in the preequilibrium, is trapped by CO to afford **3a**. Similarly, formation of **3b** and **3c** could arise from addition of the phosphines at low temperature to **2***. It is rather surprising that the reaction of triphenylphosphine with **2** at or above room temperature causes the rupture of the trinuclear unit to give the dinuclear complex **5**, since face-bridging dppm fragments have been shown to play their role in the stabilization of the Ru_3 triangle.[3,4a]

In conclusion, we believe that the previously reported[3] CO-induced transformation of $Ru_3(CO)_9(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (**2**) into $Ru_3(CO)_{10}(\mu\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (**4**) (see Scheme I) involves addition of CO as the initial reaction step to give $Ru_3(CO)_{10}(\mu_3\text{-}\eta^3\text{-}P(C_6H_5)CH_2P(C_6H_5)(C_6H_4))$ (**3a**) (Scheme II). Just as the addition of CO to bis(alkylidyne) clusters favors carbon–carbon coupling,[24] the addition of CO in the present case favors the coupling of a phosphido bridge with an adjacent aryl group. This illustrates a rather general principle in cluster chemistry: a closed metal cluster is prone to give a CO adduct via opening of a metal–metal bond; the resultant open cluster can isomerize to a closed species either by loss of ligand or by intramolecular reductive elimination and rearrangement within the ligand shell.

Acknowledgment. This research was supported by the CNRS (ATP "Chimie Fine" to J.-J.B.), by the NSF (Grant CHE-83-08076 to J.A.I.), and by the NSF/CNRS U.S.-France program (Grant INT-82-12376 to J.A.I.). We thank the Ministère des Affaires Etrangères and the Mission Scientifique de l'Ambassade de France in Washington, DC, for enabling N.L. to work in Evanston.

Registry No. **2**, 96502-43-1; **3a**, 114490-24-3; **3b**, 114466-60-3; *trans*-**3b**, 114466-61-4; **3c**, 114466-62-5; **5**, 114490-25-4; $Ru(CO)_3(P(C_6H_5)_3)_2$, 14741-36-7.

Supplementary Material Available: Tables S1, S2, and S3, anisotropic thermal parameters for compounds **3a**, **3c**, and **5**, respectively (3 pages); Tables S4, S5, and S6, structure amplitudes (×10) for compounds **3a**, **3c**, and **5**, respectively (88 pages). Ordering information is given on any current masthead page.

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[24] Chi, Y.; Shapley, J. R. *Organometallics* **1985**, *4*, 1900–1901.

From Germaphosphene to Germathia- (or Germaselena-) Phosphiranes

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Reaction of sulfur (or selenium) with the germaphosphene **1** leads to new stable three-membered heterocycles, the germathiaphosphirane **3** and the germaselenaphosphirane **14**. The structure of **3** was confirmed by X-ray crystal analysis (space group $P\bar{1}$; $a = 11.098$ (3) Å, $b = 12.329$ (3) Å, $c = 16.050$ (6) Å; $\alpha = 62.63$ (2)°, $\beta = 65.76$ (2)°, $\gamma = 70.05$ (2)°; $V = 1746$ (1) Å^3; $d_{calcd} = 1.180$ g/cm^3 for $Z = 2$; $R_w = 0.052$, 5172 reflections with $I > 2.5\ \sigma(I)$). The Ge–P (2.316 (1) Å) and Ge–S (2.227 (1) Å) bond lengths are normal. The P–S bond is slightly elongated. Germanium is nearly planar (sum of the bond angles = 358.1°).

Introduction

Compounds of groups 14 and 15 with lower coordination numbers are of current interest because of their unusual structure and reactivity.[1] The only known kinetically stable germaphosphene **1** has been synthesized,[2] its X-ray structure recently determined[3] (the Ge=P double bond length (2.138 (3) Å) is shortened by about 8.5% in relation to the standard Ge—P single bond), and some of its chemical reactions investigated. The germaphosphene **1** readily undergoes electrophilic, nucleophilic, and radical addition reactions[4a] to the germanium–phosphorus double bond, and an unexpected thermolysis reaction has been reported.[4b]

Stable metal–group 14 three-membered heterocycles are still rare: some of them have recently been isolated,[5] but only two have been structurally characterized.[6]

In this paper we report [2 + 1] cycloaddition reactions between **1** and sulfur and selenium that lead to stable novel three-membered organogermanium heterocycles, the germathiaphosphirane **3** and the germaselenaphosphirane **14**. The X-ray structure of **3** has been determined.

