chromatographed on silica. Elution with hexane gave $Ru_3(CO)_{12}$ (32 mg, 11%) and unreacted starting material (26 mg, 10%). Cluster 2 was obtained by elution with 1:3 hexane-dichloromethane solution; yield 44 mg, 16%. IR (CH_2Cl_2): 2088 (w), 2061 (s), 2040 (s), 2022 (s), 2003 (m), 1974 cm^{-1} (w). ^1H NMR spectrum: −15.6, −16.7 ppm; 2.9 ppm (s, CH_3). Anal. Calcd for $C_{14}Ru_4H_8SO_{12}$: C, 20.90; H, 1.00. Found: C, 20.96; H, 0.99.

Synthesis of $[HRu_3Co(CO)_{12}(SMe_2)]$ (3). The compounds $[HRu_3Co(CO)_{13}]$ (88 mg, 0.12 mmol) and SMe_2 (28.5 μL, 0.39 mmol) were refluxed in CH_2Cl_2 for 45 min. Chromatographic separation with hexane gave first a yellow and then a red fraction (unreacted starting material 26 mg, 0.04 mmol). Elution with 1:1 hexane-dichloromethane gave first a minor orange fraction of 2 and then the title compound. Crystallization from hexane-dichloromethane mixture gave crystals; yield 17 mg, 18%. IR (CH_2Cl_2): ν(CO) 2088 (w), 2061 (vs), 2034 (s), 2020 (s), 1835 cm^{-1} (w, br). ^1H NMR spectrum: −13.1 ppm (s, br); 3.1 and 2.8 ppm (s, CH_3, equal intensity). Anal. Calcd for $C_{14}Ru_3CoH_7SO_{12}$: C, 22.08; H, 0.93. Found: C, 22.36; H, 1.00.

Crystallographic Studies. Intensity data were collected on a Nicolet R3m diffractometer. Mo Kα radiation with λ = 0.71073 Å was used. Intensities were corrected for Lorenz, polarization, and background effects. An empirical absorption correction was made, based on ψ-scans. Table VI presents further crystallographic data.

The structures were solved by direct methods using the SHELXTL program package. Anisotropic refinement was carried out for all non-hydrogen atoms. Methyl protons were placed in idealized positions with C-H distance of 96 pm and isotropic temperature factors of 0.08. The cluster hydrides were not found in the Fourier maps.

Supplementary Material Available: Tables of atomic coordinates, temperature factors, and bond distances and angles (12 pages); listings of structure factors (39 pages). Ordering information is given on any current masthead page.

Reduction of Acyl Ligand in Transition-Metal Complexes by Catalytic Hydrosilylation

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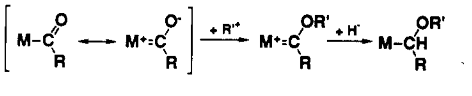
Hydrosilylation of acyl-transition-metal complexes M-C(O)R (1) with H_2SiPh_2 in the presence of a catalytic amount of $RhCl(PPh_3)_3$ leads to the formation of the corresponding α-siloxyalkyl complexes M-CH($OSiHPh_2$)R (2). In case 1 contains a ligand or a substituent which stabilizes a transient cationic alkylidene intermediate M^+=CHR (5), overreduction takes place to afford M-CH_2R (3) via 5. The mechanism of the overreduction has been studied by using α-methoxyalkyl complexes M-CH(OMe)R in place of 2. In addition, the chain propagation step in the Pichler-Schulz mechanism is mimiced by combination of the overreduction and carbonylation. Thus, the acetyl ligand in $CpFe(CO)(PPh_3)[C(O)CH_3]$ (**1f**) is elongated to the pentanoyl ligand by repeating the homologation three times. Transformation of 1 to an α-alkoxyalkyl complex and an α-hydroxycarboxylic acid ester is also described.

Introduction

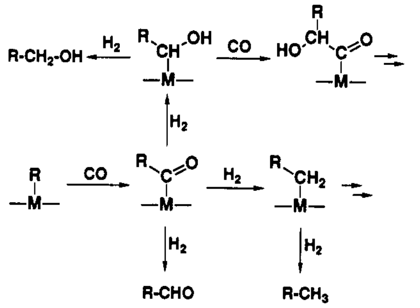
In the Pichler-Schulz mechanism (one of the plausible mechanisms proposed for catalytic hydrogenation of carbon monoxide) an acyl species is included as a key intermediate in the chain propagation step (Scheme I).[1] The acyl species is formed by carbonylation of an alkyl-metal intermediate. The fate of the acyl species is decided by the subsequent reduction step. Successive reduction to the alkyl species and CO insertion results in homologation. Complete reduction produces a hydrocarbon. On the other hand, partial reduction of the acyl species or hydrogenolysis of the metal-acyl bond may finally lead to the formation of oxygenated products such as alcohols and aldehydes.

In model reactions using discrete isolable complexes the reduction of an acyl ligand has been acheived by electrophilic activation followed by hydridic reduction[2] (eq 1).

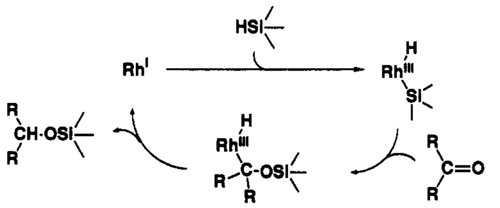


$$\left[\mathrm{M{-}C(=O)R} \longleftrightarrow \mathrm{M^{+}{=}C(O^{-})R}\right] \xrightarrow{+\,R'^{+}} \mathrm{M^{+}{=}C(OR')R} \xrightarrow{+\,H^{-}} \mathrm{M{-}CH(OR')R} \qquad (1)$$

Scheme I



Scheme II



Such activation is essential, because the electrophilicity of the acyl carbon atom is reduced by backdonation from the metal center compared to that of an organic carbonyl carbon atom. The action of strong reducing reagents such as $LiAlH_4$ results in reduction of a coexisting CO ligand.[3]

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[1] (a) Masters, C. *Adv. Organomet. Chem.* **1979**, *19*, 63. (b) Muetterties, E. L.; Rhodin, T. N.; Bard, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91. (c) Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447. (d) Herrman, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (e) Henrici-Olive, G.; Olive, S. *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide*; Springer: New York, 1984.

