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 $\sim$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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[18] P. A. Bulliner, C. O. Quicksall, and T. G. Spiro, *Inorg. Chem.*, **10**, 13 (1971).

[19] Y. Yoshino and H. J. Bernstein, *Spectrochim. Acta*, **14**, 127 (1959).

[20] M. P. Brown and W. A. Fowles, *J. Chem. Soc.*, 2811 (1958).

[21] G. Calingaert and H. Soroos, *J. Org. Chem.*, **2**, 535 (1938).

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.

(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.

(2) (a) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **9**, 1045 (1970); (b) B. Fontal and T. G. Spiro, *ibid.*, **10**, 9 (1971).

(3) H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Commun.*, 616 (1966).

(4) M. P. Brown, E. Cartmell, and G. W. A. Fowles, *J. Chem. Soc.*, 506 (1960).

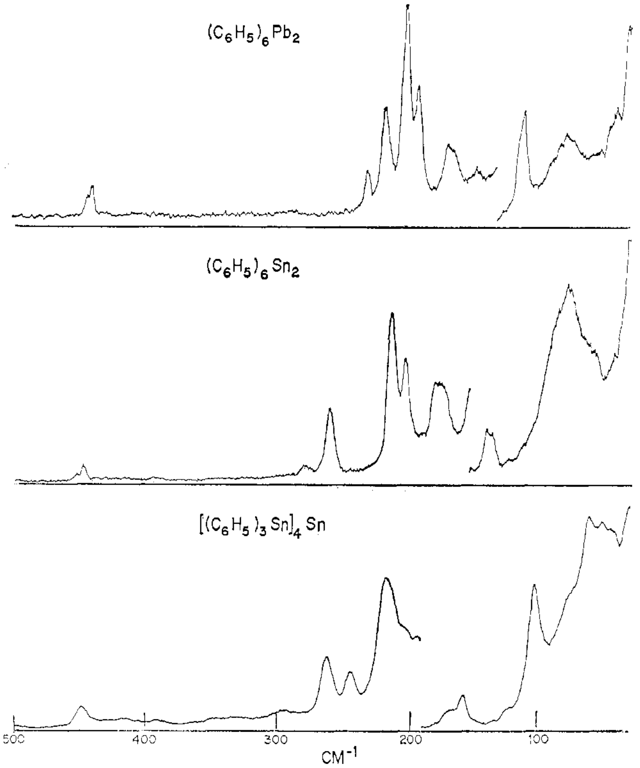

Figure 1.—Low-frequency Raman spectra for microcrystalline samples of $(C_6H_5)_6Pb_2$, $(C_6H_5)_6Sn_2$, and $[(C_6H_5)_3Sn]_4Sn$. Note scale change between 100 and 200 cm^{-1}.

it apparently escaped notice that the symmetrized *G*-matrix element for the symmetric A_1 stretch of $((C_6H_6)_3Sn)_4Sn$ is half that for $(C_6H_5)_6Sn_2$. The assignment of the same frequency for both modes thus appears inconsistent with the expected similarity in the Sn–Sn force constants.

Our preliminary comparisons of the low-frequency Raman spectra of $((C_6H_5)_3Sn)_4Sn$, $(C_6H_5)_6Sn_2$, and $(C_6H_5)_6Pb_2$ clearly suggested reassignments of the symmetric metal–metal vibrations for the two tin compounds more consistent with the different *G*-matrix elements. The reassignments however led to fresh questions about the values of the metal–metal force constants in the two hexaphenyl derivatives, with respect to each other and with respect to the hexamethyl analogs. Previous experience suggested that for metals as heavy as tin and lead, ligands made up of first-row atoms can be neglected without serious error,[5] so that a good approximation to the metal–metal force constant may be obtained directly from the observed frequency and appropriate *G*-matrix element. On the other hand, the phenyl group has vibrational modes which are much closer in frequency to the metal–metal modes than do the simple ligands considered previously, *i.e.*, methyl and carbonyl. Therefore the possibility arises that the metal–metal frequencies could be appreciably displaced by mechanical coupling.

