ORGANOMETALLICS

Organometallic compounds of the lanthanides. 43. Synthesis and x-ray crystallographic characterization of the first organolanthanide compound with a lanthanide-arsenic bond

Herbert. Schumann, Eftimios. Palamidis, Joerg. Loebel, and Joachim. Pickardt

Organometallics, **1988**, 7 (4), 1008-1010• DOI: 10.1021/om00094a035 • Publication Date (Web): 01 May 2002

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

Compound 1 is formally seven-coordinate with the three nitrogen atoms, the carbon atoms, and the hydrogen atom forming a distorted capped antiprism, $MX_3Y_3Z^9$.

The basic tetrahedral geometry of the germane Ar_3GeH is retained with the angles H–Ge–Ar = 112 (2)° and Ar–Ge–Ar = 106.8 (3)°. This last angle compares well with the average of 106.3 (5)° reported by Cameron for tri-*o*-tolylgermane.[10] This should indicate that the coordination of the three nitrogen ligands are not responsible for the decrease of the Ar–Ge–Ar angle values from the theorical 109.5°. The approach of each nitrogen ligand occurs opposite to an aryl–germanium bond. The nitrogen–germanium distance varies from 3.014 to 3.088 (7) Å (mean 3.05 Å) and the Ar–Ge–N angle from 172.5 to 176.8 (3)° (mean 174.0°). This angle is comparable to other angles measured around penta-[11] or hexacoordinated silicon species[12] and depends mainly on the geometry of the five-membered rings, e.g., Ge–C(11)–C(16)–C(17)–N(1). Other angles around the germanium atom are of two types: C(11)–Ge–N(1), mean 69.4 (3)°, and C(11)–Ge–N(2), mean 78.2 (3)°. The Ge–H bond distance 1.58 (5) Å is probably underevaluated by the X-ray technique, and the Ar–Ge bonds, ranging from 1.948 (8) to 1.969 (8) Å, are slightly shorter than that reported in ref 3, mean 1.981 (7) Å. This difference falls within the range of experimental errors and cannot be attributed to any interaction of the nitrogen dative bond with the opposite aryl–germanium bond.

The identity of the X-ray powder diagrams of compounds 1 and 2 shows the two structures are isomorphous; accordingly, the molecules (and the atoms) occupy the same places in the unit cell and this isosterism demonstrates unequivocally the identity of the two species.

Moreover, the thermal analysis diagrams of the mixtures of the two hydrides (1, mp 123.4 C; 2, mp 134.4 °C) using the Fregda method[13] show a solid solution to be produced instead of the calculated eutectic (molar fraction of 2 in the eutectic mixture, 0.407 *F* 103 °C),[14] and this result leaves no doubt as to the structural identity of these two compounds because cocrystallization of isosteric silicon and germanium compounds is well-known (cocrystallization of +α-NpMePhSiH and +α-NpMePhGeH was studied by Brook[15]).

Finally in the ^{29}Si NMR spectrum of 2 the chemical shift of the silicon appears at δ −35.3 (^1J(SiH) = 229.3 Hz) upfield from that of the model product Ph_3SiH (δ −17.8 (^1J(SiH) = 200 Hz).[16] The $\Delta\delta$ = 18 ppm between these two values is in the range of those observed for other neutral hypervalent silicon species.[17,18]

We can conclude that the silicon hydride has a geometry in which the three NMe_2 groups interact with the central silicon atom.

The structure we have observed corresponds to a tetravalent atom which has suffered, therefore, nucleophilic approach. This result confirms the possible interaction of three external donor ligands with a tetravalent silicon atom. This fact means that nucleophilic attack on an hexacoordinate silicon atom is not a chemically forbidden pathway and cannot "a priori" be eliminated in the mechanistic studies.

Registry No. 1, 113404-06-1; 2, 113404-07-2; $GeCl_4$, 10038-98-9; $HSiCl_3$, 10025-78-2; dimethylbenzylamine, 103-83-3.

