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VIBRATIONAL ASSIGNMENTS AND VALENCE FORCE FIELD CALCULATIONS FOR SOME $X_3MM'(CO)_4$ COMPLEXES (X = H, F, Cl; M = Si, C AND M′ = Co, Fe)

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Summary

The infrared and Raman spectra of $X_3MM'(CO)_4$ compounds (X = H,F,Cl; M = Si and M′ = Co,Fe) are described. Complete vibrational assignments have been made, and valence force field calculations carried out for these complexes and for $F_3CCo(CO)_4$. Evidence for π-interaction in the M—M′ bond is considered.

Introduction

In earlier papers in this series [1-3] we reported the infrared, Raman spectra and normal coordinate analysis of several $X_3MCo(CO)_4$ complexes in order to elucidate to what extent variation of the MX_3 influences the π-bonding system in these heteronuclear metal—metal bonded molecules. It was achieved that for changes in energy, due to movements of the nuclei, the changes in the π-bonding system are much more important than those in the σ-bonds.

The present work extends these studies to some other compounds of the $X_3MCo(CO)_4$ series and in addition to the $[Cl_3SiFe(CO)_4]^-$ ion, which is isoelectronic with $Cl_3SiCo(CO)_4$ to see whether the Si—Fe bond order is different from that of the Si—Co bond.

We report the complete vibrational spectra and assignments for $H_3SiCo(CO)_4$, $F_3SiCo(CO)_4$ and $[Cl_3SiFe(CO)_4]^-$ and valence force field calculations for these complexes and for $F_3CCo(CO)_4$, for which the vibrational data are taken from ref. 2.

Experimental

Starting materials were either commercially available or prepared by standard methods. All compounds were handled under an argon atmosphere. The silylcobalt tetracarbonyl was obtained through reaction of iodosilane with

$NaCo(CO)_4$ in dimethyl ether as a pale yellow liquid [4]. Trifluorosilylcobalt tetracarbonyl was prepared from SiF_3H and $Co_2(CO)_8$, as described in ref. 5. The trichlorosilyliron tetracarbonyl anion was derived from the hydride complex as the tetraethyl ammonium salt by the method used by Jetz and Graham [6,7].

The infrared spectra were recorded on Beckman IR11 and IR12 spectrophotometers at room- and liquid nitrogen-temperature with CsI and polyethylene windows as appropriate. Both spectrometers were calibrated using the IUPAC wavenumber tables [8]. Raman spectra were recorded on a Coderg PH1 spectrometer with a CRL53 mixed gas (Ar/Kr) laser, using 6471Å as the exciting line. Depolarization values were obtained from solution (CH_2Cl_2) or liquid spectra. The Ne lines were used for calibration.

TABLE 1

VIBRATIONAL FREQUENCIES (cm^{-1}) AND ASSIGNMENTS FOR $H_3SiCO(CO)_4$

Infrared		Raman		Assignment
Liquid	Solid(−160°)	Liquid	Solid (−160°)	
			2182 m	
	2152 s	2155 m P	2150 m	$A_1 + E$ ν(SiH)
			2144 w	
			2139 ms	
	2117 w	2119 w		
	2101 s	2104 m P	2103 w	A_1 ν(CO)
	2041 s	2045 s P	2042 s	A_1 ν(CO)
	2007 vs	2004 s DP	2002 m	E ν(CO)
			1997 ms	
	1975 m		1994 w	
			948 m	
944 m		945 m	944 m	A_1 $\delta(SiH_3)$
	941 m		941 m	
			910 m	
898 s	892 s	898 w	890 w	E $\delta(SiH_3)$
703 m		730 w P	730 w	?
606 s	606 s	612 w DP	604 w	E δ(HSiCo)
557 s	557 s	560 w	556 w	E $\delta(CoCO)_{out}$
			549 w	
543 s	545 s	547 w	545 w	A_1 $\delta(CoCO)_{out}$
	510 w		513 w	
500 (sh)	500 w	504 w DP	503 w	E $\delta(CoCO)_{ax} + \nu(CoC)_{eq}$
485 s	486 ms	490 w DP	488 w	E $\nu(CoC)_{eq} + \delta(CoCO)_{ax}$
460 (sh)	463 w	461 w P	464 w	A_1 $\nu(CoC)_{ax}$
419 w	423 m	426 vs P	425 vs	A_1 $\nu(CoC)_{eq}$
405 w	408 w			
375 m	378 w		378 vw	E $\delta(CoCO)_{in}$
	368 vw		367 vw	
			321 s	
	315 ms	316 vs P	318 vs	A_1 ν(SiCo)
312 ms			312 m	
			140 s	
			129 m	
		122 s DP	121 s	E δ(CCoC)
		104 s DP	112 s	E δ(CCoC)
			92 s	A_1 δ(CCoC)
			79 m	
		72 s DP	73 m	E δ(SiCoC)
			65 m	

