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Synthesis and Characterization of β-Diketiminate Germanium(II) Compounds

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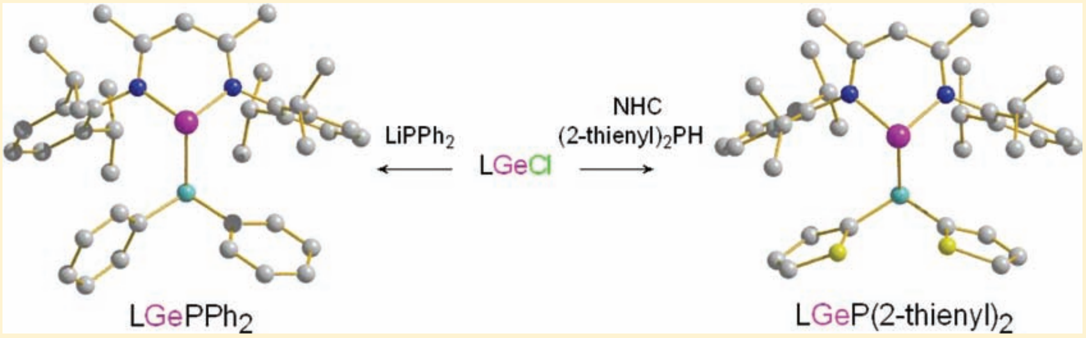
Supporting Information



ABSTRACT: Reactions of LGeCl (L = CH[C(Me)N(Ar)]$_2$; Ar = 2,6-iPr$_2$C$_6$H$_3$) with KOtBu or LiR (R = 2-thienyl, N(H)Ar, PPh$_2$) yielded the germanium(II) compounds LGeR [R = OtBu (**1**), 2-thienyl (**2**), N(H)Ar (**3**), PPh$_2$ (**4**)]. The reduction of (2-thienyl)$_2$PCl with lithium afforded the diphosphane [(2-thienyl)$_2$P]$_2$ (**5**). The treatment of (2-thienyl)$_2$PCl with LiAlH$_4$ or KHBtBu$_3$ led to the formation of (2-thienyl)$_2$PH (**6**). The NHC-assisted reaction of LGeCl and **6** resulted in the isolation of LGeP(2-thienyl)$_2$ (**7**). This is the first example where NHC is used for eliminating HCl from compounds with P−H and Ge−Cl bonds. All solid products were characterized by elemental analysis, NMR and IR spectroscopy, and single-crystal X-ray structure determination.

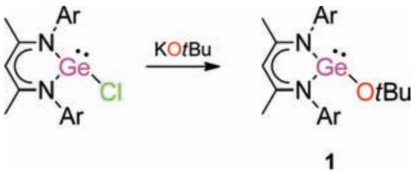
INTRODUCTION

Germylenes are heavier divalent carbene analogues[1] and contain a singlet lone pair capable of binding to transition metals in a coordinate fashion.[2] Transition metal−germylene chemistry has attracted special attention because of the increased propensity of addition reactions across the M−Ge^{II} bond for the activation of a variety of small molecules and functional groups.[3,4] Typically, group 10 metal germylene complexes have shown the feasibility to interact with H$_2$, CO$_2$,[5] O$_2$,[4,6] and COS.[7] However, the synthesis of M−Ge^{II} compounds by using the heteroleptic germylene LGeR (L = monovalent ligand) with tunable substituents R is still limited in its variety. It will be of interest to incorporate additional donor functionalities adjacent to the Ge^{II} center to provide further bonding sites for different metal fragments. The latter may compete or collaborate with each other and turn out to be efficient catalysts. In this approach, we have obtained some results by using π-donor derivatives of composition LGeC≡CR′ to generate their metal complexes with Cu^{I} and Ag^{I} acceptors.[8] To extend this work, we adopt a different strategy by preparing germylenes containing adjacent σ-donor functionalities as precursors. Therefore, we describe herein the syntheses and characterization of LGeR [L = CH[C(Me)N(Ar)]$_2$; Ar = 2,6-iPr$_2$C$_6$H$_3$; R = OtBu (**1**), 2-thienyl (**2**), N(H)Ar (**3**), PPh$_2$ (**4**), and P(2-thienyl)$_2$ (**7**)].

RESULTS AND DISCUSSION

The metathesis reaction of LGeCl (L = HC[C(Me)N(Ar)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) with 1 equiv of KOtBu was carried out in Et$_2$O to give the targeted complex LGeOtBu (**1**, Scheme 1) in moderate yield. The ^{1}H NMR resonances for the β-diketiminate ligand are similar to those observed for related germanium(II) compounds,[9] with typical isopropyl patterns of

Scheme 1. Formation of Compound 1 (Ar = 2,6-iPr$_2$C$_6$H$_3$)



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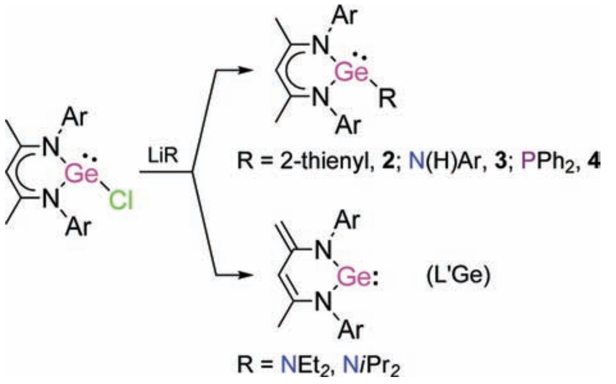
two septets for CH groups and four doublets for methyl groups. A high-field singlet (0.82 ppm) indicates the presence of the *t*Bu group. This method (elimination of alkali-metal chloride) is found to be also applicable to the synthesis of $LGeOC_6F_5$, which was alternatively accessible by the nucleophilic addition of L′Ge (L′ = $HC[\{C(CH_2)N(Ar)\}C(Me)N(Ar)]$) to C_6F_5OH.[10] In contrast, an attempt to react LGeCl with LiOAr* (Ar* = 2,6-$t\mathrm{Bu}_2$-4-MeC_6H_2) under the same conditions or even at elevated temperatures was not successful, which is presumably due to the increased steric hindrance around the LiO moiety.

