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The (β-Diketiminato)bismuth(III) Complex $[LBiCl(\mu\text{-}Cl)]_2$ {L = $HC[(CMe)(NAr)]_2$, Ar = 2,6-*i*$Pr_2C_6H_3$} and Its Derivatives: The Presence of Versatile Ligand Ligation Modes

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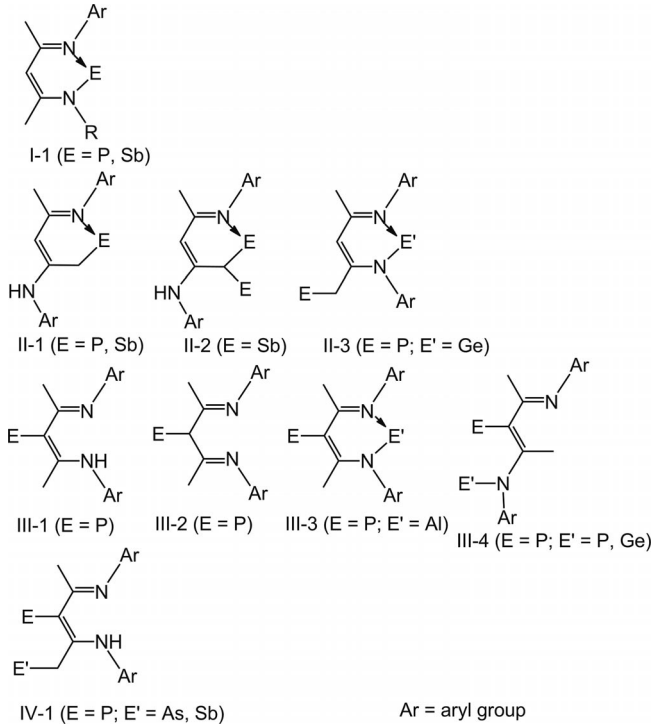
Keywords: β-Diketiminato ligands / Bismuth / Isomerization / Ligation modes / N ligands

The reaction of $BiCl_3$ with LLi {L = $HC[(CMe)(NAr)]_2$, Ar = 2,6-*i*$Pr_2C_6H_3$} in a molar ratio of 1:1 was carried out under various conditions and afforded $[LBiCl(\mu\text{-}Cl)]_2$ (**1**), $[L'BiCl(\mu\text{-}Cl)]_2$ [**4**; L′ = N(Ar)=C(Me)CH=C(NHAr)CH_2], and $L''Bi_2Cl_4$ [**5**; L′′ = N(Ar)=C(Me)CC(Me)=N(Ar)]. Compounds **1** and **4** are isomers, and a thermal conversion of **1** to **4** was realized. In this reaction system, when a little excess *n*BuLi and $BiCl_3$ were used, $[LBiCl(\mu\text{-}Cl)Bi(n\text{Bu})Cl(\mu\text{-}Cl)]_2$ (**2**) was isolated as side product after the isolation of **1**. The reaction of **1** with $AgOOCCF_3$ in the absence of light from –15 °C to room temperature generated $LBi(OOCCF_3)_2$ (**3**). Finally, the solvent-free reaction of $BiCl_3$ and LH at elevated temperature (125 °C) under vacuum gave $[LH_2]^+[BiCl_4(THF)]^-$ (**6**) in a low yield. The formulations of all these complexes have been confirmed by ^1H and ^{13}C NMR spectroscopy and X-ray crystallography, except for **6**, which was only identified by X-ray crystallography due to its insolubility in organic solvents. These complexes exhibit versatile L ligation modes at the metal atom and reveal the complexity of the reaction between $BiCl_3$ and LLi.

Introduction

β-Diketiminato ligands have been widely employed in the synthesis of main-group, transition-metal, and lanthanide complexes. This is due to the relatively rigid N,N-chelation backbone and the demanding N-substituents, which stabilize the target center electronically and/or sterically, especially with low coordination numbers and low oxidation states.[1,2] Some of these complexes can be used as precursors in reactions with various small-molecule substrates at the center,[3] efficient homogeneous catalysts,[3g,4,5] and as models for bioinorganic enzyme systems.[6] These examples prove further that β-diketiminates are promising ligands.

In recent years, progress on approaches to group 15 β-diketiminates have revealed that HC[(CMe)(NAr)][(CMe)(NHAr)] (LH) displays a variety of coordination modes in addition to N,N-chelation.[7] These ligation modes are summarized in Scheme 1 and include α-C,N-chelation (II-1),[7a,7b,8] α-C,N-chelation and α-C-ligation (II-2),[7c] α-C-ligation and N,N-chelation (II-3),[9] γ-C-ligation (III-1),[10] γ-CH-ligation (III-2),[7a] γ-C-ligation and N,N-ligation (III-3),[10c] γ-C-ligation and N-ligation (III-4),[9,10b] and γ-C-ligation and α-C-ligation (IV-1).[10a,10c] In other main-group compounds several other coordination features are also observed.[11–13] This indicates a rich coordination chemistry of β-diketiminato ligands and reflects the intriguing interactions of the ligand with a target element. However, a general viewpoint on the coordination mode of L towards



Scheme 1. Ligation modes of L in group 15 complexes (I: normal N–H activation, II: backbone Me C–H activation, III: backbone γ-CH ligation or γ-C–H activation, IV: both backbone Me and γ-CH C–H activation).

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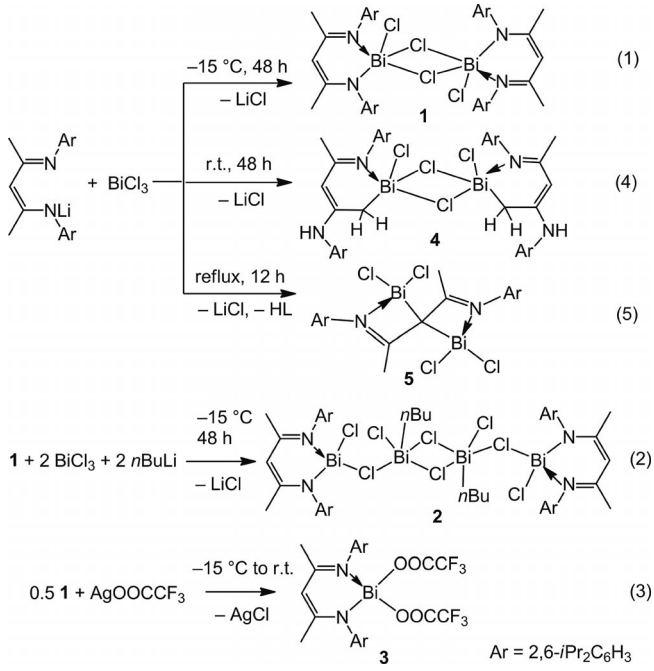
group 15 elements has not been reached, and the reaction mechanisms still remain speculative, although many experiments have been investigated, which include the use of different precursors and changing the reaction and/or isolation conditions.[7b,7c] Moreover, As and Bi complexes of L are unknown to date.[14] Recently, we successfully synthesized a series of Cu^{I}, Cr^{III}, and Bi^{III} complexes with an N,N,P ligand.[15] According to this methodology, we further investigated the reaction of $BiCl_3$ with LLi. This reaction has been reported; however, positive results have not been described.[7c] By careful control of the reaction and isolation conditions, we prepared a series of Bi^{III} compounds, which were structurally characterized and exhibited versatile L ligation modes. Herein we report these results, the isomerization of $[LBiCl(\mu\text{-}Cl)]_2$ (**1**), and a possible formation mechanism for $L''Bi_2Cl_4$ [**5**; L'' = N(Ar)=C(Me)-CC(Me)= N(Ar), Ar = 2,6-*i*$Pr_2C_6H_3$].

