

*Journal of Organometallic Chemistry*, 159 (1978) 23–30  
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

## SKELETAL STRUCTURES OF HEXA-ORGANO SUBSTITUTED TRIATOMICS $R_3XYZR_3$ : A RATIONALISATION USING THE SECOND-ORDER JAHN–TELLER EFFECT

C. GLIDEWELL

*Chemistry Department, University of St. Andrews, St. Andrews, Fife, KY16 9ST (Great Britain)*

(Received April 17th, 1978)

### Summary

In compounds of type  $R_3XYZR_3$  (R = phenyl, methyl, benzyl; X, Z = Al, Si, P, Ge, Sn; Y = C, N, O, F) linearity of the XYZ skeleton is predicted by the second-order Jahn–Teller effect in those examples where the valence orbitals of X and Z are much less tightly bound than those of Y. When the X and Z orbitals are bound more tightly than those of Y, the XYZ skeleton is predicted to be non linear at Y. The effects of varying R, X and Z, and the contribution of  $\pi$ -interactions are discussed.

### Introduction

During the course of our X-ray crystallographic studies of organometallic oxo-compounds [1–5], which are designed to test the hypothesis [6,7] that the large bond angles observed at carbon, nitrogen, oxygen, or fluorine when these atoms are bonded to two or more groups in which the ligating atom lies in the second row, or in a subsequent row, of the Periodic Table are of steric rather than of electronic origin, we observed [2] that in oxo-bis(triphenylsilicon),  $O(SiPh_3)_2$ , the SiOSi bridge is rigorously linear since the molecules lie across a centre of inversion. We had expected that the Si...Si distance would be approximately 3.10 Å, as found in a very wide range of both neutral and anionic molecular fragments  $SiYSi$  (Y = C, N, O) [6,8] and also in continuous species such as the several polymorphs of silica [8,9]; concurrently we expected an SiOSi angle of ca. 140°. Consequently the observation of a linear SiOSi fragment having an Si...Si distance of 3.232 Å was surprising, and it has prompted a comparison of the structure of this molecule with those of a number of its isoelectronic analogues, in an attempt to rationalise the geometry observed.

The triatomic array SiOSi has fourteen valence-shell electrons; assigning six to the terminal bonds to the R groups in  $R_3SiOSiR_3$ , this leaves eight electrons

for the bridge bonding. Fragments isoelectric with SiOSi, of type  $XYX$  (where  $Y$  represents an element of the first Periodic row, and  $X$  an element of the second row) are  $AlFAl^-$ ,  $SiNSi^-$ ,  $PCP$ , and  $PNP^+$ , while those of type  $XYZ$  (where  $Z$  also represents a second-row element) include  $AlFSi$ ,  $AlOP$ , and  $SiNP$ : isoelectronic fragments in which  $X$  and  $Z$  represent heavier elements follow immediately from those listed.

The structures of a number of these compounds have recently been determined by X-ray methods. In the unit-cell of  $Ph_3PCPPH_3$  [10], there are two independent molecules in which the  $PCP$  angles are  $130.1(6)^\circ$  and  $143.8(6)^\circ$  respectively, indicating that the skeletal deformation can be accomplished with the expenditure of very little energy: intermolecular forces are probably adequate to account for the difference in geometry. Many salts of the  $Ph_3PNPPh_3^+$  cation have been structurally characterised: in the majority [11–18] the  $PNP$  fragment is non-linear with the observed  $PNP$  angle falling within the range  $134.6(3)^\circ$ , as found [15] in  $[Ph_3PNPPh_3][Fe(CO)_4CN]$  to  $141.8(6)^\circ$ , as found [18] in  $[Ph_3PNPPh_3][Mo(CO)_4BH_4]$ . However, in  $[Ph_3PNPPh_3][V(CO)_6]$ , the  $PNP$  skeleton is strictly linear [19], a requirement of the space group symmetry (rhombohedral  $R\bar{3}$ ,  $Z = 1$ ): as in the example of  $Ph_3PCPPH_3$ , the observation of linear and non-linear forms suggests that skeletal deformation is not difficult, and can be accomplished simply by the intermolecular forces. This view is strongly reinforced by the observation [19] that both linear and non-linear forms of the cation occur together in the unit cell of  $[Ph_3PNPPh_3]_3[Na\{Mo_3(CO)_6(NO)_3(OCH_3)_3O\}_2]$ . The other fragments of type  $XYX$  are structurally characterised only when the  $R$  group is alkyl, rather than phenyl: thus the  $AlFAl^-$  skeleton in  $K[Et_3AlFAlEt_3]$  is linear [20]. Alkyl-substituted  $SiOSi$  and  $PCP$  skeletons also have been structurally characterised [21,22]. However, none of those of type  $XYZ$  is at present structurally characterised.

