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Kinetic Stabilization of Primary Hydrides of Main Group Elements. The Synthesis of an Air-Stable, Crystalline Arsine and Silane

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Two new, "user-friendly" derivatives of triptycene containing AsH_2 and SiH_3 fragments were synthesized. Both solids are crystalline, air-stable compounds characterized by elevated melting points and resistance toward moisture. The highly reactive As–H and Si–H bonds are protected by the presence of the surrounding phenylene hydrogen atoms, which ensure a remarkable kinetic stabilization of these primary hydrides. After X-ray irradiation of a single crystal of triptycenesilane, a persistent silyl radical was trapped and characterized.

Since the first synthesis of triptycene by Bartlett[1] in 1942, the chemistry of triptycene has gained spectacular importance, and new fields are now opened for this exciting domain, from material and polymer science,[2] to liquid crystal matrices,[3] to the synthesis of antitumor drugs[4] in medicine. The particular interest for triptycene derivatives lies in their unusually high symmetry and rigid framework. As a result, triptycene easily adopts a packed, compact structure[5] which offers an ideal organization pattern for liquid crystals or for surface polymers. Moreover, the emerging need for molecular level controlled devices has led to the development of molecular machinery, which is probably the future of nanotechnology and biotechnology. Triptycene is one of these rare molecules "par excellence", which possesses all the characteristics likely to be explored, using its derivatives as building blocks in molecular brakes or gears. Several articles devoted to triptycene-based molecular rotors have recently been published.[6]

In the past years we have reported the synthesis of stable, crystalline, primary phosphines[7] and germanes[8] using the triptycene framework as a protective group for the stabilization of the P−H and Ge−H bonds. Recently, particular interest has focused on the primary silanes, phosphines, and arsines, especially for the high reactivity of the E−H bond (E = Si, As, P) and potential uses in organic synthesis. Nevertheless, the major impediment to the use of the two latter classes of compounds lies in their extreme toxicity, unpleasant odor, and very high instability toward oxidation and hydrolysis. Most of the primary phosphines are not only air-sensitive but also pyrophoric. Several attempts were made to obtain "user-friendly" compounds, mainly by taking advantage of the stabilization of the reactive hydrogen bond by the nearby bulky substituents.

Following similar lines we have attempted the synthesis of a set of group 14 and 15 hydrides with triptycene as a stabilizing environment. In this Communication we report the synthesis of the first crystalline and air-stable silicon and arsenic derivatives of triptycene (Trip) containing free EH_n fragments ($TripSiH_3$ (**1**) and $TripAsH_2$ (**2**)) as well as preliminary EPR results on the trapping of the corresponding silyl radical in the crystal matrix. The attempted synthesis of bismuth, tin, lead, and antimony analogues is presented as Supporting Information.

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As for the reported synthesis of triptycenephosphine and triptycenegermane, we have used a simple and convenient way to synthesize Trip$-$EH_n compounds by performing an in situ reaction of the stoichiometric amount of the corresponding chloride ECl_{n+1} with the lithium derivative of triptycene[9] in THF at -100 °C and subsequent reduction with $LiAlH_4$. (**WARNING!** The evolution of highly toxic AsH_3 may occur during the reduction step.) The overall yields for this reaction vary considerably depending on the chloride used (11% for TripAsH_2 and 82% for TripSiH_3). The ^{1}H NMR spectra[10] of **1** and **2** show a characteristic signal of a single bridge proton of triptycene at 5.4 ppm. The detailed synthesis, safety warnings, and spectroscopic characterization of **1** and **2** are available in the Supporting Information.

The silane **1** and the arsine **2** are completely air-stable, solid compounds. Single crystals of **1** did not show any trace of decomposition after a 3-month exposure to air. Single crystals of **2** after the same exposure time had lost only a very little transparency on the surface, but no spectral changes in the NMR or mass spectra were observed. It is also worth noting that, for both **1** and **2**, short treatment of their respective solutions in an *n*-hexane/ether mixture with a small amount of water in the open atmosphere does not affect the yield of the crystallized product, although a systematic study of the stability in the liquid phase has not been undertaken. The crystalline samples are characterized by high melting points: 221 °C for TripSiH_3 (one of the highest melting points known for organosilicon compounds) and 293 °C for TripAsH_2. Compared with the rare SiH_3-containing compounds which have been previously reported,[11] triptycenesilane appears to be exceptionally air- and moisture-stable; nevertheless its stability is less remarkable than that of the previously synthesized triptycenegermane. In addition, as far as we know, **2** is the first free, crystalline, highly air-stable primary arsine. Only two crystal structures containing an AsH_2 group were reported in the literature, both concerning rather air-sensitive species.[12,13]

Both compounds **1** and **2** crystallize in the trigonal system in the space groups $R\bar{3}$ and $R3c$ respectively.[14] As their homologues,[7,8] the molecules are located on 3-fold axes and show disorders of the E substituents located either at the C1 (major) or C8 (minor) positions and maintaining the position of the triptycene skeleton. Moreover, the Trip$-$EH_2 compounds exhibit twinning by inversion in various ratios. These disorders and inversion twin ratios were refined and reported in Table 1. It is worth noting that TripSiH_3 shows a more ordered structure, compared to the homologous compounds TripGeH_3 and TripCH_3. In contrast, the disorder observed in TripAsH_2 is more pronounced than in the corresponding TripPH_2 and could explain the rather poor quality of the crystals.

