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1,2-Phosphagermetanes: New Precursors for the Generation of Germanephosphimines

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The first 1,2-phosphagermetanes were synthesized from β-bromogermyl phosphines by dehydrohalogenation with amines or reaction with butyllithium followed by intramolecular elimination of lithium bromide. These heterocycles lead, through a thermal β-decomposition process under reduced pressure, to germanephosphimines, $R_2Ge{=}PR'$. The latter undergo partial thermal rearrangement to P-germylated phosphinidene. Both of these intermediates insert into the germanium–phosphorus bond of 1,2-phosphagermetanes with formation of perhydrodiphosphadigermins and P-germylated diphosphagermolanes, respectively.

Introduction

The thermal decomposition of 4-membered organometallic heterocycles usually is a good source of group 4b heteroelement pπ–pπ-bonded species: germanones, $R_2Ge{=}O$,[1,2] germanethiones, $R_2Ge{=}S$,[2-4] germanimines, $R_2Ge{=}NR'$,[5] and, in the case of silicon, silanephosphimine, $Me_2Si{=}PPh$.[6]

We describe in this paper the synthesis of the first 1,2-phosphagermetanes. These proved to be good precursors of germanephosphimines, $R_2Ge{=}PPh$, intermediates with an sp^2 germanium doubly bonded to a dicoordinated phosphorus. In earlier work *P*-phenyldimethylgermanephosphimine, $Me_2Ge{=}PPh$, the first species of this type, was obtained by an exchange reaction between 1, a 1,2,5-phosphadisilolane, and dimethyldichlorogermane.[7]

Results and Discussion

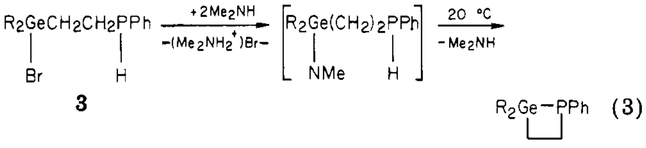
The first step of the synthesis of these heterocycles is the preparation of β-halogermylated phosphines such as 1-(phenylphosphino)-2-(dialkylbromogermyl)ethanes, **3**. These derivatives were obtained according to the reactions shown in eq 1 and 2. The diadduct **4** was formed in about

$$CH_2{=}CHMgBr + R_2Ge(H)Cl \xrightarrow[-BrMgCl]{THF} R_2Ge(H)CH{=}CH_2 \quad (1)$$

1a, R = Me[8]
1b, R = Et

$$R_2Ge(H)CH{=}CH_2 \xrightarrow[THF/0\ ^\circ C]{NBS} \underset{\mathbf{2}}{R_2Ge(Br)CH{=}CH_2} \xrightarrow[+PhPH_2]{ABN/80\ ^\circ C,\ C_6H_6} \underset{\mathbf{3}}{R_2Ge(Br)CH_2CH_2P(H)Ph} + \underset{\mathbf{4}}{(R_2Ge(Br)CH_2CH_2)_2PPh} \quad (2)$$

30% yield in the last reaction, and it was easily separated from the main product **3** by distillation. Addition of dimethylamine to **3** in benzene led to a transient germylamine, which after intramolecular elimination of dimethylamine, gave phosphagermetane (**5**) in *nearly* quantitative yield (eq 3).



3

(3)

5

The addition of n-butyllithium to 1-(phenylphosphino)-2-(dialkylbromogermyl)ethane (**3**) also gave 1,2-phosphagermetane via intramolecular elimination of

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[1] Lavayssière, H.; Barrau, J.; Dousse, G.; Satgé, J.; Bouchaut, M. *J. Organomet. Chem.* **1978**, *154*, C9.
[2] Barrau, J.; Bouchaut, M.; Lavayssière, H.; Dousse, G.; Satgé, J. *Helv. Chim. Acta* **1979**, *62*, 152.
[3] Lavayssière, H.; Dousse, G.; Barrau, J.; Satgé, J.; Bouchaut, M. *J. Organomet. Chem.* **1978**, *161*, C59.
[4] Barrau, J.; Bouchaut, M.; Lavayssière, H.; Dousse, G.; Satgé, J. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 515.
[5] Rivière-Baudet, M.; Rivière, P.; Satgé, J. *J. Organomet. Chem.* **1978**, *154*, C23.
[6] Couret, C.; Escudié, J.; Satgé, J.; Andriamizaka, J. D.; Saint-Roch, B. *J. Organomet. Chem.* **1979**, *182*, 9.
[7] Couret, C.; Satgé, J.; Andriamizaka, J. D.; Escudié, J. *J. Organomet. Chem.* **1978**, *157*, C35.
[8] The numbers with letter "**a**" refer to the products with R = Me and the numbers with letter "**b**" to the ethyl (R) analogues.

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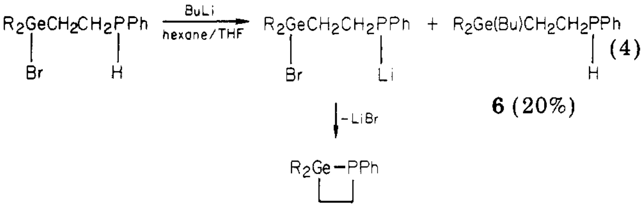
LiBr from the P-lithiated derivative. However, derivative **6** was also obtained in about 20% yield, by direct alkylation of germanium by *n*-butyllithium (eq 4).

