The analytical sample was recrystallized from pentane. When this hydride was heated in solution, it decomposed rapidly and the solution turned dark green.

Bis(trichlorosilylirontetracarbonyl), $[Cl_3SiFe(CO)_4]_2$.—A sample of 2–3 g of $Cl_3SiFeH(CO)_4$ was slowly sublimed under high vacuum into a 60–70 ml Carius tube equipped with a Teflon valve. Pentane (5.0 ml) and tetrafluoroethylene (1.2 l. at STP) were introduced at liquid nitrogen temperature. The reaction mixture was then warmed slowly to room temperature. Gentle agitation of the tube immediately precipitated a coarse, bright yellow, crystalline material. (During this process the Carius tube was kept behind a protective shield. Tetrafluoroethylene under pressure is potentially dangerous.) The excess tetrafluoroethylene and pentane were removed at reduced pressure. The remaining product, $[Cl_3SiFe(CO)_4]_2$, is pure as formed and decomposes above 90°. The infrared spectrum was complicated by the rapid decomposition of the complex in solution. The bands observed immediately after preparing a hexane solution were 2114 (w), 2079 (w), 2070 (m), 2061 (m), 2053 (s), 2049 (vs), 2037 (w), and 2011 cm^{-1} (w); additional weak bands of $Fe(CO)_5$ at 2023 and 2000 cm^{-1} were observed even in the fresh sample and increased rapidly with time.

Thermal Decomposition of $[Cl_3SiFe(CO)_4]_2$.—A sample of 0.20 g of $[Cl_3SiFe(CO)_4]_2$ (0.33 mmol) was placed in a 25-ml Carius tube equipped with a Teflon valve. The tube was evacuated and then slowly heated. At 120–130°, the compound melted to an orange-brown semisolid, which resolidified at this temperature, in approximately 10 min, to a powdery yellow solid, $[Cl_2SiFe(CO)_4]_2$, which was identified by infrared spectroscopy;[13] this reaction proceeded in high yield. The mass spectrum of the gaseous reaction products contained the ions $SiCl_4^+$ and $Fe(CO)_5^+$ as well as their fragments.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08540

Raman Spectra and Metal–Metal Bonds. Force Constants and Bond Polarizability Derivatives for Hexamethyldisilicon, -germanium, -tin, and -lead[1]

BY BERNARDO FONTAL AND THOMAS G. SPIRO*

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Raman and infrared frequencies below 700 cm^{-1} are assigned to the various skeleton modes of the hexamethyldimetal derivatives of silicon, germanium, tin, and lead. A staggered, D_{3d}, configuration is clearly indicated for $(CH_3)_6Ge_2$, while for the remaining molecules the evidence with regard to selection rules is not clear-cut. Approximate normal-coordinate analyses were carried out to obtain a consistent set of skeletal force constants for the molecules. The eigenvectors from the analyses were used to calculate bond polarizability derivatives from the absolute Raman intensities of the A_1 skeletal modes. These in turn were used to calculate bond orders, $n/2$, *via* Long and Plane's δ function model equation. While lower by a factor of 3 than the expected value of unity, the $n/2$ values for the metal–metal bonds are fairly constant despite substantial changes in the force constants. Furthermore the previously determined $n/2$ values for Hg_2^{2+} and $Re_2(CO)_{10}$ fall in the same range, with only $Mn_2(CO)_{10}$ having an exceptional (high) value. It appears that a value of $n/2 = 0.3$–0.4 may be characteristic of single homonuclear metal–metal bonds

Introduction

A recent paper[2] from this laboratory reported absolute Raman intensities and metal–metal bond polarizability derivatives for the molecules $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ and for the aquo Hg_2^{2+} ion, as well as for the bridged complexes $Bi_6(OH)_{12}^{6+}$, $Pb_4(OH)_4^{4+}$, and $Tl_4(OC_2H_5)_4$. The major conclusion was that weak metal–metal interaction in the bridged species could be readily distinguished from the genuine bonds present in the nonbridged species. For this purpose Raman intensities, interpreted with the aid of Long and Plane's semiempirical equation connecting bond polarizability derivatives with bond orders,[3] are much more useful than are vibrational frequencies and the force constants determined from them. These considerations were confirmed and extended in a study of the bridged species $[(CH_3)_3PtX]_4$, where X = OH, Cl, and I.[4] On the other hand the situation with regard to the three reference unbridged molecules was not quantitatively satisfactory, with $Mn_2(CO)_{10}$ giving, inexplicably, a substantially higher estimated metal–metal bond order than either $Re_2(CO)_{10}$ or Hg_2^{2+}, though still lower than the expected value of unity.

