

and the formation of bent bonds) and the related increases in energy. The small ring propellanes carry bond angle deformation to an extreme and lead to new types of reactions that have not been observed with mono- or bicyclic small ring systems. The remarkable stability of [1.1.1]propellane again shows the importance of driving force for a particular reaction vs. the overall strain energy. Further studies of these com-

pounds should give chemists a much better understanding of the nature of carbon-carbon bonds.

*I am indebted to my co-workers, whose names appear in the references, for their contributions to our studies of small ring chemistry. I should like to acknowledge the valuable collaboration with Prof. J. Michl in the preparation of some of the propellanes. The investigations were supported by grants from the National Science Foundation.*

## Stable Compounds with Double Bonding between the Heavier Main-Group Elements

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With the advent of modern structural techniques, compounds that were thought to possess  $P=P^1$  or  $Si=Si^2$  bonds have been shown subsequently to be cyclic oligomers.<sup>3</sup> As a consequence of these and allied observations, the consensus developed that compounds featuring (p-p) $\pi$ -bonds between the heavier main-group elements would not be stable. Such a view is often referred to as "the double-bond rule". Significant progress in the area was not forthcoming until 1965, when Gusel'nikov et al.<sup>4</sup> developed a methodology for the production of transient silaethenes. Since then, evidence for numerous other ephemeral species with implied double bonds between silicon and phosphorus atoms has been presented.<sup>5</sup> However, the isolation and characterization of *stable* compounds of this genre is a much more recent accomplishment and represents the subject matter of this Account.

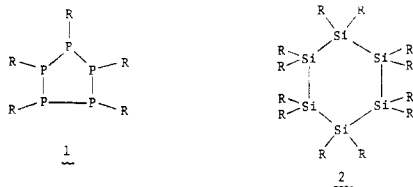
### Thermodynamic and Kinetic Factors

The basic difficulty underlying the isolation of compounds with multiple bonding between heavier main-group elements is thermodynamic. Consider the following representative bond energy data (kcal/mol) for single and multiple bonds:<sup>6</sup> N-N (39), N=N (100.1), N $\equiv$ N (225.8), P-P (48), P=P (74), P $\equiv$ P (117). Two trends are evident: (i) the relative increase in bond energy with bond order is much greater for the first-row element than for the heavier congener, and (ii) for the heavier main-group elements, it is more favorable to form two  $\sigma$ -bonds than one  $\sigma$ - and one  $\pi$ -bond. As a consequence, species of empirical composition RP or  $R_2Si$  usually exist as cyclic oligomers like 1 and 2 rather

than as diphosphenes (RP=PR) or disilenes ( $R_2Si=SiR_2$ ). One obvious way to thwart the oligomerization tendency of the doubly bonded compounds is by increasing the steric demands of the substituents, R. Although the stabilization of diphosphenes or disilenes by steric blockades might be thought of as primarily kinetic, it should be borne in mind that some of the stabilization is thermodynamic in origin since the steric interactions among the bulky groups are less in diphosphenes or disilenes than in the corresponding cyclic species. Another approach to double-bond formation is to take advantage of the enhanced stability of lower coordination numbers with increasing atomic number—the so-called "inert s-pair effect".

**Group 4A Compounds.** The group 4A alkyls,  $[(Me_3Si)_2CH]_2E$ , E = Ge, Sn, and Pb, were prepared by Lappert and co-workers several years ago.<sup>7</sup> All compounds are monomeric in the vapor phase and exhibit the anticipated V-shaped structures. However, in the solid state, the tin and germanium compounds are dimeric and feature bonding between the E atoms, viz.,  $[(Me_3Si)_2CH]_2EE[CH(SiMe_3)_2]_2$  (E = Ge (3) and Sn (4)). As will be discussed in a subsequent section, questions have arisen regarding the exact nature of the central bond. Nevertheless, these compounds represent the first examples of stable compounds involving homonuclear double bonding between the heavier group 4A or 5A elements.

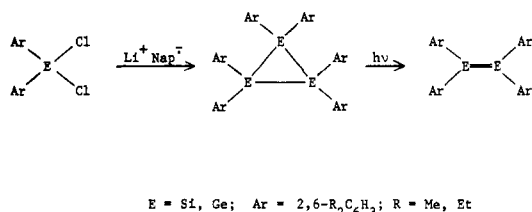
The first stable disilene,  $(Mes)_2Si=Si(Mes)_2$  (5) (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), was prepared by West et al.<sup>8</sup> via the



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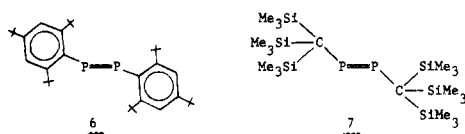
- (1) Köhler, H.; Michaelis, A. *Ber. Dtsch. Chem. Ges.* 1877, 10, 807.
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photochemical elimination of  $\text{Me}_6\text{Si}_2$  from  $(\text{Mes})_2\text{Si}(\text{SiMe}_3)_2$ . Disilene **5**, which survives brief heating to 160 °C, is presumably formed by dimerization of the silylene  $(\text{Mes})_2\text{Si}$  since the latter can be matrix isolated at low temperatures. Subsequently, the photochemical route has been used<sup>9</sup> to prepare cis/trans disilene isomers,  $(\text{Mes})(\text{R})\text{Si}=\text{Si}(\text{R})(\text{Mes})$ ,  $\text{R} = t\text{-Bu}$ ,  $(\text{Me}_3\text{Si})_2\text{N}$ , and Boudjouk et al.<sup>10</sup> have discovered that **5** can be prepared from  $(\text{Mes})_2\text{SiCl}_2$  either electrochemically or sonochemically (although this claim has been recently disputed<sup>11</sup>). Immediately following the work of West et al. Masamune et al.<sup>12</sup> described the following disilene and digermene syntheses:



