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Aluminum Complexes Containing Cyclohexane-1,2-diyl Linked Bis(ketiminato) Ligands and Proton-Promoted Demethylation

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A series of cyclohexane-1,2-diyl linked bis(ketiminato)aluminum complexes were synthesized. Reaction of a mixture of *cis*- and *trans*-diaminocyclohexane and 2,4-pentanedione gave a mixture of *cis*- and *trans*-cyclohexane-1,2-diyl linked bis(ketimine) ligands (*cis*-**1** and *trans*-**1**), which can be separated by fractional recrystallization. Reactions of *trans*-**1** with 1 and 2 equiv. $AlMe_3$ gave monoaluminum complex *trans*-C_6H_{10}[(NCMeCHCMeO)$AlMe_2$](NHCMeCHCMeO) (**2**) and dialuminum complex *trans*-C_6H_{10}[(NCMeCHCMeO)$AlMe_2$]$_2$ (**3**), respectively. Contrarily, when 1 equiv. or excess *cis*-**1** reacted with $AlMe_3$, only five-coordinate, linked bis(ketiminato)aluminum complex *cis*-C_6H_{10}[(NCMeCHCMeO)$_2$AlMe] (**4**) could be isolated in moderate yield. Heating complex **2** at reflux in a toluene solution resulted in the elimination of 1 equiv. methane to generate a five-coordinate, linked bis(ketiminato)aluminum complex, *trans*-C_6H_{10}[(NCMeCHCMeO)$_2$AlMe] (**5**). Complex **2** reacts with allyl alcohol and 2,6-dimethylphenol to form dimeric aluminum complexes [*trans*-C_6H_{10}(NCMeCHCMeO)$_2$Al]$_2$(μ-O–$CH_2CH{=}CH_2$)$_2$ (**6**) and *trans*-C_6H_{10}(NCMeCHCMeO)$_2$Al(O–C_6H_3–2,6-Me_2) (**7**), respectively. All the complexes have been characterized by ^1H and ^{13}C NMR spectroscopy and X-ray diffractometry.

Introduction

Common strategies for producing new catalysts with enhanced activities toward small molecules include changes in the types of ancillary ligand and variations in their electronic and steric effects. Numerous ligands have been used for synthesizing organometallic complexes; cyclopentadienyl (Cp) ligands dominate the field.[1–4] However, many studies have been aimed at non-Cp ligand systems, resulting in the development of many new types of ancillary ligands.[5–7] Among the non-Cp-type ancillary ligands, ligands containing heteroatoms such as O, N, S, and P have been broadly studied. Bidentate anionic ligands containing N and/or O atoms such as Schiff bases[8–15] and diketiminato ligands[16–24] have been widely used as ancillary ligands with many types of metals. However, monoanionic ketiminato or linked dianionic ketiminato ligands[25–30] have received less attention. The reasons for using ketiminato ligands instead of Schiff bases and diketiminates are: (i) ketiminato ligands contain one substituted imine, with which the electronic and steric effect of the ligands can be fine-tuned through substituted fragments; (ii) the ketiminato ligands leave an open end on the O site, which allows monomeric substrates to approach the metal center to increase the probability of successive reactions; (iii) the β-hydrogen of the ketiminato backbone presents higher acidity, and it may further react with other metal–alkyl or metal–amide complexes. In previous publications, we used ketiminato ligands as ancillary ligands to form a series of hydridoaluminum complexes.[31–33] The versatile (hydrido)bis(ketiminato)aluminum complexes react with small organic molecules through insertion or abstraction reactions. Here we extend our ketiminato–aluminum chemistry to include linked diketiminato–aluminum systems. We report the synthesis and characterization of aluminum complexes containing cyclohexane-1,2-diyl linked diketimines as ancillary ligands.

Results and Discussion

Synthesis and Characterization of Compounds 1–4

The reaction of a mixture of *cis*- and *trans*-diaminocyclohexane and 2,4-pentanedione in methanol under mild conditions gave a mixture of *cis*- and *trans*-C_6H_{10}-(NHCMeCHCMeO)$_2$ (**1**) (Scheme 1), which were then separated by fractional recrystallization. Pure *trans*-**1** and *cis*-**1** were obtained in 39.7 % and 6.0 % yield, respectively. The advantage of this method is that we can use inexpensive

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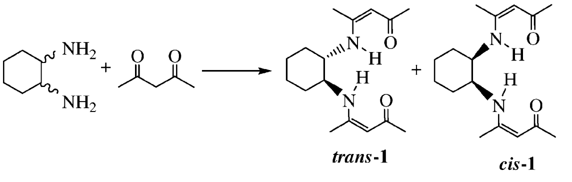
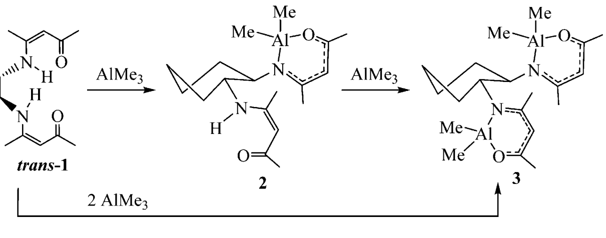
mixtures of *cis*- and *trans*-diaminocyclohexane as starting material to obtain the corresponding *cis*- and *trans*-cyclohexane-1,2-diyl linked diketimine ligands. Both *cis*- and *trans*-**1** have been characterized by ^1H and ^{13}C NMR spectroscopy (see Experimental Section).



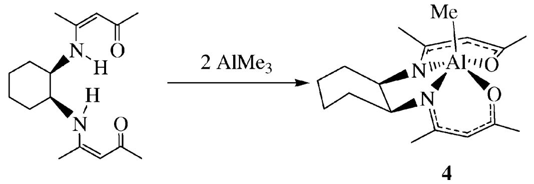
Scheme 1.

Reactions of *trans*-**1** with 1 or 2 equiv. $AlMe_3$ in dichloromethane at room temperature gave high yields of *trans*-C_6H_{10}[(NCMeCHCMeO)$AlMe_2$](NHCMeCHCMeO) (**2**) or *trans*-C_6H_{10}[(NCMeCHCMeO)$AlMe_2$]$_2$ (**3**), respectively (Scheme 2) along with the elimination of 1 or 2 equiv. methane, respectively. Complex **3** can also be obtained from the reaction of 1 equiv. $AlMe_3$ with **2**. The ^1H NMR spectrum of **2** shows two methine proton resonances at δ = 4.83 and 5.00 ppm, a clear differentiation between the ketiminato and ketimine backbones. The ^{13}C NMR spectrum of **2** shows that ketimine that is not coordinated to aluminum exhibits a more downfield-shifted resonance for C=O at δ = 194.8 ppm, whereas the resonance for the C=O of the ketiminato ligand coordinated with aluminum appears at δ = 178.9 ppm. The $AlMe_2$ fragment of **2** shows two ^{13}C NMR resonances at δ = –9.1 and –7.2 ppm, indicating the diastereotopic properties of the two methyl groups. The ^1H NMR spectrum of **3**, however, exhibited a more symmetrical pattern. Complex **3** consists of two ketiminato–$AlMe_2$ fragments linked by cyclohexane-1,2-diyl. Only one methine proton resonance of the ketiminato backbones was observed at δ = 3.88 ppm, indicating that the coordinating environments of the two ketiminato–$AlMe_2$ fragments are the same.



Scheme 2.

