Journal of Organometallic Chemistry, 78 (1974) 357—371

FORCE FIELDS OF $X_3MCo(CO)_4$ MOLECULES

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(Received April 25th, 1974)

Summary

Analysis of the complete vibrational spectra of a series of $X_3MCo(CO)_4$ molecules (M = Si, Ge, Sn; X = H, D, F, Cl, Br, I) has permitted valence force field calculations. The bonding forces can be interpreted in terms of a bonding scheme in which the metal—ligand backbonding proves to be the most important contributor. The metal—metal stretching force constant decreases in the series F > Cl > Br ≈ H, D > I for a particular metal. For a specific ligand X, the sequence is Ge > Si > Sn.

Introduction

In the last few years the growing interest in the nature of the metal—metal bond, especially between transition metals and Main Group IV elements has resulted in a number of papers being published [1]. Most of these articles have dealt with the vibrational spectra in the carbonyl stretching region and with force field calculations according to the Cotton—Kraihanzel method [2-5]. From these force fields, attempts were made to relate the changes in the carbonyl stretching force constants to bonding aspects in the metal—metal bond.

Fairly complete valence force field calculations for members of the series of $X_3MCo(CO)_4$ molecules have only been performed by Watters [6, 7] and Cyvin [8], although they used oversimplified structures with the equatorial carbonyl groups perpendicular to the molecular axis. More serious objections can be made against the method used by Watters; even in his two papers dealing with the same molecules, several numerical discrepancies can be observed and, moreover, no justification was given for the constraints in his force fields of the seven molecules. Furthermore, the calculations were based upon incorrect and

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incomplete vibrational assignments, as we have shown in two recent papers [1, 9].

Cyvin's paper also omits any description and justification of his calculation method and of the choice of the necessary constraints, and thus no significance can be attached to his force field data. Because the geometries of several molecules are now known, and as the complete series of molecules can now be treated as a whole, we have been able to calculate a reliable valence force field and to interprete the bonding forces in terms of the type of bonding.

Structures

Structural investigations have been performed for only a few members of the series of $X_3MCo(CO)_4$ molecules, viz. an electron diffraction study of $H_3SiCo(CO)_4$ [10] and X-ray analysis of $Cl_3SiCo(CO)_4$ [11] and $F_3SiCo(CO)_4$ [12], all showing a C_{3v} symmetry for the unimolecular species. This is confirmed by our determination of the crystal structure of $Cl_3GeCo(CO)_4$ [13]. There are only trivial differences between the structures of these complexes, except for a difference in the Si—Co distance of the hydride of 0.15 Å.

Since the vibrational spectra of all members of the series are very closely related, the same kind of structure is assumed throughout the whole series, and equivalent structural data for the —$Co(CO)_4$ parts of the molecules. The differences found in the metal—metal distances have been ignored, because the final force field parameters prove to be unaffected by these changes. Therefore, we have used the same values as Watters [6]. For the M—X distances we have chosen the mean values obtained for various MX_4 and MX_3Z compounds. All angles and distances are given in Table 1.

Coordinates

The C_{3v} symmetry of the unimolecular species gives rise to nine A_1-type and eleven E-type vibrations, all active in the infrared as well as in the Raman.

TABLE 1

MOLECULAR DATA FOR THE $X_3MCo(CO)_4$ MOLECULES

Bond lengths	r (Å)	Angles	
$Co—C_{eq}$	1.76	$C_{ax}—Co—C_{eq}$	95°
$Co—C_{ax}$	1.80	$C_{eq}—Co—C_{eq}$	119°15′
$C—O_{eq}$	1.15	$Co—C—O_{eq}$ and ax	180°
$C—O_{ax}$	1.14	$M—Co—C_{eq}$	85°
Si—Co	2.25	X—M—X	105°26′
Ge—Co	2.40	Co—M—X	113°15′
Sn—Co	2.50		
Ge—H	1.53		
Ge—F	1.67		
Ge—Cl	2.10		
Ge—Br	2.29		
Ge—I	2.49		
Si—Cl	2.03		
Sn—Cl	2.32		
Sn—Br	2.44		
Sn—I	2.69		

The two A_2-type vibrations are inactive. The set of 36 internal coordinates, as defined in Fig. 1, is not linearly independent and contains three redundant coordinates ($3n - 6 = 33$). The complete set of symmetry coordinates, listed in Table 2 together with the redundants, forms an orthonormal set and transforms according to the characters of the pointgroup C_{3v}, in contrast to the treatment of earlier publications [6, 7].

The inverse kinetic energy matrix *G* of the Wilson-*FG* method

Since the force field parameters and the *G*-matrix elements are numerically complementary, an exact definition of the *G*-matrix is essential. The internal *G*-matrix elements are taken from the paper of Decius [14]. The *G*-matrix in terms of symmetry coordinates is factorized in a 9×9 matrix of A_1 symmetry, a 2×2 matrix of A_2 symmetry and two identical 11×11 matrices of E symmetry. The elements of the *A* and *E* blocks are tabulated in Tables 3 and 4 respectively.

The force field

Force field calculations were performed by Wilson's *FG*-matrix method [15]. The force constants were calculated without anharmonicity corrections, and were obtained together with the calculated frequencies by an Algol computer program, suitable for a CDC 6400 computer. This program requires as input data the *G*-matrix elements as well as a "first-guess" starting force field.

The general quadratic valence force field of each complex with C_{3v} symmetry contains $45A_1 + 66E = 111$ parameters in terms of symmetry coordinates.

(continued on p. 363)

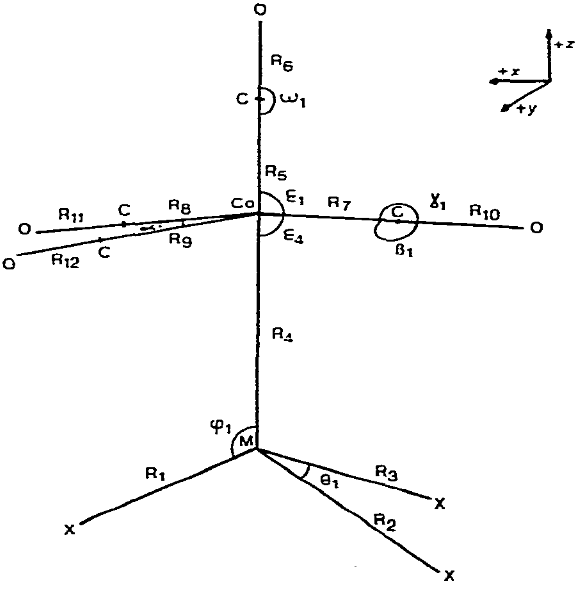

Fig. 1. The $X_3MCo(CO)_4$ staggered C_{3v} type molecule model. All the applied internal coordinates are indicated, except the torsional coordinate.

