

Air-stable crystalline primary phosphines and germanes: synthesis and crystal structures of dibenzobarellene phosphine and tribenzobarellene germane

Marcin Brynda,^a Michel Geoffroy^{*a} and Gérald Bernardinelli^b

^a Département de Chimie Physique, 30 Quai Ernest Ansermet, 1211 Genève, Switzerland

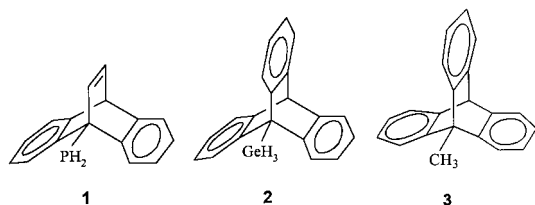
^b Laboratoire de Cristallographie, 24 Quai Ernest Ansermet, 1211 Genève, Switzerland.

E-mail: geoffroy@sc2a.unige.ch

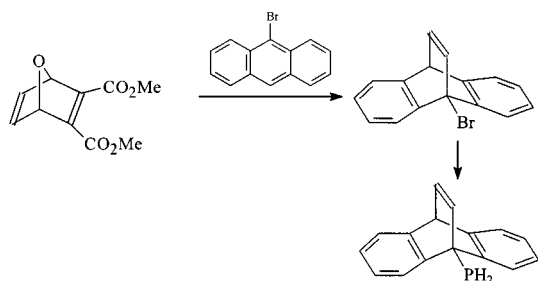
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The syntheses of dibenzobarellene phosphine and tribenzobarellene germane are described; at room temperature these primary phosphines and germanes form air-stable crystals whose structures are reported together with that of tribenzobarellene methane.

Primary phosphines are generally air-sensitive liquid compounds. Most of the reported crystal structures with an RPH₂ moiety have therefore been determined on molecules where the phosphorus atom is coordinated to a metal atom.¹ The crystal structure of free primary phosphines could be obtained in only a very limited number of cases: (1) when the phosphorus atom is bound to a cumbersome protective aryl group (Bu₃C₆H₅),² to an iron dicyclopentadienyl group³ or to a triptycyl moiety;⁴ (2) after dimerisation of anthracenephosphine;⁵ (3) after N-quaternisation of aminoalkylphosphines.⁶ Recent results⁷ indicated that benzo derivatives of barrelene were likely to lead to stable crystalline RPH₂ compounds; we have therefore taken advantage of this to attempt the synthesis of a primary phosphine which contains a double bond in the vicinity of the phosphorus atom. We report below the synthesis and the structure of the remarkably air-stable primary phosphine **1**. The synthesis of dibenzobarellene phosphine[†] is shown in Scheme 1.



In the solid state the dibenzobarellene phosphine **1**[‡] is located on a mirror plane perpendicular to the *b* axis with P1, C7, C8, C9, C10, H8, H9 and H10 in special positions 4c. All hydrogen atoms have been observed and refined without constraint. No significant electronic density corresponding to a hydrogen site located in the *trans* position relative to the C7–C8 bond was observed, meaning that only one rotamer is present and that no free rotation of the phosphine around the C–P bond occurs at 180 K. The dihedral angle between the mean planes of the phenyl moieties is 113.8° (angle between the central ethylene bridge and a phenyl moiety = 123.1°).



Scheme 1

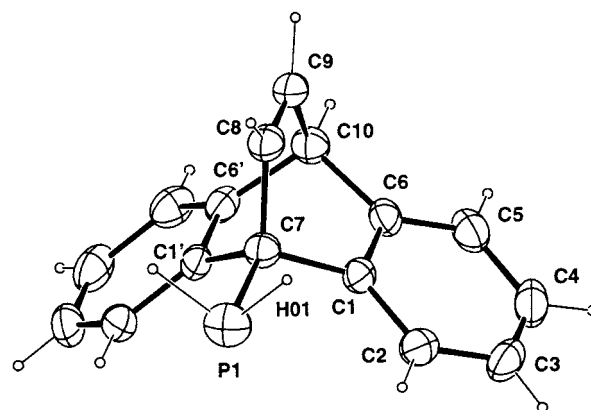
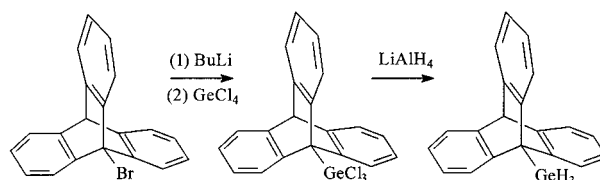


Fig. 1 Perspective view of **1**. Ellipsoids are represented with 40% probability. Selected bond distances (Å) and angles (°): P1–C7 1.859(4); C1–C6 1.402(4); C1–C7 1.536(4); C6–C10 1.522(4); C7–C8 1.539(6); C8–C9 1.314(7); C9–C10 1.520(6); P–H01 1.36(3); C1–C7–C8 105.5(2); C1–C7–C1' 103.3(3); C1–C7–P1 113.2(2); C7–C8–C9 115.2(4); C8–C9–C10 114.1(4); C6–C10–C6' 104.5(3); C6–C10–C9 106.1(2); H01–P–H01' 93(2).