[2] (a) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363. (b) Green, M. L. H.; Mitchard, L.; Swanwick, M. *J. Chem. Soc.* **1971**, 794. (c) Davison, A.; Reger, D. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (d) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.

[3] Wong, A.; Atwood, J. D. *J. Organomet. Chem.* **1981**, *210*, 395.

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Table I. Hydrosilation of 1 with H_2SiPh_2 Catalyzed by $RhCl(PPh_3)_3$

acyl complex	amt of catalyst, mol %	solvent	time	products (yield, %)
1a	5	THF	2 h	**2a** (95)[a]
1b	1	THF	1 min	**2b** (78)[b]
1c	1	C_6D_6	5 min	**2c** (95)[a]
1d	1	C_6D_6	5 min	**2d** (90)[a]
1e	5	CH_2Cl_2	10 min	**4c** (29)[b,c] + **3e** (21)[b]
			65 h	**4c** (8)[b,c] + **3e** (61)[b]
1f	2	CH_2Cl_2	6 h	**3f** (74)[b]

[a] Determined by ^{1}H NMR. [b] Isolated yield. [c] The yield of **2e** was determined after conversion to the methoxy analogue **4c** (see text).

Similar activation of a C=O functional group has been postulated in a catalytic cycle of hydrosilylation of organic carbonyl compounds[4] (Scheme II). The active species has been assumed to be a hydrido(silyl)rhodium(III) species,[4] and the M–Si bond in silyl–transition-metal complexes is polarized ($M^{\delta-}\cdots Si^{\delta+}$).[5] The highly electrophilic silyl group readily attacks the oxygen atom of the coordinated carbonyl compound to give the hydrido(siloxyalkyl)rhodium species, from which the silyl ether is reductively eliminated.

These results prompted us to examine reduction of the C=O functional group in various acyl–metal complexes (metallaketones) by catalytic hydrosilylation, and the full details are described in this paper. A preliminary communication of part of this work has already appeared.[6] Cutler et al. also reported the application of the same method to the reduction of organoiron acyl complexes.[7]

Results and Discussion

Catalytic Hydrosilylation of Acyl–Metal Complexes (1). When acetyl and benzoyl metal complexes (**1a–e**) were reacted with diphenylsilane[8] in the presence of a catalytic amount (1–5 mol%) of $RhCl(PPh_3)_3$, α-siloxyethyl and -benzyl complexes (**2a–e**) were obtained in good yields (eq 2, Table I). The molybdenum complex **2b** was isolated

$$\underset{\mathbf{1}}{\text{M-C(O)-R}} + H_2SiPh_2 \xrightarrow[\text{THF or benzene}]{\text{cat. RhCl(PPh}_3)_3} \underset{\mathbf{2}}{\text{M-CH(OSiHPh}_2\text{)-R}} + \underset{\mathbf{3}}{\text{M-CH}_2\text{-R}} \quad (2)$$

a : M = $CpFe(CO)_2$, R = CH_3; **b** : M = $CpMo(CO)_2(PPh_3)$, R = CH_3; **c** : $Mn(CO)_5$, R = CH_3; **d** : M = $Mn(CO)_5$, R = Ph; **e** : M = $CpFe(CO)_2$, R = Ph; **f** : M = $CpFe(CO)(PPh_3)$, R = CH_3.

as an analytically pure yellow powder. However, attempted purification of the iron complex **2a** by column chromatography (alumina) resulted in decomposition and its structure was determined by spectroscopic methods as well as by its transformation to stable derivatives (vide infra). The manganese complexes **2c,d** were so thermally unstable[9] that they were characterized only on the basis of their spectral data. The reaction of a benzoyliron complex (**1e**) and a phosphine-substituted acetyliron complex (**1f**) afforded overreduced products, M–CH_2R (**3e,f**)[10] (eq 2, Table I). In particular, hydrosilylation of **1f** exclusively afforded **3f**, and **2f** was not detected at all by monitoring the reaction by ^{1}H NMR. Deuteriosilylation with D_2SiPh_2 gave products in which the methylene group adjacent to the metal center was selectively deuterated (eq 3).

$$\underset{\mathbf{1e,f}}{\text{M-C(O)-R}} + D_2SiPh_2 \xrightarrow{\text{cat. RhCl(PPh}_3)_3} \underset{\mathbf{3e,f}\text{-}d_2}{\text{M-CD}_2\text{-R}} \quad (3)$$

Table II. ^{1}H NMR Data for 2[a,b]

complex	CH_3	CH	Si-H	Cp
2a	1.81 (d, 6.1)	5.88 (q, 6.1)	5.18 (s)	4.12 (s)
2b	2.40 (d, 6.6)	6.58 (dq, 2.0, 6.6)	5.94 (s)	4.72 (d, 1.5)
2c	1.82 (d, 6.6)	5.19 (q, 6.6)	5.68 (s)	
2d		6.10 (s)	5.62 (s)	
2e[c]		6.69 (s)	5.36 (s)	4.62 (s)

[a] All the spectra were recorded at 100 MHz in C_6D_6 except for **1e**. [b] Chemical shift (ppm) (multiplicity, coupling constant (Hz)). [c] In CD_2Cl_2.

Table III. ^{13}C NMR Data for 2[a,b]

complex	CH_3	CH	CO	Cp
2a[c]	35.32 (q, 125.0)	71.35 (dq, 5.9, 148.4)	217.24 217.71	86.16 (d, 179.7)
2b[d]	32.58 (q, 124.5)	69.24 (dd, 11.0, 150.2)	239.67 (d, 24.4) 241.69 (d, 23.2)	93.91 (d, 175.7)
2c[e]	33.00 (q, 125.7)	69.24 (d, 152.6)	207.88 210.92	
2d[e]		75.04 (d, 153.1)	211.12 211.15	

[a] All the spectra were recorded at 68 MHz. [b] Chemical shift (ppm) (multiplicity, coupling constant (Hz)). [c] In benzene-d_6 at 27 °C. [d] In toluene-d_8 at −20 °C. [e] In CD_2Cl_2 at 0 °C.

