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Alkylcobalt Carbonyls. 9.[1] Alkoxy-, Silyloxy-, and Hydroxy-Substituted Methyl- and Acetylcobalt Carbonyls. Reduction of Formaldehyde to Methanol by Hydridocobalt Tetracarbonyl[†,2]

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(Alkoxymethyl)-, ((silyloxy)methyl)-, and (hydroxymethyl)cobalt and (alkoxyacetyl)-, ((silyloxy)acetyl)-, and (hydroxyacetyl)cobalt tetracarbonyls and phosphine-substituted derivatives were prepared. The interconversions of these compounds by carbonylation/decarbonylation, methylation, and silylation were explored. In situ prepared hydroxymethylcobalt tetracarbonyl reacts with excess $HCo(CO)_4$ to methanol and $Co_2(CO)_8$ under mild conditions.

Introduction

An important goal in C_1 chemistry is the reduction of CO.[5] Homogeneous variants of this reaction are assisted or catalyzed by transition-metal complexes and provide a number of C_1–C_3 organics.[6] The last decade brought a breakthrough in the preparation and characterization of formyl-,[7] hydroxymethyl-,[8] alkoxymethyl-,[9] and other α-oxymethyl[10] transition-metal compounds, frequently proved and even more frequently postulated to be intermediates of CO reduction sequences.

Several transition metals were found to be active in homogeneous (stoichiometric or catalytic) carbon monoxide reduction.[11] A number of these processes, bearing imminent industrial importance, is catalyzed by cobalt carbonyls.[12] However, reports on preparation of those cobalt complexes which are widely accepted as intermediates[13] in these reactions are surprisingly few.[14] This prompts us to report here on results with the preparation and characterization of (hydroxymethyl)- (**1**) and (hydroxyacetyl)cobalt tetracarbonyl (**2**) together with their methyl- (**3** and **4**) and trimethylsilyl ether (**5** and **6**) derivatives.

Experimental Section

All operations were performed by the usual Schlenk technique,[15] using deoxygenated, dry solvents and gases and thermostated reaction vessels with magnetic stirring.

Infrared spectra were recorded by using CaF_2 cuvette on a Specord IR 75 (Carl Zeiss, Jena) spectrometer. ^1H NMR spectra were obtained on a BS-487 spectrometer (80 MHz, Tesla, Brno). Mass spectra were obtained on a JEOL IMS(01) SG-2 spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard HP 5830A type gas chromatograph using SP 2100 fused silica capillary column.

The photochemical experiments were performed in a 100-mL thermostated reaction vessel equipped by an immersed medium-pressure mercury lamp (120 W, Tungsram, Budapest) provided with a quartz cooling mantle.

Starting materials were commercial products with the exception of $Co_2(CO)_8$,[16] $HCo(CO)_4$,[17] $Na[Co(CO)_4]$,[18] $Me_3SiCo(CO)_4$,[19] diazomethane,[20] and methoxyacetyl chloride[21] which were prepared according to known procedures.

Preparation of Complexes. $HOCH_2Co(CO)_4$ (1). To 0.5 mL of a 0.6 M solution of $HCo(CO)_4$[22] in *n*-pentane was added a freshly prepared 2.0-mL solution of monomeric formaldehyde[23] containing ca. 3 mmol of CH_2O in dichloromethane at −78 °C

[†] This paper is dedicated to the 60th birthday of Prof. László Markó (Veszprêm), our friend and master in organometallic chemistry.

(1) For part 8 see ref 4.

(2) Presented at the XXIVth International Conference Coordination Chemistry; Athens, Greece, August 24–29, 1986. Abstracts, p 449.

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under Ar atmosphere. In 20 min the temperature was raised to −40 °C, and the solution was stirred for an additional 30 min at this temperature. The original pale yellow color of the mixture turned lemon yellow. The excess of formaldehyde was removed at 200 Pa and at −78 °C in 15 min. The infrared spectrum of this solution recorded at −60 °C showed the presence of **1** only. IR: ν(OH) 3580 (w); ν(CO) 2100 (w), 2050 (sh), 2021 (br, vs) cm^{-1}. Isolation attempts by crystallization failed. At −20 °C **1** decomposed into $Co_2(CO)_8$,[24] $HCo(CO)_4$,[25] and paraformaldehyde.

