Preparation and Reactivity of Tricarbonyl(η-silatranylarene)manganese Cations Bearing Functional Substrates

Su Seong Lee, Joon-Sik Lee, and Young Keun Chung*

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-742, Korea

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[{η^6-*p*-$RC_6H_4Si(OCH_2CH_2)_3N$}$Mn(CO)_3$]$^+$, **2** (R) (R = Me, Cl, OMe, and *t*-Bu), and [{$C_6H_5CH_2Si(OCH_2CH_2)_3N$}$Mn(CO)_3$]$^+$, **5**, have been obtained from the appropriate silatranyl arenes with $Mn(CO)_5ClO_4$ in CH_2Cl_2. The high reactivity of compound **2** (Cl) is utilized in the preparation of other functionally substituted silatranyl arene complexes by substitution reaction with amines or alkoxides. Nucleophilic additions of several kinds of nucleophiles to **2** have been studied. In CH_2Cl_2, the *ortho* adducts have been obtained as a sole product. In THF, *ortho* and *meta* adducts have been obtained. The ratio of *ortho* to *meta* adduct depends on the substituent on the silatranyl arene ring. The directing effect of the silatranyl group is not as great as in [{$C_6H_5Si(OCH_2CH_2)_3N$}$Mn(CO)_3$]ClO_4, **1**. Nucleophilic addition to **5** in CH_2Cl_2 or in THF has also been studied. The regioselectivity of nucleophilic addition to **5** is very different from those of compounds **2**. In most of the nucleophilic additions to **5**, *meta* adduct was obtained as a major product. The directing effect of the silatranyl group in **5** follows the directing effect of the methoxy group in (arene)$Mn(CO)_3^+$.

Introduction

Activation of aromatic compounds toward nucleophilic attack represents an attractive method for the synthesis of polyfunctionalized derivatives.[1] The use of (arene)$Mn(CO)_3^+$ cations have been established by us[2] and others.[3] The factors influencing the observed regiochemistry of nucleophilic attack are very important and need clarification.

Recently, we reported[4] the use of phenylsilatrane as a π-coordinating ligand for transition metals. The chemistry of $M(CO)_3$ (M = Cr and W) and $Mn(CO)_2L^+$ (L = CO and $P(OMe)_3$) derivatives of phenylsilatrane has been studied. The selectivity of the nucleophile addition to the phenylsilatrane derivative of $Mn(CO)_2L^+$ is strongly dependent on the nucleophile and reaction medium.

To elucidate the possible directing effect of the substituent on the coordinated phenylsilatrane ring, we have prepared [$N(CH_2CH_2O)_3SiC_6H_4R$-*p*)$Mn(CO)_3$]$^+$, **2** (R), and [{$C_6H_5CH_2Si(OCH_2CH_2)_3N$}$Mn(CO)_3$]$^+$, **5**, and studied their reactivities with nucleophiles.

Experimental Section

General Considerations. All solvents were purified by standard methods, and reagent-grade chemicals were used without further purification.

Elemental analyses were performed at the Korea Basic Science Center. Instruments used in this work were a Varian XL-200 NMR spectrometer and a Perkin-Elmer 782 infrared spectrophotometer (spectra were measured as films on NaCl by evaporation of solvent).

The synthesis and purification of the silatranes were reported earlier.[5] Compound **2** was synthesized as previously described.[4] By published procedures, nucleophilic addition of $NaBH_4$, MeLi, PhLi, MeMgBr, PhMgBr, and NaCN to compounds **2** and **5** gave the corresponding cyclohexadienyl complexes **3** and **6**, respectively. Compounds **2**, **3**, **5**, and **6** are new, and some selected analytical and spectroscopic data are given in Table I.

Synthesis of 2 (R). A typical procedure is as follows: *p*-$ClC_6H_4Si(OCH_2CH_2)_3N$ (1.71 g, 6 mmol) was added to the solution of $Mn(CO)_5OClO_3$ (1.47 g, 5 mmol) in CH_2Cl_2 (150 mL). The reaction mixture was refluxed for 20 h. After removal of any solids, the filtrate was concentrated and precipitated by using excess diethyl ether. Yield: 0.68 g (26%). The yields of **2** (Me), **2** (OMe), and **2** (*t*-Bu) were 81%, 86%, and 90%, respectively.

Reaction between 2 (Cl) and Amines or Alkoxides. A typical procedure is as follows: To a stirred solution of **2** (Cl) (0.157 g, 0.3 mmol) in 10 mL of MeOH was added NaOMe (0.05 g). After the solution was stirred for 10 min, NH_4PF_6 (0.326 g) in 10 mL of water was added. The resulting yellow precipitates were collected, washed with water, and washed with diethyl ether.

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Table I. Characterization of New Compounds

