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THE SYNTHESIS AND REACTIONS OF METHYLCHLOROSILYLCOBALT TETRACARBONYLS

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Summary

The new substances $MeSiCl_2Co(CO)_4$ and $Me_2SiClCo(CO)_4$ have been synthesized from $MeSiCl_2H$ and Me_2SiClH and dicobalt octacarbonyl. The thermal stability of these compounds and of $Me_3SiCo(CO)_4$ and $Cl_3SiCo(CO)_4$ and their interactions with HCl, HBr, $HgCl_2$, $HgBr_2$ and H_2O were investigated. All were found to react with $HgCl_2$, $HgBr_2$, and water at 90° and low pressures. Only $Me_3SiCo(CO)_4$ was found to be cleaved by HCl and HBr near atmospheric pressure. The remaining compounds underwent Si—Co cleavage with HCl and HBr at 90° and 4000 atm.

Introduction

The chemistry of the silicon—transition metal linkage has been investigated by several groups and summarized in recent review articles [1,2]. Several substances having the general formula $R_3SiCo(CO)_4$ have been reported since the first silyl—cobalt linkages were reported by Aylett and Campbell [3] and Chalk and Harrod [4]. The present study was aimed at examining substituent effects in cleavage reactions of the Si—Co bond for the series $Cl_3SiCo(CO)_4$ [4,5], $MeSiCl_2Co(CO)_4$, $Me_2SiClCo(CO)_4$ and $Me_3SiCo(CO)_4$ [6]. Experiments were carried out at a temperature at which the compounds were thermally stable to minimize extraneous reactions. When an interaction was not observed at low pressures under this restraint the system was then examined at pressures up to 4000 atm [7,8].

Results and discussion

The substances $Me_2SiClCo(CO)_4$ and $MeSiCl_2Co(CO)_4$ were synthesized from Me_2SiClH or $MeSiCl_2H$ and dicobalt octacarbonyl at room temperature in the absence of a solvent. Both compounds readily form large (1 mm) transparent golden crystals when sublimed at room temperature at a pressure of

TABLE 1

MONOISOTOPIC FRAGMENTATION PATTERN OF $MeSiCl_2Co(CO)_4$

m/e	Intensity	Ion	m/e	Intensity	Ion
284	0.6	$CH_3SiCl_2Co(CO)_4^+$	115	22.5	$SiCoCO^+$, $Co(CO)_2^+$
269	2.1	$SiCl_2Co(CO)_4^+$	102	1.6	CH_3SiCo
256	30.2	$CH_3SiCl_2Co(CO)_3^+$	101	7.9	CH_2SiCo^+
249	2.3	$CH_3SiClCo(CO)_4^+$	100	6.4	$CHSiCo^+$
241	2.5	$SiCl_2Co(CO)_3^+$	99	3.5	$CSiCo^+$
228	36.5	$CH_3SiCl_2Co(CO)_2^+$	94	5.5	$ClCo^+$
221	2.5	$CH_3SiClCo(CO)_3^+$	87	43.4	$SiCo^+$, $CoCO^+$
213	1.1	$SiCl_2Co(CO)_2^+$	71	3.1	CoC^+
200	100	$CH_3SiCl_2CoCO^+$	63	22.8	$SiCl^+$
193	1.4	$CH_3SiClCo(CO)_2^+$	57.5	1.4	$[Co(CO)_2]^{2+}$
185	30	$SiCl_2CoCO^+$	59	52.4	Co^+
172	74.6	$CH_3SiCl_2Co^+$	45	3.4	$H_2SiCH_3^+$
165	2.6	$CH_3SiClCoCO^+$	44	7.2	$HSiCH_3$
157	14.1	$SiCl_2Co^+$	43.5	1.2	$[CoCO]^{2+}$
150	1.1	$SiClCoCO^+$, $ClCo(CO)_2^+$	43	71.4	$SiCH_3^+$
143	2.3	$Co(CO)_3^+$	29	1.1	SiH^+
137	9.0	$CH_3SiClCo^+$	28	23.8	Si^+, CO^+
122	9.4	$SiClCo^+$, $ClCoCO^+$	15	0.9	CH_3^+

