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Short Communication

Tobias Böttcher* and Cameron Jones*

Synthesis and crystal structures of extremely bulky phosphinoamido and phosphinoamino germanium(II) chloride complexes

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Abstract: Reaction of an extremely bulky potassium amide complex, $KL^{\dagger}$ ($L^{\dagger}=[Ar^{\dagger}(PPh_2)N]^-$, $Ar^{\dagger}=C_6H_2\{C(H)Ph_2\}_2Pr^i$-2,6,4), with $GeCl_2$·dioxane afforded low yields of the phosphinoamido and phosphinoamino germanium(II) chloride complexes, $[GeCl_2(\kappa^1$-P-$L^{\dagger}GeCl)]$ and $[GeCl_2(\kappa^1$-P-$L^{\dagger}H)]$, respectively. The X-ray crystal structures, and limited spectroscopic data, for the complexes are reported. Both complexes represent rare examples of phosphine adducts of $GeCl_2$.

Keywords: bulky amide; germanium; germylene; low-coordinate; X-ray crystallography.

The chemistry of low-oxidation-state and/or low-coordination-number main group metal compounds has rapidly expanded since the turn of the millennium (Fischer and Power, 2010). The growing interest in such compounds stems from their intrinsically high reactivity, which has afforded them applications as 'transition metal-like' reagents in synthesis, catalysis, etc. (Power, 2010; Asay et al., 2011). The stabilization of most low-oxidation-state main group compounds has required the employment of very bulky ligand systems, which provide kinetic stabilization to those compounds. Although most attention has focused on bidentate and higher dentate ligands for this task (Jones, 2010; Tsai, 2012), we have investigated the use of extremely bulky monodentate amide ligands, e.g. $\text{-}N(Ar)(SiR_3)$, ($Ar=C_6H_2\{C(H)Ph_2\}_2R'$-2,6,4; $R'=Me$ (Ar^*) or Pr^i ($Ar^{\dagger}$); R=Me, Pr^i, Ph), in this area over the past several years (Li et al., 2011a; Wong et al., 2013). The rationale here is that such ligands have the steric bulk to stabilize very-low-oxidation-state main group systems, while leaving the main group center coordinatively unsaturated and therefore open to reaction with a variety of unsaturated substrates. This has proved to be the case, and a variety of unprecedented main group complex types have been accessed. From group 14, these include the first examples of monomeric amido-germanium halides, e.g. $[(SiMe_3)(Ar^*)NGeCl]$ (Li et al., 2011a), amido-digermynes, e.g. $[\{(SiPr^i_3)(Ar^{\dagger})NGe\}_2]$ (Li et al., 2011b; Hadlington et al., 2013), and two-coordinate germanium hydrides, e.g. $[\{Si(OBu^t)_3\}(Ar^{\dagger})NGeH]$ (Hadlington et al., 2015). Moreover, examples of the latter complex type have proven to act as efficient catalysts for the hydroboration of aldehydes and ketones, exhibiting activities that rival those of most transition metal-based catalysts used for such transformations (Hadlington et al., 2014).

We wished to extend the library of extremely bulky amide ligands at our disposal to include examples that have P-functionalities α to the amido center. The idea here was that these amides could act as hemi-labile ligands toward coordinated main group metal centers, thus increasing the stability of the metal complex without reducing its reactivity significantly. To this end, we have recently developed a range of the target ligands, e.g. $L^{\dagger}$ ($=[Ar^{\dagger}(PPh_2)N]^-$), which we have shown can act as monodentate κ^1-N-donor ligands toward low-oxidation-state silicon centers, while also exhibiting weak intramolecular P···Si interactions (Böttcher and Jones, 2015). We wished to extend the range of such complexes to those derived from germanium, e.g. $[L^{\dagger}GeCl]$, which could be used as precursors to amido-digermyne and/or amido-germanium hydride complexes. Although attempts to prepare $[L^{\dagger}GeCl]$ were not successful, they did lead to the low-yield formation of the related complexes, $[GeCl_2(\kappa^1$-P-$L^{\dagger}GeCl)]$ and $[GeCl_2(\kappa^1$-P-$L^{\dagger}H)]$, the X-ray crystal structures of which are reported herein.

