)	0.43 (d, J – 6.4 Hz, Me)
2c[c,d]		4.95 (d, J = 5.1 Hz)	5.73 (td, J = 5.1 Hz)	4.73 (t, J = 5.8 Hz)	3.07 (t, J = 5.8 Hz)	2.49 (m)	3.78 (t, J = 5.8 Hz)	2.81 (t, J = 5.8 Hz)	0.66 (t, J = 7 Hz, Me), 1.04 and 0.49 (m, CH_2)
2d		5.16 (d, J = 5.4 Hz)	5.89 (td, J = 5.4 Hz)	4.97 (t, J = 5.4 Hz)	3.1[e]	2.8[e]	3.78 (t, J = 5.8 Hz)	2.83 (t, J = 5.8 Hz)	
2e		4.97 (d, J = 5.2 Hz)	5.73 (t, J = 5.2 Hz)	4.74 (t, J = 5.8 Hz)	3.1[e]	2.8[e]	3.76 (t, J = 5.8 Hz)	2.80 (t, J = 5.8 Hz)	1.63 (d, J = 7.3 Hz, CH_2), 1.39 (s, Me)
3a	3.45[e]		5.86 (d)[b]	4.75 (t)[b]	[e]	2.5 (m)	3.81 (t, J = 5.8 Hz)	2.86 (t, J = 5.8 Hz)	7.3–7.0 (m, Ph)
3b	3.48 (d, J = 5.8 Hz)		5.88 (d, J = 5.1 Hz)	4.75 (t, J = 5.1 Hz)	3.1 (t, J = 5.9 Hz)	2.29 (m)	3.80 (t, J = 5.8 Hz)	2.83 (t, J = 5.8 Hz)	0.41 (d, J = 5.9 Hz, Me)
3c	3.46 (d, J = 6.4 Hz)		5.86 (dt, J = 5.9, 1.3 Hz)	4.72 (dd, J = 7.2, 5.9 Hz)	3.11 (dd, J = 7.2, 6.4 Hz)	[e]	3.89 (t, J = 5.8 Hz)	2.93 (t, J = 5.8 Hz)	0.65 (m, CH_2), 0.62 (t, J = 7 Hz, Me)
3e	3.45 (d)[b]		5.89 (d)[b]	4.74 (t)[b]	3.1[e]	[e]	3.81[e]	2.86[e]	1.63 (d, J = 6.8 Hz, CH_2), 1.40 (s, Me)[e]
3g	3.41 (d, J = 5.4 Hz)		5.81 (d, J = 5.1 Hz)	4.95 (t, J = 5.4 Hz)	3.13 (t)	2.78 (m)	3.80 (t, J = 5.8 Hz)	2.87 (t, J = 5.8 Hz)	0.99 (s, Me)
3h	3.5[b]		5.74 (dt, J = 5.2 Hz)	4.82 (t, J = 5.2 Hz)	3.25 (t)	[e]	3.79 (t, J = 5.8 Hz)	2.90 (t, J = 5.8 Hz)	0.55 (s, Me)
4a	3.48[b,e]	5.14 (d, J = 6.7 Hz)		5.14 (d, J = 6.7 Hz)	3.48[b,e]	*e*	3.89 (t, J = 5.8 Hz)	2.93 (t, J = 5.8 Hz)	7.3–7.0 (m, Ph)
4b	3.3 (t)[b]	4.97 (d, J = 6.9 Hz)		4.97 (d, J = 6.9 Hz)	3.3 (t)[b]	2.5 (m)	3.90 (t, J = 5.8 Hz)	2.94 (t, J = 5.8 Hz)	0.44 (d, J = 5.9 Hz, Me)
4c	3.26 (t, J = 6.6 Hz)	4.97 (d, J = 7.3 Hz)		4.97 (d, J = 7.3 Hz)	3.26 (t, J = 6.6 Hz)	2.27 (t, J = 6.6 Hz)	3.89 (t, J = 5.8 Hz)	2.91 (t, J = 5.8 Hz)	0.61 (t, J = 7 Hz, Me), 0.67 (m, CH_2)
4d	3.00 (m)	5.25 (dd, J = 6.8 Hz)		5.25 (dd, J = 6.8 Hz)	3.00 (m)	3.56 (t, J = 5.8 Hz)	3.88 (t, J = 5.8 Hz)	2.89 (t, J = 5.8 Hz)	
4e	3.25 (t, J = 7 Hz)	5.02 (dd, J = 7.2 Hz)		5.02 (dd, J = 7.2 Hz)	3.25 (t, J = 7 Hz)	2.86 (m)	3.89 (t, J = 5.8 Hz)	2.93 (t, J = 5.8 Hz)	1.63 (d, J = 7.3 Hz, CH_2), 1.38 (s, Me)
4f	3.23 (t, J = 6.9 Hz)	5.00 (d, J = 6.9 Hz)		5.00 (d, J = 6.9 Hz)	3.23 (t, J = 6.9 Hz)	3.13 (m)	3.89 (t, J = 5.8 Hz)	2.93 (t, J = 5.8 Hz)	1.95 (s, Me), 1.89 (d, J = 6.4 Hz, CH_2)
4g	3.20 (t, J = 7 Hz)	5.20 (d, J = 7 Hz)		5.20 (d, J = 7 Hz)	3.20 (t, J = 7 Hz)	2.78 (m)	3.87 (t, J = 5.8 Hz)	2.93 (t, J = 5.8 Hz)	0.98 (s, Me)
4h	3.25 (t, J = 5.7 Hz)	5.05 (dd, J = 7.4 Hz)		5.05 (dd, J = 7.4 Hz)	3.25 (t, J = 5.7 Hz)	2.32 (t, J = 5.7 Hz)	3.86 (t, J = 5.8 Hz)	2.90 (t, J = 5.8 Hz)	0.55 (s, Me)
4i	2.96 (m)	5.03 (d, J = 6.8 Hz)		5.03 (d, J = 6.8 Hz)	2.96 (m)	2.56 (m)	3.91 (t, J = 5.8 Hz)	2.96 (t, J = 5.8 Hz)	2.09 (d, J = 12.7 Hz, H)
4j	3.25 (t)[b]	5.12 (d, J = 6.8 Hz)		5.12 (d, J = 6.8 Hz)	3.25 (t)[b]	2.82 (m)	3.89 (t, J = 5.8)	2.95 (t, J = 5.8 Hz)	1.65 (d, J = 6.8 Hz, CH_2)
4k	3.41 (t, J = 6.5 Hz)	5.12 (d, J = 6.5 Hz)		5.12 (d, J = 6.5 Hz)	3.41 (t, J = 6.5 Hz)	[e]	3.88 (t, J = 5.8 Hz)	2.92 (t, J = 5.8 Hz)	2.63 (SCH_2), 1.93 (–CH_2–)

