cedures, were treated with aqueous alkaline $AgNO_3$ as previously reported.[10,13] Authentic samples of **3**[22] and **4**[23] were prepared according to the reported procedures.

Reaction of Alkenylboranes with Methylcopper. Alkenylboranes (**1a** and **1d**) were prepared by the hydroboration of 1-hexyne with disiamylborane and dicyclohexylborane,[13] respectively. Hydroboration of methyl 10-undecynoate was carried out in a similar fashion. These boranes were treated with methylcopper at 0 °C. Authentic samples of SiaI,[24] 1-cyclohexyl-1-hexene,[22] and dicyclohexyl[23] were prepared according to the known procedures. SiaH and its olefin derivatives appeared with the same retention times, and cyclohexane and cyclohexene could not be separated (SE-30).

Mechanistic Studies. The reaction of **1b** with butylcopper was carried out as described in the general procedure. Butylcopper was prepared from the reaction of CuI with butyllithium at −45 °C.[17] GLC analysis of the boranes was performed using a 1-m 5% SE-30 column. An authentic sample of *trans*-1-hexenyldi-*n*-butylborane was prepared by the reaction of *trans*-1-hexenyldichloroborane[25] with 2 equiv of *n*-butyllithium at −78 °C. This borane was not isolated. GLC examination of the reaction mixture of run 2 indicated the presence of *trans*-1-hexenyldi-*n*-butylborane. 5-Decenyldimethylborane (**18**) was prepared by the reaction of 5-decenyldichloroborane[25] with 2 equiv of methyllithium at −78 °C: bp 43-45 °C (1 mm); NMR δ 6.42 (t, 1 H, J = 8 Hz), 2.50-1.88 (m, 4 H), 1.63-1.13 (m, 8 H), 0.98 (t, 6 H, J = 7 Hz), 0.79 (s, 6 H).

References and Notes

(1) (a) For a preliminary report on some aspects of the present study see Y. Yamamoto, H. Yatagai, and I. Moritani, *J. Am. Chem. Soc.*, **97**, 5606 (1975); (b) Kyoto University; (c) Osaka University.

(2) (a) G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, **629**, 222 (1960); (b) G. Zweifel, N. L. Polston, and C. C. Whitney, *J. Am. Chem. Soc.*, **90**, 6243 (1968); (c) G. Zweifel and R. L. Miller, *ibid.*, **92**, 6678 (1970).

(3) (a) G. Zweifel and N. L. Polston, *J. Am. Chem. Soc.*, **92**, 4068 (1970); (b) E. Negishi and T. Yoshida, *J. Chem. Soc., Chem. Commun.*, 606 (1973); (c) E. Negishi, G. Lew, and T. Yoshida, *ibid.*, 874 (1973); (d) H. C. Brown and N. Ravindran, *J. Org. Chem.*, **38**, 1617 (1973).

(4) D. B. Denny and W. R. Davis, *J. Organomet. Chem.*, **24**, 537 (1970).

(5) (a) G. M. Whitesides, J. SanFilippo, Jr., C. P. Casey, and E. J. Panek, *J. Am. Chem. Soc.*, **89**, 5302 (1967); (b) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *ibid.*, **93**, 1379 (1971); (c) G. Büchi and J. A. Carlson, *ibid.*, **91**, 6470 (1969); (d) E. J. Corey, C. U. Kim, R. H. K. Chen, and M. Takeda, *ibid.*, **94**, 4395 (1972); (e) T. Kauffman and W. Sahm, *Angew. Chem., Int. Ed. Engl.*, **6**, 85 (1967); (f) F. Näf and P. Degen, *Helv. Chim. Acta*, **54**, 1939 (1971); (g) T. Cohen and T. Poeth, *J. Am. Chem. Soc.*, **94**, 4363 (1972).

(6) W. R. Moore, L. N. Bell, and G. P. Daumit, *J. Org. Chem.*, **36**, 1694 (1971).

(7) M. F. Semmelhack, P. M. Helquist, and J. D. Gorzynski, *J. Am. Chem. Soc.*, **94**, 9236 (1972).

(8) H. A. Dieck and R. F. Heck, *J. Org. Chem.*, **40**, 1083 (1975).

(9) (a) E. Vedejs and P. D. Weeks, *Tetrahedron Lett.*, 3207 (1974); (b) R. C. Larock, *J. Org. Chem.*, **41**, 2241 (1976).

(10) H. C. Brown, N. C. Hébert, and C. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1001 (1961).

(11) H. C. Brown and N. Ravindran, *J. Org. Chem.*, **38**, 1617 (1973); *J. Am. Chem. Soc.*, **98**, 1785 (1976).

(12) Copper tetraarylborates were previously prepared by cation exchange reaction: A. N. Nesmeyanov, V. A. Sazonova, G. S. Liberman, and L. I. Yemelýanova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 48 (1955). On the related cation exchange reaction of lithium tetraalkylborates, see N. Miyaura, M. Itoh, and A. Suzuki, *Tetrahedron Lett.*, 255 (1976).

(13) H. C. Brown, "Organic Syntheses via Boranes," Wiley, New York, N.Y., 1975.

(14) "Organic Syntheses," Collect. Vol. V, Wiley, New York, N.Y., 1973, p 859.

(15) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

(16) S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967).

(17) G. H. Posner, C. E. Whitten, and J. J. Sterling, *J. Am. Chem. Soc.*, **95**, 7788 (1973).

(18) M. M. Midland, J. A. Sinclair, and H. C. Brown, *J. Org. Chem.*, **39**, 731 (1974).

(19) A. L. Henne and K. W. Greenlee, *J. Am. Chem. Soc.*, **67**, 484 (1945).

(20) "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 969. 10-Undecynoic acid was converted to the corresponding methyl ester by standard procedure: bp 95–97 °C (1 mmHg); IR 2100, 1740 cm^{-1}; NMR δ 3.58 (s, 3 H), 2.40–1.93 (m, 4 H), 1.80 (t, 1 H), 1.67–1.10 (m, 12 H).

(21) J. Sicher, M. Svoboda, M. Pánková and J. Zavada, *Collect. Czech. Chem. Commun.*, **36**, 3633 (1971).

(22) G. Zweifel, R. P. Fisher, J. T. Snow, and C. C. Whitney, *J. Am. Chem. Soc.*, **93**, 6309 (1971).

(23) H. C. Brown and C. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1001 (1961).

(24) N. R. DeLue and H. C. Brown, *Synthesis*, 114 (1976).

(25) H. C. Brown and N. Ravindran, *J. Am. Chem. Soc.*, **98**, 1798 (1976).

