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Activation of gaseous $\text{PH}_3$ with low coordinate diaryltetraylene compounds

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The reaction of phosphine gas with a low coordinate diarylgermylene or diarylstannylen 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 $\text{P} – \text{H}$ 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. 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; Figure 1). Subsequent studies have shown that frustrated Lewis pairs (FLPs, ie. B), stable singlet carbenes (eg. C), diaryltetraylenes (D), heavier p-block alkyne analogues, silylenes, and group 13 dimetallenes (E) 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.

Bertrand et al. have shown that unique, stable $N$-heterocyclic carbenes (ie. C) can also insert into $\text{B} – \text{H}$, $\text{Si} – \text{H}$, and $\text{P} – \text{H}$ bonds. While primary and secondary phosphines were used in work reported previously, reactions involving phosphine ($\text{PH}_3$) are rare. Driess et al. have recently shown that a Si(II) center (F) inserts into the $\text{P} – \text{H}$ bond of phosphine to produce a ligand stabilized Si(III)($\text{PH}_3$) fragment.

The primary mode of reactivity for low valent main group centers is to undergo oxidative addition across the $\text{X} – \text{H}$ ($\text{X} = \text{H, B, N, Si, P}$) bond. For the $N$-heterocyclic carbenes and heavier analogues there are few examples to the contrary. The diaryltetraylenes (D, EAr$_2$; E = Ge, Sn; Ar = $\text{C}_6\text{H}_{12}$-2,6-$\text{Mes}_2$) 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). In this context, we report an extension of the reactivity studies on diaryltetraylenes to $\text{PH}_3$, 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 ($\text{GeAr}_2$; Ar = $\text{C}_6\text{H}_{12}$-2,6-$\text{Mes}_2$) with an excess of $\text{PH}_3$ (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 NMR spectroscopy revealed the presence of two signals ($\delta_p = -232; -180$), which integrate to an approximate 80:20 ratio. The $^{31}$P NMR spectrum was particularly informative revealing the signals to be proton coupled as a triplet of doublets and a triplet ($\delta_p = -232, J_{P-H} = 181$ Hz, $J_{P-H} = 11.2$ Hz; $\delta_p = -180, J_{P-H} = 183$ Hz), consistent with the formation of both the oxidative addition product, $\text{ArRGe(H)(PH$_3$)}$ (1), and the arene elimination product, $\{\text{ArRGe(µ-PH$_3$)}\}_2$ (2) (Scheme 2). The $^1$H NMR spectrum of a recrystallized sample of 1 revealed a doublet of triplets ($\delta_H = 5.33, J_{H-H} = 11.2$ Hz, $J_{H-P} = 4.3$ 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 $^1$H NMR spectrum ($\delta_H = 1.29, J_{H-H} = 181$ Hz, $J_{H-P} = 4.3$ Hz) and agree nicely to the other coupling constants. The FT-IR spectrum also reveals signals consistent with a P–H ($\nu = 2310$ cm$^{-1}$) and a Ge–H stretch ($\nu = 2069$ 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$_2$Ar$_2$ in the crude reaction mixture (40-50%), which cannot be efficiently separated from 1. While the origin of this species is not clear, its identity was unambiguously confirmed by $^1$H NMR and FT-IR spectroscopies as well as by single crystal X-ray diffraction. The analogous reaction of the diarylstenylene (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 again revealed two signals ($\delta_p = -249, -227$), in this case in an approximate 68:32 ratio. The phosphorus–proton coupling constants are comparable to those of the analogous germanium species ($\delta_p = -249, J_{H-H} = 174$ Hz, $J_{H-P} = 18.6$ Hz; $\delta_p = -227, J_{H-H} = 174$ Hz). Phosphorus–tin coupling is also observed with the values being consistent with a tin–phosphorus covalent bond ($\delta_p = -249, J_{P-H} = 496$ Hz, $J_{P-P} = 518$ Hz; $\delta_p = -227, J_{P-H} = 597$ Hz, $J_{P-P} = 621$ Hz). The $^1$H NMR spectrum reveals the characteristic doublet of triplets for the Sn–H ($\delta_H = 6.15, J_{H-H} = 18.6$ Hz, $J_{H-H} = 3.6$ 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, $\{\text{ArSn(µ-PH$_3$)}\}_2$, 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 Figure 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 (1.024 Å in 1). The C–E–C bond angle has increased considerably from the free diarylstenylene$^{14}$ for 3 (138.1(2)$^o$) cf. 114.7(2)$^o$ for SnAr$_2$) while the same angle in 1 is slightly smaller than in GeAr$_2$ (112.5(1)$^o$ 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 diarygmeralene 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 crystallographically. This study represents a rare example of activation of a P–H bond at a low coordinate monor group center, and the first of the heavier group 14 elements (Ge, Sn).

