ORGANOMETALLICS

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Organometallics, **1992**, 11 (3), 1408-1411• DOI: 10.1021/om00039a056 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

1408 *Organometallics* 1992, *11*, 1408–1411

Molecular Structures of a Siladigermirane and a Cyclotrigermane

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Received October 10, 1991

Summary: The crystal molecular structures of hexamesitylsiladigermirane (**1**, $SiGe_2Mes_6$, Mes = 2,4,6-trimethylphenyl) and hexamesitylcyclotrigermane (**2**, Ge_3Mes_6) have been determined by X-ray analysis. The crystals of $\mathbf{1}\cdot 2CH_2Cl_2$ (**1**) and $\mathbf{2}\cdot 2CH_2Cl_2$ (**2**) are isomorphous and isostructural and crystallize in monoclinic space group $C2/c$ with $Z = 4$ of dimensions $a = 20.659$ (3) Å, $b = 11.827$ (2) Å, $c = 23.288$ (3) Å, $\beta = 105.30$ (1)°, and $V = 5488.4$ Å^3 for **1** and $a = 20.657$ (4) Å, $b = 11.812$ (2) Å, $c = 23.289$ (3), $\beta = 105.34$ (1)°, and $V = 5479.8$ Å^3 for **2**. The three metal atoms of **2** form an equilateral triangle with a mean Ge–Ge bond length of 2.538 (2) Å. The silicon atom in the $SiGe_2$ core of **1** is evenly disordered over the three sites with a resulting metal–metal mean bond distance of 2.508 (3) Å. The molecular structures of these compounds are discussed.

Being the smallest and the most strained members of the cyclopolysilanes, cyclotrisilanes have attracted considerable attention due to their unusual physical properties[1] and chemical reactivity.[2] In particular, the photolysis of cyclotrisilanes[3,4] (and -germanes[3,5]) is of current interest because it is a valuable method for the synthesis of disilenes[6] (and digermenes[6]). We have recently reported[7] the first synthesis of a siladigermirane, hexamesitylsiladigermirane (**1**) (mesityl = 2,4,6-trimethylphenyl), and its subsequent thermolysis[8] to yield a germasilene.

To our knowledge, there are only a few examples of cyclometallanes containing both silicon and germanium in the cyclic skeleton,[9,10] and little is known about the chemistry of these species. In view of the recent interest shown in the structural chemistry of compounds containing a silicon–germanium bond,[10–12] we now describe the identification of **1** by X-ray crystallography and present a discussion of its molecular structure. During the course of this study, it was necessary to determine the molecular structure of hexamesitylcyclotrigermane (**2**),[13] and the results of this study are included.

Experimental Section

Synthesis. Hexamesitylsiladigermirane (**1**) was synthesized by the reductive cyclization of 1,2-dichlorotetramesityldigermane and dichlorodimesitylsilane with lithium naphthalenide in 1,2-dimethoxyethane.[7] Hexamesitylcyclotrigermane (**2**) is obtained as a minor product in this reaction and cannot be separated by conventional techniques. Crystals of **1**, suitable for X-ray analysis, were obtained by crystallization of the reaction mixture from hexanes/dichloromethane. An authentic sample of **2** was prepared according to a known procedure[13] and was crystallized from the same solvent mixture.

X-ray Structure Determinations. The analysis of **1** was undertaken with some concern that the highly symmetrical (C_3) shape of the molecule might result in crystallographic disorder of the Si and Ge atoms. A light yellow crystal of $\mathbf{1}\cdot 2CH_2Cl_2$ was mounted in air and transferred to an Enraf-Nonius CAD4F diffractometer. An approximate crystal density of 1.3 g·cm^{-3} was determined with difficulty by the neutral buoyancy method, as the crystals showed some solubility in all of the liquids tried. Unit cell parameters at 23 °C and an orientation matrix were determined from a least-squares treatment of 20 accurately centered high-angle reflections ($28 < 2\theta < 36°$).[14] A check on the Laue symmetry suggested a monoclinic space group, and there were four formula units per cell.

