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From multiple bonds to materials chemistry

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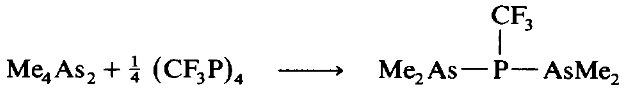
Introduction

My fascination with chemical research started in the year 1955 when, at the University of Manchester in England, I studied some thermochemical aspects of the Friedel–Crafts reaction. This was a sufficiently enjoyable experience that I decided to stay on at Manchester with the late Professor F. Fairbrother and completed my Ph.D. in 1958. The focus of my doctoral research was an examination of the Lewis acid behavior of niobium and tantalum halides together with a study of the reactivity of niobium and tantalum oxyhalides [1]. My years in Manchester provided me with a very valuable experience in handling air-sensitive materials and introduced me to modern physical methods such as X-ray diffraction.

In 1958, I was privileged to be offered a postdoctoral fellowship under the supervision of Professor H.H. Sisler at the University of Florida. It was here that I was first introduced to main-group chemistry—an interest that I have maintained to the present time. On the basis of my Floridian experiences with borazine chemistry [2], I was offered a position with Imperial Chemical Industries (Billingham Division) in England. One of the thrusts of the Exploratory Group in this era was the development of new inorganic polymers based on main-group ring systems.

In 1962 I accepted a junior faculty position at the University of Texas. One of the early projects in Austin was an examination of the structures and reactivities of ring and chain compounds in which group 15 elements are joined together [3]. I had the opportunity of delving deeper into this subject when I was fortunate enough to have a research leave with Professor Anton Burg at the University of Southern California in 1966. Here I was exposed to high vacuum line techniques and fluorocarbon ligand chemistry. It was during my sojourn in Professor Burg's laboratory that $(CF_3As)_4$, the first four-membered arsenic ring, was synthesized [4]. Upon returning to Texas, a similar approach was employed for the synthesis of $(C_2F_5P)_3$, the first three-membered phosphorus ring [5]. It was recognized that cyclopolyphosphines of the type $(RP)_n$ represent potential sources of phosphinidene (RP) units—the analogues of more familiar carbenes. For example, treatment of Me_4As_2 with the cyclotetraphosphine $(CF_3P)_4$ resulted in the formation of the first phosphorus–arsenic bond via the insertion of a trifluoromethylphosphinidene unit into an arsenic–arsenic bond [6] as shown below.



$$Me_4As_2 + \tfrac{1}{4}\,(CF_3P)_4 \longrightarrow Me_2As{-}\overset{\overset{\displaystyle CF_3}{|}}{P}{-}AsMe_2$$

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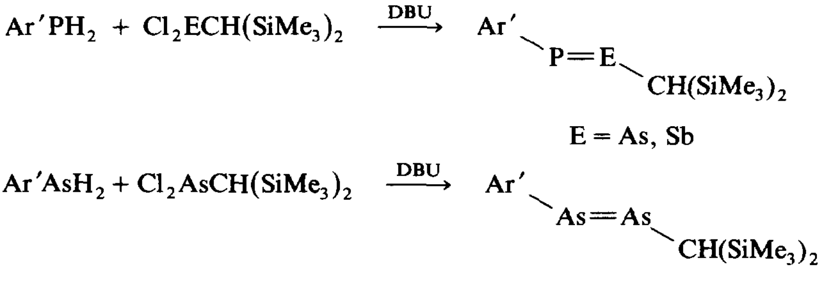
Cyclopolyphosphines and their heavier congeners also turned out to be interesting from the point of view of their electronic structures [7] and their behavior as ligands [8].

Multiple bonds

Our interest in Group 15/Group 15 bonds was rekindled in 1981 by the dramatic discovery of tetramesityldisilene, the first compound with silicon–silicon double bond, by West, Fink, and Michl [9]. It was obvious that if a phosphorus–phosphorus double bond were to be stabilized, even bulkier groups would be necessary. We therefore turned our attention to the very bulky tris(trimethylsilyl)methyl group, the usefulness of which has been elegantly demonstrated by Professor Eaborn and his colleagues [10]. Our plan was to prepare $(Me_3Si)_3CPCl_2$ and reductively couple this dichloride to produce the corresponding diphosphene:

$$(\mathrm{Me_3Si})_3\mathrm{CPCl_2} \xrightarrow{\mathrm{NaNap}} (\mathrm{Me_3Si})_3\mathrm{CP{=}PC(SiMe_3)_3}$$