$HOCH_2C(O)Co(CO)_4$ (2). This complex was formed from a solution of **1** by the equilibrium reaction with CO. Starting with solutions of **1** in a 1:4 mixture of *n*-pentane and dichloromethane gave at −40 °C and under 5 MPa of CO in 30 min a practically complete conversion into **2**. The infrared spectrum of this solution recorded at −60 °C and at atmospheric pressure of CO showed the following bands: ν(OH) 3575 (w); ν(CO) 2109 (m), 2051 (s), 2028 (vs), 2013 (vs), and 1695 (br, w) cm^{-1}. Isolation of **2** could be achieved by using Et_2O instead at CH_2Cl_2 in the preparation.[26] Thus to 0.5 mL of a 0.6 M solution of $HCo(CO)_4$ in *n*-pentane was added a freshly prepared 4.0 mL solution of ca. 3 mmol of monomeric formaldehyde in Et_2O at −78 °C under atmospheric CO pressure.

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(22) A pale yellow solution was obtained due to the presence of traces of $Co_2(CO)_8$.

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Stirring at −40 °C for 4 h gave a practically complete conversion of $HCo(CO)_4$ into **2**. Addition of 20 mL of cold *n*-pentane to the reaction mixture at −78 °C resulted in the formation of a light yellow voluminous precipitate. Filtration at −78 °C gave 0.14 g of **2** as a yellow powder. IR (Et_2O): ν(OH) 3425 (br, m); ν(CO) 2106 (m), 2045 (s), 2026 (vs), 2007 (vs), 1698 (w) cm^{-1}. ^1H NMR (toluene-d_8): δ 3.30 (br, s, 1 H, O*H*), 3.93 (s, 2 H, CH_2) ppm. Elemental analyses indicate that complex **2** was contaminated by about 15% w/w paraformaldehyde.

$MeOCH_2Co(CO)_4$ (3). To a solution of $Na[Co(CO)_4]$ prepared from 0.34 g of $Co_2(CO)_8$ and 40 g of 1.5% Na[Hg] in 30 mL of Et_2O was added 0.174 mL (1.9 mmol) methoxyacetyl chloride in two equal portions at 0 °C under Ar atmosphere with stirring. In 60 min the precipitation of NaCl was complete. After filtration the solvent was removed from the filtrate under vacuum below 0 °C. **3** (0.21 g) as a dark yellow oil was obtained. IR (*n*-octane): 2098.5 (m), 2033.3 (s), 2015.5 (vs), 2002.5 (vs) cm^{-1}. ^1H NMR (benzene-d_6): δ 3.01 (s, 3 H, CH_3), 4.90 (s, 2 H, CH_2) ppm.

$MeOCH_2C(O)Co(CO)_4$ (4). Repeating the same procedure as for **3** but under atmospheric pressure of CO gave 0.24 g of a yellow oil after the solvent was removed below −20 °C under vacuum. IR (*n*-octane): 2107.5 (m), 2049.5 (s), 2027.0 (vs), 2006.0 (vs), 1700.0 (m) cm^{-1}. ^1H NMR (benzene-d_6): δ 3.01 (s, 3 H, CH_3), 3.65 (s, 2 H, CH_2) ppm.

$Me_3SiOCH_2Co(CO)_4$ (5). Method A. In a quartz reactor for photochemical experiments 683 mg (2.8 mmol) of (trimethylsilyl)cobalt tetracarbonyl was dissolved in 80 mL of toluene. At 15 °C gaseous formaldehyde (generated by relatively mild pyrolysis of paraformaldehyde at 150–160 °C) was led over the irradiated and stirred solution by a slow (10 mL/min) Ar stream for 1.5 h. Then 0.245 mL (3.0 mmol) of pyridine was added in order to precipitate the unreacted $Me_3SiCo(CO)_4$.[28] The resulting slurry was chilled at −78 °C overnight and filtered. The filtrate was concentrated under vacuum at 0 °C and gave 210 mg of **5** (25% yield) as a light brown oil under Ar atmosphere. IR (*n*-heptane) 2100.4 (m), 2032.5 (s), 2018.7 (vs), 2007.9 (vs) cm^{-1}. ^1H NMR (toluene-d_8): δ 0.07 (s, 9 H, SiCH_3), 4.97 (s, 2 H, CH_2).

