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Raman Spectra and Metal-Metal Bonding in the Molecules X_3M'-$M(CO)_5$ ($X = CH_3$, Cl; $M' =$ Ge, Sn; $M =$ Mn, Re)[1]

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Raman frequencies below 600 cm^{-1} are assigned to various skeletal modes of the molecules X_3M'-$M(CO)_5$: $Me_3GeMn(CO)_5$, $Me_3SnMn(CO)_5$, $Me_3GeRe(CO)_5$, $Me_3SnRe(CO)_5$, and $Cl_3SnMn(CO)_5$. The symmetric X-M', M'-M, and M-C stretching frequencies are readily identifiable and were used to evaluate M'-M stretching force constants with approximate normal-coordinate calculations. The values are 0.90, 0.85, 0.73, and 0.68 mdyn/Å for Sn-Mn, Sn-Re, Ge-Mn, and Ge-Re in the trimethyl derivatives, and 1.09 for $Cl_3SnMn(CO)_5$. The trend in the trimethyl derivatives parallels the observed decrement in the M'-M distances from the mean of the corresponding M'-M' and M-M distances, but the force constants are, surprisingly, lower than the mean of the corresponding homonuclear force constants. Measured Raman intensities were used to evaluate X-M' and M'-M bond polarizability derivatives and experimental bond orders *via* the δ function potential model. The bond orders are in satisfactory accord with the mean of the corresponding homonuclear values and fail to reveal any substantial π bonding in the metal-metal bonds.

Introduction

Recent studies in this laboratory have been concerned with the examination of metal-metal bonding by evaluating metal-metal stretching force constants and polarizability derivatives from Raman spectra.[2-14] Both nonbridged[2-4] and bridged[5-13] polynuclear complexes, involving either transition[2,7-13] or main group[3-6] metal atoms, have been explored. The present work extends these studies to nonbridged heteronuclear bonds between transition and posttransition metal atoms, the examples chosen being $Me_3GeMn(CO)_5$, $Me_3SnMn(CO)_5$, $Me_3GeRe(CO)_5$ (Me = methyl), and $Cl_3SnMn(CO)_5$. These are stable molecules, well-suited for the acquisition of high-quality Raman spectra and accurate intensity measurements. Moreover, the corresponding homonuclear metal-metal bonded molecules $Mn_2(CO)_{10}$,[2] $Re_2(CO)_{10}$,[2] Me_6Ge_2,[3] and Me_6Sn_2[3] have previously been studied, so that trends in metal-metal bonding for the heteronuclear molecules can be examined in some detail. Infrared spectra and normal-coordinate calculations have been reported by Onaka[15] for $Me_3SnMn(CO)_5$ and $Cl_3SnMn(CO)_5$ as well as for $Br_3SnMn(CO)_5$.

Experimental Section

The compounds used in this study were prepared and purified by methods described in the literature.[16,17] Raman spectra, were recorded for CCl_4 or $CHCl_3$ solutions in 1-mm glass capillary tubes using transverse laser (5145-Å Ar^+ and 6471-Å Kr^+) exitation. The spectrometer was based on a Spex 1401 double monochromator equipped with a cooled ITT FW130 photomultiplier and dc amplification. The scattered light was analyzed with a polaroid disk and passed through a polarization scrambler before entering the spectrometer.

Intensities were measured from peak areas with reference to nearby solvent bands, corrected for instrumental response, and placed on an absolute scale by comparison with the intensity of the ν_1 band of CCl_4 for which $\bar{\alpha}'_Q = 0.686$ Å^2 amu$^{-1/2}$ [18]

