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Catalytic hydrosilylation of carbon monoxide with cobalt carbonyls*

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Abstract

The hydrosilylation of carbon monoxide with cobalt carbonyls under relatively mild conditions resulted in a Fischer–Tropsch-analogous reductive coupling of CO. Alkyl silyl ethers, 1,2-bis(silyloxy)-1-alkenes and higher molecular weight compounds with at least three silyloxy groups were also formed, each of these containing up to seven carbon atoms derived from CO and for the most part having a linear structure. A (silyloxycarbyne)cobalt complex was postulated as the key intermediate.

Key words: Catalysis; Hydrosilylation; Cobalt complexes; Carbonyl complexes

Introduction

The hydrogenation of carbon monoxide into oxygen containing products is an interesting new homogeneous catalytic process of potential industrial importance [1]. The procedures reported up to now, however, use forcing conditions and also the mechanistic investigations on the reaction had to be performed at high temperatures and pressures [1–3]. For the production of linear alkanes, alkenes, fatty alcohols etc. from synthesis gas, the Fischer–Tropsch synthesis, a heterogeneous, medium pressure high temperature process [4, 5] was proven to be the most useful.

The homogeneous hydrosilylation of carbon monoxide has not been reported till now, although the acceleration of CO hydrogenation by hydrosilanes is known [6]. The formal hydrosilylation of at least one CO molecule occurs in the 'silyloxymethylenylation' of olefins [7] (eqn. (1)) and the 'homologation' of CH_3OSiEt_3 [8] (eqn. (2)) as well. Both reactions are catalyzed by dicobalt octacarbonyl.

$$C_6H_{10} + HSiEt_2Me + CO \xrightarrow{5\text{–}8\ \text{MPa},\ 140\ ^\circ\text{C}} \underbrace{CH_2(CH_2)_4CH}=CHOSiEt_2Me \qquad (1)$$

$$CH_3OSiEt_3 \xrightarrow[4\text{–}8\ \text{MPa},\ 200\ ^\circ]{CO,\ HSiEt_3,\ -(Et_3Si)_2O} CH_2{=}CHOSiEt_3 + CH_3CH_2OSiEt_3 + \text{others} \qquad (2)$$

Recently we prepared the unstable hydroxymethyl- and hydroxyacetylcobalt tetracarbonyls which are possible intermediates of homogeneous CO hydrogenation [9]. Their stable derivatives, $R_3SiOCH_2(CO)_nCo(CO)_4$ ($n=0$, 1), could be obtained in their reaction with strong silylating agents and in an independent way starting from formaldehyde and $R_3SiCo(CO)_4$ [9]. In a continuation of these experiments and using an excess of $HSiR_3$ with UV irradiation in the presence of PBu_3, we observed the formation of a number of organic products:

$$HSiEt_3 + CH_2O(\text{gas}) \xrightarrow[\text{r.t.},\ h\nu]{Et_3SiCo(CO)_4,\ PBu_3} CH_3OSiEt_3 + Et_3SiOCH_2CH_2OSiEt_3 + Et_3SiOCH_2CH(OSiEt_3)CH_2OSiEt_3 + Et_3SiOH + (Et_3Si)_2O \qquad (3)$$

These results prompted us to study the possibility of the cobalt carbonyl catalyzed hydrosilylation of carbon monoxide.

Results and discussion

We succeeded in hydrosilylating CO with silanes of the type $HSiR_3$ ($R_3=Me_3$, Et_2Me, Et_3, Me_2Ph) at

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moderately elevated temperatures and pressures. The standard conditions used (120 °C, 10 MPa) are much milder than those described for the homogeneous hydrogenation of CO. The $Co_2(CO)_8$ catalyst was usually modified by adding tributyl phosphine or pyridine. A higher relative concentration of the base slowed down the reaction. The activity of the catalytic system depended strongly on the solvent: using non-polar solvents resulted in low conversions of the silane: oxygen containing solvents were, however, themselves transformed to a limited extent under the reaction conditions. The best results were achieved in dioxane and anisole.

