Inorganica Chimica Acta, 16 (1976) 219–222

The (Halomethyl)silylcobalttetracarbonyls; on the Infrared Carbonyl Stretching Frequencies of Silyl Cobalttetracarbonyls

J. M. BELLAMA and J. B. DAVISON
Department of Chemistry, University of Maryland, College Park, Maryland 20742, U.S.A.
Received July 16, 1975

The (halomethyl)silanes react with dicobaltoctacarbonyl to give the (halomethyl)silylcobalttetracarbonyls, $XCH_2SiH_2Co(CO)_4$ in which $X = Cl$, Br, I. The PMR and mass spectra suggest a similarity to the bonding in the parent XCH_2SiH_3 compounds. It was found that plots of the infrared carbonyl stretching frequencies of these and other silyl cobalttetracarbonyls vs. summed substituent electronegativities gave fair linearity, but vs. summed (modified) polarity constants produced an excellent correlation.

Introduction

Recently, a number of examples of two distinct types of organosilicon compounds have been reported. The infrared carbonyl stretching frequencies of several silyl derivatives of cobalt tetracarbonyls have been examined in attempts to learn about the structures of such species.[1–3] Also, a number of compounds of the type $XCH_2Si\equiv$ have been examined;[4] such compounds sometimes show unexpected physical properties which have led to the suggestion that some long-range intramolecular interaction may exist between an electron donor and a silicon atom to which the substituent is not directly bonded. We wish to report the synthesis and characterization of a series which is representative of both classes mentioned above, the (halomethyl)silylcobalttetracarbonyls, $XCH_2SiH_2Co(CO)_4$ (X = Cl, Br, I).

Experimental

The title compounds were prepared by the room temperature reaction of the appropriate (halomethyl) silane with $Co_2(CO)_8$ in a glass pressure vessel in the absence of solvent, a method analogous to that of Chalk and Harrod.[5]

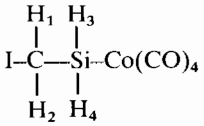
In a typical reaction, freshly sublimed $Co_2(CO)_8$ (0.289 g, 0.845 mmol) was placed in the bottom of the reaction vessel, which was then connected to a high vacuum line and evacuated for 30 min before $ClCH_2SiH_3$ (0.662 g, 8.13 mmol) was condensed into the vessel. As the mixture warmed to room temperature and the $Co_2(CO)_8$ began to dissolve in the liquid $ClCH_2SiH_3$, the solution turned dark brown and began to bubble. The contents were frozen every 30 min and noncondensible gas (H_2 and CO) was pumped off. When the bubbling ceased (three hours for the chloro-, seven hours for the bromo-, and twelve hours for the iodo-derivative) the reaction was judged to be complete. Each of the $XCH_2SiH_2Co(CO)_4$ (X = Cl, Br, I) products was isolated as a yellow oil by fractional condensation into a –23° C trap on the vacuum line. A dark brown nonvolatile oil remained in the reaction vessel after the volatile materials had been pumped off, and dark brown oily solids also remained in the vacuum traps after distillation of product, presumably due to the thermal instability of the products, which were also air sensitive. The compounds decomposed during melting, and a sharp melting point could be obtained only for the chloride (–44.7° C).

PMR spectra were obtained on a Varian A-60A spectrometer, and mass spectra were determined on a duPont Model 492 spectrometer. Infrared spectra were measured on a Digilab Model 14 Fourier Transform spectrometer; the samples were run in a 10 cm gas cell equipped with KBr windows and a cold finger so that the slightly volatile compounds could be condensed into the cell and allowed to warm to room temperature.

Results and Discussion

PMR Spectra

The chemical shifts of the $XCH_2SiH_2Co(CO)_4$ compounds are listed in Table I and are similar to those of the parent XCH_2SiH_3 compounds.[6] The spectra are not simple first order spectra, but instead are of the AA'XX' type. Computer solution of the spectra of $ICH_2SiH_2Co(CO)_4$



$$\mathrm{I{-}\underset{H_2}{\overset{H_1}{C}}{-}\underset{H_4}{\overset{H_3}{Si}}{-}Co(CO)_4}$$

TABLE I. Proton Chemical Shifts (δ) of the $XCH_2SiH_2Co(CO)_4$ Series[a].

