SHORT COMMUNICATION

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Heterobimetallic Metal-Amidinate Complexes by Stepwise Metalation of Methanetrissamidines

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Dedicated to Prof. Bernt Krebs the occasion of his 75th birthday.

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The acidity of the four N-H groups in methanetrissamidine **1c** differs significantly, hence allowing stepwise metalation by metal organic compounds such as ZnMe₂, AlMe₃ and GaMe₃. Dinuclear complexes **3a-c** were formed under kinetic control in the reactions of **1c** with two equivalents of the metal organic compound at low temperatures, whereas prolonged reaction times at elevated temperature (100 °C) with four equivalents of ZnMe₂, AlMe₃ and GaMe₃ yielded the corresponding tetranuclear complexes **4a-c**. The

different acidity of the four N-H groups also allowed the stepwise metalation of **1c** by two different metal organic complexes with formation of the heterobimetallic complexes **5a** and **5b**. In addition, transmetalation reaction with Zn/Al exchange was observed in the reaction of **3c** with AlMe₃, yielding the corresponding dinuclear aluminum complex **3a**. The complexes were characterized spectroscopically (NMR, IR) and by single crystal X-ray diffraction (**3a**, **4b**).

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Introduction

Multimetallic coordination complexes have earned great attention within the last decades due to their promising technical application in catalysis.^[1] They are expected to provide new reactivity patterns by cooperative electronic effects between the (different) metal atoms. Several bimetallic complexes have been investigated in the past for catalytic reactions such as asymmetric aldol condensation, olefin polymerization and alternating copolymerization of epoxides with CO₂.^[2-4] Moreover, the rapidly growing interest in the function, reactivity and structure of metalloenzymes, from which the concept of multimetallic catalysis was originally adapted, has led to the synthesis of an increasing number of multimetallic model complexes.^[5]

Ligand design plays a crucial role for the synthesis of tailor-made complexes, which provide different metal binding sites on the one hand and a bridging unit for adjustable metal-metal-separation on the other hand. Several multifunctional ligands based on nitrogen or oxygen donor sites such as N,N'-chelating monoanionic amidinates, guanidines, β -diketiminates or N,O chelating dianionic phenoxyamido ligands have been widely established for the synthesis of homometallic multinuclear complexes.^[6] In contrast, only a few examples of heterobimetallic complexes have been reported, to date.^[7]

We recently reported on the synthesis of two methanetrissamidines {HC[C(NR)NHR]₃} (R = *i*-Pr **1a**; Ph **1b**) and

the tautomeric form {C[C(NPh)N(Ph)H]₂[C(HNPh)₂]} **1c** (scheme 1),^[8] which were formed by hydrolysis reaction of tetranuclear zinc amidinate complexes {C[C(NR)₂ZnMe]₄} (R = *i*-Pr **2a**; Ph **2b**).^[9] Moreover, the capability of these multifunctional molecules to stabilize homometallic complexes were shown in alkane elimination reactions with aluminum organyls. The N-H groups of **1a** can be completely deprotonated under very mild conditions upon reaction with AlMe₃ and *i*-Bu₂AlH, respectively, and subsequent formation of homotrimetallic {CH[C(Ni-Pr)₂AlR₂]₃} (R = Me, *i*-Bu). In contrast, the metalation of **1c** was found to proceed gradually, and temperatures as high as 100 °C and prolonged reaction times (24 h) were required for complete deprotonation and formation of homotetrametallic {C[C(NPh)₂]₃[AlMe₂]₄} **4a**.

Scheme 1. N,C-tautomeric methanetrissamidines; potentially acidic protons are highlighted in red.

The different acidity of the amino and amidino protons in **1c** can be derived from its molecular structure. The sp²-hybridized central carbon atom allows a delocalization of the negative charge within the entire ligand, hence lowering the acidities of the remaining N-H protons with ongoing metalation. Therefore, **1c** was expected to be an ideal candidate for stepwise deprotonation reactions and we

became interested in the synthesis of heterobimetallic complexes by kinetically controlled metalation.