TABLE 2

SYMMETRY COORDINATES

A_1 vibrations:

$S_1 = \Delta r_6$
$S_2 = (\Delta r_{10} + \Delta r_{11} + \Delta r_{12})/\sqrt{3}$
$S_3 = (\Delta r_7 + \Delta r_8 + \Delta r_9)/\sqrt{3}$
$S_4 = \Delta r_5$
$S_5 = (\Delta r_1 + \Delta r_2 + \Delta r_3)/\sqrt{3}$
$S_6 = \Delta r_4$
$S_7 = (\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3)/\sqrt{3}$
$S_8 = [a(\Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3) - (\Delta\phi_1 + \Delta\phi_2 + \Delta\phi_3)]/\left\{3(1 + a^2)\right\}^{\frac{1}{2}}$
$S_9 = c(-\Delta\epsilon_1 - \Delta\epsilon_2 - \Delta\epsilon_3 + \Delta\epsilon_4 + \Delta\epsilon_5 + \Delta\epsilon_6) + b(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3)$

where $a = -3 \sin\phi \cdot \cos\phi/\sin\theta$; $b = -\frac{1}{2}\sqrt{3} \cos\epsilon \cdot \sin\epsilon/\sin\alpha$; $c = \frac{1}{4}\sqrt{2} \sin\epsilon/\sin\alpha$

E vibrations:

$S_{10a} = (2\Delta r_{10} - \Delta r_{11} - \Delta r_{12})/\sqrt{6}$
$S_{11a} = (2\Delta r_7 - \Delta r_8 - \Delta r_9)/\sqrt{6}$
$S_{12a} = (2\Delta r_1 - \Delta r_2 - \Delta r_3)/\sqrt{6}$
$S_{13a} = (2\Delta\gamma_1 - \Delta\gamma_2 - \Delta\gamma_3)/\sqrt{6}$
$S_{14a} = \Delta\omega_1$
$S_{15a} = (2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)/\sqrt{6}$
$S_{16a} = (2\Delta\theta_1 - \Delta\theta_2 - \Delta\theta_3)/\sqrt{6}$
$S_{17a} = (2\Delta\phi_1 - \Delta\phi_2 - \Delta\phi_3)/\sqrt{6}$
$S_{18a} = (2\Delta\epsilon_1 - \Delta\epsilon_2 - \Delta\epsilon_3)/\sqrt{6}$
$S_{19a} = (2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)\sqrt{6}$
$S_{20a} = (2\Delta\epsilon_4 - \Delta\epsilon_5 - \Delta\epsilon_6)/\sqrt{6}$
$S_{10b} = (\Delta r_{11} - \Delta r_{12})/\sqrt{2}$
$S_{11b} = (\Delta r_8 - \Delta r_9)/\sqrt{2}$
$S_{12b} = (\Delta r_2 - \Delta r_3)/\sqrt{2}$
$S_{13b} = (\Delta\gamma_2 - \Delta\gamma_3)/\sqrt{2}$
$S_{14b} = \Delta\omega_2$
$S_{15b} = (\Delta\beta_2 - \Delta\beta_3)/\sqrt{2}$
$S_{16b} = (\Delta\theta_2 - \Delta\theta_3)/\sqrt{2}$
$S_{17b} = (\Delta\phi_2 - \Delta\phi_3)/\sqrt{2}$
$S_{18b} = (\Delta\epsilon_2 - \Delta\epsilon_3)/\sqrt{2}$
$S_{19b} = (\Delta\alpha_2 - \Delta\alpha_3)/\sqrt{2}$
$S_{20b} = (\Delta\epsilon_5 - \Delta\epsilon_6)/\sqrt{2}$

A_2 vibrations:

$S_{21} = (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)/\sqrt{3}$

$S_{22} = \Delta\tau$

where τ is the torsional angle between MX_3 and $Co(CO)_{3\,eq}$

Redundancies:

$S' = (\Delta\epsilon_1 + \Delta\epsilon_2 + \Delta\epsilon_3 + \Delta\epsilon_4 + \Delta\epsilon_5 + \Delta\epsilon_6)/\sqrt{6} \equiv 0$
$S'' = \frac{1}{2}b\sqrt{2}(-\Delta\epsilon_1 - \Delta\epsilon_2 - \Delta\epsilon_3 + \Delta\epsilon_4 + \Delta\epsilon_5 + \Delta\epsilon_6) + c\sqrt{2}(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) \equiv 0$
$S''' = [a(\Delta\phi_1 + \Delta\phi_2 + \Delta\phi_3) + (\Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3)]/\left\{3(1 + a^2)\right\}^{\frac{1}{2}} \equiv 0$

TABLE 3. *G* MATRIX ELEMENTS FOR A_1 SPECIES[a]

