Chemistry of [(1*H*-hydronaphthalene)Mn(CO)$_3$]: The Role of Ring-Slippage in Substitution, Catalytic Hydrosilylation, and Molecular Crystal Structure of [(η^3-C$_{10}$H$_9$)Mn(CO)$_3$P(OMe)$_3$]

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Reaction of [(η^5-C$_{10}$H$_9$)Mn(CO)$_3$] (**1**) with L produced [(η^3-C$_{10}$H$_9$)Mn(CO)$_3$L] (**2**, L = P(OMe)$_3$; **5**, L = CO) in high yields. X-ray structural analysis of **2** confirmed an η^3-bonding mode of the 1-hydronaphthalene ring. Thermal treatment of **2** led to [(η^5-C$_{10}$H$_9$)Mn(CO)$_2$P(OMe)$_3$] (**3**). The η^5-1-hydronaphthalene ring in **1** is quite easily ring-slipped, $\eta^5 \leftrightarrow \eta^3$. A kinetic study of the reaction of **1** with P(OMe)$_3$ indicates that formation of **2** is first order in **1** and first order in P(OMe)$_3$ with the following activation parameters: $\Delta H^{\ddagger} = 6.9 \pm 0.4$ kcal/mol; $\Delta S^{\ddagger} = -32.6 \pm 1.5$ eu. Quantitative comparison between the reactivity of the indenyl complex [(η^5-C$_9$H$_7$)Mn(CO)$_3$] with P(OEt)$_3$ and **1** with P(OMe)$_3$ at 130 °C shows that the rate constant for **1** is 2×10^6 times faster than that of the indenyl complex. The tremendous rate enhancement in **1** was rationalized as a stabilization of **2** by the second benzene ring. The facile ring-slippage in **1** has been utilized in the synthesis of [(η^6-C$_{10}$H$_8$)Mn(CO)$_2$P(OMe)$_3$]BF$_4$ and in the catalytic hydrosilylation of ketones. Complex **1** is an effective catalyst for the hydrosilylation of alkyl and aryl ketones with Ph$_2$SiH$_2$ as a silane source. The indenyl complex [(η^5-C$_9$H$_7$)Mn(CO)$_3$] has no catalytic activity in the hydrosilylation of ketones. The facile ring-slippage in the η^5-1-hydronaphthalene ring plays a crucial role in the chemistry of **1**.

Introduction

η^5-Cyclohexadienylmanganese tricarbonyl complexes are stable and relatively inert.[1] However, reaction of (η^5-cyclohexadienyl)Mn(CO)$_3$ with strong carbanions has been reported.[2] Treatment of (η^5-cyclohexadienyl)Mn(CO)$_3$ with a nitrosyl ligand results in cationic (η^5-cyclohexadienyl)Mn(CO)$_2$(NO)$^+$ complexes,[3] which are readily attacked by nucleophiles such as phosphines, phosphites, or soft carbanions. Interestingly, there have been no reports on the chemistry of η^5-1-hydronaphthalene complex (η^5-C$_{10}$H$_9$)Mn(CO)$_3$ (**1**)[4] until the very recent publication by Kreiter et al.[5] They reported the synthesis of [(η^3-C$_{10}$H$_9$)Mn(CO)$_3$P(OMe)$_3$] (**2**), [(η^5-C$_{10}$H$_9$)Mn(CO)$_2$P(OMe)$_3$] (**3**), and [(η^5-C$_{10}$H$_9$)Mn(CO){P(OMe)$_3$}$_2$] (**4**) (Chart 1) by the reaction **1** with P(OMe)$_3$. They studied the 1,4-H shifts of 1-H$^{\text{endo}}$ in **1**, **3**, and **4** by ^{1}H NMR spectroscopy. While we studied[6] the chemistry of [(η^6-C$_{10}$H$_8$)Mn(CO)$_3$]BF$_4$, we have also found independently the formation of **2** by the reaction of **1** with P(OMe)$_3$ and interpreted the facile substitution reaction as due to the ring-slippage[7] in **1**. This observation stimulates us to study the chemistry of **1**. Herein we report our recent results of the kinetic study of CO substitution in **1**, the molecular structure of **2**, and the synthesis of [(η^3-C$_{10}$H$_9$)Mn(CO)$_4$] (**5**). The interesting novel catalytic activity of **1** in the hydrosilylation of ketones is also reported.