[a] All spectra run at 200 MHz in $CDCl_3$, with Me_4Si as internal reference, unless otherwise stated. [b] The signal was observed as broad, and the accurate coupling constant was not accessible. [c] In C_6D_6. [d] Assignments based on decoupling experiments. [e] Overlapping or obscured peaks.

Table III. Reactions of Complex 1 with Nucleophiles

nucleophile	medium	product distribution 2	3	4	combined yield, %
PhMgBr	THF	0	25	75	57.2
PhMgBr	CH_2Cl_2	100	0	0	56.7
MeMgBr	THF	0	0	100	72.5
MeMgBr	CH_2Cl_2	100	0	0	72.0
EtMgBr	THF	0	12	88	42.0
EtMgBr	CH_2Cl_2	100	0	0	56.0
MeLi	THF		9	91	42.0
MeLi	CH_2Cl_2	100	0	0	42.0
EtLi	THF	0	100	0	49.0
EtLi	CH_2Cl_2	100	0	0	52.0
NaCN	wet THF	36	0	64	56.2
$LiCH_2CO_2{}^tBu$	THF	0	0	100	62.0
$LiCH_2CO_2{}^tBu$	THF/CH_2Cl_2 (1:5)	31	10	59	62.0
$LiCH_2C(O)CH_3$	THF	35	8	57	56.5
$LiCH_2C(O)CH_3$	THF/TMEDA (1:1)	26	19	55	72.0
$LiCMe_2CN$	THF	0	46	54	52.0
$LiCMe_2CN$	THF/TMFDA (1:1)	0	50	50	74.0
$LiCMe_3$	THF	5	41	54	43.3
$NaBH_4$	THF	0	6	94	76.6
$NaBH_4$	CH_2Cl_2	0	6	94	74.0
$LiCH_2CN$	THF	0	0	100	60.0
$LiCH_2CN$	THF/CH_2Cl_2 (1:5)	46	19	35	59.0
$Li\overline{CHS(CH_2)_3S}$	THF	0	0	100	32.0

Table IV. Reactions of Complex 1 with MeLi at 0 °C in Various Solvents

solvent	product distribution 2	3	4	combined yield, %
diglyme	0	0	100	36
THF	0	9	91	42
diethyl ether	43	0	57	40
TMEDA	21	58	21	52
THF/TMEDA	0	56	44	52
CH_2Cl_2	100	0	0	42
hexane	0	0	100	40

the reaction mixture was poured into water and extracted three times with diethyl ether (100 mL). The ether extracts were dried ($MgSO_4$) and evaporated to dryness to obtain the crude product as a yellow crystalline solid.

Reaction between 1 and $LiCH_2CO_2CMe_3$. In THF. Under conditions identical with those above, a 62% yield of **4e** was obtained: mp 189–190 °C dec; EI-MS *m/z* 505 (M^+), 449 (M^+ – 2CO), 421 (M^+ – 3CO), 391 (M^+ – 3CO – $2CH_3$), 319 (M^+ – 3CO – CO_2CMe_3 – H).

In CH_2Cl_2. The reaction was carried out as before except for the reaction medium and reaction temperature (0 °C). A 62% yield of a mixture of **2e**, **3e**, and **4e** in a ratio of 3:1:6 was obtained. The above ratio was determined by the areas of the peaks of H^3, H^3, and $H^{2,4}$ appearing in the proton NMR spectrum for the isomers **2e**, **3e**, and **4e**, respectively.

Reaction between 1 and $LiCH_2C(O)CH_3$. In THF. Under conditions identical with those above, a 57% isolated yield of a mixture **2f**, **3f**, and **4f** was obtained. The isomer ratio of **2f**, **3f**, and **4f** was determined to be 4.4:1:7.1 by the areas of the peaks of H^3, H^3, and $H^{2,4}$ appearing in the proton NMR spectrum for the isomers of **2f**, **3f**, and **4f**, respectively. The mixture has the following properties: mp 153 °C; EI-MS *m/z* 390 (M^+ – 2CO – H), 363 (M^+ – 3CO), 319 (M^+ – 3CO – $CH_3C(O)$ – H), 307 (M^+ – $Mn(CO)_3$).