However, prior to the publication of our observations [11], Yoshifuji and colleagues announced the synthesis of $(2,4,6\text{-}^t\mathrm{Bu_3C_6H_2})\mathrm{P{=}P}(2,4,6\text{-}^t\mathrm{Bu_3C_6H_2})$ via magnesium coupling of the corresponding bulky aryl dichlorophosphine [12]. It soon became obvious that new approaches to Group 15 multiple bonds were very desirable. The most useful of these turned out to be base-promoted dehydrohalogenation. This method, for example, permitted the syntheses of the first examples of compounds with unsupported phosphorus–arsenic [13], phosphorus–antimony [13], and arsenic–arsenic [14] double bonds as shown below:



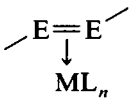
E = As, Sb

$\mathrm{Ar'} = 2,4,6\text{-}^t\mathrm{Bu_3C_6H_2}$

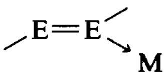
The best base for facilitation of these reactions was found to be DBU.

Fortunately, several of the new double-bonded compounds formed satisfactory crystals, thereby permitting X-ray crystal structure determinations [15]. The observed distances for P=P, P=As, and As=As bonds are 2.0, 2.1 and 2.2 Å, and thus 9–10% shorter than the corresponding single bonds. Most of the double-bonded compounds adopt a *trans* conformation and typically the R–E=E–R′ skeleton is planar. Molecular Orbital calculations at various levels of theory have been performed on the parent diphosphene [15]. The consensus view is that the HOMO is an n_+ phosphorus lone pair combination, and that the HOMO-1 is the phosphorus–phosphorus π-bond. The π-bonded description of the P–P bond is consistent with the exceptionally large chemical shift anisotropy observed in solid state ^{31}P NMR spectrum of 1,2-bis(2,4,6-^{t}butylphenyl)diphosphene [16]. A very recent deformation density study of the same compound revealed the presence of both phosphorus lone pair and π-bond electron density [17].

Interestingly, the first diphosphene complex, $(C_5H_5)_2Mo(\eta^2\text{-HPPH})$ was prepared several years prior to the isolation of double-bonded Group 15 compounds [18]. However, the availability of stable diphosphenes and their heavier congeners spurred on the coordination chemistry of these species. Fundamentally, five modes of coordination (**1**–**5**) are possible plus, of course, the possibility of incorporation of the RE=ER′ moiety into a cluster. Several groups have been active in this area and, in fact, all the foregoing modes of coordination have now been realized [15].



(1)



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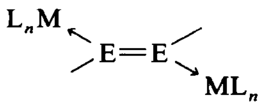

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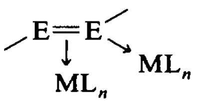

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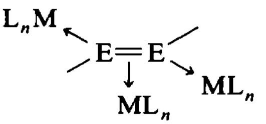
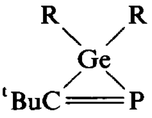


(5)

The presence of two lone pairs plus a double bond renders diphosphenes and heavier congeners reactive toward a wide variety of electrophiles such as O_2, S_8, halogens, and $HBF_4 \cdot OEt_2$ [15]. However, since such compounds also possess a relatively low-lying LUMO, they are also reactive toward nucleophiles such as H^- and alkyllithium reagents [19].

At this point, it is perhaps worth recalling that HC≡P, the first compound with a phosphorus–carbon triple bond, was prepared in 1961 [20] via the action of a carbon arc in an atmosphere of PH_3. The availability of the stable, substituted phosphaalkyne ^{t}BuC≡P (**6**) [21] has, however, prompted considerable interest in the use of this compound as a building block [22]. For example, the reaction of **6** with $[(Me_3Si)_2CH]_2Ge$ affords **7**, the first example of a phosphagermirene [23]. Curiously, the corresponding tin chemistry proceeds in a distinctly different fashion. Reaction



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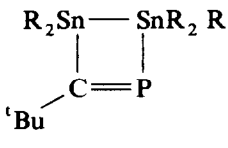
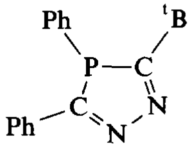


