

## Synthesis and electrophilic reactivity of $[\{\eta^5\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}6\text{-Me-C}_6\text{H}_5\}\text{Mn}(\text{CO})_2\text{NO}]\text{BF}_4$

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Received 26 January 1994; in revised form 13 April 1994

### Abstract

$[\{\eta^5\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}6\text{-Me-C}_6\text{H}_5\}\text{Mn}(\text{CO})_2\text{NO}]\text{BF}_4$  [**3(CO)**] has been synthesized by the reaction of  $[\{\eta^5\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}6\text{-Me-C}_6\text{H}_5\}\text{Mn}(\text{CO})_3]$  (**2**) with  $\text{NOBF}_4$ . The addition of phosphines or phosphite to **3(CO)** yielded  $[\{\eta^5\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}6\text{-Me-C}_6\text{H}_5\}\text{Mn}(\text{CO})(\text{L})\text{NO}]\text{BF}_4$  [**3(L)**] (L =  $\text{PPh}_3$ ,  $\text{PMePh}_2$ ,  $\text{PPhPh}_2$ , and  $\text{P(OPh)}_3$ ). Addition of excess  $\text{P(OMe)}_3$  to **3(CO)** led to  $[\{\eta^4\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}5\text{-P(O)(OMe)}_2\text{-}6\text{-Me-C}_6\text{H}_5\}\text{Mn}(\text{CO})_2\text{NO}]$  (**4**), which decomposed to liberate the 1,3-cyclohexadiene derivative of silatrane **5**. Hydride addition to **3(CO)** gave  $[\{\eta^4\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}6\text{-Me-C}_6\text{H}_5\}\text{Mn}(\text{CO})_2\text{NO}]$  (**6**) and  $[\{\eta^4\text{-}6\text{-Me-}5\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-C}_6\text{H}_5\}\text{Mn}(\text{CO})_2\text{NO}]$  (**7**). After removal of the manganese moiety from **6** and **7**, 1,3-cyclohexadiene derivatives of silatrane, **8** and **10**, were obtained. Treatment of **3(CO)** with the carbanion of ethyl cyanoacetate and then  $\text{Me}_3\text{NO}$  in refluxing benzene gave the *cis*-disubstituted cyclohexadiene derivative of silatrane, **12**. Addition of  $\text{LiCH}_2\text{CN}$  to **3(CO)** yielded  $[\{\eta^5\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}6\text{-Me-C}_6\text{H}_5\}\text{Mn}(\text{CO})(\text{C}(\text{O})\text{CH}_2\text{CN})\text{NO}]$  [**13(C(O)CH}\_2\text{CN)}**] which rearranged to the diene complex, presumably possessing an *endo* substituent. The diene compound afforded the *trans*-disubstituted cyclohexadiene derivative of silatrane **15(C(O)CH}\_2\text{CN)}**,  $\text{LiCH}_2\text{CO}_2^1\text{Pr}$ , and  $\text{LiCH}_2\text{CO}_2^1\text{Bu}$  also attacked the CO in **3(CO)**, ultimately affording **15(C(O)CH}\_2\text{CO}\_2^1\text{Pr)}** and **15(C(O)CH}\_2\text{CO}\_2^1\text{Bu)}**, respectively.

**Keywords:** Manganese; Silatranyl; Cyclohexadiene; Cyclohexadienyl; Nitrosyl; Rearrangement

### 1. Introduction

Silatrane is a siloxyalkylamine with the structure of a three-winged cage. These compounds show a wide range of toxicities in mammals and a variety of biological activities [1]. Although silatrane has been much studied, cyclohexadiene derivatives of silatrane have received little attention. To our knowledge, there have been no reports about the synthesis of cyclohexadiene derivatives of silatrane.

Recently we reported the usefulness and uniqueness of phenylsilatrane as a  $\pi$ -coordinating ligand [2]. We have also demonstrated the control of the regioselectivity of nucleophile addition to (phenylsilatrane)

$\text{Mn}(\text{CO})_3^+$  cation (**1**). Thus, compound  $[\{\eta^5\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}6\text{-Me-C}_6\text{H}_5\}\text{Mn}(\text{CO})_3]$  (**2**) was easily obtained by reaction between **1** and  $\text{MeLi}$  or  $\text{MeMgBr}$  in  $\text{CH}_2\text{Cl}_2$ . The compound **2** can be easily activated by treatment with  $\text{NOBF}_4$  or  $\text{NOPF}_6$  to give  $[\{\eta^5\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}6\text{-Me-C}_6\text{H}_5\}\text{Mn}(\text{CO})_2\text{NO}]\text{BF}_4$  [**3(CO)**].

In the present paper, we describe the synthesis and chemistry of **3(CO)**, the synthesis of several new silatranyl cyclohexadiene derivatives, and the novel migration of the  $\text{C}(\text{O})\text{R}$  group from metal to the coordinated silatranyl cyclohexadienyl ring.

### 2. Experimental section

All solvents were purified by standard methods and all synthetic procedures were done under a nitrogen

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Table 1  
Characterization of new compounds