The Structure of Trimethylphosphine Selenide by Electron Diffraction. Systematic Differences in Structure Patterns of Trimethyl and Trihalo Derivatives of Phosphorus and Arsenic

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Abstract: As determined by electron diffraction from a gaseous sample at a nozzle-tip temperature of 132–135 °C, $(CH_3)_3PSe$ has the following structure parameters (r_a basis, distances in angstroms) with estimated uncertainties, 2σ, in parentheses: $r(PSe) = 2.091$ (0.003), $r(PC) = 1.816$ (0.003), $r(CH) = 1.100$ (0.009), $\angle SePC = 113.8$ (0.3)°, $\angle PCH = 109.9$ (1.7)°. Diffraction data support a finite barrier to methyl torsion, though no quantitative measure of it comes from the analysis. Valence force constants and vibrational amplitudes were calculated to fit reported fundamental frequencies. Diffraction and spectroscopic results suggest a high degree of similarity between $(CH_3)_3PSe$ and $(CH_3)_3PS$. Structures for all pertinent $(CH_3)_3M$ and $(CH_3)_3MY$ molecules of group 5a M are examined in the light of previously established structure trends for trihalo analogues. Possible sources of the several differences found to distinguish the two classes of ligands are examined.

Simple tetracoordinate compounds, formed by coordination of the lone pair on tricoordinate phosphorus or arsenic with either a chalcogen (O, S, or Se) or an electron-deficient group such as BH_3, have received a flurry of attention from both structural and theoretical chemists in recent years. Related tricoordinate phosphorus, arsenic, and antimony derivatives have also been studied extensively. Even if one restricts consideration to molecules of C_3 or C_{3v} symmetry (i.e., with unmixed ligands), this class of compounds provides an excellent basis for testing various bonding models used by chemists. Trends in geometric parameters are well established by the large number and variety of these compounds for which high-precision structural data are known. In most cases, ancillary force field calculations are also available. One of the

Table I. Experimental Conditions for Recording Diffraction Patterns

	Camera geometry	
	I	II
Nozzle-to-plate distance, mm	750.27	300.23
Nozzle temp, °C	135	132
Reservoir temp, °C	90	97
Typical exposure time, min	1.25	5.0
Beam current, μA	0.4	0.5
Approximate accelerating voltage, kV	43.4	44.2
Range of s values, Å^{-1}	2.00-12.75	8.00-31.75
Data interval, Δs	0.25	0.25

chief points of interest is the nature of the bond to the chalcogen (or other acceptor ligand) in the tetracoordinate compounds. Subsidiary questions related to systematic substituent effects have also been raised.

One popular description of the MY bond in X_3MY molecules postulates cooperative σ donation, M $\rightarrow$ Y, and pπ-dπ back donation, M $\leftarrow$ Y. A recent determination of the gas-phase electron diffraction structures and auxiliary vibrational potential constants for the molecules $(CH_3)_3PO$, $(CH_3)_3PS$, $(CH_3)_3AsO$, and $(CH_3)_3AsS$[2] represents an attempt to obtain unambiguous experimental evidence bearing on this model. Attention in the cited report was focused on implications of combined structure, force field, and dipole moment data for the above model, in which opposed charge transfers between M and Y can result in enhanced bond strength with little accompanying change in MY bond polarity. An essential feature of the interpretation of the data offered by Wilkins et al.[2] was the assumption that methyl groups, unlike halogens, were "neutral" ligands in the following sense. By virtue of their presumed low electronegativity they should not participate in the charge redistribution that accompanies formation of the MY bond. Also, weakness of π interactions between methyl groups and adjacent atoms or groups of atoms eliminates CH_3 from competition for the M atom d orbitals which are available for back donation from the chalcogen.

The investigation of the structure of trimethylphosphine selenide, which forms the subject of this report, could be viewed merely as a postcript to the work of Wilkins,[2] graced chiefly by the novelty of a bond between phosphorus and monocoordinate selenium. Our results for $(CH_3)_3PSe$ do not qualify the conclusions reached by those investigators concerning the MY bonds in $(CH_3)_3MY$ molecules. However, combined with data for other tetracoordinated compounds, they do provide a vehicle for examining the suppositions outlined above concerning methyl groups. In a recently completed study of a set of trihalophosphine oxides and sulfides,[3] several empirical correlations between MX_3 and X_3MY geometries and ligand electronegativities were demonstrated.[4] Details of the geometries of the $(CH_3)_3M$ moieties, which received little attention in the previous work,[2] are examined below for compatibility with these correlations. The full set of data on the methylphosphines and -arsines is found to establish a characteristic pattern of behavior that is distinguishable from structure trends in halogen derivatives in several respects. These observed structure differences are shown to be consistent with expected bonding differences between methyl and halo compounds based on factors other than simple electronegativity effects.

Experimental Section

A sample of trimethylphosphine selenide was prepared for us by H. Rojhantalab using published methods.[5] IR and Raman spectra revealed no impurities. The compound was handled out of contact with air and was freshly resublimed before use.

Diffraction photographs were made in the Oregon State apparatus using Kodak Projector Slide plates (medium) of dimension 8 × 10 in. Details of the experimental conditions are summarized in Table I. A calibrated sector of nominally r^3 angular opening was used during the experiment. Incident electron wavelengths were calculated from accelerating voltages. The latter had been calibrated with CO_2 data to yield an s scale consistent with r_a(CO) = 1.1646 and r_a(O···O) = 2.3244 Å. Data from four plates at the 750-mm and two plates at the 300-mm camera distance were used in the analysis, which was carried out as described previously.[6] Smooth backgrounds were calculated[7,8] and subtracted from experimental total intensities which had been leveled by a factor of s^4, yielding molecular intensities for individual plates which are comparable to model intensities, $I_m(s)$, calculated as:

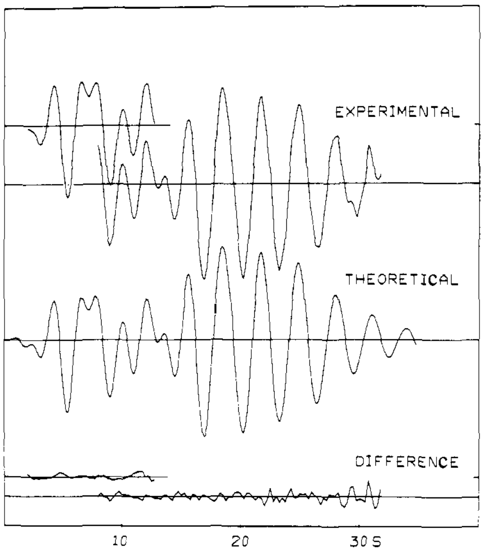

Figure 1. Intensity curves for $(CH_3)_3PSe$. The theoretical curve corresponds to the TA model of Table II. Difference curves are experimental minus theoretical.

$$sI_m(s) = k \sum_{i \neq j} n_{ij}A_iA_jr_{ij}^{-1} \exp(-l_{ij}s^2/2) \cos|\eta_i - \eta_j| \sin sr_{ij} \qquad (1)$$

In eq 1 the A's are electron scattering amplitudes[9] multiplied by s^2 and the other symbols have their usual significances. The individual intensity curves from each camera distance were combined to give an average curve for that distance to be used in structure refinements. These curves are shown in Figure 1.

Structure Analysis

The general pattern of analysis for $(CH_3)_3PSe$ paralleled that described earlier for the other $(CH_3)_3MY$ molecules,[2] and the reader is referred to that article for details. A brief description is provided below.