R = $(Me_3Si)_2CH$

(8)

of the $[(Me_3Si)_2CH]_2Sn$ monomer/dimer equilibrium mixture with **6** afforded **8**, a compound analogous to cyclobutene [24]. The reaction of **6** with Ph_2CN_2 resulted initially in a [2 + 3] cycloadduct which isomerized via un unprecedented 1,2-phenyl migration from carbon to phosphorus, thereby yielding **9** [25]. The reaction of **6** with $[(\eta\text{-}C_5H_5)_2Ti(CO)_2]$ afforded the novel heterocycle, **10**. Interestingly, the P–P distance in **10** is 0.09 Å shorter than that of a single bond, thus suggesting multiple bond character [26].



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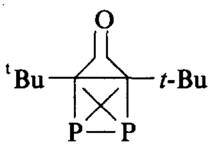
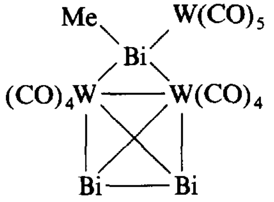


(10)

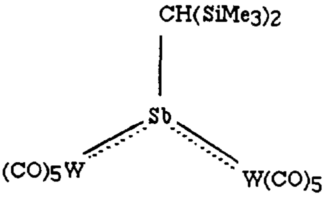
A logical outgrowth of the work on main-group/main-group multiple bonding was to explore the possibility of stabilizing compounds that feature multiple bonds between heavier Group 15 elements and transition metal fragments. One is aided greatly in this area by the isolobal principle [27], which emphasizes the similarities in the frontier orbitals of organic, main-group, and transition metal fragments. Some pertinent isolobal relationships are summarized in Table 1.

Our thrust into this area started with a study of the reactions of bulky Group 15 dihalides with organometallic anions. For example, the reaction of $(Me_3Si)_2CHBiCl_2$ with $K_2[W(CO)_5]$ produced the novel cluster **11** [28]. The bismuth–bismuth bond length of 2.795(3) Å corresponds to a bond order of approximately 2.0 and there is clearly an isolobal relationship between a Bi_2 molecule and an alkyne.



(11)

The reaction of $(Me_3Si)_2CHSbCl_2$ with $K_2[W(CO)_5]$ followed a different course to that of the bismuth analogue and resulted in the "open" stibinidene complex, **12** [29]. Like other "inidene" complexes of this type, **12** features a trigonal planar geometry at the Group 15 center and a modicum of metal–main-group multiple bonding [30]. Interestingly, the reaction of $(Me_3Si)_2CHSbCl_2$ with $Na_2[Fe(CO)_4]$ followed by treatment with $Fe_2(CO)_9$ resulted in **13**, the first example of a "closed"



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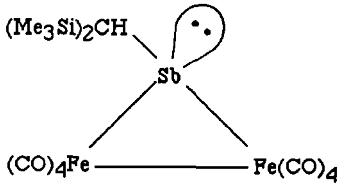


(13)

Table 1

Isolobal relationships

Main-group fragment		Organometallic fragment
R_2C R_2Si RN RP O S	$\underset{\circ}{\longleftrightarrow}$	$Cr(CO)_5$ $Mn(CO)_2(\eta\text{-}C_5H_5)$ $Fe(CO)_4$ $Co(CO)(\eta\text{-}C_5H_5)$ $Pt(PR_3)_2$ $Cr(CO)(NO)(\eta\text{-}C_5H_5)$
RC RSi N P	$\underset{\circ}{\longleftrightarrow}$	$Mo(CO)_2(\eta\text{-}C_5H_5)$ $W(O\text{-}^tBu)_3$ $Co(CO)_3$ $Mn(CO)_4$

inidene complex [29]. In terms of isolobal relationships, **12** is related to the allyl anion while **13** is analogous to cyclopropane. It occurred to us that the foregoing bonding dichotomy should also occur for fourteen- and fifteen-electron organometallic fragments. Indeed, treatment of 2,4,6-$^tBu_3C_6H_2PCl_2$ with the appropriate organometallic dianion results in the attachment of two $Mo(\eta\text{-}C_5H_5)(CO)_2$, $Co(CO)_3$, or $V(\eta\text{-}C_5H_5)(CO)_2$ moieties [31]. Each compound features a trigonal planar phosphorus atom and short metal–phosphorus distances.