3(CO)	Mp 112°C dec. IR $\nu_{\text{CO}}$ 2100, 2060 $\text{cm}^{-1}$ , $\nu_{\text{NO}}$ 1815 $\text{cm}^{-1}$ ; $^1\text{H NMR}$ ( $d_6$ -acetone) <sup>a</sup> $\delta$ 6.97 (t, 5.47 Hz, 1H, H <sup>3</sup> ), 6.01 (d, 5.47 Hz, 1H, H <sup>2</sup> ), 4.76 (m, 1H, H <sup>6</sup> ), 3.83 (t, 5.9 Hz, 6H, OCH <sub>2</sub> ), 3.08 (t, 5.9 Hz, 6H, NCH <sub>2</sub> ), 0.70 (d, 6.5 Hz, 3H, Me) ppm; Anal. Found: C, 32.06; H, 3.35; N, 5.00. C <sub>15</sub> H <sub>20</sub> BF <sub>4</sub> MnN <sub>2</sub> O <sub>6</sub> Si calc.: C, 32.6; H 3.64; N, 5.27%.
3(PPh <sub>3</sub> )	IR $\nu_{\text{CO}}$ 2020 $\text{cm}^{-1}$ , $\nu_{\text{NO}}$ 1770 $\text{cm}^{-1}$ ; $^1\text{H NMR}$ ( $d_6$ -acetone) $\delta$ 7.84–7.53 (m, 15H, Ph), 7.02 (br t, 1H, H <sup>3</sup> ), 5.36 (d, 4.6 Hz, 1H, H <sup>2</sup> ), 5.21 (br m, 1H, H <sup>4</sup> ), 3.85 (t, 5.4 Hz, 6H, OCH <sub>2</sub> ), 3.09 (t, 5.4 Hz, NCH <sub>2</sub> ), 2.76 (m, 2H, H <sup>5,6</sup> ), 0.46 (d, 5.4 Hz, 3H, Me) ppm. Anal. Found: C, 52.62; H, 4.83; N, 3.22. C <sub>32</sub> H <sub>36</sub> BF <sub>4</sub> MnN <sub>2</sub> O <sub>5</sub> Si calc.: C, 52.76; H, 4.84; N, 3.84%.
3(PPh <sub>2</sub> Me)	IR $\nu_{\text{CO}}$ 2020 $\text{cm}^{-1}$ , $\nu_{\text{NO}}$ 1770 $\text{cm}^{-1}$ ; $^1\text{H NMR}$ (CD <sub>2</sub> Cl <sub>2</sub> ) of the major isomer $\delta$ 6.47 (t, 5.6 Hz, 1H, H <sup>4</sup> ), 5.02 (d, 5.6 Hz, 1H, H <sup>2</sup> ), 3.82 (t, 5.9 Hz, 6H, OCH <sub>2</sub> ), 2.96 (t, 5.9 Hz, 6H, NCH <sub>2</sub> ), 2.67 (m, 2H, H <sup>5,6</sup> ), 2.08 (d, 9.7 Hz, 3H, PMe), 0.48 (d, 6.1 Hz, 3H, Me) ppm. $^1\text{H NMR}$ (CD <sub>2</sub> Cl <sub>2</sub> ) <sup>b</sup> of the minor isomer $\delta$ 5.93, 5.54, 4.83, 2.03 (d, 10 Hz, 3H, PMe), 0.67 (d, 6.6 Hz, 3H, Me) ppm. Anal. Found: C, 49.28; H, 5.00; N, 3.54. C <sub>27</sub> H <sub>33</sub> NF <sub>4</sub> MnN <sub>2</sub> O <sub>5</sub> Si calc.: C, 48.67; H, 4.99; N, 3.54%.
3(PPh <sub>2</sub> H)	IR $\nu_{\text{CO}}$ 2020 $\text{cm}^{-1}$ , $\nu_{\text{NO}}$ 1760 $\text{cm}^{-1}$ ; $^1\text{H NMR}$ (CD <sub>2</sub> Cl <sub>2</sub> ) of the major isomer $\delta$ 7.64–7.42 (m, 10H, Ph), 6.90 (d, 395.9 Hz, 1H, PH), 6.23 (t, 4.4 Hz, 1H, H <sup>3</sup> ), 5.49 (dd, 4.4, 6.2 Hz, 1H, H <sup>4</sup> ), 5.27 (dm, 4.4 Hz, 1H, H <sup>2</sup> ), 4.62 (t, 6.7 Hz, 1H, H <sup>5</sup> ), 3.80 (t, 5.6 Hz, 6H, OCH <sub>2</sub> ), 2.97 (t, 5.6 Hz, 6H, NCH <sub>2</sub> ), 2.80 (m, 2H, H <sup>5,6</sup> ), 0.69 (d, 6.6 Hz, 3H, Me) ppm. $^1\text{H NMR}$ (CD <sub>2</sub> Cl <sub>2</sub> ) <sup>b</sup> of the minor isomer $\delta$ 7.64–7.42 (m, Ph), 6.76 (d, 382.2 Hz, 1H, PH), 6.47 (1H, H <sup>3</sup> ), 3.17 (br t, 1H, H <sup>5</sup> ), 0.54 (d, 6.6 Hz, 3H, Me) ppm. Anal. Found: C, 47.49; H, 4.68; N, 3.85. C <sub>26</sub> H <sub>31</sub> BF <sub>4</sub> MnN <sub>2</sub> O <sub>5</sub> Si calc.: C, 47.87; H, 4.78; N, 4.29%.
3(P(OPh) <sub>3</sub> )	IR $\nu_{\text{CO}}$ 2040 $\text{cm}^{-1}$ , $\nu_{\text{NO}}$ 1780 $\text{cm}^{-1}$ ; $^1\text{H NMR}$ (CD <sub>3</sub> CN) $\delta$ 7.59–7.21 (m, 15H, Ph), 5.80 (t, 6.4 Hz, 1H, H <sup>4</sup> ), 5.58 (br t, 1H, H <sup>3</sup> ), 4.98 (d, 5.8 Hz, 1H, H <sup>2</sup> ), 3.69 (t, 6.0 Hz, 6H, OCH <sub>2</sub> ), 3.32 (t, 6.0 Hz, 1H, H <sup>5</sup> ), 2.90 (t, 6.0 Hz, 6H, NCH <sub>2</sub> ), 2.61 (m, 1H, H <sup>6</sup> ), 0.45 (d, 6.4 Hz, 3H, Me) ppm. Anal. Found: C, 50.30; H, 4.81; N, 3.41. C <sub>32</sub> H <sub>35</sub> BF <sub>4</sub> MnN <sub>2</sub> O <sub>8</sub> Si calc.: C, 49.51; H, 4.54; N, 3.61%.