Normal-coordinate calculations for the two hexaphenyl derivatives were carried out to produce more reliable estimates of the metal–metal force constants, and intensity data have been analyzed for the purpose of assessing metal–metal bond orders.

Spectra and Assignments

Raman spectra of the solids $(C_6H_5)_6Pb_2$, $(C_6H_5)_6Sn_2$, and $((C_6H_5)_3Sn)_4Sn$ in the range 30–500 cm^{-1} are shown in Figure 1, and Raman frequencies and polarizations are summarized in Table I. The frequencies above 500 cm^{-1} appear to be quite similar for all three compounds and have not been studied in detail.

Table I

Raman Frequencies[a] and Polarizations for $(C_6H_5)_6Pb_2$, $(C_6H_5)_6Sn_2$, and $((C_6H_5)_3Sn)_4Sn$ (30–500 cm^{-1})

$(C_6H_5)_6Pb_2$		$(C_6H_5)_6Sn_2$		$((C_6H_5)_3Sn)_4Sn$		Assignment
448		453	. . .[b]	449	. . .	"y modes"[c]
444		448				
233	p[d]	280	p[e]	262	nr	"t modes"
219	dp	261	dp[e]	243	nr	
203	p	214	p	216	p	"u modes"
194	dp	204	dp	204	dp?	
170	dp	178	dp	168	dp	"x mode"
				159	dp	ν_{M-M}(asym)
148	dp	150	dp	124	?[f]	?
114 sh[g]	p	140[g]	p	103	p	ν_{M-M}(sym)
111		136				
89 sh				76	?[f]	
84 sh	nr[h]	76	nr	58	nr	δ_{C-M-C}
77						
70 sh						
52	nr	56	nr			δ_{C-M-M}?
43 sh	nr					?
38						

[a] Frequencies listed are those observed in the solid state; solution values agree to within ~5 cm^{-1}. [b] Not studied in solution. [c] y, t, u, and x modes refer to Whiffen's notation for the vibrations of phenyl derivatives: D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956). [d] Abbreviations: p, polarized; dp, depolarized; sh, shoulder. [e] From CS_2 solution; all other polarizations from $CHCl_3$ solution. [f] Weak and possibly spurious lines. [g] Splitting not observable in solution and presumably due to crystal effects. [h] "nr" indicates not resolved from exciting line or other Raman lines in solution spectra.

During the course of this work, vibrational spectra for hexaphenyldilead were reported by Clark, *et al.*[6] The present results are in substantial agreement but include several additional features. The previous work lists only two polarized lines (at 109 and 203 cm^{-1}) and does not report the rather prominent feature at 194 cm^{-1}.

Table I demonstrates that the spectra of the three compounds are quite similar except for the strong polarized features at 112 ($(C_6H_5)_6Pb_2$), 138 ($(C_6H_5)_6Sn_2$), and 103 cm^{-1} [$((C_6H_5)_3Sn)_4Sn$]. On the basis of the intensity, polarization, and shifts between compounds, these lines may be confidently assigned to the respective (totally symmetric) metal–metal vibrations. The assignment for ν_{Pb-Pb} is then the same as that given by Clark,[6] and the frequency is essentially the same as for $(CH_3)_6Pb_2$.[7] The Sn–Sn frequency

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(5) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **8**, 2363 (1969).

(6) R. J. H. Clark, A. G. Davies, and R. J. Puddephatt, *ibid.*, **8**, 457 (1969).

(7) R. J. H. Clark, A. G. Davies, R. J. Puddephatt, and W. McFarlane, *J. Amer. Chem. Soc.*, **91**, 1334 (1969).

in hexaphenylditin is however ~30% lower than the value for $(CH_3)_6Sn_2$. The region previously assigned[3] to metal–metal stretching for the two tin compounds (200–220 cm^{-1}) has a very similar appearance in all three spectra, and a polarized line at 214 cm^{-1} is also observed for $(C_6H_5)_4Sn$.[8] Clearly the vibrations appearing in this region must involve predominantly the metal–phenyl unit rather than the metal–metal bonds. The asymmetric (T_2) Sn–Sn vibration of $((C_6H_5)_3Sn)_4Sn$ is tentatively associated with the Raman line at 159 cm^{-1}.