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[1] For reviews on M=M compounds, see the following. (a) Si=Si: West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (b) Si=M (M = group 14 and 15 elements): Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (c) Si=C: Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1. (d) Si=C (or N) and Ge=C (or N): Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141. (e) Ge=M (M = group 14 and 15 elements): Satge, J. *Adv. Organomet. Chem.* **1982**, *21*, 241. (f) M=M′ (M, M′ = Si, Ge, Sn, P, As, Sb): Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1. (g) P=X (X = group 14 and 15 elements): Lochschmidt, S.; Schmidpeter, A. *Phosphorus Sulfur* **1986**, *29*, 73.

[2] Escudie, J.; Couret, C.; Satge, J.; Andrianarison, M.; Andriamizaka, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 3378.

[3] Dräger, M.; Escudie, J.; Couret, C.; Ranaivonjatovo, H.; Satge, J. *Organometallics* **1988**, *7*, 1010.

[4] (a) Escudie, J.; Couret, C.; Andrianarison, M.; Satge, J. *J. Am. Chem. Soc.* **1987**, *109*, 386. (b) Andrianarison, M.; Couret, C.; Declercq, J. P.; Dubourg A.; Escudie, J.; Satge, J. *J. Chem. Soc. Chem. Commun.* **1987**, 921.

[5] For example Ge—Ge—Ge,[5a] Ge—C—S,[5b] Ge—Ge—S,[5b] Ge—Ge—Se,[5b] Ge—C=C,[5c] and Ge—P—P:[5d] (a) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191. Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1514. (b) Ando, W.; Tsumuraya, T. *Tetrahedron Lett.* **1986**, *27*, 3251. (c) Krebs, A.; Berndt, J. *Tetrahedron Lett.* **1983**, *24*, 4083. (d) Baudler, M.; Suchomel, H. *Z. Anorg. Allg. Chem.* **1983**, *503*, 7.

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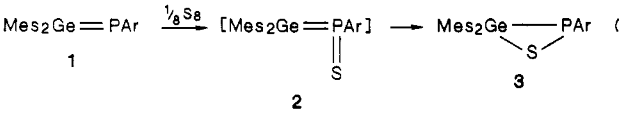
Table I. Important Interatomic Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for 3

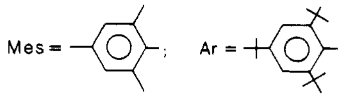
Bond Distances			
P–Ge	2.316 (1)	C(21)–C(22)	1.395 (5)
P–S	2.176 (1)	C(22)–C(23)	1.375 (5)
Ge–S	2.227 (1)	C(23)–C(24)	1.403 (4)
P–C(19)	1.880 (3)	C(24)–C(19)	1.414 (5)
Ge–C(10)	1.962 (3)	C(20)–C(25)	1.548 (5)
Ge–C(1)	1.961 (3)	C(29)–C(22)	1.527 (5)
C(19)–C(20)	1.415 (5)	C(33)–C(24)	1.555 (5)
C(20)–C(21)	1.388 (5)		
Bond Angles			
S–Ge–P	57.2 (1)	C(10)–Ge–S	119.7 (1)
S–P–Ge	59.3 (1)	C(10)–Ge–C(1)	112.2 (1)
P–S–Ge	63.5 (1)	C(19)–C(20)–C(21)	117.7 (3)
C(19)–P–S	102.5 (1)	C(20)–C(21)–C(22)	123.2 (3)
C(19)–P–Ge	106.0 (1)	C(21)–C(22)–C(23)	116.5 (3)
C(1)–Ge–P	115.6 (1)	C(22)–C(23)–C(24)	123.2 (3)
C(1)–Ge–S	107.1 (1)	C(23)–C(24)–C(19)	117.5 (3)
C(10)–Ge–P	130.3 (1)	C(24)–C(19)–C(20)	118.9 (3)
Torsion angles, ($\bar{\sigma}$ = 0.3°)			
C(1)GePS	94.6	C(1)GePC(19)	−170.2
C(10)GePS	−103.1	C(10)GePC(19)	−7.9
SGePC(19)	95.2		

Results and Discussion

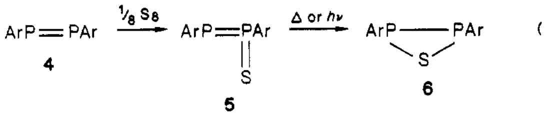
(a) Sulfur. Reaction of germaphosphene 1 with an equimolar quantity of elemental sulfur in benzene solution at room temperature produced the germathiaphosphirane 3 in good yield (eq 1).