Table 1. Space Group, Disorder, and Inversion Twin Ratios for Selected Triptycene Derivatives

compound	space group	disorder ratios (%)	inversion twin ratios (%)
TripSiH_3	$R\bar{3}$	88.6(3)/11.4(3)	
TripGeH_3[a]	$R\bar{3}$	60.0(4)/40.0(4)	
TripCH_3[a]	$R\bar{3}$	61.5(7)/38.5(7)	
TripAsH_2	$R3$c	71.8(6)/28.2(6)	74(4)/26(4)
TripPH_2[b]	$R3$c	73.4(5)/26.6(5)	65(8)/35(8)

[a] Reference 8. [b] Reference 7.

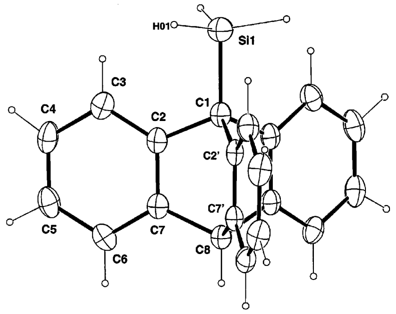

Figure 1. Perspective view of the crystal structure of triptycene$-$silane **1** with the atom numbering. Ellipsoids are represented with 40% probability. Selected bond distances (Å) and angles (deg), values for triptycene arsine **2** are given in brackets: C1$-$Si1 = 1.804(3) [2.170(18)]; Si1$-$H01 = 1.46(2) [1.38(15)], C1$-$C2 = 1.540(2) [1.458(12)]; C7$-$C8 = 1.528(2) [1.545(13)]; C2$-$C1$-$Si1 = 113.2(1) [105.7(7)]; C2$-$C1$-$C2′ = 105.5(2) [113.0(8)]; C7$-$C8$-$C7′ = 105.7(2) [102.7(7)].

We believe that the extremely high stability of **1** and **2** (compared to the usually air-sensitive primary arsines and silanes) is mostly due to the particular role that position 1 (cf. C1 in Figure 1) plays in the triptycene skeleton. This bridge position lies on the symmetry axis of the triptycene and is protected by the adjacent protons of three symmetrical phenylene rings. Such a conformation ensures a noticeable steric hindrance of the substituent attached to this particular position and is the origin of this “cage protection” effect. The average distance between three frontal phenylene protons is about 4.5 Å, derived from crystal structures of different triptycene derivatives.[7,8] That appears to be rather short taking into account the length of the dioxygen or water molecules, which are likely to approach the very reactive E$-$H bond, and could explain a high stability toward air and moisture. The same steric hindrance could also be responsible for the difficulty in including heavier elements such as bismuth or antimony at the bridge position, although their sterically protected chlorides have been reported.[15] In this context it is interesting to compare the protecting ability of the triptycene to the very similar triphenylmethyl (trityl) group

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(9) Obtained by the reaction of 1.1 equiv of *n*-BuLi with 9-bromotriptycene in THF at -78 °C.

(10) **1**: ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) $\delta_H = 4.49, 5.35, 6.90-6.99, 7.29-7.33$; ^{29}Si NMR ($CDCl_3$, 99.3 MHz, ppm) $\delta_{Si} = -62.97$, $J_{Si-H} = 204$ Hz); MS *m/z* 284 (M^+). **2**: $\delta_H = 3.34, 5.42, 6.99-7.03, 7.38-7.41$; MS *m/z* 330 ($M^+$).

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(14) X-ray data sets were collected at 200 K on a Stoe IPDS diffractometer with Mo Kα radiation. **1**: $C_{20}H_{16}Si$, $M = 284.5$; trigonal, $R\bar{3}$, $Z = 6$, $a = 11.8394(8)$ Å, $c = 17.4685(15)$ Å, $V = 2120.5(3)$ Å^3, $R = 0.032$, $R_w = 0.031$. **2**: $C_{20}H_{15}As$, $M = 330.3$; trigonal, $R3c$, $Z = 6$, $a = 12.0606(8)$ Å, $c = 17.2786(11)$ Å, $V = 2176.6(3)$ Å^3, Flack parameter $x = 0.26(4)$, $R = 0.033$, $R_w = 0.036$. (See Supporting Information for further details and ref 7 for the space group assignment of **2**.)