Results and Discussion

Molecular Structure of [(η^3-C$_{10}$H$_9$)Mn(CO)$_3$P(OMe)$_3$] (2) and Synthesis of [(η^3-C$_{10}$H$_9$)Mn(CO)$_4$] (5). Treatment of **1** with P(OMe)$_3$ in CH$_2$Cl$_2$ at room

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[1] Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525.

[2] Sheridan, J. B.; Padda, R. S.; Chaffe, K.; Wang, C.; Huang, Y.; Lalancette, R. *J. Chem. Soc., Dalton Trans.* **1992**, 1539.

[3] (a) Chung, Y. K.; Choi, H. S.; Sweigart, D. S. *J. Am. Chem. Soc.* **1982**, *104*, 4245. (b) Chung, Y. K.; Honig, E. D.; Robinson, W. T.; Sweigart, D. A.; Connelly, N. G.; Ittel, S. D. *Organometallics* **1983**, *2*, 1479. (c) Chung, Y. K.; Sweigart, D. A.; Connelly, N. G.; Sheridan, J. B. *J. Am. Chem. Soc.* **1985**, *107*, 2388. (d) Chung, Y. K.; Sweigart, D. A. *J. Organomet. Chem.* **1986**, *308*, 223. (e) Hyeon, T.-H.; Chung, Y. K. *J. Organomet. Chem.* **1989**, *372*, C12. (f) Lee, T.-Y.; Kang, Y. K.; Chung, Y. K.; Pike, R. D.; Sweigart, D. A. *Inorg. Chim. Acta* **1993**, *214*, 125. (g) Lee, S. S.; Jeong, E.; Chung, Y. K. *J. Organomet. Chem.* **1994**, *483*, 115.

[4] (a) Thompson, R. L.; Lee, S.; Rheingold, A. L.; Cooper, N. J. *Organometallics* **1991**, *10*, 1657. (b) Sun, S.; Dullaghan, C. A.; Carpenter, G. B.; Sweigart, D. A.; Lee, S. S.; Chung, Y. K. *Inorg. Chim. Acta* **1997**, *262*, 213. (c) Kreiter, C. G.; Georg, A.; Reiss, J. *Chem. Ber.* **1997**, *130*, 1197.

[5] Georg, A.; Kreiter, C. G. *Eur. J. Inorg. Chem.* **1999**, 651.

[6] (a) Sun, S.; Yeung, L. K.; Sweugart, D. A.; Lee, T.-Y.; Lee, S. S.; Chung, Y. K.; Switzer, S. R.; Pike, R. D. *Organometallics* **1995**, *14*, 2613. (b) Dullaghan, C. A.; Sun, S.; Lee, S. S.; Chung, Y. K.; Sweigart, D. A. *Inorg. Chim. Acta* **1997**, *262*, 213. (c) Son, S. U.; Paik, S. J.; Chung, Y. K. *J. Mol. Catal.*, in press.

[7] (a) Kündig, E. P.; Jeger, P.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2161. (b) Jonas, K. *Pure Appl. Chem.* **1990**, *62*, 1169.

10.1021/om9903386 CCC: $15.00

Chart 1

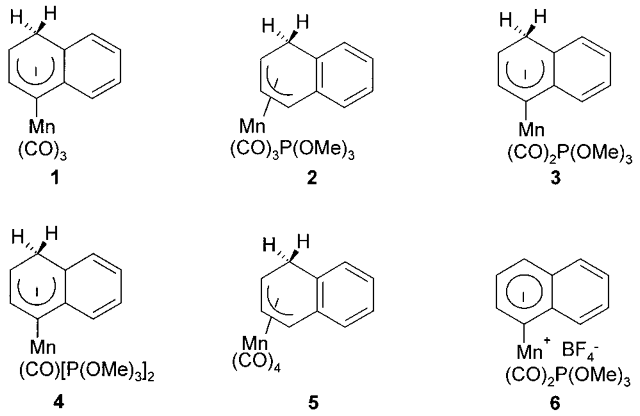


Table 1. Crystal Data and Structure Refinement for 2

empirical formula	$C_{16}H_{18}MnO_6P$
fw	392.21
crystal system	monoclinic
space group	$P2_1/a$
a, Å	10.4428(9)
b, Å	12.4612(13)
c, Å	14.325(2)
β, deg	108.679(9)
volume, Å^3	1766.0(3)
Z	4
d(calcd), Mg/m^3	1.475
2θ range, deg	4.1−50
total no. collected	3276
no. of unique data	3092
no. of params refined	222
R1 ($I > 2\sigma(I)$)	0.0419
wR2	0.1125
gof	1.030