A C_{3v} symmetry was imposed on the heavy atom framework of the molecule. Separate refinements were made using models either with hindered methyl torsions and a fitted mean torsional angle, β, (TA model, overall C_3 symmetry) or with free methyl rotation (FR model). The latter was simulated as a mixture of three equally weighted geometries corresponding to methyl groups rotated (in unison) in increments of 30° from reference positions having one hydrogen anti to the selenium atom.[10] Radial distribution curves corresponding to the best fit for each of these models are compared with the experimental curve in Figure 2. Internuclear distances are labeled in this figure by the atom indices given in the schematic representation of the molecule, Figure 3.

Structural parameters were derived by applying least-squares criteria simultaneously to differences between a given theoretical intensity curve and each of the average experimental intensity curves for the two camera distances. A diagonal weight matrix with unit weights for $sI_m(s)$ was employed. Harmonic vibrations were assumed, and shrinkage corrections were neglected. The latter were calculated from the harmonic

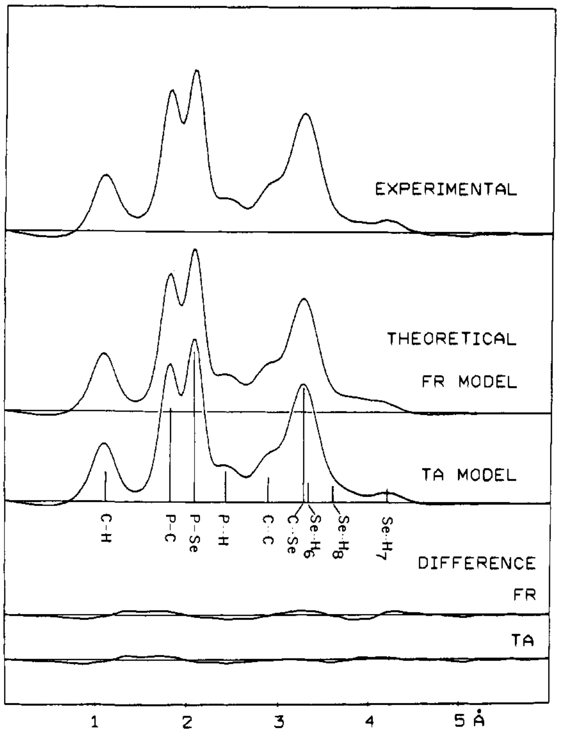

Figure 2. Radial distribution curves for $(CH_3)_3PSe$. The TA model is that given in Table II. Vertical lines indicating positions of major peaks are in length proportional to $n_{ij}Z_{ij}/r_{ij}$. Refer to Figure 3 for indexing of hydrogen atoms in the TA model.

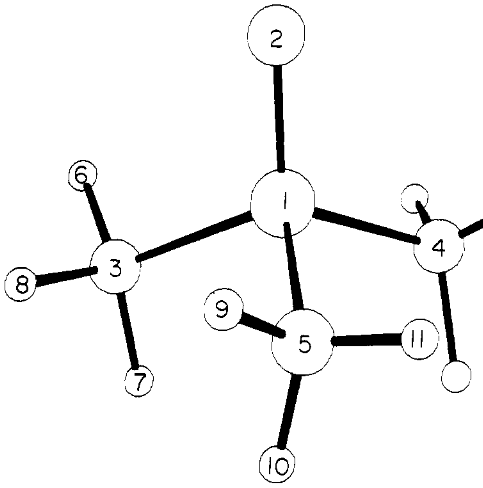

Figure 3. Schematic representation of a molecule of $(CH_3)_3PSe$ in the conformation corresponding to the TA model of Table II.

Table II. Structure Parameters for $(CH_3)_3PSe$, Restricted Rotation Model (TA)[a,b]

Internal coordinate[c]		Amplitudes, Å	
	Independent		
r(PSe)	2.091 (3)	0.044 (4)	
r(PC)	1.816 (3)	0.056 (4)	
r(CH)	1.100 (9)	0.081 (9)	
∠SePC	113.8 (4)		
∠PCH	109.9 (1.7)		
β, mean torsion angle[d]	16.4 (7.2)		
R, goodness of fit[e]	0.091		
	Dependent		
∠PCP	104.8 (4)		
∠HCH	109.0 (1.7)		
r(C···C)	2.877 (9)	0.097 (18)	
r(C···Se)	3.277 (7)	0.100 (12)	
r(P···H)	2.423 (22)	0.125 (17)	
r(Se···H)'s		0.123	(50)
r(C···H)'s		0.123	
r(H···H)'s		0.130[f]	

[a] Distances (r_a) and amplitudes are reported in angstroms, angles in degrees. [b] Values in parentheses are estimated uncertainties, 2σ, in the right-most digit(s) quoted for the respective parameters. Estimates of systematic errors and correlation among the observations are included. Bracketed amplitudes were refined as a group. [c] The "independent" coordinates are the set chosen to generate the set of r_{ij}'s to be used in constructing model intensities. Dependent distances are listed if they are associated with independently varied amplitudes of vibration. [d] β is zero for conformations in which one CH bond of each methyl group is anti to the PSe bond. The relationship between β and the parameter, δ, of ref 2 is $\beta = 60° - \delta$. [e] $R = [\Sigma\, w_i\Delta_i^2/\Sigma\, w_iI_i^2(\text{obsd})]^{1/2}$; $\Delta_i = I_i(\text{obsd}) - I_i(\text{calc})$. [f] Value is assumed and not varied.

force field (vide infra) to be smaller than the estimated uncertainties in the internuclear distances for the heavy atom skeleton of the molecule. Since positions of the hydrogens are only of secondary interest in this investigation, the lack of a force field adequate to generate vibrational corrections for distances involving hydrogen atoms was not felt to be a serious drawback. The geometrical parameter most susceptible to errors from neglect of shrinkage is the torsion angle, β, which is further contaminated by artificial model constraints both on refined structure and vibrational parameters, which affect mainly the torsion-dependent internuclear distances.

Final results for structure parameters and vibrational amplitudes for the TA model are summarized in Table II. Corresponding values for the FR model are only trivially different, so we do not include them. The overall fit for the TA model was 4% better than for the FR model, an improvement which is somewhat smaller than the reduction of R (see footnote e, Table II for definition) observed for other members of the series $(CH_3)_3MY$,[2] and is only of marginal statistical significance. Indicated error estimates were derived from formulas previously reported.[11] From the preceding discussion it is apparent that the contribution of systematic errors to the $\sigma(\beta)$ in Table II has been underestimated. The matrix of correlation coefficients for the TA model appears in Table III.