It seemed worthwhile examining a broader range of metal–metal bonds, and we report here a Raman and infrared study of the molecules $(CH_3)_6M_2$, where M = Si, Ge, Sn, and Pb. While spectra for all of these species have been reported before[5] and some simple valence force constant calculations have been carried

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* To whom correspondence should be addressed.

[1] This investigation was supported by Public Health Service Grant GM-13498 from the National Institute of General Medical Sciences and by National Science Foundation Grant GP-10122.

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out, this study appears to be the first in which all four molecules are examined as a group, and a consistent set of force constants is calculated. In addition we have measured absolute Raman intensities for the A_1 modes of principal interest and have used them, in connection with the eigenvectors from the normal-coordinate analysis, to calculate metal–metal and metal–carbon bond polarizability derivatives.

Spectra and Assignments

Raman and infrared spectra below 700 cm^{-1} for the four $(CH_3)_6M_2$ compounds are illustrated in Figure 1.

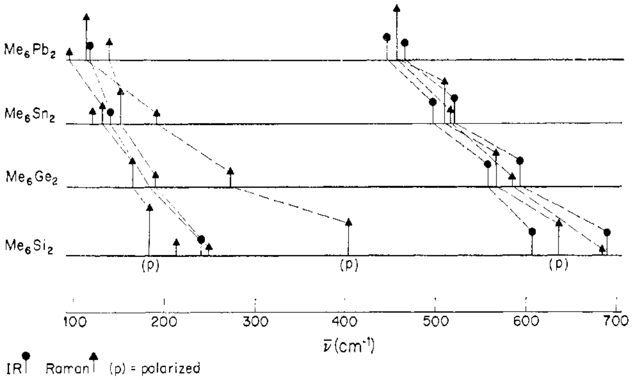

Figure 1.—Summary of vibrational spectra for $(C_6H_3)_6M_2$ compounds, below 700 cm^{-1}. The lengths of the vertical lines indicate the relative intensities of the bands in the Raman (▲) and infrared (●) spectra. The dashed lines connect bands which are assigned to analogous vibrational modes in the four compounds (see text).

The frequencies are in good agreement with those reported by previous workers. For $(CH_3)_6Sn_2$ and $(CH_3)_6Pb_2$ we were unable to examine the low-frequency (<200 cm^{-1}) infrared region, and we have utilized the infrared frequencies given by Clark, *et al.*[5d] The spectral region below 700 cm^{-1} includes the skeletal vibrations of interest here: metal–carbon stretching, metal–metal stretching, and metal–carbon deformation. Carbon–hydrogen stretching and deformation modes occur at higher frequencies. They are expected to mix somewhat with the metal–carbon modes but very little with the metal–metal modes.

Assignment of the frequencies depends on the assumed geometries for $(CH_3)_6M_2$. Staggered (D_{3d}) or eclipsed (D_{3h}) configurations are possible. The representations spanned by a set of internal skeletal coordinates in these two point groups are given in Table I. If there is free rotation about the M–M bond (point group $D_{3h'}$), the representations are the same as for D_{3h}. Previous workers have preferred D_{3d} symmetry for $(CH_3)_6Pb_2$ and $(CH_3)_6Sn_2$,[5d] but D_{3h} symmetry for $(CH_3)_6Si_2$.[5a–c] Table I shows that the expected spectral differences between the two models are not pronounced. In either case there should be three polarized Raman bands and these are readily identified in each of the spectra as the totally symmetric metal–carbon stretch, metal–metal stretch, and metal–carbon deformation (umbrella) mode, in order of decreasing frequency.