Treatment of *cis*-**1** with 2 equiv. $AlMe_3$ afforded a five-coordinate, linked bis(ketiminato)aluminum complex, *cis*-C_6H_{10}[(NCMeCHCMeO)$_2$AlMe] (**4**), in moderate yield (Scheme 3). Although the *cis*-**1** and $AlMe_3$ were employed in a 1:2 stoichiometric ratio, complex **4** was the only product isolated. Attempts to prepare an asymmetrical ketiminatoaluminum complex similar to **2** with a 1:1 *cis*-**1**/$AlMe_3$ stoichiometric ratio resulted in the isolation of only complex **4**, and no other ketiminatoaluminum complexes were found. The ^1H NMR spectrum of **4** shows that the resonances for the methyl groups attached to aluminum appear at δ = –0.88 ppm, while those for the methine protons of the ketiminato backbones appear at δ = 4.98 ppm.



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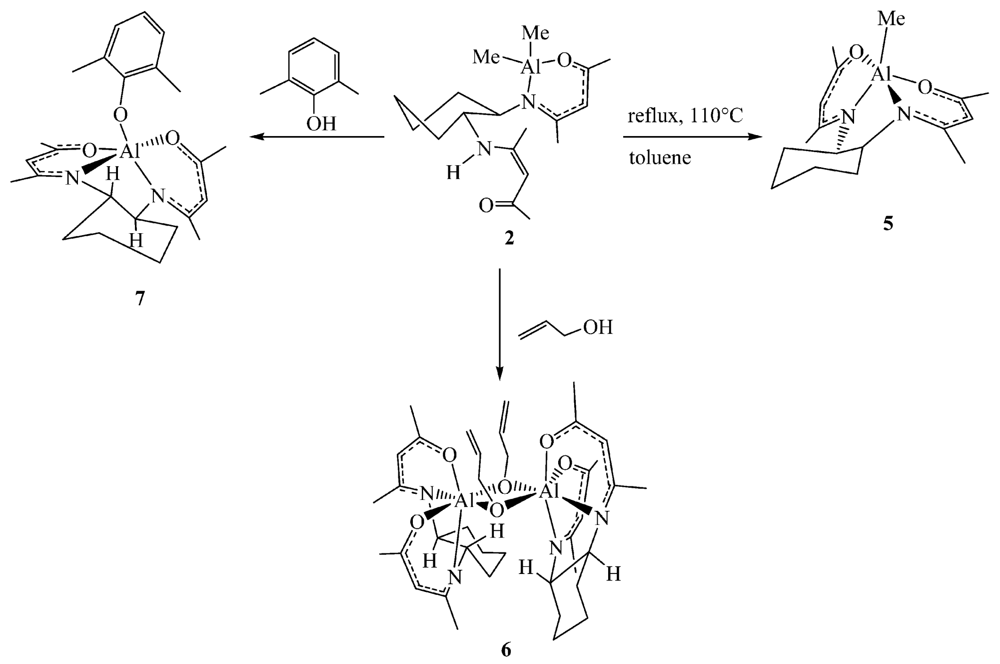
Scheme 3.

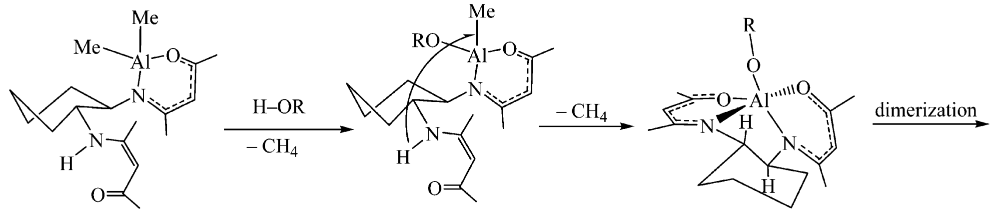
Proton-Promoted Demethylation of the Dimethylaluminum Complex

Monoketiminatodimethylaluminum complex **2** is thermally quite stable. It can be converted into a linked bis(ketiminato)methylaluminum complex, **5**, *trans*-C_6H_{10}-[(NCMeCHCMeO)$_2$AlMe], only under harsh conditions, i.e. by heating at reflux in toluene for 96 h (Scheme 4); this reaction is accompanied by the elimination of 1 equiv. methane. Pure complex **5** was obtained after recrystallization from a THF solution in high yield (80%). Unlike complex **4**, the asymmetrical complex **5** shows two methine signals for the two ketiminate fragments in the ^1H NMR spectrum. Similarly, the methine protons of the cyclohexane-1,2-diyl unit exhibited two multiplets at δ = 3.04 and 3.90 ppm.

Complex **2** reacted with alcohols to produce linked bis(ketiminato)aluminum complexes along with the elimination of methane. The reactions of **2** with 1 equiv. allyl alcohol and 2,6-dimethylphenol (Scheme 4) generated alkoxidoaluminum complexes [*trans*-C_6H_{10}(NCMeCHCMeO)$_2$Al]$_2$(μ-O–$CH_2CH=CH_2$)$_2$ (**6**) and *trans*-C_6H_{10}-(NCMeCHCMeO)$_2$Al(O–C_6H_3–2,6-Me_2) (**7**), respectively. Elemental analysis of complex **6** did not match with the calculated values, as the isolation of pure complex **6** by repeated recrystallization from a dichloromethane solution was hindered by a small amount of ketimine ligands and unknown impurities in the product. Complex **6** has been characterized by 1D and 2D ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectra of **6** show two methine signals for the ketiminato backbones at δ = 4.83 and 5.06 ppm due to the steric environment and two resonances for the cyclohexane-1,2-diyl CH protons at δ = 3.19 and 2.51 ppm. The methylene protons of O–CH_2 (δ = 5.09 and 4.87 ppm) and =CH_2 (δ = 4.28 and 4.25 ppm) for the allyl fragments all show distinguishing chemical shifts. Similarly, the ^1H NMR spectrum of **7** shows two methine signals for the linked bis(ketiminato) backbones at δ = 4.95 and 5.08 ppm and two resonances for the cyclohexane-1,2-diyl CH protons at δ = 3.13 and 4.25 ppm.



Scheme 4.



Scheme 5.

Comparing the conversions of monoketiminatoaluminum complex **2** to linked bis(ketiminato)aluminum complexes **5**, **6**, and **7**, we see that the presence of protic organic molecules has enhanced the elimination of the methyl group from the methylaluminum fragments. A possible reaction mechanism is shown in Scheme 5. The acidic proton of H–OR protonates the methylaluminum group and eliminates 1 equiv. methane to form AlMe(OR) complexes. The greater steric crowding of aluminum alkoxides enhances the further elimination of a second equivalent of methane to form the final products.

Theoretical Computations

Theoretical methods have been applied in order to understand the probable driving force that contributes to the differences in the reaction products of *cis*-**1** and *trans*-**1**. Structures and important geometrical parameters of the studied species are illustrated in Figure 1 and are compared with available X-ray data. It is seen that geometries predicted by DFT are in good agreement with the experimental data. The largest deviations occur in the Al–N and Al–O distances.

The calculation shows that adding 1 equiv. $AlMe_3$ to *trans*-**1** and *cis*-**1** to form **2** and *cis*-**2** are very exothermic; ΔE are –53.4 and –44.4 kcal/mol, respectively. For *trans*-**1** we have located two minima, an equatorial and an axial isomer. The equatorial isomer is 4.3 kcal/mol lower in energy. The complex of the equatorial *trans*-**1** with $AlMe_3$ is lower in energy than its axial counterpart by 15.5 kcal/mol. The results are consistent with the resolved X-ray structure of *trans*-**1** and -**2**.

