Specific insertion reactions of a germylene, stannylene and plumbylene into the unique P–P bond of the hexaphospha-pentaprismane cage, $P_6C_4{}^tBu_4$: Crystal and molecular structures of $P_6C_4{}^tBu_4ER_2$ (E = Ge, Sn, R = $N(SiMe_3)_2$; E = Pb, R = $(C_6H_3(NMe_2)_2$ -2,6)†

Mahmoud M. Al-Ktaifani, Peter B. Hitchcock, Michael F. Lappert, John F. Nixon* and Philip Uiterweerd

Received 11th January 2008, Accepted 4th March 2008
First published as an Advance Article on the web 4th April 2008
DOI: 10.1039/b800458g

Treatment of the cage compound $P_6C_4{}^tBu_4$ with $M\{N(SiMe_3)_2\}_2$ (M = Ge or Sn) or $Pb(C_6H_3(NMe_2)_2$-2,6) at room temperature results in their specific insertion into the P–P bond connecting the two 5-membered $P_3C_2{}^tBu_2$ rings. The products were fully characterised by multinuclear NMR spectroscopy and single crystal X-ray diffraction studies.

Introduction

Organo-phosphorus cage compounds have received considerable attention in recent years, the two major synthetic routes involving oxidative coupling of the polyphospholyl anions $P_nC_nR_{5-n}$ (n = 2, 3) and thermal or metal-mediated oligomerisation of phosphaalkynes, P≡CR, (R = Bu^t).[1,2] Cages involving tetramers, pentamers and hexamers of P≡CBu^t are shown in Fig. 1 and cages containing one or more additional hetero-atoms such as antimony,[3] silicon,[4] germanium,[4] sulfur,[5] selenium[5] and tellurium[5] are shown in Fig. 2.

The chalcogen substituted organo-phosphorus systems $P_6C_4{}^tBu_4E$ (E = S, Se Te) were easily prepared as shown in Fig. 3, by an unusually facile and specific insertion of the chalcogen into the P–P bond joining the two 5-membered rings of the hexaphospha-pentaprismane **1**.[5] Theoretical calculations on $P_6C_4H_4$, at the HF/6-31G*//B3LYP/6-31G level, show that the central P–P bond is not only involved in both the HOMO and LUMO orbitals. but also in HOMO − 1, strongly suggesting that this bond is most likely to be involved in bond cleavage reactions of **1**.

It was therefore of interest to examine the generality of this type of specific insertion reaction, by studying the interaction of **1** with other iso-electronic species such as germylenes, stannylenes and plumbylenes, MR_2 (M = Ge, Sn or Pb).

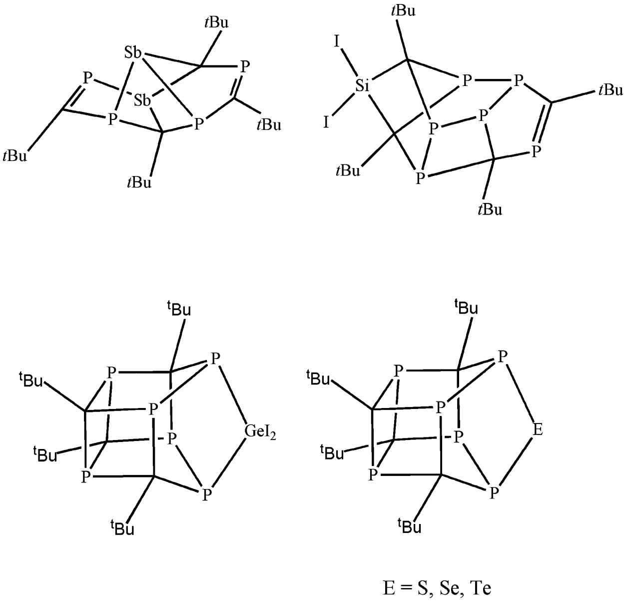


Fig. 2 Some organophosphorus cages containing other heteroatoms.

Results and discussion

Treatment of $P_6C_4{}^tBu_4$ **1** with the stable germylene and stannylene $M\{N(SiMe_3)_2\}_2$, (M = Sn or Ge), or the plumbylene $PbAr_2$ (Ar = 2,6-$(NMe_2)_2C_6H_3$)[6,7] in hexane at room temperature gave the expected products **2**, **3** and **4** *via* insertion of the MR_2 fragment into the unique P–P bond joining the two 5-membered rings

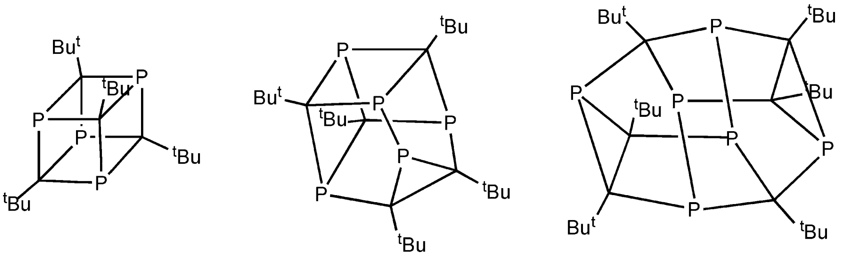


Fig. 1 Cage structures of the tetramer, pentamer and hexamer of the phosphaalkyne, P≡CBu^t.

Department of Chemistry, School of Life Sciences, University of Sussex, Brighton, Sussex, UK BN1 9QJ

† CCDC reference numbers 674809–674812. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b800458g

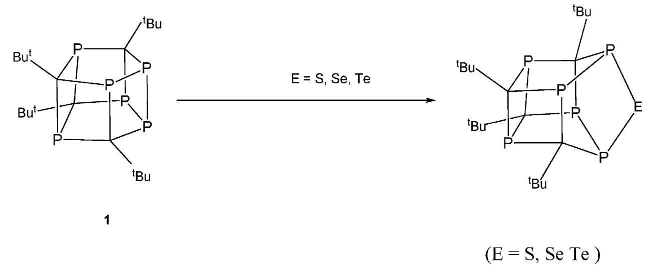
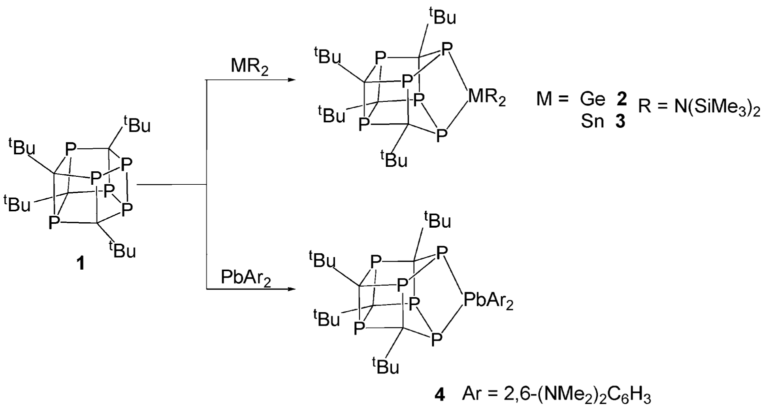


Fig. 3 Insertion of chalcogens into the hexaphospha-pentaprismane, $P_6C_4{}^tBu_4$.