In THF/TMEDA (1:1). Under conditions identical with those above except for the reaction medium (THF/TMEDA) and reaction temperature (–20 °C), a 72% isolated yield of a mixture of **2f**, **3f**, and **4f** was obtained. The isomer ratio of **2f**, **3f**, and **4f** was determined to be 1.36:1:2.9 by the areas of the peaks of H^3, H^3, and $H^{2,4}$ appearing in the proton NMR spectrum for the isomers **2f**, **3f**, and **4f**, respectively.

Reaction between 1 and $LiCMe_2CN$. In THF. Under conditions identical with those above, a 52% isolated yield of a mixture of **3g** and **4g** was obtained. The ratio of **3g** and **4g** was determined by ^1H NMR spectroscopy to be 1:1.2. Separation of the isomers was done by column chromatography on silica gel eluting with CH_2Cl_2/diethyl ether (5:1 v/v) (**3g**, R_f = 0.93; **4g**, R_f = 0.71). The mixture has the following properties: EI-MS *m/z* 457 (M^+ – H), 391 (M^+ – $Me(CN)CH_2$), 374 (M^+ – 3CO), 306 (M^+ – 3CO – CMe_2CN).

In THF/TMEDA (1:1). The reaction was carried out exactly the same as before except for the reaction medium (THF/TMEDA (1:1)) and reaction temperature (–20 °C). A 74% isolated yield of **3g** and **4g** was obtained. The isomer ratio of **3g** and **4g** was determined by to be 1:1 by comparing the integration of H^3 of **3g** with that of $H^{2,4}$ of **4g** of the ^1H NMR spectrum.

Reaction between 1 and $LiCH_2CN$. In THF. Under conditions identical with those above, a 60% isolated yield of **4j** was obtained: mp 174 °C dec; EI-MS *m/z* 390 (M^+ – CH_2CN), 346 (M^+ – 3CO), 306 (M^+ – 3CO – CH_2CN), 251 (M^+ – $Mn(CO)_3$ – CH_2CN).

In CH_2Cl_2. Under conditions identical with those above except for the reaction medium (CH_2Cl_2) and reaction temperature (0 °C), a 59% isolated yield of a mixture of **2j**, **3j**, and **4j** was obtained. The isomer ratio of **2j**, **3j**, and **4j** was determined to be 2.4:1:1.8 by the areas of the peaks of H^3, H^3, and $H^{2,4}$ appearing in the proton NMR spectrum for the isomers **2j**, **3j**, and **4j**, respectively.

Reaction between 1 and $Li\overline{CHS(CH_2)_3S}$. A solution of 1,3-dithiane (362 mg, 3.0 mmol) in 20 mL of THF was deprotonated with *n*-BuLi (1.4 mL of a 2.5 M solution in hexane) over a period of 30 min at –78 °C. A dry ice/acetone-cooled solution of 1 (0.5 mmol) in THF was then added. The reaction mixture was stirred at –78 °C for 1 h, warmed to room temperature, and poured into water and extracted three times with diethyl ether (100 mL). The ether extracts were dried ($MgSO_4$) and evaporated to dryness, yielding a yellow crystalline solid. A 32% isolated yield of **4k** was obtained: EI-MS *m/z* 425 (M^+ – 3CO), 390 (M^+ – $CH_2S(CH_2)_3S$), 306 (M^+ – 3CO – $\overline{CH_2S(CH_2)_3S}$).

X-ray Structure Analysis for 2a. Crystals of **2a** were grown at room temperature from a CH_2Cl_2/Et_2O solution of the compound. The crystal, 0.20 × 0.29 × 0.54 mm, was mounted on Enraf-Nonius CAD4 diffractometer, and the unit cell parameters were obtained from the least-squares fit of 25 reflections ($16° < 2\theta < 27°$). Data were collected with graphite-monochromated Mo Kα radiation by using the $\omega/2\theta$ scan mode.

The three intensity standards were monitored every 1 h during data collection. The data were corrected for Lorentz–polarization effects and decay. No absorption correction was applied because of the low μ value, 6.81 cm^{-1}. The crystal structure was solved by the use of the conventional heavy-atom method as well as Fourier difference techniques and refined by means of full-matrix least-squares procedures using SHELX-76.[5] All non-hydrogen atoms were refined by using anisotropic thermal factors, while most hydrogen atoms were located in a difference Fourier map. Hydrogen atoms were input in identical positions (C–H = 0.08 Å) with isotropic thermal factors and were constrained to ride on the attached atoms during subsequent refinements. The last cycle of refinement converged with R = 0.042% and R_G = 0.043%. The shift/esd ratio in the final cycle of least squares is less than 0.04 for all parameters. In the final difference Fourier map, the three largest peaks (0.89–0.61 e/Å^3) were all at chemically implausible positions. Crystal data, details of the data collection, and refinement parameters are lsited in Table V.

Results and Discussion

The phenylsilatrane coordinated to $Mn(CO)_3{}^+$ is activated to react with nucleophiles. In such reactions, cyclohexadienylmanganese tricarbonyl compounds are obtained (Scheme I and Table III). Compound 1 was insoluble in THF but soluble in CH_2Cl_2. Usually the reactions were studied in THF or CH_2Cl_2. The choice of reaction medium was critical to the distribution of products.

