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The reaction of disilenes with P_4 and As_4

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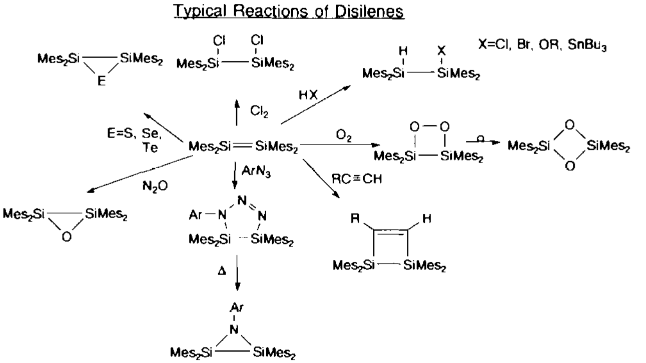
Abstract

Tetraaryldisilenes **1a–c** react with white phosphorus to give bicyclo[1.1.0] butane compounds **2a–c**. The more hindered disilene E-1,2-dimesityl-1,2-di-tert-butyldisilene (**1e**) reacts slowly with P_4 at 40 °C to give mainly a mixture of two diastereomeric intermediates with formula $Mes_4(tert\text{-}Bu)_4Si_4P_4$, **3** and **3′**, with small amounts of the *exo–endo* (**2e**) and *exo–exo* (**2e′**) isomers of the bicyclo[1.1.0]butane structure. At higher temperatures the intermediates are transformed into **2e** and **2e′** and simultaneously rearrangement of **2e** to **2e′** takes place. The X-ray crystal structure of the adduct **2e′**·$[W(CO)_5]_2$ was determined: it crystallized in the $C2/c$ space group, $Z=4$, with cell dimensions $a=18.616(4)$, $b=13.872(3)$, $c=16.815(3)$ Å and $\beta=109.95°$. Based on 2D NMR studies, structures are proposed for intermediates **3** and **3′**. Reaction of disilene **1a** with As_4 leads to a compound $Mes_8Si_4As_4$ with a tricyclic structure **7**, as well as a bicyclo[1.1.0]butane, **6**.

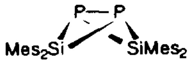
Introduction: a disiladiphosphabicyclobutane from the reaction of tetramesityldisilene with P_4

Since the discovery of disilenes in 1981, a number of chemical reactions of these multiply-bonded silicon compounds has been investigated [1, 2]. Some examples of 1,2-addition reactions of disilenes are shown in Scheme 1. Typically, disilenes react by 1,2 addition or by cycloaddition to give products in which the π bond between the silicon atoms is broken but the σ bond remains [3]. The reactions of disilenes therefore resemble those of olefins, except that disilenes are much more reactive.

As shown in Scheme 1, disilenes such as tetramesityldisilene (**1a**) react with elemental sulfur, selenium or tellurium to give products containing two silicon atoms and a chalcogen atom in a three-membered ring [4]. In 1989 we extended these studies to the Group 15 element phosphorus, as P_4. To our surprise, **1a** reacted with P_4 to give a disiladiphosphabicyclobutane (**2a**), with a novel butterfly-like structure [5]. The reaction with white phosphorus therefore differs from most other reactions of disilenes in that the σ Si–Si bond is broken as well as the π bond.



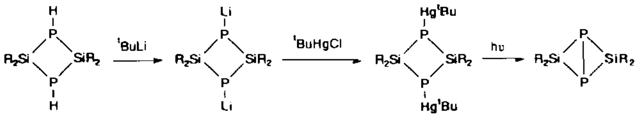
Scheme 1.



2a

A second, photolytic route to compounds with structures like **2a** has recently been described by Driess *et al.* [6] as shown in Scheme 2. The same group as also synthesized triphosphamonosilabicyclobutanes with analogous structures. Diphosphadiborabicyclobutanes with analogous structures have also been synthesized [7].

The butterfly bicyclobutanes have lone pairs on the phosphorus atoms, and so can serve as Lewis bases in further reactions, some of which lead to products having remarkable structures. With $W(CO)_5THF$, **2a** reacts to attach first one and then a second $W(CO)_5$ group, as



Scheme 2.

