Preparation, Structural Characterization, and Reactivities of (Digermanyl)lithium. Its Application to the Synthesis of Bis(1,1-diphenyl-2,2,2-trimethyldigermanyl)platinum(II)

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(Pentamethyldigermanyl)lithium ($Me_3GeGeMe_2Li$, **1a**) and (1,1-diphenyl-2,2,2-trimethyldigermanyl)lithium ($Me_3GeGePh_2Li$, **1b**) were prepared and characterized by spectroscopic methods. The structure of (digermanyl)lithium **1b** was established by X-ray diffraction. The reaction of **1b** with *cis*-$PtCl_2(PMe_2Ph)_2$ gave the expected substitution product, *trans*-$Pt(Me_3GePh_2Ge)_2(PMe_2Ph)_2$.

Group 14 element-centered alkali metals show a number of interesting and useful reactions not only in group 14 element chemistry but also in organic synthesis.[1,2] Their nucleophilicity makes them valuable reagents for introducing group 14 element groups into molecules. Group 14 element-centered anions also play important roles as one electron-transfer and reducing reagents. Kraus and Foster pioneered the preparation of triphenylgermyl alkali metal in liquid ammonia solvents,[3] and later trialkylgermyl alkali metals in hexamethylphosphoric triamide (HMPA)[2e] were introduced. Despite the large number of these reports on monogermyl alkali metals,[2] digermanyl alkali metals had never been isolated and characterized. The cleavage of germanium–germanium bonds is readily effected by alkali metals. We report herein the first preparation of (pentamethyldigermanyl)lithium, $Me_3GeGeMe_2Li$ (**1a**) and (1,1-diphenyl-2,2,2-trimethyldigermanyl)lithium, $Me_3GeGe\text{-}Ph_2Li$ (**1b**), and structural characterization of **1b** by X-ray diffraction analysis. We also describe the preparation of bis(1,1-diphenyl-2,2,2-trimethyldigermanyl)platinum(II) by the treatment of **1b** with *cis*-dichloroplatinum(II).

The treatment of pentamethyldigermane ($Me_3GeGeMe_2H$) and 1,1-diphenyl-2,2,2-trimethyldigermane ($Me_3GeGePh_2H$) in THF with one molar amount of *tert*-butyllithium in hexane at low temperature produced $Me_3GeGeMe_2Li$ (**1a**) and $Me_3GeGePh_2Li$ (**1b**), respectively, in quantitative yields (eq 1). (Digermanyl)lithium, **1a** and **1b**, were characterized by NMR analysis[4] and chemical trapping experiments.

$$Me_3GeGeR_2H \xrightarrow{t\text{-BuLi/THF}} Me_3GeGeR_2Li \qquad (1)$$

$$R = Me\ (\mathbf{1a}),\ -40\ °C,\ 10\ min;\ R = Ph\ (\mathbf{1b}),\ -10\ °C,\ 1\ h$$

The (digermanyl)lithium **1b** could be recrystallized from pentane at −15 °C as air-sensitive colorless needles. Like other organolithium compounds, **1b** was highly inflammable in the air. The (digermanyl)lithium **1a** was very unstable and its isolation failed. The molecular structure of **1b** was unequivocally confirmed by X-ray diffraction.[5] The lithium atom is coordinated by three THF molecules and Ge–Li distance of 2.683(8) Å. The Ge–Li distance of **1b** is somewhat longer than that of monogermyllithium, R_3GeLi (2.57–2.67 Å).[6–9] The Ge–Ge bond distance of 2.4601(6) Å is longer than those of $(Me_2Ge)_6$ (2.375 Å)[10] and is the same as those of $(Ph_2Ge)_6$ (2.46 Å).[11] As shown in Figure 1, one trimethylgermyl (Me_3Ge) group and two phenyl groups are arranged so as to give the eclipsed conformation relative to the three THF molecules in **1b**. The bond angles around the anionic germanium atom are contracted (the sum of the angles is 315°).