Reaction of one equivalent of the potassium amide complex, $KL^{\dagger}$, with $GeCl_2$·dioxane in THF did not give

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***Corresponding authors: Tobias Böttcher and Cameron Jones,**
School of Chemistry, Monash University, PO Box 23, Melbourne, Victoria 3800, Australia, e-mail: tobias.boettcher@ac.uni-freiburg.de (T. Böttcher), cameron.jones@monash.edu (C. Jones)

[L†GeCl], but instead led to a mixture of products that included the secondary amine L†H as the major component. Workup of the reaction mixture led to isolation of a few yellow crystals of the toluene soluble amido-germanium chloride complex, [GeCl$_2$(κ^1-*P*-L†GeCl)] **1**, and the hexane soluble amino-germanium chloride, [GeCl$_2$(κ^1-*P*-L†H)] **2** (Scheme 1). It is not known what causes the generation of L†H in this reaction, but it is reproducible and is not due to the presence of adventitious water. It is possible that compound **1** is formed *via* reaction of initially generated [L†GeCl] with GeCl$_2$·dioxane, whereas compound **2** could result from reaction of *in situ* formed L†H with GeCl$_2$·dioxane. With that said, attempts to obtain a higher isolated yield of **1** by reacting KL† with two equivalents of GeCl$_2$·dioxane were unsuccessful. Similarly, reacting L†H directly with GeCl$_2$·dioxane afforded a mixture of products containing only a small amount of **2**, as determined by a ^{31}P NMR spectroscopic analysis of the reaction solution.

Given the extremely low isolated yields of **1** and **2**, very few spectroscopic data could be obtained for the complexes. However, by monitoring both the 1:1 and 1:2 reactions by ^{31}P NMR spectroscopy (C$_6$D$_6$ solutions), broad signals at δ 45.2 and 22.3 ppm can be tentatively assigned to **1** and **2**, respectively, as the lower field signal predominates in the 1:2 reaction. The only other signal observed in these spectra is due to the secondary amine, L†H (δ=38.2 ppm), and this confirms the amine is the major component in both reaction mixtures.

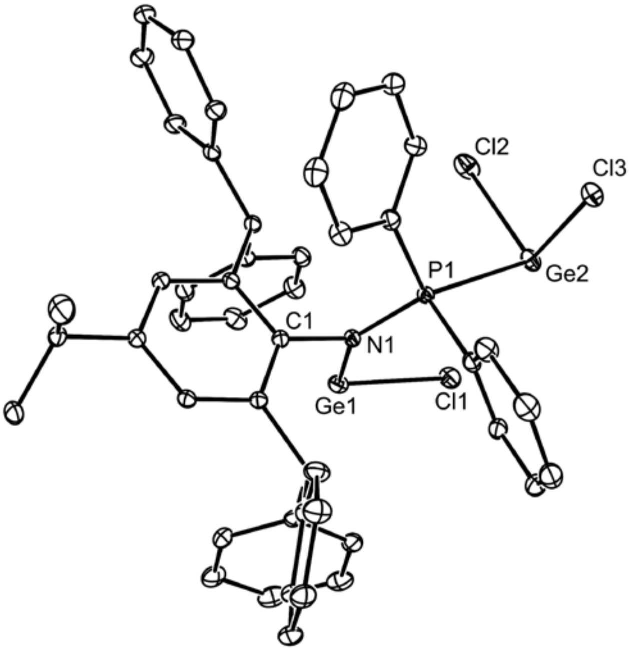
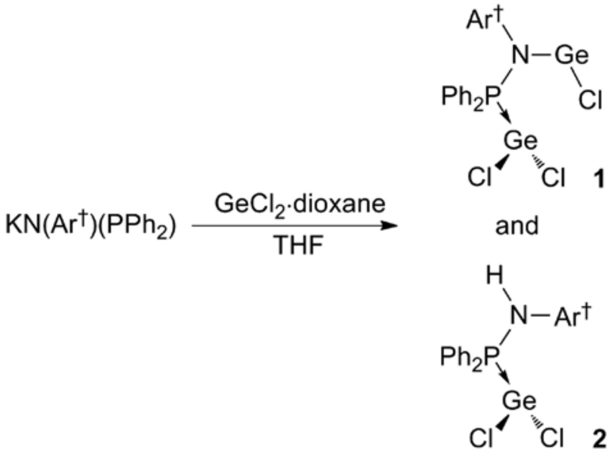


Figure 1: Thermal ellipsoid plot (30% probability surface) of the molecular structure of **1** (hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Ge(1)-N(1) 1.903(2), Ge(1)-Cl(1) 2.2405(8), P(1)-N(1) 1.706(2), P(1)-Ge(2) 2.5725(8), Ge(2)-Cl(3) 2.2785(9), Ge(2)-Cl(2) 2.3038(9), Cl(1)···Ge(2) 3.084(1), N(1)-Ge(1)-Cl(1) 96.55(6), Cl(3)-Ge(2)-Cl(2) 97.12(3), Cl(3)-Ge(2)-P(1) 91.06(3), Cl(2)-Ge(2)-P(1) 92.49(2), Ge(1)-Cl(1)···Ge(2) 108.6(1).