When we started to study the reaction between 1 and nucleophiles, we thought that the silatrane moiety would

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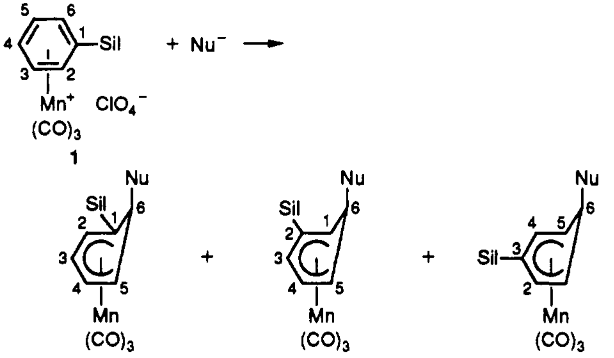
[5] Sheldrick, G. M. *SHELX 76: Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

Table V. Crystal Data, Data Collection, and Refinement of the Structure for $[\{\eta^5\text{-}1\text{-}N(CH_2CH_2O)_3Si\text{-}6\text{-}PhC_6H_5\}Mn(CO)_3]$

formula	$MnSiO_6NC_{21}H_{23}$
fw	468.446
space group	$P\bar{1}$
a, Å	9.169 (2)
b, Å	9.905 (2)
c, Å	12.353 (2)
α, deg	110.25 (2)
β, deg	97.33 (1)
γ, deg	97.70 (2)
V, Å^3	1024.6 (3)
Z	2
d_{calcd}, g cm^{-3}	1.508
cryst size, mm	0.20 × 0.29 × 0.54
μ, cm^{-1}	6.81
scan method	$\omega/2\theta$
range of data colln	$h,\pm k,\pm l$, 3° < 2θ < 50°
tot. no. of observns	3740
no. of unique data > I 3σ (I)	2856
no. of params refined	274
gof	0.8508
$R = (\sum\lvert F_o - F_c\rvert)/\sum\lvert F_o\rvert$	0.042
$R_G = ((\sum\lvert F_o - F_c\rvert)^2/(\sum\lvert F_o\rvert)^2)^{1/2}$	0.043

Scheme I



2

- 2a (Nu = Ph)
- b (Nu = Me)
- c (Nu = Et)
- d (Nu = CN)
- e (Nu = $CH_2CO_2{}^tBu$)
- f (Nu = $CH_2C(O)CH_3$)
- h (Nu = ^tBu)
- j (Nu = CH_2CN)

3

- 3a (Nu = Ph)
- b (Nu = Me)
- c (Nu = Et)
- e (Nu = $CH_2CO_2{}^tBu$)
- f (Nu = $CH_2C(O)CH_3$)
- g (Nu = CMe_2CN)
- h (Nu = ^tBu)
- i (Nu = H)
- j (Nu = CH_2CN)

4

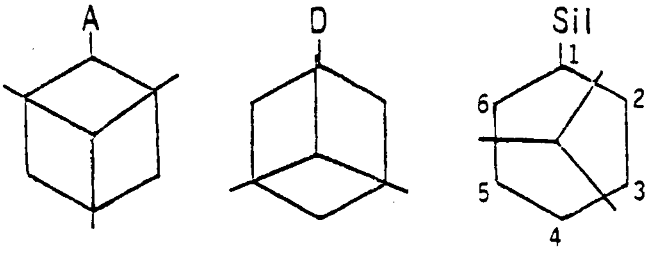
- 4a (Nu = Ph)
- b (Nu = Me)
- c (Nu = Et)
- d (Nu = CN)
- e (Nu = $CH_2CO_2{}^tBu$)
- f (Nu = $CH_2C(O)CH_3$)
- g (Nu = CMe_2CN)
- h (Nu = ^tBu)
- i (Nu = H)
- j (Nu = CH_2CN)
- k (Nu = $\overline{CHS(CH_2)_3S}$)

Sil ≡ $Si(OCH_2CH_2)_3N$

be an electron donor like a methoxy group. The CO stretching frequencies of 1 were somewhat lower than those of (anisole)$Mn(CO)_3{}^+$. The methoxy group deactivates the C-2 and C-4 positions, and the nucleophiles would exclusively attack the C-3 position.[6] However, the silatrane moiety did not follow the directional effect of the methoxy group. The attacking sites of nucleophiles in 1 showed some rather unusual trends (Table III). Reaction of 1 with RLi (R = Me, Et) and RMgBr (R = Me, Et, Ph) in CH_2Cl_2 gave products of type 2 of C-2 addition. On the other hand, reaction of 1 with MeMgBr in THF gave exclusively product 4, of C-4 addition. Reaction of 1 with EtMgBr in THF gave a mixture of C-3 and C-4 adducts in the ratio of 1:7.3. Reaction of 1 with PhMgBr in THF gave a mixture of C-3 and C-4 adducts in the ratio of 1:4.3. Reaction of 1 with MeLi in THF gave a mixture of C-3 and C-4 adducts in the ratio of 1:10. Surprisingly, reaction of 1 with EtLi gave exclusively product 3, of C-3 addition. PhLI and Ph_2CuLi did not react with 1 in any solvents. For the addition reactions of $NaBH_4$, $LiCH_2CN$, $LiCH_2CO_2CMe_3$, and 2-lithio-1,3-dithiane in THF, C-4 adducts were obtained as a major product. For the addition reaction of $LiCH_2C(O)CH_3$ in THF, a mixture of C-2, C-3, and C-4 products in a ratio of 4.4:1:7.1 was obtained. The C-4 adduct was formed in greater yield than the C-2 adduct. When the reaction medium was changed to THF/TMEDA (1:1 v/v), the C-3 adduct yield increased at the expense of that of C-2. For the addition reaction of $LiCMe_2CN$ in THF, a mixture of C-3 and C-4 adducts in a ratio of 1:1.17 was obtained. Change of the reaction medium from THF to THF/TMEDA (1:1 v/v) had no noticeable effect on the product distribution.