Results and Discussion

It has been suggested that $LMCl_2$-type complexes {L = $HC[(CMe)(NAr)]_2$, Ar = 2,6-*i*$Pr_2C_6H_3$ or 2,4,6-$Me_3C_6H_2$; M = As or Bi} are formed in a similar way to $LSbCl_2$ by the reaction of LLi and MCl_3 in tetrahydrofuran (THF) from –78 °C to room temperature. However, this has not been confirmed spectroscopically.[7c] We initially examined the synthesis by treating LLi, which was prepared in situ,[16] with $BiCl_3$ in a mixture of toluene and THF from –15 °C to room temperature. After a routine workup, which included the removal of volatiles, extraction with toluene, and concentration under vacuum, an orange-yellow solid was obtained and identified as a mixture on the basis of ^1H NMR spectroscopy. An attempt to crystallize a pure compound failed. Thus, we altered the treatment of this reaction. A mixture of a precooled (–15 °C) toluene solution of LLi and a precooled (–15 °C) THF solution of $BiCl_3 \cdot (THF)_2$ was kept at –15 °C without stirring for 48 h.

$[LBiCl(\mu\text{-}Cl)]_2$ {**1**; L = $HC[(CMe)(NAr)]_2$, Ar = 2,6-*i*$Pr_2C_6H_3$} was formed as red crystals in 64% yield [Scheme 2, Equation (1)]. In a similar manner, $[LBiCl(\mu\text{-}Cl)Bi(n\text{Bu})Cl(\mu\text{-}Cl)]_2$ (**2**) was obtained as orange-red crystals from LH, *n*BuLi, and $BiCl_3 \cdot (THF)_2$ in a molar ratio of 2.5:3.0:3.0 [Equation (2)],[17] in which **1** was isolated from the first crop in 42% yield and **2** from the second crop in a relatively low yield of 22%. This may indicate that **1** is formed during the reaction and further reacts with $BiCl_2(n\text{Bu})$, which could be generated by metathesis between $BiCl_3$ and *n*BuLi, to produce **2**. The use of excess *n*BuLi in the reaction to obtain $LBi(n\text{Bu})_2$ was not successful. Nonetheless, carboxyl group functionalized $LBi(OOCCF_3)_2$ (**3**) was prepared in good yield (87%) from the reaction of **1** with $AgOOCCF_3$ in the absence of light from –15 °C to room temperature [Equation (3)].

Compounds **1**–**3** were characterized by spectroscopy and elemental analysis and confirmed by X-ray crystallography. The ^1H NMR spectra of **1**–**3** exhibit the backbone methyl (C*Me*) and methine (γ-C*H*) proton resonances as singlets



Scheme 2. Synthesis of **1**–**5**.

at δ = 2.00 and 5.30 ppm for **1**, δ = 2.03 and 5.38 ppm for **2**, and δ = 2.03 and 5.34 ppm for **3**, which suggests an N,N-chelation mode of L at Bi. This appears to be the normal bonding feature, which is commonly known for other main group metal β-diketiminate complexes.[2a,2b,3d–3h,16] The structures of **1**–**3** are shown in Figures 1, 2, and 3, respectively, and clearly prove such a coordination mode.

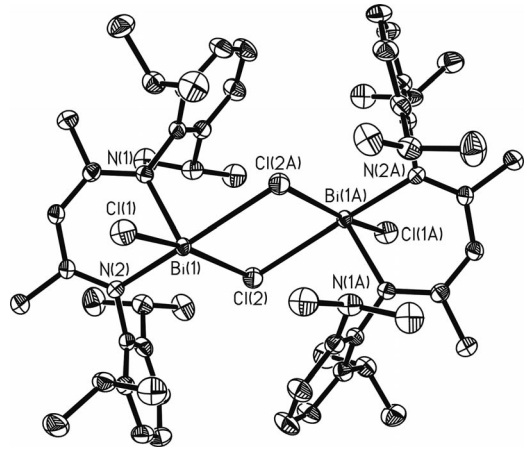


Figure 1. Crystal structure of **1** with the thermal ellipsoids at 50% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Bi(1)–N(1) 2.242(3), Bi(1)–N(2) 2.283(3), Bi(1)–Cl(1) 2.5901(12), Bi(1)–Cl(2) 2.8513(12), Bi(1)–Cl(2A) 2.8720(15), C(1)–C(2) 1.510(6), C(2)–C(3) 1.398(5), C(3)–C(4) 1.411(5), C(4)–C(5) 1.505(5), C(2)–N(1) 1.349(5), C(4)–N(2) 1.335(5); N(1)–Bi(1)–N(2) 83.40(11), N(1)–Bi(1)–Cl(1) 89.17(8), N(1)–Bi(1)–Cl(2A) 90.21(8), N(1)–Bi(1)–Cl(2) 103.86(8).