Supplementary Material Available: Table II, summary of crystal data, intensity collection, and refinement for compound 1; Table IV, atomic coordinates and thermal parameters for compound 1; Table V, atomic coordinates and thermal parameters for hydrogen atoms bonded to carbons atoms; Table VI, all bond distances and angles around the germanium atoms; Table VII, important angles and bond distances in the six germa five-membered rings; Table VIII, the other bond distances and bond angles in the two different molecules of compound 1 (10 pages); Table III, a list of structure factors amplitudes (10 pages). Ordering information is given on any current masthead page.

---

[8] Crystallographic information for germane 1: $C_{27}H_{37}GeN_3$; a = 35.046 (5) Å, *b* = 16.787 (1) Å, *c* = 8.907 (2) Å, β = 90.26 (2)°, space group $P2_1/n$; Z = 8; Mo Kα radiation; R = 0.035 for 2179 unique observed reflections. The hydrogen atoms attached to carbon atoms were positioned by calculation (SHELX-76 program); the hydrogen atoms bonded to the germanium atoms were located by difference Fourier synthesis, and their coordinates were free to move during the last least-squares refinement cycles. Full details of this structure are available as supplementary material.

[9] Mutterties, E. L.; Wrights, C. M. *Rev., Chem. Soc.* **1967**, *21*, 106.

[10] Cameron, T. S.; Mannan, K. M.; Stobart, S. R. *Cryst. Struc. Commun.* **1975**, *4*, 601.

[11] Brelière, C.; Carré, F. H.; Corriu, R. J. P.; Poirier, M.; Royo, G. *Organometallics* **1986**, *5*, 388.

[12] Brelière, C.; Carré, F.; Corriu, R. J. P.; Royo, G.; Zwecker, J., to be submitted for publication.

[13] Fredga, A. *Tetrahedron* **1960**, 126.

[14] Souchay, P. In *Thermodynamique Chimique*; Masson and Cie: Paris, 1961.

[15] Brook, A. G.; Peddle, G. J. D. *J. Am. Chem. Soc.* **1963**, *85*, 2338.

[16] Harris, R. W.; Kimber, B. J. *Adv. Mol. Relax. Processes* **1976**, *8*, 23.

[17] Boyer, J.; Brelière, C.; Carré, F.; Corriu, R. J. P.; Kpoton, A.; Poirier, M.; Royo, G. Young, J. C., submitted for publication.

[18] Tandura, ST. N.; Alekseev, N. V.; Voronkov, M. G. *Top. Curr. Chem.* **1986**, *131*, 99.

Organometallic Compounds of the Lanthanides. 43.[1] Synthesis and X-ray Crystallographic Characterization of the First Organolanthanide Compound with a Lanthanide–Arsenic Bond

Herbert Schumann,* Eftimios Palamidis, Jörg Loebel, and Joachim Pickardt

Institut für Anorganische und Analytische Chemie
Technische Universität Berlin
D-1000 Berlin 12, Federal Republic of Germany

Received January 6, 1988

Summary: $(C_5H_5)_2Lu(\mu\text{-}CH_3)_2Li$(tmed) reacts with diphenylarsine in benzene to give $(C_5H_5)_2Lu(\mu\text{-}AsPh_2)_2Li$(tmed). The molecular structure has been elucidated through complete X-ray analysis. The crystals are orthorhombic, space group *Pcnb* (nonstandard setting of *Pbcn*, No. 60), with a = 37.61 (1) Å, b = 21.065 (3) Å, c = 10.597 (1) Å, V = 8396 (3) Å^3, ρ_{calcd} = 1.526 g/cm^3, and Z = 8. The structure was solved by Patterson and Fourier techniques from 1987 observed reflections ($I \geq 3\sigma(I)$) corrected for Lorentz and polarization effects but not for absorption (μ = 37.90 cm^{-1}). The final R value is 0.0452 (R_w = 0.0395). Principal dimensions are as follows: Lu–Cp = 2.28 (2) and 2.32 (2) Å, Lu–As = 2.896 (2) and 2.870 (2) Å, Cp–Lu–Cp = 131.9 (7)°, and As–Lu–As = 81.14 (6)°.

