Synthesis of phosphine substituted β-diketiminate based isomeric Ge(II) complexes†‡

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Treatment of phosphine substituted β-diketiminate lithium, $Ph_2PC[C(Me)N(Dipp)]_2LiOEt_2$ (**1**) (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) with dioxane·$GeCl_2$resulted in a five-membered *N*,*P* chelate complex, $Ph_2PC[C(Me)N(Dipp)]_2GeCl$ (**2**). An isomer of **2** CH{[C(CH_2PPh_2)N(Dipp)][C(Me)N(Dipp)]}GeCl (**5**) was obtained from the germanium complex L′Ge (L′ = CH[C(=CH_2)N(Dipp)][C(Me)N(Dipp)])Ge (**4**) and Ph_2PCl. In **5** the PPh_2 group remains uncoordinated. Both complexes were characterized by X-ray structural analysis and in the case of **5** both enantiomers crystallize in the same unit cell.

Introduction

β-Diketiminate ligands occupy a distinct position in metal-coordination chemistry, which is evident from the number of articles published every year on these systems.[1] What makes them important is their tunability, which is both electronic and steric. The steric environment provided by these ligands, especially the 2,6-diisopropylphenyl substituted diketiminate, has been exploited in main-group chemistry for synthesizing species with low valent elements[2] and active metals.[3] Both steric and electronic factors have been utilized in developing efficient homogeneous catalysts[4] and model systems of biological relevance.[5] Barring one example[6] (Fig. 1, **B**, Dipp = 2,6-diisopropylphenyl) β-diketiminate ligands usually form chelate complexes with metals through the N atoms (**C**). Incorporation of groups like –CN and $–NO_2$ at the R^3 position (**A**) has led in some cases to the formation of either coordination polymers[7] or bimetallic systems,[8] without affecting chelation (**D**), while in most cases they have remained spectators.[9]

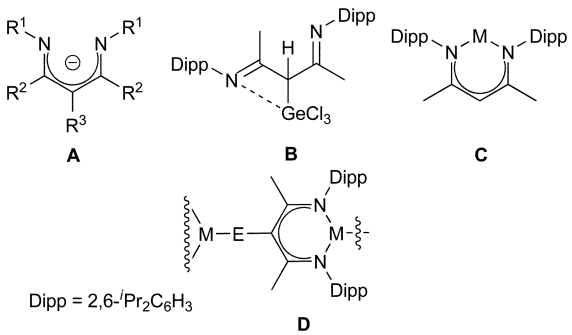

Fig. 1

Phosphines have been well known for stabilizing transition metals especially the late and heavier ones.[10] Introducing a phosphine moiety at the R^2 or R^3 position would lead to potential ligands for synthesizing heterobimetallic systems involving main-group elements and late transition metals. Recently, there have been reports on phosphine substituted β-diketiminate ligands, in which phosphine moieties occupy the R^3 position.[11] We have been interested in heterobimetallic germylenes,[12] which are potential catalysts for olefin polymerization. In continuation of our research in such systems, we explored the reaction of a phosphine substituted (at the R^3 position) β-diketiminate ligand **1** with dioxane·$GeCl_2$. In parallel, we have also designed and executed a synthetic route, *via* germylene, for making β-diketiminate Ge(II) complex with a free phosphine moiety at the R^2 position. These reactions have led to the formation of isomers, however, with different coordination modes, which will be discussed here in detail.

Results and discussion

An equimolar reaction of **1** and the dioxane complex of $GeCl_2$ in ether gives a pale yellow colored product in almost quantitative yield. The product **2** was structurally characterized as an *N*,*P* chelate complex of germanium (Scheme 1), which has been isolated and purified by washing it with *n*-hexane. Compound **2** is formed exclusively and shows a single resonance at δ 15.16 ppm in the ^{31}P NMR spectrum.

The ^{1}H NMR spectrum of **2** exhibits as many as eight doublets for isopropyl methyl groups and four multiplets for methyne protons due to the unsymmetrical nature of the molecule. Interestingly, two of the methyne protons of the isopropyl groups are quite shielded (δ 1.68 and 2.53 ppm). Upon examination of the orientation of methyne protons in the solid state we have found that two protons are in close proximity to the center of the phenyl groups of the phosphine moiety and hence fall in the shielding region of the ring current (see ESI †for orientation). This observation suggests complex **2** has the same structure both in the solid and solution state.

