dative bonding ("back bonding") π-C$_5$H$_5$ or π-C$_7$H$_7$ ligand increases the density of d electrons on the metal atom available for retrodative dπ–dπ bonding with the iodine atom.

The Far-Infrared Spectra of Some Group IV–Transition Metal Carbonyl Compounds

BY N. A. D. CAREY AND H. C. CLARK

The far-infrared spectra (100–550 cm^{-1}) of 18 compounds containing tin–transition metal bonds are presented. It is shown that reasonable assignments can be made of absorptions largely due to metal–metal vibrations. Moreover, variations in the frequencies of these absorptions can be correlated with variations in the frequencies of the transition metal carbonyl absorptions (1900–2200-cm^{-1} region). This correlation can be interpreted in terms of the π-accepting properties of the R$_3$Sn moiety and hence is related to the nature of R.

Introduction

We wish to report the far-infrared spectra (100–550 cm^{-1}) for some 18 compounds, of which five are new, containing a tin–transition metal bond. The purpose of this work has been threefold. Primarily, we have sought to obtain information for a region of the infrared that has been only briefly studied. Secondly, we wished to determine whether such a technique could be used satisfactorily to provide a reasonable assignment of the metal–metal stretching vibrations. Thirdly, we were also interested in determining whether the frequencies of the metal–metal stretching vibrations displayed a variation consistent with the shifts observed in the carbonyl stretching region for a given series of compounds. Thus, Graham, *et al.*,[1] have shown for a large number of group IV metal–transition metal compounds that the carbonyl stretching frequencies are sensitive to the nature of the ligands attached to the group IV metal. They have postulated that some form of dπ–dπ interaction may occur between the group IV metal and the transition metal and that the former acts as the π acceptor. Such an interaction, we felt, might be susceptible to observation in the metal–metal stretching vibrations, provided a reasonable series of compounds could be studied. We have examined the two distinct series of compounds (CH$_3$)$_{3-n}$Cl$_n$Sn–M, where M is Mn(CO)$_5$ and Mo(CO)$_3$(π-C$_5$H$_5$), respectively. In addition, we have examined the series (CH$_3$)$_2$XSnMn(CO)$_5$, where X = CF$_3$, (Cl), Br, and I, which may provide some information on the nature of this interaction. Finally, we have examined the far-infrared spectra of the additional metal–metal bonded compounds R$_3$SnFe(CO)$_2$(π-C$_5$H$_5$) (where R = CH$_3$ or C$_6$H$_5$), (CH$_3$)$_3$SnW(CO)$_3$(π-C$_5$H$_5$),

(CH$_3$)$_2$ClSnW(CO)$_3$(π-C$_5$H$_5$), and (CH$_3$)$_3$SnCo(CO)$_4$, which allow further useful comparisons to be made.

Experimental Section

Preparation of Starting Materials.—The preparations of (CH$_3$)$_3$SnMn(CO)$_5$, (C$_6$H$_5$)$_3$SnMn(CO)$_5$, Cl$_3$SnMn(CO)$_5$, (CH$_3$)$_3$SnCo(CO)$_4$, and (CH$_3$)$_3$SnFe(CO)$_2$(π-C$_5$H$_5$) were described by Gorsich.[2] The preparations of (CH$_3$)$_3$SnMo(CO)$_3$(π-C$_5$H$_5$), (C$_6$H$_5$)$_3$SnMo(CO)$_3$(π-C$_5$H$_5$), and (CH$_3$)$_3$SnW(CO)$_3$(π-C$_5$H$_5$) were as described by Graham.[1a] The preparations of Cl(CH$_3$)$_2$-SnMn(CO)$_5$, Cl$_2$(CH$_3$)SnMn(CO)$_5$, Cl(CH$_3$)$_2$SnW(CO)$_3$(π-C$_5$H$_5$), Cl(CH$_3$)$_2$SnMo(CO)$_3$(π-C$_5$H$_5$), Cl$_2$CH$_3$SnMo(CO)$_3$(π-C$_5$H$_5$), Cl$_3$-SnMo(CO)$_3$(π-C$_5$H$_5$), Br(CH$_3$)$_2$SnMn(CO)$_5$, I(CH$_3$)$_2$SnMn(CO)$_5$, and CF$_3$(CH$_3$)$_2$SnMn(CO)$_5$ will be described elsewhere.

Recording of Spectra.—The spectra in the carbonyl stretching region were recorded as solutions in cyclohexane, using 0.1-mm NaCl solution cells, on a Beckman IR-7 spectrometer. Calibration was made using the water line at 1942.5 cm^{-1}. The spectra for the 70–350-cm^{-1} region were recorded on a Beckman IR-11 spectrometer; 1.5-mm propathene plates were used as windows and the samples were made up in Nujol as thick pastes. Nujol in propathene possesses a weak peak at 170 cm^{-1} and a medium weak band at 250 cm^{-1}. Calibration was made using the water line at 203.6 cm^{-1}. The remaining region 350–3000 cm^{-1} was recorded on a Beckman IR-10 spectrometer. Cesium iodide windows were used and the spectra were calibrated with the characterisic bands in polystyrene.