The reactions of **2** and *cis*-**2** with the second equivalent of $AlMe_3$ are both very exothermic. In our investigation, **3** is the product of **2** and $AlMe_3$, while **4** is the only product of treating *cis*-**1** with either one or two equivalents of $AlMe_3$. A possible cause of this difference is the relative stability of **2** and *cis*-**2** with respect to the consecutive coordination (into **5** and **4**). The conversion of **2** to **5** may involve a larger reaction barrier than that of *cis*-**2** to **4**.

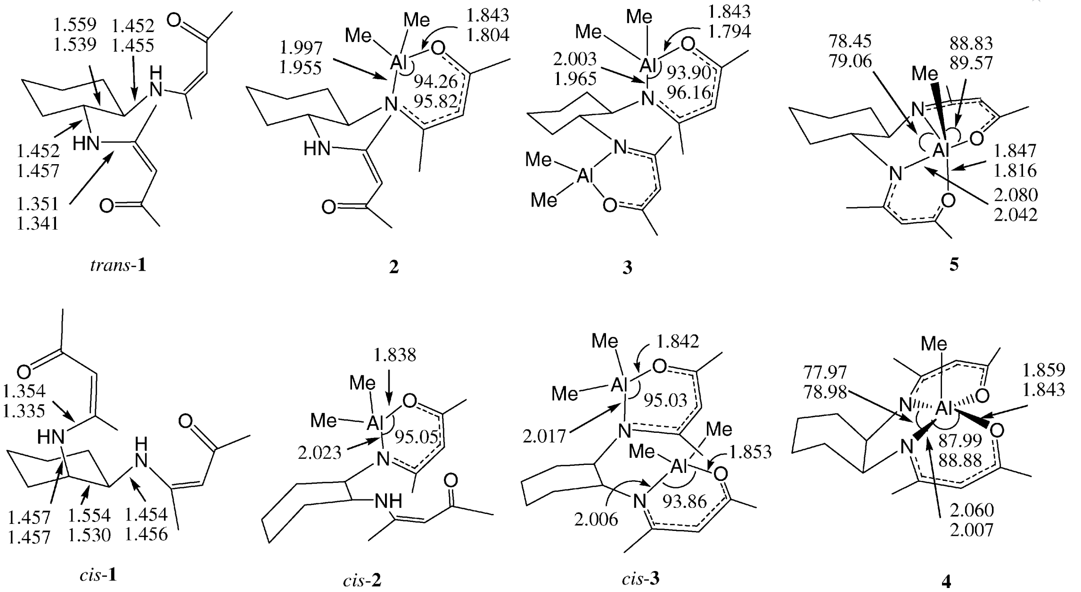


Figure 1. Structures and geometrical parameters obtained at the B3LYP/6-31G* level. The parameters obtained by X-ray diffraction data are shown in the second entries.

Molecular Structures for Complexes 1–7

The crystals of *trans*-**1** and *cis*-**1** were obtained, and their molecular structures were solved as well (Figure 2). The structure of *trans*-**1** is the same as that reported in the literature.[28] Single crystals of aluminum complexes **2**–**7** suitable for X-ray structure determination were crystallized from dichloromethane solutions at –20 °C. The collection and refinement data of the analyses are summarized in Table 1. Selected bond lengths and angles for complexes **2**–**7** are shown in Table 2. Although there are two independent molecules in a unit cell for complex **2**, the bond lengths and angles of these two molecules are relatively similar. Therefore, only one molecule is described here. Complex **2** contains one ketiminatodimethylaluminum fragment and one free ketimine (Figure 3). The ketiminate and ketimine rings are both perpendicular to the cyclohexane-1,2-diyl ring and are almost parallel to each other. The ketiminatodimethylaluminum fragment exhibits a distorted tetrahedral geometry with a biting angle of O(1)–Al(1)–N(1) equal to 106.6(3)°, which is much smaller than standard tetrahedral angles; however, it is much larger than that in normal coordinated ketiminatoaluminum complexes[22,28,29]. The free ketimine that is not coordinated to aluminum shows a mixed keto–enol form with bond lengths for C(15)–C(16) and C(17)–O(2) of 1.392(10) Å and 1.242(9) Å, respectively.

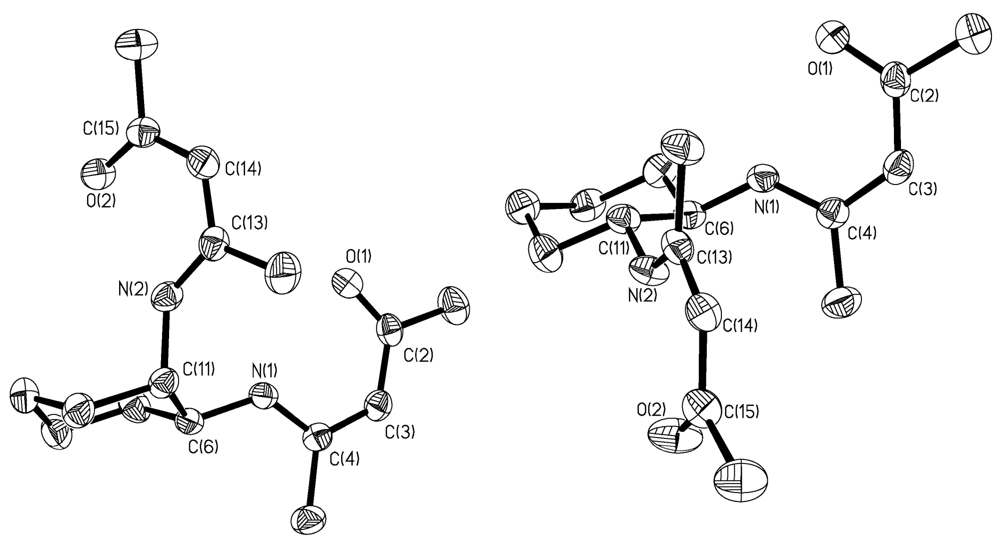


Figure 2. The comparison of the molecular structures of *cis*- and *trans*-**1**, in which thermal ellipsoids were drawn at 30% probability and all hydrogen atoms were omitted for clarity.

Table 1. Summary of crystallographic data for complexes **2**–**7**.