Organometallic compounds of the lanthanides with bonds between the lanthanide metals and soft donor atoms like sulfur, phosphorus, and silicon and its heavier ho-

---

[1] Part 43: Schumann, H.; Nickel, S.; Loebel, J.; Pickardt, J. *Organometallics*, submitted for publication.

0276-7333/88/2307-1008$01.50/0 © 1988 American Chemical Society

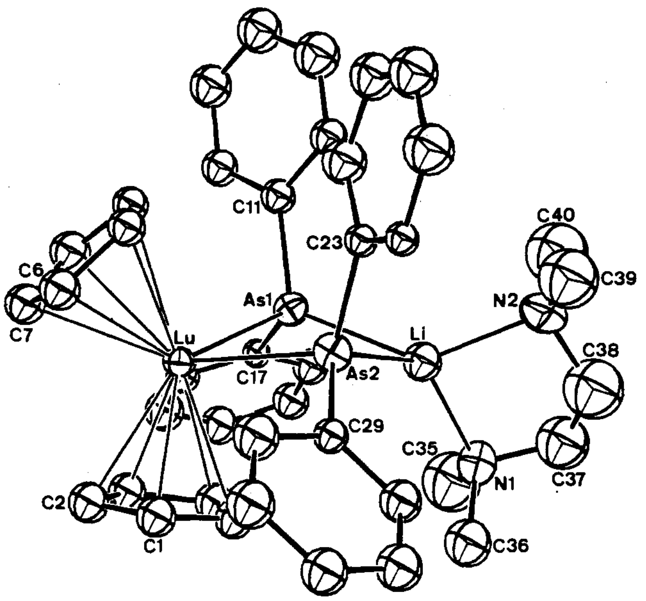
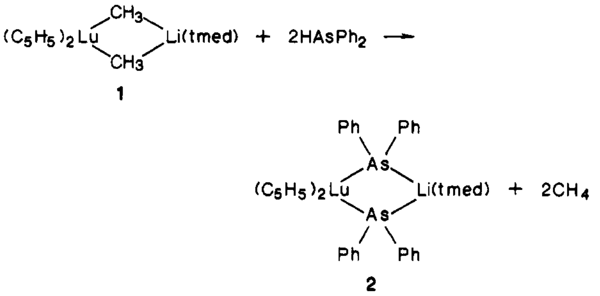


Figure 1. Crystal structure of 2 (H atoms and solvent molecules omitted for clarity; vibration ellipsoids at the 50% probability level). Selected bond lengths (Å) and angles (deg) (Cp signifies the centroid of the cyclopentadienyl ligand): Lu···Li = 3.99 (3), As1···As2 = 3.750 (3), Lu-As1 = 2.896 (2), Lu-As2 = 2.870 (2), Lu-Cp1 = 2.32 (2), Lu-Cp2 = 2.28 (2), mean value Lu-C(η^5) = 2.59, As1-C11 = 1.94 (2), As1-C17 = 1.97 (2), As2-C23 = 1.96 (2), As2-C29 = 1.95 (2), As1-Li = 2.65 (4), As2-Li = 2.73 (3), Li-N1 = 2.07 (3), Li-N2 = 2.11 (4); Cp1-Lu-Cp2 = 131.9 (7), As1-Lu-As2 = 81.14 (6), Lu-As1-Li = 91.9 (6), Lu-As2-Li = 90.8 (7), As1-Li-As2 = 88.3 (9), N1-Li-N2 = 88 (1), dihedral angle between As1-Lu-As2 and As1-Li-As2 planes = 150.8 (4).

