this bath could well prevent complete condensation of the disilapropanes. We assumed that roughly half of the disilapropane products entering the −45 °C trap passed the trap and were recirculated. The modeling results on this basis are in good agreement with the reported overall yield data (see Table IV). It is clear, from the modeling, that the proposed mechanism is a reasonable one, both qualitatively and quantitatively. While the modeling could be extended and better fits realized, such an exercise would not be instructive at this time as there are far too many unknowns in the rate constant assignments. Clearly the pressing need now is for more and better data on the elementary reactions of silylenes.

Acknowledgment. The authors are indebted to the U.S. Air Force Office of Scientific Research (AFOSR-83-0209) for financial support of this work.

Registry No. Me_2SH_2, 1111-74-6; Me_2S:, 6376-86-9; $Me_2SiHCH_2SiH_2Me$, 18148-13-5; $MeSiHCH_2SiHMeCH_2$, 1628-01-9; $Me_3SiCH_2SiH_3$, 18148-12-4; $Me_2SiCH_2SiH_2CH_2$, 38512-90-2; $Me_3SiCH_2SiH_2Me$, 18163-83-2; $Me_2SiCH_2SiHMeCH_2$, 25261-26-1; $MeSiH_2CH_2SiH_2Me$, 5654-05-7; $SiH_2CH_2SiHMeCH_2$, 80540-80-3; $Me_2SiHCH_2SiH_3$, 18145-47-6.

The Mechanism of the Formation of Silyl Enol Ethers from Hydrosilanes and Organic Carbonyl Compounds in the Presence of Cobalt Carbonyls. Kinetic Investigation of Some Reaction Steps

István Kovács,[†] Attila Sisak,[‡] Ferenc Ungváry,[†] and László Markó*[†]

Institute of Organic Chemistry, University of Veszprêm, H-8200 Veszprêm, Hungary, and Research Group for Petrochemistry of the Hungarian Academy of Sciences, H-8200 Veszprêm, Hungary

Received July 10, 1986

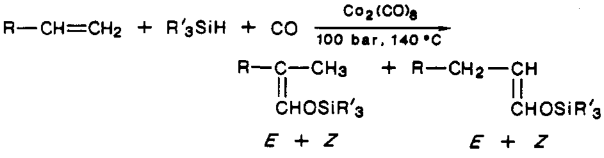
The cleavage of isobutyrylcobalt tetracarbonyl with triethylsilane gives (triethylsilyl)cobalt tetracarbonyl, isobutyraldehyde, dicobalt octacarbonyl, and the corresponding unsaturated and saturated silyl ethers. Silyl enol ether was also formed, along with order products, in the reaction of (trimethylsilyl)cobalt tetracarbonyl with isobutyraldehyde. The kinetics of both reactions were studied. The first one proceeds through an acylcobalt tricarbonyl intermediate that oxidatively adds hydrosilane in the rate-determining step and then gives the products in fast consecutive steps. The second reaction involves probably an (α-(trimethylsiloxy)isobutyl)cobalt tetracarbonyl intermediate formed from silylcobalt tetracarbonyl and aldehyde. Silyl enol ethers as main products will be provided by β-hydrogen elimination from α-siloxyalkyl complexes in both reactions.

Introduction

The formation of silyl enol ethers from ketones and hydrosilanes in good yields in the presence of dicobalt octacarbonyl and amines was described some years ago (eq 1)[1] ($RCH_2C(O)R'$ = aliphatic, cycloaliphatic, or alkyl-aromatic ketone; R''_3SiH = trialkyl-, aryldialkyl-, or trialkoxysilane; L = amine). Without use of an amine, a mixture of $RCH{=}C(R')OSiR''_3$ and $RCH_2CH(R')OSiR''_3$ results.

$$RCH_2C(O)R' + R''_3SiH \xrightarrow[50\ ^\circ C]{Co_2(CO)_8/L} RCH{=}C(R')OSiR''_3 + H_2 \qquad (1)$$

