$SeC_6H_5)_2Li(THF)_2$ (166.5°),[13] or phosphorus in the analogous compound $(C_5H_5)_2Lu(\mu\text{-}P(C_6H_5)_2)_2Li(tmed)$ (148.7°).[7] The Cp1–Lu–Cp2 angle and the mean value of the ten Lu–C(η^5) distances in **2** lie in the expected range; the cyclopentadienyl rings are planar. The length of the organolutetium–arsenic bonds (measured for the first time) are 2.896 (2) and 2.870 (2) Å.

Acknowledgment. We thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for generous support of this work.

Supplementary Material Available: Tables of data collection details, final fractional coordinates, thermal parameters, selected bond distances and angles, and calculated hydrogen positions (7 pages); a listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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[12] Schumann, H.; Albrecht, I.; Hahn, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 985.

[13] Schumann, H. *Polyhedron*, submitted for publication.

Structure of the Stable Germaphosphene $Mes_2Ge{=}PAr$: A Ge=P Connection with the Geometry of a True Double Bond

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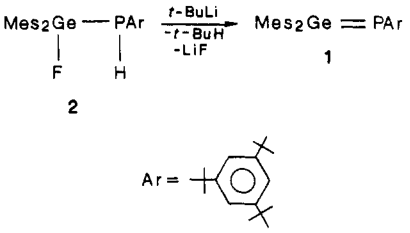
Summary: The structure of the stable germaphosphene $Mes_2Ge{=}PAr$ has been determined by X-ray crystallography (orthorhombic, $Pna2_1$; a = 1931.7 (4), b = 997.5 (2), c = 1794.6 (2) pm; $V = 3458.10^6$ pm^3; Z = 4; R = 0.0540). The germanium–phosphorus double bond length (213.8 (3) pm) is substantially shorter than the standard germanium–phosphorus single bond (~233–235 pm); this rather important shortening (about 8.5%) and the essentially planar double-bond geometry support the existence of a true germanium–phosphorus double bond. Raman emission of Ge=P bond is 503 cm^{-1}.

Compounds with double bonds to second- and third-row elements, once thought to be practically nonexistent, are now being synthesized and stabilized with increasing frequency owing to bulky substituents.[1] This is specially true for derivatives with dicoordinated phosphorus; many phosphaalkenes –P=C<,[1g] phospha imines –P=N–,[1g] diphosphenes –P=P–,[1f,g] and phosphacumulenes –P=C=X[1g] are known at the present time. But in the M_{14}=P field (M_{14} = Si, Ge, Sn), very few derivatives have been synthesized so far; some silaphosphenes[2] and a stannaphosphene[3] have been stabilized and characterized, and only the germaphosphene **1**[4a] has been isolated in a pure form.

This germaphosphene was obtained in a very good yield by dehydrofluorination of fluorogermylphosphine **2** with *tert*-butyllithium.[4a]



1 is thermally stable (until 150 °C) but is very air- and moisture-sensitive. The presence in **1** of a real double bond between germanium and phosphorus was proven by its chemical reactivity: electrophilic, nucleophilic, and radical addition reactions have been obtained[4,6] (see Scheme I).

The double-bond character of the germanium–phosphorus connection was also supported by a strong Raman emission at 503 cm^{-1} in good correlation with previous calculation[9] (481 cm^{-1} for $d_{Ge=P}$ = 216.9 pm).

However, the nature of the double bond (shortening in relation to the germanium–phosphorus single bond, planarity of germanium and phosphorus, ...) remained questionnable. Moreover, it must be noted that, if many low coordinated species of group 15 (–P=N–, –P=P–, ...) and some doubly bonded compounds of group 14 (Si=C, Si=Si, Ge=Ge, ...) have been structurally characterized, no X-ray determination have been performed until now for heavy M_{14}=M_{15} derivatives. So we report here the X-ray structure of germaphosphene **1**, first X-ray structure for this type of compound.

Experimental Section. The solutions of the germaphosphene **1** are highly air- and moisture-sensitive. So the synthesis of **1** needs high-vacuum line techniques and carefully deoxygenated solvents that must be freshly distilled over sodium/benzophenone.