Regioselectivity in the addition of carbon nucleophiles to (substituted arene)$Cr(CO)_3$ complexes has been studied experimentally and theoretically.[7] An attempt had been made to correlate the directive effect with orbital coefficients in the arene LUMO by means of INDO MO calculations. When we consider the coefficients of LUMOs, the site of attack of the nucleophile would be somewhat predictable.

Usually the (arene)$Cr(CO)_3$ compound with an electron-accepting substituent has an anti-eclipsed conformation A.[7d] The syn-eclipsed structure, B, is normally observed with an electron-donating group.[7d] Thus, (phenylsilatrane)$Cr(CO)_3$ is expected to have the syn-eclipsed conformation, B. It is, however, found experimentally to have a nearly staggered conformation, C, in which the carbonyl groups are rotated by 32.5° away from the expected syn-eclipsed form. The staggered conformation appears to arise not because of the electron-accepting nature of the silatrane moiety but because of the steric bulk of the silatrane group. $(C_6H_5CH^tBu_2)Cr(CO)_3$ has been observed to have a similar conformation in which the carbonyl groups are rotated by 44° away from the expected syn-eclipsed form.[8] The conformation of (*p*-*tert*-butylbenzoic acid)$Cr(CO)_3$, which is predicted to be syn-eclipsed, is also of a nearly staggered form.[9]



A B C

The different directive effect of the silatrane moiety from that of the methoxy group may arise from the staggered conformation, C. Albright[7d] suggested that for $(C_6H_5X)Cr(CO)_3$ the electronic effect of the metal carbonyl

---

[6] (a) Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1982**, *1*, 1053. (b) Khand, I. U.; Pauson, P. L. *J. Chem. Soc. C* **1968**, 2257.

[7] (a) Solladie-Cavallo, A. *Polyhedron* **1985**, *4*, 901. (b) Chinn, J. W., Jr.; Hall, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 4930. (c) Semmelhack, M. F.; Garcia, J. L.; Farina, R.; Hong, R.; Carpenter, B. K. *Organometallics* **1983**, *2*, 467. (d) Albright, T. A.; Carpenter, B. K. *Inorg. Chem.* **1980**, *19*, 3092. (e) Solladie-Cavallo, A.; Wipff, G. *Tetrahedron Lett.* **1980**, *21*, 3047. (f) Semmelhack, M. F.; Bisaha, J.; Czarny, M. *J. Am. Chem. Soc.* **1979**, *101*, 768. (g) Semmelhack, M. F.; Clark, G. R.; Farina, R.; Saeman, M. *Ibid.* **1979**, *101*, 217. (h) Semmelhack, M. F.; Clark, G. R. *Ibid.* **1977**, *99*, 1675. (i) Semmelhack, M. F.; Thebtranonth, Y.; Keller, L. *Ibid.* **1977**, *99*, 959. (j) Semmelhack, M. F.; Hall, H. T., Jr.; Yoshihifuji, M. *Ibid.* **1976**, *98*, 6387.

[8] van Meurs, F.; van Konigsveld, H. *J. Organomet. Chem.* **1976**, *118*, 295.

[9] van Meurs, F.; van Konigsveld, H. *J. Organomet. Chem.* **1974**, *78*, 229.

is stronger than that of any other substituent. He also suggested that as the electron-donating group becomes bulkier, the $Cr(CO)_3$ group is rotated away from the electronically favored syn-eclipsed conformation toward the less encumbered anti-eclipsed form and the site of attack is shifted from the meta to para position. The silatrane moiety is electron-donating; we feel, however, that the $Mn(CO)_3^+$ group directs nucleophilic addition on the arene ring more strongly than does the silatrane moiety. The C-2 and C-4 positions would be the most probable sites of attack by the nucleophiles.[10] However, we expected that there might be some steric hindrance to attack of C-2. It is clear that the electronic effect of the silatrane moiety on the cation plays an important role in the addition of nucleophiles.

The different regioselectivity in different reaction media might come from the different solubilities in different reaction media[11] and the availability of coordination to the oxygen atoms on the silatrane. According to the observations and calculations, we could put forward the following hypothesis: the initial formation of an oxygen–lithium or –magnesium bond would be followed by reductive elimination to give C–C bond formation at the ortho position during the addition of Grignard reagents or alkyllithiums in CH_2Cl_2, as opposed to direct alkyl group transfer to give the para adduct in THF. There is an exceptional case, e.g., the addition of EtLi in THF. We do not have any reasonable explanations for this. To verify the above hypothesis, we studied[12] the reaction between $(C_6H_5SiMe_3)Mn(CO)_3^+$ and PhMgBr in CH_2Cl_2. After workup, the para (C-4) adduct was formed as a major product. We expected that the electronic and steric effects of the $SiMe_3$ group would be similar to those of the silatrane moiety. The result shows that the oxygen in the silatrane would be very important in determining the reaction pathways.

