Synthesis and X-ray crystal structures of β -ketoiminate complexes

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Dedicated to Prof. W. Uhl on the occasion of his 65th birthday

Abstract: Heteroleptic zinc complexes containing side-arm donor-functionalized tridentate β -ketoiminate ligands were obtained from metalation reactions of β -ketoimines $L1/2/3^{Do1/2/3/4}H$ ($L1 = \{(OC(Me)C(H)C(Me)NCH_2CH_2Do)\}$, $L2 = \{(OC(Me)C(H)C(Me)NCH_2CH_2CH_2Do)\}$, $L3 = \{(OC(OMe)C(H)C(Me)NCH_2CH_2Do)\}$; $Do1 = NMe_2$, $Do2 = NEt_2$; $Do3 = Pyr$, $Do4 = OMe$) with equimolar amounts of $Zn[N(SiMe_3)_2]_2$ ($L1^{Do1}ZnN(SiMe_3)_2$ **1**, $L1^{Do2}ZnN(SiMe_3)_2$ **2**) and $ZnEt_2$ ($L1^{Do3}ZnEt$ **3**; $L2^{Do3}ZnEt$ **4**; $L3^{Do1}ZnEt$ **5**; $L3^{Do4}ZnEt$ **6**). Analogous reactions of $AlMe_3$ and Cp^*MMe_3 with $L1^{Do1/2}H$ yielded homoleptic aluminum ($L1^{Do1}AlMe_2$ **7**; $L1^{Do2}AlMe_2$ **8**; $L2^{Do1}AlMe_2$ **9**), titanium ($L1^{Do2}Ti(Me_2)Cp^*$ **10**) and zirconium complexes ($L1^{Do2}Zr(Me_2)Cp^*$ **11**). In addition, **7** reacts with an ethereal HCl solution with methane elimination and formation of $L1^{Do1}Al(Cl)Me$ (**12**) and $L1^{Do1}AlCl_2$ (**13**), while the reaction with one and two equivalents of 2,6-dimethylphenol yielded $L1^{Do1}Al(Me)O-2,6-Me_2C_6H_3$ (**14**) and $L1^{Do1}Al(O-2,6-Me_2C_6H_3)_2$ (**15**). The complexes were characterized by elemental analysis, 1H , ^{13}C NMR and IR spectroscopy and single crystal X-ray analysis (**2**, **4**, **7**, **10**, **12-14**).

modified by introducing substituents R and R' with different sizes in the backbone as well as on the imine center by using different primary amines, ranging from those containing small substituents to those containing demanding organic groups. Analogous findings were reported for β -diketimines and other N,N'-chelating substituents such as dipyrromethene ligands. The steric demand of the specific ligand not only results in a kinetic stabilization of the complexes,^[4] which sometimes become even air-stable, but also dramatically influences the activity for the stereo-regular ROP of lactide as was demonstrated by Coates et al. for specific β -diketiminate zinc complexes.^[5] In addition, the electronic properties of β -ketoimines can be controlled by using electron donating or electron withdrawing substituents R and R', as was also demonstrated for β -diketimines.^[6] Moreover, the introduction of a side-arm donor function (Do) in β -ketoimines of type **V** can further influence the structure of the resulting complexes in solution and in the solid state such as their tendency toward dimerization as well as their tendency toward ligand disproportionation reaction as was often observed for heteroleptic zinc and aluminum complexes.^[7]

Introduction

Chelating N,O ligands are well established in coordination chemistry. Aside from classical bidentate N,O ligands such as N,O-chelating β -ketoimines (**I**) and aminophenols (**II**), donor-functionalized tridentate-type O,N,N (**III**), and O,N,O (**IV**) ligands as shown in scheme 1 have also been investigated in detail.^[1] In the last two decades, these type of ligands have also been extensively applied for the synthesis of a large variety of transition metal and main group metal catalysts for the ring opening polymerization (ROP) of cyclic ethers including lactide and ϵ -caprolactone, respectively.^[2] In particular catalysts based on rather cheap and non-toxic metals such as Mg, Ti, Zn and Al as well as lanthanide metals have been widely applied.^[3] β -ketoimines (type **I**) are very promising ligands in main group metal and transition metal chemistry since their steric and electronic properties can be effectively controlled to a very large extent. The steric demand of β -ketoimines can easily be

Scheme 1. Typical bidentate N,O and tridentate O,N,N and O,N,O ligands.

We recently reported on the solid state structures of monomeric β -ketoiminate complexes $L2^{Do1}ZnR$ ($R = Me, Et$).^[8] In contrast, complex $L1^{Do2}ZnEt$ was reported to form a tetrameric structure in the solid state.^[9] Unfortunately, any attempts to structurally characterize the complexes $L1^{Do1/2}ZnMe$ and $L1^{Do1}ZnEt$ as well as $L2^{Do2}ZnR$ ($R = Me, Et$) failed.^[8] To further investigate the influence of β -ketoiminate ligand, in particular of the side-arm donor group, and of the Zn-bonded group on the structure of the resulting complexes in the solid state in more detail, we now synthesized different donor-functionalized β -ketoimines LH and reacted them with either $Zn[N(SiMe_3)_2]_2$ or $ZnEt_2$. In addition, we extended our studies on reactions of such β -ketoimines LH with other main group metal and transition metal alkyl of group 4 (Ti, Zr) and 13 (Al), respectively, since these metals are also of potential interest in ROP of cyclic ethers.

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Results and Discussion

Six donor-functionalized β -ketoimines LH (Scheme 1) were synthesized by condensation reaction between the corresponding diketone (acetylacetone, methyl acetoacetate) and the primary amine (N,N-dimethylethylenediamine, N,N-diethylethylenediamine, 1-(3-aminopropyl)pyrrolidine, 2-methoxyethylamine) according to literature known methods.^[10]

Scheme 2. Drawing of the β -ketoimines LH used in this study.

The β -ketoimines **L1**^{Do1-3}, **L2**^{Do3} and **L3**^{Do1/4} were obtained as yellow oils in almost quantitative yields after workup. Their ¹H and ¹³C NMR spectra show the expected resonances of the acetylacetone backbone, the C₂H₄ or C₃H₆ spacer and the specific donor groups (Do = NMe₂, NEt₂, Pyr, OMe).

The β -ketoimines were then reacted with equimolar amounts of Zn[N(SiMe₃)₂]₂ and ZnEt₂, respectively. The corresponding heteroleptic zinc complexes **1** - **6** (Scheme 2) were also obtained in high yields (>80 %) after workup.

Scheme 3. Drawing of the heteroleptic zinc complexes **1** - **6**.

¹H and ¹³C NMR spectra of the heteroleptic complexes **1** - **6** show the resonances of the β -ketoiminate ligands and the ZnR group (R = N(SiMe₃)₂ **1**, **2**; Et **3** - **6**) in the expected 1:1 molar ratio. In contrast, the homoleptic complex (L3^{Do4})₂Zn **7** only shows the resonances of the β -ketoiminate ligand.

Unfortunately, single crystals suitable for X-ray analyses were only obtained for **2** and **4** upon storage of solutions of **2** and **4** in *n*-hexane at -30 °C.^[11] **2** and **4** form monomeric structures in the solid state (Figures 1 and 2) and their central structural parameters are almost identical (Table 1). The zinc atoms in **2** and **4** adopt slightly distorted tetrahedral coordination

geometries as was previously observed for zinc complexes containing donor-functionalized β -ketoiminate ligands.^[8]

Figure 1. Crystal structure of **L1**^{Do2}ZnN(SiMe₃)₂ (**2**). All hydrogen atoms have been omitted for clarity. Ellipsoids are drawn to a 50 % probability level. Only one of the two independent molecules is displayed.

Figure 2. Crystal structure of **L2**^{Do3}ZnEt (**4**). Ellipsoids are drawn to a 50 % probability level and hydrogen atoms as spheres of arbitrary radii.