Method B. To a freshly prepared solution of 0.3 mmol **1** in 2 mL of dichloromethane at −40 °C under CO atmosphere was added 0.158 mL (0.6 mmol) bis(trimethylsilyl)trifluoroacetamide [BSTFA], and the mixture was stirred for 30 min at −30 °C. In another 30 min the reaction mixture was left to warm to room temperature. Concentration of this solution under vacuum resulted in 67 mg of **5** (80% yield) as a yellow-brown oil under argon atmosphere.

$Me_3SiOCH_2C(O)Co(CO)_4$ (6). Neat **5** or its solution in *n*-heptane or toluene absorbs rapidly CO at atmospheric pressure and 25 °C, leading to **6** as a light brown oil or yellow solutions respectively. IR (*n*-heptane): 2106.9 (m), 2044.0 (s), 2027.6 (vs), 2009.8 (vs), 1701 (m) cm^{-1}. ^1H NMR (toluene-d_8): δ 0.03 (s, 9 H, SiCH_3), 4.03 (s, 2 H, CH_2) ppm.

$HOCH_2C(O)Co(CO)_3PPh_3$ (7a). To a freshly prepared stirred solution of 0.3 mmol of **2** in 2 mL of CH_2Cl_2 under CO atmosphere was added 79 mg (0.3 mmol) of triphenylphosphine at −40 °C. The original lemon-yellow color of the solution turned deeper, and an orange precipitate was formed in 30 min. An infrared analysis of this precipitate in acetone after filtration showed $[Co(CO)_4]^-$ as the only cobalt carbonyl species present. The solvent from the filtrate was removed at −20 °C and reduced pressure and gave 17 mg (12% yield) of **7a** as a yellow solid. IR (toluene): ν(OH) 3575 (w), ν(CO) 2048 (w), 1982 (vs), 1960 (vs), 1650 (w, br) cm^{-1}. ^1H NMR (toluene-d_8): δ 4.35 (br s, 1 H, O*H*), 4.41 (s, 2 H, CH_2), 7.0–7.6 (m, 15 H, C_6H_5) ppm.

$HOCH_2C(O)Co(CO)_3PPh_2Cl$ (7b). To a freshly prepared solution of 0.3 mmol of **2** in 5 mL of Et_2O under CO atmosphere was added 66 mg (0.3 mmol) of PPh_2Cl at −40 °C, and the solution was stirred for 4 h. A slow formation of a crystalline precipitate was complete by storing subsequently at −78 °C overnight. This product was filtered, washed with cold *n*-pentane, and dried at −40 °C under vacuum. **7b** (83 mg, 65% yield) as a yellow thermally unstable product resulted which decomposes at −20 °C. IR (toluene): ν(OH) 3420 (m, br), ν(CO) 2050 (w), 1984 (vs), 1963 (vs), 1670 (br, w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.50 (br s, 1 H, O*H*), 4.81 (s, 2 H, CH_2), 7.4–7.9 (m, 10 H, C_6H_5) ppm. Anal. Calcd for $C_{17}H_{13}CoClO_5P$: Co, 13.89; P, 7.31. Found: Co, 13.0; P, 7.8.

$MeOCH_2C(O)Co(CO)_3PPh_3$ (8). Method A. To a freshly prepared solution of 1 mmol of **4** in 30 mL of Et_2O was added 288 mg (1.1 mmol) of PPh_3 at 25 °C, and the solution was stirred for 1 h. In the early stage of the reaction some gas evolution occurred and the color in the light yellow solution turned brown. The reaction mixture was cooled to 0 °C and filtered. The filtrate was concentrated at reduced pressure, and the resulting brown oily residue was crystallized from 20 mL of 1:1 mixture of Et_2O/*n*-pentane at −78 °C. Brown crystals of **8** were formed overnight; 85 mg (19% yield). IR (*n*-hexane); 2050.5 (w), 1984.5 (vs), 1961.5 (vs), 1685.0 (w) cm^{-1}. ^1H NMR (C_6D_6): δ 3.25 (s, 3 H, CH_3), 4.23 (br s, 2 H, CH_2), 6.9–7.7 (m, 15 H, C_6H_5) ppm.