The Bi–N bond lengths are 2.242(3)–2.283(3) Å in **1**, 2.198(10)–2.234(11) Å in **2**, and 2.230(6)–2.237(3) Å in **3**. These differences are probably due to the different coordi-

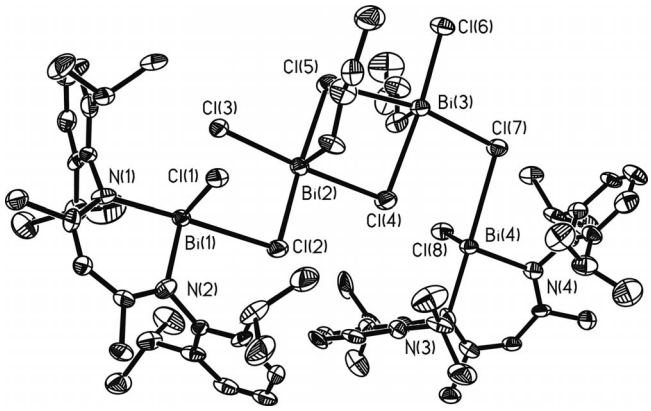


Figure 2. Crystal structure of **2** with the thermal ellipsoids at 50% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Bi(1)–N(1) 2.224(11), Bi(1)–N(2) 2.224(12), Bi(1)–Cl(1) 2.458(4), Bi(1)–Cl(2) 2.984(4), Bi(2)–C(61) 2.194(4), Bi(2)–Cl(2) 2.688(4), Bi(2)–Cl(3) 2.638(3), Bi(2)–Cl(4) 2.878(4), Bi(2)–Cl(5) 2.795(4), Bi(3)–C(65) 2.189(15), Bi(3)–Cl(4) 2.959(4), Bi(3)–Cl(5) 2.844(4), Bi(3)–Cl(6) 2.563(4), Bi(3)–Cl(7) 2.671(4), Bi(4)–N(3) 2.234(11), Bi(4)–N(4) 2.198(10), Bi(4)–Cl(7) 3.081(4), Bi(4)–Cl(8) 2.453(4); N(2)–Bi(1)–N(1) 85.7(4), N(2)–Bi(1)–Cl(1) 91.1(3), N(2)–Bi(1)–Cl(2) 94.9(3), C(61)–Bi(2)–Cl(2) 85.4(4), C(61)–Bi(2)–Cl(3) 88.7(4), C(61)–Bi(2)–Cl(4) 91.7(4), C(61)–Bi(2)–Cl(5) 89.5(4), C(65)–Bi(3)–Cl(4) 84.5(4), C(65)–Bi(3)–Cl(5) 84.2(4), C(65)–Bi(3)–Cl(6) 94.6(4), C(65)–Bi(3)–Cl(7) 88.5(4), N(4)–Bi(4)–N(3) 85.3(4), N(4)–Bi(4)–Cl(7) 96.1(3), N(4)–Bi(4)–Cl(8) 93.7(3).

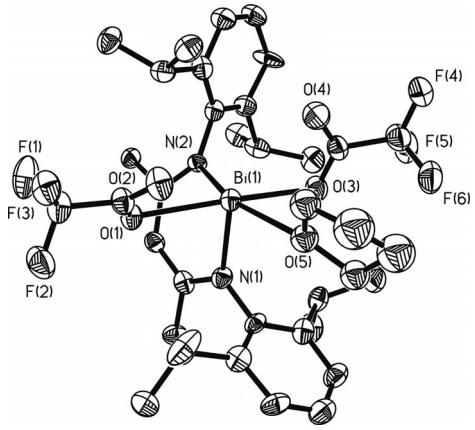


Figure 3. Crystal structure of **3** with the thermal ellipsoids at 50% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Bi(1)–N(1) 2.237(3), Bi(1)–N(2) 2.230(6), Bi(1)–O(1) 2.460(7), Bi(1)–O(3) 2.353(7), Bi(1)–O(5) 2.753(7); N(1)–Bi(1)–N(2) 85.8(3), N(1)–Bi(1)–O(1) 82.5(3), N(1)–Bi(1)–O(3) 89.8(3), N(1)–Bi(1)–O(5) 97.7(2).

nation number and the various functional groups at the Bi center. In a similar compound, L^aBiCl_2 {L^a = $HC[(CMe)(NCH_2CH_2NEt_2)]_2$}, Bi–N bond lengths of 2.232(2)–2.246(2) Å are observed.[14a] The Bi–$Cl_{terminal}$ bonds [2.5901(12) Å in **1**, 2.453(4)–2.638(3) Å in **2**] are shorter than the Bi–Cl_{bridge} bonds [2.8513(12)–2.8720(15) Å in **1**, 2.671(4)–3.081(4) Å in **2**]. However, these bond lengths are very different to those in L^aBiCl_2 [Bi–$Cl_{terminal}$ 2.675(1)–2.736(1) Å]. A similar case is observed for $L^bBiCl_2(\mu\text{-Cl})$-BiCl(THF)L^b {Bi–$Cl_{terminal}$ 2.5028(13)–2.6827(14) Å; Bi–Cl_{bridge} 2.7468(14)–2.9822(14) Å; L^b = $PhC[(CH)(NAr)]_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$}.[14b] Noteworthy features in **1**–**3** are the stereochemically active geometries of the nonbonding lone pair around the Bi^{III} centers, which are suggested to fit the 10-Bi-4 and 12-Bi-5 systems (*n*-Bi-*l*, where *n* is number of formal valence-shell electrons about a Bi atom and *l* is the number of ligands) predicted by simple valence-shell electron-pair repulsion theory.[18] Thus, square-pyramidal geometry was adopted for each five-coordinate Bi center, and triangular-pyramidal geometry was adopted for each four-coordinate Bi center, in which some degrees of geometric distortion were observed from the ideal polyhedra, probably due to the different ligation groups at the metal centers.

The formation of **1** as a crystalline product from the reaction of LLi and $BiCl_3$ can be considered as a reaction-to-crystallization process. Thus, low temperature treatment (–15 °C) and a long standing time (48 h) were of importance. The initial reactions from –15 °C to room temperature gave a product mixture, so we performed the reaction of LLi and $BiCl_3$ (1:1) with stirring at room temperature for 48 h. The yellow suspension obtained was allowed to stand at room temperature for three weeks without filtration to remove the insoluble material, and a new compound [L′BiCl(μ-Cl)]$_2$ [**4**; L′ = N(Ar)=C(Me)CH=C-(NHAr)CH$_2$], Ar = 2,6-(iPr$_2$C$_6$H$_3$) was isolated as yellow crystals in 41% yield [Scheme 2, Equation (4)].

The ^{1}H NMR spectrum of **4** shows a relatively complicated pattern compared to that of **1**. The singlets at δ = 4.09 and 1.55 ppm can be assigned to the γ-C*H* proton and C*Me*, respectively, whereas those at δ = 1.11 and 1.72 ppm are tentatively assigned to the backbone methylene protons (CCH_2) and the N*H* proton with satisfactory integrations. An absorption observed at 3294 cm^{-1} in the IR spectrum of **4** corresponds to ν(N–H).