The Zn-O (**2** 1.9815(12), 1.9769(12) Å; **4** 1.9767(8) Å) and Zn-N bond lengths (**2** 1.9943(14), 1.9949(15) Å; **4** 2.0050(10) Å) as well as the N-C, C-C and O-C bond lengths and N-C-C, C-C-C and C-C-O bond angles within the six-membered ZnNOC₃ rings

are almost identical (Table 1). Similar bond lengths and angles were observed in zinc complexes containing tridentate β -ketoiminate, amino- and iminophenolate ligands.^[12] In contrast, the endocyclic O1-Zn1-N1 bond angles (**2** 92.03(5), 92.09(6)°, **4** 94.89(4)°) significantly deviate from each other. The Zn-N bond lengths toward the coordinating amine donor group (**2** 2.1849(14), 2.1648(14) Å; **4** 2.2031(10) Å) are also comparable. In contrast, the side-arm donor groups of the homoleptic complexes (L1^{Do1})₂Zn and (L1^{Do4})₂Zn do not coordinate to the zinc atom,^[13] since the tetrahedral coordination geometry of the central zinc atom is already achieved by coordination of two N,O-chelating β -ketoiminate ligands. In contrast, the zinc atom in the related homoleptic zinc complex (L4^{Do1})₂Zn (L4^{Do1} = {(OC(Ph)C(H)C(Me)NCH₂CH₂Do)}), in which one Me group of the β -ketoiminate ligand is replaced by a Ph group, is additionally coordinated by one side-arm donor group, resulting in a distorted trigonal-bipyramidal coordination geometry.^[14]

Table 1. Selected bond lengths (Å) and bond angles (°) of L1^{Do2}ZnN(SiMe₃)₂ (**2**) and L2^{Do3}ZnEt (**4**).

	2 ^[a]	4
Zn-N	1.9943(14), 1.9949(15)	2.0050(10)
Zn-O	1.9815(12), 1.9769(12)	1.9767(8)
Zn-N _(amin)	2.1849(14), 2.1648(14)	2.2031(10)
Zn-N _(tms)	1.9280(14), 1.9314(14)	–
Zn-C	–	1.9904(11)
N1-C1	1.304(2), 1.307(2)	1.3082(15)
O1-C3	1.292(2), 1.296(2)	1.2895(14)
C1-C2	1.427(2), 1.422(3)	1.4273(16)
C2-C3	1.381(2), 1.380(3)	1.3845(16)
N-Zn-O	92.03(5), 92.09(6)	94.89(4)
N _(amin) -Zn-O	122.24(5), 125.19(6)	104.50(4)
N-Zn-N _(amin)	81.29(6), 81.52(6)	88.41(4)
Zn1-N1-C1	123.25(12), 122.61(13)	124.13(8)
Zn1-O1-C3	118.72(11), 116.72(12)	121.90(8)
C1-C2-C3	126.02(16), 126.27(17)	128.04(10)

[a] two independent molecules

Since titanium and aluminum complexes are also of potential interest as catalyst for the ROP of cyclic ethers, we became further interested to extend our studies on the synthesis of heteroleptic β -ketoiminate complexes of the general type LAIR₂ and LMR₃ (R = Ti, Zr), respectively. The reaction of AlMe₃ with LH at low temperature proceeded with smooth elimination of methane and subsequent formation of the heteroleptic aluminum complexes L1^{Do1}AlMe₂ (**7**), which has been prepared previously,^[15] L1^{Do2}AlMe₂ (**8**) and L2^{Do1}AlMe₂ (**9**), respectively. Comparable results were obtained in the reactions of LH with

Cp*MMe₃, which also occurred with methane elimination and almost quantitative formation of the heteroleptic complexes L1^{Do1}Ti(Cp*)Me₂ (**10**) and L1^{Do1}Zr(Cp*)Me₂ (**11**) (Scheme 3).

Scheme 4. Synthesis of heteroleptic aluminum and titanium β -ketiminato complexes (**7** - **11**).

¹H and ¹³C NMR spectra of the heteroleptic complexes **7** - **11** show the resonances of the β -ketiminato ligands and the MMe₂ groups (M = Al, Ti, Zr). In addition, the ¹H and ¹³C NMR spectra of **10** and **11** each show one additional resonance of the Me substituent of the Cp* ligand as well as one resonance of the ring carbon atoms (¹³C NMR), indicating a η^5 -coordination of the Cp* ligand in solution.

Reactions of L1^{Do1}AlMe₂ (**7**) with HCl in Et₂O yielded L1^{Do1}Al(Cl)Me (**12**), while L1^{Do1}AlCl₂ (**13**) was obtained by equimolar reaction of **12** with GaCl₃. **12** and **13** were isolated by fractional crystallization from solutions in *n*-hexane. **7** also reacted with one and two equivalents of ROH (R = 2,6-Me₂C₆H₃) with elimination of ethane and formation of L1^{Do1}Al(Me)O-2,6-Me₂C₆H₃ (**14**) and L1^{Do1}Al(O-2,6-Me₂C₆H₃)₂ (**15**) (Scheme 4). ¹H and ¹³C NMR spectra of the heteroleptic complexes **12** - **15** exhibit the resonances of the β -ketiminato ligand and the AlMe group (**12**, **14**) as well as the 2,6-dimethylphenoxide ligand in the expected 1:1 (**14**) and 1:2 (**15**) molar ratios.

Scheme 5. Drawing of the heteroleptic aluminum complexes (**12** - **15**).

Single crystals of the aluminum complexes **7** and **12** - **14** (Figures 3-6) were obtained from solutions in *n*-hexane upon storage at -30 °C.^[11] **7** and **12** - **14** adopt monomeric structures in the solid state (Figures 4 - 7). Their central structural parameters are summarized in table 2.

Figure 3. Crystal structure of $L1^{Do1}AlMe_2$ (**7**). Ellipsoids are drawn to a 50 % probability level and hydrogen atoms as spheres of arbitrary radii.

Table 2. Selected bond lengths (Å) and bond angles (°) of $L1^{Do1}AlMe_2$ (**7**), $L1^{Do1}Al(Cl)Me$ (**12**), $L1^{Do1}AlCl_2$ (**13**) and $L1^{Do1}Al(Me)O-2,6-Me_2C_6H_3$ (**14**).

	7	12	13	14
Al-N1	1.9857(7)	1.9658(11)	1.9414(6)	1.9719(8)
Al-O1	1.8984(7)	1.8541(11)	1.8232(6)	1.8656(7)
Al-N2	2.2283(8)	2.1468(12)	2.0921(6)	2.1441(9)
Al-C	1.9942(9) 1.9896(9)	2.036(7) ^[a]	—	1.9836(11)
Al-Cl	—	2.213(2) ^[a]	2.2179(3) 2.1774(3)	—
Al-O ^(ph)	—	—	—	1.7870(7)
N1-C1	1.3233(10)	1.3231(16)	1.3234(9)	1.3235(13)
O1-C3	1.2827(11)	1.2856(16)	1.2939(9)	1.2858(12)
C1-C2	1.4156(11)	1.4160(17)	1.4173(10)	1.4188(14)
C2-C3	1.3838(12)	1.3794(18)	1.3760(10)	1.3834(14)
N1-Al-O1	88.65(3)	89.92(5)	91.15(3)	89.23(3)
Namine-Al-O1	166.03(3)	164.93(5)	167.10(3)	165.08(4)
N1-Al-Namine	77.72(3)	79.92(4)	80.88(3)	79.16(4)
Al-N1-C1	125.62(5)	126.89(9)	126.57(5)	126.24(7)
Al-O1-C3	129.03(6)	132.52(9)	131.67(5)	130.19(6)
C1-C2-C3	123.35(8)	123.56(12)	123.84(6)	123.74(9)

[a] Restraints applied

Figure 4. Crystal structure of $L1^{Do1}Al(Cl)Me$ (**12**). Solvent and minor part of the disorder have been omitted for clarity. Ellipsoids are drawn to a 50 % probability level and hydrogen atoms as spheres of arbitrary radii.

Figure 5. Crystal structure of $L1^{Do1}AlCl_2$ (**13**). Ellipsoids are drawn to a 50 % probability level and hydrogen atoms as spheres of arbitrary radii.

Figure 6. Crystal structure of $L1^{Do1}Al(Me)O-2,6-Me_2C_6H_3$ (**14**). All hydrogen atoms have been omitted for clarity. Ellipsoids are drawn to a 50 % probability level.