Both **1** and **2** were crystallographically characterized, and their molecular structures are depicted in Figures 1 and 2 (see also Table 1). Compound **1** is monomeric and can be considered as an adduct between the tertiary phosphine center of the germanium amide, L†GeCl, and the GeCl$_2$ fragment. The geometric parameters within the L†GeCl fragment of the molecule are similar to those in [(SiPr$^{i}_{3}$)(Ar†)NGeCl] (Hadlington et al., 2013) and are suggestive of a high s-character lone pair of electrons at its germanium center [Σ angles at Ge(2)=280.7°]. The dative P→Ge bond in the compound, 2.5725(8) Å, is slightly longer than those in the handful of other crystallographically characterized phosphine adducts of GeCl$_2$, e.g. 2.5087(7) Å in [GeCl$_2$(PCy$_3$)] (Swarnakar et al., 2014), presumably due to the imposing steric bulk of the L†GeCl fragment. The intramolecular Cl(1)···Ge(2) distance (3.084(1) Å) is well within the sum of the van der Waals radii for the two elements [3.86 Å (Mantina et al., 2009), cf. sum of covalent radii=2.20 Å (Pyykkö and Atsumi, 2009)], and therefore, there is a possibility of an interaction between the atoms (cf. 4-coordinate adducts of GeCl$_2$, e.g. [(κ^2-*N*,*N′*-tmeda)GeCl$_2$] (Cheng et al., 2010). However, it is also possible that Cl(1) is directed toward Ge(2) for steric reasons.



Scheme 1: Preparation of compounds **1** and **2** (Ar†=C$_6$H$_2${C(H)Ph$_2$}$_2$Pr^{i}-2,6,4).

In the solid state, compound **2** is monomeric and can be considered as an adduct between the P-center of the protonated ligand, L†H, and the GeCl$_2$ fragment. Interestingly, the NH moiety lies on the opposite side of the molecule to the GeCl$_2$ fragment, whereas both the NGeCl

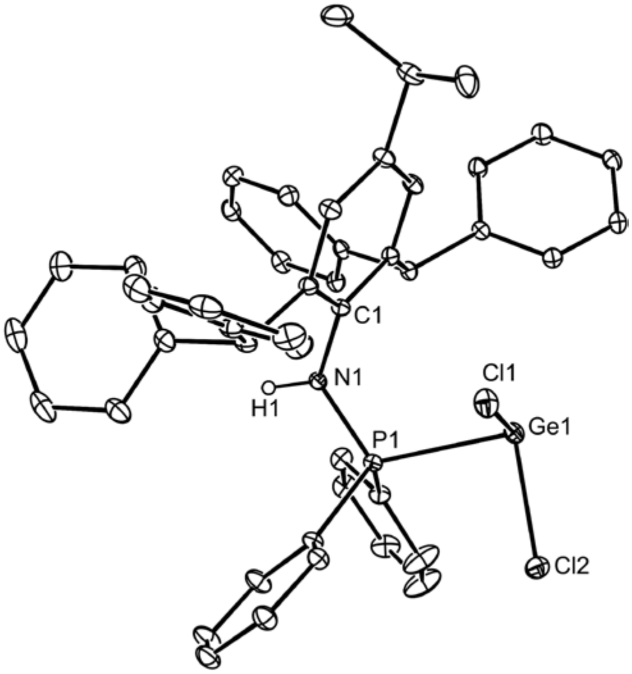


Figure 2: Thermal ellipsoid plot (30% probability surface) of the molecular structure of **2** [hydrogen atoms, except H(1), omitted]. Selected bond lengths (Å) and angles (°): Ge(1)-Cl(1) 2.2451(7), Ge(1)-Cl(2) 2.2734(8), Ge(1)-P(1) 2.5435(8), P(1)-N(1) 1.670(2), Cl(1)-Ge(1)-Cl(2) 96.32(3), Cl(1)-Ge(1)-P(1) 96.87(2), Cl(2)-Ge(1)-P(1) 90.00(3), N(1)-P(1)-Ge(1) 110.74(7).