TABLE 2

VIBRATIONAL FREQUENCIES (cm^{-1}) AND ASSIGNMENTS FOR $\mathrm{F_3SiCo(CO)_4}$

Infrared	Raman		Assignment
Solid (−160°)	Liquid	Solid (−160°)	
2128 s	2128 s P	2135 s	A_1 $\nu(\mathrm{CO})$
2072 s	2076 s	2076 s	A_1 $\nu(\mathrm{CO})$
2035 vs	2032 s DP	2037 s	E $\nu(\mathrm{CO})$
		2030 s	
922 vs		917 w(br)	E $\nu(\mathrm{SiF})$
823 vs			A_1 $\nu(\mathrm{SiF})$
555 vs	555 w P	555 w	A_1 + E δ $(\mathrm{CoCO})_{\mathrm{out}}$
		518 vw	
	510 vw DP		E $\delta(\mathrm{CoCO})_{\mathrm{ax}}$ + $\nu(\mathrm{CoC})_{\mathrm{eq}}$
506 m		503 vw	
486 w	488 w DP	489 w	E $\nu(\mathrm{CoC})_{\mathrm{eq}}$ + $\delta(\mathrm{CoCO})_{\mathrm{ax}}$
457 s	454 m P	458 m	A_1 $\delta(\mathrm{SiF_3})$
435 m		435 (sh)	A_1 $\nu(\mathrm{CoC})_{\mathrm{ax}}$
	417 vs P	423 vs	A_1 $\nu(\mathrm{CoC})_{\mathrm{eq}}$
375 w			E $\delta(\mathrm{CoCO})_{\mathrm{in}}$
332 m		326 w	E $\delta(\mathrm{SiF_3})$
246 m	245 s P	246 s	A_1 $\nu(\mathrm{SiCo})$
204 w	197 w DP	197 w	E $\delta(\mathrm{FSiCo})$
130 w			E $\delta(\mathrm{CCoC})$
	102 s DP		E $\delta(\mathrm{CCoC})$
60 w	≈60 s		E $\delta(\mathrm{SiCoC})$

TABLE 3

VIBRATIONAL FREQUENCIES (cm^{-1}) AND ASSIGNMENTS FOR $[\mathrm{Cl_3SiFe(CO)_4}]^-$