(Scheme 1). All the new compounds were fully characterised by multi-nuclear NMR spectroscopy, elemental analyses, and single crystal X-ray diffraction studies.

Compounds **2–4** all have a 2-fold rotational axis, resulting in only three different P environments and two ^{t}Bu environments. Thus P_A and $P_{A'}$ are chemically equivalent (but magnetically non-equivalent), as are the pairs P_B and $P_{B'}$, and P_C and $P_{C'}$. The $^{31}P\{^1H\}$ NMR spectra of **2–4**, which are shown in Fig. 4, 6 and 8, are typical for AA′MM′XX′ spin systems (compounds **2** and **4** also exhibit additional coupling to ^{119}Sn and ^{207}Pb nuclei respectively). Examples of this type of spin system involving six phosphorus centres are relatively uncommon and the resulting spectra are very sensitive to the magnitudes of the one and two bond J_{PP} coupling constants. The simulated spectra of **2–4** (using the shift and coupling constant data in Tables 1–4) gave reasonable fits with those experimentally observed and resulted in similar J_{PP} values within the series of compounds. The $^{119}Sn\{^1H\}$ and $^{207}Pb\{^1H\}$ NMR spectra of compounds **3** and **4** were also recorded directly.



Scheme 1

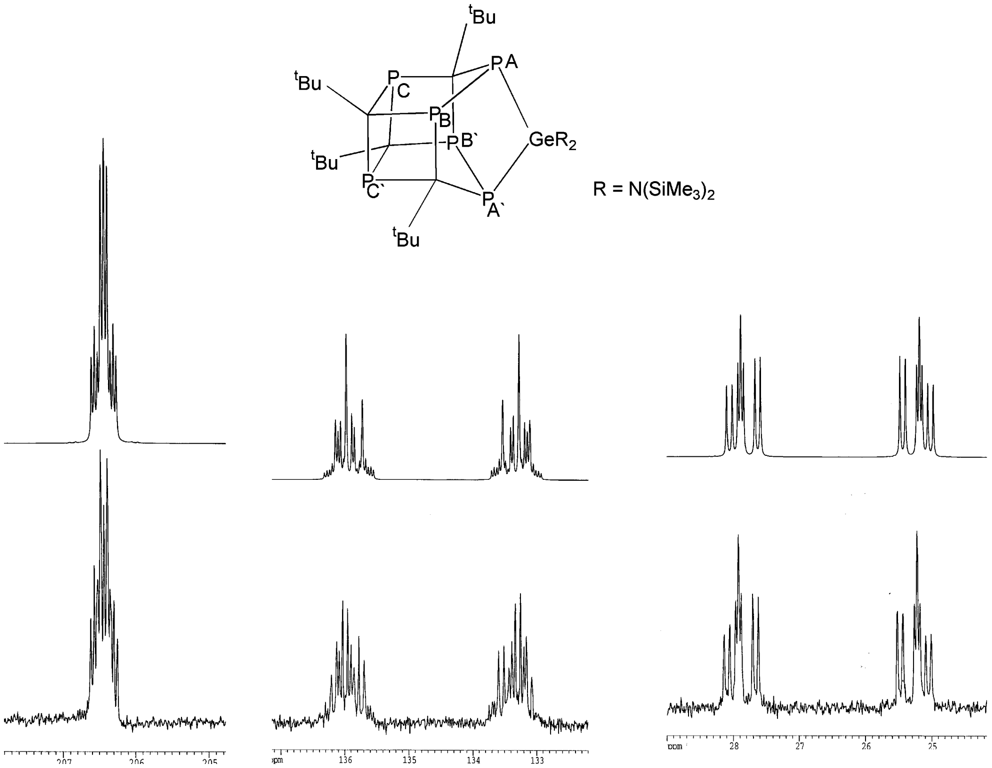
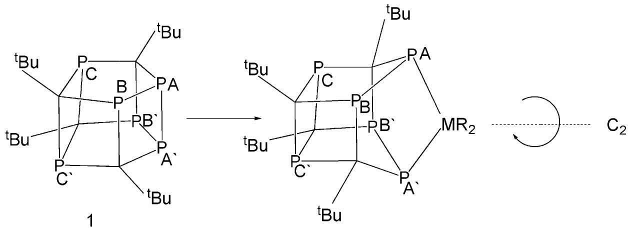


Fig. 4 Observed (lower part) and simulated (upper part) $^{31}P\{^1H\}$ NMR spectrum of $Ge\{N(SiMe_3)_2\}_2P_6C_4{}^tBu_4$ **2**.

Table 1 ^{31}P NMR data for compounds **2–4**. Chemical shifts in ppm, coupling constants in Hz (for **3**, M = Sn; For **4**, M = Pb)

Compound	$\delta P_{A,A'}$	$\delta P_{B,B'}$	$\delta P_{C,C'}$	$^1J(P_AP_B)$	$^1J(P_AM)$	$^2J(P_BM)$
2	26.5	134.5	206.4	320	—	—
3	−6.12	120.1	197.0	318	1352	—
4	−19.3	127.1	188.9	343	1737	86

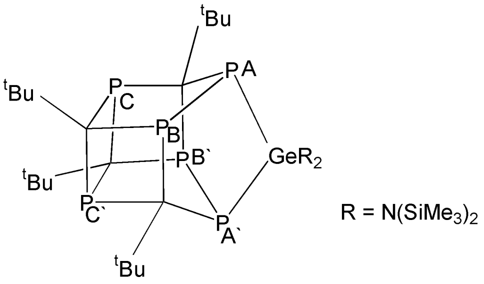


1

2 M=Ge; **3** M=Sn, R=N(SiMe$_3$)$_2$
4 M=Pb, R =2,6-(NMe$_2$)$_2$C$_6$H$_3$

The ^{31}P{^{1}H} NMR spectrum of Ge{N(SiMe$_3$)$_2$}$_2$P$_6$C$_4$^{t}Bu$_4$ **2** shows the expected three sets of widely spaced multiplets (Fig. 4). The P$_A$ resonance occurs as a large doublet of multiplets at 26.5 ppm as does the P$_B$ resonance centered at 134.5 ppm with the same large coupling.

