

Hydrosilylation of ketones catalyzed by tricarbonyl(naphthalene)manganese cation

Seung Uk Son, Se-Jung Paik, Young Keun Chung *

Department of Chemistry and Center for Molecular Catalysis, College of Natural Sciences, Seoul National University, Seoul 151-742, South Korea

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Abstract

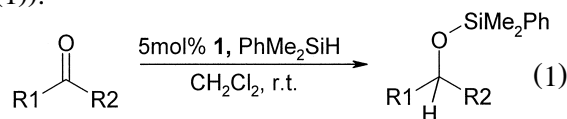
The naphthalene manganese complex $[(\eta^6\text{-C}_{10}\text{H}_8)\text{Mn}(\text{CO})_3]\text{BF}_4$ (**1**) has been used as an effective catalyst for the hydrosilylation of ketones to give the corresponding *sec*-alcohols in high yields after hydrolysis. The yields for aryl ketones are dependent on the reaction medium with the highest in CH_2Cl_2 and the steric bulkiness and electronic properties of substituents. As the steric bulkiness increases, the yield decreases and as the electron-donating ability of the substituent on the substrate increases, the yield increases. Catalytic activity of **1** is explained by the ring slippage $\eta^6 \rightarrow \eta^4$. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Manganese; Naphthalene; Catalytic; Hydrosilylation; Ring slippage

1. Introduction

Hydrosilylation of carbon–carbon and carbon–heteroatom multiple bonds has been extensively studied and many transition-metal catalysts have been shown to catalyze the reaction [1–4]. Because of their high relative reactivity, the majority of hydrosilylation catalysts are derived from group 8 metals [5–9] and relatively little efforts has been devoted to group 7 metal hydrosilylation catalysts. Recent results revealed that group 7 metal carbonyl derivatives are active catalysts precursors for ketone and ester hydrosilylation [10–12]. However, group 7 metal complexes are confined only to the metal carbonyl compounds $\text{Mn}(\text{CO})_n\text{L}_m$ (L_m is not an arene). No $(\text{arene})\text{Mn}(\text{CO})_3^+$ cationic catalysts

have ever reported. We describe here the first examples of the hydrosilylation of ketones catalyzed by $[(\text{naphthalene})\text{Mn}(\text{CO})_3]\text{BF}_4$ (**1**) (Eq. (1)).



2. Experimental

2.1. General considerations.

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

* Corresponding author.

^1H 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. Mass spectra were recorded with a Jeol JMS AX 505 WA double-focusing mass spectrometer. Complexes $[(\eta^6\text{-arene})\text{Mn}(\text{CO})_3]\text{BF}_4$ (arene = naphthalene, dibenzofuran, benzothiophene, benzene, hexamethylbenzene) and $[(\eta^5\text{-C}_{10}\text{H}_9)\text{Mn}(\text{CO})_3]$ (**2**) were reported previously [13–15].

2.2. Catalytic hydrosilylation

A typical procedure is given for acetophenone. To a mixture of **1** (15 mg, 0.043 mmol) and acetophenone (0.1 ml, 0.86 mmol) in 1.0 ml of CH_2Cl_2 was added PhMe_2SiH (0.2 ml, 1.29 mmol). The mixture was stirred at room temperature for 2 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 ^1H NMR spectrum 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. The GC-Mass spectrum of the solution confirmed the formation of PhMe_2SiF (mass number: 154). After the solvent was removed, the residue was column chromatographed on a silica gel column eluting with hexane. The first coming-out is silyl ether and the second coming-out is $[(\eta^5\text{-C}_{10}\text{H}_9)\text{Mn}(\text{CO})_3]$ (**2**). Yield of **2**: 75%. IR (CH_2Cl_2) νCO 2011, 1932 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.26–7.06 (m, 4 H), 6.47 (d, 5.5 Hz, 1 H), 5.22 (m, 1 H), 3.49 (d, 5.5 Hz, 1 H), 3.33–3.26 (m, 1 H), 2.73 (d, 12.8 Hz, 1 H) ppm.