Vibrational Calculations

Assuming a simple vibrational potential function of the form described by Wilkins[2] we calculated a set of valence force constants for framework stretching and bending vibrations (including single stretch-stretch and bend-bend interaction constants) which reproduced the reported frequencies for this molecule to within a few percent.[12] These force constants were used, in turn, to calculate parallel and perpendicular vibrational amplitudes for the distances involving only C, P, and Se atoms.[13] Calculated amplitudes and force constants for $(CH_3)_3PSe$ as well as for $(CH_3)_3PS$ and $(CH_3)_3PO$ are given in Table IV. The sulfide and oxide data are included to facilitate comparison, but more importantly to correct some inadvertent errors in their listings in ref 2. In that report the calculated amplitudes (Table I, ref 2) labeled as belonging to $(CH_3)_3PO$ are actually the preferred values for $(CH_3)_3PS$, while the superseded values for the sulfide are retained. Also, the reported force constants (Table V, ref 2) for the sulfide are a mixture of old and new results, but the force constants given by Wilkins[2] for the oxide *are* correct. Error estimates for the spectroscopic values are not known, but almost certainly some of the numbers appearing in Table IV are given to more figures than are significant. In particular, the pseudo-atom approximation for methyl groups[2] renders the nonbonded amplitudes suspect, and this may account for part of the discrepancy between diffraction and spectroscopic values for l(C···C) in these molecules.

Table III. Correlation Matrix for the Restricted Rotation Model (TA)[a]

	r_{PSe}	r_{PC}	r_{CH}	∠CPSe	∠HCP	β^c	l_{PSe}	l_{PC}	l_{CH}	$l_{C\cdots C}$	$l_{C\cdots Se}$	$l_{P\cdots H}$	$l_{Se\cdots H}$
$\sigma^b/$	*0.0006*	*0.0009*	*0.0032*	*0.12*	*0.61*	*2.53*	*0.0011*	*0.0010*	*0.0029*	*0.0062*	*0.0039*	*0.0058*	*0.0177*
	1000	−172	72	−151	160	−13	−173	−191	−25	9	−98	−193	18
		1000	−117	−64	−232	238	306	226	42	52	234	60	26
			1000	−25	−233	−59	−124	−27	−78	−3	−40	−19	−19
				1000	−74	103	45	59	1	342	110	−224	−62
					1000	−57	−128	−227	−76	−224	−111	56	−28
						1000	215	153	83	19	690	−161	122
							1000	455	291	80	413	−44	37
								1000	256	50	332	−87	41
									1000	55	172	−10	16
										1000	121	−217	−368
											1000	−51	−259
												1000	−38
													1000

[a] Matrix elements are given by $\rho_{ij} = B_{ij}^{-1}/(B_{ii}^{-1}\,B_{jj}^{-1})^{1/2}$, where the notation corresponds to that of O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27,** 1311-1317 (1957). All elements have been multiplied by 1000 for table entry. [b] Standard deviations from least-squares refinement. Distances (r) and root mean square amplitudes of vibration (l) in angstroms, angles in degrees. [c] See footnote *d*, Table II, for definition of β.

Table IV. Selected Potential Parameters for $(CH_3)_3PY$ Molecules[a]

	$(CH_3)_3PSe$	$(CH_3)_3PS$	$(CH_3)_3PO$
f(MY), mdyn Å^{-1}	2.35	3.37	8.03
f(MC), mdyn Å^{-1}	2.89	2.98	3.04
f(rr′),[b] mdyn Å^{-1}	0.027	0.043	0.126
f(CMC), mdyn Å rad^{-2}	0.535	0.494	0.740
f(YMC), mdyn Å rad^{-2}	1.226	1.071	0.924
$f(\theta\theta')$,[c] mdyn Å rad^{-2}	0.139	0.027	0.001
l(MY), Å	0.053	0.048	0.038
l(MC), Å	0.053	0.053	0.052
l(C···C), Å	0.127	0.126	0.108
l(C···Y), Å	0.091	0.092	0.084

[a] See ref 2 for details of the model force field. The calculations on $(CH_3)_3PO$ and $(CH_3)_3PS$ were made in connection with structure determinations in ref 2. Results for $(CH_3)_3PSe$ are from this work. l are amplitudes of vibration; f are valence stretching and bending force constants. [b] Stretch-stretch interaction constants for (r_{MY}/r_{MC}) and (r_{MC}/r'_{MC}) were set equal. [c] Bend-bend interaction constants for $(YMC_1)/(YMC_2)$ and $(CMC)_1/(CMC)_2$ were set equal. Interactions of the type (YMC)/(CMC) were not included.

Discussion of Results

Bonds between tetracoordinate phosphorus and monocoordinate selenium are not common. No reliable structure reports for such bonds are available for direct comparison with the $(CH_3)_3PSe$ results.[14] Reference "single bond" lengths for PO, PS, and PSe bonds were calculated from sums of covalent radii, including the Schomaker-Stevenson correction for electronegativity differences,[15,16] for comparison with the observed bond lengths in the trimethyl compounds. Resultant bond shrinkages of 0.25, 0.18, and 0.16 Å, respectively, suggest similar bond strengths for the PS and PSe bonds and a substantial disparity between strengths of these bonds and the PO bond. Stretching force constants for these bonds, as given in Table IV, reinforce this conclusion rather emphatically.

Carbon-phosphorus bond lengths and CPC angles for $(CH_3)_3PS$ and $(CH_3)_3PSe$ are the same within experimental errors. Likewise, valence force constants which characterize the $P(CH_3)_3$ portions of these molecules are nearly equal. The similarities between geometries or force fields for these species may be fortuitous, however, and may not persist in other pairs of X_3PS and X_3PSe molecules. Since MC bond lengths and CMC angles show little variation even for such different ligands Y as O and BH_3, one cannot infer similar bonding properties, e.g., similar relative acceptor and donor capacities, for sulfur and selenium from the present data. The sort of comparison made by Wilkins et al.[2] for the PS bond between bond strength and net charge transfer, M → Y, cannot be made for the PSe bond in $(CH_3)_3PSe$ until dipole moment data are available.

Although $M(CH_3)_3$ moieties are seemingly unresponsive to changes in the nature of a fourth ligand Y, they *are* sensitive to its presence or absence, with sizable changes in MC bond lengths and CMC angles accompanying conversion of $M(CH_3)_3$ to $(CH_3)_3MY$. This is in contrast to the regularity of changes in PX bond lengths and XPX angles in trihalophosphines as the ligand Y diminishes in electronegativity and finally is removed completely.

Kuchitsu and co-workers have shown[3] that the empirical correlations between structure parameters and ligand electronegativity in the fluorine and chlorine derivatives are in accord with predictions based on a simple valence shell electron pair repulsion (VSEPR) model,[17] and that they are adequately represented by linear relationships between electronegativity of Y, E(Y), and r(PX), between E(X) and r(PY), and between E(Y) and XPX angle. Our recent results for $OPBr_3$ and $SPBr_3$ support their conclusions for the most part.[18] But it is obvious that the electronegativity correlations which are so remarkably successful for halogen compounds fail for their methyl analogues. There is general acknowledgment that for the phosphine chalcogenides, and probably even for the tertiary phosphines, simple descriptions in terms of σ bonds using only s and p valence orbitals on the central atom are inadequate. Thus even though VSEPR arguments may satisfactorily account *qualitatively* for observed trends in structure parameters, to ascribe these changes in bond length and valence angles entirely to this single factor may well be unjustified. Most descriptions of the bonding in X_3MY molecules suggest a participation of halogens (and passivity of methyl groups) in pπ-dπ interactions with M. They also imply intramolecular charge shifts large enough for electrostatic interactions between pairs of charged atoms, either bonded or nonbonded, to be an important factor in determining structure parameters. As discussed below, it is possible to interpret the data for the two classes of ligands, halogen and methyl, when examined collectively, as supportive of these suppositions.