Analogously, the reaction of LGeCl with the in situ formed 2-thienyl−Li from 2-thienyl bromide and *n*BuLi allowed isolation of LGe(2-thienyl) (**2**; Scheme 2). In the ^1H NMR spectrum, three characteristic multiplets (7.35, 7.33, and 6.82 ppm) indicate the presence of a thienyl group with correct integration ratios relative to those of the *β*-diketiminato ligand backbone.

Scheme 2. Formation of Compounds 2−4 and L′Ge (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$)

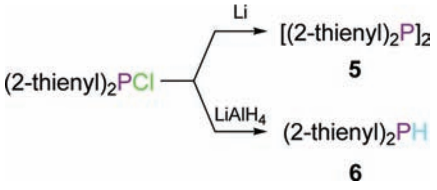


The treatment of LGeCl with $LiNEt_2$ or Li*Ni*Pr$_2$ led to an immediate color change of the reaction solution from bright yellow to brown red and finally resulted in the formation of L′Ge instead of the expected $LGeNEt_2$ or LGe*Ni*Pr$_2$ (Scheme 2). The syntheses of $LGeNH_2$ and $LGeNMe_2$ have been previously demonstrated.[11] The result obtained through the elimination of LiCl and secondary amine is exactly the same as that from the reaction of LGeCl with $LiN(SiMe_3)_2$.[12] It has also been demonstrated that L″$GeN(SiMe_3)_2$ could be isolated with the support of a smaller *β*-diketiminato ligand (L″ = $HC[\{C(CH_2)N(Ar)\}C(Me)N(Ph)]$).[13] On the contrary, the treatment of LGeCl with LiN(H)Ar smoothly afforded LGeN(H)Ar (**3**) in good yield (Scheme 2), in spite of the increased steric bulk around the N center of the lithium amide precursor. In another route, **3** was obtained by reducing LGeCl with K.[14] Consequently, we assume that LGeNR′$_2$ derivatives are only stable when R′ substituents are small enough, while LGeN(H)R′ compounds may be obtained with larger R′ groups.

A toluene solution of LGeCl was treated with the filtrate of the reaction solution of Ph_2PCl and lithium chips in tetrahydrofuran (THF). After the addition of the chips, the color of the mixture changed rapidly into a dark red. After workup, a crystalline solid of $LGePPh_2$ (**4**) was obtained from an *n*-hexane extract (Scheme 2). The ^{31}P NMR spectrum of **4** displays a low-field singlet (−14.91 ppm), which is close to that in $[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}CH_2NMe_2)P]_2Ge$ (−45.8 ppm)[15] and distinct from that found in $LGeP(SiMe_3)_2$ (−192.7 ppm).[16] The *β*-diketiminato ligand plays an important role in stabilizing compounds like **4**. Reference reactions of $GeCl_2$·dioxane with 2 equiv of $LiPPh_2$·2THF in the absence or presence of NHC gave a mixture of products consisting of diphosphane $(Ph_2P)_2$[17] as the major side product.

However, unlike the facile formation of **4**, no reaction was observed between LGeCl and the lithium-treated (2-thienyl)$_2$PCl. Therefore, we focused on this lithiation process. The treatment of (2-thienyl)$_2$PCl in THF with lithium chips was accompanied by a color change of the solution from colorless to bright yellow. After filtration, a crystalline solid of [(2-thienyl)$_2$P]$_2$ (**5**; Scheme 3) was obtained in good yield from the concentrated filtrate. The ^{31}P NMR chemical shift of **5** (−38.64 ppm) is significantly upfield-shifted when compared with that of the precursor (2-thienyl)$_2$PCl (53.23 ppm). In the ^1H and ^{13}C NMR spectra, the thienyl groups are unequivocally identified. The resulting product was **5**,[18] which was further characterized by single-crystal X-ray structural analysis.

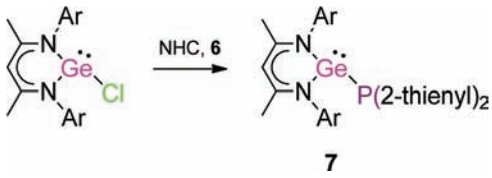
Scheme 3. Formation of Compounds 5 and 6



Therefore, we switched to secondary phosphine as the precursor[19] for preparing (2-thienyl)$_2$PLi. The treatment of (2-thienyl)$_2$PCl with $LiAlH_4$ (or KHB*t*Bu$_3$) in OEt_2 provided a colorless liquid [(2-thienyl)$_2$PH (**6**)] in low yield (Scheme 3). In the IR spectrum of **6**, the characteristic band (2285 cm^{-1}) indicates the presence of a PH group, which is in the expected range (Mes_2PH, 2361 and 2338 cm^{-1}, where Mes = 2,4,6-$Me_3C_6H_2$).[19] The ^1H NMR spectrum shows a doublet (5.49 ppm) with a $^1J_{PH}$ coupling constant of 294.1 Hz, which is consistent with the observation of a singlet (−90.06 ppm) in the ^{31}P NMR spectrum. These data are highly comparable to those for Mes_2PH (^1H, 5.36 ppm, $^1J_{PH}$ = 235 Hz; ^{31}P, −92.4 ppm).[19] However, further reaction of **6** with *n*BuLi gave a mixture of products according to NMR monitoring.