Method B. To a freshly prepared solution of 0.3 mmol of **2** in 4 mL of Et_2O was added 157 mg (0.6 mmol) of PPh_3 at −78 °C under CO atmosphere. The reaction mixture was stirred for 10 min, and 0.35 mL of a 1 M solution of diazomethane in Et_2O was added. A reddish brown precipitate appeared immediately. Maintaining continuous stirring the reaction mixture was then warmed gradually in 1 h at 25 °C and filtered. The filtrate was worked up as in method A leading to 26 mg of **8** (20% yield).

$MeOCH_2Co(CO)_3PPh_3$ (9). A solution of 250 mg (0.5 mmol) of **8** in 15 mL of *n*-heptane was stirred under Ar atmosphere at 60 °C for 1 h. The reaction mixture was then filtered at room temperature and the solvent evaporated at reduced pressure. The residue was extracted by *n*-pentane. The extract was chilled to −78 °C and gave 203 mg of **9** as a light yellow solid (90% yield). IR (*n*-hexane): 2036.0 (w), 1967.5 (vs), 1954.5 (s) cm^{-1}. ^1H NMR (benzene-d_6): δ 3.35 (s, 3 H, CH_3), 5.42 (d, J = 3 Hz, 2 H, CH_2), 6.9–7.7 (m, 15 H, C_6H_5) ppm. Anal. Calcd for $C_{23}H_{20}CoO_4P$: Co, 13.08; P, 6.88. Found: Co, 12.6; P, 7.0.

$Me_3SiOCH_2C(O)Co(CO)_3PPh_3$ (10). To a freshly prepared solution of 0.7 mmol of **6** in 10 mL of *n*-pentane under 0.1 MPa CO was added 367 mg (1.4 mmol) of PPh_3 at 25 °C, and the mixture was stirred for 30 min. Filtration and crystallization at −78 °C gave yellow crystals, which were recrystallized from toluene/pentane at 0 °C leading to 105 mg of **10** (23% yield). IR (*n*-heptane): 2051.2 (m), 1986.0 (vs), 1964.0 (vs), 1688 (m), 1672 (m) cm^{-1}. ^1H NMR (C_6D_6): δ 0.03 (s, 9 H, SiCH_3), 4.35 (s, 2 H, CH_2), 6.6–7.4 (m, 15 H, C_6H_5) ppm. Anal. Calcd for $C_{26}H_{26}CoO_5PSi$: Co, 11.01; P, 5.78. Found: Co, 10.9; P, 6.0. Mass spectrum (*m/e*, 70 eV): 452 (8%, $Me_3SiOCH_2C(O)CoPPh_3^+$ or $Me_3SiOCH_2Co(CO)PPh_3^+$), 424 (12%, $Me_3SiOCH_2CoPPh_3^+$), 321 (33%, $CoPPh_3^+$), 183 (52%, $PC_{12}H_8^+$), 103 (100%, $Me_3SiOCH_2^+$).

Reactions with $HCo(CO)_4$. (a) A solution of 50 mg (0.2 mmol) of **2** in 10 mL of *n*-hexane did not react below −20 °C under CO atmosphere with 2 mL of a 0.15 M $HCo(CO)_4$ solution in *n*-pentane. At higher temperature, however, the formation of $Co_2(CO)_8$ could be detected by IR spectroscopy,[24] and the formation of paraformaldehyde precipitate could be observed. **(b)** A 2-mL portion of a 0.15 M $HCo(CO)_4$ solution in CH_2Cl_2 (or in CD_2Cl_2) was placed in a 10-mL three-necked flask provided with a gas-inlet tube, a septum, and a gas outlet. Gaseous formaldehyde was evolved by depolymerization of paraformaldehyde at 120–130 °C in a slow (<5 mL/min) CO stream which was then chilled down to 0 °C and was introduced into the reaction flask at 0 °C. The color of the solution turned brown, and the formation of $Co_2(CO)_8$ could be detected by IR spectroscopy. Simultaneously the formation of MeOH (broad singlets at 3.38 and 4.76 ppm) was observed by ^1H NMR spectroscopy. The spectrum showed also weak, broad signals at 4.6–5.2 ppm, the intensity of which increased parallel with that of the signals of MeOH. (These latter signals can be assigned to oligomeric formaldehyde units in $(CH_2O)_n$, $HO(CH_2O)_nCH_2Co(CO)_4$ and $HO(CH_2O)_nCH_2C(O)Co(CO)_4$). $HCo(CO)_4$ was consumed in 30 min. Subsequent quantitative GLC analysis showed the presence of MeOH in 80% yield, but no methyl formate, ethylene glycol, or glycolaldehyde could be detected.