The assigned metal–metal frequencies would suggest, in the absence of mixing, that the Pb–Pb force constants are the same in the hexaphenyl and hexamethyl derivatives but that the Sn–Sn force constant is much weaker in the phenyl derivative. Furthermore, for $(C_6H_5)_6M_2$, f_{Sn-Sn} would appear to be no larger than f_{Pb-Pb}.

Other vibrations of the phenyl compounds are expected below 500 cm^{-1} and could be strongly coupled with the metal–metal vibrations. In addition to deformation and torsional modes of the M_2C_6 (or M_5C_{12}) skeleton, the modes denoted by Whiffen[9] as "u," "t," "x," "y," and "w," must be considered. To a first approximation these vibrations may be described as in-plane ring–M bending (u), M–C stretching (t), ring folding (x), out-of-plane ring–M bending (y), and ring puckering (w).

Qualitative assignments for most of the observed frequencies are included in Table I. The y modes are known to occur between 420 and 530 cm^{-1} [8] and are easily assigned to the weak Raman lines near 450 cm^{-1} in the present case. The w modes are expected to fall near 400 cm^{-1} [8] and are presumably unobserved. The assignments of the t, u, and x modes are based primarily on comparisons between $(C_6H_5)_6Sn_2$ and the series $(C_6H_5)_mSnCl_{4-m}$ (m = 1–3). In the latter compounds the ranges are as follows: t, 222–273 cm^{-1}; u, 210–218 cm^{-1}; x, 176–185 cm^{-1}.[8] Similarly, the values for iodobenzene (iodine having a mass near that of tin) are 266, 220, and 166 cm^{-1}, respectively.[9] Assignments for $((C_6H_5)_3Sn)_4Sn$ and $(C_6H_5)_6Pb_2$ then follow directly by comparison with $(C_6H_5)_6Sn_2$.

The assignments for $(C_6H_5)_6Pb_2$ arrived at in this fashion seem more consistent with other phenyl–metal spectral features and the assumed symmetry of the molecule than do those given by Clark, *et al.*[6] In any case, these descriptions must be considered approximate, as significant mixing of internal-coordinate types is expected.

Normal-Coordinate Analyses

Application of normal-coordinate methods to hexaphenylditin and hexaphenyldilead is complicated by a lack of structural information. The following assumptions can be made with some confidence.

(1) D_{3d} symmetry is assumed for the C_3M-MC_3 skeleton. This choice has been indicated for hexamethyldilead by electron diffraction[10] and is consistent with the apparent absence of infrared–Raman coincidences for hexaphenyldilead.[6]

(2) Tetrahedral (or near-tetrahedral) angles exist at the metal atoms.

(3) Bond distances estimated from similar compounds and covalent radii are as follows: Sn–Sn = 2.81 Å, Sn–C = 2.15 Å, Pb–Pb = 2.88 Å, Pb–C = 2.19 Å, C–C = 1.40 Å.

In order to perform calculations for the entire $(C_6)_6M_2$ skeleton (protons omitted for simplicity), it is necessary to choose an orientation for the planes of the phenyl rings. Since the barrier to rotation about the metal–carbon bond in solution may be small, crystal structure results for metal–phenyl compounds, which show a variety of ring orientations,[11,12] are not necessarily relevant to the present analysis. There are two ring orientations for which D_{3d} symmetry, assumed to be appropriate for the skeleton vibrations, is retained; the rings may lie either in the symmetry planes or perpendicular to them. The former choice has been made here; presumably the similarity of solid and solution spectra indicates that the degree of ring "tilt" is not a critical factor.