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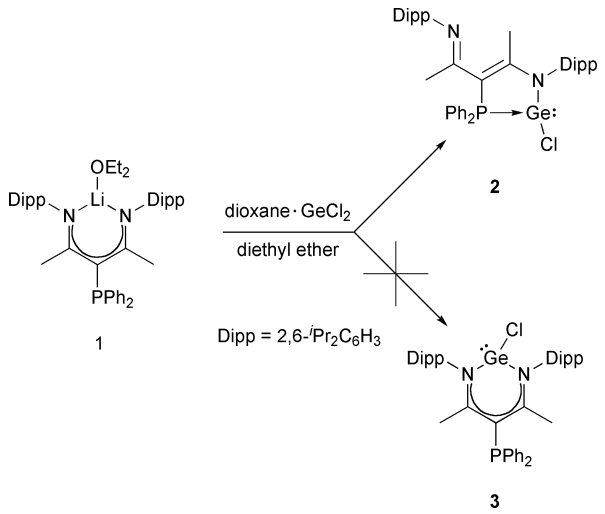
† Electronic supplementary information (ESI) available: ORTEP diagram of **2** showing proximity of methyne protons to phenyl groups. CCDC reference numbers 741341 & 741342. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b915403e

‡ Dedicated to Prof. Richard A. Walton on the occasion of his 70th birthday.



Scheme 1

Single crystals of **2** were obtained from *n*-hexane solution, and a molecular structure with selected bond distances and bond angles is given in Fig. 2. Surprisingly, a thorough search for *N*,*P* chelate complexes of germanium in CCDC resulted in one four-membered ring compound[13] and two six-membered rings,[14] and no five-membered rings were reported. Ge–N and Ge–P bond distances are in the range of those reported for such complexes.[15] The five-membered ring is slightly puckered and no four atoms in the ring fall in one plane. The N(1)–C(26), C(27)–C(28) bond lengths, typical of single bonds, and C(26)–C(27), C(28)–N(2) bond lengths, typical of double bonds, support the formulation given for **2** in Scheme 1.

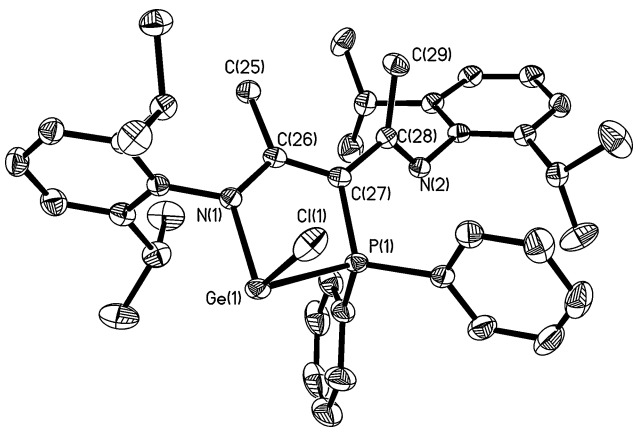


Fig. 2 Molecular structure of **2**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ge(1)–N(1) 1.9700(16), Ge(1)–Cl(1) 2.2934(8), Ge(1)–P(1) 2.4300(11), N(1)–C(26) 1.361(2), C(26)–C(27) 1.385(3), C(27)–C(28) 1.473(3), N(2)–C(28) 1.285(2); N(1)–Ge(1)–Cl(1) 95.63(6), N(1)–Ge(1)–P(1) 80.49(5), Cl(1)–Ge(1)–P(1) 93.16(3), C(26)–N(1)–Ge(1) 123.02(12), N(1)–C(26)–C(27) 121.52(16), C(27)–P(1)–Ge(1) 97.91(7), C(26)–C(27)–P(1) 114.08(14), N(2)–C(28)–C(27) 117.44(16).