Results

(A) (CH$_3$)$_{3-n}$Cl$_n$SnMn(CO)$_5$, Where n = 0, 1, 2, 3. —In Figure 1 are reproduced the spectra for the region 300–140 cm^{-1}, of the series (CH$_3$)$_{3-n}$Cl$_n$SnMn(CO)$_5$, where n = 0, 1, 2, 3, and the data are tabulated in Table I for the region 550–100 cm^{-1}. Clearly, one obvious common feature is the medium to strong intensity band in the 175–205-cm^{-1} region. The band at 182 cm^{-1} in the spectrum of (CH$_3$)$_3$SnMn(CO)$_5$ is close to the band at 180 cm^{-1} that appears in the Raman spectrum of the same compound and which has been associated with the Sn–Mn stretching vibra-

(1) (a) H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966); (b) D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 1405 (1966); (c) D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 1587 (1966); (d) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *ibid.*, **5**, 2217 (1966).

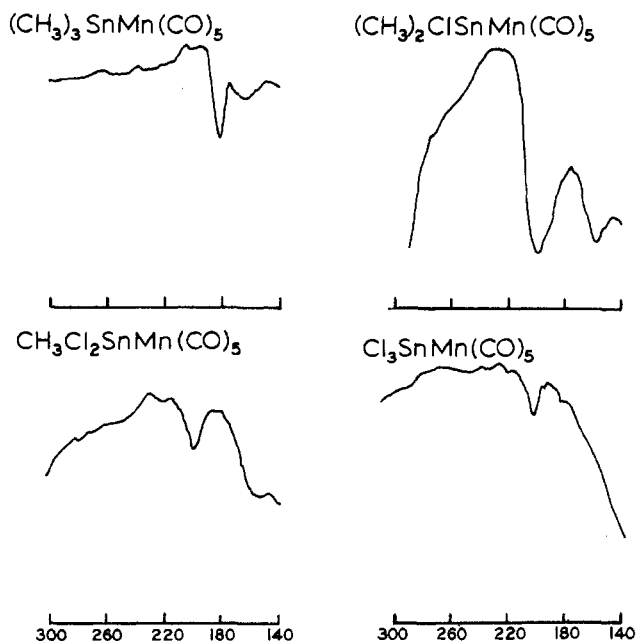(2) R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962).

Figure 1.—Spectra of $(CH_3)_{3-n}Cl_nSnMn(CO)_5$, where $n = 1, 2,$ or 3.

TABLE I

FAR-INFRARED SPECTRA (550–100 CM^{-1}) FOR
$(CH_3)_{3-n}Cl_nSnMn(CO)_5$ AND $(C_6H_5)_3SnMn(CO)_5$

$(C_6H_5)_3SnMn-(CO)_5$	$(CH_3)_3SnMn-(CO)_5$	$(CH_3)_2ClSn-Mn(CO)_5$	$(CH_3)Cl_2-SnMn(CO)_5$	$Cl_3SnMn-(CO)_5$
470 m[b]	517 s[a]	528 s[a]	530 s[a]	
440 m	500 s[a]	518 s[a]		
257 s	480 s[b]	470 s[b]	463 s[b]	451 s[b]
244 s	412 w, b	325 s[d]	330 s[d]	345 vs[d]
211 m	182 m	197 ms	201 m	201 m
174 m, b	163 ms[c]	156[e]	150[e]	
119 m, b		142 m, b	140 m	135 s[f]
		121	122	113 ms[f]

[a] Sn–C stretching vibrations: H. Kriegsmann and S. Pischtschan, *Z. Anorg. Allgem. Chem.*, **308**, 212 (1961). [b] Mn–C in Mn(CO)$_5$ stretching vibrations: N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **3**, 1123 (1964). [c] SnC$_3$ deformation mode (*e.g.*, see reference given in footnote a) and spectra of $(CH_3)_3Sn-Co(CO)_4$, $-Fe(CO)_2Cp$, $-W(CO)_3Cp$, and $-Mo(CO)_3Cp$. [d] Sn–Cl stretching vibrations; see ref 4 and the reference given in footnote a. [e] Presumably CSnCl deformations. [f] SnCl$_3$ deformations; see ref 4.

tion.[3,4] Of the three bands below 300 cm^{-1} appearing in the infrared spectrum of Cl$_3$SnMn(CO)$_5$, those at 113 and 135 cm^{-1} can be assigned to the Cl$_3$Sn group by analogy with the Raman spectrum of Cl$_3$SnCH$_3$.[5] This, then, suggests that the band at 201 cm^{-1} can be assigned to the Sn–Mn stretch. The spectrum of $(C_6H_5)SnMn(CO)_5$ (Figure 2) displays a band at 175 cm^{-1} which is in fair agreement with the band at 170 cm^{-1} appearing in the Raman spectrum of the same compound and which has been assigned to the Sn–Mn stretching vibration.[4] These results suggest that the Sn–Mn stretching vibration can be expected in the range 200–170 cm^{-1}. The spectra of both the mono- and the dichloro derivatives show bands in this region,