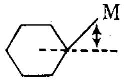
Internal coordinates appropriate to this D_{3d} model of $(C_6)_6M_2$ are given in Table II, along with the vibrational representations spanned. In view of the complexity of the problem, calculations were restricted to the totally symmetric (A_{1g}) vibrations, which are sufficient for an approximate evaluation of metal–metal

TABLE II

INTERNAL COORDINATES AND REPRESENTATIONS FOR A D_{3d} MODEL OF $(C_6)_3M-M(C_6)_3$

Coordinate	A_1	A_{2g}	E_g	A_{1u}	A_{2u}	E_u
C–C str (6 types)[a]	6	0	6	0	6	6
C–C–C bend (6 types)[a]	6	0	6	0	6	6
M–C str ("t mode")	1	0	1	0	1	1
M–M str	1	0	0	0	0	0
M–ring in-plane bend[b] ("u mode")	1	0	1	0	1	1
C–M–C bend	1	0	1	0	1	1
C–M–M bend	1	0	1	0	1	1
M–ring out-of-plane bend	0	1	1	1	0	1
C–C bond torsion (6 types)[a]	0	6	6	6	0	6
M–C bond torsion	0	1	1	1	0	1
M–M bond torsion	0	0	0	1	0	1
Total	17	8	24	9	16	25
Γ vib	13	5	18	6	12	18
Redundancies	4	3	6	3	4	7

[a] In this structure, each C–C bond (or C–C–C angle or C–C bond torsion) in a given ring is symmetrically nonequivalent to every other, so that the sets made up from the corresponding coordinates in each ring give rise to separate (but identical) representations. These contributions have been summed for brevity. [b] The actual internal coordinate used is the angle between the M–C bond and the bisector of the adjacent C–C–C angle, *i.e.*



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(8) A. L. Smith, *Spectrochim. Acta, Part A*, **24**, 695 (1968).

(9) D. H. Whiffen, *J. Chem. Soc.*, 1350 (1956).

(10) H. A. Skinner and E. L. Sutton, *Trans. Faraday Soc.*, **36**, 1209 (1940).

(11) H. P. Weber and R. F. Bryan, *Chem. Commun.*, 443 (1966).

(12) V. Busetti, M. Mammi, A. Signor, and A. Del Pra, *Inorg. Chim. Acta*, **1**, 424 (1967).

force constants and polarizability derivatives. Thus only those internal coordinates spanning A_{1g} need be considered. Examination of the vibrational representation shows that 13 A_{1g} modes are expected. Nine of these consist primarily of C–C stretching and C–C–C bending and correspond to the phenyl modes designated by Whiffen as k, l, m, n, o, p, q, r, and s.[9] All nine frequencies will lie above 500 cm^{-1}. The remaining A_{1g} vibrations may be described as a t mode ("M–C stretch"), a u mode ("M–ring in-plane bend"), the metal–metal stretch, and a deformation mode involving the C–M–C and C–M–M angles.

Calculations were carried out using Schactschneider's programs GMAT,[13a] for the construction of the *G* matrix, and FPERT,[13b] for the least-squares refinement of force constants.

As our interest is in the low-frequency modes and the associated force constants, no effort was made to account in detail for the nine high-frequency ring motions. Instead, literature values[14] for the pertinent benzene force constants (*i.e.*, f_{C-C}, f_{C-C-C}, and interaction constants) were included and held fixed. Small changes in these constants had only minor effects on the calculation of the low frequencies.

Of the remaining four A_{1g} modes, three are observed for each molecule, while the skeletal bending mode is presumably of low intensity and not resolved from the exciting line wing (see Table I). For this reason the skeletal bending constants were fixed equal to the values found for the hexamethyl analogs.[2b] The three observed frequencies were then fit by adjusting the three force constants f_{M-M}, f_{M-C}, and f_{C-C-M}.

Initial results demonstrated that for both molecules this type of three-by-three fit is very poorly conditioned. The two highest frequencies in each case show extensive mixing of f_{M-C} and f_{C-C-M} in the potential energy distribution, so that it was possible to obtain reasonable agreement (±10 cm^{-1}) with the observed frequencies with a considerable range of values for these two constants. Fortunately for our purposes, the metal–metal force constants are relatively insensitive to these uncertainties in f_{M-C} and f_{C-C-M}.