Another type of main-group–transition metal multiple bond emerged from a study of the reaction of $K[Mo(\eta\text{-}C_5H_5)(CO)_3]$ with the phosphaalkene $(Me_3Si)_2C{=}PCl$. The resulting phosphavinylidene, $(Me_3Si)_2C{=}P{=}Mo(\eta\text{-}C_5H_5)(CO)_2$ possesses an almost linear C–P–Mo skeleton (178.3(2)°) and a rather short Mo–P bond distance (2.174(1) Å) [32]. The fact that the phosphavinylidene exhibits formal double-bonding to both carbon and molybdenum results in interesting reactivity patterns. In very recent work we have been able to isolate a compound with a phosphorus–metal bond order of three [33]. The linear terminal phosphinidene complex $[WCl_2(CO)(PMePh_2)_2(\equiv PAr')]$ ($Ar' = 2,4,6\text{-}^tBu_3C_6H_2$) was produced via cleavage of the phosphorus–carbon double bond of the phosphaketene $Ar'P{=}C{=}O$.

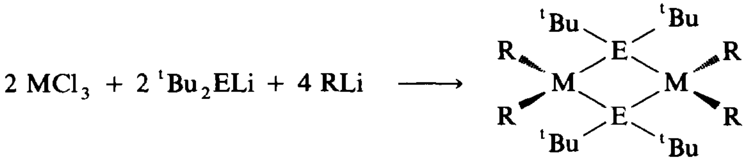
Materials science

The development of a concern with materials science can be traced to two main factors. One factor relates directly to the elegant work on bis(^{t}butyl)phosphido and arsenido chemistry by my colleague, Professor Richard Jones [34]. A logical extension of this work was to explore the usefulness of $^tBu_2E$ ligands in the context of main-group chemistry. We decided to undertake such studies collaboratively. Given the importance of III/V compound semiconductors, attention turned first to the bis(^{t}butyl)phosphido and arsenido chemistry of gallium and indium.

Interestingly, our materials science interests also relate to the concern with multiple bonds. Independently, Professor Power's group [35] and ours [36] reported the synthesis of diphospha- and diarsaboretanes. Such compounds can be regarded as head-to-tail dimers of boraphosphenes (R–B$\overset{\leftarrow}{=}$P–R′) and bora-arsenes (R–B$\overset{\leftarrow}{=}$As–R′) and indeed evidence for the former was found in a thermolysis study of a diphosphaboretane bearing very bulky substituents [37]. Interestingly, heavier congeneric compounds of the general type MeGaEH had been implied several years earlier in mechanistic studies of the thermal reaction of Me_3Ga with PH_3 or AsH_3 [38].

Thin films of gallium arsenide, indium phosphide and related ternary materials have been prepared by a variety of techniques including molecular beam epitaxy (MBE) and organometallic chemical vapor deposition (OMCVD). In its simplest form, the OMCVD method involves the thermal reaction of a Group 13 trialkyl with PH_3 or AsH_3 in the temperature range 600–700 °C. Environmental and safety concerns have arisen on account of the toxicity of PH_3 or AsH_3 and the pyrophoric nature of the Group 13 trialkyls. Moreover, the conventional OMCVD approach suffers from stoichiometry control problems and the relatively high reaction temperatures can promote interdiffusion of layers and dopants thereby preventing the achievement of sharp heterojunctions.

Professor Jones and I thought that some of the problems outlined above might be overcome by the use of single-source precursors of the general type ($L_nMEL'_n$) that feature the desired 1 : 1 stoichiometry of the Group 13 (M) and Group 15 (E) elements [39]. Our strategy was to cause the prevenient M–E bonds to be as strong as, or stronger than, any other bonds in the precursor by employing two-electron, two-center bonds rather than e.g. the donor–acceptor linkages found in adducts. Another design feature was the selection of ligands, L and L′, that are capable of thermal or photochemical elimination. Several compounds of the general type $(Me_2MEMe_2)_n$ (M = Al, Ga, In; E = P, As) had, in fact, been prepared in pioneering studies by Professor Coates and coworkers several years earlier [40]. However, in our first generation of precursors we opted to use ^tBu and ^iPr substituents because of their capability of facile alkene elimination. Treatment of $GaCl_3$ or $InCl_3$ with one equivalent of $^tBu_2ELi$ (E = P, As) and two equivalents of RLi (R = Me, ^nBu) in toluene at −78 °C affords phosphido- or arsenido-bridged dimers **16–21** in excellent yields [41].