Also the treatment of LGeCl with lithium chips was not successful. The isolated product was LLi. Subsequently, **6** was treated with LGeCl in the presence of N-heterocyclic carbene (NHC), where NHC functions as a HCl scavenger (Scheme 4).

Scheme 4. Formation of Compound 7 (NHC = [C(Me)N(*i*Pr)]$_2$C)



The same NHC-involved strategy was before successfully applied to synthesize germanium(II) hydroxide LGeOH by hydrolysis of LGeCl.[20] To a mixture of LGeCl and NHC in toluene was added a THF solution of **6**. A color change from yellow to dark red occurred almost instantly. A crystalline solid of LGeP(2-thienyl)$_2$ (**7**) was obtained from the *n*-hexane

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**, **2**, **4**, and **7**

	LGeO*t*Bu (**1**), X = O(1)	LGe(2-thienyl) (**2**), X = C(16)	$LGePPh_2$ (**4**), X = P(1)	$LGeP(2\text{-thienyl})_2$ (**7**), X = P(1)
Ge(1)−X	1.8272(14)	1.966(9)	2.4746(11)	2.4453(15)
Ge(1)−N(1)	2.0312(14)	1.993(4)	2.003(3)	2.031(3)
Ge(1)−N(2)	2.0159(14)	1.993(4)	2.029(3)	2.025(4)
O(1)−C(30)	1.431(2)			
N(1)−Ge(1)−N(2)	87.68(5)	91.7(2)	88.20(11)	88.65(14)
N(1)−Ge(1)−X	95.97(5)	99.5(3)	99.24(8)	101.39(11)
N(2)−Ge(1)−X	94.46(6)	99.5(3)	99.29(8)	97.88(11)
C(30)−O(1)−Ge(1)	121.60(11)			
C(30)−P(1)−C			99.14(16)	104.3(2)
C(30)−P(1)−Ge(1)			100.25(10)	94.26(17)
C−P(1)−Ge(1)			100.69(12)	100.04(16)

Table 2. Crystal Data, Data Collection Parameters, and Structure Refinement Details for Compounds **1**, **2**, **4**, **5**, and **7**

	LGeO*t*Bu (**1**)	LGe(2-thienyl) (**2**)	$LGePPh_2$ (**4**)	$[(2\text{-thienyl})_2P]_2$ (**5**)	$LGeP(2\text{-thienyl})_2$ (**7**)
CCDC	851949	851950	851951	851952	851953
empirical formula	$C_{33}H_{50}GeN_2O$	$C_{33}H_{44}GeN_2S$	$C_{41}H_{51}GeN_2P$	$C_{16}H_{12}P_2S_4$	$C_{37}H_{47}GeN_2PS_2$
fw	563.34	573.35	675.40	394.44	687.45
temp, K	173(2)	173(2)	173(2)	173(2)	173(2)
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	*Cmca*	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	13.341(3)	22.3720 (13)	17.202(3)	8.8941(18)	10.3778(8)
b, Å	16.611(3)	9.3145 (7)	12.099(2)	8.5353(17)	15.2472(16)
c, Å	15.085(3)	28.869 (3)	18.032(4)	11.821(2)	22.2675(18)
α, deg	90	90	90	90	90
β, deg	107.07(3)	90	99.31(3)	104.99(3)	93.784(8)
γ, deg	90	90	90	90	90
V, $Å^3$	3195.7(11)	6015.8 (8)	3703.6(13)	866.9(3)	3515.8(5)
Z	4	8	4	2	4
D_{calcd}, g/cm^3	1.171	1.266	1.211	1.511	1.299
μ, mm^{-1}	0.984	1.112	0.900	0.724	1.064
F(000)	1208	2432	1432	404	1448
cryst size, mm	0.60 × 0.45 × 0.22	0.50 × 0.40 × 0.05	0.10 × 0.10 × 0.10	0.27 × 0.20 × 0.07	0.10 × 0.10 × 0.02
θ range, deg	3.04−27.48	2.76−25.00	3.00−25.00	3.36−25.00	2.67−25.00
index range	$-17 \le h \le 17$ $-21 \le k \le 21$ $-19 \le l \le 19$	$-26 \le h \le 24$ $-6 \le k \le 11$ $-14 \le l \le 34$	$-20 \le h \le 20$ $-14 \le k \le 14$ $-19 \le l \le 21$	$-10 \le h \le 10$ $-10 \le k \le 10$ $-14 \le l \le 14$	$-11 \le h \le 12$ $-18 \le k \le 17$ $-26 \le l \le 15$
reflns collected/unique	30657/7307 [*R*(int) = 0.0379]	8440/2709 [*R*(int) = 0.0591]	28277/6499 [*R*(int) = 0.0645]	6461/1514 [*R*(int) = 0.0417]	16594/6158 [*R*(int) = 0.0970]
data/restraints/param	7307/4/364	2709/19/192	6499/0/417	1514/0/100	6158/4/399
GOF on F^2	1.081	1.080	1.165	1.234	1.027
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0319, wR2 = 0.0771	R1 = 0.0895, wR2 = 0.1778	R1 = 0.0406, wR2 = 0.0870	R1 = 0.0964, wR2 = 0.2997	R1 = 0.0732, wR2 = 0.0882
R indices (all data)	R1 = 0.0451, wR2 = 0.0823	R1 = 0.1205, wR2 = 0.1924	R1 = 0.0717, wR2 = 0.1189	R1 = 0.1151, wR2 = 0.3419	R1 = 0.1275, wR2 = 0.1005
largest diff peak/hole, e/$Å^3$	0.357/−0.299	0.867/−1.627	0.741/−0.985	2.193/−0.760	0.529/−0.499

extract in moderate yield. The ^{31}P NMR spectrum displays a singlet (−74.87 ppm), which is markedly low-field-shifted relative to that of **6** (−90.06 ppm). In the ^1H NMR spectrum of **7**, the distinct doublet for PH proton resonance of secondary phosphine disappears and three multiplets (6.85, 6.52, and 6.50 ppm) are assignable to proton resonances of the thienyl groups. In contrast, the reaction of LGeH and $(2\text{-thienyl})_2PCl$ in the presence of NHC does not yield **7**. For comparison reasons, the above-mentioned $LGeOC_6F_5$ could also not be obtained using the NHC-assisted metathesis reaction of LGeCl and C_6F_5OH.[21]