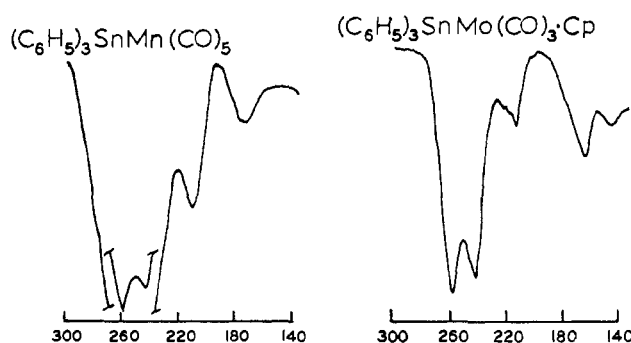(3) V. Maroni, private communication.
(4) H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Commun.*, 616 (1966).
(5) H. Kriegsmann and S. Pauly, *Z. Anorg. Allgem. Chem.*, **330**, 275 (1964).

Figure 2.—Spectra of $(C_6H_5)_3SnMn(CO)_5$ and $(C_6H_5)_3SnMo-(CO)_3(\pi-C_5H_5)$.

and these have accordingly been assigned to the Sn–Mn stretching vibration.

These assignments are further supported by a comparison with the infrared spectra of the carbonyl stretching region, the data being tabulated in Table II.

TABLE II
CARBONYL STRETCHING FREQUENCIES FOR
$(CH_3)_{3-n}Cl_nSnMn(CO)_5$

Compound	—Obsd freq, cm^{-1}—	Ref
$(CH_3)_3SnMn(CO)_5$	2089, 1998, 1991	a
$(CH_3)_2ClSnMn(CO)_5$	2101, 2015, 2006	a
$(CH_3)Cl_2SnMn(CO)_5$	2114, 2030, 2019	b
$Cl_3SnMn(CO)_5$	2126, 2046, 2039	a
$(C_6H_5)_3SnMn(CO)_5$	2093, 2002, 2002	a

[a] *Cf.* ref 1. [b] This work as a solution in CHCl$_3$.

Graham[1] has calculated the carbonyl stretching force constants and the interaction force constant for this series of compounds and the results indicate that, as chlorine replaces the methyl groups as ligands about tin, the π-accepting properties of the tin moiety increase. Accordingly, one might predict that the energy of the Sn–Mn bond will increase with successive substitution of chlorine, resulting in a shift to higher frequencies for the Sn–Mn stretching vibration. A correction for the change in reduced mass that occurs in the series $(CH_3)_{3-n}Cl_nSnMn(CO)_5$ as n shifts from 0 to 3 predicts that, all other things remaining equal, the frequency of the Sn–Mn stretching vibration should decrease as n increases. These results are shown in Table III; there is clearly a good correlation between the interaction force constants and the difference between the observed and mass-corrected Sn–Mn stretching vibrations. In effect, the observed trend in the Sn–Mn stretching vibrations, as we proceed through the series $(CH_3)_3SnMn(CO)_5$ to $Cl_3SnMn(CO)_5$, represents a competition between the increasing mass and the increasing Sn–Mn interaction, the former tending to lower the frequency and the latter tending to increase it.

(B) $(CH_3)_{3-n}Cl_nSnMo(CO)_3(\pi-C_5H_5)$, Where $n = 0, 1, 2, 3.$—By analogy with the above arguments a similar variation in $\nu(Sn–Mo)$ should be observed in this series. The observed carbonyl stretching frequencies are tabulated in Table IV, and it will be noted that the same trend occurs as with the Mn(CO)$_5$ de-

TABLE III

CORRELATION BETWEEN CARBONYL STRETCHING REGION
AND METAL–METAL STRETCHING REGION

			$\nu(Sn-Mn)_o -$	Carbonyl
	⌐—Sn–Mn str freq, cm^{-1}—⌐		$\nu(Sn-$	interaction
	Obsd,	Calcd,	$Mn)_c$	force
Compound	$\nu(Sn-Mn)_c$	$\nu(Sn-Mn)_c{}^a$	$\Delta\nu$, cm^{-1}	constant,^{b} K_i
$(CH_3)_3SnMn(CO)_5$	182	182	0	0.240
$(CH_3)_2ClSnMn(CO)_5$	197	176	21	0.234
$CH_3Cl_2SnMn(CO)_5$	201	172	29	0.213^c
$Cl_3SnMn(CO)_5$	201	168	33	0.204

^{a} Values calculated relative to $(CH_3)_3SnMn(CO)_5$ with $\nu(Sn-Mn) = 182$ cm^{-1}, using the expression

$$\nu = \left(\frac{m_s + M_m}{m_s M_m}\right)^{1/2}\left(\frac{M_s + M_m}{M_s M_m}\right)^{1/2}\nu(Sn-Mn)$$

where m_s = mass of $(CH_3)_nCl_{3-n}Sn$, M_m = mass of $Mn(CO)_5$ = 196, M_s = mass of $(CH_3)_3Sn$ = 163, and $\nu(Sn-Mn) = 182$ cm^{-1}. ^{b} Taken from ref 1, using the Cotton and Kraihanzel approximation: F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964), and references therein. ^{c} W. A. G. Graham, private communication.