The phosphine-substituted benzoyl complex CpFe(CO)(PPh_3)[C(O)Ph] remained unaffected, presumably because of steric congestion around the benzoyl group. In accord with this result, Cutler reported that sterically congested acyliron complexes such as Fp–C(O)CH(CH_3)$_2$ and Fp–C(O)CH_2CH(CH_3)$_2$ reacted sluggishly[7] [Fp = (η^5-C_5H_5)Fe$(CO)_2$].

While the hydrosilylation was also catalyzed by other group 9 metal complexes such as RhCl(CO)$(PPh_3)_2$, [Rh(C_2H_4)$_2$Cl]$_2$ + 1,4-bis(diphenylphosphino)butane (dppb),[11] and $Co_2(CO)_8$, $RhCl(PPh_3)_3$ gave better results and overreduction was not retarded by these catalysts. In addition, a remarkable solvent effect was observed for the present reaction. Benzene and THF were suitable solvents for hydrosilylation of acyl–metal complexes. Although the reaction also proceeded in CH_2Cl_2, we could not get reproducible results in this solvent, and moreover, unless CH_2Cl_2 was added to a mixture of 1, $RhCl(PPh_3)_3$, and H_2SiPh_2, the reaction did not take place at all. However, in the case of overreduction CH_2Cl_2 gave better results.[12]

The ^{1}H and ^{13}C NMR spectra data of 2 are summarized in Tables II and III. As a typical example, the structure

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(4) (a) Ojima, I.; Hirai, K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, and references cited therein. (b) Brunner, H. *Synthesis* **1988**, 645.

(5) (a) Cundy, C. S.; Kingston, B. M.; Lappert, M. F. *Adv. Organomet. Chem.* **1973**, *11*, 253. (b) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837. (c) Murai, S.; Seki, Y. *J. Mol. Catal.* **1987**, *41*, 197.

(6) Akita, M.; Mitani, O.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 527.

(7) Crawford, E. J.; Hanna, P. K.; Cutler, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 6891.

(8) Dihydrosilane exhibited higher reactivity than monohydrosilane as usually observed for hydrosilylation of organic carbonyl compounds.[4] No reaction took place with $HSiEt_3$ and $HSiPh_3$. Employment of H_3SiPh resulted in overreduction to give **3**.[7]

(9) **1c,d** decomposed within 1 h at room temperature to give a mixture of homologated hydrocarbons.[6]

(10) A hydrosilylated product Fp–CH($OSiHEt_2$)Ph was obtained by the reaction of **1e** with H_2SiEt_2.[7]

(11) Asymmetric hydrosilylation of **1a** with H_2SiPh_2 was attempted by using $[Rh(C_2H_4)_2Cl]_2$ + (−)-DIOP and [Rh(−)-DIOP)Cl]$_2$ as a catalyst. However, the obtained products showed no optical rotations. Attempted separation of (±)-**2b** by an optically active HPLC column resulted in decomposition.

(12) We could not clarify the effect of CH_2Cl_2. One of the reviewers suggested that acidic impurities in CH_2Cl_2 might induce ionic hydrogenation of **2** to give **3**. This possibility may be eliminated by the following two experiments. (i) When CH_2Cl_2 stored over Na_2CO_3 was used, the same results were obtained. (ii) In the absence of $RhCl(PPh_3)_3$ reduction of **7** with H_2SiPh_2 (eq 7) did not take place in CH_2Cl_2 (vide infra).

of **2a** was confirmed on the basis of the following spectral features: (i) ν(C=O) of the starting complex **1a** (1647 cm^{-1} in CH_2Cl_2) disappeared. (ii) Conversion of the acyl ligand to the less electron withdrawing α-siloxyalkyl ligand resulted in the shift of ν(C≡O) to lower energies by ca. 20 cm^{-1} [**2a** (CH_2Cl_2): 1997, 1940 cm^{-1}. Compare with **1a**: 2015, 1960 cm^{-1}]. (iii) The presence of the Si–H residue was confirmed by a singlet ^{1}H NMR signal at δ 5.78 as well as ν(Si–H) vibration at 2122 cm^{-1}. The latter shifted to 1220 cm^{-1} when D_2SiPh_2 was used instead of H_2SiPh_2. (iv) A pair of ^{1}H NMR signals appearing at δ 1.81 (d) and 5.88 (q) which coupled with each other with J = 6.0 Hz revealed the presence of a CH_3–CH unit. When D_2SiPh_2 was used, the signal at δ 5.88 disappeared and the signal at δ 1.81 changed to a singlet. (v) In the ^{13}C NMR spectrum the α-carbon of the siloxyalkyl moiety was observed at δ 71.35 instead of the acyl carbon in **1a** (δ 254). The coupling pattern (dq, $^3J_{C-H}$ = 5.9 Hz, $^1J_{C-H}$ = 148.4 Hz) also supported the presence of the CH_3–CH unit. (vi) The two carbonyl ligands coordinated to Fe became diastereotopic (^{13}C NMR), owing to the chiral center in the α-siloxyethyl group. Similar features were observed for **2b–e** and their structures were also assigned as the α-siloxyalkyl complexes.