The mechanism of this interesting process has not been discussed. More detailed studies were conducted by Murai and co-workers[2] to the "siloxymethylenylation" of alkenes and cycloalkenes, which was regarded as an analogue of the hydroformylation process (eq 2). The mechanistic proposals made by the authors at that time were necessarily based on rather scanty information regarding the formation and reactivity of silylcobalt carbonyl complexes[3,4] and thus need reexamination. For example, it was shown recently that reaction 3, which was proposed to be the first step of reaction 2, actually did not take place but that $R_3SiCo(CO)_4$ and H_2 are the only products in the reaction between $Co_2(CO)_8$ and R_3SiH (eq 4).[6]



$$R{-}CH{=}CH_2 + R'_3SiH + CO \xrightarrow[100\ bar,\ 140\ ^\circ C]{Co_2(CO)_8} \underset{E\ +\ Z}{R{-}C(CH_3){=}CHOSiR'_3} + \underset{E\ +\ Z}{R{-}CH_2{-}CH{=}CHOSiR'_3} \qquad (2)$$

$$Co_2(CO)_8 + R_3SiH \rightarrow R_3SiCo(CO)_4 + HCo(CO)_4 \qquad (3)$$

$$Co_2(CO)_8 + 2R_3SiH \rightarrow 2R_3SiCo(CO)_4 + H_2 \qquad (4)$$

We have recently determined the kinetics of the cleavage of *n*-butyrylcobalt tetracarbonyl and isobutyrylcobalt tetracarbonyl with H_2 and $HCo(CO)_4$ and proposed a mechanism[7] for these reactions that form a part of the catalytic hydroformylation cycle of propene. The present

---

[†] University of Veszprêm.

[‡] Research Group for Petrochemistry of the Hungarian Academy of Sciences.

(1) Sakurai, H.; Miyoshi, K.; Nakadaira, Y. *Tetrahedron Lett.* **1977**, 2671.

(2) (a) Seki, Y.; Hidaka, A.; Makino, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* **1977**, *140*, 361. (b) Seki, Y.; Murai, S.; Hidaka, A.; Sonoda, N. *Angew. Chem.* **1977**, *89*, 919. (c) Murai, S.; Sonoda, N. *Angew. Chem.* **1979**, *91*, 896.

(3) E.g.; Harrod, J. F.; Chalk, A. J. In *Organic Syntheses Via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, pp 687–692 and references therein.

(4) Important mechanistic details even about the well-documented hydroformylation reaction became known only in the eighties.[5]

(5) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1981**, *219*, 397. Markó, L. *Fundament. Res. Homogen. Catal.* **1984**, *4*, 1.

(6) Sisak, A.; Ungváry, F.; Markó, L. *Organometallics* **1986**, *5*, 1019.

(7) Kovács, I.; Ungváry, F.; Markó, L. *Organometallics* **1986**, *5*, 209.

0276-7333/88/2307-1025$01.50/0

Table I. Initial Rates of the Reaction of Isobutyrylcobalt Tetracarbonyl (1) with Triethylsilane (2a) at 25 °C in *n*-Heptane

10^2[**1**], M	10^2[**2a**], M	10^2[CO],[a] M	$10^6 r$[b], M s^{-1}	$10^6 r$,[c] M s^{-1}
0.46	1.90	1.07	1.33	0.75
0.99	1.90	1.08	2.01	1.41
1.50	1.90	1.07	3.58	2.44
2.01	1.90	1.08	4.90	3.20
3.91	1.90	1.07	9.64	5.96
0.98	1.01	1.08	1.01	0.78
1.01	3.16	1.08	3.16	2.44
0.98	5.00	1.07	4.82	3.61
0.92	6.32	1.08	5.88	4.75
0.92	3.16	0.85	3.23	2.77
1.06	3.16	1.54	2.77	1.97
0.92	3.16	2.23	1.76	1.31
0.95	3.16	2.77	1.55	1.00
0.93	3.16	3.32	1.46	0.98

[a] Calculated from p_{CO} and the solubility of CO in *n*-heptane. [b] Rate calculated from the decrease of [**1**]. [c] Rate calculated from the increase of [**3a**].