The above methodology has also been employed for the synthesis of less stable peralkylated disilenes,  $\text{R}_2\text{Si}=\text{SiR}_2$ ,  $\text{R} = t\text{-BuCH}_2$ ,<sup>13a</sup>  $i\text{-Pr}$ ,<sup>13b</sup> and  $\text{Et}_2\text{CH}$ .<sup>14</sup> The  $t\text{-Bu}$  analogue can also be formed as an unstable material.<sup>11</sup>

**Group 5A Compounds.** Recognizing the stoichiometries of a disilene and a diphosphene, it is clear that stabilization of the latter requires somewhat bulkier substituents. Two particularly useful groups in this regard are 2,4,6- $(t\text{-Bu})_3\text{C}_6\text{H}_2$  and  $(\text{Me}_3\text{Si})_3\text{C}$ . Thus, the first arylated diphosphene, **6**, was prepared by Yoshifuji et al.<sup>15</sup> This development was followed by the synthesis of the first alkylated diphosphene, **7**, by our group<sup>16</sup> and



Escudié and co-workers.<sup>17</sup> Both **6** and **7** were prepared by reductive coupling of the respective dichlorides. However, the <sup>31</sup>P NMR chemical shifts reported initially for **6** (-59 ppm)<sup>15</sup> and **7** (+599.6 ppm)<sup>16,17a</sup> were strikingly different. The unanticipated upfield <sup>31</sup>P chemical shift for **6** prompted the curiosity of several workers<sup>18</sup> who noted that the value for **6** was erroneous

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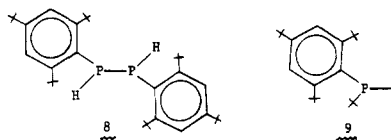
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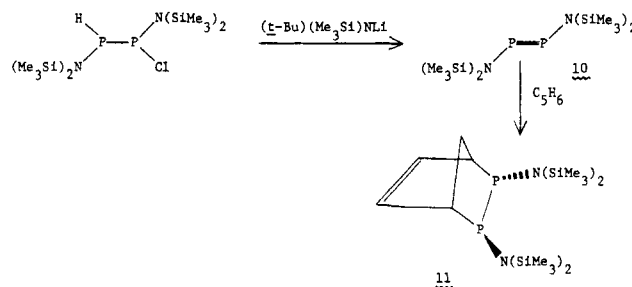
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(17) (a) Couret, C.; Escudié, J.; Satgé, J. *Tetrahedron Lett.* **1982**, 23, 4941. (b) Jaud, J.; Couret, C.; Escudié, J. *J. Organometal. Chem.* **1983**, *249*, C25.

and should, in fact, be +494 ppm. Furthermore, our reinvestigation of the reaction of  $(2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2)\text{-PCl}_2$  with Mg in THF revealed that it is not straightforward and yields **8** and **9** in addition to **6**.<sup>19</sup> Improved syntheses of **6** have now been developed.<sup>19</sup>

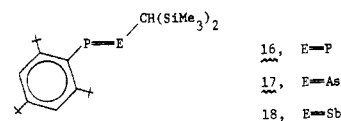


As indicated below, base-promoted dehydrochlorination represents an alternative strategy for diphosphene synthesis.<sup>20</sup>



As a consequence of the modest bulk of the  $(\text{Me}_3\text{Si})_2\text{N}$  moiety, **10** dimerizes readily at ambient temperature; accordingly, it is best stored as the thermally dissociable cyclopentadiene adduct **11**. Other amido-substituted diphosphenes have been prepared subsequently by a similar approach.<sup>21</sup>

The first unsymmetrically substituted diphosphene, 2,4,6- $t\text{-Bu}_3\text{C}_6\text{H}_2\text{P}=\text{PC}(\text{SiMe}_3)_3$  (**15**), was synthesized by reductive coupling of mixtures of  $(\text{Me}_3\text{Si})_3\text{CPCl}_2$  and  $(2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2)\text{PCl}_2$ .<sup>22</sup> The unsymmetrical diphosphene is appreciably less stable than the corresponding symmetrical compounds. Furthermore, the yields of **15** were only modest; hence a new unsymmetrical diphosphene synthesis was sought. Base-promoted dehydrochlorination of a mixture of  $(\text{Me}_3\text{Si})_3\text{CPCl}_2$  and  $(2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2)\text{PH}_2$  resulted somewhat surprisingly in **16** rather than **15**.<sup>23</sup> Pre-



sumably, **16** is formed by  $\text{Cl}^-$  attack of a  $\text{Me}_3\text{Si}$  group of **15** followed by protonation of the resulting carbanion. Three other research groups have also reported synthesis of unsymmetrical diphosphenes.<sup>21,24</sup>

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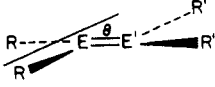
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(21) Niecke, E.; Rüger, R.; Lysek, M.; Pohl, S.; Schoeller, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 486.

