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METAL-METAL AND METAL-LIGAND VIBRATIONS OF SOME TIN-COBALT COMPOUNDS

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ABSTRACT--Two series of compounds containing, respectively, tetracarbonylcobalt and triphenylphosphinetricarbonylcobalt derivatives of tin with general formulas $X_{4-n}Sn[Co(CO)_4]_n$ and $X_{4-n}Sn[Co(CO)_3PPh_3]_n$ (where X = Cl, Br, or I and n = 1, 2, or 3) were prepared and their low-frequency infrared spectra studied. Assignments were made for tin-cobalt, cobalt-phosphorus, and tin-halogen stretching frequencies.

INTRODUCTION

Organometallic compounds containing covalent metal-metal bonds are of great interest. Recently, the infrared spectra of some organometallic compounds containing the triphenylphosphinetricarbonylcobalt derivatives of tin have been reported and the carbonyl stretching frequencies assigned (Hall, 1974). However, in order to identify the vibrations associated primarily with metal-metal and metal-ligand stretchings, it is necessary to look into the low-

frequency region of the infrared spectra, which also contain metal-ligand deformation modes. In the present work, two series of compounds, one series containing the tetracarbonylcobalt derivatives of tin, and the other containing the triphenylphosphinetricarbonylcobalt derivatives, were prepared and their low-frequency infrared spectra studied.

METHODS AND MATERIALS

All reactions were carried out under a static nitrogen atmosphere, and solid products were handled with minimum exposure to air. Microanalyses were performed by the Alfred Bernhardt Mikroanalytisches Laboratorium.

The low-frequency infrared spectra for the 33-800 cm^{-1} region were measured in Nujol and recorded on a Beckman IR-11 spectrometer. Calibration was made using the water line at 203.6 cm^{-1}. High density polyethylene plates were used as windows for the region below 200 cm^{-1} and cesium iodide was used for the region above 200 cm^{-1}. Spectral data are summarized in Table 1. Representative spectra are displayed in Figure 1.

Trichloro(tetracarbonylcobalt)tin(IV), $Cl_3SnCo(CO)_4$. This compound, the tribromo and the triiodo compound, $Br_3SnCo(CO)_4$ and $I_3SnCo(CO)_4$ were prepared by the method of Patmore (1968).

Dichlorobis(tetracarbonylcobalt)tin(IV), $Cl_2Sn[Co(CO)_4]_2$. This compound was prepared by the method described by Bonati (1966). The dibromo and diiodo compound, $Br_2Sn[Co(CO)_4]_2$ and $I_2Sn[Co(CO)_4]_2$, were similarly prepared.

Chlorotris(tetracarbonylcobalt)tin(IV), $ClSn[Co(CO)_4]_3$. This compound, the bromo and the iodo compound,

Table 1

Low-Frequency Infrared Spectral Data and Assignments *

COMPOUND	ν(Co-C) + δ(Co-C-O)							ν(Co-P)	ν(Sn-X)		ν(Sn-Co)
$Cl_3SnCo(CO)_4$	546s	538s,sh	486s	456s	412w	362w	360s		355s	350s	205m
$Cl_3SnCo(CO)_3PPh_3$	560s	524s	517s,sh	482m	470m			436w	345s	335s	195w
$Br_3SnCo(CO)_4$	546s	536s,sh	486m	457s	410m	365m			260s	251s	205m
$Br_3SnCo(CO)_3PPh_3$	558s	525s	520s,sh	480m	469m			434w	240s	228m	190w
$I_3SnCo(CO)_4$	543s	534s,sh	486m	456s	408w	366w			210w	200w	205w
$I_3SnCo(CO)_3PPh_3$	564m	526s	518s,sh	480m	472m			433w	226w	210w	180w
$Cl_2Sn[Co(CO)_4]_2$	540s	504m	492m	468s	408m	370w	366w,sh		336m	327m	213m
$Cl_2Sn[Co(CO)_3PPh_3]_2$	570m	558s	524s,sh	520s	499m	490m,sh	477w	435w	316w	304m	168m
$Br_2Sn[Co(CO)_4]_2$	544s	507m	487s	466s	408m	370w,sh	363w		237m	225s	209m

Table 1 (Continued)