The single-crystal X-ray structural analysis of **4** unambiguously discloses a C,N-chelation bonding mode, which is completely different to those in **1**–**3**. The same coordination feature has been found in P and Sb compounds.[7a,7b,8] As shown in Figure 4, the Bi–N bonds [2.333(6)–2.368(5) Å] are a little longer than those in **1**–**3**. Bi–$Cl_{terminal}$ distances of 2.544(2)–2.6056(19) Å and Bi–Cl_{bridge} distances of 2.7846(19)–2.9310(18) Å were found. The Bi–C bonds are 2.225(6) and 2.228(7) Å long, which is a little longer than those in **2** [2.189(15) and 2.194(4) Å]. The C–Bi–N bite angles [78.8(2)–79.8(2)°] are smaller than the N–Bi–N bite angles in **1**–**3** [83.40(11)–85.8(3)°]. Compared to the matrix data of the ligation backbone in **1** [C(1)–C(2) 1.510(6), C(2)–C(3) 1.398(5), C(3)–C(4) 1.411(5), C(4)–C(5) 1.505(5), C(2)–N(1) 1.349(5), C(4)–N(2) 1.335(5) Å], in **4** the C(1)–C(2), C(2)–C(3), C(3)–C(4), C(4)–C(5), C(2)–N(2), and C(4)–N(1) bond lengths are 1.483(8) [1.455(9) (in another ligand backbone)], 1.337(8) [1.394(9)], 1.415(8) [1.432(8)], 1.515(8) [1.521(9)], 1.359(7) [1.333(7)], and 1.320(7) [1.271(1)] Å, respectively, which indicates a big change in the ligand backbone geometry.

Compounds **1** and **4** are isomers that were isolated from different conditions. Stirring a THF solution of pure **1** at room temperature for 24 h led to quantitative conversion to **4**, which indicates a thermal structural conversion. Simi-

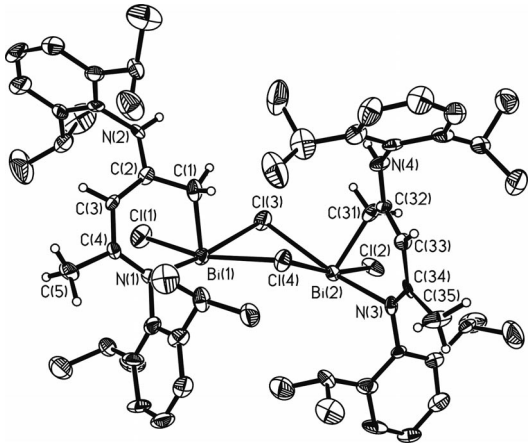
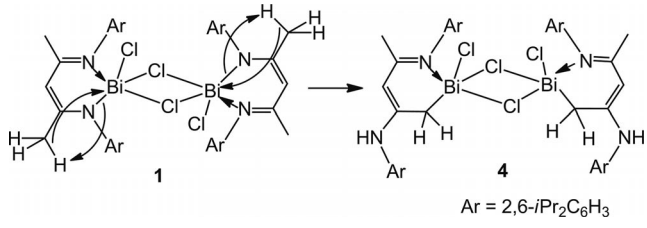


Figure 4. Crystal structure of **4** with the thermal ellipsoids at 50% probability. H atoms of the aryl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Bi(1)–C(1) 2.225(6), Bi(1)–N(1) 2.368(5), Bi(1)–Cl(1) 2.544(2), Bi(1)–Cl(3) 2.8456(19), Bi(1)–Cl(4) 2.882(2), Bi(2)–C(31) 2.228(7), Bi(2)–N(3) 2.333(6), Bi(2)–Cl(2) 2.6056(19), Bi(2)–Cl(3) 2.9310(18), Bi(2)–Cl(4) 2.7846(19), C(1)–C(2) 1.483(8), C(2)–C(3) 1.337(8), C(3)–C(4) 1.415(8), C(4)–C(5) 1.515(8), C(2)–N(2) 1.359(7), C(4)–N(1) 1.320(7), C(31)–C(32) 1.455(9), C(32)–C(33) 1.394(9), C(33)–C(34) 1.432(8), C(34)–C(35) 1.521(9), C(32)–N(4) 1.333(7), C(34)–N(3) 1.271(1); C(1)–Bi(1)–N(1) 78.8(2), C(1)–Bi(1)–Cl(1) 90.68(19), C(1)–Bi(1)–Cl(3) 90.59(18), C(1)–Bi(1)–Cl(4) 80.68(18), C(31)–Bi(2)–N(3) 79.8(2), C(31)–Bi(2)–Cl(2) 84.66(19), C(31)–Bi(2)–Cl(3) 90.70(18), C(31)–Bi(2)–Cl(4) 86.89(18).

larly, $[L'SbBr(\mu\text{-}Br)]_2$ was thought to undergo intramolecular C–H activation due to the presence of the active Sb–X (X = halide).[7c] It is reasonable to deduce that such activation may be induced from structural isomerization, which is probably due to the active Bi–N bond (Scheme 3). The high reactivity of such a bond has been well documented by Roesky et al. and shows insertion reactions with a series of carbon-containing unsaturated molecules.[19]

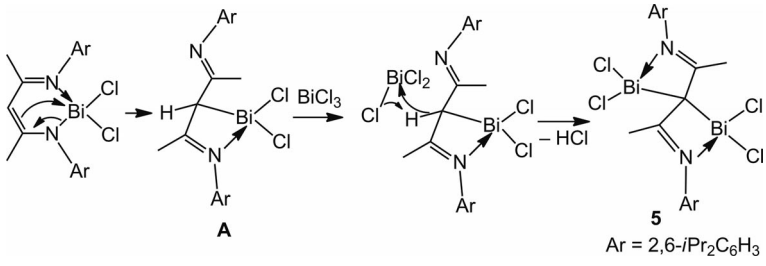


Scheme 3. Isomerization of **1** to **4**.

We further investigated the reaction of LLi with 1 equiv. of $BiCl_3$ in toluene under reflux conditions to see if a new compound could be generated. $L''Bi_2Cl_4$ [**5**; L'' = N(Ar)=C(Me)CC(Me)=N(Ar), Ar = 2,6-*i*Pr$_2$C$_6$H$_3$] was formed as a light brown solid in 45% yield [Scheme 2, Equation (5)]. Free ligand was found as a byproduct in a nonnegligible amount (**5**/LH ≈ 1:0.7)[20] by ^{1}H NMR spectral analysis. Due to the production of a considerable amount of LH, we tried the reaction with LLi again, in which the LLi was ensured to have been formed in situ by ^{1}H NMR measurements of the reaction mixture by using 2 equiv. of $BiCl_3$. However, almost the same results were obtained with the yield of **5** always less than 50%.