Infrared		Raman		Assignment
Solution	Solid	Solution	Solid	
2033 s	2036 s	2035 m P	2034 w	A_1 $\nu(\mathrm{CO})$
1952 s	1957 s	1952 m	1946 s	A_1 $\nu(\mathrm{CO})$
1918 vs	1925 s	1920 m	1923 w	E $\nu(\mathrm{CO})$
	1905 vs		1909 m	
			1896 w	
			638 w	E $\delta(\mathrm{FeCO})_{\mathrm{out}}$
631 s		630 s P?		
	627 vs		625 w	A_1 $\delta(\mathrm{FeCO})_{\mathrm{out}}$
550 m	549 w	550 w DP	551 w	E $\nu(\mathrm{SiCl})$
	517 s		524 w	E $\nu(\mathrm{FeC})_{\mathrm{eq}}$
512 s	512 s	515 w P	512 w	A_1 $\nu(\mathrm{SiCl})$
			491 w	
481 m	481 s	485 w DP	483 (sh)	E $\delta(\mathrm{FeCO})_{\mathrm{ax}}$
	≈460 (sh)	455 vs P	458 vs	A_1 $\nu(\mathrm{FeC})_{\mathrm{eq}}$
	306 w	305 vs P	310 vs	A_1 $\nu(\mathrm{SiFe})$
	207 m	205 m DP	212 m	E $\delta(\mathrm{SiCl_3})$
	188 s	190 s P	190 m	A_1 $\delta(\mathrm{SiCl_3})$
	144 w	140 w DP	148 m	E $\delta(\mathrm{ClSiFe})$
	110 w		110 w	E $\delta(\mathrm{CFeC})$
	104 w	≈100 (br)		
	98 w		97 m	E $\delta(\mathrm{CFeC})$

Results and discussion

Vibrational assignment

The vibrational frequencies obtained under various conditions are listed in Tables 1, 2 and 3 for $H_3SiCo(CO)_4$, $F_3SiCo(CO)_4$ and $[Cl_3SiFe(CO)_4]^-$, respectively, together with approximate descriptions of the observed fundamentals. Values are considered to be accurate to within ± 1 cm^{-1} over the whole range.

As has previously been pointed out [1,2] a C_{3v} symmetry is assumed for this type of molecule, and this leads to the following vibrational representation:

$$\Gamma_{vib} = 9A_1 + 2A_2 + 11E$$

A_1 = infrared and Raman allowed, polarized; A_2 = forbidden; E = infrared and Raman allowed, depolarized. The vibrational assignments for the silylcobalt complexes, following the arguments described for other members of the Group IV—cobalt series [1,2], are straightforward, but some special comments are necessary. The degenerate equatorial carbonyl stretching mode for the hydride and fluoride complexes is lower in frequency than expected; this was also observed, although to a lesser extent, for the chlorosilyl complex. Thus, there must be a difference in the interaction between the silyl groups and the equatorial carbonyl groups compared with that for the other MX_3 groups.

Another irregularity is observed for the trifluorosilyl compound, for which, as for $F_3CCo(CO)_4$ and $F_3GeCo(CO)_4$, one expects values as follows in the middle frequency region:

≈ 480 cm^{-1} E $\delta(CoCO)_{ax} + \nu(CoC)_{eq}$
≈ 460 E $\nu(CoC)_{eq} + \delta(CoCO)_{ax}$
≈ 435 A_1 $\nu(CoC)_{ax}$
≈ 400 A_1 $\nu(CoC)_{eq}$.

The frequencies actually observed are respectively 506, 488, 435 and 420 cm^{-1}. Except for the 435 cm^{-1} mode the values look more like those of a hydride complex.

To what extent mixing with the SiF_3 deformation modes or a different type of interaction of the SiF_3 group with the equatorial carbonyl group contribute to this effect is considered in the discussion below of the valence force field calculations.

In the vibrational assignment of $[Cl_3SiFe(CO)_4]^-$ (Table 3, the values for the tetraethylammonium cation are omitted) we use the same arguments as for the cobalt series. In the light of the knowledge that, for iron carbonyl complexes, the FeCO bending modes are higher in frequency than the corresponding CoCO modes for cobalt complexes [9], the assignment is straightforward.

For comparison the vibrational spectra of $Cl_3SiFeH(CO)_4$ a molecule with C_s symmetry, are also shown. With the assumption of local C_{3v} symmetry for the Cl_3SiFe moiety a comparison can be made between the Si—Cl stretching and deformation modes and Si—M' stretching modes of both molecules and the cobalt analogue $Cl_3SiCo(CO)_4$.