Low-Frequency Infrared Spectral Data and Assignments *

COMPOUND	ν(Co-C) + δ(Co-C-O)							ν(Co-P)	ν(Sn-X)		ν(Sn-Co)
$Br_2Sn[Co(CO)_3PPh_3]_2$	568m	558s	524s,sh	520s	497m	491m,sh	476w	434w	221m	210m	164w
$I_2Sn[Co(CO)_4]_2$	541s	510m,sh	483s	467s	370w,sh	363w			195m	187m	202m
$I_2Sn[Co(CO)_3PPh_3]_2$	566m	556s	521s	496m	487m,sh	475w		432w	181w	172w	160w
$ClSn[Co(CO)_4]_3$	540s	505s	472s	412m	371w	367w,sh			302m		180m
$ClSn[Co(CO)_3PPh_3]_3$	578w	563s	540s,sh	521s	500m,sh	478w		433w	290w		152w
$BrSn[Co(CO)_4]_3$	546s	505s	472s	411m	373w	366w			216m		181m
$BrSn[Co(CO)_3PPh_3]_3$	576w	562s	540s,sh	521s	498m,sh	478w		434w	208w		152w
$ISn[Co(CO)_4]_3$	543s	508s	500s,sh	472m	410m	370w			177m		180m
$ISn[Co(CO)_3PPh_3]_3$	576w	562s	540s,sh	520s	503s,sh	478w		435w	167w		146w

* m - medium; s - strong; sh - shoulder; w - weak

$BrSn[Co(CO)_4]_3$ and $ISn[Co(CO)_4]_3$, were prepared by the method of Patmore (1966b).

Trichloro(triphenylphosphinetricarbonylcobalt)tin(IV), $Cl_3SnCo(CO)_3PPh_3$. This compound, the tribromo and the triiodo compound, $Br_3SnCo(CO)_3PPh_3$ and $I_3SnCo(CO)_3PPh_3$, were prepared by the method described earlier (Hall, 1974).

Dichlorobis(triphenylphosphinetricarbonylcobalt)tin(IV), $Cl_2Sn[Co(CO)_3PPh_3]_2$. This compound, the dibromo and diiodo compound, $Br_2Sn[Co(CO)_3PPh_3]_2$ and $I_2Sn[Co(CO)_3PPh_3]_2$, were prepared by insertion reaction as described by Patmore (1966a).

Chlorotris(triphenylphosphinetricarbonylcobalt)tin(IV), $ClSn[Co(CO)_3PPh_3]_3$. This compound, the bromo and the iodo compound, $BrSn[Co(CO)_3PPh_3]_3$ and $ISn[Co(CO)_3PPh_3]_3$, were prepared by the method described earlier (Hall, 1974).

RESULTS AND DISCUSSION

The spectral range investigated in this work was 33-800 cm^{-1}. No important feature other than the choppy baseline and the Nujol band at 70 cm^{-1} was observed in the 33-100 cm^{-1} region. The characteristic bands associated with triphenylphosphine as described by Edgell (1965) were present in all the $Co(CO)_3PPh_3$ derivatives in the 690-750 cm^{-1} region. Such bands were of course absent in the $Co(CO)_4$ derivatives. It is interesting to point out that the number and position of the bands for triphenylphosphine were independent of the number of $Co(CO)_3PPh_3$ groups.

The low-frequency region of infrared spectra of metal carbonyls has received very little attention. Consequently, very few assignments have been made. In the 300-600 cm^{-1}

region are found metal-carbon stretching vibrations, ν(M-C), and metal-carbonyl deformation modes, δ(M-C-O). The distinction between the δ(M-C-O) deformation and the ν(M-C) stretching vibrations is not clearcut although there can be little doubt that the higher frequency bands are essentially δ(M-C-O) and the lower frequency bands are ν(M-C) stretching vibrations (Jones, 1963; Edgell, 1963). The extent of overlapping between δ(M-C-O) and ν(M-C) and coupling of vibrations of the same symmetry types is probably extensive. Standard group theory treatment reveals a total of 5 infrared-active bands of ν(M-C) and δ(M-C-O) for mono-$Co(CO)_3PPh_3$ derivatives and 7 bands for mono-$Co(CO)_4$ while the bis- and tris-derivatives of $Co(CO)_3PPh_3$ and $Co(CO)_4$ possess 14 or more infrared-active bands. Only in the mono-$Co(CO)_3PPh_3$ derivatives were the predicted number of infrared-active ν(M-C) and δ(M-C-O) bands observed. The bis- and tris-derivatives of both $Co(CO)_4$ and $Co(CO)_3PPh_3$ revealed only 6 or 7 bands.