The following types of compounds were identified as products:

- alkyl silyl ethers, $R'OSiR_3$ (**1**), $R' = CH_3(CH_2)_{n-1}$, $n = 2$–7
- 1,2-bis(silyloxy)-1-alkenes, $R''C(OSiR_3)=CHOSiR_3$ (**2**) (mixture of *E*- and *Z*-isomers), $R'' = CH_3(CH_2)_{m-1}$, $m = 1$–4
- disiloxanes, $R_3SiOSiR_3$ (**3**)

Interestingly, some H_2 could be detected but no methane, methyl silyl ether (**4**) or disilanes were formed. The catalytic results are listed in Table 1.

It is obvious from the compiled data that the selectivity of CO hydrosilylation under the conditions used is low. Table 1 shows that a large part of the starting silane was built into high molecular weight products which could not be identified unequivocally. Mass spectral data suggest the presence of polysilyloxy alkanes and alkenes with at least three silyloxy groups.

The product distributions show that **3** was the main identified product practically in all examined cases. This is a consequence of the formal 'overall reaction'

$$n\mathrm{CO} + 2n\mathrm{HSiR_3} \longrightarrow (\mathrm{CH_2})_n + n\mathbf{3} \qquad (4)$$

related to that of the Fischer–Tropsch synthesis. The methylene groups formed are involved in the alkyl groups of products **1** and **2**. In all cases compounds containing at least two carbon atoms were obtained. In the case of compounds **1**, linear saturated C_3, C_5 and C_6 chains dominated, but also minor amounts of branched chain products and traces of unsaturated compounds were found. Compounds **2** contained predominantly ethyl, propyl and isopropyl groups. The averages of *n* and *m* together with other data characterizing the chain growth are listed in Table 2. In dioxane *n* decreased with increasing PBu_3/Co ratio, but *m* was practically independent of it. The ability to produce $(CH_2)_n$ chains in **1** correlates with the bulkiness of silane (see ref. 10). The smallest one, $HSiMe_2Ph$, provided the longest alkyl groups, and the largest one $HSiEt_3$, gave the greatest share of **2**. Table 2 shows that $TO_{CO} \gg TO_{CH_2}$, which is a consequence of the high share of high molecular weight products with a much higher R_3SiO/CH ratio than that of **1**.

The formation of compounds **1** needs hydrogen. We, therefore, tried to replace the silane at least in part with H_2. Using a gas mixture $H_2/CO = 1/2$ instead of CO increased the share of **1** at the expense of **2** (experiments 5 and 10).

TABLE 1. Catalytic hydrosilylation of carbon monoxide[a]

Run	R_3	Solvent	$B/Co_2(CO)_8$	$HSiR_3$ conv. (%)	Products from CO (mol%)[b]				Products from the solvent (mol%)[c]
					1	2	3	Others	
1	$MeEt_2$		1.0	62	8	6	51	35	
2	$MeEt_2$	toluene	1.0	18	16	2	59	23	
3	$MeEt_2$	dioxane	0	100	5	<1	30	54	10[d]
4	$MeEt_2$	dioxane	0.4	100	5	2	21	59	13[d]
5	$MeEt_2$	dioxane	1.0	100	5	6	23	48	18[d]
6	$MeEt_2$	dioxane	1.5	78	3	4	18	65	10[d]
7	$MeEt_2$	acetonitrile	1.0	46	10	3	53	33	<1
8	$MeEt_2$	diethyl ether	1.0	100	5	5	24	50	16[f]
9	$MeEt_2$	acetic anhydride[e]	1.0	100	8	1	50	19	22
10[g]	$MeEt_2$	dioxane	1.0	100	12	<1	27	47	14[d]
11	Et_3	dioxane	1.0	63	9	12	24	35	20[d]
12	Me_2Ph	dioxane	1.0	100	11	<1	24	49	15[d]
13	Me_3[h]	$CH_3CH(OSiMe_3)$-CH_2OSiMe_3	1.0	94	6	4	41	49	
14	$MeEt_2$[i]	anisole	1.0[j]	100	4	1	34	48	13[k]
15	Et_3[i]	anisole	1.0[j]	100	4	1	32	55	9[k]
16	Me_2Ph[i]	anisole	1.0[j]	100	4	<1	23	62	10[k]

[a] 120 °C, 10 MPa CO (cold), 20 mmol of $HSiR_3$, 1.7 ml of solvent, 0.5 mmol of $Co_2(CO)_8$, $B = PBu_3$, 5 h. [b] Σ (products from CO) = 100%, mol% of silane transformed into these products (see text). [c] mol% of the converted silane. [d] $(R_3SiOCH_2)_2$. [e] 0.9 ml of solvent. [f] $EtOSiMeEt_2$. B = py. [g] $H_2/CO = 1/2$, 12 MPa (cold). [h] 16 mmol of $HSiMe_3$. [i] 12 mmol of $HSiR_3$. [j] B = py. [k] $PhOSiR_3$.