Results

Spectra and Assignments. The observed Raman frequencies are listed in Table I. Only the region below 600 cm^{-1} is reported because it contains all the bands of principal interest to the evaluation of the metal-metal bonds. Assignment of the frequencies can be made on the basis of local C_{3v} and C_{4v} symmetry for the Me_3M'- (M' = Ge, Sn) portion and the -$M(CO)_5$ (M = Mn, Re) portion of the molecule, respectively. Bands in the 400-600-cm^{-1} region arise from metal-carbon stretching and carbonyl bending vibrations. The bands at 557 and 586 cm^{-1} remain essentially unshifted from $Me_3GeMn(CO)_5$ to $Me_3GeRe(CO)_5$ so they must arise from Ge-C rather than Mn-C or Re-C stretching vibrations. The band at 557 cm^{-1} is strongly polarized and is assigned to the A_1 mode and the one at 586 cm^{-1} to the E mode. On the same basis the bands at 504 and 519 cm^{-1} in $Me_3SnMn(CO)_5$ and $Me_3SnRe(CO)_5$ are assigned to the A_1 and E Sn-C stretching modes, respectively. These assignments agree well with the reported frequencies[3] of the A_{1g} and E_g modes at 569 and 586 cm^{-1}, respectively, in Me_6Ge_2 and at 509 and 519 cm^{-1} in Me_6Sn_2.

For the -$M(CO)_5$ portion of the molecules, M-C stretching and MCO bending modes are expected in the regions 350-500 and 500-650 cm^{-1}, respectively. M-C stretching should give rise to two A_1 modes and MCO bending to one. Yet only one strong polarized mode was found, at 398, 414, and 418 cm^{-1} in the $Mn(CO)_5$ derivatives and at 462 and 463 cm^{-1} in the $Re(CO)_5$ derivatives. We assign it to symmetric M-C stretching and assume that the two expected M-C A_1 modes are accidentally coincident. The MCO bending mode may be too weak to be identified. A number of weak bands, of questionable polarization were observed in the spectra. A polarized band of medium intensity at 352 cm^{-1} in the spectrum of $Cl_3SnMn(CO)_5$ can be assigned to the Sn-Cl

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Table I. Observed Raman Frequencies[a] (cm^{-1}) in CCl_4 or $CHCl_3$ Solution

Assignment[b]	Me_3Ge-$Mn(CO)_5$	Me_3Ge-$Re(CO)_5$	Cl_3Sn-$Mn(CO)_5$	Me_3Sn-$Mn(CO)_5$	Me_3Sn-$Re(CO)_5$
$\nu_{M'-Me}(E)$	586 w, dp	581 w, dp		519 w, dp	518 w, dp
$\nu_{M'-Me}(A_1)$	557 m, p	556 m, p		504 s, p	504 s, p
	430 vw, sh			430 vw, sh	
$\nu_{M-CO}(A_1)$	414 s, p	462 s, p	398 m, p	418 s, p	463 s, p
		452 vvw, sh			452 vvw
$\nu_{Sn-Cl}(A_1)$			352 m, p		
$\delta_{C-M'-C}(E)$	197 w, sh	194 vw, dp		163 w, br, dp	161 w, dp, sh
$\nu_{M'-M}(A_1)$	191 s, p	169 s, p	198 s, p	179 s, p	147 s, p
δ_{C-M-C}	104 s, br, dp	97 s, br, dp		102 s, br, dp	98 s, br, dp

[a] Symbols: s, strong; m, medium; w, weak; v, very; sh, shoulder; p, polarized; dp, depolarized; br, broad. [b] On the basis of local C_{3v} and C_{4v} symmetry for the X_3M'- and -$M(CO)_5$ portions of the molecules, respectively.

