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Kinetics and Mechanism of the Silylation of Dicobalt Octacarbonyl by Triethylsilane. Effect of Lewis Bases on the Reaction

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The mechanism of the known reaction between $Co_2(CO)_8$ and Et_3SiH leading to $Et_3SiCo(CO)_4$ and H_2 has been reinvestigated. In contrast to earlier reports, $HCo(CO)_4$ is not an intermediate of this reaction. Catalytic amounts of pyridine or tributylphosphine increase the rate and change the kinetics of the reaction. A general scheme involving cobalt carbonyl radical species is proposed for the mechanisms of the uncatalyzed and catalyzed reaction pathways.

Introduction

The reaction of dicobalt octacarbonyl with an excess of hydrosilane leads to silylcobalt tetracarbonyls (eq 1).

$$Co_2(CO)_8 + 2R_3SiH \rightarrow 2R_3SiCo(CO)_4 + H_2 \quad (1)$$

When equimolar amounts of silane were used, the formation also of hydridocobalt tetracarbonyl was reported.[1] In spite of the importance of the reaction both from a practical (catalytic hydrosilylation of olefins and related processes; cf. ref 2 and 3) and from a theoretical viewpoint (activation of a less polar Y–H bond by a transition-metal complex; cf. ref 4), no kinetic work has been performed until now, however, and, consequently, mechanistic considerations were based mainly on speculation.[2] Catalytic processes probably involving the above reaction often were carried out in the presence of phosphines, but the role of these Lewis bases was not thoroughly discussed to date.

We have studied the kinetics of the reaction between $Co_2(CO)_8$ and Et_3SiH both in the absence and in the presence of catalytic amounts of Lewis bases and report our results below.

Results

The formation of $Et_3SiCo(CO)_4$ from Et_3SiH and $Co_2(CO)_8$ under CO in *n*-heptane at 30–40 °C was followed by IR spectroscopy. The results of the kinetic measurements are compiled in Table I. The reaction was found to be of first order for $Co_2(CO)_8$ as well as Et_3SiH and of negative first order for CO. To check the exact stoichiometry of the reaction, we followed in some cases also the consumption of $Co_2(CO)_8$ and found that the initial rate of $Et_3SiCo(CO)_4$ formation was twice as high as the initial rate of $Co_2(CO)_8$ consumption, in the case of both a 1:1 and a 10:1 ratio of Et_3SiH to $Co_2(CO)_8$. This is in accord with eq 1.

Under the conditions examined, neither under CO nor under Ar could $HCo(CO)_4$ be detected in the reaction mixture by IR spectroscopy. This is in sharp contrast to earlier reports, and therefore we tried to clarify the role of this proposed[1] intermediate. First we measured the rate of reaction 1 under CO in the presence of initially added $HCo(CO)_4$. Surprisingly, the rate of $Et_3SiCo(CO)_4$ formation was not affected by $HCo(CO)_4$; it corresponded only to that determined by the concentration of $Co_2(CO)_8$ (Figure 1). Next, we tried to react $HCo(CO)_4$ and Et_3SiH under CO in the absence of $Co_2(CO)_8$ (i.e., $[Co_2(CO)_8] \leq 5 \times 10^{-4}$ M), but the concentrations of both reactants remained practically unchanged for ~1 h. When $Co_2(CO)_8$ was added, $Et_3SiCo(CO)_4$ was formed, $HCo(CO)_4$ decomposed to $Co_2(CO)_8$ (this reaction is catalyzed by $Co_2(CO)_8$[6]), and the rate of $HCo(CO)_4$ decomposition[7] corresponded to the literature data.[6]

Table I. Hydrosilylation of $Co_2(CO)_8$ in *n*-Heptane[a]

$10^2[Co_2(CO)_8]_0$, M	$10^2[Et_3SiH]_0$, M	$10^2[CO]$,[b] M	$10^6 r_0$, M s^{-1}	$10^4 k_{obsd}$,[c] s^{-1}
0.99	2.04	1.07	2.29	1.39
0.99	4.06	1.07	4.78	1.31
0.99	6.08	1.07	7.31	1.34
0.50	4.06	1.07	2.29	1.25
1.98	2.04	1.07	5.07	1.39
3.86	5.11	1.07	23.57	1.32
5.14	7.04	1.07	44.45	1.36
5.20	8.10	1.07	54.01	1.41
7.88	8.10	1.07	81.26	1.40
0.99	4.07	1.57	3.68	1.49
0.99	4.06	2.30	2.25	1.40
0.99	4.06	3.31	1.43	1.22
3.81	5.13	1.06[d]	6.79	0.368
3.81	5.13	1.07[e]	12.33	0.675
0.17[f]	5.95	1.07	1.15	1.21
1.67[g]	5.36	1.07	13.05	1.56
1.57	6.26	1.07	15.44[h]	1.68
3.14	6.28	1.05[i]	2.87[h]	0.153
5.71[j]	7.55	1.07	57.98	1.44
0.89	9.50	0[k]	10[l]	