The P$_C$ resonance exhibits a smaller multiplet at 206.4 ppm. The ^{31}P{^{1}H} NMR spectrum of **2** was simulated (Fig. 4) and the resulting J_{PP} coupling constants are listed in Table 2.



The ^{1}H NMR spectrum showed the expected two singlets for the different ^{t}Bu environments at 1.21 and 1.49 ppm respectively, but interestingly *two* resonances for the SiMe$_3$ protons at 0.63 and 0.51 ppm. The latter behaviour presumably results from restricted rotation of the bulky –N(SiMe$_3$)$_2$ groups around the N–Ge bonds which results in an orientation in which one SiMe$_3$ group is aligned close to a P atom of one 5-membered ring while the other SiMe$_3$ group lies adjacent to a C atom of the second ring, as subsequently confirmed in the solid state structure (*vide infra*).

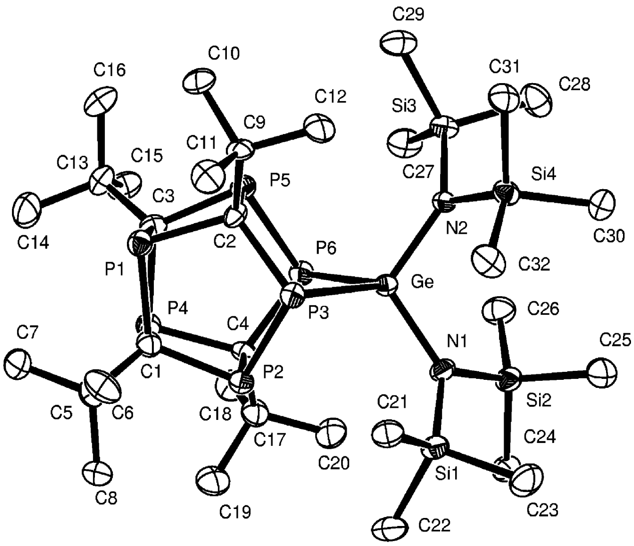


Fig. 5 Molecular structure of Ge{N(SiMe$_3$)$_2$}$_2$P$_6$C$_4$^{t}Bu$_4$ **2**. Selected bond distances (Å) and angles (°): Ge–N(1) 1.876(4), Ge–N(2) 1.883(4), Ge–P(3) 2.3915(12), Ge–P(6) 2.4091(12); P(3)–Ge–P(6) 90.65(4), N(1)–Ge–N(2) 109.28(1), N(1)–Ge–P(3) 110.33(11), N(1)–Ge–P(6) 117.79(11), N(2)–Ge–P(6) 111.06(11), N(2)–Ge–P(3) 110.33(10), Ge–P(3)–C(2) 101.53(14), Ge–P(3)–P(2) 91.60(5), C(2)–P(3)–P(2) 99.60(15), Ge–P(6)–C(4) 100.31(14), Ge–P(6)–P(5) 92.69(5), P(5)–P(6)–C(4) 99.21(15).

The molecular structure of **2** was confirmed by a single crystal X-ray diffraction study and is shown in Fig. 5. The germanium centre lies in a distorted tetrahedral environment (P(3)–Ge–P(6) angle = 90.65(4)°), which is slightly smaller than that found in the cage compound P$_6$C$_4$^{t}Bu$_4$GeI$_2$[4] made by treatment of GeI$_4$ with KP$_3$C$_2$^{t}Bu$_2$. The mean Ge–P bond length in **2** (2.4003 Å) is longer than that in P$_6$C$_4$^{t}Bu$_4$GeI$_2$ (2.337 Å) or in (H$_3$Ge)$_3$P[8] (2.308 Å). Interestingly there is hardly any change in the geometry of Ge{N(SiMe$_3$)$_2$}$_2$ in forming the insertion product **2** even though there is a formal oxidation state change of two for Ge. Thus, the mean Ge–N distance in Ge{N(SiMe$_3$)$_2$}$_2$ is 1.876(5) Å[9] and in **2** is 1.878(4) Å, while the N–Ge–N bond angle in Ge{N(SiMe$_3$)$_2$}$_2$ is 107.1(2)° and in **2** is 109.28(1)°.

The analogous tin compound Sn{N(SiMe$_3$)$_2$}$_2$P$_6$C$_4$^{t}Bu$_4$ **3** shows very similar ^{31}P{^{1}H}, ^{1}H and ^{13}C{^{1}H} NMR spectroscopic features to **2** (see Fig. 6). The P$_A$ resonance is a widely spaced doublet of multiplets centered at −6.12 ppm as is the P$_B$ resonance at 120.1 ppm both exhibiting the same large coupling. The P$_C$ resonance gives a smaller multiplet at 197.0 ppm. The ^{119}Sn{^{1}H} NMR spectrum shows a well-resolved triplet at 130.4 ppm {$^1J(P_ASn)$ = 1352 Hz}. The simulated ^{31}P{^{1}H} NMR spectrum of **3** is shown in Fig. 6 and J_{PP} coupling constants are listed in Table 3.

The ^{1}H NMR spectrum of **3**, like that of **2**, showed the expected two resonances for the two ^{t}Bu environments and two resonances for the two stereo-inequivalent SiMe$_3$ groups.

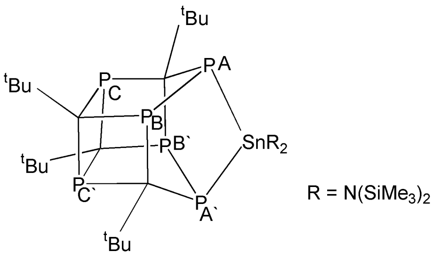
The molecular structure of **3** was confirmed by a single crystal X-ray diffraction study (Fig. 7). It is similar to that of the Ge analogue and reveals that the Sn centre is in a distorted tetrahedral environment with a mean Sn–P bond length of (2.589 Å) which is comparable to the Sn–P bond distance in [^{t}Bu$_2$Sn(PPh)$_3$] (2.5435 Å),[10] and in (^{t}Bu$_2$SnPH)$_2$ (2.546 Å).[11] The P(3)–Sn–P(6) angle is 86.02(6)° and the N–Sn–N angle is 105.2(2)°.