A_1 stretch (compare 365 cm^{-1} for Cl_3Sn-$Co(CO)_4$[19]). The strong polarized lines at 191, 179, 147, 169, and 198 cm^{-1} are assigned to the metal-metal modes of $Me_3GeMn(CO)_5$, $Me_3SnMn(CO)_5$, $Me_3SnRe(CO)_5$, $Me_3GeRe(CO)_5$, and $Cl_3SnMn(CO)_5$, respectively. The metal-metal frequency for $Me_3SnMn(CO)_5$ has been observed previously at 179 cm^{-1} in the Raman[20] and ir spectra[15] while the analogous 198-cm^{-1} band of $Cl_3SnMn(CO)_5$ has also been seen in the ir.[15]

The weak depolarized line at 163 cm^{-1} for $Me_3SnMn(CO)_5$ and at 165 cm^{-1} for $Me_3SnRe(CO)_5$ is assigned to the C-Sn-C bending vibration of E symmetry. This mode is observed at 152 cm^{-1} in Me_6Sn_2. The A_1 C-Sn-C bending mode must have very little intensity because it was not observed. In Me_6Sn_2 it appears at 135 cm^{-1}. The E C-Ge-C bending mode in $Me_3GeRe(CO)_5$ is observed as a weak depolarized line at 194 cm^{-1} and it is probably hidden under the strong band at 191 cm^{-1} of $Me_3GeMn(CO)_5$. In Me_6Ge_2[3] it is observed at 191 cm^{-1}. Again the A_1 C-Ge-C bending mode was not observed. It appears at 165 cm^{-1} in Me_6Ge_2. All the compounds showed a strong and broad band centered around 100 cm^{-1}. This band must be a superposition of the M-C deformation modes.[21] Since it shows no polarization, it may be assumed that the A_1 deformation modes are very weak.

Force Constants. Approximate normal-coordinate analyses were carried out on all five molecules. The methyl groups were treated as single atoms of mass 15. All the molecules were assumed to have C_s symmetry, which is consistent with the crystal structure of $Me_3SnMn(CO)_5$.[22] Molecular parameters are listed in Table II and labeled in Figure 1. For $Me_3GeMn(CO)_5$, $Me_3GeRe(CO)_5$ and $Me_3SnRe(CO)_5$, we used the crystallographically determined metal-metal distances available for the *phenyl* analogs,[23] in view of the observation[22] that the Sn-Mn distances are identical in $Me_3SnMn(CO)_5$ and $Ph_3SnMn(CO)_5$. The M'-C, M-C, and C-O distances and the bond angles were taken from related molecules.

The primary aim of the analyses was to obtain reliable force constants and eigenvectors for the metal-metal stretching modes. Only the A' block was calculated, using Schachtschneider's program FPERT,[24] and only the frequencies below 600 cm^{-1} were fit with precision. Since A' C-M'-C or Cl-Sn-Cl modes were not observed, we used the reported frequencies for the analagous modes in Me_6Sn_2,[3] Me_6Ge_2,[3] and $Cl_3SnCo(CO)_4$.[19] Valence force constants were transferred from related molecules[3,19,21,25] and, for the most part, were held fixed (see Table III). The M'-M stretching force constant was allowed to vary, as were the force constants for M'-C stretching and C-M'-C bending, which displayed the largest interactions with the M'-M force constant. Their final values are listed in Table III. The uncertainties are estimated to be on the order of 0.05 mdyn/Å.

Table II. Molecular Parameters for Me_3M'-$M(CO)_5$

		Distances, Å				Angles, deg		
M'	M	M'-M	M'-C	M-C	C-O	M'-M-C	C-M-C	C-M'-C
Ge	Mn	2.60[a]	1.98[d]	1.80[c]	1.15[c]	90	90	108
Ge	Re	2.69[a]	1.98[d]	1.95[f]	1.15[f]	90	90	108
Sn	Mn	2.674[b]	2.14[b]	1.80[b]	1.15[b]	90	90	108[b]
Sn	Re	2.74[a]	2.14[c]	1.95[f]	1.15[f]	90	90	108
			$Cl_3SnMn(CO)_5$					
Sn	Mn	2.67[c]	2.32[e]	1.80	1.15[c]	90	90	108

[a] From ref 23. [b] From ref 22. [c] Transferred from $Me_3SnMn(CO)_5$.[22] [d] Transferred from Me_4Ge [L. O. Brockway and H. O. Jenkins, *J. Amer. Chem. Soc.*, 58, 2036 (1936)]. [e] Sn-Cl distance, transferred from $Cl_3SnCo(CO)_4$.[19] [f] Transferred from $Re_2(CO)_{10}$ [L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, 26, 7150 (1957)].