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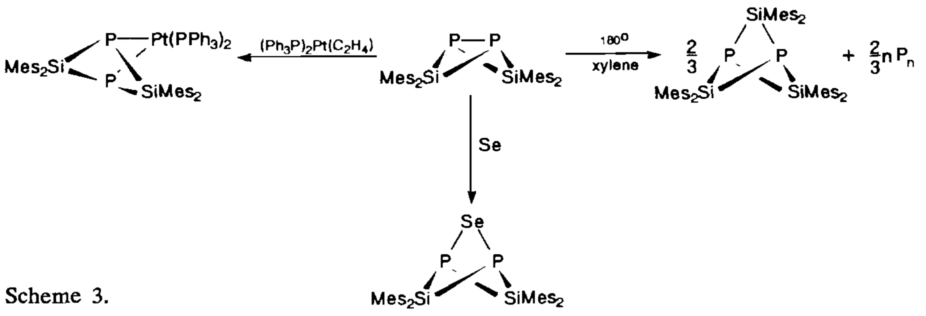
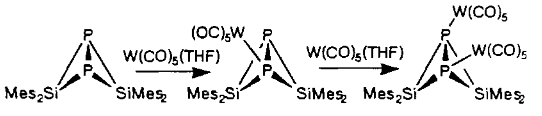


Scheme 3.

shown in eqn. (1) [5]. The P–P bond is retained in these tungsten complexes, but in reaction with $(Ph_3P)_2PtC_2H_4$ the P–P bond is broken, giving a phosphido complex with a propellane structure [8]. This unusual structure type is also obtained in the reaction of **2a** with elemental selenium. And most remarkably, thermolysis of **2a** at 180 °C gives only two products, red phosphorus and the symmetrical Si_3P_2 propellane (Scheme 3).

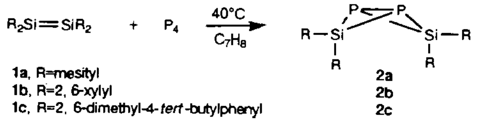


(1)

In this paper we will describe the reaction of P_4 with several other disilenes, leading in one case to the formation of intermediate compounds, and provide a preliminary account of the reaction of **1a** with As_4.

Reaction of P_4 with other disilenes

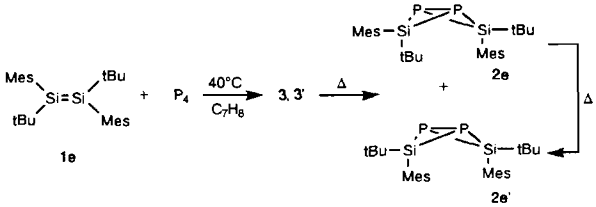
We anticipated that other disilenes might react with white phosphorus, and in fact tetra-2,6-xylyldisilene (**1b**) and tetrakis(2,6-dimethyl-4-tert-butylphenyl)disilene (**1c**) reacted similarly to **1a** to give the bicyclo[1.1.0]butane products, **2b** and **2c**. These reactions proceeded at 40 °C in toluene with no indication of the formation of detectable intermediates (eqn. (2)). The highly hindered tetrakis(2,4,6-tri-iso-propylphenyl)disilene (**1d**), however did not react with P_4, even after 3 days at 120 °C in toluene.



(2)

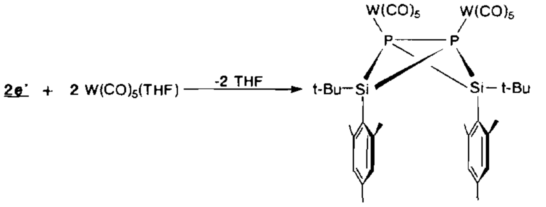
In other reactions, E-1,2-dimesityl-1,2-di-tert-butyldisilene (**1e**) is more reactive than **1d**, but less so than **1a**. Similar **1e** is intermediate in its reactivity toward P_4. The reaction of **1e** with P_4 in toluene-d_8 at 40 °C proceeded slowly over 12 h, producing a mixture of products. In the mixture were identified small amounts of two [1.1.0] bicyclobutanes, the tBu–tBu *exo–endo* product **2e** and the rearranged tBu–tBu *exo–exo* compound **2e′**. These compounds can easily by distinguished by symmetry, since **2e** has two different ^1H resonances for the tert-butyl protons while **2e′**, which contains a symmetry plane, has only one.

The major product in the reaction of **1e** and P_4, however, were compounds with a more complex structure, each containing four silicon and four phosphorus atoms. These compounds, **3** and **3′**, serve as intermediates in the reaction leading to **2e** and **2e′**. Further heating of the reaction mixture to 130 °C led to gradual disappearance of **3**,**3′** and formation of **2e**,**2e′** (eqn. (3)). At the same time, rearrangement of **2e** into the *exo–exo* isomer **2e′** took place. After 3 days at 130 °C, the reaction contained **2e** and **2e′** in a ratio of 1:4 by ^{31}P NMR, with only traces of **3**,**3′** remaining. This is the first example of a disilene reaction in which the major product is formed with inversion of configuration at silicon.