γ-CH ligation of L has been reported for P (Scheme 1, III-2)[7a] and Ge compounds,[11] which have been suggested to form through elimination of NaCl or LiCl from the reaction of LNa and PCl_3 or LLi and $GeCl_4$ followed by distinct diimine rearrangement within the C_5N_2 ligand backbone. The P compound can be quickly converted into the III-1-type species in solution by γ-CH proton migration to one of the imine N-atoms to reestablish the π-electron conjugation of the ligand backbone, and is thus considered as an intermediate.[10c] The stable formation of many III-1 complexes and their derivatives has also been reported.[7b,9,10] Comparably, **5** exhibits γ-C double ligation under the diimine framework, which may involve further γ-C–H activation based on coordination similar to that of the Ge compound.[11] To the best of our knowledge, this is a new L ligation feature for β-diketiminato complexes.[1–11] Considering the prior formation of **1** in this reaction system, we propose that the formation of **5** might undergo an isomerization of partial **1** to **A**, and **A** further reacted with another molecule of $BiCl_3$ by γ-C–H activation to give **5** with the release of HCl (Scheme 4). C–H activation within the L backbone has been observed in P,[7–10] As,[10a,10c] Sb,[7,8,10a,10c] Si,[13] and Ge[13b] complexes, some of which can occur even in the presence of a relatively active NH functionality.[7c,10] The HCl generated could acidify the unreacted LLi to produce LH. This is in agreement with the isolation of LH from the reaction. Moreover, the production of a considerable amount of LH and less than 50% yield of **5** suggests the consumption of LLi and $BiCl_3$ in a degree too larger for further reactions even when changing the molar ratio of the reactants.

The formulation of **5** was confirmed by spectroscopy and X-ray crystallography. The ^{1}H NMR spectrum exhibits only



Scheme 4. Plausible mechanism for the formation of **5**.

one singlet resonance for the C*Me* protons at δ = 1.96 ppm within the ligand backbone. The crystal structure shown in Figure 5 illustrates the γ-C double ligation, which presents γ-C,N-chelation at each Bi^{III} center. The Bi–N [2.500(13)–2.539(11) Å] and Bi–C [2.311(16)–2.315(14) Å] bonds are a little longer than those in **1**–**4** for the former and in **2** and **4** for the latter, whereas the Bi–Cl bond lengths [2.504(4)–2.653(4) Å] are comparable to the related terminal distances. The matrix data for the ligand backbone [C(1)–C(2) 1.48(2), C(2)–C(3) 1.46(2), C(3)–C(4) 1.544(17), C(4)–C(5) 1.46(2), C(2)–N(1) 1.301(16), and C(4)–N(2) 1.301(18) Å] match well with the diimine arrangement.

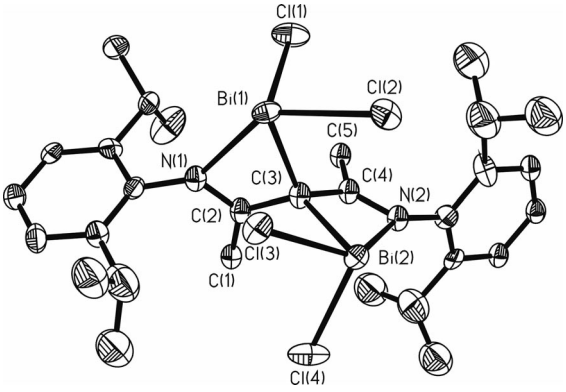


Figure 5. Crystal structure of **5** with the thermal ellipsoids at 50% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Bi(1)–N(1) 2.500(13), Bi(1)–C(3) 2.315(14), Bi(1)–Cl(1) 2.519(4), Bi(1)–Cl(2) 2.653(4), Bi(2)–N(2) 2.539(11), Bi(2)–C(3) 2.311(16), Bi(2)–Cl(3) 2.648(3), Bi(2)–Cl(4) 2.504(4), C(1)–C(2) 1.48(2), C(2)–C(3) 1.46(2), C(3)–C(4) 1.544(17), C(4)–C(5) 1.46(2), C(2)–N(1) 1.301(16), C(4)–N(2) 1.301(18); Cl(1)–Bi(1)–N(1) 99.6(3), Cl(1)–Bi(1)–C(3) 95.6(4), Cl(1)–Bi(1)–Cl(2) 95.69(15), Cl(4)–Bi(2)–N(2) 97.3(3), Cl(4)–Bi(2)–C(3) 92.8(4), Cl(4)–Bi(2)–Cl(3) 96.05(15).

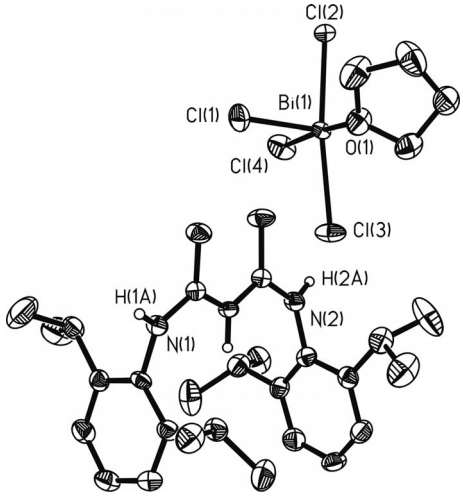


Figure 6. Crystal structure of **6** with the thermal ellipsoids at 50% probability. H atoms are omitted for clarity except NH and γ-CH. Selected bond lengths [Å] and angles [°]: Bi(1)–O(1) 2.637(3), Bi(1)–Cl(1) 2.4901(11), Bi(1)–Cl(2) 2.6663(11), Bi(1)–Cl(3) 2.7868(11), Bi(1)–Cl(4) 2.5166(12), N(1)–C(2) 1.336(4), N(2)–C(4) 1.330(4), C(2)–C(3) 1.392(4), C(3)–C(4) 1.392(4); Cl(1)–Bi(1)–O(1) 81.96(6), Cl(1)–Bi(1)–Cl(2) 88.26(3), Cl(1)–Bi(1)–Cl(3) 97.72(3), Cl(1)–Bi(2)–Cl(4) 93.29(4).

Finally, we tested the solvent-free reaction of $BiCl_3$ and LH at 125 °C under vacuum. Extraction with THF followed by crystallization at –20 °C afforded $[LH_2]^+$-$[BiCl_4(THF)]^-$ (**6**) as colorless crystals in a very low yield (9.3%). Most of the residues were insoluble in organic solvents. $[LH_2]^+Cl^-$ is known as a precursor in the base-neutralized formation of LH.[21] The formation of **5** is thought to involve the generation of HCl, which could react with $BiCl_3$ and LH to give **6**. Because of the ionic character, **6** is insoluble in organic solvents, and its NMR spectrum was silent. Nonetheless, X-ray crystallography clearly evidences an ionic pair (Figure 6).