The similarity between these molecules is remarkable as far as these modes are concerned, in contrast to the patterns for the CO and M'C stretching modes,

$[Cl_3SiFe(CO)_4]^-$	$Cl_3SiHFe(CO)_4$	$Cl_3SiCo(CO)_4$	Assignment
550 cm^{-1}	556 cm^{-1}	570 cm^{-1}	E $\nu(SiCl)$
514	506	506	A_1 $\nu(SiCl)$
308	304	308	A_1 $\nu(SiM')$
208	208	202	E $\delta(SiCl_3)$
189	186	181	A_1 $\delta(SiCl_3)$

which are respectively much lower and higher in the case of the anion. This leads to the conclusion that the extra electron density in the anion is completely transferred to the antibonding carbonyl π-orbitals, which is confirmed by the force field calculations below.

Valence force field calculations

Structural investigations on $H_3SiCo(CO)_4$ [10], and $F_3SiCo(CO)_4$ [11] did not reveal any significant differences in the structures of these molecules, except for the Si—Co distance; this difference has been ignored in the calculations because the force field parameters proved to be unaffected by small changes in the metal—metal bond distances. Thus the value for the fluorine complex of 2.25Å was taken for both siliconcobalt molecules. The same value was used for the metal—metal distance in the iron complex, since no structural data are available for the anion complexes. The CO and FeC distances used are those deduced from an electron diffraction study of $Fe(CO)_5$ [12]. All angles and distances used in the calculations are given in Table 4.

The force field calculations were performed by Wilson's *FG*-matrix method [13]. The same set of orthonormal internal symmetry coordinates and *G*-matrix elements were used as in ref. 3. Again, the general valence force field, containing 111 parameters, had to be constained and the attempt was made to use the same assumptions as in ref. 3, i.e.:

(1) All bend—bend interaction constants are set at zero, except for $f_{M'CO_{out},M'CO_{out}}$.

(2) All stretch—stretch interactions not directly linked are neglected, except for the carbonyl stretching system.

(3) All interactions between a bending mode and stretching vibrations not involving the apical atom of this bending mode are neglected.

TABLE 4

MOLECULAR DATA FOR THE $X_3MM'(CO)_4$ COMPLEXES

$r(CoC_{eq})$ = 1.76 Å	$r(FeC_{eq})$ = 1.83 Å
$r(CoC_{ax})$ = 1.80	$r(FeC_{ax})$ = 1.81
$r(CO_{eq})$ = 1.15	$r(CO_{eq})$ = 1.14
$r(CO_{ax})$ = 1.14	$r(CO_{ax})$ = 1.14
$\angle C_{ax}M'C_{eq}$ = 95°	$\angle MM'C_{eq}$ = 85°
$\angle C_{eq}M'C_{eq}$ = 119°15	$\angle M'MX$ = 113°15'
$\angle M'CO_{eq}$ and ax = 180°	$\angle XMX$ = 105°26'
$r(SiF)$ = 1.56 Å	$r(SiM')$ = 2.25 Å
$r(SiH)$ = 1.48	$r(CF)$ = 1.33
$r(SiCl)$ = 2.03	$r(CmCo)$ = 1.80

(4) Where necessary, a van der Waals interaction is introduced between the MX_3 group and the equatorial carbonyl groups.

(5) For $F_{MX,MM'}$, F_{MX,MX_3} and F_{MM',MX_3} the relation of Becher [14] is used.

These assumptions lead to a force field of 37 parameters.

Except for the few modifications as outlined below these assumptions could be sustained, even for $[Cl_3SiFe(CO)_4]^-$, although in this complex some numerical values for the FeCO bending modes had to be adjusted. Also, another interaction constant $F_{CO_{ax},CO_{eq}}$ was needed because a different amount of mixing of the carbonyl stretching modes from that in the Co complexes was revealed by calculations based on the potential energy distribution.