The composition of compounds **1**, **2**, **4**, **5**, and **7** was further confirmed by single-crystal X-ray structural analysis. Selected bond lengths and angles are reported in Table 1 (except for compound **5**), and crystal data and collection parameters are listed in Table 2. The Ge and P centers are all three-coordinate, and each adopts a pyramidal geometry. Pyramidalization was measured by calculating the angle (θ) at the center of the pyramid.[22] The obtained θ_{Ge} angles [123.3° (**1**), 120.1° (**2**), 121.1° (**4**), 120.8° (**7**)] indicate an evident deviation from planarity ($\theta = 90°$) and are more or less close to the ideal case with three mutually perpendicular Ge 4p atomic orbitals ($\theta \approx 125.3°$). It is suggested that the germanium σ orbital owns a high 4p character in the Ge−X (X = O, C, P) bond, while a lone pair of electrons occupies the germanium vertex with high 4s character.[16,23] The θ_P angles [117.8° (**4**), 117.6° (**5**), 118.1°

(7)] are found in a narrow range and suggest a situation for P vertexes similar to those for Ge sites. Compounds **1**, **2**, **4**, and **7** each consist of a puckered C_3N_2Ge six-membered ring in boat conformation. Compound **2** shows the structural features of the parent LGeCl in terms of the orientation of substituents at the Ge center as well as the comparable folding angle between N(1)−C(2)−C(4)−N(2) (denoted as N_2C_2) and N_2Ge planes [19.18° (**2**), 21.18° (LGeCl)]. In contrast, the folding angles for compounds **1**, **4**, and **7** are much wider [34.34° (**1**), 36.59° (**4**), 39.19° (**7**)], and the corresponding substituents are all bent down relative to the prow atom.

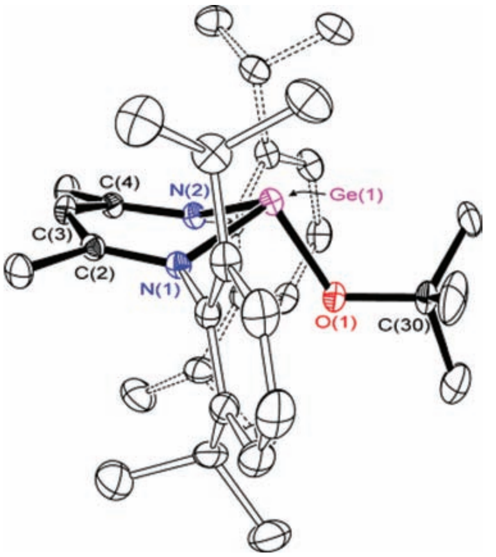


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% level, and all H atoms are omitted for clarity.

Compound **1** crystallizes from *n*-hexane in the monoclinic space group $P2_1/n$ (Table 2). The molecular structure of **1** (Figure 1) features a nearly right angle of N−Ge−O (95.21° av) and a bent Ge−O−C linkage [121.60(11)°]. These data are marginally larger but still comparable to those of the phenyl analogue LGeOPh [93.88 and 117.5(4)°].[10] It is noted that the Ge−O bond length [1.8272(14) Å] is evidently shorter than those observed for $(C_5H_5)Sn(\mu\text{-O}t\text{Bu})_2\text{GeO}t\text{Bu}$ [1.839(10) Å],[24] NHC·Ge(O*t*Bu)$_2$ [1.874(5) Å],[25] and aryl-substituted analogues LGeOPh [1.860(4) Å] and $LGeOC_6F_5$ [1.9515(14) Å].[10] Comparable Ge−O distances are found in LGeOH [1.828(1) Å][20] and Ge(OAr′)$_2$ [1.826(1) and 1.827(1) Å; Ar′ = 2,3,5,6-Ph_4C_6H].[26] In addition, the O−C bond separation of **1** [1.431(2) Å] is longer than those of terminal alkoxyl groups in compounds mentioned above (1.319−1.424 Å).[10,24,25]

Compound **2** represents the first structurally characterized complex with a thienyl group bound directly to the Ge^{II} center. The crystal structure of **2** (Figure 2) is of higher symmetry (orthorhombic, *Cmca*) than that of **1**. A mirror plane passes through C(3), Ge(1), and the thienyl group. The imposed symmetry implies that the thienyl ring is exactly planar and perpendicular to the N_2C_2 plane. The S atom is directed opposite to the lone pair of electrons on the Ge center. The N−Ge−C angle [99.5(3)°] is a little wider than the N−Ge−O angle in **1** (95.25° av), and the Ge−C bond length [1.966(9) Å] is slightly longer than those found in germanium(IV) thienyl compounds (1.94−1.95 Å).[27]

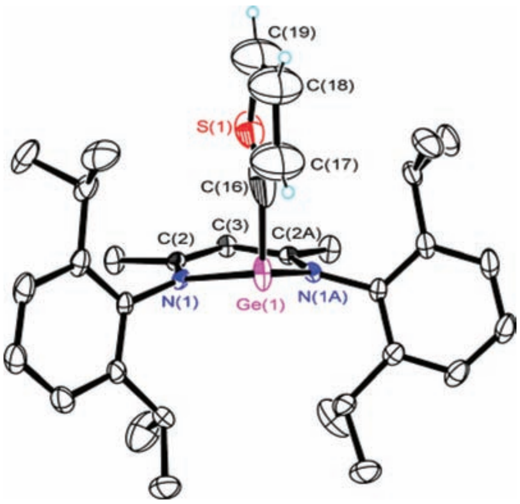


Figure 2. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% level, and all H atoms, except those of the thienyl group, are omitted for clarity.

