Two Quasi-Stable Lead(II) Hydrides at Ambient Temperature

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Two Quasi-Stable Lead(II) Hydrides at Ambient Temperature

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Simple reactions of their terphenyl lead bromide precursors with DIBAL-H in diethyl ether solution at ca. -78°C leads to the isolation of the hydrides {Pb(μ-H)Ar$^{Pr^i}_4$}$_2$ (Ar$^{Pr^i}_4$ = C$_6$H$_3$-2,6 (C$_6$H$_3$-2,6-Pr$^i_2$)$_2$) (1) and {Pb(μ-H)Ar$^{Me}_6$}$_2$ (Ar $^{Me}_6$ = C$_6$H$_3$-2,6(C$_6$H$_2$-2,4,6-Me$_3$)$_2$) (2) in good yield(60-80%). The isolated solids are stable at up to 5°C for several weeks but are thermally labile in solution. Hydride 1 decomposes to the diplumbyne Ar$^{Pr^i}_4$PbPbAr$^{Pr^i}_4$, while 2 decomposes to the plumbylene Pb(Ar$^{Me}_6$)$_2$. The decomposition of 1 was determined to be zero order with a rate constant of ca. 2.0×10^{-5} M min^{-1} at 298K..

Since the initial report of a stable tin(II) hydride in 2000[1], low valent hydride derivatives of the heavy group 14 elements have become well established for the elements Si-Sn[1–14] over the past two decades. They display a diverse range of structures and are of particular interest for their reactivity with small molecules[15–18] and potential uses in catalysis.[19,20] The existence of an unstable lead(II) hydride "Pb(H)Ar$^{Pr^i}_6$" (Ar$^{Pr^i}_6$ = C$_6$H$_3$-2,6-(C$_6$H$_2$-2,4,6-Pr$^i_3$)$_2$) was implicated in the synthesis of the terphenyl substituted diplumbyne Ar$^{Pr^i}_6$PbPbAr$^{Pr^i}_6$ which was obtained via treatment of {Pb(μ-Br)Ar$^{Pr^i}_6$}$_2$ with LiAlH$_4$.[21] However, it wasn't until recently that the existence of the lead(II) hydride was established by Wesemann and coworkers[22] who synthesized it by treatment of Ar$^{Pr^i}_6$Pb{CH(Ph)(PPh$_2$)} with catechol borane, and showed that it has the symmetrically bridged hydride structure {Pb(μ-H)Ar$^{Pr^i}_6$}$_2$ (3) and converts to the diplumbyne Ar$^{Pr^i}_6$PbPbAr$^{Pr^i}_6$ above -40°C in solution with H$_2$ elimination.

In related work on Sn(II) hydrides we have shown that they can be stabilized by a variety of terphenyl substituents.[1,23–25] Moreover, the structure of the hydride product was found to be dependent on the aryl substituent used.[24] and that bulkier substituents favoured the unsymmetrical ArSnSn(H)$_2$Ar (Ar = terphenyl group) over the symmetric {Sn(μ-H)Ar}$_2$ structure. We applied this approach to the
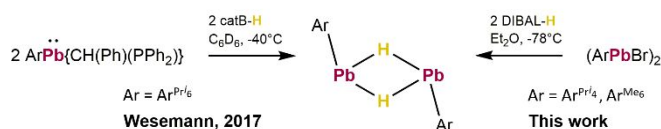
Scheme 1 Current known synthetic routes to terphenyl substituted lead(II) hydrides.

synthesis of lead(II) hydrides and their subsequent conversions to diplumbynes[26] and other low-valent lead species. We found that some of the intermediate lead hydrides that were formed precipitated out of diethyl ether as relatively stable solids and can be isolated in good yields (60-80%). We now report the isolation of the aryl lead(II) hydrides {Pb(μ-H)Ar$^{Pr^i}_4$}$_2$ (Ar$^{Pr^i}_4$ = C$_6$H$_3$-2,6 (C$_6$H$_3$-2,6-Pr$^i_2$)$_2$) (1) and {Pb(μ-H)Ar$^{Me}_6$}$_2$ (Ar $^{Me}_6$ = C$_6$H$_3$-2,6(C$_6$H$_2$-2,4,6-Me$_3$)$_2$) (2) and show that although 1 converts to the expected diplumbyne Ar$^{Pr^i}_4$PbPbAr$^{Pr^i}_4$ in solution,[26] 2 is transformed to the diarylplumbylene Pb(Ar$^{Me}_6$)$_2$.[27]