TABLE 2. Data of the alkyl chains of $CH_3(CH_2)_{n-1}OSiMeEt_2$ and $CH_3(CH_2)_{m-1}C(OSiMeEt_2){=}CHOSiMeEt_2$ formed in the reaction of CO and $HSiMeEt_2$[a]

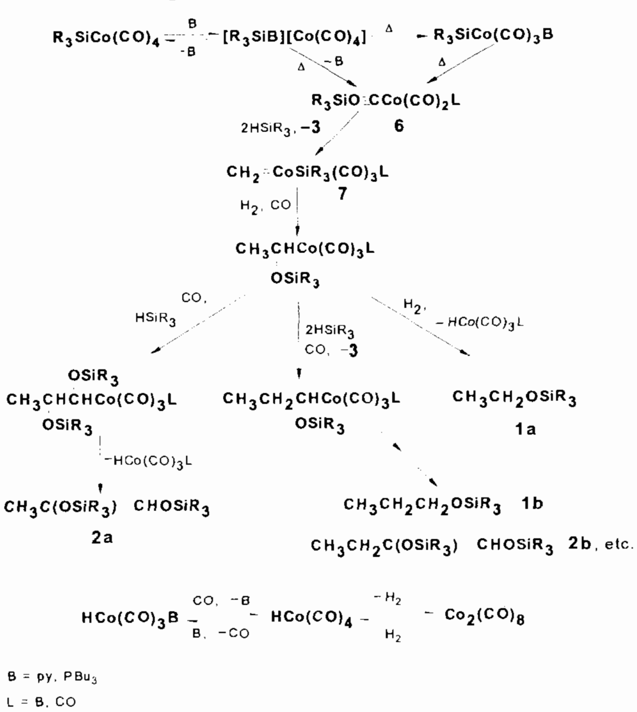
Run	PBu_3/ $Co_2(CO)_8$	$HSiMeEt_2$ conv. (%)	$\bar{n}$	$\bar{m}$	TO_n[b]	TO_m[b]	TO_{CH_2}[c]	TO_{CO}[d]
1[e]	1.0	62	2.8[f]	3.0[g]	1.4	1.2	2.6	8
3	0	100	4.7	3.0	2.5	<0.1	2.5	13
4	0.4	100	4.8	2.5	2.4	0.6	3.0	15
5	1.0	100	3.2	2.4[g]	1.7	1.5	3.2	14
6	1.5	78	2.6	2.4	0.5	0.6	1.1	12
10[h]	1.0	100	5.3	3.0	6.9	<0.1	6.9	10
11	1.0	63[i]	3.4[f]	2.5[g]	2.1	2.0	4.1	16
12	1.0	100[j]	5.2	3.0	6.3	0.3	6.6	16

[a] For conditions see Table 1, dioxane solvent. [b] Turnover CH_2/Co/5 h. [c] $TO_{CH_2} = TO_n + TO_m$. [d] Turnover converted CO/Co/5 h. [e] Without solvent. [f] $(CH_3)_2CHOSiR_3$ was found up to 10 mol% of **1**. [g] $(CH_3)_2CHC(OSiR_3){=}CHOSiR_3$ was found up to 6 mol% of **2**. [h] $H_2/CO = 1/2$ was used. [i] $HSiEt_3$ was used. [j] $HSiMe_2Ph$ was used.

The formation of silyl ethers from the ethers used as solvents was observed (cf., e.g. ref. 7); these side reactions consumed a minor part of the silane, however. 1,2-Bis(silyloxy)ethanes could also have been real products in the CO hydrosilylation (*vide supra*); a control experiment in dioxane-d_8, however, showed the formation of 1,2-bis(silyloxy)ethane-d_4, i.e. a product formed from the solvent. Analogously, diethyl ether provided some ethyl silyl ether, and anisole some phenyl silyl ether, respectively (Table 1).