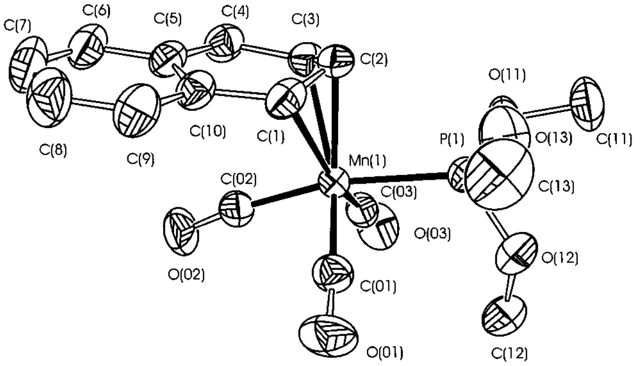
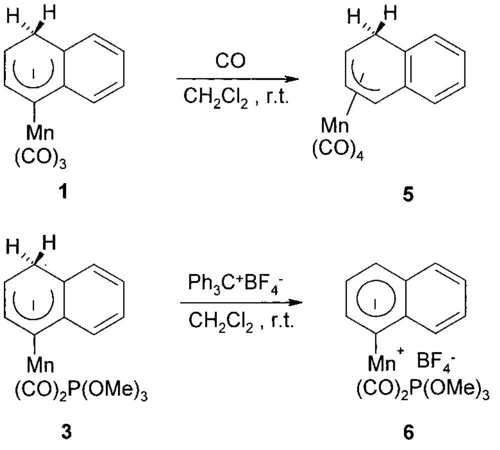


Figure 1. ORTEP drawing of **2** with the atomic labeling scheme. Thermal ellipsoids are drawn at the 40% probability level.

Scheme 1



temperature afforded **2**[5] in 94% yield. Single crystals of **2** suitable for X-ray crystallography were grown by slow evaporation of a pentane solution of **2** at −15 °C. Crystal data and structure refinement details are given in Table 1 and selected bond lengths and angles in Table 2. The X-ray structural determination of **2** confirmed the η^3-bonding mode of the 1-hydronaphthalene ring (Figure 1). The Mn−C2 bond length is significantly shorter than the Mn−C1 and Mn−C3 bond distances. The dihedral angle between plane C1−C2−C3 and plane C10−C9−C8−C7−C6−C5 is 32.1(0.3)°. Similar coordination was observed for the η^3-indenyl ligand of $(\eta^3\text{-}C_9H_7)Ir(PMe_3)_3$ and $(\eta^3\text{-}C_9H_7)IrH_2(PPr^i{}_3)_2$.[8,9] Contrary to our expectation, **2** is relatively stable. At room temperature, **2** does not rearrange to η^5-1-hydronaphthalene complex. Refluxing **2** at 40 °C for 4 h led to **3** in 86% yield. Kreiter et al.[5] obtained **3** by the photochemical reaction of **2**.

Treatment of **1** in CH_2Cl_2 under a CO atmosphere gave **5** in 74% yield (Scheme 1).

Compound **5** is air-stable but thermally unstable. When **5** is heated to melt, it is converted to **1**. The facile ring-slippage in **1** has been utilized in the synthesis of the $[(\eta^6\text{-}C_{10}H_8)Mn(CO)_2L]^+$ cation. Complex $[(\eta^6\text{-}C_{10}H_8)Mn(CO)_2L]^+$ cannot be synthesized directly from $[(\eta^6\text{-}C_{10}H_8)Mn(CO)_3]^+$ due to the easy loss of the naphthalene ring (a L_3 type ligand).[10] However, in **1**, the 1-hydronaphthalene ring is a L_2X type ligand. Hence, the 1-hydronaphthalene ring tolerates the reaction condition as in the synthesis of **2** or **3**. Hence, treatment of **1** with $P(OMe)_3$ followed by addition of Ph_3CBF_4 gave a high yield of $[(\eta^6\text{-}C_{10}H_8)Mn(CO)_2P(OMe)_3]^+$ (**6**).