Synthesis of the Fluorogermylphosphine $Mes_2Ge(F)P(H)Ar$ (2). The lithiophosphide ArP(H)Li was prepared by addition of 11.3 mL (15.8 mmol) of a solution of *tert*-butyllithium (1.4 M in pentane) to a solution of 2,4,6-tri-*tert*-butylphenyl phosphine (4.40 g, 15.8 mmol) in 20 mL of diethyl ether. After 1 h at room temperature, the red solution of lithiophosphide was slowly added to a suspension of dimesityldifluorogermane (5.50 g, 15.8 mmol) in pentane (30 mL). The reaction was immediate as shown by a rapid decoloration; the reaction mixture was stirred for 1 h at room temperature and filtered to eliminate LiF. After elimination of the solvents in vacuo, crude **2** was recrystallized in pentane at –20 °C to afford white crystals (8.60 g, yield 90%; mp 124 °C).

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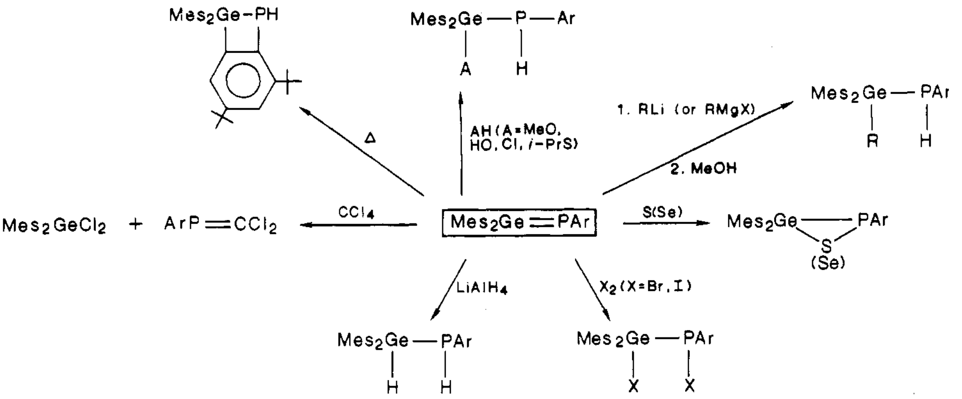
[1] For reviews on M=M compounds, see the following. (a) Si=Si: West, R. *Science (Washington, D.C.)* **1984**, *225*, 1109–14. West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201–11. (b) Si=M (M = group 14 and 15 elements): Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419–509. (c) Si=C: Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1–44. (d) Si=C (or N) and Ge=C (or N): Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141–77. (e) Ge=M (M = group 14 and 15 elements): Satge, J. *Adv. Organomet. Chem.* **1982**, *21*, 241–87. (f) M=M′ (M, M′ = Si, Ge, Sn, P, As, Sb): Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1–63. (g) P=X (X = group 14 and 15 elements): Lochschmidt, S.; Schmidpeter, A. *Phosphorus Sulfur* **1986**, *29*, 73–109.

[2] Smit, C. N.; Lock, F. M.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, *25*, 3011. Smit, C. N.; Bickelhaupt, F. *Organometallics* **1987**, *6*, 1156.

[3] Couret, C.; Escudie, J.; Satge, J.; Raharinirina, A.; Andriamizaka, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 8280. Escudie, J.; Couret, C.; Raharinirina, A.; Satge, J. *Nouv. J. Chim.* **1987**, *11*, 627.

[4] (a) Escudie, J.; Couret, C.; Satge, J.; Andrianarison, M.; Andriamizaka, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 3378. (b) Escudie, J.; Couret, C.; Andrianarison, M.; Satge, J. *J. Am. Chem. Soc.* **1987**, *109*, 390.