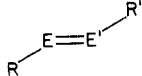
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Table I.  
Summary of Structural Data for Double-Bonded Compounds of Groups 4A and 5A

	RER bond angles, deg	REE' bond angles, deg	$\theta$ , <sup>a</sup> deg	$\phi$ , <sup>b</sup> deg	EE' bond lengths, Å	sum of double bond covalent radii, Å	EE' single bond lengths, Å	% shortening	ref
	(2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ) <sub>2</sub> Si=Si(2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ) <sub>2</sub>	115.5	113.9, 126.9	18	5	2.160	2.14	2.32 <sup>c</sup>	8
(2,6-Et <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> Si=Si(2,6-Et <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub>	117.6 (2)	117.6 (2), 124.8 (2)	0	10	2.133 (3)	2.14	2.32 <sup>c</sup>	9.2	12c
<i>trans</i> -( <i>t</i> -Bu)(2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> )Si=Si-( <i>t</i> -Bu)(2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> )	113.2 (1)	123.86 (8), 122.77 (8)	0	0	2.143	2.14	2.32 <sup>c</sup>	8.8	23b,c
(Me <sub>3</sub> Si) <sub>2</sub> CH <sub>2</sub> Ge=Ge(CH(Me <sub>3</sub> Si)) <sub>2</sub>	112.5 (3)	113.7 (3), 122.3 (2)	32	0	2.347 (2)	2.24	2.44 <sup>c</sup>	4	30
((Me <sub>3</sub> Si) <sub>2</sub> CH) <sub>2</sub> Sn=Sn(CH(SiMe <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub>	112 (av)	115 (av)	41	0	2.764 (2)	2.60	2.81 <sup>c</sup>	2	7

	REE' and R'E'E bond angles, deg	EE' bond lengths, Å	sum of double bond covalent radii, Å	EE' single bond lengths, Å	% shortening	ref
(2,4,6-( <i>t</i> -Bu) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> )P=P(2,4,6-( <i>t</i> -Bu) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> )	102.8 (1)	2.034 (2)	2.00	2.21 <sup>c</sup>	8	15
(Me <sub>3</sub> Si) <sub>3</sub> CP=PC(SiMe <sub>3</sub> ) <sub>3</sub>	108.2 (4), 108.9 (4) <sup>d</sup>	2.014 (6), 2.004 (6) <sup>d</sup>	2.00	2.21 <sup>c</sup>	9	33, 17b
(Me <sub>3</sub> Si)( <i>t</i> -Bu)NP=PN( <i>t</i> -Bu)(SiMe <sub>3</sub> )	102.2	2.034	2.00	2.21 <sup>c</sup>	8	21
(2,4,6-( <i>t</i> -Bu) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> )P=AsCH(SiMe <sub>3</sub> ) <sub>2</sub>	96.4 (2), 101.2 (2)	2.124 (2)	2.11	2.32–2.36 <sup>e</sup>	9–10	25
(2,4,6-( <i>t</i> -Bu) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> )As=AsCH(SiMe <sub>3</sub> ) <sub>2</sub>	93.6 (3), 99.9 (3)	2.224 (2)	2.22	2.43–2.46 <sup>f</sup>	9–10	26
(Me <sub>3</sub> Si) <sub>3</sub> CAs=AsC(SiMe <sub>3</sub> ) <sub>3</sub>	106.2 (2), 106.4 (2) <sup>d</sup>	2.243 (1), 2.245 (1) <sup>d</sup>	2.22	2.43–2.46 <sup>f</sup>	9–10	g

<sup>a</sup> $\theta$ , the fold angle, is the angle between the RER or R'ER' plane and the EE' axis. <sup>b</sup> $\phi$ , the twist angle, is the angle between the RER and R'ER' planes (along the EE' axis). <sup>c</sup>"Tables of Interatomic Distances and Configuration in Molecules and Ions"; Chemical Society: London; Spec. Publ.-Chem. Soc. 11 and 18, 1958 and 1965, respectively. <sup>d</sup>Two crystallographically independent molecules per unit cell. <sup>e</sup>Sheldrick, W. S. *Acta Crystallogr., Sect. B* 1975, B31, 1789. Baudler, M.; Aktalay, Y.; Heinlein, T.; Tebbe, K.-F. *Z. Naturforsch. B* 1982, B37, 299. <sup>f</sup>Rheingold, A. L.; Sullivan, P. J. *Organometallics* 1983, 2, 327. <sup>g</sup>Cowley, A. H.; Norman, N. C.; Pakulski, M. *J. Chem. Soc., Dalton Trans.*, in press.

It was recognized that the dehydrochlorination approach might make available compounds with heteronuclear double bonding. Thus, the reaction of (2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)PH<sub>2</sub> with (Me<sub>3</sub>Si)<sub>2</sub>CHAsCl<sub>2</sub> in THF in the presence of DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) afforded phospharsene 17, a stable orange crystalline solid.<sup>25</sup> An analogous reaction with (Me<sub>3</sub>Si)<sub>2</sub>CHSbCl<sub>2</sub> afforded 18, the first example of a phosphorus-antimony double bond.<sup>25</sup> However, phosphastibene 18 is less stable than 16 or 17 and decomposes in solution to diphosphene 6. Attempts to prepare a phosphabis-muthene by this route have not been successful.

