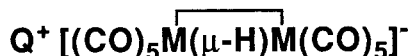


**GROUP 6 ANIONIC μ -HYDRIDE COMPLEXES $[\text{HM}_2(\text{CO})_{10}]^-$ (M = Cr, Mo, W):
NEW CATALYSTS FOR HYDROGENATION AND HYDROSILYLATION**

Takamasa FUCHIKAMI*, Yumiko UBUKATA, and Yasutaka TANAKA
Sagami Chemical Research Center,
Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan

Summary: Group 6 anionic μ -hydride complexes catalyze hydrogenation of conjugated olefins, aldehydes, ketoesters, and alkynes, and hydrosilylation of aldehydes and conjugated olefins with high regio- and stereoselectivity. Ketones are converted into silyl ethers and silyl enol ethers with monohydrosilanes and dihydrosilanes, respectively.

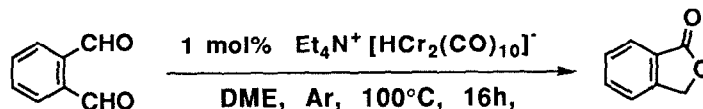
Complex metal hydrides of main Groups such as LiAlH_4 and NaBH_4 are in common use as powerful and chemoselective reducing agents in organic syntheses although these reactions require stoichiometric amounts of the reagents and less attractive from both practical and economical viewpoints. Two types of Group 6 anionic hydride complexes, monomeric $[\text{HM}(\text{CO})_5]^-$ (**1**) and dimeric $[\text{HM}_2(\text{CO})_{10}]^-$ (**2**) (M = Cr, Mo, W), also have been of use as reducing reagents, but reactivities are quite different: Monomeric complexes **1** have been reported to reduce acid chlorides,^{1b} organic halides,^{1a} aldehydes and ketones,^{1c} whereas dimeric **2** can convert α,β -unsaturated ketones and nitriles into saturated ones.² Moreover, there are quite interesting reports that dimeric complexes **2** are unreactive with benzaldehyde or cyclohexanone under stoichiometric conditions,^{1c} but act as a catalyst for hydrogenation of them with turnovers less than 18.^{3a} Nevertheless, little is known about the catalytic reactivity³ of these anionic bimetallic complexes **2** with a great electrodensity at the hydrogen atom bonded to two metals. We report here catalytic utilities of the dimeric complexes **2** in organic syntheses.



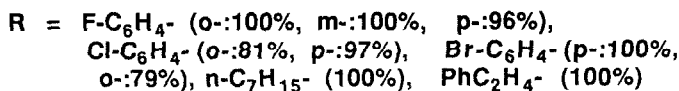
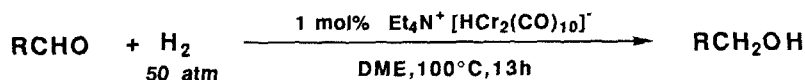
2a: Q = Et_4N , M = Cr; **2b:** Q = Et_4N , M = Mo;

2c: Q = Et_4N , M = W; **2d:** Q = $(\text{Ph}_3\text{P})_2\text{N}$, M = Cr

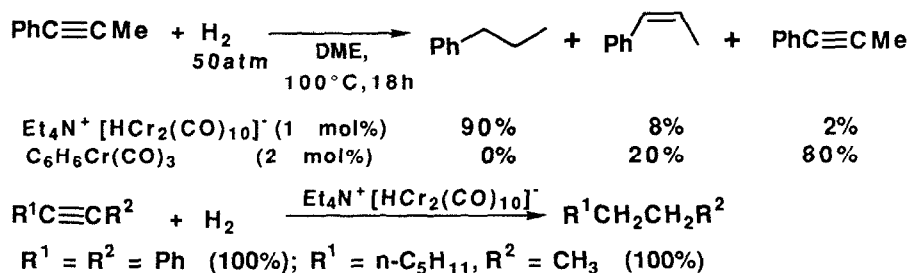
Initially we re-examined the stoichiometric reaction with $\text{Et}_4\text{N}[\text{HCr}_2(\text{CO})_{10}]$ (**2a**) and benzaldehyde in THF, and no reaction took place at 50 °C as reported by Darensbourg et al.^{1c} However, on using DME as solvent benzylalcohol was obtained in 85-94 % conversion yield, in addition to benzyl benzoate (6-15%). The order of reactivity of dimeric complexes was **2a** (Cr) = **2b** (Mo) \gg **2c** (W). The formation of benzyl benzoate can be explained in terms of a nucleophilic attack of benzyloxy-chromium species to second benzaldehyde followed by elimination of the metal hydride (**2a**). Indeed, phthalic dicarbaldehyde can be converted into phthalide in 80 % yield in the presence of 1 mol% of **2a** at 100 °C.