compd	
2 (Cl)	mp 202 °C dec; IR ν_{CO} 2070, 2015 cm^{-1}; ^1H NMR[a] δ 7.03 (d, 7.1 Hz, 2 H), 6.75 (d, 7.1 Hz, 2 H), 3.94 (t, 5.5 Hz, 6 H, OCH_2), 3.23 (t, 5.5 Hz, 6 H, NCH_2) ppm
2 (Me)	mp 191 °C dec; IR ν_{CO} 2050, 2000 cm^{-1}; ^1H NMR[a] δ 6.83 (d, 6.7 Hz, 2 H), 6.35 (d, 6.7 Hz, 2 H), 3.93 (t, 5.7 Hz, 6 H, OCH_2), 3.21 (t, 5.7 Hz, 6 H, NCH_2), 2.51 (s, 3 H, Me) ppm
2 (OMe)	mp 193 °C dec; IR ν_{CO} 2075, 1997 cm^{-1}; ^1H NMR[a] δ 6.94 (d, 6.0 Hz, 2 H), 6.20 (d, 6.0 Hz, 2 H), 4.10 (s, 3 H, OMe), 3.93 (t, 5.5 Hz, 6 H, OCH_2), 3.20 (t, 5.5 Hz, 6 H, NCH_2) ppm. Anal. Calcd for $C_{16}H_{19}ClMnNO_{11}Si$: C, 33.99; H, 3.39; N, 2.48. Found: C, 33.94; H, 3.43; N, 2.42
2 (*t*-Bu)	mp 211 °C dec; IR ν_{CO} 2050, 2000, 1985 cm^{-1}; ^1H NMR[a] δ 6.74 (d, 7.3 Hz, 2 H), 6.63 (d, 7.3 Hz, 2 H), 3.95 (t, 6.1 Hz, 6 H, OCH_2), 3.24 (t, 6.1 Hz, 6 H, NCH_2), 1.46 (s, 9 H, *t*-Bu) ppm. Anal. Calcd for $C_{19}H_{25}ClMnNO_{10}Si$: C, 41.81; H, 4.62; N, 2.57. Found: C, 41.94; H, 4.65; N, 2.58
2 (OEt)	IR ν_{CO} 2060, 2000 cm^{-1}; ^1H NMR[a] δ 6.93 (d, 7.3 Hz, 2 H), 6.17 (d, 7.3 Hz, 2 H), 4.39 (q, 6.8 Hz, 2 H, OCH_2), 3.93 (t, 5.8 Hz, 6 H, OCH_2), 3.21 (t, 5.8 Hz, 6 H, NCH_2), 1.45 (t, 6.8 Hz, 3 H, CH_3) ppm
2 (NH_2)	mp 219 °C dec; IR ν_{CO} 2050, 1995, 1960 cm^{-1}; ^1H NMR[a] δ 7.07 (br 2 H, NH_2), 6.69 (d, 7.4 Hz, 2 H), 5.67 (d, 7.4 Hz, 2 H), 3.90 (t, 6.0 Hz, 6 H, OCH_2), 3.17 (t, 6.0 Hz, 6 H, NCH_2) ppm. Anal. Calcd for $C_{15}H_{18}ClMnN_2O_{10}Si$: C, 35.69; H, 3.59; N, 5.55. Found: C, 35.21; H, 3.69; N, 5.41
2 (NEt_2)	IR ν_{CO} 2045, 1970 cm^{-1}; ^1H NMR[a] δ 6.66 (d, 7.6 Hz, 2 H), 5.66 (d, 7.6 Hz, 2 H), 3.92 (t, 5.6 Hz, 6 H, OCH_2), 3.62 (q, 7.2 Hz, 4 H, NCH_2), 3.18 (t, 5.6 Hz, 6 H, NCH_2), 1.30 (t, 7.2 Hz, 6 H, CH_3) ppm
2 (NH-*n*-Pr)	mp 160 °C dec; IR ν_{CO} 2040, 1975 cm^{-1}; ^1H NMR[a] δ 7.4 (br, 1 H, NH), 6.67 (d, 6.8 Hz, 2 H), 5.61 (d, 6.8 Hz, 2 H), 3.90 (t, 6.1 Hz, 6 H, OCH_2), 3.33 (m, 2 H, NCH_2), 3.17 (t, 6.1 Hz, 6 H, NCH_2), 1.72 (m, 2 H, $-CH_2-$), 0.98 (t, 7.6 Hz, 3 H, CH_3) ppm. Anal. Calcd for $C_{18}H_{25}FMnN_2O_{10}PSi$: C, 36.50; H, 4.08; N, 4.73. Found: C, 36.19; H, 4.40; N, 4.34.
2 (NH-*n*-Bu)	mp 181 °C dec; IR ν_{CO} 2030, 1975 cm^{-1}; ^1H NMR[a] δ 7.36 (br, 1 H, NH), 6.65 (d, 7.4 Hz, 2 H), 5.63 (d, 7.4 Hz, 2 H), 3.90 (t, 6.0 Hz, 6 H, OCH_2), 3.34 (m, 2 H, NCH_2), 3.16 (t, 6.0 Hz, 6 H, NCH_2), 1.59 (m), 1.39 (m), 0.92 (m) ppm. Anal. Calcd for $C_{19}H_{26}ClMnN_2O_{10}Si$: C, 40.69; H, 4.67; N, 4.99. Found: C, 40.52; H, 4.91; N, 5.14.
5[b]	IR ν_{CO} 2058, 1993 cm^{-1}; ^1H NMR[a] δ 6.83 (d, 6.7 Hz, 2 H, Ph), 6.37 (m, 3 H, Ph), 3.74 (t, 5.9 Hz, 6 H, OCH_2), 3.00 (t, 5.9 Hz, 6 H, NCH_2), 1.90 (s, 2 H, CH_2) ppm. Anal. Calcd for $C_{16}H_{19}ClMnNO_{10}Si$: C, 38.14; H, 3.80; N, 2.78. Found: C, 39.36; H, 4.02; N, 2.93
3 (R = Me, Nu = Me)	HRMS M^+ calcd 419.0584, obsd 419.0591 ^1H NMR of **3a**[c] δ 5.65 (dd, 1.7, 5.1 Hz, 1 H, H^3), 4.94 (d, 5.1 Hz, 1 H, H^2), 3.76 (t, 5.8 Hz, 6 H, OCH_2), 2.99 (dd, 1.7, 5.1 Hz, 1 H, H^5), 2.79 (t, 5.8 Hz, 6 H, NCH_2), 2.7 (m, 1 H, H^6), 1.79 (s, 3 H, CH_3), 0.40 (d, 6.4 Hz, 3 H, CH_3) ppm. IR of 3a ν_{CO} 1990, 1920, 1890 cm^{-1} ^1H NMR of **3b**[c,d] δ 5.75 (d, 1 H, H^3), 4.45 (d, 1 H, H^4), 3.80 (t, 5.8 Hz, 6 H, OCH_2), 3.35 (dd, 1 H, H^1), 2.81 (t, 5.8 Hz, 6 H, NCH_2), 1.61 (s, 3 H, CH_3), 0.43 (d, 3 H, Me) ppm ^1H NMR of **3b**[c,d] δ 5.75 (d, 1 H, H^3), 4.45 (d, 1 H, H^4), 3.80 (t, 5.8 Hz, 6 H, OCH_2), 3.35 (dd, 1 H, H^1), 2.81 (t, 5.8 Hz, 6 H, NCH_2), 1.61 (s, 3 H, CH_3), 0.43 (d, 3 H, Me) ppm