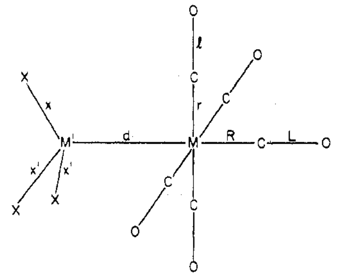

Figure 1. Idealized structure of $X_3M'M(CO)_5$ (X = Me or Cl) molecules, with labeling of internal coordinates. The assumed mirror symmetry is close to what is observed in the crystal structure of $Me_3SnM(CO)_5$.[22]

Bond Polarizability Derivatives. Measured Raman intensities and depolarization ratios of totally symmetric modes can be used to calculate mean molecular polarizability derivatives, $\bar{\alpha}'_Q$, *via* the usual intensity equation.[26] These derivatives can in turn be decomposed into contributions from *internal* coordinates *via* the transformation[26]

$$\bar{\alpha}'_{Q_i} = \sum_u \sqrt{N_u} l_{ui} \bar{\alpha}'_u \qquad (1)$$

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Table III. Valence Force Constants[a] for $X_3M'-M(CO)_5$

	$Me_3GeMn(CO)_5$	$Me_3GeRe(CO)_5$	$Cl_3SnMn(CO)_5$	$Me_3SnMn(CO)_5$	$Me_3SnRe(CO)_5$
	Values Estimated from the Literature[19,21,25] and Held Constant				
$K_r{}^b$	2.40	2.90	2.40	*c*	*d*
K_R	2.50	3.10	2.50		
K_l	16.60	16.60	16.60		
K_L	15.90	16.00	15.90		
K_{C-M-C}^{eq}	0.60	0.66	0.60		
K_{C-M-C}^{ax}	0.34	0.40	0.34		
$K_{C-M-M'}$	0.10	0.09	0.10		
K_{M-C-O}^{ip}	0.48	0.48	0.48		
K_{M-C-O}^{op}	0.48	0.48	0.48		
K_{M-C-O}^{ax}	0.48	0.48	0.48		
$K_{X-M'-M}$	0.10	0.08	0.17		
K_{rr}^{trans}	0.47	0.61	0.47		
K_{rr}^{cis}	−0.02	0.05	−0.02		
K_{rR}	−0.02	0.05	−0.02		
$K_{rl(neighbor)}$	0.69	0.84	0.69		
$K_{rl(opposite)}$	−0.10	−0.09	−0.10		
$K_{rl(adjacent)}$	−0.09	−0.11	−0.09		
K_{rL}	−0.09	−0.11	−0.09		
K_{RL}	0.69	0.84	0.69		
$K_{ll(opposite)}$	0.08	0.11	0.08		
$K_{ll(adjacent)}$	0.17	0.19	0.17		
K_{lL}	0.17	0.19	0.17		
	Values Obtained by Least-Squares Fit				
$K_{M'-M}$	0.73	0.68	1.09	0.90	0.85
$K_{M'-C}$	2.53	2.54	2.26	2.14	2.15
$K_{C-M'-C}$	0.33	0.32	0.22	0.27	0.26

[a] Units are mdyn/Å for stretching force constants and mdyn Å/radian² for bending force constants. [b] See Figure 1 for coordinate labeling. [c] Values in this column are the same as for $Me_3GeMn(CO)_5$. [d] Values in this column are the same as for $Me_3GeRe(CO)_5$.