For reference we have summarized in Table V the three geometrical parameters which describe the MX_3 fragments in series of X_3MY molecules for which the reported structures are of sufficient precision for useful comparison, including several borane adducts. Trimethylarsine was included in Table V even though no complete structure determination has been reported for it. Without its structure for reference much of the value to the present discussion of the structures reported for

Table V. Structure Parameters Characterizing MX_3 Groups in MX_3 and X_3MY Molecules[a,b]

Y	$(CH_3)_3PY$	$(CH_3)_3AsY$	Br_3PY	Cl_3PY	F_3PY
MX Bond Lengths, r_g,[c] Å					
lp[d]	1.846 (3)	1.964 (8)	2.220 (3)	2.040 (1)	1.570 (1)
BH_3	1.819 (10)/MW	1.945 (10)/MW			1.538 (8)/MW
Se	1.818 (3)				
S	1.819 (2)	1.941 (3)	2.193 (2)	2.011 (3)	1.538 (3)
O	1.811 (2)	1.939 (2)	2.175 (2)	1.993 (3)	1.524 (3)
$\Delta(MX)$[e]	−0.035 (3)	−0.025 (8)	−0.045 (3)	−0.047 (3)	−0.046 (3)
XMX Angle,[f] deg					
lp[d]	98.6 (2)/g	96.0 (1.5)/	101.0 (4)/α	100.4 (1)/α	97.8 (2)/α
BH_3	105.0 (4)/MW	105.0 (2.0)/MW			99.8 (1.0)/MW
Se	104.8 (3)/a				
S	104.5 (2)/a	105.3 (4)/a	101.9 (2)/α	101.8 (2)/α	99.6 (3)/α
O	104.1 (7)/a	106.2 (1.3)/a	104.1 (1)/α	103.3 (2)/α	101.3 (2)/α
$\Delta(\angle XMX)$[e]	6.2 (3)	10.2 (1.5)	3.1 (4)	2.9 (2)	3.5 (3)
X···Distances, r_g,[c] Å					
lp[d]	2.800 (5)	2.92 (4)	3.424 (6)	3.132 (3)	2.364 (3)
BH_3	2.886 (10)/MW	3.086 (44)/MW			2.353 (21)/MW
Se	2.880 (11)				
S	2.877 (8)	3.089 (15)	3.405 (5)	3.118 (4)	2.346 (7)
O	2.858 (16)	3.103 (30)	3.427 (4)	3.129 (6)	2.355 (4)
$\Delta(X\cdots X)$[e]	0.08 (1)	0.18 (4)	−0.019 (6)	−0.014 (6)	−0.018 (7)

[a] Primary references for structures represented above as follows: $P(CH_3)_3$, ref 22; $(CH_3)_3PSe$, this work; $(CH_3)_3PO$, $(CH_3)_3PS$, $(CH_3)_3AsO$, and $(CH_3)_3AsS$, ref 2; $As(CH_3)_3$, see Appendix; PF_3, ref 27; PCl_3, r_a's reported in ref 28 transformed to r_α's using perpendicular amplitude corrections given in ref 29; PBr_3, ref 30; SPF_3, ref 3a, POF_3, $POCl_3$, and $SPCl_3$, ref 3b; $POBr_3$ and $SPBr_3$, ref 18; $(CH_3)_3PBH_3$, ref 31; $(CH_3)_3AsBH_3$, ref 32; PF_3BH_3, ref 33. [b] Numbers in parentheses are estimated uncertainties in the least significant digit(s) as given by the original authors. These represent variously σ, 2σ, or they are of unspecified statistical significance. [c] In some cases, r_g's tabulated were calculated from reported r_a and l values. The structures of $As(CH_3)_3$ and the borane adducts do not represent any direct determination via a standard definition or type of data treatment. See Appendix and primary references for details. [d] lp denotes a lone pair of electrons; i.e., the molecule is an uncoordinated MX_3 species. [e] The parameters $\Delta(MX)$, $\Delta(\angle XMX)$, and $\Delta(X\cdots X)$ are the differences between the values for an MX_3 molecule and for the corresponding X_5MY molecule which show the greatest deviation. [f] The letter designations a, g, or α following each angle refer to the conventional definitions used in reporting electron diffraction distances and derived angles. See the Appendix for further qualifications on the labels for reported angles. The angle reported for $As(CH_3)_3$ carries no letter designation, since it does not derive from a direct determination. Angles for the BH_3 derivatives are microwave values, but are not properly r_0, r_s, or r_z values.

$(CH_3)_3AsO$ and $(CH_3)_3AsS$ is lost. We have reevaluated the available data pertinent to the $As(CH_3)_3$ structure (see Appendix) and feel that the error limits we place on its parameters in Table V are justified. Also outlined in the Appendix are our choices of vibrational averages to be reported for most reliable comparisons among these molecules. Phosphorus-oxygen and phosphorus-sulfur bond lengths are compared graphically in Figure 4.

The connection between $E(X)$ and the extent of $p\pi$-$d\pi$ bonding in these molecules is twofold. The withdrawal of electrons from the central atom by highly electronegative ligands is generally supposed to result in energy lowering and spatial contraction of d orbitals on the central atom, which in turn encourages back donation from the acceptor ligand Y. At the same time it increases the tendency of lone pair electrons on halogen ligands to feed into this π system. Roughly speaking, the relative abilities of the halogens to participate in π bonding parallel their relative electronegativities. Methyl groups provide no stabilization of the central atom d orbitals, and may even destabilize them if the methyls are sufficiently electron donating in character. As a result we can expect MY bonds in trimethyl compounds to appear abnormally long on plots of $r(MY)$ vs. $E(X)$. Shrinkages of bonds to carbon and to halogens, measured against appropriate individual reference values, should also bear witness to the extra source of bond strength for the halogens, even in the uncoordinated MX_3 species. Furthermore, the absence of significant coupling of CH_3 and Y through π interactions with M should result in reduced sensitivity of $r(MC)$ to changes in $E(Y)$ compared with sensitivities of MX bonds in halogen compounds.

The discontinuities in the plots of $r(PO)$ vs. $E(X)$ and $r(PS)$ vs. $E(X)$ in Figure 4 show clearly that the experimental bond lengths do indeed exaggerate the apparent electronegativity differences between methyl groups and halogens. The points for $(CH_3)_3PO$ and $(CH_3)_3PS$ lie 0.02 and 0.04 Å, respectively, above the least-squares lines through the points for trihalo compounds, discrepancies far in excess of experimental uncertainties. Alternatively one could say that the methyl compounds affect the PO and PS distances as though they had electronegativities of about one on the Pauling scale. The maximum range of values for these inferred apparent electronegativities allowed by experimental uncertainties in the individual points for X = F, Cl, and Br is indicated by the horizontal line for each plot in Figure 4.