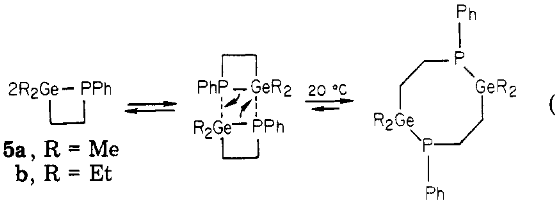


(4)

6 (20%)

5 (80%)

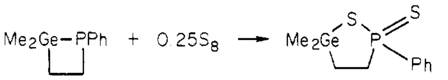
As in the case of the 1,2-phosphasiletane, chemical and physicochemical studies of this heterocycle showed the existence of an equilibrium between the monomeric form **5** (1,2-phosphagermetane) and the dimeric form **5′** (1,5,2,6-diphosphadigermocane; eq 5). At 20 °C and atmospheric pressure, this heterocycle is nearly completely converted to the dimeric form, which is the only observable form under these conditions. Thus the ^{31}P NMR spectrum exhibits a broad singlet at about δ_P −70 attribuable to a tricoordinated phosphorus atom bonded to a germanium atom in a virtually unstrained heterocycle. Moreover, cryometry in benzene gave a molecular weight of 510, close to the calculated mass of the dimeric form for **5′** (533). The monomer–dimer equilibrium is normally influenced by pressure; an increase in pressure displaces the equilibrium toward the dimeric form: **5′** was recovered in quantitative yield after being heated in a sealed tube at 200 °C for 48 h. A decrease in pressure displaces the equilibrium toward the monomeric form which decomposes by a *β*-elimination process (eq 10). The high chemical reactivity of **5**/**5′** confirmed the presence of the monomeric form **5**. Thus, the addition of sulfur to heterocycle **5a** produced the corresponding germylated dithiophosphinate **7a** (eq 6).



(5)

5a, R = Me
b, R = Et

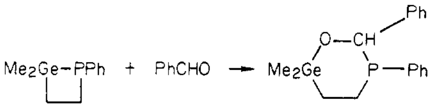
5′a, R = Me
b, R = Et



(6)

7a

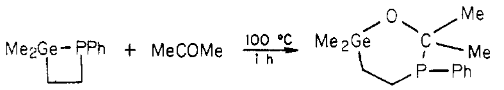
Insertion of benzaldehyde into the germanium–phosphorus bond of the same 1,2-phosphagermetane gave the expected 6-membered heterocycle **8a** in its two diastereoisomeric forms (eq 7). However, it is impossible to assert, as in the case of its silylated analogue,[6] that these two reactions involve the 1,2-phosphagermetane **5** rather than its dimer **5′**, although the monomeric form should be much more reactive than the dimeric form.



(7)

8a

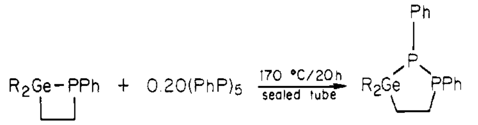
A good argument for the equilibrium and the existence of 1,2-phosphagermetane is given by the reaction with acetone. Acyclic germylphosphines, $R_3Ge–PR'_2$ (R = alkyl, aryl; R′ = aryl), and relatively unstrained heterocycles such as 1,2-phosphagermolanes do not react with acetone even upon heating to 150 °C.[9] However, 2,2-dimethyl-1-phenyl-1,2-phosphagermetane undergoes facile ring expansion with acetone in excellent yield (eq 8).



(8)

9a

1,2-Phosphagermetanes as Germanephosphimine Precursors. As in the case of some other 4-membered germanium-containing heterocycles, 1,2-phosphagermetanes decompose thermally by a *β*-elimination process. At about 120 °C and under low pressure, they lead, after loss of ethylene, to *P*-phenyldialkylgermanephosphimines (**10**; eq 10). The transient germanephosphimine **10** adds to the 1,2-phosphagermetane with the formation of a perhydro-1,3,2,4-diphosphadigermin (**11**). The latter leads, by loss of dialkylgermylene, to 1,2,3-diphosphagermolane **12** (eq 10a). Moreover, germanephosphimine **10** gives, after phenyl migration, the more stable phosphinidenic form **13** (eq 10b). This germylated phosphinidene then inserts into the Ge–P bond of the 1,2-phosphagermetane (eq 10b) to give 1,2,3-diphosphagermolane **14**. This type of insertion reaction is known; in earlier work we described the insertion of phenylphosphinidene into various Ge–P bonds,[10,11] and particularly into the Ge–P bond of 1,2-phosphagermetanes,[10] the best route to 1,2,3-diphosphagermolanes (eq 9).



(9)

12

We must emphasize that the formation of the silylated analogue of **14** has not been observed in the thermal decomposition of 2,2-dimethyl-1-phenyl-1,2-phosphasiletane. This difference can be rationalized in terms of the more polar character of the $[>Si^{\delta+}=P^{\delta-}–]$ species than the $[>Ge=P–]$ species.[12] The latter seems more capable of rearranging to the phosphinidene form at temperatures of 150 °C or above (eq 10).

The type of decomposition of 2,4-dialkylperhydro-1,3,2,4-diphosphadigermins (**11**) obtained in eq 10a was confirmed by independent synthesis of **11**. When heated to 130–150 °C under low pressure, this compound gave, via loss of dialkylgermylene, the same 3,3-dialkyl-1,2,3-diphosphagermolane (**12**; eq 11 and 12).

The structure of derivative **14** was established by NMR and was confirmed by reduction with lithium aluminium hydride (eq 13). The germylene formed in eq 10a led to polygermanes $(R_2Ge)_n$.

The highly reactive 1,2-phosphagermetanes could be used to trap the group 4b phosphorus double-bonded species at low temperature. Thus *P*-phenyldimethyl-

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[9] Satgé, J.; Couret, C.; Escudié, J. *J. Organomet. Chem.* **1970**, *24*, 633.