4	IR $\nu_{\text{CO}}$ 2020, 1960 $\text{cm}^{-1}$ , $\nu_{\text{NO}}$ 1720 $\text{cm}^{-1}$ , $\nu_{\text{P=O}}$ 1250 $\text{cm}^{-1}$ ; $^1\text{H NMR}$ ( $d_8$ -THF) <sup>c</sup> $\delta$ 5.58 (d, 3.9 Hz, 1H, H <sup>2</sup> ), 5.38 (br t, 1H, H <sup>3</sup> ), 3.53 (t, 5.8 Hz, 6H, OCH <sub>2</sub> ), 2.62 (t, 5.8 Hz, 6H, NCH <sub>2</sub> ), 2.27 (dd, 9.7, 24.6 Hz, H <sup>5</sup> ), 1.12 (d, 6.5 Hz, 3H, Me) ppm. Anal. Found: C, 39.21; H, 5.14; N, 5.09. C <sub>17</sub> H <sub>26</sub> MnN <sub>2</sub> O <sub>9</sub> PSi calc.: C, 39.54; H, 5.07; N, 5.42%.
5	IR $\nu_{\text{P=O}}$ 1250 $\text{cm}^{-1}$ , $\nu_{\text{Si-O}}$ 1080, 1120 $\text{cm}^{-1}$ ; $^1\text{H NMR}$ (CDCl <sub>3</sub> ) $\delta$ 6.39 (d, 4.6 Hz, 1H, H <sup>2</sup> ); 6.05 (m, 1H, H <sup>3</sup> ), 5.59 (t, 10 Hz, 1H, H <sup>4</sup> ), 3.80 (t, 5.8 Hz, 6H, OCH <sub>2</sub> ), 3.79 (d, 14 Hz, 6H, POME), 3.01 (dm, 26 Hz, 1H, H <sup>5</sup> ), 2.82 (t, 5.8 Hz, 6H, NCH <sub>2</sub> ), 1.05 (d, 6.8 Hz, 3H, Me) ppm. Anal. Found: C, 47.16; H, 6.75; N, 3.62. C <sub>15</sub> H <sub>26</sub> NO <sub>6</sub> PSi calc.: C, 47.99; H, 6.98; N, 3.37%.
8	IR $\nu_{\text{CO}}$ 2020, 1960 $\text{cm}^{-1}$ , $\nu_{\text{NO}}$ 1730 $\text{cm}^{-1}$ ; $^1\text{H NMR}$ (CD <sub>2</sub> Cl <sub>2</sub> ) $\delta$ 5.70 (dd, 0.73, 4.4 Hz, 1H, H <sup>2</sup> ), 5.59 (ddd, 0.73, 4.7, 6.3 Hz, 1H, H <sup>3</sup> ), 3.71 (t, 5.86 Hz, 6H, OCH <sub>2</sub> ), 2.75 (t, 5.86 Hz, 6H, NCH <sub>2</sub> ), 2.47 (m, 1H, H <sup>6</sup> ), 1.94 (ddd, 2.9, 10.0, 15 Hz, 1H, H <sup>5-endo</sup> ), 1.47 (dd, 2.4, 15 Hz, 1H, H <sup>5-exo</sup> ), 1.02 (d, 6.8 Hz, 3H, Me) ppm. Anal. Found: C, 44.37; H, 5.12; N, 6.68. C <sub>15</sub> H <sub>20</sub> MnN <sub>2</sub> O <sub>6</sub> Si calc.: C, 44.12; H, 5.18; N, 6.86%.
7	IR $\nu_{\text{CO}}$ 2020, 1960 $\text{cm}^{-1}$ , $\nu_{\text{NO}}$ 1730 $\text{cm}^{-1}$ ; $^1\text{H NMR}$ (CD <sub>2</sub> Cl <sub>2</sub> ) $\delta$ 5.42 (m, 1H, H <sup>2</sup> ), 5.36 (m, 1H, H <sup>3</sup> ), 3.84 (m, 1H, H <sup>1</sup> ), 3.68 (t, 5.86 Hz, 6H, OCH <sub>2</sub> ), 3.37 (m, 1H, H <sup>4</sup> ), 2.75 (t, 5.86 Hz, 6H, NCH <sub>2</sub> ), 2.40 (m, 1H, H <sup>5</sup> ), 1.45 (dd, 3.1, 10.5 Hz, 1H, H <sup>6</sup> ), 1.11 (d, 6.8 Hz, 3H, Me) ppm. Anal. Found: C, 44.37; H, 5.12; N, 6.68. C <sub>15</sub> H <sub>20</sub> MnN <sub>2</sub> O <sub>6</sub> Si calc.: C, 44.12; H, 5.18; N, 6.86%.
8(H)	Mp 138°C. $^1\text{H NMR}$ (CDCl <sub>3</sub> ) $\delta$ 6.39 (d, 4.88 Hz, 1H, H <sup>2</sup> ), 5.89 (ddd, 2.2, 4.88, 9.2 Hz, 1H, H <sup>3</sup> ), 5.65 (t, 8.3 Hz, 1H, H <sup>4</sup> ), 3.80 (t, 5.7 Hz, 6H, OCH <sub>2</sub> ), 2.81 (t, 5.7 Hz, 6H, NCH <sub>2</sub> ), 2.38 (dd, 5.6, 13.7 Hz, 1H, H <sup>5-endo</sup> ), 1.95 (dd, 5.86, 14.2 Hz, 1H, H <sup>5-exo</sup> ), 1.01 (d, 6.6 Hz, 3H, Me) ppm. Anal. Found: 58.64; H, 7.41; N, 5.00. C <sub>13</sub> N <sub>21</sub> NO <sub>3</sub> Si calc.: C, 58.39; H, 7.91; N, 5.24%.
8(D)	$^1\text{H NMR}$ (CDCl <sub>3</sub> ) $\delta$ 6.40 (d, 6.4 Hz, 1H, H <sup>2</sup> ), 5.89 (dd, 4.88, 9.52 Hz, 1H, H <sup>3</sup> ), 5.65 (dd, 5.86, 9.28 Hz, 1H, H <sup>4</sup> ), 3.81 (t, 5.86 Hz, 6H, OCH <sub>2</sub> ), 2.82 (t, 5.85 Hz, 6H, NCH <sub>2</sub> ), 2.44 (m, 1H, H <sup>6</sup> ), 1.93 (dd, 3.2, 5.6 Hz, 1H, H <sup>5-exo</sup> ), 1.02 (d, 7.1 Hz, 3H, Me) ppm.
10(H)	$^1\text{H NMR}$ (CDCl <sub>3</sub> ) $\delta$ 5.86–5.72 (m, 4H, H <sup>2,3,4,5</sup> ), 3.75 (t, 5.9 Hz, 6H, OCH <sub>2</sub> ), 2.78 (t, 5.9 Hz, 6H, NCH <sub>2</sub> ), 2.42 (m, 1H, H <sup>6</sup> ), 1.85 (dt, 2.2, 8.3 Hz, 1H, H <sup>1</sup> ), 0.90 (d, 7.1 Hz, 3H, Me) ppm.