The various experimental MX bond lengths can be compared with sums of covalent radii,[16] r_{cov}. The differences, $(r_g - r_{cov})$, are plotted in Figure 5 as functions of $|E(X) - E(M)|$ for PX_3 and AsX_3 species. Included on the graphs are the calculated Schomaker-Stevenson corrections to r_{cov}[15,16] for each of the PX and AsX bonds. The MC bond shrinkages are 0.06 Å *greater* than those predicted by extrapolations of the linear fits to the halogen data suggested by Karakida and Kuchitsu,[3a] a result which at first glance seems to contravene the π bonding argument. However, the MC, MCl, and MBr shrinkages are all remarkably consistent with the Schomaker-Stevenson corrections, whereas the experimental PF and AsF shrinkages are respectively 0.10 and 0.07 Å greater than the calculated values. This creates anomalously steep slopes for the lines through the halogen data.[19] One could argue that it is fluorine and not methyl which is the deviant ligand in this comparison, presumably as a result of appreciable π character in the MF bonds of trifluoro compounds.

It has already been suggested that the near constancy observed for MC bond lengths in coordinated species is compatible with a lack of π-bond coupling between the methyl and chalcogen ligands. This argument requires some slight modi-

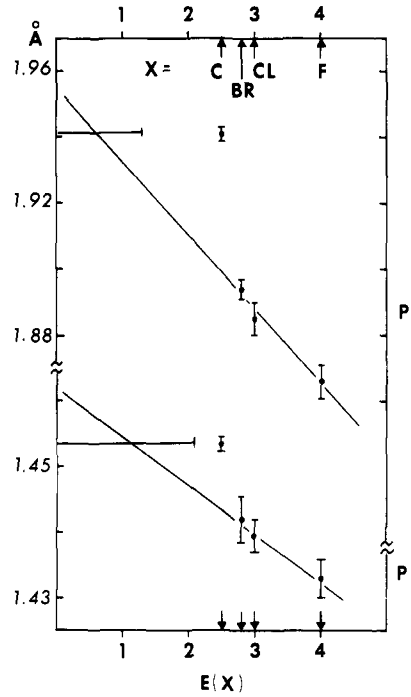

Figure 4. r(PO) vs. E(X) and r(PS) vs. E(X). Vertical bars are experimental uncertainties. Horizontal bars give the allowable range of intersections between lines through the halogen points with r values for the trimethyl compounds.

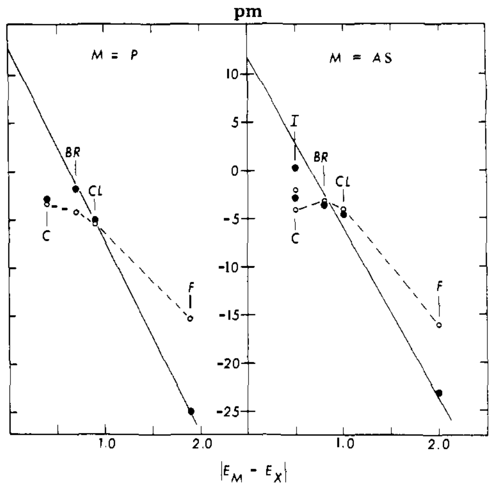

Figure 5. MX bond shrinkages in MX_3 molecules vs. electronegativity differences, $|E(M) - E(X)|$. Solid circles are $(r_g - r_{cov})$. Solid lines are linear regressions through the halogen points. Open circles are Schomaker-Stevenson corrections according to ref 16. Dashed lines connect the X = CH_3, Br, Cl, and F points in each figure. 1 pm = 0.01 Å.

fication, however, since diminished VSEP repulsions between MY and MX bonds are predicted for increased E(Y) regardless of the relative electronegativities of M and X. One factor which could operate to reverse this trend for bonds to methyls, but augment it for halogens, is bond polarity. As E(Y) increases, the charge on M undoubtedly becomes more positive. This would increase the charge separation across bonds to halogens and tend to strengthen and contract those bonds. However if, as seems likely, the methyl groups carry slight positive charges, MC bonds would experience increasingly repulsive electrostatic interactions along the bond as E(Y) increased,[20] which would offset VSEPR relaxations.

The same two factors, namely π interactions and electrostatic atom-atom interactions, can account for most of the differences in patterns observed in XMX angles for the two classes of ligands as described below.

For the halogen species moderate but steady increases in XPX angles parallel the decreases in r(PX) with increasing E(Y), including the E(lp) = 0 cases. Every series of molecules with fixed Y or with Y = lp shows a subsidiary pattern of regular decreases in XMX angle with increases in E(X).[21] This latter trend holds for all known trihalo MX_3 compounds with M any group 5a atom except nitrogen. Both patterns are consistent with VSEPR predictions. On the other hand, the CMC angles, both for M = P and As, show sizable increases upon coordination of $M(CH_3)_3$ to the least electronegative ligand Y (6-9° in trimethyl compounds compared with increases of 1-2° in the analogous halides), but they show no statistically significant change as more electronegative Y's are substituted. If electronegativity effects or ligand size were the sole determinant of XMX angles, the CMC angles should be as large or larger than the BrMBr angles in molecules with the same ligand Y or in the simple MX_3 species. That this is not the case for PX_3 molecules was observed and commented upon some years ago.[22] Since then additional data for tricoordinate arsenic and antimony species have confirmed a general elevation of XMX angles in trihalides relative to CMC angles in trimethyl compounds. Trisilyl and Trigermyl derivatives have even smaller XMX angles than the trimethyl species, while angles in the parent phosphine, arsine, and stibine molecules are smallest of all. Clearly, neither ligand size nor ligand electronegativity can explain *all* these data.

Qualitatively, partial double bond character in bonds to halogens, but not in bonds to methyl carbons, can satisfactorily account for anomalously large angles in the uncoordinated trihalides. The difficulty with this argument is in finding a logical extension of it to the four coordination cases, which is in accord with experiment. Presumably the π character of the halogen bonds increases upon addition of a fourth ligand Y, with this cooperative interaction among the ligands increasing along with E(X) and E(Y). The smaller angular increases experienced by the halogen compounds upon coordination and the resultant restoration of methyl compounds to their place relative to the halogens as predicted by a VSEPR model does not accord well with this picture. Furthermore, the order of XMX angles among the halogens remains that of the VSEPR model, in four- as well as three-coordinate species, rather than the reverse order predicted by relative π-bonding tendencies, i.e., F > Cl > Br.