One might expect that the open pentadienyl ligand undergoes even more facile associative ligand substitutions involving η^5 to η^3 interconversion, and so they do.[11] The η^3-intermediate is isolable and has been characterized crystallographically. However, curiously, the related η^3-allyl complex $(\eta^3\text{-}C_3H_4X)Mn(CO)_4$ (X = H, Me, Ph, t-Bu, Cl)[12] does not undergo associative ligand substitutions, at least not with the moderate nucleophile PPh_3. It is well-known[7] that the η^5-1-hydronaphthalene ligand can undergo a facile haptotropic rearrangement to an η^3-enyl coordination mode. As expected from the facile ring-slippage in 1-hydronaphthalene complexes, the 1-hydronaphthalene iron(II) complex $[(\eta^5\text{-}C_{10}H_9)FeCp]$ is considerably more reactive than (η^5-cyclopentadienyl)(η^5-cyclohexadienyl)iron(II) $[(\eta^5\text{-}C_6H_7)FeCp]$.[7a] For the same reason as the organoiron complex, the benzocyclohexadienylmanganese(I) complex $[(\eta^5\text{-}C_{10}H_9)Mn(CO)_3]$ is expected to be considerably more reactive than cyclohexadienylmanganese complexes [(*exo*-R-η^5-C_6H_6)Mn(CO)$_3$]. In fact, it is not a facile process to substitute one of carbonyls in [(*exo*-R-η^5-C_6H_6)Mn(CO)$_3$]

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(8) Merola, J. S.; Kacmarcik, R. T.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 329.

(9) Husebo, T. L.; Jensen, C. M. *Organometallics* **1995**, *14*, 1087.

(10) Crabtree, R. H. *The Organometallic Chemistry of Transition Metals*, 2nd ed.; John Wiley & Sons: New York, 1993; p 129.

(11) Paz-Sandoval, M. A.; Powell, P.; Drew, M. G.; Perutz, R. N. *Organometallics* **1984**, *3*, 1026.

(12) Palmer, G. T.; Basolo, F. *J. Am. Chem. Soc.* **1985**, *107*, 3122.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2

Mn(1)−C(01)	1.793(3)	Mn(1)−C(02)	1.825(3)	Mn(1)−P(1)	2.243(9)
Mn(1)−C(1)	2.235(3)	Mn(1)−C(2)	2.112(3)	C(1)−C(2)	1.405(5)
C(2)−C(3)	1.380(5)	C(3)−C(4)	1.504(5)	C(1)−C(10)	1.407(5)

C(1)−C(2)−C(3)	117.3(3)	C(1)−C(10)−C(5)	119.6(3)
C(4)−C(5)−C(10)	120.4(3)	C(3)−C(4)−C(5)	114.1 (3)
P(1)−Mn(1)−C(02)	167.49(11)	Mn−C(01)−O(01)	176.9(3)

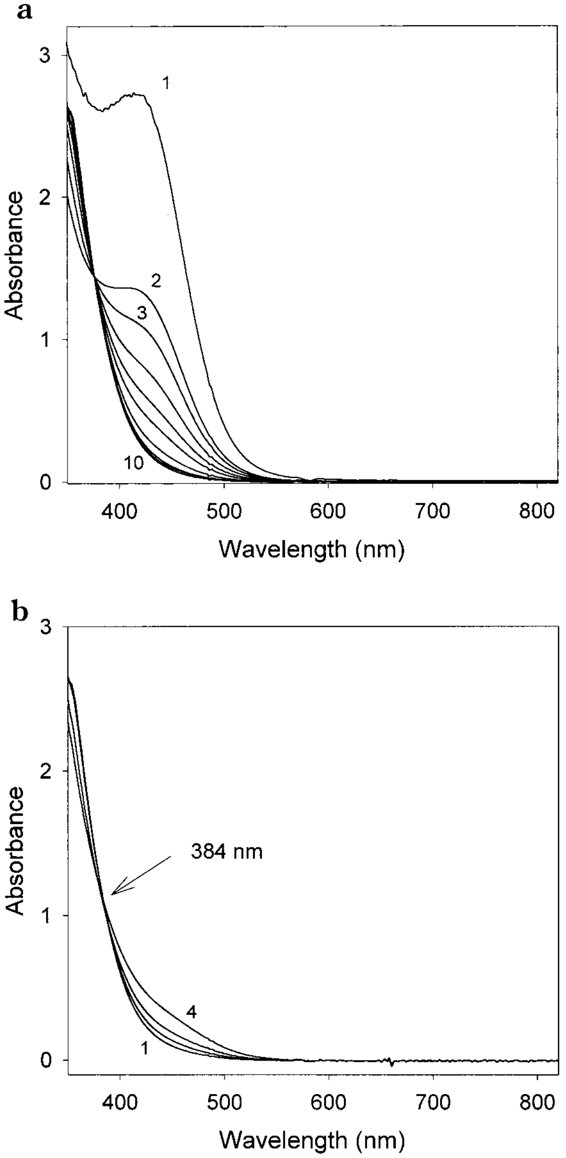

Figure 2. Successive spectral changes observed during the reaction of **1** (initially 0.93 mM) by P(OMe)$_3$ (initially 4.66 mM) in CH$_2$Cl$_2$ at 298 K. (a) The first stage of the reaction showing the absorbance decrease at 415 nm; (1) **1** only; (2) 10 s; (3) 30 s; (4) 60 s; (5) 90 s; (6) 2 min; (7) 3 min; (8) 4 min; (9) 5 min; (10) 30 min. (b) The second stage showing the increase at 415 nm: (1) 0.5 h; (2) 1 h; (3) 3 h; (4) 6 h.

