Adjacent planes are also mutually perpendicular in the alternating chain compound $[Cu(3,6\text{-dithiaoctane})Cl_2]_\infty$, and although the exchange coupling constants were negative as expected, the absolute magnitudes of the coupling constants were smaller than expected.[21] That observation, coupled with the results of the present work, suggests that the relative orientation of the Cu_2X_2 planes in chain compounds is important in determining the sign and magnitude of the exchange coupling constant. It appears that ferromagnetic contributions predominate when adjacent Cu_2X_2 planes are mutually perpendicular or nearly perpendicular. Additional data on other compounds with this structural feature must be collected so that this effect can be understood.

Although the out-of-plane Cu···Cl interatomic separation is relatively long, it is the shortest bond distance in such bis(μ-chloro)-bridged copper(II) chain compounds.[18] The longest comparable copper–chloride separation in an exchange-coupled chain is 3.21 Å in $[Cu(4\text{-Etpy})_2Cl_2]_\infty$,[22] while the longest such distance in a dimeric chloride-bridged molecule is 3.37 Å in $[Cu(2\text{-Mepy})_2Cl_2]_2$.[23] It is clear that exchange interactions in these compounds can be transmitted through long interatomic separations.

It has been pointed out that a universal ϕ/R_0 correlation for a series of chemically and structurally related complexes is unexpected and that the magnetic and structural correlation should involve a family of J vs. ϕ/R_0 curves.[18] Such a family of curves would lead to a surface as described by Willett and co-workers.[24]

Acknowledgment. This research was supported by the National Science Foundation through Grant No. CHE 83 08129 (W.E.H.) and by Stiftung Volkswagenwerk (FRG) through its Partnership Program AZ: I/38 154 (M.M.-B.).

Registry No. Cu(DPG)Cl_2, 90791-12-1.

Supplementary Material Available: Tables of temperature factors and calculated and observed structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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(23) (a) Duckworth, V. F.; Stephenson, N. C. *Acta Crystallogr., Sect. B* **1969**, *B25*, 1795. (b) Marsh, W. E.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1982**, *21*, 2679–2684.

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Contribution from the Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, and University of Alabama, University, Alabama 35486

Synthesis and Structures of Compounds Containing Double Bonds between the Heavier Group 5A Elements: Diphosphenes, Diarsenes, Phosphaarsenes, and Phosphastibenes

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and WILLIAM E. HUNTER‡

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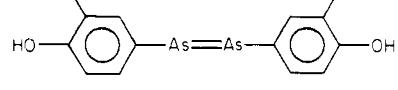
The syntheses of the symmetrical diphosphene $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**2**), the unsymmetrical diphosphenes $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]P{=}PC(SiMe_3)_3$ (**5**) and $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]P{=}PCH(SiMe_3)_2$ (**7**), the phosphaarsene $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]P{=}AsCH(SiMe_3)_2$ (**12**), the phosphastibene $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]P{=}SbCH(SiMe_3)_2$ (**14**), and the diarsene $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]As{=}AsCH(SiMe_3)_2$ (**18**) are described. X-ray diffraction studies have been performed on **2**, **12**, and **18**. Diphosphene **2** crystallizes in space group $P\bar{1}$ (No. 2) with a = 15.629 (7) Å, b = 9.155 (5) Å, c = 12.486 (6) Å, α = 91.58 (4)°, β = 111.42 (5)°, and γ = 90.02 (4)°. Phosphaarsene **12** crystallizes in space group $P\bar{1}$ (No. 2) with a = 9.991 (4) Å, b = 10.452 (9) Å, c = 15.140 (15) Å, α = 89.72 (7)°, β = 85.03 (5)°, and γ = 77.72 (5)°. Diarsene **18** crystallizes in space group $P\bar{1}$ (No. 2) with a = 9.955 (9) Å, b = 10.393 (7) Å, c = 15.159 (5) Å, α = 89.56 (4)°, β = 85.39 (6)°, and γ = 78.31 (9)°. The nature of the bonding in these and related double-bonded compounds is discussed with use of the available molecular structural and electronic spectral information. An extensive compilation of ^{31}P NMR spectroscopic data is presented and discussed.

Introduction

The history of the present subject dates back to 1877, when Köhler and Michaelis[1] treated $C_6H_5PH_2$ with $C_6H_5PCl_2$ and isolated a compound of empirical composition C_6H_5P, which they dubbed "phosphobenzene" and formulated as $C_6H_5P{=}PC_6H_5$ by analogy with azobenzene. This field lay essentially dormant until 1957, when, in a pioneering study, Mahler and Burg[2] reported the preparation of the cyclopolyphosphines $(CF_3P)_4$ and $(CF_3P)_5$ and suggested an oligomeric structure for "phosphobenzene". This postulate was confirmed almost simultaneously by Kuchen and Buchwald[3] on the basis of molecular weight measurements. Subsequent X-ray diffraction studies have revealed that "phosphobenzene" adopts pentameric or hexameric structures in the solid state.[4] A somewhat similar situation arose with arsenicals. Thus, Erlich,[5] the originator of the chemotherapeutic drug "Salvarsan", formulated his compound as



but once again, X-ray crystallographic work indicated that, e.g., compounds of empirical composition C_6H_5As are, in fact, oligomeric.[6]

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† University of Texas at Austin.

‡ University of Alabama.

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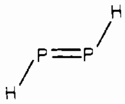
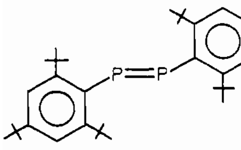
From these beginnings, the consensus developed that compounds featuring double bonds between the heavier main-group elements would not be isolable. Such a view is sometimes referred to as "the classical double-bond rule", according to which elements having a principal quantum number greater than 2 should not be able to form a p_π–p_π bond with themselves or with other elements.[7]

A compound of composition P_2H_2, which is presumably the parent diphosphene of structure

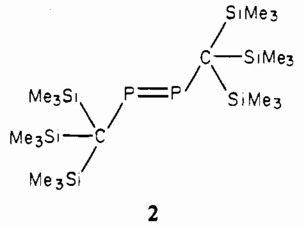


was first detected[8] by mass spectrometry as a product of thermolysis of P_2H_4. Diphosphene is unstable under ambient conditions and undergoes decomposition to PH_3 and P_4. Subsequent studies revealed that diphosphene is formed from P_2H_4 at room temperature[9] and by photolysis of P_2H_4.[10]

Let us now turn to the isolation of stable compounds featuring double bonding between the group 5A elements. One way of accomplishing such an objective is by incorporation of otherwise labile molecules into the coordination sphere of a transition metal. This approach has been successful, and a number of complexes featuring RPPR (R = H,[11] Me_3Si,[12] C_6H_5,[13] C_6F_5[14]) RAsAsR (R = C_6H_5,[15] C_6F_5[16]), and PhSbSbPh[17] have been isolated. Obviously, though, these compounds do not involve unsupported multiple bonds between the group 5A atoms. The first examples of unsupported double bonds stemmed from the realization that if the steric bulk of ligands became sufficiently large, oligomerization would be thwarted. Accordingly, the first stable aryl- and alkyl-substituted diphosphenes, **1**[18] and **2**,[19] were prepared by using the

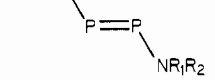


1



2

very bulky 2,4,6-tri-*tert*-butylphenyl and tris(trimethylsilyl)methyl groups, respectively. Intense activity is now apparent in the stabilized diphosphene field, some of it prompted by an error in the initially reported ^{31}P NMR chemical shift of **1**.[20] Independent syntheses of **1**[21] and **2**[22] have appeared, and Niecke and co-workers[23,24] have reported the first heteroatom-substituted diphosphenes, **3**. The first examples of unsymmetrical diphosphenes have been reported,[24-28] and preliminary studies of the reactivities[22b,23,29,30] and ligative behavior[31] of diphosphenes have started to appear. Very recent work has established that it is possible to isolate appropriately sterically protected compounds with P=As[32] and As=As[33,34] bonds. A significantly less stable phosphastibene, $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]P{=}SbCH(SiMe_3)_2$, has been identified spectroscopically.[32] In this, the first full paper on the subject, we discuss (i) the synthetic approaches to P=P, P=As, and As=As bonds, (ii) the structural chemistry of these compounds, (iii) the nature of the bonding as deduced from electronic spectroscopy, and (iv) ^{31}P NMR spectroscopic data.



3a, $R_1 = R_2 = Me_3Si$
b, $R_1 = Me_3Si$, $R_2 = t$-Bu
c, $R_1 = R_2 = t\text{-BuMe}_2Si$

Results and Discussion

(i) Synthesis of Diphosphenes, Phosphaarsenes, Phosphastibenes, and Diarsenes. The synthesis of **1** by Yoshifuji et al.[18] was achieved by magnesium coupling of the precursor

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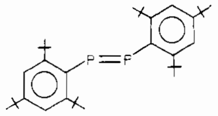
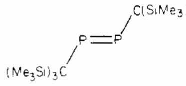
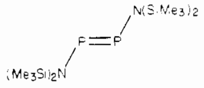
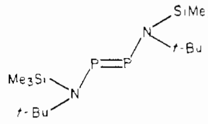
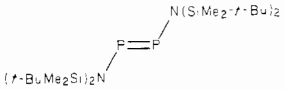
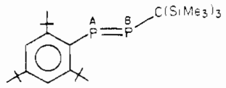
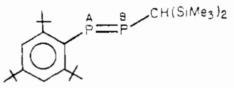
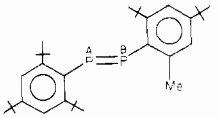
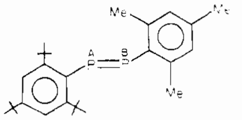
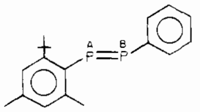
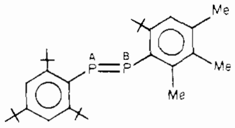
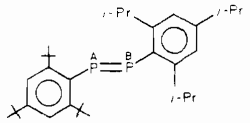
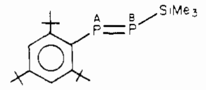
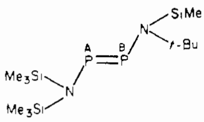
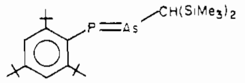
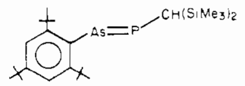
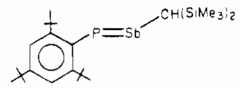
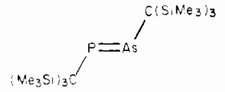
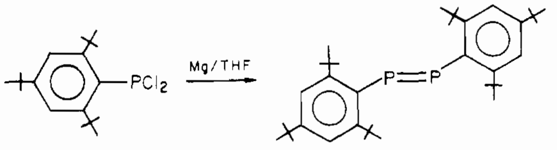
Table I. ^{31}P NMR Data for Diphosphenes, Phosphaarsenes, and Phosphastibenes

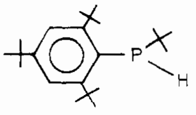
compd	δ_P	$^1J_{P_AP_B}$, Hz	ref
	494 493.6 493 492.4		19 21b 21c 20
	599.6 598.6		19 22
	572		23
	499		24
	561		24
	530.0 (P_A) 533.1 (P_B)	619.7	25
	493.0 (P_A) 513.0 (P_B)	577.5	26
	480.1 (P_A) 517.0 (P_B)	583.5	27
	467.6 (P_A) 540.4 (P_B)	573.7	27
	463 (P_A) 541 (P_B)	571	28
	455.5 (P_A) 525.5 (P_B)	548.7	27
	470 (P_A) 535 (P_B)	572	28
	463 (P_A) 541 (P_B)	571	28
	486.8 (P_A) 628.2 (P_B)	575	28[a]
	544 (P_A) 507 (P_B)	670	24
	575		32
	533		33
	620		32
	668		37

[a] Identity of compound not certain.

dichlorophosphine, and its stability is ascribable to the steric blockade afforded by the 2,4,6-$(t\text{-Bu})_3C_6H_2$ groups. We have also synthesized **1** for reactivity studies[29] but have found a different synthetic route to be preferable (see Experimental Section). In our hands, the synthesis of Yoshifuji et al. using magnesium also produces the diphosphine [2,4,6-$(t\text{-Bu})_3C_6H_2PH]_2$ and the secondary phosphine **4**. On the other hand, we find the sodium naphthalenide reduction of [2,4,6-$(t\text{-Bu})_3C_6H_2]PCl_2$ to be a convenient source of pure **1**.