(1)



The first step of this reaction probably is the formation of the germaphosphene sulfide 2. A similar addition has been demonstrated by Yoshifuji in the reaction of sulfur with the diphosphene 4[7] in which the stable intermediate 5 isomerizes thermally or photochemically to 6 (eq 2).



(2)

In our case we have never observed, even on following the reaction by NMR, the intermediate compound 2, which isomerizes, probably very quickly, to 3 due to the great affinity of sulfur for germanium.

Compound 3 is a colorless, crystalline solid, soluble in organic solvents, which has been identified on the basis of its physicochemical data: in the ^{31}P NMR spectrum its P atom shows a high-field chemical shift of −85.6 ppm characteristic of a three-membered heterocycle.[8] The molecular structure of 3 was confirmed by an X-ray crystal structure determination.

Description of the Structure. The molecular structure of 3 and the numbering of the atoms are shown in Figure 1 (PLUTO[9]). Important bond lengths and angles are given in Table I. Crystal structure data and fractional atomic coordinates with equivalent isotropic temperature factors are displayed in Tables II and III .

Table II. Crystal Structure Data for 3[a]

formula	$C_{36}H_{51}GePS$
M_r	619.406
cryst system	triclinic
space group	$P\bar{1}$
cryst dimensions, mm	0.3 × 0.3 × 0.4
a, Å	11.098 (3)
b, Å	12.329 (3)
c, Å	16.050 (6)
α, deg	62.63 (2)
β, deg	65.76 (2)
γ, deg	70.05 (2)
V, Å^3	1746 (1)
Z	2
D(calcd), g/cm^3	1.180
μ(Mo Kα), mm^{-1}	1.04
F(000)	660
radiatn	Mo Kα
λ, Å	0.71069
ω scan width, deg	1.4
ω scan speed, deg/min	1.4–30
measd data	6873
obsd data [$I > 2.5\sigma(I)$]	5172

[a] $R = 0.046$. $R_w = 0.052$. $w = 1/\sigma^2(F) + 0.00168F^2$. Maximum and minimum values of the electron density in the final difference synthesis: +0.50/−0.37 e Å^{-3}.

Table III. Fractional Atomic Coordinates (×10^6) and Equivalent Isotropic Temperature Factors (Å^2) for 3

	x/a	y/b	z/c	B_{eq}[a]
Ge	449 (1)	982 (1)	2362 (1)	3.32
P	186 (1)	3121 (1)	1812 (1)	3.90
S	−896 (1)	2064 (1)	3309 (1)	4.42
C(1)	−711 (3)	395 (3)	2071 (2)	3.34
C(2)	−956 (4)	931 (4)	1153 (3)	4.14
C(3)	−1808 (4)	437 (4)	1033 (3)	4.67
C(4)	−2411 (4)	−541 (4)	1759 (3)	4.53
C(5)	−2155 (4)	−1052 (4)	2654 (3)	4.28
C(6)	−1329 (4)	−600 (3)	2820 (3)	3.64
C(7)	−326 (5)	1978 (5)	308 (3)	6.29
C(8)	−3319 (5)	−1050 (5)	1600 (4)	6.64
C(9)	−1113 (5)	−1245 (4)	3832 (3)	5.32
C(10)	1926 (3)	−340 (3)	2771 (2)	3.24
C(11)	2502 (4)	−1235 (3)	2331 (3)	3.69
C(12)	3386 (4)	−2286 (4)	2699 (3)	4.71
C(13)	3757 (5)	−2479 (4)	3494 (3)	5.02
C(14)	3247 (4)	−1577 (3)	3888 (3)	4.39
C(15)	2346 (4)	−510 (3)	3547 (2)	3.55
C(16)	2203 (4)	−1106 (4)	1439 (3)	4.85
C(17)	4742 (6)	−3639 (5)	3879 (5)	8.04
C(18)	1872 (4)	428 (4)	4033 (3)	4.54
C(19)	1607 (4)	3409 (3)	1989 (3)	3.63
C(20)	2961 (4)	3058 (3)	1468 (3)	3.74
C(21)	3947 (4)	2842 (4)	1877 (3)	4.27
C(22)	3675 (4)	3057 (3)	2723 (3)	3.87
C(23)	2390 (4)	3640 (3)	3083 (3)	4.00
C(24)	1337 (4)	3873 (3)	2718 (3)	3.76
C(25)	3458 (4)	3000 (4)	434 (3)	4.36
C(26)	2452 (5)	3781 (6)	−152 (3)	7.65
C(27)	3798 (6)	1654 (5)	495 (4)	7.46
C(28)	4737 (5)	3541 (5)	−173 (3)	6.31
C(29)	4795 (4)	2746 (4)	3161 (3)	4.81
C(30)	5323 (7)	1390 (5)	3507 (6)	9.86
C(31)	5928 (7)	3387 (9)	2400 (5)	14.51
C(32)	4327 (6)	3115 (8)	4030 (6)	11.09
C(33)	41 (4)	4738 (4)	3104 (4)	5.10
C(34)	516 (6)	5932 (4)	2865 (5)	7.83
C(35)	−602 (5)	4126 (5)	4222 (4)	6.94
C(36)	−1026 (5)	5217 (4)	2572 (4)	6.90