(3)

Our earlier studied showed that **2a** reacts with $W(CO)_5(THF)$ to form the Lewis acid–base adducts $\mathbf{2a}\cdot W(CO)_5$ and $\mathbf{2a}\cdot[W(CO)_5]_2$ (**4**) [5]. Compound **2e′** reacts similarly (eqn. (4)); an X-ray crystal structure study was carried out for the complex $\mathbf{2e'}\cdot[W(CO)_5]_2$ (Table 1). A thermal ellipsoid diagram for **5** is shown in Fig. 1, along with important bond lengths and angles. The structure of **5** is similar to that previously reported for **4**. The P–P distances, 234 pm for **4** and 232 pm



(4)

5

TABLE 1. Crystal and refinement data

Formula	$C_{36}H_{40}O_{10}P_2Si_2W_2$
Color, habit	orange plates
Crystal size (mm)	0.10×0.24×0.30
Crystal system	monoclinic
Space group	$C2/c$
Cell dimensions	
a (Å)	18.616(4)
b (Å)	13.872(3)
c (Å)	16.815(3)
β (°)	109.95(3)
V (Å^3)	4081.7(14)
Z	4
Formula weight	1118.5
D_{calc} (g/cm^3)	1.820
Absorption coefficient (cm^{-1})	5.821
Radiation	Mo Kα (λ=0.71072 Å)
Temperature (K)	295
Monochromator	highly oriented graphite crystal
2θ Range (°)	3.0–50.0
Scan type, range (°)	Wyckoff, ω 0.60
Scan speed (°/min)	variable; ω 2.00–12.00
Background	2 measurements for 25% of total scan time
Reflections collected	4724
Independent data	3594 (R_{int}=7.14%)
Observed data	2909 ($F > 4.0\sigma(F)$)
Hydrogen atoms	riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0006F^2$
R_1, R_w (obs. data)	R=3.42%, R_w=4.11%
Goodness-of-fit	1.14
Largest and mean Δ/σ	0.002, 0.000
Data-to-parameter ratio	12.3:1
Largest difference peak and hole (e/Å^3)	0.88 and −2.64

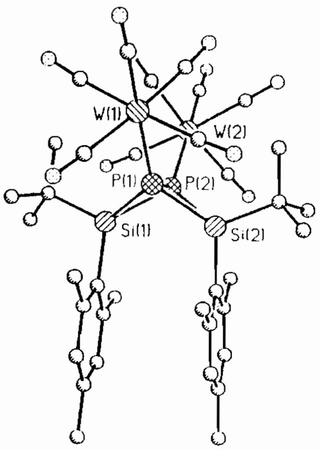


Fig. 1. Structural diagram for **5** from X-ray diffraction. Important bond lengths (pm) and angles (°): P–P 231.8(1), Si–P 226.4(1), 222.5(1), P–W 255.6(1), P–Si–P 62.2(1), Si–P–P 59.7(1), Si–P–P 89.1(1), interplane SiPP–SiPP 110.0(1). Hydrogen atoms have been omitted for clarity.

in **5**, are both somewhat longer than the normal distance of ~222 pm for diphosphanes [9]. The structures of **4** and **5** differ in the torsional angles between the P–W vectors, which are 30.9° for **4** but only 2.6° for **5**. The small W–P–P–W torsional angle in **5** may reflect steric interaction between the *exo* tert-butyl and the $W(CO)_5$ groups.

Compounds **4** and **5** also have quite similar NMR properties. Both compounds show rather low values for $^1J(^{31}P–^{183}W)$ of 129.7 (**4**) and 134.6 (**5**) Hz, consistent with a smaller s-orbital contribution from phosphorus than in typical phosphorus–transition metal complexes [10]. Similar $^1J(^{31}P–^{183}W)$ values have been previously observed in small ring systems [11] and are in accordance with MO calculations indicating that bridgehead P atoms in di-, tri- and tetraphosphabicyclo[1.1.0]butanes possess donor orbitals with very high p-character [12].

NMR and structure of intermediates 3 and 3′

The formula of intermediates **3** and **3′** was determined by FAB-MS which gave an $[M+1]$ parent peak at $m/z = 941$, corresponding to $Mes_4(t\text{-}Bu)_4P_4Si_4$. Elucidation of the structure of **3** and **3′** posed difficulties, however, because we were unable to crystallize either compound in pure form for X-ray analysis. Our structural study was therefore limited to NMR spectroscopy. ^{31}P NMR resonances are given in Table 2.