3 (R = Me, Nu = Ph)	Anal. Calcd for $C_{22}H_{24}MnNO_6Si$: C, 55.00; H, 5.06; N, 2.85. Found: C, 54.88; H, 5.02; N, 2.91 ^1H NMR of **3a**[c] δ 7.08 (m, 5 H, Ph), 5.64 (dd, 1.5, 5.1 Hz, 1 H, H^3), 5.09 (d, 5.1 Hz, 1 H, H^2), 4.04 (d, 5.8 Hz, 1 H, H^6), 3.68 (t, 5.8 Hz, 6 H, OCH_2), 3.17 (dd, 1.5, 5.8 Hz, 1 H, H^5), 2.75 (t, 5.8 Hz, 6 H, NCH_2), 1.84 (s, 3 H, CH_3) ppm; mp of **3a** 184 °C dec; IR of **3a** ν_{CO} 1995, 1916 cm^{-1} ^1H NMR of **3b**[4]c δ 7.13 (m, 5 H, Ph), 5.76 (dd, 1.3, 5.3 Hz, 1 H, H^3), 4.51 (d, 5.3 Hz, 1 H, H^4), 3.81 (t, 5.8 Hz, 6 H, OCH_2), 3.75 (d, 5.8 Hz, 1 H, H^6), 3.53 (dd, 1.3, 5.8 Hz, 1 H, H^1), 2.84 (t, 5.8 Hz, 6 H, NCH_2), 1.68 (s, 3 H, CH_3) ppm
3 (R = Me, Nu = H)	Anal. Calcd for $C_{16}H_{20}MnNO_6Si$: C, 47.41; H, 4.97; N, 3.34. Found: C, 47.23; H, 4.97; N, 3.46; IR of mixture ν_{CO} 1993, 1899 cm^{-1} ^1H NMR of **3a**[c,d] δ 5.79 (dd, 1.3, 5.1 Hz, 1 H, H^3), 5.00 (d, 5.1 Hz, 1 H, H^2), 3.76 (t, 5.9 Hz, 6 H, OCH_2), 2.80 (t, 5.9 Hz, 6 H, NCH_2), 1.96 (d, 11.3 Hz, 1 H, $H^{6\text{-}e}_{xo}$), 1.79 (s, 3 H, CH_3) ppm ^1H NMR of **3b**[c] δ 5.85 (dd, 1.3, 5.3 Hz, 1 H, H^3), 4.53 (d, 5.3 Hz, 1 H, H^4), 3.81 (t, 5.9 Hz, 6 H, OCH_2), 3.16 (dt, 1.3, 5.8 Hz, 1 H, H^1), 2.85 (t, 5.9 Hz, 6 H, NCH_2), 2.54 (ddd, 1.2, 5.8, 12.6 Hz, 1 H, H^6), 2.19 (d, 12.6 Hz, 1 H, $H^{6\text{-exo}}$), 1.54 (s, 3 H, CH_3) ppm
3 (R = Me, Nu = CN)	Anal. Calcd for $C_{17}H_{19}MnN_2O_6Si$: C, 47.44; H, 4.45; N, 6.51. Found: C, 48.06; H, 4.32; N, 6.02. IR of mixture ν_{CN} 2208 cm^{-1}, ν_{CO} 2000, 1905 cm^{-1} ^1H NMR of **3a**[c,d] δ 5.82 (dd, 1.4, 5.2 Hz, 1 H, H^3), 5.16 (d, 5.2 Hz, 1 H, H^2), 3.80 (t, 5.8 Hz, 6 H, OCH_2), 2.84 (t, 5.8 Hz, 6 H, NCH_2), 1.91 (s, 3 H, CH_3) ppm ^1H NMR of **3b**[c] δ 5.94 (dd, 1.1, 5.5 Hz, 1 H, H^3), 4.75 (d, 5.5 hz, 1 H, H^4), 3.83 (t, 5.8 Hz, 6 H, OCH_2), 3.46 (dd, 1.1, 5.6 hz, 1 H, H^1), 3.22 (dd, 1.3, 5.6 Hz, 1 H, H^6), 2.81 (t, 5.8 Hz, 6 H, NCH_2), 1.66 (s, 3 H, CH_3) ppm
3 (R = Cl, Nu = Me)	HRMS M^+ calcd 439.0046, obsd 439.0075 ^1H NMR of **3a**[c,d] δ 6.00 (d, 2.0, 5.4 Hz, 1 H, H^3), 4.91 (d, 5.4 Hz, 1 H, H^2), 3.76 (t, 5.9 hz, 6 H, OCH_2), 3.33 (dd, 5.9 Hz, 1 H, H^6), 2.81 (t, 5.9 Hz, 6 H, NCH_2), 0.46 (d, 6.6 Hz, 3 H, CH_3) ppm; mp of **3a** 174 °C dec; IR of **3a** ν_{CO} 2000, 1905 cm^{-1}
3 (R = Cl, Nu = Ph)	Anal. Calcd for $C_{21}H_{21}ClMnNO_6Si$: c, 50.26; H, 4.22; N, 2.79. Found: C, 50.62; H, 4.34; N, 2.70 ^1H NMR of **3a**[c] δ 7.1 (m, 5 H, Ph), 5.98 (dd, 2.0, 5.2 Hz, 1 H, H^3), 5.05 (dd, 0.8, 5.2 Hz, 1 H, H^2), 4.20 (d, 6.1 Hz, 1 H, H^6), 3.68 (t, 5.9 Hz, 6 H, OCH_2), 3.52 (dd, 2.0, 6.1 Hz, 1 H, H^5), 2.76 (t, 5.9 Hz, 6 H, NCH_2) ppm; mp of **3a** 203 °C; IR of **3a** ν_{CO} 2010, 1915 cm^{-1} ^1H NMR of **3b**[c] δ 7.26 (m, 5 H, Ph), 5.73 (dd, 1.6, 5.7 Hz, 1 H, H^3), 5.01 (dd, 1.6, 5.7 Hz, 1 H, H^4), 4.18 (dd, 1.6, 5.2 Hz, 1 H, H^1), 3.82 (t, 5.7 Hz, 6 H, OCH_2), 2.94 (t, 5.7 Hz, 6 H, NCH_2) ppm
3 (R = Cl, Nu = H)	Anal. Calcd for $C_{15}H_{17}ClMnNO_6Si$: C, 42.31; H, 4.02; N, 3.29. Found: C, 42.54; H, 4.08; N, 3.28. IR of mixture ν_{CO} 2000, 1920 cm^{-1} ^1H NMR of **3a**[c,d] δ 6.11 (dd, 1.8, 5.1 Hz, 1 H, H^3), 4.96 (d, 5.1 Hz, 1 H, H^2), 3.76 (t, 5.8 Hz, 6 H, OCH_2), 2.80 (t, 5.8 Hz, 6 H, NCH_2), 2.06 (d, 11.1 Hz, 1 H, $H^{6\text{-exo}}$) ppm ^1H NMR of **3b**[c] 5.83 (dd, 1.5, 5.7 Hz, 1 H, H^3), 5.10 (dd, 1.5, 5.7 Hz, 1 H, H^4) 3.81 (t, 5.8 Hz, 6 H, OCH_2), 3.51 (dt, 1.5, 5.2 Hz, 1 H, H^1), 3.04 (ddd, 1.6, 5.2, 12.3 Hz, 1 H, $H^{6\text{-exo}}$), 2.86 (t, 5.8 Hz, 6 H, NCH_2), 2.55 (d, 12.3 Hz, 1 H, $H^{6\text{-exo}}$) ppm