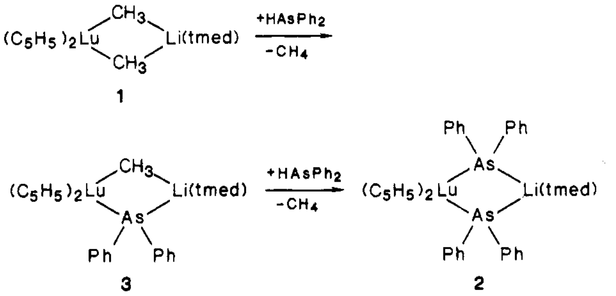
mologues have been described in the literature, but most of them are only very poorly characterized.[2] The structure of the organolanthanide-phosphane compounds $(C_5H_2)_2LnP(t\text{-}C_4H_9)_2$,[3,4] $(C_5H_5)_2LnP(C_6H_{11})_2$,[5] $(C_5H_5)_2LnP(C_6H_5)(t\text{-}C_4H_9)$,[2] and $(CH_3C_5H_4)_2SmP(C_6H_5)_2$[6] was hitherto derived from analytical and spectroscopic data alone, only $(C_5H_5)_2Lu(\mu\text{-}P(C_6H_5)_2)_2Li(tmed)$[7] could be characterized by an X-ray crystallographic investigation. Also the structure of some homoleptic lanthanide-arsenic compounds of the type $Ln(As(t\text{-}C_4H_9)_2)_3$[8] could not be determined because of disordered crystals.

An excellently crystalline dicyclopentadienyllutetium-arsine compound could be prepared from (tetramethylethylenediamine)lithium dimethylbis(cyclopentadienyl)lutetate(III)[9] (1) and diphenylarsine at room temperature in benzene with elimination of methane (eq 1).[10]



(1)

Di-*tert*-butylarsine, $HAs(t\text{-}C_4H_9)_2$, does not react with 1, even in boiling benzene. When the reaction of diphenylarsine with 1 was monitored by NMR spectroscopy, it was observed that only one CH_3 bridge is initially replaced by a diphenylarsine group; the singlet for six protons of the two bridging methyl groups (δ −0.89 for 1) is replaced by a singlet (δ −0.51 for 3) which upon further addition of $HAsPh_2$ disappears completely, indicating the substitution of both CH_3 bridges by diphenylarsine groups (eq 2).



(2)

According to the X-ray structure analysis, 2 is a bis(diphenylarsino)-bridged, dinuclear lutetium–lithium complex (Figure 1).[11] The lutetium atom is surrounded by a distorted tetrahedral array of the centroids of the two cyclopentadienyl rings and the two bridging arsenic atoms. At the same time these two arsenic atoms together with the two nitrogen atoms of the tmed ligand coordinate the lithium atom tetrahedrally. In addition, the crystal contains one molecule of benzene per asymmetric unit. The As1–Lu–As2 and As1–Li–As2 planes form an angle of 150.8 (4)°; i.e., a bent four-membered ring is formed, as observed in analogous compounds with other soft donor atoms bridging lutetium and lithium, like sulfur in the pentamethylcyclopentadienyl complex $(C_5Me_5)_2Lu(\mu\text{-}S\text{-}t\text{-}C_4H_9)_2Li(THF)_2$ (168.1 (7)°),[12] selenium in $(C_5H_5)_2Lu(\mu\text{-}$

---

(2) For the most recent comprehensive reviews on organolanthanide chemistry see: (a) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474. (b) Schumann, H.; Genthe, W. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Eyring, L., Eds.; Elsevier: Amsterdam, 1984; Vol. 7, p 445. (c) Schumann, H. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds.; D. Reidel Publishing: Dordrecht, Holland, 1985; p 1. More recent, but more speciallized reviews are as follows. (d) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131. (e) Kagan, H. B., Namy, J. L. *Tetrahedron* **1986**, *42*, 6573. (f) Evans, W. J. *Polyhedron* **1987**, *6*, 803.