Table IV. A_1 Eigenvectors for $X_3M'-M(CO)_5$

	$Q_{M'-M}{}^a$	$Q_{M'-C}$
	$Me_3Ge-Mn(CO)_5$	
$S_{M-C}{}^b$	0.0171	0.0223
$S_{M'-M}$	0.1365	−0.0474
$S_{M'-C}$	0.0133	0.4601
	$Me_3Ge-Re(CO)_5$	
S_{M-C}	0.035	0.0022
$S_{M'-M}$	0.1164	−0.0335
$S_{M'-C}$	0.0106	0.4623
	$Me_3Sn-Mn(CO)_5$	
S_{M-C}	0.0195	−0.0155
$S_{M'-M}$	0.1274	−0.0134
$S_{M'-C}$	0.0093	0.4550
	$Me_3Sn-Re(CO)_5$	
S_{M-C}	0.0042	0.0053
$S_{M'-M}$	0.1060	−0.0211
$S_{M'-C}$	0.0070	0.4559
	$Cl_3Sn-Mn(CO)_5$	$Q_{M'-Cl}$
S_{M-C}	0.0246	−0.0138
$S_{M'-M}$	0.1211	−0.0381
$S_{M'-Cl}$	0.0321	0.3051

[a] *Q* is the normal coordinate identified according to the internal coordinate which is the primary contributor. [b] *S* is the symmetry coordinate, constructed from the indicated internal coordinate.

Table V. Raman Intensity Data and Results

Compd	$\nu(A')$, cm^{-1}	ρ^a	$\bar{\alpha}'_Q$,[b] Å^2/amu$^{1/2}$	$\bar{\alpha}'_u$,[c] Å^2	$n/2^d$
$Me_3Ge-Mn(CO)_5$	191 (Ge–Mn)	0.24	0.47	2.97	0.54
	557 (Ge–C)	0.0	0.80	1.91	0.64
$Me_3Ge-Re(CO)_5$	165 (Ge–Re)	0.23	0.35	2.74	0.45
	556 (Ge–C)	0.0	0.72	1.73	0.58
$Me_3Sn-Mn(CO)_5$	179 (Sn–Mn)	0.50	0.47	3.07	0.51
	504 (Sn–C)	0.0	1.25	2.93	0.77
$Me_3Sn-Re(CO)_5$	147 (Sn–Re)	0.45	0.38	3.79	0.58
	504 (Sn–C)	0.0	1.15	2.65	0.62
$Cl_3Sn-Mn(CO)_5$	198 (Sn–Mn)	0.24	0.61	2.56	0.43
	352 (Sn–Cl)	0.26	0.88	1.95	0.42

[a] Depolarization ratio: analyzed scattered radiation with linearly polarized excitation. [b] Polarizability derivative for the indicated normal mode. [c] Bond polarizability derivative for the indicated bond. [d] Bond orders calculated with the Long and Plane equation $\bar{\alpha}'_u = {}^2/_3(g\sigma/za_0)r^3(n/2)$. See ref 18 for definitions. The following constants were used: $z_{Re} = z_{Mn} = 7$; $z_C = z_{Sn} = z_{Ge} = 4$; $X_{Re} = 1.9$, $X_{Mn} = 1.8$, $X_{Sn} = X_{Ge} = 1.7$, $X_C = 2.5$. X = Pauling electronegativity, used in calculating g and σ.[18]

where $\bar{\alpha}'_u$ is the mean polarizability derivative with respect to the internal coordinate u, N_u is the number of such internal coordinates in a set, and l_{ui} is the eigenvector element connecting the normal mode with the symmetry coordinate constructed from the internal coordinate set.