Table I (Continued) Characterization of New Compounds

compd	
3 (R = Cl, Nu = CN)	Anal. Calcd for $C_{16}H_{16}ClMnN_2O_6Si$: 42.63; H, 3.58; N, 6.21. Found: C, 42.53; H, 3.86; N, 5.39. IR of mixture ν_{CN} 2206 cm^{-1}, ν_{CO} 2000, 1915 cm^{-1} ^1H NMR of **3a**[c,d] δ 6.18 (dd, 1.9, 5.5 Hz, 1 H, H^3), 5.15 (d, 5.7 Hz, 1 H, H^2), 3.85 (t, 6.1 Hz, 6 H, OCH_2), 3.16 (dd, 1.9, 5.7, Hz, 1 H, H^5), 2.93 (t, 6.1 Hz, 6 H, NCH_2) ppm ^1H NMR of **3b**[c] δ 5.92 (dd, 1.5, 5.8 Hz, 1 H, H^3), 5.26 (dd, 1.4, 5.8 Hz, 1 H, H^4), 3.90 (dd, 6.3, 1.5 Hz, 1 H, H^6), 3.81 (t, 6.1 Hz, 6 H, OCH_2), 3.57 (dd, 1.5, 6.3 Hz, 1 H, H^1), 2.89 (t, 6.1 Hz, 6 H, NCH) ppm
3 (R =OMe, Nu = Me)	mp 200 °C dec; IR ν_{CO} 2000, 1925, 1890 cm^{-1}. Anal. Calcd for $C_{17}H_{22}MnNO_7Si$: C, 46.90; H, 5.09; N, 3.22. Found: C, 46.81; H, 5.09; N, 3.19 ^1H NMR of **3a**[c] δ 5.70 (d, 5.1 Hz, 1 H, H^3), 4.99 (m, 1 H, H^2), 3.76 (t, 5.1 Hz, 6 H, OCH_2), 3.44 (s, 3 H, OMe), 2.99 (m, 1 H, H^5), 2.80 (t, 5.1 Hz, 6 H, NCH_2), 0.43 (d, 6.3 hz, 3 H, CH_3) ppm
3 (R = OMe, Nu = Ph)	mp 204 °C dec; IR ν_{CO} 1995, 1915 cm^{-1}. Anal. Calcd for $C_{22}H_{24}MnNO_7Si$: C, 53.12; H, 4.86; N, 2.82. Found: C, 53.26; H, 4.96; N, 2.76 ^1H NMR of **3a**[c] δ 7.16 (m, 5 H, Ph), 5.69 (dd, 2.3, 5.5 Hz, 1 H, H^3), 5.13 (dd, 0.7, 5.5 Hz, 1 H, H^2), 4.16 (d, 6.1 Hz, 1 H, H^6), 3.69 (t, 5.9 Hz, 6 H, OCH_2), 3.44 (s, 3 H, OMe), 3.20 (dd, 2.3, 6.1 Hz, 1 H, H^5), 2.77 (t, 5.9 Hz, 6 H, NCH_2) ppm
3 (R = OMe, Nu = CN)	mp 131 °C dec; IR ν_{CN} 2212 cm^{-1}, ν_{CO} 2000, 1935, 1915 cm^{-1}. Anal. Calcd for $C_{17}H_{19}MnN_2O_7Si$: C, 45.74; H, 4.29; N, 6.28. Found: C, 45.68; H, 4.30; N, 6.00 ^1H NMR of **3a**[c,d] δ 5.84 (dd, 2.2, 5.6 Hz, 1 H, H^3), 5.23 (d, 5.6 Hz, 1 H, H^2), 3.91 (d, 5.4 Hz, 1 H, H^5), 3.79 (t, 5.9 Hz, 6 H, OCH_2), 3.52 (s, 3 H, OMe), 2.85 (t, 5.9 Hz, 6 H, NCH_2) ppm
3 (R = OMe, Nu = H)	Anal. Calcd for $C_{16}H_{20}MnNO_7Si$: C, 45.61; H, 4.78; N, 3.32. Found: C, 45.76; H, 4.81; N, 3.32. IR of mixture ν_{CO} 2000, 1905 cm^{-1} ^1H NMR of **3a**[c,d] δ 5.80 (dd, 2.2, 5.6 Hz, 1 H, H^3), 5.03 (d, 5.6 hz, 1 H, H^2), 3.74 (t, 5.6 hz, 6 H, OCH_2), 3.43 (s, 3 H, OMe), 2.78 (t, 5.6 Hz, 6 H, NCH_2), 2.71 (dd, 5.8, 2.2 Hz, 1 H, H^5), 2.04 (s, 12.7 Hz, 1 H,$H^{6\text{-exo}}$) ppm ^1H NMR of **3c**[c,d] δ 5.20 (dd, 6.8, 0.6 Hz, 2 H, $H^{2,4}$), 3.91 (t, 5.8 Hz, 6 H, OCH_2), 3.34 (s, 3 H, OMe), 2.96 (t, 5.8 Hz, 6 H, NCH_2) ppm
3 (R = *t*-Bu, Nu = H)	Anal. Calcd for $C_{19}H_{26}MnNO_6Si$: C, 51.00; H, 5.86; N, 3.13. Found: C, 51.09; H, 5.98; N, 3.05. IR of mixture ν_{CO} 1990, 1890 cm^{-1} ^1H NMR of **3a**[c,d] δ 5.83 (d, 1 H, H^3), 5.0 (d, 1 H, H^2), 3.77 (t, 5.9 Hz, 6 H, OCH_2), 2.81 (t, 5.9 Hz, 6 H, NCH_2), 1.90 (d, 8.6 Hz, 1 H, $H^{6\text{-exo}}$), 1.16 (s, 9 H, *t*-Bu) ppm ^1H NMR of **3b**[c] δ 5.85 (dd, 0.7, 5.6 Hz, 1 H, H^3), 4.70 (d, 5.6 Hz, 1 H, H^4), 3.82 (t, 5.9 Hz, 6 H, OCH_2), 3.15 (d, 5.9 Hz, 1 H, H^1), 2.87 (t, 5.9 Hz, 6 H, NCH_2), 2.78 (m, 1 H, H^6), 2.11 (d, 13.2 Hz, 1 H, $H^{6\text{-exo}}$), 1.01 (s, 9 H, *t*-Bu) ppm
3 (R = *t*-Bu, Nu = Me)	mp 205 °C dec; IR ν_{CO} 1990, 1925, 1875 cm^{-1}. Anal. Calcd for $C_{20}H_{28}MnNO_6Si$: C, 52.06; H, 6.12; N, 3.04. Found: C, 52.05; H, 6.20; N, 2.92 ^1H NMR of **3a**[c] δ 5.71 (dd, 1.7, 5.4 Hz, 1 H, H^3), 4.89 (d, 5.4 Hz, 1 H, H^2), 3.75 (t, 5.9 Hz, 6 H, OCH_2), 2.96 (dd, 1.7, 5.9 Hz, H^5), 2.79 (t, 5.9 Hz, 6 H, NCH_2), 2.69 (m, 1 H, H^6), 1.14 (s, 9 H, *t*-Bu), 0.33 (d, 6.3 Hz, 3 H, CH_3) ppm