In attempting both to rationalise the geometries observed and also to predict those which are as yet unknown as a test of the rationalisation, the approach adopted is to use the second-order Jahn–Teller effect to investigate the propensity of a particular linear triatomic skeleton to undergo a deformation of  $\Pi_u$  symmetry, that is, to bend. The relative atomic orbital binding energies in the atoms  $X$  (and  $Z$ ) on the one hand, and  $Y$  on the other, prove to be crucial in this respect.

## Method

Suppose for the linear geometry, the symmetry classes (in  $D_{\infty h}$  or  $C_{\infty v}$ ) of the HOMO and LUMO are  $\Gamma_0$  and  $\Gamma_1$  respectively: restricting attention, as is usual [23], to a single electronic excited state, then the force constant,  $f_q$ , for the vibration along a coordinate  $q$  is

$$f_q = \frac{1}{2} \left\langle \Psi_0 \left| \frac{\partial^2 U}{\partial q^2} \right| \Psi_1 \right\rangle - \frac{\left[ \left\langle \Psi_0 \left| \frac{\partial U}{\partial q} \right| \Psi_1 \right\rangle \right]^2}{(E_1 - E_0)}$$

where  $\Psi_0$  and  $\Psi_1$  are the wavefunctions for the ground and excited states, of energies  $E_0$  and  $E_1$  respectively, and  $U$  is the total potential energy of the sys-

tem. Both terms in  $f_q$  are positive, but depending on the relative magnitudes of the two terms  $f_q$  may be: (1) positive in which case the system executes vibrations of small amplitude and the skeleton is rigid and linear; (2) approximately zero, when the vibrational amplitudes are large and the skeleton is flexible; or (3) negative, especially if  $(E_1 - E_0)$  is small, in which case the system distorts along a vibrational coordinate  $q$  such that  $\Gamma_q$  is contained in  $\Gamma_0 \times \Gamma_1$ , giving a skeleton which is bent and rigid.

In the molecules in question, the atoms X and Z are always four-coordinate so that, as a first approximation, they each contribute only a single  $\sigma$  orbital, which may be regarded as similar to an atomic  $p$  orbital, to the bridge bonding. The atom Y contributes  $ns$  and  $np$  orbitals of symmetry classes (in  $D_{\infty h}$ )  $\Sigma_g^+(ns)$ ,  $\Sigma_u^+(np_z)$ , and  $\Pi_u(np_x, np_y)$  (where the molecular axis is taken to be  $z$ ): the in-phase and out-of-phase combinations of the X( $\sigma$ ) orbitals belong to symmetry classes  $\Sigma_g^+$  and  $\Sigma_u^+$  respectively. Whatever the relative binding energies, within chemically plausible limits, the electronic configuration for the bridge is:

$$(1\sigma_g^+)^2(1\sigma_u^+)^2(1\pi_u)^4(2\sigma_g^+)^0(2\sigma_u^+)^0$$

precisely as for an  $MH_2$  molecule [24]. Hence if any distortion of the skeleton is to occur, it will involve the vibrational coordinate  $\Pi_u \times \Sigma_g^+ = \Pi_u$ , so that the only distortion to be expected is a skeletal bend, as observed in eight electron  $MH_2$  species such as  $OH_2$ .