The probable charge distributions in the methyl and halogen compounds differ in just the proper way to provide an alternative or complementary rationale for observed differences in valence angles in terms of electrostatic interactions. Examination of nonbonded distances, r(XX), lends support to the argument. All ligands X in a given molecule obviously carry the same charge, and hence repel each other. Halogens are expected to be negatively charged, while a net positive charge on the methyl groups is reasonable. In the coordinated species, the acceptor ligand Y can be expected to bear a negative charge in all cases, including the boranes. Attractions between Y and CH_3 would then act to reinforce any tendency toward expansion of the triad of methyl groups, while repulsive Y···X interactions would suppress such a tendency in the trihalo compounds. An order-of-magnitude calculation shows that net atomic charges of a few tenths of an electron generate electrostatic forces consistent with angular displacements of several degrees in these systems. In accord with this analysis are the slight contractions of interhalogen distances upon coordination of the central atom lone pair (0.017 ± 0.004 Å for sulfides and 0.003 ± 0.004 Å for oxides), and the appreciable expansion of intercarbon distances in the methyl compounds (from 0.06 to 0.18 Å). This differentiation cannot logically be attributed to van der Waals repulsions, since all of the X···Y and Y···X distances, including the shortest H···H distances, are modestly repulsive both in MX_3 and X_3MY species.

The above discussion serves as a reminder of the *caveat* which should, but seldom does, accompany any empirical parametrization of molecular structures in terms of electronegativities or electronegativity differences. Success in fitting restricted data sets for molecules having ligands which closely resemble each other chemically merely allows one to *include* the chosen parameter, e.g., $E(X)$ or $E(Y)$, in the list of possible contributors to changes in bond lengths and valence angles. It does not *preclude* other factors. Thus there is no assurance that the adjustable coefficients (e.g., slopes in linear regressions) represent the true influence of variation of the parameter on molecular structure. In the present instance, if one discards the interpretation that methyl groups have effective Pauling electronegativities as low as one, one is led to the conclusion that the originally proposed correlations between observed bond lengths and ligand electronegativities[3a] have buried within them parallel correlations between ligand electronegativity and π character for halogen ligands, but not methyl groups. The superficially simple correlation between XMX angles and $E(Y)$ invoked for the halogen series seems to be similarly contaminated, both with π bonding and with electrostatic ligand-ligand interactions, thus making nonsense of any attempt to predict XMX angles for nonhalogen ligands by extrapolation. Given the multiplicity of factors contributing to the structure patterns in the symmetrically substituted phosphines, phosphine chalcogenides, and their arsine analogues, it seems unlikely that simple interpolation schemes would successfully predict structures of mixed halo-methyl derivatives, or even mixed halogen compounds of these systems.

A final comment on the electron diffraction results for $(CH_3)_3PSe$ should be made. One can interpret the bias in the data in favor of the TA model as tenuous evidence for hindered methyl torsions. The non-zero value of the parameter β is an expression of torsional shrinkage. There is no need to suppose the equilibrium configuration to be other than the staggered one, i.e., $\beta = 0°$. Despite the direct correlation between the barriers to methyl rotation inferred from the spectroscopic data[12] and the percent reduction in R (see Table II, footnote *e*) achieved by restricting the methyl torsion angle in the diffraction model for the three trimethylphosphines, the value of β does not change significantly over the series. Hence, it would be inappropriate to claim that β gives even a semiquantitative measure of the barrier height.

Appendix

Reevaluation of the Structure of Trimethylarsine. In the absence of a high precision electron diffraction study or of measurements of microwave spectra for isotopic species, the single moment of inertia, $I^0{}_b$, reported by Lide[23] remains the pivotal datum for determining structure parameters for $As(CH_3)_3$.

Our procedure for deriving values for r(AsC) and ∠CAsC does not differ materially from Lide's. Starting with various assumed methyl geometries, curves of r(AsC) vs. ∠CAsC (denoted hereafter by ϕ) which reproduce $I^0{}_b$ were generated. These curves are steep and nearly linear in the region of interest, with positive slopes in the range 4.0-4.4 deg pm^{-1} (1 pm = 0.01 Å). Lide's quoted error estimates on ϕ and r of ±3° and ±1 pm, respectively, are consistent with these slopes. Auxiliary data were then used to limit the range of "expected" values of ϕ, hence sharply restricting the range of compatible r(AsC) values.

We differ from Lide only in the selection of CH_3 parameters and in our estimate of bracketing values for ϕ. Subsequent to Lide's report, in which the microwave geometry of CH_3 groups in $P(CH_3)_3$[24] was transferred to $As(CH_3)_3$, structures for $(CH_3)_3AsO$ and $(CH_3)_3$ AsS have been reported.[2] These latter suggest that a slightly longer r(CH) and a considerably larger HCH angle than used previously are appropriate for $As(CH_3)_3$, even taking into account the probable difference between r_0(CH) and r_g(CH). Altering the CH_3 parameters translates the (r, ϕ) curve by 0.008 Å to higher r values.

There are two independent sources of data from which limits on ϕ can be derived. First, the C···C distance reported in the old visual-method electron diffraction study of $As(CH_3)_3$, adjusted for an apparent scale-factor error,[25] is 2.91 ± 0.05 Å, which restricts the microwave data to a 4° spread in ϕ, centered on 95.5° for the revised CH_3 geometry.

A second estimate of ϕ comes from plots of XMX angles in MX_3 molecules vs. atomic number, or covalent radius, for respective M atoms belonging to group 5a. Plots for X = F, Cl, Br, H, or SiH_3 are all monotonically decreasing, with a relatively narrow range of slopes. The entire spread of slopes, together with the known value of ∠CPC in $P(CH_3)_3$, generates an estimate for ∠CAsC of 96.0° (+1.5°, −1.0°).

Although our final preferred values of r(AsC) and ϕ, as given in Table V, agree with Lide's values of 1.959 Å and 96° to well within *his* quoted error estimates, we are confident that the reduced error limits for ϕ are justified. We note further that *our* estimated uncertainty in r(AsC) is due as much to the uncertainty in the methyl geometry as it is to the uncertainty in ϕ. We feel that this additional source of uncertainty in r(AsC) was not adequately accounted for in the previous analysis.

Choice of Vibrational Averages for Parameters in Table V. Ideally all the entries in Table V for a given type of parameter (e.g., r(MX), ∠XMX, r(XX)) would represent the same vibrational average and would have resulted from least-squares refinements in which vibrational corrections to Euclidean self-consistency were made in a uniform manner. Because of the different methods of analysis for the various experiments, it would be impossible to report parameters, all of which are rigorously comparable without reanalyzing much of the data. The compromises made in selecting entries for Table V are outlined below.

In Table V parameters derived from electron diffraction investigations are labeled by vibrational average using conventional notations, r_g, r_a, and r_α. These labels are not rigorously correct in cases where geometric consistency has been imposed on an inherently non-Euclidean set of internuclear distances. The molecules under consideration are grouped below according to the model used for least squares refinement:

(a) No geometric constraints imposed, and either r_g or r_a refined, then converted to r_α for calculation of valence angles: PF_3, PCl_3, PBr_3, $OPBr_3$, (SPF_3[26]).

(b) Geometric constraints imposed in an r_a basis: POF_3, $POCl_3$, SPF_3, $SPCl_3$, $SPBr_3$.

(c) Geometric constraints imposed in an uncorrected r_a basis: $(CH_3)_3PO$, $(CH_3)_3PS$, $(CH_3)_3PSe$, $(CH_3)_3AsO$, $(CH_3)_3AsS$.

