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Chelating triarylgermyl anions as ligands in lanthanide chemistry: synthesis of Ln[GeAr$_3$]$_2$ [Ar = $C_6H_4(2\text{-}CH_2NMe_2)$; Ln = Sm, Yb] and the crystal structure of an unusual μ-(*o*-tolylene)digermane byproduct

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Abstract

The synthesis of substituted triarylgermyl potassium reagents KGeAr$_3$ [Ar = $C_6H_4(2\text{-}CH_2NMe_2)$ and $C_6H_3(2\text{-}OMe)(5\text{-}Me)$] and their reactions with YbI$_2$ and SmI$_2$ are described. Clean formation of Ln[GeAr$_3$]$_2$ complexes is observed for Ar = $C_6H_4(2\text{-}CH_2NMe_2)$ in which the lanthanide centre is six-coordinate with each germyl anion functioning as a tridentate ligand. Reaction of KGeAr$_3$ [Ar = $C_6H_3(2\text{-}OMe)(5\text{-}Me)$] with LnI$_2$ did not produce Ln[GeAr$_3$]$_2$ complexes cleanly. This failure was traced to competing metallation of the diethyl ether solvent. Crystals of a μ-*o*-tolylenedigermane byproduct were however isolated from the YbI$_2$ reaction and crystallographically characterized. The latter compound represents the first example of the μ-*o*-phenylenedigermane class of compounds to be reported.

Keywords: Germanium; Lithium; Samarium; Ytterbium; Lanthanides

1. Introduction

In contrast to the efforts devoted to investigation of the lanthanide–carbon bond [1], considerably less attention has been focused on compounds containing bonds between lanthanides and the heavier Group 14 elements. In particular, few compounds containing divalent Ln–Si [2], Ln–Ge [2,3], and Ln–Sn [4] bonds have been characterized and their reactivity is virtually unknown. We therefore embarked on a program to investigate the synthesis and reactivity of silyl, germyl, and stannyl lanthanide derivatives.

In this contribution, we report the synthesis of two chelating triarylgermyl anions $K^+[GeAr_3]^-$ [Ar = $C_6H_4(2\text{-}CH_2NMe_2)$ and $C_6H_3(2\text{-}OMe)(5\text{-}Me)$] and their reactions with LnI$_2$ to produce Ln[GeAr$_3$]$_2$ [Ln = Sm, Yb]. Triarylgermyl anions were chosen because they are easily accessible in excellent purity by deprotonation of the parent germanes. In our hands, the corresponding triarylsilanes could not be deprotonated [5], in contrast to a literature report that claims deprotonation of triphenylsilane with KH [6]. We have not yet succeeded in preparing chelating triarylsilyl anions of sufficient purity from the triarylsilyl chlorides or hexaaryldisilanes. A chelating anion was chosen in an effort to stabilize the bis(germyl) lanthanide product and to allow future elaboration to RLn[GeAr$_3$]. Chelate stabilization is likely to be particularly important for the latter class of compounds since the typical R groups [e.g. Me, Ph, ^{t}Bu, CH$_2$SiMe$_3$, etc.] offer comparatively little steric shielding of the metal centre.

2. Experimental section

2.1. General procedures

All manipulations were carried out under an argon atmosphere, with the rigorous exclusion of oxygen and water, using standard glovebox (Braun MB150-GII) or Schlenk techniques, except as noted. Tetrahydrofuran (THF), diethyl ether, hexane and toluene were dried by distillation from sodium benzophenone ketyl under

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argon immediately prior to use. Anhydrous metal iodides (Sm and Yb) were prepared as described in the literature [7,8]. $GeCl_4$ was purchased from Aldrich and used without further purification. 2-Bromo-4-methylanisole was prepared from the commercially available 4-methylanisole by direct bromination with Br_2 [9]. 2-((*N*,*N*-dimethylamino)methyl)phenyl lithium was prepared by direct metallation of *N*,*N*-dimethylbenzyl amine with ^{n}BuLi as reported in the literature [10]. Benzylpotassium was prepared according to a published procedure [11].

^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM-250 MHz or a Bruker AMX-360 MHz spectrometer. Mass spectra were recorded on a Finnegan 3300 or a Kratos Concept H spectrometer using a chemical ionization or electron impact (70 eV) source, respectively. Infrared spectra were recorded using a Bruker IFS 25 FT instrument as Nujol mulls on KBr plates. Melting points were recorded using a Reichert hot stage and are not corrected. Elemental analyses were performed by Canadian Microanalytical, Delta, BC. Lanthanides were analyzed by the method of Flaschka [12].