Conclusions

We investigated the reaction of LLi and $BiCl_3$ and, with careful control of the reaction and isolation conditions, we prepared a series of bismuth(III) complexes **1**, **2**, **4**, and **5**, the formulations of which were confirmed by structural characterization, which showed versatile L ligation modes at the metal atom. This reveals a complexity of the reaction system and may reasonably explain the unsuccessful isolation of pure compounds previously mentioned due to the complexity of products.[7c] The temperature-dependent conversion of **1** to **4** suggests easy isomerization of the β-diketiminato ligand, especially in ligating group 15 elements.[7a,7b,8] On changing the functionality at the Bi^{III} center, e.g. the carboxyl group in **3**, the N,N-ligation of L appears to be stable. Multiple coordination sites in the N-substituents or avoidance of an active group in the backbone may have the same function. The former has been demonstrated by Roesky et al. with the preparation of L^aBiCl_2,[14a] and the latter by Lappert et al. with the synthesis of $L^b{}_2Bi_2X_4$ (X = Cl, Br, and I).[14b] With respect to the salt-elimination metathesis, routine operations of removal of the salt followed by crystallization or recrystallization seem to be unworkable for obtaining pure **1**, **2**, and **4**. In contrast, an unusual workup of not separating the LiCl salt does well. This method will be applied to the isolation of other Bi complexes.

Experimental Section

General Procedures: All syntheses and manipulations of air- and moisture-sensitive materials were carried out under nitrogen by using Schlenk techniques or inside an MBraun Unilab glovebox filled with argon, in which the calibrated values of O_2 and H_2O were strictly controlled below 1.2 ppm. Organic solvents including toluene, *n*-hexane, and THF were predried with fine sodium wire and then heated with sodium/potassium benzophenone under nitrogen prior to use. CH_2Cl_2 and $CHCl_3$ were heated with CaH_2 for at least 3 d before use. Deuterated $CDCl_3$ was degassed, dried with CaH_2, and filtered before use. NMR spectra were recorded with a Bruker Avance II 500 spectrometer. IR spectra were measured with a Nicolet 300 spectrometer. Melting points were measured in sealed glass tubes by using a Büchi-540 instrument. Elemental analysis

was performed with a Thermo Quest Italia SPA EA 1110 instrument. Commercially available reagents were purchased from Aldrich, Acros, Alfa Aesar, and Lvyin Chemical Co. and used as received. LH[21] and $BiCl_3(THF)_2$[22] were prepared according to published procedures.

Preparation of [LBiCl(μ-Cl)]$_2$ (1): Inside the glovebox, *n*BuLi (1.04 mL, 2.4 M in *n*-hexane, 2.50 mmol) was added dropwise to a precooled (–15 °C) solution of LH (1.05 g, 2.50 mmol) in toluene (20 mL). The mixture was stirred and warmed to room temperature. After stirring for 12 h to allow the complete formation of LLi, the solution was cooled to –15 °C and added to a precooled (–15 °C) solution of $BiCl_3(THF)_2$ (1.15 g, 2.50 mmol) in THF (20 mL). The mixture was allowed to stand at –15 °C for 48 h. Red crystals of **1** were formed. After decanting the solution, the residue was extracted with cooled CH_2Cl_2 (30 mL, –15 °C). The extract was concentrated to dryness under vacuum, and the residue was washed with *n*-hexane (5 mL) to give **1** as a red solid. Yield: 1.12 g, 64%. M.p. 147 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 1.23 (d, $^3J_{HH}$ = 6.5 Hz, 24 H), 1.36 (d, $^3J_{HH}$ = 6.5 Hz, 24 H) (CH*Me*$_2$), 2.00 (s, 12 H, C*Me*), 3.37 (sept, $^3J_{HH}$ = 6.5 Hz, 8 H, C*H*Me$_2$), 5.30 (s, 2 H, γ-C*H*), 7.05–7.33 (m, 12 H, (C_6H_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 24.60, 25.49, 26.24, 28.49 (*C*H*Me*$_2$, C*Me*), 111.48 (γ-*C*H), 124.55, 128.21, 128.91, 129.02, 138.75, 145.22 (C_6H_3), 165.65 (*C*N) ppm. $C_{58}H_{82}Bi_2Cl_4N_4$ (1395.07): calcd. C 49.93, H 5.92, N 4.02; found C 49.89, H 5.64, N 3.92.

Preparation of [LBiCl(μ-Cl)Bi(*n*Bu)Cl(μ-Cl)]$_2$ (2): The preparation of **2** was similar to that of **1**, and *n*BuLi (1.25 mL, 2.4 M in *n*-hexane, 3.00 mmol), LH (1.26 g, 2. 50 mmol), and $BiCl_3(THF)_2$ (1.38 g, 3.00 mmol) were used. The LLi formed in situ, *n*BuLi, and $BiCl_3(THF)_2$ mixture was allowed to stand at –15 °C for 48 h. Red crystals of **1** (0.73 g, 42%) were collected. The mother liquor was concentrated to half its volume under vacuum and then kept at –15 °C for 72 h to afford orange-red crystals of **2**, which were collected by filtration and washed with *n*-hexane (2 mL). Yield: 0.24 g, 22% (based on quantitative formation of **2** at a 0.25 mmol scale on account of 0.50 mmol excess of *n*BuLi). M.p. 142 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 0.88–0.93 (m, 6 H), 1.26–1.30 (m, 4 H), 2.50–2.55 (m, 4 H), 3.15–3.22 (m, 4 H) (C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_3$), 1.22 (d, $^3J_{HH}$ = 6.5 Hz, 24 H), 1.37 (d, $^3J_{HH}$ = 6.5 Hz, 24 H) (CH*Me*$_2$), 2.03 (s, 12 H, C*Me*), 3.12 (sept, $^3J_{HH}$ = 6.5 Hz, 8 H, C*H*Me$_2$), 5.38 (s, 2 H, γ-C*H*), 7.14–7.29 (m, 12 H, C_6H_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 14.11, 21.39, 24.67, 25.46, 25.91, 27.47, 28.70, 36.35 (*C*H*Me*$_2$, C*Me*, *C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$), 93.70 (γ-*C*H), 111.15, 124.79, 125.23, 128.15, 128.96, 129.36, 138.58, 144.37 (C_6H_3), 165.67 (*C*N) ppm. $C_{66}H_{100}Bi_4Cl_8N_4$ (2069.07): calcd. C 38.31, H 4.87, N 2.71; found C 38.51, H 5.08, N 2.63.