Scheme I



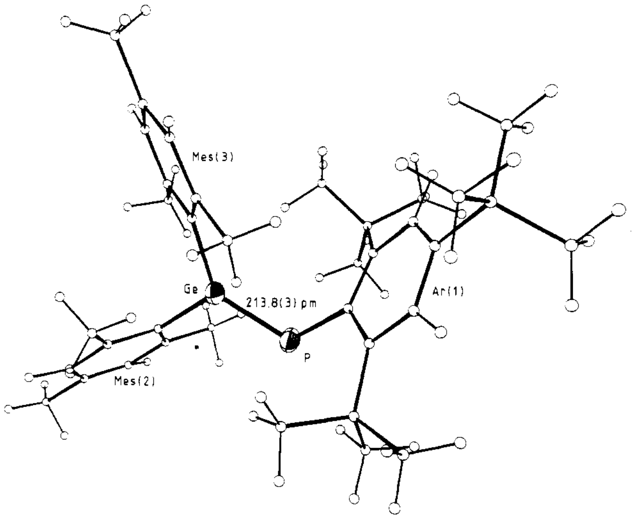


Figure 1. ORTEP drawing of $Mes_2Ge{=}PAr$. Numbering scheme as given in Table II. Thermal ellipsoids for Ge and P are scaled to enclose 30% of the electron density probability; C and H atoms are isotropic spheres with radii of 9 pm.

Synthesis of the Germaphosphene 1. To a solution of fluorogermylphosphine $Mes_2Ge(F)P(H)Ar$ (7.60 g, 12.52 mmol) in pentane (30 mL), cooled at −20 °C, was slowly added 8.95 mL (12.52 mmol) of a solution of *tert*-butyllithium (1.4 M in pentane). The reaction mixture becomes orange immediately; around −10 °C, a precipitate of lithium fluoride appears. The reaction mixture is then allowed to warm to room temperature, filtered to eliminate LiF, and partly concentrated. Crystallization at −20 °C in pentane afforded 5.52 g of pure germaphosphene (yield 75%) in the form of orange aggregates.

Single crystals were obtained by heating in a sealed tube at 100 °C 1 g of 1 in 5 mL of pentane until dissolution (after the solution was cooled to room temperature, orange-red crystals were formed). The solvent was decanted off, and the crystals were dried in vacuo. They are air- and moisture-sensitive, but much less than in solution, and can be handled in air for a short time (mp 155–160 °C; $\delta(^{31}P)$ +175.4).[4a]

Table I summarizes crystal data and experimental details. Coordinates are given in Table II. Table III contains the most important bond lengths and angles. Figure 1 shows the molecule found. A Raman spectrum was obtained with a spectrometer SPEX-1403 (Kr laser, 647 nm) from crystalline material in a sealed tube.

Results and Discussion. The most significant feature of this structure is the short germanium–phosphorus double bond length (213.8 (3) pm). So, the shortening (about 20 pm) in relation to the typical germanium–phosphorus single bond (2.30–2.36 pm)[5] is nearly 8.5%.

Table I. Crystallographic Data for $Mes_2Ge{=}PAr$ and Structure Determination Details

Crystal Data (Mo $K\alpha_1$, λ = 70.926 pm)	
formula, M_r	$C_{36}H_{51}GeP$, 587.37
cryst habit, faces (dist from a common origin inside the crystal (mm))	plate, 100 ± $\bar{1}00$ (0.22), $0\bar{1}0$ (0.35), $01\bar{1}$ (0.25), 001 + $00\bar{1}$ (0.50)
cryst color	orange-red
symmetry	orthorhombic, $Pna2_1$ (No. 33)
unit cell dimension (pm) (least-squares fit to 25 reflctns with 17° < θ(Mo) < 21°)	a = 1931.7 (4), b = 997.5 (2), c = 1794.6 (2)
packing: V (pm^3), Z, $F(000)$	3458 (2) × 10^6, 4, 1255.96
D_{calcd}, D_{exptl} (g cm^{-3})	1.128, 1.12 (2)
Experimental Data (Mo $K\bar{\alpha}$, λ = 71.069 pm, Graphite Monochromator)	
density	neutral buoyancy (Thoulet)
preparatn	sealed capillary (Ar)
symmetry	film methods
diffractometer	CAD4 (Enraf-Nonius)
collectn mode, range of θ(deg)	$\omega/2\theta$-scans, 1.5–30.0
ref reflctns	three, every 60 min
loss of intensity, correctn	47% (6 days), direct fit
independent reflctns	5155
unobservable reflctns	3008 with $I < 2\sigma(I)$
μ (cm^{-1}), abs correctn	9.12, calcd by face indices (transmissn 0.49–0.68)
Solution and Refinement	
soln	Patterson, Fourier
least-squares refinement	full matrix
enantiomorph by anomalous disp	significance R_2:R_1 = 1.04
hydrogen atoms	calcd, CH and CH_3 rotating rigid groups
no. of variables (Ge and P anisotr, C and H common isotr)	227
reflctns used	2147 with $F > 4\sigma(F)$
final R, R_w	0.054, 0.074
weighting scheme	$w = 1/(\sigma^2(F) + 0.003\,873F^2)$
final diff Fourier maxima	0.6–0.4 e/A^3 near Ge
computing, program	HB-DPS-8/70, SHELX76