Table 1 (continued)

10(D)	$^1\text{H NMR}$ ( $\text{CDCl}_3$ ) $\delta$ 5.86–5.73 (m, 4H, $\text{H}^{2,3,4,5}$ ), 3.77 (t, 5.9 Hz, 6H, $\text{OCH}_2$ ), 2.81 (t, 5.9 Hz, 6H, $\text{NCH}_2$ ), 2.42 (m, 1H, $\text{H}^6$ ), 0.92 (d, 7.1 Hz, 3H, Me) ppm.
11	IR $\nu_{\text{CN}}$ 2240 $\text{cm}^{-1}$ , $\nu_{\text{CO}}$ 2020, 1960 $\text{cm}^{-1}$ , $\nu_{\text{NO}}$ 1730 $\text{cm}^{-1}$ .
12 <sup>e</sup>	IR $\nu_{\text{CN}}$ 2240 $\text{cm}^{-1}$ . $^1\text{H NMR}$ ( $\text{CDCl}_3$ ) $\delta$ 6.40 (d, 4.6 Hz, 1H, $\text{H}^2$ ), 6.01 (m, 1H, $\text{H}^3$ ), 5.63 (d, 9.8 Hz, 1H, $\text{H}^4$ minor isomer), 5.31 (d, 9.8 Hz, 1H, $\text{H}^4$ major isomer), 4.27 (q, 7.3 Hz, 2H, $\text{CH}_2$ ), 3.82 (t, 5.9 Hz, 6H, $\text{OCH}_2$ major isomer), 3.80 (t, 5.9 Hz, 6H, $\text{OCH}_2$ minor isomer), 3.56 (d, 8.8 Hz, 1H, CH minor isomer), 3.53 (d, 11.7 Hz, 1H, CH major isomer), 3.15 (m, 1H, $\text{H}^6$ ), 2.85 (t, 5.9 Hz, 6H, $\text{NCH}_2$ minor isomer), 2.78 (t, 5.9 Hz, 6H, $\text{NCH}_2$ major isomer), 2.45 (t, 6.5 Hz, 1H, $\text{H}^5$ minor isomer), 1.33 (t, 7.1 Hz, 3H, Me minor isomer), 1.31 (t, 7.1 Hz, 3H, Me major isomer), 0.94 (d, 7.1 Hz, 3H, Me major isomer), 0.93 (d, 7.1 Hz, 3H, Me major isomer) ppm.
13( $\text{CO}$ ) $\text{CH}_2\text{CN}$	IR $\nu_{\text{CN}}$ 2240 $\text{cm}^{-1}$ , $\nu_{\text{CO}}$ 2000 $\text{cm}^{-1}$ , $\nu_{\text{NO}}$ 1725 $\text{cm}^{-1}$ , $\nu_{\text{C=O}}$ 1620 $\text{cm}^{-1}$ . $^1\text{H NMR}$ ( $\text{CDCl}_3$ ) $\delta$ 6.25 (t, 4.5 Hz, 1H, $\text{H}^3$ ), 4.89 (m, 2H, $\text{H}^{2,4}$ ), 3.79 (t, 5.86 Hz, 6H, $\text{OCH}_2$ ), 3.64 (1H, $\text{CH}_2$ ), 3.55 (d, 15.6 Hz, 1H, $\text{CH}_2$ ), 3.43 (t, 6.0 Hz, 1H, $\text{H}^6$ ), 2.84 (t, 5.86 Hz, 6H, $\text{NCH}_2$ ), 2.51 (t, 6.0 Hz, 1H, $\text{H}^6$ ), 0.48 (d, 6.8 Hz, 3H, Me) ppm. Anal. Found: C, 45.62; H, 5.24; N, 8.44. $\text{C}_{17}\text{H}_{22}\text{MnN}_3\text{O}_6\text{Si}$ calc.: C, 45.64; H, 4.95; N, 9.39%.
13( $\text{CO}$ ) $\text{CH}_2\text{CO}_2t\text{Bu}$ <sup>f</sup>	IR $\nu_{\text{CO}}$ 1995 $\text{cm}^{-1}$ , $\nu_{\text{NO}}$ 1723 $\text{cm}^{-1}$ , $\nu_{\text{C=O}}$ 1620 $\text{cm}^{-1}$ . $^1\text{H NMR}$ ( $\text{CDCl}_3$ ) $\delta$ 6.18 ( $\text{H}^2$ ), 4.88 ( $\text{H}^{3,4}$ ), 3.68 ( $\text{CH}_2$ ), 3.40 ( $\text{H}^5$ ) ppm.
13( $\text{CO}$ ) $\text{CH}_2\text{CO}_2Pr$ <sup>f</sup>	IR $\nu_{\text{CO}}$ 1980 $\text{cm}^{-1}$ , $\nu_{\text{NO}}$ 1720 $\text{cm}^{-1}$ , $\nu_{\text{C=O}}$ 1618 $\text{cm}^{-1}$ , $\nu_{\text{Si-O}}$ 1098, 1120 $\text{cm}^{-1}$ . $^1\text{H NMR}$ ( $\text{CD}_3\text{Cl}$ ) $\delta$ 6.19 ( $\text{H}^2$ ), 4.88 ( $^{3,4}$ ), 3.4 ( $\text{H}^5$ ), 3.74 ( $\text{CH}_2$ ), 0.48 (Me) ppm.
15( $\text{CO}$ ) $\text{CH}_2\text{CN}$	IR $\nu_{\text{CN}}$ 2248 $\text{cm}^{-1}$ , $\nu_{\text{C=O}}$ 1705 $\text{cm}^{-1}$ , $\nu_{\text{Si-O}}$ 1092, 1121 $\text{cm}^{-1}$ . $^1\text{H NMR}$ ( $\text{CDCl}_3$ ) $\delta$ 6.38 (d, 4.9 Hz, 1H, $\text{H}^2$ ), 6.11 (ddd, 1.0, 5.1, 9.4 Hz, 1H, $\text{H}^3$ ), 5.53 (ddd, 1.0, 6.4, 9.4 Hz, 1H, $\text{H}^4$ ), 4.08 (d, 20 Hz, 1H, $\text{CH}_2\text{CN}$ ), 3.82 (t, 5.8 Hz, 6H, $\text{OCH}_2$ ), 3.80 (d, 20 Hz, 1H, $\text{CH}_2\text{CN}$ ), 2.95 (d, 6.3 Hz, 1H, $\text{H}^5$ ), 2.86 (t, 5.9 Hz, 6H, $\text{NCH}_2$ ), 2.68 (q, 7.1 Hz, 1H, $\text{H}^6$ ), 1.13 (d, 7.0 Hz, 3H, Me) ppm. Anal. Found: C, 57.05; H, 6.67; N, 9.17. $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_4\text{Si}$ calc.: C, 57.46; H, 6.63; N, 8.38%. HRMS Foun: 266.1220. $\text{M}^+ - \text{C}(\text{O})\text{CH}_2\text{CN}$ calc.: 226.1220. Mp 143.4°C. IR $\nu_{\text{CO}}$ , $\nu_{\text{CO}_2}$ 1730, 1702 $\text{cm}^{-1}$ , $\nu_{\text{Si-O}}$ 1100, 1128 $\text{cm}^{-1}$ . $^1\text{H NMR}$ ( $\text{CD}_3\text{Cl}$ ) $\delta$ 6.35 (dd, 1.0, 4.9 Hz, 1H, $\text{H}^2$ ), 6.01 (ddd, 0.6, 4.9, 9.8 Hz, 1H, $\text{H}^3$ ), 5.62 (dd, 6.2, 9.4 Hz, 1H, $\text{H}^4$ ), 3.80 (t, 5.9 Hz, 6H, $\text{OCH}_2$ ), 3.61 (d, 16.3 Hz, 1H, $\text{CH}_2$ ), 3.53 (d, 16.3 Hz, 1H, $\text{CH}_2$ ), 3.00 (d, 7.0 Hz, 1H, $\text{H}^5$ ), 2.83 (t, 5.9 Hz, 6H, $\text{NCH}_2$ ), 1.45 (s, Bu), 1.12 (d, 7.0 Hz, 3H, Me) ppm. $^{13}\text{C NMR}$ ( $\text{CD}_3\text{Cl}$ ) $\delta$ 205.4 (C=O), 167.61 ( $\text{CO}_2$ ), 145.7 ( $\text{C}^1$ ), 128.44 ( $\text{C}^2$ ), 126.82 ( $\text{C}^3$ ), 120.81 ( $\text{C}^4$ ), 80.96 (CMe <sub>3</sub> ), 57.68 ( $\text{OCH}_2$ ), 54.50 ( $\text{CH}_2$ ), 51.15 ( $\text{NCH}_2$ ), 47.90 ( $\text{C}^5$ ), 31.97 ( $\text{C}^6$ ), 28.02 (C(CH <sub>3</sub> ) <sub>3</sub> ), 19.19 ( $\text{CH}_3$ ) ppm. Anal. Found: C, 58.65; H, 7.63; N, 3.42. $\text{C}_{20}\text{H}_{31}\text{NO}_6\text{Si}$ calc.: C, 58.14; H, 7.54; N, 3.13%.
15( $\text{CO}$ ) $\text{CH}_2\text{CO}_2t\text{Bu}$	Mp 104.4°C. IR $\nu_{\text{CO}}$ , $\nu_{\text{CO}_2}$ 1737, 1705 $\text{cm}^{-1}$ , $\nu_{\text{Si-O}}$ 1100(br) $\text{cm}^{-1}$ . $^1\text{H NMR}$ ( $\text{CD}_3\text{Cl}$ ) $\delta$ 6.36 (d, 4.9 Hz, 1H, $\text{H}^2$ ), 6.08 (ddd, 0.6, 4.9, 9.4 Hz, 1H, $\text{H}^3$ ), 5.61 (dd, 6.2, 9.4 Hz, 1H, $\text{H}^4$ ), 5.03 (m, $\text{CHMe}_2$ ), 3.80 (t, 5.8 Hz, 6H, $\text{OCH}_2$ ), 3.69 (d, 16.8 Hz, 1H, $\text{CH}_2$ ), 3.63 (d, 16.8 Hz, 1H, $\text{CH}_2$ ), 2.91 (d, 5.9 Hz, 1H, $\text{H}^5$ ), 2.83 (t, 5.8 Hz, 6H, $\text{NCH}_2$ ), 1.23 (d, 6.2 Hz, 6H, $\text{CHMe}_2$ ), 1.12 (d, 7.1 Hz, 3H, Me) ppm. $^{13}\text{C NMR}$ ( $\text{CD}_3\text{Cl}$ ) $\delta$ 205.1 (C=O), 167.92 ( $\text{CO}_2$ ), 145.75 ( $\text{C}^1$ ), 128.42 ( $\text{C}^2$ ), 126.93 ( $\text{C}^3$ ), 120.67 ( $\text{C}^4$ ), 68.18 ( $\text{CHMe}_2$ ), 57.67 ( $\text{OCH}_2$ ), 54.60 ( $\text{CH}_2$ ), 51.14 ( $\text{NCH}_2$ ), 46.84 ( $\text{C}^5$ ), 31.97 ( $\text{C}^5$ ), 21.77 (CMe <sub>2</sub> ), 19.20 ( $\text{CH}_3$ ) ppm. Anal. Found: C, 57.70; H, 7.39; N, 3.54. $\text{C}_{19}\text{H}_{26}\text{NO}_6\text{Si}$ calc.: C, 57.34; H, 7.43; N, 3.22%.
15( $\text{CO}$ ) $\text{CH}_2\text{CO}_2i\text{Pr}$	

<sup>a</sup> The signals of  $\text{H}^4$  and  $\text{H}^6$  overlapped with the peaks of  $\text{H}^2$  and  $\text{NCH}_2$ , respectively, and obscured.

<sup>b</sup> We could not determine the position and the splitting pattern of each peaks because of trace existence.

<sup>c</sup> The signals of  $\text{P}(\text{O})(\text{OMe})_2$ ,  $\text{H}^4$ , and  $\text{H}^6$  were overlapped with other signals and obscured.

<sup>d</sup> The signal of  $\text{H}^4$  overlapped the signal of silatrane (2.75 ppm) and was obscured.

<sup>e</sup> We failed to obtain analytical data.