Preparation of LBi(OOCCF$_3$)$_2$ (3): Inside the glovebox, a precooled solution of $AgOOCCF_3$ (0.09 g, 0.40 mmol) in toluene (5 mL) was added dropwise to a precooled (–15 °C) solution of **1** (0.14 g, 0.10 mmol) in THF (20 mL) in a dark brown vial. Precipitation of solid from the solution was immediately observed. This mixture was allowed to stand at –15 °C for 24 h and then warmed to room temperature. After stirring for 1.5 h, the mixture was filtered to remove insoluble material, and the filtrate was dried under vacuum. The residue was washed with *n*-hexane (3 mL) to give **3** as an orange solid, which was analytically pure by ^{1}H NMR spectroscopy. Yield: 0.16 g, 87%. M.p. 154 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 1.21 (d, $^3J_{HH}$ = 6.5 Hz, 12 H), 1.45 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, CH*Me*$_2$), 2.03 (s, 6 H, C*Me*), 3.23 (sept, $^3J_{HH}$ = 6.5 Hz, 4 H) (C*H*Me$_2$), 5.34 (s, 1 H, γ-C*H*), 7.12–7.30 (m, 6 H, C_6H_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 22.65, 24.21, 24.81, 28.58, 28.67, 31.59 (*C*H*Me*$_2$, C*Me*, *C*F$_3$), 93.25 (γ-*C*H), 123.02, 124.64, 125.07, 129.21, 140.74, 142.47, 145.17 (C_6H_3), 161.19 (OO*C*), 166.49 (*C*N) ppm. ^{19}F NMR (470 MHz, $CDCl_3$, 298 K): δ = –77.01 (s) ppm. $C_{37}H_{49}BiF_6N_2O_5$ (**3**·THF, 924.77): calcd. C 48.05, H 5.34, N 3.03; found C 48.43, H 5.56, N 2.87. The X-ray quality single crystals of **3**·1.75THF were obtained by recrystallization of **3** from a THF/*n*-hexane (5 mL/5 mL) mixture at –15 °C.

Preparation of [L′BiCl(μ-Cl)]$_2$ [4; L′ = N(Ar)=C(Me)CH=C(NHAr)CH$_2$, Ar = 2,6-(*i*Pr$_2$C$_6$H$_3$)]: LLi (2.5 mmol) in toluene (30 mL), prepared as described above, was added to a suspension of $BiCl_3$ (0.79 g, 2.5 mmol) in toluene (10 mL) at room temperature. The mixture was stirred for 48 h. After workup, the yellow suspension was concentrated (ca. 10 mL) and allowed to stand at room temperature without filtration. After 3 weeks, yellow crystals of **4** were formed and collected together with the insoluble material. The solids were extracted with toluene (20 mL), and the extract was dried under vacuum and washed with *n*-hexane (5 mL) to give **4** as a yellow crystalline solid. Yield: 0.72 g, 41%. M.p. 170 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 1.07 (d, $^3J_{HH}$ = 7.0 Hz, 12 H), 1.13 (d, $^3J_{HH}$ = 7.0 Hz, 12 H), 1.21 (d, $^3J_{HH}$ = 7.0 Hz, 12 H), 1.22 (d, $^3J_{HH}$ = 7.0 Hz, 12 H) (CH*Me*$_2$), 1.11 (s, 4 H, C=C*H*$_2$), 1.55 (s, 6 H, C*Me*), 1.72 (s, 2 H, N*H*), 3.21 (sept, $^3J_{HH}$ = 7.0 Hz, 4 H), 3.41 (br., 4 H) (C*H*Me$_2$), 4.09 (s, 2 H, γ-C*H*), 7.12–7.35 (m, 12 H, C_6H_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 1.02 (C=*C*H$_2$), 20.75, 23.22, 23.62, 24.21, 24.35, 24.62, 25.37, 28.09, 28.19, 28.65 (C*Me*, *C*H*Me*$_2$), 99.71 (γ-*C*H), 123.01, 123.89, 124.50, 125.06, 140.72, 142.46 (C_6H_3, *C*NH), 161.19 (*C*N) ppm. IR (KBr plate, Nujol mull): $\tilde{\nu}$ = 3294 [w, ν(NH)] cm^{-1}. $C_{71}H_{104}Bi_2Cl_4N_4$ (**4**·toluene·*n*-hexane, 1573.39): calcd. C 54.20, H 6.66, N 3.56; found C 55.09, H 6.68, N 3.30.

Isomerization of 1 to [L′BiCl(μ-Cl)]$_2$ (4): At room temperature, **1** (0.13 g, 0.20 mmol) was dissolved in THF (6 mL). The solution was stirred for 24 h, and a yellow solution developed. The solution was concentrated to dryness under vacuum to give a yellow solid. The ^{1}H NMR spectroscopic analysis confirmed almost quantitative formation of **4**.

Preparation of L′′Bi$_2$Cl$_4$ [5; L′′ = N(Ar)=C(Me)CC(Me)=N(Ar), Ar = 2,6-*i*Pr$_2$C$_6$H$_3$]: A precooled (–15 °C) solution of LLi (1.25 mmol) in toluene (30 mL), prepared as described above, was added to a precooled (–15 °C) suspension of $BiCl_3$ (0.40 g, 1.25 mmol) in toluene (10 mL). The mixture was heated slowly to reflux with stirring and kept at this temperature for 12 h. After workup, the reaction suspension was cooled to room temperature. After filtration to remove insoluble material, the filtrate was concentrated to dryness under vacuum to give a grey-yellow residue, which was identified as a mixture of **5** and LH in a molar ratio of ca. 1:0.7 by ^{1}H NMR spectroscopy. The residue was washed with a large amount of *n*-hexane (3 × 10 mL) to remove LH, and **5** (0.42 g) was obtained as a light brown solid. The washings were added to THF (0.5 mL) and allowed to stand at room temperature for slow concentration; 2 weeks later, light brown crystals of **5**$_2$·3.7THF (0.15 g) were grown. Total yield: 0.55 g (based on **5**), 45%. M.p. 178 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 1.14 (d, 6 H, $^3J_{HH}$ = 6.5 Hz), 1.16 (d, 6 H, $^3J_{HH}$ = 6.5 Hz), 1.24 (d, 6 H, $^3J_{HH}$ = 6.5 Hz), 1.28 (d, 6 H, $^3J_{HH}$ = 6.5 Hz) (CH*Me*$_2$), 1.96 (s, 6 H, C*Me*), 3.22 (sept, 2 H, $^3J_{HH}$ = 6.5 Hz), 3.24 (sept, 2 H, $^3J_{HH}$ = 6.5 Hz) (C*H*Me$_2$), 7.14–7.42 (m, 6 H, C_6H_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 1.01 (*C*Bi), 23.37, 24.22, 24.39, 25.98, 27.53, 28.65, 33.28 (*C*H*Me*$_2$, C*Me*), 123.26, 124.31, 127.84, 136.38, 141.82, 142.83 (C_6H_3), 173.30 (*C*N) ppm. $C_{29}H_{40}Bi_2Cl_4N_2$

Table 1. Crystallographic data for **1**–**6**.