$$G_{1,1} = \mu_{\mathrm{O}} + \mu_{\mathrm{C}}$$
$$G_{1,4} = -\mu_{\mathrm{C}}$$
$$G_{2,2} = \mu_{\mathrm{O}} + \mu_{\mathrm{C}}$$
$$G_{2,3} = -\mu_{\mathrm{C}}$$
$$G_{2,7} = 0$$
$$G_{2,9} = 0$$
$$G_{3,3} = \mu_{\mathrm{C}} + 3\cos^2\epsilon \cdot \mu_{\mathrm{Co}}$$
$$G_{3,4} = \sqrt{3}\mu_{\mathrm{Co}} \cdot \cos\epsilon$$
$$G_{3,6} = -\sqrt{3}\mu_{\mathrm{Co}} \cdot \cos\epsilon$$
$$G_{3,7} = 3\rho_{\mathrm{CoC_{eq}}} \cdot \mu_{\mathrm{Co}} \cdot \cos\epsilon \cdot \sin\epsilon$$
$$G_{3,9} = 3\rho_{\mathrm{CoC_{eq}}} \cdot \mu_{\mathrm{Co}} \cdot \cos\epsilon \cdot \sin\epsilon \left\{ \frac{1 + 2\cos\alpha}{1 + \cos\alpha} + \tfrac{1}{2}\sqrt{6}\,\frac{\sin\epsilon}{\sin\alpha} \right\}$$
$$G_{4,4} = \mu_{\mathrm{C}} + \mu_{\mathrm{Co}}$$
$$G_{4,6} = -\mu_{\mathrm{Co}}$$
$$G_{4,7} = \sqrt{3}\rho_{\mathrm{CoC_{eq}}} \cdot \mu_{\mathrm{Co}} \cdot \sin\epsilon$$
$$G_{4,9} = \sqrt{3}\rho_{\mathrm{CoC_{eq}}} \cdot \mu_{\mathrm{Co}} \cdot \sin\epsilon \left\{ \frac{1 + 2\cos\alpha}{1 + \cos\alpha} + \tfrac{1}{2}\sqrt{6}\,\frac{\sin\epsilon}{\sin\alpha} \right\}$$
$$G_{5,5} = \mu_{\mathrm{X}} + 3\cos^2\phi\mu_{\mathrm{M}}$$
$$G_{5,6} = \sqrt{3}\mu_{\mathrm{M}} \cdot \cos\phi$$
$$G_{5,8} = 3\rho_{\mathrm{MX}} \cdot \mu_{\mathrm{M}} \cdot \sin\phi \cdot \cos\phi \sqrt{\frac{3 + 5\cos\theta}{1 + \cos\theta}}$$
$$G_{6,6} = \mu_{\mathrm{M}} + \mu_{\mathrm{Co}}$$
$$G_{6,7} = -\sqrt{3}\rho_{\mathrm{CoC_{eq}}} \cdot \mu_{\mathrm{Co}} \cdot \sin\epsilon$$
$$G_{6,8} = \sqrt{3}\rho_{\mathrm{MX}} \cdot \mu_{\mathrm{M}} \cdot \sin\phi \sqrt{\frac{3 + 5\cos\theta}{1 + \cos\theta}}$$
$$G_{6,9} = -\sqrt{3}\rho_{\mathrm{CoCeq}} \cdot \mu_{\mathrm{Co}} \cdot \sin\epsilon \left\{ \frac{1 + 2\cos\alpha}{1 + \cos\alpha} + \tfrac{1}{2}\sqrt{6}\,\frac{\sin\epsilon}{\sin\alpha} \right\}$$
$$G_{7,7} = \rho^2_{\mathrm{CoC_{eq}}} \cdot \mu_{\mathrm{O}} + (\rho_{\mathrm{CO_{eq}}} + \rho_{\mathrm{CoC_{eq}}})^2 \mu_{\mathrm{C}} + (2 - 2\cos\alpha)\rho^2_{\mathrm{CoC_{eq}}} \cdot \mu_{\mathrm{Co}}$$
$$G_{7,9} = \left\{ 2(1 - \cos\alpha)\rho^2_{\mathrm{CoC_{eq}}} \cdot \mu_{\mathrm{Co}} + (\rho^2_{\mathrm{CoC_{eq}}} + \rho_{\mathrm{CoC_{eq}}} \cdot \rho_{\mathrm{CO_{eq}}})\mu_{\mathrm{C}} \right\} \left\{ \frac{1 + 2\cos\alpha}{1 + \cos\alpha} + \tfrac{1}{2}\sqrt{6}\,\frac{\sin\epsilon}{\sin\alpha} \right\}$$
$$G_{8,8} = \rho^2_{\mathrm{MX}}(\mu_{\mathrm{X}} + 3\sin^2\phi \cdot \mu_{\mathrm{M}}) \left\{ \frac{3 + 5\cos\theta}{1 + \cos\theta} \right\}$$
$$G_{9,9} = \left\{ 2\mu_{\mathrm{Co}} \cdot \rho^2_{\mathrm{CoC_{eq}}} (1 - \cos\alpha) + \mu_{\mathrm{C}} \cdot \rho^2_{\mathrm{CoC_{eq}}} \right\} \left\{ \frac{1 + 2\cos\alpha}{1 + \cos\alpha} + \tfrac{1}{2}\sqrt{6}\,\frac{\sin\epsilon}{\sin\alpha} \right\}^2$$

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[a] μ_i is the reciprocal of the mass of atom i and ρ_{ij} is the reciprocal of the distance between atoms i and j.

TABLE 4. *G*-MATRIX ELEMENTS FOR *E*-SPECIES[a]

$$G_{10,10} = \mu_{\mathrm{O}} + \mu_{\mathrm{C}}$$
$$G_{10,11} = -\mu_{\mathrm{C}}$$
$$G_{10,13} = 0$$
$$G_{10,15} = 0$$
$$G_{10,18} = 0$$
$$G_{10,19} = 0$$

$$G_{11,11} = \mu_{\mathrm{C}} + \mu_{\mathrm{Co}}(1 - \cos\alpha)$$
$$G_{11,13} = -\frac{3}{2}\rho_{\mathrm{CoC_{eq}}} \cdot \mu_{\mathrm{Co}} \cdot \sin\epsilon \cdot \cos\epsilon$$
$$G_{11,14} = -\frac{1}{2}\sqrt{6}\rho_{\mathrm{CoC_{ax}}} \cdot \mu_{\mathrm{Co}} \cdot \sin\epsilon$$
$$G_{11,15} = 0$$
$$G_{11,17} = -\frac{3}{2}\rho_{\mathrm{MCo}} \cdot \mu_{\mathrm{Co}} \cdot \sin\epsilon$$
$$G_{11,18} = \frac{3}{2}\rho_{\mathrm{CoC_{eq}}} \cdot \mu_{\mathrm{Co}} \cdot \sin\epsilon \left\{ \cos\epsilon - (\rho_{\mathrm{CoC_{ax}}}/\rho_{\mathrm{CoC_{eq}}}) \right\}$$
$$G_{11,19} = \rho_{\mathrm{CoC_{eq}}} \cdot \mu_{\mathrm{Co}}(1 - \cos\alpha)^2/\sin\alpha$$

TABLE 4 (continued)

$$G_{11,20} = -\tfrac{3}{2}\,\rho_{\mathrm{CoC_{eq}}}\cdot\mu_{\mathrm{Co}}\cdot\sin\epsilon\,\left\{\cos\epsilon + (\rho_{\mathrm{MCo}}/\rho_{\mathrm{CoC_{eq}}})\right\}$$

$$G_{12,12} = \mu_{\mathrm{X}} + \mu_{\mathrm{M}}(1-\cos\theta)$$

$$G_{12,16} = \rho_{\mathrm{MX}}\cdot\mu_{\mathrm{M}}(1-\cos\theta)^2/\sin\theta$$

$$G_{12,17} = \tfrac{3}{2}\,\rho_{\mathrm{MX}}\cdot\mu_{\mathrm{M}}\cdot\sin\phi(\cos\phi - \rho_{\mathrm{MCo}}/\rho_{\mathrm{MX}})$$

$$G_{12,20} = -\tfrac{3}{2}\,\rho_{\mathrm{MCo}}\cdot\mu_{\mathrm{M}}\cdot\sin\phi$$

$$G_{13,13} = \rho^2_{\mathrm{CO_{eq}}}\cdot\mu_{\mathrm{O}} + (\rho_{\mathrm{CO_{eq}}} + \rho_{\mathrm{CoC_{eq}}})^2\mu_{\mathrm{C}} + (\tfrac{1}{2} + \cos\alpha)\rho^2_{\mathrm{CoC_{eq}}}\cdot\mu_{\mathrm{Co}}$$

$$G_{13,14} = \tfrac{1}{2}\,\sqrt{6}\mu_{\mathrm{Co}}\cdot\rho_{\mathrm{CoC_{ax}}}\cdot\rho_{\mathrm{CoC_{eq}}}\cdot\cos\epsilon$$

$$G_{13,15} = 0$$

$$G_{13,17} = \tfrac{3}{2}\,\rho_{\mathrm{CoC_{eq}}}\cdot\rho_{\mathrm{MCo}}\cdot\mu_{\mathrm{Co}}\cdot\cos\epsilon$$