The lead hydrides were synthesized in a simple manner by treatment of {Pb(μ-Br)Ar$^{Pr^i}_4$}$_2$[28] or {Pb(μ-Br)Ar$^{Me}_6$}$_2$[29] with DIBAL-H (di-isobutyl aluminium hydride) in diethyl ether solution at -78°C (Scheme 1). This resulted in the precipitation of 1 and 2 as yellow-green solids. Decanting the supernatant liquid and washing the solid with ether and hexanes gave 1 in ca. 80% and 2 in ca. 60% yield. Extraction of a portion of the solids with either toluene or THF at ca. 0°C and storage of the resulting solutions at ca. -30°C gave yellow blocks of 1 or yellow-green blocks of 2 that were suitable for X-ray diffraction studies (see photos in Supporting Information). Both 1 and 2 (Figure 1) display dimeric hydrogen-bridged structures with planar Pb$_2$H$_2$ cores (sum of the internal angles = 360°), which are similar to that seen for the structure of 3 reported by Wesemann and coworkers.[22] The dimeric structure of 2 contrasts with the analogous Sn hydride {Sn(H)Ar$^{Me}_6$}$_4$,[25] which has a tetrameric structure containing four Sn–Sn bonds and a terminal hydrogen bound to each tin. The Pb–H distances are in the range 2.04(3) Å to 2.09(4) Å, similar to the distances reported in 3 (1.98(4)-2.03(5) Å). The ligands are

{Pb(μ-H)Ar$^{Pr^i_4}$}$_2$ (**1**)
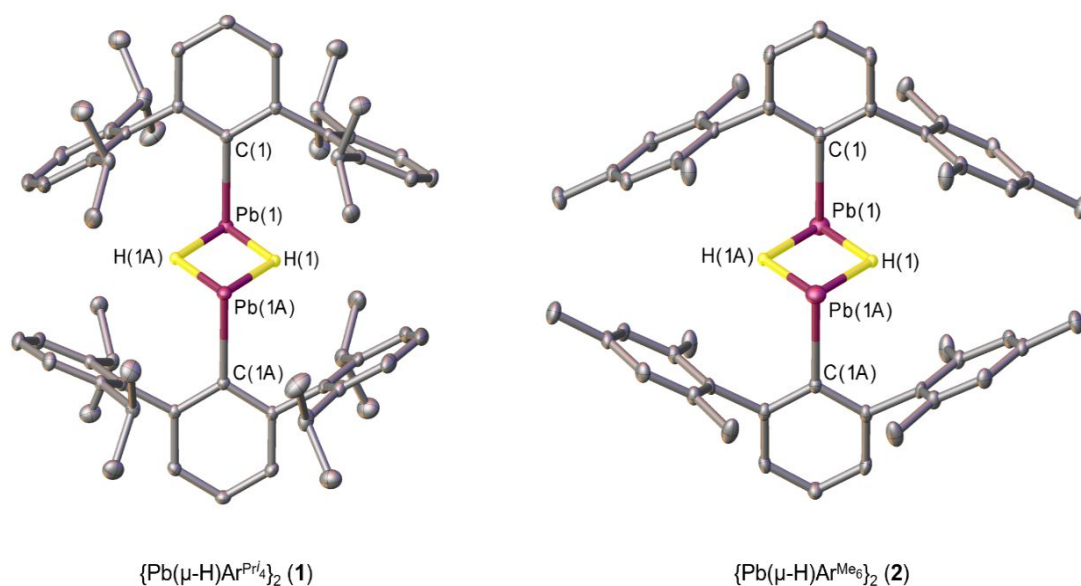
{Pb(μ-H)Ar^{Me_6}}$_2$ (**2**)