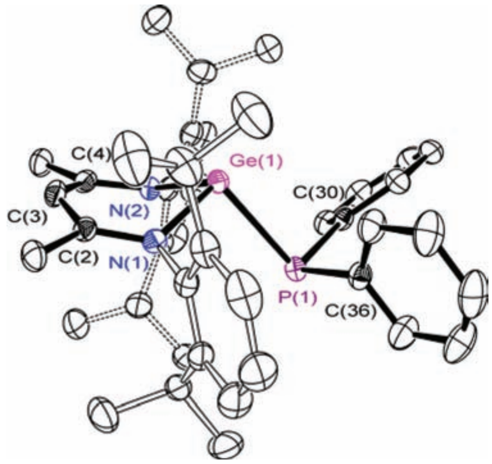


Figure 3. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% level, and all H atoms are omitted for clarity.

Compound **4** (Figure 3) crystallizes as bright-yellow crystals in the monoclinic space group $P2_1/c$. The N−Ge−P (99.26° av), Ge−P−C (100.47° av), and C−P−C [99.14(16)°] angles are very close to each other. The chemically active lone pairs at the respective Ge and P apexes are located in a trans arrangement along the Ge−P vector. Two phenyl planes are almost mutually perpendicular (87.55°), while their angles relative to the N_2C_2 quasi-plane are quite different (48.61 vs 69.27°). Although some other compounds containing the $-GePPh_2$ moiety have been previously structurally characterized, none of them has a three-coordinate P atom bound to the Ge^{II} center.[28] The Ge−P bond length [2.4746(11) Å] of **4** is substantially longer than those found in related germanium(II) compounds [2.333(1)−2.4300(11) Å][15,16,29] and slightly shorter than those in dimeric (tBu$_2$PGeCl)$_2$ [2.4876(8) Å][30] as well as in the adduct $Ph_3P\cdot GeCl_2$ [2.5084(7) Å].[31] The product of the reaction of (2-thienyl)$_2$ PCl and Li is [(2-thienyl)$_2$P]$_2$ (**5**). The single-crystal X-ray structural analysis of **5** is shown in Figure 4. The P(1)−P(1A) bond length of 2.241(3) Å falls in the expected range of compounds with P−P single bonds.

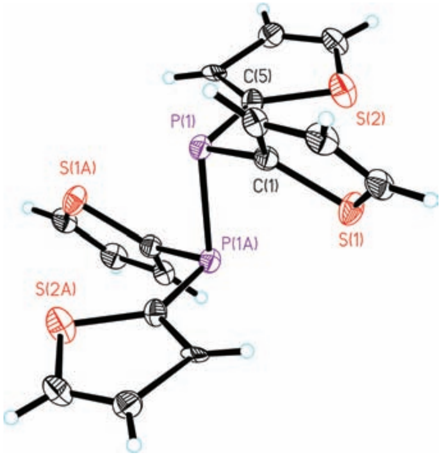


Figure 4. Molecular structure of **5**. Thermal ellipsoids are drawn at the 50%. Selected bond lengths (Å) and angles (deg): P(1)−P(1A) 2.241(3), P(1)−C(1) 1.822(7), P(1)−C(5) 1.822(6); C(1)−P(1)−C(5) 104.6(3), C(1)−P(1)−P(1A) 97.5(2), C(5)−P(1)−P(1A) 98.7(2).

Compound **7** (Figure 5) crystallizes in the monoclinic space group $P2_1/n$. The C−P−C angle of **7** [104.3(2)°] is a little wider than that of **4** [99.03(19)°], while the angle between the two thienyl planes (135.98°) is much broader than that for their phenyl counterparts in **4** (87.93°). The two thienyl planes show similar angles of 78.15° and 79.71° relative to the N_2C_2 quasi-plane, respectively. The Ge−P bond length [2.4453(15) Å] of **7** is a little shorter than that in **4** [2.4746(11) Å]. In line with **4**, the lone pairs of electrons at Ge and P sites are directed to the opposite direction. As such, the S atoms on thienyl groups gain the chance of being aligned with the Ge center,[32] creating a bowl-like environment with potential chelating ability.

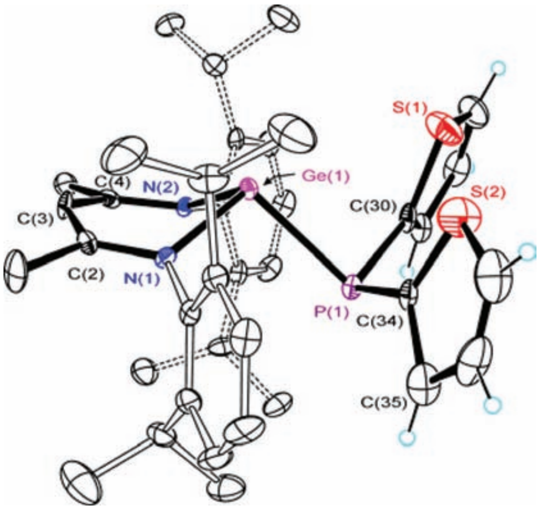


Figure 5. Molecular structure of **7**. Thermal ellipsoids are drawn at the 50% level, and all H atoms, except those of the thienyl groups, are omitted for clarity.