3. Results and discussion

Complex **1** was synthesized by the reaction of naphthalene with $\text{Mn}(\text{CO})_5\text{BF}_4$ in CH_2Cl_2 and can be handled in air without any noticeable decomposition [14].

Treatment of a mixture of 1 eq of **1** and 20 eq of acetophenone in CH_2Cl_2 with 30 eq of silane gave the expected hydrosilylation product silyl ether. Formation of other product such as enol silyl ether was not observed. The yields for aryl ketones were dependent on the silane itself (entries 1–3 in Table 1) as Ojima et al. demonstrated [16–18] the reactivity order of the hydrosilane, $\text{RSiH}_3 > \text{R}_2\text{SiH}_2 > \text{R}_3\text{SiH}$. For convenience, PhMe_2SiH was used as a hydrosilylation source. The yields for aryl ketones are quite dependent on the reaction medium (entries 4–6 in Table 1), with the activity highest (> 99%) in CH_2Cl_2 and lowest in Et_2O (37%) for the hydrosilylation of acetophenone. Thus, CH_2Cl_2 was chosen as a reaction medium. The scope of the reaction was examined with a number of aryl ketones and alkyl ketones. The results are shown in Table 1. The yields for aryl ketones are dependent on the steric bulkiness (entries 1 and 7–9 in Table 1). As the steric bulkiness increases, the yield decreases and the reaction time is lengthened. The yields for aryl ketones are dependent on the electronic properties (entries 1 and 10–11 in Table 1) of the substrates. As the electron donating ability of the substituent on the substrate increases, the yield increases and the reaction time is shortened. Alkyl ketones were hydrosilylated almost quantitatively (entries 12–15 in Table 1).

We have screened the catalytic activities of $(\text{arene})\text{Mn}(\text{CO})_3^+$ and found the following reactivity order (entry 1 in Table 1 and entries 1–4 in Table 2): **1** > (benzothiophene) $\text{Mn}(\text{CO})_3^+ \gg$ (dibenzofuran) $\text{Mn}(\text{CO})_3^+ \gg$ $(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$, $(\text{C}_6\text{Me}_6)\text{Mn}(\text{CO})_3^+$. Complex $(\text{arene})\text{Mn}(\text{CO})_3^+$ (arene = C_6H_6 and C_6Me_6) have no catalytic activities. Although there is no clear explanation for the reactivity difference, the reactivity difference is likely related to the ease of $\eta^6 \leftrightarrow \eta^4$ ring slippage in the $(\text{arene})\text{Mn}(\text{CO})_3^+$ complexes [21,22]. Previous work has shown that the ability of (polyarene) $\text{Mn}(\text{CO})_3^+$ to undergo nucleophilic attack is largely dictated by the ease of $\eta^6 \rightarrow \eta^4$ ring slippage, which follows the order: arene = naphthalene > benzothiophene >

Table 1
Catalytic hydrosilylation of ketones by **1**^a

Entry	Substrate	Silane	Sol.	Time (h)	Yield (%) ^b
1	Acetophenone	PhMe ₂ SiH	CH ₂ Cl ₂	2	> 99
2	Acetophenone	Et ₃ SiH	CH ₂ Cl ₂	5	95
3	Acetophenone	Ph ₂ SiH ₂	CH ₂ Cl ₂	0.5	> 99
4	Acetophenone	PhMe ₂ SiH	THF	18	41
5	Acetophenone	PhMe ₂ SiH	Et ₂ O	18	37
6 ^c	Acetophenone	PhMe ₂ SiH	CH ₂ Cl ₂	2	> 99
7	2-Acetonaphthone	PhMe ₂ SiH	CH ₂ Cl ₂	2	> 99
8	1-Acetonaphthone	PhMe ₂ SiH	CH ₂ Cl ₂	18	35
9	Benzophenone	PhMe ₂ SiH	CH ₂ Cl ₂	18	15
10	4-Methoxyacetophenone	PhMe ₂ SiH	CH ₂ Cl ₂	0.8	> 99
11	4-Nitroacetophenone	PhMe ₂ SiH	CH ₂ Cl ₂	2	18
12	2-Pentanone	PhMe ₂ SiH	CH ₂ Cl ₂	2	> 99
13	Cyclopentanone	PhMe ₂ SiH	CH ₂ Cl ₂	2	> 99
14	Cyclohexanone	PhMe ₂ SiH	CH ₂ Cl ₂	2	> 99
15	Cyclopropyl methyl ketone	PhMe ₂ SiH	CH ₂ Cl ₂	2	> 99