2.2. *Syntheses*

2.2.1. $HGe[C_6H_4(2\text{-}CH_2NMe_2)]_3$ *(1)*

A solution of $LiC_6H_4(2\text{-}CH_2NMe_2)$ (10.73 g, 76.0 mmol) in 100 ml of THF was added dropwise to a stirred solution of $GeCl_4$ (5.35 g, 25.0 mmol) in 100 ml of THF cooled to 0°C. After the addition was complete, the solution was allowed to stir at room temperature for 4 h. Lithium aluminum hydride (0.75 g, 20 mmol) was added directly to the reaction mixture and stirring was continued overnight. The reaction mixture was carefully quenched with water (500 ml) and extracted with CH_2Cl_2 (3×300 ml). The combined extracts were dried over anhydrous $MgSO_4$, filtered and the filtrate taken to dryness by rotary evaporation (water aspirator). The resulting white solid was recrystallized 3 times from Et_2O to remove the more soluble H_2GeAr_2 impurity. Large white crystals of **1** were obtained. Yield: 8.15 g (17.1 mmol, 68.5%). Mp: 121–122°C. ^{1}H NMR (C_6D_6): δ 7.46 (d, 3H, 3- or 6-arylC*H*, ^{3}J(HH) = 7.4 Hz), 7.25 (d, 3H, 3- or 6-arylC*H*, ^{3}J(HH) = 7.4 Hz), 7.15 (t, 3H, 4- or 5-arylC*H*, ^{3}J(HH) = 7.4 Hz), 7.02 (t, 3H, 4- or 5-arylC*H*, ^{3}J(HH) = 7.4 Hz), 6.11 (s, 1H, Ge*H*), 3.48 (s, 6H, C*H*$_2$N), 1.86 (s, 18H, N*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 136.4, 128.8, 127.6, 126.5 (aryl*C*H), 144.7, 140.5 (quaternary aryl*C*), 65.2 (*C*H$_2$N), 44.4 (N*Me*$_2$). IR: 2080 (m) cm^{-1} (ν Ge–H) MS(CI): *m/z* (relative intensity) 477(100) [M^{+} + 1], 343(95) [M^{+} − $C_6H_3(CH_2NMe_2)$]. Anal. Found: C, 68.03; H, 7.85; N, 8.80. $C_{27}H_{37}GeN_3$ calc.: C, 68.11; H, 7.83; N, 8.82%.

2.2.2. $HGe[C_6H_3(2\text{-}OMe)(5\text{-}Me)]_3$ *(2)*

The preparation of **2** was carried out using the Grignard reagent, prepared in Et_2O, rather than the lithium salt because this resulted in better yields and a cleaner product. The workup procedure was similar to **1**. Yield: 57.3%. Mp: 126–128°C. ^{1}H NMR (C_6D_6): δ 7.36 (d, 3H, *J*(HH) = 2.0 Hz, aryl*H*), 7.03 (dd, 3H, *J*(HH) = 2.0 and 6.3 Hz, aryl*H*), 6.57 (d, 3H, *J*(HH) = 6.3 Hz), 6.56 (s, 1H, Ge*H*), 3.26 (s, 9H, O*Me*), 2.04 (s, 9H, aryl*Me*). ^{13}C{^{1}H} NMR (C_6D_6): δ 161.8 (aryl*C*OMe), 137.5, 131.3, 110.1 (aryl*C*H), 129.8, 125.2 (quaternary aryl*C*), 55.2 (O*Me*), 20.5 (aryl*Me*). IR: 2027 (s) cm^{-1} (ν Ge–H). MS(CI): *m/z* (relative intensity) 465(12) [M^{+} + 29], 437(100) [M^{+} + 1]. Anal. Found: C, 65.83; H, 6.49; O, 11.36. $C_{24}H_{28}GeO_3$ calc.: C, 65.96; H, 6.46; O, 10.98%.

2.2.3. $K^{+}\{Ge[C_6H_4(2\text{-}CH_2NMe_2)]_3\}$ *(3)*

A solution of **1** (1.66 g, 3.49 mmol) in 50 ml of THF was added rapidly by canula to a stirred solution of benzyl potassium (0.464 g, 3.54 mmol) in 50 ml of THF. The reaction mixture rapidly faded in colour from deep red to yellow. After 1 h, the solvent was removed under reduced pressure and the glassy yellow solid removed to the glove box. The hydrocarbon-insoluble potassium salt **3** was isolated as a bright yellow powder by repeated hexane washing followed by vacuum drying. Yield: 1.322 g (2.57 mmol, 73.7%). Mp: dec. 209–211°C.

2.2.4. $K^{+}\{Ge[C_6H_3(2\text{-}OMe)(5\text{-}Me)]_3\}$ · *toluene (4)*

The preparation of **4** was the same as **3** except that the product was crystallized from toluene at −30°C. This salt was isolated as a toluene solvate which readily lost solvent on exposure to vacuum. Compound **4** is stable indefinitely as a solid at room temperature under argon but slowly decomposes to the germane on stirring in ethereal solvents. Yield: 92.5%. Mp: 204–205°C. ^{1}H NMR (C_6D_6): δ 6.91 (br m, 6H, aryl*H*), 6.62 (d, 3H, aryl*H*, *J*(HH) = 8.4 Hz), 2.89 (s, 9H, O*Me*), 1.93 (s, 9H, aryl*Me*). ^{13}C{^{1}H} NMR (C_6D_6): δ 161.5 (aryl*C*OMe), 144.6 (quaternary aryl*C*Ge), 131.0 (quaternary aryl*C*Me), 138.6, 127.8, 110.6 (aryl*C*H), 54.8 (O*Me*), 20.7 (aryl*Me*). The downfield chemical shift of the aryl carbon bound to Ge (C1) is 14.8 or 19.4 ppm relative to the parent germane, depending on which quaternary aryl carbon in **2** represents C1. This value is consistent with the literature observation that the ipso C of $Et_2PhGeLi$ shifts downfield by 35.44 ppm relative to the parent germane [13].