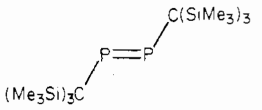


1



4

Our own work in this area focused initially on the tris(trimethylsilyl)methyl group, $(Me_3Si)_3C$, as a potential stabilizing ligand for diphosphenes. Reduction of the dichlorophosphine $(Me_3Si)_3CPCl_2$[35] with sodium naphthalenide in THF at −78 °C does indeed lead to the desired diphosphene, **2**, in good yield.[19] Compound **2** was characterized initially by high-resolution mass spectrometry (HRMS) and ^{31}P NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **2** comprises a singlet at $\delta = +599.6$. This degree of deshielding is characteristic of diphosphenes as evidenced by this and other work, details of which are collected in Table I. In order to establish more fully the nature of **2**, an X-ray crystal structure determination was carried out. Structural details will be presented in the following section. An alternative synthesis of **2** was achieved by the reaction of $(Me_3Si)_3CPCl_2$ with $(Me_3Si)_3CLi$ in a 1:4 molar ratio in THF/Et_2O solution. Couret, Escudié, and Satgé[22] have reported an independent synthesis of **2** using t-BuLi as the reducing agent.



2

In an effort to extend the foregoing synthetic methodology, a crossover experiment was attempted. When treated with sodium naphthalenide, equimolar quantities of [2,4,6-$(t\text{-Bu})_3C_6H_2]PCl_2$ and $(Me_3Si)_3CPCl_2$ in THF solution produce predominantly **1** and **2** but also afforded a 20% yield of the first unsymmetrical diphosphene, **5**.[25]

Compound **5** was characterized by HRMS and ^{31}P NMR spectroscopy. This diphosphene is of particular interest since the two phosphorus atoms are chemically inequivalent and thus

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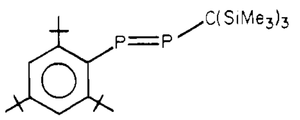
[35] Issleib, K.; Schmidt, H.; Wirkner, C. *Z. Chem.* **1980**, *20*, 153.

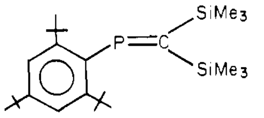


5

permitted measurement of a P–P coupling constant for the phosphorus–phosphorus double bond. The 81.03-MHz $^{31}P\{^1H\}$ NMR spectrum of **5** consists of an AB system with δ_{P_A} = +530.0, δ_{P_B} = +533.1, and $^1J_{PP}$ = 619.7 Hz. For single-bonded trivalent phosphorus compounds, $^1J_{PP}$ falls typically in the range 200–300 Hz.[36] The significantly larger $^1J_{PP}$ value for **5** is attributed to double bonding between the phosphorus atoms. While the average chemical shift of **5** falls between those of **1** and **2**, the chemical shift difference between P_A and P_B is only 3 ppm.

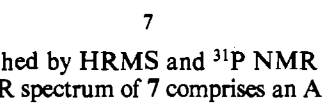
Unlike the symmetrical diphosphenes **1** and **2**, which exhibit "deceptively simple" triplet $^{13}C\{^1H\}$ patterns for the ortho $2,4,6\text{-}(t\text{-Bu})_3C_6H_2$ and $(Me_3Si)_3C$ carbons,[18,19] the corresponding resonances for **5** comprise doublets of doublets (see Experimental Section). The unsymmetrical diphosphene **5** is not as stable as its symmetrical counterparts **1** and **2** and undergoes decomposition in ~2 days at room temperature to afford the primary phosphine $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]PH_2$ as the major product. The mechanism of this decomposition has not been established.

Since **2** can be prepared from $(Me_3Si)_3CPCl_2$ and $(Me_3Si)_3CLi$, an analogous crossover reaction was attempted by treating an equimolar mixture of $(Me_3Si)_3CPCl_2$ and $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]PCl_2$ with $(Me_3Si)_3CLi$ in THF. However, no **5** could be detected and the major product was, in fact, the new phosphaalkene **6**.[25] Details of the synthesis and structure of **6** will be reported elsewhere.



6

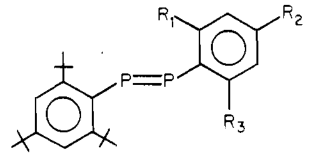
The diphosphenes discussed thus far have all been prepared by reduction of the corresponding dichlorophosphines with organolithium, sodium, or magnesium reagents. A new approach to diphosphenes was therefore sought. The strategy adopted was to treat the appropriate $RPCl_2$ and RPH_2 compounds in equimolar quantities with an organic base in order to achieve a double dehydrochlorination. (In passing we note that this dehydrochlorination approach was used initially by Köhler and Michaelis[1] to prepare "phosphobenzene"!) DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) was found to be the most successful base in this context. The first reaction to be attempted featured $(Me_3Si)_3CPCl_2$ and $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]PH_2$. Treatment of these two phosphines with a 5% excess of DBU in THF, followed by purification using column chromatography (silica gel/*n*-hexane), afforded not **5** but a 78% yield of the new unsymmetrical diphosphene **7**.[26] The constitution



7

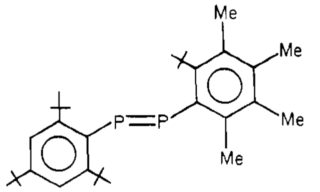
of **7** was established by HRMS and ^{31}P NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum of **7** comprises an AB system with δ_{P_A} = 513.0, δ_{P_B} = 493.0, and $^1J_{PP}$ = 577.5 Hz. The corresponding proton-coupled ^{31}P spectrum consists of the AB portion of an ABX spin system (with J_{AX} = 17 Hz, J_{BX} = −0.5 Hz) owing to coupling with the α proton of the $(Me_3Si)_2CH$ group. It is presumed, though not demonstrated, that **5** is the initial product of this reaction. If so, **5** could be converted into **7** via Cl^- attack on the $(Me_3Si)_3C$ group followed by elimination of Me_3SiCl and protonation of the resulting carbanion. The unsymmetrical diphosphene **7** is more readily prepared by reaction of $(Me_3Si)_2CHPCl_2$ and $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]PH_2$ with DBU in THF. The ^{31}P NMR spectra of the products of both reactions ($(Me_3Si)_3CPCl_2$ or $(Me_3Si)_2CHPCl_2$) are identical.

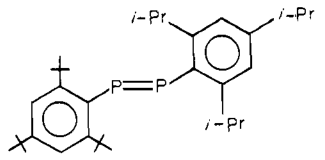
Yoshifuji et al.[27] have also reported a similar synthetic route, which provides access to unsymmetrically substituted aryldiphosphenes (**8**). Other examples of unsymmetrical di-



8a, $R_1 = R_2 = t\text{-Bu}$, R_3 = Me
b, $R_1 = R_2 = R_3$ = Me
c, $R_1 = R_2 = R_3$ = H

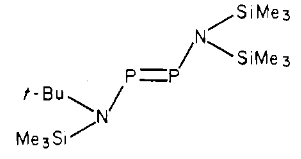
phosphenes have been reported more recently by two groups. Bickelhaupt et al.[28] prepared **8b**, **9**, and **10** via magnesium





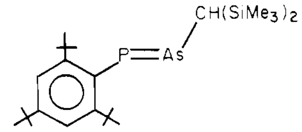
9 10

coupling of the respective dichlorides (and in the case of **10** by a Me_3SiCl elimination method also). Niecke et al.[24] discovered that treatment of a mixture of the lithium amides $(Me_3Si)_2NLi$ and $(t\text{-Bu})(Me_3Si)NLi$ with PCl_3, $LiAlH_4$, and Et_3N produced **11**.



11

Having extended the number of synthetic routes to diphosphenes by means of the DBU reaction, we attempted the synthesis of a phosphaarsene. Treatment of $(Me_3Si)_2CHAsCl_2$ and $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]PH_2$ with DBU in THF afforded a yield of orange crystalline **12**.[32] The $^{31}P\{^1H\}$ NMR spectrum



12

of **12** consists of a singlet at δ = 575.0 analogous to the shifts observed in diphosphenes while the proton-coupled ^{31}P spectrum shows a doublet ($^3J_{PH}$ = 8.9 Hz) due to coupling with the α proton of the $(Me_3Si)_2CH$ group. The structure of the phosphaarsene **12** was confirmed by an X-ray crystallographic study described in the next section.

The success of this synthetic route, which produced the first structurally characterized phosphaarsene,[37] prompted us to

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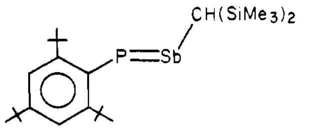
[36] Harris, R. K.; Norval, E. M.; Fild, M. *J. Chem. Soc., Dalton Trans.* **1979**, 826.

extend the approach to the antimony analogue. The starting compound for this reaction, $(Me_3Si)_2CHSbCl_2$ (**13**) was unknown prior to this study. It is, however, easily prepared from $SbCl_3$ and $(Me_3Si)_2CHMgCl$ and is described in the Experimental Section.[38]

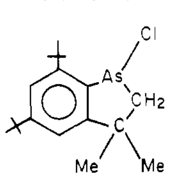
Treatment of **13** with $[2,4,6\text{-}(t\text{-}Bu)_3C_6H_2]PH_2$ and DBU afforded the first phosphastibene, **14**, which was characterized by HRMS and ^{31}P NMR spectroscopy.[32] The ^{31}P NMR spectrum of **14** showed an extremely deshielded signal at $\delta = 620.0$, one of the lowest field ^{31}P chemical shifts recorded (Table I) for a diamagnetic phosphorus compound.[39]



14

While the phosphaarsene **12** is stable in solution, the corresponding phosphastibene, **14**, is not. Solutions of orange crystalline **14** decompose slowly in solution to yield the symmetrical diphosphene **1**. The reaction can be followed by ^{31}P NMR spectroscopy and suggests that **14** is a source of free phosphinidine (RP), which, in the absence of a capturing group, dimerizes to give **1**. Attempts to prepare P=Bi compounds by this route have been unsuccessful thus far, presumably because such compounds are thermally unstable.