■ CONCLUSION

Germanium(II) compounds of composition LGeR (L = CH[C(Me)N(Ar)]$_2$; Ar = 2,6-iPr$_2$C$_6$H$_3$) containing adjacent σ-donating functionalities [R = OtBu (**1**), 2-thienyl (**2**), N(H)Ar (**3**), PPh$_2$ (**4**)] were obtained from the reaction of LGeCl with the corresponding alkali-metal precursors. The preparation of the (2-thienyl)$_2$PLi precursor was not successful by the treatment of (2-thienyl)$_2$PCl with lithium. Instead, the diphosphane **5** was formed in this reduction. **7** was successfully prepared from the NHC-assisted reaction of LGeCl and **6**. This is the first example where NHC is used for eliminating HCl from compounds with P−H and Ge−Cl functionalities. The Ge as well as the P centers exhibit pyramidal geometry and accommodate a lone pair of electrons with high 4s character. **1** represents an interesting example with short Ge−O and long O−C bond lengths. Germanium(II) compounds with 2-thienyl (**2**), PPh$_2$ (**4**), and P(2-thienyl)$_2$ (**7**) substituents are interesting precursors for coordination compounds.

■ EXPERIMENTAL SECTION

Materials and Methods. All manipulations were carried out under nitrogen using Schlenk techniques or inside a Mbraun glovebox filled with argon, in which the calibrated values of O_2 and H_2O were controlled below 1.2 ppm. Organic solvents including toluene, n-hexane, THF, and Et$_2$O were predried with sodium wire and then heated with sodium/potassium benzophenone under nitrogen prior to use. C$_6$D$_6$ was degassed, dried with a sodium/potassium alloy, and filtered before use. NMR spectra were recorded on a Bruker AV 500 spectrometer. Melting points were measured in a sealed glass tube using a Büchi B-540 instrument without correction. IR spectra were recorded on a Nicolet 380 (Thermo Fisher Scientific) spectrometer. Elemental analysis was performed with a Thermo Quest Italia SPA EA 1110 instrument. Chemicals commercially available were purchased from Aldrich and used as received. GeCl$_2$·dioxane,[33] LGeCl (L = HC[C(Me)N(Ar)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$),[9] LGeH,[34] L′Ge (L′ = HC[{C(CH$_2$)N(Ar)}C(Me)N(Ar)]),[12] LiPPh$_2$·2THF,[35] (2-thienyl)$_2$PCl,[36] LiOAr* (Ar* = 2,6-tBu$_2$-4-MeC$_6$H$_2$),[37] LiOC$_6$F$_5$, LiNEt$_2$, LiNiPr$_2$, LiN(H)Ar,[38] and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (abbreviated as NHC)[39] were prepared as described in the literature or by modified methods.

*LGeOtBu (**1**).* At −18 °C, a suspension of KOtBu (0.12 g, 1 mmol) in Et$_2$O (20 mL) was added drop by drop to a solution of LGeCl (0.53 g, 1 mmol) in Et$_2$O (30 mL). The mixture was stirred and warmed to room temperature. After stirring for additional 12 h, the solvent was removed under vacuum and the residue was extracted with n-hexane (8 mL). The extract was stored at −18 °C in a freezer for 2 days, and X-ray-quality pale-yellow block crystals of **1** were obtained (0.41 g, 73%). Mp: 216 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$, ppm): δ 7.05−7.20 (m, Ar), 4.64 (s, 1 H, γ-C*H*), 3.86 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*Me$_2$), 3.37 (sept, $^3J_{HH}$ = 7.0 Hz, 2 H, C*H*Me$_2$), 1.54 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 1.54 (s, 6 H, β-*Me*), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH*Me*$_2$), 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 0.82 (s, 9 H, C*Me*$_3$). ^{13}C NMR (126 MHz, C$_6$D$_6$, ppm): δ 163.66 (CN), 145.20, 144.23, 139.69, 126.50, 124.02, 123.73 (*Ar*), 94.73 (γ-CH), 69.74 (CMe$_3$), 33.24 (C*Me*$_3$), 28.50, 28.33 (*C*HMe$_2$), 25.87, 24.60, 24.37, 24.08 (CH*Me*$_2$), 22.47 (β-*Me*). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1658.52 (vw), 1621.28 (vw), 1562.66 (w), 1554.89 (w), 1520.4 (w), 1322.76 (m), 1173.01 (w), 1099.79 (vw), 1057.79 (vw), 1019.26 (w), 935.43 (w), 891.32 (vw), 850.2 (vw), 793.87 (w), 765.43 (w), 608.33 (vw). Anal. Calcd for C$_{33}$H$_{50}$GeN$_2$O (563.4): C, 70.35; H, 8.95; N, 4.97. Found: C, 68.78; H, 8.73; N, 4.94.

*LGe(2-thienyl) (**2**).* At −50 °C, nBuLi (0.52 mL, 2.4 M, 1.25 mmol) was added drop by drop to a solution of 2-bromothiophene (0.20 g, 1.25 mmol) in Et$_2$O (30 mL). The mixture was stirred and warmed to room temperature. Additional stirring for 12 h ensured the complete formation of 2-thienyllithium. The light-brown suspension of 2-thienyllithium obtained was added to a solution of LGeCl (0.53 g, 1 mmol) in Et$_2$O (30 mL) at −18 °C. After stirring for 12 h, the solvent was removed under vacuum and the residue was treated upon quick washing with cold n-hexane (2 × 2 mL) and then extracted with n-hexane (10 mL). The extract was kept at −18 °C for 2 days, and X-ray-quality pale-yellow crystals of **2** were obtained (0.37 g, 65%). Mp: 191