2.2.5. $Yb\{Ge[C_6H_4(2\text{-}CH_2NMe_2)]_3\}_2$ · *toluene (5)*

A Schlenk tube equipped with a stir bar was loaded with **3** (0.785 g, 1.53 mmol) and YbI_2 (0.326 g, 0.764 mmol) in the glove box. After removal to the vacuum line, diethyl ether (60 ml) was added and the yellow suspension stirred at room temperature overnight. The resulting clear orange supernatant was filtered away from the beige precipitate which formed using a Schlenk frit and the filtrate evaporated to dryness under reduced pressure. The glassy orange residue was transferred to the glove box and recrystallized from a mixture of toluene and hexane at −30°C. Deep orange crystals of **5** were collected by filtration and dried under vacuum. Yield: 0.392 g (42.2%). Mp: 114–117°C. ^{1}H NMR (C_6D_6, +50°C): δ 7.57 (d, 6H, 3- or 6-aryl*H*, *J*(HH) = 7.2 Hz), 7.37 (d, 6H, 3- or 6-aryl*H*, *J*(HH) = 6.9 Hz), 7.12 (m, 6H, 4- or 5-aryl*H*), 7.02 (m, 6H, 4- or 5-aryl*H*), 3.50 (br s, 12H, CH_2N), 1.99 (s, 36H, NMe_2). ^{13}C{^{1}H} NMR (C_6D_6, +50°C): δ 153.5, 143.6 (quaternary aryl*C*), 137.8, 129.8, 127.1, 126.7 (aryl*C*H), 66.4 (*C*H_2N), 44.9 (NMe_2). Anal. Found: C, 59.90; H, 6.85; N, 6.82; Yb, 14.0. $C_{61}H_{80}Ge_2N_6Yb$ calc.: C, 60.27; H, 6.63; N, 6.91; Yb, 14.2%.

2.2.6. *Sm{Ge[C_6H_4(2-CH_2NMe_2)]$_3$}$_2$ · 0.5 toluene (6)*

The preparation of **6** was the same as that described for **5**. Purple crystals of **6** were isolated by layering a toluene solution of the crude product with hexane and cooling at −30°C. Yield: 82%. Mp: 134–136 °C. ^{1}H NMR (C_7D_8, +80°C): δ 7.14 (t, 6H, 4- or 5-aryl*H*, *J*(HH) = 6.7 Hz, $w_{1/2}$ = 4 Hz), 6.81 (d, 6H, 3- or 6-aryl*H*, *J*(HH) = 6.8 Hz, $w_{1/2}$ = 5 Hz), 6.02 (t, 6H, 4- or 5-aryl*H*, *J*(HH) = 6.9 Hz, $w_{1/2}$ = 5 Hz), 4.65 (s, 36H, NMe_2, $w_{1/2}$ = 13 Hz), 3.78 (d, 6H, 3- or 6-aryl*H*, J_{HH} = 6.7 Hz, $w_{1/2}$ = 5.5 Hz), −0.58 (s, 12H, CH_2N, $w_{1/2}$ = 14 Hz). Anal. Found: C, 59.92; H, 6.89; N, 7.06; Sm, 13.1. $C_{57.5}H_{76}Ge_2N_6Sm$ calc.: C, 60.22; H, 6.68; N, 7.32; Sm, 13.1%.

2.2.7. *Attempted preparation of Ln{Ge[C_6H_3(2-OMe)(5-Me)]$_3$}$_2$ [Ln = Yb (7), Sm (8)]*

Several attempts were made to prepare **7** and **8** by the procedure employed for the synthesis of **5**. In all cases, a red-orange (**7**) or black (**8**) powder was isolated from toluene-hexane mixtures. In addition, a small yield of red-orange crystals (**9**) were consistently isolated in the YbI_2 reaction, as described in 2.2.8 below. Neither powder could be purified sufficiently to allow characterization although deuterolysis (see 2.3 below) seemed to suggest that Ar_3Ge^- was present. The major impurity present in both compounds was $HGeAr_3$, presumably formed by metallation of diethyl ether by $KGeAr_3$ as mentioned in 2.2.4.