Table II. Initial Rates of the Reaction of (Trimethylsilyl)cobalt Tetracarbonyl (3b) with Isobutyraldehyde (5) at 25 °C in *n*-Heptane[a]

10^2[**3b**], M	10^2[**5**], M	$10^6 r_0$, M s^{-1}
0.92	2.00	2.15
1.40	2.00	2.90
2.06	2.00	3.84
3.17	2.00	5.13
4.01	2.00	5.46
5.95	2.00	7.30
1.98	0.90	1.66
2.02	4.00	7.14
2.04	6.00	9.33
2.02	8.00	11.52
1.12	8.28	7.32
1.59	8.24	10.51
1.88	8.40	12.70
2.04	2.00	3.85[b]
1.01	4.40	0.09[c]
0.88	19.50	1.00[d]
1.60	4.00	0.13[e]

[a] [CO] = 1.07 × 10^2 M. [b] Experiment under 1 bar of Ar. [c] Starting complex **3a**. The conversion of **3a** was 3% in 1 h. [d] Starting complex **3a** at 40 °C. [e] Starting complex **3c**. The conversion of **3c** was 3% in 1 h.

work deals with the kinetics and the mechanism of the reaction between isobutyrylcobalt tetracarbonyl and triethylsilane and between (trialkylsilyl)cobalt tetracarbonyls and isobutyraldehyde.

Results

We found that an excess of triethylsilane reacts smoothly with isobutyrylcobalt tetracarbonyl at 25 °C under CO in *n*-heptane solution leading to not only the expected[8] isobutyraldehyde and $Co_2(CO)_8$ but to $Me_2C{=}CHOSiEt_3$, $Me_2CHCH_2OSiEt_3$, $Et_3SiCo(CO)_4$, and traces of $HCo(CO)_4$ as well (eq 5).

$$\underset{\mathbf{1}}{Me_2CHC(O)Co(CO)_4} + \underset{\mathbf{2a}}{Et_3SiH} \xrightarrow{r} \underset{\mathbf{3a}}{Et_3SiCo(CO)_4} + \underset{\mathbf{4}}{Co_2(CO)_8} + \underset{\mathbf{5}}{Me_2CHCHO} + \underset{\mathbf{6a}}{Me_2C{=}CHOSiEt_3} + \underset{\mathbf{7a}}{Me_2CHCH_2OSiEt_3} \quad (5)$$

The kinetics of reaction 5 were measured, because of probable consecutive reactions, by the initial rate method. Clear first-order kinetics for both **1** and **2a** and negative first order kinetics for CO were found.[10] The initial rate of formation of **3a** amounted to only about 60% of the rate of consumption of **1** (Table I). The rate of formation of the organic products could not be measured exactly. Nevertheless, it was evident that **5**, **6a**, and **7a** were formed as main products up to ~65% conversion. Although **5** slowly disappeared during long reaction times, forming partly silylated oligomeric products, the ratio of **6a** to **7a** remained unchanged (~1.2:1).

The reaction between silylcobalt tetracarbonyls and aldehydes leading to silyl enol ethers and $HCo(CO)_4$ was suggested[2] to play an important role in catalytic siloxymethylenylation (eq 2) and seemed to be involved also in reaction 1. We proved experimentally that **5** and **3a** indeed react with each other but only at a negligible rate as compared with that of reaction 5 under the same conditions. We tried therefore to find a more reactive silyl complex that would allow the study of this reaction under mild conditions. Actually, (trimethylsilyl)cobalt tetracarbonyl (**3b**) was found to react with **5** at 25 °C under argon or CO in *n*-heptane at a rate convenient for kinetic measurements (eq 6). Under argon, fast decomposition of **9** to **4** and **10**