This shortening is of course less important than in the case of carbon (13% between >C—C< and >C=C<) and indicates a smaller π-bonding caused by less efficient p

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(5) Andrianarison, M.; Couret, C.; Declercq, J. P.; Dubourg, A.; Escudie, J.; Ranaivonjatovo, H.; Satge, J., submitted for publication. Fritz, G.; Hoppe, K. D.; Honle, 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**, *C40*, 254. Tebbe, K. F.; Frohlich, 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. Andrianarison, M.; Couret, C.; Declercq, J. P.; Dubourg, A.; Escudie, J.; Satge, J. *J. Chem. Soc., Chem. Commun.* **1987**, 921.

Table II. Fractional Coordinates for the Non-Hydrogen Atoms of $\mathrm{Mes_2Ge{=}PAr}$, Anisotropic Temperature Factors for Ge and P, and Isotropic Temperature Factors for C

atom	*x*	*y*	*z*	*U*, Å^2	atom	*x*	*y*	*z*	*U*, Å^2
Ge	−0.11360 (4)	−0.7534 (1)	0.00000		P	−0.0929 (1)	−0.5706 (2)	−0.0580 (1)	
					Aryl(1)				
C(11)	−0.0541 (3)	−0.4513 (7)	0.0102 (5)	0.043 (1)	C(142)	0.0928 (7)	−0.1230 (13)	0.1573 (7)	0.091 (4)
C(12)	0.0193 (3)	−0.4287 (7)	0.0040 (6)	0.046 (1)	C(143)	0.1142 (7)	−0.3490 (16)	0.2136 (9)	0.103 (4)
C(121)	0.0637 (4)	−0.4656 (9)	−0.0647 (5)	0.056 (2)	C(144)	0.0146 (7)	−0.2143 (13)	0.2564 (7)	0.089 (4)
C(122)	0.1352 (5)	−0.3958 (11)	−0.0601 (7)	0.074 (2)	C(15)	−0.0530 (4)	−0.3283 (9)	0.1252 (5)	0.052 (2)
C(123)	0.0322 (6)	−0.4181 (12)	−0.1371 (6)	0.076 (3)	C(16)	−0.0914 (4)	−0.3912 (8)	0.0685 (5)	0.044 (1)
C(124)	0.0787 (5)	−0.6173 (10)	−0.0682 (7)	0.075 (3)	C(161)	−0.1704 (5)	−0.3766 (10)	0.0743 (6)	0.062 (2)
C(13)	0.0511 (4)	−0.3623 (9)	0.0630 (5)	0.051 (2)	C(162)	−0.2093 (7)	−0.3767 (15)	0.0020 (10)	0.111 (4)
C(14)	0.0179 (4)	−0.3186 (9)	0.1248 (5)	0.052 (2)	C(163)	−0.1904 (10)	−0.2386 (16)	0.1067 (10)	0.119 (5)
C(141)	0.0584 (5)	−0.2528 (10)	0.1893 (6)	0.063 (2)	C(164)	−0.2008 (7)	−0.4884 (13)	0.1247 (7)	0.087 (3)
					Mesityl(2)				
C(21)	−0.1387 (4)	−0.8972 (8)	−0.0677 (5)	0.044 (1)	C(241)	−0.1797 (8)	−1.2229 (15)	−0.2194 (9)	0.105 (4)
C(22)	−0.1924 (5)	−0.8865 (10)	−0.1206 (6)	0.058 (2)	C(25)	−0.1108 (5)	−1.1191 (11)	−0.1163 (6)	0.067 (2)
C(221)	−0.2392 (6)	−0.7634 (11)	−0.1220 (7)	0.075 (3)	C(26)	−0.0951 (4)	−1.0140 (9)	−0.0670 (5)	0.053 (2)
C(23)	−0.2032 (5)	−0.9947 (12)	−0.1675 (6)	0.068 (2)	C(261)	−0.0353 (5)	−1.0285 (12)	−0.0158 (6)	0.073 (3)
C(24)	−0.1642 (6)	−1.1054 (12)	−0.1669 (7)	0.079 (3)					
					Mesityl(3)				
C(31)	−0.1163 (5)	−0.8079 (11)	0.1046 (5)	0.057 (2)	C(341)	−0.1239 (7)	−0.9671 (16)	0.3268 (8)	0.100 (4)
C(32)	−0.1770 (5)	−0.8708 (11)	0.1306 (6)	0.061 (2)	C(35)	−0.0640 (6)	−0.8493 (12)	0.2223 (7)	0.075 (3)
C(321)	−0.2412 (5)	−0.8772 (12)	0.0856 (6)	0.075 (3)	C(36)	−0.0580 (5)	−0.7956 (10)	0.1515 (5)	0.058 (2)
C(33)	−0.1774 (5)	−0.9205 (11)	0.2039 (6)	0.065 (2)	C(361)	0.0072 (6)	−0.7296 (11)	0.1253 (7)	0.075 (3)
C(34)	−0.1215 (5)	−0.9128 (12)	0.2481 (7)	0.072 (3)					