For the $F_3SiCo(CO)_4$ compound it was necessary to introduce an interaction constant $F_{4,8}$ (F_{CoC_{ax},MX_3}) because of evidence for strong mixing between these two modes. There was no need to take account of an interaction between

TABLE 5

THE SYMMETRY FORCE CONSTANTS FOR ALL MOLECULES IN mdyne/Å

F	$H_3SiCo(CO)_4$	$F_3SiCo(CO)_4$	$F_3CCo(CO)_4$	$[Cl_3SiFe(CO)_4]^-$	Description
1,1	17.05	17.70	17.65	15.50	CO_{ax}
1,2[a]	0.2	0.2	0.2	0.35	
1,3[a]	−0.17	−0.17	−0.17	−0.17	
1,4[a]	0.55	0.55	0.55	0.55	
2,2	16.95	17.40	17.60	15.60	CO_{eq}
2,3[a]	0.41	0.41	0.41	0.41	
2,4[a]	−0.17	−0.17	−0.17	−0.17	
3,3	3.10	3.0	2.75	3.55	$M'C_{eq}$
3,4[a]	0.05	0.05	0.05	0.05	
4,4	2.45	2.1	2.00	2.90	$M'C_{ax}$
4,6	0	0	0.1	0	
4,7[a]	−0.1	−0.1	−0.1	0	
4,8	0	0.1	0	0	
5,5	2.72	6.0	5.6	3.2	MX
5,6	0.26	0.45	0.47	0.29	
5,8	0.16	0.32	0.75	0.26	
6,6	1.50	2.00	2.35	1.35	MM'
6,8	−0.15	−0.22	−0.33	−0.21	
7,7[a]	0.62	0.62	0.62	0.80	$M'CO_{out}$
8,8	0.49	0.85	1.65	1.05	MX_3
8,9	0	0	−0.10	0	
9,9	0.33	0.36	0.35	0.35	CM'C
10,10	16.25	16.65	17.05	14.80	CO_{eq}
10,11[a]	0.62	0.62	0.62	0.62	
11,11	2.50	2.45	2.10	2.45	$M'C_{eq}$
11,14[a]	0.1	0.1	0.1	0.1	
12,12	2.61	4.80	3.1	2.05	MX
12,16	0	0	−0.21	0	
13,13[a]	0.75	0.75	0.75	1.00	$M'CO_{out}$
14,14[a]	0.55	0.55	0.55	0.60	$M'CO_{ax}$
15,15[a]	0.35	0.35	0.35	0.40	$M'CO_{in}$
16,16	0.41	0.98	2.10	1.20	MX_3
17,17	0.56	0.60	0.72	0.68	XMM'
17,20	0	0	−0.08	0	
18,18[a]	0.40	0.40	0.40	0.40	CM'C
19,19[a]	0.09	0.09	0.09	0.09	CM'C
20,20	0.30	0.35	0.30	0.32	MM'C

[a] Force constants fixed in the calculations.

CoC_{eq} and MX_3 ($F_{3,8}$), since no interaction was observed and use of a plausible interaction constant did not influence the calculated vibrational frequencies.