Results and Discussion

Reactions of **1c** with two equivalents of either AlMe₃, GaMe₃ or ZnMe₂ at -80 °C in toluene gave the twofold metalated complexes {C[C(NPh)₂MMe_n]₂[C(HNPh)₂]} (MMe_n = AlMe₂ **3a**, GaMe₂ **3b**, ZnMe **3c**) in quantitative yield (scheme 2). **3a** was also obtained by reaction of **1c** with two equivalents of *t*-BuLi/TMEDA and subsequent reaction with two equivalents of Me₂AlCl.

Scheme 2. Synthesis of **3a-c** by stepwise metalation reaction of **1c**.

The ¹H NMR spectra of **3a** and **3b** in C₆D₆ each show two singlets (δ -0.98, -0.14 ppm **3a**; -0.98, -0.14 ppm **3b**) for the diastereotopic MMe moieties, whereas **3c** shows only one ZnMe singlet at -0.20 ppm. Additional singlet resonances (**3a** δ 5.42 ppm; **3b** δ 5.38 ppm; **3c** δ 5.34 ppm) could be clearly assigned to the remaining amidino N-H-groups using different spectroscopic methods (e.g. C,H-COSY and deuteration experiments).^[10]

Figure 1. Molecular structure of **3a** (thermal ellipsoids at 50% probability levels; hydrogen atoms at arbitrary radii; phenyl hydrogen atoms omitted for clarity).

Colorless crystals of **3a** were obtained from a solution in *n*-hexane at -30 °C (Table 1).^[11] **3a** crystallizes in the monoclinic space group *P*2₁/*c* with one molecule in the asymmetric unit. The

central carbon atom C1 binds to three other carbon atoms of two neighboring amidine groups and one amidinate group forming a trigonal planar C₄ moiety (C1 0.0131(18) Å above C2/C3/C4 plane). Two AlMe₂ moieties are coordinated by the amidinate group in a bridging μ-η¹,η¹ binding mode (Al1-N6 1.8956(14) Å, Al2-N5 1.9015(14) Å). Each aluminum atom is further coordinated by one imino nitrogen atom of a neighboring amidine group (Al1-N1 1.9220(14) Å, Al2-N4 1.9272(14) Å).

The comparison of the central structural parameters of twofold-metalated **3a** with those of the fourfold metalated complex {C[C(NPh)₂]₃[AlMe₂]₄} **4a** shows slightly different C-C bond lengths within the central C₄ moiety (Table 2, 3). The C-C bond lengths in **3a** (C1-C2 1.4564(19) Å, C1-C3 1.453(2) Å, C1-C4 1.446(2) Å) are very similar and their values are in between typical C-C single and double bonds indicating complete delocalization of π-electron density within this C₄-moiety. In contrast, in the fourfold metalated complex {C[C(NPh)₂]₃[AlMe₂]₄} **4a** two short (1.4191(15) Å) and one elongated C-C bonds (1.506(2) Å) were observed.^[8] The Al-N bond lengths in **3a** (av. 1.912 Å) are within the typical range observed for fourfold-coordinated Al atoms and the N-Al-N (av. 91.92°) and C-Al-C bond angles (118.58(9), 115.46(11)°) are comparable to those previously reported for the bridging AlMe₂ moieties in the tetrametalated Al complex {C[C(NPh)₂]₃[AlMe₂]₄} **4a** (av. Al-N 1.9587 Å; C-Al-C 119.60(6)°; N-Al-N 90.67(5)°).^[8]

In order to prove the general applicability of **3a-c** for further alkane elimination reactions, we investigated their reactions with different metal alkyls. Reactions of **3a-c** with two equivalents of their corresponding metal alkyls MMe_n at 100 °C and prolonged reaction times yielded the homometallic tetranuclear complexes {C[C(NPh)₂]₃[MMe_n]₄} (MMe_n = AlMe₂ **4a**, GaMe₂ **4b**, ZnMe **4c**). **4a**, which was previously reported, was identified by NMR spectroscopy, whereas **4b** and **4c** were characterized by NMR and single crystal X-ray diffraction. Since the quality of the crystal of **4c** was poor, only the connectivity of the model could be established.