The structures of **2a,e** were also confirmed by derivatization to α-alkoxyalkyl complexes (eq 4). Addition of

$$\underset{\mathbf{2}}{\text{Fp-CH(OSiHPh}_2\text{)-R}} \xrightarrow[-(\text{Ph}_2\text{HSi})_2\text{O}]{[\text{Rh-SiHPh}_2]} \underset{\mathbf{5}}{\text{Fp}^+\text{=CHR}} \xrightarrow{\text{R'OH}} \underset{\mathbf{4}}{\text{Fp-CH(OR')-R}} \qquad (4)$$

4a : R = CH_3, R' = Me (97 %)
4b : R = CH_3, R' = Et (86 %)
4c : R = Ph, R' = Me (29 %)
Yields based on 1.

alcohol to a reaction mixture containing **2a,e** readily produced the corresponding α-alkoxyalkyl complex **4a,b** in good yields. Formation of **4** should be explained by eq 4. Initial ionization of **2** by the action of a Lewis acidic component such as Rh species gives a cationic alkylidene intermediate **5**, which is trapped by alcohol to afford **4**. **4** serves as a useful starting compound for generation of a cationic alkylidene intermediate Fp$^+$ = CHR which transfers its alkylidene moiety to olefins to afford substituted cyclopropanes.[13] The present method provides an efficient one-pot transformation of **1** to **4** which has been so far prepared by a two-step reaction according to eq 1.

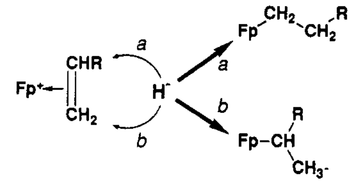
Overreduction. As mentioned above, overreduction took place in the case of **2e,f**. Transformation of **2** to **3** may be interpreted by eq 5. The electrophilic attack of

$$\underset{\mathbf{2}}{\text{M-CH(OSiHPh}_2\text{)-R}} \xrightarrow[-(\text{Ph}_2\text{HSi})_2\text{O}]{[\text{Rh-SiHPh}_2]} \underset{\mathbf{5}}{\text{M}^+\text{=CHR}} \xrightarrow[\text{or [Si-H]}]{[\text{Rh-H}]} \underset{\mathbf{3}}{\text{M-CH}_2\text{-R}} \qquad (5)$$

the oxophilic Rh$^{\delta-}$···Si$^{\delta+}$ part in the hydrido(silyl)rhodium(III) intermediate to the siloxy oxygen atom ionizes **2** to form the cationic alkylidene intermediate **5**, which is reduced by the action of Rh–H species or hydrosilane to produce **3**. Therefore, in the case where the acyl complex **1** contains a ligand or a substituent which stabilizes **5**, overreduction may take place. Actually, the phenyl substituent in **2e** would stabilize the alkylidene ligand in **5** by conjugation with the π-electrons of the phenyl group and the electron-donating PPh_3 ligand in **2f** would neutralize the positive charge on the alkylidene carbon.

In order to confirm this mechanism, some model reactions using isolable α-alkoxyalkyl complexes were carried out. While no reaction took place between the dicarbonyl(methoxymethyl)iron complex **6** and H_2SiPh_2 in the presence of $RhCl(PPh_3)_3$ (5 mol %) even under forcing conditions (in benzene-d_6 for 5 h at 60 °C) (eq 6), the phosphine-substituted derivative **7** was readily reduced to the methyl complex at room temperature (eq 7). Similarly, the α-methoxyethyl complex **9** gave the ethyl complex **10** with concomitant formation of the vinyl complex **11** (eq 8). Treatment of **9** with a catalytic amount of $RhCl(PPh_3)_3$ in the absence of H_2SiPh_2 also produced **11** (eq 9). On the other hand, the dicarbonyl(α-methoxybenzyl)iron complex **12** remained unaffected under the hydrosilylation conditions (eq 10).

Chart I



14
15

$$\underset{\mathbf{6}}{\text{CpFe(CO)}_2\text{-CH}_2\text{OMe}} \xrightarrow[\substack{\text{C}_6\text{D}_6\\ 60^\circ\text{C, 5 h}}]{\text{H}_2\text{SiPh}_2\,/\,[\text{Rh}]} \text{No reaction} \qquad (6)$$

$$\underset{\mathbf{7}}{\text{CpFe(CO)(PPh}_3\text{)-CH}_2\text{OMe}} \xrightarrow[\substack{\text{C}_6\text{D}_6\\ \text{r. t., 4 h}}]{\text{H}_2\text{SiPh}_2\,/\,[\text{Rh}]} \underset{\mathbf{8}}{\text{CpFe(CO)(PPh}_3\text{)-CH}_3}\ (87\ \%) \qquad (7)$$

$$\underset{\mathbf{9}}{\text{CpFe(CO)(PPh}_3\text{)-CH(OMe)CH}_3} \xrightarrow[\substack{\text{C}_6\text{D}_6\\ \text{r. t., 2.5 h}}]{\text{H}_2\text{SiPh}_2\,/\,[\text{Rh}]}$$

$$\underset{\mathbf{10}}{\text{CpFe(CO)(PPh}_3\text{)-CH}_2\text{CH}_3}\ (45\ \%) + \underset{\mathbf{11}}{\text{CpFe(CO)(PPh}_3\text{)-CH=CH}_2}\ (40\ \%) \qquad (8)$$

$$\mathbf{9} \xrightarrow[\substack{\text{C}_6\text{D}_6\\ \text{r. t, 6 h}}]{[\text{Rh}]} \mathbf{11}\ (80\%) \qquad (9)$$

$$\underset{\mathbf{12}}{\text{CpFe(CO)}_2\text{-CH(OMe)Ph}} \xrightarrow[\text{CD}_2\text{Cl}_2\text{, r. t.}]{\text{H}_2\text{SiPh}_2\,/\,[\text{Rh}]} \text{No reaction} \qquad (10)$$

The dramatic change in reactivity induced by the phosphine ligand supports the postulated mechanism (eq 5). And when an α-alkoxyalkyl complex contains a stabilizing ligand or a substituent, the alkoxy moiety is readily ionized even by such a weak Lewis acid as $RhCl(PPh_3)_3$ under mild conditions to give **5**. In the absence of a hydride donor **9** affords **11** and MeOH via deprotonation of **5**. Formation of variable amounts of **11** was also observed on hydrosilylation of **1e**, and the formation of a vinyl complex on hydrosilylation of CpFe(CO)[P(OMe)$_3$][C(O)CH$_3$] was also mentioned by Cutler.[7] The sluggish reactivity of **12** may correspond to that of **2e**.