Intensity data for 4140 reflections were collected in the range $0 < 2\theta < 46°$, in θ-2θ mode, at variable scan speeds of 1.5–3.3° min^{-1} and scan widths of $1.0 + 0.35 \tan \theta$, with a maximum time per datum of 60 s. Standard reflections 002, 020, and $\bar{2}00$ were monitored every 180 min of X-ray exposure time and showed 5.2% decay over the total period of 85.7 h. Corrections were made for Lorentz, monochromator, and crystal polarization, background radiation effects, and decay using the Structure Determination Package[15] running on a PDP11/23+ computer. A p factor of 0.04 was applied to the data.[16] Twelve crystal faces were identified by optical goniometry and the crystal dimensions measured. An absorption correction was made using the program ABSCOR.[17] The systematic absences suggested that the space group was either Cc or $C2/c$,[18a] and a zero-moment test[19] strongly indicated the centrosymmetric space group. The data were averaged accordingly; 165 symmetry-related observations gave $R = 0.012$ on F and left 3805 unique observations for solution and refinement of the structure.

The structure was solved with MULTAN82,[20] and the remaining atoms were located by least-squares refinements and difference Fourier techniques. Full-matrix least-squares refinement on F was carried out with the SHELX-76 software[21] running on a SUN 3/80 work-station. Scattering factors for the neutral Ge atom were taken from ref 18b. With $Z = 4$, the molecule has imposed 2-fold symmetry, and in an ordered structure the Si atom should occupy special position Wyckoff *e*. However, during the initial

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[1] Watanabe, H.; Nagai, Y. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, England, 1985; p. 107. Grev, R. S.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1987**, *109*, 6569.

[2] Weidenbruch, M.; Schäfer, A.; Grimm, F.-T.; Thom, K.-L. *Phosphorus, Sulfur, Silica* **1989**, *41*, 229. Weidenbruch, M. *Comments Inorg. Chem.* **1986**, *5*, 247.

[3] Masamune, S. In *Silicon Chemistry*; Corey, E. R.; Corey, J. Y.; Gaspar, P. P., Eds.; Ellis Horwood: Chichester, U.K., 1988; p 257.

[4] Weidenbruch, M.; Lesch, A.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1990**, *123*, 1795. Weidenbruch, M.; Flintjer, B.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 95.

[5] Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1990**, *9*, 2061. Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1989**, *8*, 161.

[6] For reviews on M═M systems, see the following studies. Si═Si: West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. Si═M: Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1015. Ge═M: Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283.

[7] Baines, K. M.; Cooke, J. A. *Organometallics* **1991**, *10*, 3419.

[8] Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1989**, 770. N.B.: Thermolysis of hexamesitylcyclotrigermane yields tetramesityldigermene and dimesitylgermylene.

[9] Carberry, E.; Dombek, B. D. *J. Organomet. Chem.* **1970**, *22*, C43. Hengge, E.; Brychcy, U. *Monatsh. Chem.* **1966**, *97*, 1309.

[10] Suzuki, H.; Fukuda, Y.; Sato, N.; Ohmori, H.; Goto, M.; Watanabe, H. *Chem. Lett.* **1991**, 853.

[11] Pannell, K. H.; Kapoor, R. N.; Raptis, R.; Pårkånyi, L.; Fülöp, V. *J. Organomet. Chem.* **1990**, *384*, 41.

[12] Pårkånyi, L.; Hernandez, C.; Pannell, K. H. *J. Organomet. Chem.* **1986**, *301*, 145.

[13] Synthesis: Ando, W.; Tsumuraya, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1514.

[14] *CAD4 Diffractometer Manual*; Enraf-Nonius: Delft, The Netherlands, 1982 and 1988.

[15] Enraf-Nonius Structure Determination Package, Version 3.0; SDP-PLUS, 1985.

[16] Busing, W. R.; Levy, H. A. *J. Chem. Phys.* **1957**, *26*, 563.

[17] Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1968**, *18*, 1035.

[18] *International Tables for X-ray Crystallography*: (a) D. Reidel Publishing Co.: Boston, MA, 1983; Vol. A.; (b) Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

[19] Howells, E. R.; Phillips, D. C.; Rogers, D. *Acta Crystallogr.* **1950**, *3*, 210.

[20] Main, P. MULTAN 82 Manual, July, 1982.

[21] Sheldrick, G. M. SHELX-76. Programme for Crystal Structure Determination. University of Cambridge, U.K., 1976.

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stages of the refinement the isotropic thermal parameter of the Si atom refined to a negative value, indicating the presence of a greater number of electrons at that site. Furthermore, all the bond distances in the $SiGe_2$ core were equal, and our earlier concerns regarding disorder were borne out.