$$\underset{\mathbf{3b}}{Me_3SiCo(CO)_4} + \underset{\mathbf{5}}{Me_2CHCHO} + CO \xrightarrow{r'} \underset{\mathbf{6b}}{Me_2C{=}CHOSiMe_3} + \underset{\mathbf{7b}}{Me_2CHCH_2OSiMe_3} + \underset{\mathbf{8b}}{Me_2CHCH(OSiMe_3)CHO} + \underset{\mathbf{9}}{HCo(CO)_4} + \underset{\mathbf{4}}{Co_2(CO)_8} + \underset{\mathbf{10}}{Co_4(CO)_{12}} \quad (6)$$

took place as a consecutive reaction. Under CO, however, not only **6b** (62%) but also **7b** (7%) and **8b** (23%) were formed as well, together with the corresponding amounts of **9** and **4**. Simultaneous volumetric, IR, and GC measurements showed that the formation of **8b** was connected with CO uptake and the source of **8b** was the starting product **3b** and not **6b**. No **8b** was formed at 25 °C under CO in either the presence or the absence of **4** (cf. ref 5) in attempted reactions of **6b** with **5** or **9**, respectively. Thus the formation of the aldehyde **8b** by hydroformylation of **6b** could be excluded. The yield of **8b** in reaction 6 could be increased by raising the CO pressure. For example, the product mixture obtained from nearly equimolar amounts of **3b** and **5** at 50 bar of CO pressure in 1 h gave **8b** by vacuum distillation in 36% isolated yield.

The rate of **3b** consumption was found to be independent of CO concentration and first order in **5**. The order in **3b** was less than 1 at low [**5**]:[**3b**] ratios, but it approached 1 at higher relative concentrations of **5** (Table II).

The catalytic hydrosilylation of **5** in the presence of **4** (an analogue of reaction 1) was carried out at 50 °C under CO in *n*-heptane. Since we did not use basic additives, a 4:3 mixture of **6a** and **7a** was obtained in accord with the results of Sakurai and co-workers.[1] We note here that no catalytic process related to that described in eq 2 could be observed under ambient conditions if we used aliphatic alkenes, **2a**, and **4** as catalysts.

---

[8] According to a recent report,[9] $MeC(O)Co(CO)_3PPh_3$ and Et_3SiH give only MeCHO as the organic product. We repeated this experiment using $Me_2CHC(O)Co(CO)_3PPh_3$ and Et_3SiH and found that at 60 °C both Me_2CHCHO (**5**) and $Me_2C{=}CHOSiEt_3$ (**6a**) were formed even at the initial stages of the reaction. At higher conversions the amount of **5** decreased and further amounts of **6a** appeared in the product, probably as a result of a reaction analogous to that described in eq 6. The formation of the cobalt–carbonyl containing products could not be followed exactly by IR spectroscopy because of the overlap of their bands with those of the starting complex. At the end of the reaction most of the cobalt was present in form of the well-known complex $Co_2(CO)_6(PPh_3)_2$.

[9] Wegman, R. W. *Organometallics* **1986**, *5*, 707.

[10] At low CO pressures a very fast initial rate was observed, but the reaction slowed down in a few minutes.

Table III. Initial Rates of the Reactions of Isobutyrylcobalt Tetracarbonyl (1) with H_2, $HSiEt_3$, and $HCo(CO)_4$ at 25 °C in *n*-Heptane under 1 atm of CO and H–X (X = H, Si, Co) Bond Strengths, *D*[a]

	$10^6 r$, M s^{-1}	$10^3 k_2/k_{-1}$[b]	D^0_{298}, kcal mol^{-1}
H_2	0.93	0.26	104.2[c]
$HSiEt_3$	3.36	2.5 ± 0.1	90 ± 3[d]
$HCo(CO)_4$	11.10	6.3	58[e]

[a] [1] = [H_2] = [$HSiEt_3$] = [$HCo(CO)_4$] = 2×10^{-2} M. [b] See text; calculated from rate of formation of isobutyraldehyde. [c] See ref 12a. [d] Given for $HSiMe_3$, see ref 12b. [e] See ref 12c.