Fig. 1 Thermal ellipsoid plots (50%) of **1** and **2**. Terphenyl hydrogen atoms and co-crystallized solvent molecules are not shown for clarity. Selected bond lengths [Å] and angles [°]: 1: Pb1–C1: 2.3066(12), Pb1–H1: 2.04(3), Pb1–H1A: 2.05(2), Pb1···Pb1A: 3.2662(3), Pb1–H1–Pb1A: 105.9(1), H1–Pb1–H1A: 74.1(1), (Pb1–C1)–(Pb2H2): 93.44(3). 2: Pb1–C1: 2.289(4), Pb1–H1: 2.08(4), Pb1–H1A: 2.09(4), Pb1···Pb1A: 3.2791(5), Pb1–H1–Pb1A: 104(3), H1–Pb1–H1A: 76(3), (Pb1–C1)–(Pb$_2$H$_2$): 89.61(11).

bound to the lead atoms almost perpendicularly to the Pb$_2$H$_2$ core with Pb–C$_{ipso}$ angles of 89.61(11)° to 93.44(3)° (cf. 92.3(6) in the case of **3**) with respect to the Pb$_2$H$_2$ plane.

Wesemann and co-workers reported two observable ^{1}H NMR signals in solution for the lead hydride **3** at 35.83 ppm and 31.43 ppm in d_8-toluene, which were attributed to the presence of rotamers of **3** in solution.[22] The more downfield shifted signal is the prominent signal at 298 K while the more upfield signal is more prominent at 193 K, indicative of an equilibrium between the two rotamers in solution. The extreme downfield chemical shift of the hydride resonance has been determined by relativistic DFT methods to be due to the spin-orbit coupling effects of the heavy lead atoms.[30] Essentially, it was found that the relatively low HOMO-LUMO gap of low valent 6p elements allows for efficient magnetic coupling of the frontier orbitals; combined with the primarily 6p character of the metal contribution to the bonding orbitals, the result is a drastic deshielding of the bonded hydrogen atom.[31]

Our previous work on tin(II) hydrides showed that increasing the size of the terphenyl ligand affects the solution structure,[24] e.g. the symmetric hydrogen bridged structure of {Sn(μ-H)Ar$^{Pr^i_6}$}$_2$ in the solid state converts to the deep blue asymmetric structure Ar$^{Pr^i_6}$SnSn(H)$_2$Ar$^{Pr^i_6}$ in solution. The ^{1}H NMR spectra of yellow solutions of **1** and **2** at 298 K display only one downfield singlet at 33.91 ppm (^1J ^{207}$_{Pb-}^{1}_H$ = 696 Hz) in C$_6$D$_6$ for **1** and at 33.91 ppm in C$_6$D$_6$ or 33.65 ppm in d_8-THF (^1J ^{207}$_{Pb-}^{1}_H$ = 708Hz) for **2** corresponding to the hydride signal. The signals are slightly upfield in comparison to that of the lead hydride ^{1}H chemical shift for **3** at 35.83 ppm (^1J ^{207}$_{Pb-}^{1}_H$ = 725 Hz) reported at 298 K and are in close agreement with the chemical shift calculated for the symmetric bridging hydride structure in solution.[30] The ATR-FTIR spectra of **1** and **2** both display a near identical feature in the range ca. 950 to 1050 cm^{-1} which match Pb-H bands determined for **3** (900-1100 cm^{-1}).[22]