2.2.8. *{Ge[C_6H_3(2-OMe)(5-Me)]$_2$}$_2${μ-o-C_6H_3(4-Me)} (9)*

Red-orange crystals of **9** were isolated from the reaction of **4** with YbI_2 as described in 2.2.7 by recrystallization of the crude product from toluene layered with hexane at room temperature. Compound **9** crystallized out prior to precipitation of the red-orange powder (impure **7**). Yields varied from 5–15%. ^{1}H NMR (C_6D_6): δ 7.94 (d, 1H, tolylene*H*, *J*(HH) = 7.6 Hz), 7.82 (s, 1H, tolylene*H*), 7.59 (s, 4H, *p*-methylanisolyl*H*), 7.25 (d, 1H, tolylene*H*, *J*(HH) = 7.7 Hz), 6.94 (d, 4H, *p*-methylanisolyl*H*, *J*(HH) = 7.9 Hz), 6.45 (d, 4H, *p*-methylanisolyl*H*, *J*(HH) = 8.2 Hz), 3.13 (s, 6H, O*Me*), 3.12 (s, 6H, O*Me*), 2.27 (s, 3H, tolylene*Me*), 2.04 (s, 12H, *p*-methylanisolyl*Me*). ^{13}C{^{1}H} NMR (C_6D_6): δ 161.3, 159.4, 155.8, 137.7, 137.3, 134.7, 133.9, 130.6, 130.5, 129.8, 129.5, 129.0, 128.8, 109.7 (aryl*C*), 54.0 (O*Me*), 21.9 (μ-tolylene*Me*), 20.5 (aryl*Me*). MS (EI, 70 eV): 720 M^+ (28%), 705 M^+ − Me (27), 689 M^+ − OMe (22), 599 M^+ − C_6H_3(2-OMe)(5-Me) (100), 567 M^+ − C_6H_3(2-OMe)(5-Me) − OMe (89). Anal. Found: C, 64.73; H, 5.69; O, 9.15. $C_{39}H_{42}Ge_2O_4$ calc.: C, 65.06; H, 5.88; O, 8.89%.

2.3. *Hydrolysis and deuterolysis experiments*

Hydrolysis of compounds **3–8** was carried out by addition of 0.5 ml of H_2O to a solution of the compound (40–75 mg) in 2 ml of C_6D_6 under argon. The organic phase was separated, dried over 4 Å sieves and examined by ^{1}H NMR spectroscopy. In all cases, only peaks due to the germane (**1** or **2**) were observed. Deuterolysis experiments were performed in an analogous fashion using D_2O in C_6H_6 followed by examination of the organic phase by ^{2}D NMR. In all cases, deuterium incorporation was found exclusively at the Ge–D site.

2.4. *X-ray crystal structure determination of (9)*

Crystallographic data for **9** is summarized in Table 1. A red-orange crystal of **9** (0.4 × 0.25 × 0.2 mm) was

Table 1
Summary of crystallographic data for **9**

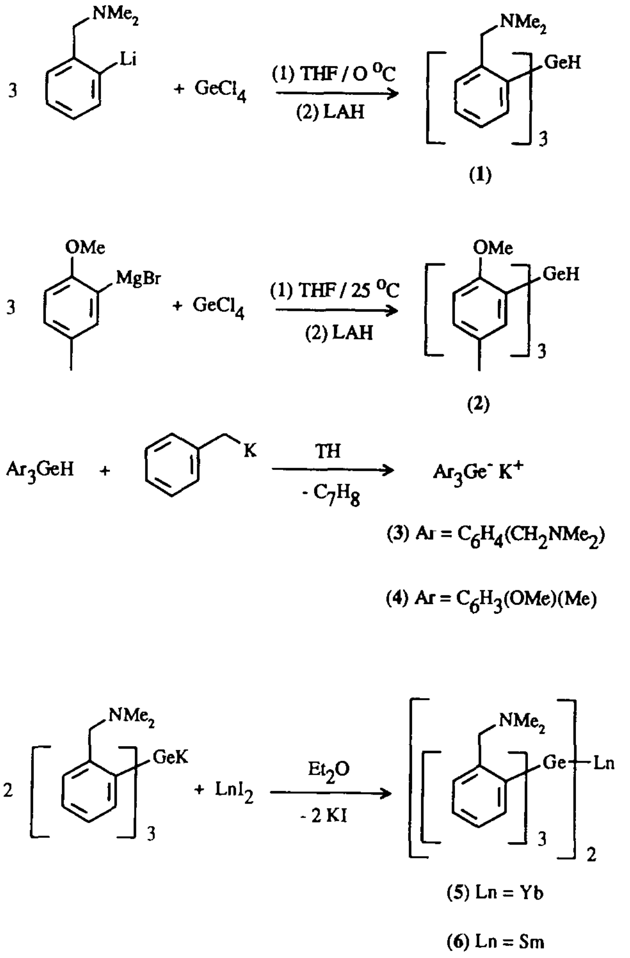
Empirical formula	$C_{39}H_{41}Ge_2O_4$	*Z*	4
*F*w	718.9	ρ (calcd) (g cm^{-3})	1.338
Cryst syst	Monoclinic	μ (cm^{-1})	23.37
Space group	*I*2/*a* (No. 15) [a]	radiation, λ (Å)	Cu K_α, 1.542
a (Å)	15.158(3)	T	295 K
b (Å)	13.118(1)	$2\theta_{max}$ (deg)	60
c (Å)	18.074(6)	no. of obsd reflcns	2514
α (°)	90	no. of unique reflcns	1962
β (°)	96.78(2)	*R* [b]	0.071
γ (°)	90	R_w [c]	0.091
V (Å^3)	3568.8		

[a] Unique axis b, cell choice 3 (see: T. Hahn (ed.) *International Tables for Crystallography, Volume A: Space Group Symmetry*, D. Reidel, Dordrecht, 1983, p. 185).