The ^{31}P NMR spectrum of the reaction mixture of **1e** and P_4 after 12 h at 40 °C showed two singlets with ^{29}Si satellites, representing the bicyclobutanes **2e** ($\delta = -313.30$ ppm) and **2e′** ($\delta = -350.30$). In addition, a complex spectrum exhibiting extensive $^{31}P–^{31}P$ coupling appears between −165 and −210 ppm (Fig. 2). These multiplets, as will be shown, are due to two asymmetric molecules (diastereomers), each present as a racemic mixture of enantiomers.

The sample was first analyzed by performing a two-dimensional homonuclear ^{31}P J-resolved spectrum over the multiplet region (Fig. 3). It is evident by looking down the F2 dimension that eight magnetically non-equivalent nuclei are responsible for the spectrum in

TABLE 2. ^{31}P NMR Resonances for **3**, **3′**

	d (ppm)
P^1	−168.26
P^2	−171.35
P^3	−172.78
P^4	−180.19
P^5	−184.96
P^6	−185.41
P^7	−195.87
P^8	−206.68

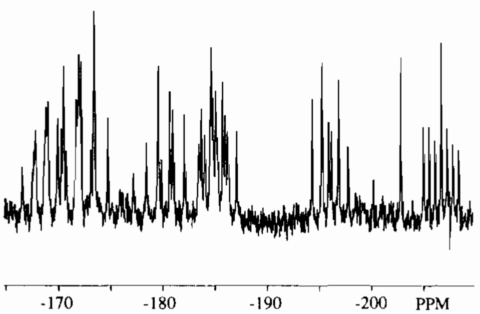


Fig. 2. ^{31}P NMR spectrum of intermediates **3** and **3′**. The single peak at −203 ppm is an impurity.

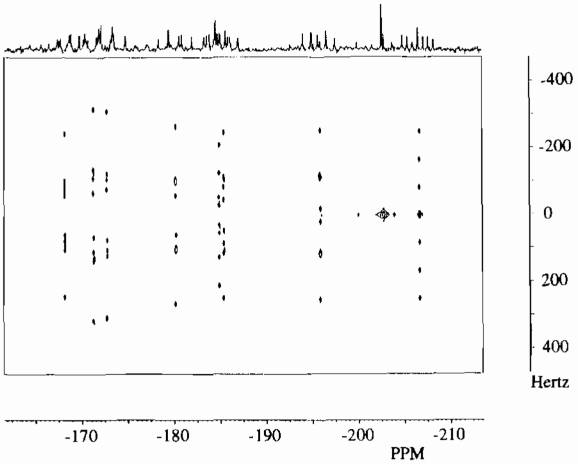
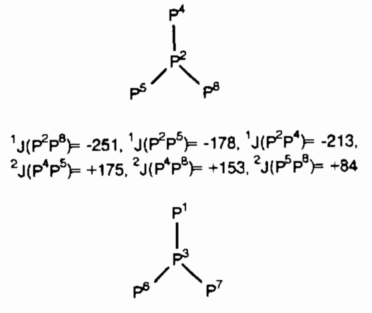


Fig. 3. Homonuclear two-dimensional *J*-resolved spectrum ^{31}P of the multiplets shown in Fig. 2.

Fig. 2. Since spectra such as these containing non-first couplings will be distorted, the individual coupling patterns for each resonance were only used as guides.

The spectrum shown in Fig. 2 could also be simulated by computer as two independent spin systems, each containing four chemically non-equivalent ^{31}P nuclei. Each group has three large negative couplings which must be due to $^{1}J(^{31}P–^{31}P)$, as well as three positive, longer range $^{n}J(^{31}P–^{31}P)$ couplings. The latter were also large in magnitude, indicating that $n=2$. Intermediates **3** and **3′** therefore each have a phosphorus connectivity resembling a Mercedes star, as shown in Fig. 4. The fact that the absolute values of ^{1}J and $^{2}J(^{31}P–^{31}P)$ coupling constants are quite similar for the two compounds leads us to conclude that **3** and **3′** are diastereomers.

The connectivity results of the computer simulation were confirmed by performing a COSY-45 spectrum on the reaction mixture (Fig. 5). This NMR experiment not only gives information about coupled nuclei, but also about the signs of the various coupling constants [13]. Since $^{1}J(^{31}P–^{31}P)$ are known to be negative [14] and longer range couplings between phosphorus nuclei are positive, it is possible to determine the connectivity based on the direction of the ‘tilts’ of the various correlations. It has been observed that $^{1}J(^{31}P–^{31}P)$ couplings give a tilt in a direction perpendicular to the diagonal while longer range couplings have a tilt in a parallel direction. In each instance the tilt of the observed correlation matched the prediction of the computer simulation.