Similarly, the metal–metal force constants appear to be nearly independent of the values chosen for the skeletal bending force constants. The problem was studied for a range of values of $(f_{C-M-C} + f_{C-M-M})$[15] from 0 to 1.05 mdyn-Å (the appropriate values for $(CH_3)_6Sn_2$ and $(CH_3)_6Pb_2$ are 0.43 and 0.35 mdyn-Å, respectively). As expected, f_{M-C} and f_{C-C-M} remain poorly defined, but the changes in f_{M-M} are reasonably small.

Table III summarizes the results of the calculations. The force constants are expressed as a range of values for which acceptable agreement with the three observed frequencies was obtained. The ranges are not intended to represent total uncertainties in any general sense; for example, no consideration of uncertainties arising from the assumed geometry is included.

TABLE III

RANGES OF VALUES OF f_{M-C}, f_{C-C-M}, AND f_{M-M} (MDYNE/Å) COMPATIBLE WITH ASSUMED GEOMETRY AND OBSERVED FREQUENCIES

	$(C_6H_5)_6Sn_2$	$(C_6H_5)_6Pb_2$
f_{M-C}	3.03 ± 0.55	2.74 ± 0.41
f_{C-C-M}	0.18 ± 0.07	0.16 ± 0.05
f_{M-M}	1.17 ± 0.06	1.01 ± 0.05

Within the limitations of the model, the metal–metal force constants are reasonably well defined. The value of f_{Sn-Sn} is slightly lower (16%) than the value for hexamethylditin (1.39 mdyn/Å),[2b] whereas it would be lower by a factor of 2.6 if the Sn–Sn frequencies were treated in isolation. On the other hand, the present estimate of f_{Pb-Pb} is the same as that found for the hexamethyl analog (0.98 mdyn/Å),[2b] as are the Pb–Pb frequencies. The present results are consistent with the steady decrease in f_{M-M} with increasing atomic number of M found for $(CH_3)_6M_2$ (M = Si, Ge, Sn, Pb).

The metal–carbon force constants are, as noted earlier, poorly defined, and may be quite sensitive to the assumed geometry. For these reasons it seems unwise to attribute any significance to the fact that the values appear to be higher than the corresponding values in the hexamethyl analogs ($f_{Sn-C} = 2.08$, $f_{Pb-C} = 1.74$ mdyn/Å).

Raman Intensities and Bond Polarizability Derivatives

Raman intensities for the three A_{1g} lines of interest were determined for each compound. These were placed on an absolute basis by comparison with ν_6 of the chloroform solvent, which was subsequently compared with ν_1 of CCl_4, for which the absolute intensity has been reported.[16] Calculation of mean polarizability derivatives with respect to the normal coordinates, $\bar{\alpha}_{Q_i}{}^2$, requires that the exciting frequency, ν_0, be much less than the frequency of the first electronic transition, ν_e. The recent finding[2a] that the $\nu_0 \ll \nu_e$ condition fails for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, producing a resonance enhancement of the intensities of the respective "metal–metal" lines, suggested that this effect might also be observable for hexaphenylditin and -dilead, since all four compounds have electronic absorptions in the near-uv region which have been assigned to transitions involving "metal–metal" electrons.[17,18] Studies of the intensities of the 112-cm^{-1} line of $(C_6H_5)_6Pb_2$ and the 138-cm^{-1} line of $(C_6H_6)_6Sn_2$ as a function of exciting frequency did in fact reveal a significant dependence for the former line but a negligible effect for the latter. In order to obtain valid $\bar{\alpha}'_Q$ values in cases where the Raman intensity includes a resonance contribution it is necessary to estimate $\bar{\alpha}'_Q$

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[13] J. H. Schachtschneider, Shell Development Co., Emeryville, Calif.: (a) Technical Report No. 231-64; (b) Technical Report No. 57-65.

[14] J. R. Scherer, *Spectrochim. Acta*, **20**, 345 (1964) (set ii of Table IV).

[15] Because of the redundancy condition relating the A_{1g} C–M–C and C–M–M symmetry coordinates, f_{C-M-C} and f_{C-M-M} are essentially inseparable in this calculation. Thus only one variable need be treated, *i.e.*, the sum of the two constants.