The stability of the phosphaarsene **12** and observation of the phosphastibene **14** prompted us to investigate the synthesis of a diarsene (RAs=AsR). Our initial strategy involving reductive coupling of $[2,4,6\text{-}(t\text{-}Bu)_3C_6H_2]AsCl_2$ was unsuccessful.[33] The reaction of $2,4,6\text{-}(t\text{-}Bu)_3C_6H_2Li$ with 1 equiv of $AsCl_3$ in THF at −78 °C afforded the heterocycle **15** rather than $[2,4,6\text{-}(t\text{-}Bu)_3C_6H_2]AsCl_2$ due to attack by the As on an *o*-*t*-Bu group.[40] Although the corresponding difluoride $[2,4,6\text{-}(t\text{-}Bu)_3C_6H_2]AsF_2$ (**16**) can be prepared by reaction of $2,4,6\text{-}(t\text{-}Bu)_3C_6H_2Li$ with AsF_3, this compound fails to produce a diarsene upon treatment with sodium naphthalenide. However, **16** can be reduced with $LiAlH_4$ to the primary arsine $[2,4,6\text{-}(t\text{-}Bu)_3C_6H_2]AsH_2$ (**17**). Treatment of **17** and $(Me_3Si)_2CHAsCl_2$ with DBU then affords the orange crystalline diarsene **18** in good yield.[33] The diarsene was characterized initially by HRMS. The above structure assignment was confirmed by an X-ray diffraction study, details of which are presented in the following section.



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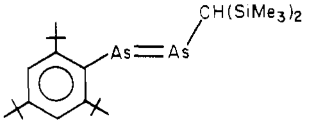

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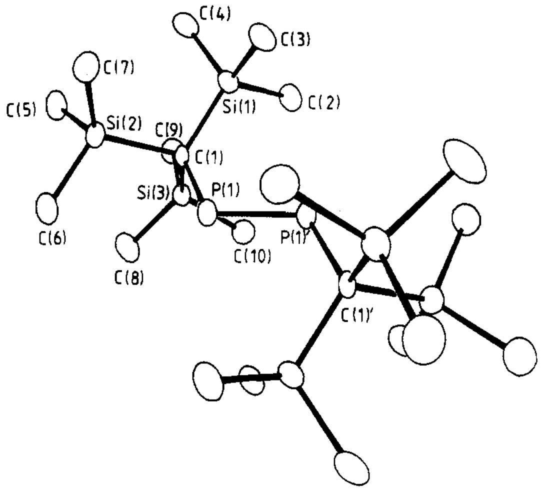


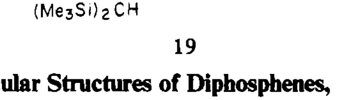
Figure 1. Molecular structure of $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**2**) showing 50% probability thermal ellipsoids.

Table II. Atomic Coordinates for $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**2**)[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*
P(1)A	0.0687 (2)	0.4880 (3)	0.5339 (3)
Si(1)A	0.0386 (2)	0.5708 (4)	0.7674 (3)
Si(2)A	0.2314 (2)	0.5100 (4)	0.7441 (3)
Si(3)A	0.0871 (2)	0.2503 (3)	0.7074 (3)
C(1)A	0.1018 (6)	0.453 (1)	0.6890 (8)
C(2)A	−0.0760 (7)	0.488 (1)	0.753 (1)
C(3)A	0.0152 (8)	0.761 (1)	0.714 (1)
C(4)A	0.1050 (8)	0.593 (1)	0.924 (1)
C(5)A	0.2990 (8)	0.437 (1)	0.888 (1)
C(6)A	0.2901 (7)	0.445 (1)	0.645 (1)
C(7)A	0.2444 (8)	0.712 (1)	0.752 (1)
C(8)A	0.1723 (8)	0.137 (1)	0.669 (1)
C(9)A	0.1006 (8)	0.205 (1)	0.856 (1)
C(10)A	−0.0275 (7)	0.176 (1)	0.613 (1)
P(1)B	0.5077 (2)	−0.0227 (3)	0.4251 (3)
Si(1)B	0.4149 (3)	−0.0845 (5)	0.1797 (3)
Si(2)B	0.2912 (2)	−0.0533 (5)	0.3291 (3)
Si(3)B	0.3920 (3)	0.2230 (4)	0.2838 (3)
C(1)B	0.3983 (6)	0.019 (1)	0.3043 (8)
C(2)B	0.5335 (8)	−0.078 (2)	0.180 (1)
C(3)B	0.392 (1)	−0.291 (1)	0.190 (1)
C(4)B	0.3374 (8)	−0.026 (1)	0.035 (1)
C(5)B	0.2524 (8)	0.086 (2)	0.418 (1)
C(6)B	0.1919 (7)	−0.080 (1)	0.190 (1)
C(7)B	0.3069 (8)	−0.222 (1)	0.409 (1)
C(8)B	0.4820 (9)	0.278 (2)	0.218 (1)
C(9)B	0.4178 (9)	0.339 (1)	0.413 (1)
C(10)B	0.2788 (8)	0.280 (1)	0.178 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Finally, the primary arsine **17** proved useful for the synthesis of a second phosphaarsene. Thus, treatment of an equimolar quantity of **17** and $(Me_3Si)_2CHPCl_2$ with DBU afforded the phosphaarsene **19**, which was characterized by HRMS and ^{31}P NMR spectroscopy ($\delta_P = 533$).



19

(ii) Molecular Structures of Diphosphenes, Phosphaarsenes, and Diarsenes. Prior to the present work, only one diphosphene, **1**, had been structurally characterized by X-ray diffraction.[18] Due to the novel nature of diphosphenes, an

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(37) For an independent synthesis of a phosphaarsene, see: Escudié, J.; Couret, C.; Ranaivonjatovo, H.; Wolf, J.-G. *Tetrahedron Lett.* **1983**, *24*, 3625.

(38) While the present work was in progress, a publication appeared describing the synthesis of $(Me_3Si)_2CHSbCl_2$ by a similar route: Breunig, H. J.; Kanig, W.; Soltani-Neshan, A. *Polyhedron* **1983**, *2*, 291.

(39) The largest ^{31}P chemical shift of which we are aware is $\delta_P = +1362$ in the phosphinidene complex $t\text{-}BuP[Cr(CO)_5]_2$: Huttner, G.; Borm, J.; Zsolnai, L. *J. Organomet. Chem.* **1984**, *263*, C33.

(40) For ring closures of $2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$–phoshorus compounds, see: (a) Baceiredo, A.; Bertrand, G.; Mazerolles, P.; Majoral, J.-P. *J. Chem. Soc., Chem. Commun.* **1981**, 1197. (b) Yoshifuji, M.; Shima, I.; Ando, K.; Inamoto, N. *Tetrahedron Lett.* **1983**, *24*, 933.

Table III. Bond Lengths (Å) for $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**2**)[a]

	dist			dist	
atoms	molecule A	molecule B	atoms	molecule A	molecule B
P(1)-P(1)′	2.014 (6)	2.004 (6)	Si(2)-C(5)	1.86 (1)	1.91 (1)
P(1)-C(1)	1.85 (1)	1.87 (1)	Si(2)-C(6)	1.87 (1)	1.87 (1)
Si(1)-C(1)	1.93 (1)	1.90 (1)	Si(2)-C(7)	1.86 (1)	1.83 (1)
Si(1)-C(2)	1.89 (1)	1.85 (1)	Si(3)-C(1)	1.90 (1)	1.89 (1)
Si(1)-C(3)	1.87 (1)	1.94 (1)	Si(3)-C(8)	1.88 (1)	1.94 (1)
Si(1)-C(4)	1.86 (1)	1.86 (1)	Si(3)-C(9)	1.85 (1)	1.83 (1)
Si(2)-C(1)	1.95 (1)	1.93 (1)	Si(3)-C(10)	1.86 (1)	1.86 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Bond Angles (deg) for $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**2**)[a]

	angle	
atoms	molecule A	molecule B
P(1)′-P(1)-C(1)	108.2 (4)	108.9 (4)
C(1)-Si(1)-C(2)	112.0 (5)	114.9 (5)
C(1)-Si(1)-C(3)	113.7 (5)	109.2 (6)
C(2)-Si(1)-C(3)	106.6 (5)	103.8 (7)
C(1)-Si(1)-C(4)	112.6 (5)	114.1 (5)
C(2)-Si(1)-C(4)	106.2 (6)	106.9 (6)
C(3)-Si(1)-C(4)	105.1 (6)	107.4 (6)
C(1)-Si(2)-C(5)	113.0 (5)	110.2 (5)
C(1)-Si(2)-C(6)	112.8 (5)	111.2 (5)
C(5)-Si(2)-C(6)	106.1 (5)	105.9 (6)
C(1)-Si(2)-C(7)	110.6 (5)	115.7 (5)
C(5)-Si(2)-C(7)	108.9 (6)	104.7 (7)
C(6)-Si(2)-C(7)	105.0 (6)	108.5 (6)
C(1)-Si(3)-C(8)	112.0 (5)	108.4 (6)
C(1)-Si(3)-C(9)	113.0 (5)	116.8 (5)
C(8)-Si(3)-C(9)	106.9 (6)	105.3 (7)
C(1)-Si(3)-C(10)	113.2 (5)	112.3 (5)
C(8)-Si(3)-C(10)	104.7 (6)	105.7 (6)
C(9)-Si(3)-C(10)	106.4 (5)	107.7 (6)
P(1)-C(1)-Si(1)	114.9 (5)	101.2 (5)
P(1)-C(1)-Si(2)	100.1 (5)	112.7 (5)
Si(1)-C(1)-Si(2)	109.8 (5)	110.8 (5)
P(1)-C(1)-Si(3)	108.8 (5)	108.6 (5)
Si(1)-C(1)-Si(3)	111.4 (5)	112.1 (5)
Si(2)-C(1)-Si(3)	111.3 (5)	111.1 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

X-ray crystallographic study of the alkyl derivative, **2**, was undertaken. Virtually simultaneously with our communication, an independent report of the X-ray structure of **2** appeared[41] and Niecke et al.[24] published the X-ray crystal structure of $[(t\text{-}BuMe_2Si)_2N]_2P_2$ (**3c**). The molecular structure of **2** is illustrated in Figure 1 along with the atom-numbering scheme. Tables of atomic positional parameters, bond lengths, and bond angles are collected in Tables II–IV, respectively.

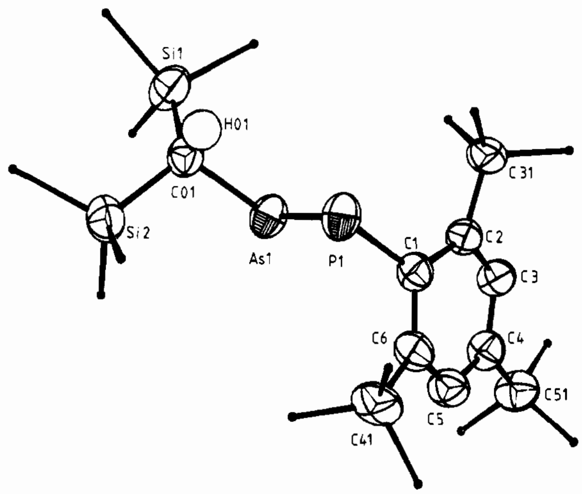

Figure 2. Molecular structure of $[2,4,6\text{-}(t\text{-}Bu)_3C_6H_2]P{=}AsCH(SiMe_3)_2$ (**12**) showing 50% probability thermal ellipsoids. Methyl carbons are of reduced size for clarity.