^a5 mol% **1** used at 25°C unless noted.

^bCalculated yield by ¹H NMR.

^c0.5 mol% used.

dibenzofuran. Thus, we suggest that ring-slippage may play an important role in the hydrosilylation reaction by allowing coordination of the silane and/or the ketone. Since η^2 -coordination or oxidative addition of the silane is a likely initial step, π -hydrocarbon ring slippage could help the initial step through providing low energy pathways to unsaturated intermediates. There are many examples of ring slippage in the associative ligand substitution or addition reactions of indenyl complexes [19–22]. Recently, Garrett and Fu reported [23] η^5 - to η^3 -indenyl ring-slippage in a rhodium-catalyzed olefin hydroboration. In general, however, relatively little attention has been paid to the application of ring-slippage in the catalytic reactions.

We have screened other naphthalene transition metal complexes as a catalyst in a hydrosilylation of ketones (entries 5 and 6 in Table 2). Our results show that $(\eta^6\text{-C}_{10}\text{H}_8)\text{Cr}(\text{CO})_3$ has a moderate catalytic activity, but $[(\eta^6\text{-C}_{10}\text{H}_8)\text{FeCp}]\text{BF}_4$ does not have a catalytic activity presumably due to a robust bonding structure.

In the beginning, we expected that the real catalyst would be $\text{Mn}(\text{CO})_3^+$ which might be generated from **1**. However, after a catalytic reaction, we could isolate $[(\eta^5\text{-C}_{10}\text{H}_9)\text{Mn}(\text{CO})_3]$

(**2**) in 75% yield instead of free naphthalene. Compound **2** does not function as a catalyst with PhMe₂SiH. Thus, no naphthalene dissociation occurs during the reaction. The formation of **2** involves a formal hydride transfer to the π -coordinated arene ring in **1**. Thus, two reactions occur simultaneously- hydrosilylation of the ketone catalyzed by **1** and a hydride addition

Table 2
Catalytic hydrosilylation of acetophenone by arene transition metal complexes^a

Entry	Catalyst	Silane	Yield (%) ^b
1	[(Benzothiofene) Mn(CO) ₃]BF ₄	PhMe ₂ SiH	84
2	[(Dibenzofuran) Mn(CO) ₃]BF ₄	PhMe ₂ SiH	13
3	[(Benzene) Mn(CO) ₃]BF ₄	PhMe ₂ SiH	N.R. ^c
4	[(Hexamethylbenzene)- Mn(CO) ₃]BF ₄	PhMe ₂ SiH	N.R. ^c
5	[(Naphthalene) FeCp]BF ₄	Ph ₂ SiH ₂	N.R. ^c
6	(Naphthalene) Cr(CO) ₃	Ph ₂ SiH ₂	66

^aAll the reactions were carried out in the presence of catalyst (5 mol%) with silane (1.3 mmol) and acetophenone (0.86 mmol) in CH₂Cl₂ at 25°C for 18 h.

^bCalculated yield by ¹H NMR.

^cNo reaction.

to **1**. However, good substrates were found to be completely consumed before a noticeable amount of **2** was detected.