For the addition reaction of $NaBH_4$ in CH_2Cl_2 or THF, we were not able to see any noticeable medium effects. The reason might be the insolubility of $NaBH_4$ in both solvents. For the addition reaction of $LiCH_2CN$ and $LiCH_2CO_2CMe_3$ in CH_2Cl_2, the medium effect was not so great as for the addition of RLi and RMgBr. We might expect that for the stabilized carbanions there would be no need of stabilization via coordination as much as for RLi and RMgBr. However, we expected some stabilization during the reaction.

For the addition of *tert*-butyllithium, the meta and para adducts were obtained in a ratio of 1:1.2. The change of reaction medium from THF to THF/TMEDA (1:1 v/v) did not affect the isomer ratio. The anion of 2-lithio-2-methylpropionitrile gave a similar pattern under identical conditions. Changing the reaction medium increased the total yield, and the meta adducts increased in yield at the expense of para addition.

Table VI. Positional Parameters and Equivalent Isotropic Thermal Factors for $[\{\eta^5\text{-1-N}(CH_2CH_2O)_3\text{Si-6-Ph}C_6H_5\}Mn(CO)_3]$

atom	*x/a*	*y/b*	*z/c*	U_{eq},[a] Å²
Mn	0.1895 (1)	0.4945 (1)	0.8013 (1)	0.047 (<1)
Si	0.3357 91)	0.1605 (1)	0.7028 (1)	0.043 (1)
C(1)	0.1485 (5)	0.4280 (4)	0.9151 (4)	0.059 (3)
O(1)	0.1261 (4)	0.3918 (4)	0.9909 (3)	0.094 (3)
C(2)	0.1536 (4)	0.6688 (5)	0.8895 (4)	0.056 (3)
O(2)	0.1353 (3)	0.7807 (3)	0.9489 (3)	0.070 (2)
C(3)	0.3868 (5)	0.5481 (4)	0.8621 (4)	0.057 (3)
O(3)	0.5113 (4)	0.5881 (4)	0.9031 (3)	0.080 (2)
N	0.4617 (4)	0.0179 (4)	0.7585 (3)	0.056 (2)
O(4)	0.2987 (3)	0.0230 (3)	0.5741 (2)	0.058 (2)
C(4)	0.3414 (6)	-0.1147 (5)	0.5581 (4)	0.070 (4)
C(5)	0.4738 (6)	-0.0948 (5)	0.6490 (4)	0.075 (4)
O(5)	0.2407 (3)	0.1437 (3)	0.8039 (2)	0.064 (2)
C(6)	0.2820 (5)	0.0746 (5)	0.8834 (4)	0.062 (3)
C(7)	0.3642 (6)	-0.0444 (6)	0.8238 (4)	0.085 (4)
O(6)	0.5021 (3)	0.2683 (3)	0.7374 (3)	0.063 (2)
C(8)	0.6359 (4)	0.2333 (5)	0.7820 (4)	0.070 (3)
C(9)	0.5978 (6)	0.1118 (6)	0.8300 (5)	0.087 (4)
C(11)	0.2250 (4)	0.2889 (4)	0.6605 (3)	0.043 (2)
C(12)	0.2861 (4)	0.3772 (4)	0.5891 (3)	0.049 (2)
H(12)	0.3501 (4)	0.3307 (4)	0.6421 (3)	0.119 (9)
C(13)	0.2326 (5)	0.5210 (4)	0.6385 (4)	0.053 (3)
C(14)	0.0834 (5)	0.5197 (4)	0.6471 (4)	0.058 (3)
C(15)	-0.0007 (4)	0.3991 (4)	0.6616 (4)	0.057 (3)
C(16)	0.0759 (4)	0.2868 (4)	0.6722 (3)	0.049 (2)
C(21)	0.2388 (4)	0.3071 (4)	0.4573 (3)	0.052 (2)
C(22)	0.2943 (5)	0.3821 (5)	0.3893 (4)	0.069 (3)
C(23)	0.2533 (6)	0.3234 (7)	0.2675 (5)	0.091 (5)
C(24)	0.1577 (6)	0.1889 (7)	0.2122 (5)	0.088 (5)
C(25)	0.1027 (5)	0.1150 (6)	0.2785 (4)	0.074 (3)
C(26)	0.1415 (5)	0.1728 (5)	0.3993 (4)	0.061 (3)

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV shows the yield and product distribution for MeLi addition in several solvents. Usually C-4 adducts were obtained as the major product in nonpolar solvents such as cyclohexane and hexane. There were some differences for ethereal solvents, e.g., THF, diglyme, and diethyl ether. In diethyl ether, the C-2 and C-4 adducts were obtained in the ratio of 43:57. In THF, C-3 and C-4 adducts were obtained in a ratio of 1:10. However, in diglyme, the C-4 adduct was obtained as a sole product. We do not have a plausible explanation for these ethereal solvent effects. When the reaction medium changed to THF/TMEDA (1:1 v/v), the C-3 adducts increased in yield at the expense of C-4 addition. Since compound 1 is completely soluble in TMEDA, the formation of C-2 adducts in TMEDA was expected. In TMEDA, C-2, C-3, and C-4 adducts were obtained in a ratio of 1:2.7:1. The above results show that the charge-controlled reaction would be predominant in the nonpolar solvents and the orbital-controlled reaction would become significant in TMEDA.

