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Activation of gaseous PH_3 with low coordinate diaryltetrylene compounds†

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The reaction of phosphine gas with a low coordinate diaryl germylene or diarylstannylene results in both oxidative addition and arene elimination at the group 14 atom. The products were characterised by ^{31}P NMR spectroscopy and X-ray crystallography, and represent the first P–H bond activation by a heavy group 14 element compound.

The activation of small molecule substrates by coordinatively unsaturated main group molecules is a continuously expanding area of research.[1] Of particular intrigue is the fact that these commodity, and typically unreactive, chemicals can be activated directly without the use of transition metals. The activation of dihydrogen by a main group compound under ambient conditions was first achieved by using a digermyne (**A**; Fig. 1).[2] Subsequent studies have shown that frustrated Lewis pairs (FLPs, *i.e.* **B**),[3] stable singlet carbenes (*e.g.* **C**),[4] diaryltetrylenes (**D**),[5] heavier p-block alkyne analogues,[2,6] silylenes,[7] and group 13 dimetallenes (**E**)[8] can also accomplish the same feat. Several of these unique systems also activate ammonia under ambient conditions, a feature that is not as common for transition metals.[9]

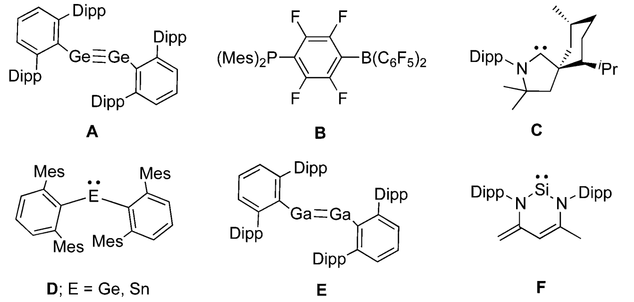
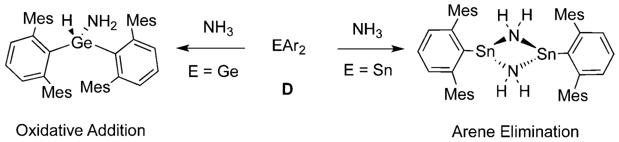


Fig. 1 Examples of main group compounds that activate small molecules. Note that Dipp = 2,6-diisopropylphenyl and that Mes = 2,4,6-trimethylphenyl.

Bertrand *et al.* have shown that unique, stable N-heterocyclic carbenes (*i.e.* **C**) can also insert into B–H, Si–H, and P–H bonds.[10] While primary and secondary phosphines were used in work reported previously, reactions involving phosphine (PH_3) are rare.[11] Driess *et al.* have recently shown that a Si(II) center (**F**)[12] inserts into the P–H bond of phosphine to produce a ligand stabilized $Si(H)(PH_2)$ fragment.[13]

The primary mode of reactivity for low valent main group centers is to undergo oxidative addition across the X–H (X = H, B, N, Si, P) bond. For the N-heterocyclic carbenes and heavier analogues there are few examples to the contrary. The diaryltetrylenes (**D**, EAr_2; E = Ge, Sn; Ar = C_6H_3-2,6-Mes_2)[13] however, have displayed different reactivity based on the group 14 element. In the reaction with ammonia, germanium exclusively favours the oxidative addition pathway, while tin exclusively favours arene elimination to remain in the +2 oxidation state (Scheme 1).[5] In this context, we report an extension of the reactivity studies on diaryltetrylenes to PH_3, ammonia's heavier congener. In contrast to ammonia, both oxidative addition and arene elimination products are observed for germanium and tin, and also in different ratios relative to each other.

The reaction of the diarylgermylene ($GeAr_2$; Ar = C_6H_3-2,6-Mes_2) with an excess of PH_3 (80 psi) in a stainless steel pressure reactor for three hours results in the complete consumption of the purple starting material to give a colourless solution.‡ Analysis of a fraction of the concentrated reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy revealed the presence of two signals (δ_P = −232; −180), which



Scheme 1 Reactivity of ammonia with a diarylgermylene (left) and a diarylstannylene (right) highlighting the oxidative addition and reduction elimination pathways (Ar = C_6H_3-2,6(C_6H_2-2,4,6-Me_3)$_2$ = C_6H_3-2,6-Mes_2).