$L1^{Do1}AlMe_2$ **7** is a new polymorph of the known structure of $L1^{Do1}AlMe_2$ ^[15] and the bonding parameters (Al-O, Al-N and Al-C bond length, endo- and exocyclic bond angles) of both polymorphs are almost identical. In addition, the solid state structures of $L1^{Do1}Al(Cl)Me$ (**12**) and $L1^{Do1}AlCl_2$ (**13**) are comparable to those of $L1^{Do2}Al(Me)Cl$ ^[16] and $L1^{Do2}AlCl_2$ ^[17] respectively, and their central Al-N (**7** 1.9857(7) Å; **12** 1.9658(11) Å; **13** 1.9414(6) Å; **14** 1.9719(8) Å) and Al-O (**7** 1.8984(7) Å; **12** 1.8541(11) Å; **13** 1.8232(6) Å; **14** 1.8656(7) Å) bond lengths and O-Al-N bond angles (**7** 88.65(3)°; **12** 89.92(5)°; **13** 91.15(3)°; **14** 89.23(3)°) within the six-membered AlONC₃ metallacycle also agree very well. The Al atoms in the complexes are fivefold coordinated and show distorted trigonal-bipyramidal (tbp) coordination modes. The central aluminum atom in **7** and **12-14** is coordinated by N1 and two further heteroatoms X (X = C, Cl, O) in a trigonal planar mode, whereas the O1 and N2 (amine) atoms always adopt the axial positions of the distorted tbp coordination. The O1-Al-N2 bond angles deviated from linearity by roughly 15° (table 2).

Penta-coordinated aluminum complexes have been prepared and structurally characterized in the past and the bonding situation in such complexes including chelating tri- or tetradentate N,O-based ligands was analyzed by quantum chemical calculations.^[18] Lewiński et al. demonstrated the *trans-effect* in five-coordinated aluminum complexes containing O,O'-chelating substituents, clearly revealing the influence on the resulting structure in solution and in the solid state as well as the stability of such complexes.^[19] Several dimeric complexes of the general type $[R_2Al(O,O')]_2$ derived from α - and β -hydroxy carbonyl compounds were structurally characterized and a strong relation between the two axial Al-O bond lengths was revealed: The stronger (shorter) the external axial Al-O_{ax/ex} bond, the weaker (longer) the internal axial Al-O_{ax/br} bond toward the bridging alkoxide.^[20] In addition, the formation of an envelope-type C₃O₂Al six-membered ring as observed in the 4-methylpyridine adduct of $Me_2Al[OC(Me)C_6H_4-2-O]$, which also contains a penta-coordinate aluminum atom, was addressed to the *trans-effect* of the axial substituents, even though no bond weakening was observed in this case.^[7b] It should be noted, that the C₃NOAl six membered rings in **7** and **12-14** each form envelope-like structures.

The side-arm donor group (NMe₂) coordinates in all complexes to the Lewis-acidic aluminum atom, resulting in the formation of five-membered AlN₂C₂ rings, and the Al-N bond lengths (2.2283(8) Å **7**, 2.1468(12) Å **12**, 2.0921(6) Å **13**, 2.1441(9) Å **14**) are comparable to those reported for $L1^{Do2}Al(Me)Cl$ (2.252(2) Å)^[16] and $L1^{Do2}AlCl_2$ (2.171(3) Å).^[17] The axial Al-N2 are significantly elongated compared to the equatorial Al-N1 bond lengths. As was expected, the introduction of two electronegative, electron withdrawing Cl substituents increases the Lewis acidity of the central Al atom, resulting in the shortest Al-N bond distances.

Single crystals of $L1^{Do2}Ti(Cp^*)Me_2$ **10** were obtained upon storage of a concentrated solution of **10** in *n*-hexane at -30 °C.^[11] **10** adopts a monomeric structure in the solid state (Figure 7).

Figure 7. Crystal structure of $L1^{Do2}Ti(Cp^*)Me_2$ (**10**). All hydrogen atoms have been omitted for clarity. Ellipsoids are drawn to a 50 % probability level.

Even though a large number of β -ketoiminate complexes of group 4 metal have been synthesized in the past,^[21] only one compound containing a Cp* substituent has been structurally characterized. The mixed ketoiminate-ketoimine zirconium complex $Cp^*(Cl)_2Zr(L5)L5H$, which contains a para-CF₃-substituted phenyl substituent at the imine N atom, was obtained from the reaction of Cp^*ZrCl_3 with an equimolar mixture of LiL5 and L5H (L5 = $\{(OC(Me)C(H)C(Me)N-4-CF_3Ph)\}$).^[22] The Cp* substituent in **10** adopts a η^5 coordination mode as was expected from the ¹H and ¹³C NMR spectra and as was also observed in $Cp^*(Cl)_2Zr(L5)L5H$. The Ti-O (1.963(2) Å), Ti-N (2.226(8) Å) and Ti-Cp*_{centr.} bond lengths (2.402(8) Å) of **10** are shorter compared to the values observed for $Cp^*(Cl)_2Zr(L5)L5H$ (Zr-O (2.054(5)Å), Zr-N (2.418(6) Å) and Zr-Cp*_{centr.} (2.602(8) Å)), reflecting the larger atom radii of Zr compared to Ti. The amine donor group in **10** does not bind to the Lewis-acidic metal center most likely due to the presence of the η^5 -coordinated Cp* ligand, which transfers enough electron density to the Ti atom. As a consequence, the Ti atom is fivefold coordinated and adopts a distorted square-pyramidal coordination geometry.

Conclusions

Metalation reactions of donor-functionalized β -ketoiminines $L1-3^{Do1-4}H$ with main group (Al) and transition metal complexes (Ti, Zr, Zn) yielded heteroleptic metal β -ketoiminate complexes **1-15**. The complexes were characterized by heteronuclear NMR (¹H, ¹³C) and IR spectroscopy, elemental analysis as well as single crystal X-ray analyses (**2**, **4**, **7**, **10**, **12-14**). Except for the heteroleptic Ti complex **10**, the donor side-arm of the β -ketoimininate ligands was found to coordinate to the metal atom, resulting in the formation of monometallic complexes containing tetrahedrally-coordinated zinc and penta-coordinated aluminum atoms.

Experimental Section

General: All manipulations involving air-sensitive materials were performed using standard vacuum techniques and inert gas atmosphere (argon, < 0.3 ppm O₂) or in a glove box (MBraun Unilab V2.0). Solvents were carefully dried over CaH₂ (CH₂Cl₂) or Na/K alloy (pentane, hexane), respectively, degassed and stored in teflon-sealed glass vessel over molecular sieve. Zn[N(SiMe₃)₂]₂^[23] and Cp*MMe₃ (M = Ti, Zr)^[24] were synthesized according to literature methods. ¹H (300 MHz) and ¹³C{¹H} (75.5 MHz) NMR spectra (δ in ppm) were recorded using a Bruker Avance DPX-300 spectrometer and the spectra were referenced to internal C₆D₅H (¹H: δ = 7.16; ¹³C: δ = 128.06), C₆D₅CHD₂ (¹H: δ = 2.08; ¹³C: δ = 20.43), CDCl₃ (¹H: δ = 7.26; ¹³C: δ = 77.16) and CD₂Cl₂ (¹H: δ = 5.32; ¹³C: δ = 53.84)).^[25] Microanalyses were performed at the Elemental Analysis Laboratory of the University of Duisburg-Essen. IR spectra were measured in an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. The melting points were measured using a Thermo Scientific 9300 apparatus.

General procedure for the synthesis of β-ketoimines LH. A solution of the acetylacetone derivative in 15 mL of dichloromethane was cooled to 0 °C, the amine dropwise added and the resulting solution stirred for additional 2 h. The as-formed water as well as the solvent and the remaining acetylacetonate was removed in vacuo and the β-ketoimines were obtained as yellow oils.