Table 3. Some of Typical Kinetic Data for the Initial Step in the Reaction of 1 with P(OMe)$_3$ in CH$_2$Cl$_2$

$10^3 \times$ [**1**], M	$10^2 \times$ [P(OMe)$_3$], M	k,^{a} M^{-1} s^{1-}	temp, °C
1.04	3.73	1.95 (±0.02)	10.0
0.93	7.46	2.45 (±0.03)	15.0
1.04	14.8	3.09 (±0.02)	20.0
0.93	1.87	3.58 (±0.01)	25.0
1.04	3.73	4.86 (±0.03)	30.0

^{a} Each rate constant is the average of four or more experimental results. Second-order rate constants were calculated from k_{obs}/[P(OMe)$_3$] under pseudo-first-order conditions in excess P(OMe)$_3$, where k_{obs} is the pseudo-first-order rate constant.

by phosphines.[1] In the similar manner, the well-known indenylmanganese complex [(η^5-C$_9$H$_7$)Mn(CO)$_3$] is much more reactive than the cyclopentadienylmanganese complex [CpMn(CO)$_3$].[13] [CpMn(CO)$_3$] has been known to be thermally inert toward CO substitution.[14] The above studies stimulated our curiosity to compare the reactivities of [(η^5-C$_9$H$_7$)Mn(CO)$_3$] and **1**.

Kinetic Study of [(η^5-C$_{10}$H$_9$)Mn(CO)$_3$] with P(OMe)$_3$. In Figure 2 are shown the spectral changes that occur with time in CH$_2$Cl$_2$ solution with 0.93 mM of **1** and 0.466 mM of P(OMe)$_3$. After mixing, the reaction occurs in a stepwise fashion via an intermediate, which forms in an initial rapid step and slowly loses CO to give the product. The formation of the intermediate was observed by the fast disappearance of the broad peak around 415 nm with an isobestic point at 376 nm. The structure of the intermediate was identified as [(η^3-C$_{10}$H$_9$)Mn(CO)$_3$P(OMe)$_3$] (**2**), as shown in Figure 1. The kinetics of the initial step of the reaction of **1** with P(OMe)$_3$ in CH$_2$Cl$_2$ was studied by a stopped-flow spectrometer. The kinetics of formation of **2** are first order in **1** and first order in P(OMe)$_3$. Under pseudo-first-order conditions with P(OMe)$_3$ in excess, rate constant data for the reaction at each temperature are summarized in Table 3. At 25.0 °C, $k = 3.58$ M^{-1} s^{-1} was averaged over four or more concentrations of P(OMe)$_3$ in pseudo-first-order excess. From rate constant measurements as a function of temperature and the plot of ln(k/T) vs 1/T over the temperature range of 10−30 °C according to reaction rate theory,[15] $\Delta H^{\ddagger} = 6.9 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -32.6 \pm 1.5$ eu were obtained. Using the Arrhenius equation, $E_a = 7.5 \pm 0.4$ kcal/mol was also obtained.

The results shown in Table 3 would clearly suggest an associative mechanism with a huge negative entropy. The next step slowly proceeds to give the product **3**; k(25 °C) = ~10^{-5} s^{-1} was obtained. The rate of the second step was independent of the concentration of added P(OMe)$_3$.

Quantitative comparison between the reactivity of the indenyl complex [(η^5-C$_9$H$_7$)Mn(CO)$_3$] with P(OEt)$_3$ and that of **1** with P(OMe)$_3$ at 130 °C shows that the rate constant for the latter is 2×10^6 times faster (!) than the indenyl complex ([(η^5-C$_9$H$_7$)Mn(CO)$_3$], 4.7×10^{-5} M^{-1} s^{-1}; **1**, 97.3 M^{-1} s^{-1}).[13] The tremendous rate enhancement of **1** compared to [(η^5-C$_9$H$_7$)Mn(CO)$_3$] can be explained by a stabilization of the η^3 intermediate

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(13) (a) Rerek, M. E.; Ji, L.-N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208. (b) Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372. (c) Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740.