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Notes and references


10 Both products are hexanes soluble and crystallize from hexanes solution at -35°C. Therefore, the products cannot be consistently isolated free of each other in usable quantities.

11 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.

Notes and references

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†All manipulations were performed in a nitrogen filled MBraun glovebox with solvents stored over 4A molecular sieves or a potassium mirror.

Phosphine (Cytec) was loaded into a stainless steel Parr reactor and excess gas was swept with N2 and controllably burnt after the desired reaction time. The product distribution was determined from integration of the 31P{1H} NMR spectrum of the isolated crude powder in CD2Cl2.

Experimental Data: 1H NMR (400 MHz, CD2Cl2, δ): 1.29 (dd, 2H, JH,H = 181 Hz, JH,H = 4.3 Hz), 1.79 (s, 12H), 1.84 (s, 12H), 2.19 (s, 12H), 5.33 (dt, 1H, JH,H = 11.2 Hz, JH,H = 4.3 Hz), 6.71 (d, 2H, JH,H = 6.4 Hz), 6.75 (s, 4H), 6.83 (s, 4H), 7.02 (t, 1H, JH,H = 7.6 Hz); 31P{1H} NMR (161.8 MHz, CD2Cl2, δ): -232; 31P NMR (161.8 MHz, CD2Cl2, δ): -232 (td, JH,P = 181 Hz, JH,P = 11.2 Hz); FT-IR (cm-1): 2069 (Ge-H), 2310 (PH); 3: 1H NMR (400 MHz, CD2Cl2, δ): resonances that could assigned to 3 are listed: 0.84 (dd, 2H, JH,H = 174 Hz, JH,H = 3.6 Hz, JH,P = 61.8 Hz, 6P{1H} = 68.7 Hz), 6.15 (dt, 1H, JH,H = 18.6 Hz, JH,H = 1.76 Hz); 31P{1H} NMR (161.8 MHz, CD2Cl2, δ): -249 (JH,P = 496 Hz, JH,P = 518 Hz); 31P NMR (161.8 MHz, CD2Cl2, δ): -249 (JH,P = 174 Hz, JH,H = 18.6 Hz); HRMS: found (calculated) for C6H12N4P5Sn 803.2867 (803.2800).

Crystallographic Details: I: CaH6GeP, C5H5; FW = 819.64 g/mol; colourless block; Size: 0.052 x 0.061 x 0.130 mm; Monoclinic, P21/c; Unit Cell: a = 14.813(3) Å, b = 19.868(4) Å, c = 16.899(3) Å, β = 111.25(3) °, V = 4655.1(16) Å3; Z = 4; p = 1.175; T = 150°C; K = 0.71073 nm (MoKa); F(000) = 1752; μ = 0.729; 20max = 55.12; 20min = 3.30; 35818 reflections, 10616 unique (Rint = 0.0449); parameters = 538; restraints = 5; R1 = 0.0583; wR2 = 0.1449; R1(all data) = 0.0751; wR2(all data) = 0.1563; Goof = 1.017; percent complete: 99.3%; 2: CaH6GeP; FW = 779.56 g/mol; colourless block; Size: 0.040 x 0.055 x 0.131 mm; Triclinic, P21/c; Unit Cell: a = 10.3576(11) Å, b = 22.4612(2) Å, c = 17.5165(19) Å, β = 99.453(3) °, V = 4019.8(7) Å3; Z = 4; p = 1.288; T = 150°C; λ = 0.71073 nm (MoKa); F(000) = 1624; μ = 0.707; 20max = 55.0; 20min = 2.98; 45865 reflections, 9226 unique (Rint = 0.0442); parameters = 474; restraints = 4; R1 = 0.0661; wR2 = 0.1475; R1(all data) = 0.1692; wR2(all data) = 0.1888; Goof = 1.007; percent complete: 99.9%.