However the crucial factor is the  $1\pi_u - 2\sigma_g^+$  gap. In assessing this, without resort to computation, several classes of behaviour may be distinguished:

*Class 1.* The  $\sigma$  orbitals of Y are tighter bound than the orbitals of X; consequently the  $1\sigma_u^+ - 1\pi_u$  gap is large, but the  $1\pi_u - 2\sigma_g^+$  gap is small, that is  $E(2\sigma_g^+) - E(1\pi_u)$  is small,  $f(\Pi_u)$  is negative, and the system is expected to distort along the bending vibration  $\Pi_u$ .

*Class 2.* The  $\sigma$  orbitals of Y are bound less tightly than the orbitals of X: in this case the  $1\sigma_u^+ - 1\pi_u$  gap is generally small, but the  $1\pi_u - 2\sigma_g^+$  gap is generally large. Hence  $E(2\sigma_g^+) - E(1\pi_u)$  is large,  $f(\Pi_u)$  is positive, and neither a distortion along  $\Pi_u$ , nor vibrations of large amplitude are expected.

*Class 3.* This is in effect a special case of Class 2 which gives rise to Class 1 behaviour. If the X( $\sigma$ ) orbitals are comparable in binding energy with the Y( $np$ ) orbitals but the Y( $ns$ ) orbital is much tighter bound, then the  $\Sigma_g^+$  interaction will be small, yielding a small  $1\pi_u - 2\sigma_g^+$  gap, so that, as in Class 1, the system distorts along the  $\Pi_u$  bending vibration.

*Class 4.* For some intermediate range of relative atomic orbital binding energies, (between those giving rise to classes 1 and 2),  $f(\Pi_u)$  may be expected to be close to zero, so that large amplitude bending vibrations occur. It is a characteristic of such vibrations that the skeletal inter-bond angle can be markedly changed with the expenditure of very little energy.

In summary, if the X( $\sigma$ ) binding energy is similar to or greater than the binding energy of Y( $np$ ), a non-linear skeleton is to be expected: if the binding energy of X( $\sigma$ ) is less than that of Y( $np$ ), then a linear skeleton is expected.

## Results

Atomic orbital binding energies [25,26] for selected neutral atoms are listed in Table 1: for positive and negative species, the binding energies increase and

TABLE 1

ATOMIC ORBITAL BINDING ENERGIES (eV) FOR VALENCE-SHELL ELECTRONS IN SELECTED NEUTRAL ATOMS<sup>a</sup>

Atom	ns	np
H	13.60	
Li	5.39	3.54
C	21.01	11.27
N	27.63	13.94
O	34.96	17.28
F	38.24	20.86
Al	12.27	6.47
Si	17.31	9.19
P	19.55	10.73
S	22.47	12.39
Ga	14.58	6.75
Ge	18.57	9.43
As	18.77	9.36
Se	22.27	11.68
Sn	16.16	8.32
Sb	18.02	8.75

<sup>a</sup> Refs. 25, 26.

decrease respectively. Using these data, crude predictions of geometry can be made, subject to refinement when the effect of changing the substituent is considered.

(a) *AlFAl*<sup>-</sup>. The binding energy of Al(3*p*) is much less than that of F<sup>-</sup>(2*p*): hence this is an example of Class 2, and linearity is expected.

(b) *SiOSi*. The binding energy of Si(3*p*) is much less than that of O(2*p*): this is another example of Class 2, and linearity is again expected.

(c) *PCP*. The binding energies of P(3*p*) and C(2*p*) are comparable: this is an example either of Class 3 or of Class 4.

(d) *PNP*<sup>+</sup>. If this is regarded as P—N<sup>+</sup>—P, with P(3*p*) much less tightly bound than N<sup>+</sup>(2*p*), then this fragment falls into Class 2, and a linear skeleton is expected. However an ESCA study [27] of a series of salts [Ph<sub>3</sub>PNPPh<sub>3</sub>]X (X<sup>-</sup> = F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NCO<sup>-</sup>, NCS<sup>-</sup>, N<sub>3</sub><sup>-</sup>, and V(CO)<sub>6</sub><sup>-</sup>) concluded that the best description is P<sup>+</sup>—N<sup>-</sup>—P<sup>+</sup>: here the orbitals P<sup>+</sup>(3*p*) is tighter bound than N<sup>-</sup>(2*p*) so that this fragment then belongs to Class 1 with a non-linear skeleton predicted. In each of these salts the N(1s) and P(2*p*) binding energies were found [27] to be essentially independent of the counter ion: it has been pointed out [19] that this implies either that in all these salts the geometry is identical, with a linear PNP fragment as found [19] in [Ph<sub>3</sub>PNPPh<sub>3</sub>][V(CO)<sub>6</sub>], or that the binding energies are independent of the angle in which case no conclusion about the charge distribution or the geometry can be reached from the ESCA data.