	1·2toluene	**2**	**3**·1.75THF	**4**·toluene	$\mathbf{5}_2$·3.7THF	**6**
Empirical formula	$C_{72}H_{98}Bi_2Cl_4N_4$	$C_{66}H_{100}Bi_4Cl_8N_4$	$C_{40}H_{55}BiF_6N_2O_{5.75}$	$C_{65}H_{90}Bi_2Cl_4N_4$	$C_{72.8}H_{109.6}Bi_4Cl_8N_4O_{3.7}$	$C_{33}H_{51}BiCl_4N_4O$
Formula mass	1579.30	2069.02	978.84	1487.17	2219.56	842.54
Temperature [K]	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	triclinic	monoclinic	triclinic,	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$P2(1)$	$P2(1)/c$
a [Å]	10.303(2)	17.666(4)	10.583(2)	14.6999(17)	14.1084(7)	10.379(2)
b [Å]	13.035(3)	21.075(4)	15.651(3)	15.9145(18)	19.0622(7)	21.808(4)
c [Å]	14.361(3)	22.312(5)	16.799(3)	17.7187(19)	16.2781(8)	16.543(3)
α [°]	72.14(3)		111.84(3)	96.965(9)		
β [°]	73.93(3)	111.01(3)	100.11(3)	114.316(11)	110.393(6)	94.48(3)
γ [°]	74.32(3)		101.66(3)	112.658(11)		
V [Å^3]	1727.4(6)	7755(3)	2431.5(8)	3287.1(6)	4103.4(3)	3732.8(13)
Z	1	4	2	2	2	4
$\rho_{calcd.}$ [Mg/m^3]	1.518	1.772	1.337	1.503	1.796	1.499
μ [mm^{-1}]	5.284	9.363	3.687	5.549	8.857	5.036
$F(000)$	792	3968	984	1484	2144	1688
θ range [°]	3.05–27.46	3.01–27.48	3.01–27.48	2.74–26.00	2.79–26.00	3.04–27.47
Index ranges	$-13 \le h \le 13$	$-22 \le h \le 22$	$-13 \le h \le 13$	$-17 \le h \le 18$	$-17 \le h \le 17$	$-13 \le h \le 13$
	$-16 \le k \le 16$	$-27 \le k \le 27$	$-20 \le k \le 20$	$-19 \le k \le 19$	$-23 \le k \le 23$	$-28 \le k \le 28$
	$-18 \le l \le 18$	$-28 \le l \le 28$	$-21 \le l \le 21$	$-21 \le l \le 21$	$-15 \le l \le 20$	$-21 \le l \le 19$
No. of reflns. collected	16928	74146	23646	34507	19034	35786
No. of indep. reflns. (R_{int})	7827 (0.0446)	17678 (0.2286)	10932 (0.0931)	12904 (0.0874)	13820 (0.075)	8507 (0.0679)
No. of data/restraints/params.	7827/0/381	17678/0/754	10932/123/513	12904/0/661	13820/1443/719	8507/0/380
Completeness to θ	98.8%	99.5%	97.9%	99.9%	99.8%	99.3%
GOF/F^2	1.010	0.966	1.089	0.710	0.972	1.102
$R1$,[a] $wR2$[b] [$I > 2\sigma(I)$]	0.0344, 0.0902	0.0813, 0.1251	0.0744, 0.1702	0.0427, 0.0584	0.0634, 0.0940	0.0303, 0.0450
$R1$,[a] $wR2$[b] (all data)	0.0362, 0.0916	0.1965, 0.1593	0.1135, 0.2137	0.1026, 0.0640	0.0852, 0.1031	0.0540, 0.0547
Largest diff. peak/hole [e/Å^3]	2.464/–3.310	1.538/–1.785	2.485/–2.471	1.449/–1.301	1.938/–1.322	1.391/–1.433

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$.

(976.41): calcd. C 35.67, H 4.13, N 2.87; found C 35.23, H 4.65, N 2.60.

Preparation of $[LH_2]^+[BiCl_4(THF)]^-$ (6): LH (0.70 g, 1.68 mmol) and $BiCl_3(THF)_2$ (0.89 g, 1.68 mmol) were placed into a 50 mL Schlenk flask and subjected to evacuation. The mixture was heated slowly to 125 °C and kept at this temperature for 5 h. After cooling to room temperature, the resultant solid was extracted with THF (15 mL). The extract was concentrated (ca. 5 mL) and then layered with *n*-hexane (0.5 mL). After keeping at –20 °C for 72 h, colorless crystals of **6** were obtained from the solution. Yield: 0.13 g, 9.3%. M.p. 143 °C. Due to the poor solubility of **6**, the resonance signals in the NMR spectra (^{1}H and ^{13}C) were hard to assign. IR (KBr plate, Nujol mull): $\tilde{\nu}$ = 3248 [w, ν(NH)] cm^{-1}. $C_{33}H_{51}BiCl_4N_2O$ (842.56): calcd. C 47.04, H 6.10, N 3.32; found C 46.10, H 5.01, N 3.33.

X-ray Structure Determination and Refinement: The crystallographic data for **1**–**6** were collected with a Rigaku R-Axis Spider IP system (**1**–**3** and **6**) or an Oxford Gemini S Ultra (**4** and **5**). In all cases graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used. Absorption corrections were applied by using the spherical harmonics program (multiscan type). The structures were solved by direct methods (SHELXS-96)[23] and refined against F^2 using SHELXL-97.[24] In general, the non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included by using the riding model with U_{iso} tied to the U_{iso} of the parent atoms unless otherwise specified. The carbon atoms of the THF solvent molecules in **3** and **5** and of the toluene molecule in **4** were isotropically refined. A summary of cell parameters, data collection, and structure solution and refinement is given in Table 1. CCDC-837123 (for **1**·2toluene), -837124 (for **2**), -837125 (for **3**·1.75THF), -837126 (for **4**·toluene), -837127 (for $\mathbf{5}_2$·3.7 THF), and -837128 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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