<sup>f</sup> Due to the presence of *ortho*-methylsilatranylbenzene and of  $15(\text{CH}_2\text{CO}_2\text{R})$ , we could not assign the splitting pattern of each peaks and could not obtain analytical data.

atmosphere. THF (tetrahydrofuran) was distilled freshly from sodium benzophenone ketyl prior to use, and other solvents were purified according to standard methods. Reagent grade chemicals were used without further purification.

Elemental analyses were performed at the Korea

Basic Science Center.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained with a Varian XL-200 instrument. Infrared spectra were recorded on a Perkin-Elmer spectrometer. Characterizations are summarised in Table 1.

Compounds 1 and 2 were synthesized as previously described [2].

### 2.1. Synthesis of $[\{\eta^5\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}6\text{-Me-C}_6\text{H}_5\}\text{-Mn}(\text{CO})_2\text{NO}]\text{BF}_4$ (**3**) [**3(CO)**]

To **2** (0.787 g, 1.94 mmol) in 30 ml of  $\text{CH}_2\text{Cl}_2$  at room temperature was added a slight excess of  $\text{NOBF}_4$  and the mixture was stirred for 30 min. Several drops of  $\text{CH}_3\text{NO}_2$  were added and then the solution was filtered. Excess diethyl ether was added to precipitate the product as yellow orange solids, which were washed with diethyl ether and dried. Yield: 0.708 g (81%).

### 2.2. Synthesis of $[\{\eta^5\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}6\text{-Me-C}_6\text{H}_5\}\text{-Mn}(\text{CO})(\text{NO})\text{L}]\text{BF}_4$ , (**3**) [**3(L)**]( $\text{L} = \text{PPh}_3$ , $\text{PPh}_2\text{Me}$ , $\text{PPh}_2\text{H}$ , and $\text{P(OPh)}_3$ )

In a typical experiment, stirring with excess  $\text{PPh}_3$  (1.44 g, 5.51 mmol) and **3(CO)** (0.272 g, 0.551 mmol) in 25 ml of  $\text{CH}_2\text{Cl}_2$  for 5 h followed by addition of diethyl ether gave **3(PPh<sub>3</sub>)** (0.295 g, 86%).

### 2.3. Synthesis of $[\{\eta^4\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}5\text{-P(O)}(\text{O-Me})_2\text{-}6\text{-Me-C}_6\text{H}_5\}\text{-Mn}(\text{CO})_2\text{NO}]$ (**4**)

Five equivalents of  $\text{P(OMe)}_3$  were added to the solution of **3(CO)** in 20 ml of  $\text{CH}_2\text{Cl}_2$  at room temperature under  $\text{N}_2$ . After stirring for 2.5 h, the solution was concentrated and put through neutral alumina with diethyl ether to separate the product from the excess  $\text{P(OMe)}_3$ . The product, **4**, was obtained as solids after removal of the solvent.

Compound **4** was unstable in  $\text{CDCl}_3$  and led to demetallated product, *cis*-5-dimethylphosphono-6-methyl-1-silatranyl-1,3-cyclohexadiene (**5**). The overall yield from **3(CO)** to **5** was 80%.

### 2.4. Addition of hydride donor to **3(CO)**

A little excess  $\text{NaBH}_3\text{CN}$  was added to the solution of **3(CO)** (0.562 g, 1.14 mmol) in 30 ml of THF at room temperature under nitrogen. After stirring for 1 h, the solution was allowed to warm to room temperature and extracted with diethyl ether. The ether extracts were dried ( $\text{MgSO}_4$ ) and concentrated to give the crude product as a mixture of two regioisomers,  $[\{\eta^4\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{-Si-}6\text{-Me-C}_6\text{H}_6\}\text{-Mn}(\text{CO})_2\text{NO}]$  (**6**) and  $[\{\eta^4\text{-}6\text{-Me-}5\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-C}_6\text{H}_6\}\text{-Mn}(\text{CO})_2\text{NO}]$  (**7**). Compounds **6** and **7** were separated by column chromatography on silica gel using diethyl ether as eluant. The total yield of **6** and **7** was 95% and the ratio of **6** : **7** was 91 : 4.

By the same method as the addition of  $\text{NaBH}_3\text{CN}$ , a little excess  $\text{NaBD}_4$  was added to compound **3(CO)** (0.364 g, 0.737 mmol). After work-up, two products,  $[\{\eta^4\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{-Si-}6\text{-Me-C}_6\text{H}_5\text{D}\}\text{-Mn}(\text{CO})_2\text{NO}]$

**[6(D)]** and  $[\{\eta^4\text{-}6\text{-Me-}5\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-C}_6\text{H}_5\text{D}\}\text{-Mn}(\text{CO})_2\text{NO}]$  (**[7(D)]**) were obtained in the ratio of 4 : 3 (total yield: 77%).

#### 2.4.1. Demetallation of **6**

Ten equivalents of  $\text{Me}_3\text{NO}$  were added to a stirred solution of **6** (0.145 g, 0.354 mmol) in 20 ml of benzene. The mixture was refluxed for 2 h and then cooled to room temperature. After filtration, the filtrate was washed with water (30 ml  $\times$  3) and then extracted with diethyl ether (30 ml  $\times$  3). The combined extracts were dried ( $\text{MgSO}_4$ ), and then concentrated to give the crude product. Purification by column chromatography (silica gel, diethyl ether) gave the product. Demetallation of **6(H)** gave (*R*)-6-methyl-1-silatranyl-1,3-cyclohexadiene [**8(H)**] (82%), and that of **6(D)** gave (*R*)-6-deuterio-6-methyl-1-silatranyl-1,3-cyclohexadiene [**8(D)**] (75%).

#### 2.4.2. Demetallation of **7**

This was done in a similar way to that described above. Demetallation of **7(H)** gave **8(H)**, *ortho*-methyl-silatranyl benzene [**9(H)**] and *cis*-5-methyl-6-silatranyl-1,3-cyclohexadiene [**10(H)**] in the ratio of 2 : 1 : 2.7 (total yield: 72%), and that of **7(D)** led to **8(D)**, **9(D)**, and *cis*-6-deuterio-5-methyl-6-silatranyl-1,3-cyclohexadiene [**10(D)**] in the ratio of 4 : 1 : 13 (total yield: 72%).

### 2.5. Addition of $\text{NaCH}(\text{CO}_2\text{Et})\text{CN}$ to **3(CO)**

To a stirred solution of  $\text{NaH}$  (40 mg, 1.67 mmol) in 15 ml of THF at  $0^\circ\text{C}$  under  $\text{N}_2$  was added ethyl cyanoacetate (0.18 ml). The mixture was stirred for 10 min, after which time the solution became clear. The resulting solution was added via syringe to the suspension of **3(CO)** (0.56 g, 1.13 mmol) in 30 ml of THF at  $0^\circ\text{C}$ . Stirring was continued for 15 min, and then the reaction mixture was allowed to warm to room temperature. The mixture was poured into saturated  $\text{NH}_4\text{Cl}$  solution (50 ml) and extracted with diethyl ether (30 ml  $\times$  3), dried ( $\text{MgSO}_4$ ), and evaporated in vacuo to yield crude product. The pure product  $[\{\eta^4\text{-}1\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-}5\text{-N}(\text{C}(\text{EtO}_2\text{C})\text{CH-}6\text{-Me-C}_6\text{H}_5\text{Mn})\text{-CO})_2\text{NO}]$  (**11**) (0.183 g, 31%, red oil) was obtained by column chromatography on silica gel eluting with diethyl ether.

#### 2.5.1. Demetallation

Demetallation of **11** was done by the similar method as the demetallation of **6** except using 4-methylmorpholine *N*-oxide instead of  $\text{Me}_3\text{NO}$ . Compound *cis*-5-(1-cyano-1-ethoxycarbonyl)-methyl-6-methyl-1-silatranyl-1,3-cyclohexadiene (**12**) was obtained in 41% yield.