$$G_{13,18} = -\rho_{\mathrm{CoC_{eq}}}\,\left\{(\rho_{\mathrm{CoC_{eq}}} + \rho_{\mathrm{CO_{eq}}})\mu_{\mathrm{C}} + (\tfrac{3}{2}\cos^2\epsilon\cdot\rho_{\mathrm{CoC_{eq}}} - \tfrac{3}{2}\cos\epsilon\cdot\rho_{\mathrm{CoC_{ax}}})\mu_{\mathrm{Co}}\right\}$$

$$G_{13,19} = \tfrac{3}{2}\cos\epsilon\cdot\sin\epsilon\cdot\rho_{\mathrm{CoC_{eq}}}\,\left\{(\rho_{\mathrm{CoC_{eq}}} + \rho_{\mathrm{CO_{eq}}})\mu_{\mathrm{c}} - (1-\cos\alpha)\rho_{\mathrm{CoC_{eq}}}\cdot\mu_{\mathrm{Co}}\right\}/\sin\alpha$$

$$G_{13,20} = \rho_{\mathrm{CoC_{eq}}}\,\left\{(\rho_{\mathrm{CoC_{eq}}} + \rho_{\mathrm{CO_{eq}}})\mu_{\mathrm{C}} + (\tfrac{3}{2}\cos^2\epsilon\cdot\rho_{\mathrm{CoC_{eq}}} + \tfrac{3}{2}\cos\epsilon\cdot\rho_{\mathrm{MCo}})\mu_{\mathrm{Co}}\right\}$$

$$G_{14,14} = \rho^2_{\mathrm{CO_{ax}}}\cdot\mu_{\mathrm{O}} + (\rho_{\mathrm{CO_{ax}}} + \rho_{\mathrm{CoC_{ax}}})^2\,\mu_{\mathrm{C}} + \rho^2_{\mathrm{CoC_{ax}}}\cdot\mu_{\mathrm{Co}}$$

$$G_{14,15} = 0$$

$$G_{14,17} = \tfrac{1}{2}\sqrt{6}\rho_{\mathrm{CoC_{ax}}}\cdot\rho_{\mathrm{MCo}}\cdot\mu_{\mathrm{Co}}$$

$$G_{14,18} = \tfrac{1}{2}\,\sqrt{6}\rho_{\mathrm{CoC_{ax}}}\,\left\{(\rho_{\mathrm{CoC_{ax}}} - \rho_{\mathrm{CoC_{eq}}}\cdot\cos\epsilon)\mu_{\mathrm{Co}} + (\rho_{\mathrm{CoC_{ax}}} + \rho_{\mathrm{CO_{ax}}})\mu_{\mathrm{C}}\right\}$$

$$G_{14,19} = \tfrac{1}{2}\sqrt{6}\,\sin\epsilon(\cos\alpha - 1)\rho_{\mathrm{CoC_{eq}}}\cdot\rho_{\mathrm{CoC_{ax}}}\cdot\mu_{\mathrm{Co}}/\sin\alpha$$

$$G_{14,20} = \tfrac{1}{2}\,\sqrt{6}\rho_{\mathrm{CoC_{ax}}}\cdot\mu_{\mathrm{Co}}(\rho_{\mathrm{MCo}} + \cos\epsilon\cdot\rho_{\mathrm{CoC_{eq}}})$$

$$G_{15,15} = \rho^2_{\mathrm{CO_{eq}}}\cdot\mu_{\mathrm{O}} + (\rho_{\mathrm{CO_{eq}}} + \rho_{\mathrm{CoC_{eq}}})^2\mu_{\mathrm{C}} + \tfrac{3}{2}\,\rho^2_{\mathrm{CoC_{eq}}}\cdot\mu_{\mathrm{Co}}$$

$$G_{15,17} = 0$$

$$G_{15,18} = 0$$

$$G_{15,19} = 0$$

$$G_{15,20} = 0$$

$$G_{16,16} = \rho^2_{\mathrm{MX}}\,\left\{\mu_{\mathrm{X}}\;\frac{2+\cos\theta}{1+\cos\theta} + \mu_{\mathrm{M}}\;\frac{(1-\cos\theta)^3}{\sin^2\theta}\right\}$$

$$G_{16,17} = -\tfrac{3}{2}\sin\phi\cdot\cos\phi\cdot\rho^2_{\mathrm{MX}}\,\left\{\mu_{\mathrm{X}} - \mu_{\mathrm{M}}(\cos\phi - \rho_{\mathrm{MCo}}/\rho_{\mathrm{MX}})\,(1-\cos\theta)/\cos\phi\right\}/\sin\theta$$

$$G_{16,20} = \tfrac{3}{2}\sin\phi(\cos\theta - 1)\rho_{\mathrm{MX}}\cdot\rho_{\mathrm{MCo}}\cdot\mu_{\mathrm{M}}/\sin\theta$$

$$G_{17,17} = \rho^2_{\mathrm{MX}}\,\left\{\mu_{\mathrm{X}} + \tfrac{3}{2}\mu_{\mathrm{M}}(\cos\phi - \rho_{\mathrm{MCo}}/\rho_{\mathrm{MX}})^2 + \tfrac{3}{2}\mu_{\mathrm{Co}}(\rho_{\mathrm{MCo}}/\rho_{\mathrm{MX}})^2\right\}$$

$$G_{17,18} = \tfrac{3}{2}(\rho_{\mathrm{CoC_{ax}}} - \rho_{\mathrm{CoC_{eq}}}\cdot\cos\epsilon)\rho_{\mathrm{MCo}}\cdot\mu_{\mathrm{Co}}$$

$$G_{17,19} = \tfrac{3}{2}\,\sin\epsilon(\cos\alpha - 1)\rho_{\mathrm{CoC_{eq}}}\cdot\rho_{\mathrm{MCo}}\cdot\mu_{\mathrm{Co}}/\sin\alpha$$

$$G_{17,20} = \tfrac{3}{2}\rho_{\mathrm{MCo}}\,\left\{(\rho_{\mathrm{MCo}} - \rho_{\mathrm{MX}}\cdot\cos\phi)\mu_{\mathrm{M}} + (\rho_{\mathrm{MCo}} + \rho_{\mathrm{CoC_{eq}}}\cdot\cos\epsilon)\mu_{\mathrm{Co}}\right\}$$

$$G_{18,18} = \rho^2_{\mathrm{CoC_{eq}}}\,\left\{\mu_{\mathrm{C}} + \tfrac{3}{2}\,\mu_{\mathrm{Co}}\,(\cos\epsilon - \rho_{\mathrm{CoC_{ax}}}/\rho_{\mathrm{CoC_{eq}}})^2 + \tfrac{3}{2}\mu_{\mathrm{C}}(\rho_{\mathrm{CoC_{ax}}}/\rho_{\mathrm{CoC_{eq}}})^2\right\}$$

$$G_{18,19} = -\tfrac{3}{2}\sin\epsilon\cdot\cos\epsilon\cdot\rho^2_{\mathrm{CoC_{eq}}}\,\left\{\mu_{\mathrm{C}} - \mu_{\mathrm{Co}}(\cos\epsilon - \rho_{\mathrm{CoC_{ax}}}/\rho_{\mathrm{CoC_{eq}}})\,(1-\cos\alpha)/\cos\epsilon\right\}/\sin\alpha$$