$^{1}J(P^2P^8)$= -251, $^{1}J(P^2P^5)$= -178, $^{1}J(P^2P^4)$= -213,
$^{2}J(P^4P^5)$= +175, $^{2}J(P^4P^8)$= +153, $^{2}J(P^5P^8)$= +84

$^{1}J(P^1P^3)$= -186, $^{1}J(P^3P^6)$= -214, $^{1}J(P^3P^7)$= -245,
$^{2}J(P^1P^6)$= +176, $^{2}J(P^1P^7)$= +153, $^{2}J(P^6P^7)$=+138

Fig. 4. Phosphorus connectivity and coupling constants (in Hz) for the intermediates **3** and **3′**.

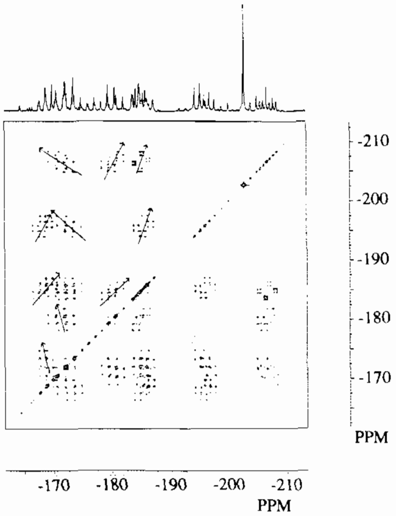
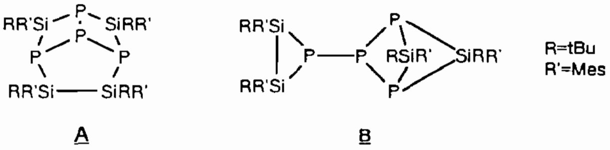


Fig. 5. COSY-45 spectrum of the multiplet region form Fig. 2 with arrows showing the direction of the tilts for various cross-peaks. Tilts with a positive slope represent long range $^{1}J(^{31}P–^{31}P)$ coupling and tilts with negative slope represent $^{2}J(^{31}P–^{31}P)$ coupling.

From the formula as well as the phosphorus connectivity determined by the NMR experiments, only two structural isomers appeared possible, shown below as **A** and **B**. Either **A** and **B** could exist as a mixture



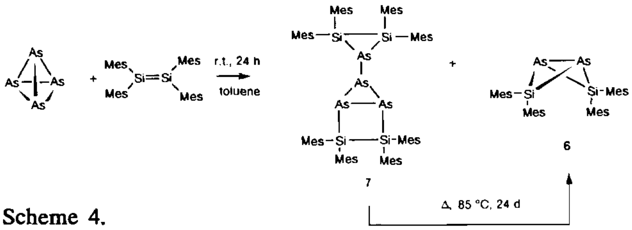
of two stereoisomers with the t-butyl groups on the two silicon atoms in the bicyclopentane ring having the *endo-endo* and *endo-exo* configurations. Now if the t-butyl groups on the upper silicon atoms are in a *trans* relationship to one another (especially likely for structure **B**) the two phosphorus atoms in the bicyclopentane ring are disastereotopic and hence magnetically inequivalent. Four different ^{31}P NMR signals are then expected for each diastereomer, or eight resonances for **3** and **3'** together.

Although structures **A** and **B** are both consistent with the NMR evidence, structure **B** seemed more likely because it has a logical pathway for fragmentation to **2e** and **2e'**, through breaking of two P–P bonds. A more involved pathway would be required for fragmentation of structure **A** to give **2e** and **2e"**. Further consideration of the mechanism is best postponed until the end of following section.

Reaction of tetramesityldisilene with As_4

Since such interesting and unusual products were obtained in the reactions of silenes with phosphorus it seems worthwhile to attempt similar reactions with arsenic. Ordinary gray arsenic was unreactive with disilene **1a**, even after long heating. However As_4, prepared by the sublimation of metallic arsenic into toluene [15], reacted with **1a** at a similar rate to P_4.

In the reaction of **1a** with As_4 two products were formed in a ratio of about 3:1, which together made up more than 90% of the reaction mixture (small amounts of minor products were also formed). Of the two major products the one initially present in a smaller amount had composition $Mes_4Si_2As_2$, and showed ^1H and ^{29}Si NMR spectra similar to those of **2a**. As shown in Scheme 4, we assign to this compound the bicyclobutane structure **6**.



Scheme 4.