X	*CH_2*	*SiH_2*
Cl	2.92	4.29
Br	2.76	4.78
I	2.43	4.83
H[b]	0.20	4.06

[a] Neat liquids; ±0.01 ppm; δ = ppm downfield from external TMS. [b] Also reported in benzene at infinite dilution as δ1.02 (CH_2) and δ4.85 (SiH_2), ref. 3.

TABLE II. Mass Spectral Fragmentation Pattern for $ICH_2SiH_2Co(CO)_4$[a].

m/e	% Intensity	Assignment
314	100	$ICH_2SiH_2Co(CO)_3^+$
286	85	$ICH_2SiH_2Co(CO)_2^+$
258	92	$ICH_2SiH_2Co(CO)^+$
230	78	$ICH_2SiH_2Co^+$
214	81	$ISiCo^+$, $ICo(CO)^+$
172	16	$HCo(CO)_4^+$, $ICH_2SiH_3^+$
171	12	$ICH_2SiH_2^+$, $Co(CO)_4^+$
131	14	$CH_2SiH_2Co(CO)^+$
115	55	$Co(CO)^+$
103	36	$CH_2SiH_2Co^+$
102	16	CH_2SiHCo^+
101	32	CH_2SiCo^+
100	15	$CHSiCo^+$
87	75	$Co(CO)^+$
59	38	Co^+
43	35	CH_2SiH^+

[a] Only fragment ions having a relative abundance > 10% are listed.

yielded "best-fit" values of $J_{1-2} = -12.36$ Hz, $J_{3-4} = -11.19$ Hz, $J_{1-3} = J_{2-4} = 1.43$ Hz, and $J_{1-4} = J_{2-3} = 8.62$ Hz (rms error = 0.176).

Mass Spectra

Since the compounds are temperature sensitive, the inlet was cooled to room temperature (30° C) before a sample was introduced; nevertheless, the observation of peaks due to $HCo(CO)_4$ indicate that some thermal decomposition did occur, a process also noted by other authors with analogous compounds.[7,8] The m/e values, % intensity, and assignments are given in Table II for $ICH_2SiH_2Co(CO)_4$. The chloro- and bromo-compounds gave similar fragmentation patterns. No parent ions were observed, although fragments corresponding to the molecular ion minus 1, 2, and 3 carbonyl groups were the most abundant ions (with $CH_3SiH_2Co(CO)_4$ also, no parent ion was observed; the highest m/e value reported was 104, corresponding to $CH_3SiH_2Co^+$ [3]). In addition, rearranged ions of the type XSi^+ and $XSiH_2^+$ are observed for the $XCH_2SiH_2Co(CO)_4$ compounds, a phenomenon also noted with the parent XCH_2SiH_3 compounds.[4a]

Infrared Spectra

Both the chloride and bromide, when warmed enough to produce sufficient volatility for the measurement of infrared spectra, underwent some thermal decomposition and thus the spectra showed the presence of $HCo(CO)_4$,[9] a known thermal decomposition product of silylcobalttetracarbonyls.[3,10] The infrared spectrum of $ICH_2SiH_2Co(CO)_4$ was not obtained because of the very limited volatility of the compound and the ease with which it decomposed; only ICH_2SiH_3[6] and $HCo(CO)_4$[9] were observed. Difficulties were also reported in obtaining the infrared spectra of $(CH_3)_3SiCo(CO)_4$ and $CH_3SiH_2Co(CO)_4$; it was suggested that decomposition was hastened by the melting of the sample.[2] The CO stretching frequencies for the $XCH_2SiH_2Co(CO)_4$ (X = Cl, Br) compounds are given in Table III, along with the frequencies of several analogous silyl cobalttetracarbonyls.

Infrared CO stretching frequencies of metal carbonyl compounds generally occur between 2150 and 1650 cm^{-1} with absorption below about 1850 cm^{-1} often indicating the presence of bridging carbonyl

TABLE III. Gas-phase Carbonyl Stretching Vibrations, Substituent Electronegativities, and Polarity Constants for Selected Silyl Cobalttetracarbonyls.