	2	**3**	**4**·CH_2Cl_2	**5**	**6**·CH_2Cl_2	**7**
Formula	$C_{18}H_{31}AlN_2O_2$	$C_{20}H_{36}AlN_2O_2$	$C_{18}H_{29}AlCl_2N_2O_2$	$C_{17}H_{27}AlN_2O_2$	$C_{39}H_{60}Al_2Cl_2N_4O_6$	$C_{24}H_{33}AlN_2O_3$
Formula weight	334.43	390.47	403.31	318.39	805.77	424.50
T [K]	150(2)	150(1)	150(1)	150(2)	150(2)	150(2)
Crystal system	triclinic	orthorhombic	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	*Pccn*	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a [Å]	12.117(4)	11.1513(4)	8.0184(1)	8.0963(5)	11.7913(9)	10.8736(6)
b [Å]	12.417(4)	11.5438(4)	10.9668(2)	9.8450(7)	13.4011(10)	19.3299(10)
c [Å]	13.965(4)	17.6683(7)	12.5820(2)	21.4805(14)	13.6351(11)	11.5527(7)
α [deg]	80.003(5)	90	84.8258(10)	90	77.041(2)	90
β [deg]	75.081(5)	90	76.1238(8)	96.762(2)	83.100(2)	111.075(3)
γ [deg]	73.492(5)	90	70.4327(8)	90	83.473(2)	90
V [Å^3]	1935.2(10)	2274.41(14)	2530.39(6)	1700.26(19)	2076.1(3)	2265.8(2)
Z	4	4	2	4	2	4
d_c [Mg/m^3]	1.148	1.140	1.324	1.244	1.289	1.244
μ [mm^{-1}]	0.116	0.143	0.378	0.128	0.248	0.117
F(000)	728	848	428	688	860	912
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
No. of rflns. collected	13636	28118	17890	16630	33818	24463
Ind. rflns.	8416	2619	4643	4539	11060	6002
R_{int}	0.0371	0.0380	0.0397	0.0204	0.0428	0.0421
Data/restraints/params.	8416/0/415	2619/0/122	4643/0/227	4539/0/204	11060 /0/ 486	6002/0/ 277
Goodness-of-fit on F^2	0.871	1.061	1.054	1.037	1.075	1.077
R_1, wR_2 [$I > 2\sigma(I)$]	0.0609, 0.1721	0.0417, 0.1087	0.0490, 0.1405	0.0330, 0.0935	0.0544, 0.1419	0.0423, 0.1027
R_1, wR_2 (all data)	0.1589, 0.2064	0.0486, 0.1137	0.0584, 0.1500	0.0401, 0.0973	0.0849, 0.1572	0.0725, 0.1118
Largest diff peak, hole [e/Å^3]	0.508, –0.464	0.356, –0.189	0.651, –0.499	0.338, –0.276	1.444, –1.098	0.262, –0.311

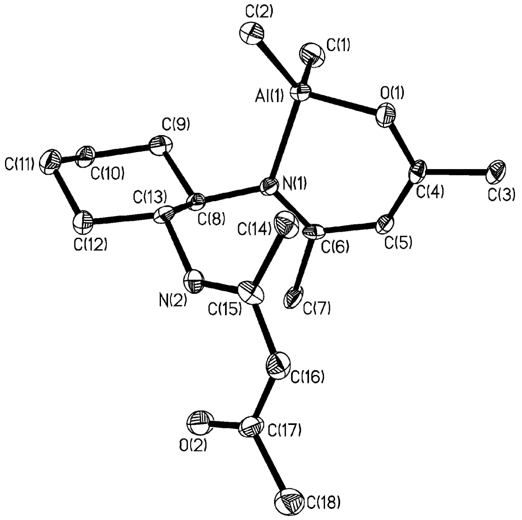


Figure 3. The molecular structure of complex **2**, in which thermal ellipsoids were drawn at 30% probability and all hydrogen atoms were omitted for clarity.

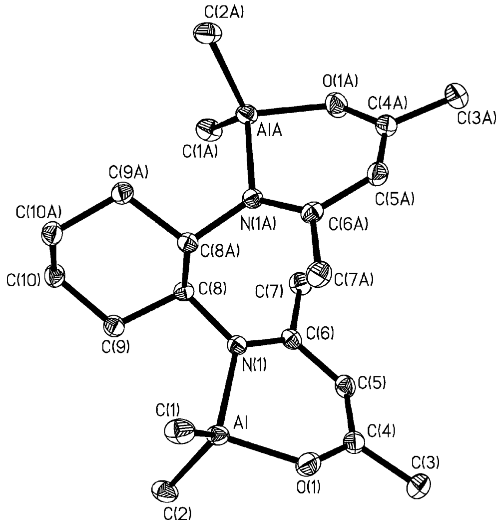


Figure 4. The molecular structure of complex **3**, in which thermal ellipsoids were drawn at 30% probability and all hydrogen atoms were omitted for clarity.

The molecular structure of complex **3** (Figure 4) is very similar to that of **2** except that the two ketiminate rings are now both bound to aluminum atoms and form two ketiminatodimethylaluminum fragments. Again, the biting angle of the ketiminatoaluminum fragment, O(1)–Al(1)–N(1), is 96.16(5)°, which is smaller than the bond angle for regular tetrahedral geometry.

In the molecular structure of complex **4** (Figure 5), the five-coordinate aluminum atom adopts a square-pyramidal geometry in which the two ketiminato ligands occupy the square base and the methyl group takes the apical position. The cyclohexane-1,2-diyl fragment exhibits a boat conformation. The deviation of the aluminum atom from the square base formed by the nitrogen and oxygen atoms of two ketiminate fragments is ca. 0.53 Å. The bond lengths of aluminum to the ketiminate N and O atoms, 1.9974–2.0067 Å and 1.8501–1.8428 Å, respectively, are apparently longer than those in complexes **2** and **3** (1.954–1.965 Å and 1.794–1.804 Å, respectively). Presumably, the more electron-rich ketiminato ligands lessen the electrophilicity of the high oxidation state of the aluminum atom.

The linked bis(ketiminato) fragments of complex **5** are bound to an aluminum atom along with a methyl group, forming a five-coordinate trigonal bipyramidal geometry (Figure 6). The nitrogen atom of one ketiminate group and the oxygen atom of the other ketiminate group occupy the axial positions with an angle of 167.53(4)°. The cyclohexane-1,2-diyl fragment is arranged in the chair conformation.

Table 2. The selected bond distances [Å] and angles [°] for complexes **2**–**7**.