Catalytic hydrogenation of aldehydes (1 mmol) was run with dimeric complex **2** (0.01 mmol) in DME (1 ml) under 50 atm. of hydrogen at 100 °C for 13 hr. A pronounced solvent effect was observed: The turnovers in the reaction with benzaldehyde were 100 (**2d**) and 83 (**2b**) in DME (100 °C, 13 hr), whereas 14.4 (**2d**) and 8.6 (**2b**) in THF (125 °C, 24 hr).² It is noteworthy that no hydrogenolysis of carbon-halogen bond takes place at all under these reaction conditions.



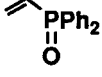
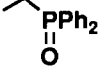
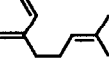
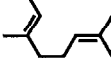

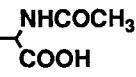
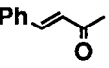
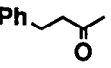








Unique feature of these catalysts was observed in hydrogenation of alkynes, where alkanes were obtained in excellent yields by using **2a** as a catalyst, and no or trace of alkenes were formed even under lower hydrogen pressure. This result may seem to suggest hydrogenation of initially formed alkenes is much faster than that of starting alkynes. However, (*E*)- and (*Z*)-stilbenes, (*E*)- and (*Z*)-*a*-methylstyrenes, (*E*)- and (*Z*)-2-octenes, and 1-octene were recovered unchanged under the same reaction conditions, indicating alkanes are directly derived from alkynes. This result shows a sharp contrast to that of arene tricarbonyl complexes, which lead to a selective formation of (*Z*)-alkenes.⁴

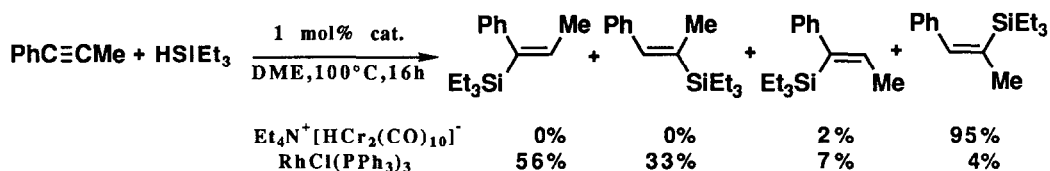


Although having no reactivity toward the hydrogenation of nonfunctionalized alkenes, the complex **2a** showed a remarkable catalytic activity in the reduction of olefins bearing electron-withdrawing groups because of a great electron density at the hydrogen atom of the anionic complex. Thus, conjugated ketones, vinylphosphine oxide, and dehydroamino acid derivative were hydrolyzed in good yields. Moreover, myrcene underwent 1,4-reduction exclusively, and α -ketoesters were converted into the corresponding hydroxy esters in good yield in spite of its' poor reactivity toward simple ketones such as cyclohexanone and acetophenone.

Table I. Hydrogenation of Unsaturated Compounds Catalyzed by Complex **2a**

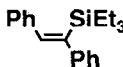

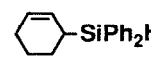

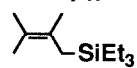
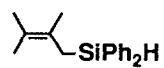

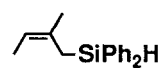
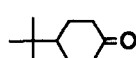
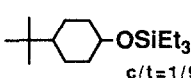
Substrate	Product (yield, %)	Substrate	Product (yield, %)
	 (60)		 (100)
	 (90)		 (100)
	 (82)		 (91)
	 (60)		 (99)