The only discrepancy is that $(CH_3)_6Pb_2$ has only two observably polarized Raman bands. Noting this, Clark, *et al.*,[5d] assumed that the lower of these, at 116 cm^{-1}, is a superposition of both the M–M stretch and the C–M–C umbrella mode. However their own simple valence force calculation predicts the umbrella mode some 20 cm^{-1} lower, and our calculations (*vide infra*) show that even with several interaction constants it is very difficult to force the two A_1 modes into a predicted degeneracy. There is a weak Raman band at 97 cm^{-1}, of uncertain polarization, which we prefer to assign to the umbrella mode.

Table I

Distribution and Description of Normal Modes for the C_6M_2 Skeleton of $(CH_3)_6M_2$[a]

	D_{3h}				
	A_1' (R)	A_1'' (inactive)	A_2'' (ir)	E' (ir, R)	E'' (R)
	D_{3d}				
Internal coordinate	A_{1g} (R)	A_{1u} (inactive)	A_{2u} (ir)	E_u (ir)	E_g (R)
MM str	1	0	0	0	0
MC str	1	0	1	1	1
CMM bend	1	0	1	1	1
CMC bend	1	0	1	1	1
Torsion	0	1	0	0	0
Total	3	1	2	3	3
Redundancies	1	0	1	0	0

[a] Abbreviations: ir, infrared active; R, Raman active.

In both the D_{3d} and D_{3h} point groups, four modes are expected for both the M–C stretching and C–M–C bending coordinates. For D_{3d} geometry one expects two Raman (A_{1g}, E_g) and two infrared (A_{2u}, E_u) bands, for each set of coordinates, with no coincidences. The *only* change on going to D_{3h} selection rules is that the ir mode of E symmetry (now E′) becomes Raman active as well. Aside from contributions to modes which can, through redundancies, be expressed in terms of the other coordinates, the C–M–M bending coordinate contributes to two modes of E symmetry. In D_{3d} they are mutually exclusive, while in D_{3h} the ir mode becomes Raman active as well. The torsional coordinate contributes only to a spectroscopically inactive mode in either point group.

Examining first the $(CH_3)_6Ge_2$ spectra (Figure 1) we see that the bands in the C–M stretching region (550–600 cm^{-1}) are consistent only with D_{3d} selection rules. There is no evidence for a third Raman band coincident with one of the ir bands. Likewise in the C–M–C bending region, 160–240 cm^{-1}, only two Raman bands occur, although we were unsuccessful in finding the ir bands. The C–M–M modes were not observed nor have they been reported elsewhere. Both $(CH_3)_6Sn_2$ and $(CH_3)_6Si_2$ show two Raman and two ir bands in the M–C stretching region. However the higher of the two Raman frequencies is coincident, within experimental error, with the higher of the ir frequencies. For $(CH_3)_6Si_2$ this coincidence has been the basis for inferring a D_{3h} (or $D_{3h'}$) configuration.[5a–c] The difficulty with this interpretation is that if the coincident Raman and ir bands arise from the same mode (E′), then the fourth mode (E″) is missing and must be assumed to be degenerate with the E′ mode. There seems little to choose between a D_{3h} or a D_{3d} model since either way there is apparently an accidental degeneracy of the two E type modes. In the bending region both compounds have three Raman bands and only one ir band. The third Raman band, if assigned to a C–M–C mode, could be taken to confirm D_{3h} configuration, or it could be assigned to a C–M–M mode. Unfortunately neither assignment is easy to reconcile with quantitative calculations. Despite a good deal of trial and error we have been unable to calculate the 215-cm^{-1} band of $(CH_3)_6Si_2$ or the 122-cm^{-1} band of $(CH_3)_6Sn_2$ satisfactorily. They have not been reported by others and may possibly be due to impurities. For $(CH_3)_6Pb_2$ the M–C stretching region shows two ir bands but only one, noncoincident, Raman band. The bending region shows two Raman bands and one ir band, again without coincidences. Because in each region at least one band is missing, there can be no clear inference of symmetry.