[a] $B_{eq} = {}^8/_3\,\pi^2\sum_i\sum_j U_{ij}a_i^*\,a_j^*a_ia_j$.

In the three-membered heterocycle, the Ge–S bond length (2.227 (1) Å) is normal.[10b] The Ge–P bond length

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[6] (a) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *22*, 6136. (b) Egorov, M. P.; Kolesnikov, S. P.; Struchkov, Yu. T.; Antipin, M. Yu.; Sereda, S. V.; Nefedov, O. M. *J. Organomet. Chem.* **1985**, *290*, C27.

[7] Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Chem. Soc., Chem. Commun.* **1983**, 862.

[8] Baudler, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 492.

[9] Motherwell, S.; Clegg, W. PLUTO; University of Cambridge: Cambridge, England, 1978.

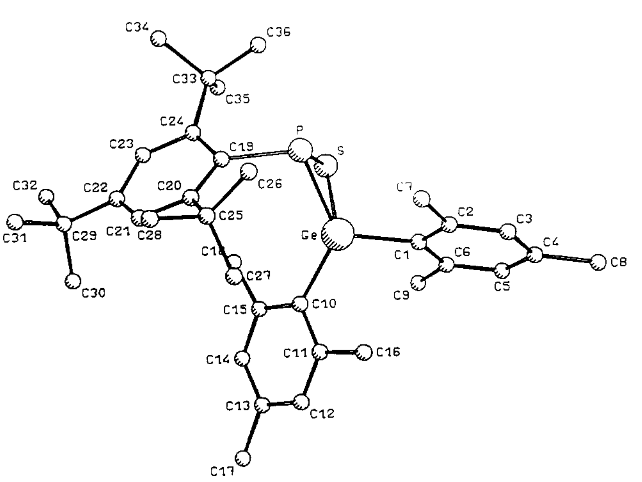
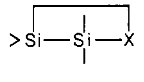


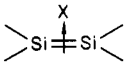
Figure 1. PLUTO drawing of germathiaphosphirane 3.

(2.316 Å) lies in the lower limit of the normal range (2.31–2.36 Å)[4b,10a] and is shorter than expected for a bond between very crowded germanium and phosphorus atoms; this bond should be, of course, elongated to decrease the steric bulk due to mesityl and 2,4,6-tri-*tert*-butylphenyl groups. The P–S bond length (2.176 (1) Å) is slightly longer than expected: the normal values lie in the range 2.10–2.14 Å.[10c] A slight elongation is also observed for P–C(19) (1.880 (3) Å) in relation to the standard P–C bond length (1.86 Å), probably due to the steric bulk of the substituent on phosphorus. The 57.2 (1)° S–Ge–P angle is a normal value for a three-membered heterocycle, close to that observed in a cyclotrigermane (Ge–Ge–Ge = 59.9 and 60.1°)[6a] but much larger than that in germirene (C–Ge–C = 40.5°).[6b] Germanium, phosphorus, and the three ipso carbons of the aromatic rings (C(1), C(10), and C(19)) are nearly in the same plane: the distances from germanium and phosphorus to the plane $C_1C_{10}C_{19}$ are 0.20 and 0.09 Å, respectively. Germanium is nearly planar: the sum of the bond angles P–Ge–C(10), C(10)–Ge–C(1), and P–Ge–C(1) around the germanium atom is 358.1°. Surprisingly, its geometry is very close to that observed in the starting germaphosphene 1, where the five atoms Ge, P, C(1), C(10), and C(19) are also coplanar, as expected for a compound with a double bond between germanium and phosphorus.[3] The torsion angles are very similar in the two cases (C(1)GePC(19) = −170.2° in 3 and −169.7° in 1;[3] C(10)GePC(19) = −7.9° in 3 and −12.9° in 1[3]). The least-squares plane GePC(1)C(10)C(19) is nearly perpendicular (86°) to the three-membered germathiaphosphirane ring (see also torsion angles in Table I).