Table 2 J_{PP} coupling constants (in Hz) for Ge{N(SiMe$_3$)$_2$}P$_6$C$_4$^{t}Bu$_4$ **2**

	$P_{C'}$	P_C	$P_{B'}$	P_B	$P_{A'}$
P_A	0	10	7	320	52
P_B	13	−14	0		
P_C	5				

Table 3 J_{PP} coupling constants (in Hz) for Sn{N(SiMe$_3$)$_2$}P$_6$C$_4$^{t}Bu$_4$ **3**

	$P_{C'}$	P_C	$P_{B'}$	P_B	$P_{A'}$
P_A	−4	5	8	318	51
P_B	23	−12	6		
P_C	−2				



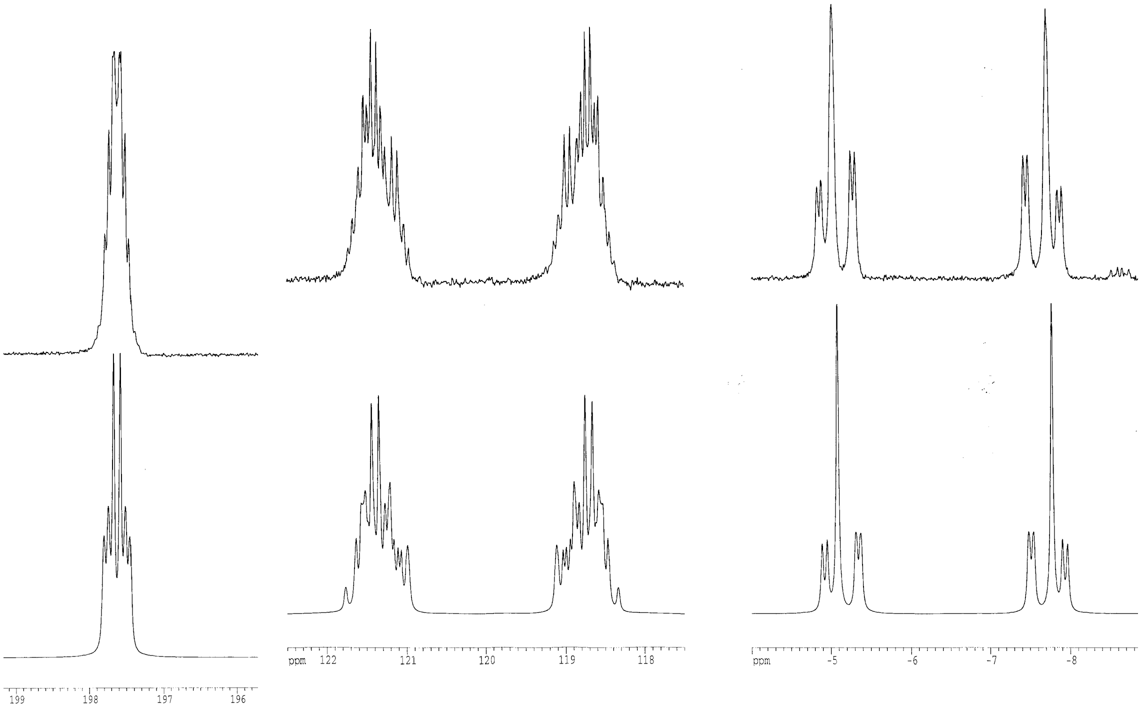


Fig. 6 Experimental (upper part) and simulated (lower part) $^{31}P\{^1H\}$ NMR spectra of $Sn\{N(SiMe_3\}_2P_6C_4{}^tBu_4$ **3**.

Interestingly, as in the case of the Ge system, there is no significant change in the geometry of $Sn\{N(SiMe_3)_2\}_2$ in forming the insertion product **3**. The mean Sn–N distance in crystalline $Sn\{N(SiMe_3)_2\}_2$ is 2.09(1) Å[12] and in **3** is 2.080 Å, while the N–Sn–N bond angle in $Sn\{N(SiMe_3)_2\}_2$ is 104.7(2)° and in **3** is 105.2(2)°

The lead compound $Pb\{C_6H_3(NMe_2)_2\text{-}2,6\}_2P_6C_4{}^tBu_4$ **4** was made from **1** by treatment with the plumbylene $Pb\{C_6H_3(NMe_2)_2\}_2$ and is a rather rare example of a compound containing a Pb(IV)–P bond. As can be seen in Fig. 8, its $^{31}P\{^1H\}$ NMR spectrum is very similar to those discussed above for the Ge and Sn analogues **2** and **3** exhibiting doublets of multiplets at −19.3, 127.1 and 188.9 ppm for P_A, P_B and P_C respectively. The simulated $^{31}P\{^1H\}$ NMR spectrum of **4** is shown in Fig. 8 and J_{PP} coupling constants are listed in Table 4.

Table 4 J_{PP} coupling constants (in Hz) for $Pb\{2,6\text{-}(NMe_2)_2C_6H_3\}_2P_6C_4{}^tBu_4$ **4**

	$P_{C'}$	P_C	$P_{B'}$	P_B	$P_{A'}$
P_A	−13	13	9	343	37
P_B	11	2	8		
P_C	−7				

The ^1H NMR spectrum of **4** showed the expected two resonances for the ᵗBu groups and two resonances for the two stereo-inequivalent NMe_2 groups (as a result of restriction of the free rotation around the C–Pb bond). The $^{207}Pb\{^1H\}$ NMR spectrum showed a triplet of triplets, which corresponds to one bond coupling $^1J(P_APb) = 1737$ Hz, and two bond coupling $^2J(P_BPb) = 86$ Hz.

The molecular structure of $Pb\{2,6\text{-}(NMe_2)_2C_6H_3\text{-}2,6\}_2P_6C_4{}^tBu_4$ **4** was confirmed by a single crystal X-ray diffraction study (Fig. 9) and is similar to that of the analogous Sn and Ge structures. The Pb centre lies in a distorted tetrahedral environment with a P(3)–Pb–P(6) angle of 84.55(4)° and a mean Pb–P bond length of 2.6295 Å, which is comparable to the Pb–P bond distance (2.611 Å) in $P_7[(PbMe_3)_3$.[13] The P–C and P–P distances in **2**, **3** and **4** are very close to their counterparts in $P_6C_4{}^tBu_4$ **1**.