Figure 2. Molecular structure of **4b** (#1 -x,y,-z+1/2 symmetry equivalent atoms displayed in pale colors; thermal ellipsoids at 50% probability levels; hydrogen atoms omitted for clarity).

Yellow crystals of **4b** were obtained from a solution in toluene at $-30\text{ }^{\circ}\text{C}$. **4b** is isostructural to **4a** and crystallizes in the monoclinic space group $C2/c$ with C1 and C2 on a twofold axis (Fig. 2). One amidinate group (N1-C1-N1#1) adopts a bridging position and two serve as chelating units. The C atoms of the amidinate groups bind to trigonal-planar-coordinated C1 (because of symmetry exactly on the C2/C3/C3#1 plane) with two short bonds and one long C-C bond, showing a delocalized- π electron system within the N3-C3-C1-C3#1-N3#1 unit. The C-N bond lengths within these two amidinate groups differ owing to different coordination numbers of the N atoms, whereas the C-N bond lengths within the N1-C2-N1#1 unit indicate delocalized π -electrons. The Ga-N bond lengths are within the typical range observed for fourfold-coordinated Ga atoms. The N-Ga-N bond angle of the chelating amidinate group (N(3)-Ga(2)-N(2) $65.45(5)^{\circ}$) is smaller compared to the bridging N-Ga-N moiety (N(1)-Ga(1)-N(2) $88.08(5)^{\circ}$) as was expected. In fact, the formation of bridging N-metal-N units decrease the ring strain within the molecules and most likely is responsible for the general formation of this structural motif, which is typically observed in these tetrametalated complexes.

The reaction of **3c** with two equivalents of AlMe_3 at $-80\text{ }^{\circ}\text{C}$ proceeded with transmetalation and quantitative formation of **3a** and ZnMe_2 (scheme 3) rather than the expected heterobimetallic complex. This reaction pathway can be explained by the somehow favored formation of Al-N bonds (ΔH_f^0 : $297 \pm 96\text{ kJ/mol}$ Al-N, 203 kJ/mol Zn-N)^[12] and an entropic effect arising from the formation of monomeric ZnMe_2 in the course of this reaction. Moreover, transmetalation reactions between a metal salt (i.e. **3a**) and an organometallic compound (i.e. AlMe_3) are known to proceed with formation of the thermodynamically more stable metal-carbon bond, typically the more covalent bond (i.e. Zn-Me). As a consequence, zinc has been intensely used in transmetalation reactions in the last decade, in particular in the synthesis of organocuprates.^[13] However, Zn/Al exchange reactions are rather rare. Goldberg et al. reported on the reaction of a bis(imino)pyridyl-thiolate zinc(II) complex with LiAlH_4 , which proceeded with reduction of the imino groups in the ligand backbone and Zn/Al metal exchange and subsequent formation of the corresponding aluminum complex.^[14]

Scheme 3. Transmetalation reaction of **3c** with AlMe_3 at $-80\text{ }^{\circ}\text{C}$ in toluene.