TABLE 2

MONOISOTOPIC FRAGMENTATION PATTERN OF $Me_2SiClCo(CO)_4$

m/e	Intensity	Ion	m/e	Intensity	Ion
264	0.6	$(CH_3)_2SiClCo(CO)_4^+$	103	1.6	CH_3SiHCo^+
249	1.4	$CH_3SiClCo(CO)_4^+$	102	5.8	CH_3SiCo^+
236	28.0	$(CH_3)_2SiClCo(CO)_3^+$	101	21.7	CH_2SiCo^+
229	2.3	$(CH_3)_2SiCo(CO)_4^+$	100	11.8	$CHSiCo^+$
221	1.7	$CH_3SiClCo(CO)_3^+$	99	4.3	$CSiCo^+$
208	36.2	$(CH_3)_2SiClCo(CO)_2^+$	94	58.9	$ClCo^+$
201	2.6	$(CH_3)_2SiCo(CO)_3^+$	89	2.6	SiH_2Co^+
193	16.6	$CH_3SiClCo(CO)_2^+$	88	3.5	$SiHCo^+$
180	83.1	$(CH_3)_2SiClCoCO^+$	87	52.5	$CoCO^+$, $SiCo^+$
173	1.8	$(CH_3)_2SiCo(CO)_2^+$	71.5	0.3	$[Co(CO)_3]^{2+}$
165	1.8	$CH_3SiClCoCO^+$	71	2.4	CoC^+
152	100	$(CH_3)_2SiClCo^+$	63	12.6	$SiCl^+$
145	1.4	$(CH_3)_2SiCoCO^+$	59	45.4	Co^+
143	1.4	$Co(CO)_3^+$, $SiCo(CO)_2^+$	57.5	0.9	$[Co(CO)_2]^{2+}$
138	2.8	$CH_3SiHClCo^+$	45	1.7	$H_2SiCH_3^+$
137	21.6	$CH_3SiClCo^+$	44	2.5	$HSiCH_3^+$
123	10.0	$HSiClCo^+$	43.5	0.5	$CoCO^{2+}$
122	12.2	$SiClCo^+$	43	25.4	$SiCH_3^+$
117	5.3	$(CH_3)_2SiCo^+$	29	3.2	SiH^+
116	1.5	$HSiCoCO^+$	28	48.9	Si^+, CO^+
115	23.3	$Co(CO)_2^+$, $SiCoCO^+$	15	0.9	CH_3^+

1 mmHg. When they were heated in a sealed tube at 90° for 6 h, only about 5% of the original material was not recovered in each case, which is comparable to the thermal stability of freshly sublimed $Cl_3SiCo(CO)_4$ as determined under the same identical conditions in this laboratory. Trimethylsilylcobalt tetracarbonyl at the same conditions underwent 40% decomposition to give $(Me_3Si)_2O$ as the volatile product of decomposition. A more detailed study [9] of this compound has shown that $Me_3SiOCCo_3(CO)_9$ and $(Me_3SiOC)_4Co_2(CO)_4$ are the major nonvolatile products when it is heated at 105° for 50 h.

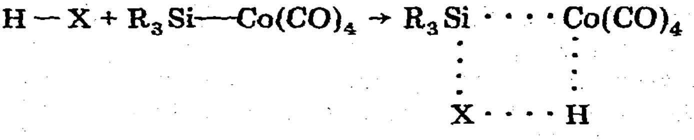
The reactivity or lack of reactivity of the silicon—transition metal linkage with anhydrous hydrogen halides has been noted previously [1]. The results of this study demonstrate that the properties of compounds often cannot be predicted from the behavior of a closely related compound. For example, previous reports have shown that the Si—Co linkage in $H_3SiCo(CO)_4$ was cleaved by HCl at 20° [10].