Compound		A_1^e (cm^{-1})	A_1^a (cm^{-1})	E (cm^{-1})	$\Sigma\chi_R$[a]	$\Sigma\sigma^*$ (Si)[b]	Ref.
$F_3SiCo(CO)_4$	(8)[d]	2128	2073	2049	12.00	4.05	2
$Cl_3SiCo(CO)_4$	(7)	2125	2071	2049	9.00	3.60	2
$CH_3F_2SiCo(CO)_4$	(6)	2116	2061	2035, 2026	10.27	2.70	3
$ClCH_2SiH_2Co(CO)_4$	(5)	2108		2022	6.67	1.25	*c*
$BrCH_2SiH_2Co(CO)_4$	(4)	2107	2050	2021	6.60	1.10	*c*
$H_3SiCo(CO)_4$	(3)	2106	2051	2026	6.30	1.47	1
$CH_3SiH_2Co(CO)_4$	(2)	2102	2043	2021, 2015	6.47	0.98	3
$(CH_3)_3SiCo(CO)_4$	(1)	2100	2041	2009	6.81	0.00	2

[a] Group electronegativities from ref. 11. [b] σ* (Si) values calculated according to ref. 12. [c] This work, ±2 cm^{-1}, 500 scans.
[d] Numbers identify compounds depicted in Figures 1 and 2.

groups.[13] An axial trigonal bipyramidal C_{3v} structure has been established for $H_3SiCo(CO)_4$ in the gas phase by electron diffraction[14] and for $Cl_3SiCo(CO)_4$[15] and $F_3SiCo(CO)_4$[16] in the solid phase by X-ray diffraction. The gas phase infrared spectra of these symmetrical compounds exhibit three CO stretching vibrations, A_1^a, A_1^e, and E, as expected for C_{3v} symmetry.[1,2]

Several unsymmetrically substituted compounds of the type $R'R_2MCo(CO)_4$ where (a) M = Si, R' = CH_3, R = H or F, and (b) M = Ge, R' = C_6H_5, Cl, or I, R = CH_3, C_6H_5, Cl, or I, have been synthesized and their infrared spectra reported.[2,3,17,18] The result of unsymmetric substitution on the Si or Ge is a change of symmetry for the molecule: from C_{3v} with three CO bands to (at most) C_s with four CO bands,[17] the E mode having split into two components of comparable intensity.[2,17] All of the unsymmetrically substituted Ge compounds listed above show four CO bands in solution;[17] the gas phase spectra of these compounds have not been reported. The gas phase spectra of the two Si compounds also show four CO bands.

It has been observed that symmetrically substituted $R_3SiCo(CO)_4$ compounds, where R = Cl, CH_3O, C_6H_5, and C_2H_5, exhibit four bands in the CO stretching region when dissolved in heptane.[5] Adams points out that it is possible to have a change in the selection rules due to solvent–solute interactions which can lead to the appearance of additional bands.[19] Furthermore, one generally observes a difference in the CO stretching frequencies when the infrared spectrum of a carbonyl compound is taken in the gas phase[2] and in solution.[5] For these reasons, the data discussed in this report are taken only from infrared spectra in the gas phase.

The frequency of the CO stretching vibration is determined by the CO bond order, which in turn reflects the metal–carbon bond order; and the metal–carbon bond order is directly affected by the other ligands bound to the metal. It is known that electronegative substituents (*e.g.* halogen, F_3C–) usually raise the CO stretching frequencies above those in the unsubstituted carbonyl.[20] Electron-donating substituents usually lower the CO stretching frequencies when they replace CO groups.[16] Thus it is to be expected that the three carbonyl stretching frequencies observed for the isostructural silyl cobalttetracarbonyls, $R_3SiCo(CO)_4$, reflect to some extent the sum of the electronegativities of the substituent R groups.

Table III lists the gas-phase CO stretching frequencies for some $R_3SiCo(CO)_4$ compounds, plus the sum of the electronegativities, $\Sigma\chi_R$, of the substituent R groups. It is obvious from Table III that, in general, the more electronegative the substituents on the Si, the higher the CO stretching frequencies. The data from Table III is graphically presented in Figure 1 where the sums of the R group electronegativities are plotted *vs.* the CO stretching frequencies. While this plot (R = .88) shows a relationship between the electronegativity of the R substituents and the CO stretching frequencies, it also seems to indicate that other factors in addition to electronegativity may be important.