$$G_{18,20} = -\rho^2_{\mathrm{CoC_{eq}}}\,\left\{\mu_{\mathrm{C}} + \tfrac{3}{2}\,\mu_{\mathrm{Co}}\,(\cos\epsilon - \rho_{\mathrm{CoC_{ax}}}/\rho_{\mathrm{CoC_{eq}}})\,(\cos\epsilon + \rho_{\mathrm{MCo}}/\rho_{\mathrm{CoC_{eq}}})\right\}$$

$$G_{19,19} = \rho^2_{\mathrm{CoC_{eq}}}\,\left\{\mu_{\mathrm{C}}\left(\frac{2+\cos\alpha}{1+\cos\alpha}\right) + \mu_{\mathrm{Co}}\,\frac{(1-\cos\alpha)^3}{\sin^2\alpha}\right\}$$

$$G_{19,20} = \tfrac{3}{2}\cos\epsilon\cdot\sin\epsilon\cdot\rho^2_{\mathrm{CoC_{eq}}}\,\left\{\mu_{\mathrm{C}} - \mu_{\mathrm{Co}}\,(\cos\epsilon + \rho_{\mathrm{MCo}}/\rho_{\mathrm{CoC_{eq}}})\,(1-\cos\alpha)/\cos\epsilon\right\}/\sin\alpha$$

$$G_{20,20} = \rho^2_{\mathrm{CoC_{eq}}}\,\left\{\mu_{\mathrm{C}} + \tfrac{3}{2}\,\mu_{\mathrm{Co}}(\cos\epsilon + \rho_{\mathrm{MCo}}/\rho_{\mathrm{CoC_{eq}}})^2 + \tfrac{3}{2}\,\mu_{\mathrm{M}}\,(\rho_{\mathrm{MCo}}/\rho_{\mathrm{CoC_{eq}}})^2\right\}$$

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[a] μ_i is the reciprocal of the mass of atom i and ρ_{ij} the reciprocal of the distance between atoms i and j.

The number of available data is not sufficient to fit all the parameters for each molecule. Therefore, we have to constrain our force field. This constrained valence force field was obtained by the following general assumptions:

(1) All bend—bend interaction constants are taken as zero.

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

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

(4) The signs of the interaction constants are confirmed by Hybrid Orbital Following arguments.

For the discussion of the restrictions in detail, we divide the molecules into several parts.

The —Co(CO)$_4$ part

The force field parameters in the cobalt tetracarbonyl part of the molecules were fixed as far as possible. This fixing was not successful for the CO stretching diagonal force constants nor, although to a lesser extent, for the CoC stretching constants. The reason for this will be discussed within the framework of the bonding scheme. The starting values of the diagonal and the off-diagonal elements in terms of internal coordinates for a "first-guess" force field, have been taken from Jones's calculations for the parent molecules $M(CO)_6$, $M(CO)_5$ and $M(CO)_4$ [16]. Small corrections were applied for the changes in the bonding angles of our molecules with respect to these latter. We chose the off-diagonal elements following the same arguments as Jones, contrary to the Cotton—Kraihanzel method [17, 18].

The MX$_3$ part

The starting diagonal force constants were taken from general valence force field calculations on the parent MX_4 molecules [19, 20] and other MX_3Z molecules [21, 22] as far as the f_{MX}, f_{MX_3} and $f_{MX,\,MX}$ constants are concerned. Force constants were introduced by combining both the above parts. Among these are the diagonal force constants f_{MCo}, f_{XMCo} and f_{MCoC}.

The f_{MCo} starting values are taken from Watters [6, 7]. For the interaction constants $f_{MX,\,MCo}$, $f_{MX,\,MX_3}$ and $f_{MCo,\,MX_3}$, we used the assertion of Becher [24], that in a series of closely related molecules the following relations between diagonal and off-diagonal elements in terms of symmetry coordinates can be used:

$F_{ij} = q_{ij}\sqrt{F_{ii} \times F_{jj}}$ (q_{ij} is constant through the whole series).

In order for our first assumption, that all bend—bend interactions are zero, to hold the following relations must be valid:

$F_{8,8} = 0.56\ F_{16,16} + 0.44\ F_{17,17}$. $F_{9,9} = 0.5\ F_{18,18} + 0.5\ F_{20,20}$.

For several members of this series of molecules, the assumption can only be maintained by introducing a Van der Waals interaction between the MX_3 group and the equatorial CO groups. The order of magnitude of this interaction ($F_{8,9}$ and $F_{17,20}$) is determined by the distance between the halogen atoms and the equatorial carbon atoms. However, it was still necessary to introduce a very

TABLE 5

RELATIONS BETWEEN SYMMETRY FORCE CONSTANTS AND VALENCE FORCE CONSTANTS

A_1 block

$F_{1,1} = f_{\mathrm{CO_{ax}}}$

$F_{1,2} = \sqrt{3} f_{\mathrm{CO_{ax}},\, \mathrm{CO_{eq}}}$

$F_{1,3} = \sqrt{3} f_{\mathrm{CO_{ax}},\, \mathrm{CoC_{eq}}}$

$F_{1,4} = f_{\mathrm{CO_{ax}},\, \mathrm{CoC_{ax}}}$

$F_{2,2} = f_{\mathrm{CO_{eq}}} + 2 f_{\mathrm{CO_{eq}},\, \mathrm{CO_{eq}}}$

$F_{2,3} = f_{\mathrm{CO_{eq}},\, \mathrm{CoC_{eq}}} + 2 f_{\mathrm{CO_{eq}},\, \mathrm{CoC'_{eq}}}$

$F_{2,4} = \sqrt{3} f_{\mathrm{CO_{eq}},\, \mathrm{CoC_{ax}}}$

$F_{3,3} = f_{\mathrm{CoC_{eq}}} + 2 f_{\mathrm{CoC_{eq}},\, \mathrm{CoC_{eq}}}$

$F_{3,4} = \sqrt{3} f_{\mathrm{CoC_{eq}},\, \mathrm{CoC_{ax}}}$

$F_{4,4} = f_{\mathrm{CoC_{ax}}}$

$F_{4,6} = f_{\mathrm{CoC_{ax}},\, \mathrm{MCo}}$

$F_{4,7} = \sqrt{3} f_{\mathrm{CoC_{ax}},\, \mathrm{CoCO_{out}}}$

$F_{5,5} = f_{\mathrm{MX}} + 2 f_{\mathrm{MX},\, \mathrm{MX}}$

$F_{5,6} = \sqrt{3} f_{\mathrm{MX},\, \mathrm{MCo}}$

$$F_{5,8} = \frac{a}{\sqrt{(1+a^2)}} \left(f_{\mathrm{MX},\, \mathrm{X'MX''}} + 2 f_{\mathrm{MX},\, \mathrm{X'MX}}\right) - \frac{1}{\sqrt{(1+a^2)}} \left(f_{\mathrm{MX},\, \mathrm{XMCo}} + 2 f_{\mathrm{MX},\, \mathrm{X'MCo}}\right)$$