The stability of 17 and the observation of 18 prompted us to attempt the synthesis of a diarsene. Our initial approach to this objective was frustrated by the fact that the reaction of 2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Li with AsCl<sub>3</sub> results in heterocycle formation rather than the desired dichloroarsine.<sup>26</sup> However, the analogous difluoroarsine (2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)AsF<sub>2</sub> is stable and can be reduced to (2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)AsH<sub>2</sub> by standard methods. In turn, the DBU-promoted reaction of the latter with (Me<sub>3</sub>Si)<sub>2</sub>CHAsCl<sub>2</sub> afforded the orange, crystalline diarsene, (2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)As=AsCH(SiMe<sub>3</sub>)<sub>2</sub> (19) in good yields. Independent of our work, French workers<sup>27</sup> have reported the synthesis of (Me<sub>3</sub>Si)<sub>3</sub>CAs=AsC(SiMe<sub>3</sub>)<sub>3</sub> and the corresponding phospharsene via *t*-BuLi-induced coupling of the respective dichlorides.

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## Structural Information

The available structural data for the double-bonded compounds of group 4A and 5A have been assembled in Table I. One obvious feature in group 4A is that the *trans*-bent conformation is favored progressively as the group is descended. This trend is apparent from increases in  $\theta$ , the fold angle. The increasing pyramidal-ity is further evident from the diminishing sums of bond angles at the heteroatom. Increased pyramidal-ity is accompanied by a relative elongation of the E=E' bond. Thus, the silicon-silicon bond length in (Mes)<sub>4</sub>Si<sub>2</sub> is ~7% shorter than that of a typical silicon-silicon single bond.<sup>28</sup> However, the percent shortening diminishes rapidly with the heavier congeners. The disilene bond lengths are close to the sum of Pauling's double-bond covalent radii,<sup>29</sup> but, as expected from the foregoing discussion, the E=E' bond lengths for [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>Ge<sub>2</sub> and [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>Sn<sub>2</sub> are considerably in excess of the respective sums of double-bond covalent radii. Interestingly, [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>Sn, [4-Me-2,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>Sn, and [2,4,6-(*t*-Bu)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O]<sub>2</sub>Sn are monomeric in the solid state.<sup>30-32</sup>

All the group 5A compounds adopt a *trans* structure, and in each case the R-E=E'-R' skeleton is planar within experimental error. Comparing the R-P-P bond angles of the diphosphenes, one notices that those of

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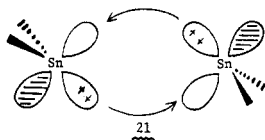
7 are  $\sim 6^\circ$  larger than the other two. This structural feature is due to the extraordinary bulk of the  $(\text{Me}_3\text{Si})_3\text{C}$  moiety. Obviously, pyramidalities has no meaning from the group 5A compounds. Nevertheless, it is clear that the  $\text{R}-\text{E}-\text{E}'$  and  $\text{R}'-\text{E}'-\text{E}$  bond angles decrease with increasing atomic number of the heteroatom. In contrast to group 4A, however, the  $\text{E}=\text{E}'$  bond length exhibits a fairly consistent shortening in relation to corresponding single bond lengths. Furthermore, there is a remarkably good agreement between all observed  $\text{E}=\text{E}'$  bond lengths and those computed by summation of the respective double-bond covalent radii.

### Are They Really Double Bonds?

The significant nonplanarity of the digermene and distanene, coupled with the fact that the Ge-Ge and Sn-Sn bond distances for these compounds are close to those of the corresponding single bonds, led Pauling to imply that these compounds do not possess double bonds.<sup>34</sup> Pauling postulated a stannylene dimer, **20a, b**, in which a donor-acceptor bond is formed by interaction of a lone pair of one stannylene with a vacant orbital of the other. Resonance between **20a** and **20b** then results in delocalization of the lone pair and an esti-



mated bond order of 1.1. Interestingly, this valence-bond description was suggested several years earlier by Lappert et al.<sup>7b</sup> In addition, these authors postulated an alternative structure, **21**, which is formed by pairwise overlap of the occupied  $\text{sp}_x\text{p}_y$  "lone pair" orbital of one stannylene unit with the vacant  $\text{p}_z$  orbital of the other.



A PMO argument can also be used to explain the structural trends observed from the group 4A compounds. The argument is similar to that used to explain the trends in pyramidal inversion barriers of  $\text{R}_3\text{E}$  compounds.<sup>35</sup> In a planar  $\text{E}_2\text{H}_4$  molecule the  $\pi(\text{b}_{1u})$  and  $\sigma^*(\text{b}_{3u})$  orbitals are orthogonal and cannot mix. However, upon trans bending of the structure, these two orbitals begin to interact and the stabilization energy (SE) which results from this interaction is

$$\text{SE} = \frac{n \langle \psi_{\text{b}_{1u}} | \text{H} | \psi_{\text{b}_{3u}} \rangle^2}{\Delta E}$$

where  $n$  is the number of electrons involved. The energy gap between the  $\text{b}_{1u}$  and  $\text{b}_{3u}$  MO's,  $\Delta E$ , decreases as group 4A is descended, thus the trans-bent geometry is progressively favored in agreement with the structural data in Table I. Furthermore, since the  $\text{b}_{3u}$  MO is a  $\sigma$ -antibonding, admixture of this MO with the HOMO

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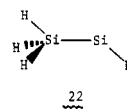
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will result in a diminished bond order between the E atoms as observed. The foregoing argument leads to the conclusion that, in general,  $\text{R}_4\text{E}_2$  molecules are expected to be trans bent. Obviously, the antisymmetry plane is lost upon bending of an  $\text{R}_4\text{E}_2$  molecule; hence in a traditional sense the  $\pi$ -bond is lost. However, it should be recalled that nonplanar organic  $\pi$ -systems are known. Furthermore, it seems more consistent to consider a compound like  $[(\text{Me}_3\text{Si})_2\text{CH}]_4\text{Sn}_2$  as a distannene rather than a bis(stannylene) even though the bond order between the tin atoms is considerably less than two.