## 2.6. Addition of $\text{LiCH}_2\text{CN}$ to $3(\text{CO})$

To the LDA solution was added dropwise 0.06 ml of  $\text{CH}_3\text{CN}$  (1.12 mmol). The resulting solution was added dropwise to  $3(\text{CO})$  (0.492 g, 0.996 mmol) at  $-78^\circ\text{C}$ . The reaction mixture was stirred for 30 min, poured into water and then extracted with diethyl ether (30 ml  $\times$  3). The ether extracts were dried ( $\text{MgSO}_4$ ), evaporated to dryness, and purified by column chromatography on silica gel eluting with diethyl ether. After removal of the solvent,  $[\{\eta^5\text{-1-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-6-Me-C}_6\text{-H}_5\}\text{Mn}(\text{CO})\{\text{C}(\text{O})\text{CH}_2\text{CN}\}\text{NO}]$  [ $13(\text{C}(\text{O})\text{CH}_2\text{CN})$ ] was obtained in the yield of 0.287 g (64%).

### 2.6.1. Demetallation

When  $13(\text{C}(\text{O})\text{CH}_2\text{CN})$  was refluxed in benzene overnight, two kinds of compound were obtained. One compound, *trans*-5-cyanomethylcarbonyl-6-methyl-1-silatranyl-1,3-cyclohexadiene [ $15(\text{C}(\text{O})\text{CH}_2\text{CN})$ ], was formed via migration of the  $\text{C}(\text{O})\text{CH}_2\text{CN}$  group from metal to the  $\pi$ -hydrocarbon ring. We failed to isolate the other compound in the pure form.

## 2.7. Addition of $\text{LiCH}_2\text{CO}_2^t\text{Bu}$ to $3(\text{CO})$

To the LDA solution was added dropwise 0.41 ml of tert-butyl acetate (3.0 mmol). The resulting solution was added dropwise to  $3(\text{CO})$  (0.184 g, 0.373 mmol) in dry THF (30 ml) at  $-78^\circ\text{C}$ . The reaction mixture was stirred for 30 min at  $-78^\circ\text{C}$ , and then poured into water and extracted three times with diethyl ether. The ether extracts were dried ( $\text{MgSO}_4$ ), evaporated to dryness, and purified by column chromatography on silica gel eluting with diethyl ether and THF. After removal of the solvent the residue was washed with hexane to give pure  $[\{\eta^5\text{-1-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-6-Me-C}_6\text{-H}_5\}\text{Mn}(\text{CO})\{\text{C}(\text{O})\text{CH}_2\text{CO}^t\text{Bu}\}\text{NO}]$  [ $13(\text{C}(\text{O})\text{CH}_2\text{CO}_2^t\text{Bu})$ ].

### 2.7.1. Demetallation

Compound  $13(\text{C}(\text{O})\text{CH}_2\text{CO}_2^t\text{Bu})$  soaked with THF was kept under  $\text{N}_2$  for several days in the freezer. Then, to ensure demetallation, the compound was stirred in  $\text{CH}_2\text{Cl}_2$  at room temperature overnight. After purification by flash column chromatography, *trans*-5-tert-butoxycarbonylmethylcarbonyl-6-methyl-1-silatranyl-1,3-cyclohexadiene [ $15(\text{C}(\text{O})\text{CH}_2\text{CO}_2^t\text{Bu})$ ] was obtained in the analytically pure form. The overall yield from  $3$  to  $15(\text{C}(\text{O})\text{CH}_2\text{CO}_2^t\text{Bu})$  was 15%.

## 2.8. Addition of $\text{LiCH}_2\text{CO}_2^i\text{Pr}$ to $3(\text{CO})$

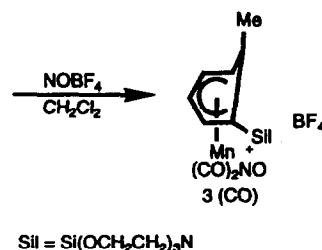
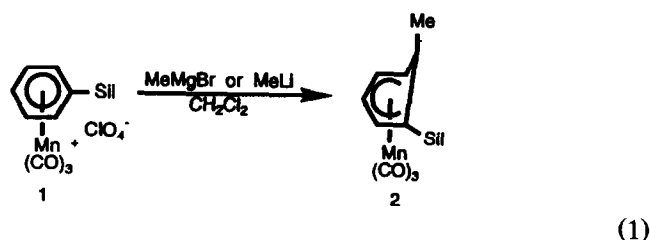
The same procedure as the addition of  $\text{LiCH}_2\text{CO}_2^t\text{Bu}$  was followed except using  $\text{LiCH}_2\text{CO}_2^i\text{Pr}$  instead of  $\text{LiCH}_2\text{CO}_2^t\text{Bu}$ .

### 2.8.1. Demetallation

Demetallation of  $[\{\eta^5\text{-1-N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Si-6-Me-C}_6\text{-H}_5\}\text{Mn}(\text{CO})\{\text{C}(\text{O})\text{CH}_2\text{CO}_2^i\text{Pr}\}\text{NO}]$  [ $13(\text{C}(\text{O})\text{CH}_2\text{CO}_2^i\text{Pr})$ ] was done by the same method as the demetallation of  $\text{M-C}(\text{O})\text{CH}_2\text{CO}_2^i\text{Bu}$ . The overall yield from  $3(\text{CO})$  to *trans*-5-isopropoxycarbonylmethylcarbonyl-6-methyl-1-silatranyl-1,3-cyclohexadiene [ $15(\text{C}(\text{O})\text{CH}_2\text{CO}_2^i\text{Pr})$ ] was 17%.

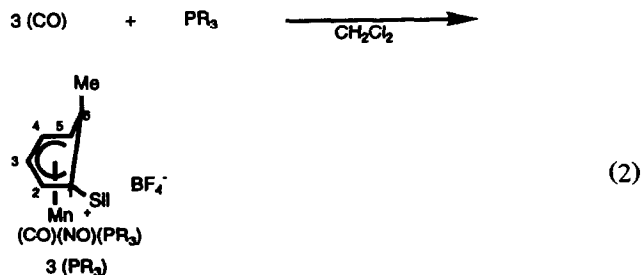
## 3. Results and discussion

Compound  $3(\text{CO})$  was synthesized by reaction between  $2$  and  $\text{NOBF}_4$  in  $\text{CH}_2\text{Cl}_2$  (Eq. 1). Compound  $3(\text{CO})$  is thermally stable, but rather unstable in air.



### 3.1. Addition of $\text{PPh}_3$ , $\text{P}(\text{O}Ph)_3$ , $\text{PMePh}_2$ and $\text{PPhPh}_2$ to $3(\text{CO})$

Phosphines or phosphites attacked the metal of  $3(\text{CO})$  with CO displacement (Eq. 2) [3]. Displacement of carbonyl by a phosphorus ligand generates a chiral-