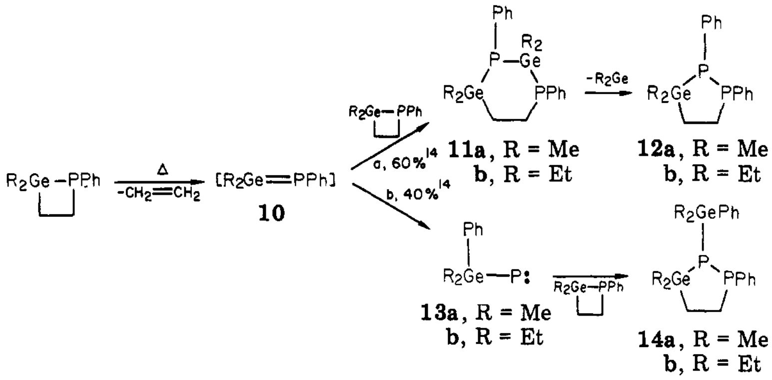
[10] Andriamizaka, J. D.; Couret, C.; Escudié, J.; Satgé, J. *Phosphorus Sulfur*, in press.

[11] Escudié, J.; Couret, C.; Satgé, J. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 461.

[12] This difference of polar character between $[>Si=P–]$ and $[>Ge=P–]$ seems particularly attribuable to differences of electronegativity between silicon and germanium.[13]

[13] Allred, A. L.; and Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 269. Allred, A. L. *Ibid.* **1961**, *17*, 215.

[14] Calculated from relative percentages of 11, 12, and 14%. These relative percentages are almost unchanged as the reaction proceeds, as proved by periodical ^{31}P NMR analyses taken during the thermolysis of **5a** or **5b** under 10^{-2} mmHg in a static system.

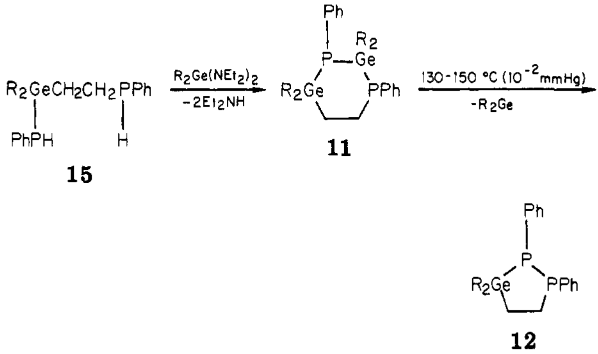


(10a)

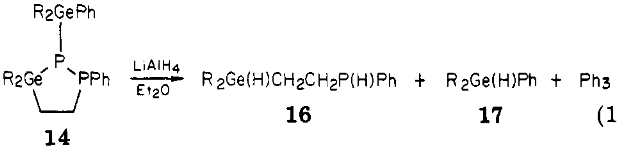
(10b)

$$\underset{3}{R_2Ge(Br)CH_2CH_2P(H)Ph} + PhPHLi \xrightarrow[-LiBr]{THF} R_2Ge(PhPH)CH_2CH_2P(H)Ph \quad (11)$$

15a, R = Me
15b, R = Et

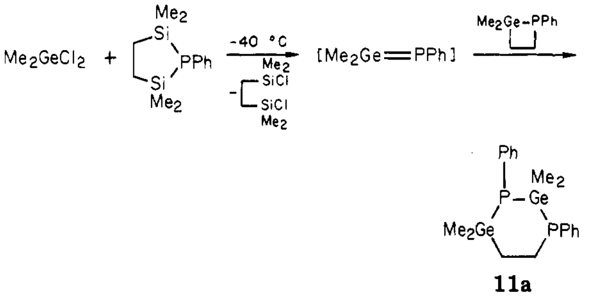


(12)



(13)

germanephosphimine, obtained by an exchange reaction between 1,2,5-phosphadisilolane and dimethyldichlorogermane[7] in the presence of 1,2-phosphagermetane, gave 1,3,2,4-diphosphadigermin (**11a**; eq 14). This last type of



(14)

reaction has the advantage of giving germanephosphimines at very low temperatures in excellent yield (60–70%). Trapping of *P*-phenyldimethylstannanephosphimine, $Me_2Sn{=}PPh$, by 1,2-phosphagermetanes also has been observed previously.[15]

Experimental Section

General Comments. All reactions were carried out in a standard high vacuum system. Proton NMR spectra were recorded in C_6D_6 at 60.0 MHz with Varian T 60 and EM 360 A spectrometers. Chemical shifts are reported relative to internal Me_4Si. Phosphorus-31 NMR spectra were obtained at 36.4 MHz on a Bruker WP 90 instrument. Positive δ values indicate shifts downfield from 85% H_3PO_4 used as an external standard. Infrared spectra were recorded with Perkin-Elmer Model 337 and 457 spectrometers using neat samples. Mass spectra were obtained with a Varian MAT 311A spectrometer. Elemental analyses were carried out at the "Laboratoire Central de Microanalyse du CNRS" at Vernaison, France.

Synthesis of Dimethylvinylgermane (1a). Dimethylvinylgermane (**1a**) was prepared (like its diethyl homologue **1b**[4]) by reaction of 3.50 g (252 mmol) of dimethylchlorogermane[16] and a solution of vinylmagnesium bromide (obtained from 29.60 g (277 mmol) of vinyl bromide and 6.64 g (277 mmol) of magnesium) in 200 mL of THF. Distillation after 2 h of stirring at room temperature gave 29.60 g (90%) of **1a**: bp 42 °C (760 mmHg); ^1H NMR δ 0.30 (d, ^3J(MeGeH) = 3.4 Hz, 6 H, Me_2Ge), 4.17 (d sept, ^3J(HGeCH) = 3.6 Hz, ^3J(MeGeH) = 3.4 Hz, 1 H, GeH), 5.47–6.70 (m, 3 H, $CH{=}CH_2$). Anal. Calcd for $C_4H_{10}Ge$: C, 36.75; H, 7.71. Found: C, 36.37; H, 7.70.