14 M = Ga, E = P, R = Me
15 M = Ga, E = P, R = ^nBu
16 M = Ga, E = As, R = Me
17 M = Ga, E = As, R = ^nBu
18 M = In, E = P, R = Me
19 M = In, E = P, R = ^nBu
20 M = In, E = As, R = Me
21 M = In, E = As, R = ^nBu

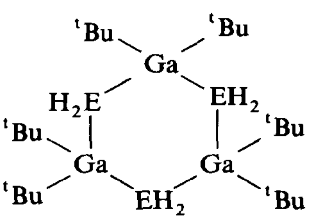
Compounds **14**, **16**, **18**, and **20** can also be made by methane elimination and redistribution reactions [41]. X-ray crystallographic studies reveal that e.g. **14** and **15** possess diborane-like skeletal structures. The geometries at Ga and As are approximately tetrahedral and the Ga–As distances are indicative of a bond order of unity. There is no evidence for Ga- - -Ga or As- - -As cross-ring interactions.

Similar structural features have been found for other Ga_2As_2 dimers [42] and analogous Ga–P [43] and In–P compounds [44].

The use of smaller substituents or heavier Group 13 or 15 elements results in trimer formation. Examples include $(Me_2InAsMe_2)_3$ [45] and $[Me_2InSb(^tBu)_2]_3$ [46]. The case of $[Me_2GaE(^iPr)_2]_x$ is particularly intriguing [47]. As prepared by salt-elimination methods, $(Me_2GaP\,^iPr_2)_3$ and $(Me_2InP\,^iPr_2)_3$ adopt distorted boat trimeric structures in the solid state. However, upon vacuum sublimation the trimers are converted into the corresponding dimers.

Deposition studies of the first generation precursors have focussed on $[Me_2GaAs(^tBu)_2]_2$ (**16**) and $[^nBu_2GaAs(^tBu)_2]_2$ (**17**). Both complexes are colorless, crystalline materials that exhibit short term stability in air. Preliminary evidence reveals that neither compound is highly toxic. OMCVD studies of **16** were carried out on a collaborative basis with Professor John Ekerdt using a specially designed cold wall reactor [48]. With saturator and reactor temperatures of 145 °C and 525 °C respectively, it was possible to achieve film growth rates of 0.75 μm/h as determined by profilometry. The XPS of GaAs films grown from **16** are indistinguishable from those of electronic grade samples. Moreover, within experimental error, the Ga : As mole ratios are 1 : 1 and no carbon peaks are detectable, thus implying that the carbon content is less than 1000 ppm. Examination of the SIMS spectra indicates that the carbon content of our films is comparable to that of commercial GaAs wafers. Initial X-ray diffraction studies of the GaAs films deposited on α-$Al_2O_3(0001)$ and GaAs(100) show very similar diffraction patterns to that of a GaAs(111) wafer. Pole figure analysis indicates that our films are highly (111) oriented in the sample plane, but are polygrained with the grains aligned cylindrically. Photoluminescence spectra (5 K) of the GaAs films deposited on α-Al_2O_3 exhibit the typical GaAs band gap, but reveal that the samples are degeneratively doped. Finally, since the volatile by-products of the deposition are methane and isobutylene, we conclude that the thermolysis of **16** proceeds via a β-hydride shift mechanism.

Since the ^{t}Bu substituent undergoes thermolysis by alkene elimination, it can be considered to be a "masked" hydrogen. There was obvious interest, therefore, in preparing hydrogen-substituted single source precursors since it was anticipated that they would possess even lower decomposition temperatures than the corresponding alkylated derivatives. These second generation precursors, **18** and **19**, were isolated from the reaction of $^tBu_3Ga$ with PH_3 or AsH_3 at low temperatures [49]. Interestingly, **18** adopts a planar structure in the solid state with the ^{t}Bu groups eclipsed above and below the molecular plane. A similar structure can be proposed for **19** on the basis of spectroscopic data. Thermal decomposition studies in the solid state show that **19** produces GaAs at 250 °C. Refluxing a toluene solution of **19** for 20 minutes resulted in the formation of amorphous GaAs containing trapped organic