°C. ^{1}H NMR (500.13 MHz, C_6D_6, ppm): δ 7.35 (m, 1H, *H*C5), 7.33 (m, 1H, *H*C3), 6.83−7.20 (m, Ar), 6.82 (m, 1H, *H*C4), 5.10 (s, 1 H, *γ*-C*H*), 3.64 (sept, $^3J_{HH}$ = 7.0 Hz, 2 H, C*H*Me$_2$), 2.98 (sept, $^3J_{HH}$ = 7.0 Hz, 2 H, C*H*Me$_2$), 1.63 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, CH*Me*$_2$), 1.41 (s, 6 H, *β-Me*), 1.17 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, CH*Me*$_2$), 1.07 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, CH*Me*$_2$), 0.69 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, CH*Me*$_2$). ^{13}C NMR (126 MHz, C_6D_6, ppm): δ 165.93 (CN), 146.67, 143.33, 141.24 (*Ar*), 137.16 (*C*5), 130.02 (*C*3), 127.09 (*Ar*), 125.53 (*C*4), 124.59, 123.94 (*Ar*), 98.93 (*γ*-CH), 29.01, 28.10 (CHMe$_2$), 25.54, 24.50, 24.34, 23.80 (CH*Me*$_2$), 23.22 (*β-Me*). IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1658.3 (vw), 1621.73 (vw), 1551.76 (w), 1529.15 (w), 1316.22 (m), 1256.18 (w), 1170.76 (w), 1098.75 (w), 1056.95 (w), 1019.84 (w), 968.25 (w), 934.97 (w), 852.04 (w), 794.37 (w), 757.06 (w), 636.56 (vw), 520.32 (vw). Anal. Calcd for $C_{33}H_{44}GeN_2S$ (573.42): C, 69.12; H, 7.73; N, 4.89. Found: C, 68.57; H, 7.58; N, 4.91.

LGeN(H)Ar (3). The preparation of **3** is similar to that of **2** using ArHNLi (2.4 mmol), which is in situ formed from the reaction of $ArNH_2$ (0.5 mL, 2.4 mmol), *n*BuLi (1 mL, 2.4 M in *n*-hexane, 2.4 mmol), and LGeCl (1.26 g, 2.4 mmol) as starting materials. Compound **3** was obtained as colorless crystals (1.1 g, 69%). Spectroscopic data are identical with those previously reported.[14]

LGePPh$_2$ (4). Finely divided lithium chips (0.07 g, 10 mmol)) were added to a solution of Ph_2PCl (0.44 g, 2 mmol) in THF (30 mL) at room temperature. The mixture was vigorously stirred for 6 h, and Ph_2PLi was formed and added via filtration to a solution of LGeCl (1.05 g, 2 mmol) in Et_2O (40 mL) at −18 °C. The mixture was stirred and warmed to room temperature. After additional stirring for 12 h, all volatiles were removed under vacuum and the residue was extracted with *n*-hexane (15 mL). The solution was concentrated (ca. 5 mL) and then stored at −18 °C in a freezer. After 2 days, dark-red crystals of **4** were obtained (0.96 g, 71%). Mp: 202 °C. ^{1}H NMR (500.13 MHz, C_6D_6, ppm): δ 6.75−7.02 (m, *Ar*), 4.73 (s, 1 H, *γ-CH*), 4.14 (m, 2 H, C*H*Me$_2$), 3.23 (sept, $^3J_{HH}$ = 7.0 Hz, 2 H, C*H*Me$_2$), 1.69 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH*Me*$_2$), 1.44 (s, 6 H, *β-Me*), 1.20 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH*Me*$_2$), 1.07 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH*Me*$_2$), 0.98 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, CH*Me*$_2$). ^{13}C NMR (126 MHz, C_6D_6, ppm): δ 166.42 (CN), 144.98, 143.16, 141.25 (*Ar*), 140.75 (d, J_{PC} = 27.9 Hz, *Ph*), 135.38 (d, J_{PC} = 16.9 Hz, *Ph*), 134.50 (d, J_{PC} = 13.0 Hz, *Ph*), 134.40 (d, J_{PC} = 12.8 Hz, *Ph*), 127.00, 125.70, 124.92 (*Ar*), 124.22 (*Ph*), 96.97 (*γ*-CH), 29.00, 28.93, 28.40 (CHMe$_2$), 25.18, 24.90, 24.46, 24.07, 23.99 (CH*Me*$_2$), 22.58 (*β-Me*). ^{31}P NMR (202 MHz, C_6D_6, ppm): δ −14.91. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2668.8 (w), 1555.19 (w), 1513.4 (w), 1319.14 (m), 1257.2 (m), 1174.6 (w), 1096.81 (w), 1058.43 (w), 1017.62 (w), 965.87 (w), 933.92 (w), 853.24 (w), 792.56 (w), 758.11 (w), 736.9 (m), 694.79 (m), 519.4 (vw), 498.68 (vw), 475.86 (vw), 445.02 (vw). Anal. Calcd for $C_{41}H_{51}GeN_2P$ (675.47): C, 72.9; H, 7.61; N, 4.15. Found: C, 71.81; H, 7.56; N, 4.19.

[(2-Thienyl)$_2$P]$_2$ (5). Finely divided lithium chips (0.04 g, 5 mmol)) were added to a solution of (2-thienyl)$_2$PCl (0.23 g, 1 mmol) in THF (20 mL) at room temperature. The mixture was vigorously stirred for 6 h. All volatiles were removed under vacuum, and the residue was extracted with *n*-hexane (10 mL). The extract was concentrated (ca. 5 mL) and stored at −18 °C in a freezer. After 2 days, pale-yellow crystals of **5** were obtained (0.34 g, 87%). Mp: 136 °C. ^{1}H NMR (500.13 MHz, C_6D_6, ppm): δ 7.24 (m, 1H, *H*C5), 6.59 (m, 1H, *H*C3), 6.58 (m, 1H, *H*C4). ^{13}C NMR (126 MHz, C_6D_6, ppm): δ 136.41 (t, J_{PC} = 15.7 Hz, *C*5), 132.13 (*C*3), 128.95 (*C*2), 128.18 (*C*4). ^{31}P NMR (202 MHz, C_6D_6, ppm): δ −38.64. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1623.14 (m), 1552.6 (s), 1321.57 (s), 1276.05 (m), 1259.37 (m), 1220.93 (w), 1174.31 (m), 1100.4 (m), 1057.63 (m), 1021.81 (m), 974.83 (w), 935.12 (w), 889.51 (vw), 854.09 (w), 796.32 (m), 758.35 (m), 596.15 (vw), 524.52 (vw). Anal. Calcd for $C_{16}H_{12}P_2S_4$ (394.47): C, 48.72; H, 3.07. Found: C, 48.35; H, 3.13.

