Reaction of a diarylgermylene with a phosphaalkyne: formation of a germadiphosphacyclobutene with an exocyclic C=Ge double bond

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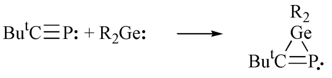
The reaction of bis(2-*tert*-butyl-4,5,6-trimethylphenyl)germylene (Ar_2Ge:) with *tert*-butylphosphaalkyne furnishes a germadiphosphacyclobutene derivative with an exocyclic –C(Bu^t)=$GeAr_2$ group at one phosphorus atom, which was characterised by an X-ray structure analysis.

The addition of dialkyl-silylenes and -germylenes to the P≡C triple bonds of thermally stable phosphaalkynes represents a simple method for the synthesis of three-membered ring systems containing a P=C double bond that are difficult to prepare by other routes. For example, the silylene R_2Si**:** (R = CMe_3) reacts smoothly with phosphaalkynes to afford the corresponding phosphasilirenes.[1] The dialkylgermylene **1**[2,3] also undergoes a [2 + 1] cycloaddition reaction with *tert*-butylphosphaalkyne from which the germaphosphirene **2** can be isolated (Scheme 1).[4] The diarylsilylene Mes_2Si**:** behaves differently and furnishes a phosphadisilacyclobutene *via* stepwise addition of two silylene molecules to the phosphaalkyne.[5]



1 R = $(Me_3Si)_2CH$ **2**

Scheme 1

We have now addressed the question if, similar to the silylenes, the use of a diarylgermylene would furnish a different result. Thus, from the reaction of the germylene **4** (which, in analogy to **1**,[6] exists as the digermene **3** in the solid state)[7] with *tert*-butylphosphaalkyne gave orange-coloured crystals which were isolated in 59% yield. The analytical data for these crystals were indicative of a 1 : 1 adduct composed of **4** and the phosphaalkyne. However, the ^{31}P NMR spectrum revealed the presence of both two- and three-coordinated phosphorus atoms, thus excluding the formation of a three-membered ring system analogous to **2** and suggesting the presence of a larger ring system (Scheme 2).

In agreement with the analytical and spectral data, an X-ray crystallographic analysis (Fig. 1)‡ revealed that two molecules each of the phosphaalkyne and **4** had reacted to furnish compound **5**† comprised of a germadiphosphacyclobutene with an additional, exocyclic Ge=C double bond. The bond lengths of both the exocyclic Ge=C and the endocyclic P=C double bonds were in accord with those of previously reported, similar bonds. The remaining bond lengths and angles also did not reveal any unusual features.

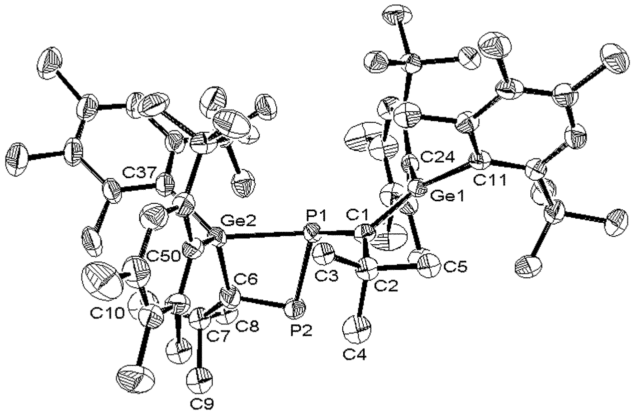
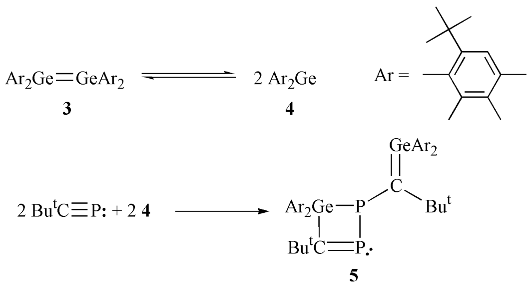