TABLE IV

CARBONYL STRETCHING FREQUENCIES FOR
$(CH_3)_{3-n}Cl_nSnMo(CO)_3(\pi\text{-}C_5H_5)$

Compound	⌐—Obsd freq, cm^{-1}—⌐	Ref
$(CH_3)_3SnMo(CO)_3(\pi\text{-}C_5H_5)$	1997, 1922, 1895	a
$Cl(CH_3)_2SnMo(CO)_3(\pi\text{-}C_5H_5)$	2013, 1947, 1913	a
$Cl_2CH_3SnMo(CO)_3(\pi\text{-}C_5H_5)$	2038, 1970, 1941	b
$Cl_3SnMo(CO)_3(\pi\text{-}C_5H_5)$	2060, 1996, 1972	c
$(C_6H_5)_3SnMo(CO)_3(\pi\text{-}C_5H_5)$	2004, 1934, 1909	a

^{a} Cf. ref 1. ^{b} Obtained from a solution in $CHCl_3$. ^{c} F. Bonati and C. Wilkinson, *J. Chem. Soc.*, 179 (1964).

rivatives—a shift to higher frequencies as chlorine replaces methyl around the tin. In Figure 3 are reproduced the spectra for the region 300–140 cm^{-1}, and in Table V the values observed between 550 and 100 cm^{-1} are listed. Originally,[6] the weak band at 156 cm^{-1} was assigned to the Sn–Mo stretch in $(CH_3)_4$-$SnMo(CO)_3(\pi\text{-}C_5H_5)$, since it was felt that this was consistent with the change in mass from $(CH_3)_3SnM$-$(CO)_5$ to $(CH_3)_3SnMo(CO)_3(\pi\text{-}C_5H_5)$. However, with the additional information available from the spectra of the complete series, the stronger band at 172 cm^{-1} is assigned to the Sn–Mo stretching vibration while the band at 156 cm^{-1} is consistent with a C_3Sn deformation [of $(CH_3)_3SnMn(CO)_5$]. The spectrum of Cl_3SnMo-$(CO)_3(\pi\text{-}C_5H_5)$ contains three bands below 250 cm^{-1} of which the two bands at 142 and 113 cm^{-1} can be assigned to Cl_3Sn deformation and rocking modes,[4] leaving the band at 190 cm^{-1} to be associated with $\succ Sn\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$. Since there are no bands in the region 140–250 cm^{-1} for the far-infrared spectrum[7] of $CH_3Mo(CO)_3(\pi\text{-}C_5H_5)$, it seems reasonable to associate this band with the Sn–Mo stretching vibration. Comparing the spectra reproduced in Figure 3 with those in Figure 1, a set of values for $\nu(Sn-Mo)$ is apparent that is very similar to the set obtained for $\nu(Sn-Mn)$ (Table VI). The two sets are consistent both with each other and with the values of the carbonyl streching frequencies.

(6) N. A. D. Carey and H. C. Clark, *Chem. Commun.*, 292 (1967).
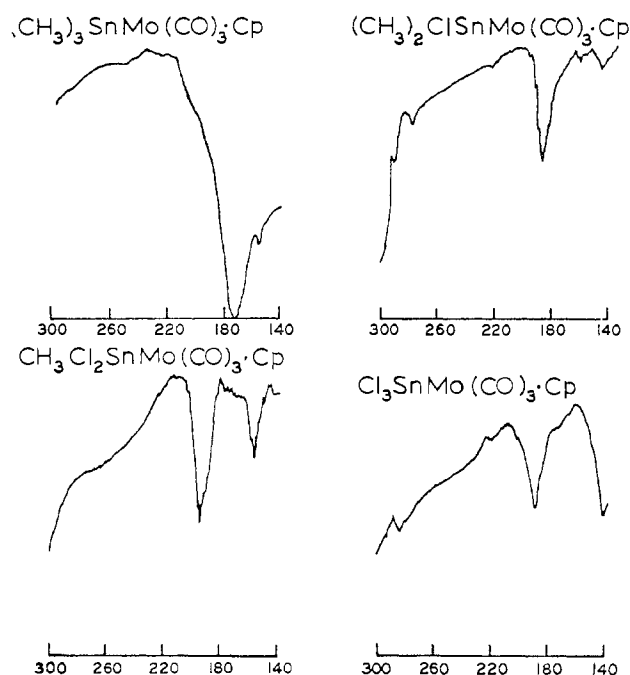(7) N. A. D. Carey and H. C. Clark, unpublished observations.

Figure 3.—Spectra of $(CH_3)_{3-n}Cl_nSnMo(CO)_3(\pi\text{-}C_5H_5)$, where $n = 1, 2,$ or 3.