As might be expected, for $F_3CCo(CO)_4$, several modifications were needed,

TABLE 6

VIBRATIONAL FREQUENCIES CALCULATED FOR SOME $X_3MM'(CO)_4$ MOLECULES

	$H_3SiCo(CO)_4$			$F_3SiCo(CO)_4$		
Mode	ν_{exp}	ν_{calc}	Δ	ν_{exp}	ν_{calc}	Δ
$\nu(CO)\ A_1$	2102	2100	+2	2130	2127	+3
$\nu(CO)\ A_1$	2043	2047	−4	2074	2077	−3
$\nu(CO)\ E$	2004	2013	−9	2035	2036	−1
$\delta(CoCO)_{out}\ E$	557	558	−1	555	559	−4
$\delta(CoCO)_{out}\ A_1$	546	554	−8	555	556	−1
$\delta(CoCO)_{ax} + \nu(CoC)_{eq}\ E$	502	504	−2	506	507	−1
$\nu(CoC)_{eq} + \delta(CoCO)_{ax}\ E$	486	474	+12	487	474	+13
$\nu(CoC)_{ax}\ A_1$	462	469	−7	435	430	+5
$\nu(CoC)_{eq}\ A_1$	423	424	−1	420	416	+4
$\delta(CoCO)_{in}\ E$	370	368	+2	375	368	+7
$\nu(MX)\ E$	2152	2153	−1	920	917	+3
$\nu(MX)\ A_1$	2152	2154	−2	823	823	0
$\nu(MCo)\ A_1$	315	310	+5	245	234	+11
$\delta(MX_3)\ E$	944	945	−1	329	332	−3
$\delta(MX_3)\ A_1$	898	902	−4	456	459	−3
$\delta(CCoC)\ E$	122	121	+1		119	
$\delta(CCoC)\ E$	106	103	+3	102	101	+1
$\delta(CCoC)\ A_1$	92	98	−6		95	
$\delta(XMCo)\ E$	606	608	−2	200	200	0
$\delta(MCoC)\ E$	73	81	−8	60	62	−2
	Δtot = 81			Δtot = 65		
	Δmean = 4.1			Δmean = 3.6		

	$F_3CCo(CO)_4$			$[Cl_3SiFe(CO)_4]^-$		
Mode	ν_{exp}	ν_{calc}	Δ	ν_{exp}	ν_{calc}	Δ
$\nu(CO)\ A_1$	2135	2129	+6	2034	2034	0
$\nu(CO)\ A_1$	2075	2076	−1	1952	1959	−7
$\nu(CO)\ E$	2052	2053	−1	1921	1921	0
$\delta(M'CO)_{out}\ E$	562	559	+3	632	629	+3
$\delta(M'CO)_{out}\ A_1$	555	544	+11	626	625	+1
$\delta(M'CO)_{ax} + \nu(M'C)_{eq}\ E$	477	483	−6	520	518	+2
$\nu(M'C)_{eq} + \delta(M'CO)_{ax}\ E$	460	465	−5	483	491	−8
$\nu(M'C)_{ax}\ A_1$	438	438	0	483	489	−6
$\nu(M'C)_{eq}\ A_1$	400	400	0	457	452	+5
$\delta(M'CO)_{in}\ E$	376	368	+8		391	
$\nu(MX)\ E$	1080	1085	−5	550	554	−4
$\nu(MX)\ A_1$	1045	1049	−4	513	511	+2
$\nu(MM')\ A_1$	281	281	0	307	312	−5
$\delta(MX_3)\ E$	532	533	−1	208	209	−1
$\delta(MX_3)\ A_1$	711	701	+10	189	183	+6
$\delta(CM'C)\ E$	126	120	+6	110	111	−1
$\delta(CM'C)\ E$	109	104	+5	97	98	−1
$\delta(CM'C)\ A_1$	78	79	−1		87	
$\delta(XMM')\ E$	258	260	−2	144	149	−5
$\delta(MM'C)\ E$		95			49	
	Δtot = 75			Δtot = 57		
	Δmean = 4.1			Δmean = 3.35		

because this is the only $X_3MCo(CO)_4$ compound studied in which there can be no π-bonding into d-orbitals of M. An interaction constant $F_{4,6}$ (F_{CoC_{ax},CoC_M}) seemed reasonable. Becher's relation [14] did not hold for this complex, because of a considerable degree of mixing between the CF stretching and bending modes in the A_1 and E block. Hence, a larger value for $F_{5,8}$ (F_{CF,CF_3}) was used and a non-zero interaction constant between these modes in the E block ($F_{12,16}$) was introduced.

All calculated fixed and non-fixed symmetry force constants are listed in Table 5. For clarity a brief description of the symmetry coordinates is presented in terms of the diagonal force constants.

The calculated vibrational frequencies are listed in Table 6 together with the experimental values.