(14) Nyholm, R. S.; Shandu, S. S.; Stiddard, M. H. *J. Am. Chem. Soc.* **1963**, *85*, 5916.

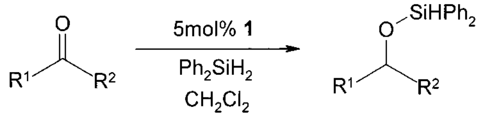
(15) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981.

Table 4. Catalytic Hydrosilylation of Ketones by Manganese Tricarbonyl Compounds of π-Hydrocarbons[a]

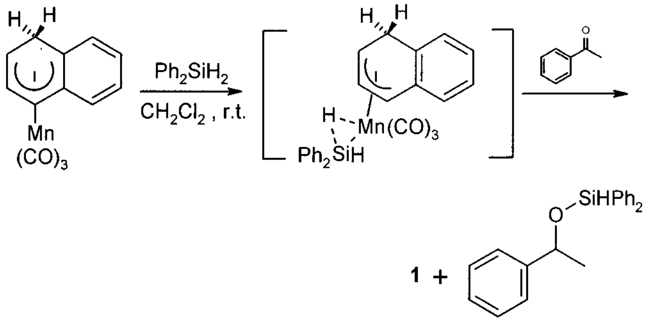
entry	cat.	substrate	silane	time (h)	yield (%)[b]
1	**1**	2-pentanone	Ph_2SiH_2	3	>99
2	**1**	cyclopentanone	Ph_2SiH_2	3	>99
3	**1**	acetophenone	Ph_2SiH_2	3	>99
4	**1**	4-methyl acetophenone	Ph_2SiH_2	3	>99
5	**1**	4-methoxy acetophenone	Ph_2SiH_2	7	28
6	**1**	4-bromo acetophenone	Ph_2SiH_2	7	>99
7	**1**	4-cyano acetophenone	Ph_2SiH_2	18	N.R.[c]
8	**1**	4-nitro acetophenone	Ph_2SiH_2	18	N.R.
9	**1**	2-acetonaphthone	Ph_2SiH_2	3	>99
10	**1**	1-acetonaphthone	Ph_2SiH_2	3	N.R.
11	(η^5-cyclohexadienyl)Mn(CO)$_3$	acetophenone	Ph_2SiH_2	18	N.R.
12	(η^5-indenyl)Mn(CO)$_3$	acetophenone	Ph_2SiH_2	18	N.R.

[a] In CH_2Cl_2, 5 mol % catalyst used at 25 °C. [b] Conversion yield calculated by ^1H NMR. [c] No reaction.

Scheme 2



Scheme 3



by the second benzene ring. This argument is similar to that used in the tremendous rate enhancement observed for the carbonyl substitution reaction of indenyl complexes over cyclopentadienyl complexes. One major difference between indenyl and 1-hydronaphthalene systems is that η^3-indenyl prefers to reverse back to the η^5 coordination (i.e., to restore the aromaticity), while the 1-hydronaphthalene ligand has little tendency to go back to η^5 coordination because of the nonaromaticity of 1-hydronaphthalene ligand. Besides the indenyl complex, the 1-pyrindinyl complex [(η^5-C_8H_6N)Mn(CO)$_3$] and the fluorenyl complex [(η^5-$C_{13}H_9$)Mn(CO)$_3$] also undergo substitution reaction with 40 times and 67 times faster rates, respectively, than the indenyl complex [(η^5-C_9H_7)Mn(CO)$_3$] due to the extent of stabilization of the coordinated ene fragment in the allyl, ene η^3 intermediate.[13,16] The ease of the CO substitution is in the order cyclopentadienyl ≪ indenyl ≪ 1-hydronaphthalene. The tremendous rate enhancement of **1** stimulates us to study the application of **1** in catalytic reactions.

Catalytic Hydrosilylation. To be an active catalyst, the low-energy pathway to the the requisite coordinative unsaturation is quite required. Ring-slippage could be a good breakthrough to this purpose. However, little attention has been paid to the use of ring-slippage in the catalytic reactions.[17] Especially, there have been no reports on the use of complexes containing a 1-hydronaphthalene ring in the catalytic reactions.

Hydrosilylation of ketones catalyzed by **1** has been studied (Scheme 2). Experimental results are summarized in Table 4.