[a] 40.0 °C, 1 bar total pressure, unless otherwise noted. [b] [CO] was calculated from p_{CO} by using solubility data from ref 5. [c] $k_{obsd} = r_0[CO]/([Co_2(CO)_8][Et_3SiH])$. [d] At 30.2 °C. [e] At 35.2 °C. [f] $[HCo(CO)_4]_0 = 0.033$ M. [g] $[HCo(CO)_4]_0 = 0.022$ M. [h] With UV irradiation. [i] At 21.3 °C. [j] 1% galvinoxyl was added. [k] The reaction was started under argon, at 14.5 °C. [l] Reproducibility low.

The silylation of $Co_2(CO)_8$ was found to be a strongly temperature-dependent reaction with an E_a value of 105 kJ/mol. UV irradiation with a low power, medium-pressure mercury lamp accelerated $Et_3SiCo(CO)_4$ formation by

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[1] Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640. Baay, Y. L.; MacDiarmid, A. G. *Inorg. Chem.* **1969**, *8*, 986.

[2] Harrod, J. F.; Chalk, A. J. In "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P. Eds.; Wiley: New York, 1977; Vol. II. pp 687–690.

[3] Murai, S.; Sonoda, N. *Angew. Chem.* **1979**, *91*, 896.

[4] Sailard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.

[5] Ungváry, F. *J. Organomet. Chem.* **1972**, *36*, 363.

[6] Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1980**, *193*, 383.

[7] We found a $HCo(CO)_4$ consumption rate of 2.27×10^{-7} M s^{-1}, at $[HCo(CO)_4] = 0.022$, $[Co_2(CO)_8] = 0.017$, and $Et_3SiH = 0.054$ M, at 40 °C, under CO atmosphere (~1 bar). From Ungváry's data (measured in the absence of Et_3SiH, but otherwise under similar conditions[6]), a value of 2.43×10^{-7} M s^{-1} can be calculated. At lower temperatures an unknown species could be detected in solutions of $HCo(CO)_4$ and excess Et_3SiH with a broad IR absorption between 1960 and 1860 cm^{-1}. The reversible formation of this species did not seem to influence the decomposition of $HCo(CO)_4$ to $Co_2(CO)_8$.

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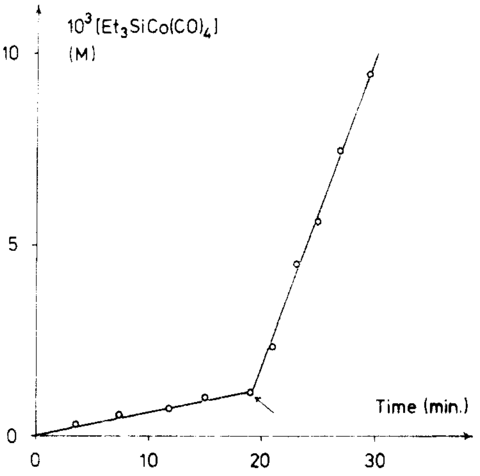

Figure 1. Time course of $Et_3SiCo(CO)_4$ formation in a mixture of $HCo(CO)_4$ (0.033 M), $Co_2(CO)_8$ (0.0017 M), and Et_3SiH (0.0595 M) under CO atmosphere at 40 °C. At the time shown by the arrow a solution of $Co_2(CO)_8$ was added changing the actual concentrations to 0.022, 0.0167 and 0.0536 M, respectively.

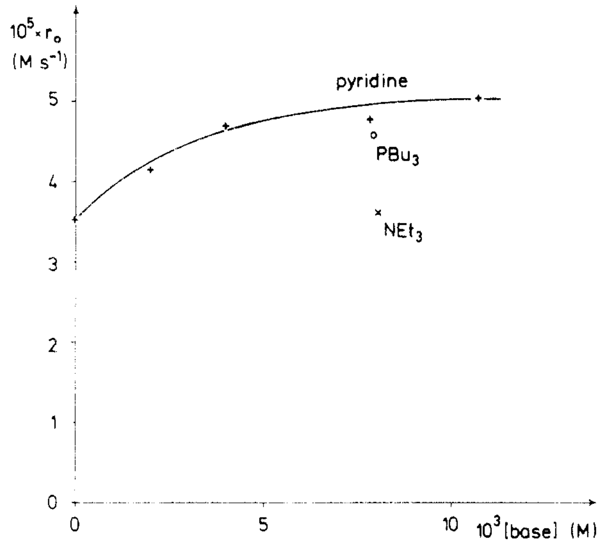

Figure 2. Initial rates of $Et_3SiCo(CO)_4$ formation in the presence of bases at 30 °C under CO. Initial concentrations of $Co_2(CO)_8$ and Et_3SiH are 0.0407 and 0.080 M, respectively.