Hydrosilylation of Other Oxygen-Containing Ligands. Hydrosilylation of a β-oxopropyl complex **13a** gave an isopropyl complex **15a** in low yield. On the other hand, hydrosilylation of a β-oxophenethyl complex **13b** gave an inseparable mixture of two isomeric alkyl complexes **14b** and **15b** with a variable ratio of the two isomers (eq 11).

$$\underset{\substack{\mathbf{13a}\ (\text{R = Me})\\ \mathbf{13b}\ (\text{R = Ph})}}{\text{Fp-CH}_2\text{-C(O)-CH}_3} \xrightarrow[\text{THF}]{\text{H}_2\text{SiPh}_2\,/\,[\text{Rh}]} \underset{\substack{\mathbf{14a}\ (0\ \%)\\ \mathbf{14b}}}{\text{Fp-CH}_2\text{CH}_2\text{-CH}_3} + \underset{\substack{\mathbf{15a}\ (13\ \%)\\ \mathbf{15b}}}{\text{Fp-CH(CH}_3\text{)-CH}_3} \qquad (11)$$

(ca. 1 : 1 ; 26 % yield)

The formation of the isoalkyl complex **15** indicates that the reaction proceeds via hydridic reduction of a transient cationic olefin complex which is generated by ionization of an initially formed β-siloxyalkyl complex Fp–CH$_2$CH(OSiHPh$_2$)R (Chart I). The addition to the less hindered

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[13] Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.

Table IV. Oxidative Methanolysis of 2[a]

complex	R	yield of 19, % oxidizing agent Br_2	yield of 19, % oxidizing agent $CuCl_2 \cdot H_2O$
2a	CH_3	74	20
2b	CH_3	5	0
2c	CH_3	13	0
2d	Ph	94	3

[a] Yields were based on 1.

methylene carbon atom was favored over that to the internal carbon atom. The lower selectivity in the hydridic reduction of an [$Fp^+(\eta^2$-olefin)] complex was already reported by Rosenblum.[14]

Hydrosilylation of a μ-ketene diiron complex **16**[15] gave Fp_2 and $CH_2{=}CHOSiHPh_2$ **17** (a silyl enol ether of acetaldehyde) as major products in addition to small amounts of ethylene (4%) and ethane (2%) (eq 12). Hydrosilylation of the C=O group followed by metal–metal bond formation would release **17**. We have already reported conversion of the bridging ketene ligand in **16** to an acetaldehyde equivalent (methyl enol ether) via a two-step reaction sequence similar to eq 1.[15]

$$\underset{\mathbf{16}}{\text{Fp-CH}_2\text{CO-Fp}} + H_2SiPh_2 \xrightarrow[CD_2Cl_2]{[Rh]} \underset{\mathbf{17}\,(50\,\%)}{CH_2{=}CHOSiHPh_2} + Fp_2 \tag{12}$$

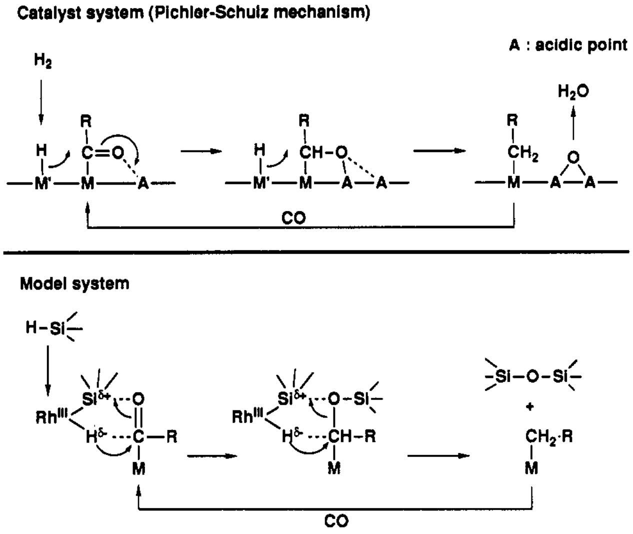
The μ-methoxymethylene ligand in a diiron complex **18** was reduced to the μ-methylene ligand by hydrosilylation with $H_3SiPh/RhCl(PPh_3)_3$ in CH_2Cl_2 (eq 13). H_2SiPh_2 was not effective in this case. Attempted reduction of a bridgehead alkoxy group in $(\mu_3\text{-MeO-C})Co_3(CO)_9$ by H_2SiPh_2 or $H_3SiPh/Rh(I)$ resulted in recovery of the starting complex presumably because of the instability of a bridgehead carbocationic intermediate. Bridging and semibridging carbonyl ligands in $[CpFe(CO)(\mu\text{-CO})]_2$, $[Me_2Si(C_5H_4)_2]Fe_2(CO)_2(\mu\text{-CO})_2$, $Cp_2Fe_2(dppe)(\mu\text{-CO})_2$, $Cp_2Ni_2(\mu\text{-CO})_2$, $(CpNi)_3(\mu_3\text{-CO})_3$, and $Mn_2(dmpe)_2(\mu\text{-CO})$ could not be reduced by the present method.

$$\underset{\mathbf{18}}{Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-CHOMe})} \xrightarrow[CH_2Cl_2]{H_3SiPh\,/\,[Rh]} \underset{38\,\%\text{ yield}}{Cp_2Fe_2(CO)_2(\mu\text{-CO})(\mu\text{-CH}_2)} \tag{13}$$