It appears therefore that only for $(CH_3)_6Ge_2$ is the evidence regarding molecular geometry clear-cut, and it favors the staggered, D_{3d}, configuration. The spectra of the remaining molecules correlate satisfactorily with those of $(CH_3)_6Ge_2$, as the dashed lines in Figure 1 show. It seems reasonable to assume that they all adopt the staggered configuration. It is particularly difficult to understand on physical grounds why $(CH_3)_6Si_2$ should adopt a D_{3h} or $D_{3h'}$ configuration since, being at least as crowded as $(CH_3)_6Ge_2$, it would be expected to prefer the staggered configuration at least as much.

Force Constants

Approximate normal-coordinate analyses were carried out on all four $(CH_3)_6M_2$ molecules, using an eight-atom ethane-like model with methyl groups treated as single atoms of mass 15. The aim was to obtain a consistent set of metal–metal force constants and also to fit the spectra with sufficient accuracy to produce reliable eigenvectors for the A_1 skeletal modes, for use in calculating bond polarizability derivatives from the measured Raman intensities.

TABLE II

MOLECULAR PARAMETERS FOR $(CH_3)_6M_2$

M	Distances, Å MM	MC	CMC angles, deg	Ref
Si	2.34	1.90	109.5	6
Ge	2.42	1.98	109.5	7
Sn	2.80	2.18	109.5	7
Pb	2.88	2.25	109.5	8

Molecular parameters are listed in Table II.[6-8] These were used to construct the G matrices using Schachtschneider's program GMAT.[9] Both G and F matrices were factored using symmetry coordinates generated by standard group theoretical methods. Schachtschneider's program FPERT[9] was used to solve the secular equations, with least-squares adjustment of the force constants. The principal valence force constants were initially chosen to fit the different spectral regions approximately. Interaction force constants were then added as needed to improve the agreement between observed and calculated frequencies. Since no frequency could be assigned with confidence primarily to C–M–M bending, the associated force constant was set equal to zero in order to avoid an ill-conditioned fit of the frequencies. Its effect is absorbed primarily by the C–M–C bending constant.

The final calculated frequencies are compared with the observed frequencies in Table III, while Table IV lists the adjusted force constants and Table V shows the A_1 eigenvectors. The results given are for an assumed staggered, D_{3d}, configuration of the molecules. For $(CH_3)_6Si_2$, calculations were also performed using an eclipsed, D_{3h}, configuration. The frequency fit was of the same quality and the changes in the force constants and eigenvectors were negligible. It seems safe to assume that for the other molecules as well the assumed configuration is of no great consequence to the normal-coordinate analysis results.

TABLE III

OBSERVED AND CALCULATED FREQUENCIES FOR $(CH_3)_6M_2$ (D_{3d} SYMMETRY)

	$(CH_3)_6Si_2$		$(CH_3)_6Ge_2$		$(CH_3)_6Sn_2$		$(CH_3)_6Pb_2$	
Species	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
			Raman Bands					
E_g	688	688	586	590	519	519	458	462
A_{1g}	638	639	569	567	509	505	458	453
A_{1g}	404	395	273	270	192	190	116	117
E_g	251	248	192	192	152	147	141	130
A_{1g}	184	163	165	164	135	126	97	103
E_g[a]	215?	0	. . .	0	122?	0	. . .	0
			Infrared Bands					
E_u	691	698	595	590	520	519	467	463
A_{2u}	610	607	560	562	499	503	448	452
A_{2u}	243	248	. . .	217	142	147	118	113
E_u	243	247	. . .	192	142	147	118	130
E_u[a]	. . .	0	. . .	0	. . .	0	. . .	0

[a] Calculated values constrained by setting $f_{CMM} = 0$.

TABLE IV

ADJUSTED VALENCE FORCE CONSTANTS FOR $(CH_3)_6M_2$ (MDYN/Å)[a]

	$(CH_3)_6Si_2$	$(CH_3)_6Ge_2$	$(CH_3)_6Sn_2$	$(CH_3)_6Pb_2$
	Principal Force Constants			
f_{MM}	1.70	1.54	1.39	0.98
f_{MC}	2.49	2.47	2.08	1.74
f_{CMC}	0.20	0.17	0.09	0.07
	Interaction Force Constants			
$k_{CM,CM}$(str–str)	0.11	0.07	0.04	0.02
$k_{MM,CMC}$(str–bend)	−0.05	−0.05	−0.05	−0.04
$k_{CMC,CMC}$(bend–bend)	0.03	0.05	0.02	0.01

[a] Principal force constants for torsion and for CMM bending and all other interaction constants were constrained to zero.