L1^{D03}H. Reagents: 6.2 mL (61 mmol) acetylacetone, 7.6 mL (60 mmol) 1-(3-aminopropyl)pyrrolidine. Yield 11.01 g (93 %). Elemental analysis calcd (%) for C₁₁H₂₀N₂O: C, 67.3; H, 10.3; N, 14.3; found (%): C, 66.8, H, 10.2, N, 14.4. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ = 1.49 (s, 3H, CCH₃), 1.51 (m, 4H, N^{pyr}CH₂CH₂), 1.98 (s, 3H, CCH₃), 2.24 (m, 4H, N^{pyr}CH₂CH₂), 2.27 (t, ³J_{HH} = 6.6 Hz, 2H, NCH₂CH₂), 2.90 (q, ³J_{HH} = 5.8 Hz, 2H, NCH₂CH₂), 4.88 (s, 1H, CH), 11.13 (s, 1H, NH). ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ = 18.6 (CCH₃), 23.9 (N^{pyr}CH₂CH₂), 28.9 (CCH₃), 42.3 (NCH₂CH₂), 54.2 (N^{pyr}CH₂CH₂), 55.8 (NCH₂CH₂), 96.2 (CH), 161.6 (CN), 193.9 (CO). IR: ν = 3025, 2955, 2889, 2804, 1609, 1546, 1519, 1297, 1174, 1122, 1010, 712, 633 cm⁻¹.

L2^{D03}H. Reagents: 6.2 mL (61 mmol) acetylacetone, 6.8 mL (60 mmol) 1-(3-aminopropyl)pyrrolidine. Yield 12.15 g (96 %). Elemental analysis calcd (%) for C₁₂H₂₂N₂O: C, 68.5; H, 10.5; N, 13.3; found (%): C, 69.0, H, 10.6, N, 13.2. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ = 1.38 (m, ³J_{HH} = 6.8 Hz, 2H, NCH₂CH₂CH₂), 1.53 (s, 3H, CCH₃), 1.55 (m, ³J_{HH} = 3.6 Hz, 4H, N^{pyr}CH₂CH₂), 1.96 (s, 3H, CCH₃), 2.24 (t, ³J_{HH} = 6.6 Hz, 6H, N^{pyr}CH₂), 2.92 (q, ³J_{HH} = 5.8 Hz, 2H, NCH₂CH₂CH₂), 4.85 (s, 1H, CH), 11.10 (s, 1H, NH). ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ = 18.0 (CCH₃), 23.9 (N^{pyr}CH₂CH₂), 28.9 (CCH₃), 29.6 (NCH₂CH₂CH₂), 40.7 (NCH₂CH₂CH₂), 53.0 (N^{pyr}CH₂CH₂), 54.1 (NCH₂CH₂CH₂), 95.1 (CH), 162.2 (CN), 193.7 (CO). IR: ν = 2974, 2952, 2831, 2822, 2740, 1638, 1574, 1423, 1307, 1089, 1062, 795, 637 cm⁻¹.

L3^{D01}H. Reagents: 6.50 mL (61 mmol) methyl acetoacetate, 6.62 mL (60 mmol) N,N-dimethylethylenediamine. Yield 10.84 g (97 %). Elemental analysis calcd (%) for C₉H₁₈N₂O₂: C, 58.0; H, 9.7; N, 15.0; found (%): C, 57.7; H, 10.0; N, 15.0. ¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 1.85 (s, 3H, CCH₃), 2.18 (s, 6H, N(CH₃)₂), 2.39 (m, 2H, NCH₂CH₂), 3.20 (m, 2H, NCH₂CH₂), 3.53 (s, 3H, OCH₃), 4.36 (s, 1H, CH), 8.55 (s, 1H, NH). ¹³C-NMR (75 MHz, CDCl₃, 25 °C): δ = 19.6 (CCH₃), 41.0 (NCH₂CH₂), 45.5 (N(CH₃)₂), 49.9 (OCH₃), 59.0 (NCH₂CH₂), 81.9 (CH), 161.5 (CN), 170.7 (CO). IR: ν = 3354, 3266, 2945, 2861, 2820, 2768, 1654, 1593, 1499, 1443, 1242, 1168, 1119, 1051, 920, 782, 699 cm⁻¹.

L3^{D04}H. Reagents: 6.50 mL (61 mmol) methyl acetoacetate, 4.78 g (60 mmol) 2-methoxyethylamine. Yield 7.63 g (96%). Elemental analysis calcd (%) for C₈H₁₅NO₃: C, 55.5; H, 8.7; N, 8.1; found (%): C, 55.9; H, 8.9; N, 7.8. ¹H-NMR (300 MHz, CDCl₃, 25 °C): δ = 1.89 (s, 3H, CCH₃), 3.34 (s, 3H, OCH₃), 3.44 (dt, ³J_{HH} = 5.6 Hz, 2H, NCH₂CH₂), 3.47 (t, ³J_{HH} = 5.6 Hz, 2H, NCH₂CH₂), 3.57 (s, 3H, COCH₃), 4.42 (s, 1H, CH), 8.62 (s, 1H, NH). ¹³C-NMR (75 MHz, CDCl₃, 25 °C): 19.5 (CCH₃), 42.9 (NCH₂CH₂), 49.9 (OCH₃), 59.1 (NCH₂CH₂), 71.9 (COCH₃), 82.3 (CH), 161.8 (CN), 170.9 (CO). IR: ν = 3353, 3291, 2929, 2880, 2833, 1652, 1598, 1502, 1443, 1257, 1170, 1115, 1055, 1003, 923, 782, 698 cm⁻¹.

General procedure for the synthesis of heteroleptic complexes

LZn(N(SiMe₃)₂)₂: A solution of the β-ketoimine in *n*-hexane (20 mL) was slowly added to a cooled (-50 °C) solution of Zn[N(SiMe₃)₂]₂ (0.33 g, 0.84 mmol) in *n*-hexane (20 mL) and slowly warmed to ambient temperature within 3 h. The solution was concentrated to 5 mL and stored at -30 °C, yielding colorless crystalline solids within 24 h.

L1^{D01}ZnN(SiMe₃)₂ 1: Reagent: 0.14 g (0.84 mmol) L1^{D01}H. Yield 0.29 g (82%). Mp 87 °C. Elemental analysis calcd (%) for C₁₅H₃₅N₃OSi₂Zn: C 45.6, H 8.9, N 10.6; found (%): C 45.2, H 8.8, N 10.4. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 0.01 (s, 18H, SiMe₃), 1.87 (s, 6H, CCH₃), 2.39 (s, 6H, N(CH₃)₂), 2.64 (t, ³J_{HH} = 6.3 Hz, 2H, NCH₂CH₂), 3.39 (t, ³J_{HH} = 6.3 Hz, 2H, NCH₂CH₂), 4.48 (s, 1H, CH). ¹³C NMR (75 MHz, CD₂Cl₂, 25 °C): δ = 5.0 (SiMe₃), 21.2 (CCH₃), 27.6 (CCH₃), 44.0 (NCH₂CH₂), 45.4 (N(CH₃)₂), 58.8 (NCH₂CH₂), 96.9 (CH), 172.3 (CN), 182.9 (CO). IR: ν 2912, 1584, 1509, 1396, 1281, 1067, 1000, 948, 799, 675, 552, 464, 420.

L1^{D02}ZnN(SiMe₃)₂ 2: Reagent: 0.17 g (0.84 mmol) L1^{D02}H. Yield 0.31 g (86%). Mp 31 °C. Elemental analysis calcd (%) for C₁₇H₃₉N₃OSi₂Zn: C 48.3, H 9.3, N 9.9; found (%): C 47.9, H 9.2, N 9.8. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 0.43 (s, 18H, SiMe₃), 0.79 (t, ³J_{HH} = 7.2 Hz, 6H, N(CH₂CH₃)₂), 1.44 (s, 3H, CCH₃), 2.00 (s, 3H, CCH₃), 2.20 (t, ³J_{HH} = 6.4 Hz, 2H, NCH₂CH₂), 2.39 (q, ³J_{HH} = 7.2 Hz, 4H, N(CH₂CH₃)₂), 2.81 (t, ³J_{HH} = 6.4 Hz, 2H, NCH₂CH₂), 4.84 (s, 1H, CH). ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ = 6.2 (SiMe₃), 9.6 (N(CH₂CH₃)₂), 21.3 (CCH₃), 28.4 (CCH₃), 43.7 (NCH₂CH₂), 45.6 (N(CH₂CH₃)₂), 52.3 (NCH₂CH₂), 97.7 (CH), 172.0 (CN), 184.0 (CO). IR: ν 2945, 1595, 1499, 1387, 1342, 1241, 992, 880, 815, 740, 664, 610, 439, 403.