Table 1: Summary of crystallographic data for compounds **1** and **2**.

	1	2
Empirical formula	$C_{47}H_{41}Cl_3Ge_2NP$	$C_{47}H_{42}Cl_2GeNP$
Formula weight	902.31	795.28
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	14.029(3)	9.0920(18)
b (Å)	13.926(3)	19.908(4)
c (Å)	21.395(4)	21.674(4)
α (deg)	90	90
β (deg)	99.59(3)	92.21(3)
γ (deg)	90	90
Volume (Å^3)	4121.5(14)	3920.2(14)
Z	4	4
ρ (calcd) (g/cm^3)	1.454	1.347
μ (mm^{-1})	1.727	0.993
F(000)	1840	1648
Reflections collected	38 032	36 921
Unique reflections	9646	9325
R_{int}	0.0791	0.0471
R1 indices [$I>2\sigma(I)$]	0.0433	0.0427
*w*R2 indices (all data)	0.1166	0.1095
Largest peak/hole (e/Å^3)	0.48, -1.20	1.39, -0.96
CCDC no.	1419563	1419564

and $GeCl_2$ units in **1** lie on the same side of that molecule. This might add weight to the proposal of a weak intramolecular Cl···Ge interaction in the latter. The Ge center in **2** (Σ angles=283.2°) exhibits a similar degree of pyramidalization to Ge(2) in **1**, although its P-Ge distance (2.5435(8) Å) is slightly shorter, presumably because of the lesser steric strain in **2**.

In summary, complexes of extremely bulky phosphinoamido and phosphinoamino ligands with germanium(II) chloride fragments have been prepared and structurally characterized. The complexes represent rare examples of phosphine adducts of $GeCl_2$, and one possibly exhibits an intramolecular Cl···Ge interaction in the solid state. We continue to develop the application of bulky amides to the stabilization of low oxidation state/low coordination number main group compounds and will report on our efforts in this direction in due course.

Experimental details

General

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. THF, hexane, and toluene were distilled over potassium. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance III 400 spectrometer and were referenced to the residual proton resonance of the solvent used or external 85% H_3PO_4. The compound $KL^\dagger$ was prepared by the literature procedure (Böttcher and Jones, 2015), whereas all other reagents were used as received.

Preparation of [$GeCl_2(\kappa^1$-*P*-$L^\dagger GeCl)$] 1 and [$GeCl_2(\kappa^1$-*P*-$L^\dagger H)$] 2

A solution of $KL^\dagger$ (0.30 g, 0.43 mmol) in THF (50 mL) was added to a solution of $GeCl_2$·dioxane (0.093 g, 0.40 mmol) in THF (20 mL) at -80°C. The reaction mixture was then warmed to ambient temperature and stirred overnight, yielding a yellow solution. Volatiles were removed from this under vacuum, and the residue washed with hexane (ca. 15 mL). Placing the hexane washings at -30°C overnight led to deposition of a small number of yellow crystals of **2** (<2% yield). The hexane insoluble residue from the washing was dissolved in toluene (ca. 10 mL) and the extract placed at -30°C overnight to give a small number of yellow crystals of **1** (<2% yield). Data for **1**: ^1H NMR (400 MHz, 298 K, C_6D_6): δ 0.84 [d, *J*=6.8 Hz, 6H, $CH(CH_3)_2$], 2.34 (sept, *J*=6.8 Hz, 1H, $CH(CH_3)_2$), 5.89 (s, 2H, $CHPh_2$), 6.79–7.50 (m, 32H, *Ar*H); $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 296 K), δ=45.2 (br.). Data for **2**: $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 296 K), δ=22.3 (br.). N.B. (1) Due to the very low yields of the compounds, no further characterizing data could be obtained. (2) The $L^\dagger H$ by-product can be recrystallized from the reaction mixture if required.

X-ray crystallography

Crystals of 1 and 2 suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were carried out at 100(2) K and were made using the MX1 beamline of the Australian Synchrotron (λ=0.71080 Å). All structures were solved by direct methods and refined on F^2 by full-matrix least squares (SHELX97) (Sheldrick, 1997) using all unique data. All non-hydrogen atoms are anisotropic, with hydrogen atoms included in calculated positions (riding model), except the amine proton, H(1) of 2, whose the positional and isotropic thermal parameters were freely refined. Crystal data, details of data collections, and refinement are given in Table 1. Crystallographic data (excluding structure factors) for all structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1419563 and 1419564). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; website: http://www.ccdc.cam.ac.uk).

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