

## Unusual Formation of a Tricyclic Compound from a Phosphaalkyne and an Arylgermene exhibiting 1,3-Diene Characteristics<sup>1</sup>

Mohamed Lazraq,<sup>a</sup> Jean Escudie,<sup>\*a</sup> Claude Couret,<sup>a</sup> Uwe Bergsträsser<sup>b</sup> and Manfred Regitz<sup>\*b</sup>

<sup>a</sup> Laboratoire de Chimie des Organominéraux, URA No. 477, Université P. Sabatier, F-31062 Toulouse Cedex, France

<sup>b</sup> Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrodinger-Strasse, D-6750 Kaiserslautern, Germany

The phosphaalkyne **2** reacted with the germene **1** in a molar ratio of 2 : 1 with formation of the germadiphosphatricyclooctene **5**; this is rationalised in terms of a Diels–Alder reaction of the substrates followed by an ene reaction and intramolecular cycloaddition.

Compounds possessing low-coordinated phosphorus or germanium atoms—such as the phosphaalkynes  $\text{RC}\equiv\text{P}^2$  and germenes  $\text{R}_2\text{Ge}=\text{CR}_2^3$ —are highly reactive despite the kinetic stabilization effects of the spatially demanding substituents. In cycloaddition reactions, such compounds play an important part in the construction of phosphorus<sup>2</sup> and germanium<sup>3</sup> heterocyclic systems. To date, cycloaddition reactions of, among others, the [2 + 2]-, [2 + 3]- and [2 + 4]-types have been realized for both classes of compounds.

We now report on the reaction of the germene **1**<sup>4</sup> with the phosphaalkyne **2** which was expected to furnish principally a germaphosphacyclobutene by way of a [2 + 2] cycloaddition. Instead, we observed the formation of the unusual polycyclic product **5**; hence the germene has reacted as a 1,3-diene with participation of one C=C double bond of the fluorenylidene group.

The reaction of **1** (0.95 g, 2 mmol) with **2** (0.20 g, 2 mmol) was performed in benzene (5 ml) in a glass pressure tube under a nitrogen atmosphere at 170 °C and was complete after 5 h. <sup>31</sup>P NMR spectroscopic analysis of the reaction mixture revealed the presence of the polycyclic compound **5** as the major product (ca. 70%); the as yet not identified by-products gave rise to <sup>31</sup>P NMR signals at very low field ( $\delta = 423, 415, 355, 266$ ). Evaporation under reduced pressure and recrystallisation of the residue from  $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$  (9 : 1) finally gave **5** as colourless, analytically pure crystals (yield: 0.23 g, 34% based on **2**) with m.p. 258–259 °C.<sup>†‡</sup>