All of the substances (Me_3Si-, Me_2SiCl-, $MeSiCl_2$- and Cl_3Si-$Co(CO)_4$) in this study were combined with HCl and HBr at 90°/4 atm. At these conditions the Si—Co bond in $Me_3SiCo(CO)_4$ was cleaved and Me_3SiCl or Me_3SiBr are formed; however, no cleavage was observed for the other compounds. When the pressure was increased to 4000 atm at 90° the Si—Co linkage of the remaining compounds was readily cleaved by both HBr and HCl with the halogen substituted substance being recovered, e.g.,

$$Me_2SiClCo(CO)_4 + HBr \rightarrow Me_2SiClBr + HCo(CO)_4$$

The $HCo(CO)_4$ was not recovered; however, this was not unexpected since in a previous study [11] and in this, pure samples of $HCo(CO)_4$ were observed to be highly unstable above 35°. Experiments were carried out at pressures in the range 100 to 4000 atm and the reactions were first detectable by mass spectroscopy at 1500 atm. However, the yields increased rapidly with the pressure increase, with the best results being observed at the limits of the apparatus (4000 atm).

The effect of pressure on the reaction between anhydrous HCl or HBr and the silicon—cobalt linkage in $Cl_3SiCo(CO)_4$, $MeSiCl_2Co(CO)_4$ and $Me_2SiClCo(CO)_4$ was of importance since it provided a new kinetic pathway for the cleavage reaction, since the expected change in free energy for the reaction (or equilibrium constant) at 4000 atm would not be expected to be greater than 2 - 3 kcal [12]. The improved rate could simply arise because of the great increase in concentration of the gaseous reactant, which approaches the density of common organic solvents or to more subtle factors such as the formation of an activated complex that has a smaller volume than the reactants. Such an intermediate could possibly be a four-centered species, viz.,



$$H-X + R_3Si—Co(CO)_4 \rightarrow \begin{array}{ccc} R_3Si & \cdots & Co(CO)_4 \\ \vdots & & \vdots \\ X & \cdots & H \end{array}$$

as has been proposed for other silicon exchange reactions [13,14].

The substances Me_xSiCl_{4-x} ($x = 0 - 3$) were combined with HBr at

90°/4000 atm to confirm that the exchange reaction was with the silicon—transition metal bond and not with small amounts of methylchlorosilane that may form from thermal decomposition. In each case no halogen exchange was observed.

The reactions with water demonstrate that both the Si—Cl and the silicon—transition metal linkages are cleaved. The exact mechanism of the reaction has not been determined. In the course of this study substances resulting from the initial hydrolysis of the Si—Cl bond, viz.,

$$2\ Me_2SiClCo(CO)_4 + H_2O \rightarrow [Me_2SiCo(CO)_4]_2O + 2\ HCl\ ,$$

were sought; however, none were isolated.

The reactions with mercuric chloride and mercuric bromide result in cleavage of the silicon—transition metal linkage, providing a good synthetic procedure for $MeSiCl_2Br$ [15,16] and $Me_2SiClBr$ [16]. All of the substances investigated underwent this exchange.

The behavior of $Me_3SiCo(CO)_4$ with respect to the selected reagents employed in this study was found to be influenced by the competing 90° thermal decomposition reaction. When this compound was combined with $HgCl_2$ or $HgBr_2$ the major silicon containing product was $(Me_3Si)_2O$, which presumably formed from thermal decomposition. In addition small amounts of Me_3SiCl or Me_3SiBr were also recovered. However, when $Me_3SiCo(CO)_4$ was combined with anhydrous HCl or HBr only trace amounts of $(Me_3Si)_2O$ were detected by infrared spectroscopy and high yields of Me_3SiCl or Me_3SiBr were obtained.

Attempts were made to insert carbon monoxide into the Si—Co linkage in each compound under investigation; however, no carbonylated product was isolated even after increasing the CO pressure to 4000 atm.