2			
Al(1)–O(1)	1.804(5)	Al(1)–C(2)	1.946(7)
Al(1)–C(1)	1.951(9)	Al(1)–N(1)	1.954(6)
O(1)–Al(1)–C(2)	106.0(3)	O(1)–Al(1)–C(1)	109.7(3)
C(1)–Al(1)–C(2)	119.0(3)	O(1)–Al(1)–N(1)	106.6(3)
C(2)–Al(1)–N(1)	117.1(3)	C(1)–Al(1)–N(1)	106.6(3)
3			
Al(1)–O(1)	1.7935(12)	Al(1)–C(1)	1.9640(16)
Al(1)–N(1)	1.9649(12)	Al(1)–C(2)	1.9657(17)
O(1)–Al(1)–C(2)	111.13(7)	O(1)–Al(1)–C(1)	106.77(7)
C(1)–Al(1)–C(2)	116.44(7)	O(1)–Al(1)–N(1)	96.16(5)
C(2)–Al(1)–N(1)	109.03(6)	C(1)–Al(1)–N(1)	115.39(6)
4			
Al(1)–O(1)	1.8501(13)	Al(1)–O(2)	1.8428(13)
Al(1)–N(1)	1.9974(16)	Al(1)–C(1)	1.9807(19)
Al(1)–N(2)	2.0067(15)	O(2)–Al(1)–O(1)	85.59(6)
O(2)–Al(1)–C(1)	104.99(7)	O(1)–Al(1)–C(1)	102.11(7)
O(2)–Al(1)–N(1)	143.17(6)	O(1)–Al(1)–N(1)	89.33(6)
C(1)–Al(1)–N(1)	111.74(7)	O(2)–Al(1)–N(2)	88.88(6)
O(1)–Al(1)–N(2)	152.24(7)	C(1)–Al(1)–N(2)	105.60(7)
N(1)–Al(1)–N(2)	78.98(6)		
5			
Al(1)–O(1)	1.8162(8)	Al(1)–O(2)	1.8581(8)
Al(1)–N(2)	1.9732(9)	Al(1)–N(2)	1.9732(9)
Al(1)–C(17)	1.9857(11)	Al(1)–N(1)	2.0425(9)
O(1)–Al(1)–O(2)	90.82(4)	O(1)–Al(1)–N(2)	117.84(4)
O(2)–Al(1)–N(2)	89.57(4)	O(1)–Al(1)–C(17)	114.93(4)
O(2)–Al(1)–C(17)	95.35(4)	N(2)–Al(1)–C(17)	126.89(4)
O(1)–Al(1)–N(1)	89.99(4)	O(2)–Al(1)–N(1)	167.53(4)
N(2)–Al(1)–N(1)	79.06(4)	C(17)–Al(1)–N(1)	95.59(4)
6			
Al(1)–O(2)	1.8582(15)	Al(1)–O(1)	1.8682(15)
Al(1)–O(6)	1.8994(15)	Al(1)–O(5)	1.9107(14)
Al(1)–N(2)	2.0205(18)	Al(1)–N(1)	2.0535(17)
Al(2)–O(3)	1.8490(15)	Al(2)–O(4)	1.8742(15)
Al(2)–O(5)	1.9035(15)	Al(2)–O(6)	1.9077(15)
Al(2)–N(3)	2.0402(18)	Al(2)–N(4)	2.0453(17)
O(5)–C(33)	1.431(2)	O(6)–C(36)	1.431(2)
C(34)–C(35)	1.321(3)	C(36)–C(37)	1.494(3)
C(37)–C(38)	1.246(4)	O(1)–Al(1)–O(5)	91.01(6)
O(1)–Al(1)–O(6)	92.42(6)	O(6)–Al(1)–O(5)	75.94(6)
O(2)–Al(1)–N(2)	88.88(7)	O(6)–Al(1)–N(2)	168.04(7)
O(5)–Al(1)–N(2)	95.51(7)	O(2)–Al(1)–N(1)	165.40(7)
O(1)–Al(1)–N(1)	88.18(7)	O(4)–Al(2)–O(5)	92.40(6)
O(4)–Al(2)–O(6)	168.17(7)	O(5)–Al(2)–O(6)	75.92(6)
O(3)–Al(2)–N(3)	89.17(7)	O(5)–Al(2)–N(3)	167.83(7)
O(3)–Al(2)–N(4)	166.08(7)	O(4)–Al(2)–N(4)	87.99(7)
C(35)–C(34)–C(33)	124.1(2)	C(38)–C(37)–C(36)	128.1(3)
7			
Al(1)–O(3)	1.7417(11)	Al(1)–O(1)	1.7947(10)
Al(1)–O(2)	1.8474(10)	Al(1)–N(2)	1.9453(12)
Al(1)–N(1)	2.0221(12)	O(3)–Al(1)–O(1)	111.91(5)
O(3)–Al(1)–O(2)	98.58(5)	O(1)–Al(1)–O(2)	90.88(5)
O(3)–Al(1)–N(2)	122.16(5)	O(1)–Al(1)–N(2)	125.15(5)
O(2)–Al(1)–N(2)	89.82(5)	O(3)–Al(1)–N(1)	90.21(5)
O(1)–Al(1)–N(1)	91.17(5)	O(2)–Al(1)–N(1)	169.48(5)
N(2)–Al(1)–N(1)	80.57(5)		

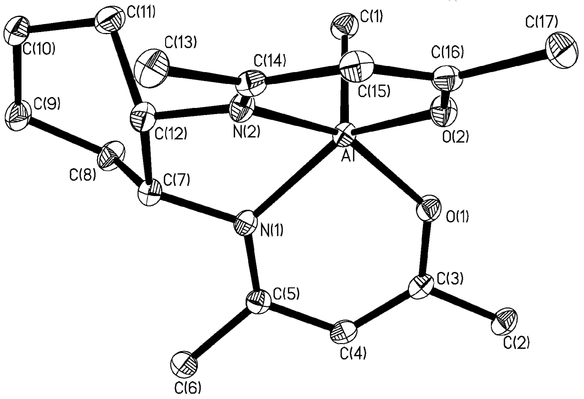


Figure 5. The molecular structure of complex **4**, in which thermal ellipsoids were drawn at 30% probability and all hydrogen atoms and one dichloromethane molecule were omitted for clarity.

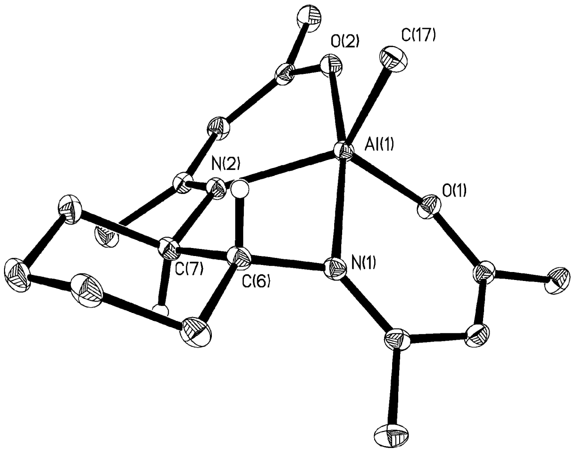


Figure 6. The molecular structure of complex **5**, in which thermal ellipsoids were drawn at 30% probability and all hydrogen atoms (excepting those on C5 and C6) and one dichloromethane molecule were omitted for clarity.

The crystal of **6** contains one molecule of **6** and one molecule of dichloromethane, which is omitted in Figure 7 for clarity. The molecular structure of **6** can be described as an edge-shared bi-octahedron in which the two oxygen atoms of the allyloxide groups occupy the sharing edge and the two allyl fragments extend in the same direction. All of the Al–O(bridge) bond lengths in complex **6** are very similar and lie in the range 1.8994(15)–1.9107(14) Å. They are much longer than the Al–O(ketiminate) bond lengths reported here, which range from 1.8490(15) Å to 1.8742(15) Å. Here, the Al–O(ketiminate) bond lengths are longer than the Al–O bond length in Schiff base aluminum complexes.[34,35] The Al_2O_2 core in complex **6** forms a perfect square plane with a dihedral angle of 7.8°, which is similar to the core structure of alkoxidodiketiminatoaluminum complexes reported by Wengrovius.[36]

Unlike the dimeric molecular structure of **6**, aryloxidoaluminum complex **7** exhibits a five-coordinate trigonal bipyramidal geometry in which the bulky 2,6-dimethylphenoxido ligand occupies the axial position (Figure 8). The short aryloxido–Al [1.7417(11) Å] bond length along with the large Al(1)–O(3)–C(17) [139.66(9)°] bond angle indicate that the delocalized O(p_π) electrons move towards the

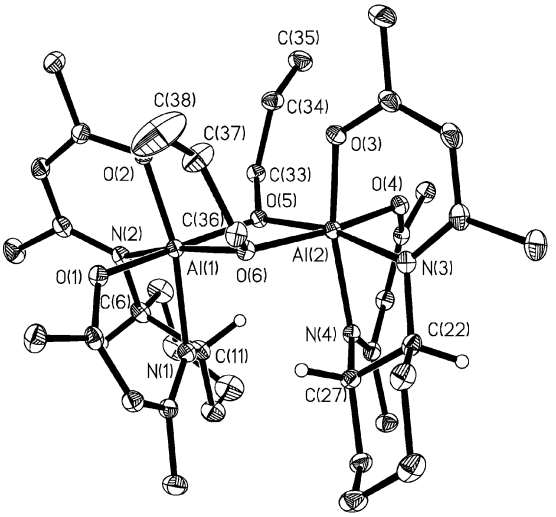


Figure 7. The molecular structure of complex **6**, in which thermal ellipsoids were drawn at 30% probability and all hydrogen atoms (excepting those on C6, C11, C22, and C27) and one dichloromethane molecule were omitted for clarity.

high-oxidation-state aluminum atom. A comparison of the structures of **6** and **7** shows that the bulkier aryloxide group of **7** is bound to the aluminum atom and occupies a large space in the Al coordination sphere, preventing complex **7** from forming a dimeric structure. In contrast, in complex **6**, the smaller allyloxide fragments are bridged to two aluminum atoms, forming a more stable dimeric structure.