From the work of Westland (1965), and Rivest (1967), metal-phosphorus stretching frequency appears to lie in the range of 430-480 cm^{-1}. In all the $Co(CO)_3PPh_3$ derivatives of tin, the band that appeared in the range of 432-436 cm^{-1} was assigned the ν(Co-P) stretching. This band was of course absent in the $Co(CO)_4$ derivatives. It is interesting to note that the position and intensity of the ν(Co-P) stretching was not affected by the halo-group on tin nor by the number of $Co(CO)_3PPh_3$ groups.

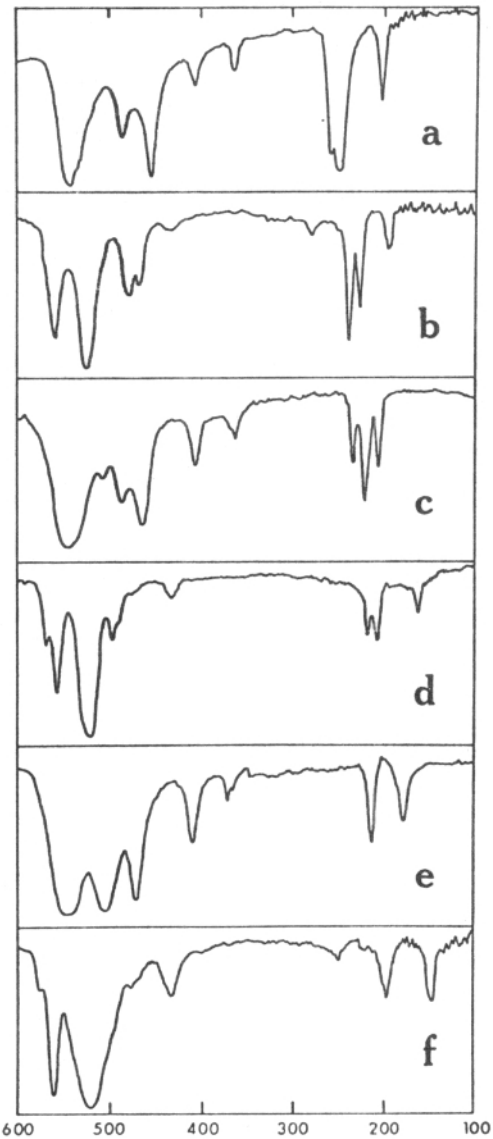
On the basis of available information on metal-halogen stretching frequencies (Brasch, 1968; Nakamoto, 1970), some useful empirical rules for assignment can be given as follows: 280-350 cm^{-1} for ν(M-Cl); 190-250 cm^{-1} for ν(M-Br); and 150-200 cm^{-1} for ν(M-I). Assignments for ν(Sn-Cl), ν(Sn-Br) and ν(Sn-I) are summarized in Table 1. Wherever two bands were observed, the higher frequency band was

assigned the asymmetric stretching while the lower frequency band, the symmetric stretching of the tin-halogen bond.

Tin-halogen deformation modes are generally very weak and occur at much lower frequencies than the stretching vibrations. The choppiness of the baseline in the spectra below 150 cm^{-1} made assignments difficult as small features must be treated with doubt. No attempt was thus made in such assignments.

Owing to the synthetic effort at present being expended on heteronuclear metal-metal bonded systems, there is increasing interest in stretching frequencies associated with such bonds. Clark (1965) examined the compound $(CH_3)_3SnCo(CO)_4$, and assigned the band at 176 cm^{-1} the ν(Sn-Co) stretching frequency. In the present work, the band in the 180-210 cm^{-1} region for the $Co(CO)_4$ derivatives is assigned the ν(Sn-Co) stretching and the band in the 150-195 cm^{-1} region for the $Co(CO)_3PPh_3$ derivatives is assigned the ν(Sn-Co) stretching. When the terminal carbonyl group is replaced by a triphenylphosphine group, the tin-cobalt stretching frequency is at a lower frequency. The higher ν(Sn-Co) stretching frequencies in the $Co(CO)_4$ derivatives are probably due to configuration interaction or coupling of vibrational modes of the same symmetry type. While the ν(Sn-Co) stretching frequencies do not seem to depend on the type of halogen present, it does depend on the number present. The ν(Sn-Co) vibrations shift to lower frequency as the number of halogen decreases.

Figure 1. Low-Frequency Infrared Spectra of Some Tin-Cobalt Compounds.



(a) $Br_3SnCo(CO)_4$

(b) $Br_3SnCo(CO)_3PPh_3$

(c) $Br_2Sn[Co(CO)_4]_2$

(d) $Br_2Sn[Co(CO)_3PPh_3]_2$

(e) $BrSn[Co(CO)_4]_3$

(f) $BrSn[Co(CO)_3PPh_3]_3$

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