3 (R = *t*-Bu, Nu = Ph)	mp 208 °C dec; IR ν_{CO} 1995, 1930, 1900 cm^{-1}. Anal. Calcd for $C_{25}H_{30}MnNO_6Si$: C, 57.36; H, 5.78; N, 2.68. Found: C, 57.64; H, 5.81; N, 2.64 ^1H NMR of **3a**[c] δ 7.0 (m, 5 H, Ph), 5.72 (dd, 1.7, 5.6 Hz, 1 H, H^3), 5.21 (d, 5.6 Hz, 1 H, H^2), 4.05 (d, 6.0 Hz, 1 H, H^6), 3.69 (t, 5.9 Hz, 6 H, OCH_2), 3.26 (dd, 1.7, 6.0 Hz, 1 H, H^5), 2.76 (t, 5.9 Hz, 6 H, NCH_2), 1.02 (s, 9 H, *t*-Bu) ppm
3 (R = *t*-Bu, Nu = CN)	Anal. Calcd for $C_{20}H_{25}MnN_2O_6Si$: C, 50.85; H, 5.33; N, 5.93. Found: C, 50.62; H, 5.40; N, 5.57. IR of mixture ν_{CN} 2216 cm^{-1}, ν_{CO} 2000, 1915 cm^{-1} ^1H NMR of **3a**[c,d] δ 5.91 (dd, 1 H, H^3), 5.15 (d, 5.6 Hz, 1 H, H^2), 3.81 (t, 5.9 Hz, 6 H, OCH_2), 2.87 (t, 5.9 Hz, 6 H, NCH_2), 2.79 (dd, 1.7, 5.9 Hz, 1 H, H^5), 1.22 (s, 9 H, *t*-Bu) ppm ^1H NMR of **3b**[c] δ 5.93 (dd, 1.2, 5.9 Hz, 1 H, H^3), 4.93 (dd, 0.5, 5.2 Hz, 1 H, H^4), 3.82 (t, 5.9 Hz, 6 H, OCH_2), 3.72 (dd, 0.5, 6.2 hz, 1 H, H^6), 3.15 (dd, 1.2, 6.2 Hz, 1 H, H^1), 2.89 (t, 5.9 Hz, 6 H, NCH_2), 1.15 (s, 9 H, *t*-Bu) ppm
3 (R = NH_2, Nu = H)	mp 191 °C dec; IR ν_{CO} 1990, 1880 cm^{-1}; HRMS M^+ calcd 406.0388, obsd 406.0389 ^1H NMR of **3a**[c,d] δ 5.56 (dd, 1.2, 5.4 Hz, 1 H, H^3), 5.08 (d, 5.4 Hz, 1 H, H^2), 3.76 (t, 5.9 Hz, 6 H, OCH_2), 2.95 (br, 2 H, NH_2), 2.80 (t, 5.9 Hz, 6 H, NCH_2), 2.52 (dd, 5.6, 1.2 Hz, 1 H, H^5), 2.09 (d, 12.9 Hz, 1 H, $H^{6\text{-exo}}$) ppm
6 (Nu = Me)	Anal. Calcd for $C_{17}H_{22}MnNO_6Si$: C, 48.71; H, 5.25; N, 3.34. Found: C, 48.37; H, 5.26; N, 3.21 ^1H NMR of **6a**[c,d] δ 5.56 (td, 1 H, H^4), 4.91 (d, 1 H, H^3), 4.64 (t, 1 H, H^5, 1.42 (d, 1 H, CH_2), 1.15 (d, 1 H, CH_2), 0.53 (d, 6.35 Hz, 3 H, CH_3) ppm ^1H NMR of **6b**[c] δ 5.73 (d, 5.1 Hz, 1 H, H^2), 4.70 (t, 6.3 Hz, 1 H, H^3), 3.78 (t, 5.8 Hz, 6 H, OCH_2), 3.17 (d, 5.4 Hz, 1 H, H^6), 3.08 (t, 6.3 Hz, 1 H, H^4), 2.85 (t, 5.8 Hz, 6 H, NCH_2), 2.56 (m, 1 H, H^5), 1.54 (d, 12.4 Hz, 1 H, CH_2), 1.03 9d, 12.4 Hz, 1 H, CH_2), 0.41 (d, 6.3 Hz, 3 H, CH_3) ppm; mp of **3a** 174 °C dec; IR of **3a** ν_{CO} 1996, 1904 cm^{-1}
6 (Nu = Ph)	Anal. Calcd for $C_{22}H_{27}MnN_6OSi$: C, 54.89; H, 4.99; N, 2.91. Found: C, 54.85; H, 5.06; N, 2.76 ^1H NMR of **6a**[c] δ 7.17 (m, 2 H, Ph), 7.02 (m, 3 H, Ph), 5.60 (td, 1.5, 5.4 Hz, 1 H, H^3), 4.94 (d, 5.1 Hz, 1 H, H^2), 4.65 (td, 1.0, 5.4 Hz, 1 H, H^4), 4.00 (d, 5.6 Hz, 1 H, H^6), 3.57 (dt, 5.6, 1.6.6 hz, 3 H, OCH_2), 3.40 (dt, 5.6, 16.6 Hz, 3 H, OCH_2), 3.25 (td, 1.2, 5.9 Hz, 1 H, H^5), 2.62 (t, 5.9 Hz, 6 H, NCH_2), 1.40 (d, 13.7 Hz, 1 H, CH_2), 1.13 (d, 13.7 Hz, 1 H, CH_2) ppm ^1H NMR of **6b**[c,d] δ 5.73 (d, 4.15 Hz, 1 H, H^3), 4.92 (t, 6.1 Hz, 1 H, H^4), 3.25 (t, 1 H, H^5), 2.69 (t, 5.8 Hz, 6 h, NCH_2), 1.53 (d, 12.7 Hz, 1 H, CH_2), 1.08 (d, 12.7 Hz, 1 H, CH_2) ppm; mp of **6b** 195 °C dec; IR of **6b** ν_{CO} 1998, 1912 cm^{-1} ^1H NMR of **6c**[c,d] δ 5.09 (d, 6.6 Hz, 2 H, $H^{2,}$), 4.74 (t, 6.1 Hz, 1 H, H^6), 2.85 (t, 5.8 Hz, 6 H, NCH_2), 1.94 (s, 2 H, CH_2) ppm
6 (Nu = H)	Anal. Calcd for $C_{16}H_{20}MnNO_6Si$: C, 47.41; H, 4.94; N, 3.46. Found: C, 47.88; H, 4.70; N, 3.23. IR of mixture ν_{CO} 1997, 1900 cm^{-1} ^1H NMR of **6a**[c,d] δ 5.68 (t, 1 H, H^3), 4.52 (t, 5.1 Hz, 1 H, H^2), 3.71 (t, 5.9 Hz, 6 H, OCH_2), 2.00 (d, 10.0 Hz, 1 H, $H^{6\text{-exo}}$), 1.36 (d, 13.3 Hz, 1 H, CH_2), 1.07 (d, 13.3 Hz, 1 H, CH_2) ppm ^1H NMR of **6b**[c] δ 5.90 (d, 5.1 Hz, 1 H, H^3), 4.78 (t, 6.3 Hz, 1 H, H^4), 3.79 (t, 5.9 Hz, 6 H, OCH_2), 2.85 (t, 5.9 Hz, 6 H, NCH_2), 2.70 (m, 3 H, $H^{1,4,6\text{-endo}}$), 2.10 (d, 12.7 Hz, 1 H, $H^{6\text{-exo}}$), 1.56 (d, 12.7 Hz, 1 H, CH_2), 0.97 (d, 12.7 Hz, 1 H, CH_2) ppm

