1,3-Digermacyclobutanes with exocyclic C=P and C=P=S double bonds†

Petronela Maria Petrar,[ab] Gabriela Nemes,[a] Ioan Silaghi-Dumitrescu,*[a] Henri Ranaivonjatovo,[b] Heinz Gornitzka[b] and Jean Escudié*[b]

Received (in Cambridge, UK) 1st June 2007, Accepted 6th July 2007
First published as an Advance Article on the web 3rd August 2007
DOI: 10.1039/b708308d

New 1,3-digermacyclobutanes, with two exocyclic C=PMes* bonds, and the corresponding first bis(methylenethioxo)phosphoranes with C=P(S)Mes* moieties have been synthesized.

1,3-Dimetallacyclobutanes featuring two exocyclic main group element–carbon double bonds, **I** (Chart 1) are poorly documented in the literature. This finding is illustrated by the relatively limited number of such silicon heterocycles (**I**, M = Si, X = CR_2,[1a–c] C=CR_2,[1d] NR,[1e,f] PR[1g] and PR_3[1h]) and turns out to be particularly true for the germanium analogues, since only one example has been reported so far (**I**, M = Ge, X = PR). Moreover, this sole 2,4-diphosphinylidene-1,3-digermacyclobutane was obtained in a very low yield.[2]

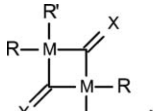
We have been successful in the synthesis of a new representative (**I**, M = Ge, X = PMes*, R = R′ = *t*Bu) and present the first molecular X-ray structure of such a germanium heterocycle. This molecule prompted us to investigate the accessibility of related 2,4-bis(thioxophosphoranylidene)-1,3-digermacyclobutane (**I**, M = Ge, X = P(S)R). Since the report of the first stable thioxomethylenephosphorane, a structure containing the P(=S)=C skeleton,[3] no counterpart featuring more than a single P(=S)=C unit has been described. Here, we also detail the synthesis and the X-ray structure of the first bis(thioxomethylenephosphorane) linked by two germanium atoms. Such heterocycles could be interesting building blocks in heterochemistry owing to the reactivity of their P=C double bonds; these double bonds, next to the lone pairs of phosphorus, oxygen or sulfur atoms, represent interesting coordination sites for transition metals.

The reaction of *t*BuLi with phosphagermapropene **1**,‡ prepared from *C*,*C*-dichlorophosphaalkene Mes*P=CCl_2 (Mes* = 2,4,6-tri-*tert*-butylphenyl) (**2**) and tBu_2GeF_2, affords the 2,4-diphosphinylidene-1,3-digermacyclobutane (**3**) in a near quantitative yield§ (Scheme 1).

The *cis* and *trans* isomers, **3a** and **3b** are formed in a 3 : 1 ratio (relative to the P=C···C=P axis). An equilibrium between the two geometrical isomers is established at room temperature in less than 1 h after dissolving crystals of either **3a** or **3b**. This kind of geometrical isomerism has previously been described for similar compounds.[1g,2] DFT B3LYP/6-31G(d) calculations on several model systems for **3** (see Table S2-1 in the ESI†) show the *trans* isomer to be slightly lower in energy; unlike the *trans* isomer, the *cis* isomer has a non-zero dipole moment and thus better solvation in polar solvents (THF, $CDCl_3$), explaining the reverse trend in solution.

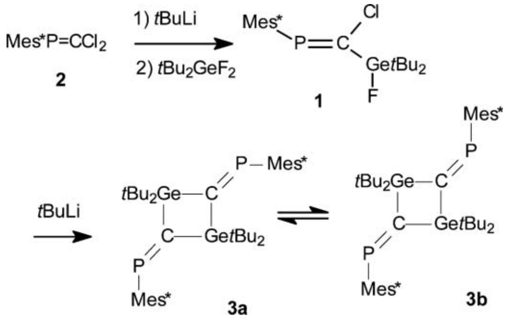
Both isomers **3a** and **3b** have been characterized by X-ray diffraction.¶ As they present approximately the same geometrical data, only the structure of the *trans* isomer **3b** is discussed (see Fig. 1 for the molecular structure of **3b** and the ESI for that of **3a**†). The endocyclic Ge–C bond lengths lie slightly beyond the upper limit of the standard range (1.93–1.97 Å[4]) due to the high steric hindrance, but are almost comparable to those reported for 1,3-digermacyclobutanes (2.009–2.010 Å[5a] and 1.97–1.98 Å[5b]). The shape of the four-membered ring is rather different from that of 1,3-digermacyclobutanes without exocyclic double bonds since the Ge···Ge distance is longer (2.918 Å *vs.* 2.77–2.80 Å[5]) while the C···C distance is shorter (2.755 Å *vs.* 2.904 Å[5a]) as a consequence of the sp^2 hybridization of the cyclic carbon atoms. The four-membered ring is planar, in contrast to its silicon analogue with two C=PMes* exocyclic bonds which is slightly folded by about 5° along the C···C or Si···Si axes.[1g]