A number of different models were tried in space group $C2/c$. If a Ge_3 core was assumed, then refinement of the structure proceeded smoothly. Anisotropic thermal parameters were assigned to the methyl carbon atoms and the Ge atoms. The phenyl ring carbon atoms were constrained to a regular hexagon with C–C = 1.392 Å. All the hydrogen atoms (except those in the solvent molecule) were located by difference Fourier techniques and introduced in idealized positions (C–H = 0.90 Å). A disorder in the dichloromethane solvent molecule was successfully resolved. With the use of 2300 observations with $I \geq 3\sigma(I)$ and with utilization of weights of the form $w = 1/\sigma^2(F_o) + gF^2$, where $g = 0.002\,093$, refinement of 163 variables converged at agreement factors $R = 0.0705$ and $R_w = 0.0776$. The magnitudes of all three "Ge" atom anisotropic thermal parameters were rather small but essentially indistinguishable. The metal–metal distances (2.510 (2) and 2.505 (2) Å) were identical, significantly smaller than the Ge–Ge distances reported[22] for Ge_3R_6 (where R = 2,6-dimethylphenyl) and larger than the expected Si–Ge distance calculated from the covalent radii.[23] These results suggest that the Si atom in the $SiGe_2$ core is probably disordered over the three sites.

This assumption was employed in the final model. For a disorder over the three sites of equal probability, with a Si/Ge ratio of 1/2 in each site, the Ge atom occupancy factors at the general and the special positions will be 0.8125 and 0.40625, respectively. Using conditions identical to those described above, 2300 observations with $I \geq 3\sigma(I)$, and utilizing weights of the form $w = 1/\sigma^2(F_o) + gF^2$, where $g = 0.000\,287$, refinement of 163 variables converged at agreement factors $R = 0.059$ and $R_w = 0.063$. Given the successful refinement, no attempt was made to refine the structure in the alternative space group Cc.

Since there was some residual uncertainty that the crystal chosen was really the siladigermirane, and not by some mischance one of the cyclotrigermane crystals picked from the reaction product, it was decided to carry out a structure determination of an authentic sample of hexamesitylcyclotrigermane (2).

Crystals of $2{\cdot}2CH_2Cl_2$ were found to be both isomorphous and isostructural with 1. The intensity data collection for 2 was performed under conditions as closely identical to those for 1 as were possible. A total of 4132 reflections and 66 standards were collected over total period of 56.7 h. The intensities showed a 2.6% decay, for which a linear decay correction was applied.[15] For the data crystal 12 faces were identified by optical goniometry. A numerical absorption correction was applied to the data using the program AGNOST.[24] The data were averaged, yielding $R = 0.018$ for 144 symmetry-related observation. In all, 3797 data remained for the structure refinement. The positional parameters for 1 were used as a starting point, and the refinement proceeded smoothly to convergence. With the use of 1921 observations with $I \geq 3\sigma(I)$, and weights of the form $w = 1/\sigma^2(F_o) + gF^2$, where $g = 0.000\,102$, refinement of 159 variables converged at agreement factors $R = 0.059$ and $R_w = 0.057$. An analysis of variance showed no unusual details, and secondary extinction was not significant.

The experimental details and crystal data for both analyses are given in Table I. Atomic positional and U(equiv) thermal parameters are listed in Tables II and III. Tables of anisotropic thermal parameters, calculated hydrogen atom parameters, root-mean-square amplitudes of anisotropic displacement, weighted least-squares planes and dihedral angles, and structure amplitudes have been included in the supplementary material.

Table I. Summary of X-ray Structure Determinations

	2	1
compd	$C_{54}H_{66}Ge_3{\cdot}2CH_2Cl_2$	$C_{54}H_{66}SiGe_2{\cdot}2CH_2Cl_2$
fw	1102.76	1058.26
cryst system; space group	monoclinic; $C2/c$ (No. 15)	
cell dimens		
a, Å	20.657 (4)	20.659 (3)
b, Å	11.812 (2)	11.827 (2)
c, Å	23.289 (3)	23.288 (3)
β, deg	105.34 (1)	105.30 (1)
V, Å^3; Z	5479.8; 4	5488.4; 4
calcd density, g·cm^{-3}	1.337	1.281
$F(000)$ electrons	2280	2208
diffractometer; monochromator	Enraf Nonius CAD4F; graphite	
radiation; wavelength, Å	Mo K$\bar{\alpha}$; 0.710 73	
approx cryst dimens, mm	0.18 × 0.20 × 0.20	0.28 × 0.32 × 0.32
cryst vol, mm^{-3}	76.37×10^{-2}	21.33×10^{-1}
face indices	{001}, {111}, {$\bar{1}$11}	{001}, {$\bar{1}$11}, (111)
index	$-22 < h < 22, -13 < k < 0, 0 < l < 25$	
θ ranges	$0 < 2\theta < 46°$	
abs coeff, cm^{-1}	17.9	12.8
max, min abs	0.778, 0.756	0.739, 0.537
av $R(F)$	0.018	0.012
no. of obsd reflns averaged	144	165
no. of unique data	3797 > 0	3805 > 0
no. of observns	1921 ($I \geq 3\sigma(I)$)	2300 ($I > 3\sigma(I)$)
no. of variables	159	163
final model: R; R_w	0.0590; 0.0575	0.059; 0.0629
resid electron density range, e·A^{-3}	0.844 to −0.661	0.548 to −0.570
largest shift/esd param	z of Cl(2), 0.0238	U_{11} of C(10), −0.0025