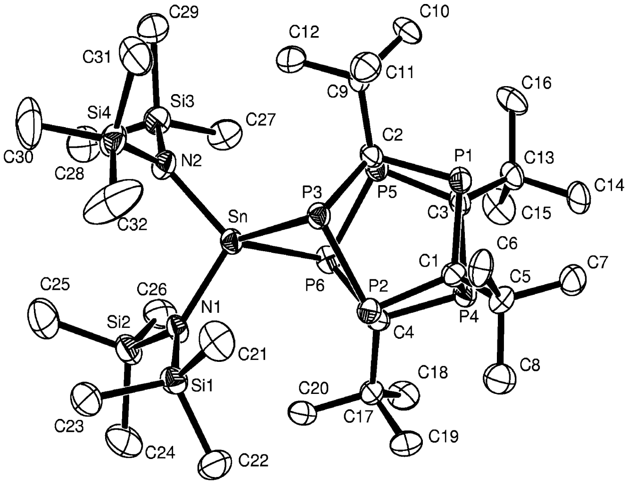


Fig. 7 Molecular structure of $Sn\{N(SiMe_3)_2\}_2P_6C_4{}^tBu_4$ **3**. Selected bond distances (Å) and angles (°): Sn–N(1) 2.077(6), Sn–N(2) 2.083(6), Sn–P(3) 2.554(2), Sn–P(6) 2.624(2); P(3)–Sn–P(6) 86.02(6), N(1)–Sn–N(2) 105.2(2), N(1)–Sn–P(3) 116.57(16), N(1)–Sn–P(6) 111.92(18), N(2)–Sn–P(6) 123.18(17), N(2)–Sn–P(3) 113.83(19), Sn–P(3)–C(2) 100.5(2), Sn–P(3)–P(2) 91.07(9), C(2)–P(3)–P(2) 99.3(2), Sn–P(6)–C(4) 98.8(2), Sn–P(6)P(5) 94.09(10), P(5)–P(6)–C(4) 97.9(3).

We have also carried out a single crystal X-ray analysis of $Pb\{2,6\text{-}(NMe_2)_2C_6H_3\}_2$ **5** and its molecular structure is shown in Fig. 10. It can be seen that the structural features in **5** are hardly changed from those in the insertion product **4**. Thus, the Pb–C average distance in **4** is 2.232(5) Å and in **5** is 2.327(5) Å; likewise the C–Pb–C bond angle in **4** is 104.48(18)° and in **5** is 102.19(17)°. This behaviour parallels that of compounds **2** and **3** discussed earlier.

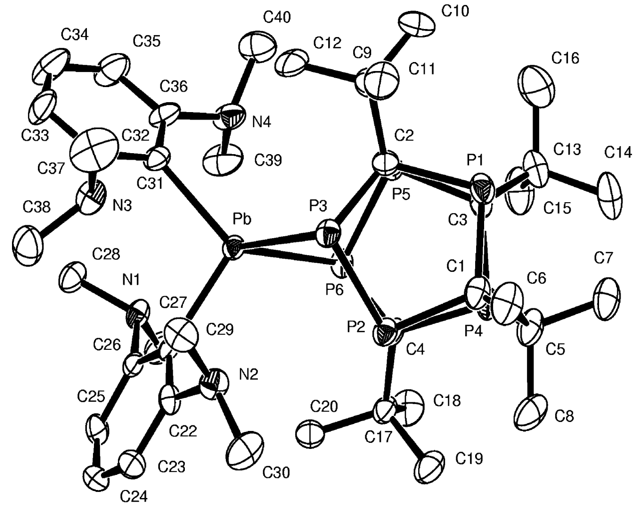


Fig. 9 Molecular structure of $Pb\{C_6H_3(NMe_2)_2\text{-}2,6\}_2P_6C_4{}^tBu_4$ **4**. Selected bond distances (Å) and angles (°): Pb–P(3) 2.626(1), Pb–P(6) 2.633(1), Pb–C(21) 2.224(5), Pb–C(31) 2.241(5); P(3)–Pb–P(6) 84.55(4), C(21)–Pb–C(31) 104.48(18), C(21)–Pb–P(3) 115.97(13), C(21)–Pb–P(6) 111.28(12), C(31)–Pb–P(6) 119.96(14), C(31)–Pb–P(3) 120.23(14), Pb–P(3)–C(2) 99.21(19), Pb–P(3)–P(2) 93.59(6), C(2)–P(3)–P(2) 99.13(16), Pb–P(6)–C(4) 100.47(16), Pb–P(6)P(5) 92.23(6), P(5)–P(6)–C(4) 99.04(17).

Several attempts were made to carry out analogous reactions of $P_6C_4{}^tBu_4$ **1** with silylenes $Si(NCH^tBu)_2(C_6H_4\text{-}1,2)$[14] or $Si(N^tBuCH)_2$[15] under various reaction conditions, but unexpectedly no reaction was observed. Treatment of **1** with the carbene $C(N^tBuCH)_2$[16] gave an unidentified product with a very complicated $^{31}P\{^1H\}$ NMR spectrum indicating no simple insertion of