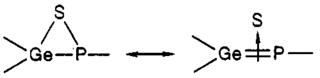
Similar observations (short Si–Si bond and nearly planar silicon atoms) were made by West in the three-membered heterocyles



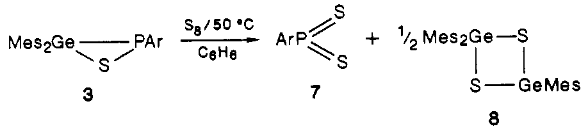
(X = O,[20] S[21]) obtained from a starting disilene, $R_2Si{=}SiR_2$. A contribution from the form



was postulated[1a] and was supported by calculations.[22] So it seems that in the case of 3, where a short Ge—P bond length and the planarity of the GePC(1)C(10)C(19) skeleton are observed, the hybridization at germanium may be better represented as sp^2 than sp^3 and partial π-bonding may exist between the germanium and phosphorus atoms. So the bonding may be intermediate between that in a normal three-membered ring and that of a π-complex:

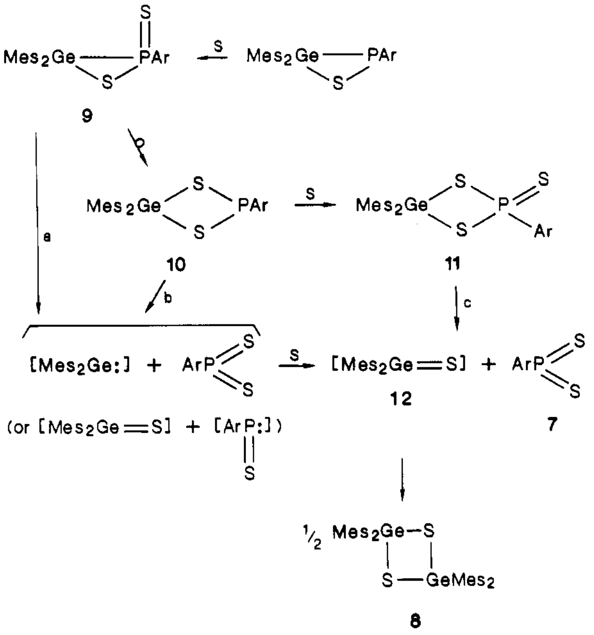


Reactivity of 3. Heating 3 with an excess of sulfur leads not only to the metadithiophosphonate 7[11] and to the 2,4-digerma-1,3-dithietane 8[12] but also to a few unidentified products in minor quantities (less than 10%) (eq 3).



(3)

Formation of 7 and 8 might be explained by the mechanisms involving the decomposition of the three- or four-membered heterocycles 9–11; 8 arises probably from the dimerization of the germathione intermediate 12 (eq 4).



(4)

We have been unable until now to determine which mechanism (a, b, or c) leads to 7 and 8. Attempts to trap