In contrast, reactions of **3a** and **3b** with ZnMe_2 in toluene at $110\text{ }^{\circ}\text{C}$ gave the heterobimetallic tetranuclear complexes $\{\text{C}[\text{C}(\text{NPh})_2]_3[\text{MMe}_2]_2[\text{ZnMe}_2]\}$ ($\text{M} = \text{Al}$ **5a**, Ga **5b**) in quantitative yield (scheme 4). Atwood et al. reported on a similar stepwise metalation reaction using salen-type ligands.^[7d] Bimetallic group 13 metal complexes containing Al and Ga were prepared, but their solid state structures remained unknown. The ^1H NMR spectra of **5a** and **5b** in C_6D_6 each show three singlets due to the diastereotopic MMe_2 moieties ($\text{M} = \text{Al}$ δ $-1.12, 0.13$; Ga δ $-0.78, 0.46$) and one Zn-Me resonance (**5a**: -1.2 ppm , **5b** -1.08 ppm). Disappearance of the NH resonances in both spectra clearly proves the complete metalation of the organic ligand. The ^{13}C NMR

spectrum of **5a** shows two broadened AlMe resonances at -6.4 and -9.8 ppm and one sharp Zn-Me resonance at -14.8 ppm . The corresponding ^1H NMR signals were assigned by C,H-COSY experiments (SI).^[10]

Scheme 4. Complete metalation of **3a-b** by stepwise alkane elimination reaction.

Yellow crystals of **5a** were obtained from a solution in toluene at $-30\text{ }^{\circ}\text{C}$. **5a** crystallizes in the monoclinic space group $C2$ with two independent molecules of which one is placed on a twofold axis (Fig. 3). **5a** also contains highly disordered toluene molecules in the crystal lattice. Two of these could be modeled properly (one on twofold axis) the others have been removed by calculation using SQUEEZE.^[15]

Figure 3. Molecular structure of **5a** (#2 $-x,y,z+1$ symmetry equivalent atoms displayed in pale colors; thermal ellipsoids at 50% probability levels, hydrogen atoms and solvent molecules omitted for clarity).

The structural motif of **5a** is in accordance to that of $\{\text{C}[\text{C}(\text{NPh})_2]_3[\text{AlMe}_2]_4\}$ **4a** and $\{\text{C}[\text{C}(\text{NPh})_2]_3[\text{GaMe}_2]_4\}$ **4b** (*vide supra*). Three amidinate carbon atoms are bonded to the central trigonal-planar carbon atom C1 (C2-C1-C4 $122.85(15)^{\circ}$, C2-C1-C4 $121.02(16)^{\circ}$, C3-C1-C4 $116.12(15)^{\circ}$) and C101 (C102-C101-C103#2 $121.76(12)^{\circ}$, C102-C101-C103 $121.76(12)^{\circ}$), respectively. The C-C bond lengths within the C_4 moiety are in between typical values observed for C-C single and double bonds (C1-C2 $1.434(2)\text{ \AA}$, C1-C3 $1.456(2)\text{ \AA}$, C1-C4 $1.464(2)\text{ \AA}$ and C101-C103#2 $1.464(2)\text{ \AA}$, C101-C103 $1.464(2)\text{ \AA}$) indicating a distinct charge delocalization within the ligand. One amidinate moiety coordinates to two AlMe_2 units in a bridging $\mu\text{-}\eta^1\text{-}\eta^1$ -binding mode (Al1-N1 $1.8822(17)\text{ \AA}$, Al2-N2 $1.8901(17)\text{ \AA}$ and Al3-N8 $1.883(2)\text{ \AA}$), whereas the other amidinates bind one ZnMe moiety in a chelating $\eta^1\text{-N},\eta^3\text{-Aryl}$ coordination (Zn1-N5 $1.9067(16)\text{ \AA}$, Zn1...C31 $2.551(2)\text{ \AA}$, Zn2-N4 $1.9159(16)\text{ \AA}$, Zn2...C61 $2.514(2)\text{ \AA}$ and Zn3-N7 $1.9249(18)\text{ \AA}$, Zn3...C91 $2.512(2)\text{ \AA}$) as was previously reported for zinc amidinate complexes.^[14] Both nitrogen atoms N6 and N3 show an additional bonding to Al1 or Al2, respectively (Al1-N6 $1.9146(17)\text{ \AA}$, Al2-N3 $1.9146(17)\text{ \AA}$). The C-N bond lengths in the bridging N1-C2-N2 moiety are very similar (C2-N1 $1.366(2)\text{ \AA}$, C2-N2 $1.352(2)\text{ \AA}$) and because of symmetry equivalence identical in the respective N8-C102-N8#2