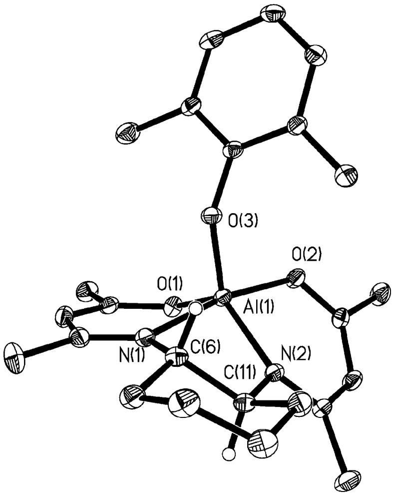


Figure 8. The molecular structure of complex **7**, in which thermal ellipsoids were drawn at 30% probability and all hydrogen atoms (excepting those on C6 and C11) and one dichloromethane molecule were omitted for clarity.

Conclusions

A series of aluminum complexes containing *cis*- and *trans*-cyclohexane-1,2-diyl linked bis(ketiminato) ligands has been synthesized. These ligands exhibit versatile coordination modes and the ability of forming mono- or dialuminum complexes. The allyloxido and aryloxidoaluminum complexes can be useful in olefin or lactide polymerization chemistry, and we are currently developing their applications.

Experimental Section

General Procedure: All reactions were performed under a dry nitrogen atmosphere by using standard Schlenk techniques or in a glove box. Toluene, heptane, diethyl ether, and tetrahydrofuran were dried by heating at reflux over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_2O_5. 1,2-diaminocyclohexane (99%, mixture of *cis* and *trans*) and 2,4-pentanedione were obtained from Aldrich and used as received. All solvents were distilled and stored in solvent reservoirs that contained 4-Å molecular sieves and were purged with nitrogen. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 spectrometer. Chemical shifts for ^1H and ^{13}C NMR spectra were recorded in ppm relative to the residual protons and the ^{13}C isotope of $CDCl_3$ (δ = 7.24 and 77.0 ppm, respectively) and C_6D_6 (δ = 7.16 and 128.0 ppm, respectively). Elemental analyses were performed with a Heraeus CHN–OS Rapid Elemental Analyzer at the Instrument Center, NCHU.

***cis*- and *trans*-C_6H_{10}[(NHCMeCHCMeO)]$_2$ (*cis*- and *trans*-1):** A mixture of *cis*- and *trans*-diaminocyclohexane (87.7 g, mmol) was dissolved in ethanol (30 mL), and a solution of 2,4-pentanedione (50.0 g, mmol) in methanol (30 mL) was added slowly. A few drops of formic acid were added to the mixed solution as catalyst. The solution was stirred at room temperature for another 12 h. Pure *trans*-**1** was first obtained from recrystallization (48.4 g, 39.7% yield), and *cis*-**1** was obtained from the last crop of recrystallization (7.2 g, 6.0% yield).

***trans*-1:** ^1H NMR ($CDCl_3$): 1.31 (m, 4 H, C*H*$_2$CH$_2$CHN), 1.79–2.03 (m, 4 H, CH$_2$C*H*$_2$CHN), 1.93 (s, 6 H, CC*H*$_3$), 1.98 (s, 6 H, CC*H*$_3$), 3.18 (m, 2 H, CH$_2$CH$_2$C*H*N), 4.84 (s, 2 H, CC*H*C), 10.95 (s, 2 H, N*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.7 (q, J_{CH} = 128 Hz, C*C*H$_3$), 24.4 (t, J_{CH} = 129 Hz, *C*H$_2$CH$_2$CHN), 28.7 (q, J_{CH} = 126 Hz, C*C*H$_3$), 32.9 (t, J_{CH} = 130 Hz, CH$_2$*C*H$_2$CHN), 57.7 (d, J_{CH} = 137 Hz, CH$_2$CH$_2$*C*HN), 95.3 (d, J_{CH} = 161 Hz, C*C*HC), 162.8 (s, *C*–N), 194.9 (s, *C* = O) ppm. $C_{16}H_{26}N_2O_2$ (278.39): calcd. C 69.03, H 9.41, N 10.06; found C 69.16, H 10.17, N 10.46.

***cis*-1:** ^1H NMR ($CDCl_3$): δ = 1.44 (m, 2 H, C*H*HCH$_2$CH), 1.67 (m, 2 H, CH*H*CH$_2$CHN), 1.67 (m, 4 H, CH$_2$C*H*$_2$CHN), 1.88 (s, 6 H, CC*H*$_3$), 1.95 (s, 6 H, CC*H*$_3$), 3.62 (m, 2 H, CH$_2$CH$_2$C*H*N), 4.98 (s, 2 H, CC*H*C), 11.12 (s, 2 H, O*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.5 (q, J_{CH} = 128 Hz, C*C*H$_3$), 21.6 (t, J_{CH} = 128 Hz, *C*H$_2$CH$_2$CHN), 28.5 (q, J_{CH} = 126 Hz, C*C*H$_3$), 29.5 (t, J_{CH} = 126 Hz, CH$_2$*C*H$_2$CHN), 52.9 (d, J_{CH} = 137 Hz, CH$_2$CH$_2$*C*HN), 96 (d, J_{CH} = 160 Hz, C*C*HC), 161.5 (s, *C*–N), 194.7 (s, *C* = O) ppm. $C_{16}H_{26}N_2O_2$ (278.39): calcd. C 69.03, H 9.41, N 10.06; found C 69.02, H 10.15, N 10.18.

***trans*-C_6H_{10}[(NCMeCHCMeO)AlMe$_2$](NHCMeCHCMeO) (2):** To a 30-mL Schlenk flask charged with dichloromethane (15 mL) and *trans*-**1** (3.0 g, 10.8 mmol), was added $AlMe_3$ toluene solution (5.4 mL, 2 M, 10.8 mmol) at –78 °C. The solution was stirred for 10 h, and the volatiles were removed under vacuum. The solid was recrystallized from a saturated dichloromethane solution at –20 °C to yield a white solid of **2** (2.67 g) in 74% yield. ^1H NMR ($CDCl_3$): δ = –0.99 (s, 3 H, Al*Me*), –0.61 (s, 3 H, Al*Me*), 1.33 (br.m, 4 H, cyclohexane-1,2-diyl-C*H*$_2$), 1.76–2.04 (br.m, 4 H, cyclohexane-1,2-diyl-C*H*$_2$), 1.80 (s, 3 H, C*Me*), 1.91 (s, 3 H, C*Me*), 1.94 (s, 3 H, C*Me*), 1.97 (s, 3 H, C*Me*), 3.54 (br.m, 2 H, cyclohexane-1,2-diyl-C*H*-N), 4.83 (s, 1 H, NCMeC*H*CMeO), 5.00 (s, 1 H, NCMeC*H*CMeO), 10.91 (br. s, 1 H, N*H*) ppm. ^{13}C NMR ($CDCl_3$):