The chelation mode of the β-diketiminate in **2** was unexpected, since we were aiming at complex **3** (Scheme 1) in which the phosphine moiety remains a spectator. However, recently it has been demonstrated by Burford and coworkers that the β-diketiminate ligand **1** is in a unusual coordination mode in its As(III) and Sb(III) complexes (Fig. 3, **I**). The Al(III) forms an *N*,*N'* chelate complex, in which the –PPh_2 remains uncoordinated (Fig. 3, **II**).[11b] It is evident from their observation that the mode of coordination depends upon the nature of the metal. In addition to the coordination modes observed so far (**I** and **II** in ref. 11b, **III** in this paper), there is also another mode possible (**IV**).

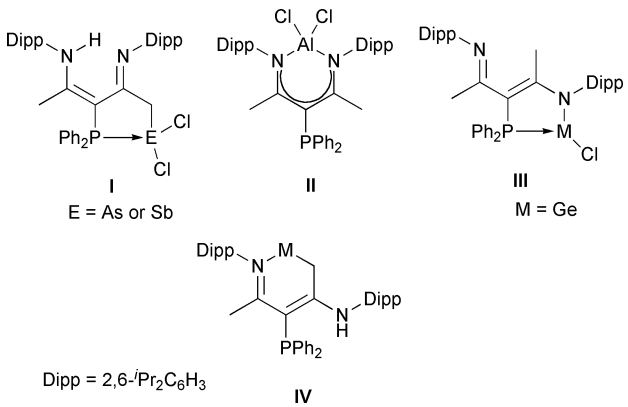
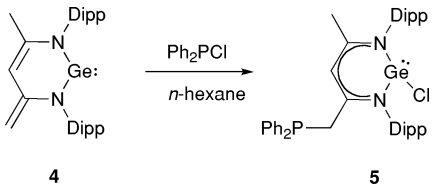


Fig. 3

Recently, from the work of Driess and coworkers[3j] as well as from our results[16] we have learnt that the germylene **4** can be utilized for effecting substitution at the α carbon of the ligand back-bone. In order to introduce the Ph_2P group at this position we have employed Ph_2PCl. A quantitative reaction has occurred when a solution of **4** in *n*-hexane is treated with Ph_2PCl. Product **5** was characterized by NMR and single crystal X-ray studies (Scheme 2).



Scheme 2

As shown in Fig. 4, the *N*,*N'*-chelation mode of the ligand is retained and the Ph_2P group does not interact with Ge(II). As with the previously reported β-diketiminate Ge(II) complexes,[3j,17] Ge deviates away from the plane of the ring, and Ge–N and Ge–Cl bonds are also typical of such complexes. As given in Fig. 4, unlike in **2**, all the C–C and C–N bond lengths of the β-diketiminate skeleton in **5** are almost equal.

The ^{31}P NMR chemical shifts of **2** (15.16 ppm) and **5** (–13.47 ppm) are diagnostic of the coordination mode in these complexes. The complexes **2** and **5** are chiral and the chirality is due to the presence of the out of plane Ge–Cl bond as well as the way the ligand coordinates in **2**, and the unsymmetrical nature of the ligand in **5**. Interestingly, in **5** both enantiomers are present in the same unit cell (Fig. 4).