General procedure for the synthesis of heteroleptic complexes

LZnEt. 10 mL (10 mmol) of a 1M solution of Et₂Zn in *n*-hexane was cooled to -35 °C and a solution of the corresponding β-ketoimine in 25 mL of *n*-hexane was added dropwise. The solution was slowly warmed to ambient temperature and stirred for additional 2 h, until ethane evolution has stopped. The solvent was removed in vacuo and the remaining crystalline solid recrystallized from solutions in *n*-hexane at -30 °C. The complexes were obtained as light-yellow crystals.

L1^{D03}ZnEt 3: Reagent: 1.96 g (10 mmol) L1^{D03}H. Yield: 2.43 g (84 %). Mp 83 °C. Elemental analysis calcd (%) for C₁₃H₂₄N₂OZn: C, 53.9; H, 8.4; N, 9.7; found (%): C, 54.0; H, 8.3; N, 9.9. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 0.63 (q, ³J_{HH} = 7.9 Hz, 2H, ZnCH₂CH₃), 1.61 (m, 4H, N^{pyr}CH₂CH₂), 1.62 (s, 3H, CCH₃), 1.81 (t, ³J_{HH} = 7.9 Hz, 3H, ZnCH₂CH₃), 2.14 (s, 3H, CCH₃), 2.30 (m, 6H, N^{pyr}CH₂CH₂ and NCH₂CH₂), 2.91 (t, ³J_{HH} = 6.3 Hz, 2H, NCH₂CH₂), 4.97 (s, 1H, CH). ¹³C NMR (75 MHz, C₆D₆, 25 °C): δ = -2.8 (ZnCH₂CH₃), 13.5 (ZnCH₂CH₃), 20.6 (CCH₃), 22.7 (N^{pyr}CH₂CH₂), 27.6 (CCH₃), 45.5 (NCH₂CH₂), 52.8 (N^{pyr}CH₂CH₂), 54.0 (NCH₂CH₂), 96.9 (CH), 170.4 (CN), 182.3 (CO). IR: ν = 2922, 2851, 1560, 1506, 1405, 1310, 1006, 937, 753, 594, 494, 434 cm⁻¹.

L2^{D03}ZnEt 4: Reagent: 2.10 g (10 mmol) L2^{D03}H. Yield: 2.43 g (80 %). Mp 62 °C. Elemental analysis calcd (%) for C₁₄H₂₆N₂OZn: C, 55.4; H, 8.6;

N, 9.2; found (%): C, 55.9; H, 8.8; N, 9.3. ^1H NMR (300 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = 0.54 (q, $^3J_{\text{HH}}$ = 7.8 Hz, 2H, ZnCH_2CH_3), 1.16 (m, $^3J_{\text{HH}}$ = 4.8 Hz, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.52 (s, 3H, CCH_3), 1.64 (m, $^3J_{\text{HH}}$ = 5.9 Hz, $\text{N}^{\text{pyr}}\text{CH}_2\text{CH}_2$), 1.71 (t, $^3J_{\text{HH}}$ = 7.9 Hz, 3H, ZnCH_2CH_3), 1.98 (s, 3H, CCH_3), 2.18 (t, $^3J_{\text{HH}}$ = 6.2 Hz, 4H, $\text{N}^{\text{pyr}}\text{CH}_2\text{CH}_2$), 2.31 (t, $^3J_{\text{HH}}$ = 6.0 Hz, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 3.20 (t, $^3J_{\text{HH}}$ = 4.5 Hz, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 4.67 (s, 1H, CH). ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$): δ = -4.2 (ZnCH_2CH_3), 14.2 (ZnCH_2CH_3), 19.3 (CCH_3), 22.6 ($\text{N}^{\text{pyr}}\text{CH}_2\text{CH}_2$), 27.7 (CCH_3), 29.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 50.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 55.0 ($\text{N}^{\text{pyr}}\text{CH}_2\text{CH}_2$), 58.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 96.1 (CH), 167.9 (CN), 181.7 (CO). IR: ν = 2905, 2858, 1545, 1499, 1422, 1307, 1036, 978, 596, 565, 471, 432 cm^{-1} .

L3^{Do1}ZnEt 5: Reagent: 1.86 g (10 mmol) L3^{Do1}H. Yield: 3.70 g (93%). Mp. 80 $^\circ\text{C}$. Elemental analysis calcd (%) for $\text{C}_{11}\text{H}_{22}\text{N}_2\text{O}_2\text{Zn}$: C, 47.2; H, 7.9; N, 10.0; found (%): C, 47.3; H, 7.8; N, 10.0. ^1H -NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 0.13 (q, $^3J_{\text{HH}}$ = 8.02 Hz, 2H, ZnCH_2CH_3), 1.22 (t, $^3J_{\text{HH}}$ = 8.2, 3H, ZnCH_2CH_3), 1.92 (s, 3H, CCH_3), 2.38 (s, 6H, $\text{N}(\text{CH}_3)_2$), 2.57 (t, $^3J_{\text{HH}}$ = 6.1 Hz, 2H, NCH_2CH_2), 3.39 (t, $^3J_{\text{HH}}$ = 5.8 Hz, 2H, NCH_2CH_2), 3.65 (s, 3H, OCH_3), 4.33 (s, 1H, CH). ^{13}C -NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = -2.3 (ZnCH_2CH_3), 1.2 (ZnCH_2CH_3), 12.8 (CCH_3), 45.1 (NCH_2CH_2), 47.4 ($\text{N}(\text{CH}_3)_2$), 50.7 (OCH_3), 58.9 (NCH_2CH_2), 78.0 (CH), 129.2 (CN), 172.0 (CO). IR: ν = 2925, 2873, 2844, 2801, 1561, 1516, 1438, 1367, 1326, 1286, 1179, 1065, 1025, 957, 883, 773, 598, 542, 502, 410 cm^{-1} .

L3^{Do4}ZnEt 6: Reagent: 1.63 g (10 mmol) L3^{Do4}H. Yield: 2.88 g (72%). Mp. 73 $^\circ\text{C}$. Elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{19}\text{NO}_3\text{Zn}$: C, 45.1; H, 7.2; N, 5.3; found (%): C, 44.7; H, 7.1; N, 5.1. ^1H -NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 0.29 (q, $^3J_{\text{HH}}$ = 8.13 Hz, 2H, ZnCH_2CH_3), 1.19 (t, $^3J_{\text{HH}}$ = 8.2, 3H, ZnCH_2CH_3), 1.96 (s, 3H, CCH_3), 3.31 (s (br), 3H, OCH_3), 3.50 (s (br), 4H, NCH_2CH_2), 3.63 (s, 3H, COCH_3), 4.37 (s, 1H, C_αH). ^{13}C -NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 0.3 (ZnCH_2CH_3), 1.1 (ZnCH_2CH_3), 12.0 (CCH_3), 22.8 (OCH_3), 49.8 (NCH_2CH_2), 51.4 (NCH_2CH_2), 59.0 (COCH_3), 72.3 (CH), 126.4 (CN), 172.4 (CO). IR: ν = 2939, 2876, 2853, 1422, 1287, 1259, 1203, 1130, 1059, 993, 906, 769, 607, 513, 446 cm^{-1} .

Synthesis of heteroleptic complexes LAIME₂: A solution of L1^{Do1}H (2.72 g, 16 mmol) in *n*-pentane (20 mL) was slowly added to a solution of AIME₃ (1.64 mL, 94 %, 16 mmol) in 20 mL of *n*-pentane at 0 $^\circ\text{C}$, and the mixture was stirred for 5 h at ambient temperature. The solvent was removed in vacuo, yielding yellow waxy solids, which were recrystallized from solutions in *n*-pentane at -80 $^\circ\text{C}$. Light yellow crystalline solids were formed after storage for 24 h.