Potential  $\pi$ -donor substituents are expected to have a profound effect on the E-E  $\pi$ -bond. Consider, for example, a planar group 4A molecule,  $(\text{R}_2\text{N})_2\text{E}=\text{E}(\text{NR}_2)_2$ . The nitrogen lone-pair orbitals can be arranged parallel or perpendicular to the molecular plane. With a perpendicular arrangement, the  $\text{N}(2\text{p})$  lone pair AO's transform as  $\text{b}_{2g}$ ,  $\text{b}_{3g}$ ,  $\text{a}_u$ , and  $\text{b}_{1u}$ ; hence a four-electron destabilizing interaction can take place between the  $\text{b}_{1u}$  combination and the HOMO which destabilizes the latter and weakens the  $\text{E}=\text{E}$  bond. In the case of Ge and Sn this is enough to prevent dimerization when the substituents are  $(\text{Me}_3\text{Si})_2\text{N}$ . However, in the case of silicon, attachment of one  $(\text{Me}_3\text{Si})_2\text{N}$  substituent does not prevent dimerization. Nevertheless the  $\pi$ -bond of  $(\text{Mes})(\text{Me}_3\text{Si})_2\text{NSiSiN}(\text{SiMe}_3)_2(\text{Mes})$  appears to be weaker than the *t*-Bu analogue as evidenced by the lower barrier for *cis*-*trans* interconversion.<sup>9</sup> Similar arguments to the foregoing presumably apply to other  $\pi$ -donor substituents like RO and RS.

### Molecular Orbital Calculations

In agreement with the above qualitative arguments and the general trends in pyramidal inversion barriers, MO calculations on the group 4A molecules  $\text{E}_2\text{H}_4$  (E = C, Si, Ge, and Sn)<sup>7c,36</sup> revealed progressive favoring of the trans-bent structure with increasing atomic number. Disilene has, however, been investigated much more extensively than the heavier molecules. Early semi-empirical and *ab initio* studies assumed or predicted a planar geometry for disilene.<sup>37</sup> However, using a 4-31G basis set, Snyder and Wasserman<sup>38</sup> concluded that the silylsilylene structure, **22**, represents the global minimum.<sup>39</sup> Structure **22** also emerged as the global min-



imum in a Hartree-Fock study by Poirier and Goddard;<sup>40</sup> however, when correlation energy contributions were included, the relative stabilities of the disilene and silylsilylene structures were reversed. A similar con-

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clusion has been reached by Krogh-Jespersen,<sup>41</sup> viz., when correlation energy corrections are included, the trans-bent structure is the global minimum. Sensitivity of the results to basis-set size has also been demonstrated.<sup>42</sup>

Ab initio MO calculations on  $P_2H_2$  indicate that the trans conformation is favored over the cis by 3–5 kcal/mol regardless of the size of the basis set.<sup>24a,43</sup> The sequencing of the first two occupied MO's (the phosphorus lone pair combination,  $n_+$ , and the P–P  $\pi$ -bond) depends on (i) the conformation and (ii) the calculational method. Electronic spectral data on substituted diphosphenes (and heavier congeners) tend to support the view that the HOMO is the phosphorus lone pair combination.

### Comments on Spectroscopic Properties

The <sup>31</sup>P NMR chemical shifts of diphosphenes, phospharsenes, and phosphastibenes fall in the range +500–670 ppm and are thus among the largest chemical shifts reported for this nucleus. When measurable, the one-bond <sup>1</sup>J<sub>PP</sub> coupling constants are also unusually large (~550–650 Hz). These trends parallel, although they are greater than, those observed in <sup>13</sup>C NMR spectroscopy. The <sup>29</sup>Si NMR chemical shifts of disilenes are also deshielded (~50–90 ppm) with respect to saturated analogues. The reason for the observed deshielding of the double-bonded compounds is presumably due to the increased importance of the paramagnetic terms,  $\sigma_P$ , on account of the existence of low-lying excited states. The enhanced <sup>1</sup>J<sub>PP</sub> values for diphosphenes are attributable to increases in the Fermi contact term resulting from changes in valence s character of the phosphorus atoms.

At this point rather few vibrational spectroscopic data are available. However,  $\nu_{PP}$  falls in the range 610–624  $cm^{-1}$ <sup>24a,b,44,45</sup> and the  $\nu_{SiSi}$  for **5** is 529  $cm^{-1}$ .<sup>8,28c</sup> As expected, these values exceed those for analogous single-bonded species. A Raman band at 300  $cm^{-1}$  has been assigned to  $\nu_{GeGe}$ .<sup>7b</sup>

**Reactivity Studies.** In some respects, disilenes behave like typical alkenes, particularly in regard to addition reactions (Scheme I). For example, **5** reacts with  $Cl_2$  (in  $C_6H_6$ )<sup>46</sup> and HCl to give the anticipated addition products **23** and **24**, respectively.<sup>47</sup> Likewise, tetrakis(2,6-dimethylphenyl)disilene reacts with  $Br_2$  to afford the corresponding 1,2-dibromosilane.<sup>12a</sup> Steric effects play an obvious role in disilene chemistry since while **5** undergoes cycloaddition with  $PhC\equiv CH$  to produce **25**, it fails to react with more hindered dienes such as 2,3-dimethyl-1,3-butadiene.<sup>47</sup> On the other hand, less bulky alkylated disilenes react with this diene to afford **26** and **27**.<sup>11,14</sup> The arylated disilenes also react with  $PhN_3$  and  $CH_2N_2$  to afford the corresponding disilaziridine<sup>28c</sup> and disilacyclopropane,<sup>48</sup> respectively.