(d) No geometric constraints imposed; angles derived from an uncorrected r_g basis: $P(CH_3)_3$.

Proper r_g's are usually considered acceptable indicators of real changes in electronic structures. For the molecules in classes a, b, and d, unbiased values for r_g(MX) and r_g(XX) are accessible. In the case of class c molecules, pseudo-r_g's can be calculated from reported r_a's and amplitudes of vibration. There are probably negligible model errors associated with such corrections for r(MX). While this is less likely to hold for r(XX), the quoted uncertainties in the C···C distances for the $(CH_3)_3MY$ molecules are large enough to swamp such effects. Angles XMX are most susceptible to model errors, especially those for class c molecules. No simple transformation between θ_α and the pseudo-θ_a's is possible, so angles are quoted in their original form. In large part vertical comparisons in Table V are among molecules which received the same type of data treatment. There is further assurance of the validity of comparisons among the angles as quoted in the fact that for the molecules in class a the correction from θ_g or θ_a to θ_α is found to be 0.1-0.3°, which is comparable to the quoted error limits on these angles.

The parameters selected for presentation in Table V do not, in most cases, comprise a Euclidean set (except for the borane adducts, studied by microwave). However, it is felt that the numbers for a given type of coordinate, viz. r(MX), r(XX), and ∠XMX, give as faithful a representation of actual trends in parameters as is possible under the circumstances, and they do permit valid conclusions to be drawn from comparisons between series of molecules.

Structures of the borane adducts are based on partial isotopic substitution in combination with assumed values of selected parameters, e.g., for the methyl groups. Thus they correspond to none of the accepted operationally or vibrationally defined parameter types, r_0, r_s, or r_z. The large error limits reported probably exceed any correction for these parameters to some basis suitable for comparison with the diffraction-based structures.

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Supplementary Material Available: The data for experimental intensities and calculated backgrounds (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) To whom correspondence should be addressed at the University of Toledo.

(2) C. J. Wilkins, K. Hagen, L. Hedberg, Q. Shen, and K. Hedberg, *J. Am. Chem. Soc.*, **97**, 6352-6358 (1975).

(3) (a) K. Karakida and K. Kuchitsu, *Inorg. Chim. Acta*, **16**, 29-34 (1976). (b) T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, **10**, 344-350 (1971).

(4) Systematics of bond angles are also examined in S. Konaka and M. Kimura, *Bull. Chem. Soc. Jpn.*, **46**, 413-416 (1973).

(5) R. A. Zingaro and R. E. McGlothin, *J. Chem. Eng. Data*, **8**, 226-229 (1963).

(6) G. Gundersen and K. Hedberg, *J. Chem. Phys.*, **51**, 2500-2507 (1969).

(7) L. Hedberg, Abstracts, Fifth Austin Symposium on Gas Phase Molecular Structure, Austin, Texas, March 1974, p 37.

(8) Inelastic scattering factors used in background calculations were taken from D. T. Cromer, *J. Chem. Phys.*, **50**, 4857-4859 (1969), except for hydrogen, which was taken from C. Tavard, D. Nicholas, and M. Rouault, *J. Chim. Phys.*, **64**, 540-554 (1967).

(9) Elastic scattering factors were interpolated to 44 kV from values tabulated by L. Shafer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, **55**, 3055-3056 (1971).

(10) Rotation of 60° spans all unique orientations in terms of r_{ij} distributions.

(11) V. Plato, W. D. Hartford, and K. Hedberg, *J. Chem. Phys.*, **53**, 3488-3494 (1970).

(12) H. Rojhantalab, J. W. Nibler, and C. J. Wilkins, *Spectrochim. Acta, Part A*, **32**, 519-533 (1976).

(13) R. Stølevik, H. M. Seip, and S. J. Cyvin, *Chem. Phys. Lett.*, **15**, 263-265 (1972).

(14) An x-ray study of triethylphosphine sulfide and triethylphosphine selenide has been reported. See M. van Meerssche and A. Léonard, *Bull. Soc. Chim. Belg.*, **68**, 683-698 (1959); **69**, 45-56 (1960). However, abnormally long PC bonds and unreasonably short PS, PSe, and CC bonds were reported therein, and we consider those results to be erroneous.

(15) V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37-40 (1941).

(16) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960, pp 93, 224-229.

(17) See, for example, R. J. Gillespie, *Angew. Chem., Int. Ed. Engl.*, **6**, 819 (1967), and references cited therein.

(18) E. J. Jacob, S. Samdal, and D. D. Danielson, to be submitted for publication.

(19) The coefficients for $|\Delta E|$ in the r(PO) and r(PS) plots in Figure 4 are respectively 0.194 and 0.175. By contrast, coefficients recommended by Pauling (see ref 16) for $|\Delta E|$ in Schomaker-Stevenson type expressions range from 0.04 to 0.08.

(20) This is admittedly a grossly oversimplified view of the charge distributions in the methyl compounds. A counter claim could be made that even though the methyl groups carry a net positive charge, the carbons themselves may be slightly negative. Thus the addition of sulfur to $(CH_3)_3M$ would reverse the charge on M, converting the M-C interaction from a repulsive to an attractive one.

(21) Kuchitsu has shown (see ref 3a) that a satisfactory representation of XMX angles in most of these molecules can also be obtained by replacing E(X) with the covalent radius of X as the parameter.

(22) See, for example, L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **32**, 512-515 (1960), and references cited therein.

(23) D. R. Lide, Jr., *Spectrochim. Acta*, **15**, 473-476 (1959).

(24) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **29**, 914-920 (1958). For a more recent microwave determination of the structure of $P(CH_3)_3$, see P. S. Bryan and R. L. Kuczkowski, *J. Chem. Phys.*, **55**, 3049-3051 (1971).

(25) H. D. Springall and L. O. Brockway, *J. Am. Chem. Soc.*, **60**, 996-1000 (1938). A 1-2% reduction of all internuclear distances reported for both $P(CH_3)_3$ and $As(CH_3)_3$ in the cited reference brings them into substantially better agreement with more recent structure determinations.

(26) Parameters preferred by the authors of ref 3a resulted from the constrained, vibrationally corrected fit, which was said not to differ from the unconstrained fit by more than the estimated σ's.

(27) Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, **8**, 867-871 (1969).

(28) K. Hedberg and M. Iwasaki, *J. Chem. Phys.*, **36**, 589-593 (1962).

(29) S. J. Cyvin, B. N. Cyvin, and A. Müller, *J. Mol. Struct.*, **4**, 341-349 (1969).

(30) K. Kuchitsu, T. Shibata, A. Yokozeki, and C. Matsumura, *Inorg. Chem.*, **10**, 2584-2587 (1971).

(31) P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, **11**, 553-559 (1972).

(32) J. R. Durig, B. A. Hudgens, and J. D. Odom, *Inorg. Chem.*, **13**, 2306-2312 (1974).

(33) R. L. Kuczkowski and D. R. Lide, Jr., *J. Chem. Phys.*, **46**, 357-365 (1967).