Description of bonding properties

Even these more extreme examples in the series of molecules studied show the same features in the force constants as previously described [3]. As can be seen from Table 5, the results of the force field calculations give further indications that changes in the π-bonding system in this kind of complexes is by far the most important factor. The bonding scheme of diminishing π-backbonding, leading to a stronger CO bond, a weaker CoC bond and a stronger metal—metal bond, can be applied throughout the whole series including the iron-derivative. However, attention must be drawn to some special features, and more clearly than in our previous paper [3], we can distinguish a series of additional bonding mechanisms. These are:

(a) An extra $d\pi_{Co}$—σ^*_{MX} bonding between Co(Fe) and the Group IV metal, as proposed by Cotton [15], which results in a stronger Co—M bond and lower MX frequencies. In Table 7 we compare the mean values of MX vibrational frequencies for several MX_4 molecules with the mean values in our $X_3MCo(CO)_4$ compounds. The decrease in the MX frequencies in our complexes indicates that the degree of π—σ^* bonding interaction decreases in the order F > Cl,H > Br > I.

(b) On a closer look at Table 7 we see deviations from the proposed $d\pi_{Co}$—

TABLE 7

MEAN MX FREQUENCIES IN SEVERAL COMPLEXES

MX	MX_4	$X_3MCo(CO)_4$	Δ
Si—H	2189	2152	+37
Ge—H	2111	2079	+32
Ge—D	1516	1488	+28
C—F	1175	1068	+107
Si—F	974	888	+86
Ge—F	785	685	+100
Si—Cl	562	549	+13
Ge—Cl	441	402	+39
Sn—Cl	397	361	+36
Ge—Br	305	299	+6
Sn—Br	265	256	+9
Ge—I	238	249	—11
Sn—I	201	212	—11

σ^*_{MX} trends for SiCl and to a lesser extent for SiF. This can be explained by a certain amount of $d\pi$—$p\pi$ interaction in the M—X bond, which strengthens the M—X bond in the order SiCl > SiF > rest of the series. This sequence has also been revealed by NQR, NMR and UV photoelectron spectroscopy [16-20]. This $d\pi$—$p\pi$ interaction competes with other possible bonding contributions from the d orbitals of the silicon atom. The trends in the force constants F_{MX} and $F_{MM'}$ are opposite to the trends in the $d\pi_{Co}$—σ^*_{MX} bonding scheme.

(c) With the introduction of a direct through-space bonding interaction between the Si d orbitals and orbitals from C_{eq}, which was revealed by MacDiarmid [21,22] from extended Hückel MO calculations and mass spectroscopy for silicon—cobalt complexes, we can explain several unexpected irregularities in the force constant values. In our earlier paper [3] on force field calculations, including those on $Cl_3SiCo(CO)_4$, the need for the introduction of such an interaction was not obvious, although the equatorial CO stretching frequencies for $Cl_3SiCo(CO)_4$ were lower than expected, and this could indeed indicate a small Si—C_{eq} interaction, which would result in higher $F_{CoC_{eq}}$ and F_{SiCo} and lower $F_{CO_{eq}}$ force constants. This influence is probably obscured by the strong $d\pi$—$p\pi$ interaction between Si and Cl. In the silicon fluoride complex and, to a lesser extent, in the hydride complex, where $d\pi$—$p\pi$ bonding is relatively small or absent, such an interaction can account for the following features of Table 5: (1) The smaller $F_{CO_{eq}}$ and larger $F_{CoC_{eq}}$ values compared with those of the corresponding axial constants (for which this effect is absent), and (2) the large metal—metal force constants for the Si—Co compounds.

The extremely large F_{SiCo} constants can thus be accounted for in terms of the through space interaction along with $d\pi$—σ^* interaction.

The $F_3CCo(CO)_4$ complex behaves, as far as the —$Co(CO)_4$ part of the molecule is concerned, as expected for a fluoride complex with no $d\pi$—$p\pi$ bonding, a strong electron withdrawing capacity, and a strong $d\pi$—σ^* interaction. Because of strong mixing between the CF stretching and bending modes we had to adjust $F_{5,8}$ and $F_{12,10}$ to get good agreement with the experimental vibrational data.