TABLE V

FAR-INFRARED SPECTRA (550–100 CM^{-1}) FOR
$(CH_3)_{3-n}Cl_nSnMo(CO)_3(\pi\text{-}C_5H_5)$ AND $(C_6H_5)_3SnMo(CO)_3(C_5H_5)$

$(C_6H_5)_3$-SnMo(CO)$_3$-$(\pi\text{-}C_5H_5)$	$(CH_3)_3$-SnMo(CO)$_3$-$(\pi\text{-}C_5H_5)$	$Cl(CH_3)_2$-SnMo(CO)$_3$-$(\pi\text{-}C_5H_5)$	Cl_2CH_3-SnMo(CO)$_3$-$(\pi\text{-}C_5H_5)$	Cl_3SnMo-(CO)$_3$-$(\pi\text{-}C_5H_5)$
495 s	520 s	510 m	550 s	540 s
470 m	505 s	493 vs	525 m	470 s
450 m, sh	480 s	465 s	485 s	450 s
440 s	440 w		440 m	
420 w		420 w	405 mw	415 w
380 vs	350 w	350 w	350 vw	375 w
340 vw				360 m
258 s		304 s	325 s	340 s
242 s			310 s	324 s
214 mw				285 m
169 m	172 s	186 ms	195 ms	190 m
152 w	156 ms	149 mw	158 m	142 ms
148 w	138 m	126 mw	122 m	
	125 m			

TABLE VI

CORRELATION BETWEEN $\nu(Sn-Mn)$ AND $\nu(Sn-Mo)$ IN THE TWO
SERIES $(CH_3)_{3-n}Cl_nSnMn(CO)_5$ AND $(CH_3)_{3-n}SnMo(CO)_3(\pi\text{-}C_5H_5)$

| | ⌐————Metal–metal str freq, cm^{-1}————⌐ | | |
| | Mo(CO)$_3$- | Mn(CO)$_5$- | W(CO)$_3$- |
Ligand	$(\pi\text{-}C_5H_5)$	$(\pi\text{-}C_5H_5)$	$(\pi\text{-}C_5H_5)$
$(CH_3)_3Sn$	172	182	169
$Cl(CH_3)_2Sn$	186	197	175
Cl_2CH_3Sn	195	201	
Cl_3Sn	190	201	
$(C_6H_5)_3Sn$	169	175	

(C) $(CH_3)_2XSnMn(CO)_5$ Where X = Cl, Br, I, or CF_3.—The carbonyl stretching frequencies are listed in Table VII. For X = Cl, Br, or I, these frequencies are almost identical. This would not be expected if only the electron-withdrawing properties of the substituents about tin are involved, so that this factor must be relatively unimportant. The alternative is

TABLE VII

CARBONYL STRETCHING REGION FOR (CH3)2XSnMn(CO)5

Compound	Obsd freq, cm⁻¹
Cl(CH3)2SnMn(CO)5	2101, 2015, 2006
Br(CH3)2SnMn(CO)5[a]	2099, 2014, 2005
I(CH3)2SnMn(CO)5	2100, 2014, 2005
CF3(CH3)2SnMn(CO)5	2105, 2048, 2010

[a] There were present in this spectrum a number of additional bands which were considered due to impurities.

to conclude that the π-accepting properties of (CH3)2-XSn, where X = Cl, Br, or I, are the same. This is reasonable since Graham, et al.,[1] have already concluded that the π-accepting properties of Cl3Sn and Br3Sn groups attached to Mn(CO)5 are much the same. It is, however, noticeable that substitution of the perfluoromethyl group shifts the carbonyl absorptions to higher frequencies than those of the monohalogen analogs. The far-infrared spectra for the perfluoromethyl, bromo, and iodo derivatives are reproduced in Figure 4 for the region 300–140 cm⁻¹, and the absorption frequencies for the region 550–100 cm⁻¹ are given in Table VIII. The band at 226 cm⁻¹ in the spectrum of Br-(CH3)2SnMn(CO)5 can be assigned to the Sn–Br stretch by analogy with the spectrum[4,8] of (CH3)3SnBr, while by comparison with the spectra reproduced in Figure 1, the band at 191 cm⁻¹ is most probably due to the Sn–Mn stretching vibration. The two bands at 178 and 189 cm⁻¹ in the spectrum of I(CH3)2SnMn-(CO)4 are presumably the Sn–I and the Sn–Mn stretching vibrations, the 178-cm⁻¹ band perhaps containing the main contribution of the Sn–Mn stretching vibration.
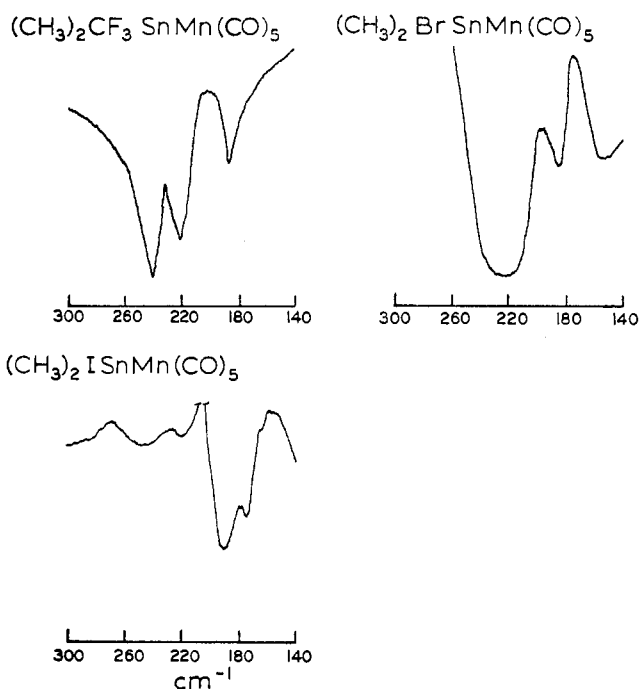