Synthesis of Dimethylvinylbromogermane (2a). This derivative was prepared by the same method as **2b**.[4] A 39.81-g (224-mmol) sample of *N*-bromosuccinimide was slowly added in portions to 29.21 g (224 mmol) of dimethylvinylgermane (**1a**) in 500 mL of THF at 0 °C, under N_2. After completion of the addition, the reaction mixture was allowed to rise to room temperature and then centrifuged to eliminate succinimide. Fractionation gave 36.0 g (77%) of **2a**: bp 66 °C (80 mmHg); ^1H NMR δ 0.87 (s, 6 H, Me_2), 5.67–6.83 (m, 3 H, $CH{=}CH_2$). Anal. Calcd for C_4H_9BrGe: C, 23.02; H, 4.34; Br, 37.85. Found: C, 23.00; H, 4.28; Br, 37.75.

Preparation of 1-(Phenylphosphino)-2-(dimethylbromogermyl)ethane (3a). A solution of 7.18 g (34 mmol) of dimethylvinylbromogermane (**2a**), 4.51 g (41 mmol) of phenylphosphine (10% excess), and 0.10 g of azobis(isobutyronitrile) in 30 mL of benzene was refluxed for 1 h. After removal of the solvent, fractionation gave 6.50 g (59%) of a colorless derivative which quickly became dark in the light and which was identified as the expected adduct **3a**: bp 110 °C (0.3 mmHg); IR ν(PH) 2302 cm^{-1}; ^1H NMR δ 0.70 (s, 6 H, Me_2), 1.07–1.57 (m, 2 H, CH_2Ge), 1.80–2.13 (m, 2 H, CH_2P), 4.36 (dt, ^1J(PH) = 206 Hz, ^3J($HPCH_2$) = 7.0 Hz, 1 H, PH); $^{31}P\{^1H\}$ NMR δ −43.5. Anal. Calcd for $C_{10}H_{16}BrGeP$: C. 37.67; H, 5.06; Br, 24.78. Found: C, 37.72; H, 5.08; Br, 24.10.

The diadduct **4a** also was isolated: 3.60 g, 20% yield; bp 192 °C (0.3 mmHg); ^1H NMR δ 0.76 (s, 6 H, Me_2Ge); ^{31}P NMR −16.1 ppm. Anal. Calcd for $C_{14}H_{25}Br_2Ge_2P$: C, 31.87; H, 4.78; Br, 29.95. Found: C, 31.82; H, 4.69; Br, 29.63.

Preparation of 1-(Phenylphosphino)-2-(diethylbromogermyl)ethane (3b). This adduct was synthesized by the method previously described for **3a** from 50.92 g (214 mmol) of **2b**, 23.57 g (214 mmol) of phenylphosphine, and 0.10 g of azobis(isobutyronitrile). A 40.0-g (54%) sample of **3b** was obtained by distillation: bp 174 °C (1.5 mmHg); ^1H NMR δ 1.0 (br s, 10 H, Et_2Ge), 0.86–1.40 (m, 2 H, CH_2Ge), 1.60–2.10 (m, 2 H, CH_2P), 4.07 (dt, ^1J(PH) = 204 Hz, ^3J($HPCH_2$) = 7.0 Hz, 1 H, PH); $^{31}P\{^1H\}$ NMR δ −42.4. Anal. Calcd for $C_{12}H_{20}BrGeP$: C, 41.55; H, 5.81; Br, 27.78. Found: C, 41.07; H, 5.56; Br, 22.88.

The diadduct **4b** also was obtained: 19.60 g, 16% yield; bp 230 °C (1.5 mmHg); ^1H NMR δ 1.23 (br s, 10 H, Et_2Ge); ^{31}P NMR

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(15) Couret, C.; Andriamizaka, J. D.; Escudié, J.; Satgé, J. *J. Organomet. Chem.* **1981**, *208*, C3.

(16) Drake, J. E.; Glavincevski, B. M.; Hemmings, R. T.; Henderson, H. E. *Inorg. Synth.* **1978**, *18*, 154.

δ −15.2. Anal. Calcd for $C_{18}H_{33}Br_2Ge_2P$: C, 37.04; H, 5.70; Br, 27.07. Found: C, 36.89; H, 5.66; Br, 27.12.

Synthesis of 5a/5′a. (a) Action of Dimethylamine on 3a. A solution of 11.86 g (37 mmol) of **3a** in 150 mL of anhydrous benzene was stirred in a 250-mL flask equipped with an alcohol–dry ice reflux condenser at −30 °C. Dimethylamine (6.66 g, 148 mmol, a twofold excess) was allowed to bubble through the solution. Dimethylamine hydrobromide was formed immediately and was removed by centrifugation. The solvent then was evaporated under reduced pressure, leaving a viscous residue. This was washed twice with benzene and then with pentane: cryometry in benzene calcd for **5′a** 477, found 468; ^{1}H NMR δ 0.17–0.50 (m, 12 H, 2 Me_2Ge), 0.67–2.33 (m, 4 H, CH_2CH_2), 7.10–7.33 (m, 5 H, Ph); ^{31}P NMR δ −70.2 (br s); mass spectrum, *m/e* 236–242 (**5a**). Anal. Calcd for $(C_{10}H_{15}GeP)_n$: C, 50.30; H, 6.33. Found: C, 50.67; H, 6.58. Distillation gave a viscous oil (7.91 g; bp 130–180 °C (0.2 mmHg)). Separation of **5a**, **11a**, **12a**, and **14a** as rigorously pure compounds was impossible by distillation. Many fractions were collected, and every fraction was distilled again twice, leading to many fractions with different percentages of every compound (some of them more than 80% pure). Comparison of ^{1}H and ^{31}P NMR spectra and GC analyses between all these fractions allowed us to characterize unambiguously these derivatives.