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Table 2. Melting Points of Selected Primary Phosphines

primary phosphine	MW	mp (°C)
phenylphosphine[a]	110	*b*
9-anthracenylphosphine	210	88
$Bu^t{}_3C_6H_2$ phosphine	278	114
dibenzobarrelenephosphine	236	108
diphenyldibenzobarrelenephosphine	388	141
triptycylphosphine	286	222

[a] At room temperature exists in liquid phase. [b] Bp 160 °C.

which has been used to stabilize a number of previously unisolable compounds.[16] The trityl moiety possesses similar characteristics; although it is not as symmetrical as triptycene, its C−X bond (related to the methyl carbon bearing substituent) lies on the "pseudo" 3-fold axis and is surrounded by three benzenic rings. In the trityl unit the average distance between the three frontal phenylene protons (4.4 Å) is also very close to that observed in the triptycene moiety. In order to explain the differences in the stabilizing "cage effect" between triptycyl and trityl groups, the shortest distance between the bridgehead carbon in triptycene (or analogous methyl carbon in the trityl unit) and the plane containing the three frontal phenylene hydrogens of the triptycyl unit (respectively the three frontal hydrogens of the trityl group) has been estimated on the basis of the crystal structures of the various triptycene and trityl derivatives. In trityl, this distance is ∼0.35 Å, while in the triptycyl fragment it is noticeably longer (∼0.60 Å). Bearing in mind that both protecting groups have almost the same molecular weight, this difference in the "cage" dimension is most probably responsible for the more pronounced stabilizing effect in the case of the triptycyl moiety.[17]

We believe that the "cage" effect is also one of the reasons for the previously mentioned high melting points of **1** and **2**. Together with a high rigidity, another important factor for increasing the melting point,[18] the "cage effect" can explain this unusually high physicochemical property of various triptycene derivatives; the majority of the triptycene-based molecules with bridgehead substituents melt above 200 °C. The tandem influence of the rigidity and "cage" protection on the melting point is nicely illustrated by the trend observed in the increase of the melting point of primary phosphines (Table 2). The molecular frames of the dibenzobarrelenephosphine[8] (DBB−PH_2, MW = 236) and the diphenyldibenzobarrelenephosphine[19] (DPDBB−PH_2, MW = 388) do not allow a "cage" protection, and, additionally, both compounds exhibit a higher degree of flexibility than the corresponding triptycylphospine (MW = 286). This is directly reflected by their melting points: 108 °C for DBB−PH_2, 141 °C for DPDBB−PH_2, and 222 °C for triptycylphosphine, respectively.

As previously reported, upon X-ray irradiation of single crystals of main group hydrides, homolytic scission of the E−H bond occurs; in the case of R−EH_3 hydrides, R−$E^{\bullet}H_2$ radicals have been detected by EPR. Examples of such radicals are triptycenegermyl[20] and triptycenemethyl[21] radicals; the corresponding spectra exhibit a simple 1−2−1 triplet due to hyperfine coupling with two protons. A similar spectrum is obtained with an X-ray irradiated single crystal of **1** and is consistent with the trapping of the persistent (more than a few weeks) $TripSi^{\bullet}H_2$ (**R1**) radical. The optimized proton hyperfine tensors (25, 34, and 35 MHz) are mostly isotropic and consistent with the coupling constants reported for other $RSi^{\bullet}H_2$ radicals.[22] The anisotropy of the **g**-tensor is not very marked ($g_x = 2.0036$, $g_y = 2.0039$, $g_z = 2.0045$), and the corresponding mean value ($g_{mean} = 2.0040$) is close to the free electron value. In accordance with the spin−orbit coupling constants of the central atom, this g_{mean} value is slightly higher than that measured for $TripC^{\bullet}H_2$ ($g_{mean} = 2.0017$) but lower than the value observed for $TripGe^{\bullet}H_2$ ($g_{mean} = 2.011$). The slightly different pyramidality[23] and the difference in the C−Si (1.794 Å) and C−Ge (1.861 Å) bond lengths are probably responsible for the lower values of the proton coupling constant compared to those of $TripGe^{\bullet}H_2$.

In conclusion, we present here the synthesis of two new, crystalline and "user-friendly" derivatives of triptycene with high melting points, containing AsH_2 and SiH_3 fragments. Highly reactive bonds (such as arsenic−hydrogen or silicon−hydrogen bonds) can thus be efficiently protected by the presence of the surrounding phenylene hydrogen atoms of the triptycyl moiety, which ensure a remarkable kinetic stabilization of the primary hydrides. The potential use of the novel primary arsine and silane as building blocks for the synthesis of liquid crystals or polymers, as well as the use of the triptycene unit as a protecting group for the stabilization of other highly reactive species, is currently under investigation.

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Supporting Information Available: Detailed synthesis, characterization, and crystallographic data of **1** and **2**, EPR spectra of **R1** (PDF), and CIFs. Attempted synthesis of bismuth, tin, lead, and antimony analogues. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) For example, trityl−PH_2 was isolated (see ref 16c) as an only moderately stable solid (mp 76 °C) while Trip−PH_2 is a crystalline, highly air- and moisture-stable compound (mp 222 °C). For the melting points of selected triptycene derivatives, see Table S1 in the Supporting Information.

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(23) DFT optimized structures show that in $TripE^{\bullet}H_2$ (E = Si or Ge) the out-of-plane angle (angle between the normal to the HEH plane and the E−C bond direction) is equal to 37.6° for $TripSi^{\bullet}H_2$ and 52.6° for $TripGe^{\bullet}H_2$.