Table V. Positional Parameters and Their Estimated Standard Deviations for $[2,4,6\text{-}(t\text{-}Bu)_3C_6H_2]P{=}AsCH(SiMe_3)_2$ (**12**)[a]

atom	*x*	*y*	*z*	*B*, Å^2
As1	0.18709 (7)	0.03983 (6)	0.26971 (4)	4.22 (1)
P1	0.1825 (2)	−0.1590 (2)	0.2964 (1)	4.35 (4)
Si1	0.1828 (2)	0.2422 (2)	0.4227 (1)	5.24 (4)
Si2	−0.1004 (2)	0.2020 (2)	0.3505 (1)	5.01 (4)
C01	0.0805 (6)	0.1293 (5)	0.3776 (4)	3.9 (1)
C1	0.2870 (5)	−0.2285 (5)	0.1940 (4)	3.5 (1)
C2	0.4332 (5)	−0.2521 (5)	0.1898 (4)	3.4 (1)
C3	0.5038 (5)	−0.2578 (6)	0.1064 (4)	3.9 (1)
C4	0.4441 (5)	−0.2492 (5)	0.0278 (4)	3.8 (1)
C5	0.3037 (6)	−0.2471 (6)	0.0351 (4)	4.3 (1)
C6	0.2246 (5)	−0.2407 (6)	0.1151 (4)	3.8 (1)
C11	0.1121 (8)	0.2984 (7)	0.5359 (5)	6.5 (2)
C12	0.3633 (8)	0.1554 (9)	0.4299 (7)	10.2 (2)
C13	0.184 (1)	0.3818 (8)	0.3502 (6)	8.9 (2)
C21	−0.1925 (7)	0.3288 (8)	0.4330 (6)	7.5 (2)
C22	−0.1957 (8)	0.0717 (9)	0.360 (1)	13.8 (4)
C23	−0.102 (1)	0.279 (1)	0.2436 (6)	9.9 (3)
C31	0.5207 (6)	−0.2763 (6)	0.2701 (4)	4.1 (1)
C32	0.5763 (9)	−0.1576 (8)	0.2896 (6)	9.3 (2)
C33	0.4474 (9)	−0.302 (1)	0.3571 (6)	9.7 (3)
C34	0.6403 (9)	−0.3894 (9)	0.2507 (5)	8.4 (2)
C41	0.0717 (6)	−0.2540 (7)	0.1125 (5)	5.2 (2)
C42	−0.0211 (8)	−0.124 (1)	0.1150 (8)	12.0 (3)
C43	0.0293 (8)	−0.329 (1)	0.1864 (7)	16.1 (3)
C44	0.0594 (9)	−0.325 (1)	0.0259 (8)	18.7 (3)
C51	0.5242 (6)	−0.2508 (6)	−0.0629 (4)	4.8 (1)
C52	0.460 (1)	−0.136 (1)	−0.1152 (7)	17.0 (4)
C53	0.525 (1)	−0.374 (1)	−0.1070 (7)	18.2 (4)
C54	0.6732 (8)	−0.245 (1)	−0.0562 (6)	9.5 (3)
H01*	0.077 (5)	0.062 (5)	0.421 (3)	
H3*	0.581 (5)	−0.270 (5)	0.104 (3)	
H5*	0.269 (5)	−0.243 (5)	−0.015 (3)	

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with half of two crystallographically independent molecules (A and B) in the asymmetric unit. Each molecule features a crystallographically imposed center of symmetry at the midpoint of the P=P bond. The phosphorus–phosphorus bond length in molecule A is 2.014 (6) Å while that in molecule B is 2.004 (6) Å (cf. 2.034 (2) Å in **1**[18] and 2.034 Å in **3c**[24]). All four bond lengths are significantly shorter than the range 2.21–2.22 Å found in singly bonded diphosphines[42] but close to the sum of double-bond covalent radii (2.00 Å) suggested by Pauling.[43] The geometry about the double bond in **2** is planar and trans, analogous to that found in **1** although the P–P–C angles in **2** are approximately 6° larger than those in **1** and **3**. This is presumably a result of the larger steric bulk of the $(Me_3Si)_3C$ group compared to that of $2,4,6\text{-}(t\text{-}Bu)_3C_6H_2$ or $(t\text{-}BuMe_2Si)_2N$. However, all three groups are of sufficient size that a trans geometry is required (see section on stability). The P–P–C bond angles are significantly smaller than the idealized 120° expected for sp^2-hybridized phosphorus. Thus in **2** the angles are 108.2 (4)° for A and 108.9 (4)° for B while in **1** and **3c** the angles are 102.8 (1) and 102.2°, respectively. This more acute angle reflects an increase in p character in the P–C

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(41) Jaud, J.; Couret, C.; Escudié, J. *J. Organomet. Chem.* **1983**, *249*, C25. See also ref 22b.

(42) See, for example: Cowley, A. H. "Compounds Containing Phosphorus-Phosphorus Bonds"; Dowden, Hutchinson, and Ross Inc.: Strondsbury, PA, 1973.

(43) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY.

Table VI. Bond Distances (Å) for $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]P{=}AsCH(SiMe_3)_2$ (**12**)[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
As1	P1	2.125 (1)	C01	H01	0.972 (3)	C6	C41	1.567 (4)
As1	C01	1.991 (3)	C1	C2	1.425 (4)	C31	C32	1.503 (6)
P1	C1	1.852 (3)	C1	C6	1.412 (4)	C31	C33	1.502 (5)
Si1	C01	1.883 (3)	C2	C3	1.388 (4)	C31	C34	1.501 (5)
Si1	C11	1.845 (4)	C2	C31	1.547 (4)	C41	C42	1.473 (6)
Si1	C12	1.850 (5)	C3	C4	1.370 (4)	C41	C43	1.447 (6)
Si1	C13	1.822 (5)	C3	H3	0.751 (3)	C41	C44	1.535 (7)
Si2	C01	1.885 (3)	C4	C5	1.393 (4)	C51	C52	1.498 (7)
Si2	C21	1.861 (4)	C4	C51	1.527 (4)	C51	C53	1.453 (6)
Si2	C22	1.818 (6)	C5	C6	1.382 (4)	C51	C54	1.514 (6)
Si2	C23	1.804 (5)	C5	H5	0.862 (3)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Bond Angles (deg) for $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]P{=}AsCH(SiMe_3)_2$ (**12**)[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
P1	As1	C01	101.35 (9)	Si2	C01	H01	108.7 (2)	C2	C31	C32	110.6 (3)
As1	P1	C1	96.37 (9)	P1	C1	C2	120.0 (2)	C2	C31	C33	116.5 (3)
C01	Si1	C11	110.5 (2)	P1	C1	C6	120.9 (2)	C2	C31	C34	110.1 (3)
C01	Si1	C12	110.4 (2)	C2	C1	C6	118.4 (3)	C32	C31	C33	103.5 (4)
C01	Si1	C13	110.4 (2)	C1	C2	C3	117.3 (3)	C32	C31	C34	108.1 (4)
C11	Si1	C12	107.1 (2)	C1	C2	C31	125.7 (3)	C33	C31	C34	107.6 (4)
C11	Si1	C13	110.4 (2)	C3	C2	C31	117.0 (2)	C6	C41	C42	110.5 (3)
C12	Si1	C13	107.9 (3)	C2	C3	C4	125.0 (3)	C6	C41	C43	111.5 (3)
C01	Si2	C21	112.4 (2)	C2	C3	H3	117.4 (3)	C6	C41	C44	108.4 (3)
C01	Si2	C22	107.2 (2)	C4	C3	H3	117.6 (3)	C42	C41	C43	108.7 (5)
C01	Si2	C23	111.5 (2)	C3	C4	C5	115.4 (3)	C42	C41	C44	109.0 (5)
C21	Si2	C22	105.0 (3)	C3	C4	C51	123.7 (3)	C43	C41	C44	108.7 (6)
C21	Si2	C23	106.9 (2)	C5	C4	C51	120.9 (3)	C4	C51	C52	109.7 (4)
C22	Si2	C23	113.7 (4)	C4	C5	C6	123.6 (3)	C4	C51	C53	108.1 (3)
As1	C01	Si1	108.0 (1)	C4	C5	H5	113.3 (3)	C4	C51	C54	112.5 (3)
As1	C01	Si2	109.0 (2)	C6	C5	H5	122.8 (3)	C52	C51	C53	111.9 (6)
As1	C01	H01	106.2 (2)	C1	C6	C5	118.6 (3)	C52	C51	C54	108.0 (4)
Si1	C01	Si2	118.0 (2)	C1	C6	C41	124.0 (3)	C53	C51	C54	106.6 (5)
Si1	C01	H01	106.3 (2)	C5	C6	C41	117.3 (3)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

or P–N bond and that the phosphorus atoms are approaching sp hybrid character. This is the reverse of the trend expected from steric considerations alone and therefore probably reflects an emerging inert s-pair effect for heavier atoms. The geometry of the $(Me_3Si)_3C$ group is not surprising and deserves no special comment.

Since no bond lengths have been reported for the phosphorus–arsenic double bond, it was of interest to perform an X-ray diffraction study of the phosphaarsene **12**. The structure of **12** is shown in Figure 2, and compilations of atomic positional parameters, bond lengths, and bond angles appear in Tables V–VII, respectively. The structural assay revealed a phosphorus–arsenic distance of 2.124 (2) Å. This distance is consistent with its formulation as a double bond and, as in the case of diphosphenes, is significantly shorter than the values reported for P–As single bonds (~2.32–2.36 Å[44]) but close to the sum of double-bond covalent radii (2.11 Å).[43] The phosphorus is bonded to a $2,4,6\text{-}(t\text{-Bu})_3C_6H_2$ group (P1–C1 = 1.847 (5) Å) while the arsenic bonds to a $(Me_3Si)_2CH$ ligand (As1–C01 = 1.995 (5) Å). The central atoms, C01, As1, P1, and C1, are planar (mean deviation 0.010 (7) Å), and the conformation is trans. The geometry about the double bond is thus analogous to that for the structurally characterized diphosphenes **1**, **2**, and **3c**. The bond angle at P1 (C1–P1–As1) is 96.37 (9)° and thus considerably smaller than that in **1** (102.8 (1)°).[18] This difference may be the result of (a) a longer As=P bond in **12** compared to the P=P bond length in **1** and (b) the smaller steric bulk of the $(Me_3Si)_2CH$ group