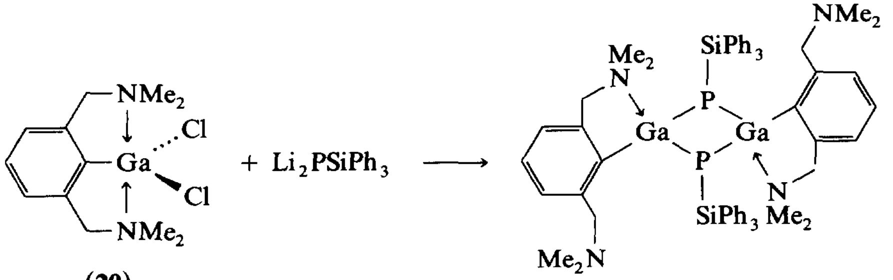


18 E = P **19** E = As

impurities. Of related interest are similar materials prepared by Theopold et al. via the reaction of $(Me_5C_5)_2GaAs(SiMe_3)_2$ with ^tBuOH [50].

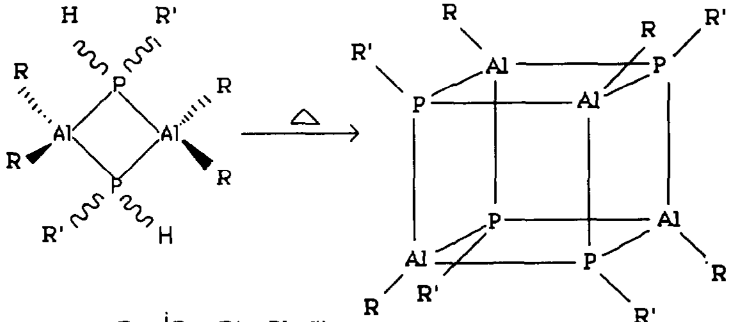
More recently, our attention has turned to compounds of empirical composition RMER′. Such compounds are of interest for both intrinsic and practical reasons. Theoretical interest stems from the potentially rich variety of structural forms and the possibility of novel bonding modes. Potential practical importance is associated with the possibility that such compounds might represent a third generation of single source precursors. Previous examples of compounds of the type $(RMER')_n$ had been confined to cases where M = B, Al and E = N [51]. We have recently been able to prepare compounds where both M and E are heavier main-group elements.

Our initial attempts to prepare the desired compounds were frustrated by the apparently high Lewis acidities of the products. Accordingly, it seemed appropriate to attempt to stabilize the products by Lewis base blocking. Treatment of Li[2,5-$\{Me_2NCH_2\}_2C_6H_3$] [52] with $GaCl_3$ in toluene afforded **20** which, in turn reacted with Li_2PSiPh_3 to produce **21** [53]. The central Ga_2P_2 core of **21** is planar and resides on a center of symmetry. The Ga–P bond length of 2.338(1) A is over 0.1 Å shorter than those found in dimers or trimers of the type RR′GaPR″R‴. It should be noted, however, that the phosphorus geometry is pyramidal, hence, if there is any delocalization in the Ga_2P_2 ring, it is much less than that in diazadiboretidenes which are therefore much closer analogues of cyclobutadiene.



(20)

(21)



R = ^iBu; R' = Ph3Si

(22)

(23)

The reaction of $^{i}Bu_2AlH$ with Ph_3SiPH_2 also proved to be interesting. The first product isolated, **22**, resulted from the elimination of molecular hydrogen at room temperature. However, refluxing **22** in toluene solution for 12 hours caused alkane elimination. An X-ray crystallographic study revealed that the product (**23**) possesses a cubane structure [54]. As in the case of the recently isolated tetraphosphacubanes [55,56] the cube of **23** is distorted in the sense that the internal bond angles at phosphorus are < 90% (av. 88.2(2)°). The average Al–P bond distance in the cubane (2.414(4) Å) is slightly less than those observed in dimers of the type $(R_2AlPR'_2)_2$. Preliminary thermolysis studies indicate that the new Al_4P_4 cubane represents a potentially interesting precursor to aluminum phosphide.

Acknowledgements

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