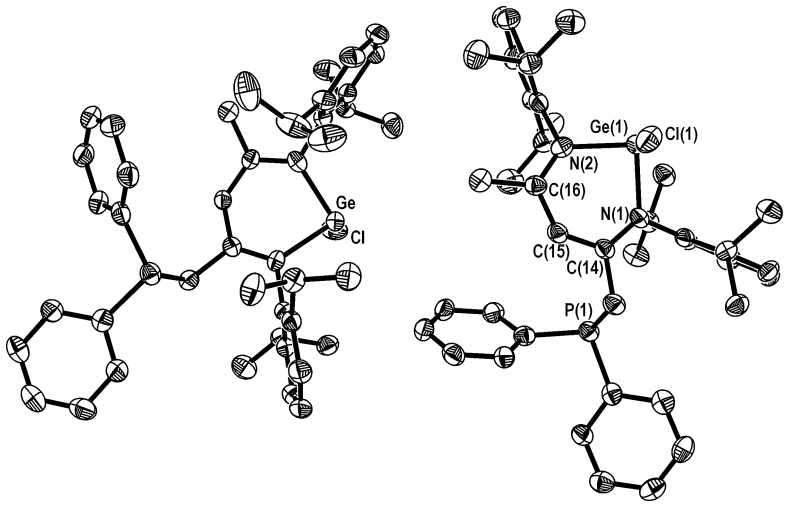


Fig. 4 Molecular structure of **5**, showing both the enantiomers. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ge(1)–N(1) 1.984(3), Ge(1)–N(2) 1.967(3), Ge(1)–Cl(1) 2.3250(11), N(1)–C(14) 1.348(4), C(14)–C(15) 1.400(5), C(15)–C(16) 1.387(5), N(2)–C(16) 1.351(5); N(2)–Ge(1)–N(1) 91.35(12), N(2)–Ge(1)–Cl(1) 93.70(9), N(1)–Ge(1)–Cl(1) 94.61(8).

Experimental

General considerations

All manipulations were performed in a dry and oxygen-free atmosphere (N_2 or Ar) by using Schlenk-line and glove-box techniques. Solvents were purified with the M-Braun solvent drying system. Compounds **1**[11b] (used MeLi in ether) and **4**[16a] were prepared by literature methods. Other chemicals were procured and used as received. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker 500 or 300 MHz instrument and referenced to the deuterated solvent in the case of the ^{1}H and ^{13}C NMR spectra. ^{31}P NMR spectra were referenced to 85% H_3PO_4. Elemental analyses were performed by the Analytisches Labor des Institut für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument and are not corrected.

Crystallographic details. Suitable crystals of **2** and **5** were mounted on a glass fiber and data were collected on an IPDS II Stoe image-plate diffractometer (graphite monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å) at 133(2) K. The data were integrated with X-Area. The structures were solved by Direct Methods (SHELXS-97)[18] and refined by full-matrix least square methods against F^2 (SHELXL-97). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in calculated positions and refined by using a riding model. Crystallographic data are given in Table 1.

Table 1 Crystal data for complexes **2** and **5**

Empirical formula, CCDC-No.	**2** $C_{41}H_{50}ClGeN_2P$, 741342	**5** $C_{41}H_{50}ClGeN_2P$, 741341
T/K	133(2)	133(2)
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
a/Å	11.003(2)	10.060(2
b/Å	11.678(2)	25.670(5)
c/Å	16.335(3)	29.272(6)
α (°)	86.03(3)	90
β (°)	87.29(3)	90
γ (°)	67.40(3)	90
V/Å^3	1932.7(7)	7559(3)
Z	2	8
ρ_c/Mg m^{-3}	1.220	1.247
μ/mm^{-1}	0.932	0.954
F(000)	748	2992
Crystal size/mm	0.49 × 0.36 × 0.34	0.50 × 0.12 × 0.10
θ range [°]	1.89–27.04	1.39–26.02
Reflections collected/unique	17957/8316 [R(int) = 0.0832]	59909/14663 [R(int) = 0.1146]
Reflections observed [$I > 2\sigma(I)$]	7725	12018
Data/restraints/parameters	8316/0/425	14663/0/847
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0439, 0.1177	0.0480, 0.0861
R_1, wR_2 (all data)[a]	0.0467, 0.1199	0.0635, 0.0911
GoF	1.068	1.000
Residual density max./min./e Å^{-3}	1.211/–1.222	0.453/–0.492

[a] $R1 = \sum\|F_o\| - \|F_c\|/\sum\|F_o\|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