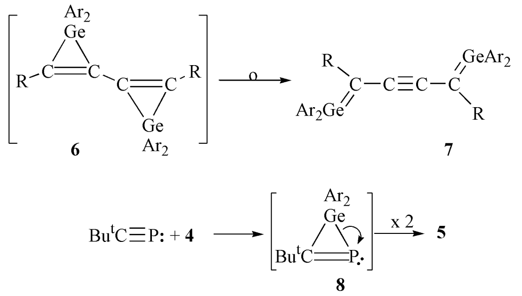
Fig. 1 Molecular structure of **5** (50% probability ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): P(1)–P(2) 2.1703(14), P(2)–C(6) 1.702(4), C(6)–Ge(2) 1.982(4), P(1)–Ge(2) 2.4351(9), P(1)–C(1) 1.822(3), C(1)–Ge(1) 1.833(4); P(2)–P(1)–Ge(2) 78.73(4), P(1)–Ge(2)–C(6) 79.15(11), Ge(2)–C(6)–P(2) 105.0(2), C(6)–P(2)–P(1) 93.39(15).

The unexpected formation of **5** is without precedence in the chemistry of germylenes and phosphaalkynes. It is, at best, comparable with the addition of the germylene **4** to 1,3-diynes, a process proceeding through the C–C bridged bis(germacyclopropenes) **6** as the intermediate on the way to the rearranged, acetylene-linked bis(germaethenes) **7** (Scheme 3).[8] In analogy to the formation of **7**, it may be assumed that here also the reaction sequence is initiated by the addition of **4** to the phosphaalkyne to afford a three-membered ring system of type **8** with subsequent opening of the P–Ge single bond. Cyclodimerisation of this intermediate would then yield compound **5**.

A cyclodimerisation of this type should produce several conformers with varying orientations of the substituents on the exocyclic C atom. In fact, the ^{31}P NMR spectrum of **5** contains two doublets for two-coordinate phosphorus atoms at δ 269.0 and 271.5 as well as two doublets in the high-field region at δ -8.1 and -34.4. These signals remain unchanged even on heating a sample to 80 °C, presumably on account of the steric crowding at the exocyclic carbon atom. The existence of two conformers in solution is further supported by the observation



Scheme 2



Scheme 3

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of numerous, in part overlapping, signals in the ^{1}H and ^{13}C NMR spectra that cannot be assigned unambiguously. The $^{1}J_{PP}$ coupling constants of 16 and 21 Hz for the two conformers are inexplicably small; related ring systems[9] have values of *ca.* 250 Hz.

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Notes and references

† *Preparation* of **5**: to a suspension of **3** (0.35 g, 0.41 mmol) in *n*-hexane (20 mL) was added a solution of *tert*-butylphosphaalkyne (0.30 g, 3.0 mol) in *n*-hexane (20 mL) and the mixture was stirred for 24 h at room temperature. The mixture was then filtered, the filtrate concentrated to a volume of 20 mL, and cooled to −30 °C to furnish 0.255 g (59% yield) of orange crystals of **5**, mp 118–120 °C. ^{31}P{^{1}H} NMR: δ 271.5, −34.4 ($^{1}J_{PP}$ 16 Hz), 269.0, −8.1 ($^{1}J_{PP}$ 21 Hz). UV–VIS (THF): λ_{max}/nm (ε/dm^{3} mol^{-1} cm^{-1}) 366 (29000) nm. Anal. Calc. for $C_{62}H_{94}Ge_2P_2$: C, 71.16; H, 9.05. Found: C, 71.27, H, 9.22%.

‡ *Crystal data* for **5**: $C_{62}H_{94}Ge_2P_2 \cdot n\text{-}C_6H_{14}$, M = 1132.66, crystal dimensions 0.32 × 0.21 × 0.15 mm, triclinic, space group $P\bar{1}$, a = 12.1315(6), b = 15.3937(8), c = 17.6016(7) Å, α = 87.207(5), β = 80.276(5), γ = 87.056(6)°, V = 3232.9(3) Å^{3}, Z = 2, D_c = 1.164 g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, T = 193(2) K, $2\theta_{max}$ = 52°, 11735 unique reflections, 6979 observed [$I > 2\sigma(I)$] 6979, 624 parameters. The structure was solved by direct methods (SHELXS-97) and refined by the full-matrix least-squares techniques against F^2 (SHELXL-97). The *tert*-butyl groups C2–C5 and C7–C10 are disordered and were refined on two positions with an occupancy factor of 0.5 each. Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically; $R1$ = 0.0455, $wR2$ (all data) = 0.1064. CCDC 186/1877. See http://www.rsc.org/suppdata/cc/b0/b008472g/ for crystallographic files in .cif format

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