Table VIII. Positional Parameters and Their Estimated Standard Deviations for $[2,4,6\text{-}(t\text{-Bu})_3\text{-}C_6H_2]As{=}AsCH(SiMe_3)_2$ (**18**)[a]

atom	*x*	*y*	*z*	*B*, Å²
As1	0.1858 (2)	0.0417 (2)	0.2708 (1)	5.13 (4)
As2	0.1803 (2)	−0.1665 (2)	0.3009 (1)	5.34 (5)
Si1	−0.1006 (6)	0.2023 (5)	0.3499 (4)	5.8 (1)
Si2	0.1835 (6)	0.2458 (6)	0.4224 (4)	6.1 (1)
C01	0.081 (2)	0.128 (2)	0.378 (1)	4.5 (4)
C1	0.291 (2)	−0.232 (2)	0.193 (1)	4.4 (4)
C2	0.229 (1)	−0.245 (2)	0.112 (1)	4.3 (4)
C3	0.307 (2)	−0.246 (2)	0.031 (1)	4.6 (4)
C4	0.448 (2)	−0.251 (2)	0.026 (1)	4.6 (4)
C5	0.510 (2)	−0.258 (1)	0.105 (1)	4.2 (4)
C6	0.436 (1)	−0.257 (1)	0.186 (1)	3.9 (4)
C11	−0.197 (2)	0.328 (2)	0.434 (1)	7.5 (6)
C12	−0.097 (3)	0.277 (2)	0.239 (2)	9.1 (7)
C13	−0.201 (2)	0.064 (2)	0.357 (2)	11.8 (9)
C21	0.183 (2)	0.389 (2)	0.348 (2)	9.5 (7)
C22	0.109 (2)	0.301 (2)	0.536 (1)	7.0 (5)
C23	0.367 (2)	0.154 (3)	0.430 (2)	10.7 (7)
C31	0.073 (2)	−0.260 (2)	0.110 (1)	6.1 (5)
C32	−0.020 (2)	−0.128 (2)	0.106 (2)	10.6 (7)
C33	0.032 (2)	−0.342 (3)	0.185 (2)	12.2 (7)
C34	0.062 (2)	−0.333 (3)	0.023 (2)	11.8 (7)
C41	0.526 (2)	−0.283 (2)	0.269 (1)	4.9 (4)
C42	0.575 (2)	−0.156 (2)	0.289 (1)	9.6 (5)
C43	0.456 (2)	−0.332 (3)	0.351 (1)	10.2 (8)
C44	0.653 (2)	−0.391 (2)	0.243 (1)	8.7 (6)
C51	0.526 (2)	−0.247 (2)	−0.063 (1)	5.5 (5)
C52	0.524 (3)	−0.373 (3)	−0.115 (2)	11.7 (8)
C53	0.462 (3)	−0.134 (3)	−0.119 (2)	10.3 (8)
C54	0.673 (2)	−0.236 (3)	−0.058 (2)	11.3 (8)
H01*	0.08 (1)	0.04 (1)	0.425 (8)	

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

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(44) Sheldrick, W. S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1789. Baudler, M.; Aktalay, Y.; Heinlein, T.; Tebbe, K.-F. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 299.

Table IX. Bond Distances (Å) for $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]As{=}AsCH(SiMe_3)_2$ (**18**)[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
As1	As2	2.224 (2)	Si2	C23	1.897 (12)	C6	C41	1.595 (12)
As1	C01	1.976 (10)	C01	H01	1.14 (7)	C31	C32	1.51 (2)
As2	C1	1.946 (10)	C1	C2	1.440 (11)	C31	C33	1.50 (2)
Si1	C01	1.900 (9)	C1	C6	1.409 (11)	C31	C34	1.55 (2)
Si1	C11	1.888 (11)	C2	C3	1.393 (12)	C41	C42	1.539 (13)
Si1	C12	1.849 (14)	C2	C31	1.591 (12)	C41	C43	1.516 (15)
Si1	C13	1.906 (12)	C3	C4	1.399 (12)	C41	C44	1.539 (14)
Si2	C01	1.908 (9)	C4	C5	1.373 (12)	C51	C52	1.546 (15)
Si2	C21	1.860 (14)	C4	C51	1.506 (13)	C51	C53	1.51 (2)
Si2	C22	1.868 (11)	C5	C6	1.381 (12)	C51	C54	1.501 (15)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table X. Bond Angles (deg) for $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]As{=}AsCH(SiMe_3)_2$ (**18**)[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
As2	As1	C01	99.9 (3)	Si1	C01	H01	110 (4)	C2	C31	C33	111.6 (9)
As1	As2	C1	93.6 (3)	Si2	C01	H01	110 (4)	C2	C31	C34	107.6 (9)
C01	Si1	C11	113.4 (5)	As2	C1	C2	121.3 (7)	C32	C31	C33	113. (1)
C01	Si1	C12	110.1 (6)	As2	C1	C6	122.8 (6)	C32	C31	C34	107. (1)
C01	Si1	C13	106.6 (5)	C2	C1	C6	115.5 (8)	C33	C31	C34	107. (1)
C11	Si1	C12	109.6 (6)	C1	C2	C3	119.7 (8)	C6	C41	C42	107.6 (8)
C11	Si1	C13	104.4 (7)	C1	C2	C31	122.7 (9)	C6	C41	C43	115.7 (8)
C12	Si1	C13	112.6 (7)	C3	C2	C31	117.6 (8)	C6	C41	C44	108.1 (8)
C01	Si2	C21	111.0 (5)	C2	C3	C4	121.8 (9)	C42	C41	C43	111. (1)
C01	Si2	C22	109.2 (5)	C3	C4	C5	117.3 (9)	C42	C41	C44	108.5 (9)
C01	Si2	C23	108.4 (5)	C3	C4	C51	119.4 (9)	C43	C41	C44	106. (1)
C21	Si2	C22	110.5 (6)	C5	C4	C51	123.3 (9)	C4	C51	C52	109. (1)
C21	Si2	C23	109.3 (8)	C4	C5	C6	122.5 (9)	C4	C51	C53	113. (1)
C22	Si2	C23	108.3 (6)	C1	C6	C5	121.0 (8)	C4	C51	C54	113.9 (9)
As1	C01	Si1	108.7 (5)	C1	C6	C41	123.5 (8)	C52	C51	C53	106. (1)
As2	C01	Si2	107.7 (5)	C5	C6	C41	115.5 (8)	C52	C51	C54	108. (1)
As1	C01	H01	103 (4)	C2	C31	C32	110.4 (9)	C53	C51	C54	106. (1)
Si1	C01	Si2	116.1 (5)								

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

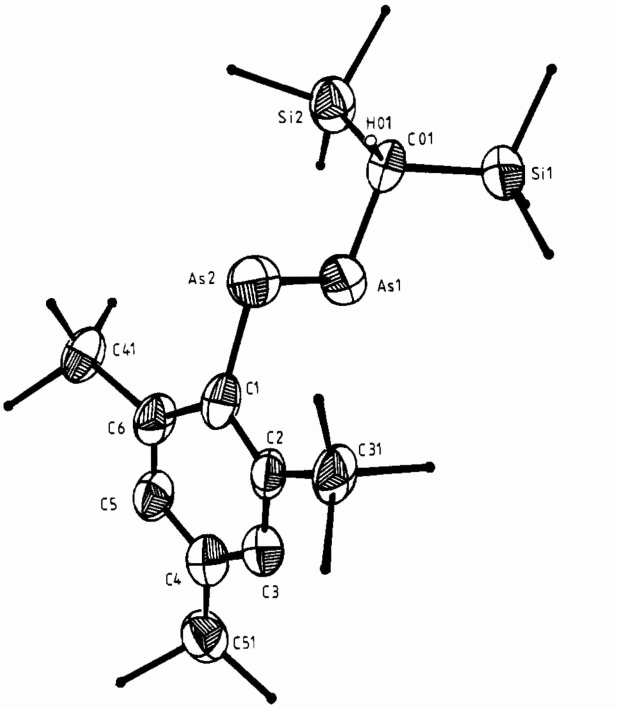


Figure 3. Molecular structure of $[2,4,6\text{-}(t\text{-Bu})_3C_6H_2]As{=}AsCH(SiMe_3)_2$ (**18**) showing 50% probability thermal ellipsoids. Methyl carbons are of reduced size for clarity.

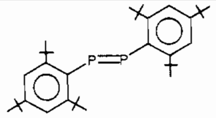
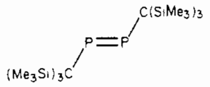
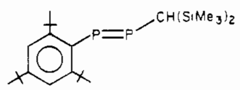
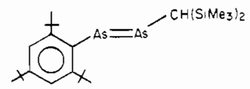
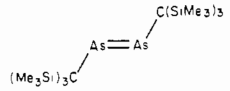
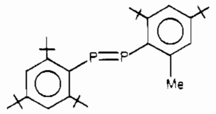
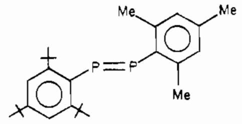
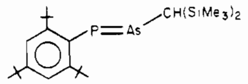
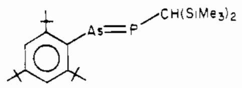
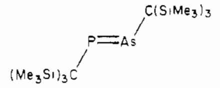
Table XI. Summary of Crystal Data, Data Collection Parameters, and Least-Squares Residuals for Compounds **2**, **12**, and **18**

	2	**12**	**18**
formula	$P_2Si_6C_{20}H_{54}$	$AsPSi_2C_{25}H_{48}$	$As_2Si_2C_{25}H_{48}$
fw	525.1	510.22	554.17
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	15.629 (7)	9.991 (4)	9.955 (9)
b, Å	9.155 (5)	10.452 (9)	10.393 (7)
c, Å	12.482 (6)	15.140 (15)	15.159 (5)
α, deg	91.58 (4)	89.72 (7)	89.56 (4)
β, deg	111.42 (5)	85.03 (5)	85.39 (6)
γ, deg	90.02 (4)	77.72 (5)	78.31 (9)
V, Å^3	1662 (2)	1539 (3)	1530 (3)
Z	2	2	2
d_{calcd}, g/cm^3	1.049	1.310	1.199
cryst size, mm	1.0 × 0.6 × 0.3	0.5 × 0.4 × 0.4	0.5 × 0.5 × 0.3
μ(Mo Kα), cm^{-1}	3.1	12.8	22.6
radiation	Mo Kα ($\lambda\bar{\alpha}$ = 0.71073 Å; graphite monochromated)		
ω scan width, deg	0.8 + 0.2 tan θ	0.8 + 0.2 tan θ	0.9 + 0.2 tan θ
decay of stds	<3%	<4%	<2%
std reflcns	600, 008, 040	$\bar{1}\bar{3}\bar{2}$, $\bar{1}\bar{1}\bar{1}$	403, 314
reflcns measd	2275	5397	5384
reflcns obsd	2046	3862	2508
data omission	$I > 2\sigma(I)$	$I > 3\sigma(I)$	$I > 2.5\sigma(I)$
2θ range, deg	2–36	2–50	2–50
no. of parameters varied	253	406	265
R	0.086	0.057	0.0867
R_w	0.086	0.061	0.1062

(see later). These two factors combine to allow a decrease in the angle at P1, which is presumably the point of an electronic energy minimum. The angle at arsenic (C01–As1–P1) is 101.35 (9)°.