The proton chemical shift for the methyl grouping in the compounds $Me_xSiCl_{3-x}Co(CO)_4$ $(x = 1 - 3)$ was found to move downfield as methyl groups were replaced by chlorine atoms (all values are in ppm upfield from C_6H_{12} used as standard and solvent: $x = 1$, 0.18; $x = 2$, 0.50; $x = 3$, 0.83). This trend has also been reported for the series Me_xSiCl_{4-x} $(x = 1 - 4)$ [18] and has been assigned to an inductive effect of the chloro groups. The gas phase infrared spectra for the new compounds exhibited the expected four bands in the carbonyl stretching region [19] as well as the characteristic methyl deformation mode near 1255 cm^{-1} and SiCl modes.

The mass spectra of these substances exhibited parent peaks in addition to fragmentation patterns dominated by the consecutive eliminations of the carbonyl groups without destroying the $SiMe_xCl_y$ grouping. In earlier communications mass spectral evidence for the direct interaction between silicon and the equatorial carbonyl groups was provided by an examination of the ratio $Co(CO)_x^+/R_3SiCo(CO)_{x-1}^+$ for the corresponding ion currents [20,21]. If it is assumed [20,21] that the observed mass spectral patterns arise from an initial ionization of a species which then fragments, the ratios show that as long as there are two carbonyl groups attached to the cobalt it is easier to break the Co—CO linkage than the Si—Co linkage.

Similar calculations for $MeSiCl_2Co(CO)_4$ and $Me_2SiClCo(CO)_4$ are compared with the substances investigated in both this and the previous studies in

TABLE 3

RATIOS OF $Co(CO)_x^+/R_3SiCo(CO)_{x-1}^+$ ION CURRENTS

Compound	$Me_3SiCo(CO)_4$[a]	$Me_2SiClCo(CO)_4$	$MeSiCl_2Co(CO)_4$	$Cl_3SiCo(CO)_4$[a]
$Co(CO)_4^+/RCo(CO)_3^+$	0	0	0	0
$Co(CO)_3^+/RCo(CO)_2^+$	0	0.04	0.07	0
$Co(CO)_2^+/RCo(CO)^+$	2.4	0.28	0.22	0.03
$Co(CO)^+/RCo^+$	2.1	2.4	0.58	0.85

[a] Calculated from data in Ref. 21.

Table 3. The data indicate that these new compounds also exhibit the property of not breaking their Si—Co linkage until after at least one carbonyl grouping had been removed and that most of the bond breaking takes place after two and three carbonyls are ejected [20,21].

TABLE 4

MONISOTOPIC MASS SPECTRA

Only peaks having an intensity greater than 2% are reported

m/e	$Me_2SiClBr$	$MeSiCl_2Br$	Ion
192		3.0	$H_3CSiCl_2Br^+$
177		12.6	$SiCl_2Br^+$
172	8.9		$(H_3C)_2SiClBr^+$
157	41.1		$H_3CSiClBr^+$
137	3.3		$(H_3C)_2SiBr^+$
113		71.4	$H_3CSiCl_2^+$
112		3.8	H_2CSiCl_2
107	7.7	3.6	$SiBr^+$
98		9.5	H_3CSiCl^+
93	100.0		$(H_3C)_2SiCl^+$
80		4.0	HBr^+
79		11.1	Br^+
63	75.6	100.0	$SiCl^+$
43	15.6	30.9	H_3CSi^+
42	11.1	44.8	H_2CSi^+
41	6.6	42.9	$HCSi^+$
40		14.3	CSi^+
36	28.9	83.8	HCl^+
35	3.3	44.8	Cl^+
28	82.3	72.0	Si^+
15		10.3	H_3C^+

Experimental

All work was carried out in a borosilicate glass vacuum system constructed with Teflon stopcocks (Fisher & Porter Co., Warminster, Pa.). High pressures were generated using a gas pressure booster (High Pressure Equipment Co., Erie, Pa.). The samples were usually contained in sealed ampules made from 3 mm diameter thin-walled gold tubing which were placed in a high pressure micro reactor (Autoclave Engineers, Erie, Pa.). Nitrogen gas was used to generate the desired pressure. At the end of a reaction period the micro reactor was cooled to −196° before releasing the pressure. Then the frozen ampule was placed in an opening device attached to the vacuum line. After warming to room temperature, water, CO_2, and other condensable materials on the surface of the gold tubing were pumped away and then the ampule was opened. The substances which volatilized were then transferred directly into the vacuum line.