Synthesis of 2. To a cooled (–30 °C) suspension of dioxane·$GeCl_2$ complex (1.50 g, 6.47 mmol) in ether (40 mL) was added a suspension of **1** (4.44 g, 6.51 mmol) in ether (40 mL) using a L-bent tube. The resultant mixture was stirred at room temperature overnight and filtered using Celite®. All the volatiles were removed from the filtrate and 50 mL of *n*-hexane was added to the residue. The mixture was stirred well for about 30 min and filtered to obtain a yellow colored powder (2.82 g). The filtrate was kept at room temperature and after one day pale yellow colored crystals were obtained (1.50 g). Total yield 4.32 g (94%). Mp. 288–290 °C. ^{1}H NMR (300.01 MHz, C_6D_6) δ 0.62 (d, 3H, $CH(CH_3)_2$), 0.71 (d, 3H, $CH(CH_3)_2$), 0.81–0.84 (two doublets, 6H, $CH(CH_3)_2$), 1.17–1.21 (two doublets, 6H, $CH(CH_3)_2$), 1.28 (d, 3H, $CH(CH_3)_2$), 1.54 (d, 3H, $CH(CH_3)_2$), 1.68 (m, 1H, $CH(CH_3)_2$), 1.77 (s, 3H, CCH_3), 1.91 (s, 3H, CCH_3), 2.53 (m, 1H, $CH(CH_3)_2$), 3.02 (m, 1H, $CH(CH_3)_2$), 3.98 (m, 1H, $CH(CH_3)_2$), 6.95–7.20 (m, 12H, Ph), 7.82–7.90 (m, 2H, Ph), 8.03–8.11 (m, 2H, Ph) ppm; $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6) δ 21.64, 21.80, 23.03, 23.77, 24.06, 24.29, 24.32, 24.43, 24.49, 24.57, 24.62, 26.81, 27.61, 28.35, 28.54, 28.91, 91.37, 92.03, 123.30–147.32 (28 resonances), 167.45,

167.48, 173.62, 173.97 ppm; $^{31}P\{^{1}H\}$ NMR (121.50 MHz, C_6D_6) δ 15.16 ppm. Elemental analysis for $C_{41}H_{50}ClGeN_2P$ (%): Calcd.: C, 69.37; H, 7.10; N, 3.95. Found: C, 69.65; H, 7.66; N, 3.96.

Synthesis of 5. To a cooled (−60 °C) solution of **4** (1.40 g, 2.86 mmol) in *n*-hexane (30 mL) was added a solution of Ph_2PCl (0.64 g, 2.90 mmol) in *n*-hexane (20 mL). The solution turned yellow and a yellow precipitate started forming while the mixture was brought to rt. After stirring the mixture overnight it was filtered and the precipitate was dried under vacuum (0.80 g). Keeping the filtrate at rt for one day also afforded orange yellow crystals along with some powder (1.02 g). Total yield 1.82 g (90%). Mp. 173–175 °C. ^{1}H NMR (500.13 MHz, C_6D_6) δ 1.09 (d, 3H, $CH(CH_3)_2$), 1.15 (d, 3H, $CH(CH_3)_2$), 1.26–1.32 (three doublets, 9H, $CH(CH_3)_2$), 1.39 (s, 3H, CCH_3), 1.42 (d, 3H, $CH(CH_3)_2$), 1.47 (d, 3H, $CH(CH_3)_2$), 1.52 (d, 3H, $CH(CH_3)_2$), 3.14 (q, 2H, CH_2), 3.23 (m, 1H, $CH(CH_3)_2$), 3.39 (m, 1H, $CH(CH_3)_2$), 3.93 (m, 1H, $CH(CH_3)_2$), 4.03 (m, 1H, $CH(CH_3)_2$), 4.92 (d, 1H, CH), 6.88–8.05 (several multiplets, 16H, Ph) ppm; $^{13}C\{^{1}H\}$ NMR (125.77 MHz, C_6D_6) δ 23.32, 23.97, 24.22, 24.47, 24.82, 24.89, 26.77, 27.75, 28.21, 28.28, 28.66, 29.18, 29.41, 37.12, 37.31, 101.86, 101.92, 124.00–147.21 (23 resonances), 164.31, 166.16 ppm; $^{31}P\{^{1}H\}$ NMR (121.50 MHz, C_6D_6) δ -13.47 ppm. Elemental analysis for $C_{41}H_{50}ClGeN_2P$ (%): Calcd.: C, 69.37; H, 7.10; N, 3.95. Found: C, 69.45; H, 7.08; N, 3.34.

Conclusions

In summary, we have synthesized two isomeric β-diketiminate based Ge(II) complexes by two entirely different methods and they have been structurally characterized. Ligand **1** has shown versatile coordination modes and the way in which it coordinates to Ge(II) in **2** is the first of its kind. The presence of a free phosphine moiety in complex **5** can be exploited to coordinate further with other metals to obtain heterometallic Ge(II) complexes. Currently, we are exploring the route to incorporate two phosphine moieties in the backbone of the β-diketiminate ligand.

Acknowledgements

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