Table I. (Continued)

compd	
6 (Nu = CN)[e]	IR of mixture ν_{CN} 2216 cm^{-1}, ν_{CO} 2008, 1942, 1910 cm^{-1} ^1H NMR of **6a**[c,d] δ 5.75 (t, 1 H, H^3), 4.76 (d, 1 H, H^2) ppm ^1H NMR of **6b**[c] δ 5.91 (d, 5.37 Hz, 1 H, H^3), 4.99 (t, 6.11 Hz, 1 H, H^4), 3.83 (t, 5.86 Hz, 6 H, OCH_2), 3.59 (t, 5.6 Hz, 1 H, H^5), 3.0 (d, 4.1 Hz, 1 H, H^1), 2.85 (t, 5.86 Hz, 6 H, NCH_2), 1.63 (d, 12.0 Hz, 1 H, CH_2), 1.11 (d, 12.0 Hz, 1 H, CH_2) ppm ^1H NMR of **6c**[b,c] δ 5.18 (d, 2 H, $H^{2,4}$) ppm

[a] Measured in acetone-d_6. *J* values are given in Hz. [b] According to the elemental analysis, the ratio of compound **5** to $N(CH_2CH_2O)_3SiCH_2C_6H_5$ was 95:5. [c] $CDCl_3$. [d] Due to the existence of trace amount or to the overlapping with other peaks, we failed to assign completely. [e] Due to the same R_f values of aromatized compound and product, we failed to obtain the analytically pure product. According to the elemental analysis, the ratio of **6** (Nu = CN) to $N(CH_2CH_2O)_3SiCH_2C_6H_5$ was 72:28. The ratio was also confirmed by the comparison of ^1H NMR spectra.

Yield of **2** (OMe): 99 mg (58%). The yields of **2** (OEt), **2** (PrNH), **2** (BuNH), **2** (Et_2N), and **2** (NH_2) were 10%, 20%, 20%, 20%, and 77%, respectively.

Synthesis of 5. $C_6H_5CH_2Si(OCH_2CH_2)_3N$ (2.90 g, 11 mmol) was refluxed with $Mn(CO)_5ClO_4$ (2.94 g, 10 mmol) in 200 mL of CH_2Cl_2 overnight. After filtration of the reaction mixture, the filtrate was concentrated and precipitated by treatment with excess diethyl ether. Yield: 68%.

Reaction between 2 (or 5) and Nucleophile. Nu = MeLi, MeMgBr, PhMgBr, and $NaBH_4$. In CH_2Cl_2. A typical procedure is as follows: Compound **2** (0.3 mmol) was stirred in dry CH_2Cl_2 under N_2 at 0 °C while Nu was added dropwise. After being stirred for 30 min, 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 residue. Recrystallization (hexane/CH_2Cl_2) gave compounds **3** and **4** (R). The distribution of products was determined by integration of ^1H NMR peaks.

Nu = MeLi, MeMgBr, PhMgBr and $NaBH_4$. In THF. The reaction was carried out under conditions identical with those described above except for the reaction medium (THF).

Nu = NaCN. To a stirred solution of **2** (0.3 mmol) and a slight excess NaCN is 30 mL of THF at 0 °C was added 1 mL of water. After being stirred for 50 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.