The principal product, **7**, had the composition $Mes_8Si_4As_4$. Crystals of **7** were grown from warm toluene and analyzed by X-ray crystallography. The results, which will be described in detail elsewhere, establish the connectivity beyond doubt. Compound **7** has the tricyclic structure shown in Scheme 4. Note that the structure of compound **7** is related to, but distinctly different from, structure **B** proposed for the phosphorus compounds **3** and **3'**. Just as **3** and **3'** undergo thermal conversion to **2e** and **2e'**, **7** fragments form **6** when heated. A solution of **7** kept at 85 °C for 24 days was completely (>98%) converted to **6**.

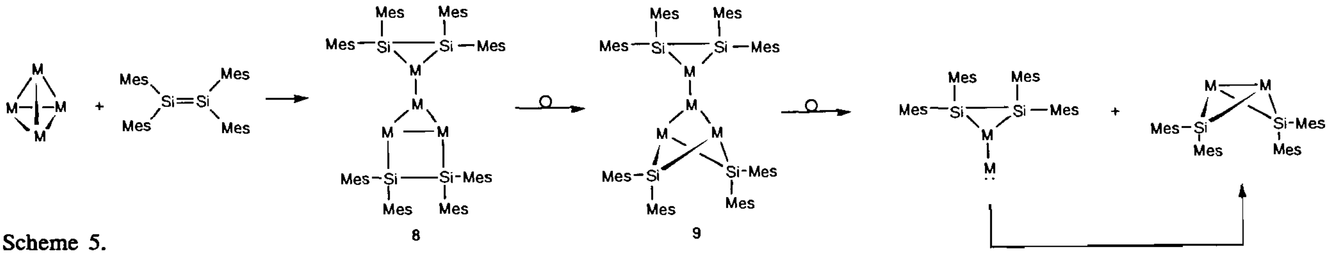
What is the relationship between the disilene reactions with P_4 and As_4? Many additional experiments are called for, but tentatively we propose that both **3,3'** (structure **B**) and **7** may lie on a similar reaction coordinate, shown in Scheme 5. The initial reaction with M_4 might lead to a structure of type **8**, which could possibly result from the breaking of two bonds in the M_4 tetrahedron followed by trapping of the intermediate by two disilene molecules. Rearrangement could then take place to the more open structure **9**, which could ultimately fragment into two bicyclobutane-type molecules, perhaps by the pathways shown. It is only necessary than to suppose that in the arsenic reactions, **8** is stable and can be isolated, while in the phosphorus series structure **9** is the more stable intermediate and so is the one observed.

Experimental

General procedures

All reactions were done under an atmosphere of dry nitrogen or argon. Solvents were distilled from Na/benzophenone and stored in a dry box or used immediately. All glassware was oven dried at 130 °C. Mass spectra were obtained with a Kratos MS-80 mass spectrometer (El) or sent to the University of Illinois for FAB and FD ionization.

^1H NMR spectra were recorded on a Bruker WP-200 and ^{31}P and ^{29}Si NMR were determined on a Bruker AM-360 (145.79 and 71.55 MHz, respectively). ^{29}Si NMR spectra were acquired using the INEPTRD



Scheme 5.

(INEPT with refocussing for ^{1}H decoupled spectra) pulse sequence. The two-dimensional homonuclear *J*-resolved spectrum was acquired with a 4 s relaxation delay, SI2 = 2K, SI1 = 256W, TD2 = 2K, TD1 = 128W, NE = 128 and NS = 32. The COSY-45 spectrum was acquired with a 4 s relaxation delay, SI2 = 1K, SI2 = 512W, TD2 = 1K, TD1 = 256W, NE = 256 and NS = 32. All two-dimensional spectra were processed with a squared cosine curve in both dimensions (WDW1 = Q, WDW2 = Q, SSB1 = 2, SSB2 = 2). The processed homonuclear *J*-resolved spectrum was symmetrized and tilted and the processed COSY-45 spectrum was symmetrized with the appropriate software. The ^{31}P NMR spectra of **3** and **3′** were simulated with the use of the PANIC85 program (Bruker). Initial choices of shifts and coupling were refined by iteration. The final parameters gave a fit to within 1.5% r.m.s.