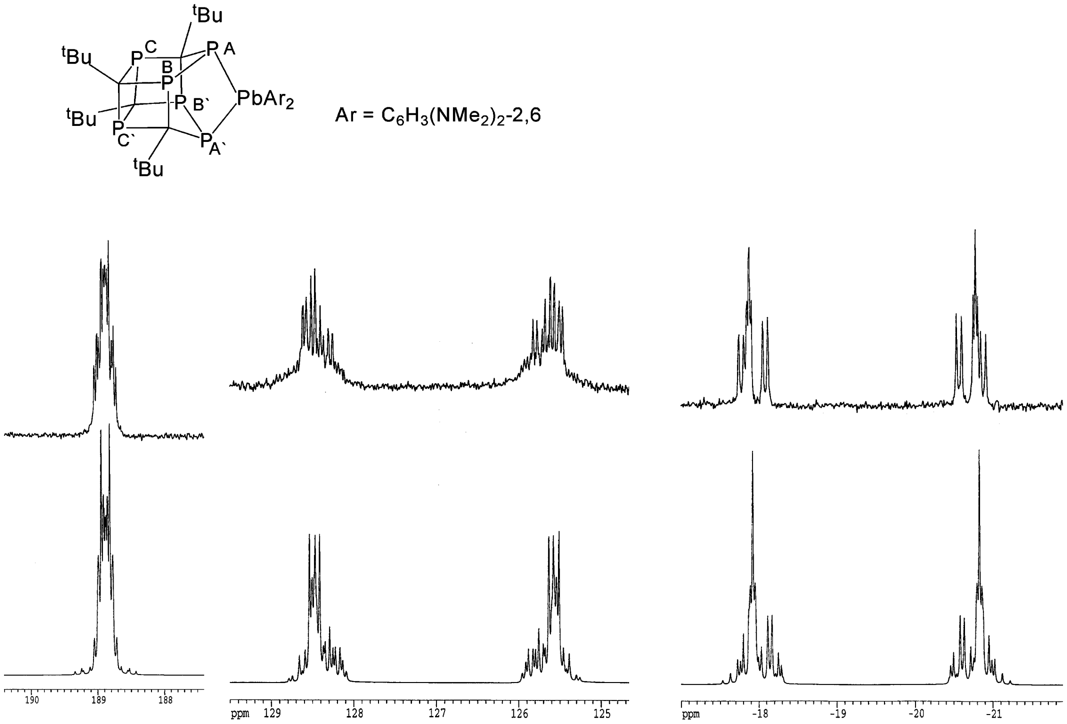


Fig. 8 Experimental (upper part) and simulated (lower part) $^{31}P\{^1H\}$ NMR spectra of $Pb\{C_6H_3(NMe_2)_2\text{-}2,6\}_2P_6C_4{}^tBu_4$ **4**.

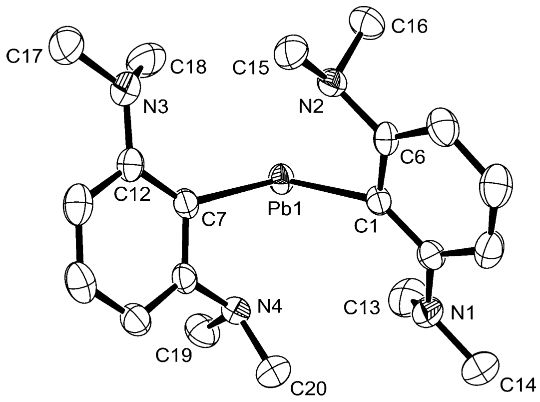


Fig. 10 Molecular structure of Pb{(NMe$_2$)$_2$C$_6$H$_3$-2,6}$_2$ **5**. Selected bond distances (Å) and angles (°): Pb(1)–C(1) 2.328(5), Pb(1)–C(7) 2.325(5); C(1)–Pb–C(7) 102.19(17).

the carbene into the unique P–P bond of **1** had occurred as in the case of germylenes, stannylenes or plumbylenes.

Conclusions

The specific insertion of the "heavy carbenes" MR$_2$ (M = Ge, Sn or Pb) into the unique P–P bond between the two 5-membered rings of the pentaphospha-prismane cage P$_6$C$_4{}^t$Bu$_4$. has been shown to parallel the behaviour of the isoelectronic chalcogen systems S, Se and Te suggesting that a common reaction mechanism obtains.

Experimental

All manipulations of air-and/or moisture-sensitive compounds were carried out under rigorously anhydrous and oxygen-free conditions using standard high vacuum Schlenk line techniques or in an inert atmosphere. Glassware and Schlenk tubes were flame dried before used. Solvents were dried and distilled before use. NMR solvents were purified by refluxing over a suitable drying agent, and vacuum-transferred into ampoules. ^{31}P and ^{1}H NMR spectra were acquired on a Bruker Avance 300DPX spectrometer operating at 300 MHz for ^{1}H measurements, and 121.49 MHz for ^{31}P measurements. ^{1}H NMR spectra are referenced to the residual proton chemical shift of the internal deuterated solvent (which in turn is referenced to TMS). ^{31}P NMR spectra are referenced to H$_3$PO$_4$ (87% H$_3$PO$_4$ in D$_2$O as an external standard). All spectra were recorded at room temperature. Mass spectra (EI and FAB) were recorded by Dr A. Abdul-Sada at the University of Sussex. Single crystal X-ray diffraction studies were carried out using an Enraf Nonius KAPPACCD diffractometer.

Ge{N(SiMe$_3$)$_2$}$_2$, Sn{N(SiMe$_3$)$_2$} and Pb{C$_6$H$_3$(NMe$_2$)$_2$-2,6}$_2$ were synthesised by literature methods.[6,7]

Synthesis of P$_6$C$_4{}^t$Bu$_4$ 1

In an alternative synthesis to those already described in the literature,[1] a THF solution of I$_2$ (0.47 g, 1.85 mmol in 10 ml THF) was added to K(P$_3$C$_2{}^t$Bu$_2$) (1 g, 3.7 mmol in 15 ml THF) at −40 °C and the mixture warmed to room temperature. The solution became orange and was stirred for a further 96 h. Solvent was removed and the product extracted with hexane. Cooling to −40 °C afforded orange crystals of **1** (300 mg, 20%).

Synthesis of Ge{N(SiMe$_3$)$_2$}$_2$P$_6$C$_4{}^t$Bu$_4$ 2

A mixture of P$_6$C$_4{}^t$Bu$_4$ (0.06 g, 0.13 mmol) and Ge{N(SiMe$_3$)$_2$}$_2$ (0.05 g, 0.13 mmol) was stirred in hexane (15 ml) for 48 h. The solvent was then removed *in vacuo* to give Ge{N(SiMe$_3$)$_2$}$_2$P$_6$C$_4{}^t$Bu$_4$, which was crystallised from Et$_2$O to afford colourless crystals (mp 225 °C, 0.66 g, 60%). Found: C 45.17, H 8.37, N 3.32. C$_{32}$H$_{72}$N$_2$GeP$_6$Si$_4$ requires C 44.92, H 8.48, N 3.27%.

Spectroscopic data. (C$_6$D$_6$, 25 °C), ^{31}P{^{1}H} NMR (121.49 MHz): δP$_{A,A'}$ = 26.5 (dm), δP$_{B,B'}$ = 134.5 (dm), δP$_{C,C'}$ = 206.4 (m). ^{1}H NMR (300 MHz): δH(^{t}Bu) = 1.49 (s, 18H), δH(^{t}Bu) = 1.21 (s, 18H), δH(SiMe$_3$) = 0.63 (s, 18H), δH(SiMe$_3$) = 0.51 (s, 18H). ^{29}Si{^{1}H}NMR (99.36 MHz): δSiMe$_3$ = 6.11 (s), δSiMe$_3$ = 5.77 (s). ^{13}C{^{1}H} NMR (125.76 MHz): δC(SiMe$_3$) = 8.77 and 8.69, δC(CH$_3$) = 31.84 and 27.53, δC(^{t}Bu) = 35.96 and 37.81 ppm. MS (EI): *m/z* 856 (50%, [M]$^+$), 841 (100%, [M − Me]$^+$).