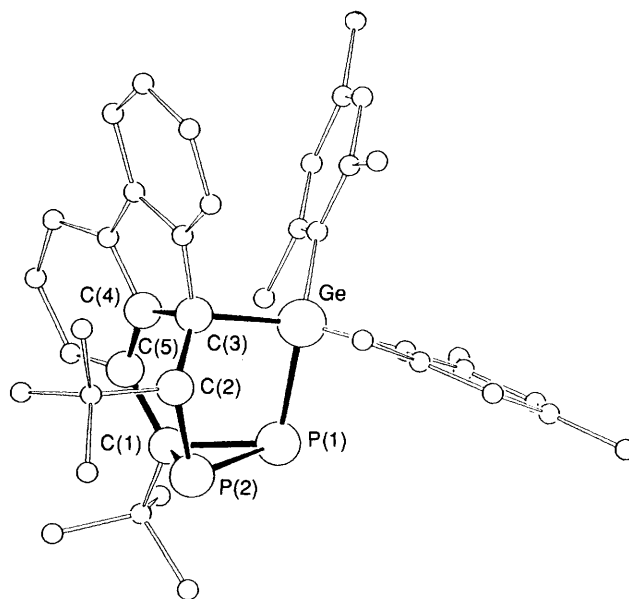
<sup>†</sup> Spectroscopic data for **5**:  $\text{C}_{41}\text{H}_{48}\text{GeP}_2$ ; MS (desorption chemical ionization,  $\text{CH}_4$ , <sup>74</sup>Ge),  $m/z$  705 ( $\text{M}^+ + 29, 7\%$ ), 677 ( $\text{M}^+ + 1, 88\%$ ), 676 ( $\text{M}^+, 100\%$ ), 619 [ $\text{M}^+ - \text{CMe}_3, 14\%$ ], 577 [ $\text{M}^+ - \text{C}_6\text{H}_2\text{Me}_3, 76\%$ ]; <sup>1</sup>H NMR ( $\text{CDCl}_3, 300 \text{ MHz}$ )  $\delta$  0.63 (d, <sup>4</sup> $J_{\text{H,P}}$  1.5 Hz, 9H, diphosphirane-Bu<sup>t</sup>), 1.10 (s, 3H, mesityl-Me), 1.67 (s, broad, 9H, germadiphosphacyclopentane-Bu<sup>t</sup>), 1.67 (s, 3H, mesityl-Me), 2.00 (s, 6H, mesityl-Me), 2.26, 3.02 (each s, each 3H, mesityl-Me), 3.09 (d, <sup>2</sup> $J_{\text{H,P}}$  6.1 Hz, 1H, CHBu<sup>t</sup>), 6.11, 6.32, 6.70, 6.98 (each s, each 1H, mesityl-H), 7.20–7.94 (m, 7H, fluorenyl-H); <sup>13</sup>C NMR ( $\text{CDCl}_3, 50.3 \text{ MHz}$ )  $\delta$  20.58, 20.70 (each s, each mesityl-*p*-CH<sub>3</sub>), 23.71 (s, mesityl-*o*-CH<sub>3</sub>), 23.72 (d, <sup>4</sup> $J_{\text{C,P}}$  9.1 Hz, mesityl-*o*-CH<sub>3</sub>), 24.02 (d, <sup>4</sup> $J_{\text{C,P}}$  13.4 Hz, mesityl-*o*-CH<sub>3</sub>), 27.27 (s, mesityl-*o*-CH<sub>3</sub>), 29.60 [s, broad, diphosphirane-C(CH<sub>3</sub>)<sub>3</sub>], 32.30 [d, <sup>3</sup> $J_{\text{C,P}}$  12.2 Hz, germadiphosphacyclopentane-C(CH<sub>3</sub>)<sub>3</sub>], 37.38 (t, <sup>2</sup> $J_{\text{C,P}}$  13.3 Hz, C-Ge), 38.85 [d, <sup>2</sup> $J_{\text{C,P}}$  11.2 Hz, germadiphosphacyclopentane-C(CH<sub>3</sub>)<sub>3</sub>], 47.53 (d, <sup>1</sup> $J_{\text{C,P}}$  56.2 Hz, CHBu<sup>t</sup>), 58.01 (dd, <sup>1</sup> $J_{\text{C,P}}$  22.5 and 75.0 Hz, respectively, diphosphirane-C), 115.75–129.56 (fluorenyl-CH/mesityl-*m*-C), 137.35–145.90 (fluorenyl-*C*/mesityl-*C*); <sup>31</sup>P NMR ( $\text{CDCl}_3, 32.4 \text{ MHz}$ )  $\delta$  -231.88 (d, <sup>1</sup> $J_{\text{P,P}}$  186.8 Hz, P-Ge), -107.61 (d, <sup>1</sup> $J_{\text{P,P}}$  186.8 Hz, P-C). Satisfactory elemental analyses were obtained.

<sup>‡</sup> Crystal data for **5**:  $\text{C}_{41}\text{H}_{48}\text{GeP}_2$ ,  $M = 675.4$ , triclinic space group  $\bar{P}1$ ,  $a = 12.662(11)$ ,  $b = 13.377(4)$ ,  $c = 12.235(6) \text{ \AA}$ ,  $\alpha = 107.35(3)$ ,  $\beta = 107.70(5)$ ,  $\gamma = 80.97(4)^\circ$ ;  $V = 1878.0(17) \text{ \AA}^3$ ;  $Z = 2$ ;  $D_c = 1.194 \text{ g cm}^{-3}$ ;  $\mu = 9.0 \text{ cm}^{-1}$ ;  $F(000) = 712.0$ . Data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ , ambient temperature), and 5883 reflections were measured, 5023 of which with  $I \geq 2\sigma(I)$  were employed for the calculations. The structure was solved by direct methods (SHELXS 86). All non-hydrogen atoms were refined anisotropically, 397 parameters were refined with a weighting scheme [ $w^{-1} = \sigma^2(F) + 0.0002 F_o^2$ ]. The final values for  $R$  and  $R_w$  were 0.0728 and 0.0971, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to the Authors, Issue No. 1.