For the XYZ species, predictions can be made for the neutral species:

(e) *SiNP*. The binding energies of Si(3*p*) and P(3*p*) are 9.19 eV and 10.73 eV respectively: when these two orbitals interact (at the Si...P distance) they will yield an out-of-phase combination somewhat less tightly bound than 9.2 eV, and an in-phase combination somewhat more tightly bound than 10.7 eV, in other words, quite close to N(2*p*) at 13.9 eV. So that this skeleton may be a member of either of Class 2 or of Class 3.

(f) *AlOP*. The binding energies of Al( $3p$ ) and P( $3p$ ) are 6.47 eV and 10.73 eV respectively whereas O( $2p$ ) has a binding energy of 17.28 eV. Hence this is an example of Class 2 behaviour, and a linear skeleton is expected.

### *Effect of substituent*

Any substituent on the atom X which is a net electron donor, such as alkyl or oxide, will render the orbitals of X less tightly bound, and so will tend to shift a Class 1 system into Classes 3 or 4, and a Class 3 or 4 system into Class 2, that is the skeleton will tend towards linearity. Conversely any substituent on X which is a net electron acceptor will perturb the system in the opposite sense, towards a non-linear rigid skeleton.

### *Effect of $d\pi$ orbitals on X*

Regardless of the relative binding energies of X( $np$ ) and Y( $np$ ), X( $nd$ ) will be less tightly bound than X( $np$ ). The perturbation of the  $np\pi$  orbitals of Y will always have the effect of increasing the  $1\pi_u - 2\sigma_g^+$  gap, and therefore it will reinforce any tendency of the skeleton to remain linear. This is consistent with the popular MO picture of  $p_\pi - d_\pi$  interactions in these molecules. The role of the  $d\pi$  orbitals on X will be greatest when the energy gap X( $nd$ )—Y( $np$ ) is least, that is when X is more electronegative than Y, for example in PCP or PNP<sup>+</sup>. In cases where Y is more electronegative than X, such as in AlFAl<sup>-</sup> or SiOSi, the  $p_\pi - d_\pi$  interactions will be least significant: as shown above, with ligands of low electronegativity the  $\sigma$  bonding alone predicts a linear skeleton.

### *Effect of heavier atoms X*

On going to the subsequent rows of the Periodic Table, the binding energies of the valence shell orbitals of the atoms X exhibit very little change from those of the second row atoms, so that analogous considerations apply, with analogous deductions.

## Discussion

Ph<sub>3</sub>PCPPh<sub>3</sub> [10] has a skeleton which is easily deformed, with the lower limit of the PCP angle determined by the non-bonded P...P contact [6]. On changing the organic substituent to the more electron donating methyl group, the structure is expected to tend more to linearity. In an electron diffraction study of Me<sub>3</sub>PCPMe<sub>3</sub> [22] an apparent PCP angle of 147.6(5)<sup>o</sup> was determined: however the best fit to the experimental intensity data was obtained for a model having free rotation of the Me<sub>3</sub>P groups about the P—C bonds. From this, the authors concluded that the vibrational ground state was linear, and that the apparent PCP angle resulted from the shrinkage effect observed in the presence of a large amplitude skeletal vibration of low frequency (estimated in this example to be no more than 80 cm<sup>-1</sup>). Hence Me<sub>3</sub>PCPMe<sub>3</sub> exhibits Class 4 behaviour.