Bond Polarizability Derivatives.—The intensities and depolarization ratios of the three A_1 Raman bands were measured for each molecule in CCl_4 solution and used to calculate mean polarizability derivatives for the normal modes, $\partial\alpha/\partial Q_i = \bar{\alpha}'_{Q_i}$, as described previ-

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(9) J. H. Schachtschneider, Technical Report No. 231-64 and 57-65, Shell Development Co., Emeryville, Calif., 1964 and 1965.

TABLE V

A_{1g} EIGENVECTORS FOR $(CH_3)_6M_2$

	Q_1[a]	Q_2	Q_3
		$(CH_3)_6Si_2$	
S_{MC}[b]	0.2668	0.0849	0.0011
S_{MM}	−0.1732	0.2011	0.0281
S_{CMC}	−0.4390	0.5510	−0.4880
		$(CH_3)_6Ge_2$	
S_{MC}	0.2659	0.0201	0.0019
S_{MM}	−0.0540	0.1496	0.0474
S_{CMC}	−0.1400	0.5250	−0.4040
		$(CH_3)_6Sn_2$	
S_{MC}	0.2632	0.0089	0.0005
S_{MM}	−0.0304	0.1251	0.0167
S_{CMC}	−0.0764	0.3800	−0.5060
		$(CH_3)_2Pb_2$	
S_{MC}	0.2610	0.0029	0.00001
S_{MM}	−0.0162	0.0969	0.0011
S_{CMC}	−0.0396	0.2440	−0.5480

[a] Q is the normal coordinate, numbered in the order of decreasing frequency of the corresponding A_{1g} modes. [b] S is the symmetry coordinate, constructed from the indicated internal coordinates.

ously.[2] Unfortunately $(CH_3)_6Pb_2$ decomposed rapidly in the laser beam of the Raman spectrometer and no meaningful intensities could be obtained for it.

The normal mode polarizability derivatives can be decomposed into contributions from each of the internal coordinates *via* the transformation[10]

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

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 the set, and l_{ui} is the eigenvector element connecting the normal mode with the symmetry coordinate constructed from the internal coordinate set. Since there are three skeletal A_1 modes, the transformation involves three simultaneous equations, involving the unknowns $\bar{\alpha}'_{CM}$, $\bar{\alpha}'_{MM}$, and $\bar{\alpha}'_{CMC}$.[11] Furthermore the sign of $\bar{\alpha}_{Q_i}$ is undetermined because the intensity is proportional to $(\bar{\alpha}'_{Q_i})^2$. Consequently there are four possible pairs of solutions to the three simultaneous equations, the members of each pair differing only in sign. For each molecule it was found that only one pair of solutions gave reasonable magnitudes for $\bar{\alpha}'_{CM}$ and $\bar{\alpha}'_{MM}$. Table VI gives the more positive set for each of these solutions. Reorientation of bonds, *i.e.*, a bending coordinate, is assumed not to contribute to $\bar{\alpha}'_{Q_i}$ in the Wolkenstein bond polarizability theory.[12] When subject to test this assumption has been found to be reasonably valid.[4,13] The $\bar{\alpha}'_{CMC}$ values are indeed quite small. Table IV also gives bond orders, $n/2$, calculated from the bond polarizability derivatives with the δ function model equation of Long and Plane.[3]