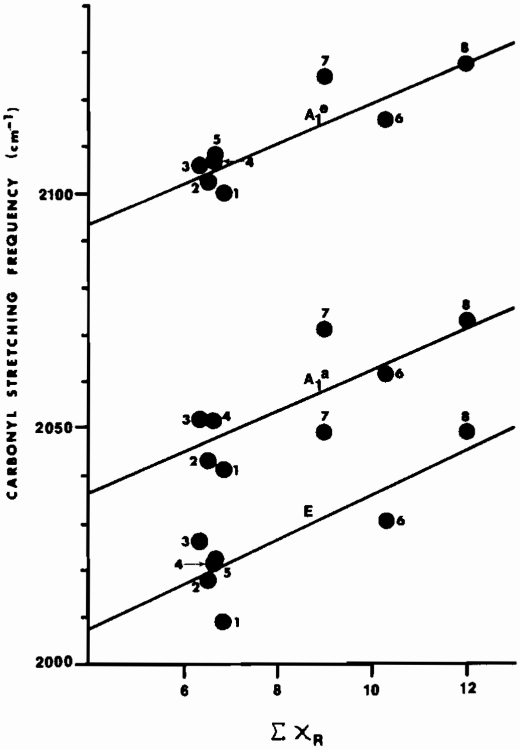


Figure 1. Plot of summed substituent electronegativities[11] *vs.* CO stretching frequencies for $R_3SiCo(CO)_4$ compounds. See Table III for identity of compounds.

Stone and co-workers[18] have shown that a linear relationship exists between the force constants of the CO stretching vibration and the Taft polarity constant, σ^*, for a series of $R_3GeCo(CO)_4$ complexes. The Taft polarity constant reflects the charge distribution in a molecule (or activated complex) and is thus related to the electronegativity of substituent groups.[21] Attridge[12] has modified σ^* somewhat to account for variations in the Si–H stretching frequencies of various silanes. He noted that these variations were not due solely to the inductive influences of the substituents. Therefore he calculated a modified polarity constant, $\sigma^*(Si)$,

$$\sigma^*(\mathrm{Si}) = \sigma^* - \Theta$$

where σ^* is the Taft polarity constant for a substituent and Θ is an empirical constant. While the significance of Θ is a matter of speculation, Attridge suggests that Θ may be a measure of the (p→d)π bonding between the R substituent and the Si.

The sums of the modified polarity constants, $\Sigma\sigma^*(\mathrm{Si})$, are also listed in Table III for the $R_3SiCo(CO)_4$ compounds. The $\sigma^*(\mathrm{Si})$ values for the $ClCH_2SiH_2$– and $BrCH_2SiH_2$– groups were calculated using the Si–H stretching frequencies for $ClCH_2SiH_3$ and $BrCH_2SiH_3$ as given in reference 6. In Figure 2 the $\Sigma\sigma^*(\mathrm{Si})$ values are plotted *vs.* the CO stretching frequencies. The close fit to linearity (R = .98) would suggest that the CO stretching frequencies are very sensitive to whatever factors determine the value of Θ in Attridge's equation. Therefore, from a comparison of the data presented in Figures 1 and 2, it is apparent that the CO stretching frequencies of the $R_3SiCo(CO)_4$ compounds are not dependent on simply the inductive effects of R groups, but also on some other factor, possibly, as Attridge suggests,[12] the $(p\rightarrow d)\pi$ bonding capability of the R group to the silicon.