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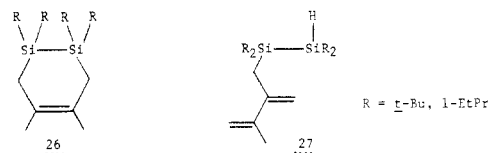
(44) Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Hirotsu, K.; Higuchi, J. *J. Chem. Soc., Chem. Commun.* **1983**, 862.

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(46) If the chlorination is done in alkane solvents, HCl addition occurs, presumably via a radical-chain process.

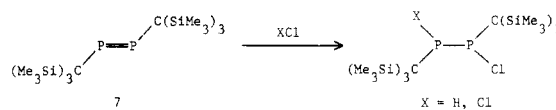
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(48) Masamune, S.; Murakami, S.; Tobita, H.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 7776.

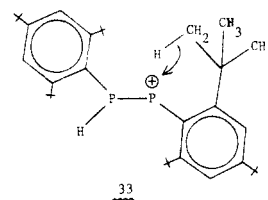


One facet of the chemistry that differentiates alkenes from their heavier congeners is oxophilicity. Thus, disilenes and digermenes react readily with alcohols and water via addition across the  $E=E$  bond (**28**). Likewise, **5** reacts readily with  $O_2$ , acetone, and benzil to afford cyclic products **29**, **30**, and **31**, respectively (Scheme I).<sup>28c,47,49</sup>

Given that diphosphenes and heavier congeners possess two lone pairs of electrons in addition to the double bond, it is anticipated that these compounds will be reactive toward electrophiles. This is indeed in the case. For example, careful treatment of **7** with HCl or  $Cl_2$  results in addition across the phosphorus-phosphorus double bond in a manner reminiscent of an alkene.<sup>33</sup> In general, however, the reactivity of **7** is not



high due to the steric demands of the  $(Me_3Si)_3C$  groups. The arylated diphosphene **6** is much less sterically encumbered and for this reason has been used more extensively for reactivity studies. Protonation of **6** with  $HBF_4 \cdot OEt_2$  results eventually in complete cleavage of the P=P bond (as does halogenation<sup>50</sup>). However, at  $-78^\circ C$  it is possible to detect phosphonium salt **32** by NMR (Scheme II).<sup>33a</sup> It is believed that initial protonation of **7** forms **33**, which is an electron-deficient phosphonium ion. Like other highly electrophilic



species (vide infra), this cationic center inserts into a C–H bond of an *o-t*-Bu group by an intramolecular oxidative addition. Reaction of **6** with  $Ag^+$  or  $Et_3PAu^+$ , which are isolobal with  $H^+$ , affords the novel cations **34–36**.<sup>51</sup>

Oxidation of **6** with *m*-chloroperbenzoic acid is believed to yield diphosphosene monoxide **37** as the initial product.<sup>52</sup> On the other hand, photolytic oxidation of **6** results in the bicyclic compounds **38** and **39**.<sup>53</sup> In turn, these products may arise from intramolecular C–H insertion reactions of **40** and **41**, respectively. Some support for this interpretation is provided by the fact that flash vacuum pyrolysis (FVP) of **42** results in **39**.<sup>53</sup>

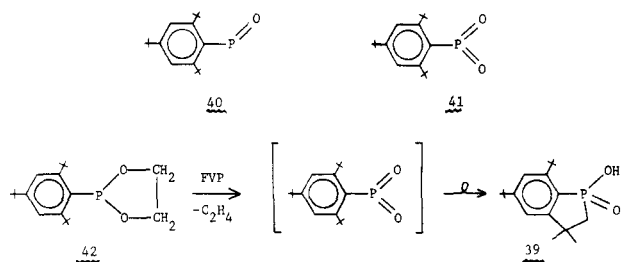
(49) Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 822.

(50) Yoshifuji, M.; Shima, I.; Shibayama, K.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 411.

(51) Cowley, A. H.; Norman, N. C.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1054.

(52) Yoshifuji, M.; Ando, K.; Toyota, K.; Shima, I.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1983**, 419. Compound **37** can be prepared by an independent route.

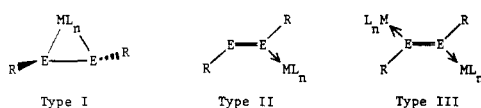
(53) Cadogan, J. I. G.; Cowley, A. H.; Gosney, I.; Pakulski, M.; Yaslek, S. *J. Chem. Soc., Chem. Commun.* **1983**, 1408.