The structure of the diarsene **18** is illustrated in Figure 3, and compilations of atomic positional parameters, bond lengths, and bond angles are presented in Tables VIII–X, respectively. The structure differs in no fundamental manner from that of the phosphaarsene **12**. Indeed, the two compounds are almost isostructural as evidenced by the pertinent crystallographic data assembled in Table XI. The geometry of **18** is planar and trans with an arsenic–arsenic separation

Table XII. Electronic Spectral Data for Diphosphenes, Phosphaarsenes, and Diarsenes

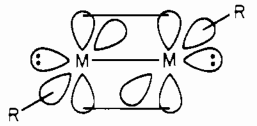
compd	λ_1, nm[a]	λ_2, nm[a]	λ(other), nm[a]	ref
	460 (1360)	340 (7690)	284 (15660)	18
	484 (62.8)	353 (9474)	241.3 (8532)	this work
	427 (370)	325 (13000)	261 (15500)	this work
	449 (180)	368 (6960)	255 (12660)	33
	505 (10)	380 (5000)		34
	461 (468)	330 (5080)	279 (13800)	27
	456 (220)	326 (2500)	273 (9830)	27
	454 (280)	353 (7500)	263 (10320)	this work
	431 (220)	354 (8400)	254 (10440)	33
	497 (20)	361 (7900)		37

[a] ε values are in parentheses.

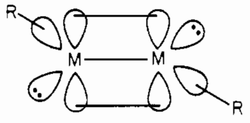
of 2.224 (2) Å. This is the shortest arsenic–arsenic bond reported[45] and agrees well with the sum of double-bond covalent radii (2.22 Å)[43] and the value of ~2.3 Å that Dahl et al.[46] have suggested for the As=As double bond. The bond angles at arsenic are As1 = 99.9 (3)° and As(2) = 93.6 (3)°, significantly smaller than those in the phosphaarsene **12**.

The most noteworthy feature about these three structures is the P=P, P=As, and As=As bond lengths. These are shorter than the sums of the respective covalent radii and structurally characterized examples of single bonds but close to the sum of double-bond covalent radii. Formulating these compounds as double bonded therefore seems warranted by the available structural data.

The other features of interest concerns the angles at either phosphorus or arsenic. The structures of **2**, **12**, and **18** show that the angles decrease as the double bond lengthens and the steric demands of the ligands decrease. It thus appears that an angle approaching 90° is preferred, presumably for electronic reasons. While olefinic double bonds are considered to feature sp^2 hybridized carbon atoms, it would appear that in diphosphenes, phosphaarsenes, and diarsenes a tendency toward sp hybridization occurs on going from phosphorus to arsenic, i.e. form A over form B. As previously mentioned,



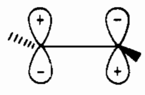
A



B

this may reflect the emergence of an inert s-pair effect on moving from phosphorus to arsenic, where sp hybridization is preferred to sp^2.

(iii) Electronic Structures of Diphosphenes, Phosphaarsenes, and Diarsenes. Electronic spectral data for the diphosphenes, phosphaarsenes, and diarsenes have been assembled in Table XII. Each compound exhibits two UV-vis maxima at wavelengths >300 nm, i.e. in the region outside aromatic $\pi \rightarrow \pi^*$ transitions. Ab initio MO calculations on the model diphosphene *trans*-P_2H_2 reveal that the $2b_g$ MO is the LUMO



$2b_g$

and that this orbital possesses appreciable P–P π^* character.[27,47] The calculation of a low-lying LUMO (+0.24 eV)

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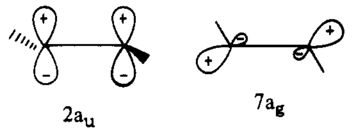
(45) The arsenic–arsenic single-bond length is 2.43–2.46 Å. See: (a) Maxwell, L. K.; Hendricks, S. B.; Mosely, V. M. *J. Chem. Phys.* **1935**, *3*, 699. (b) Burns, J. H.; Waser, J. *J. Am. Chem. Soc.* **1957**, *79*, 259. (c) Hedberg, K.; Hughes, E. W.; Waser, J. *Acta Crystallogr.* **1961**, *14*, 369. (d) Rheingold, A. L.; Sullivan, P. J. *Organometallics* **1983**, *2*, 327.

(46) Foust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 5633. (b) Foust, A. S.; Campana, C. F.; Sinclair, J. D.; Dahl. L. F. *Inorg. Chem.* **1979**, *18*, 3047.

(47) (a) Lee, J.-G.; Cowley, A. H.; Boggs, J. E. *Inorg. Chim. Acta* **1983**, *77*, L61. (b) Galasso, V. *Chem. Phys.* **1984**, *83*, 407.

is consistent with the observation that it undergoes facile one-electron reduction to the corresponding anion radical.[21b] The two highest occupied MO's, $2a_u$ (P–P π bond) and $7a_g$ (n_+ phosphorus lone pairs), are closely spaced and their order



depends on the calculational method. $X\alpha$–scattered-wave calculations[48] on *trans*-P_2H_2 produce the sequence $7a_g$ (–6.41 eV) and $2a_u$ (–6.55 eV). We consider that the electronic spectral data support the $X\alpha$–SW calculation and indicate that the $7a_g$ (n_+) MO is the HOMO. Note that for all the molecules listed in Table XII λ_1 is considerably less intense than λ_2. We attribute this observation to the fact that the $n_+ \rightarrow \pi^*$ transition (i.e., $7a_g \rightarrow 2b_g$) is symmetry forbidden, while the $\pi \rightarrow \pi^*$ transition (i.e. $2a_u \rightarrow 2b_g$) is symmetry allowed. The conclusion that the n_+ lone-pair combination represents the HOMO is supported by UV PES data for **1**[21b,49] and **2**.[49] Although the spectral interpretation is complicated by the occurrence of overlapping bands, both spectra exhibit a low-intensity first peak at ~7 eV that has the appearance of a lone-pair ionization.

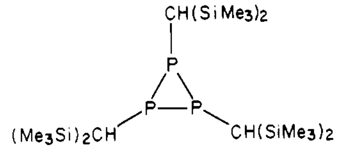
Finally, we note that λ_1 and λ_2 occur at longer wavelengths for the diarsenes than for the corresponding diphosphenes. This occurs because the π bonding is less strong in the diarsenes; hence, the $n_+ \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ energy gaps are diminished. The fact that λ_1 and λ_2 are very similar for the alkylated and arylated diphosphenes or diarsenes suggests that there is relatively little conjugation between the aryl π systems and the P=P or As=As chromophore.

(iv) ^{31}P NMR Data. All ^{1}H and ^{13}C NMR data are given in the Experimental Section, and ^{31}P NMR data are summarized in Table I. Two aspects of the data deserve special comment. First, the ^{31}P chemical shifts for diphosphenes, phosphaarsenes, and phosphastibenes are among the lowest field shifts known in ^{31}P NMR spectroscopy,[39] typically in the range 500–670 ppm. Second, the values of $^1J_{PP}$ obtained directly from the spectra of unsymmetrical diphosphenes are also large and fall in the range 550–650 Hz. These effects parallel, although they are greater than, those observed in ^{13}C NMR spectroscopy. Thus olefinic carbons resonate at lower field than saturated carbons and $^1J_{CC}$ values are greater for C=C double bonds than for C—C single bonds.[50]

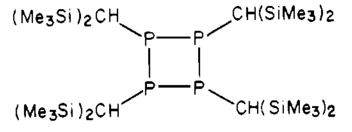
The reason for the low-field ^{31}P chemical shifts is assumed to be a large increase in the paramagnetic shielding term (σ_P), which dominates the overall shielding in multiply bonded compounds. This effect is well-known in ^{13}C NMR spectroscopy and is also evident in the ^{29}Si chemical shift of $(mesityl)_2Si{=}Si(mesityl)_2$ compared to that of a disilane.[51] We have attempted to correlate the ^{31}P chemical shifts with the electronic spectral data to determine whether the paramagnetic term is dominated by the $n_+ \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transition of the diphosphene. However, no such relationship is apparent.

The larger $^1J_{PP}$ values for doubly bonded compounds stem principally from increases in the Fermi contact term, which, in turn, result from the changes in valence s character of the phosphorus atoms.

(v) Concluding Remarks on Bonding and Stability. The stabilities of the double-bonded compounds described in this work are ascribable to the kinetic stabilization afforded by the sterically demanding substituents. The resistance of e.g. diphosphenes toward oligomerization diminishes with decreasing ligand bulk. Thus, although it is possible to isolate a diphosphene with one $(Me_3Si)_2CH$ group, this moiety is not sufficiently bulky to permit isolation of the diphosphene $(Me_3Si)_2CHP{=}PCH(SiMe_3)_2$; hence, the reaction of $(Me_3Si)_2CHPCl_2$ with Mg in THF results in a mixture of the oligomerized products **20** and **21**.[26]

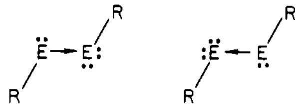


20



21

In a recent article, Pauling[52] has suggested that distannenes and digermenes do not feature double bonding between the tin or germanium atoms but rather that these atoms are connected by a single covalent bond and that an unshared pair resonates between the fourth sp^3 orbitals of the two atoms. Obviously, resonating structures can be written for the group 5A compounds, viz.



However, we prefer a double-bonded formualtion because the P=P, P=As, and As=As bond lengths are considerably shorter (~0.2 Å) than the corresponding single-bond lengths. In fact, the observed bond lengths for diphosphenes, phosphaarsenes, and diarsenes are remarkably close to those predicted with use of Pauling's double-bond covalent radii.[43] Furthermore, the double-bonded formulation permits a facile interpretation of electronic, photoelectronic, and NMR spectral data. Likewise, the observation[22a,29a] that $(Me_3Si)_3CP(H)P(Cl)C(SiMe_3)_3$ can be produced by addition of HCl to the diphosphene $[(Me_3Si)_3C]_2P_2$ is most easily accommodated by postulating double bonding between the phosphorus atoms.

Experimental Section

General Considerations. All experiments were performed under an atmosphere of dry dinitrogen with use of standard Schlenk techniques. All solvents used were freshly distilled over CaH_2 prior to use. Microanalytical data were obtained from the Canadian Microanalytical Service Ltd.

Spectroscopic Measurements. UV spectra were recorded on a Cary Model 15 spectrophotometer, and the data are summarized in Table XII. ^{1}H NMR spectra were recorded on Varian EM390 and Nicolet NT200 instruments operating at spectrometer frequencies of 90.0 and 200.0 MHz, respectively. ^{13}C spectra were recorded on Varian FT80A and Bruker WH90 instruments at spectrometer frequencies of 20.0 and 22.615 MHz, respectively. ^{31}P NMR spectra were recorded on Varian FT80A and Nicolet NT200 instruments at spectrometer frequencies of 32.384 and 81.03 MHz, respectively. ^{1}H and ^{13}C spectra are referenced to Me_4Si (0.0 ppm) while ^{31}P spectra are referenced to external 85% H_3PO_4 with positive values to high frequency in all cases. The ^{31}P NMR data are summarized in Table I. All NMR spectra were obtained in CH_2Cl_2 or CD_2Cl_2 as solvent unless otherwise stated and were run at room temperature. Medium- and high-res-

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(48) Lattman, M.; Cowley, A. H., to be submitted for publication.

(49) Gonbeau, D.; Pfister-Guillouzo, G.; Escudié, J.; Couret, C.; Satgé, J. *J. Organomet. Chem.* **1983**, *247*, C17.

(50) See, for example: Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.

(51) (a) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. (b) Zilm, K. W.; Grant, D. M.; Michl, J.; Fink, M. J.; West, R. *Organometallics* **1983**, *2*, 193. (c) West, R. *Pure Appl. Chem.* **1984**, *56*, 163.