(1) *trans*-3,3-dimethyl-1,2-diphenyl-1,2,3-diphosphagermolane (**12a**):[10] 32%;[17] ^{1}H NMR[18] δ −0.02 (d, ^3J(MeGeP) = 2.0 Hz, 3 H, MeGe), 0.29 (d, ^3J(MeGeP) = 6.0 Hz, 3 H, MeGe); ^{31}P{^{1}H} NMR δ 3.5 (d, ^1J(PP) = 270.9 Hz, PC), −101.2 (d, PGe).

(2) 3,3-Dimethyl-2-(dimethylphenylgermyl)-1-phenyl-1,2,3-diphosphagermolane (**14a**): 20%; ^{1}H NMR δ 0.19 (d, ^3J(MeGeP) = 1.1 Hz, 3 H, MeGeC), 0.35 (d, ^3J(MeGeP) = 6.5 Hz, 3 H, MeGeC), 0.30 (d, ^3J(MeGeP) = 5.2 Hz, 6 H, Me_2GePh); ^{31}P{^{1}H} NMR δ 7.8 (d, ^1J(PP) = 273.9 Hz, PC), −115.6 (d, PGe). This compound has also been characterized by reduction with $LiAlH_4$ (see below).

(3) 2,4-Dimethyl-1,3-diphenylperhydro-1,3,2,4-diphosphadigermin (**11a**): 18%; ^{1}H NMR δ 0.27 (d, ^3J(MeGeP) = 1.0 Hz, 3 H, MeGeC), 0.55 (d, ^3J(MeGeP) = 6.2 Hz, 3 H, MeGeC), 0.28–0.60 (m, 6 H, Me_2GeP); ^{31}P{^{1}H} NMR δ −126.2 (s, GePGe), −74.3 (br s, GePC). This compound has also been synthesized by a different route and characterized by reduction by $LiAlH_4$ (see below).

(4) About 5% higher polymers of **10a** were also obtained and characterized by reduction by $LiAlH_4$, leading exclusively to dimethylgermane and phenylphosphine (see below).

(5) The starting product **5′a** (18%) was recovered after distillation.

(b) Action of *n*-Butyllithium on 3a. Dropwise addition of 15.50 mL of a solution of *n*-butyllithium in Et_2O (83.2 g/L; 20 mmol) to a solution of 6.50 g (20 mmol) of **3a** in 50 mL of THF resulted in an orange coloration that immediately disappeared. After completion of the addition, 30 mL of pentane was added. LiBr was removed by centrifugation, and the solvents were distilled under reduced pressure, leaving a viscous oil which was identified as **5a/5′a**, previously described, and 2-(dimethyl-*n*-butylgermyl)-1-(phenylphosphino)ethane (**6a**). This byproduct was isolated in the first fraction of the distillation: bp 102 °C (0.1 mmHg); 0.89 g, 15%; ^{1}H NMR δ 0.07 (s, 6 H, Me_2Ge), 4.13 (dt, ^1J(PH) = 205.0 Hz, ^3J($HPCH_2$) = 6.5 Hz, 1 H, PH); ^{31}P NMR δ −41.1 (d, ^1J(PH) = 205.0 Hz). The other fractions were similar (with slight differences in percentages) to fractions obtained from the distillation of **5a** (see paragraph a).

Reduction of a Mixture of 12a and 14a by Lithium Aluminium Hydride. Mixtures of **12a** and **14a** were obtained in different percentages after several distillations of **5a/5′a** (from 85% of **12a** and 15% of **14a** to 20% of **12a** and 80% of **14a**).

To a mixture of **12a** (60%) and **14a** (40%) (4.0 g) in 50 mL of Et_2O was added in portions 0.94 g (twofold excess) of lithium aluminium hydride. The reaction mixture was refluxed for 6 h, then hydrolyzed, extracted with Et_2O, and dried over Na_2SO_4. Distillation gave the following derivatives.

Phenylphosphine ($PhPH_2$;[19] from **12a**): 0.38 g, 56%; bp 156 °C; ^{1}H NMR δ 3.85 (d, ^1J(PH) = 198 Hz, 1 H, PH); ^{31}P{^{1}H} NMR δ −122.4.

Dimethylphenylgermane (**17a**;[20] from **14a**): 0.38 g, 52%; bp 80 °C (50 mmHg); ^{1}H NMR δ 0.37 (d, ^3J(MeGeH) = 3.7 Hz, 6 H, Me_2Ge), 4.50 (sept, 1 H, GeH); IR ν(GeH) 2025 cm^{-1}.

2-(Dimethylgermyl)-1-(phenylphosphino)ethane (**16a**; from **12a** and **14a**): 1.92 g, 78%; bp 74–76 °C (1 mmHg); ^{1}H NMR δ 0.09 (d, ^3J(MeGeH) = 3.60 Hz, 6 H, Me_2Ge), 0.90–1.33 (m, 2 H, CH_2Ge), 1.50–2.07 (m, 2 H, CH_2P), 4.13 (dt, ^1J(PH) = 205.9 Hz, ^3J(CH_2PH) = 6.5 Hz, 1 H, PH), 3.93 (m, 1 H, GeH); ^{31}P{^{1}H} NMR δ −42.4; IR ν(GeH) 2046 cm^{-1}, ν(PH) 2302 cm^{-1}. Anal. Calcd for $C_{10}H_{17}GeP$: C, 49.88; H, 7.12. Found: C, 49.57; H, 6.96.