[b] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$.

loaded into a glass capillary in the glove box and subsequently examined using Weissenberg and Precession cameras. The crystal was transferred to a Nonius CAD4F diffractometer equipped with Ni-filtered Cu Kα radiation. The unit cell was refined by least squares using 25 reflections in the 2θ range 22–80°. The experimental density was not obtained because of the air sensitivity of the compound. Three standard reflections (0,0,14; 0,10,0; 12,0,0), measured periodically during data collection, showed no significant decline in intensity. Intensity measurements were collected over one quarter of the sphere. After the usual data reduction procedures, including an absorption correction according to a measured Ψ scan, the structure was solved using SHELXS and refined using SHELX76 (refinement minimized $\Sigma w((|F_o| - |F_c|)^2)$ [14]. The criterion for inclusion of reflections was $I > 2\sigma(I)$ and the weighting scheme was determined by counting statistics using $w = 1/(\sigma^2(F) + 0.001F^2)$. Convergence proceeded to an R value of 0.13 at which point the methyl group of the μ-tolylene unit was found to be disordered. This disorder was modeled by using an occupancy factor of 0.5 for the methyl group in each site (bonded to C(19) and C(19Y)); refinement proceeded satisfactorily to R = 0.071, and convergence was attained: max shift/esd = 0.02. A total of 208 parameters (23 atoms × 9 parameters per atom + scale) was refined in a single block. No intermolecular contacts shorter than 3.5 Å were observed. The structural perspective plot was drawn using ORTEP [15].



Scheme 1.

3. Results and discussion

The crystalline triarylgermanes, $HGeAr_3$ [1: Ar = $C_6H_4(2\text{-}CH_2NMe_2)$; 2: Ar = $C_6H_3(2\text{-}OMe)(5\text{-}Me)$], were prepared from the aryllithium or Grignard reagents and $GeCl_4$, for 1 and 2 respectively, followed by reduction with LAH. The steric bulk of the aryl moieties resulted in good yields of the triarylgermanes without contamination due to Ar_4Ge. Preparation of the potassium salts, $K^{+-}GeAr_3$ [3: Ar = $C_6H_4(2\text{-}CH_2NMe_2)$; 4: Ar = $C_6H_3(2\text{-}OMe)(5\text{-}Me)$], proceeded smoothly with benzyl potassium in THF (Scheme 1). Both salts are very soluble in THF but only 4 is soluble in toluene and diethyl ether. Recrystallization of 4 from toluene-hexane mixtures yielded colourless crystals. In contrast, 3 was isolated as an insoluble bright yellow powder. The low solubility of 3 can be attributed to polymer formation through bridging dimethylaminomethyl arms of the aryl substituents. It seems likely that the less flexible methoxy groups in 4 are incapable of interacting with a neighbouring K^+ ion without incurring unfavourable steric interactions with aryl groups of the adjacent triarylgermyl anion. The absence of the Ge–H function was confirmed by ^{1}H NMR (4) and IR. As expected, hydrolysis and deuterolysis generated exclusively $HGeAr_3$ and $DGeAr_3$, respectively. Satisfactory elemental analyses were precluded by the extreme air sensitivity of 3 and the presence of variable amounts of toluene of solvation in 4.

Reaction of 2 equivalents of 3 with LnI_2 proceeded slowly in diethyl ether to produce good yields of very air and moisture sensitive $Ln[Ge(C_6H_4(2\text{-}CH_2NMe_2))_3]_2 \cdot n$ toluene [5: Ln = Yb, n = 1, orange; 6: Ln = Sm, n = 0.5, purple] (Scheme 1). Complexes 5 and 6 were characterized by ^{1}H, ^{13}C (5) NMR and elemental analysis. Unfortunately, despite the crystallinity of these compounds (particularly 6), we were unable to obtain a crystal structure of either complex. Hydrolysis and deuterolysis experiments produced exclusively $HGeAr_3$ and $DGeAr_3$, respectively, by NMR. The presence of residual K^+ and I^- was ruled out on the basis of negative flame (K^+) and silver halide (I^-) tests as well as elemental analysis (C, H, N and lanthanide).

In the absence of a crystal structure determination it is difficult to predict the structures of 5 and 6 with

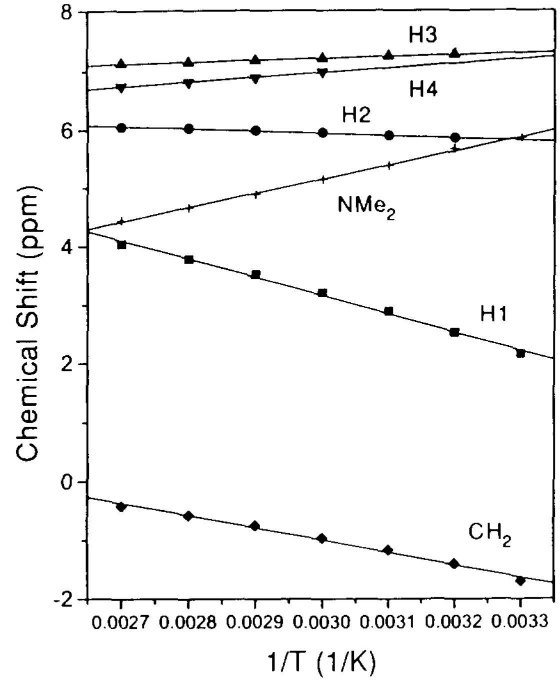


Fig. 1. Plot of chemical shift (δ) versus $1/T$ for **6** in the 30–90°C range. H1–H4 are reference labels for the aryl H resonances; no assignments are implied.