L1^{Do1}AIME₂ 7: Reagent: 2.72 g (16 mmol) L1^{Do1}H. Yield 3.40 g (94 %). Mp 62 $^\circ\text{C}$. Elemental analysis calcd (%) for $\text{C}_{11}\text{H}_{23}\text{N}_2\text{OAl}$: C 58.4, H 10.2, N 12.4%; found (%): C 58.1, H 10.2, N 12.2. ^1H NMR (300 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = -0.32 (s, 6H, $\text{Al}(\text{CH}_3)_2$), 1.35 (s, 3H, CCH_3), 1.81 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.86 (s, 3H, CCH_3), 2.10 (t, $^3J_{\text{HH}}$ = 6.6 Hz, 2H, NCH_2CH_2), 2.55 (t, $^3J_{\text{HH}}$ = 6.5 Hz, 2H, NCH_2CH_2), 4.84 (s, 1H, CH). ^{13}C NMR (75 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = -7.9 ($\text{Al}(\text{CH}_3)_2$), 21.9 (CCH_3), 25.5 (CCH_3), 44.2 ($\text{N}(\text{CH}_3)_2$), 44.6 (NCH_2CH_2), 55.0 (NCH_2CH_2), 98.1 (CH), 174.3 (CN), 182.5 (CO). IR: ν 2916, 1581, 1522, 1181, 1029, 941, 754, 658, 535, 440 cm^{-1} .

L1^{Do2}AIME₂ 8: Reagent: 3.17 g (16 mmol) L1^{Do2}H. Yield 3.44 g (91 %). Mp 30 $^\circ\text{C}$. Elemental analysis calcd (%) for $\text{C}_{13}\text{H}_{27}\text{N}_2\text{OAl}$: C 61.4, H 10.7, N 11.0; found (%): C 61.2, H 10.6, N 10.9. ^1H -NMR (300 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = -0.27 (s, 6H, $\text{Al}(\text{CH}_3)_2$), 0.85 (t, $^3J_{\text{HH}}$ = 7.3 Hz, 6H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 1.45 (s, 3H, CCH_3), 1.78 (s, 3H, CCH_3), 2.31 (q, $^3J_{\text{HH}}$ = 7.0 Hz, 4H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 2.39 (t, $^3J_{\text{HH}}$ = 7.8 Hz, 2H, NCH_2CH_2), 3.10 (t, $^3J_{\text{HH}}$ = 7.5 Hz, 2H, NCH_2CH_2), 4.73 (s, 1H, CH). ^{13}C -NMR (75 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = -8.9 ($\text{Al}(\text{CH}_3)_2$), 11.7 ($\text{N}(\text{CH}_2\text{CH}_3)_2$), 20.7 (CCH_3), 25.4 (CCH_3), 46.9 ($\text{N}(\text{CH}_2\text{CH}_3)_2$), 47.7 (NCH_2CH_2), 52.4 (NCH_2CH_2), 99.9 (CH), 174.8

(CN), 179.7 (CO). IR: ν = 2970, 2926, 2814, 1602, 1515, 1404, 1186, 674 cm^{-1} .

L2^{Do1}AIME₂ 9: Reagent: 2.95 g (16 mmol) L2^{Do1}H. Yield 3.70 g (95 %). Mp. 26 $^\circ\text{C}$. Elemental analysis calcd (%) for $\text{C}_{12}\text{H}_{25}\text{N}_2\text{OAl}$: C 60.0, H 10.5, N 11.7; found (%): C 60.3, H 10.7, N 11.6. ^1H NMR (300 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$): δ = -0.85 (s, 6H, $\text{Al}(\text{CH}_3)_2$), 1.71 (m, 2H, NCH_2CH_2), 1.95 (s, 3H, CCH_3), 2.08 (s, 3H, CCH_3), 2.21 (s, 6H, $\text{N}(\text{CH}_3)_2$), 2.28 (t, $^3J_{\text{HH}}$ = 6.8 Hz, 2H, NCH_2CH_2), 3.38 (t, $^3J_{\text{HH}}$ = 6.8 Hz, 2H, NCH_2CH_2), 5.07 (s, 1H, CH); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$): δ = -10.5 ($\text{Al}(\text{CH}_3)_2$), 20.6 (CCH_3), 25.1 (CCH_3), 28.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 45.2 ($\text{N}(\text{CH}_3)_2$), 46.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 56.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 99.8 (CH), 174.6 (CN), 177.7 (CO). ATR-IR: ν 2928, 2886, 2859, 2816, 2767, 2723, 1600, 1515, 1458, 1405, 1186, 946, 769, 713, 674, 580, 387 cm^{-1} .

Synthesis of heteroleptic complexes L1^{Do2}M(Me₂)Cp* (M = Ti, Zr): A solution of L1^{Do2}H (0.65 g, 3.3 mmol) in 5 mL of *n*-pentane was slowly added to a cooled (-60 $^\circ\text{C}$) solution of Cp*MMe₃ (0.75 g, 3.3 mmol) in 10 mL of *n*-pentane. The resulting red solutions were stirred for 2 h at -60 $^\circ\text{C}$ and then warmed to ambient temperature. The solvent was reduced in vacuo to 3 mL and the solution was stored at -30 $^\circ\text{C}$, yielding red crystalline solids after 24 h.

L1^{Do2}Ti(Me₂)Cp* 10: Reagent: 0.75 g (3.3 mmol) Cp*TiMe₃. Yield 1.02 g (95%). Mp 54 $^\circ\text{C}$. Elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{42}\text{N}_2\text{OTi}$: C 65.7, H 10.0, N 7.3; found (%): C 65.6, H 10.2, N 7.1. ^1H NMR (300 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = 0.83 (s, 6H, $\text{Ti}(\text{CH}_3)_2$), 0.92 (t, $^3J_{\text{HH}}$ = 7.1 Hz, 6H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 1.88 (s, 15H, $\text{C}_5(\text{CH}_3)_5$), 1.91 (s, 3H, CCH_3), 1.98 (s, 3H, CCH_3), 2.35 (q, 4H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 2.38 (m, 2H, NCH_2CH_2), 3.26 (m, 2H, NCH_2CH_2), 5.23 (s, 1H, CH). ^{13}C NMR (75 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = 12.4 ($\text{C}_5(\text{CH}_3)_5$), 12.8 ($\text{N}(\text{CH}_2\text{CH}_3)_2$), 23.3 (CCH_3), 25.8 (CCH_3), 48.1 (NCH_2CH_2), 53.1 ($\text{N}(\text{CH}_2\text{CH}_3)_2$), 53.5 (NCH_2CH_2), 102.3 (CH), 122.9 ($\text{C}_5(\text{CH}_3)_5$), 170.9 (CN), 176.7 (CO). IR: ν 2969, 2801, 1584, 1508, 1370, 1281, 1201, 1068, 1000, 952, 791, 675, 483, 432.

L1^{Do2}Zr(Me₂)Cp* 11: Reagent: 0.90 g (3.3 mmol) Cp*ZrMe₃. Yield 0.31 g (61%). Mp 62 $^\circ\text{C}$. Elemental analysis calcd (%) for $\text{C}_{23}\text{H}_{42}\text{N}_2\text{OZr}$: C 60.8, H 9.3, N 6.2; found (%): C 60.7, H 9.3, N 6.0. ^1H NMR (300 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = 0.44 (s, 6H, $\text{Zr}(\text{CH}_3)_2$), 0.93 (t, $^3J_{\text{HH}}$ = 7.1 Hz, 6H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 1.78 (s, 3H, CCH_3), 1.85 (s, 3H, CCH_3), 1.92 (s, 15H, $\text{C}_5(\text{CH}_3)_5$), 2.37 (q, $^3J_{\text{HH}}$ = 7.1 Hz, 2H, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 2.40 (m, 4H, NCH_2CH_2), 2.40 (m, 2H, NCH_2CH_2), 3.44 (m, 2H, NCH_2CH_2), 5.03 (s, 1H, CH). ^{13}C NMR (75 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = 11.0 ($\text{C}_5(\text{CH}_3)_5$), 12.1 ($\text{N}(\text{CH}_2\text{CH}_3)_2$), 22.2 (CCH_3), 25.0 (CCH_3), 47.3 (NCH_2CH_2), 51.0 ($\text{N}(\text{CH}_2\text{CH}_3)_2$), 53.0 (NCH_2CH_2), 102.3 (CH), 119.0 ($\text{C}_5(\text{CH}_3)_5$), 172.1 (CN), 174.9 (CO). IR: ν 2912, 1584, 1509, 1396, 1281, 1067, 1000, 948, 799, 675, 552, 464, 420.