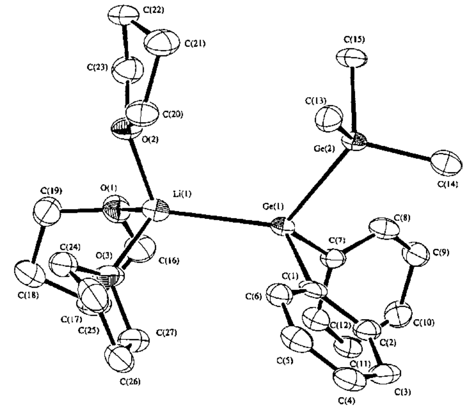

Figure 1. Molecular structure of **1b**.

The NMR spectrum shows that **1b** has three THF molecules coordinated to the lithium atom. The ^7Li NMR chemical shift observed at δ 0.36 is reasonable for the completely THF solvated monomer **1b**.

Hydrolysis of **1** with D_2O gave the corresponding deuteriodigermanes quantitatively. On reaction of **1** with trimethylchlorosilane (Me_3SiCl), substitution reactions occurred to give the corresponding Me_3Si-substituted digermanes (**1a** 59%, **1b** 83%). The reaction of **1b** with alkyl, phenyl, and benzyl halides gave the corresponding substitution products. These results are summarized in Table 1.

As shown in Table 1, (digermanyl)lithium **1b** is a useful nucleophilic reagent for formation of the Ge–Ge–C bond under mild conditions.

Continuously, we have undertaken hitherto unknown Ge–Ge–Pt bond formation by the treatment of Pt–Cl bond with **1b**. Complex *cis*-$PtCl_2(PMe_2Ph)_2$ reacted with two molar amounts

Table 1. Reactions of $Me_3GeGePh_2Li$ (**1b**) with electrophiles[a]

Reagent	Product	Yield/%[b]
D_2O	$Me_3GeGePh_2D$	100
Me_3SiCl	$Me_3GeGePh_2SiMe_3$	83
Me_3GeCl	$(Me_3Ge)_2GePh_2$	63
MeI	$Me_3GeGePh_2Me$	100
EtBr	$Me_3GeGePh_2Et$	100
$PhCH_2Cl$	$Me_3GeGePh_2CH_2Ph$	100
PhBr	$Me_3GeGePh_3$	19

[a]Reactions were carried out at r.t. for 30 min in hexane. [b]GC yields.

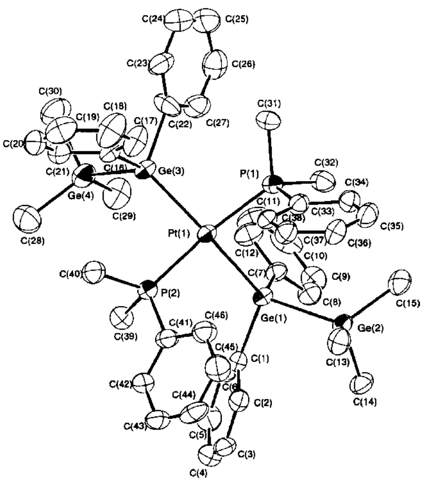

Figure 2. Molecular structure of **2**.

of **1b** in benzene at room temperature for 1 h to give *trans*-Pt($GePh_2GeMe_3$)$_2$(PMe_2Ph)$_2$ (**2**) as pale yellow crystals.

$$cis\text{-}PtCl_2(PMe_2Ph)_2 + \underset{\mathbf{1b}}{2Me_3GeGePh_2Li} \xrightarrow[\text{benzene}]{\text{r.t., 1 h}} \underset{\mathbf{2}}{trans\text{-}Pt(Me_3GeGePh_2)_2(PMe_2Ph)_2} \quad (2)$$

Complex **2** in C_6D_6 was stable and did not isomerize to the cis isomer at room temperature for a few days. The structure of **2** was established by spectroscopic methods[12] coupled with X-ray analysis.[13]

Complex **2** has distorted square-planar trans geometry with the dihedral angles between the planes composed of P(1)–Pt(1)–Ge(1) and P(2)–Pt(1)–Ge(3) being 29.4°. The deformation from planarity is considered to be caused by a steric repulsion between the bulky ligands. The sum of four angles about platinum was 367° (Figure 2).