group (1.360(2) Å). In contrast, the C-N bond distances of the other two amidinate units clearly differ (C3-N3 1.338(2) Å, C3-N5 1.364(2) Å, C4-N6 1.333(2) Å, C4-N4 1.359(2) Å and N7-C103 1.360(3) Å, N9-C103 1.341(3) Å), most likely due to the coordination to different metal atoms. The C-N bond lengths of the zinc bonded nitrogen atoms N4, N5 and N7, respectively, rather show single bond character, indicating an increased negative charge localization that results in a stronger ionic character of the corresponding Zn-N bonds. As a consequence, the Zn-N bonds are rather short and at the lower range of Zn-N bonds of three-coordinate Zn centers, which typically range from 1.88 to 2.20 Å.^[15]

Conclusions

We have successfully demonstrated that methanetrissamidines are an interesting new class of organic ligands. They were applied for the synthesis of binuclear and tetranuclear homometallic complexes due to the different acidity of the N-H groups. In addition, they can be stepwise metalated by different organometallic reagents, hence allowing the synthesis of heterobimetallic complexes.

Experimental Section

All manipulations were performed in a glovebox under an Ar atmosphere or using standard Schlenk techniques. Solvents were dried over Na/K and degassed prior to use. **1c** was prepared according to literature methods.^[8] ¹H and ¹³C NMR spectra were recorded on a Bruker DMX 300 spectrometer and are referenced to internal C₆D₆H (¹H: δ = 7.154; ¹³C: δ = 128.0) and CD₂Cl₂ (¹H: δ = 5.32; ¹³C: δ = 53.8). IR spectra were recorded on an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the *Elementaranalyse Labor*, University of Essen.

{[C(NPh)NHPPh]₂[C(N(Ph)AlMe₂)₂]}₂, **3a. Procedure A) **1c** (0.5 g, 0.8 mmol) was dissolved in 15 mL of toluene and cooled to -80 °C. 1.67 mL of a 2 M solution of AlMe₃ in toluene (1.6 mmol) was added dropwise and the reaction mixture was stirred for 24 h. All volatiles were then removed under reduced pressure and the resulting yellowish solid was washed with 10 mL of *n*-hexane, yielding pure **3a**. Colorless crystals of **3a** were obtained from a solution in *n*-hexane at ambient temperature after storage for 24 h. Yield: 0.50 g (84.7%).**

Procedure B) **1c** (0.5 g, 0.8 mmol) was dissolved in 20 mL of toluene. 0.24 mL TMEDA (1.6 mmol) were added and the resulting yellow solution was cooled to -80 °C. 0.94 mL of a 1.7 M solution of *t*-BuLi in *n*-hexane (1.6 mmol) were added slowly to the reaction mixture, resulting in the formation of an orange solution. After 2 h, 0.21 mL AlMe₂Cl (1.6 mmol) were added at -80 °C and the reaction mixture was continuously stirred for 24 h. The resulting suspension was filtrated and all volatiles of the filtrate were removed under reduced pressure, yielding a yellowish solid, that was purified as described in Procedure A. Yield: 0.42 g (70.8%). Mp.: 125.3 °C (dec.). Elemental analysis calculated (%) for C₄₄H₄₄N₆Al₂ (710.82 g/mol): H 6.24, C 74.35, N 11.82; found: H 5.95, C 73.98, N 11.62. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ -0.99 (s, 6 H, AlC^aH₃), 0.14 (s, 6 H, AlC^bH₃), 5.41 (s, 2 H, NH), 6.58 (m, 4 H, Ph), 6.77 (m, 4 H, Ph), 6.92 (m, 9 H, Ph), 7.19 (m, 4 H, Ph), 7.49 (m, 9 H, Ph). ¹³C-NMR (75 MHz, C₆D₆, 25 °C): δ -9.7 (AlCH₃), -7.5 (AlCH₃), 82.6 (C), 120.9 (Ar), 122.7 (Ar), 126.6 (Ar), 129.6 (Ar), 130.0 (Ar), 139.2 (*ipso*-Ar), 142.9 (*ipso*-Ar), 148.8 (*ipso*-Ar), 160.8 (NCN), 170.4 (AlNCNAI). ATR-IR: ν 3370 (N-H), 3055, 3022, 2922, 2884, 1592, 1539, 1483, 1459, 1406, 1368, 1333, 1256, 1230, 1180, 1068, 1024, 953, 906, 747, 688, 662, 565, 506, 456 cm⁻¹.