For the molecules in question, metal-metal stretching is reasonably well isolated in the "metal-metal" mode, although there is a moderate contribution from M′–C (or M′–Cl) stretching. Raman intensities and depolarization ratios, in CCl_4 or $CHCl_3$ solution, were measured for these two modes and subjected to the analysis described in the preceding paragraph. The relevant eigenvector elements obtained from the normal-coordinate analyses are given in Table IV. There are small contributions to each of the two modes from M–C stretching on the pentacarbonyl portions of the molecules. These were entered in eq 1, along with an estimate for $\bar{\alpha}'_{M-C}$, 2.5 Å² obtained from a previous study of hexacarbonyl complexes,[27] to serve as a (small)

Table VI. Trends in Metal-Metal Force Constants, Bond Distances, and Bond Orders

	Sn-Mn (Δ%)[a]	Sn-Re (Δ%)	Ge-Mn (Δ%)	Ge-Re (Δ%)
		$K_{M\text{-}M}$, mdyn/Å		
Mean[b]	0.99	1.10	1.06	1.18
Me_3M'-$M(CO)_5$	0.90 (−9)	0.85 (−23)	0.73 (−32)	0.68 (−42)
Cl_3Sn-$Mn(CO)_5$	1.09 (+9)			
		$R_{M\text{-}M}$, Å		
Mean[b]	2.86	2.91	2.67	2.72
Me_3M'-$M(CO)_5$	2.67 (−0.19)	2.74 (−0.17)	2.60 (−0.07)	2.69 (−0.03)
		$n/2_{M\text{-}M}$		
Mean[b]	0.54	0.51	0.52	0.48
Me_3M'-$M(CO)_5$	0.51 (−6)	0.58 (+14)	0.54 (+4)	0.45 (−6)
Cl_3Sn-$Mn(CO)_5$	0.43 (−20)			

[a] Δ% is the per cent deviation (absolute deviation for the bond distance, R) of the observed value from the mean value. [b] The mean of the $K_{M\text{-}M}$, R, or $n/2$ values for the appropriate homonuclear pairs $Me_6M'_2$ and $(CO)_{10}M_2$ (see text).

correction to the $\bar{\alpha}'_{Q_i}$. The only other significant contributor to the eigenvectors was C-M′-C bending. Polarizability derivatives with respect to bending coordinates are expected,[28] and found,[3] to be small, however, so that their contribution to the $\bar{\alpha}'_{Q_i}$ can be neglected. Therefore, the transformation (1) was treated as a pair of simultaneous equations in two unknowns, $\bar{\alpha}'_{M\text{-}M'}$ and $\bar{\alpha}'_{M'\text{-}C}$. The signs of the $\bar{\alpha}'_{Q_i}$ are undetermined, since the Raman intensity is proportioned to $(\bar{\alpha}'_{Q_i})^2$. Consequently there are two pairs of solutions to the simultaneous equations, differing only in sign. Only one choice of signs (both plus) for $\bar{\alpha}'_{Q_1}$ and $\bar{\alpha}'_{Q_2}$ was found to give positive values for both $\bar{\alpha}'_{M\text{-}M'}$ and $\bar{\alpha}'_{M'\text{-}C}$, however. This solution, along with the intensity data, is tabulated in Table V. Also listed in Table V are estimates of M-M′ and M′-C bond orders, $n/2$, obtained with the δ function potential model of Long and Plane.[18]

Discussion

The adjusted force constants in Table III all have reasonable values. Thus, the M′-X and X-M′-X force constants compare well with analogous force constants[3,19] in Me_6Ge_2, Me_6Sn_2, and $Cl_3SnCo(CO)_4$. The M′-M force constants are in the vicinity of 1.0 mdyn/Å, a value typical for metal-metal single bonds.[14,19] Onaka[15] calculated Urey-Bradley force constants for M′-M stretching in $Me_3SnMn(CO)_5$ and $Cl_3SnMn(CO)_5$, 0.7 and 1.0 mdyn/Å, which are somewhat smaller than the valence force constants reported here but are in the same order.