$F_{6,6} = f_{\mathrm{MCo}}$

$$F_{6,8} = \frac{a\sqrt{3}}{\sqrt{(1+a^2)}} f_{\mathrm{MCo},\, \mathrm{XMX}} - \frac{\sqrt{3}}{\sqrt{(1+a^2)}} f_{\mathrm{MCo},\, \mathrm{XMCo}}$$

$F_{7,7} = f_{\mathrm{CoCO_{out}}} + 2 f_{\mathrm{CoCO_{out}},\, \mathrm{CoCO_{out}}}$

$F_{8,8} = 0.56\, f_{\mathrm{XMX}} + 0.44\, f_{\mathrm{XMCo}}$

$F_{8,9} =$ Van der Waals

$F_{9,9} = 0.5\, f_{\mathrm{C_{ax}CoC_{eq}}} + 0.5\, f_{\mathrm{MCoC_{eq}}}$

E Block

$F_{10,10} = f_{\mathrm{CO_{eq}}} - f_{\mathrm{CO_{eq}},\, \mathrm{CO_{eq}}}$

$F_{10,11} = f_{\mathrm{CoC_{eq}},\, \mathrm{CO_{eq}}} - f_{\mathrm{CO_{eq}},\, \mathrm{CoC'_{eq}}}$

$F_{11,11} = f_{\mathrm{CoC_{eq}}} - f_{\mathrm{CoC_{eq}},\, \mathrm{CoC_{eq}}}$

$F_{11,14} = \sqrt{6}/3 f_{\mathrm{CoC'_{eq}},\, \mathrm{CoCO_{ax}}} - \sqrt{6}/3 f_{\mathrm{CoC''_{eq}},\, \mathrm{CoCO_{ax}}}$

$F_{12,12} = f_{\mathrm{MX}} - f_{\mathrm{MX},\, \mathrm{MX}}$

$F_{13,13} = f_{\mathrm{CoCO_{out}}} - f_{\mathrm{CoCO_{out}},\, \mathrm{CoCO_{out}}}$

$F_{14,14} = f_{\mathrm{CoCO_{ax}}}$

$F_{15,15} = f_{\mathrm{CoCO_{in}}}$

$F_{16,16} = f_{\mathrm{XMX}}$

$F_{17,17} = f_{\mathrm{XMCo}}$

$F_{17,20} =$ Van der Waals

$F_{18,18} = f_{\mathrm{C_{ax}CoC_{eq}}}$

$F_{19,19} = f_{\mathrm{C_{eq}CoC_{eq}}}$

$F_{20,20} = f_{\mathrm{MCoC_{eq}}}$

TABLE 6a

THE FIXED SYMMETRY FORCE CONSTANTS FOR ALL MOLECULES IN MDYN/Å

$F_{1,2} = 0.20$
$F_{1,3} = -0.17$
$F_{1,4} = 0.55$
$F_{2,3} = 0.41$
$F_{2,4} = -0.17$
$F_{3,4} = 0.05$
$F_{4,6} = 0$
$F_{4,7} = -0.10$

$F_{7,7} = 0.62$
$F_{10,11} = 0.62$
$F_{11,14} = 0.10$
$F_{13,13} = 0.75$
$F_{14,14} = 0.55$
$F_{15,15} = 0.35$
$F_{18,18} = 0.40$
$F_{19,19} = 0.09$

small difference between $F_{7,7}$ and $F_{13,13}$, both standing for the f_{CoCO} out of plane bending constant, which means that an $f_{\mathrm{CoCO\text{-}out,\,CoCO\text{-}out}}$ interaction constant with a very small negative value had to be introduced. Otherwise the vibrational assignment would have had to be reversed, contrary to the experimental depolarization ratio obtained. These assumptions lead to a force field of 34 parameters with physical significance. The calculations are then carried out with the set of symmetry coordinates as basis set. The relations between the calculated force constants in terms of symmetry coordinates and the internal valence force constants are given in Table 5. In these relations all the neglected bend-bend interactions are omitted.

The calculated fixed and non-fixed symmetry force constants are tabulated in Tables 6a and 6b, respectively. The calculated vibrational frequencies are listed in Table 7, together with experimental published values [1, 9].

(continued on p. 369)

TABLE 6b

THE NON-FIXED SYMMETRY FORCE CONSTANTS IN MDYN/Å

F	H_3Ge or D_3Ge	F_3Ge	Cl_3Ge	Br_3Ge	I_3Ge	Cl_3Si	Cl_3Sn	Br_3Sn	I_3Sn
1, 1	17.05	17.70	17.45	17.40	17.30	17.35	17.45	17.35	17.25
2, 2	17.05	17.65	17.45	17.40	17.30	17.35	17.40	17.35	17.25
3, 3	3.10	2.75	2.90	2.90	2.90	2.90	2.90	2.90	2.90
4, 4	2.50	2.05	2.25	2.25	2.25	2.25	2.25	2.25	2.25
5, 5	2.53	4.65	2.76	2.55	2.10	3.30	2.40	2.25	2.0
5, 6	0.24	0.36	0.27	0.25	0.18	0.29	0.24	0.22	0.18
5, 8	0.14	0.28	0.20	0.15	0.13	0.26	0.16	0.14	0.12
6, 6	1.30	1.73	1.52	1.30	0.85	1.45	1.30	1.20	0.85
6, 8	− 0.12	− 0.22	− 0.18	− 0.14	− 0.10	− 0.21	− 0.15	− 0.13	− 0.10
8, 8	0.40	0.85	0.74	0.46	0.41	0.98	0.52	0.42	0.37
8, 9	0	0	− 0.13	− 0.16	− 0.14	− 0.14	− 0.10	− 0.14	− 0.10
9, 9	0.33	0.36	0.35	0.33	0.33	0.35	0.35	0.33	0.32
10,10	16.55	17.15	16.95	16.90	16.80	16.85	16.90	16.85	16.75
11,11	2.45	2.10	2.20	2.20	2.20	2.20	2.20	2.20	2.20
12,12	2.54	3.90	2.05	1.65	1.35	2.25	2.00	1.63	1.35
16,16	0.40	1.10	0.85	0.64	0.58	1.15	0.68	0.58	0.55
17,17	0.46	0.59	0.54	0.30	0.26	0.60	0.40	0.26	0.24
17,20	0	0	− 0.10	− 0.12	− 0.10	− 0.12	− 0.08	− 0.11	− 0.08
20,20	0.30	0.35	0.32	0.26	0.24	0.32	0.32	0.26	0.24