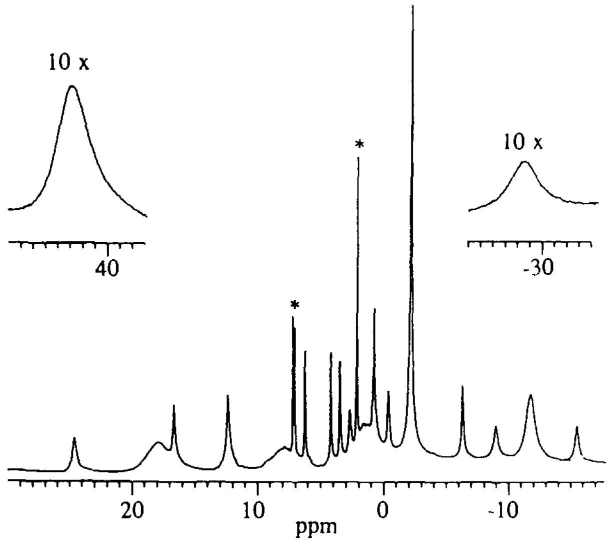


Fig. 2. 250 MHz ^1H NMR Spectrum of **6** at −60°C (*d_8-toluene residual protonresonances).

certainty. However, the fluxional behaviour of these compounds observed by variable temperature ^1H NMR is quite informative. At temperatures above ambient, **5** and **6** display a single environment for all aryl groups (i.e. six resonances in 1:1:1:1:2:6 ratio). A plot of chemical shift versus temperature (Fig. 1) for paramagnetic **6** shows straight line behaviour in the 30–90°C range [16] for all six resonances, providing good evidence that a single fluxional species is present throughout this temperature regime. When the samples are cooled to 0°C, the NMR spectra of both **5** and **6** collapse. Cooling to −20°C results in reappearance of the spectra as complex patterns. Further cooling to −80°C results in no additional changes other than the expected temperature-dependent paramagnetic shifts for **6**. The pattern of resonances observed at low temperature is illustrated for **6** at −60°C in Fig. 2.

The inequivalence of the aryl groups evident in the low temperature ^1H NMR spectra can be explained if octahedral coordination is assumed at the lanthanide centre with one chelate arm of each germyl anion noncoordinating. In this case, *trans* (C_{2h}) and *cis* (C_2) configurations are possible for the germanium atoms (Fig. 3). A total of 14 resonances are expected for the *trans* geometry while 22 resonances are predicted for the *cis* configuration. Additionally, *three* methyl resonances in 12:12:12 ratio are expected for the *trans* geometry while the *cis* isomer should give rise to *five* methyl resonances in 12:6:6:6:6 ratio. Inspection of Fig. 2 seems to support the *cis* geometry since at least 18 resonances are visible and five larger resonances (δ 43.0, 18.0, 7.8, −2.2 and −11.8 ppm), attributable to the methyl groups, are observed with the −2.2 ppm resonance being twice as large as the others. Not surprisingly, given the large number and broadness of the resonances, four of the expected signals of integration 2 are not observed. It is noteworthy that Bochkarev and co-workers have confirmed crystallographically that $Yb[GePh_3]_2[THF]_4$ possesses an octahedral ytterbium centre albeit with a *trans* disposition of germyl anions [2].

Attempts to prepare analogous Yb and Sm complexes using **4** met with failure. In both cases air sensitive powders heavily contaminated with $HGeAr_3$ (**2**) were obtained. The main reason for the failure of this reaction appears to be the tendency of **4** to metallate the diethyl ether solvent (see Section 2.2.7 for

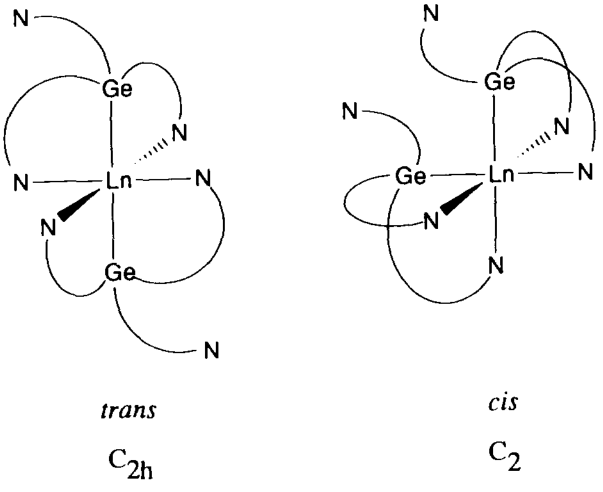


Fig. 3. Possible structures for compounds **5** and **6**.