Crystal data for 2. C$_{32}$H$_{72}$GeN$_2$P$_6$Si$_4$, *M* = 855.69, triclinic, space group $P\bar{1}$ (No. 2), a = 18.0331(4), b = 18.1166(5), c = 24.3208(7) Å, α = 82.831(2), β = 69.414(2), γ = 65.093(2)°; V = 6743.9(3) Å^3, T = 173(2) K, Z = 6, $D_{c=}$ 1.26 Mg m^{-3}, μ = 1.03 mm^{-1}, λ = 0.71073 Å, F(000) = 2736, crystal size 0.20 × 0.20 × 0.05 mm, 46958 measured reflections, 23675 independent reflections (R_{int} = 0.063), 16354 reflections with $I > 2\sigma(I)$, Final indices $R1$ = 0.053, $wR2$ = 0.100 for $I > 2\sigma(I)$, $R1$ = 0.094, $wR2$ = 0.116 for all data. Data collection: KappaCCD. Program package WinGX.[17] Refinement using SHELXL-97.[18]

Synthesis of Sn{N(SiMe$_3$)$_2$}$_2$P$_6$C$_4{}^t$Bu$_4$ 3

A mixture of P$_6$C$_4{}^t$Bu$_4$ (0.0 4 g, 0.09 mmol) and Sn{N(SiMe$_3$)$_2$}$_2$ (0.04 g, 0.09 mmol) was stirred in hexane (15 ml) for 24 h. The solvent was then removed *in vacuo* to give Sn{N(SiMe$_3$)$_2$}$_2$P$_6$C$_4{}^t$Bu$_4$, which was crystallised from hexane at −35 °C to afford yellow crystals (mp 226 °C, 0.05 g, 60%). Found: C 42.10, H 7.51, N 2.97. C$_{32}$H$_{72}$ N$_2$P$_6$Si$_4$Sn requires C 42.62, H 8.05, N 3.11%.

Spectroscopic data. (C$_6$D$_6$, 25 °C), ^{31}P{^{1}H} NMR (121.49 MHz): δP$_{A,A'}$ = −6.12 (dm), δP$_{B,B'}$ = 120.1 (dm), δP$_{C,C'}$ = 197 (m). ^{1}H NMR (300 MHz): δH(^{t}Bu) = 1.48 (s, 18H), δH(^{t}Bu) = 1.26 (s, 18H), δH(SiMe$_3$) = 0.52 (s, 18H), δH(SiMe$_3$) = 0.47 (s, 18H). ^{29}Si{^{1}H} NMR (99.36 MHz): δSiMe$_3$ = 5.4 (s), δSiMe$_3$ = 5.2 (s). ^{13}C{^{1}H} NMR (125.76 MHz): δC(SiMe$_3$) = 7.55 and 7.46, δC(CH$_3$) = 27.5 and 31.5, δC(^{t}Bu) = 36.0 and 37.9. ^{119}Sn{^{1}H} NMR (186.5 MHz): δSn = 130.4 (t) ppm. ^1J(P$_A$Sn) = 1352 Hz. MS (EI), *m/z*: 902 (80%, [M]$^+$).

Crystal data for 3. C$_{32}$H$_{72}$N$_2$P$_6$Si$_4$Sn, *M* = 901.79, triclinic, space group $P\bar{1}$ (No. 2), a = 11.9453(17), b = 13.7446(14), c = 15.126(2) Å, α = 114.191(7), β = 93.524(5), γ = 94.335(9)°; V = 2247.2(5) Å^3, T = 173(2) K, Z = 2, $D_{c=}$ 1.33 Mg m^{-3}, μ = 0.91 mm^{-1}, λ = 0.71073 Å, F(000) = 948, crystal size 0.40 × 0.05 × 0.02 mm, 13494 measured reflections, 6186 independent reflections (R_{int} = 0.096), 4261 reflections with $I > 2\sigma(I)$, Final indices $R1$ = 0.061, $wR2$ = 0.120 for $I > 2\sigma(I)$, $R1$ = 0.102, $wR2$ = 0.136 for all data. Data collection: KappaCCD. Program package WinGX. Refinement using SHELXL-97.

Synthesis of Pb$\{C_6H_3(NMe_2)_2\text{-}2,6\}_2P_6C_4{}^tBu_4$ 4

A solution of $P_6C_4{}^tBu_4$ (0.07 g, 0.15 mmol) and Pb$\{C_6H_3(NMe_2)_2\text{-}2,6\}_2$ (0.08 g, 0.15 mmol) was stirred in hexane (20 ml) for 48 h. The solvent was then removed *in vacuo* to give Pb$\{C_6H_3(NMe_2)_2\}_2P_6C_4{}^tBu_4$ which was crystallised from Et_2O to give pale orange crystals (mp 140 °C decomp., 0.075 g, 50%). Found: C 48.13, H 6.66. $C_{40}H_{66}N_4P_6Pb$ requires C 48.24, H 6.68%.

Spectroscopic data. (C_6D_6, 25 °C), $^{31}P\{^1H\}$ NMR (121.49 MHz): $\delta P_{A,A'} = -19.3$ (dm), $\delta P_{B,B'} = 127.1$ (dm), $\delta P_{C,C'} = 188.9$ (m). ^1H NMR (300 MHz): $\delta H(^tBu) = 1.42$ (s, 18H), $\delta H(^tBu) = 1.24$ (s, 18H), $\delta H(NMe_2) = 2.88$ (s, 12H), $\delta H(NMe_2) = 2.20$ (s, 12H), $\delta H(C_6H_3) = 6.9$ (m, 6H). $^{13}C\{^1H\}$ (125.76 MHz): $\delta C(CH_3) = 28.20$ and 30.50, $\delta C(^tBu) = 37.70$ and 36.00, $\delta C(NCH_3) = 40.60$ (m) and 46.41 (m). $^{207}Pb\{^1H\}$ NMR (104.68 MHz): $\delta Pb = 530.9$ (tt) ppm $^1J(P_APb) = 1737$ Hz, $^2J(P_BPb) = 86$ Hz. MS (EI), m/z: 996 (10%, $[M]^+$).

Crystal data for 4. $C_{40}H_{66}N_4P_6Pb$, $M = 995.98$, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.2177(3)$, $b = 33.3392(11)$, $c = 13.1175(4)$ Å, $\beta = 112.074(2)°$, $V = 4546.2(2)$ Å^3, $T = 173(2)$ K, $Z = 4$, $D_c = 1.46$ Mg m^{-3}, $\mu = 3.95$ mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 2024$, crystal size 0.2 × 0.1 × 0.1 mm, 23962 measured reflections, 10524 independent reflections ($R_{int} = 0.070$), 7750 reflections with $I > 2\sigma(I)$, Final indices $R1 = 0.046$, $wR2 = 0.093$ for $I > 2\sigma(I)$, $R1 = 0.075$, $wR2 = 0.103$ for all data. Data collection: KappaCCD. Program package WinGX. Refinement using SHELXL-97.