The Ph<sub>3</sub>PNPPh<sub>3</sub><sup>+</sup> cation is another example to Class 4. It is unfortunate that no other R<sub>3</sub>PNPR<sub>3</sub><sup>+</sup> cations appear to have been structurally characterised. One can predict that the cation Cl<sub>3</sub>PNPCl<sub>3</sub><sup>+</sup>, obtained in the early stages of the reaction between PCl<sub>5</sub> and NH<sub>4</sub>Cl [28], will fall into Class 1 and will have a non-linear skeleton with a P...P distance of ca. 2.90 Å [6], whereas Me<sub>3</sub>PNPMe<sub>3</sub><sup>+</sup> may well be linear (Class 2).

$\text{Ph}_3\text{SiOSiPh}_3$  falls into either Class 2 or Class 4. There is a single molecule in the unit cell [2] so that no assessment of the flexibility of the skeleton is possible. However some support for Class 4 behaviour may be drawn from an electron diffraction study of  $\text{Me}_3\text{SiOSiMe}_3$ , which revealed an apparent SiOSi angle of  $148(3)^\circ$ . The radial distribution curve was far too complex to yield any information on the shape of the SiOSi bending potential function, so that again no direct indication of the flexibility of the skeleton is available.

No study has been made of the anion  $\text{Ph}_3\text{AlFAlPh}_3^-$ : however the potassium salt of the ethyl analogue  $\text{K}[\text{Et}_3\text{AlFAlEt}_3]$  has been studied [20] and the AlFAl skeleton found to be linear. This is almost certainly an example of Class 2 behaviour: this conclusion could readily be tested by making structural analyses of salts containing other cations of various sizes. For Class 2, the skeleton is rigid, so that the geometry should be independent of the counterion (unlike  $\text{Ph}_3\text{PNPPH}_3^+$ ).

It is interesting to note that those species for which  $p_\pi-d_\pi$  interactions are expected to be the least important are the linear AlFAl<sup>-</sup> and SiOSi, while those for which they are expected to be most important are the most easily deformed, namely PCP and PNP<sup>+</sup>. It may be concluded from these observations that the structural significance of  $\pi$ -interactions in molecules of this type is negligible since such interactions will necessarily render the molecular skeletons more rigid, rather than less.

The compounds  $\text{Ph}_3\text{SiNPPH}_3$  and  $\text{Ph}_3\text{AlOPPh}_3$  have not been structurally investigated. From the foregoing analysis, both may be predicted to have linear skeletons, although that of  $\text{Ph}_3\text{SiNPPH}_3$  may possibly exhibit Class 3 behaviour.

Very few analogues of the above-mentioned species are characterised which contain elements heavier than those of the second Periodic row.  $\text{Ph}_3\text{GeOGePh}_3$  is found to have a GeOGe angle of  $135.2(2)^\circ$  [1], and hence appears to exhibit Class 1 behaviour, as does  $\text{H}_3\text{GeOGeH}_3$  where the skeletal angle is  $126.5(3)^\circ$  [29]: in this latter molecule there is no evidence from the gas phase study of any large amplitude skeletal vibration. In  $\text{Me}_3\text{GeOGeMe}_3$ , the apparent GeOGe angle is  $141.0^\circ$  [30], but as in  $\text{Me}_3\text{SiOSiMe}_3$ , the radial distribution curve is too complex to yield any evidence either for or against such a vibration. It is to be

TABLE 2

GEOMETRICAL COMPARISON OF  $\text{R}_3\text{XYZR}_3$  WITH  $\text{R}_3\text{XYCO}$  AND  $\text{R}_3\text{XYCS}$ ; SKELETAL ANGLES AT Y IN DEGREES