Oxidative Methanolysis of 2. Oxidative alcoholysis of acyl–metal complexes leading to esters has been well-documented.[16] Similarly, oxidative methanolysis of **2** gave methyl α-hydroxycarboxylate **19** (eq 14, Table IV). Of the three α-siloxyethyl complexes, **2a** produced methyl lactate in 74% yield, when Br_2 was used as an oxidant. **2d** gave methyl mandelate in an almost quantitative yield. Because the migrating ability of the α-siloxyalkyl group is reduced by the electron-withdrawing siloxy group,[17a] the reaction should be conducted under pressure of CO (10 atm). **19** was not formed at all under atmospheric pressure of CO. Thus, it is revealed that an acyl–metal complex serves not only as an ester equivalent but also as an α-alkoxycarboxylate ester equivalent [M–C(O)R ≡ R′OC(O)R ≡ R′OC(O)CH(OH)R].

$$\underset{\mathbf{2}}{\text{M-CH(OSiHPh}_2\text{)-R}} \xrightarrow[MeOH]{oxid.} \underset{\mathbf{19}}{\text{MeO-C(O)-CH(OH)-R}} \tag{14}$$

Scheme III



Modeling the Pichler–Schulz Mechanism by Repeating Overreduction and CO Insertion. It has been well-known that a phosphine-substituted alkyliron complex is readily carbonylated by the action of a catalytic amount of an oxidizing agent.[17] Combination of the overreduction with the carbonylation would lead to construction of a model system for the chain propagation step in the Pichler–Schulz mechanism. Actually, the acetyliron complex **1f**, which was prepared by the reaction of $Fp{-}CH_3$ with PPh_3, was converted to the pentanoyl complex in 12% yield (based on **1f**) by repeating the homologation three times[18] (eq 15).

$$\begin{aligned}
&\underset{\mathbf{1f}}{FE\text{-C(O)-CH}_3} \xrightarrow{a} \underset{77\,\%}{FE\text{-CH}_2\text{-CH}_3} \xrightarrow{b} \underset{77\,\%}{FE\text{-C(O)-CH}_2\text{CH}_3} \\
&\xrightarrow{a} \underset{62\,\%}{FE\text{-CH}_2\text{CH}_2\text{CH}_3} \xrightarrow{b} \underset{66\,\%}{FE\text{-C(O)-CH}_2\text{CH}_2\text{CH}_3} \\
&\xrightarrow{a} \underset{80\,\%}{FE\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3} \xrightarrow{b} \underset{\substack{71\,\% \\ (12\,\%\text{ from }\mathbf{1f})}}{FE\text{-C(O)-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3}
\end{aligned} \tag{15}$$

FE = CpFe(CO)(PPh_3)

a : H_2SiPh_2 / cat. $RhCl(PPh_3)_3$. b : CO (1atm) / cat. $[Cp_2Fe]BF_4$.

As shown in Scheme III, there are several similarities between the Pichler–Schulz mechanism and the present model system. In the actual system an acid point (A) on the catalyst surface may activate the acyl part to facilitate transfer of hydride which is formed by adsorption of hydrogen. In the model system, the hydrosilane is, at first, activated by oxidative addition to Rh(I) species. In the resulting hydrido(silyl)rhodium(III) species the hydrosilane may be apparently polarized like $Rh(H^{\delta-})(Si^{\delta+})$. The electrophilic Si center would activate the acyl C=O part in a manner similar to the acid point on the catalyst surface. Hydride transfer from Rh to the acyl carbon atom completes the first step to give the α-siloxyalkyl complex. The formed siloxy group is reductively replaced with hydride in a manner similar to the first step to give the overreduced alkyl species, and the acyl oxygen atom originating from carbon monoxide is finally removed as si-

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loxane (silylated water). The driving force for reduction of an acyl group should be attributed to the thermodynamic stability of the H–O bond in H_2O and the Si–O bond in a siloxane, compared to that of the C–O bond in the acyl group.

Experimental Section

General Data. All manipulation were performed under argon atmosphere by using standard Schlenk tube techniques.

THF and CH_2Cl_2 were dried over NaK/benzophenone and P_2O_5, respectively, distilled, and stored under argon atmosphere. Deuterated solvents were dried over molecular sieves and distilled in vacuo.

$RhCl(PPh_3)_3$,[19] the acyl complexes (1),[20] α-methoxyalkyl complex (6, 7, 9, and 12),[2,21] 13,[22] 16,[15] and 18[23] were prepared according to the published methods. H_2SiPh_2 and H_3SiPh were prepared by the reduction of the corresponding chlorosilanes with $LiAlH_4$.

^1H and ^{13}C NMR spectra were recorded on a JEOL FX-100 (100 MHz) and a JEOL GX-270 (68 MHz) spectrometer, respectively. IR spectra were obtained on a Hitachi 260-50 spectrophotometer. The GLC analyses of the reaction products were made on a Hitachi 163 gas chromatograph using columns packed with Porapak Q (gas) and Silicon SE-30 (others). Column chromatography was performed on alumina (activity II-IV; Merck Art. 1097).

Hydrosilylation of Fp–C(O)CH$_3$ (1a). **1a** (653 mg, 2.97 mmol) and $RhCl(PPh_3)_3$ (164 mg, 0.18 mmol) were dissolved in THF (2 mL). Upon addition of H_2SiPh_2 (0.72 mL, 3.9 mmol) gas evolution was observed and the color of the mixture darkened. After the mixture was stirred for 2 h at room temperature, the volatiles were removed under reduced pressure and the product was extracted with ether. Filtration through a short alumina column followed by evaporation of ether gave crude **2a** (1.13 g) as dark red oil.

The yield of **2a** was determined by a separate reaction. Hydrosilylation of **1a** (44 mg, 0.20 mmol) was carried out as described above by using $RhCl(PPh_3)_3$ (2 mg, 0.002 mmol) and H_2SiPh_2 (55 μL, 0.3 mmol) in THF (2 mL). Removal of the volatiles under reduced pressure, extraction with ether, and filtration through an alumina pad followed by evaporation of the filtrate gave dark red oily residue, to which was added benzene-d_6 (0.5 mL) and cyclohexane (5 mg; internal standard). The yield of **2a** was determined to be 95% by comparison of the intensity of the Cp signal of **2a** with that of cyclohexane.