Table II. Atomic Positional (×10^4) and Thermal (×10^3) Parameters for 2

atom	x	y	z	U, Å^2 [a]
Ge(1)	0	4919.6 (14)	2500	41.7 (6)*
Ge(2)	−166.9 (5)	3058.7 (10)	1936.0 (5)	40.7 (4)*
C(1)	−787 (4)	5992 (6)	2400 (3)	45 (3)
C(2)	−1193 (4)	6039 (6)	2792 (3)	53 (3)
C(3)	−1689 (4)	6866 (6)	2722 (3)	64 (3)
C(4)	−1779 (4)	7647 (6)	2261 (3)	68 (4)
C(5)	−1373 (4)	7600 (6)	1869 (3)	66 (4)
C(6)	−877 (4)	6772 (6)	1938 (3)	58 (3)
C(7)	−1114 (6)	5229 (10)	3298 (6)	79 (6)*
C(8)	−2285 (7)	8617 (11)	2202 (7)	106 (7)*
C(9)	−477 (6)	6782 (11)	1484 (5)	77 (5)*
C(11)	437 (3)	2700 (6)	1413 (3)	46 (3)
C(12)	262 (3)	3162 (6)	843 (3)	54 (3)
C(13)	677 (3)	2996 (6)	466 (3)	73 (4)
C(14)	1268 (3)	2369 (6)	659 (3)	66 (4)
C(15)	1443 (3)	1908 (6)	1229 (3)	69 (3)
C(16)	1028 (3)	2073 (6)	1606 (3)	55 (3)
C(17)	−354 (5)	3850 (11)	589 (5)	69 (5)*
C(18)	1763 (7)	2215 (14)	254 (6)	112 (7)*
C(19)	1261 (6)	1558 (10)	2209 (5)	75 (5)*
C(21)	−1062 (4)	2376 (4)	1492 (3)	40 (3)
C(22)	−1649 (4)	3002 (4)	1280 (3)	48 (3)
C(23)	−2235 (4)	2474 (4)	952 (3)	60 (3)
C(24)	−2232 (4)	1319 (4)	836 (3)	61 (3)
C(25)	−1645 (4)	693 (4)	1048 (3)	59 (3)
C(26)	−1059 (4)	1221 (4)	1376 (3)	53 (3)
C(27)	−1697 (6)	4243 (10)	1399 (6)	79 (5)*
C(28)	−2862 (6)	753 (12)	451 (6)	87 (6)*
C(29)	−449 (6)	468 (9)	1613 (6)	67 (5)*
C(10)	4445 (10)	4288 (17)	4399 (9)	139 (7)
Cl(1) [b]	4029 (11)	4222 (18)	4896 (9)	331 (10)*
Cl(2)	4054 (4)	3546 (7)	3790 (3)	233 (4)*
Cl(1a) [b]	4000 (6)	4130 (10)	4950 (6)	51 (3)

[a] Parameters marked with an asterisk were assigned anisotropic thermal parameters given as the isotropic equivalent displacement parameter defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j$. [b] Occupancy 80/20.

Results and Discussion

Crystals of 1 and 2 are isomorphous and isostructural. The crystal structure of each compound consists of discrete molecules, and the shortest intermolecular distances are for 1 and 2 respectively 2.316 and 2.296 Å between H(72) and H(82) ($-x - 0.5, y + 0.5, 0.5 - z$) and 2.390 and 2.447 Å between H(83) and H(193) ($-x, y, -z - 0.5$). Figure 1

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(22) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136.

(23) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; p 258.

(24) Cahen, D.; Ibers, J. A. *J. Appl. Crystallogr.* **1972**, *5*, 298.