Discussion

Our results allow the following conclusions concerning the mechanisms of the investigated reactions.

i. Reaction 5, as expected, begins with the dissociative loss of CO followed by the rate-determining oxidative addition of hydrosilane and fast product formation (eq 7–9). Applying the steady-state treatment and assuming

$$1 \underset{k_1}{\overset{k_1}{\rightleftharpoons}} Me_2CHC(O)Co(CO)_3 + CO \qquad (7)$$

$$Me_2CHC(O)Co(CO)_3 + \mathbf{2a} \xrightarrow[\text{slow}]{k_2} Me_2CHC(O)Co(CO)_3(H)(SiEt_3) \qquad (8)$$

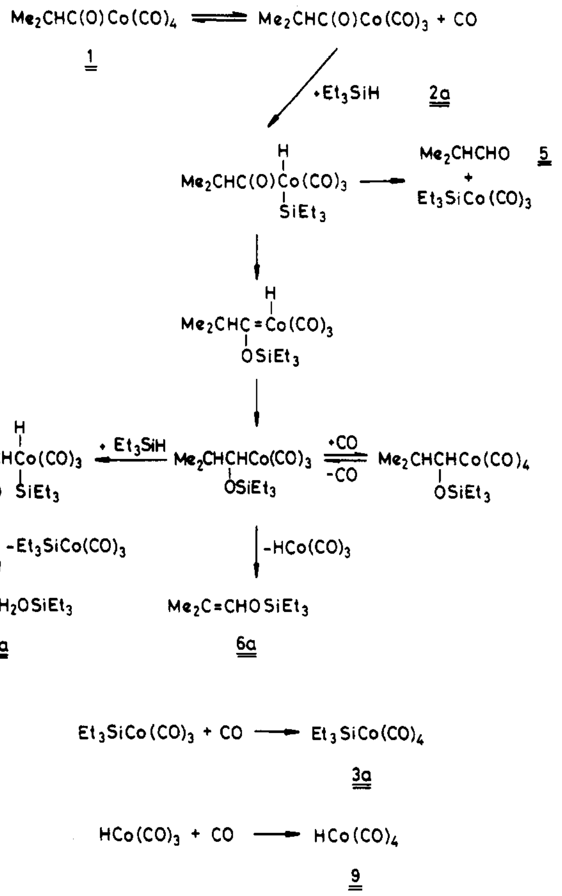
$$Me_2CHC(O)Co(CO)_3(H)(SiEt_3) \xrightarrow[\text{fast}]{} \text{products} \qquad (9)$$

that $k_2 \ll k_{-1}$, this mechanism leads to the rate expression found experimentally. Such a treatment has been already repeatedly used for reactions of acylcobalt tetracarbonyls.[7,11] The cleavage of **1** by **2a** was found to be faster than by H_2 but slower than by **9** (Table III). This finding is in accordance with the increase of bond strengths in the order H–Co < H–Si < H–H. Our kinetic results are also consistent with the recent ones reported by Wegman[9] on the reaction of triphenylphosphine-substituted acetylcobalt carbonyl with HMR_3 (M = Si, Sn; R = Bu, Ph) compounds. The different rate laws observed in the two cases derive from the different relative values of k_1, k_{-1}, and k_2 for the substituted and unsubstituted complexes.

ii. The three "inorganic" (**3a**, **4**, **9**) and three "organic" (**5**, **6a**, **7a**) products of reaction 5 can be explained only by a mechanism in which several parallel and consecutive steps follow the rate-determining reaction (eq 8). A possible pathway is shown in Scheme I.[13,14] It has to be considered that the reactions between **3a** and **5** and between **4** and **2a** are slow under the conditions of reaction 5. On the other hand, the reduction of **1** by **9** (Table III) is fast; i.e., the most probable pathway for the formation of **4** is the consecutive step (10), which may also account for the higher rate of **1** consumption in comparison to the rate of formation for **3a**.

$$\underset{\mathbf{1}}{Me_2CHC(O)Co(CO)_4} + \underset{\mathbf{9}}{HCo(CO)_4} \rightarrow \underset{\mathbf{5}}{Me_2CHCHO} + \underset{\mathbf{4}}{Co_2(CO)_8} \qquad (10)$$