Hydrosilylation of CpMo(CO)$_2$(PPh$_3$)–C(O)CH$_3$ (1b). **1b** (1.32 g, 2.35 mmol) and $RhCl(PPh_3)_3$ (23 mg, 0.024 mmol) were dissolved in THF (2 mL). Upon addition of H_2SiPh_2 (0.52 mL, 2.8 mmol) to the mixture gas was evolved, and the reaction was completed within 1 min as revealed by TLC. Filtration through a short alumina column (2 cm × 2 cm) and evaporation of the volatiles gave yellow powders **2b**, which was washed with ether and dried in vacuo. **2b**·THF (1.43 g, 1.84 mmol, 78% yield): IR (KBr) δ(C≡O) 1933, 1845, ν(Si–H) 2126 cm^{-1}. Anal. Cald. for $C_{39}H_{35}MoPSi{\cdot}C_4H_8O$: C, 66.31; H, 5.56. Found C, 65.91; H, 5.11.

Hydrosilylation of Mn(CO)$_5$–C(O)R (1c,d). To an NMR tube containing **1c** (34 mg, 0.15 mmol) and $RhCl(PPh_3)_3$ (2 mg, 0.002 mmol) was added benzene-d_6 (0.5 mL), H_2SiPh_2 (55 μL, 0.3 mmol), and cyclohexane (4 mg; internal standard). After several minutes gas was suddenly evolved and an exothermic reaction took place with the color change from pale yellow to black. **2c** was formed in 95% yield as confirmed by ^1H NMR. The reaction of **2d** was similarly carried out. IR (C_6H_6) ν(C≡O): (**2c**) 2108, 2045, 1999; (**2d**) 2109, 2045, 2005 cm^{-1}.

Hydrosilylation of CpFe(CO)(PPh$_3$)[C(O)CH$_3$] (1f) (Overreduction). To a mixture of **1f**·CH_2Cl_2 (658 mg, 1.27 mmol), $RhCl(PPh_3)_3$ (28 mg, 0.03 mmol), and H_2SiPh_2 (0.56 mL, 3.0 mmol) was added CH_2Cl_2 (3 mL). After the complete consumption of **1f** was checked by TLC after 6 h at room temperature, the mixture was passed through a short Celite column. The product **3f**[24] (412 mg, 0.963 mmol, 74% yield) was precipitated by the addition of hexanes. When THF was used as a solvent, the yield of **3f** was reduced to 10–30% and variable amount of **11** was formed.

Hydrosilylation Catalyzed by Group 9 Complexes. 1a/RhCl(CO)(PPh$_3$)$_2$. To a mixture of **1a** (40 mg, 0.18 mmol) and $RhCl(CO)(PPh_3)_2$ (5 mg, 0.007 mmol) in THF (2 mL) was added H_2SiPh_2 (55 mL, 0.3 mmol), and the mixture was stirred for 6 h. After evaporation of the volatiles the products were extracted with ether. Filtration through an alumina pad followed by evaporation left deep red oil, to which was added benzene-d_6 (0.5 mL) and cyclohexane (4 mg; internal standard). The yield of **2a** was estimated to be 92%.

1f/RhCl(CO)(PPh$_3$)$_2$. To a mixture of **1f** (262 mg, 0.487 mmol) and $RhCl(CO)(PPh_3)_2$ (20 mg, 0.03 mmol) in THF (2 mL) was added H_2SiPh_2 (0.19 mL, 1.0 mmol) via a syringe. The mixture was stirred for 1 h, and then consumption of **1f** was checked by TLC. Chromatographic separation (eluent: CH_2Cl_2–hexanes) gave red and green bands. **3e** (30 mg, 0.068 mmol, 14% yield) was isolated from the red band, and an unknown product which contained only Cp and PPh_3 signals was isolated from the green band.

1e/Co$_2$(CO)$_8$. To a mixture of $Co_2(CO)_8$ (31 mg, 0.091 mmol) and H_3SiPh (0.53 mL, 4.3 mmol) under CO (1 atm) was added **1e** (337 mg, 1.20 mmol) dissolved in CH_2Cl_2 (2 mL). After the mixture was stirred for 4 h, **3e** (124 mg, 0.462 mmol, 38% yield) was isolated by column chromatography.

The reaction of **1a** with H_2SiPh_2 in the presence of $Co_2(CO)_8$ gave a complicated mixture containing a small amount of **2a**.

1b/[Rh(CH$_2$=CH$_2$)$_2$Cl]$_2$ + dppb. To an NMR tube containing a mixture of **1b** (52 mg, 0.100 mmol), $[Rh(CH_2{=}CH_2)_2Cl]_2$ (0.8 mg, 0.002 mmol), and dppb (1.6 mg, 0.004 mmol) in benzene-d_6 (0.5 mL) was added H_2SiPh_2 (35 μL, 0.18 mmol) via a microsyringe. After 1 h, ^1H NMR of the mixture showed the formation of **2b** in 90% yield (unreacted **1b** (10%) was also observed).

One-Pot Synthesis of 4a,b from 1a. A THF solution (4 mL) of **2a** was prepared by the reaction of **1a** (413 mg, 1.88 mmol), $RhCl(PPh_3)_3$ (95 mg, 0.102 mmol), and H_2SiPh_2 (1.0 mL, 5.4 mmol) as described above (1 h). To the resulting mixture was added MeOH (8 mL), and the mixture was further stirred for 2 h at room temperature. After evaporation of the volatiles the product was isolated by column chromatography (eluent: CH_2Cl_2–hexanes). The first eluting yellow band was collected, from which **4a**[25] (428 mg, 1.81 mmol, 97% yield) was isolated after recrystallization from ether–hexanes. When EtOH was used in place of MeOH, **4b**[26] was obtained in 86% yield.

Hydrosilylation of 1e Followed by Methanolysis. To a mixture of **1e** (388 mg, 1.38 mmol), $RhCl(PPh_3)_3$ (60 mg, 0.065 mmol), and H_2SiPh_2 (0.64 mL, 3.4 mmol) was added 3 mL of CH_2Cl_2. After the resulting mixture was stirred for 66 h, MeOH (1.5 mL) was added and the mixture was further stirred for 1 h. Separation by column chromatography gave **3e**[27] (225 mg, 0.839 mmol, 61% yield) and **4c**[28] (32 mg, 0.107 mmol, 8% yield).