a factor of ~1.5; galvinoxyl (1% based on $Co_2(CO)_8$) had no effect on the rate.

The reaction of Et_3SiH and $Co_2(CO)_8$ in toluene at 25–35 °C was studied also in the presence of catalytic amounts of pyridine (5–30 mol % based on $Co_2(CO)_8$) and some other Lewis bases. The correct measurement of $Et_3SiCo(CO)_4$ concentration was not possible in these cases because of the presumably rapid equilibrium reaction (2) (B = pyridine), which has been described for B = NR_3 or PR_3 and R = alkyl.[8,9] We therefore followed Et_3SiH consumption by GLC or by H_2 evolution measured volumetrically.

$$\mathrm{Et_3SiCo(CO)_4 + B \rightleftarrows \underset{1}{[Et_3SiB]^+[Co(CO)_4]^-}} \qquad (2)$$

Table II. Hydrosilylation of $Co_2(CO)_8$ in the Presence of Pyridine (py)[a]

$10^2[Co_2(CO)_8]_0$, M	$10^3[py]_0$, M	$10^2[Et_3SiH]_0$, M	p_{CO}, bar	$10^5 r_0$,[b] M s^{-1}
4.13	7.8	4.02	0.93	1.19
4.10	7.8	7.99	0.93	1.89
4.07	7.7	11.90	0.93	3.06
4.15	7.7	15.80	0.93	3.89
4.13		8.04	0.93	1.40
4.27	2.0	8.31	0.93	1.63
4.20	4.0	8.18	0.93	1.87
3.95	11.7	7.69	0.93	2.00
2.03	7.7	7.94	0.93	0.93
6.15	7.8	7.99	0.93	2.40
8.20	7.8	7.99	0.93	2.76
4.07	7.7	7.94	1.80	1.98
4.07	7.7	7.94	2.40	1.64
4.07	7.7	7.94	0.94[c]	0.91
4.07	7.7	7.94	0.92[d]	3.12
3.95	7.9[e]	7.69	0.93	1.78
3.95	8.1[f]	7.69	0.93	1.46
2.07		8.38	0.93	0.65[g]
4.91		9.47	0.93	1.98[g]
2.03	4.4[h]	8.20	0.93	0.60[g]
4.07[i]	7.7	7.94	0.93	1.25

[a] 30.0 °C, 1 bar total pressure, toluene solution, unless otherwise noted. [b] Measured by GLC, unless otherwise noted. [c] At 25.3 °C. [d] At 35.0 °C. [e] PBu_3 was added. [f] NEt_3 was added. [g] Measured by H_2 evolution volumetrically. [h] PPh_3 was added. [i] 1% galvinoxyl was added.

In the presence of pyridine the infrared spectrum showed the formation of both $HCo(CO)_4$ and $Et_3SiCo(CO)_4$. The rate of $Et_3SiCo(CO)_4$ formation was in this case, however, first order in Et_3SiH and fractional order (between 0.5 and 1) in $Co_2(CO)_8$ and depended only slightly on the concentrations of pyridine and CO (Table II and Figure 2).[11] Galvinoxyl (1% based on $Co_2(CO)_8$) slowed down the reaction by about one-third.

The influence of some other Lewis bases on the silylation of $Co_2(CO)_8$ also was tested. No effect was shown by 10 mol % PPh_3 or NEt_3 on the reaction rate. Addition of PPh_3 resulted in the evolution of an equivalent amount of CO, and $Co_2(CO)_7PPh_3$ was found as an additional product. NEt_3 gave the known derivative 1 with the $Et_3SiCo(CO)_4$ formed (vide supra). On the other hand, PBu_3 accelerated Et_3SiH consumption practically to the same extent as pyridine. Immediately some $HCo(CO)_4$ and $[Co(CO)_4]^-$ [13] appeared in the reaction mixture.