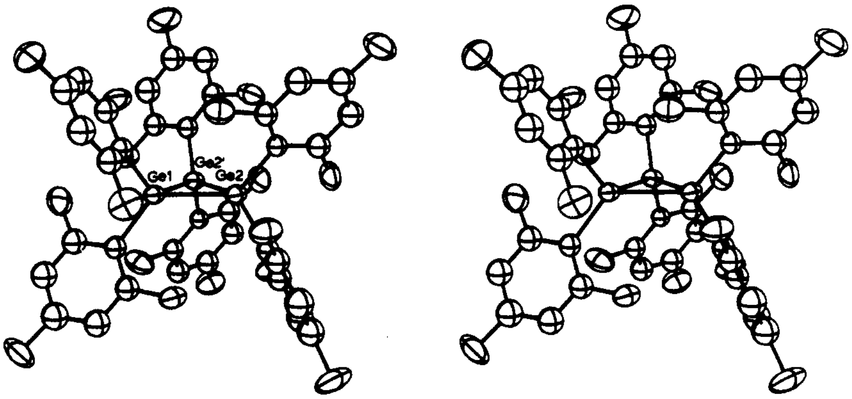

Figure 1. Stereoview of compound 2. Atoms are drawn as 50% probability thermal ellipsoids.

Table III. Atomic Positional ($\times10^4$) and Thermal ($\times10^3$) Parameters for 1

atom	*x*	*y*	*z*	*U*, Å^{2} [b]
M(1)[a]	0	4926.9 (12)	2500	43.3 (5)*
M(2)[a]	−162.3 (4)	3087.8 (9)	1942.4 (4)	43.9 (3)*
C(1)	−780 (3)	5994 (4)	2403 (2)	49 (2)
C(2)	−1189 (3)	6044 (4)	2791 (2)	56 (2)
C(3)	−1680 (3)	6877 (4)	2720 (2)	65 (2)
C(4)	−1762 (3)	7660 (4)	2260 (2)	74 (3)
C(5)	−1354 (3)	7610 (4)	1872 (2)	71 (3)
C(6)	−863 (3)	6778 (4)	1943 (2)	61 (2)
C(7)	−1127 (4)	5254 (8)	3283 (4)	80 (4)*
C(8)	−2268 (5)	8639 (9)	2209 (6)	115 (5)*
C(9)	−465 (5)	6779 (9)	1479 (4)	84 (4)*
C(11)	443 (2)	2716 (4)	1420 (2)	52 (2)
C(12)	263 (2)	3168 (4)	847 (2)	61 (2)
C(13)	677 (2)	3008 (4)	470 (2)	72 (3)
C(14)	1270 (2)	2396 (4)	664 (2)	76 (3)
C(15)	1450 (2)	1945 (4)	1236 (2)	69 (2)
C(16)	1036 (2)	2105 (4)	1614 (2)	57 (2)
C(17)	−358 (4)	3861 (9)	594 (4)	79 (4)*
C(18)	1749 (6)	2231 (11)	253 (5)	117 (6)*
C(19)	1274 (4)	1574 (8)	2230 (4)	79 (4)*
C(21)	−1047 (3)	2415 (3)	1499 (2)	48 (2)
C(22)	−1634 (3)	3036 (3)	1288 (2)	55 (2)
C(23)	−2215 (3)	2503 (3)	960 (2)	64 (2)
C(24)	−2209 (3)	1350 (3)	843 (2)	68 (2)
C(25)	−1622 (3)	729 (3)	1054 (2)	67 (2)
C(26)	−1041 (3)	1262 (3)	1382 (2)	56 (2)
C(27)	−1691 (4)	4266 (8)	1406 (4)	79 (4)*
C(28)	−2852 (5)	767 (9)	454 (4)	93 (4)*
C(29)	−432 (4)	490 (7)	1612 (4)	74 (3)*
C(10)	4462 (9)	4300 (16)	4408 (8)	172 (6)
Cl(1)[c]	4022 (7)	4221 (13)	4880 (6)	359 (8)*
Cl(2)[c]	4105 (7)	3435 (13)	3897 (7)	419 (10)*
Cl(1a)[c]	4001 (5)	4139 (8)	4954 (5)	35 (2)
Cl(2a)[c]	4009 (6)	3635 (10)	3712 (5)	41 (2)

[a] M = Si/Ge in the ratio 1:2. $SiGe_2$ is disordered over the three sites equally (see the text) with occupancy 0.40625 and 0.81250 for M(1) and M(2), respectively. [b] Parameters marked with an asterisk were assigned anisotropic thermal parameters given as the isotropic equivalent displacement parameter defined as $U_{eq} = {}^1/{}_3\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j$. [c] Occupancy 80/20.