TABLE VI

Compound[a]	$\nu(A_{1g})$, cm^{-1}	ρ_l[b]	$\bar{\alpha}'_Q$, Å^2	$\bar{\alpha}'_u$, Å^2	$n/2$
$(CH_3)_6Si_2$	184 (CMC)	0.658	0.141	−0.05	. . .
	404 (MM)	0.018	0.553	1.69	0.31
	628 (MC)	0.037	0.627	1.33	0.48
$(CH_3)_6Ge_2$	165 (CMC)	0.649	0.143	−0.03	. . .
	273 (MM)	0.066	0.380	2.20	0.37
	569 (MC)	0.021	1.07	1.81	0.58
$(CH_3)_6Sn_2$	135 (CMC)	0.425	0.339	−0.21	. . .
	192 (MM)	0.081	0.348	3.89	0.42
	509 (MC)	0.181	1.81	2.93	0.70

[a] Extensive decomposition prevented intensity studies with $(CH_3)_6Pb_2$. [b] Depolarization ratio from analyzed scattered radiation from polarized incident radiation.

Discussion

The force constants obtained from the normal-coordinate analysis are all reasonable. The MC stretching and CMC deformation force constants are in good agreement with those reported for the analogous $(CH_3)_4M$ species[14] as are the interaction constants $k_{CM,CM}$ and $k_{CMC,CMC}$. The metal–metal force constants are substantially higher than those calculated by Brown, *et al.*,[5a] and by Clark, *et al.*,[5d] using A_{1g} frequencies only. For $(CH_3)_6Si_2$ and $(CH_3)_6Ge_2$ the present values of f_{M-M} are in good agreement with the values given for disilane (1.75 mdyn/Å)[15] and digermane (1.60 mdyn/Å).[16] The metal–metal force constants decrease smoothly with increasing atomic number from Si to Pb, in accord with expectation based on the homonuclear bond strengths of the group IV elements.[17]

The main point of interest here concerns the estimate of bond orders from bond polarizability derivatives *via* the Long and Plane equation.[3] This equation can be criticized on the grounds that it is based on a vastly oversimplified model of the chemical bond. On the other hand it has proved quite successful in calculating bond polarizability derivatives, within about 30%, for a wide range of molecules without any adjustable parameters.[3] Even if bond orders calculated with this equation are not meaningful in an absolute sense, they may at least be useful in comparing chemically related systems.

Such comparisons are quite revealing for the $(CH_3)_6M_2$ molecules. Table VI shows that, although the metal–metal bond polarizability derivatives more than double on going from M = Si to M = Sn, the calculated bond orders vary by only 30%. The absolute values of $n/2$ (0.32–0.42) are about one-third as large as they should be, since we are clearly dealing with single bonds. The important point is, however, that the $n/2$ values are nearly constant and that they do not correlate with the force constants. It is clear that while the force constants reflect changes in the metal–metal bond

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(10) R. E. Hester in "Raman Spectroscopy," H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1967, Chapter 4.

(11) There is actually a fourth unknown since C–M–M bending also contributes to the A_1 block. Because of the form of the redundancy, however, $l_{CMM,i} = -l_{CMC,i}$. Therefore we set $\bar{\alpha}'_{CMM} = -\bar{\alpha}'_{CMC}$, and the contribution to eq 1 from angle bending becomes $2\sqrt{6} l_{CMC,i} \bar{\alpha}'_{CMC}$.

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(16) E. A. Clark, Thesis, Fordham University, 1966.

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strengths, the $n/2$ values reflect, at least roughly, the expected constancy in the number of bonding electrons, even if the actual electron count is off by a factor of 3.

Of still greater interest is the fact that two out of the previous three $n/2$ values[2] for single metal-metal bonds fall in the same range, even though the molecules are quite different in electronic structure. For Hg_2^{2+} $n/2 = 0.38$, while for $Re_2(CO)_{10}$ $n/2 = 0.36$. The only exceptional value is given by $Mn_2(CO)_{10}$ for which $n/2 = 0.66$. We can offer no explanation at present of the $Mn_2(CO)_{10}$ anomaly, although a possibility is suggested in the succeeding paper.[18] However, with five apparently well-behaved representatives from a fairly wide range of metal-metal bonded molecules, it now becomes a reasonable conjecture that a metal-metal bond of unit bond order will give $n/2 = 0.3$–0.4 as calculated with the Long and Plane equation.