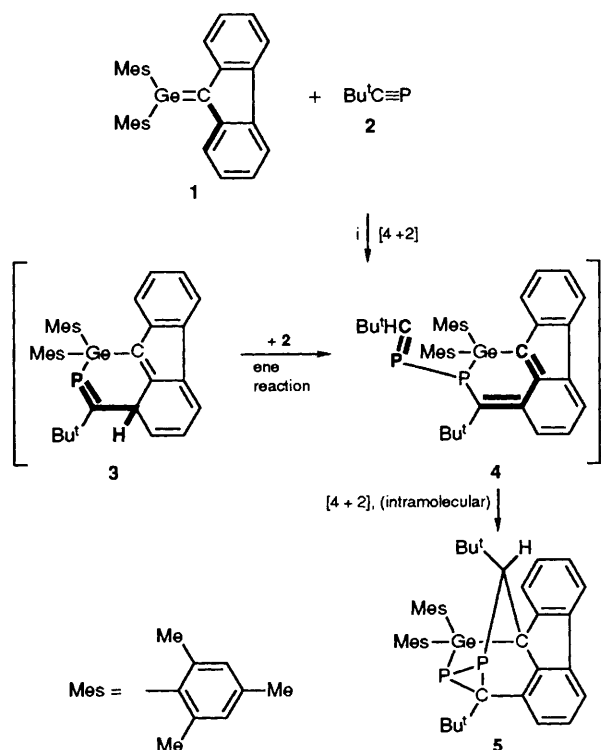
Concordant elemental analysis and the mass spectrum confirm the 1 : 2 stoichiometry of the reaction product. The fact that one benzene ring of the fluorenylidene group of **1** has participated in the reaction is further substantiated by the <sup>1</sup>H NMR spectrum of **5**, which contains signals for only seven aromatic hydrogen atoms. The high field signals of the two phosphorus atoms and the magnitude of the P–P coupling constant<sup>5</sup> are indicative of the formation of the diphosphirane ring element. In both the <sup>1</sup>H and the <sup>13</sup>C NMR spectra of **5**, the signals for the Me groups of the *tert*-butyl substituents on the diphosphirane ring appear as broad singlets; this is attributed to slow rotation. Steric hindrance of rotation of the mesityl substituents about the Ge–C bond is also apparently responsible for the fact that the *ortho*-methyl groups and the aromatic *meta*-hydrogen atoms are no longer magnetically equivalent in the NMR spectra. The assignments of the signals in the <sup>13</sup>C NMR spectrum are based primarily on <sup>31</sup>P decoupling experiments.

The unequivocal structural elucidation of **5** was provided by the X-ray crystal structure analysis.<sup>‡</sup> Selected bond lengths and bond angles are listed in Fig. 1.

The absence of the Ge=C double bond of **1** [1.803(4) Å]<sup>6</sup> and the P≡C triple bond of **2** [1.542(2) Å]<sup>7</sup> is unambiguously revealed. The diphosphirane ring has P–P [2.187(3) Å] and P–C bond lengths [1.867(7) and 1.882(7) Å, respectively] that



**Fig. 1** Molecular structure of  $\text{C}_{41}\text{H}_{48}\text{GeP}_2$ , **5**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Ge–P(1) 2.308(2); P(1)–P(2) 2.187(3); P(2)–C(1) 1.867(7); C(1)–C(5) 1.512(9); C(4)–C(3) 1.495(9); Ge–C(3) 2.038(6); P(1)–C(1) 1.882(7); P(2)–C(2) 1.872(7); C(5)–C(4) 1.403(9); C(3)–C(2) 1.528(9); C(3)–Ge–P(1) 94.7(2); Ge–P(1)–P(2) 94.5(1); Ge–P(1)–C(1) 103.4(2); P(2)–P(1)–C(1) 54.0(2); C(2)–P(2)–P(1) 106.5(2); C(2)–P(2)–C(1) 105.0(3); P(1)–P(2)–C(1) 56.6(2); P(2)–C(1)–P(1) 71.4(2); P(2)–C(1)–C(5) 115.2(5); P(1)–C(1)–C(5) 117.3(5); C(1)–C(5)–C(4) 119.4(6); C(4)–C(3)–C(2) 109.8(5); C(3)–C(2)–P(2) 111.1(4); C(5)–C(4)–C(3) 127.7(6); C(4)–C(3)–Ge 99.0(4).