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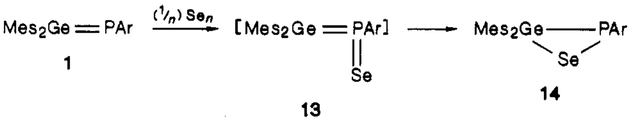
(10) (a) Fritz, G.; Hoppe, K. D.; Hönle, W.; Weber, D.; Mujica, C.; Manriquez, V.; von Schnering, H. G. *J. Organomet. Chem.* **1983**, *249*, 63. Tebbe, K. F.; Freckmann, B. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1984**, *40*, 254. Tebbe, K. F.; Fröhlich, R. *Z. Anorg. Allg. Chem.* **1983**, *506*, 27. Veith, M.; Grosser, M.; Huch, V. *Z. Anorg. Allg. Chem.* **1984**, *513*, 89. Dahl, A. R.; Norman, A. D.; Shenav, H.; Schaeffer, R. *J. Am. Chem. Soc.* **1975**, *97*, 6364. (b) Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M.; Beagley, B.; Cradock, S. *J. Chem. Soc. A* **1970**, 315. Ebsworth, E. A. V.; Huntley, C. M.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1983**, 835. (c) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J.; Goldwhite, H. *J. Chem. Soc. Chem. Commun.* **1982**, 691. Lensch, C.; Sheldrick, G. M. *J. Chem. Soc., Dalton. Trans.* **1984**, 2855. Navech, J.; Majoral, J. P. *Phosphorus Sulfur* **1983**, *15*, 51 and references cited therein.

(11) 7 has been characterized by NMR, particularly by its $\delta(^{31}P)$ (+295 ppm), as the metadithiophosphonate already prepared by other authors: Navech, J.; Majoral, J. P.; Kraemer, R. *Tetrahedron Lett.* **1983**, *24*, 5885. Appel, R.; Knoch, F.; Kunze, U. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1004. Yoshifuji, M.; Toyota, K.; Ando, K.; Inamoto, N. *Chem. Lett.* **1984**, 317.

(12) 8 has been characterized by GC and ^1H NMR by comparison to an authentic sample prepared by H. Lavayssiere (unpublished results).

the germylene Mes_2Ge: (routes a and b) or the phosphinidene sulfide ArP(S): (routes a and b) failed due to the presence of sulfur in the reaction mixture. Moreover, independent synthesis of heterocyles **9**, **10**, and **11** in order to study their decomposition behavior has unfortunately not been possible so far.

(b) Selenium. Reaction of selenium with the germaphosphene **1** in benzene solution affords exclusively the stable germaselenaphosphirane **14** (eq 5).



(5)

As in the case of sulfur, the first step of this reaction probably is the formation of intermediate **13**. The driving force of the transposition **13** → **14** is probably the great energy of the germanium–selenium bond (115 kcal/mol).[19] In the ^{31}P NMR spectrum the high-field chemical shift (−97.8 ppm) of the P atom is close to that observed for **3**; the coupling constant with ^{77}Se (41.2 Hz) is normal for a single bond between phosphorus and selenium. Similar values have been observed by Yoshifuji,[13] Baudler,[14] and Weber[16c] in selenadiphosphiranes $\overline{\mathrm{RP{-}PR{-}Se}}$. On the other hand, the coupling constant for a phosphorus–selenium double bond is generally between 750 and 900 Hz.[15,16] Mass spectrometry gives added proof of the structure of **14**. The most important fragment corresponds to $(Mes_2Ge{=}Se + H)^+$ and proves that a germanium–selenium bond is present in **14**, thereby excluding **13**.

Experimental Section

General Comments. All syntheses were performed under an atmosphere of dry nitrogen using standard Schlenk or high-vacuum lines techniques. Solvents were dried by distillation from sodium–benzophenone immediately prior to use. Highly pure sulfur and selenium were purchased respectively from Janssen and Fluka.

Germaphosphene 1 was prepared as previously described.[2,3] ^{1}H NMR spectra were recorded on a Varian EM 360 A spectrometer at 60 MHz and ^{31}P NMR spectra on a Bruker WH 90 spectrometer at 36.44 MHz. Chemical shifts are reported in parts per million from internal Me_4Si for ^{1}H and from external 85% H_3PO_4 for ^{31}P. Downfield shifts are noted positive in all cases. Mass spectra were performed on a Varian MAT 311 A spectrometer. Experimental molecule peak patterns were assigned after comparison with theoretical peak patterns calculated on a Tektronics 4051. Melting points were determined on a Reichert apparatus. Elemental analyses were done by the Service Central de Microanalyse du CNRS, Vernaison, France.