$\text{R}_3\text{XYZR}_3$	$\text{R}_3\text{XYCO}$	$\text{R}_3\text{XYCS}$
$\text{Ph}_3\text{PCPPH}_3$ 130.1, 143.8 <sup>a</sup>	$\text{Ph}_3\text{PCCO}$ 145.5 <sup>c</sup>	$\text{Ph}_3\text{PCCS}$ 168.0 <sup>e</sup>
$\text{Ph}_3\text{PNSiPh}_3$	$\text{Ph}_3\text{SiNCO}$	$\text{Ph}_3\text{SiNCS}$ 170.7 <sup>f</sup>
$\text{Ph}_3\text{PNPPH}_3^+$ 134.6–180.0 <sup>b</sup>	$\text{Ph}_3\text{PNCO}^+$	$\text{Ph}_3\text{PNCS}^+$
$\text{Ph}_3\text{PNGePh}_3$	$\text{Ph}_3\text{GeNCO}$ 150.7 <sup>d</sup>	$\text{Ph}_3\text{GeNCS}$
$\text{Ph}_3\text{PNSnPh}_3$	$\text{Ph}_3\text{SnNCO}$	$\text{Ph}_3\text{SnNCS}$ 161 <sup>g</sup>

<sup>a</sup> Ref. 10. <sup>b</sup> See text. <sup>c</sup> Ref. 31. <sup>d</sup> Ref. 32. <sup>e</sup> Ref. 33. <sup>f</sup> Ref. 34. <sup>g</sup> Ref. 35.

expected that alkyl substitution causes the system to tend from Class 1 behaviour towards Class 4 and thence to Class 2, and indeed  $(\text{PhCH}_2)_3\text{GeOGe}(\text{CH}_2\text{Ph})_3$  appears [5] to have a linear skeleton (rhombohedral,  $Z = 1$ ). An entirely parallel series of observation has been made for SnOSn species: in the solid state  $\text{Ph}_3\text{SnOSnPh}_3$  has an SnOSn angle of  $137.3(1)^\circ$  [4], in the gas phase  $\text{Me}_3\text{SnOSnMe}_3$  has a skeletal angle of  $140.8^\circ$  [30], while in the solid state  $(\text{PhCH}_2)_3\text{SnOSn}(\text{CH}_2\text{Ph})_3$  is [5] again rhombohedral, with  $Z = 1$ . We predict from these observations that  $(\text{PhCH}_2)_3\text{PCP}(\text{CH}_2\text{Ph})_3$  and  $(\text{PhCH}_2)_3\text{PNP}(\text{CH}_2\text{Ph})_3^+$  will both have linear skeletons (Class 2).

Isoelectronic with  $\text{R}_3\text{P}$  and  $\text{R}_3\text{Si}^-$  are the groups CO and CS: in Table 2 are listed some examples of  $\text{R}_3\text{XYXR}_3$  and  $\text{R}_3\text{XYZR}_3$  molecules, together with their analogues  $\text{R}_3\text{XYCO}$  and  $\text{R}_3\text{XYCS}$ , with the skeletal angles at Y where these are known. The  $\text{R}_3\text{XYCS}$  species all have skeletons which are close to linear.

## Conclusions

In any complex of type  $\text{R}_3\text{XYZR}_3$ , the skeleton will be non-linear at Y if the ligands  $\text{R}_3\text{X}$  and  $\text{R}_3\text{Z}$  have their valence-shell orbitals tighter bound than those of Y. If they are markedly less tightly bound than those of Y the skeleton will be linear at Y regardless of whether Valence Bond descriptions require the presence of unshared pairs on Y. This prediction of stereochemical inactivity of lone pairs in the presence of ligands of low electronegativity is an important modification to the Valence-Shell Electron-Pair Repulsion model of molecular geometry: its application to other systems  $(\text{R}_3\text{X})_p\text{Y}$  ( $p \geq 3$ ) is under investigation.