**Scheme 1** Reagents and conditions: i,  $\text{C}_6\text{H}_6$ , 5 h in a sealed Schlenk-tube at  $170^\circ\text{C}$

are in the same range as those for comparable polycyclic diphosphiranes.<sup>1,5</sup>

A feasible explanation for the course of the reaction  $\mathbf{1} + \mathbf{2} \rightarrow \mathbf{5}$  involves an initial Diels-Alder reaction in which the germane **1** plays the part of the 1,3-diene ( $\rightarrow \mathbf{3}$ ). Although the germane **1** is known to be extremely susceptible to cycloaddition reactions,<sup>3,8</sup> a germa-1,3-diene behaviour of this type has not been reported previously. This is also true for similarly constructed 1,3-dienes containing other main group elements such as phosphorus,<sup>9</sup> boron<sup>10</sup> or tin<sup>11</sup> ( $\text{RP}=\text{}$ ,  $\text{RB}=\text{}$ , or  $\text{R}_2\text{Sn}=\text{}$  in place of  $\text{R}_2\text{Ge}=\text{}$ ). However, this 1,3-diene behaviour of **1** is comprehensible on consideration of the crystal structure analysis of the molecule: this reveals a somewhat shortened ( $\text{Ge}-\text{C}(\text{fluorenylidene})$ ) bond,<sup>6</sup> which is expressed in terms of diene-typical conjugation between the  $\text{Ge}=\text{C}$  and one of the  $\text{C}=\text{C}$  double bonds.

The cycloaddition step is followed by an ene reaction of **3** with the second equivalent of **2** acting as an enophile,<sup>1,5,12</sup> which furnishes **4**. The latter species cannot be isolated since it undergoes a rapid, intramolecular Diels-Alder reaction to yield the final product **5**. As shown by a  $^{31}\text{P}$  NMR spectroscopic analysis of the crude reaction mixture, the polycyclic compound is formed in approximately 70% yield, hence the individual steps must each proceed with a high selectivity. A similar reaction of buta-1,3-dienes with phosphalkynes has been reported.<sup>5</sup>

M. R. is grateful to the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for generous financial support.

Received, 7th December 1992; Com. 2/06509F

## References

- 1 This communication is part 67 of the series of papers on *Organophosphorus Compounds* started by M. Regitz; for part 66, see: A. Marinetti, L. Ricard, F. Mathey, M. Slany and M. Regitz, *Tetrahedron*, in the press.
- 2 Reviews: (a) M. Regitz and P. Binger, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1484; (b) M. Regitz, *Chem. Rev.*, 1990, **90**, 191; M. Regitz, in *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme, Stuttgart, 1990, p. 58.
- 3 Review: J. Barrau, J. Escudié and J. Satgé, *Chem. Rev.*, 1990, **90**, 283.
- 4 C. Couret, J. Escudié, J. Satgé and M. Lazraq, *J. Am. Chem. Soc.*, 1987, **109**, 4411.
- 5 E. P. O. Fuchs, W. Rösch and M. Regitz, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1011.
- 6 M. Lazraq, J. Escudié, C. Couret, J. Satgé, M. Dräger and R. Dammel, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 829.
- 7 A. N. Chernega, M. Y. Antipin, Y. T. Struchkov, M. F. Meidine and J. F. Nixon, *Heteroatom Chemistry*, 1991, 665.
- 8 M. Lazraq, C. Couret, J. Escudié, J. Satgé and M. Dräger, *Organometallics*, 1991, **10**, 1771; M. P. Egorov, S. P. Kolesnikov, O. M. Nefedov and A. Krebs, *J. Organomet. Chem.*, 1989, **375**, C5; M. Lazraq, J. Escudié, C. Couret, J. Satgé and M. Soufiaoui, *J. Organomet. Chem.*, 1990, **397**, 1; M. Lazraq, J. Escudié, C. Couret, J. Satgé and M. Soufiaoui, *Organometallics*, 1992, **11**, 555.
- 9 T. A. Van der Knaap and F. Bickelhaupt, *Chem. Ber.*, 1984, **117**, 915.
- 10 B. Glaser and H. Nöth, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 416.
- 11 G. Anselme, H. Ranaivonjatovo, J. Escudié, C. Couret and J. Satgé, *Organometallics*, 1992, **11**, 2748.
- 12 U. Annen and M. Regitz, *Tetrahedron Lett.*, 1988, **29**, 1681.