{[C(NPh)NDPh]₂[C(N(Ph)AlMe₂)₂]}₂, **3aD₂. **3aD₂** was prepared in a similar way as described for **3a** by using 0.5 g (0.8 mmol) of deuterated **1c** (**1cD₄**), which was formed in the reaction of **1c** and MeOD at ambient temperature for 3 d. The resulting solution of **1cD₄** was dried over MgSO₄ and **1cD₄** was isolated after filtration and removing of all volatiles under reduced pressure in high yield (0.53 g, 89.6%). Mp.: 125.3 °C (dec.). C₄₄H₄₂D₂N₆Al₂ (712.84 g/mol). ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ -0.99 (s, 6 H, AlC^aH₃), 0.14 (s, 6 H, AlC^bH₃), 6.58 (m, 4 H, Ph), 6.77 (m, 4 H, Ph), 6.92 (m, 9 H, Ph), 7.19 (m, 4 H, Ph), 7.49 (m, 9 H, Ph). ¹³C-NMR (75 MHz, C₆D₆, 25 °C): δ -9.7 (AlCH₃), -7.5 (AlCH₃), 82.6 (C), 120.9 (Ar), 122.7 (Ar), 126.6 (Ar), 129.6 (Ar), 130.0 (Ar), 139.2 (*ipso*-Ar), 142.9 (*ipso*-Ar), 148.8 (*ipso*-Ar), 160.8 (NCN), 170.4 (AlNCNAI). ATR-IR: ν 3055, 3022, 2922, 2884, 2502 (N-D), 1592, 1539, 1483, 1459, 1406, 1368, 1333, 1256, 1230, 1180, 1068, 1024, 953, 906, 747, 688, 662, 565, 506, 456 cm⁻¹.**

{[C(NPh)NHPPh]₂[C(N(Ph)GaMe₂)₂]}₂, **3b. The synthesis of **3b** is similar to that of **3a** using 0.5 g **1c** (0.8 mmol) and 0.18 g GaMe₃ (1.6 mmol). Yield: 0.38 g (83.8%). Mp.: 146.2 °C (dec.). Elemental analysis calculated (%) for C₄₄H₄₄N₆Ga₂ (796.30 g/mol): H 5.57, C 66.36, N 10.55; found: H 6.36, C 68.05, N 9.15. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ -0.68 (s, 6 H, GaMe), 0.46 (s, 6 H, GaMe), 5.38 (s, 2 H, NH), 6.53 (m, 4 H, Ph), 6.69 (m, 4 H, Ph), 6.91 (m, 9 H, Ph), 6.99 (m, 4 H, Ph), 7.18 (m, 9 H, Ph). ¹³C-NMR (75 MHz, C₆D₆, 25 °C): δ -8.19 (GaMe), -5.06 (GaMe), 83.03 (C), 120.95 (Ar), 120.95 (Ar), 123.66 (Ar), 126.09 (Ar), 129.55 (Ar), 129.94 (Ar), 139.93 (*ipso*-Ar), 144.51 (*ipso*-Ar), 150.37 (*ipso*-Ar), 159.71 (NCN), 170.20 (GaNCNGa). ATR-IR: ν 3378 (NH), 3057, 3028, 2922, 2852, 1593, 1537, 1486, 1464, 1399, 1336, 1306, 1291, 1276, 1258, 1069, 1025, 942, 900, 795, 748, 688, 568, 534, 500, 446, 412 cm⁻¹.**