*1,3-Diphospha-2,4-disilabicyclo[1.1.0]butanes (**2a–c**)*

A solution of Mes_4Si_2, **1a** [16] (500 mg, 0.94 mmol) in toluene (10 ml) was treated with white phosphorus (58.2 mg, 0.47 mmol) and the solution was stirred for 24 h at 40 °C. During this time, the orange solution gradually decolorized to a clear pale yellow. The solution was concentrated to *c.* 5 ml, benzene (5 ml) was added and 2a was recrystallized from the hot (60 °C) solvent mixture as a pale yellow powder (516 mg, 87%): m.p. = 217–218 °C. ^{1}H NMR (C_6D_6, 300 K): δ 1.98 (s, 6H, *p*-Me), 2.09 (br. s, 6H, *p*-Me), 2.46 (s, 12H, *o*-Me), 2.82 (s, 12H, *o*-Me), 6.31 (s, 4H, $C_6H_2Me_3$), 6.68 (s, 4H, $C_6H_2Me_3$). ^{29}Si{^{1}H} NMR (INEPT-pulse sequence, C_6D_6): δ −49.50 (t, $|^{1}J$(Si–P)$|$ = 77 Hz). ^{31}P{$_{1}$H} NMR (C_6D_6): δ −324.0 (s). HRMS (El) *m/z* calc. (M^+) 594.2456, found 594.2453 (23%).

In the same manner, 500 mg **1b** (1.05 mmol) and **1c** (0.72 mmol) were reacted with P_4 (68 mg, 0.53 mmol or 46 mg, 0.36 mmol, respectively) to yield 463 mg **2b** (82%) and 405 mg **2c** (74%).

3b: ^{1}H NMR (C_6D_6, 300 K): δ 2.38 (s, 12H, *o*-Me), δ 2.76 (s, 12H, *o*-Me), 6.47–7.04 (m, 12H, ArH). ^{29}Si{^{1}H} NMR (INEPT pulse sequence, C_6D_6): δ −48.76(t), $|^{1}J$(SI–P)$|$ = 78.6 Hz. ^{31}P{^{1}H} NMR (C_6D_6): δ: −320.5. HRMS (El) *m/z* calc. (M^+) 538.1831, found 538.1847 (51%).

2c: ^{1}H NMR (toluene-d_8, 300 K): δ 1.23 (s, 18H, tBu), 1.27 (s, 18H, t-Bu), 2.44 (s, 12H, *o*-Me), 2.82 (s, 12H, *o*-Me), 6.68 (s, 4H, ArH), 6.99 (s, 4H, ArH). ^{29}Si{^{1}H} NMR (INEPT pulse sequence, toluene-d_8): δ −49.8(t), $|^{1}$J(Si–P)$|$ = 76.4 Hz. ^{31}P{^{1}H} NMR (toluene-d_8): δ −324.6, HRMS (El) *m/z* calc. (M^+) 762.4335, found 762.4327 (10%).

*Reaction of **1e** with P_4 at 40 and 120 °C*

A solution of 180 mg **1e** (0.44 mmol) in 1 ml toluene-d_8 was reacted with 28 mg P_4 (0.22 mmol) at 40 °C for 12 h in a sealed NMR tube. This produced about 8% **2e** and 15% **2e′** by ^{31}P NMR along with reaction intermediates **3**, **3′**.

2e: ^{31}P{^{1}H} NMR (toluene-d_8): δ −313.30 ppm.

3: $P^2(P^8)(P^5)(P^4)$ ^{31}P{^{1}H} NMR (toluene-d_8): δ −171.35 (P^2,m: $^{1}J(P^2–P^8)$ = −251 Hz, $^{1}J(P^2–P^5)$ = −178 Hz $^{1}J(P^2–P^4)$ = −213 Hz), −180.19 (P^4, m; $^{2}J(P^4–P^5)$ = 176 Hz, $^{2}J(P^4–P^8)$ = 153 Hz), −184.96 (P^5, m; $^{2}J(P^5–P^8)$ = 83.6), −206.68 (P^8, m).

3′: $P^3(P^7)(P^6)(P^1)$ ^{31}P{^{1}H} NMR (toluene-d_8): δ −168.26 (P^1, m: $^{1}J(P^1–P^3)$ = −186 Hz, $^{2}J(P^1–P^6)$ = 176 Hz, $^{2}J(P^1–P^7)$ = 153 Hz), δ −172.78 (P^3, m; $^{1}J(P^3–P^6)$ = −213 Hz, $^{2}J(P^3–P^7)$ = −245 Hz), δ −185.41 (P^6, m; $^{2}J(P^6 – P^7)$ = 138 Hz), δ −195.87 (P^7, m). MS [FAB, 3-$NO_2(C_6H_4)CH_2OH$ matrix]: *m/z* 941 (3%, $[M+1]^+$, 910 (1%, $[M-2Me+1]^+$), 119 (100%, Mes^+).

Increasing the heat to 120 °C for three days gave **2e′** in 80% yield by ^{31}P NMR.