The hydrides **1** and **2** can be stored as solids under anaerobic and anhydrous conditions at 5°C in the absence of light but decompose slowly over several days if kept at ambient temperature. When dissolved in hydrocarbon or ethereal solvents they both immediately begin to release H$_2$ and decompose. Monitoring the degradations by ^{1}H NMR spectroscopy, we observed that **1** converts to the expected amber diplumbyne Ar$^{Pr^i_4}$PbPbAr$^{Pr^i_4}$[26] and determined the rate to be zero order with a rate constant of ca. 2.0×10^{-5} M min^{-1} (1.2×10^{-3} M hr^{-1}). The hydride **2** instead converts to the purple plumbylene Pb(Ar^{Me_6})$_2$[27] with concomitant deposition of Pb metal. This suggests the putative diplumbyne "Ar^{Me_6}PbPbAr^{Me_6}" that may form upon elimination of H$_2$ from **2** is not sufficiently stabilized by the smaller groups on the flanking rings of the terphenyl ligands compared to Ar$^{Pr^i_6}$PbPbAr$^{Pr^i_6}$ and Ar$^{Pr^i_4}$PbPbAr$^{Pr^i_4}$ and instead a rearrangement is preferred. We have previously found that Ar^{Me_6} is not sufficiently large to stabilize the digermyne Ar^{Me_6}GeGeAr^{Me_6} and instead the cyclotregermenyl radical (GeAr^{Me_6})$_3$· is obtained.[32] Ziegler and co-workers have demonstrated computationally that isopropyl substituents on the terphenyl ligands play a crucial role in stabilizing group 14 dimetallynes through intramolecular London dispersion interactions which overcome the Pb–Pb bond dissociation energy (cf. -44 kcal·mol^{-1}).[33] Working with Stefan Grimme's group on a series of diplumbynes bearing terphenyl ligands of varying size, we have further confirmed that the Pb–Pb bond dissociation energy is compensated for by dispersion force attractions between ligands on opposing Pb atoms.[26]

Attempts to apply this protocol to the preparation of other terphenyl supported lead(II) hydrides has so far been unsuccessful and we have not observed any precipitation of other lead(II) hydride systems. We attribute this to the low solubility of **1** and **2** compared to other terphenyl lead systems we have investigated.[26] Examining the crystal structure of **2**, a

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network of close interligand H···H contacts can be observed between molecules with distances of 2.368(25) Å, (see ESI– Figure S8) shorter than twice the van der Waals radius of hydrogen ($2r_H$ = 2.40 Å).[34] Such an interaction is not observed in the structure of **1** recrystallized from toluene, as several solvent molecules surround the structure which presumably contribute to the stability of the crystals. However, these crystals were found to be much more prone to thermal decomposition than crystals of **2** or powdered **1**. The results strongly suggest that as isolated solids, **1** and **2** may be stabilized by intermolecular London dispersion force energies (i.e. 'packing' forces) which stabilize the molecular structures.[35] When these are removed by dissolution of **1** or **2** in hydrocarbon or ethereal solvents, decomposition to the diplumbyne or plumbylene ensues.

Compounds **1** and **2** are very rare examples of hydride derivatives from the 6th period p-block elements that are isolable under ambient or near ambient conditions, the other notable example BiH(Ar^{Me_6})$_2$.[36]

In summary, the treatment of {Pb(μ-Br)Ar$^{Pr^i_4}$}$_2$ and {Pb(μ-Br)Ar^{Me_6}}$_2$ with DIBAL-H in diethyl ether at -78° gives the lead(II) hydrides **1** and **2** in ca. 60-80% yield as green-yellow powders. The products are thermally unstable in solution and degrade to diplumbyne Ar$^{Pr^i_4}$PbPbAr$^{Pr^i_4}$ in the case of **1** and plumbylene Pb(Ar^{Me_6})$_2$ in the case of **2** . However, they can be stored in the solid state under a nitrogen or argon atmosphere and in low light conditions at ≤ 5°C for several weeks without noticeable decomposition.

Conflicts of interest

There are no conflicts to declare.

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Two quasi stable lead(II) hydrides appear to be stabilized by intermolecular dispersion forces in the crystal phase.

ChemComm

:PbAr₂

$-H_2$, $-Pb^0$

Ar =

ArPb(μ-Br)₂PbAr ⟶ ArPb⟨H / H⟩PbAr

Stable Solid < 5°C !

Ar =

$-H_2$

ArPbPbAr