{[C(NPh)NHPPh]₂[C(N(Ph)ZnMe₂)₂]}₂, **3c. The synthesis of **3c** is similar to that of **3a** and **3b**, using 0.5 g **1c** (0.8 mmol) and 1.4 mL of a 1.2 M solution of ZnMe₂ in toluene (1.6 mmol). Yield: 0.56 g (89.3%). Mp.: 132.5 °C (dec.). Elemental analysis calculated (%) for C₄₂H₃₈N₆Zn₂ (757.55 g/mol): H 5.06, C 66.59, N 11.09; found: H 4.87, C 66.84, N 10.75. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ -0.20 (s, 6 H, ZnCH₃), 5.34 (s, 2 H, NH), 6.62 (m, 12 H, ArH), 6.76 (m, 12 H, ArH), 6.96 (m, 3 H, ArH), 7.18 (m, 3 H, ArH). ¹³C-NMR (75 MHz, C₆D₆, 25 °C): δ -13.6 (ZnCH₃), 82.1 (C), 121.4 (Ar), 122.4 (Ar), 123.5 (Ar), 124.2 (Ar), 124.5 (Ar), 124.6 (Ar), 128.7 (Ar), 129.6 (Ar), 129.9 (Ar), 141.3 (*ipso*-Ar), 146.2 (*ipso*-Ar), 149.5 (*ipso*-Ar), 161.5 (NCN), 164.3 (ZnNCNZn). ATR-IR: ν 3375 (NH), 3055, 3025, 2960, 2896, 2831, 1586, 1530, 1480, 1397, 1341, 1256, 1233, 1171, 1071, 1021, 929, 865, 791, 688, 656, 541, 503, 485 cm⁻¹.**

{[C(NPh)₂]₃[GaMe₂]₄}₂, **4b. 0.57 g GaMe₃ (5 mmol) were added to a solution of 0.5 g **1c** (0.84 mmol) in 15 mL of toluene, resulting in gas evolution and formation of a brown solution. The resulting reaction mixture was stirred for 7 d at 100 °C in a sealed pressure reactor. Thereafter, all volatiles were removed under reduced pressure, yielding crude **4b** as a yellowish solid. Washing with 15 mL of *n*-hexane and filtration gave pure **4b**. Colorless crystals were formed within 24 h at -30 °C from a toluene solution. Yield: 0.5 g (58.7%). Mp.: 223 °C (dec.). Elemental analysis calculated (%) for C₄₈H₅₄N₆Ga₄ (993.87 g/mol): H 5.48, C 58.01, N 8.46; found: H 6.11, C 59.23, N 8.15. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ -0.65 (s, 6 H, GaC^aH₃), -0.15 (s, 6 H, GaC^bH₃), 0.01 (s, 6 H, GaC^cH₃), 0.37 (s, 6 H, GaC^dH₃), 5.52 (m, 2 H, ArH), 6.37 (m, 2 H, ArH), 6.56 (m, 2 H, ArH), 6.72 (m, 6 H, ArH), 6.82 (m, 2 H, ArH), 7.02 (m, 6 H, ArH), 7.30 (m, 2 H, ArH), 7.63 (m, 8 H, ArH). ¹³C-NMR (75 MHz, C₆D₆, 25 °C): δ -10.0 (GaC^aH₃), -8.9 (GaC^bH₃), -8.7 (GaC^cH₃), -7.8 (GaC^dH₃), 97.2 (C), 121.7 (Ar), 123.2 (Ar), 124.5 (Ar), 125.0 (Ar), 125.8 (Ar), 126.1 (Ar), 128.0 (Ar), 128.1 (Ar), 128.5 (Ar), 129.0 (Ar), 129.6 (Ar), 139.9 (*ipso*-Ar), 143.5 (*ipso*-Ar), 143.9 (*ipso*-Ar), 160.8 (NCN), 161.9 (GaNCNGa). ATR-IR: ν 3058, 3022, 2952, 1592, 1521, 1483, 1421, 1347, 1280, 1233, 1197, 1074, 1027, 1012, 941, 924, 750, 729, 691, 579, 538, 509, 426 cm⁻¹.**