Reaction of 4 with $NaOCH_3$. To a solution of 1.9 mmol of **4** in 30 mL of Et_2O was added 130 mg (2.4 mmol) sodium methoxide in 1.8 mL of methanol under CO atmosphere at 25 °C with stirring. Infrared spectra and gas chromatography of the

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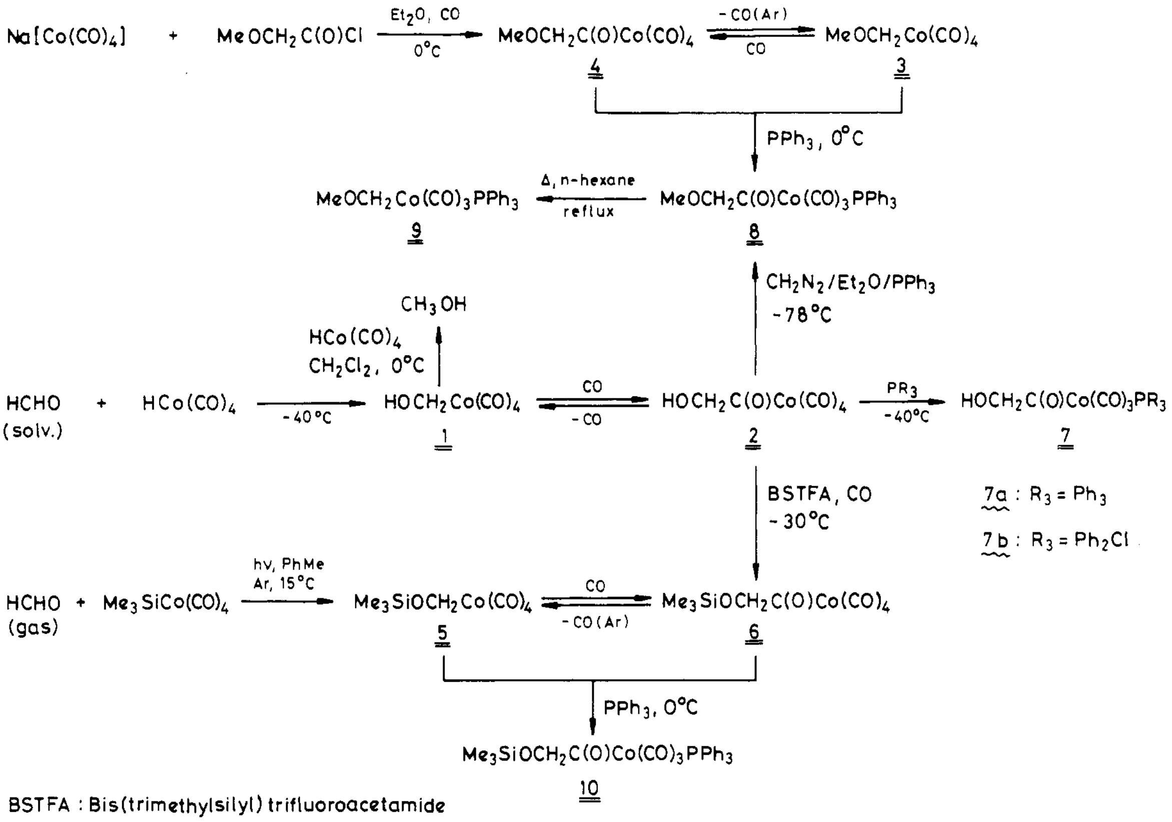
[28] The insertion of an aldehyde into a M–H bond is very rarely observed, see ref 8e,d,r,s and additional results with Th (where, however, the oxophilic character of the metal dominates): (a) Maatta, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *103*, 3576. (b) Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723.

Scheme I



BSTFA : Bis(trimethylsilyl) trifluoroacetamide

reaction mixture revealed a complete conversion of 4 in 1 h into $Na[Co(CO)_4]$ and methyl methoxyacetate as the only organic product.