Hydrosilylation of α-Alkoxyalkyl Complexes 6, 7, 9, and 12. **7** (31 mg, 0.069 mmol) and $RhCl(PPh_3)_3$ (3 mg, 0.004 mmol) were weighed in an NMR tube. After addition of cyclohexane (internal standard, 2 mg), benzene-d_6 (0.5 mL), and H_2SiPh_2 (25 μL) under argon the tube was sealed. The formatioin of **8** and $(MeO)SiHPh_2$ was monitored by ^1H NMR. Other reactions were similarly carried out. **8**,[29] **10**[30] and **11**[31] were identified by com-

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parison with authentic samples.

Hydrosilylation of 13a. To a mixture of **13a** (193 mg, 0.822 mmol) and $RhCl(PPh_3)_3$ (35 mg, 0.038 mmol) in THF (1.5 mL) was added H_2SiPh_2 (0.45 mL, 2.4 mmol). After the mixture was stirred for 30 min, **15a**[32] (23 mg, 0.105 mmol, 13% yield) was isolated by column chromatography (eluent:hexanes).

Hydrosilylation of 13b. **13b** (419 mg, 1.41 mmol) was treated with $RhCl(PPh_3)_3$ (21 mg, 0.023 mmol) and H_2SiPh_2 (0.52 mL, 2.8 mmol) in THF (3 mL) in a manner similar to **13a**. Chromatographic separation gave an inseparable isomeric mixture of **14b** and **15b** in 26% yield (103 mg, 0.365 mmol). The ratio of **14b**[33] and **15b**[34] was determined to be ca. 1:1 on the basis of the intesities of the Cp signals (^1H NMR).

Hydrosilylation of Fp–$CH_2C(O)$Fp (16). The reaction was carried out in an NMR tube with use of **16** (36 mg, 0.091 mmol), $RhCl(PPh_3)_3$ (11 mg, 0.012 mmol), and H_2SiPh_2 (36 μL, 0.20 mmol) in CD_2Cl_2 (0.5 mL). **17**[35] was identified by comparison of its ^1H NMR spectrum with that of the authentic sample. **17**: ^1H NMR (CD_2Cl_2) δ 4.21 (1 H, dd, $J = 1.2, 5.9$ Hz, $=CH$ trans to the SiO group), 4.55 (1 H, dd, $J = 1.2$ Hz, 13.7 Hz $=CH$ cis to the SiO group), 5.55 (1 H, s, SiH), 6.52 (1 H, dd, $J = 5.9, 13.7$ Hz, $=CH$ gem to the SiO group), 7.37 (10 H, m, Ph × 2).

Reduction of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHOMe)$ (18). To a mixture of **18** (307 mg, 0.676 mmol), $RhCl(PPh_3)_3$ (50 mg, 0.054 mmol), and H_3SiPh (0.25 mL, 2.0 mmol) was added 5 mL of CH_2Cl_2, and the mixture was stirred for 2 days. Chromatographic separation gave $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$[23] (86 mg, 0.254 mmol, 38% yield) and the starting complex (33 mg, 0.089 mmol, 13% recovery).

Oxidative Methanolysis of 2. A THF solution (1 mL) of **2a** was prepared as described above starting from **1a** (88 mg, 0.40 mmol), $RhCl(PPh_3)_3$ (18.5 mg, 0.002 mmol), and H_2SiPh_2 (0.11 mL, 0.60 mmol). The volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (5 mL) and was filtered through a Celite pad, which was subsequently washed with CH_2Cl_2. The resulting solution was transfered to a 50-mL glass autoclave with a rubber septum filled with argon and was frozen under CO by immersing it in an liquid nitrogen bath. Then Br_2 (1.8 mL, 2.0 mmol) was added through the rubber septum. After pressurizing CO at 10 atm the bulb was closed and the frozen mixture was melted and stirred for 30 min at -20 °C. MeOH (1 mL) was added to the mixture, which was stirred for 20 min at room temperature. 1-Octene (0.16 mL, 2.0 mmol) and a MeOH solution (0.5 mL) of KF (70 mg, 1.2 mmol) were added to the mixture to destroy excess Br_2 and silyl ether, respectively. The yield of the product was determined by GLC with 1-hexanol (methyl lactate) and *n*-dodecane (methyl mandelate) as an internal standard.

Chain Propagation of 1f. **3f** (321 mg, 0.728 mmol) was prepared from **1f** (490 mg, 0.942 mmol) as described above. **3f** was placed in a two-necked Schlenk tube with a rubber septum and a V-shaped glass tube containing $[Cp_2Fe]BF_4$ (20 mg, 0.07 mmol). After evacuation CO was introduced through the stopcock from a rubber balloon. CH_2Cl_2 (15 mL) was added through the rubber septum, and the Schlenk tube was cooled to 0 °C in an ice bath. $[Cp_2Fe]BF_4$ was added to the solution by rotating the V-shaped glass tube. The mixture was stirred overnight, and $CpFe(CO)(PPh_3)[C(O)CH_2CH_3]$ (263 mg, 0.563 mmol) was isolated in 77% yield as a sole product by column chromatography. Repetition of hydrosilation (average yield, 68%) and carbonylation (average yield, 71%) three times gave $CpFe(CO)(PPh_3)C(O)\text{-}CH_2CH_2CH_2CH_3]$ (56 mg, 0.113 mmol) in 12% yield based on **1f**. The products $[CpFe(CO)(PPh_3)[C(O)(CH_2)_nCH_3]$ (n = 1,[36], 2,[36] 3[37]), $CpFe(CO)(PPh_3)\text{-}(CH_2)_nCH_3$ (n = 2,[30] 3,[38] 4[38])] were identified by comparison with authentic samples.

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