When the germanium atom was substituted by bulky Tip (2,4,6-triisopropylphenyl) and *t*Bu groups, the analogous reaction led to the stable phosphagermaallene Mes*P=C=Ge(Tip)*t*Bu.[6] With two



(M = Si, Ge)

Chart 1



Scheme 1

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[a] Babes-Bolyai University, 1, Kogalniceanu Street, Cluj-Napoca, Romania. E-mail: isi@chem.ubbcluj.ro; Fax: +40 264 590818; Tel: +40 264 590482
[b] Hétérochimie Fondamentale et Appliquée (UMR CNRS 5069), Université Paul Sabatier, 118 Rte de Narbonne, 31062 Toulouse Cedex 9, France. E-mail: escudie@chimie.ups-tlse.fr; Fax: +33 561558204; Tel: +33 561558347

† Electronic supplementary information (ESI) available: S1 includes full physicochemical data for **1**, **3a**, **3b**, **5a** and **5b**, and X-ray data for **3a**, **3b**, **5a** and **5b**. S2 includes the calculated energies for **3a**, **3b**, **5a** and **5b**.

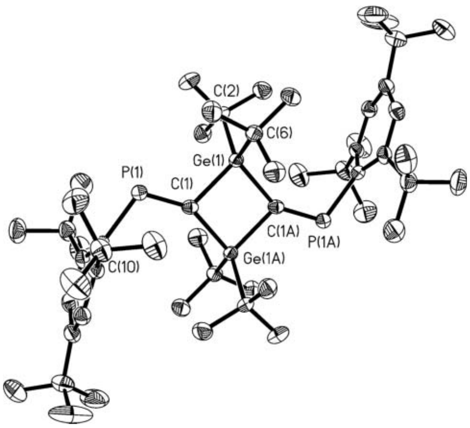
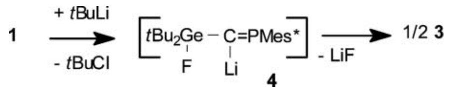


Fig. 1 Molecular structure of **3b** (50% probability ellipsoids). Hydrogen atoms, solvent molecules and rotation disorder of the *p*-*t*Bu moieties on the aryl groups are omitted for clarity. "A" letters in the atom labels correspond to the symmetry operation ½ − *x*, ½ − *y*, −*z*. Selected bond lengths (Å) and bond/torsion angles (°): Ge(1)–C(1) 2.005 (3), C(1)–P(1) 1.665(3), P(1)–C(10) 1.872(3), Ge(1)–C(2) 2.016(3), Ge(1)···Ge(1A) 2.918, C(1)···C(1A) 2.755, C(1)–Ge(1)–C(1A) 86.71(11), Ge(1)–C(1)–Ge(1A) 93.29(11), Ge(1)–C(1)–P(1) 117.45(15), C(1)–Ge(1)–C(1A)–Ge(1A) 0.

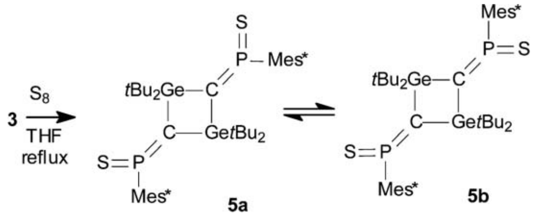
less bulky Mes (2,4,6-trimethylphenyl) groups, the transient phosphagermaallene Mes*P=C=GeMes$_2$[2] could be observed by ^{31}P NMR experiments. The latter readily lead to the corresponding 1,3-digermacyclobutane derivative **I** (M = Ge, X = PMes*, R = R′ = Mes). The same phenomenon could be observed in the silicon series since the 1,3-disilacyclobutanes **I** (M = Si, X = PMes*, R = Ph, R′ = Tip) were also formed *via* the phosphasilaallene intermediate Mes*P=C=Si(Ph)Tip.[1g] In the case of **1**, monitoring the reaction by ^{31}P NMR spectroscopy between −80 °C and room temperature showed the initial formation of **4** (Scheme 2) (δ_P = 381.6, $^3J_{PF}$ = 10.1 Hz), leading to a new asymmetric intermediate (δ_P = 286.7 and 443.8, $^4J_{PP}$ = 38.5 Hz), and finally to **3** at −40 °C; no phosphagermaallene could be observed. These preliminary results seem to indicate that at least one stabilizing aryl group on the group 14 metal atom favours the observation of the phosphametallaallene.