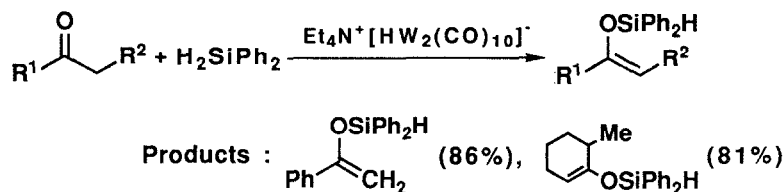
These dimeric anionic complexes **2** also exhibited unique catalytic reactivities toward the reactions of unsaturated compounds with hydrosilanes. The hydrosilylation of alkynes are most characteristic, in which stereo- and regio-selective addition of hydrosilane to carbon-carbon triple bond took place. Exclusive trans-addition⁵ to triple bond were observe in all cases of the reaction with alkynes such as 1-phenylpropyne and diphenylacetylene using **2a** as a catalyst. As shown in the reaction with 1-phenylpropyne, a silyl group was introduced into less hindered site in excellent selectivity. This forms a striking contrast to the result using Wilkinson's catalyst, in which cis-addition is favored without regioselectivity. Again, hydrosilylation of nonfunctionalized olefins didn't proceed at all, however, regio- and stereo-selective 1,4-addition was observed in the reaction of isoprene with diphenylsilane using molybdenum complex **2b** as a catalyst, giving (*Z*)-2-methyl-2-butenyl-diphenylsilane exclusively.



Although aldehydes easily underwent the hydrosilylation under the identical conditions, the dramatic change of the reaction sequence depending upon a sort of employed hydrosilanes was observed in the reaction of ketones. The hydrosilylation took place exclusively on using monohydrosilanes to give silyl ethers, while silyl enol ethers were obtained selectively with dihydrosilanes. The tungsten complex **2c** showed high selectivity for this dehydrogenative silylation.⁶ Highly regiospecific dehydrogenative silylation occurred in the case of 2-methylcyclohexanone leading to 2-methyl-1-diphenylsiloxy-1-cyclohexane exclusively. Thus, this catalyst offers a very facile method for the preparation of silyl enol ethers.

Table II. Hydrosilylation of Unsaturated Compounds Catalyzed by Complexes 2

Substrate	Cat.	Product (yield, %)	Substrate	Cat.	Product (yield, %)
PhC≡CPh	2 a	 (53)		2 b	 (99)
	2 b	 (94)	C ₇ H ₁₅ CHO	2 c	C ₇ H ₁₅ CH ₂ OSiEt ₃ (90)
	2 b	 (75)	PhCHO	2 b	PhCH ₂ OSiEt ₃ (97)
	2 b	 (97)		2 a	 (66) c/t=1/9



In conclusion, group 6 anionic μ -hydride complexes display regio- and/or stereospecific hydrogenation and hydrosilylation of alkynes and conjugated olefins, and afford silylenol ether from ketones in a regiospecific manner. Therefore, these complexes are very unique and useful catalysts for organic syntheses. Further applications of these complexes are in progress.

References and Notes

- (1). (a) Kao, S. C., Darensbourg, M. Y. *Organometallics*, **1984**, *3*, 646; (b) Kao, S. C., Gaus, P. L., Youngdahl, K., Darensbourg, M. Y. *Organometallics*, **1984**, *3*, 1601; (c) Gause, P. L., Kao, S. C., Youngdahl, K., Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428.
- (2) Boldrine, G. P., Umani-Ronchi, A., Panunzio, M. *Synthesiss*, **1976**, 596.
- (3) (a) Tooley, P. A., Ovalles, C., Kao, S. C., Darensbourg, D. J., Darensbourg, M. Y. *J. Am. Chem. Soc.* **1986**, *108*, 5465. (b) Darensbourg, D. J., Ovalles, C. *J. Am. Chem. Soc.* **1984**, *106*, 3750. (c) Darensbourg, D. J., Ovalles, C. *J. Am. Chem. Soc.* **1987**, *109*, 3330.
- (4) Sodeoka, M., Shibasaki M. *J. Org. Chem.* **1985**, *50*, 1149.
- (5) Example of trans addition, see: (a) Ojima, I, Kumagai, M, Nagai, Y. *J. Organomet. Chem.* **1974**, *66*, C64. (b) Dickers, H.M., Haszeldine, R. N., Mather, A. P., Parish, R. V. *Ibid.* **1978**, *161*, 91. (c) Brady, K. A., Nile, T. A. *Ibid.* **1981**, *206*, 299.
- (6) Example of the catalytic dehydrogenative silylation of ketones under basic conditions, see; Sakurai, H, Miyoshi, K., Nakadaira, Y. *Tetrahedron Lett.* **1977**, 2971. Ketones bearing an electron-withdrawing group on the α -carbon also undergo the dehydrogenative silylation, see; Ojima, I, Nihonyanagi, M, Kogure, T, Kumagai, M, Horiuchi, S, Nakatsugawa, K. *J. Organomet. Chem.* **1975**, *94*, 449.

(Received in Japan 14 December 1990)