(52) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 3871.

olution mass spectra were measured on Du Pont-Consolidated Model 21-491 and 21-100 instruments, respectively. Perfluorokerosene was used as the calibrant for HRMS.

Starting Materials. The compounds PCl_3, $AsCl_3$, AsF_3, $SbCl_3$, and $LiAlH_4$ were procured commercially and used without subsequent purification. The halides $(Me_3Si)_2CHMCl_2$ (M = P, As),[53,54] [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]PCl$_2$,[18] and $(Me_3Si)_3CPCl_2$[35] were prepared and purified according to the literature procedures.

Preparation of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]PH$_2$. The chlorophosphine [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]PCl$_2$ (13.9 g, 40 mmol) in 170 mL of THF was added via a double-tipped needle to a stirred slurry of $LiAlH_4$ (3 g, 80 mmol) in 180 mL of THF at 0 to −5 °C. The suspension was refluxed for a further 2 h and cooled, and 120 mL of 20% HCl was added carefully. The organic layer was dried over $MgSO_4$, and after filtration, the THF was removed in vacuo to afford the crude product. Recrystallization from *i*-PrOH afforded 8.9 g (80%) of the pure phosphine, mp 144–146 °C dec. ^{31}P NMR (32.384 MHz): δ −132 (t, $^1J_{PH}$ = 209 Hz). ^1H NMR (90 MHz): δ 1.32 (s, 9 H, *p-t*-Bu), 1.60 (s, 18 H, *o-t*-Bu), 4.22 (d, 2 H, PH, $^1J_{PH}$ = 209 Hz), 7.52 (d, 2 H, C_6H_2, $^4J_{PH}$ = 2.3 Hz). The NMR data are in good agreement with those of Issleib et al.[55]

Preparation of $(Me_3Si)_2CHSbCl_2$ (13).[38] The Grignard reagent $(Me_3Si)_2CHMgCl$ was prepared from $(Me_3Si)_2CHCl$ (19.5 g, 100 mmol) and Mg (2.6 g, 107 mmol) in 65 mL of Et_2O under reflux for 2 h. The resulting Grignard solution was added dropwise at −40 to −50 °C to a solution of $SbCl_3$ (22.8 g, 100 mmol) in 70 mL of Et_2O. The reaction mixture was allowed to warm to room temperature, and stirring was continued for an additional 2 h. Filtration followed by distillation afforded 26 g (74%) of **13** as a colorless liquid, bp 83–85 °C (0.03 torr), which solidified slowly on standing (mp 42–44 °C). The spectroscopic properties were in good agreement with those in ref 38.

Preparation of 15. Arsenic trichloride (1.8 g, 10.0 mmol) was added dropwise at −78 °C to a solution of 2.5 g (10.0 mmol) of 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$Li in 40 mL of THF. The reaction mixture was stirred for a further 2 h and then allowed to warm to room temperature. Removal of the solvent in vacuo followed by sublimation (80 °C, 0.025 torr) afforded 1.5 g (42%) of **15** as a white crystalline solid, mp 146–148 °C. ^1H NMR data for **15**: δ 1.40 (s, 9 H, *t*-Bu), 1.60 (s, 9 H, *t*-Bu), 1.45 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 2.15 (d, 1 H, CH_2, $^2J_{HH}$ = 15 Hz), 2.75 (d, 1 H, CH_2, $^2J_{HH}$ = 15 Hz), 7.45 (m, 2 H, C_6H_2). The mass spectrum showed a parent peak at *m/e* 354.

Preparation of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]AsF$_2$ (16). A THF solution of 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$Li (2.5 g, 10 mmol) was added dropwise to a solution of AsF_3 (1.33 g, 10 mmol) in THF (10 mL) at −78 °C. The reaction mixture was stirred at room temperature overnight. Removal of solvent followed by sublimation gave 2.9 g (81%) of white crystalline **16**, mp 119–121 °C. The mass spectrum showed a parent peak at *m/e* 358.

Preparation of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]AsH$_2$ (17). A THF solution of **16** (9 g, 25 mmol) was added dropwise to a stirred suspension of $LiAlH_4$ (1.9 g, 50 mmol) in 100 mL of THF at 0 °C. The stirred reaction mixture was then heated to 40 °C for 2 h. After filtration (Celite), the solvent was removed in vacuo. Recrystallization of the residue from *i*-PrOH at 0 °C afforded 3.2 g (40%) of white crystalline **17**, mp 146–150 °C dec. ^1H NMR data for **17**: δ 1.40 (s, 9 H, *p-t*-Bu); 1.60 (s, 18 H, *o-t*-Bu); 4.00 (s, 2 H, AsH_2); 7.50 (s, 2 H, C_6H_2).

Preparation of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]$_2$P$_2$ (1). A solution of sodium naphthalenide (25 mL, 0.8 M) was added dropwise to a THF solution of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]PCl$_2$ (3.5 g, 10 mmol) at −78 °C. This solution was stirred for 1 h, after which time the solvent and naphthalene were removed in vacuo. Purification of the residue by column chromatography (silica gel/*n*-hexane) afforded 1.4 g (51%) of orange crystalline **1** after recrystallization from *n*-pentane. ^1H and ^{31}P NMR and melting point data were in agreement with those given in ref 18 and 20.

Preparation of $[(Me_3Si)_3C]_2P_2$ (2). This compound has been prepared by several routes. Reported here are reductions involving sodium naphthalenide and $(Me_3Si)_3CLi$. A synthesis involving *t*-BuLi has been reported elsewhere.[22]

(i) Sodium Naphthalenide (NaNp) Route. A solution of $(Me_3Si)_3CPCl_2$ (1.26 g, 3.77 mmol) in dry, degassed THF (25 mL) was added to a nitrogen-filled 100-mL flask and cooled to −70 °C. In a separate flask, a solution of NaNp (9.6 mL, 0.79 M) in THF was also cooled to −70 °C. The NaNp solution was transferred dropwise to the flask containing $(Me_3Si)_3CPCl_2$ and the temperature maintained at −70 °C. Following completion of the transfer, the mixture was allowed to stir and warm to room temperature overnight. Removal of the solvent in vacuo produced a brown residue, from which excess naphthalene was removed by vacuum sublimation at 60 °C for 12 h. After the residue was dissolved in *n*-hexane, the NaCl was removed by filtration (Celite column). The resulting solution was purified further by column chromatography on silica gel with *n*-hexane as eluant. The leading yellow-orange band comprised compound **2** and was taken to dryness and recrystallized from toluene at 0 °C (resulting in 0.30 g (30%) of orange crystalline **2**). While this yield is reproducible, the method has not proved suitable for scale-up. NMR data for **2**: ^1H δ 0.3 (t, $(CH_3)_3Si$, $|^4J_{PH} + {}^5J_{PH}|$ = 0.8 Hz); $^{13}C\{^1H\}$ (ppm) 33.2 (t, $((CH_3)_3Si)_3C$, $|^1J_{PC} + {}^2J_{PC}|$ = 41.5 Hz), 4.88 (t, $((CH_3)_3Si)_3C$, $|^3J_{PC} + {}^4J_{PC}|$ = 4.91 Hz). Anal. Calcd for $C_{20}H_{54}Si_6P_2$: C, 45.76; H, 10.37. Found: C, 45.80; H, 10.95. HRMS: calcd mol wt for $C_{20}H_{54}P_2Si_6$, 524.2315; found, 524.2333.

(ii) $(Me_3Si)_3CLi$ Route. To a flask containing $(Me_3Si)_3CPCl_2$ (1.89 g, 5.68 mmol) in 25 mL of THF at 0 °C was added a solution of $(Me_3Si)_3CLi$ (46.1 mL, 0.37 M) in THF/Et_2O. The initially light orange solution changed to dark red on warming to room temperature and stirring overnight. After removal of solvent, the liquid residue was heated to 50 °C under high vacuum for 12 h to remove the $(Me_3Si)_3CH$ that had formed in the reaction. Analysis by ^{31}P NMR spectroscopy showed the reaction to be virtually quantitative. Purification of **2** produced by this method was accomplished by dissolving the residue in *n*-hexane followed by filtering to remove LiCl. Recrystallization from toluene at 0 °C afforded orange crystals of **2**.

The above method is amenable to scale-up and is the preferred method of synthesis for **2**.

Preparation of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]P=PC(SiMe$_3$)$_3$ (5). A solution of NaNp (17.6 mL, 0.49 M in an extra 50 mL of THF) was added to a flask containing $(Me_3Si)_3CPCl_2$ (0.97 g, 2.9 mmol) and [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]PCl$_2$ (0.50 g, 1.45 mmol) in 50 mL of THF at −78 °C. The stirred reaction mixture was allowed to warm to room temperature overnight. After removal of solvent and naphthalene (as for **2**), the brown residue was chromatographed on silica gel with *n*-hexane as eluant. The first and third fractions were identified as **2** and **1**, respectively, by use of ^{31}P NMR spectroscopy. The second fraction contained **5** and after recrystallization from toluene afforded orange crystals of **5** in 30% yield. HRMS: calcd mol wt for $C_{28}H_{56}P_2Si_3$, 538.3164; found, 538.3172. $^{13}C\{^1H\}$ NMR: δ 33.9 (dd, *o-t*-Bu, $|^4J_{PC} + {}^5J_{PC}|$ = 6.5 Hz), 35.3 (dd, $(Me_3Si)_3C$, $|^1J_{PC} + {}^2J_{PC}|$ = 128.0 Hz).

Preparation of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]P=PCH(SiMe$_3$)$_2$ (7). DBU (0.96 g, 6.3 mmol)[56] was added dropwise to a solution of $(Me_3Si)_2CHPCl_2$ (0.8 g, 3.06 mmol) and [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]PH$_2$ (0.43 g, 1.54 mmol) in 30 mL of THF at 0 °C. The reaction mixture was stirred overnight, resulting in a white precipitate and a yellow supernatant liquid. Filtration (Celite) and removal of solvent gave a yellow residue that was purified further by column chromatography (silica gel/*n*-hexane). Recrystallization from *n*-pentane at 0 °C gave 0.56 g (78%) of yellow crystalline **7**, mp 114–116 °C. ^1H NMR data for **7**: δ 0.20 (s, 18 H, H_A),[57] 1.40 (s, 9 H, H_C), 1.55 (s, 18 H, H_D),

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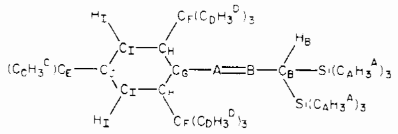
(53) (a) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1976**, 623. (b) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428.

(54) The preparation of the $(Me_3Si)_2CH$ derivatives was facilitated by the one-pot synthesis of the precursor $(Me_3Si)_2CHCl$: Cowley, A. H.; Kemp, R. A. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 591.

(55) Issleib, K.; Schmidt, H.; Wirkner, C. *Z. Anorg. Allg. Chem.* **1982**, *488*, 75.

(56) In all reactions using the DBU route, an excess of the dichlorophosphine was employed. This results in higher yields of the coupled product. The reason for this is unclear at the present time.