Results and Discussion

Syntheses of Compounds 2. Refluxing of *para*-substituted arylsilatrane with $Mn(CO)_5ClO_4$ in CH_2Cl_2 formed the expected complexes with reasonable to high yields. However, the *p*-chloro-substituted arylsilatrane gave a poor yield of the expected complex (eq 1).

$$\text{arylsilatrane} + Mn(CO)_5OClO_3 \rightarrow [(\text{arylsilatrane})Mn(CO)_3]ClO_4 \quad (1)$$
$$\text{2 and 5}$$

2: aryl = *p*-ClC_6H_4, *p*-$CH_3OC_6H_4$, *p*-BuC_6H_4, *p*-MeC_6H_4

5: aryl = $C_6H_5CH_2$

Nucleophilic substitution of the chlorine atom in **2** (Cl) proceeded readily with a variety of nucleophiles (eq 2).[6]

$$[\{p\text{-}ClC_6H_4Si(OCH_2CH_2)_3N\}Mn(CO)_3^+] + NuH \rightarrow [\{p\text{-}NuC_6H_4Si(OCH_2CH_2)_3N\}Mn(CO)_3^+] \quad (2)$$
$$\text{2 (R)}$$

Nu = OMe, OEt, NH_2, NEt_2, NH-*i*-Pr, NH-*t*-Bu

Of the nucleophilic reagents tried, methoxide, ethoxide, ammonia, ethylamine, *n*-propylamine, and *n*-butylamine gave the expected substitution products. However, due to competing demetalation by the solvent, the yields were very poor.

Reactivities of Compounds 2 and 5. Nucleophilic addition reactions to complexes **2** were studied in THF or CH_2Cl_2 in order to compare the reaction medium effect on the regioselectivity with those found[4b-d] in the reaction between compound **1** and nucleophiles. The results are shown in Table II. In the beginning of this study, we expected that the conformation of the $Mn(CO)_3^+$ for the arene ring in **2** would be similar to that in **1** and *ortho* or *para* positions to the silatranyl group would be attacked by nucleophiles.[4] However, the regioselectivity of nucleophilic addition to **2** is much more complicated than we expected.

(1) Reactivities of Compound 2 (Me). With RMgBr (R = Me, Ph) nucleophiles in CH_2Cl_2, we found **3a** as a major product. However, with RMgBr addition in THF, a mixture of **3a** and **3b** was obtained and the ratio of **3a** and **3b** varied with R. As the size of the nucleophile decreased, we could see an increase in the formation of **3a**. Due to the insolubility of $NaBH_4$ in CH_2Cl_2, the addition of $NaBH_4$ in CH_2Cl_2 was not regioselective. When we compare the regioselectivity of **2** (Me) with that of (*p*-$MeC_6H_4OMe)Mn(CO)_3^+$, the results are rather disappointing. Addition of PhMgBr to (*p*-$MeC_6H_4OMe)$-$Mn(CO)_3^+$ in THF favors the position *meta* to MeO as a sole product.[7] In the beginning, we expected that the *meta*-directing effect of methyl[8] and the *ortho*- and *para*-directing effect of the silatranyl group in THF would dominate to produce **3a**. However, the directing effect of silatranyl group in THF is not as great as we expected.

(2) Reactivities of Compound 2 (Cl). In the reaction between **2** (Cl) and MeLi, no isolable product was obtained. Addition of RMgBr (R = Me and Ph) in CH_2Cl_2 was regioselective and was found to be directed exclusively *ortho* to the silatranyl group. However, in THF, the situation was very different. Addition of MeMgBr resulted in the demetalation and afforded *p*-chloroarylsilatrane **4** (Cl). Treatment of **2** (Cl) with PhMgBr resulted in the formation of **3a** and **3b** in a ratio of 1:4. With the addition of $NaBH_4$ to **2** (Cl) in CH_2Cl_2, **3b** was obtained as a major product, and with the addition of $NaBH_4$ in THF, a mixture of **3a** and **3b** was obtained in a ratio of 3:3.7.

In the addition of carbanions to (arene)$Cr(CO)_3$ complexes, chloride shows a directing effect similar to methyl: *meta* is preferred.[8] Thus, we expected that the *meta*-directing effect of chloride and the *ortho*- and *para*-

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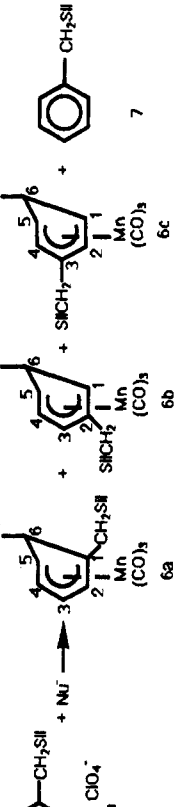
Table II. Reaction of Complexes 1, 2, and 5 with Nucleophiles



Sil = $Si(OCH_2CH_3)_3N$

nucliphile	medium	complex 1[a] product distribn 3a	3b	3c	combined yield (%)	complex 2 (Me) product distribn 3a	3b	combined yield (%)	complex 2 (Cl) product distribn 3a	3b	combined yield (%)	complex 2 (OMe) product distribn 3a	3b	3c	combined yield (%)	complex 2 (t-Bu) product distribn 3a	3b	combined yield (%)	complex 2 (NH_2) product distribn 3a	3b	combined yield (%)	complex 5 product distribn 6a	6b	6c	combined yield (%)
MeLi	THF	0	9	91	42	52	48	47			NR[b]				NR[b]			NR[b]			NR[b]	0	100	0	6
MeLi	CH_2Cl_2	100	0	0	42	100	0	95			NR[b]				NR[b]			NR[b]			NR[b]	23	77	0	13
MeMgBr	THF	0	0	100	72.5	64	36	18	0	0	49[c]	0	0	0	76[c]	0	0	76[c]			NR[b]	0	100	0	29
MeMgBr	CH_2Cl_2	100	0	0	72	100	0	84	>98	t	89	100	0	0	67	100	0	66			NR[b]	0	100	0	48
PhMgBr	THF	0	25	75	57	26	74	26	20	80	24	100	0	0	31	100	0	49			NR[b]	6	63	31	39
PhMgBr	CH_2Cl_2	100	0	0	56.7	100	0	76	100	0	92	100	0	0	82	100	0	62			NR[b]	100	0	0	50
$NaBH_4$	THF	0	6	94	76.6	29	71	88	45	55	77	62	0	38	58	11	89	59	100	0	45	5	92	3	45
$NaBH_4$	CH_2Cl_2	0	6	94	74	55	45	72	t	>95	39	90	0	10	64	37	63	58	100	0	91	8	77	15	35
NaCN	wet THF	36	0	64	56	86	14	66	25	75	40	100	0	0	68	39	61	68			NR[b]	>8	>91	t	45

[a] These data are reproduced from ref 4c for comparison. [b] After reaction, no isolable compound was obtained. NR = no reaction. t = trace. [c] 4 (R) was obtained.

directing effect of silatranyl would dominate to produce **3a**. However, the regioselectivity of nucleophilic addition to **2** (Cl) in THF shows no special trends.