Discussion

Silylation of $Co_2(CO)_8$ in *n*-Heptane. Earlier studies[1,2] on the silylation of $Co_2(CO)_8$ suggested that the reaction begins with oxidative addition of hydrosilane on the dinuclear metal carbonyl, which leads to the cleavage of the cobalt–cobalt bond (eq 3). The fact that the overall

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

reaction between Et_3SiH and $Co_2(CO)_8$ is described by eq 1 was explained by the secondary reaction (4). Such a

$$\mathrm{Et_3SiH + HCo(CO)_4 \rightarrow Et_3SiCo(CO)_4 + H_2} \qquad (4)$$

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[8] Bald, J. F.; MacDiarmid, A. G. *J. Organomet. Chem.* **1970**, *22*, C22.

[9] We found an analogous product with B = pyridine, which could not be isolated, however. Compounds 1 are soluble in toluene showing IR spectra related to those of the contact ion pair type molecules $[R_3NH]^+[Co(CO)_4]^-$;[10] e.g., $[Et_3NSiEt_3]^+[Co(CO)_4]^-$, ν_{CO} (cm^{-1}, toluene): 2019 m, 1934 s, 1895 vs, br; $[C_5H_5NSiEt_3]^+[Co(CO)_4]^+$, ν_{CO} (cm^{-1}, toluene) 2017 mw, 1936 s, 1900 vs, br.

[10] Fachinetti, G.; Balocchi, L.; Secco, F.; Venturini, M. *Angew. Chem.* **1981**, *93*, 215. Calderazzo, F.; Fachinetti, G.; Marchetti, F. *J. Chem. Soc., Chem. Commun.* **1981**, 181.

[11] At longer reaction times (>10 min) the formation of a new species was observed by IR spectroscopy. On the basis of its ν_{CO} spectrum (2098 m, 2045 vs, br, 2033 s, 2010 m, 1995 w, sh cm^{-1} (*n*-heptane)), we suggest the formula $Et_3SiOCCo_3(CO)_9$ (cf. ref 12) for this product which, however, could not be isolated.

[12] Fieldhouse, S. A.; Cleland, A. J.; Freeland, B. H.; Mann, C. D. M.; Obrien, R. J. *J. Chem. Soc. A* **1971**, 2536.

[13] $[Co(CO)_4]^-$ came presumably from $[Bu_3PSiEt_3]^+[Co(CO)_4]^-$.[8] The presence of $Co_2(CO)_7PBu_3$ could not be unequivocally shown, because its bands were covered by those of other species.

Table III. Hydrogenation and Hydrosilylation of $Co_2(CO)_8$ in the Presence of Catalytic Amounts of Bases. Comparison of Kinetic Data

observn	hydrogenation (ref 21)	hydrosilation (this work)
primary products	$HCo(CO)_4$	$Et_3SiCo(CO)_4$, $HCo(CO)_4$ (>1:1)
effective catalysts at $[B]/[Co_2(CO)_8] = 0.1$	pyridine and not chelating derivatives, PR_3 (R = alkyl),[a] halide ions	pyridine, PBu_3
inhibition by 1% galvinoxyl	yes	yes
rate[b] at 50 °C in toluene		
without pyridine	1.8×10^{-6} M s^{-1}	4×10^{-4} M s^{-1}[c]
with 10 mol % pyridine	6.9×10^{-5} M s^{-1}	5.6×10^{-4} M s^{-1}
rate equation (B = pyridine)	$r = k_{obsd}[Co_2(CO)_8]^{1/2}[B]^{1/2}p_{H_2}{}^{\sim 1}p_{CO}{}^{>-1}$[d]	$r = k_{obsd}[Co_2(CO)_8)]^{<1}[B]^{<<1}[Et_3SiH]p_{CO}{}^{\sim 0}$
secondary/byproducts	$[HB]^+[Co(CO)_4]^-$ (B = pyridine), $Co_2(CO)_7B$ (B = PR_3)	$[Et_3SiB]^+[Co(CO)_4]^-$ (B = pyridine, PBu_3), $Co_2(CO)_7B$ (?) (B = PBu_3), $Et_3SiOCCo_3(CO)_9$ (in all cases)

[a] Tertiary phosphines with p$K_a \geq 5$ were effective. [b] Calculated for the following concentrations (M): $[Co_2(CO)_8] = 0.08$, [pyridine] = 0.008, $p_{CO} = 0.9$ bar, $p_{H_2} = 24$ bar (i.e., $[H_2] \approx 0.08$), $[Et_3SiH] = 0.08$. [c] Calculated from the measured temperature dependence. [d] $p_{H_2}{}^{1.5}p_{CO}{}^{-1}$ was published.

reaction was described by Chalk and Harrod as well as by Baay and MacDiarmid.[1] These authors carried out their experiments under nitrogen or argon. More recent investigations[6,14,15] proved, however, that the reactions of $HCo(CO)_4$ or $Co_2(CO)_8$ cannot be reliably investigated in an inert gas atmosphere because both complexes are rapidly transformed in the absence of CO into other reactive species. These side reactions at the same time make the determination of the acutal p_{CO} impossible (see last experiment in Table I). Thus the reactions mentioned above had to be reinvestigated under CO.