## References

- 1 C. Glidewell and D.C. Liles, *Acta Cryst.*, B, 34 (1978) 1119.
- 2 C. Glidewell and D.C. Liles, *Acta Cryst.*, B, 34 (1978) 124.
- 3 C. Glidewell and D.C. Liles, *Acta Cryst.*, B, 34 (1978) 696.
- 4 C. Glidewell and D.C. Liles, *Acta Cryst.*, B, 34 (1978) 1693.
- 5 C. Glidewell and D.C. Liles, unpublished work.
- 6 C. Glidewell, *Inorg. Chim. Acta*, 12 (1975) 219.
- 7 C. Glidewell, *Inorg. Chim. Acta*, 20 (1976) 113.
- 8 C. Glidewell, *Inorg. Chim. Acta*, 25 (1977) 77.
- 9 C. Glidewell, *Inorg. Nuclear Chem. Lett.*, 13 (1977) 65.
- 10 A.T. Vincent and P.J. Wheatley, *J. Chem. Soc. Dalton*, (1972) 617.
- 11 L.B. Handy, J.K. Ruff and L.F. Dahl, *J. Amer. Chem. Soc.*, 92 (1970) 7312.
- 12 L.B. Handy, J.K. Ruff and L.F. Dahl, *J. Amer. Chem. Soc.*, 92 (1970) 7327.
- 13 J.K. Ruff, R.P. White and L.F. Dahl, *J. Amer. Chem. Soc.*, 93 (1971) 2159.
- 14 M.B. Smith and R. Bau, *J. Amer. Chem. Soc.*, 95 (1973) 2388.
- 15 S.A. Goldfield and K.N. Raymond, *Inorg. Chem.*, 13 (1974) 770.
- 16 H.B. Chin, M.B. Smith, R.D. Wilson and R. Bau, *J. Amer. Chem. Soc.*, 96 (1974) 5285.
- 17 J. Chiang, M.S. Thesis, University of Southern California, 1974.
- 18 S.W. Kirtley, M.A. Andrews, R. Bau, G.W. Grynkewich, T.J. Marks, D.L. Tipton and B.R. Whittlesey, *J. Amer. Chem. Soc.*, 99 (1977) 7154.
- 19 R.D. Wilson and R. Bau, *J. Amer. Chem. Soc.*, 96 (1974) 7401.
- 20 G. Natta, G. Allegra, G. Perego and A. Zambelli, *J. Amer. Chem. Soc.*, 83 (1961) 5033.
- 21 B. Csákvári, Z.S. Wagner, P. Gömöry, F.C. Mijlhoff, B. Rozsondai and I. Hargittai, *J. Organometal. Chem.*, 107 (1976) 287.
- 22 E.A.V. Ebsworth, T.E. Fraser, D.W.H. Rankin, O. Gasser and H. Schmidbaur, *Chem. Ber.*, 110 (1977) 3508.
- 23 R.G. Pearson, *Symmetry Rules for Chemical Reactions*, John Wiley, New York, 1976.

- 24 A.D. Walsh, *J. Chem. Soc.*, (1953) 2260.
- 25 J. Hinze and H.H. Jaffé, *J. Amer. Chem. Soc.*, 84 (1962) 540.
- 26 J. Hinze and H.H. Jaffé, *J. Phys. Chem.*, 67 (1963) 1501.
- 27 W.E. Swartz, Jr., J.K. Ruff and D.M. Hercules, *J. Amer. Chem. Soc.*, 94 (1972) 5227.
- 28 J. Emsley and P.B. Udy, *J. Chem. Soc. A*, (1970) 3025.
- 29 C. Glidewell, D.W.H. Rankin, A.G. Robiette, G.M. Sheldrick, B. Beagley and S. Craddock, *J. Chem. Soc. A*, (1970) 315.
- 30 L.V. Vilkov and N.A. Tarasenko, *Zh. Strukt. Khim.*, 10 (1969) 1102.
- 31 J.J. Daly and P.J. Wheatley, *J. Chem. Soc. A*, (1966) 1703.
- 32 L.E. Nikolaeva, T.N. Tarkhova, E.V. Chuprunov and O.V. Matskevich, In Yu.T. Struchkov and Ya.Ya. Bleidelis (Eds.), *Tezisy Dokl. -Vses. Soveshch. Org. Kristallokhim.*, 1974; *Chem. Abstr.*, 87 (1977) 75667q.
- 33 J.J. Daly, *J. Chem. Soc., A*, (1967) 1913.
- 34 G.M. Sheldrick and R. Taylor, *J. Organometal. Chem.*, 87 (1975) 145.
- 35 A.M. Domingos and G.M. Sheldrick, *J. Organometal. Chem.*, 67 (1974) 257.