(3) Reactivities of Compound 2 (OMe). For the addition of MeLi to **2** (OMe), the expected product was not isolated. The reactant was completely decomposed. Addition of RMgBr (R = Me and Ph) in CH_2Cl_2 resulted in **3a** as a sole product. Treatment of **2** (OMe) with MeMgBr in THF led to **4** (OMe) in 28% yield after workup, and addition of PhMgBr in THF gave **3a** as an isolable organometallic compound. Addition of $NaBH_4$ to **2** (OMe) led to the isolation of a mixture of **3a** and **3c**. The ratio of **3a** to **3c** was 6:4 in THF and 9:1 in CH_2Cl_2. The *ipso* addition is not popular. However, Sutherland *et al.*[9] mentioned the formation of *ipso* adducts in the hydride addition to (arene)$FeCp^+$, and Watts *et al.*[10] reported the formation of (η^5-6,6-dimethoxycyclohexadienyl)$Mn(CO)_3$ by slow addition of methoxide to $(MeOC_6H_5)Mn(CO)_3^+$. Addition of NaCN to **2** (OMe) in wet THF gave **3a** in 68% yield.

According to the study of substituent effects in the addition of carbanions to (arene)$M(CO)_3^{n+}$ (M = Cr, n = 0; M = Mn, n = 1) complexes, methoxy favors *meta*.[2a,11] Thus, we expected that the *meta*-directing effect of methoxy and the *ortho*- and *para*-directing effect of silatranyl would reinforce to produce **3a**. The regioselectivity of nucleophilic addition to **2** (OMe) in THF follows the expected trend.

(4) Reactivities of Compound 2 (*t*-Bu). The regioselectivities of RMgBr addition to **2** (*t*-Bu) were similar to those found in **2** (OMe). However, there was no similarity in the hydride addition. Addition of NaCN to **2** (*t*-Bu) in wet THF resulted in a mixture of **3a** and **3b** in a ratio of 2:3.

In the addition of carbanions to (arene)$M(CO)_3^{n+}$ (M = Cr, n = 0; M = Mn, n = 1) complexes, *tert*-butyl favors *meta* and *para*.[8,11,12] Thus, we expected that the *meta*- and *para*-directing effect of *tert*-butyl and the *ortho*- and *para*-directing effect of silatranyl can reinforce the production of **3a**. However, with the sterically less bulky nucleophiles (H^- and CN^-), **3b** becomes important.

(5) Reactivities of Compound 2 (NH_2). For the addition of nucleophiles to **2** (NH_2), only hydride addition was observed. The reason would be that upon coordination the acidities of amine protons would be enhanced and could be easily deprotonated by nucleophilic reagents.[13]

In the addition of carbanions to (arene)$Cr(CO)_3$ complexes, dialkylamino favors *meta*.[8] Thus, we expected that the *meta*-directing effect of dialkylamino and the *ortho*- and *para*-directing effect of silatranyl can reinforce the production of **3a**. As was expected, **3a** was obtained as the sole product for hydride addition.

(6) Reactivities of Compound 5. Addition of MeMgBr to **5** in CH_2Cl_2 or THF resulted in the formation of *meta* adduct **6b**. However, addition of PhMgBr to **5** in CH_2Cl_2 gave an *ortho* adduct **6a**, and in THF *meta* and *para* adducts were obtained in a ratio of 2:1. Addition of MeLi

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to **5** in CH_2Cl_2 afforded a mixture of *meta* and *para* adducts in a ratio of 5:1.5, and in THF only *meta* adduct was obtained in a low yield. The low yield was due to the demetalation of **5** in the reaction. Treatment of **5** with $NaBH_4$ in CH_2Cl_2 led to isolation of a mixture of *meta* and *ortho* adducts in the ratio of 5:1, and in THF a mixture of *ortho*, *meta*, and *para* adducts in the ratio of 2:35:1 was obtained. Addition of NaCN to **5** in wet THF led to isolation of a mixture of *ortho* and *meta* adducts in a ratio of 1:10. The regioselectivity of nucleophile addition to **5** is very different from those of compounds **1** and **2**. For the addition of nucleophile to **1** or **2** in CH_2Cl_2, we expect that the initial formation of an oxygen–magnesium bond would be followed by intramolecular nucleophilic addition to give C–C bond formation at the *ortho* position.[2c] However, for the addition of nucleophile to **5** in CH_2Cl_2, we do not expect the initial formation of the oxygen–magnesium bond because of long distances between oxygens of the silatranyl group and arene ring. Instead we expect the direct R^- group transfer to give *meta* adduct. The $CH_2Si(OCH_2CH_2)_3N$ moiety in **5** is an electron-donating group and would deactivate the *ortho* and *para* positions.[2a,11] Thus, the nucleophilic attack would occur at the *meta* position. However, it seems that $CH_2Si(OCH_2CH_2)_3N$ is a weaker *meta*-directing group than the methoxy group.

In conclusion, it is noted that the regioselectivities of nucleophilic addition to **2** were strongly dependent upon the substituent on the ring, the reaction medium, and the nature of nucleophile. The different regioselectivities in different reaction media might come from the different solubilities in different reaction media and the availability of coordination to the oxygen atoms on the silatranyl group. The regioselectivities of **2** (Cl), **2** (OMe), and **2** (*t*-Bu) were rather similar. However, the effect of substituent on the regioselectivity seems to be very complex. To verify the substituent effect more clearly, we have to do further studies. The $CH_2Si(OCH_2CH_2)_3N$ moiety is an electron-donating group and would deactivate the *ortho* and *para* positions. Thus, for the addition of nucleophiles to **5**, the nucleophilic attack would occur at the *meta* position.

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