Our results demonstrate clearly the following: (i) the stoichiometry of $Et_3SiCo(CO)_4$ formation corresponds to eq 1 even at the beginning of the reaction; (ii) no $HCo(CO)_4$ appears in the reaction mixture in the absence of bases; (iii) the rate of the formation of $Et_3SiCo(CO)_4$ does not depend on $HCo(CO)_4$, and (iv) the presence of Et_3SiH does not affect the decomposition of $HCo(CO)_4$ into $Co_2(CO)_8$.

These facts are incompatible with earlier assumptions about the reaction of $Co_2(CO)_8$ and hydrosilanes because they exclude $HCo(CO)_4$ as an intermediate of reaction 1. The decomposition (eq 5) of $HCo(CO)_4$ (which was claimed

$$2HCo(CO)_4 \xrightarrow{Co_2(CO)_8(cat.)} Co_2(CO)_8 + H_2 \tag{5}$$

to be formed as primary product according to eq 3) into $Co_2(CO)_8$ and H_2 cannot be so fast, even in the presence of $Co_2(CO)_8$[6] that no $HCo(CO)_4$ would be detected in the reaction mixture. To prove this statement quantitatively, we calculated the time courses of the expected concentrations of $Co_2(CO)_8$, $Et_3SiCo(CO)_4$, and $HCo(CO)_4$ assuming reaction 1 to run over reactions 2 and 5 (Figure 3). As can be seen, large concentrations of $HCo(CO)_4$ would be expected to occur, which is, however, definitely not the case.

We propose, therefore, that activation of hydrosilane takes place through the radical species $Co(CO)_4$ and/or $Co(CO)_3$, which can be generated under our reaction conditions.[17a,18] If the reaction pathway contains two such mononuclear radical species up to the rate determining step the formal order in $Co_2(CO)_8$ would be one. A possible pathway is given in Scheme I (running over k_3 and k_4). The slight increase of rate under the effect of irradiation may be explained by an increase in the $Co(CO)_4$ radical concentration. The ineffectiveness of galvinoxyl as an inhibitor is also in accordance with this mechanism which—although partly radical in character—is not a radical chain mechanism.[20]

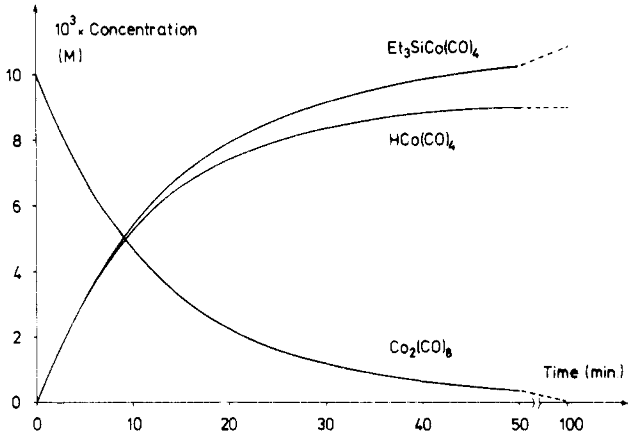

Figure 3. Calculated concentration vs. time plot for a reaction mixture composed of $Co_2(CO)_8$ (0.01 M) and Et_0SiH (0.10 M) (initial concentrations) using measured rate data for reaction 1 (this work) and reaction 5 (ref 7), under CO atmosphere and at 40 °C.

These results also question the assumption[2,3] that the key step of the hydrosilylation of olefins is the reaction between $HCo(CO)_4$ and olefin. Hydrosilylation and related reactions of alkenes in the presence of $Co_2(CO)_8$ obviously need further thorough mechanistic studies.

In this connection it may be of interest to note that although the dissociation of CO from $HCo(CO)_4$, producing the 16e complex $HCo(CO)_3$, is very fast,[22] the reactivity

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(14) Ungváry, F.; Markó, L. *J. Organomet. Chem.* **1974**, *71*, 283.