Scheme I



iii. Our findings concerning reaction 6 are closely related to those of Gladysz and co-workers[15b] for the analogous reactions of $Me_3SiMn(CO)_5$. As it is to be expected on the basis of the generally higher reactivity of cobalt carbonyls as compared with that of analogous manganese compounds, reaction 6 takes place much faster than that described for $Me_3SiMn(CO)_5$, which requires several weeks at 5 °C in the case of aliphatic aldehydes and ketones.[15b] The reaction pathway we propose (Scheme II) is similar to that already suggested for analogous Mn complexes.[15] The independence of the rate of CO pressure can be explained if the (α-siloxyisobutyl)cobalt tetracarbonyl intermediate is formed in a rate-determining step in which a tricarbonylcobalt complex is not involved. The acyl complex $Me_2CHCH(OSiMe_3)C(O)Co(CO)_4$ is similar to the complexes $RCH(OSiMe_3)C(O)Mn(CO)_5$ prepared by Gladysz and co-workers.[15b] In our case, however, the acylcobalt complex could be detected only at high CO pressures, presumably because of the fast formation of **8b**. This finding is consistent with our previous results[11] concerning the easy formation of acylcobalt tricarbonyls and, consequently, their ready reduction to aldehydes by **9**.[16]

On the basis of our results, we propose therefore that α-siloxyalkyl complexes are the key intermediates in reaction 5 as well as in reaction 6: they lead to silyl enol ethers through β-hydrogen elimination. The differences found between the two systems studied, Et_3Si and Me_3Si complexes in the case of reactions 5 and 6, respectively, can be explained by the size of these two groups: the larger

---

[11] (a) Hoff, C. D.; Ungváry, F.; King, R. B.; Markó, L. *J. Am. Chem. Soc.* **1985**, *107*, 666. (b) Kovács, I.; Hoff, C. D.; Ungváry, F.; Markó, L. *Organometallics* **1985**, *4*, 1347.

[12] (a) Weast, R. c. *CRC Handbook of Chemistry and Physics*; CRC Press: West Palm Beach, FL, 1978; p F-223. (b) *Ibid.* p F-232. (c) Ungváry, F. *J. Organomet. Chem.* **1972**, *36*, 363.

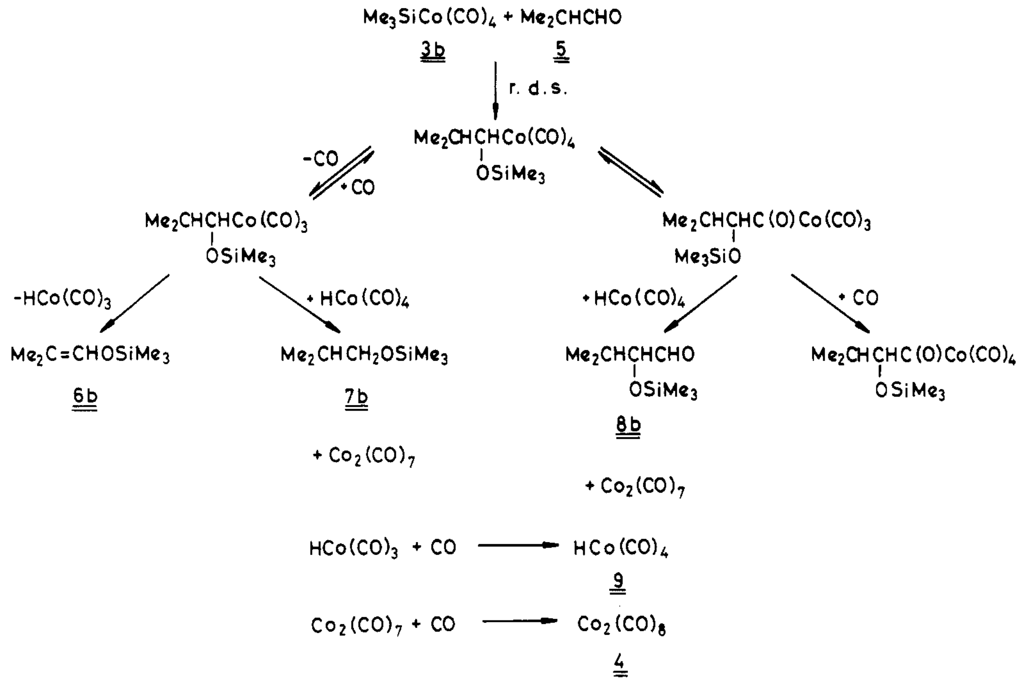
[13] More details related to those of Scheme I were suggested by Murai et al. as possible steps of the catalytic siloxymethylenylation of olefins (cf. ref 2c).