Table IV. Selected Bond Distances (Å) and Angles (deg)

	M = Ge	M = Si/Ge (1:2)
M(1)–M(2)	2.539 (2)	2.510 (2)
M(2)–M(2)	2.535 (2)	2.505 (2)
M(1)–C(1)	2.020 (7)	2.013 (5)
M(2)–C(11)	2.003 (7)	2.010 (5)
M(2)–C(21)	2.025 (7)	2.011 (5)
C(2)–C(7)	1.495 (12)	1.458 (9)
C(4)–C(8)	1.531 (13)	1.543 (10)
C(6)–C(9)	1.504 (12)	1.520 (10)
C(12)–C(17)	1.490 (12)	1.507 (9)
C(14)–C(18)	1.572 (12)	1.560 (10)
C(16)–C(19)	1.490 (13)	1.525 (10)
C(22)–C(27)	1.501 (12)	1.491 (9)
C(24)–C(28)	1.521 (13)	1.557 (9)
C(26)–C(29)	1.518 (12)	1.532 (9)
C(10)–Cl(1)	1.616 (24)	1.605 (19)
C(10)–Cl(2)	1.681 (19)	1.595 (20)
C(10)–Cl(1a)	1.773 (25)	1.789 (22)
C(10)–Cl(2a)		1.823 (24)

	M = Ge	M = Si/Ge (1:2)
M(2)–M(1)–M(2)	59.89 (6)	59.88 (6)
C(1)–M(1)–M(2)	119.31 (22)	119.45 (16)
C(11)–M(2)–M(1)	118.55 (22)	118.90 (17)
C(21)–M(2)–M(1)	126.14 (16)	125.99 (13)
C(21)–M(2)–C(11)	103.4 (3)	103.21 (21)
C(2)–C(1)–M(1)	123.40 (15)	123.91 (12)
C(6)–C(1)–M(1)	116.38 (15)	115.86 (12)
C(12)–C(11)–M(2)	116.85 (17)	116.39 (12)
C(16)–C(11)–M(2)	123.06 (17)	123.48 (12)
C(22)–C(21)–M(2)	123.76 (16)	124.20 (12)
C(26)–C(21)–M(2)	116.16 (16)	115.73 (12)
C(7)–C(2)–C(3)	117.7 (5)	117.2 (4)
C(7)–C(2)–C(1)	122.3 (5)	122.8 (4)
C(8)–C(4)–C(3)	120.9 (6)	120.2 (5)
C(8)–C(4)–C(5)	118.9 (6)	119.7 (5)
C(9)–C(6)–C(5)	115.7 (5)	115.3 (4)
C(9)–C(6)–C(1)	124.3 (5)	124.6 (4)
C(17)–C(12)–C(13)	115.2 (5)	115.4 (4)
C(17)–C(12)–C(11)	124.8 (5)	124.6 (4)
C(18)–C(14)–C(13)	121.2 (6)	120.8 (5)
C(18)–C(14)–C(15)	118.8 (6)	119.2 (5)
C(19)–C(16)–C(15)	116.1 (5)	116.1 (3)
C(19)–C(16)–C(11)	123.9 (5)	123.9 (3)
C(27)–C(22)–C(23)	116.8 (5)	116.4 (4)
C(27)–C(22)–C(21)	123.2 (5)	123.6 (4)
C(28)–C(24)–C(23)	120.0 (6)	119.8 (4)
C(28)–C(24)–C(25)	119.9 (6)	120.1 (4)
C(29)–C(26)–C(25)	116.6 (5)	115.6 (3)
C(29)–C(26)–C(21)	123.4 (5)	124.4 (4)
Cl(2)–C(10)–Cl(1)	110.8 (14)	103.9 (13)
Cl(1a)–C(10)–Cl(2)	109.5 (12)	
Cl(2a)–C(10)–Cl(1a)		109.9 (10)

gives a perspective stereoview of compound 2. Selected bond distances and bond angles are given in Table IV.

In space group *C*2/*c*, crystallographic 2-fold symmetry is imposed on the molecules and the three central atoms form essentially equilateral triangles. In compound 2 the Ge–Ge bond distances are 2.539 (2) and 2.535 (2) Å, mean 2.538 (2) Å, and the Ge–Ge–Ge angles are 59.89 (6) and 60.05 (6)°. These Ge–Ge distances are closely comparable to those of 2.543 (1), 2.543 (1), and 2.537 (1) Å found in Ge_3R_6 (where R = 2,6-dimethylphenyl).[22] The Ge–C bond lengths are range from 2.003 (7) to 2.025 (7) Å.