Phosphine (PH_3;[21] from **14a**) was also obtained (trapped at −196 °C): ^{31}P NMR (C_6H_6) δ −240 (q, ^1J(PH) = 180 Hz).

Synthesis of 2,4-Dimethyl-1,3-diphenylperhydro-1,3,2,4-diphosphadigermin (11a). (a) Synthesis of 1-(Phenylphosphino)-2-(dimethyl(phenylphosphino)germyl)ethane (15a). To a solution of 4.55 g (14 mmol) of **3a** in 10 mL of C_6H_6 was added dropwise a solution of lithium phenylphosphide prepared from 1.57 g (14 mmol) of phenylphosphine and 6.07 g of a 15% solution of BuLi in hexane (14 mmol). After completion of the addition, the solvent was removed under vacuum, leaving a colorless liquid which was identified as **15a**: ^{1}H NMR δ 0.23 (d, ^3J(MeGeP) = 3.5 Hz, 6 H, Me_2Ge), 3.37 (d, ^1J(PH) = 206.0 Hz, 1 H, GePH), 4.10 (dt, ^1J(PH) = 207.0 Hz, ^3J(CH_2PH) = 6.5 Hz, 1 H, CPH): ^{31}P NMR δ −123.9 (d, GePH), −41.9 (d, HPC). Anal. Calcd for $C_{16}H_{22}GeP_2$: C, 55.08; H, 6.36. Found: C, 54.81; H, 5.99.

(b) Action of Dimethylbis(diethylamino)germane on 15a. Solutions of 14 mmol of **15a** in 10 mL of C_6H_6 and 3.51 g (14 mmol) of dimethylbis(diethylamino)germane, $Me_2Ge(NEt_2)_2$, in 10 mL of the same solvent were added simultaneously by means of two addition funnels to 15 mL of C_6H_6. The reaction was exothermic. The reaction mixture then was refluxed for 2 h and the solvent distilled away under reduced pressure. ^{31}P NMR spectrum showed four signals: −126.2 and −74.3 (attributed to a first diastereoisomeric form of **11a** (**11′a**), 90%) and −126.0 (shoulder) and −69.2 (attributed to a second diastereoisomeric form of **11a** (**11″a**), 10%). ^{1}H NMR signals of **11″a** were under those of **11′a** (see data above) and could not be obtained. Elemental analysis, reduction, and decomposition by heating seem to prove that **11″a** is a second diastereoisomeric form of **11a**. Anal. Calcd for $C_{18}H_{26}Ge_2P_2$: C, 48.09; H, 5.83. Found: C, 48.50; H, 5.77. Reduction by $LiAlH_4$ gave only Me_2GeH_2, $PhPH_2$, and $Me_2Ge(H)CH_2CH_2P(H)Ph$. Cryometry in benzene: calcd 449.2; found 455. Reduction gave only Me_2GeH_2, $PhPH_2$, and $Me_2Ge(H)CH_2CH_2P(H)Ph$.

Thermal Decomposition of 11a. A 1.28-g sample of a mixture of **11′a** and **11″a** was heated at 150 °C under 0.01 mmHg in a 20-mL flask connected to a trap cooled at −196 °C and filled with 5 g of MeSSMe. Decomposition reaction was analyzed by ^{31}P NMR. After 0.5 h, about 20% of **11′a** and more than 50% of **11″a** were decomposed. Reaction was complete after 6 h. ^{31}P NMR of the reaction mixture showed the quantitative formation (no other signal) of **12a**. Distillation of products trapped led to 0.14 g (25%) of $Me_2Ge(SMe)_2$,[22] bp 74 °C (10 mmHg), identified by GC by comparison with a sample previously prepared.[24]

Reduction of 11a by LiAlH$_4$. Reaction was performed in a 100-mL flask equipped with an alcohol–dry ice reflux condenser. A solution of 4.18 g (9.3 mmol) of **11a** in 20 mL of Et_2O was added to an excess of lithium aluminium hydride (0.70 g, 18.6 mmol) in 20 mL of Et_2O. Reaction was slightly exothermic. The reaction mixture was refluxed for 2 h, hydrolyzed, extracted with Et_2O, and dried over Na_2SO_4. Distillation gave the following derivatives.

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(17) Relative percentages.

(18) In ^{1}H NMR, only characteristic signals are given; we have not reported signals of Et_2Ge (A_6B_1-type spectrum), CH_2CH_2P (AA′BB′X-type spectrum), and Ph which appear as very complex multiplets. In all cases, integrations are in good agreement.

(19) Kosolapoff, G. M.; Maier, L. Eds. "Organic Phosphorus Compounds"; Wiley-Interscience: New York, 1972; Vol. 1, Chapter 1, p 111.

(20) Satgé, J.; Rivière, P. *Bull. Soc. Chim. Fr.* **1966**, 1773.

(21) Jones, R. A. Y.; Katritzky, A. R. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 32.

(22) Dimethyl disulfide is a good trapping reagent of germylenes.[23]

(23) Rivière, P.; Satgé, J.; Castel, A. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1975**, *281*, 835.

(24) Moedritzer, K.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1965**, *87*, 2360.