The reaction conditions have not been optimized yet. For convenience, we used 5 mol % of catalyst for the reactions. Alkyl ketones were hydrosilylated almost quantitatively at 25 °C in 3 h (entries 1 and 2). The yields for aryl ketones are highly dependent on the electronic properties (entries 3−8) of the substrates. As the electron-donating ability of the substituent on the substrate decreases, the yield decreases. Reactions did not occur with a strong electron-withdrawing substituent such as cyano and nitro (entries 7 and 8). The oxygen of the methoxy group of 4-methoxyacetophenone may compete with ketone for coordinating to the manganese atom and interrupt the hydrosilylation of 4-methoxyacetophenone. This argument may be related to the observation that no hydrosilylation reaction occurs in tetrahydrofuran. The same reason may apply to explain the cases for cyano- and nitroacetophenone. The yields for aryl ketones are dependent on the steric bulkiness (entries 3, 9, and 10). With 1-acetonaphthone (entry 10), no reaction occurred. Thus, the yields for the hydrosilylation of aryl ketones are quite dependent on the electronic and steric effect of the substituent of the aryl ring. As expected, neither the cyclohexadienyl complex [(η^5-C_6H_7)Mn(CO)$_3$] (entry 11) nor the indenyl complex [(η^5-C_9H_7)Mn(CO)$_3$] (entry 12) is active in the hydrosilylation of ketones.

After hydrosilylation, the catalyst was recovered as intact because there were no deactivation pathways. The recovered catalyst can be reused as a catalyst as long as the ketone substrate is supplied.

Treatment of **1** with acetophenone in $CDCl_3$ yielded no reaction products. Thus, the first step of the hydrosilylation may be the formation of Mn(η^2-H−Si) species, and then the Mn(η^2-H−Si) species would react with ketone. A plausible mechanism (Scheme 3) has been proposed, which is based on other previous studies.

Complex **1** is a good catalyst for the hydrosilylation of ketones. Usually, the catalyst precursor has to be transformed to coordinatively unsaturated species. When ring-slippage occurs to a π-bound ligand as the η^5-1-hydronaphthalene in **1**, its hapticity falls and coordi-

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(16) (a) Ji, L.-N.; Kershner, D. L.; Rerek, M. E.; Basolo, F. *J. Organomet. Chem.* **1985**, *296*, 83. (b) Sweigart, D. A. In *Mechanisms of Inorganic and Organometallic Reactions*; Twigg, M. V., Ed.; Plenum Press: New York, 1985; Vol. 3, p 269.

(17) (a) Marder, T. B.; Roe, D. C.; Milstein, D. *Organometallics* **1988**, *7*, 1451. (b) Garrett, C. E.; Fu, G. *J. Org. Chem.* **1998**, *63*, 1370.

(18) (a) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90. (b) Sun, J.; Lu, R. S.; Bau, R.; Yang, G. K. *Organometallics* **1994**, *13*, 1317. (c) Scharrer, E.; Chang, S.; Brookhart, M. *Organometallics* **1995**, *14*, 5686.

native unsaturation is created. Hence, it is not a prerequisite for **1** to be transformed to the coordinatively unsaturated species. Hence, the catalytic reactivity of **1** may be due to the facile ring-slippage $\eta^5 \rightarrow \eta^3$. The endurance of **1** in the catalytic reaction may come from its low electrophilicity and its L_nX type character.

Conclusion

We have demonstrated that the η^5-1-hydronaphthalene ring in $[(\eta^5\text{-}C_{10}H_9)Mn(CO)_3]$ (**1**) has a special property, i.e., a facile ring-slippage between η^5 and η^3. The ring-slippage has been verified by the molecular structure of $[(\eta^3\text{-}C_{10}H_9)Mn(CO)_3P(OMe)_3]$ and the kinetic study of CO substitution in **1**. The facile ring-slippage is reflected in the associative substitution of CO with $P(OMe)_3$ and the tremendous substitution rate enhancement compared to that of (indenyl)$Mn(CO)_3$. Finally, we have explicitly demonstrated the role of ring-slippage in the catalytic hydrosilylation of ketones.

Experimental Section

General. All solvents were purified by standard methods, and all synthetic procedures were done under nitrogen atmosphere. Reagent grade chemicals were used without further purification.

^{1}H NMR spectra were obtained with a Bruker DPX-300 or a Bruker AMX-500 instrument. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer. Elemental analyses were done at the Chemical Analytic Center, College of Engineering, Seoul National University. The syntheses of $[(\eta^6\text{-naphthalene})\text{-}Mn(CO)_3]BF_4$, **1**, **2**, and **3** were previously reported.[4,5,6a]

Routine UV−visible spectra and slow kinetic runs were recorded on a Hewlett-Packard 8452A diode array spectrophotometer using HP 89532A general scanning and HP 89532K kinetic software. Fast kinetic measurements were carried out by a Photal RA-401 stopped-flow spectrophotometer. The system was interfaced with an IBM-compatible computer system employing an RA-451 data processor. The temperature of the reaction was controlled within ±0.2 °C by a Brinckman Lauda K-2/RD water bath circulator.