In conclusion, it is noted, by using the appropriate nucleophile, either type of adduct, 2 or 4, can be obtained in good yield and, by using the appropriate reaction medium with the same nucleophile, either type of adduct, 2 or 4, can be obtained. The above results indicate that the regioselectivity of nucleophilic addition to 1 is dependent on the nature of the nucleophile and the reaction medium.

Molecular Structure of 2a. The single-crystal X-ray structure of **2a** confirms that Ph nucleophile attacks at the ortho position to the silatrane moiety in the phenyl ring of compound 1 in CH_2Cl_2. An ORTEP drawing of the molecule is shown in Figure 1. Positional parameters and equivalent isotropic thermal factors and bond distances and angles are listed in Tables VI and VII, respectively. The coordination sphere around the manganese atom in **2a** is essentially that of a piano stool, as in the compound $CpMn(CO)_3$.[13] The angles between C(1)–Mn–C(2), C-

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[10] We did some EHT calculations on (phenylsilatrane)$Mn(CO)_3^+$. The parameters for the EHT calculations for the Mn complex are taken from: Albright, T. A.; Hoffmann, P.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3411. The geometry determined for the Cr complex is used. The calculated charge densities for arene carbons for complex 1 are as follows: −0.3615 (C_1), 0.0705 (C_2), 0.0551 (C_3), 0.0706 (C_4), 0.0564 (C_5), 0.0763 (C_6).

[11] A reviewer has suggested that an electron-transfer mechanism (solvent dependent) might occur in some of the addition reactions. Thus, this could be the source of selectivity changes with solvent.

[12] Lee, Y.-A.; Jung, E. H.; Chung, Y. K. Unpublished results.

[13] Berndt, A. F.; Marsh, R. E. *Acta Crystallogr.* **1963**, *16*, 118.

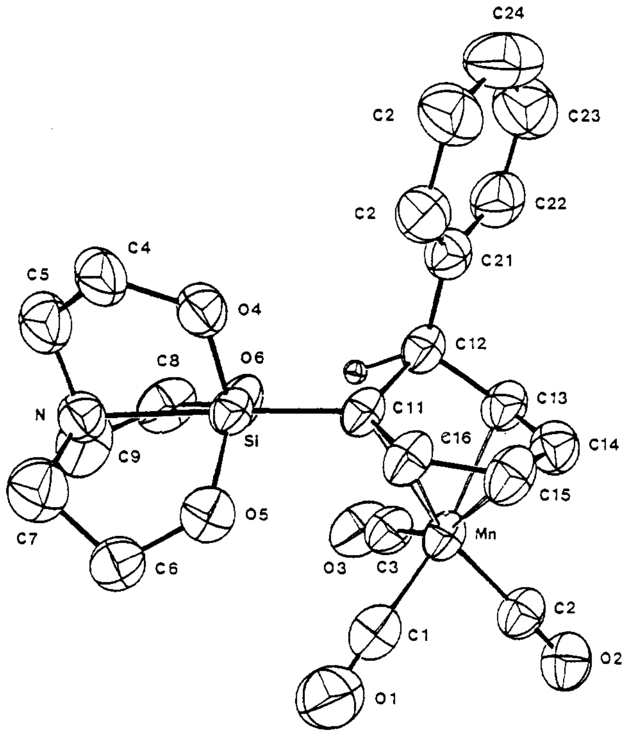

Figure 1. ORTEP drawing of $[\{\eta^5\text{-}1\text{-}N(CH_2CH_2O)_3Si\text{-}6\text{-}PhC_6H_5\}\text{-}Mn(CO)_3]$.

(1)–Mn–C(3), and C(2)–Mn–C(3) of 88.3 (2), 92.9 (2), and 92.2 (2)° are all nearly perpendicular to each other. The dienyl carbon atoms, C(11), C(13), C(14), C(15), and C(16), define a nearly perfect plane (maximum deviation 0.022 (3) Å). The cyclohexadienyl ring is folded about C(11)–C(13) with a dihedral angle of 42.2 (3)°, which is larger than 36.5° in $[\eta^5\text{-}PhC_6H_5]Mn(CO)_3$.[14] The phenyl substituent is positioned exo as expected. Due to the steric congestion of the silatrane and phenyl groups, the bond distance C(11)–C(12) is somewhat longer than the bond distance C(12)–C(13). The carbon–carbon bond distances in the cyclohexadienyl ring are not significantly different from one another, indicating the delocalization of electrons in this portion of the ring, and are very similar to those in $[\eta^5\text{-}PhC_6H_5]Mn(CO)_3$.[14] The carbon–carbon distances in the bent back portion are normal single bond lengths (1.543 (5) and 1.518 (5) Å). The interior angle (103.2 (3)°) at the saturated carbon, C(12), is significantly smaller than the ideal tetrahedral angle. The metal–carbon distances in the cyclohexadienyl ring show a pattern in which the metal atom is significantly closer to the central atom, C(15), of the delocalized set than to the two terminal carbon atoms, C(11) and C(13) [Mn–C(15) = 2.139 (4) Å, Mn–C(11) = 2.269 (4) Å, and Mn–C(13) = 2.193 (4) Å]. The Si atom is displaced significantly from the dienyl plane toward the Mn atoms. The introduction of $Mn(CO)_3^+$ and the addition of Ph^- to phenylsilatrane do not affect the silatrane ring geometry appreciably. The bond lengths of N–Si (2.170 (3) Å) and Si–C(11) (1.896 (3) Å) are similar to those in phenylsilatrane (2.193 (5) and 1.882 (6) Å, respectively).[15] However, the bond length N–Si in **2a** is longer than that (2.127 (6) Å) in $[\eta^5\text{-}3\text{-}(N(CH_2CH_2O)_3Si)\text{-}6\text{-}(Me_3CO_2CCH_2)C_6H_5]Mn(CO)_3$ (**4e**) and the bond length Si–C(11) is similar to that (1.898 (6) Å) in **4e**.[3b] However, other numerical parameters of **2a** are similar to those of **4e**.[3b]