(15) $HCo_3(CO)_9$, a reactive, paramagnetic complex, could be obtained from $HCo(CO)_4$ at 20 °C under low CO partial pressure.[10] The same species was detected in the mixture of $HCo(CO)_4$ and $Co_2(CO)_8$ under similar conditions.[16]

(16) Tannenbaum, R. Dissertation, ETH Zürich, No. 6970, 1980.

(17) (a) Pályi, G.; Ungváry, F.; Galamb, V.; Markó, L. *Coord. Chem. Rev.* **1984**, *53*, 37. (b) Absi-Halabi, M.; Brown, T. L. *J. Am. Chem. Soc.* **1977** *99*, 2982. Absi-Halabi, M.; Atwood, J. D.; Forbus, N. P.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 6248.

(18) Such steps were postulated earlier for photochemically generated rhenium and manganese radicals or phosphine-substituted cobalt carbonyl radicals in the activation of H_2 or Et_3SiH.[19]

(19) (a) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; pp 186–188. (b) Reichel, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6789.

(20) A reviewer suggested that the kinetics of the reaction (in the absence of bases) may be also explained by the following mechanism:

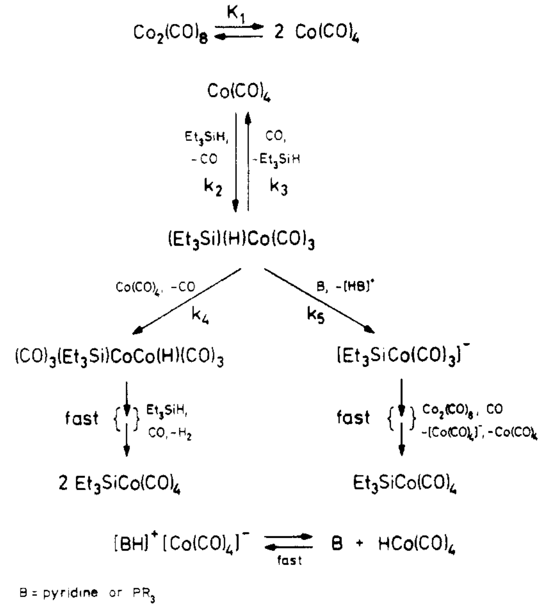
$$Co_2(CO)_8 \rightleftharpoons Co_2(CO)_7 + CO$$

$$Co_2(CO)_7 + Et_3SiH \rightarrow \text{products (rate-determing step)}$$

There is no convincing argument against this mechanism, but were prefer the mechanism proposed in Scheme I. Both hydrosilylation (this work) and hydrogenation[21] of $Co_2(CO)_8$ in the absence and presence of bases show characteristics which suggest that the "uncatalyzed" reaction can be regarded as a "catalyzed" one extrapolated to zero concentration of base (compare Figure 2). This suggests common intermediates.

(21) (a) Sisak, A.; Ungváry, F.; Markó, L. *Organometallics* **1983**, *2*, 1244. (b) Sisak, A.; Ungváry, F.; Markó, L. *Acta Chim. Hung.* **1985**, *119*, 115.

Scheme I



of this "unsaturated" complex toward various HY molecules (hydrosilane, H_2, or D_2[16] and $HCo(CO)_4$ itself[6]) is apparently rather low. This may be perhaps due to the fact that the equilibria (6) (Y = H, Et_3Si, or $Co(CO)_4$) are shifted far to the left and cannot play a role, e.g., in the formation of $Et_3SiCo(CO)_4$.

$$HCo(CO)_3 + HY \rightleftarrows (HY)(H)Co(CO)_3 \rightleftarrows (Y)(H)_2Co(CO)_3 \quad (6)$$

Mechanistic Considerations on Hydrogenation and Hydrosilylation of $Co_2(CO)_8$ in the Presence of Lewis Bases. Recently we described the catalytic effect of several Lewis bases on the hydrogenation of $Co_2(CO)_8$ and investigated also the kinetics of the pyridine-catalyzed reaction.[21] Table III shows the qualitative and quantitative comparison of the published data and the present results. It can be seen that the slower hydrogenation reaction is accelerated more strongly by catalytic amounts of Lewis bases than the faster reaction of hydrosilylation. Other features of the two reactions are, however, in many respects analogous. These analogies encourage us to assume that identical or similar species operate in the two reactions. Both reactions presumably involve 17e and 15e cobalt carbonyl species like $Co(CO)_4$ or $Co(CO)_3B$ (B = PR_3 or pyridine[17b]). The role of such mononuclear species is supported by the fractional order in $[Co_2(CO)_8]$, and the moderate inhibiting effect of galvinoxyl suggests that the reaction should have a mechanism with some radical chain character. A possible mechanism for the hydrosilylation reaction in the presence of bases in accordance with these premises is shown in Scheme I (running over k_3 and k_5, cf. ref 17, 19, and 23).