Figure 4.—Spectra of (CH3)2XSnMn(CO)5, where X = CF3, Br, or I.

ligands around tin, it seems more consistent to assign the shoulder at 186 cm⁻¹ in the spectrum of (CH3)3-SnFe(CO)2(π-C5H5) and the band at 174 cm⁻¹ in the spectrum of (C6H5)3SnFe(CO)2(π-C5H5) to the Sn–Fe stretching vibration rather than the bands at 208 and 209 cm⁻¹ that are also present, respectively, in the spec-

TABLE VIII

FAR-INFRARED SPECTRA (550–100 CM⁻¹)

Br(CH3)2Sn-Mn(CO)5	I(CH3)2Sn-Mn(CO)5	CF3(CH3)2Sn-Mn(CO)5	(CH3)3Sn-Fe(CO)2Cp[a]	(C6H5)3Sn-Fe(CO)2Cp[a]	(CH3)3Sn-W(CO)3Cp[a]	Cl(CH3)2Sn-W(CO)3Cp[a]	(CH3)3Sn-Co(CO)4
523 m	520 w	520 m	510 ms	515 w	515 ms	550 m	548 s
513 m	505 w	510 m			500 m	520 mw	525 m
			490 m		485 ms	505 mw	500 m
470 m	470 w	465 ms			470 ms	473 ms	
			450 w	441 m	450 sh	450 ms	420 mw
		305 mw			365 w	430 w	370 mw
		240 ms	299 w	256 ms	340 w	355 w	
226 ws	189 ms	222 ms	208 mw	209 w	323 w	303 m	
191 m	178 ms	189 m	186 m, sh	174 w	168 ms	174 m	176 m
162 m			159 ms, b	150 w, b	130 m, b	140 w	160 m
138 mw	139 mn					136	142
126					106 m, b	110 w, b	

[a] Cp = π-C5H5.

(D) Compounds Containing Sn–Fe, Sn–W, and Sn–Co Bonds.—The spectra in the region 300–140 cm⁻¹ are reproduced in Figure 5 and the results for the region 550–100 cm⁻¹ are tabulated in Table VIII. Comparison of the spectra of (C6H5)3SnFe(CO)2(π-C5H5) and (CH3)3SnFe(CO)2(π-C5H5) suggests that the bands at 208 or 180 cm⁻¹ are the Sn–Fe stretching vibrations. Since an approximate 10-cm⁻¹ difference has been observed in Sn–Mn stretching vibrations when phenyl groups rather than methyl groups are present as

(8) H. Kriegsmann and S. Pischtschan, *Z. Anorg. Allgem. Chem.*, **308**, 212 (1961).

tra of both compounds. In addition, a value of 186 cm⁻¹ for the Sn–Fe stretching vibration seems entirely reasonable when compared with the Sn–Mn stretching vibrations.

By analogy with the spectra of Cl(CH3)3Sn- and (CH3)3Sn-containing compounds considered in sections A and B, the Sn–W stretching vibration would be expected to be slightly higher in Cl(CH3)2SnW(CO)3(π-C5H5) than in (CH3)3SnW(CO)3(π-C5H5). If it is assumed that the only difference between (CH3)3SnW-(CO)3(π-C5H5) and its molybdenum analog is in the masses of tungsten and molybdenum, then the Sn–W