[16] T. V. Long, II, and R. A. Plane, *J. Chem. Phys.*, **43**, 457 (1965).

[17] R. Levenson and H. B. Gray, private communication.

[18] W. Drenth, M. J. Janssen, G. J. M. Van der Kerk, and J. A. Vliegenthart, *J. Organometal. Chem.*, **2**, 265 (1964).

at zero exciting frequency. This is most easily accomplished[2a] by plotting the *apparent* $\bar{\alpha}'_Q$ values, obtained from the observed intensities as a function of the frequency parameter[19]

$$X = \frac{1 + (\nu_0/\nu_e)^2}{[1 - (\nu_0/\nu_e)^2]^2}$$

and extrapolating to $X = 1$ (*i.e.*, $\nu_0 = 0$].

The results for the present case are shown in Figure 2. For hexaphenyldilead, the correction for $\bar{\alpha}_{112\,\text{cm}^{-1}}$ from $\nu_0 = 14{,}784$ cm^{-1}, the lowest exciting frequency available, to $\nu_0 = 0$ amounts to ~20%.

Some resonance enhancement of the A_{1g} lines of $(C_6H_5)_6Pb_2$ at 203 and 233 cm^{-1} might also be expected if the metal–metal coordinate is mixed into these normal modes. Studies of intensity in the 190–240-cm^{-1} region as a function of exciting frequency did reveal changes, but as these were small and irregular, no correction was deemed necessary. Values of $\bar{\alpha}'_Q$ used in subsequent calculations of bond polarizability derivatives are collected in Table IV. The three measured $\bar{\alpha}'_Q$'s for each compound were used to solve for three mean polarizability derivatives with respect to internal coordinates,[2b] $\bar{\alpha}'_{\text{M-M}}$, $\bar{\alpha}'_{\text{M-C}}$, and $\bar{\alpha}'_{\text{C-C-M}}$.

TABLE IV

NORMAL MODE POLARIZABILITY DERIVATIVES FOR HEXAPHENYLDITIN AND HEXAPHENYLDILEAD

$(C_6H_5)_6Sn_2$		$(C_6H_5)_6Pb_2$	
ν, cm^{-1}	$\bar{\alpha}_Q$, Å^2 amu$^{-1/2}$	ν, cm^{-1}	$\bar{\alpha}'_Q$, Å^2 amu$^{-1/2}$
280	0.135	233	0.465
214	0.534	203	0.940
138	0.502[a]	112	0.764[a]

[a] Corrected for resonance enhancement.

Allowance for the contribution of C–C stretching to the observed intensities was made by assuming all $\bar{\alpha}'_{\text{C-C}} = 2.05$ Å^2, an approximate average of the experimental and theoretical values for benzene.[16] The equations giving the normal mode polarizability derivatives in terms of derivatives with respect to internal coordinates then take the form

$$\bar{\alpha}'_{Q_i} = \sqrt{6}L_{\text{M-C},i}\bar{\alpha}'_{\text{M-C}} + L_{\text{M-M},i}\bar{\alpha}'_{\text{M-M}} + \sqrt{12}L_{\text{C-C-M},i}\bar{\alpha}'_{\text{C-C-M}} + \sum_{j=1}^{6}\sqrt{6}L_{(\text{C-C})j,i}$$

where the L's are the eigenvector elements linking the indicated symmetry coordinate (*i.e.*, M–C, M–M, etc.) with the normal mode Q_i. The sum in the last term is over the six types of (formally) nonequivalent C–C bonds.

Since each $\bar{\alpha}'_Q$ may have either a positive or negative value ($\bar{\alpha}'_Q$ is proportional to $\sqrt{I}$), there are a total of eight possible sets of values for $\bar{\alpha}'_{\text{M-M}}$, $\bar{\alpha}'_{\text{M-C}}$, and $\bar{\alpha}'_{\text{C-C-M}}$. Calculations were carried out for all eight sign possibilities, and the most reasonable choice was determined by requiring $\bar{\alpha}'_{\text{M-C}}$ and $\bar{\alpha}'_{\text{M-M}}$ positive and $\bar{\alpha}'_{\text{C-C-M}}$ small. Fortunately the absolute magnitudes of $\bar{\alpha}'_{\text{Sn-Sn}}$ and $\bar{\alpha}'_{\text{Pb-Pb}}$ are nearly independent of the choice of signs, so that the qualitative interpretation of metal–metal bond strengths to follow would not be modified by a different choice.