δ = –9.1 (q, J_{CH} = 119 Hz, Al*Me*), –7.2 (q, J_{CH} = 118 Hz, Al*Me*), 19.1 (q, J_{CH} = 128 Hz, C*Me*), 22.8 (q, J_{CH} = 128 Hz, C*Me*), 24.5 (t, J_{CH} = 128 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 24.7 (t, J_{CH} = 127 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 25.3 (q, J_{CH} = 127 Hz, C*Me*), 28.8 (q, J_{CH} = 126 Hz, C*Me*), 31.7 (t, J_{CH} = 128 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 33.9 (t, J_{CH} = 133 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 55.9 (d, J_{CH} = 137 Hz, cyclohexane-1,2-diyl-*C*H-N), 63.7 (d, J_{CH} = 135 Hz, cyclohexane-1,2-diyl-*C*H-N), 95.2 (d, J_{CH} = 161 Hz, OCMe*C*HCMeNH), 101.2 (d, J_{CH} = 162 Hz, OCMe*C*HCMeN), 162.9 (s, OCMeCH*C*MeNH), 175.2 (s, OCMeCH*C*MeN), 178.9 (s, O*C*MeCHCMeN), 194.8 (s, O*C*MeCHCMeNH) ppm. $C_{18}H_{31}AlN_2O_2$ (334.43): calcd. C 64.65, H 9.34, N 8.38; found C 64.58, H 8.85, N 8.41.

***trans*-C$_6$H$_{10}$[(NCMeCHCMeO)AlMe$_2$]$_2$ (3):** A similar reaction procedure to that used for synthesizing **2** was applied here. *trans*-**1** (1.0 g, 3.6 mmol) and AlMe$_3$ (2 M, 3.6 mL, 7.2 mmol) were used, and 1.21 g product was isolated (86% yield). ^{1}H NMR (CDCl$_3$): δ = –1.00 (s, 6 H, Al*Me*), –0.55 (s, 6 H, Al*Me*), 1.30 (br.m, 2 H, cyclohexane-1,2-diyl-C*H*$_2$), 1.83–2.00 (br.m, 6 H, cyclohexane-1,2-diyl-C*H*$_2$), 1.92 (s, 6 H, C*Me*), 1.93 (s, 6 H, C*Me*), 3.88 (br.m, 2 H, cyclohexane-1,2-diyl-C*H*-N), 4.99 (s, 2 H, NCMeC*H*CMeO) ppm. ^{13}C NMR (CDCl$_3$): δ = –9.3 (q, J_{CH} = 112 Hz, Al*Me*), –7.0 (q, J_{CH} = 112 Hz, Al*Me*), 23.4 (q, J_{CH} = 128 Hz, C*Me*), 24.3 (t, J_{CH} = 128 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 25.3 (q, J_{CH} = 127 Hz, C*Me*), 31.8 (t, J_{CH} = 126 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 61.9 (d, J_{CH} = 133 Hz, cyclohexane-1,2-diyl-*C*H-N), 101.0 (d, J_{CH} = 161 Hz, OCMe*C*HCMeN), 175.4 (s, OCMeCH*C*MeN), 178.8 (s, O*C*MeCHCMeN) ppm. $C_{20}H_{36}Al_2N_2O_2$ (390.48): calcd. C 61.52, H 9.29, N 7.17; found C 60.79, H 9.33, N 7.20.

***cis*-C$_6$H$_{10}$[(NCMeCHCMeO)$_2$AlMe] (4):** A similar reaction procedure to that used for synthesizing **2** is applied here. *cis*-**1** (1.0 g, 3.6 mmol) and excess AlMe$_3$ (2 M, 3.6 mL, 7.2 mmol) were used, and 0.21 g product was isolated (86% yield). ^{1}H NMR (CDCl$_3$): δ = –0.88 (br. s, 3 H, Al*Me*), 1.40 (br.m, 2 H, cyclohexane-1,2-diyl-C*H*$_2$), 1.54–1.69 (br.m, 4 H, cyclohexane-1,2-diyl-C*H*$_2$), 1.86–1.96 (m, 2 H, cyclohexane-1,2-diyl-C*H*$_2$), 1.951 (s, 6 H, C*Me*), 1.954 (s, 6 H, C*Me*), 1.96 (s, 3 H, C*Me*), 3.74 (br.m, 2 H, cyclohexane-1,2-diyl-C*H*-N), 4.98 (s, 2 H, NCMeC*H*CMeO) ppm. ^{13}C NMR (CDCl$_3$): δ = 19.3 (t, J_{CH} = 127 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 20.9 (q, J_{CH} = 128 Hz, C*Me*), 25.6 (q, J_{CH} = 127 Hz, C*Me*), 27.1 (t, J_{CH} = 128 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 55.0 (d, J_{CH} = 140 Hz, cyclohexane-1,2-diyl-*C*H-N), 99.6 (d, J_{CH} = 160 Hz, OCMe*C*HCMeN), 170.6 (s, OCMeCH*C*MeN), 179.1 (s, O*C*MeCHCMeN) ppm. $C_{17}H_{27}AlN_2O_2$ (318.39): calcd. C 64.13, H 8.55, N 8.80; found C 64.32, H 8.59, N 8.86.

***trans*-C$_6$H$_{10}$[(NCMeCHCMeO)$_2$AlMe] (5):** A toluene (20 mL) solution of **2** (0.30 g,) was heated at reflux for 4 d, and the volatiles were removed under vacuum. The resulting solid was recrystallized from a THF solution to yield 0.23 g (80.4%) final product. ^{1}H NMR (CDCl$_3$): δ = –0.88 (s, 3 H, Al*Me*), 1.36 (br.m, 3 H, cyclohexane-1,2-diyl-C*H*$_2$), 1.75–2.05 (br.m, 4 H, cyclohexane-1,2-diyl-C*H*$_2$), 1.85 (s, 3 H, C*Me*), 1.92 (s, 3 H, C*Me*), 1.94 (s, 3 H, C*Me*), 1.97 (s, 3 H, C*Me*), 2.48 (m, 1 H, cyclohexane-1,2-diyl-C*H*$_2$), 3.04 (br.m, 1 H, cyclohexane-1,2-diyl-C*H*-N), 3.90 (br.m, 1 H, cyclohexane-1,2-diyl-C*H*-N), 4.77 (s, 1 H, NCMeC*H*CMeO), 5.03 (s, 1 H, NCMeC*H*CMeO) ppm. ^{13}C NMR (CDCl$_3$): δ = 21.3 (q, J_{CH} = 128 Hz, C*Me*), 23.3 (q, J_{CH} = 128 Hz, C*Me*), 24.6 (t, J_{CH} = 124 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 25.66 (q, J_{CH} = 127 Hz, C*Me*), 25.74 (q, J_{CH} = 127 Hz, C*Me*), 26.5 (t, J_{CH} = 127 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 32.8 (t, J_{CH} = 132 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 33.6 (t, J_{CH} = 130 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 63.28 (d, J_{CH} = 135 Hz, cyclohexane-1,2-diyl-*C*H-N), 63.30 (d, J_{CH} = 135 Hz, cyclohexane-1,2-diyl-*C*H-N), 99.3 (d, J_{CH} = 161 Hz, OCMe*C*HCMeN), 101.1 (d, J_{CH} = 156 Hz, OCMe*C*HCMeN), 165.2 (s, OCMeCH*C*MeN), 173.8 (s, OCMeCH*C*MeN), 176.1 (s, O*C*MeCHCMeN) 180.8 (s, O*C*MeCHCMeN) ppm. $C_{17}H_{27}AlN_2O_2$ (318.39): calcd. C 64.13, H 8.55, N 8.80; found C 63.95, H 8.08, N 8.60.