2e′: ^{1}H NMR (toluene-d_8, 300 K): δ 1.15 (s, 18H, tBu), 2.11 (s, 6H, *p*-Me), 2.46 (s, 12H, *o*-Me), 6.26 (s, 4H, $C_6H_2Me_3$). ^{29}Si{^{1}H} NMR (INEPT pulse sequence, toluene-d_8): δ −19.9(t), $|^{1}J$(Si–P)$|$ = 77.8 Hz. ^{31}P{^{1}H} NMR (toluene-d_8): δ −350.3. HRMS (El) *m/z* calc. (M^+) 470.2144, found 470.2146 (26%).

*Synthesis of **2e′** · [W(CO)$_5$ (**5**)*

The reaction mixture from above was added to a freshly prepared solution of 350 mg $W(CO)_5(THF)$ (1.0 mmol) in THF and stirred at room temperature overnight. After removal of solvent, the residue was recrystallized from benzene giving 165 mg **5** as orange plates. ^{1}H NMR (toluene-d_8, 300 K): δ 1.28 (s, 18H, tBu), 1.89 (s, 6H, *p*-Me, 2.37 (s, 12H, *o*-Me), 6.19 (s, 4H, ArH). ^{19}Si{^{1}H} NMR (INEPT pulse sequence, toluene-d_8): δ −30.38 (t, $^{1}J(^{31}P–^{29}Si)$ = 49.5 Hz). ^{31}P{^{1}H} NMR (toluene-d_8): δ −260.12 (s, $[^{1}J(^{31}P–^{183}W) + {}^{2}J(^{31}P–^{29}Si)]$ = 134.6 Hz). MS (FD, 3mA) *m/z* 1118 (10%, M^+).

*Synthesis of **7***

Tetramesityldisilene (400 mg, 0.93 mmol) was added to 120 ml of a toluene solution of As_4 (excess) in a drybox. The solution immediately turned orange. After sitting in the box for 24 h, the toluene was removed under vacuum. The residue was redissolved in toluene and decanted to remove excess arsenic, present as a black precipitate. The toluene solvent was then stripped, leaving an orange residue. Proton NMR of this orange residue showed about a 3:1 ratio of compounds **7** and **6**.

The residue was transferred to a glass frit and washed with hexane, leaving a light yellow solid on the glass frit (200 mg, 32%). The light yellow solid was identified as **7**. ^{1}H NMR (200 MHz, C_6D_6): δ 1.99–2.63 (multiplet, 72H, *o*-CH_3, *p*-CH_3), 6.58, 6.61, 6.65, 6.82 (16H, Ar–H).

$^{29}\mathrm{Si}\{^1\mathrm{H}\}$ (INEPT, 99.4 MHz, C_6D_6): δ -6.6, -64.0. MS (FD), m/z mass calc. for $^{12}C_{72}{}^1H_{88}{}^{28}Si_4{}^{75}As_4$ 1364.283, found 1364.3. The orange mother liquor contained a mixture of products, of which compound **6** was the main component; compound **6** was however not isolated from this mixture.

Synthesis of 2.2.4.4-tetramesityl-1,3-diarsa-2,4-disilabicyclo[1.1.0]butane (6)

Compound **7** (15 mg) in 2 ml of benzene-d_6 was placed in an NMR tube and heated at 85 °C; the reaction was followed by ^{1}H NMR. After 24 days, compound **7** was almost completely converted to a yellow compound, identified as **6**: ^{1}H NMR (200 MHz, C_6D_6): δ 2.01 (s, 6H, p-CH_3), 2.05 (s, 6H, p-CH_3), 2.43 (s, 12H, o-CH_3), 2.77 (s, 12H, o-CH_3), 6.35 (s, 4H, Ar–H), 6.68 (s, 4H, Ar–H). $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ (INEPT, 99.4 MHz, C_6D_6): δ -35.1. MS (30 eV), m/z (relative intensity) 682 (M^+, 94.3), 487 (M^+ $-$Mes $-$As $+1$, 6.3), exact mass calc. for $^{12}C_{36}{}^1H_{44}{}^{28}Si_2{}^{75}As_2$ 682.1413, found 682.1420.

Crystal structure determination of 5

X-ray diffraction was carried out on a Siemens R3m/v diffractometer with Mo Kα radiation. The structure was solved by direct methods using Siemens SHELXTL PLUS (VMS) and refined by full-matrix least-squares to final values of $R = 0.0458$, $R_w = 0.0437$. Additional information about the data collection is given in Table 1.

Supplementary material

Tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, H-atoms coordinates and isotropic displacement coefficients, 5 pages; and structure factors, 13 pages are available from the authors on request.

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