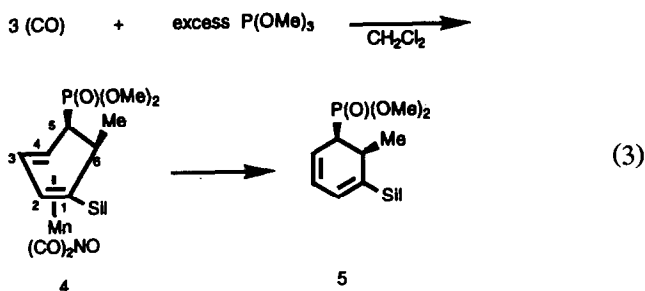


ity on the metal centre. In the  $^1\text{H}$  NMR spectra of  $3(\text{L})$ , ( $\text{L} = \text{PMePh}_2, \text{PPhPh}_2$ ), we could see two kinds of diastereomers, i.e. the methyl peak appeared at  $\delta$  0.48 and 0.67 ppm for  $3(\text{PMePh}_2)$  and  $\delta$  0.54 and 0.69 ppm for  $3(\text{PPhPh}_2)$ . For other  $3(\text{L})$  ( $\text{L} = \text{PPh}_3$  and  $\text{P}(\text{O}Ph)_3$ )

compounds, there might be a chance that the methyl peaks of two diastereomers coincide (0.45 and 0.46 ppm for  $3(\text{P}(\text{OPh})_3)$  and  $3(\text{PPh}_3)$ , respectively), in the  $^1\text{H}$  NMR spectra and that it might exist as a single diastereomer. We could not decide which was more probable. However, depending upon the phosphorus ligand, the ratio of two diastereomers would be varied. Temporarily, we assign the term A diastereomer for the case where the methyl peak appeared at ca. 0.5 ppm and B diastereomer for when the methyl peak appeared at 0.68 ppm. Then, the A:B ratios were 3.5:1 and 1:1.75 for the complexes of  $3(\text{PPh}_2\text{Me})$  and  $3(\text{PPh}_2\text{H})$ , respectively. At first, we expected that the steric bulk of phosphorus ligand would be a factor controlling diastereoselectivity. However, the available data on steric bulk of phosphorus ligands [4] (the cone angles of  $\text{PPh}_2\text{H}$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{PMePh}_2$  and  $\text{PPh}_3$  are  $128^\circ$ ,  $128^\circ$ ,  $136^\circ$ , and  $145^\circ$ , respectively) are not consistent with the diastereoselectivity. Other factors may also influence the diastereoselectivity.

### 3.2. Addition of $\text{P}(\text{OMe})_3$ to $3(\text{CO})$

IR studies showed that at room temperature  $\text{P}(\text{OMe})_3$  reacts with  $3(\text{CO})$  to give a mixture of the product derived from CO substitution,  $3(\text{P}(\text{OMe})_3)$  ( $\nu_{\text{CO}}$  2025 and  $\nu_{\text{NO}}$  1780  $\text{cm}^{-1}$ ), and the product derived from addition to the cyclohexadienyl ring, **4** ( $\nu_{\text{CO}}$  2020, 1960  $\text{cm}^{-1}$ ,  $\nu_{\text{P=O}}$  1250 and  $\nu_{\text{NO}}$  1720  $\text{cm}^{-1}$ ). However, treatment of  $3(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$  with 5 equiv. of  $\text{P}(\text{OMe})_3$  gave exclusively compound **4** [5] in a reasonable yield (Eq. 3).

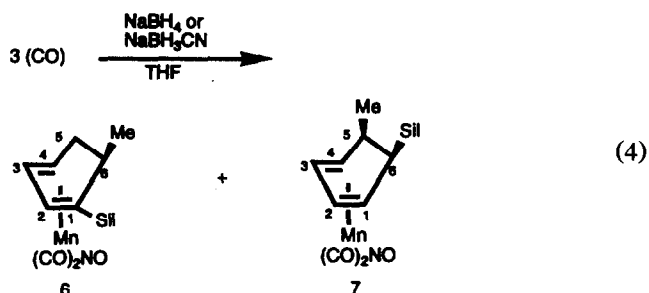


The *exo* position of the  $\text{P}(\text{O})(\text{OMe})_2$  group was confirmed by checking the coupling constant between  $\text{H}^5$  and  $\text{H}^6$ . If both protons were situated as *trans*, then the coupling constant would be 2–3 Hz. If both protons were situated as *cis*, then the coupling constant would be 9–10 Hz. According to the  $^1\text{H}$  NMR spectrum, the coupling constant was 9.7 Hz. Thus both protons were situated as *cis* and  $\text{P}(\text{O})(\text{OMe})_2$  group was situated in *exo* fashion. Compound **4** is apparently derived from the spontaneous Michaelis-Arbusov reaction of the  $\text{P}(\text{OMe})_3$  adduct [6]. Thus, this reaction provides an easy and viable synthetic route to the silatranyl phosphonate cyclohexadienyl complex. The phosphonate complex is highly sensitive to oxygen and rapidly de-

composed in solution. After demetallation of **4**, silatranyl phosphonate cyclohexadiene derivative (**5**) was obtained quantitatively.

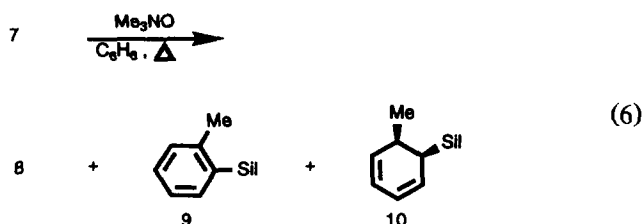
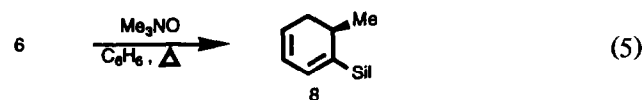
### 3.3. Addition of hydride to $3(\text{CO})$

The reaction of  $\text{NaBH}_3\text{CN}$  with  $3(\text{CO})$  occurred cleanly to give diene complexes **6** and **7** (Eq. 4) [7]. The hydride added at the C-1 or C-5 position of the dienyl



ring. The ratio of **6** and **7** was dependent upon the reaction temperature. When  $\text{NaBH}_3\text{CN}$  was added at room temperature, the ratio of **6** and **7** was 91:4. When  $\text{NaBH}_3\text{CN}$  was added at  $-15^\circ\text{C}$ , this ratio was 1:1. As the reaction temperature was further lowered, the formation of **7** seemed to be more favourable. However, when the reaction temperature was below  $-40^\circ\text{C}$ , the reactant was recovered. Compounds **6** and **7** can be handled in air and separated by column chromatography. The hydride is situated *endo* in compounds **6** and **7**. This was ascertained by deuteration and demetallation experiments. For compound **7**, the added hydride gave a clean doublet that was coupled to H-5 hydrogen ( $J = 10.5$  Hz) and H-6 hydrogen ( $J = 3.1$  Hz).

Demetallation of **6** was performed by using  $\text{Me}_3\text{NO}$  in refluxing benzene [8] and gave a cyclohexadiene derivative **8** (Eq. 5). However, when **7** was treated with  $\text{Me}_3\text{NO}$  in refluxing benzene, a mixture of **8**, **9**, and **10** was obtained in the ratio of 2:1:2.7 for **7**(H) and 4:1:13 for **7**(D) (Eq. 6). Compound **8** could be ob-



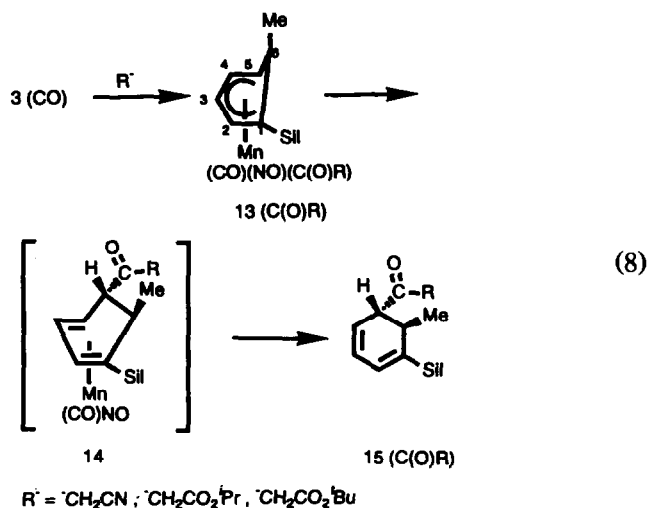
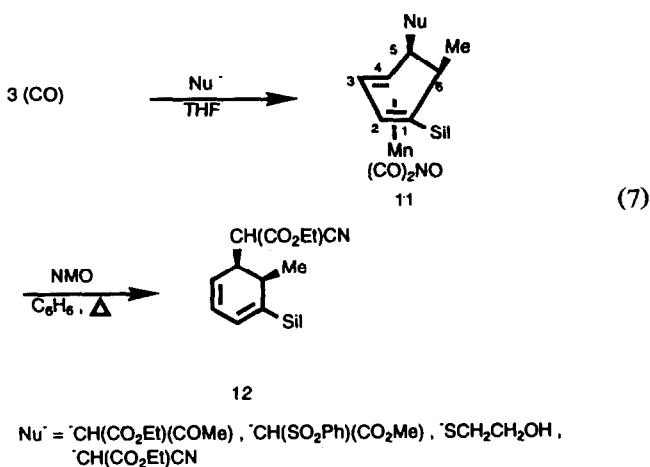
tained by hydride migration followed by demetallation or by removal and readdition of hydrogen while refluxing in benzene. The formation of **9** could be understandable in terms of removal of one of the hydrogens.