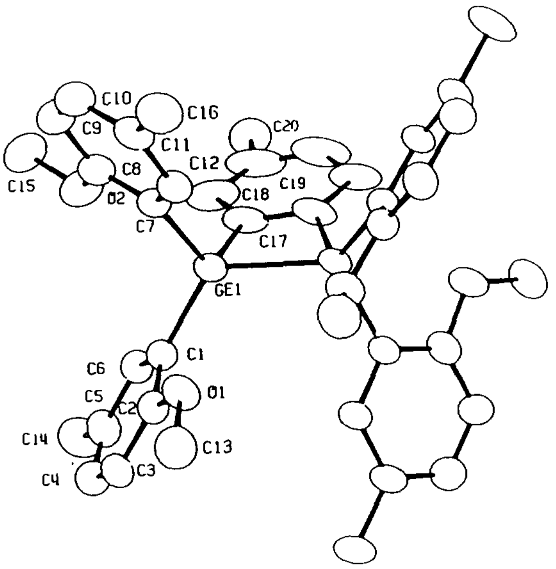


Fig. 4. ORTEP drawing of **9** (note: C(20) is disordered between sites on C(19) and C(19)′ but has been shown here in a single site for clarity. Please refer to the text for further details).

details). While potassium salt **4** is stable in hydrocarbon solvents such as toluene, the insolubility of YbI_2 and SmI_2 in these solvents does not allow the reaction to proceed. The greater tendency of **4** to metallate ethereal solvents, relative to **3**, is likely due to destabilization of the germyl anion by the more electron rich C_6H_3(2-OMe)(5-Me) groups.

Of more interest is the red-orange crystalline byproduct (**9**) consistently isolated (5–15% yield) as the less soluble material during recrystallization of Yb{Ge[C_6H_3(2-OMe)(5-Me)]$_3$}$_2$ (**7**) from toluene layered with hexane. Initially we believed this material to be **7** since it was air sensitive and the appropriate colour. However, the elemental analysis and NMR spectra were inconsistent with this formulation. An X-ray crystallographic study revealed that **9** was in fact {Ge[C_6H_3(2-OMe)(5-Me)]$_2$}$_2$[μ-*o*-C_6H_3(4-Me)]. An ORTEP drawing of **9** is shown in Fig. 4. Fractional atomic coordinates are given in Table 2 while selected bond lengths and angles are collected in Table 3. To our knowledge **9** is the first example of a μ-phenylenedigermane to be reported. Silicon analogues [17] and the digermacyclobutenes **I** and **II** [18,19] are known.

Table 2

Fractional atomic coordinates [a] and equivalent isotropic temperature [b].

Factors for **9** (estimated standard deviations in parentheses)

Atom	*x*	*y*	*z*	U_{eq}
Ge(1)	1743(1)	2331(1)	148(1)	66(1)
O(1)	1259(4)	218(4)	−349(3)	85(2)
O(2)	451(5)	3179(5)	1134(3)	108(2)
C(1)	740(5)	1884(6)	−543(4)	69(2)
C(2)	631(5)	848(6)	−705(4)	74(3)
C(3)	−99(6)	488(7)	−1192(5)	88(3)
C(4)	−704(6)	1186(8)	−1516(5)	97(3)
C(5)	−596(6)	2223(8)	−1390(5)	99(3)
C(6)	126(5)	2572(6)	−890(4)	80(3)
C(7)	1596(5)	1974(6)	1174(4)	69(2)
C(8)	972(6)	2474(6)	1538(5)	87(3)
C(9)	897(7)	2273(7)	2300(5)	93(3)
C(10)	1450(7)	1547(7)	2665(5)	97(3)
C(11)	2071(6)	1020(7)	2307(5)	87(3)
C(12)	2145(5)	1234(6)	1550(4)	74(2)
C(13)	1203(7)	−842(7)	−499(6)	110(3)
C(14)	−1246(7)	3016(9)	−1776(6)	133(3)
C(15)	−190(8)	3758(9)	1518(6)	130(3)
C(16)	2696(7)	221(7)	2708(5)	105(3)
C(17)	2049(6)	3773(6)	58(5)	91(3)
C(18)	1562(8)	4688(6)	113(5)	123(3)
C(19)	2053(9)	5610(7)	30(7)	167(3)
C(20)	1877(14)	6703(13)	−7(12)	116(4)

[a] $\times 10^4$;

[b] $U_{eq} = 1/3\ \Sigma_i \Sigma_j U_{ij} a_i * a_j * (a_i \cdot a_j)$ (Å × 10^3).

In the structure of **9**, the methyl group of the μ-tolylene unit is disordered. The disorder was successfully modeled by using an occupancy factor of 0.5 for the methyl carbon and refining the structure in the space group *I*2/*a*. In this space group, the molecule is bisected by a 2-fold axis passing through the centre of the Ge(1)–Ge(1)′ bond and the tolylene ring (i.e. bisecting C(17)–C(17)′ and C(19)–C(19)′). The methyl carbon is disordered between site C(20) and site C(20)′ which are related by the 2-fold axis although it has been drawn in only one site in Fig. 4 for clarity. Obviously an individual molecule cannot possess the 2-fold axis. If a perfectly ordered crystal could be obtained it would not have this unit cell and space group combination. The space group *I*2/*a* is being used merely to describe the disordered molecule which we have encountered.