The Pt–Ge distances of **2** (2.4882(8) and 2.5269(8) Å) are similar to those of Pt(R_3Ge)$_2$(*tert*-phosphine)$_2$ (2.44–2.52 Å).[14] The Ge–Ge distances of **2** (2.4698(11) and 2.4748(13) Å) are somewhat longer than those of (Ph_2Ge)$_6$ (2.46 Å).[11]

The ^{1}H NMR of complex *trans*-**2** displayed two methyl signals of the platinum-bound $GePh_2GeMe_3$ at 0.31 (s) ppm and PMe_2Ph ligands at 1.38 ppm (virtual triplet). The ^{31}P NMR showed a singlet with satellites at −11.4 ppm ($^1J_{\text{Pt–P}} =$ 2788 Hz).

Further applications of the (digermanyl)lithium species in organogermanium synthesis will be reported soon.

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References and Notes

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4 **1a**·3thf: ^{1}H NMR (δ, C_6D_6) 0.54 (s, 9H), 0.68 (s, 6H), 1.23 (m, 12H), 3.39 (m, 12H); ^{7}Li NMR (δ, C_6D_6) 0.54. **1b**·3thf: ^{1}H NMR (δ, C_6D_6) 0.58 (s, 9H), 1.25 (m, 12H), 3.38 (m, 12H), 7.12–8.00 (m, 10H); ^{13}C NMR (δ, C_6D_6) 1.1, 25.4 (THF), 68.4 (THF), 124.4, 127.2, 137.0, 137.6; ^{7}Li NMR (δ, C_6D_6) 0.36.

5 Crystallographic data for **1b**•3thf: $C_{27}H_{43}O_3Ge_2Li$, $M_r =$ 567.73, monoclinic, $P2_1/n$, $a = 10.7550(6)$, $b = 15.0150(18)$, $c = 17.7410(17)$ Å, $\beta = 95.931(6)°$, $V = 2849.6(5)$ Å^3, $Z =$ 4, $D_{\text{calcd}} = 1.323$ g cm^{-3}, $F(000) = 1184$, $\mu = 2.133$ mm^{-1}, $R = 0.0612$ ($I > 2\sigma(I)$), $wR_2 = 0.1576$ (all data), GOF = 1.277.

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12 **2**: ^{1}H NMR (δ, C_6D_6) 0.31 (s, 9H), 1.38 (vt with two satellites, $J_{\text{Pt–P}} = 32.8$ Hz, $J_{\text{P–H}} = 3.1$ Hz, 10H), 7.26–7.62 (m, 20H); ^{13}C NMR (δ, C_6D_6) 1.8, 18.8, 125.7, 126.7, 127.7, 129.4, 131.0, 135.8, 137.5, 149.5; ^{31}P NMR (δ, C_6D_6) −11.4 (s, with two satellites, $J_{\text{Pt–P}} = 2788$ Hz).

13 Crystallographic data for **2**: $C_{46}H_{60}Ge_4P_2Pt$, $M_r = 1160.33$, triclinic, $P\bar{1}$, $a = 10.411(3)$, $b = 10.7140(14)$, $c =$ 23.617(6) Å, $\alpha = 94.738(13)$, $\beta = 96.092(11)$, $\gamma =$ 115.097(13)°, $V = 2348.2(9)$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.641$ g cm^{-3}, $F(000) = 1144$, $\mu = 5.596$ mm^{-1}, $R = 0.0768$ ($I > 2\sigma(I)$), $wR_2 = 0.2170$ (all data), GOF = 1.345.

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