The $n/2$ values for the metal-carbon bonds in the $(CH_3)_6M_2$ molecules show a greater variation, ranging from 0.48 for $(CH_3)_6Si_2$ to 0.70 for $(CH_3)_6Sn_2$. Part of the variation may be due to neglect of the carbon-hydrogen modes in the analysis. In particular the HCH umbrella mode, which occurs at ~750 cm^{-1}, may mix appreciably with the A_1 MC stretch. Since CH deformation is not expected to contribute to $\bar{\alpha}'_Q$, the effect of mixing would be mainly to lower the MC eigenvector element for the A_1 MC stretching mode and therefore to raise the calculated $\bar{\alpha}'_{MC}$. Since mixing should be greatest for $(CH_3)_6Si_2$, which has the highest MC stretching frequencies, the effect of this correction would be to compensate some of the observed variation in $\bar{\alpha}'_{MC}$ and in the associated $n/2$ values. We note that for the CC bond in ethane $n/2$ is 0.76 or 0.50,[3] depending on which of two available sets of force constants is chosen.[19]

Experimental Section

Preparations.—Hexamethyldisilane was obtained from Peninsular Chemical Research Inc. (PCR) and distilled before use. Hexamethyldigermane was prepared from $(CH_3)_3GeBr$ using the method described by Brown and Fowles[20] ($((CH_3)_3GeBr$ in molten potassium), and distilled in a vacuum line. Hexamethylditin was purchased from Alfa Inorganics and distilled in a vacuum line prior to use and the solutions were kept under an inert atmosphere. Hexamethyldilead was synthesized following the method of Calingaert and Soroos[21] ($PbCl_2$ and CH_3MgBr at −10° in ether) and recrystallized from ether before use.

Physical Measurements.—Infrared spectra (190–1000 cm^{-1}) were measured for $(CH_3)_6Si_2$ and $(CH_3)_6Ge_2$ as neat liquids between CsI plates using a Beckman IR-12 infrared spectrophotometer. Raman spectra were recorded using a spectrometer described previously,[2] employing the 6764-Å (red) line from a mixed-gas Ar-Kr ion laser (Coherent Radiation Lab, Model 52) for excitation. Raman intensities were measured in CCl_4 solution using the 459-cm^{-1} (ν_1) line of the solvent as an internal standard. The spectrum of $(CH_3)_6Pb_2$ was taken in ether, but extensive decomposition prevented accurate intensity measurements.

Polarization measurements were made using a polaroid filter placed before the entrance slit. The spectrometer was equipped with a polarization scrambler. Overlapping bands were resolved using Lorentzian-shaped lines employing a Du Pont 310 curve resolver. Areas were measured directly with a polar planimeter and corrected for instrumental response.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08540

Raman Spectra and Metal-Metal Bond Strengths for Hexaphenylditin and Hexaphenyldilead[1]

BY P. ALAN BULLINER, CARL O. QUICKSALL, AND THOMAS G. SPIRO*

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Low-frequency Raman spectra of hexaphenylditin, hexaphenyldilead, and tetrakis(triphenyltin)tin are reported and assigned. Normal-coordinate calculations have been carried out for the totally symmetric vibrations of the two ethane analogs, using an assumed D_{3d} model for the $(C_6)_6M_2$ skeletons. The derived metal-metal force constants and eigenvectors appear rather insensitive to the approximations made. The eigenvectors were combined with absolute Raman intensities, corrected for resonance enhancement, to allow the estimation of metal-metal bond polarizability derivatives and bond orders. The metal-metal bonds appear to be quite similar to those occurring in the hexamethyl analogs, contrary to the impression gained from considering only the metal-metal frequencies themselves.

Introduction

This report is one of a series[2] from this laboratory concerned with force constants and polarizability derivatives for metal-metal bonds. Our interest in the phenyl derivatives of tin and lead arose from a report[3] that the symmetric Sn-Sn stretching frequencies for $(C_6H_5)_6Sn_2$ and $((C_6H_5)_3Sn)_4Sn$ were 208 and 207 cm^{-1}. While these frequencies were in reasonable accord with the previously reported ν_{Sn-Sn} 190 cm^{-1} for $(CH_3)_6Sn_2$,[4]

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* To whom correspondence should be addressed.

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