atom	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
Ge	0.0570 (5)	0.0402 (4)	0.0508 (5)	−0.0029 (5)	−0.0005 (7)	−0.0064 (4)
P	0.065 (1)	0.042 (1)	0.056 (1)	0.003 (1)	−0.003 (1)	−0.010 (1)

Table III. Bond Lengths (pm) and Angles (deg) with Esd's in Parentheses for $\mathrm{Mes_2Ge{=}PAr}$

atoms	bond lengths	atoms	bond angles	atoms	torsion angles
Ge=P	213.8 (3)	Ar(1)-P-Ge	107.5 (3)	Ar(1)P-Ge-Mes(2)	-169.7 (4)
P—Ar(1)	186 (1)	P-Ge-Mes(2)	111.8 (3)	Ar(1)P-Ge-Mes(3)	+12.9 (5)
Ge—Mes(2)	194 (1)	P-Ge-Mes(3)	135.2 (4)	GeP-Ar(1)($\mathrm{C_{ipso} + C_{ortho}}$)	−70.8 (5)
Ge—Mes(3)	196 (1)	Mes(2)-Ge-Mes(3)	112.9 (4)	PGe-Mes(2)($\mathrm{C_{ipso} + C_{ortho}}$)	−53.7 (5)
				PGe-Mes(3)($\mathrm{C_{ipso} + C_{ortho}}$)	−59.1 (5)