Results and Discussion

The preparative results obtained in course of the present work are shown in Scheme I.

Compound 1 was obtained by the reaction[28] of $HCo(CO)_4$ with H_2CO in CH_2Cl_2 solution at −40 °C. 1 could be carbonylated[29,30] to 2 under 5 MPa CO pressure. The hydroxyacetyl complex 2 was further characterized by reactions.

Compound 2 reacts with diazomethane and PPh_3 to 8, which can smoothly (and reversibly) be decarbonylated to 9.[31] Complex 3 or 4 was obtained from methoxyacetyl chloride and $Na[Co(CO)_4]$ under Ar or CO atmosphere, respectively. Both 3 and 4 gave complex 8 by their reaction with PPh_3.

The hydroxyacetyl complex 2 was also silylated[32] to 6. The product 6 could be decarbonylated[33] to 5. The (silyloxy)methyl complex 5 was obtained also by an independent photochemical reaction from formaldehyde and $Me_3SiCo(CO)_4$.[34] Complexes 5 or 6 when reacted with PPh_3 yielded exclusively 10.

Compound 1 decomposes[35] while 2 provides CO substitution product 7 when reacted with PPh_2X (X = Ph, Cl).

Compounds **7b**, 8, 9, and 10 were solids and could be isolated in analytically pure form (almost pure samples of 2 were contaminated with paraformaldehyde). Crystals suitable for X-ray study could not be obtained. These compounds were further characterized by spectra. Compounds 1, 3, 4, 5, 6 and **7a** were oils. These complexes were characterized by clean spectra obtained from their solutions.

The infrared spectra of the tetracarbonyls $RCo(CO)_4$ and $RC(O)Co(CO)_4$ can be satisfactorily assigned to trigonal-bipyramidal (with axial R) structures on the basis of almost identical ν(CO) patterns of several analogous complexes,[4,36] based even on the X-ray structural study of a benzylcobalt tetracarbonyl derivative[36e] and a C–O force field analysis of the $XCo(CO)_4$ type.[37]

The ν(CO) spectra of the tricarbonyls $RCo(CO)_3(PR'_3)$ and $RC(O)Co(CO)_3(PR'_3)$ were closely similar to those of analogous compounds with R and PR'_3 in trans positions and the three CO groups in the equatorial plane as dem-

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(29) Carbonylation/decarbonylation reactions of hydroxymethyl and -acetyl derivatives of transition metals were observed in a few cases. [Mn]: ref 8d,e,f (0.1–3 MPa) strongly depending on non-CO ligands), [Fe]: ref 8k (≈0.1 MPa) but a (hydroxymethyl)ruthenium complex resisted to carbonylation up to 27 MPa CO pressure.[8j]

(30) The assistance to carbonylation of H bridging between the OH and the acyl CO group was assumed at Mn[8f] and Rh.[8r] It seems to play a more restricted role at Co, since 3 and 5 could be carbonylated at milder conditions than 1.

(31) Examples of carbonylation/decarbonylation studies of alkoxymethyl transition-metal complexes include Mn, Fe, and Mo.[9a,c] Mild conditions can be used. Probably "in situ" carbonylation happens at the reported preparation of 8.[14a]

(32) Silylation of hydroxymethyl complexes has some precedent with Ru[8j,q] and Ir.[8z] Desilylation of the (silyloxy)methyl derivatives is well documented for Mn,[8d,e,g] Fe,[8k] Re,[8c,d,g] and Ru;[8j,q] this latter reaction could not be realized, however, with Co.

(33) Carbonylation/decarbonylation of (siloxy)methyl complexes is well documented at Mn[8f,h,10d,e] (1–13 MPa) but could not be realized at Fe and Ru up to 27 MPa CO pressure.[8j]

(34) This important reaction has precedent only at Mn in the very clean work of Gladysz.[8e,10e,g]

(35) It has been observed that hydroxymethyl complexes easily deinsert H_2CO, Mn,[8b] Rh,[8r,s] and Ir.[8z] The macroscopic reversibility of the H_2CO + MH reaction has been even demonstrated.[8s] An interesting philosophy of avoiding the deinsertion has been worked out on the basis of comparison with the reactivity of organic hemiacetals.[8g]

(36) (a) Markó, L.; Bor, G.; Almásy, G.; Szabó, P. *Brennst.-Chem.* **1963**, *44*, 184. (b) Galamb, V.; Pályi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1981**, *209*, 183. (c) Galamb, V.; Pályi, G. *Acta Chim.* (*Budapest*) **1982**, *111*, 141. (d) Tasi, M.; Pályi, G. *Organometallics* **1985**, *4*, 1523. (e) Galamb, V.; Pályi, G.; Ungváry, F.; Markó, L.; Boese, R.; Schmid, G. *J. Am. Chem. Soc.* **1986**, *108*, 3344.