(57) Labeling system:



7, A = B = P
12, A = P, B = As
18, A = B = As
19, A = As, B = P

2.85 (1 H, H_B, X part of ABX, J_{AX} = 17 Hz, J_{BX} = −0.5 Hz), 7.50 (s, 2 H, H_I). $^{13}C\{^1H\}$ NMR: δ 1.2 (bm, nonequivalent C_A),[57] 17.4 (X part of ABX, $|J_{AX} + J_{BX}|$ = 164 Hz, C_B), 31.2 (s, C_C), 32.5 (s, C_E), 34.0 (m, nonequivalent C_D), 38.4 (s, C_F), 121.9 (s, C_I), 135.3 (X part of ABX, $|^1J_{PC} + {}^2J_{PC}|$ = 57 Hz, C_G), 149.2 (s, C_J), 153.2 (d, C_H, $^2J_{PC}$ = 7.5 Hz). Anal. Calcd for $C_{25}H_{48}P_2Si_2$: C, 64.33; H, 10.37. Found: C, 64.02; H, 10.98. HRMS: calcd mol wt for $C_{25}H_{48}P_2Si_2$, 466.2771; found, 466.2764.

Preparation of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]P═AsCH(SiMe$_3$)$_2$ (17). This compound was prepared in a manner analogous to that for **7** but with $(Me_3Si)_2CHAsCl_2$ (1.53 g, 5.0 mmol), [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]PH$_2$ (0.84 g, 3.0 mmol), and DBU (1.6 g, 10.5 mmol)[56] in 30 mL of THF. Purification by filtration (Celite) and column chromatography (silica gel/*n*-hexane) afforded 0.72 g (47%) of **12** as an orange crystalline material, mp 108–109 °C, after recrystallization from *n*-pentane. ^1H NMR data for **12**: δ 0.20 (s, 18 H, H_A),[57] 1.40 (s, 9 H, H_C), 1.50 (s, 18 H, H_D), 2.95 (d, 1 H, H_B, $^3J_{PH}$ = 13.0 Hz), 7.60 (s, 2 H, H_I). ^{13}C NMR data for **12**: δ 1.7 (m, nonequivalent C_A),[57] 18.3 (d, C_B, $^2J_{PC}$ = 171.2 Hz), 31.3 (s, C_C), 33.3 (s, C_E), 34.0 (m, nonequivalent C_D), 38.5 (s, C_F), 121.8 (s, C_I), 140.2 (d, C_G, $^1J_{PC}$ = 70 Hz), 149.2 (s, C_J), 152.2 (s, C_H). Anal. Calcd for $C_{25}H_{48}AsPSi_2$: C, 58.79; H, 9.47. Found: C, 57.95; H, 9.85. HRMS: calcd mol wt for $C_{25}H_{48}AsPSi_2$, 510.2248; found, 510.2256.

Preparation of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]P═SbCH(SiMe$_3$)$_2$ (14). DBU (0.9 g, 5.9 mmol)[56] was added dropwise to a solution of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]PH$_2$ (0.4 g, 1.4 mmol) and $(Me_3Si)_2CHSbCl_2$ (1 g, 2.8 mmol) in 18 mL of THF at 0 °C. The solution immediately became dark orange, and a white precipitate formed. Compound **14** was not successfully purified due to its instability in solution (see text) but was characterized by ^{31}P NMR spectroscopy (see Table I) and mass spectroscopy. HRMS: calcd mol wt for $C_{25}H_{48}PSbSi_2$, 556.2070; found, 556.2092.

Preparation of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]As═AsCH(SiMe$_3$)$_2$ (18). DBU (1.6 g, 10.5 mmol)[56] was added dropwise to a mixture of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]AsH$_2$ (0.97 g, 3 mmol) and $(Me_3Si)_2CHAsCl_2$ (1.52 g, 5 mmol) in 30 mL of THF. Purification by column chromatography (silica gel/*n*-hexane) gave, after recrystallization from *n*-pentane, 1.1 g (66%) of orange crystalline **18**, mp 110–113 °C. Anal. Calcd for $C_{25}H_{48}As_2Si_2$: C, 54.14; H, 8.72. Found: C, 55.83; H, 8.85. HRMS: calcd mol wt for $C_{25}H_{48}As_2Si_2$, 554.1726; found, 554.1795. ^1H NMR data for **18**: δ 0.2 (s, 18 H, H_A),[57] 1.35 (s, 9 H, H_C), 1.50 (s, 18 H, H_D), 3.00 (s, 1 H, H_B), 7.50 (s, 2 H, H_I). $^{13}C\{^1H\}$ NMR data for **18**: δ 1.1 (m, nonequivalent C_A),[57] 18.9 (s, C_B), 29.5 (s, C_C), 32.6 (s, C_E), 33.4 (m, nonequivalent, C_D), 34.7 (s, C_F), 122.2 (s, C_I), 144.0 (s, C_G), 149.6 (s, C_J), 152.5 (s, C_H).

Preparation of (Me$_3$Si)$_2$CHP═As[2,4,6(*t*-Bu)$_3$C$_6$H$_2$] (19). A mixture of [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]AsH$_2$ (0.97 g, 3 mmol) and $(Me_3Si)_2CHPCl_2$ (1.31 g, 5 mmol) in 30 mL of THF was treated with 1.6 g (10.4 mmol)[56] of DBU as described above. Purification by column chromatography (silica gel, *n*-hexane) gave, after recrystallization from *n*-pentane, 0.8 g (52%) of orange crystalline **19**, mp 118–120 °C. Anal. Calcd for $C_{25}H_{48}AsPSi_2$: C, 58.79; H, 9.47. Found: C, 58.24; H, 9.85. HRMS: calcd mol wt for $C_{25}H_{48}AsPSi_2$, 510.2248; found, 510.2256. ^1H NMR data for **19**: δ 0.20 (s, 18 H, H_A),[57] 1.40 (s, 9 H, H_C), 1.50 (s, 18 H, H_D), 3.20 (d, 1 H, H_B, $^2J_{PH}$ = 3.7 Hz), 7.55 (s, 2 H, H_I). $^{13}C\{^1H\}$ NMR data for **19**: δ 1.2 (m, nonequivalent C_A),[57] 17.6 (d, C_B, $^1J_{PC}$ = 169.7 Hz), 31.2 (s, C_C), 33.6 (s, C_E), 34.2 (m, nonequivalent C_D), 38.8 (s, C_F), 122.3 (s, C_I), 142.1 (d, C_G, $^2J_{PC}$ = 8.0 Hz), 148.9 (s, C_J), 153.7 (d, C_H, $^3J_{PC}$ = 6.4 Hz).

X-ray Crystallography. (Me$_3$Si)$_3$CP═PC(SiMe$_3$)$_3$ (2). Single crystals of **2** were grown from toluene solution at 0 °C. A suitable data crystal was sealed in a Lindemann capillary under a nitrogen atmosphere and mounted on an Enraf-Nonius CAD-4 diffractometer. Initial lattice parameters were determined with use of 25 reflections obtained from the SEARCH program[58] in the range 10° ≤ 2θ ≤ 20° and subsequently refined with use of higher angle data. Data were collected with graphite-monochromated radiation by use of the ω–2θ scan method with 1.0° ≤ 2θ ≤ 36.0°. The scan rate was varied according to a 20° min^{-1} prescan, the intensity of which was used to calculate final scan speeds, which varied from 20 to 0.8° min^{-1}. The scan range was determined by the equation scan range = $A + B \tan \theta$ with A = 0.8° and B = 0.2°. Aperture settings were determined in a similar manner with A = 4.0 mm and B = 1.0 mm. As a check on crystal stability, three reflections were measured periodically but showed only 3% overall intensity diminution.

One independent half of data was collected, giving a total of 2275 unique measured reflections, of which 2046 were considered observed ($I > 2\sigma(I)$). The data were corrected for Lorentz and polarization effects but not for absorption (μ = 3.1 cm^{-1}).

The structure was solved with use of MULTAN[59] in the triclinic space group $P\bar{1}$ and refined with use of the SHELX[60] program package on a UNIVAC 1100/60 computer. Difference Fourier maps were used to locate all non-hydrogen atoms, which were refined (full-matrix least squares)[61] with anisotropic thermal parameters. Hydrogen atoms were not located but were constrained to idealized geometries 0.96 Å from their respective carbon atoms with fixed isotropic temperature factors. In the final least-squares cycles, refinement converged smoothly to give final residuals R = 0.086, R_w = 0.086 with use of unit weights. No chemically significant peaks were observed in the final difference map. Complex neutral-atom scattering factors were used throughout.[62] Atomic positional parameters, bond lengths, and bond angles are given in tables in the text. Details of hydrogen atom positions, thermal parameters, and tables of observed and calculated structure factors are available as supplementary material.

[2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]P═AsCH(SiMe$_3$)$_2$ (12). Data were collected on an Enraf-Nonius CAD-4 diffractometer analogously to the method described for **2**. Relevant crystallographic information is collected in Table XI.

The structure was solved with use of a Patterson map, which located the As atom. Subsequent difference Fourier maps revealed the positions of all non-hydrogen atoms, and these were refined (full-matrix least squares) with anisotropic thermal parameters. Most hydrogen atoms were located and positionally refined with fixed isotropic temperature factors. Those not found were calculated and refined as described above. Structure solution and refinement were carried out with use of the Enraf-Nonius SDP Plus program package[63] on a PDP 11/44 computer system. Tables of hydrogen atom coordinates, thermal parameters, and observed and calculated structure factors are available as supplementary material.

[2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]As═AsCH(SiMe$_3$)$_2$ (18). The data collection procedures used were the same as for **2** and **12**. Relevant crystallographic information is collected in Table XI.

The two As atoms were located from a Patterson map. All non-hydrogen atoms were located from subsequent difference Fourier maps and refined with use of anisotropic thermal parameters. While **18** is almost isostructural with **12**, the crystal quality was inferior, leading to far fewer observed data for **18**. As a result of a low data:parameter ratio, the hydrogen atoms were not located with the exception of H01. Tables of atomic positional parameters, bond lengths, and bond angles are given in the text. Thermal parameters and tables of observed and calculated structure factors are available as supplementary material.

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Registry No. 1, 83466-54-0; **2**, 86120-22-1; **4**, 88765-98-4; **5**, 90507-73-6; **7**, 89746-77-0; **12**, 88652-82-8; **13**, 86509-03-7; **14**, 88652-83-9; **15**, 86528-35-0; **16**, 86528-36-1; **17**, 86528-37-2; **18**, 86528-38-3; **19**, 86746-78-1; [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]PH$_2$, 83115-12-2; [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]AsH$_2$, 86528-37-2; [2,4,6-(*t*-Bu)$_3$C$_6$H$_2$]PCl$_2$, 79074-00-3; $(Me_3Si)_3CPCl_2$, 75235-85-7; $(Me_3Si)_2CHPCl_2$, 76505-20-9; $(Me_3Si)_2CHAsCl_2$, 76505-21-0; $(Me_3Si)_2CHSbCl_2$, 86509-03-7; $AsCl_3$, 7784-34-1; AsF_3, 7784-35-2; $SbCl_3$, 10025-91-9; $(Me_3Si)_2CHCl$, 5926-35-2; 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$Li, 35383-91-6; $(Me_3Si)_3CLi$, 28830-22-0.

Supplementary Material Available: Tables of thermal parameters and observed and calculated structure factors for compounds **2**, **12**, and **18** (85 pages). Ordering information is given on any current masthead page.

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(58) A program that finds and centers reflections automatically for unit cell determination.

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(62) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104; "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. 3.

(63) SDP Plus package of programs.