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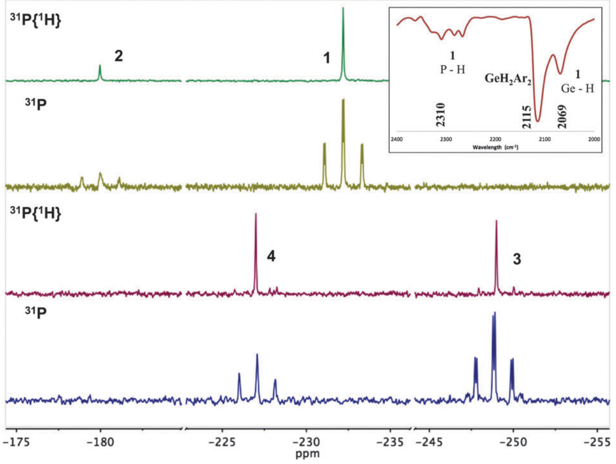
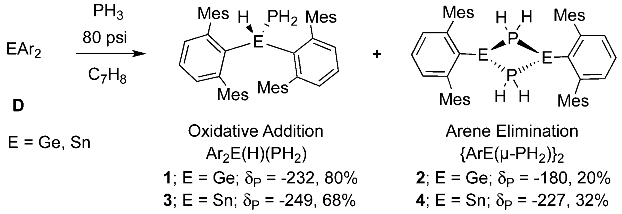


Fig. 2 Plots of $^{31}P\{^1H\}$ and ^{31}P NMR spectra for the reaction of EAr_2 (E = Ge, Sn) with phosphine. Inset: FT-IR spectrum of **1** focusing on hydride vibrations.



Scheme 2 The reaction of phosphine with the diaryltetrylenes (E = Ge, Sn) to give both the oxidative addition (**1** or **3**) and arene elimination (**2** or **4**) products. Ratios determined by $^{31}P\{^1H\}$ NMR spectroscopy of the crude reaction mixture.

integrate to an approximate 80 : 20 ratio (Fig. 2). The ^{31}P NMR spectrum was particularly informative revealing the signals to be proton coupled as a triplet of doublets and a triplet (δ_P = −232, $^1J_{P\text{–}H}$ = 181 Hz, $^2J_{P\text{–}H}$ = 11.2 Hz; δ_P = −180, $^1J_{P\text{–}H}$ = 183 Hz), consistent with the formation of both the oxidative addition product, $Ar_2Ge(H)(PH_2)$ (**1**), and the arene elimination product, $\{ArGe(\mu\text{-}PH_2)\}_2$ (**2**) (Scheme 2). The ^1H NMR spectrum of a recrystallized sample of **1** revealed a doublet of triplets (δ_H = 5.33, $^2J_{P\text{–}H}$ = 11.2 Hz, $^3J_{H\text{–}H}$ = 4.3 Hz), consistent with a germanium hydride adjacent to a PH_2 functionality. The phosphorus hydrides were also observed as a doublet of doublets in the ^1H NMR spectrum (δ_H = 1.29, $^1J_{P\text{–}H}$ = 181 Hz, $^3J_{H\text{–}H}$ = 4.3 Hz) and agree nicely to the other coupling constants. The FT-IR spectrum also reveals signals consistent with a P–H (ν = 2310 cm^{-1}) and a Ge–H stretch (ν = 2069 cm^{-1}). Confirmation of the solid-state structure of **1** was obtained from an X-ray diffraction study on single crystals grown from a saturated hexane solution at −35 °C. There is a significant presence of GeH_2Ar_2 in the crude reaction mixture (40–50%), which cannot be efficiently separated from **1**.[15] While the origin of this species is not clear, its identity was unambiguously confirmed by ^1H NMR and FT-IR spectroscopies as well as by single crystal X-ray diffraction. The analogous reaction of the diarylstannylene ($SnAr_2$) with PH_3 (80 psi) requires longer reaction times (24 hours) to go to completion, as evidenced by the disappearance of the characteristic purple colour. The proton decoupled and coupled ^{31}P NMR spectra (Fig. 2) again revealed two signals (δ_P = −249, −227), in this case in an approximate 68 : 32 ratio. The phosphorus–proton coupling constants are comparable to those of the analogous germanium species (δ_P = −249, $^1J_{P\text{–}H}$ = 174 Hz, $^2J_{P\text{–}H}$ = 18.6 Hz; δ_P = −227, $^1J_{P\text{–}H}$ = 174 Hz). Phosphorus–tin coupling is also observed with the values being consistent with a tin–phosphorus covalent bond (δ_P = −249, $^1J_{^{117}Sn\text{–}P}$ = 496 Hz, $^1J_{^{119}Sn\text{–}P}$ = 518 Hz; δ_P = −227, $^1J_{^{117}Sn\text{–}P}$ = 597 Hz, $^1J_{^{119}Sn\text{–}P}$ = 621 Hz). The ^1H NMR spectrum reveals the characteristic doublet of triplets for the Sn–H (δ_H = 6.15, $^2J_{P\text{–}H}$ = 18.6 Hz, $^3J_{H\text{–}H}$ = 3.6 Hz) while the FT-IR spectrum displayed resonances consistent the P–H and Sn–H bond vibrations. The solid-state structure of the oxidative addition product, $Ar_2Sn(H)(PH_2)$, **3**, was obtained as structural confirmation, while unfortunately structural verification of the arene elimination product, $\{ArSn(\mu\text{-}PH_2)\}_2$, **4**, has proven elusive despite considerable effort. This is likely a result of the fact that completely separating **3** and **4** was not possible under the conditions employed.