[14] 1,3-Silatropic shift from metal to acyl oxygen (shown also in Scheme I) was proposed to Gladysz and co-workers.[15a] The suggested intermediate $Me_2CHCH(OSiMe_3)Co(CO)_4$ is related to the manganese complex $RCH(OSiMe_3)Mn(CO)_5$ supposed also by the above group[15b] to be formed in the reaction of $Me_3SiMn(CO)_5$ and aliphatic aldehydes.

[15] (a) Brinkman, K. C.; Blakeney, A. C.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325. (b) Jonsson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508. Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147.

[16] Ungváry, F. *J. Chem. Soc., Chem. Commun.* **1984**, 824.

Scheme II



Et_3Si facilitates β-elimination and does not favor alkyl migration. Consequently "homologues" of aldehyde 8 are not formed in reaction 5.

Our results concerning reactions 5 and 6 should contribute to a better understanding of the rather complex catalytic processes 1 and 2.

Experimental Section

General Data. IR spectra were recorded on a Carl Zeiss Jena IR 75 spectrophotometer using 0.124- or 0.060-mm CaF_2 cuvettes. ^1H NMR spectra were recorded on a Tesla BS 487/c 80-MHz spectrometer. GC–MS analyses of samples were performed on a JMS 01-SG-2 JEOL spectrometer. Gas chromatograms were recorded on a Hewlett-Packard Model 5830 A chromatograph equipped with FID detector using SP 2100 glass capillary column.

All manipulations were carried out under CO atmosphere by using anaerobic techniques.

Materials. *n*-Heptane was distilled under CO from sodium wire. Isobutyrylcobalt tetracarbonyl[16] (**1**), (triethylsilyl)cobalt tetracarbonyl[17] (**3a**), (trimethylsilyl)cobalt tetracarbonyl[18] (**3b**), and (triphenylsilyl)cobalt tetracarbonyl[17] (**3c**) as well as authentic samples of silyl enol ethers **6a** and **6b**[19] were prepared by published methods. Triethylsilane (**2a**) and isobutyraldehyde (**5**) (Fluka) were commercially available compounds and were freshly distilled before use.

Kinetic runs were performed in the same way as reported earlier.[7] Initial rates were determined for **1**, **3a**, **3b**, and **3c** by using the IR bands at 2044, 2088, 2090, and 2094 cm^{-1}, respectively. The increase of **4** could be followed at 2069 cm^{-1}. IR absorbances in *n*-heptane: 2044 (ϵ_M(**1**) 2645), 2088 (ϵ_M(**3a**) 2530),[6] 2090 (ϵ_M(**3b**) 1820), 2027 (ϵ_M(**3b**) 3720), 1995.5 (ϵ_M(**3b**) 11 200), 2094 (ϵ_M(**3c**) 3740), 2033 (ϵ_M(**3c**) 4040), 2005 cm^{-1} (ϵ_M(**3c**) 12 300 $cm^2\ mmol^{-1}$).