As can be seen from Table 6 all the bonding characteristics described for the cobalt complexes are also valid for the iron anion complex. The differences between the force constants of $Cl_3SiCo(CO)_4$ and the $[Cl_3SiFe(CO)_4]^-$ anion complex are small for the MX and metal—metal stretching modes, but strikingly large for the CO and FeC stretching modes. The extra electron in the iron complex is obviously located more in the CO region than on the Fe atom itself. The conclusion may be drawn that the effective charge on iron is closer to zero than to minus one.

The values of the force constants of the $[Cl_3SiFe(CO)_4]^-$ anion, i.e. smaller CO and Fe—Si and large FeC force constants, can only be explained by the role of the π-bonding system. This conclusion is completely the opposite to that reached by Risen [23] for some other $[X_3MFe(CO)_4]^-$ anions. The changes in the σ-bonding system apparently have no important influence on the force field parameters.

Conclusion

By a simplified approach to a very complicated bonding situation we have been able to show for the whole series of cobalt complexes, as well as for the iso-electronic iron anion complex, that changes in the π-bonding system are the most important in determining the intramolecular forces in the molecules.

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References

1 G.C. van den Berg, A. Oskam and K. Vrieze, J. Organometal. Chem., 57 (1973) 329.
2 G.C. van den Berg, A. Oskam and K. Vrieze, J. Organometal. Chem., 69 (1974) 169.
3 G.C. van den Berg and A. Oskam, J. Organometal. Chem., 78 (1974) 357.
4 B.J. Aylett and J.M. Campbell, J. Chem. Soc. A, (1969) 1910.
5 Inorg. Syn., Vol. 13.
6 W. Jetz and W.A.G. Graham, Inorg. Chem., 10 (1971) 4.
7 W. Jetz and W.A.G. Graham, Inorg. Chem., 10 (1971) 1647.
8 IUPAC Tables of Wavenumbers for the Calibration of Infrared Spectrometers, Butterworths, London, 1961.
9 O. Kahn and M. Bigorgne, J. Organometal. Chem., 10 (1967) 137.
10 A.G. Robiette, G.M. Sheldrick, R.N.F. Simpson, B.J. Aylett and J.A. Campbell, J. Organometal. Chem., 14 (1968) 279.
11 K. Emerson, P.R. Ireland and W.T. Robinson, Inorg. Chem., 9 (1970) 436.
12 B. Beagley, D.W.J. Cruickshank, P.M. Pinder, A.G. Robiette and G.M. Sheldrick, Acta Crystallogr., Sect. B, 25 (1969) 737.
13 E.B. Wilson, J.C. Decius and P.C. Cross, Molecular Vibrations, McGraw—Hill, New York, 1955.
14 H.J. Becher, Fortschr. Chem. Forsch., 10 (1967) 156.
15 F.A. Cotton and R.M. Wing, J. Organometal. Chem., 9 (1967) 511.
16 D.D. Spencer, J.L. Kirsch and T.L. Brown, Inorg. Chem., 9 (1970) 235.
17 T.L. Brown, P.A. Edwards, C.B. Harris and J.L. Kirsch, Inorg. Chem., 8 (1969) 763.
18 H.W. Spiess and R.K. Sheline, J. Chem. Phys., 53 (1970) 3036.
19 D.F. van de Vondel, H. Willemen and G.P. van der Kelen, J. Organometal. Chem., 63 (1973) 205.
20 P.J. Bassett and D.R. Lloyd, J. Chem. Soc. A, (1971) 641.
21 A.D. Berry, E.R. Corey, A.P. Hagen, A.G. MacDiarmid, F.E. Saalfield and B.B. Wayland, J. Amer. Chem. Soc., 92 (1970) 1940.
22 F.E. Saalfield, M.V. McDowell and A.G. MacDiarmid, J. Amer. Chem. Soc., 92 (1970) 2324.
23 W.M. Butler, W.A. McAllister and W.M. Risen, Inorg. Chem., 13 (1974) 1702.