(2-Thienyl)$_2$PH (6). The preparation of **6** was accomplished like that of Mes_2PH[19] from (2-thienyl)$_2$PCl (0.47 g, 2 mmol) and $LiAlH_4$ (0.08 g, 2 mmol) to give a colorless liquid. Yield: 0.09 g (23%). ^{1}H NMR (500.13 MHz, C_6D_6, ppm): δ 7.12−7.14 (m, 1 H, *H*C5), 6.98 (m, 1 H, *H*C3), 6.63 (m, 1 H, *H*C4), 5.49 (d, $^1J_{PH}$ = 294.11 Hz, 1 H). ^{13}C NMR (126 MHz, C_6D_6, ppm): δ 136.27 (d, J_{PC} = 27.8 Hz, *C*5), 133.03 (d, J_{PC} = 24.1 Hz, *C*2), 131.97 (*C*3), 127.98 (*C*4). ^{31}P NMR (202 MHz, C_6D_6, ppm): δ −90.06. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2284.96 (w, *PH*), 1408.22 (m), 1334.8 (w), 1219.34 (s), 1083.91 (m), 1053.9 (vw), 1002.94 (s), 895.61 (w), 851.56 (m), 831.97 (w), 796.56 (m), 742.06 (w), 703.81 (vs), 501.39 (w), 424.22 (m).

LGeP(2-thienyl)$_2$ (7). At −18 °C, KBH*t*Bu$_3$ (1 mL, 1 M in Et_2O, 1 mmol) was added to a solution of (2-thienyl)$_2$PCl (0.23 g, 1 mmol) in Et_2O (30 mL). This mixture was stirred and warmed to room temperature. After additional stirring for 12 h, the complete formation of **6** was observed, and the suspension obtained was added to a mixture of LGeCl (0.53 g, 1 mmol) and NHC (0.18 g, 1 mmol) in Et_2O (40 mL) at −18 °C. The mixture was vigorously stirred and warmed to room temperature. After additional stirring for 12 h, all volatiles were removed under vacuum to give an oily paste. A small portion of *n*-hexane (3 mL) was layered on this paste. By storing the oily paste at room temperature for 1 week, dark-red crystals of **7** were obtained (0.26 g, 38%). Mp: 198 °C. ^{1}H NMR (500.13 MHz, C_6D_6, ppm): δ 6.83−7.20 (m, *Ar*), 6.85 (m, 1H, *H*C5), 6.52 (m, 1H, *H*C3), 6.50 (m, 1H, *H*C4), 4.70 (s, 1 H, *γ-CH*), 4.03 (m, 2 H, C*H*Me$_2$), 3.25 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, C*H*Me$_2$), 1.78 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 1.42 (s, 6 H, *β-Me*), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$), 1.09 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, CH*Me*$_2$), 1.06 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH*Me*$_2$). ^{13}C NMR (126 MHz, C_6D_6, ppm): δ 166.42 (*C*N), 144.90, 143.07, 140.48 (*Ar*), 140.11 (d, J_{PC} = 42.2 Hz, *C*2), 136.40 (*C*5), 133.35 (d, J_{PC} = 19.7 Hz, *C*4), 128.93 (*C*3), 127.03, 124.78, 124.25 (*Ar*), 96.63 (*γ*-CH), 28.70, 28.70 (CHMe$_2$), 25.06, 24.95, 24.51, 24.27 (CH*Me*$_2$), 22.48 (*β-Me*). ^{31}P NMR (202 MHz, C_6D_6, ppm): δ −74.87. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2669 (m), 1709.76 (vw), 1691.65 (vw), 1658.99 (vw), 1641.71 (vw), 1620.57 (vw), 1553.48 (w), 1513.75 (w), 1316.64 (s), 1215.64 (w), 1170.14 (m), 1096.55 (w), 1079.23 (w), 1055.53 (w), 1014.84 (w), 966.33 (w), 934.14 (w), 890.97 (w), 845.03 (w), 822.71 (w), 792.62 (w), 704.01 (w), 692.71 (w), 570.22 (vw), 516.23 (vw), 498.9 (vw), 428.11 (vw). Anal. Calcd for $C_{37}H_{47}GeN_2PS_2$ (687.53): C, 64.64; H, 6.89; N, 4.07. Found: C, 64.01; H, 6.73; N, 4.11.

Structure Determination. Data were collected on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer for **1**, **4**, and **5** and an Oxford Gemini S Ultra system for **2** and **7**. In all cases, graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) was used in ω-scan mode. Absorption corrections were applied using the spherical harmonics program (multiscan type). The structures were solved by direct methods (*SHELXS-97*)[40] and were refined by full-matrix least squares on F^2 with the program *SHELXL-97*.[41] In general, the non-H atoms were located by difference Fourier synthesis and refined anisotropically, and H atoms were included using the riding model with U_{iso} tied to U_{iso} of the parent atoms unless otherwise specified. A summary of cell parameters, data collection, and structure solution and refinement is given in Table 2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal data (CIF) for compounds **1**, **2**, **4**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(32) One of the thienyl rings exhibits disorder at the S(2) and C(35) sites because the same crystallographic position of them is settled by C(35′) and S(2′), respectively. This disorder could not be removed by reducing the symmetry of the space group. Thus, the structure of **7** is best described with the help of the occupation factors 0.64 and 0.36.

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