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onstrated by X-ray[4,36b,e,38b] and spectroscopic[4,38b] studies. This picture was complemented by the ν(OH) bands of **1**, **2**, **7a** and **7b** as well as by the ^{1}H NMR spectra showing close similarities to the ^{1}H NMR behavior of other $XCH_2[C(O)]_nCo(CO)_3L$ (X = Ph, substituted COOR, Cl; L = CO, PR_3; n = 0, 1) complexes.[4,36,38]

The preparative results described here apparently provide a starting point for mechanistic studies. As an example it should be pointed out that the regiochemistry of the formation of **1** from H_2CO and $HCo(CO)_4$ (i.e. the absence of regioisomer $MeOCo(CO)_4$ or its carbonylation product $MeOC(O)Co(CO)_4$[36d,39]) hints at a nonradical pathway of the addition of $HCo(CO)_4$ to H_2CO according to the argumentation of Fahey.[13b]

The carbonylation/decarbonylation equilibria described in this paper find only a few precedents in the case of other metals.[29–33] The ease of attaining these equilibria (realized with other metals sometimes only by sophisticated and ingenious approaches[40]) point at one of the possible reasons why just cobalt is playing such a pivotal role in carbonylation chemistry.

Two "synthetic" aspects of this chemistry were also tested.

Complex **2** did not react with $HCo(CO)_4$ at −20 °C. A direct reaction of gaseous formaldehyde with excess of $HCo(CO)_4$, however, resulted in the high-yield stoichiometric (≈80%) formation of methanol at 0 °C within 1 h. This remarkably mild reduction of formaldehyde to MeOH with a transition-metal hydride finds only a few precedents.[41]

The connection with alkoxycarbonylation[42] was tested by reacting **4** with the methoxide ion under CO. This reaction yielded 95% methyl methoxyacetate at room temperature and 0.1 MPa CO pressure.

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Registry No. **1**, 119146-93-9; **2**, 119146-94-0; **3**, 119146-95-1; **4**, 93063-71-9; **5**, 119146-96-2; **6**, 119146-97-3; **7a**, 119146-98-4; **7b**, 119147-01-2; **8**, 101546-13-8; **9**, 119146-99-5; **10**, 119147-00-1; **11**, 64519-62-6; BSTFA, 21149-38-2; HCHO, 50-00-0; $Na[CO(CO)_4]$, 14878-28-5; $MeOCH_2C(O)Cl$, 38870-89-2; $Me_3SiCo(CO)_4$, 52730-61-7; MeOH, 67-56-1; $NaOCH_3$, 124-41-4; $MeOCH_2C(O)OMe$, 6290-49-9.

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(40) See, e.g., ref 8d–g.

(41) Basis of comparison: ref 6a,b,d–g,i,p, 8r, 10i,h, 11b,c 13b–d, and (a) Herberich, G. E.; Okuda, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 402. (b) Knifton, J. F.; Grigsby, R. A.; Lin, J. J. *Organometallics* **1984**, *3*, 62. (c) Green, M. L. H.; Parkin, G.; Moynihan, K.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1540. (d) Klier, K. *Adv. Catal.* **1982**, *31*, 243. (e) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959. (f) Spencer, A. *J. Organomet. Chem.* **1980**, *194*, 113. (g) Kung, H. *Catal. Rev.—Sci. Eng.* **1980**, *22*, 235. (h) Ichikawa, M. *J. Chem. Soc., Chem. Commun.* **1978**, 566. (i) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544. (j) Shoer, L. I.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 5831. (k) Gray, D. R.; Brubaker, C. H. *Inorg. Chem.* **1971**, *10*, 2143.

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