Synthesis of L1^{Do1}Al(CI)Me 12: A solution of ethereal HCl (1 mL, 2N, 2 mmol) was slowly added to a solution of 0.45 g (2.0 mmol) L1^{Do1}AIME₂ 7 in 15 mL of CH_2Cl_2 . The solution was stirred for 2 h, until gas evolution has stopped. The solvent was removed in vacuo and the resulting light-yellow solid was recrystallized from a solution in toluene. Light-yellow crystals of **12** were formed within 24 h upon storage at -30 $^\circ\text{C}$. Yield 0.43 g (87%). Mp 117 $^\circ\text{C}$. Elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{20}\text{AlClIN}_2\text{O}$: C 48.7, H 8.2, N 11.4; found (%): C 49.1, H 8.1, N 11.2. ^1H NMR (300 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$): δ = -0.81 (s, 3H, $\text{Al}(\text{CH}_3)_2$), 1.94 (s, 3H, CCH_3), 2.03 (s, 3H, CCH_3), 2.36 (s, 6H, $\text{N}(\text{CH}_3)_2$), 2.84 (t, $^3J_{\text{HH}}$ = 6.4 Hz, 2H, NCH_2CH_2), 3.37 (t, $^3J_{\text{HH}}$ = 6.4 Hz, 2H, NCH_2CH_2), 5.17 (s, 1H, CH). ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$): δ = 22.9 (CCH_3), 25.4 (CCH_3), 44.1 ($\text{N}(\text{CH}_3)_2$), 44.9 (NCH_2CH_2), 54.5 (NCH_2CH_2), 99.0 (CH), 177.0 (CN), 182.4 (CO). IR: ν 1586, 1526, 1433, 1396, 1344, 1300, 1181, 1036, 944, 770, 679, 652, 611, 464.

L1^{Do1}AlCl₂ 13: A solution of GaCl₃ (0.13 g, 0.75 mmol) in 5 mL of CH₂Cl₂ was added to a solution of 0.18 g (0.76 mmol) **12** in 5 mL of CH₂Cl₂ at room temperature and the resulting solution was stirred for additional 30 minutes. Thereafter, all volatiles were removed in vacuum yielding a red solid. Colorless crystals were formed after storage of a solution in CH₂Cl₂ at 0 °C for 12 h. Yield 0.152 g (75%). Mp 172 °C. Elemental analysis calcd (%) for C₉H₁₇AlN₂O: C 40.5, H 6.1, N 10.1; found (%): C 39.8, H 6.3, N 9.6. ¹H (300 MHz, CDCl₃, 25 °C): δ = 2.02 (s, 3H, CCH₃), 2.05 (s, 3H, CCH₃), 2.54 (s, 6H, N(CH₃)₂), 3.01 (t, ³J_{HH} = 6.5 Hz, 2H, CH₂N(CH₃)₂), 3.44 (t, ³J_{HH} = 6.4 Hz, 2H, CNCH₂), 5.25 (s, 1H, CH). ¹³C (75 MHz, CDCl₃, 25 °C): δ = 23.4 (CCH₃), 26.0 (CCH₃), 43.7 (CH₂N(CH₃)₂), 46.0 (N(CH₃)₂), 100.7 (CH), 177.9 (CN), 183.9 (CO). IR: ν 1590, 1528, 1397, 1346, 1306, 1017, 957, 768, 683, 492, 456, 417.

Synthesis of L1^{Do1}Al(Me)O-2,6-Me₂C₆H₃ 14: A solution of 2,6-dimethylphenol (0.24 g (2 mmol)) in 4 mL of toluene was added to a solution of 0.45 g (2.0 mmol) L1^{Do1}AlMe₂ **7** in 10 mL of toluene. The solution was warmed to ambient temperature and stirred for one additional hour. The solvent was reduced in vacuo to 2 mL and the solution stored at -10 °C, yielding colorless crystalline solids. Yield 0.51 g (77%). Mp 97 °C. Elemental analysis calcd (%) for C₁₈H₁₉AlN₂O₂: C 65.0, H 8.8, N 8.4; found (%): C 64.7, H 8.7, N 8.4. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = -0.84 (s, 3H, AlCH₃), 1.52 (s, 3H, CCH₃), 2.02 (s, 3H, CCH₃), 2.06 (s, 6H, C_{Ar}CH₃), 2.46 (s, 6H, N(CH₃)₂), 2.90 (m, 2H, NCH₂CH₂), 3.44 (m, 2H, NCH₂CH₂), 5.05 (s, 1H, CH), 6.45 (t, ³J_{HH} = 7.4 Hz, 1H, CH), 6.81 (d, ³J_{HH} = 7.4 Hz, 2H, *m*-CH). ¹³C NMR (75 MHz, CD₂Cl₂, 25 °C): δ = 17.9 (C_{Ar}CH₃), 23.1 (CCH₃), 25.4 (CCH₃), 45.0 (N(CH₃)₂), 45.8 (NCH₂CH₂), 55.3 (NCH₂CH₂), 98.9 (CH), 116.6 (C_{Ar-p}H), 127.8 (C_{Ar-q}CH₃), 128.0 (C_mH), 159.2 (C_{Ar}O), 176.4 (CN), 182.9 (CO). IR: ν 2914, 1580, 1522, 1461, 1397, 1341, 1278, 1237, 1189, 1091, 1027, 954, 868, 791, 751, 719, 654, 621, 584, 543, 470.

Synthesis of L1^{Do1}Al(O-2,6-Me₂C₆H₃)₂ 15: A solution of 2,6-dimethylphenol (0.49 g (4 mmol)) in 4 mL of toluene was added to a solution of 0.45 g (2.0 mmol) L1^{Do1}AlMe₂ **7** in 10 mL of toluene. The solution was warmed to ambient temperature and stirred for one additional hour. The solvent was reduced in vacuo to 2 mL and the solution stored at -10 °C, yielding colorless crystalline solids. Yield 0.79 g (90%). Mp. 197 °C. Elemental analysis calcd (%) for C₂₅H₃₅AlN₂O₃: C 68.5, H 8.0, N 6.4; found (%): C 68.8, H 8.1, N 6.4. ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ = 1.27 (s, 3H, CH₃), 2.07 (s, 3H, CH₃), 2.11 (s, 12H, C_{Ar}CH₃), 2.70 (s, 6H, N(CH₃)₂), 3.00 (t, ³J_{HH} = 6.5 Hz, 2H, NCH₂CH₂), 3.56 (t, ³J_{HH} = 6.5 Hz, 2H, NCH₂CH₂), 5.09 (s, 1H, CH), 6.49 (t, ³J_{HH} = 7.3 Hz, 1H, *p*-CH), 6.82 (d, ³J_{HH} = 7.3 Hz, 2H, *m*-CH). ¹³C NMR (75 MHz, CD₂Cl₂, 25 °C): δ = 18.1 (C_{Ar}CH₃), 23.1 (CCH₃), 24.9 (CCH₃), 44.7 (N(CH₃)₂), 47.1 (NCH₂CH₂), 56.0 (NCH₂CH₂), 99.7 (CH), 117.2 (C_{Ar-p}H), 127.7 (C_{Ar}CH₃), 128.4 (C_mH), 158.2 (C_{Ar}O), 176.9 (CN), 183.8 (CO). IR: ν 1583, 1460, 1393, 1339, 1275, 1237, 1092, 1028, 953, 902, 876, 789, 751, 736, 681, 615, 575, 487.

Single crystal X-ray diffraction. Crystallographic data of **2**, **4**, **7**, **10** and **12-14**, which were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (MoK α radiation, λ = 0.71073 Å) at 100(2) K, are summarized in Table S1 (SI). The solid-state structures of **2**, **4**, **7**, **10** and **12-14** are shown in Figures 1 to 7, bond lengths and angles of **2**, **4**, **7**, **10** and **12-14** are summarized in Tables 1 and 2. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F² (SHELXL-2014).^[26,27] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2).

Hydrogen atoms were refined using a riding model or rigid methyl groups. In **12** the toluene molecule is disordered over a center of inversion. Its atoms' adp were restraint with RIGU. The methyl and chlorine substituent

are disordered. The carbon atom could only be refined isotropically and the geometric parameters of the disordered parts cannot be regarded meaningful. Lowering the symmetry does not resolve the disorder.