(C₆H₅)₃Sn Fe(CO)₂Cp
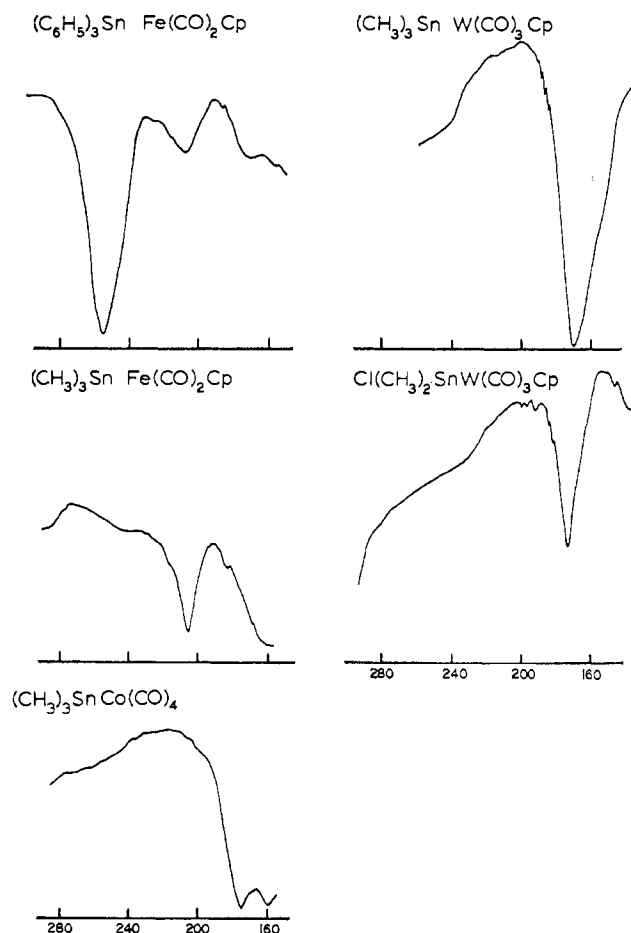
(CH₃)₃Sn W(CO)₃Cp

(CH₃)₃Sn Fe(CO)₂Cp

Cl(CH₃)₂SnW(CO)₃Cp

(CH₃)₃Sn Co(CO)₄

Figure 5.—Spectra of some Sn–Fe, Sn–Co, and Sn–W compounds.

stretching vibration in $(CH_3)_3SnW(CO)_3(\pi\text{-}C_5H_5)$ can be calculated to be 162.7 cm^{-1} since the Sn–Mo stretching vibration in the analogous molecule is considered to be 172 cm^{-1}. Of the two possible bands occurring in the far-infrared spectrum of $(CH_3)_3SnW(CO)_3(\pi\text{-}C_5H_5)$, this calculated result would suggest that the band at 168 cm^{-1} be assigned to the Sn–W stretching vibration rather than the band at 130 cm^{-1}. Similarly the band at 174 cm^{-1} occurring in the spectrum of $Cl(CH_3)_2$-$SnW(CO)_3(\pi\text{-}C_5H_5)$ seems reasonable as the Sn–W stretching vibration. These results are summarized in Table VI.

Only the one Sn–Co compound, $(CH_3)_3SnCo(CO)_4$, has been studied. A tentative assignment for the Sn–Co stretching vibration, by analogy with the spectra of the Sn–Mn-containing compounds, would be the band at 176 cm^{-1}.

Discussion

While it is almost certain that none of the bands that we have assigned as metal–metal stretching frequencies are pure vibrations, the results do form a remarkably self-consistent set, from which a number of conclusions can be reached.

(i) The far-infrared absorption region can provide useful spectroscopic information, on the basis of which reasonable assignments can be made for metal–metal stretching vibrations. Such assignments have the

same degree of reliability as other qualitative infrared assignments, and certainly, as in other cases, problems due to coupling, etc., cannot be avoided. In other words, the assignments cannot be more than tentative and do not imply that the particular absorptions are associated with pure vibrational modes.

(ii) The metal–metal stretching frequencies for the series $(CH_3)_{3-n}Cl_nSn\text{-}M$ (where M = Mn(CO)$_5$ and Mo(CO)$_3(\pi\text{-}C_5H_5)$ for n = 0, 1, 2, 3 and W(CO)$_3$-$(\pi\text{-}C_5H_5)$ for n = 0, 1) appear to represent a balance between the increasing reduced mass of the substituted tin groups and the increasing interaction between the tin and transition metal as chlorine successively replaces the methyls around the tin. This result is consistent with the carbonyl stretching frequencies observed for these compounds, supporting the idea that the metal–metal interaction is affected by the nature of the ligand attached to the tin.

(iii) The metal–metal interaction is independent of the type of halogen present. Thus the carbonyl stretching region in $(CH_3)_2XSnMn(CO)_5$ is the same whether X is Cl, Br, or I, and the variation in the Sn–Mn stretching vibration cannot be explained by the change in reduced mass of the tin group for the different halogen derivatives. This result suggests that the interaction depends on something more subtle than the electron-withdrawing properties of the ligands, although this presumably plays its part. We feel that π-donor properties of the halogens cannot be ignored and that the π-accepting properties of the tin moiety reflects a balance between the electron-withdrawing properties of the ligands and their ability to act as π donors. That the metal–metal interaction may depend on the $(p \rightarrow d)\pi$ character of the Sn–L bond is given some support in that introduction of a perfluoromethyl group does shift the carbonyl stretching absorptions to higher frequencies than those observed for the monohalogen derivatives. This would be expected if it is assumed that the $(p \rightarrow d)\pi$ character of the Sn–C bond (in Sn–CF$_3$) is negligible.

(iv) The metal–metal stretching frequencies decrease when phenyl replaces methyl around the tin. This has been observed in $R_3SnMn(CO)_5$, R_3SnMo-$(CO)_3(\pi\text{-}C_5H_5)$, and $R_3SnFe(CO)_2(\pi\text{-}C_5H_5)$. Although the difference is of the order of 10 cm^{-1}, this is small enough to suggest that the metal–metal interaction is greater in the triphenyltin derivatives than the corresponding trimethyltin compounds. This is also consistent with the carbonyl stretching region for these compounds.

Finally, it must be stressed again that conclusions ii–iv above involve the assumption that the absorptions assigned to metal–metal vibrations approximate reasonably pure vibrational modes. The validity of this assumption cannot be established until more extensive vibrational information is available.

part of a joint program with Professor G. J. M. van der Kerk, Utrecht, Holland, with the aid of a NATO research grant. The generous cooperation and assistance

of Professor G. Wright, University of Toronto, in the use of the Beckman IR-11 spectrometer is gratefully acknowledged.