TABLE 7

VIBRATIONAL FREQUENCIES CALCULATED FOR SOME $X_3MCo(CO)_4$ MOLECULES

Mode	$H_3GeCo(CO)_4$			$D_3GeCo(CO)_4$			$F_3GeCo(CO)_4$		
	ν_{exp}	ν_{calc}	Δ	ν_{exp}	ν_{calc}	Δ	ν_{exp}	ν_{calc}	Δ
$\nu(CO)A_1$	2105	2105	0	2103	2104	− 1	2135	2133	+ 2
$\nu(CO)A_1$	2054	2050	+ 4	2047	2050	− 3	2085	2080	+ 5
$\nu(CO)E$	2036	2031	+ 5	2033	2031	+ 2	2060	2060	0
$\delta(CoCO_{out})E$	565	558	+ 7	565	558	+ 7	553	559	− 6
$\delta(CoCO_{out})A_1$	555	550	+ 5	552	549	+ 3	553	550	+ 3
$\delta(CoCO_{ax}) + \nu(CoC_{eq})E$	500	493	+ 7	505	506	− 1	484	482	+ 2
$\nu(CoC_{eq}) + \delta(CoCO_{ax})E$	478	473	+ 5	485	473	+12	466	463	+ 3
$\nu(CoC_{ax})A_1$	464	467	− 3	467	467	0	440	440	0
$\nu(CoC_{eq})A_1$	420	424	− 4	420	424	− 4	411	401	+10
$\delta(CoCO_{in})E$	370	368	+ 2	368	368	0	370	368	+ 2
$\nu(MX)E$	2083	2087	− 4	1495	1492	+ 3	690	688	+ 2
$\nu(MX)A_1$.	2070	2072	− 2	1474	1471	+ 3	675	671	+ 4
$\nu(MCo)A_1$	223	222	+ 1	223	221	+ 2	222	218	+ 4
$\delta(MX_3)E$	872	869	+ 3	624	618	+ 6	313	316	− 3
$\delta(MX_3)A_1$	805	810	− 5	588	583	+ 5	313	313	0
$\delta(CCoC)E$	128	121	+ 7	128	121	+ 7	122	118	+ 4
$\delta(CCoC)E$	104	100	+ 4	104	100	+ 4	104	101	+ 3
$\delta(CCoC)A_1$	84	91	− 7	84	91	− 7	90	91	− 1
$\delta(XMCo)E$	532	534	− 2	383	378	+ 5	164	170	− 6
$\delta(MCoC)E$	66	67	− 1	63	66	− 3	63	60	+ 3
	Δtot = 78 Δmean = 3.90			Δtot = 78 Δmean = 3.90			Δtot = 63 Δmean = 3.15		
	$Cl_3GeCo(CO)_4$			$Br_3GeCo(CO)_4$			$I_3GeCo(CO)_4$		
$\nu(CO)A_1$	2124	2124	0	2121	2121	0	2115	2115	0
$\nu(CO)A_1$	2071	2069	+ 2	2067	2066	+ 1	2063	2061	+ 2
$\nu(CO)E$	2052	2050	+ 2	2049	2047	+ 2	2042	2041	+ 1
$\delta(CoCO_{out})E$	557	558	− 1	554	557	− 3	550	556	− 6
$\delta(CoCO_{out})A_1$	548	551	− 3	548	547	+ 1	543	543	0
$\delta(CoCO_{ax}) + \nu(CoC_{eq})E$	488	485	+ 3	486	484	+ 2	487	484	+ 3
$\nu(CoC_{eq}) + \delta(CoCO_{ax})E$	464	469	− 5	460	468	− 8	458	468	−10
$\nu(CoC_{ax})A_1$	443	452	− 9	442	450	− 8	445	446	− 1
$\nu(CoC_{eq})A_1$	416	411	+ 5	410	411	− 1	410	411	− 1

$\delta(\mathrm{CoCO_{in}})E$	370	368	+ 2	368	368	0	368	368	0
$\nu(\mathrm{MX})E$	407	408	− 1	302	300	+ 2	253	252	+ 1
$\nu(\mathrm{MX})A_1$	392	394	− 2	292	289	+ 3	241	236	+ 5
$\nu(\mathrm{MCo})A_1$	242	244	− 2	199	203	− 4	161	161	0
$\delta(\mathrm{MX_3})E$	162	165	− 3	97	92	+ 5	82	66	+16
$\delta(\mathrm{MX_3})A_1$	162	152	+10	82	83	− 1	65	62	+ 3
$\delta(\mathrm{CCoC})E$	123	126	− 3	125	121	+ 4	124	121	+ 3
$\delta(\mathrm{CCoC})E$	108	104	+ 4	107	100	+ 7	108	100	+ 8
$\delta(\mathrm{CCoC})A_1$	81	86	− 5	68	79	−11	70	77	− 7
$\delta(\mathrm{XMCo})E$	90	97	− 7	44	44	0	43	36	+ 7
$\delta(\mathrm{MCoC})E$	58	53	+ 5	57	54	+ 3	55	48	+ 7
	Δtot = 74 Δmean = 3,70			Δtot = 66 Δmean = 3,30			Δtot = 81 Δmean = 4,05		

	$\mathrm{Cl_3SnCo(CO)_4}$			$\mathrm{Br_3SnCo(CO)_4}$			$\mathrm{I_3SnCo(CO)_4}$		
$\nu(\mathrm{CO})A_1$	2123	2121	+ 2	2119	2118	+ 1	2112	2112	0
$\nu(\mathrm{CO})A_1$	2070	2069	+ 1	2065	2063	+ 2	2060	2057	+ 3
$\nu(\mathrm{CO})E$	2049	2047	+ 2	2045	2044	+ 1	2037	2037	0
$\delta(\mathrm{CoCO_{out}})E$	558	558	0	552	557	− 5	549	556	− 7
$\delta(\mathrm{CoCO_{out}})A_1$	548	548	0	545	545	0	542	542	0
$\delta(\mathrm{CoCO_{ax}}) + \nu(\mathrm{CoC_{eq}})E$	488	485	+ 3	487	484	+ 3	488	484	+ 4
$\nu(\mathrm{CoC_{eq}}) + \delta(\mathrm{CoCO_{ax}})E$	459	468	− 9	460	468	− 8	459	468	− 9
$\nu(\mathrm{CoC_{ax}})A_1$	446	450	− 4	444	449	− 5	449	446	+ 3
$\nu(\mathrm{CoC_{eq}})A_1$	416	411	+ 5	410	411	− 1	410	411	− 1
$\delta(\mathrm{CoCO_{in}})E$	370	368	+ 2	366	368	− 2	366	368	− 2
$\nu(\mathrm{MX})E$	364	366	− 2	259	258	+ 1	216	212	+ 4
$\nu(\mathrm{MX})A_1$	353	355	− 2	250	247	+ 3	204	202	+ 2
$\nu(\mathrm{MCo})A_1$	205	201	+ 4	186	188	− 2	158	158	0
$\delta(\mathrm{MX_3})E$	135	131	+ 4	88	81	+ 7	64	60	+ 4
$\delta(\mathrm{MX_3})A_1$	112	116	− 4	80	73	+ 7	57	54	+ 3
$\delta(\mathrm{CCoC})E$	124	123	+ 1	124	121	+ 3	122	121	+ 1
$\delta(\mathrm{CCoC})E$	106	101	+ 5	107	100	+ 7	103	99	+ 4
$\delta(\mathrm{CCoC})A_1$	75	83	− 8	74	78	− 4	76	76	0
$\delta(\mathrm{XMCo})E$	88	80	+ 8	47	40	+ 7	39	32	+ 7
$\delta(\mathrm{MCoC})E$	59	51	+ 8	52	50	+ 2	50	48	+ 2
	Δtot = 74 Δmean = 3,70			Δtot = 71 Δmean = 3,55			Δtot = 56 Δmean = 2,80		