Synthesis of Germathiaphosphirane 3. To a solution of 1 (1.80 g, 3.22 mmol) in 10 mL of C_6H_6 was slowly added in portions, at room temperature, an equivalent of sulfur (0.10 g, 3.22 mmol). The initially orange solution turned yellow after 5 min of stirring. NMR analysis showed the exclusive formation of **3**. After elimination of benzene in vacuo, the residue was crystallized from 10 mL of pentane at −20 °C to afford colorless crystals (1.30 g, 65%) identified as **3**: mp 153–155 °C dec; ^{1}H NMR (C_6D_6) δ 1.65 (s, 9 H, *p*-*t*-Bu), 2.07 (br s, 18 H, *o*-*t*-Bu), 2.32 (s, 3 H, *p*-Me), 2.43 (s, 9 H, *o*-Me and *p*-Me), 2.93 (s, 6 H, *o*-Me), 6.83 (s, 2 H, arom Mes), 6.98 (s, 2 H, arom Mes), 7.48 (s, 2 H, arom Ar); ^{31}P{^{1}H} NMR (C_6D_6) δ −85.6; mass spectrum (EI, 70 eV, ^{74}Ge), *m/e* (relative intensity) 620 (M^+, 20), 563 $(M - t\text{-Bu})^+$, 100), 345 $(Mes_2Ge{=}S + H)^+$, 20). Anal. Calcd for $C_{36}H_{51}GePS$: C, 69.80; H, 8.30. Found: C, 69.71; H, 8.24.

Synthesis of Germaselenaphosphirane 14. To a suspension of selenium (0.26 g, 3.41 mmol) in 5 mL of C_6H_6 was added at room temperature a solution of 1 (2.00 g, 3.41 mmol) in 15 mL of C_6H_6. The reaction mixture became yellow. ^{31}P NMR analysis of the solution showed the disappearance of 1. Benzene was evaporated in vacuo and the residue crystallized from 10 mL of pentane at −20 °C to afford light yellow crystals (1.11 g, 49%) identified as **14**: mp 153–157 °C; ^{1}H NMR (C_6D_6) δ 1.23 (s, 9 H, *p*-*t*-Bu), 1.66 (d, ^5J(PH) = 1.2 Hz, 18 H, *o*-*t*-Bu), 1.97 (s, 3 H, *p*-Me), 2.03 (s, 6 H, *o*-Me), 2.05 (s, 3 H, *p*-Me), 2.57 (s, 6 H, *o*-Me), 6.57 (s, 2 H, arom Mes), 6.70 (s, 2 H, arom Mes), 7.17 (d, ^4J(PH) = 2.0 Hz, 2 H, arom Ar); ^{31}P{^{1}H} NMR (C_6D_6) δ −97.8 (^1J(P–^{77}Se) = 41.2 Hz); mass spectrum (EI, 70 eV, ^{74}Ge, ^{80}Se), *m/e* (relative intensity) 666 (M^+), 80), 609 $(M - t\text{-Bu})^+$, 90), 390 $(Mes_2Ge{=}Se + H)^+$, 100). Anal. Calcd for $C_{36}H_{51}GePSe$: C, 64.89; H, 7.72. Found: C, 65.01; H, 7.80.

X-ray Structure Determination. Single crystals of **3** were obtained by cooling a solution of **3** (0.50 g) in 2 mL of pentane to −20 °C for 2–3 days. The solvent was decanted, and the slightly air- and moisture-sensitive crystals were dried in vacuo.

Data were collected on a Syntex $P2_1$ four-circle diffractometer with monochromatized Mo $K\alpha$ radiation at room temperature. Accurate cell dimensions were obtained from the centering of 15 reflections ($3° < 2\theta < 26°$). A standard reflection measured every 50 reflections showed no significant variation. The coordinates of the germanium atoms were obtained by the interpretation of the Patterson function. This model was expanded to the complete structure by direct methods using SHELXS-86.[17] The least-squares refinement was performed by SHELX 76[18] with the H atoms in calculated positions.

Registry No. 1, 96481-35-5; 3, 114552-12-4; 7, 88001-79-0; 8, 114552-14-6; 14, 114552-13-5; S, 7704-34-9; Se, 7782-49-2.

Supplementary Material Available: Tables of fractional atomic coordinates, bond lengths, bond angles, torsion angles, thermal parameters, and H-atom coordinates (8 pages); a listing of observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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[15] For example, 854.5 Hz in $ArP(Se)_2$,[13] 890 Hz in xylyl-P(Se)=CPh_2,[16a] 960 Hz in $Me_3Si(t\text{-Bu})P(Se){=}N\text{-}t\text{-Bu}$,[16b] and 753 Hz in ArP=P(Se)Fe$(CO)_2(\eta^5\text{-}C_5Me_5)$.[16c]

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