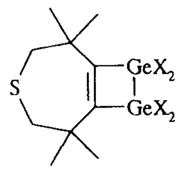
The Ge(1)–Ge(1)′ distance of 2.416(2) Å is typical of Ge–Ge single bonds [20]. The Ge(1)–C(17) distance of 1.958(8) Å is identical within experimental error with the Ge(1)–C(1) and Ge(1)–C(7) distances of 1.941(8) and 1.952(8) Å. The acute C(17)–Ge(1)–Ge(1)′ angle of 75.0(3)° is necessitated by the formation of a four-membered ring and the very different Ge(1)–Ge(1)′ and C(17)–C(17)′ distances of 2.416(2) and 1.41(2) Å, respectively. The narrow C(17)–Ge(1)–Ge(1)′ angle al-

Table 3

Selected distances (Å) and angles (°) for **9** [a]

Distances			
Ge(1)–Ge(1)′	2.416(2)	C(17)–C(18)	1.419(11)
Ge(1)–C(1)	1.941(8)	C(18)–C(19)	1.44(2)
Ge(1)–C(7)	1.952(8)	C(19)–C(19)′	1.37(3)
Ge(1)–C(17)	1.958(8)	C(19)–C(20)	1.46(2)
C(17)–C(17)′	1.41(2)		
Angles			
C(1)–Ge(1)–Ge(1)′	123.3(3)	C(7)–Ge(1)–C(17)	111.5(3)
C(1)–Ge(1)–C(7)	111.7(3)	C(17)–Ge(1)–Ge(1)′	75.0(3)
C(1)–Ge(1)–C(17)	114.4(3)	Ge(1)–C(17)–C(17)′	104.8(8)
C(7)–Ge(1)–Ge(1)′	115.4(3)	Ge(1)–C(17)–C(18)	132.9(8)

[a] Estimated standard deviation in parentheses.

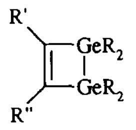


I

a $X = Cl$

b $X = Me$

c $X_2 = (t\text{-}BuN)_2SiMe_2$



II

	R	R'	R''
a	Me	n-Bu	H
b	Me	CF_3	CF_3
c	Ar'	Ph	H
d	Ar''	Ph	H

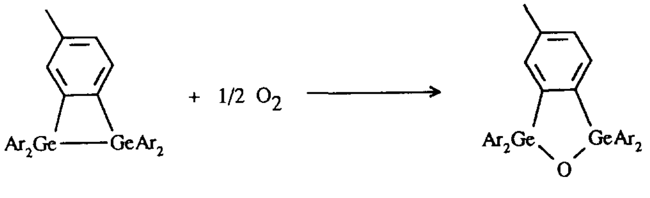
$Ar' = 2,6\text{-}Et_2C_6H_3$

$Ar'' = 2,4,6\text{-}Me_3C_6H_2$

Form 1.

lows opening of the other angles about Ge(1) from tetrahedral (111.5(3)–123.3(3)°). Similarly, the Ge(1)–C(17)–C(17)' and Ge(1)–C(17)–C(18) angles of 104.8(8) and 132.9(8)°, respectively, deviate significantly from the ideal 120° as a result of ring formation. These angular distortions suggest that the Ge_2C_2 ring in **9** is highly strained. The methoxy groups on each aryl ring are oriented such that the methoxy oxygen is directed towards germanium (interatomic distances: Ge(1)–O(1), 2.979(9) and Ge(1)–O(2), 3.012(8) Å). This may indicate a weak interaction between O and Ge although packing forces may also play a role in determining the observed geometry.

The formation of **9** is surprising since it requires loss of a methoxy group from one aryl ring, complete loss of one aryl group and formation of a Ge–Ge bond. The reaction does not occur in the absence of YbI_2 and the red-orange powder **7**, while thermally sensitive, does not decompose to **9** under prolonged reflux. All attempts to maximize the yield of **9** have been unsuccessful and this has precluded reactivity studies. However, the observed air sensitivity of **9** could be due to formation of a 1,3-digerma-2-oxacyclopentene (**III**) by reaction with O_2. This reaction is well-known for the silicon analogues of **9** [17a,17b] but since we have been unable to observe **III** by mass spectroscopy of the decomposition products of **9**, the ultimate fate of this compound in air is still open to speculation.



9

III

While we realize that a wide range of mechanisms could explain the formation of **9**, the product is at least suggestive of a [2 + 2] coupling between a digermene and a benzyne. Although no attempts to trap benzynes with digermenes have been reported, the latter have been shown to react readily with alkynes to form digermacyclobutenes, **I** and **II** [18,19]. Formation of digermenes could occur by decomposition of $KGeAr_3$ to KAr and GeR_2 followed by germene coupling. Germene coupling reactions have been reported previously [19a,19b,21]. Benzyne formation could perhaps occur by decomposition of KAr to 4-methylbenzyne and KOMe. It is not clear what role YbI_2 plays in this reaction but it may catalyze the decomposition of $KGeAr_3$ or KAr (or both). It is clear however that this process represents a minor reaction pathway. Work is currently under way to design a rational route to **9** and related digermacyclobutenes as well as to investigate the reactivity of complexes **5** and **6**.

Supplementary material available

Full tables of distances (S1), angles (S2) and anisotropic thermal parameters (S3) for **9** (3 pages). Ordering information is given on any current masthead page.

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