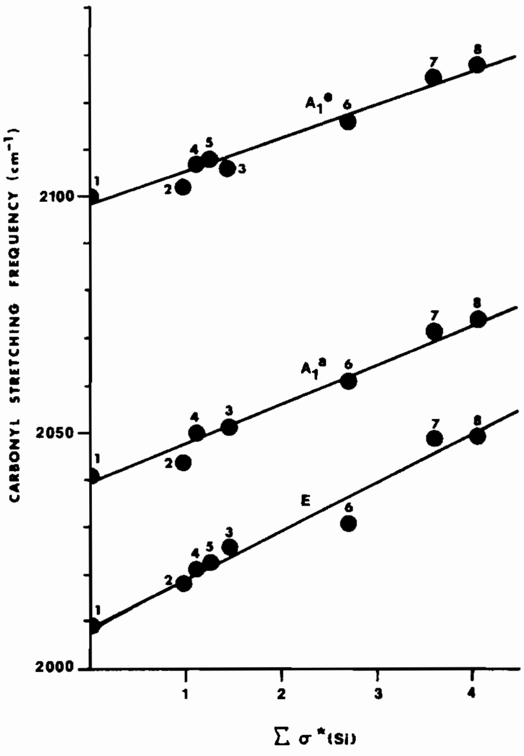


Figure 2. Plot of summed (modified) polarity constants[12] *vs.* CO stretching frequencies for $R_3SiCo(CO)_4$ compounds. See Table III for identity of compounds.

Acknowledgments

This work was supported in part by the Center of Materials Research of the University of Maryland.

References

1 B.J. Aylett and J.M. Campbell, *Chem. Comm.*, 159 (1967).
2 A.P. Hagen and A.G. MacDiarmid, *Inorg. Chem.*, *6*, 686 (1967); ibid., *6*, 1941 (1967).
3 S.K. Gondal, A.G. MacDiarmid, F.E. Saalfeld, and M.V. McDowall, *Inorg. Nucl. Chem. Lett.*, *5*, 413 (1969).
4 The groups of Chvalovský and of Voronkov have been particularly active in studying this interaction. See for example, (a) J.M. Bellama and A.G. MacDiarmid, *J. Organometal. Chem.*, *24*, 91 (1970); (b) M.G. Voronkov, V.P. Feshin, V.F. Mironov, S.A. Mikhailyants and T.K. Gar, *J. Gen. Chem. USSR*, *41*, 2237 (1971); (c) J. Pola, J.M. Bellama and V. Chvalovský, *Coll. Czech. Chem. Comm.*, *39*, 3705 (1974).
5 A.J. Chalk and J.F. Harrod, *J. Am. Chem. Soc.*, *87*, 1133 (1965).
6 J.M. Bellama and A.G. MacDiarmid, *J. Organometal. Chem.*, *18*, 275 (1968).
7 F.E. Saalfeld, M.V. McDowell, S.K. Gondal and A.G. MacDiarmid, *Inorg. Chem.*, *7*, 1465 (1968).
8 R.E. Winters and R.W. Kiser, *J. Phys. Chem.*, *69*, 1618 (1965).
9 W.F. Edgell, C. Magee and G. Gallup, *J. Am. Chem. Soc.*, *78*, 4185 (1956).
10 B.J. Aylett and J.M. Campbell, *Chem. Comm.*, 217 (1965).
11 J.E. Huheey, *J. Phys. Chem.*, *69*, 3284 (1965).
12 C.J. Attridge, *J. Organometal. Chem.*, *13*, 259 (1968).
13 T.A. Manuel in *Advances in Organometallic Chemistry*, v. 3, F.G.A. Stone and R. West, Eds., Academic Press, New York, (1965).
14 A.G. Robiette, G.M. Sheldrick, R.N.F. Simpson, B.J. Aylett and J.A. Campbell, *J. Organometal. Chem.*, *14*, 279 (1968).
15 W.T. Robinson and J.A. Ibers, *Inorg. Chem.*, *6*, 1208 (1967).
16 K. Emerson, P.R. Ireland and W.T. Robinson, *Inorg. Chem.*, *9*, 436 (1970).
17 D.J. Patmore and W.A.G. Graham, *Inorg. Chem.*, *6*, 981 (1967).
18 J. Dalton, I. Paul, J.G. Smith and F.G.A. Stone, *J. Chem. Soc. (A)*, 199 (1968).
19 D.M. Adams, "Metal–Ligand and Related Vibrations", St. Martin's Press, New York, 1968.
20 E. Pitcher and F.G.A. Stone, *Spectrochim. Acta*, *18*, 585 (1962).
21 R.W. Taft, "Steric Effects in Organic Chemistry", M.S. Newman, ed., Wiley, New York, 1966.