All reagents were commercially available except $Cl_3SiCo(CO)_4$ and $Me_3SiCo(CO)_4$ which were synthesized according to literature procedures [22].

Infrared absorption spectra were recorded on a Beckman Model IR-10 double beam grating spectrophotometer. Volatile materials were confined in a 10 cm cell fitted with KBr windows sealed with rubber O-rings at reduced pressure. Mass spectra were taken at 70 eV on a Hitachi - Perkin - Elmer RMU-6E mass spectrometer at 150°. For each reaction the products were identified by two or more techniques including vapor pressure, molecular weight, infrared spectral or mass spectral measurements. All transfers of non-volatile reagents were carried out in a nitrogen filled glove bag.

Synthesis of $MeSiCl_2Co(CO)_4$

Methyldichlorosilane (1.403 g, 10.02 mmol) was condensed into a 25 ml glass pressure vessel in which had been placed (in a nitrogen filled glove bag) $Co_2(CO)_8$ (2.38 g, 6.98 mmol). The vessel was closed and allowed to warm to room temperature. After 28 h the reactor was cooled to −23° (CCl_4 slush) and the excess methyldichlorosilane condensed out of the vessel into the vacuum system and trapped at −196°. The solid in the vessel was sublimed at room temperature (0.1 mmHg) on to a cold finger cooled to −78° (dry-ice/acetone mixture). The sublimate consisted of pure $MeSiCl_2Co(CO)_4$ (1.35 g, 3.98 mmol; m.p. 40.0 - 41.5°; found: C, 20.90; H, 1.16; Cl, 24.62. $C_5H_3Cl_2CoO_4Si$ calcd.: C, 20.07; H, 1.06; Cl, 24.88%). Infrared spectrum: (gaseous, 1 mmHg); 2990 w, 2100 m, 2050 m, 2025 vs, 2015 vs, 1405 w, 1260 s, 795 vs, 735 s, 555 vs, 510 vs, 360 m cm^{-1}.

Synthesis of $Me_2SiClCo(CO)_4$

The same procedure was used to react dimethylchlorosilane (2.033 g, 17.83 mmol) and $Co_2(CO)_8$ (2.181 g, 6.387 mmol). The solid product was sublimed at room temperature (0.1 mmHg) on to a cold finger cooled to −196° to give $Me_2SiClCo(CO)_4$ (1.130 g, 4.267 mmol; m.p. 45.5-46.4°; found: C, 27.29; H, 2.43; Cl, 13.47; $C_6H_6ClCoO_4Si$ calcd.: C, 27.24; H, 2.29; Cl, 13.40%). Infrared spectrum: (gaseous, 1 mmHg) 2960 w, 2080 s, 2020 vs, 2005 vs, 1990 vs, 1400 w, 1250 m, 1075 w, 1015 w, 825 m, 795 s, 765 w, 685 s, 650 w, 530 vs, 500 w, 480 w, 380 w, cm^{-1}.

Reactions with $HgCl_2$

Mercuric chloride (1.060 g, 3.905 mmol) and $MeSiCl_2Co(CO)_4$ (0.444 g, 1.56 mmol) were placed in a 25 ml glass pressure reactor in a nitrogen filled glove bag. The vessel was then evacuated and heated at 90° for one h. The vessel was cooled to room temperature and the volatile material collected in a trap cooled to −196°. The volatile material consisted of a small amount of $MeSiCl_2Co(CO)_4$ and $MeSiCl_3$ (197 mg, 1.32 mmol).

Mercuric chloride (499.4 mg, 1.839 mmol) and $Me_2SiClCo(CO)_4$ (461.4 mg, 1.744 mmol) were heated at 60° for 90 minutes in a similar manner. The volatile products were passed through traps cooled to −46° and −130°, and then collected in a −196° trap. The latter contained a trace of HCl, the −46° trap contained unreacted $Me_2SiClCo(CO)_4$ and the −130° trap contained Me_2SiCl_2 (123.3 mg, 0.9514 mmol).