Dimethylgermane[25] trapped at −78 °C (0.65 g, 67%): ^{1}H NMR ($CHCl_3$) δ −0.14 (t, ^{3}J(MeGeH) = 3.8 Hz, 6 H, Me_2Ge), 3.34 (sept, ^{3}J(MeGeH) = 3.8 Hz, 2 H, GeH).

Phenylphosphine ($PhPH_2$): 0.77 g, 75% (see data above).

2-(Dimethylgermyl)-1-(phenylphosphino)ethane (**16a**): 1.66 g, 74% (see data above). No other compound was detectable.

Reduction of Polymers of 10a by $LiAlH_4$. We used the same procedure as that for the reduction of **11a** from 0.70 g of $(Me_2GePPh)_n$. Only dimethylgermane (0.22 g, 64%) and phenylphosphine (0.24 g, 67%) were obtained by distillation.

Synthesis of 5b/5′b. (a) Action of Diethylamine on 3b. **5b/5′b** was obtained as viscous oil by the method previously described for **5a/5′a** from 16.28 g (224 mmol) of diethylamine and 19.35 g (56 mmol) of **3b** in 30 mL of benzene: cryometry in C_6H_6 calcd 533, found 510; mass spectrum, *m/e* 264–270 (**5b**). Distillation gave a very viscous liquid (12.51 g; bp 180–220 °C (0.05 mmHg)). As in the case of distillation of **5a/5′a** separation of **5′b**, **11b**, **12b**, and **14b** as pure compounds was impossible. Comparison between NMR data and GC analyses of several fractions isolated after three distillations and chemical reactivity study (reduction by $LiAlH_4$, thermolysis, etc.) allowed us to identify every compound.

(1) **12b**: 42%[10,17,18] ^{31}P{^{1}H} NMR δ 1.5 (d, ^{1}J(PP) = 270.6 Hz, PC), −103.7 (d, PGe).

(2) **14b**: 31%; ^{31}P{^{1}H} NMR δ 8.6 (d, ^{1}J(PP) = 276.5 Hz, PC), −115.6 (d, PGe). This compound has also been characterized by reduction by $LiAlH_4$ (see below).

(3) **11b**: 10%; ^{31}P{^{1}H} NMR δ −76.1 (s, GePC), −146.4 (s, GePGe). **11b** has also been characterized by an independant synthesis and by reduction with $LiAlH_4$ (see below).

(4) **5′b**: 9% of the starting product was recovered.

(5) Higher polymers of **10b** ($(Et_2GePPh)_n$; 5%) were also obtained and characterized by reduction with $LiAlH_4$ (see below).

(b) Action of *n*-Butyllithium on 3b. The reaction of a solution of 15% of *n*-butyllithium (6 mmol) in hexane with 2.17 g (6 mmol) of **3b** in 20 mL of THF gave **5b/5′b** previously described and about 20% of **6b** (2-(diethylbutylgermyl)-1-(phenylphosphino)ethane). This byproduct was obtained in the first fraction of distillation: bp 110 °C (0.1 mmHg); 0.33 g 17%; ^{1}H NMR δ 4.10 (td, ^{1}J(PH) = 210.1 Hz, ^{3}J($HPCH_2$) = 6.5 Hz, 1 H, PH); ^{31}P δ −41.1 (d, ^{1}J(PH) = 210.1 Hz, PH). The other fractions were similar to those obtained in the precedent distillation (see above).

Reduction of a Mixture of 12b and 14b by Lithium Aluminium Hydride. A mixture of **12b** (65%) and **14b** (35%) (5.21 g) in 60 mL of Et_2O was reduced by 1.22 g of lithium aluminium hydride (large excess) according to the method previously described for the reduction of **12a** and **14a**. The following derivatives were obtained.

Phenylphosphine ($PhPH_2$;[19] from **12b**): 0.60 g, 68%; bp 156 °C; ^{1}H NMR δ 3.85 (d, ^{1}J(PH) = 198 Hz, 1 H, PH); ^{31}P{^{1}H} NMR δ −122.

Diethylphenylgermane (**17b**;[26] from **14b**): 0.97 g, 79%; ^{1}H NMR δ 1.03–1.16 (m, 10 H, Et_2Ge), 4.40–4.60 (m, 1 H, GeH), 7.20–7.60 (m, 5 H, Ph).

2-(Diethylgermyl)-1-(phenylphosphino)ethane (**16b**; from **12b** and **14b**): 2.51 g, 73%; bp 105–108 °C (0.5 mmHg); ^{1}H NMR δ 0.72–1.42 (m, 12 H, Et_2Ge and $GeCH_2$), 1.62–2.12 (m, 2 H, CH_2P), 3.87 (m, 1 H, GeH), 4.03 (dt, ^{1}J(PH) = 204.8 Hz, ^{3}J(CH_2PH) = 6.8 Hz, 1 H, PH); ^{31}P NMR δ −42.0. Anal. Calcd for $C_{12}H_{21}GeP$: C, 53.61; H, 7.87. Found: C, 53.98; H, 8.09.

Phosphine (PH_3; from **14b**) was trapped at −196 °C (see data above).

Synthesis of 2,4-Diethyl-1,3-Diphenylperhydro-1,3,2,4-diphosphadigermin (11b). This derivative was synthesized by the method previously described for **11a** from 5.18 g (15 mmol) of **3b**, 1.64 g (15 mmol) of phenylphosphine, and 6.40 g of a 15% solution of *n*-BuLi in hexane (15 mmol). To this mixture was added 4.12 g (15 mmol) of diethylbis(diethylamino)germane in benzene to give 5.91 g (78%) of **11b** (see data above): cryometry in C_6H_6 calcd 505.2, found 501. Anal. Calcd for $C_{22}H_{34}Ge_2P_2$: C, 52.26; H, 6.78. Found: C, 51.87; H, 6.62.