Synthesis of 5. Compound **1** (0.15 g, 0.56 mmol) was dissolved in 3 mL of CH_2Cl_2. The solution was bubbled with CO for 5 min. During the bubbling, the color of the solution changed to yellow. Then the solvent was removed by flushing with CO. The residue was dissolved in pentane. Slow evaporation of the solvent at −15 °C under CO in a freezer gave a yellow solid (0.12 g, 74%): mp 48−50 °C (conversion to **1**); IR (pentane) νCO 2059, 1988, 1970, 1934 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.07 (d, 7.0 Hz, 1 H), 7.01 (t, 7.4 Hz, 1 H), 6.92 (t, 7.1 Hz, 1 H), 6.80 (d, 7.3 Hz, 1 H), 5.07 (t, 6.4 Hz, 1 H), 4.71 (m, 2 H), 3.73 (dd, 4.6, 21.9 Hz, 1 H), 3.35 (d, 21.5 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 224.0, 140.6, 133.4, 129.4, 128.2, 26.8, 125.9, 84.4, 63.9, 61.9, 33.8 ppm. Anal. Calcd for $C_{14}H_9MnO_4$: C, 56.78; H, 3.06. Found: C, 56.72; H, 3.02.

Synthesis of 6. Ph_3CBF_4 (0.15 g, 0.45 mmol) was added to a solution of **1** (0.15 g, 0.41 mmol) in 5 mL of CH_2Cl_2. The solution was stirred at room temperature for 1 h and quenched with 20 mL of Et_2O. After the solution was filtered, the precipitate was washed with Et_2O (3 × 10 mL) and dried. The yield was 95% (0.18 g): IR (NaCl) νCO 1994, 1942 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 8.17 (m, 2 H), 8.06 (m, 2 H), 7.47 (m, 2 H), 6.68 (m, 2 H), 3.68 (d, 11.7 Hz, 9 H) ppm. Anal. Calcd for $C_{15}H_{17}BF_4MnO_5P$: C, 40.04; H, 3.81. Found: C, 39.98; H, 3.53.

X-ray Crystal Structure Determination of 2. Crystals of **2** were grown by slow evaporation of a pentane solution of **2**. Diffraction was measured by an Enraf-Nonius CAD4 diffractometer with a $\omega-2\theta$ scan method. Unit cells were determined by centering 25 reflections in the approximate 2θ range. The structure was solved by direct methods using SHELX-86 and refined by full-matrix least-squares with SHELXL-93. All non-hydrogen atoms were refined with anisotropic temperature factors; hydrogen atoms were refined isotropically using a riding model with 1.2 times the equivalent isotropic temperature factors of the atoms to which they are attached. Details on crystal and intensity data for **2** are given in Table 1.

Kinetic Study. The substitution reaction of **1** by $P(OMe)_3$ in CH_2Cl_2 rapidly afforded an intermediate, which slowly lost CO to give the product. The rate of the rapid conversion of **1** to an intermediate in the initial step was monitored from the absorbance change against time at 415 nm using a stopped-flow spectrometer. Pseudo-first-order conditions were maintained throughout the experiments with $P(OMe)_3$ in excess. Reported values of the rate constants were the average of four or more experiments in which the same solution reacted under the reaction conditions employed. The solvolysis rate of the intermediate in CH_2Cl_2 at room temperature was determined from the absorbance change against time at 415 nm using a HP 8452A diode array spectrophotometer.

Catalytic Hydrosilylation. A typical procedure is given for acetophenone. To a mixture of **1** (10 mg, 0.037 mmol) and acetophenone (0.09 mL, 0.75 mmol) in 3.0 mL of CH_2Cl_2 was added Ph_2SiH_2 (0.21 mL, 1.13 mmol). The mixture was stirred at room temperature for 3 h. Complete consumption of acetophenone was verified by TLC. Excess diethyl ether was added to extract the organic products. The extract was evaporated to dryness, and the ^{1}H NMR spectrum was recorded after dissolution in $CDCl_3$ (with anisole present as an internal standard). The yield was calculated by comparing the methyl peaks of the products with the methoxy peak of the anisole.

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Supporting Information Available: Tables of atomic coordinates, displacement parameters, and bond distances and angles for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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