The reaction of **3** with an excess of sulfur in refluxing THF affords a new type of bis(methylenethioxophosphoranes),[3] **5a** (*cis*) and **5b** (*trans*), bridged by two germanium atoms (Scheme 3). The two isomers are also in equilibrium, and at the room temperature the ratio **5a** : **5b** is 3 : 1. The electropositive germanium atoms (2.0–2.1 on the Pauling scale) bonded to the thioxophosphaalkene carbons cause the phosphorus nuclei in compound **5** to resonate at low fields (δ_P **5a** = 184.4, **5b** = 183.7), as in the case of MesP(S)=C(SiMe$_3$)$_2$ (190.9 pm)[3i] bearing two electropositive silicon atoms. The ^{31}P NMR spectra of such compounds substituted by alkyl or aryl groups generally exhibit chemical shifts between 107 and 160 ppm.[3f–m]

Derivatives **5**‖ are the first examples of compounds containing two C=P=S units in a same molecule. They showed very good thermal stability and did not undergo valence isomerization to give the corresponding thiaphosphirane *via* a [1 + 2] cycloaddition of sulfur with the P=C double bond; the further addition of sulfur to give a thiaphosphirane P-sulfide derivative was not observed. The high steric congestion in **5** might be responsible for its stability since, in other instances, depending on the substituents at C and P, the C=P=S moieties are either stable, rearrange to a thiaphosphirane or further add sulfur.[3]



Scheme 2



Scheme 3

Both **5a** and **5b** have been characterized by X-ray diffraction¶ (see Fig. 2 for the molecular structure of **5b** and the ESI for that of **5a**†). Close similarities in geometry between **5a** and **5b**, and the starting **3a** and **3b** were noticed.

The presence of sulfur atoms and the P=C double bonds makes derivatives **5a** and **5b** of interest in the synthesis of novel transition metal complexes. Their ability to act as versatile ligands is currently under investigation. Theoretical calculations that could give us insight into the electronic structure of the S=P=C unit and its potential coordinative properties, the likely mechanism of the *cis–trans* isomerisation and a study into the possible interactions between the two coordinative moieties are now in progress.

We thank the French Ministry of Foreign Affairs (AI Brancusi n^o 08581TK (Fr) and 18015 (Ro), and Eiffel grant to P. M. P.), the CNRS, and the French and Romanian Ministry of Education and

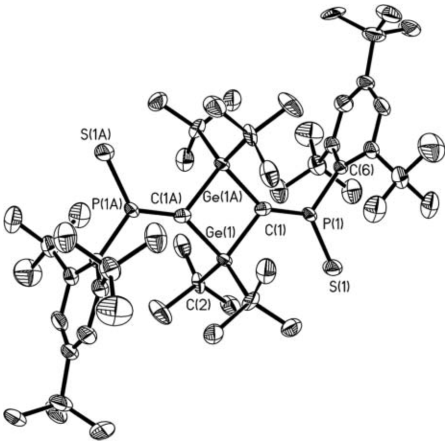


Fig. 2 Molecular structure of **5b** (50% probability ellipsoids). Hydrogen atoms, solvent molecules, rotation disorder of the *p*-*t*Bu on the aryl groups and disorder of the whole *t*Bu group on the germanium atom over two positions are omitted for clarity. "A" letters in the atom labels correspond to the symmetry operation 1 − *x*, −*y*, *z*. Selected bond lengths (Å) and bond/torsion angles (°): Ge(1)–C(1) 2.008(6), C(1)–P(1) 1.652(6), P(1)–S(1) 1.937(2), P(1)–C(6) 1.827(6), Ge(1)–C(2) 2.105(19), Ge(1)···Ge(1A) 2.956, C(1)···C(1A) 2.712, C(1)–Ge(1)–C(1A) 85.1(3), Ge(1)–C(1)–Ge(1A) 94.9(3), Ge(1)–C(1)–P(1) 121.9(3), C(1)–P(1)–S(1) 124.8(2), C(1)–Ge(1)–C(1A)–Ge(1A) 0.

Research (CEEX project SUPRACOM) for their financial support of this work.

Notes and references

‡ Synthesis of phosphagermapropene **1**. To 1.0 g (2.7 mmol) of dichlorophosphaalkene **2** in 30 mL of THF cooled at −90 °C was added dropwise 1.9 mL of 1.6 M *n*BuLi in hexane (1 equiv.). After half an hour at −85 °C, 0.62 g (2.7 mmol) of $t\mathrm{Bu_2GeF_2}$ in 20 mL of THF were canulated. The reaction mixture was then allowed to warm to room temperature, and the solvent was removed under vacuum and replaced by pentane. Lithium salts were removed by filtration. **1** precipitated from methanol as a white solid (1.47 g, 78%, mp = 118 °C). Only the *E*-isomer was obtained. NMR data for **1** (solvent $\mathrm{CDCl_3}$). δ_H (300 MHz): 1.23 (d, ${}^4J_\mathrm{HF}$ = 1.2 Hz, *t*BuGe), 1.29 (s, *p*-*t*Bu), 1.47 (s, *o*-*t*Bu), 7.38 (d, ${}^4J_\mathrm{PH}$ = 1.4 Hz, ArH); δ_C (75.5 MHz): 165.27 (dd, ${}^1J_\mathrm{CP}$ = 91.0 Hz, ${}^2J_\mathrm{CF}$ = 4.5 Hz, C=P); δ_F (188.3 MHz, $\mathrm{CF_3COOH}$): −135.4; δ_P (121.5 MHz): 293.5 (d, ${}^3J_\mathrm{PF}$ = 45.8 Hz).