Crystal data for 5[6]

$C_{23}H_{33}N_4Pb$, $M = 572.72$, monoclinic, space group $P2_1/n$ (No. 14), $a = 13.714(4)$, $b = 10.324(3)$, $c = 17.259(5)$ Å, $\beta = 109.372(4)°$, $V = 2305.1(11)$ Å^3, $T = 173(2)$ K, $Z = 4$, $D_c = 1.65$ Mg m^{-3}, $\mu = 7.334$ mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 1124$, crystal size 0.3 × 0.2 × 0.2 mm, 14598 measured reflections, 5471 independent reflections ($R_{int} = 0.0494$), 4226 reflections with $I > 2\sigma(I)$, Final indices $R1 = 0.0365$, $wR2 = 0.0837$ for $I > 2\sigma(I)$, $R1 = 0.0547$, $wR2 = 0.0962$ for all data. Data collection: Bruker SMART. Program package WinGX. Refinement using SHELXL-97.

Acknowledgements

We acknowledge Dr Peter Loennecke for determining the crystal and molecular structure of compound **5** and the late Dr A. G. Avent for the simulation of the ^{31}P NMR spectra. M. M. Al-K. thanks the Syrian Atomic Energy Commission for a studentship and P.U. thanks the Euopean Commision for a TMR grant. J.F.N. acknowledges continuing financial support from the EPSRC for phospha-organometallic chemistry at Sussex University.

References

1 (*a*) K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus, The Carbon Copy: From Organophosphorus to Phospha-organic Chemistry*, Wiley, New York, 1998; (*b*) *Phosphorous-Carbon Heterocyclic Chemistry: The Rise of a New Domain*, ed. F. Mathey, Pergamon, Oxford, 2001; (*c*) F. Mathey, *Angew. Chem., Int. Ed.*, 2003, **42**, 1578.

2 (*a*) R. Streubel, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 436 and references therein; (*b*) A. Mack and M. Regitz, in *Carbocyclic and Heterocyclic Cage Compounds and Their Building Blocks*, ed. K. K. Laali, J. A. I. Press, Stamford, CT, USA, 1999, p. 199; (*c*) J. F. Nixon, in *Carbocyclic and Heterocyclic Cage Compounds and Their Building Blocks*, ed. K. K. Laali, J. A. I. Press, Stamford, CT, USA, 1999, p. 257; (*d*) L. Weber, *Adv. Organomet. Chem.*, 1997, **41**, 1; (*e*) M. Regitz, A. Hoffmann and U. Bergsträsser, in *Modern Acetylene Chemistry*, ed. P. J. Stang and F. Diederich, VCH, Weinheim, 1995; (*f*) R. Appel, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. Scherer, Georg Thieme Verlag, New York, 1990, p. 153; (*g*) R. Bartsch, P. B. Hitchcock and J. F. Nixon, *J. Organomet. Chem.*, 1989, **375**, C31; (*h*) V. Caliman, P. B. Hitchcock, J. F. Nixon, M. Hofmann and P. von R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2202; (*i*) B. Geissler, T. Wettling, S. Barth, P. Binger and M. Regitz, *Synthesis*, 1994, 1337; (*j*) F. Tabellion, A. Nachbauer, S. Leininger, C. Peters, F. Preuss and M. Regitz, *Angew. Chem., Int. Ed.*, 1998, **37**, 1233; (*k*) T. Wettling, J. Schneider, O. Wagner, C. G. Kreiter and M. Regitz, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1013; (*l*) B. Geissler, S. Barth, U. Bergsträsser, M. Slany, J. Durkin, P. B. Hitchcock, M. Hofmann, P. Binger, J. F. Nixon, P. von R. Schleyer and M. Regitz, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 484; (*m*) M. M. Al-Ktaifani, W. Bauer, U. Bergsträsser, B. Breit, M. D. Francis, F. W. Heinemann, P. B. Hitchcock, A. Mack, J. F. Nixon, H. Pritzkow, M. Regitz, M. Zeller and U. Zenneck, *Chem.–Eur. J.*, 2002, **8**, 2622; (*n*) A. G. Avent, F. G. N. Cloke, M. D. Francis, P. B. Hitchcock and J. F. Nixon, *Chem. Commun.*, 2000, 879; (*o*) M. M. Al- Ktaifani, P. B. Hitchcock and J. F. Nixon, *Inorg. Chim. Acta*, 2003, **356**, 103.

3 S. J. Black, M. D. Francis and C. Jones, *Chem. Commun.*, 1997, 305.

4 A. G. Avent, F. G. N. Cloke, M. D. Francis, P. B. Hitchcock and J. F. Nixon, *Chem. Commun.*, 2000, 879.

5 M. M. Al-Ktaifani, D. P. Chapman, M. D. Francis, P. B. Hitchcock, J. F. Nixon and L. Nyulászi, *Angew. Chem., Int. Ed.*, 2001, **40**, 3474.

6 C. Drost, P. B. Hitchcock, M. F. Lappert and L. J- M. Pierssens, *Chem. Commun.*, 1997, 1141.

7 P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1976, 2268.

8 D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, B. Beagley and T. G. Hewitt, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2351.

9 R. W. Chorley, P. B. Hitchcock, M. F. Lappert, W.-P. Leung, P. P. Power and M. M. Olmstead, *Inorg. Chim. Acta*, 1992, **200**, 203.

10 T. L. Breen and D. W. Stephan, *Organometallics*, 1997, **16**, 365.

11 D. Hänssgen, H. Aldenhoven and M. Nieger, *Chem. Ber.*, 1990, **123**, 1837.

12 T. Fjeldberg, H. Hope, M. F. Lappert, P. P. Power and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1983, 639.

13 D. Weber, C. Mujica and H. G. Schnering, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 863.

14 B. Gehrhus, M. F. Lappert, J. Heinicke, R. Boese and D. Bläser, *J. Chem. Soc., Chem. Commun.*, 1995, 1931.

15 R. West and M. Denk, *Pure Appl. Chem.*, 1996, **68**, 785.

16 A. J. Arduengo, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.

17 L. J. Farrugia, WinGX, *J. Appl. Crystallogr.*, 1999, **32**, 837.

18 G. M. Sheldrick, *SHELXL-97*, University of Gottingen, Gottingen, 1997.