In conclusion, we have demonstrated that [(naphthalene)Mn(CO)₃]BF₄ is a good hydrosilylation catalyst precursor to ketones. As far as we are aware, this is the first explicit demonstration of the use of ring-slippage in the hydrosilylation reaction. The mechanism of the hydrosilylation catalyzed by **1** and an asymmetric hydrosilylation using [(naphthalene)Mn(CO)₂PR₃^{*}]BF₄ are currently under investigation.

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References

- [1] B. Marciniec, J. Gulinski, *J. Organomet. Chem.* 446 (1993) 15.
- [2] I. Ojima, *The Chemistry of Organic Silicon Compounds*, Part 2, Chap. 25, in: S. Patai, Z. Rappoport (Eds.), Wiley Interscience, New York, 1989.
- [3] P.A. Chaloner, *Handbook of Coordination Catalysis in Organic Chemistry*, Chap. 7.2, Butterworths, Boston, MA, 1986.
- [4] B. Marciniec (Ed.), *Comprehensive Handbook on Hydrosilylation*, Pergamon, Oxford, UK, 1992.
- [5] I. Ojima, R.J. Donovan, N. Clos, *Organometallics* 10 (1991) 2606.
- [6] S.B. Duckett, R.N. Perutz, *Organometallics* 11 (1992) 90.
- [7] Y. Nishibayashi, K. Segawa, J.D. Singh, S.-i. Fukuzawa, K. Ohe, S. Uemura, *Organometallics* 15 (1996) 370.
- [8] K. Tamao, K. Kobayashi, Y. Ito, *J. Am. Chem. Soc.* 111 (1989) 6478.
- [9] X. Coqueret, G. Wegner, *Organometallics* 10 (1991) 3139.
- [10] M.D. Cavanaugh, B.T. Gregg, A.R. Cutler, *Organometallics* 15 (1996) 2764.
- [11] P.K. Hanna, B.T. Gregg, D.L. Tarazano, J.R. Pinkes, A.R. Cutler, *Homogeneous Transition Metal catalyzed Reactions*, in: W.R. Moser, D.W. Slocum (Eds.), *Advances in Chemistry Series No. 230*, American Chemical Society, Washington, DC, 1992, p. 491.
- [12] Z. Mao, B.T. Gregg, A.R. Cutler, *J. Am. Chem. Soc.* 117 (1995) 10139.
- [13] P.L. Pauson, J.A. Segal, *J. Chem. Soc., Dalton Trans.*, 1975, 1677.
- [14] S. Sun, L.K. Yeung, D.A. Sweigart, T.-Y. Lee, S.S. Lee, Y.K. Chung, S.R. Switzer, R.D. Pike, *Organometallics* 14 (1995) 2613.
- [15] S. Sun, C.A. Dullaghan, G.B. Carpenter, D.A. Sweigart, S.S. Lee, Y.K. Chung, *Inorg. Chim. Acta* 262 (1997) 213.
- [16] I. Ojima, M. Nihonyanagi, M. Kogure, M. Kumagai, S. Horiuchi, K. Nakatsugawa, *J. Organomet. Chem.* 94 (1975) 449.
- [17] I. Ojima, T. Kogure, M. Kumagai, S. Horiuchi, T. Sato, *J. Organomet. Chem.* 122 (1976) 83.
- [18] I. Ojima, T. Kogure, *Organometallics* 1 (1982) 1390.
- [19] M.E. Rerek, F. Basolo, *Organometallics* 2 (1983) 372.
- [20] M.E. Rerek, F. Basolo, *J. Am. Chem. Soc.* 106 (1984) 5908.
- [21] A. Habib, R.S. Tanke, E.M. Holt, R.H. Crabtree, *Organometallics* 8 (1989) 1225.
- [22] D. Monti, M. Bassetti, *J. Am. Chem. Soc.* 115 (1993) 4658.
- [23] C.E. Garrett, G. Fu, *J. Org. Chem.* 63 (1998) 1370.