The crystallographic data of **2**, **4**, **7**, **10** and **12-14** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1855741 (**2**), -1855740 (**4**), -1855739 (**7**), -1855742 (**10**), -1855743 (**12**), -1855744 (**13**) and -1855745 (**14**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): A CIF file giving X-ray crystallographic data of **2**, **4**, **7**, **10**, **12-14**, spectroscopic details (¹H, ¹³C NMR; IR) and crystallographic details of **2**, **4**, **7**, **10**, **12-14**.

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- [11] **2**: [C₁₇H₃₉N₃OSi₂Zn], *M* = 423.06, colorless crystal, (0.250 × 0.134 × 0.102 mm); monoclinic, space group *P2₁/c*; *a* = 16.8067(4) Å, *b* = 18.0457(4) Å, *c* = 17.1775(4) Å; $\alpha = 90^\circ$, $\beta = 117.4450(10)^\circ$, $\gamma = 90^\circ$, *V* = 4623.40(19) Å³; *Z* = 8; $\mu = 1.175 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.216 \text{ g cm}^{-3}$; 48147 reflexes ($\theta_{\text{max}} = 30.577^\circ$), 14035 unique (*R*_{int} = 0.0324); 453 parameters; largest max./min in the final difference Fourier synthesis 0.599 e-Å⁻³/ -0.556 e-Å⁻³; max./min. transmission 0.63/0.75; *R*₁ = 0.0343 (*I* > 2 σ (*I*)), *wR*₂ = 0.0861 (all data). **4**: [C₁₄H₂₆N₂OZn], *M* = 303.74, colorless crystal, (0.390 × 0.340 × 0.280 mm); monoclinic, space group *P2₁/c*; *a* = 11.0419(12) Å, *b* = 11.2385(12) Å, *c* = 13.0253(13) Å; $\alpha = 90^\circ$, $\beta = 113.447(3)^\circ$, $\gamma = 90^\circ$, *V* = 1482.9(3) Å³; *Z* = 4; $\mu = 1.648 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.360 \text{ g cm}^{-3}$; 33130 reflexes ($\theta_{\text{max}} = 29.658^\circ$), 4114 unique (*R*_{int} = 0.0316); 166 parameters; largest max./min in the final difference Fourier synthesis 0.594 e-Å⁻³/ -0.232 e-Å⁻³; max./min. transmission 0.58/0.75; *R*₁ = 0.0229 (*I* > 2 σ (*I*)), *wR*₂ = 0.0617 (all data). **7**: [C₁₆H₂₈N₂O₄Zn], *M* = 377.77, colorless crystal, (0.552 × 0.328 × 0.194 mm); orthorhombic, space group *Pca2₁*; *a* = 21.752(3) Å, *b* = 5.6648(7) Å, *c* = 14.5039(19) Å; $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, *V* = 1787.2(4) Å³; *Z* = 4; $\mu = 1.395 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.404 \text{ g cm}^{-3}$; 37941 reflexes ($\theta_{\text{max}} = 30.548^\circ$), 5416 unique (*R*_{int} = 0.0406); 215 parameters; Flack-Parameter *x* = 0.197(12); largest max./min in the final difference Fourier synthesis 0.306 e-Å⁻³/ -0.405 e-Å⁻³; max./min. transmission 0.55/0.90; *R*₁ = 0.0258 (*I* > 2 σ (*I*)), *wR*₂ = 0.0591 (all data). **8**: [C₁₁H₂₃AlN₂O], *M* = 226.29, orange crystal, (0.430 × 0.380 × 0.320 mm); monoclinic, space group *P2₁/n*; *a* = 8.1748(8) Å, *b* = 16.1174(15) Å, *c* = 10.4904(10) Å; $\alpha = 90^\circ$, $\beta = 97.528(2)^\circ$, $\gamma = 90^\circ$, *V* = 1370.3(2) Å³; *Z* = 4; $\mu = 0.129 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.097 \text{ g cm}^{-3}$; 29264 reflexes ($\theta_{\text{max}} = 25.242^\circ$), 4766 unique (*R*_{int} = 0.0250); 136 parameters; largest max./min in the final difference Fourier synthesis 0.459 e-Å⁻³/ -0.253 e-Å⁻³; max./min. transmission 0.67/0.75; *R*₁ = 0.0338 (*I* > 2 σ (*I*)), *wR*₂ = 0.0988 (all data). **11**: [C₂₃H₄₂N₂OTi], *M* = 410.48, orange crystal, (0.280 × 0.200 × 0.100 mm); orthorhombic, space group *Pbca*; *a* = 8.1915(3) Å, *b* = 23.6657(8) Å, *c* = 24.0318(8) Å; $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, *V* = 4658.7(3) Å³; *Z* = 8; $\mu = 0.382 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.170 \text{ g cm}^{-3}$; 82506 reflexes ($\theta_{\text{max}} = 33.228^\circ$), 8840 unique (*R*_{int} = 0.0533); 255 parameters; largest max./min in the final difference Fourier synthesis 0.757 e-Å⁻³/ -0.632 e-Å⁻³; max./min. transmission 0.63/0.75; *R*₁ = 0.0458 (*I* > 2 σ (*I*)), *wR*₂ = 0.1252 (all data). **13**: [C_{13.53}H_{24.04}AlClN₂O], *M* = 293.24, colorless crystal, (0.281 × 0.220 × 0.172 mm); monoclinic, space group *P2₁/c*; *a* = 8.9805(9) Å, *b* = 14.1884(11) Å, *c* = 11.9568(10) Å; $\alpha = 90^\circ$, $\beta = 90.216(4)^\circ$, $\gamma = 90^\circ$, *V* = 1523.5(2) Å³; *Z* = 4; $\mu = 0.302 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.278 \text{ g cm}^{-3}$; 37860 reflections ($\theta_{\text{max}} = 33.207^\circ$), 5631 unique (*R*_{int} = 0.0263); 214 parameters; largest max./min in the final difference Fourier synthesis 0.624 e-Å⁻³/ -0.404 e-Å⁻³; max./min. transmission 0.75/0.70; *R*₁ = 0.0440 (*I* > 2 σ (*I*)), *wR*₂ = 0.1220 (all data). **14**: [C₉H₁₇AlCl₂N₂O], *M* = 267.12, colorless crystal, (0.522 × 0.202 × 0.114 mm); monoclinic, space group *P2₁/n*; *a* = 6.9716(4) Å, *b* = 13.7557(7) Å, *c* = 13.3773(7) Å; $\alpha = 90^\circ$, $\beta = 100.188(2)^\circ$, $\gamma = 90^\circ$, *V* = 1262.65(12) Å³; *Z* = 4; $\mu = 0.561 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.405 \text{ g cm}^{-3}$; 72519 reflexes ($\theta_{\text{max}} = 36.336^\circ$), 5749 unique (*R*_{int} = 0.0299); 140 parameters; largest max./min in the final difference Fourier synthesis 0.617 e-Å⁻³/ -0.270 e-Å⁻³; max./min. transmission 0.62/0.75; *R*₁ = 0.0244 (*I* > 2 σ (*I*)), *wR*₂ = 0.0666 (all data). **15**: [C₁₈H₂₆AlN₂O₂], *M* = 332.41, colorless crystal, (0.231 × 0.161 × 0.122 mm); orthorhombic, space group *Pbca*; *a* = 14.5393(6) Å, *b* = 15.3238(6) Å, *c* = 16.6689(7) Å; $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, *V* = 3713.8(3) Å³; *Z* = 8; $\mu = 0.120 \text{ mm}^{-1}$; $\rho_{\text{calc}} = 1.189 \text{ g cm}^{-3}$; 59816 reflexes ($\theta_{\text{max}} = 33.153^\circ$), 7091 unique (*R*_{int} = 0.0377); 215 parameters; largest max./min in the final difference Fourier synthesis 0.542 e-Å⁻³/ -0.284 e-Å⁻³; max./min. transmission 0.66/0.75; *R*₁ = 0.0388 (*I* > 2 σ (*I*)), *wR*₂ = 0.1135 (all data).
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*Dennis Dittrich, Phillip Steiniger,
Christoph Wölper, and Stephan Schulz**

Page No. – Page No.

**Synthesis and X-ray crystal
structures of β -ketoiminate
complexes**

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