We investigated the IR spectra of the catalytic reaction mixtures. In a chilled mixture containing PBu_3 as additive, $HCo(CO)_4$ and *trans*-$R_3SiCo(CO)_3PBu_3$ could be detected as well as $R_3SiCo(CO)_4$. Catalytically inactive systems with $PBu_3/Co > 5$ showed $[Co(CO)_3(PBu_3)_2][Co(CO)_4]$ as the main component. After total conversion of the silane, however, only $Co_2(CO)_8$ and $Co_2(CO)_7PBu_3$ could be detected. In chilled mixtures containing pyridine in toluene as solvent, IR bands characteristic for the carbene bridged dinuclear complex, $Co_2(CO)_7(\mu\text{-}C(OSiR_3)CH_2OSiR_3)$ (**5**) could be observed as well as $Co_2(CO)_8$. Complex **5** has been prepared recently in an independent way [11].

On the basis of earlier theoretical considerations [12] and related experimental results both in complex chemistry [13a] and in catalysis [13b], we propose the formation of a silyloxycarbyne species (**6**) as the key intermediate. This may be formed both from ionic and from covalent complexes of known types as shown in Scheme 1. **6** may be reduced by silane to the methylene complex, $CH_2{=}CoSiR_3(CO)_3$ (**7**) or its substituted derivative. The chain propagation resulting in the formation of products **1** and **2** proceeds probably by the known [4] 'CO insertion' pathway. This interpretation explains also the observed formation of $HCo(CO)_4$. The mechanism of hydrosilylation of the intermediate acyl- and (α-silyloxyalkyl)cobalt carbonyls was discussed earlier on the basis of kinetic measurements [14]. For similar reactions of complexes containing other transition metals, beautiful examples have been given recently by Cutler and co-workers [15] and Akita *et al.* [16].



Scheme 1.

Compounds **2** can be regarded as homologation products of aliphatic aldehydes [7]:

$$R''CHO + 2HSiR_3 + CO \longrightarrow \mathbf{2} + H_2 \qquad (5)$$

Aldehydes, however, could not be observed in the reaction mixtures although their transformation to **2** would need temperatures >100 °C [7]. Consequently, they are probably not intermediates leading to **2**. Similarly, compounds **1** may not be formed through **4** (see ref. 7) because reaction (2) takes place only at $\sim$200 °C. This latter supposition was proven by an independent experiment starting from **4** at 120 °C.

Experimental

Materials

Solvents were purchased from Reanal (Hungary), dried over sodium wire (toluene, heptane, diethyl ether, dioxane, anisole), calcium hydride (dichloromethane) or potassium hydroxide pellets (pyridine), and distilled. Hydrosilanes, chlorosilanes, aldehydes and tributyl phosphine were purchased from Fluka (Switzerland), and distilled before use. Dicobalt octacarbonyl was prepared by the usual method [17], and recrystallized from dichloromethane and then from heptane. Authentic samples of silylated derivatives of alcohols (**1**) were prepared by modified literature methods starting from hydrosilanes [18] or chlorosilanes [19]. 1,2-Bis(silyloxy)-1-alkenes (**2**) were obtained from aldehydes and hydrosilanes according to the procedure of Murai and co-workers [7, 20].

General techniques

Gas chromatograms were recorded on a Hewlett-Packard model 5830 A chromatograph using an SP 2100 fused silica capillary column. GC-MS analyses were performed on a JMS 01-SG-2 JEOL spectrometer and a Hewlett-Packard 5890 Series II GC-MSD equipment. IR spectra were obtained on a Carl Zeiss Jena IR 75 spectrophotometer using 0.060 mm CaF_2 cuvettes.

Hydrosilylation of carbon monoxide

In a 15 ml teflon coated stainless steel autoclave equipped with manometer and valve were added under argon with cooling $Co_2(CO)_8$ (171 mg, 0.5 mmol), solvent (1.7 ml), hydrosilane (20 mmol), base and cyclohexane (internal standard, 216 μl). The autoclave was purged twice with CO, pressurized to 10 MPa, and shaken for 5 h in a heating mantle thermostated at 120 °C. After cooling the pressure was released and the reaction mixture was analyzed by IR spectroscopy and GC-MS. **1**–**3** and the products formed from the solvents were identified by comparison of their GC-MS data with those of authentic samples.

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