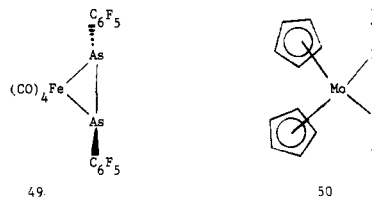
As expected, treatment of **6** with 1 equiv of sulfur results in **43**, the thio analogue of **37**.<sup>44</sup> Interestingly, thermolysis or photolysis converts **43** to the corresponding episulfide **44**. Other episulfides have been formed by thiation of other diphosphenes,<sup>20,33b</sup> a phospharsene, and a diarsene.<sup>27</sup> Excess sulfur, however, leads to complete P=P cleavage and formation of the thio analogue of **39**.<sup>54</sup> Further evidence of the reactivity of diphosphenes toward electrophiles is provided by the fact that **6** reacts with *t*-BuO· and *t*-BuS· radicals to form novel phosphinyl radicals **45** and **46**.<sup>55</sup> So far, the only example of the reactivity of a diphosphene toward C=C or C≡C bonds is provided by the reaction of **10** with cyclopentadiene to form **11**.<sup>20</sup>

Cyclic voltammetric studies in our laboratory and elsewhere<sup>18c</sup> revealed that diphosphenes possess a relatively accessible LUMO [ $E_{1/2} = -1.74$  V (**6**),  $-1.70$  V (**7**)]. This observation, along with MO calculations on the model diphosphene, *trans*-HPPH,<sup>43</sup> led us to surmise that the P=P bond should be susceptible to nucleophilic attack. Indeed, **6** reacts readily with an equimolar quantity of MeLi at  $-78$  °C to form the deep red anion, **47**.<sup>56a</sup> Quenching of the latter with MeOH produces diphosphine **48**, which can be regarded as the product of adding CH<sub>4</sub> across the phosphorus-phosphorus double bond. It has also been discovered that **6** is reactive toward other nucleophiles such as *n*-Bu<sup>-</sup> and H<sup>-</sup> resulting in Ar(H)P-P(Ar)(*n*-Bu) and Ar(H)P-P(H)(Ar), respectively.<sup>56</sup> When, however, the nucleophile becomes extremely large, as in the case of naphthalenide,<sup>55</sup> reaction with **6** generates the corresponding anion radical, [ArPPAr]<sup>-</sup> via electron transfer. In turn, this observation suggests that nucleophilic attack of **6** may proceed by initial electron transfer.

**Coordination Chemistry.** Thus far, there have been no reports of group 4A compounds functioning as intact ligands. Diphosphenes and their heavier congeners are expected to exhibit the following modes of coordination:

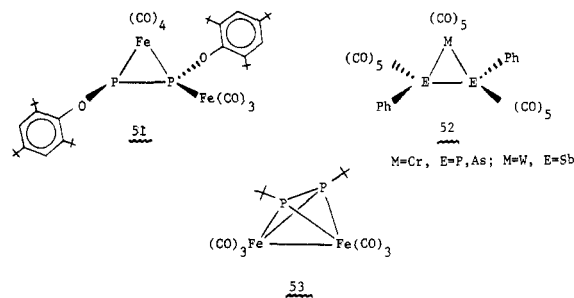


All three types of coordination behavior, combinations thereof, and the incorporation of diphosphenes into metal clusters have now been achieved. Type I coordination was, in fact, the first to be recognized. The diarsene complex **49**, for example, resulted from cleavage of the cyclotetraarsene (C<sub>6</sub>F<sub>5</sub>As)<sub>4</sub> with Fe(CO)<sub>5</sub>.<sup>57</sup> This was followed by the synthesis of **50** from reaction of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>MoH<sub>2</sub> with elemental phosphorus,



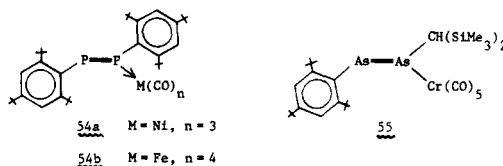
a development of special interest since it is a complex of the parent diphosphene.<sup>58</sup> Other approaches to the preparation of type I complexes include the decomposition of labile bis(phosphido)nickel complexes<sup>59</sup> and the reaction of Pt or Pd dichlorides with the [PhPPPPh]<sup>2-</sup> anion.<sup>60</sup> In each of the type I complexes, the ligand adopts a *trans* conformation, and as in the case of η<sup>2</sup>-alkenes, the E-E bond lengths fall between typical single- and double-bond values.

Provided the steric demands of the ligands are not excessive, it is possible to achieve concomitant coordination of additional organometallic moieties. Compounds **51**<sup>61</sup> and **52**,<sup>62</sup> which result from reaction of the appropriate dihalides with organometallic dianions, feature four- and six-electron donation, respectively, on the part of the ligands. Six-electron donation has also



been realized in the novel cluster derivative **53**.<sup>63</sup> Note that **53** can be regarded as a complex of (*t*-BuP-PtBu)<sup>2+</sup>[Fe<sub>2</sub>(CO)<sub>6</sub>]<sup>2-</sup>. A higher degree of clusterification has been observed recently by Power et al.<sup>64</sup> by treatment of (Me<sub>3</sub>Si)<sub>2</sub>CHPCl<sub>2</sub> with Na<sub>2</sub>Ni(CO)<sub>12</sub>.