Similar experiments were carried out with $Cl_3SiCo(CO)_4$ and $Me_3SiCo(CO)_4$. In each case the corresponding chloro derivative was formed; however, with $Me_3SiCo(CO)_4$ the yield was very low with a large amount of $(Me_3Si)_2O$ being recovered.

Reactions with $HgBr_2$

Mercuric bromide (0.5448 g, 1.512 mmol) and $MeSiCl_2Co(CO)_4$ (0.3530 g, 1.239 mmol) were heated at 90° for two h using the above procedure. The vessel was cooled to room temperature and the material which volatilized was passed through a trap cooled to −46° into a trap cooled to −196°. The former trap contained $MeSiCl_2Co(CO)_4$ (181.2 mg, 0.934 mmol). The trap at −196 ° contained $MeSiCl_2Br$ (147.9 mg, 0.7625 mmol; identified by mass spectrum and confirmed by infrared spectrum). Infrared Spectrum: (gaseous; 2 mmHg) 3000 w, 1260 m, 790 vs, 640 s, 560 vs, 515 vs, and 365 w, cm^{-1}.

Mercuric bromide (533.1 mg, 1.479 mmol) and $Me_2SiClCo(CO)_4$ (205.1 mg, 0.775 mmol), when allowed to react under similar conditions gave volatile products which were passed through a trap cooled to −64° (chloroform slush) and collected in a trap cooled to −196°. The latter trap contained $Me_2SiClCo(CO)_4$ (111.6 mg, 0.4218 mmol). The former trap contained $Me_2SiClBr$ (53.4 mg, 0.308 mmol; identified by mass spectrum and confirmed by infrared spectrum). IR: (gaseous, 2 mmHg); 2970 m, 1255 s, 1055 s, 1020 s, 790 vs, 760 m, 500 s, 450 w, 375 w, cm^{-1}.

Similar experiments were carried out with $Cl_3SiCo(CO)_4$ and $Me_3SiCo(CO)_4$. In each case the corresponding bromo derivative was formed; however, with $Me_3SiCo(CO)_4$ the yield was very low with a large amount of $(Me_3Si)_2O$ being recovered.

Reactions with HCl and HBr

Anhydrous HCl (118.3 mg, 3.25 mmol) was condensed into a 25 ml glass reactor containing $MeSiCl_2Co(CO)_4$ (132.1 mg, 0.464 mmol). The vessel was heated for one hour at 90° in a water bath and then cooled to −196°. Only a trace of non-condensable gas was present. The vessel was warmed to room temperature and the HCl (117.2 mg, 3.21 mmol) recovered. The $MeSiCl_2Co(CO)_4$ had not undergone any reaction or decomposition. In a series of similar experiments HBr and HCl were found not to react with $Me_2SiClCo(CO)_4$, $MeSiCl_2Co(CO)_4$, and $Cl_3SiCo(CO)_4$. However, $Me_3SiCo(CO)_4$ was found to react with both HCl and HBr, forming Me_3SiCl and Me_3SiBr respectively, with only a very small amount of $(Me_3Si)_2O$ being formed.

High pressure reactions with HCl

Anhydrous HCl (44.2 mg, 1.21 mmol) was condensed into a gold tube containing $MeSiCl_2Co(CO)_4$ (91.5 mg, 0.321 mmol). The tube was sealed and held at 90°/4000 atm for 12 h. The ampule was opened into the vacuum system and the volatile materials trapped at −196°. A small amount of non-condensable material was present. The material which stopped at −196° was passed through traps cooled to −46° (chlorobenzene slush) and −130° (pentane slush), into a −196° trap. The latter trap contained HCl (31.1 mg, 0.851 mmol), the −130° trap contained $MeSiCl_3$ (43.1 mg, 0.288 mmol), and the −46° trap contained a very small amount of unreacted $MeSiCl_2Co(CO)_4$.