(continued)

TABLE 7 (continued)

Mode	$Cl_3SiCo(CO)_4$		
	ν_{exp}	ν_{calc}	Δ
$\nu(CO)A_1$	2119	2118	+ 1
$\nu(CO)A_1$	2066	2063	+ 3
$\nu(CO)E$	2040	2040	0
$\delta(CoCO_{out})E$	560	558	+ 2
$\delta(CoCO_{out})A_1$	551	562	−11
$\delta(CoCO_{ax}) + \nu(CoC_{eq})E$	485	485	0
$\nu(CoC_{eq}) + \delta(CoCO_{ax})E$	472	469	+ 3
$\nu(CoC_{ax})A_1$	440	450	−10
$\nu(CoC_{eq})A_1$	414	411	+ 3
$\delta(CoCO_{in})E$	373	368	+ 5
$\nu(MX)E$	571	568	+ 3
$\nu(MX)A_1$	506	505	+ 1
$\nu(MCO)A_1$	308	309	− 1
$\delta(MX_3)E$	202	205	− 3
$\delta(MX_3)A_1$	181	171	+10
$\delta(CCoC)E$	120	112	+ 8
$\delta(CCoC)E$	103	100	+ 3
$\delta(CCoC)A_1$	86	89	− 3
$\delta(XMCo)E$	137	133	+ 4
$\delta(MCoC)E$	59	55	+ 4
	$\Delta tot = 78$ $\Delta mean = 3.90$		

Discussion

The most striking features of Table 6b are the variations in the stretching force constants of the metal—metal bonds, ($F_{6,6}$), of the C—O bonds, ($F_{1,1}$ and $F_{2,2}$) and to a lesser extent of the Co—C bonds, ($F_{3,3}$ and $F_{4,4}$). The strength of the metal—metal bond decreases with decreasing electron withdrawing capacity of the MX_3 group except for the hydride complex. This sequence in the force constants can only be explained by a relatively strong influence of the π-bonding system, as shown by the following analysis.

The diminishing π-backbonding causes a shift in the electron density from the antibonding carbonyl orbital to the metal—metal bond, which strengthens this bond and also the C—O bond, and weakens the Co—C bond, thus leading to an increase in $F_{M,M}$ and F_{CO} and a decrease in F_{CoC}. Thus the strong metal—metal bond in the trifluorogermyl compound may be caused by lack of transferability of electron density from the metal—metal bond due to the absence of $d\pi$—$p\pi$ bonding between Ge and F, which itself is associated with the strong electronegativity of the F atom. The weakening of the Ge—F bond with respect to the bond in fluorogermanes [19, 23] can be explained by an extra $d\pi$—σ* bonding between Co and Ge, as proposed by Cotton for $CF_3Mn(CO)_5$ [25] and by MacDiarmid [26] (from MO calculations) for $SiF_3Co(CO)_4$. The difficulty of $d\pi$—$p\pi$ bonding can also be used to explain the unexpectedly strong Ge—Co bond in the germyl complex, although the electronegativity of bromine is greater than that of hydrogen. The metal—metal bond strengths of the trichloro compounds show an irregular order compared with that of Watters [6, 7]. The Si—Co bond is weaker than might be at first expected. The small $f_{Si—Co}$ in the series suggests a stronger $d\pi$—$p\pi$ bonding between Si and Cl, competing with the $d\pi_{Si}$—$d\pi_{Co}$ bonding. This relatively strong $d\pi$—$p\pi$ bonding character, especially in the $SiCl_3$ compound, has also been revealed by analysis of photoelectron spectra, dissociation energies [27], NQR studies [28, 29] and ^{59}Co NMR paramagnetic shift measurements [30]. Table 6b also shows the sequence of $F_{CO_{ax}}$ and $F_{CO_{eq}}$, which is the same as for the metal—metal bond. This is consistent with the mutually inverse trends along the series for the CO and CoC bonds observed from the calculations, and also from the finding that $f_{CO_{ax}} > f_{CO_{eq}}$, while $f_{CoC_{ax}} < f_{CoC_{eq}}$.

An explanation can be found in the participation of the d orbitals of cobalt in the π-interactions. In the axial group, bonding mainly involves the d_{xz} and d_{yz} orbitals. In the equatorial group, four d orbitals (d_{xz}, d_{yz}, d_{xy} and $d_{x^2-y^2}$) are involved, shared however by three carbonyl groups. Therefore, the changes along the series in the axial and in the equatorial force constants are of the same order of magnitude.

Further evidence for the importance of π-backbonding is provided by the larger values of the $f_{CoC_{eq}, CoC_{eq}}$ and $f_{CO_{eq}, CO_{eq}}$ force constants compared to those of $f_{CoC_{eq}, CoC_{ax}}$ and $f_{CO_{eq}, CO_{ax}}$ respectively. The interaction constant $f_{CO_{eq}, CO_{ax}}$ is certainly not zero in this kind of five-coordinate complex, since only a strong mixing between the two C—O stretching modes in the A_1 species can explain the abnormal infrared activities and Raman depolarization ratio which we discussed previously [1]. According to Bor [5], these vibrations have to be assigned to in-phase and out-of-phase combinations. These features are not consistent with changes in the σ-skeleton [31].

From our calculated L matrix, which transforms symmetry into normal coordinates, we deduce that there is a mixing of 50% between the CO stretching modes of A_1 symmetry and of 10% between the Co—C stretching modes of A_1 symmetry. $F_{\mathrm{CoC_{ax}},\,\mathrm{MCo}}$ ($F_{4,6}$) is taken to be zero, since small values (up to 0.1) did not have any influence on the calculated vibrational frequencies.

The final set force constants were not very different from our first-guess constants. All the stretch-stretch interaction constants are consistent with considerations based on Hybrid Orbital Following Force Field arguments.

Conclusion

All the results point clearly to the conclusion that change in the π-bonding system is by far the most important factor in the explanation of the intramolecular forces in these molecules. Changes in the σ-bonding system due to differences in substituent electronegativity would result in trends in the same direction for all the bond strengths, in conflict with the results.

This first complete normal-coordinate calculation, based upon complete assignments of the whole series of $X_3MCo(CO)_4$ molecules, shows several disagreements with earlier publications in which the calculations were based upon the Cotton—Kraihanzel method and which refer to specific parts of the spectra only. Most of the vibrations are mixed, as is shown in calculated L-matrices. Thus assignments in terms of internal symmetry coordinates are sometimes rather arbitrary.

Acknowledgement

We wish to thank Mrs. W. de Blécourt for assistance with the computer programs.

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