In the formation of $HCo(CO)_4$ from $Co_2(CO)_8$ and H_2 the effectiveness of phosphines was found to be strongly dependent on their pK_a values.[21a] This suggests that an important factor in determining the efficiency of the base as catalyst should be its proton affinity. Accordingly, as shown on Scheme I, the deprotonation of the paramagnetic hydridic intermediate $(Et_3Si)(H)Co(CO)_3$ is suggested as the point at which the base enters the reaction. Such a reaction is not necessarily very fast,[24] and, therefore, a competition between the base B (k_5) and the radical $Co(CO)_4$ (k_4) seems reasonable. On the other hand, the very strong basicity of the tertiary amines is already disadvantageous, presumably because of the high stability of $[R_3NSiEt_3]^+[Co(CO)_4]^-$ (and $[R_3NH]^+[Co(CO)_4]^-$).

The rate equation derived from the mechanism on Scheme I is shown in eq 7. Our data provide the constants

$$-\frac{d[Et_3SiH]}{dt} = k_2K_1^{1/2}[Co_2(CO)_8]^{1/2}[Et_3SiH] \times \frac{2k_4K_1^{1/2}[Co_2(CO)_8]^{1/2} + k_5\,[py]}{k_4K_1^{1/2}[Co_2(CO)_8]^{1/2} + k_3[CO] + k_5\,[py]} \quad (7)$$

$k_2K_1^{1/2} = 1.25 \times 10^{-3}$, $k_4K_1^{1/2}/k_3 = 1.77 \times 10^{-2}$, and $k_5/k_3 = 7.14$, with a standard deviation of ±13%. We do not wish to discuss these values further because the rate constants for most of the proposed steps are not known.

A similar reaction pathway may be possible also for the hydrogenation of $Co_2(CO)_8$ in the presence of Lewis bases[26] (H_2 instead of Et_3SiH in Scheme I). The decreased reactivity of H_2 as compared to that of Et_3SiH (Table III) is consistent with the stronger H–H bond.

Experimental Section

Materials. Triethylsilane and tri-*n*-butylphosphine were purchased from Fluka AG (Switzerland) and distilled before use. Pyridine and triethylamine (Reanal, Hungary) were dried over KOH pellets, distilled, and stored under CO atmosphere. All solvents were dried on sodium wire, distilled, and stored under argon or CO.

Dicobalt octacarbonyl was doubly recrystallized first from CH_2Cl_2 and then from *n*-heptane. $Et_3SiCo(CO)_4$ as well as stock solutions of $HCo(CO)_4$ in *n*-heptane and toluene were prepared from $Co_2(CO)_8$ by literature methods.[1,27]

General Techniques. Infrared spectra were recorded on a Carl Zeiss Jena IR 75 spectrophotometer. GLC analyses were performed on Carlo Erba Fractovap Model GT and Hewlett-Packard Model 5830 A gas chromatographs using 100-m stainless-steel and 20-m glass capillary columns with squalene and OV-1 stationary phases, respectively.

Hydrosilylation of $Co_2(CO)_8$ in *n*-Heptane. All reactions were run in thermostated vessels at 21.5–40 °C and generally under CO (1 bar total pressure). In reactions at higher CO pressures a 10-dm^3 puffer flask was used, additionally. Experiments with UV irradiation were performed in a vessel with an immersed quartz cooling coat containing a medium-pressure lamp (125 W, Tungsram). The reactions were initiated by injecting the silane into the vigorously stirred solution of $Co_2(CO)_8$. The course of the reaction was followed by taking samples with a gas-tight syringe and injecting them by the aid of a three-way valve into the thermostated IR cell. We measured the log (I_0/I) values of the 2088 cm^{-1} band ($\epsilon_M = 2530 \pm 40\ M^{-1}\ cm^{-1}$) of $Et_3SiCo(CO)_4$[28] and (in some cases) the 2116 cm^{-1} band ($\epsilon_M = 330 \pm 10\ M^{-1}\ cm^{-1}$) of $HCo(CO)_4$ as well as the 1858 cm^{-1} band ($\epsilon_M = 1735 \pm 20\ M^{-1}\ cm^{-1}$) of $Co_2(CO)_8$.[16] Initial rates were calculated from graphical plots below 10% conversion and were reproducible within ±10% by using different IR cells and stock solutions.