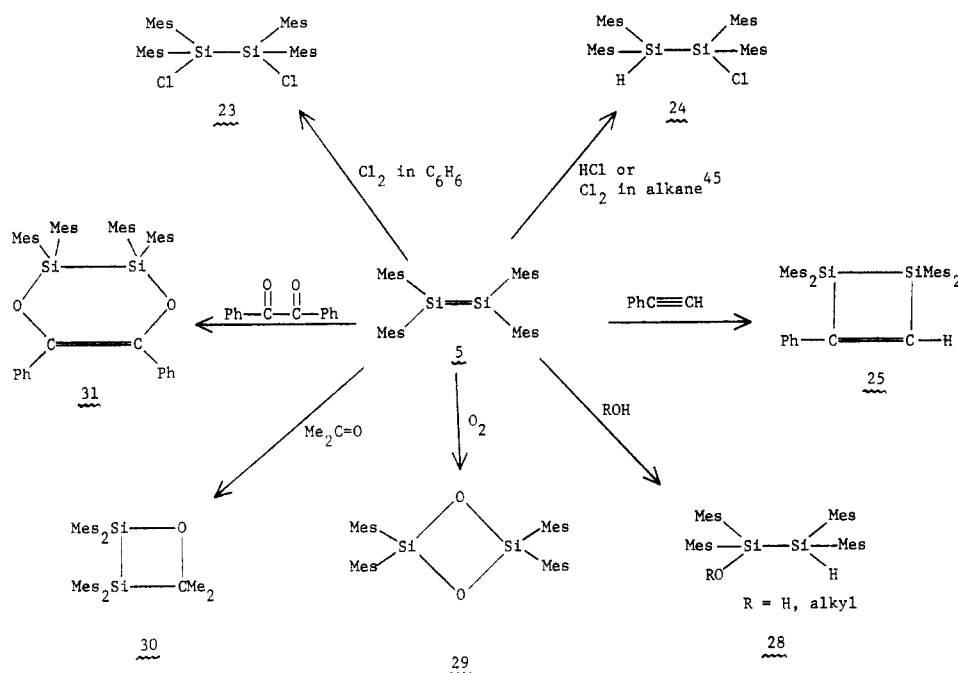
Having ligands with preformed double bonds at our disposal, we realized that new modes of coordination might be attainable. As expected, the results are highly dependent on steric requirements. Thus, while **7** fails to react with Ni(CO)<sub>4</sub>, the less bulky aryl analogue **6** reacts readily with this carbonyl and Fe<sub>2</sub>(CO)<sub>9</sub> to afford **54a,b**, the first examples of type II complexes.<sup>65</sup> Vir-



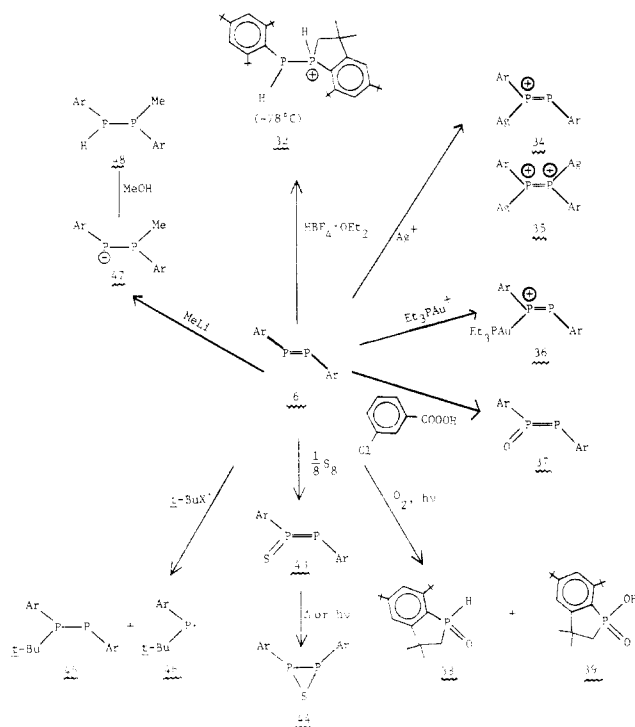
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Scheme I



Scheme II



tually simultaneously, Power et al.<sup>66</sup> reported the synthesis of  $(\text{Me}_3\text{Si})_2\text{CH}$ - or  $(\text{Me}_3\text{Si})_2\text{N}$ -substituted  $\text{Cr}(\text{CO})_5$  complexes with type II structures (55) from the reaction of the appropriate phosphorus dichlorides with  $[\text{Cr}(\text{CO})_5]^{2-}$ . Although 6 fails to react with  $\text{THFCr}(\text{CO})_5$ , the less sterically encumbered diarsene 17 does react with this reagent to produce 55.<sup>67</sup> Yoshifuji and Inamoto<sup>68</sup> have found subsequently that 6 undergoes aryl

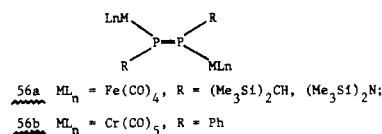
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ring attack when treated with  $\text{Cr}(\text{CO})_6$  under forcing conditions.

Finally, these examples of type III complexes, 56, have been reported. Complexes 56a<sup>69</sup> were prepared via the reaction of the appropriate phosphorus dichloride with  $[\text{Fe}(\text{CO})_4]^{2-}$  and 56b<sup>62c</sup> was produced by thermolysis of 52 ( $\text{M} = \text{Cr}$ ,  $\text{E} = \text{P}$ ). It is clear from



X-ray crystallographic studies that in type II or type III complexes, donation of the diphosphene or diarsene lone pair(s) leaves the  $\text{E}=\text{E}$  distance essentially unchanged.

## Conclusions and Outlook

Double-bonded compounds of the heavier main-group elements are less stable thermodynamically than the corresponding  $\sigma$ -bonded oligomers. However, the use of sterically demanding substituents has permitted the recent isolation of several double-bonded compounds involving group 4A and 5A elements. Interestingly, despite the requisite steric blockades, compounds such as diphosphenes or disilenes exhibit a versatile reaction chemistry. The group 5A compounds have also proved to be useful ligands. Many new multiply bonded main-group compounds await discovery. Another area of great promise is the synthesis of compounds featuring multiple bonding between main-group and transition elements.

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