Reduction of 11b by $LiAlH_4$. We used the same procedure as that for the reduction of **11a** from 4.55 g (9 mmol) of **11b** and 0.68 g (18 mmol) of lithium aluminium hydride. Distillation gave the following derivatives.

Diethylgermane:[27] bp 74 °C; 0.79 g, 67%; ^{1}H NMR δ 0.57–1.23 (m, 10 H, Et_2Ge), 3.76 (quint, ^{3}J(CH_2GeH) = 2.7 Hz, 2 H, GeH).

Phenylphosphine ($PhPH_2$): 0.71 g, 72% (see data above).

2-(Diethylgermyl)-1-(phenylphosphino)ethane (**16b**): 1.66 g, 69% (see data above).

Reduction of Polymers of 10b by $LiAlH_4$: same procedure as that for the reduction of **11a** from 0.68 g of $(Et_2GePPh)_n$. Only diethylgermane (0.26 g, 68%) and phenylphosphine (0.18 g, 56%) were obtained by distillation.

Reactions of 2,2-Dimethyl-1-phenyl-1,2-phosphagermetane (5a). (a) Sulfuration. Sulfur (0.35 g (1.4 mmol) as S_8) was added slowly in portions to 1.32 g (5 mmol) of **5a/5′a**. The reaction was exothermic. A light yellow liquid, **7a**, was isolated by distillation: 0.90 g, 56%; bp 130–135 °C (0.4 mmHg)); ^{1}H NMR δ 0.50 (br s, 6 H, Me_2Ge); ^{31}P NMR δ +84.4; osmometry in C_6H_6 calcd 302.8, found 298. Anal. Calcd for $C_{10}H_{15}GePS_2$: C, 39.65; H, 4.99; S, 21.16. Found: C, 39.13; H, 4.84; S, 21.28.

(b) Action of Benzaldehyde. A solution of 0.64 g (6 mmol) of benzaldehyde in 2 mL of benzene was added slowly to 1.44 g (6 mmol) of **5a/5′a** in 5 mL of the same solvent. The reaction mixture was stirred for 1 h and distilled to give **8a** (1.61 g, 77%; bp 151–154 °C (0.5 mmHg)). First diastereoisomeric form (75%): ^{1}H NMR δ 0.36 (s, 3 H, MeGe), 0.38 (s, 3 H, MeGe), 5.11 (d, ^{2}J(HCP) = 6.0 Hz, 1 H, OCH); ^{31}P NMR δ −18.2. Second diastereoisomeric form (25%): ^{1}H NMR δ 0.28 (s, 3 H MeGe), 0.30 (s, 3 H, MeGe), 5.73 (d, ^{2}J(HCP) = 16.0 Hz, 1 H, OCH); ^{31}P NMR δ −19.2. Anal. Calcd for $C_{17}H_{21}GeOP$ (mixture of two diastereoisomers): C, 59.20; H, 6.14. Found: C, 59.12; H, 6.10.

(c) Action of Acetone. A solution of 1.44 g (6 mmol) of **5a/5′a** in a large excess of acetone (2 mL) was heated in a sealed tube for 1 h at 100 °C. Fractionation gave 1.50 g (88%) of **9a**: bp 130–132 °C (0.4 mmHg); ^{1}H NMR δ 0.33 (s, 6 H, Me_2Ge), 1.27 (d, ^{3}J(PCMe) = 7.0 Hz, 3 H, MeC), 1.48 (d, ^{3}J(PCMe) = 15.6 Hz, 3 H, MeC), 1.50–2.50 (m, 2 H, CH_2P), 0.90–1.50 (m, 2 H, CH_2Ge); ^{31}P NMR δ −11.9. Anal. Calcd for $C_{13}H_{21}GeOP$: C, 52.59; H, 7.13. Found: C, 52.23; H, 7.10.

Registry No. **1a**, 82312-12-7; **1b**, 77031-54-0; **2a**, 35935-19-4; **2b**, 77031-54-0; **3a**, 82312-13-8; **3b**, 82322-80-3; **4a**, 82312-14-9; **4b**, 82312-15-0; **5a**, 82312-16-1; **5b**, 82312-17-2; **5′a**, 82312-18-3; **5′b**, 82312-19-4; **6a**, 82312-20-7; **6b**, 82312-21-8; **7a**, 82312-22-9; **8a**, 82312-23-0; **9a**, 82312-24-1; **10a**, 68160-18-9; **10b**, 82312-25-2; **11a**, 81744-50-5; **11b**, 81744-51-6; **12a**, 78665-55-1; **12b**, 81744-45-8; **13a**, 82312-26-3; **13b**, 82312-27-4; **14a**, 82312-28-5; **14b**, 82312-29-6; **15a**, 82312-30-9; **15b**, 82312-31-0; **16a**, 82312-32-1; **16b**, 82312-33-2; **17a**, 7366-21-4; **17b**, 79301-90-9; $Me_2Ge(H)Cl$, 21961-73-9; $CH_2{=}CHBr$, 593-60-2; $PhPH_2$, 638-21-1; PhPHLi, 51918-34-4; $Me_2Ge(NEt_2)_2$, 3058-23-9; Me_2GeH_2, 1449-64-5; Et_2GeHz, 1631-46-5; PhCHO, 100-52-7; MeCOMe, 67-64-1.

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(25) Van de Vondel, D. F. *J. Organomet. Chem.* **1965**, *3*, 400.

(26) Rivière, P.; Castel, A.; Satgé, J.; Cazes, A. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 443.

(27) Mac Kay, K. M.; Watt, R. *J. Organomet. Chem.* **1966**, *6*, 336.