orbital overlap due to the larger size of the germanium and phosphorus atoms. But this shortening is in a typical range for organometallic doubly bonded compounds: similar values have been obtained in the case of silaalkenes >Si=C<,[1b,c] disilenes >Si=Si<,[1a,b] and diphosphenes -P=P-.[1f,g] In the germene $\mathrm{Mes_2Ge{=}CR_2}$ ($\mathrm{CR_2}$ = fluorenylidene) recently synthesized,[6a] the shortening is slightly larger (10.4%).[6b] In the cases of digermenes $\mathrm{R'_2Ge{=}GeR'_2}$, very different values are obtained according to substituents on germanium. When R′ is a 2,6-diethylphenyl group,[7] the shortening is similar (about 8.5%), but when R′ is a bis(trimethylsilyl)methyl group,[8] the difference between the double- and single-bond length is only 4%: in this case, the Ge–Ge bond is exceedingly labile and the chemical properties of $\mathrm{Ge_2R'_4}$ in solution are those of the monomer $\mathrm{GeR'_2}$. Moreover, the Ge=P bond length is in good agreement with calculations by Barthelat[9] (SCF level with configuration interactions, 216.9 pm; ab initio using pseudopotential, 213.6 pm), and the Ge=P bond length agrees well with the sum of covalent radii (212 pm) of sp^2 germanium (112 pm) and sp^2 phosphorus (100 pm).[1f]

The molecule adopts a nearly planar conformation of the central atoms $\mathrm{C_2Ge{=}PC}$ (mean deviation 7 pm; individual displacements; Ge, −1.3 (1); P, −13.2 (3); C, +7.6 (8), −3.6 (9), and +10.6 (8) pm). The deviation of the germanium atom from its direct coordination $\mathrm{(Mes{-}C_{ipso})_2}$ + P is only 2 pm (sum of angles on germanium 360°). The twist between the cis and trans ligands at the Ge=P bond is 10 and 13°, respectively.

The angle at phosphorus of 107.5° is significantly smaller than the idealized 120° expected for sp^2-hybridized phosphorus. It is the reverse of the trend expected from steric consideration alone; this more acute angle, observed also in diphosphenes and phosphaalkenes, reflects an increase in p character in the P–C bond. The widened angle P–Ge–cis-Mes of 135° (vs 112° trans) demonstrates the steric repulsion between the cis mesityl and the 2,4,6-tri-*tert*-butylphenyl group. The geometry of mesityl and Ar groups shows standard bond lengths and angles and deserves no special comment.

Torsion of aryl and the two mesityl groups around the Ge=P center is approximately equal in sign and magnitude. The aromatic groups form a kind of a three-bladed propeller. There are no short intermolecular interactions between Ge and P: the bulky ligands shield the Ge=P bond well against other molecules and can explain the stability in a monomeric form of this germaphosphene while other compounds of this type are generally highly polymerisable and could only be characterized by trapping reactions.[10]

The results of this X-ray structure are in good agreement with a true germanium–phosphorus double bond already postulated after the study of the germaphosphene chemical

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(6) (a) Couret, C.; Escudie, J.; Satge, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, *109*, 4411. (b) Lazraq, M.; Escudie, J.; Couret, C.; Satge, J.; Drager, M.; Dammel, R., submitted for publication.

(7) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191.

(8) Hitchcock, P. B.; Lappert, M. F.; Miles, J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480.

(9) Barthelat, J. C., private communication; cited in ref 1e.

(10) Couret, C.; Satge, J.; Andriamizaka, J. D.; Escudie, J. *J. Organomet. Chem.* **1978**, *157*, C35.

reactivity: we have only observed for 1 behavior of doubly bonded compound and never behavior of germylene Mes_2Ge and phosphinidene ArP, as if the germanium–phosphorus connection was very weak.

Registry No. 1, 96481-35-5; 2, 96481-37-7; ArP(H)Li, 83115-13-3; 2,4,6-tri-*tert*-butylphenylphosphine, 83115-12-2; dimesityldifluorogermane, 96481-36-6.

Supplementary Material Available: A listing of the hydrogen atom positions (1 page); a listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

Synthesis of a Stable Disulfur Monoxide Precursor and Trapping of Disulfur Monoxide with Transition-Metal Complexes

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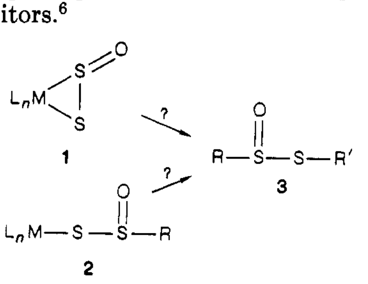
Received January 21, 1988