The solid-state structures of the oxidative addition products **1**, and **3** are shown in Fig. 3.§ The structures are nearly identical, and also similar to the ammonia insertion product, with the tetrel center in a distorted tetrahedral geometry. The Ge–H and Sn–H distances are 1.58(4) and 1.90(5) Å. The Ge–C bond lengths are 1.981(3) and 2.003(3) Å, while the Ge–P bond length is 2.3194(11) Å. The analogous bond lengths for **3** are 2.193(6), 2.181(6), and 2.5997(17) Å, respectively. For both **1** and **3** the phosphorus–hydrogen bond lengths fall within the range of 1.32 and 1.42 Å with the exception of one very short outlier (1.02(4) Å in **1**).[16] The C–E–C bond angle has increased considerably from the free diaryltetrylene[14] for **3** (138.1(2)° *cf.* 114.7(2)° for $SnAr_2$) while the same angle in **1** is slightly smaller than in $GeAr_2$ (112.5(1) *cf.* 114.4(2) for $GeAr_2$). The P–E–H bond angles are much smaller in comparison, consistent with the use of unhybridized p-orbitals in the bonding, and also an obvious result of the steric pressure of the terphenyl substituents.

In conclusion, a diarylgermylene and a diarylstannylene react with phosphine gas under ambient conditions to produce both oxidative addition and arene elimination products, the structures of the oxidative addition products being confirmed

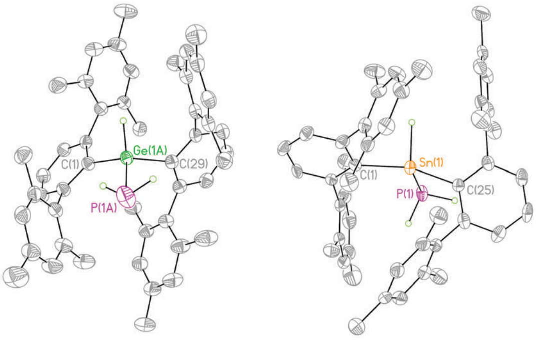


Fig. 3 The solid-state structure of **1** (left) and **3** (right). Ellipsoids are drawn at 50% probability, hydrogen atoms, with exception to the main group hydrides, and hexane solvate (**1**) are removed for clarity. Selected bond lengths (Å) and angles (°): **1** Ge–H 1.58(4), Ge–P 2.3194(11), P–H 1.34(4), P–H 1.02(4), C–Ge–C 112.5(1), P–Ge–H 102.1(13); **3** Sn–H 1.90(5), Ge–P 2.5997(17), P–H 1.391(10), P–H 1.384(10), C–Sn–C 138.1(2), P–Sn–H 96.1(14).

crystallographically. This study represents a rare example of activation of a P–H bond at a low coordinate main group center, and the first of the heavier group 14 elements (Ge, Sn).