In compound 1 the dimensions in the metal core are entirely reasonable, if we assume a 3-fold disorder of the Si atom. Thus, the metal–metal distances in 1 are identical (2.510 (2) and 2.505 (2) Å, mean 2.508 (3) Å) and lie between reported average values of 2.541 (3) Å for Ge–Ge distances in cyclotrigermanes (ref 22 and this work) and

2.407 (28) Å for Si–Si distances in a cyclotrisilane, Si_3R_6 (where R = 2,6-dimethylphenyl).[25] Using the values for Si_3 and Ge_3 clusters, Si and Ge "cluster covalent radii" of 1.2035 and 1.2705 Å may be calculated, leading to a predicted Si–Ge cluster bond distance of 2.474 Å. On the assumption that the disorder is 3-fold and that the Ge–Ge distance (from **2**) is 2.538 Å, we can calculate a Si–Ge distance of 2.493 Å from the expression $^1/_3[d(\text{Ge–Ge}) + 2d(\text{Si–Ge})] = 2.508$ Å. This value differs little from that predicted above of 2.474 Å but is also much longer than the mean Si–Ge distances reported for $Ph_3Si–GeMe_3$ (2.394 (1) Å),[11] $Me_3Si–GePh_3$ (2.384 (1) Å),[12] and a germatrisilacyclobutane (2.457 (7) Å).[10] It is interesting to note that the Ge–Ge distances observed in cyclotrigermanes (ref 22 and this work) are also longer than those found for linear and less strained molecules. This elongation of bond lengths is probably to be expected for three-membered rings with bulky substituents, due to steric congestion.[22,25] The M–C distances within compound **1** are 2.013, 2.010, and 2.011 Å, mean 2.011 (2) Å. Other distances and angles within both compounds are normal.

Acknowledgment. We thank the NSERC of Canada and the University of Western Ontario for financial support of this work in the form of grants to K.M.B. and N.C.P.

Registry No. 1, 138432-97-0; 2, 138432-98-1.

Supplementary Material Available: For 1 and 2, listings of anisotropic thermal parameters, calculated hydrogen atom parameters, root-mean-square amplitudes of anisotropic displacement, and weighted least-squares planes and dihedral angles (6 pages); listings of structure amplitudes (25 pages). Ordering information is given on any current masthead page.

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[25] Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, M. F. *J. Am. Chem. Soc.* 1982, *104*, 1150.

(2-Phosphino)phospholyls: A New Type of η^1,η^5-Heterodifunctional Ligand for Transition-Metal Chemistry

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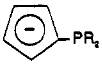
Received October 21, 1991

Summary: The anion obtained by metalation of 1-phenyl-3,4-dimethylphosphole sulfide reacts with chlorodiphenylphosphine to give the corresponding 2-(diphenylphosphino)phosphole sulfide. A migration of sulfur slowly takes place between the two phosphorus atoms of this compound. The resulting tervalent phosphole reacts with lithium in THF to yield the 3,4-dimethyl-2-(diphenylphosphino)phospholyl anion. This anion is converted into the corresponding 2,2′-bis(diphenylphosphino)-1,1′-diphosphaferrocene by reaction with iron(II) chloride. The difunctional diphosphaferrocene thus obtained gives a $Mo(CO)_4$ chelate by reaction with molybdenum hexacarbonyl.

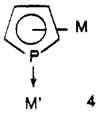
Phosphino-substituted cyclopentadienyls (**1**) have recently found a widespread use in coordination chemistry.[1] Their interest stems from the fact that they allow two types of transition metals to be held in close proximity in order to study their cooperativity in various reactions. On the other hand, phospholyls (phosphacyclopentadienyls) (**2**) have been shown to be able to replace cyclopentadienyls in a variety of η^5-complexes[2] (**3**) and to have the additional ability to coordinate a second metal via their phosphorus lone pair[2] (**4**). The previously unknown phosphino-substituted phospholyls (**5**) were thus a target of obvious interest for coordination chemists. We describe here the synthesis of the first such ligand, i.e. the 3,4-dimethyl-(2-diphenylphosphino)phospholyl anion (**6**) and some of its transition-metal complexes.