In the context of this study, we envisaged using benzobarellene derivatives to form a crystalline primary germane. Although less reactive than their silicon homologues, primary germanes are generally air-sensitive liquid (or gaseous) compounds at room temperature. As far as we know, the only crystal structure reported for RGeH₃ was obtained at 160 K on cyclopentadienyl germane, which melts at 200 K.⁸ We report below the synthesis[†] (Scheme 2) and the crystal structure[‡] of tribenzobarellene germane **2** which forms air-stable crystals with a melting point of 232 °C.

This compound is isostructural with tribenzobarellene methane **3**,⁹ whose structure,[‡] to the best of our knowledge, has never been published. Both **2** and **3** show disordered structures. The molecules are located on 3-fold axes with C1, C8, Ge (resp. C9) and H8 atoms in special positions 6c of the space group R $\bar{3}$. The disorder consists of an inversion of the molecule approximately maintaining the position of the tribenzobarellene skeleton and mainly affecting the germanium (resp. C9) atom. The refinement of such models fixing the sum of the occupations of the Ge (resp. C9) sites to 1 shows disorder ratios of 60.0(4)/40.0(4)% and 61.5(7)/38.5(7)% for **2** and **3** respectively. The relatively high values of the *R* factors and uncertainties obtained for **2** show that this compound is more affected than **3** by the disorder. Indeed, in the crystal packing,



Scheme 2

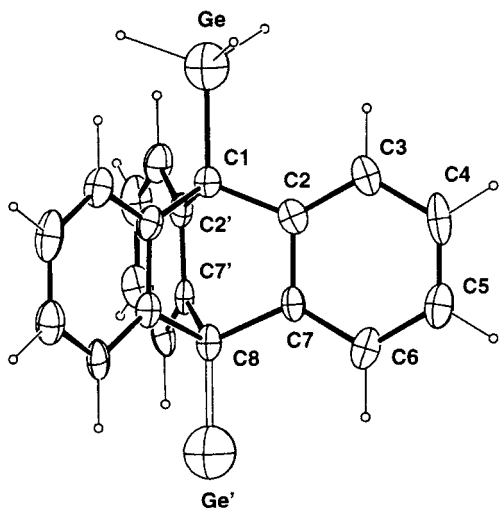


Fig. 2 Perspective view of **2**. Ellipsoids are represented with 40% probability. Selected bond distances (Å) and angles (°): C1–Ge 1.861(8); C1–Ge' 1.77(1); C1–C2 1.513(8); C7–C8 1.541(5); C2–C1–Ge 111.8(3); C7–C8–Ge' 114.0(3); C2–C1–C2' 107.1(5); C7–C8–C7' 104.6(5) [for the isostructural **3** (Ge \leftrightarrow C9): C1–C2 1.529(2); C1–C9 1.546(5); C1–C9' 1.546(6); C7–C8 1.524(2); C2–C1–C2' 105.0(1); C2–C1–C9 113.62(9); C7–C8–C9' 113.07(8); C7–C8–C7' 105.6(1)].

the shortest distances between two disordered sites of the Ge (resp. C9) atoms located along *c* axis (on both sides of a centre of inversion) are 1.557(7) and 2.065(8) Å for **2** and **3** respectively. It should be noted that a refinement of **2** in the noncentrosymmetric space group *R*3 leads to a final value of the Flack parameter¹⁰ of $x = 0.47(28)$, large values of Δ/σ , non-positive values of $\|U_{ij}\|$ and a value of *R* of about 13%. These observations lead us to exclude the presence of a non-centrosymmetric, twinned and disordered structure as observed for the analogous tribenzobarrelenephosphine compound.⁴

EPR experiments on the dynamics of radicals produced from **1** and **2** are currently in progress.

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Notes and references

† *Syntheses*: All experiments were performed under dry N₂.

Bromodibenzobarellene was synthesized following a slight modification of the method reported by Mori *et al.* (ref. 11): 3.57 g (14 mmol) of 9-bromoanthracene and 3.48 g (17 mmol) of the furan–acetylene adduct in 20 ml of triglyme were sealed in a glass tube and placed in an autoclave. Very vigorous stirring was applied and the mixture was heated at 120 °C for 48 h and then at 200 °C for 24 h. The oily brown solution was washed with water (3 × 30 ml) to remove the solvent. After the usual work-up bromodibenzobarellene was separated by chromatography on silica gel using hexane–Et₂O (10 : 1) as eluant. The yellow powder was recrystallised from CH₂Cl₂–EtOH (68%): transparent crystals, mp 105 °C; δ_{H} (CDCl₃, 200 MHz) 5.13 (dd, 1H), 7.05 (m, 6H), 7.26 (d, 2H), 7.71 (d, 2H); *m/z* (M⁺), 282, 256, 203, 176, 150, 101, 75.