Preparative Runs. Reaction 5. 2a (0.45 mL, 2.82 mmol) was added to a 5.85-mL stock solution of **1** (0.94 mmol) in *n*-heptane under atmospheric pressure of CO. The reaction vessel was thermostated at 25 °C. The color of the mixture changed rapidly from yellow to dark brown, indicating the formation of **4**. After a 15-min reaction time the organometallic products were identified and analyzed by IR spectroscopy, and the other products were analyzed by GC–MS after all the cobalt-containing compounds were precipitated with excess pyridine at 0 °C. This showed the following product distribution: **1** (0.00 mmol), **4** (0.22 mmol), **3a** (0.49 mmol), **9** (0.00 mmol), **5** (0.42 mmol), **6a** (0.26 mmol), **7a** (0.20 mmol), Et_3SiOH (0.07 mmol).

Reaction 6. 5 (0.10 mL, 1.1 mmol) was added to a 5.0-mL stock solution of **3b** (1.0 mmol) in *n*-heptane under atmospheric CO pressure at 25 °C. Until the disappearance of **3b** (detected by IR, ~30 min) 4.2 mL of CO was consumed with less and less rate; then it turned to slow gas evolution (decomposition of the formed **9**). The reaction mixture was stirred further for ~1 h until the gas evolution ceased. Meanwhile the light brown color of the solution turned dark, characteristic for **4**. The GC-MS analysis of the mixture showed nearly quantitative conversion of **5**. Besides **6b** (0.62 mmol) and **7b** (0.07 mmol) the additional main product was **8b** (0.25 mmol). Mass spectrum, *m*/*e* (relative intensity); highest fragment, 159 (95); other characteristic fragments, 145 (471), 117 (109), 75 (200), and 73 (1000).

To obtain preparative amounts of **8b**, 11 mmol of **5**, 10 mmol of **3b**, and 3 mL of *n*-pentane were charged in a 10 mL Teflon-coated stainless-steel autoclave under CO at −10 °C. The autoclave was pressurized with CO up to 50 bar and then shaken at room temperature for 1 h. The reaction mixture was cooled to −78 °C in order to remove **4** by crystallization. The IR spectrum of the solution showed besides a strong aldehyde band at 1741 cm^{-1} new ν_{CO} bands at 2103 (m), 2050 (s), 2025 (vs), 2005 (vs), and 1705 (w) cm^{-1} characteristic for an acylcobalt tetracarbonyl. The filtered mixture was distilled in vacuo which gave 0.69 g of **8b** (bp 25–30 °C (2 mmHg)) in 91% purity (GC): yield 36%; ^1H NMR ($CDCl_3$, δ) 0.14 (s 9 H), 0.91 (d, 6 H, *J* = 7.2 Hz), 1.75 (m, 1 H), 3.55 (m, 1 H), 9.44 (d, 1 H, *J* = 2 Hz).

Catalytic Hydrosilylation of 5. 2a (0.32 mL, 2.0 mmol) and **5** (0.36 mL, 4.0 mmol) were dissolved in a 5.0-mL stock solution of **4** (0.1 mmol) in *n*-heptane at 50 °C under CO atmosphere. The reaction was followed by IR spectroscopy. After a 70-min reaction time the solution contained **3a** (0.125 mmol) and **9** (0.025 mmol) besides **4** and some **10**. A complete conversion of **2a** was achieved after a 6-h reaction time. The GC–MS analysis of this mixture showed as main products **6a** (0.76 mmol), **7a** (0.54 mmol), and Et_3SiOH (0.28 mmol).

Registry No. 1, 38784-32-6; **2a**, 617-86-7; **3a**, 14049-72-0; **3b**, 15693-82-0; **3c**, 14095-19-3; **4**, 15226-74-1; **5**, 78-84-2; **6a**, 7031-16-5; **6b**, 6651-34-9; **7a**, 18132-87-1; **7b**, 1825-66-7; **8b**, 112969-05-8; **9**, 16842-03-8; Et_3SiOH, 597-52-4.

---

[17] Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640.

[18] Baay, I. L.; MacDiarmid, A. G. *Inorg. Chem.* **1969**, *8*, 986.

[19] House, H. O.; Czuba, L. J.; Gal, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.