(3) Schumann, H.; Jarosch, H. *Z. Anorg. Allg. Chem.* **1976**, *426*, 127.

(4) Schumann, H.; Frisch, G. M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 1294.

(5) Bielang, G.; Fischer, R. D. *J. Organomet. Chem.* **1978**, *161*, 335.

(6) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 709.

(7) Schumann, H.; Palamidis, E.; Schmid, G.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 718.

(8) Schumann, H.; Frisch, G. M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 168.

(9) Schumann, H.; Reier, F.-W.; Hahn, E. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1985**, *40B*, 1289.

(10) $(C_5H_5)_2Lu(\mu\text{-}CH_3)_2Li(tmed)$ (0.88 g, 1.92 mmol) was dissolved in 10 mL of benzene, and $HAs(C_6H_5)_2$ (0.88 g, 3.84 mmol) was added dropwise at room temperature. A yellow solution was obtained and stirred for 24 h. The solution volume was carefully reduced to 2 mL by solvent evaporation under reduced pressure. The procedure yielded 1.44 g (78%) of yellow crystals of $(C_5H_5)_2Lu(\mu\text{-}As(C_6H_5)_2)_2Li(tmed)\cdot C_6H_6$, suitable for X-ray analysis; decomp pt 168 °C. Anal. Calcd for $C_{46}H_{52}N_2As_2LiLu$: C, 57.26; H, 5.44; N, 2.90. Found: C, 56.21; H, 5.11; N, 3.3. Satisfactory microanalytical data were difficult to obtain since the crystalline product loses benzene when dried in vacuo. ^1H NMR (C_6D_6, 25 °C, 80 MHz): δ 1.62 (s, NCH_2), 1.75 (s, NCH_3), 6.19 (s, C_5H_5), 7.0–7.9 (m, C_6H_5). ^{13}C NMR (C_6D_6, 25 °C, 20.15 MHz): δ 45.23 (s, NCH_3), 56.02 (s, NCH_2), 110.62 (s, C_5H_5), 131 (m, C_6H_5).

(11) Crystal data: space group *Pcnb* (alternate setting of *Pbcn*, No. 60) $a = 37.61$ (1) Å, $b = 21.065$ (3) Å, $c = 10.297$ (1) Å, $V = 8396$ (3) Å^3, $\rho_{calcd} = 1.526$ g·cm^{-1}, $Z = 8$; Mo Kα radiation, graphite monochromator, ω–2θ scans in the 2θ range up to 40° at 173 (5) K; raw data corrected for Lorentz and polarization effects; solution by heavy-atom methods; full-matrix least-squares refinement based on 1987 observed reflections ($I \geqslant 3\sigma(I)$) led to final $R = 0.0452$ and $R_w = 0.0395$ ($w = 2.3233/(\sigma^2(F) + 0.000148F^2)$). Further details of the structure investigations are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-53022, the authors, and the full citation of the journal.

1010 *Organometallics* **1988,** *7,* 1010–1013

$SeC_6H_5)_2Li(THF)_2$ (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.

---

(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

Martin Dräger

Institut für Anorganische Chemie und Analytische
Chemie der Johannes Gutenberg-Universität
Johann-Joachim-Becher-Weg 24, D-6500 Mainz, Germany

Jean Escudie,* Claude Couret, Henri Ranaivonjatovo, and Jacques Satge

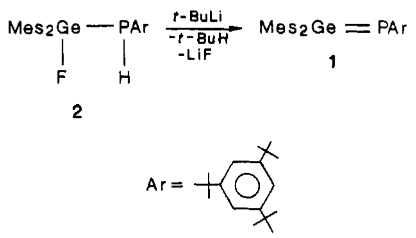
Laboratoire de Chimie des Organominéraux
Université Paul Sabatier, 118, route de Narbonne
31062 Toulouse Cedex, France

Received November 10, 1987

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).

---

(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.

0276-7333/88/2307-1010$01.50/0