1

2

3



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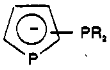

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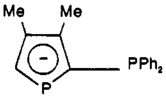

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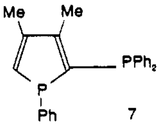

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Results and Discussion

The classical synthesis of phospholyl anions involves the cleavage of the exocyclic P–Ph bond of 1-phenylphospholes

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[1] (a) Selected references: Mathey, F.; Lampin, J. P. *J. Organomet. Chem.* 1977, *128*, 297. Rudig, A. W.; Lichtenberg, D W.; Katcher, M. L.; Davison, A. *Inorg. Chem.* 1978, *17*, 2859. Casey, C. P.; Bullock, R. M.; Fultz, W. C.; Rheingold, A. L. *Organometallics* 1982, *1*, 1591. Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* 1983, *105*, 7574. Casey, C. P.; Nief, F. *Organometallics* 1985, *4*, 1218. Rausch, M. D.; Edwards, B. H.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* 1983, *105*, 3882. Moise, C.; Maisonnat, A.; Poilblanc, R.; Charrier, C.; Mathey, F. *J. Organomet. Chem.* 1984, *231*, C43. Tikkanen, W.; Fujita, Y.; Petersen, J. L. *Organometallics* 1986, *5*, 888. Du Bois, D. L.; Eigenbrot, C. W., Jr.; Miedaner, A.; Smart, J. C.; Haltiwanger, R. C. *Organometallics* 1986, *5*, 1405. He, X. D.; Maisonnat, A.; Dahan, F.; Poilblanc, R. *Organometallics* 1987, *6*, 678. Anderson, G. K.; Lin, M. *Inorg. Chim. Acta* 1988, *142*, 7. He, X. D.; Maisonnat, A.; Dahan, F.; Poilblanc, R. *Organometallics* 1989, *8*, 2618. Rausch, M. D.; Spink, W. C.; Atwood, J. L.; Baskar, A. J.; Bott, S. G. *Organometallics* 1989, *8*, 2627. Deacon, G. B.; Dietrich, A.; Forsyth, C. M.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 1370. He, X. D.; Maisonnat, A.; Dahan, F.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* 1990, 670. Szymoniak, J.; Kubicki, M. M.; Besançon, J.; Moise, C. *Inorg. Chim. Acta* 1991, *180*, 153. Schenk, W. A.; Neuland-Labude, C. *Z. Naturforsch* 1991, *46B*, 573. Anderson, G. K.; Lin, M.; Chiang, M. Y. *Organometallics* 1990, *9*, 288. Anderson, G. K.; Lin, M.; Rath, N. P. *Organometallics* 1990, *9*, 2880. Tikkanen, W.; Ziller, J. W. *Organometallics* 1991, *10*, 2266. He, X. D.; Maisonnat, A.; Dahan, F.; Poilblanc, R. *Organometallics* 1991, *10*, 2443. Wong, W.-K.; Chow, F. L.; Chen, H.; Wang, R.-J.; Mak, T. C. W. *Polyhedron* 1990, *9*, 2469.

[2] Review: Mathey, F. *New J. Chem.* 1987, *11*, 585. Recent references: Nief, F.; Mathey, F.; Ricard, L.; Robert, F. *Organometallics* 1988, *7*, 921. Nief, F.; Mathey, F. *J. Chem. Soc., Chem. Commun.* 1988, 770. Nief, F.; Ricard, L.; Mathey, F. *Organometallics* 1989, *8*, 1473. Nief, F.; Mathey, F. *J. Chem. Soc., Chem. Commun.* 1989, 800; Nief, F.; Mathey, F.; Ricard, L. *J. Organomet. Chem.* 1990, *384*, 271. Baudry, D.; Ephritikhine, M.; Nief, F.; Ricard, L.; Mathey, F. *Angew Chem., Int. Ed. Engl.* 1990, *29*, 1485. Nief, F.; Mathey, F. *Synlett* 1991, 745. Kershner, D. L.; Basolo, F. *J. Am. Chem. Soc.* 1987, *109*, 7396. Roberts, R. M. G.; Silver, J.; Wells, A. S. *Inorg. Chim. Acta* 1989, *155*, 197. Roberts, R. M. G.; Silver, J.; Wells, A. S. *Inorg. Chim. Acta* 1989, *157*, 45. Lemoine, P. *J. Organomet. Chem.* 1989, *359*, 61. Metternich, H. J.; Niecke, E. *Angew. Chem., Int. Ed. Engl.* 1991, *30*, 312. Chase, K. J.; Bryan, R. F.; Woode, M. K.; Grimes, R. N. *Organometallics* 1991, *10*, 2631.

0276-7333/92/2311-1411$03.00/0