§ Synthesis of 2,4-diphosphinylidene-1,3-digermacyclobutane (**3**). To 1.0 g (1.89 mmol) of **1** in 20 mL of THF cooled at −95 °C was added dropwise 1.38 mL of 1.5 M *t*BuLi in hexane (10% excess). The reaction mixture was left at low temperature for 15 min and then allowed to warm slowly to room temperature. After removal of the lithium salts and solvents, 20 mL of pentane was added. A mixture of **3a**/**3b** precipitated (0.67 g, 75%). The yellow mixture was dissolved in 20 mL of THF. Yellow acicular crystals of the *trans* isomer of **3** were obtained after a few days, while the *cis* isomer crystallized from pentane through slow evaporation. mp = 309 °C (**3a**), mp = 301 °C (**3b**).

NMR data for **3** (solvent $\mathrm{CDCl_3}$). **3a** δ_H (300 MHz): 0.56 (s, *t*BuGe), 1.23 and 1.32 (2 s, *p*-*t*Bu and *t*BuGe), 1.47 (s, *o*-*t*Bu), 7.07 (s, ArH); δ_C (75.5 MHz): 204.0 (dd, ${}^1J_\mathrm{CP}$ = 96.6 Hz, ${}^3J_\mathrm{CP}$ = 25.7 Hz, C=P); δ_P (121.5 MHz): 367.4.

3b δ_H (300 MHz): 0.94, 1.19 and 1.50 (3 s, *t*Bu), 7.13 (s, ArH); δ_C (75.5 MHz): 204.3 (dd, ${}^1J_\mathrm{CP}$ = 92.0 Hz, ${}^3J_\mathrm{CP}$ = 24.9 Hz, C=P); δ_P (121.5 MHz): 367.7.

¶ Crystal data for **3b** and **5b**.

3b: $\mathrm{C_{58}H_{104}Ge_2O_1P_2}$, M = 1024.54, monoclinic, a = 35.416(2), b = 10.6099(7), c = 16.2868(11) Å, β = 101.109(1)°, V = 6005.3(7) Å^3, T = 173(2) K, space group *C*2/*c*, Z = 4, 14909 reflections measured, 5077 unique (R_int = 0.0577). The final R_1 (for $I > 2\sigma(I)$) was 0.0386 and w$R2$ (all data) was 0.0847 with $R_1 = \Sigma||F_\mathrm{o}| - |F_\mathrm{c}||/\Sigma|F_\mathrm{o}|$ and $\mathrm{w}R_2 = (\Sigma \mathrm{w}(F_\mathrm{o}^2 - F_\mathrm{c}^2)^2/\Sigma \mathrm{w}(F_\mathrm{o}^2)^2)^{0.5}$.

5b: $\mathrm{C_{62}H_{110}Ge_2O_2P_2S_2}$, M = 1158.74, orthorhombic, a = 20.440(3), b = 16.670(2), c = 19.133(3) Å, V = 6519.2(15) Å^3, T = 173(2) K, space group *Ibam*, Z = 4, 14548 reflections measured, 2491 unique (R_int = 0.1131). The final R_1 (for $I > 2\sigma(I)$) was 0.0504 and w$R2$ (all data) was 0.1217.

Data for all structures represented in this paper were collected at low temperatures using an oil coated shock cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods[7] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2.[8] CCDC 649323 (**3a**), 649324 (**3b**), 649325 (**5a**) and 649326 (**5b**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708308d

‖ Synthesis of 2,4-bis(thioxophosphoranylidene)-1,3-digermacyclobutane (**5**). To 0.60 g (0.63 mmol) of a mixture of *cis*/*trans* **3** in 10 mL of THF were added 3 equivalents of sulfur; the reaction mixture was refluxed for 3 h. An NMR study showed the quantitative formation of **5**. After removal of THF, 20 mL of pentane was added and the reaction mixture was filtered to eliminate the excess sulfur; a mixture of **5a**/**5b** was isolated (0.52 g, 81%). Crystals of the *trans* isomer were obtained from the THF solution at −20 °C while the *cis* isomer crystallized from pentane. δ_P (121.5 MHz): 184.4 (**5a**), 183.7 (**5b**).

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