Similar experiments were carried out with $Cl_3SiCo(CO)_4$ and $Me_2SiClCo(CO)_4$. In each case the $Co(CO)_4$ grouping was replaced by a chloro substituent.

High pressure reactions with HBr

Anhydrous HBr (107 mg, 1.32 mmol) was condensed into a gold tube containing $MeSiCl_2Co(CO)_4$ (132 mg, 0.462 mmol). The tube was sealed and held at 90°/4000 atm for 12 h. The ampule was opened into the vacuum system and the volatile materials trapped at −196°. A small amount of non-condensable material was present. The material which stopped at −196° was passed through traps cooled to −46° and −130° into a −196° trap. The latter trap contained HBr (69.0 mg, 0.852 mmol), the −130° trap contained $MeSiCl_2Br$ (81.6 mg, 0.421 mmol), and the −46° trap contained a small amount of unreacted $MeSiCl_2Co(CO)_4$.

In a series of similar experiments, $MeSiCl_3$, Me_2SiCl_2, and $SiCl_4$ were found not to react with HBr; however, $Cl_3SiCo(CO)_4$ and $Me_2SiClCo(CO)_4$ did react forming Cl_3SiBr and $Me_2SiClBr$ respectively

Reactions with H_2O

In a nitrogen filled glove bag $Me_2SiClCo(CO)_4$ (321 mg, 1.22 mmol) was placed into a 25 ml glass pressure reactor. The vessel was then evacuated and degassed water (0.898 g, 50.0 mmol) was condensed into the reactor. The stopcock was closed and the vessel was permitted to warm to and held at room temperature for one hour. The vessel was then cooled to −196° and opened to a manometer. No non-condensable gas was observed. The vessel was then warmed to room temperature. The material which volatilized (in addition to water and H_2O/HCl) was $HCo(CO)_4$ (160 mg, 0.93 mmol; identified by gaseous IR spectrum [23] and confirmed by mass spectrum). Upon heating the reactor in a water bath, $[Me_2SiO]_3$ was collected (55 mg, 0.25 mmol). The mass spectrum indicated that a small amount of the tetramer was also present.

A similar experiment with $MeSiCl_2Co(CO)_4$ also formed $HCo(CO)_4$ and a solid substance which had the same infrared spectrum as $[MeSiO_{1.5}]_x$ obtained by the hydrolysis of $MeSiCl_3$.

Thermal stability

A sample of $MeSiCl_2Co(CO)_4$ (378.4 mg, 1.328 mmol) was placed in a 25 ml glass pressure reactor in a nitrogen filled glove bag. The vessel was then evacuated and heated at 90° for 8 h. The vessel was cooled to −196° and opened to a manometer. Only a small amount of non-condensable material was observed. Upon warming to room temperature no other volatile material was observed except for unreacted starting material (366.5 mg, 1.285 mmol).

Similar experiments with $Me_2SiClCo(CO)_4$ and $Cl_3SiCo(CO)_4$ indicated that these substances also have a high thermal stability. However, at 240° $MeSiCl_2Co(CO)_4$, $Me_2SiClCo(CO)_4$, and $Cl_3SiCo(CO)_4$ were found to decompose to metallic cobalt, a complex solid, and $MeSiCl_3$, Me_2SiCl_2 and $SiCl_4$ respectively.

High pressure reaction with CO

A sample of $MeSiCl_2Co(CO)_4$ (445.7 mg, 1.564 mmol) was placed in a gold cup and placed in a high pressure microreactor. Carbon monoxide was then added to the reactor until a pressure of 4000 atm at 90° had been attained. This pressure was held for 24 hours, and then the reactor was cooled to −196°. Four traps in series were cooled to −196°, and then the reactor was opened into the vacuum system and permitted to warm to room temperature. No new substances were stopped in the traps after all of the CO had been removed. Almost all of the $MeSiCl_2Co(CO)_4$ (441.2 mg, 1.548 mmol) was recovered.

Similar experiments with $Me_2SiClCo(CO)_4$ and $Cl_3SiCo(CO)_4$ also resulted in almost complete recovery of the starting material.

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