Hydrosilylation of $Co_2(CO)_8$ in the Presence of Bases in Toluene. These reactions were initiated by injecting at first the silane and then (within 30 s) a stock solution of the base. The reaction was quenched by taking 0.5-mL samples with a syringe and injecting them into micro test tubes containing 5 µL of pyridine each. The samples were reacted for 30 s at 0 °C and

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[24] The deprotonation rate constants of some transition metal hydrides were reported[25] to be 10^1–10^4 $M^{-1}\ s^{-1}$.

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[26] An alternative route going through $Co(CO)_3B$ (B = pyridine or PR_3) was suggested recently.[21b]

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[28] A value of 2700 $M^{-1}\ cm^{-1}$ was published.[29].

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then cooled to −80 °C. The clear upper layer was analyzed by GLC using heptane as internal standard. The initial rates were reproducible within ±10%. The volumetric measurements of evolved H_2 were carried out by using a described gasometric apparatus.[22]

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Registry No. $Co_2(CO)_8$, 15226-74-1; $Et_3SiCo(CO)_4$, 14049-72-0; Et_3SiH, 617-86-7.

Thermally Induced Reaction of a Group 4 Bent Metallocene Unit with Elemental Sulfur and Selenium: The Formation of Four-Membered Metallacycles

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(Butadiene)bis(η-*tert*-butylcyclopentadienyl)zirconium has been obtained by reacting $(\eta\text{-}C_5H_4CMe_3)_2ZrCl_2$ (**3**) with (butadiene)magnesium. The (diene)zirconium complex exists in two stable isomeric forms, (s-cis-η^4-butadiene)$Zr(C_5H_4CMe_3)_2$ (**5**) and (s-$trans$-η^4-butadiene)$Zr(C_5H_4CMe_3)_2$ (**7**). At room temperature the **5** $\rightleftarrows$ **7** equilibrium ratio is 95/5. UV irradiation of **5** at low temperature leads to almost pure **7**. The activation barrier of the thermally induced **7** → **5** rearrangement has been determined being $\Delta G^{\ddagger}_{-10\,°C}$ = 19.5 ± 0.2 kcal/mol. The **5** $\rightleftarrows$ **7** equilibrium mixture reacts with elemental selenium (ambient temperature, 6 days) to give the four-membered metallacycle $(Cp'_2ZrSe)_2$ (**2**). With stoichiometric amounts of sulfur a similar reaction of the (butadiene)$ZrCp'_2$ system is observed to give the analogous butadiene-free product $(Cp'_2ZrS)_2$ (**9**). With a tenfold excess of sulfur the reaction of the thermodynamic **5**/**7** mixture yields only a small amount of the four-membered metallacycle **9**. The six-membered metallacycle Cp'_2ZrS_5 (**8**) now is the major reaction product (**8**/**9** ≈ 10/1). **8** in turn is converted to **9** upon treatment with a stoichiometric amount of the (butadiene)metallocene mixture **5** $\rightleftarrows$ **7** at ambient temperature. The (butadiene)Zr(η-$C_5H_4CMe_3)_2$ system appears to be a reliable source for transferring the elusive group 4 bent metallocene unit for preparative purposes.

Deoligomerization of the stable forms of the chalcogen elements can be achieved in a number of ways. Substantial knowledge has been accumulated concerning the methodology and mechanisms of cleaving, e.g., sulfur to sulfur linkages starting from the S_8 molecule.[1] Many of the synthetic methods developed in sulfur chemistry have turned out to be suitable to prepare interesting selenium compounds as well.[2] Most notable among the published procedures are the reactions of the chalcogen rings and chains (or fragments derived thereof) with many transition-metal complexes to form new metallacyclic complexes of various ring sizes.[3] Examples of compounds containing "three"- to eight-membered rings containing sulfur have been reported.[4,5]

Frequently, late-transition-metal complexes are able to cleave the elemental chalcogens directly forming the stable metallacyclic deoligomerization products.[3] In addition, the same transition-metal–main-group element complexes can be obtained by stepwise reaction sequences. In this case, e.g., *cyclo*-S_8 is first transformed to an oligosulfide, S_n^{2-}, which is then treated with the corresponding transition-metal dihalide complex.[6]

Variations of this route have for a long time been the best way of preparing the structurally as well as chemically most interesting examples of metallacyclic oligosulfides and -selenides of many early transition metals.[5,6] In principle, early-transition-metal complexes should be able to directly cleave the chalcogen element–element linkage similar to the many reagents derived from the late transition metals. To us, the crucial point seems to be the availability of

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