[*trans*-C$_6$H$_{10}$(NCMeCHCMeO)$_2$Al]$_2$(μ-O–CH$_2$CH=CH$_2$)$_2$ (6): To a 100-mL Schlenk flask charged with **2** (1.0 g, 2.99 mmol) and toluene (50 mL) was added allyl alcohol (0.174 g, 2.99 mmol), and the solution was heated at reflux for additional 4.5 h. Volatiles were removed, and the residue was recrystallized from a CH$_2$Cl$_2$/heptane solvent system to yield 1.53 g (71%) pale yellow crystals. A small amount of the original cyclohexane-1,2-diyldiketimine ligand was observed in the final product even when repetitive recrystallization was performed. ^{1}H NMR (C$_6$D$_6$): δ = 1.32 (br., 16 H, C*H*$_2$ cyclohexane-1,2-diyl), 1.84 (s, 6 H, C*H*$_3$), 1.96 (s, 6 H, C*H*$_3$), 1.97 (s, 6 H, C*H*$_3$), 2.02 (s, 6 H, C*H*$_3$), 2.48 (d, 2 H, C*H* cyclohexane-1,2-diyl), 3.06 (d, 2 H, C*H* cyclohexane-1,2-diyl), 4.18 (br., 4 H, OC*H*$_2$), 4.86 (d, 2 H, C*H* allyl), 5.09 (d, 2 H, C*H* allyl), 5.03 (s, 2 H, CC*H*C), 5.25 (s, 2 H, CC*H*C), 6.01 (m, 2 H, C*H* allyl) ppm. ^{13}C NMR (C$_6$D$_6$): δ = 21.3 (q, J_{CH} = 128 Hz, C*C*H$_3$), 23.6 (q, J_{CH} = 128 Hz, C*C*H$_3$), 25.6 (q, J_{CH} = 128 Hz, C*C*H$_3$), 24.7 (t, *C*H$_2$ cyclohexane-1,2-diyl), 26.5 (t, *C*H$_2$ cyclohexane-1,2-diyl), 32.8 (t, J_{CH} = 122 Hz, *C*H$_2$ cyclohexane-1,2-diyl), 33.4 (t, J_{CH} = 129 Hz, *C*H$_2$ cyclohexane-1,2-diyl), 63.0 (d, J_{CH} = 138 Hz, CH cyclohexane-1,2-diyl), 64.0 (d, J_{CH} = 137 Hz, CH cyclohexane-1,2-diyl), 64.3 (t, J_{CH} = 138 Hz, O*C*H$_2$), 99.4 (d, J_{CH} = 161 Hz, C*C*HC), 101.8 (d, J_{CH} = 159 Hz, C*C*HC), 111.5 (t, J_{CH} = 155 Hz, *C*H$_2$ allyl), 142.6 (d, J_{CH} = 155 Hz, *C*H allyl), 167.0 (s, N-*C*), 174.4 (s, N-*C*), 176.3 (s, O =*C*), 181.7 (s, O =*C*) ppm.

***trans*-C$_6$H$_{10}$(NCMeCHCMeO)$_2$Al(O–C$_6$H$_3$–2,6-Me$_2$) (7):** To a 30-mL Schlenk flask charged with toluene (15 mL) and *trans*-**1** (0.50 g, 1.50 mmol) was added a toluene solution of 2,6-dimethylphenol (0.183 g, 1.50 mmol in 10 mL toluene) at 0 °C. The solution was stirred for 20 min and heated at reflux for additional 14 h. The volatiles were removed under vacuum, and the solid was recrystallized from a saturated dichloromethane solution at –20 °C to afford a white solid of **7** (0.47 g) in 79% yield. ^{1}H NMR (C$_6$D$_6$): δ = 1.37 (br.m, 4 H, cyclohexane-1,2-diyl-C*H*$_2$), 1.67–2.53 (m, Me and cyclohexane-1,2-diyl-C*H*$_2$), 3.13 (br.m, 1 H, cyclohexane-1,2-diyl-C*H*-N), 4.25 (br.m, 1 H, cyclohexane-1,2-diyl-C*H*-N), 4.95 (s, 1 H, NCMeC*H*CMeO), 5.08 (s, 1 H, NCMeC*H*CMeO), 6.48-6.87 (m, 3 H, Ph) ppm. ^{13}C NMR (C$_6$D$_6$): δ = 17.52 (q, J_{CH} = 128 Hz, Ph-*Me*), 21.54 (q, J_{CH} = 128 Hz, *Me*), 23.73 (q, J_{CH} = 128 Hz, *Me*), 24.56 (t, J_{CH} = 128 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 25.50 (q, J_{CH} = 127 Hz, *Me*), 26.36 (t, J_{CH} = 127 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 32.77 (t, J_{CH} = 132 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 33.34 (t, J_{CH} = 133 Hz, cyclohexane-1,2-diyl-*C*H$_2$), 63.03 (d, J_{CH} = 137 Hz, cyclohexane-1,2-diyl-*C*H-N), 64.41 (d, J_{CH} = 137 Hz, cyclohexane-1,2-diyl-*C*H-N), 99.36 (d, J_{CH} = 161 Hz, OCMe*C*HCMeNH), 102.3 (d, J_{CH} = 162 Hz, OCMe*C*HCMeN), 116.64, 127.25, 127.46, 157.2 (Ph), 166.9 (s, OCMeCH*C*MeNH), 174.62 (s, OCMeCH*C*MeN), 175.9 (s, O*C*MeCHCMeN), 182.4 (s, O*C*MeCHCMeNH) ppm. $C_{22}H_{33}AlN_2O_3$ (400.49): calcd. C 67.90, H 7.84, N 6.60; found C 67.78, H 7.28, N 5.90.

X-ray Structure Determination of Complexes 1–7: The crystals were sealed in glass fibers under nitrogen and transferred to a goniostat. Data were collected with a Bruker SMART CCD diffractometer with graphite-monochromated Mo-K_α radiation with a radiation wavelength of 0.71073 Å. Structural determinations were made by using the SHELXTL package of programs.[37] A SADABS absorption correction was made.[38] All refinements were carried out by full-matrix least-squares and by using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were placed with the use of a riding model. The crystal data are summarized in Table 1.

CCDC-665882 (*cis*-**1**), -665881 (*trans*-**1**), -665879 (**2**), -665875 (**3**), -665880 (**4**), -665876 (**5**), -665877 (**6**), and -665878 (**7**) 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.

Theoretical Computations: The gradient-corrected hybrid density functional theory (DFT), B3LYP, along with the 6-31G* basis set was used in the computations. All calculations were carried out with the Gaussian 03 program, Revision C.02.[39] Predicted reaction energies are summarized in Table 3.

Table 3. Reaction energies computed by using the B3LYP/6-31G*level of theory.

Reactions			Δ*E* [kcal/mol]
trans-**1** + $AlMe_3$	→	**2** + CH_4	–53.4
2 + $AlMe_3$	→	**3** + CH_4	–51.7
2	→	**5** + CH_4	–28.3
cis-**1** + $AlMe_3$	→	*cis*-**2** + CH_4	–44.4
cis-**2** + $AlMe_3$	→	*cis*-**3** + CH_4	–48.7
cis-**2**	→	**4** + CH_4	–42.1

Acknowledgments

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