Examination of the M-M′ force constants reveals a distinct trend in the order Sn-Mn > Sn-Re > Ge-Mn > Ge-Re. Moreover all the M′-M force constants for the Me_3M'-$M(CO)_5$ molecules are *smaller* than the average of the force constants associated with the stretching of the corresponding pairs of homonuclear bonds: Mn-Mn, Re-Re, Ge-Ge, and Sn-Sn (0.59, 0.81, 1.54, and 1.39 mdyn/Å, respectively, in $Mn_2(CO)_{10}$,[2] $Re_2(CO)_{10}$,[2] Me_6Ge_2,[3] and Me_6Sn_2[3]), as shown in Table VI. This is surprising, inasmuch as the metal-metal bonds in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ are generally thought to be weak and long,[29] because of buildup of negative charge on the metal atoms and repulsion of their filled dπ orbitals. This repulsion would be absent in the heteronuclear M-M′ bonds, and indeed the latter *are* contracted with respect to the mean of the corresponding pairs of homonuclear bonds, as is also shown in Table VI. While the sign of the force constant deviations from the mean values is opposite to what might have been expected from the bond length deviation, the direction of the *trend* is consistent for the two parameters, *i.e.*, the force constants increase as the decrement in bond length with respect to the mean value increases, from Ge-Re to Sn-Mn. The physical origin of this trend is not altogether clear, although it probably relates to overlap considerations. The metal-metal bonding orbitals are 4p and 5p for Ge and Sn and 3d and 5d for Mn and Re. It would appear that the best match is between the Sn 5p and Mn 3d orbitals, and the worst match is between the Ge 4p and Re 5d orbitals. It may be objected that substitution of Cl for CH_3 on $Me_3SnMn(CO)_5$ would be expected to contract the Sn 4p orbital and worsen the match with Mn 3d orbital, yet a pronounced *increase* in M-M′ force constant is observed on going from $Me_3SnMn(CO)_5$ to $Cl_3SnMn(CO)_5$. This increase may, however, be due to increased polarity (ionic contribution) of the Sn-Mn bond. Graham has suggested,[30] on the basis of an analysis of C-O stretching frequencies, that Cl_3Sn is a much poorer σ donor (better σ acceptor) than Me_3Sn, with respect to $Mn(CO)_5$.

Bond orders calculated from bond polarizability derivatives using the δ function potential model are frequently incorrect in absolute magnitude but appear to provide a reliable basis for comparing related bonds with respect to the number of electron pairs they contain.[2,3] The $n/2$ values given in Table V are obviously much lower than the actual bond orders of the bonds in question, but they can be usefully compared with those of related molecules. The X-M′ bonds all have essentially the same values as those found elsewhere (compare[3] $n/2_{C\text{-}Ge} = 0.58$ in Me_6Ge_2 and $n/2_{C\text{-}Sn} = 0.70$ in Me_6Sn_2). As shown in Table VI, the values for the M′-M bonds agree quite well with the averages of previously determined homonuclear $n/2$ values (0.66, 0.59,[31] 0.37, and 0.42 for $Mn_2(CO)_{10}$,[2] $Re_2(CO)_{10}$,[2] Me_6Ge_2,[3] and Me_6Sn_2,[3] respectively). The deviations are small and do not correlate with the force constant trend. The present $n/2$ values provide no indication of a significant amount of π bonding in the M′-M bonds. If π bonding were quantitatively important, the $n/2$ values would have been expected to exceed significantly the averages for the corresponding pairs of homonuclear bonds, since the latter are incapable of significant π bonding.

Registry No. $Me_3GeMn(CO)_5$, 37843-69-9; $Me_3GeRe(CO)_5$, 51051-55-9; $Me_3SnMn(CO)_5$, 14126-94-4; $Me_3SnRe(CO)_5$, 15219-90-6; $Cl_3SnMn(CO)_5$, 16165-09-6.

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(31) The previously reported value,[2] 0.36, has been found to be in error, as has the corresponding $\alpha'_{Re\text{-}Re}$ (2.2 Å^2) whose redetermined value is 3.6 Å^2 (B. Fontal and T. G. Spiro, unpublished results).