The *endo* stereochemistry observed in the hydride addition reaction suggests an initial interaction with the metal to form a M–H or M–CHO species [9,10], followed by hydride migration to give the diene products **6** and **7**. Sweigart reported [9] the spectral evidence for the formation of formyl complex in the reaction of (6-*exo*-PhC<sub>6</sub>Me<sub>5</sub>H)Re(CO)<sub>2</sub>NO<sup>+</sup> with [Bu<sub>4</sub>N]BH<sub>4</sub> in CH<sub>3</sub>CN at –35°C. Recently, Eyman reported [10] the intermediary of a metal formyl, in the reactions of NaBD<sub>4</sub> (–83°C) with [(C<sub>6</sub>Me<sub>6</sub>)Mn(CO)<sub>3</sub>]PF<sub>6</sub> in CH<sub>3</sub>OD and NaBH<sub>4</sub> (–50°C) with [(C<sub>6</sub>H<sub>6</sub>)Mn(CO)<sub>3</sub>]<sup>+</sup> in CH<sub>3</sub>OH by the detection of down-field <sup>2</sup>H and <sup>1</sup>H NMR signals. It is probable that for the addition of hydride to compound **3**(CO) a reactive formyl species is formed initially, followed by hydride migration to the cyclohexadienyl ring. The carbanion addition to **3**(CO) (presented later) would be indirect evidence for the formation of a formyl intermediate.

### 3.4. Addition of carbon nucleophiles to **3**(CO)

The addition reactions of several kinds of carbon nucleophiles were studied. Addition of RMgX or RLi (R = Me and Ph) to **3**(CO) resulted in poor yield [11]. Addition of the carbanions of ethyl acetoacetate, methyl phenylsulfonylacetate and mercaptoethanol to **3**(CO) gave diene complexes **11** [11] (when the reaction was checked by IR) (Eq. 7). However, the diene complexes, **11**, decomposed rather rapidly in solution. Treatment of the diene complexes with Me<sub>3</sub>NO in benzene gave *ortho*-methylsilatranylbenzene. However, the product of reaction between **3** and the carbanion of ethyl cyanoacetate was rather stable and could be demetallated by treating with 4-methylmorpholine *N*-oxide (NMO) to yield the cyclohexadiene derivative of silatrane, **12**.

When compound **3**(CO) was treated with LiCH<sub>2</sub>CN, the acyl complex **13**(C(O)CH<sub>2</sub>CN) was isolated in 64% yield (Eq. 8). We could see the  $\nu(\text{C}=\text{O})$  stretching at



1622 cm<sup>-1</sup> [12] and the methylene protons at 3.55 and ca. 3.6 ppm, respectively. Due to the overlapping with the signals of silatranyl OCH<sub>2</sub>, it is not easy to assign the exact peak position of the proton at ca. 3.6 ppm. The peak at 3.55 ppm was doublet due to the geminal coupling (*J* = 15.6 Hz). **13**(C(O)CH<sub>2</sub>CN) rearranged very slowly to diene compound, presumably **14**, that the C(O)CH<sub>2</sub>CN group was situated at *endo*. Compound **14** decomposed ultimately to afford *trans*-disubstituted cyclohexadiene derivatives of silatrane, **15**(C(O)CH<sub>2</sub>CN). The rearrangement continued in solution and even in the solid state. The same kind of rearrangement was observed [12] in the reaction of (*exo*-R- $\eta^5$ -C<sub>6</sub>H<sub>6</sub>)Mn(CO)<sub>2</sub>NO<sup>+</sup> (R = Me or Ph) with carbon nucleophiles such as LiPh and LiMe. MeLi or PhLi attacked the carbonyl group in (*exo*-R- $\eta^5$ -C<sub>6</sub>H<sub>6</sub>)Mn(CO)<sub>2</sub>NO<sup>+</sup> (R = Me or Ph), ultimately affording *trans*-disubstituted cyclohexadienes. However, the metal carbonyl-attacked complex was not observed in this case because of its instability. However, when LiCH<sub>2</sub>CN was reacted with (*exo*-Me- $\eta^5$ -C<sub>6</sub>H<sub>6</sub>)Mn(CO)<sub>2</sub>NO<sup>+</sup>, we could see the formation of acyl compound by checking IR ( $\nu(\text{C}=\text{O})$  1622 cm<sup>-1</sup>) [13]. The acyl compound ultimately decomposed during separation.

The same kind of nucleophilic addition and rearrangement occurred with complexes **13**(C(O)CH<sub>2</sub>CO<sup>i</sup><sub>2</sub>Bu) and **13**(C(O)CH<sub>2</sub>CO<sup>i</sup><sub>2</sub>Pr). The rearrangement could be accelerated by treatment with polar solvent or silica gel. However, when the rearrangement was speeded up, the yield of aromatized compound, *ortho*-methylsilatranylbenzene, increased. Thus, to decrease the distribution of aromatized product, the compound was soaked with THF under N<sub>2</sub> and kept in a freezer for several days and then stirred in CH<sub>2</sub>Cl<sub>2</sub> overnight. After column chromatography, we obtained the analytically pure rearranged products, **15**(C(O)CH<sub>2</sub>CO<sup>i</sup><sub>2</sub>Bu) and **15**(C(O)CH<sub>2</sub>CO<sup>i</sup><sub>2</sub>Pr), which were characterized.

The rearrangement of complex **13**(C(O)R) to **15**(C(O)R) occurred even at low temperature and in the solid phase.

The regioselectivities of carbon nucleophile addition to **3**(CO) and (*exo*-R- $\eta^5$ -C<sub>6</sub>H<sub>6</sub>)Mn(CO)<sub>2</sub>NO<sup>+</sup> were almost the same. However, there were big differences in the stabilities of the reaction products. In particular the acyl compounds **13** had a degree of stability. Thus we could characterize **13** and observe the rearrangement of **13** to the diene complex, presumably **14**, ultimately affording *trans*-disubstituted cyclohexadiene derivatives of silatrane, **15**. However, the acyl compound derived from the reaction between (*exo*-R- $\eta^5$ -C<sub>6</sub>H<sub>6</sub>)Mn(CO)<sub>2</sub>NO<sup>+</sup> and LiCH<sub>2</sub>CN had only marginal stability. We envisaged that the introduction of the silatranyl group improved the stability of the acyl compound **13**. However, we are not sure how the silatranyl group helps to enhance the stability of acyl compounds. We are now continuing to clarify the effect of the silatranyl group on the stability of the acyl compound.

In conclusion, we have demonstrated that the manganese system discussed in this paper is a versatile means for the synthesis of new silatranyl derivatives via difunctionalization of phenylsilatrane.

#### Acknowledgement

Financial support from the Korea Science and Engineering Foundation (Grant No. 90-03-00-18) is gratefully acknowledged.

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