The eigenvectors for the three observed A_{1g} frequencies of each compound were examined throughout the range of variations described in the normal-coordinate analysis section. The changes found are surprisingly small. The metal–metal frequency in each case is a nearly "pure" vibration with some contribution from deformation of the C–C–M angles. Polarizability derivatives with respect to internal coordinates are given in Table V. The ranges of values arise from the differences in eigenvectors associated with different possible values of the uncertain force constants, and are rather small. The values of $\bar{\alpha}'_{\text{C-C-M}}$ are essentially zero. The assumption of the Wolkenstein theory[20] that $\bar{\alpha}'$ is invariant to angle bending has been found valid in several cases.[21,22] Table V also gives values for bond orders ($n/2$) calculated from the δ function potential equation of Long and Plane.[16]

TABLE V

BOND POLARIZABILITY DERIVATIVES AND BOND ORDERS FOR HEXAPHENYLDITIN AND HEXAPHENYLDILEAD

Internal coord	$\bar{\alpha}'$, Å^2	$n/2$
	$(C_6H_5)_6Sn_2$	
M–M	4.1 ± 0.4	0.43 ± 0.04
M–C	3.1 ± 0.2	0.76 ± 0.05
C–C–M	−0.02 ± 0.03	
	$(C_6H_5)_6Pb_2$	
M–M	7.9 ± 0.6	0.78 ± 0.06
M–C	5.8 ± 0.6	1.36 ± 0.15
C–C–M	0.01 ± 0.11	

The $n/2$ value for the Sn–Sn and Sn–C bonds in hexaphenylditin are indistinguishable from those found in hexamethylditin, 0.42 and 0.70, respectively.[2b] The stronger M–C bonding for hexamethylditin which is indicated by the force constants is not borne out in the intensity analysis. Similar comparisons unfortunately cannot be made for hexaphenyl- and hexamethyldilead, as accurate intensity measurements for the latter compound are not available.[2b] The values of $n/2$(M–C) and $n/2$(M–M) for hexaphenyldilead bear the same relationship as in hexaphenylditin, but both are nearly a factor of 2 higher.

Conclusions

One major conclusion to be drawn from the present work is the danger inherent in estimating metal–metal force constants from a single metal–metal frequency when other low-lying totally symmetric vibrations are present. In the present case, this type of estimate is 25% low even for the sixth-period element lead and is seriously in error for the lighter tin.

The normal-coordinate methods employed for these phenyl derivatives necessarily involve a number of

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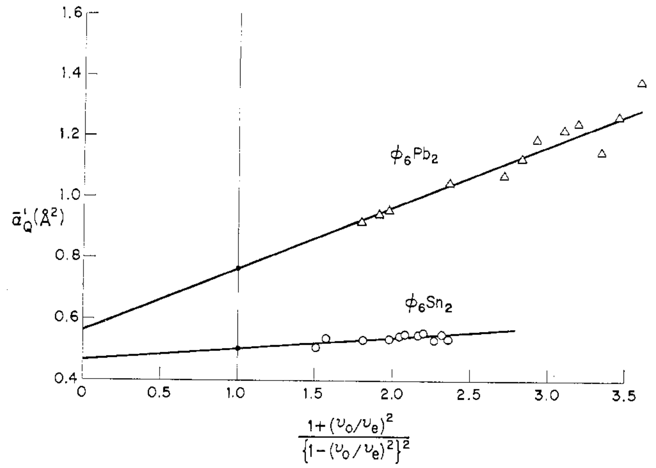