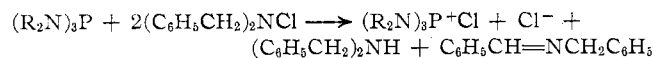# Reactions of Tris(dialkylamino)phosphines with Dialkylchloramines[1]

BY DONALD B. DENNEY AND STEPHEN M. FELTON

Tris(dialkylamino)phosphines react with dialkylchloramines to give tris(dialkylamino)chlorophosphonium chlorides, a Schiff base derived from the dialkylchloramine, and the parent amine. The reaction is thought to proceed by initial displacement on halogen to give a tris(dialkylamino)chlorophosphonium dialkylamide. This salt is in equilibrium with the starting materials. Reaction of the dialkylamide anion with dialkylchloramine yields the Schiff base and the parent amine.

Introduction

The reaction of "positive halogen" containing compounds with trialkylphosphines and phosphites have been shown to lead in many cases to phosphonium salts.[2] Sisler and his co-workers have made an extensive study of the reactions of a variety of phosphines with chloramine.[3] In general, aminophosphonium chlorides are the products. One exception involves the reaction of tris(dimethylamino)phosphine with dimethylchloramine which yielded tris(dimethylamino)-chlorophosphonium chloride.[3] The other products of this reaction were not investigated; however, it was suggested that tetramethylhydrazine was probably formed.

The study now being reported was aimed at preparing tetrakis(dialkylamino)phosphonium halides by allowing tris(dialkylamino)phosphines to react with dialkylchloramines. It has been found that the reaction does not yield these products but as previously reported by Sisler, *et al.*,[3] yields the tris(dialkylamino)-chlorophosphonium chloride. It has been shown that, in the N-chlorodibenzylamine reaction, the other products are the Schiff base derived from the dibenzylchloramine and dibenzylamine rather than the tetraalkylhydrazine suggested by Sisler, *et al.*[3]

$$(R_2N)_3P + 2(C_6H_5CH_2)_2NCl \longrightarrow (R_2N)_3P^+Cl + Cl^- +$$
$$(C_6H_5CH_2)_2NH + C_6H_5CH=NCH_2C_6H_5$$

Experimental Section

Materials.—N-Chlorodialkylamines were prepared by the method of Coleman.[4] The tris(dialkylamino)phosphines were prepared by condensing the appropriate amine with phosphorus trichloride.[5]

Spectra.—The nuclear magnetic resonance spectra were re-

corded with a Varian Associates A-60 spectrometer at 60 MHz. The spectra were run in a variety of solvents with tetramethylsilane as an internal standard. Chemical shifts are reported in ppm relative to tetramethylsilane. Infrared spectra were recorded with Perkin-Elmer Models 21 and 137 and a Beckman IR-5A instrument.

Reaction of Tris(diethylamino)phosphine (1 Mol) with N-Chlorodiethylamine (2 Mol).—Tris(diethylamino)phosphine, 8.25 g (0.0345 mol) was added to a chilled hexane solution, 75 g, containing 0.0691 mol of N-chlorodiethylamine. The reaction mixture warmed and became milky. The mixture was stirred at room temperature. A yellow-orange oil formed and after 16 hr in the refrigerator two distinct phases were present. An aliquot of the hexane phase gave no iodine when treated with potassium iodide solution. The oil and the hexane phase were separated by decantation and the oil was washed with 50 ml of hexane. The oil was dried in a vacuum oven to give 7.0 g of material. The nmr spectrum was identical in its major absorptions with that of an authentic sample of tris(diethylamino)-chlorophosphonium chloride. This reaction was conducted many times with identical results. When the oil was further dried at 90° (2 mm) for 16 hr and then triturated with dry ether, the oil became semicrystalline. The infrared and nmr spectra of this material were identical with that of an authentic sample of tris(diethylamino)chlorophosphonium chloride prepared by allowing chlorine to react with tris(diethylamino)phosphine which is the method used by Nöth and Vetter to prepare tris(dimethylamino)chlorophosphonium chloride.[6] The materials obtained by both methods were extremely hygroscopic. The nmr spectra showed a triplet at 1.30 ppm ($J = 7$ cps) and an apparent sextet centered at 3.34 ppm. The 1.30-ppm absorption is due to the methyl group and the absorption at 3.34 ppm is due to the methylene group hydrogens which are coupled to the methyl group hydrogens and phosphorus ($J_{PH} = 14$ cps). The relative areas under these absorptions were 18:12.

Both materials were converted to their hexafluorophosphate derivatives by allowing the salts to react with saturated aqueous solutions of potassium hexafluorophosphate. The salts were recrystallized from ethanol, mp 332–333°. The yield of hexafluorophosphate from the dialkylchloramine reaction was 56%.
Anal. Calcd for [(C_2H_5)_2N]_3PClPF_6: C, 33.70; H, 7.02. Found: C, 34.55; H, 7.20.

The hexane solution was treated with a solution of 6.4 g of 2,4-dinitrophenylhydrazine in 30 ml of concentrated sulfuric acid, 48 ml of water, and 160 ml of ethanol. A yellow solid formed

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