Dibenzobarellene-phosphine: 4.9 ml of BuLi (1.6 M, hexane) were very slowly introduced, at –80 °C, into a solution containing 2 g (7.1 mmol) of bromodibenzobarellene dissolved in 30 ml of dry THF. After 10 min the temperature was slowly raised up to –60 °C. Then the solution was quickly cooled to –100 °C and 1.1 ml of PCl₃ (12.5 mmol) was added all at once; the solution was vigorously stirred for 30 min and gently refluxed for 1 h. The solution was then cooled in an ice bath and 0.53 g (14 mmol) of LiAlH₄ were carefully added. After refluxing for 2 h, the reaction was quenched with a few drops of HCl/H₂O and the residual phosphine was extracted with Et₂O (3 × 30 ml). The final product was purified by chromatography on silica gel using hexane–Et₂O (9 : 1) as eluant. Small, thin crystals were obtained directly from this solution (42%): mp 108 °C; δ_{P} (CDCl₃, 80 MHz) 143.6 (t, *J*_{PH} 199); δ_{H} (CDCl₃, 200 MHz) 3.55 (d, *J*_{PH} 200, 1H, PH), 5.13 (dd, 2H), 6.76 (ddd, 1H), 7.05 (m, 6H), 7.32 (m, 2H), 7.50 (m, 2H).

Tribenzobarellene-germane: 2 g (6.0 mmol) of bromotriptycene were dissolved in 30 ml of dry THF. Then 4.1 ml of BuLi (1.6 M hexane) were introduced very slowly into the solution during a few minutes at –78 °C. After 10 min the temperature was slowly raised up to 0 °C and then cooled quickly to –80 °C. 1.93 g of GeCl₄ (9.0 mmol) was added all at once and the solution was vigorously stirred. After 30 min a gentle reflux was applied during 1.5 h. The solution was cooled in an ice bath and 0.4 g (10.6 mmol) of LiAlH₄ was carefully added. After refluxing for 2 h the reaction was quenched with a few drops of HCl/H₂O and the residual germane was extracted with Et₂O (3 × 30 ml). The final product was purified via silica gel chromatography using hexane–Et₂O (9 : 1) as eluant. Small transparent crystals were obtained directly from this solution (35%), mp 232 °C; δ_{H} (CDCl₃, 200 MHz) 2.37 (s, 3H), 4.44 (s, 1H), 6.96–7.04 (m, 6H), 7.33–7.42 (m, 6H); *m/z* 330 (M⁺), 253, 226, 176, 126.

‡ *Crystal data* for **1**: C₁₆H₃₁P, *M* = 236.3; orthorhombic, *Pnma*, *Z* = 4, *a* = 11.7836(5), *b* = 14.3232(7), *c* = 7.2002(5) Å, *V* = 1215.2(1) Å³, *T* = 180 K, μ = 1.753 mm^{–1} for Cu–K α radiation (*A** min., max. = 1.174, 1.585), *F*₀₀₀ = 496, *D*_c = 1.291 g cm^{–3}, 1560 measured reflections, 780 unique reflections of which 665 were observable [*I*(*F*_o) > 4 σ (*F*_o)]. Full-matrix least-squares refinement based on *F* using weight of 1/ σ^2 (*F*_o) + 0.0001(*F*_o)² gave final values *R* = 0.038, ωR = 0.037 for 115 variables and 665 contributing reflections. Hydrogen atoms were observed and refined. For **2**: C₂₀H₁₆Ge, *M* = 328.9; trigonal, *R*3, *Z* = 6, *a* = 11.8154(7), *c* = 17.7571(7) Å, *V* = 2146.8(3) Å³, *T* = 200 K, μ = 2.794 mm^{–1} for Cu–K α radiation (*A** min., max. = 1.661, 2.898), *F*₀₀₀ = 1008, *D*_c = 1.527 g cm^{–3}, 1872 measured reflections, 593 unique reflections of which 563 were observables [*I*(*F*_o) > 4 σ (*F*_o)]. Full-matrix least-squares refinement based on *F* using weight of 1/ σ^2 (*F*_o) gave final values *R* = 0.086, ωR = 0.060 for 69 variables and 563 contributing reflections. Hydrogen atoms were calculated. For **3**: C₂₁H₁₆, *M* = 268.4; trigonal, *R*3, *Z* = 6, *a* = 11.7919(7), *c* = 17.5871(8) Å, *V* = 2117.8(2) Å³, *T* = 170 K, μ = 0.538 mm^{–1} for Cu–K α radiation (*A** min., max. = 1.083, 1.165), *F*₀₀₀ = 852, *D*_c = 1.263 g cm^{–3}, 1985 measured reflections, 634 unique reflections of which 629 were observables [*I*(*F*_o) > 4 σ (*F*_o)]. Full-matrix least-squares refinement based on *F* using weight of 1/ σ^2 (*F*_o) gave final values *R* = 0.038, ωR = 0.036 for 95 variables and 629 contributing reflections. Hydrogen atoms were observed and refined. CCDC 182/1228. See <http://www.rsc.org/suppdata/cc/1999/961/> for crystallographic files in .cif format.

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