Table VII. Bond Distances (Å) and Bond Angles (deg) for $[\{\eta^5\text{-}1\text{-}N(CH_2CH_2O)_3Si\text{-}6\text{-}PhC_6H_5\}Mn(CO)_3]$

C(1) – Mn	1.806 (4)	C(6) – C(7)	1.509 (6)
C(2) – Mn	1.794 (4)	C(7) – N	1.487 (6)
C(3) – Mn	1.800 (4)	O(6) – C(8)	1.415 (4)
C(11) – Mn	2.269 (4)	C(8) – C(9)	1.535 (7)
C(13) – Mn	2.193 (4)	C(9) – N	1.429 (6)
C(14) – Mn	2.135 (4)	C(11) – C(12)	1.543 (5)
C(15) – Mn	2.139 (4)	C(11) – H(12)	1.242 (5)
C(16) – Mn	2.143 (4)	C(12) – C(13)	1.518 (5)
N – Si	2.170 (3)	C(13) – C(14)	1.384 (5)
O(4) – Si	1.655 (3)	C(14) – C(15)	1.411 (6)
O(5) – Si	1.651 (3)	C(11) – C(16)	1.391 (5)
O(6) – Si	1.653 (3)	C(15) – C(16)	1.426 (5)
C(11) – Si	1.896 (3)	C(12) – C(21)	1.509 (5)
C(1) – O(1)	1.144 (5)	C(21) – C(22)	1.400 (5)
C(2) – O(2)	1.146 (5)	C(22) – C(23)	1.391 (7)
C(3) – O(3)	1.144 (5)	C(23) – C(24)	1.383 (8)
O(4) – C(4)	1.424 (4)	C(24) – C(25)	1.373 (7)
C(4) – C(5)	1.486 (6)	C(21) – C(26)	1.392 (6)
C(5) – N	1.454 (5)	C(25) – C(26)	1.378 (6)
O(5) – C(6)	1.420 (4)		

C(2) – Mn – C(1)	88.3 (2)	C(6) – O(5) – Si	124.8 (2)
C(3) – Mn – C(1)	92.9 (2)	C(7) – C(6) – O(5)	108.1 (3)
C(3) – Mn – C(2)	92.2 (2)	C(6) – C(7) – N	105.7 (3)
O(4) – Si – N	83.7 (1)	C(8) – O(6) – Si	123.9 (3)
O(5) – Si – N	82.1 (1)	C(9) – C(8) – O(6)	109.6 (3)
O(5) – Si – O(4)	117.3 (2)	C(8) – C(9) – N	107.6 (4)
O(6) – Si – N	83.1 (1)	C(12) – C(11) – Si	120.8 (2)
O(6) – Si – O(4)	116.2 (2)	C(16) – C(11) – Si	121.4 (3)
O(6) – Si – O(5)	122.0 (2)	C(16) – C(11) – C(12)	116.7 (3)
C(11) – Si – N	177.7 (2)	C(13) – C(12) – C(11)	103.2 (3)
C(11) – Si – O(4)	98.4 (1)	C(21) – C(12) – C(11)	116.4 (3)
C(11) – Si – O(5)	96.1 (1)	C(21) – C(12) – C(13)	111.8 (3)
C(11) – Si – O(6)	96.7 (1)	C(14) – C(13) – C(12)	119.7 (4)
O(1) – C(1) – Mn	176.8 (4)	C(15) – C(14) – C(13)	119.3 (3)
O(2) – C(2) – Mn	177.4 (4)	C(16) – C(15) – C(14)	117.5 (3)
O(3) – C(3) – Mn	177.1 (4)	C(15) – C(16) – C(11)	122.0 (3)
C(5) – N – Si	104.0 (2)	C(22) – C(21) – C(12)	118.2 (4)
C(7) – N – Si	104.7 (2)	C(26) – C(21) – C(12)	123.8 (3)
C(7) – N – C5	110.8 (4)	C(26) – C(21) – C(22)	117.9 (4)
C(9) – N – Si	104.9 (3)	C(23) – C(22) – C(21)	120.7 (5)
C(9) – N – C5	117.0 (4)	C(24) – C(23) – C(22)	120.1 (5)
C(9) – N – C7	113.9 (4)	C(25) – C(24) – C(23)	119.5 (5)
C(4) – O(4) – Si	122.8 (2)	C(26) – C(25) – C(24)	120.9 (5)
C(5) – C(4) – O(4)	109.7 (4)	C(25) – C(26) – C(21)	120.9 (4)
C(4) – C(5) – N	109.1 (4)		

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Supplementary Material Available: Tables of anisotropic thermal parameters, positional and thermal parameters of hydrogen atoms, and least-squares planes for $[\{\eta^5\text{-}1\text{-}N(CH_2CH_2O)_3Si\text{-}6\text{-}PhC_6H_5\}Mn(CO)_3]$ (**2a**) (3 pages); a listing of observed and calculated structure factors for **2a** (14 pages). Ordering information is given on any current masthead page.

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