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Notes and references

‡ All manipulations were performed in a nitrogen filled MBraun glovebox with solvents stored over 4 Å molecular sieves or a potassium mirror. Phosphine (Cytec) was loaded into a stainless steel Parr reactor and excess gas was swept with N_2 and controllably burnt after the desired reaction time. The product distribution was determined from integration of the $^{31}P\{^{1}H\}$ NMR spectrum of the isolated crude powder in C_6D_6. Experimental data: **1:** ^{1}H NMR (400 MHz, C_6D_6, δ): 1.29 (dd, 2H, $^{1}J_{P\text{–}H}$ = 181 Hz, $^{3}J_{H\text{–}H}$ = 4.3 Hz), 1.79 (s, 12H), 1.84 (s, 12H), 2.19 (s, 12H), 5.33 (dt, 1H, $^{2}J_{P\text{–}H}$ = 11.2 Hz, $^{3}J_{H\text{–}H}$ = 4.3 Hz), 6.71 (d, 2H, $^{3}J_{H\text{–}H}$ = 6.4 Hz), 6.75 (s, 4H), 6.83 (s, 4H), 7.02 (t, 1H, $^{3}J_{H\text{–}H}$ = 7.6 Hz); $^{31}P\{^{1}H\}$ NMR (161.8 MHz, C_6D_6, δ): −232; ^{31}P NMR (161.8 MHz, C_6D_6, δ): −232 (td, $^{1}J_{P\text{–}H}$ = 181 Hz, $^{2}J_{P\text{–}H}$ = 11.2 Hz); FT-IR (cm^{-1}); 2069 (Ge–H), 2310 (P–H); **3:** ^{1}H NMR (400 MHz, C_6D_6, δ): resonances that could assigned to **3** are listed: 0.84 (dd, 2H, $^{1}J_{P\text{–}H}$ = 174 Hz, $^{3}J_{H\text{–}H}$ = 3.6 Hz, $^{2}J_{^{117}Sn\text{–}H}$ = 61.8 Hz, $^{2}J_{^{119}Sn\text{–}H}$ = 68.7 Hz), 6.15 (dt, 1H, $^{2}J_{P\text{–}H}$ = 18.6 Hz, $^{3}J_{H\text{–}H}$ = 3.6 Hz); $^{31}P\{^{1}H\}$ NMR (161.8 MHz, C_6D_6, δ): −249 ($^{1}J_{^{117}Sn\text{–}P}$ = 496 Hz, $^{1}J_{^{119}Sn\text{–}P}$ = 518 Hz); ^{31}P NMR (161.8 MHz, C_6D_6, δ): −249 (td, $^{1}J_{P\text{–}H}$ = 174 Hz, $^{2}J_{P\text{–}H}$ = 18.6 Hz); HRMS: found (calculated) for $C_{48}H_{53}NaPSn$ 803.2687 (803.2800).

§ Crystallographic details: **1:** $C_{48}H_{53}GeP$, C_6H_{14}; FW = 819.64 g mol^{-1}; colourless block; size: 0.052 × 0.061 × 0.130 mm; monoclinic, $P2_1/c$; unit cell: a = 14.813(3) Å, b = 19.868(4) Å, c = 16.899(3) Å, β = 111.25(3)°, V = 4635.1(16) Å; Z = 4; ρ = 1.175; T = 150 K; λ = 0.71073 nm (MoKα); F(000) = 1752; μ = 0.729; $2\theta_{max}$ = 55.12; $2\theta_{min}$ = 3.30; 35 818 reflections, 10 616 unique (R_{int} = 0.0449); parameters = 538; restraints = 5; R_1 = 0.0583; wR_2 = 0.1449; R_1(all data) = 0.0751; wR_2(all data) = 0.1563; GooF = 1.017; percent complete: 99.3%; **3:** $C_{48}H_{53}SnP$; FW = 779.56 g mol^{-1}; colourless block; size: 0.040 × 0.055 × 0.131 mm; triclinic, $P2_1/c$; unit cell: a = 10.3576(11) Å, b = 22.461(2) Å, c = 17.5165(19) Å, β = 99.453(3)°, V = 4019.8(7) Å; Z = 4; ρ = 1.288; T = 150 K; λ = 0.71073 nm (MoKα); F(000) = 1624; μ = 0.707; $2\theta_{max}$ = 55.0; $2\theta_{min}$ = 2.98; 45 865 reflections, 9226 unique (R_{int} = 0.1763); parameters = 474; restraints = 4; R_1 = 0.0661; wR_2 = 0.1475; R_1(all data) = 0.1692; wR_2(all data) = 0.1888; GooF = 1.007; percent complete: 99.9%.

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16 There is disorder about the germanium and phosphorus atoms, with the major component refining to 91% occupancy. While the hydride refines to a logical location by bond angle, the bond distance is much shorter than one would expect, potentially a result of this disorder.