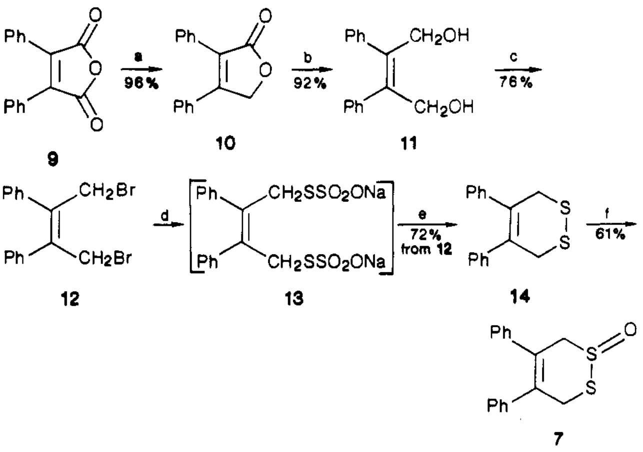
Summary: A five-step synthesis of 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide starting from 2,3-diphenylmaleic anhydride is described. When the dithiin 1-oxide was treated with coordinatively unsaturated transition-metal complexes, a transition-metal disulfur monoxide complex and 2,3-diphenylbutadiene were isolated.

The ability of transition metals to stabilize small, reactive sulfur fragments such as sulfur monoxide (SO),[1] disulfur (S_2),[2] and trisulfur (S_3)[2b,3] offers chemists a chance to explore the reactivity of these molecules under mild, controlable conditions. Our goal within this active area of research is to synthesize transition-metal complexes containing the disulfur monoxide (S_2O) moiety in a variety of different bonding modes. Only two (1 and 2) of a variety of possibilities are shown below. Our hope is that the complexed S_2O can be used as a template for the synthesis of thiosulfinate esters (3). The thiosulfinate esters (3) have shown interesting biological activities as antibacterials,[4] antifungals,[4] plant growth inhibitors,[5] and platelet aggregation inhibitors.[6]

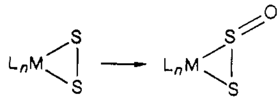


There are no reports in the literature of transition-metal S_2O complexes obtained through the trapping of S_2O and few reports of transition-metal S_2O complexes 1 obtained through the oxidation of S_2 complexes 4.[1,2a,7] The reported mononuclear S_2O complexes are presumed to contain η^2-S_2O in all cases. Comparatively little is known about the reactivity of S_2O in these complexes. Methylation on oxygen with methyl fluorosulfonate has been reported for an iridium complex.[7c] Reaction with triphenylphosphine and oxidation of complexed S_2O have also been reported.[7b,e]

Scheme I[a]

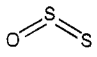


[a] (a) $LiAlH_4$, Et_2O, −20 °C. (b) $LiAlH_4$, Et_2O, −20 °C. (c) PBr_3, C_6H_6, 25–45 °C, 1 h. (d) $Na_2S_2O_3$, THF/H_2O, 1:1, reflux, 1.5 h; (e) I_2, reflux, 1 h. (f) mCPBA, CH_2Cl_2, 0–25 °C, 1 h.



4 1

In order to be able to trap S_2O and study its reactivity, a method for clean, reproducible S_2O generation is required. Free disulfur monoxide (5), structurally similar to sulfur dioxide (6),[8] is an extremely reactive molecule



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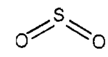

6

unless stored at very low pressures in the gas phase.[9] Disulfur monoxide has been produced in the past for synthetic purposes by the vacuum pyrolysis of $SOCl_2$ over Ag_2S at 160 °C,[10] by pyrolysis of thiirane 1-oxide,[11] and by pyrolysis of a mixture of cupric oxide and sulfur.[11] All of these methods produce S_2O which is contaminated to varying degrees with SO_2 and SO, making them impractical as S_2O sources for transition-metal complex trapping studies. We set out to synthesize an air-stable, crystalline compound (7) which we hoped would yield S_2O via a transition-metal-induced retro Diels–Alder reaction.[12]

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