Figure 2.—Apparent molecular polarizability derivatives for the 112-cm^{-1} line of $(C_6H_5)_6Pb_2$ and the 138-cm^{-1} line of $(C_6H_5)_6$-Sn_2 *vs.* $[1 + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2]^2$. ν_0 is the laser exciting frequency; ν_e is the effective absorption frequency. $\nu_e((C_6H_5)_6Sn_2) = 40{,}468$ cm^{-1} (247 mμ); $\nu_e((C_6H_5)_6Pb_2) = 34{,}014$ cm^{-1} (294mμ).

uncertainties, but the metal–metal force constants found appear to be largely independent of the assumptions made. Comparison of these force constants with the corresponding quantities for hexamethylditin and -dilead indicates that the metal–metal bonding is very similar for both ligands. For the tin compounds this interpretation is borne out by the intensity analyses.

For $(C_6H_5)_6Sn_2$, the value of $n/2$(M–M) falls in the "normal range,[2b] 0.3–0.4, for single homonuclear metal–metal bonds. The value for $(C_6H_5)_6Pb_2$, however, is well above this range. This is the second exceptional case, along with $(CO)_{10}Mn_2$ ($n/2 = 0.66$),[2a] out of eight metal–metal bonds for which $n/2$ values have been determined.[2b] The only obvious characteristic that $(C_6H_5)_6Pb_2$ and $(CO)_{10}Mn_2$ have in common[23–25] is significant intensity enhancement through the resonance Raman effect. The possibility arises, therefore, that the extrapolation procedure (Figure 2) used to compensate for this effect does not in fact do so adequately. Further exploration of this question is needed.

Experimental Section

Hexaphenylditin and -dilead were purchased from Alfa Inorganics, Inc., and used without purification. Tetrakis(triphenyltin)tin, $[(C_6H_5)_3Sn]_4Sn$, was prepared by the method given by Willemsens and Van der Kerk.[26] The crude product was purified by extracting hexaphenylditin, the major impurity, with small, rapid washings of chloroform. The extraction procedure was monitored *via* uv spectra (Beckman DB-G) using the spectral information given in the literature.[18] The product was then recrystallized from toluene, yielding large opaque crystals.

The Raman instrument used has been described.[2a] Preliminary spectra were excited with the 6328-Å line of a Spectra Physics Model 125 He–Ne laser. The studies of Raman intensity as a function of exciting frequency were performed with a Coherent Radiation Model 52 Ar–Kr ion laser producing lines of usable power throughout the region from 6764 to 4765 Å.

Spectra were obtained from the microcrystalline solids and from saturated solutions in $CHCl_3$ or CS_2. Absolute Raman intensities were measured as described in the earlier report.[2a]

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(23) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, Chapter 3.

(24) A referee has pointed out that if Allred's[25] modification of Pauling's[23] electronegativity value for lead is used ($X = 2.33$ instead of 1.8), then $(n/2)$(Pb–Pb) is reduced to 0.68, a value even closer to $(n/2)$(Mn–Mn).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WESTERN ONTARIO, LONDON, CANADA

Insertion Reactions into the Methyl–Platinum Bond.
II.[1] Intermediate π Complexes

BY H. C. CLARK* AND R. J. PUDDEPHATT

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π complexes of tetrafluoroethylene and hexafluorobut-2-yne with *trans*-$PtXCH_3L_2$ (X = halogen, L = tertiary phosphine, arsine, or stibine) have been prepared, and their structures and stabilities investigated. In some cases, the complexes may rearrange to give the products of insertion of the olefin or acetylene into the methyl–platinum bond. Reactions of tetrafluoroethylene and hexafluorobut-2-yne with *cis*-$Pt(CH_3)_2L_2$ and *trans*-$PtHClL_2$ are also described.

Introduction

The current interest in the use of transition metal complexes for the homogeneous catalysis of polymerization or hydrogenation of unsaturated compounds has led to several attempts to isolate the types of intermediates involved in these processes.[2–7] Thus, Bailar[2] isolated a hydridoplatinum(II) cyclooctadiene complex which was believed to be an intermediate in the catalytic hydrogenation of the diene, and, more recently, Baddley reported[3] that similar

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* To whom correspondence should be addressed.

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