{[C(NPh)₂]₃[ZnMe₂]₄}₂, **4c. 1.88 mL of a 1.2 M ZnMe₂/toluene solution (2.2 mmol) were added to a solution of 0.3 g **1c** (0.5 mmol) in 15 mL of toluene, immediately forming a yellow solution under gas evolution. The**

reaction mixture was stirred for 3 d at 110 °C in a sealed pressure reactor. Thereafter, all volatiles were removed under reduced pressure yielding crude **4c** as a yellowish solid. Washing with 15 mL of *n*-hexane followed by filtration gave pure **4c**. Yield: 0.35 g (76.5%). Mp.: 137.5 °C (dec.). Elemental analysis calculated (%) for C₄₄H₄₂N₆Zn₄ (916.36 g/mol): H 4.62, C 57.67, N 9.17; found: H 5.13, C 59.12, N 8.89. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ -0.98 (s, 6 H, ZnCH₃), -0.18 (s, 6 H, ZnCH₃), 6.61 (m, 4 H, ArH), 6.80 (m, 4 H, ArH), 6.89 (m, 4 H, ArH), 7.00 (m, 14 H, ArH), 7.24 (m, 4 H, ArH). ¹³C-NMR (75 MHz, C₆D₆, 25 °C): δ -14.8 (ZnCH₃), -13.0 (ZnCH₃), 87.1 (C), 121.0 (Ar), 121.3 (Ar), 123.7 (Ar), 124.4 (Ar), 125.6 (Ar), 128.6 (Ar), 130.4 (Ar), 132.2 (Ar), 145.7 (*ipso*-Ar), 150.0 (*ipso*-Ar), 151.4 (*ipso*-Ar), 165.7 (NCNZn), 170.7 (ZnNCNZn). ATR-IR: ν 3055, 3022, 2955, 2896, 1589, 1542, 1477, 1453, 1436, 1377, 1324, 1268, 1233, 1168, 1074, 1024, 941, 897, 868, 747, 688, 644, 585, 568, 538, 512, 494 cm⁻¹.

{C[C(NPh)₂]₃[AlMe₂]₂[ZnMe]₂} **5a**. 2 mL of a 1.2 M solution of ZnMe₂ in toluene (2.4 mmol) were added to a solution of 0.3 g **3a** (0.42 mmol) at ambient temperature. The reaction mixture was heated to 110 °C for 3 d in a sealed pressure reactor. Thereafter, all volatiles were removed under reduced pressure, yielding crude **5a** as a yellowish solid. Purification of **5a** was accomplished by washing with 5 mL of *n*-hexane and filtration. Colorless crystals of **5a** were obtained from a solution in toluene at -30 °C after 3 d. Yield: 0.27 g (73.6%). Mp.: 220 °C (dec.). Elemental analysis calculated (%) for C₄₆H₄₈Al₃N₆Zn₂ (869.64 g/mol): H 5.56, C 63.53, N 9.66; found: H 5.91, C 64.54, N 8.83. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ -1.12 (s, 6 H, ZnCH₃), -1.11 (s, 6 H, AlC^aH₃), 0.13 (s, 6 H, AlC^bH₃), 6.35 (m, 6 H, ArH), 6.61 (m, 3 H, ArH), 6.75 (m, 3 H, ArH), 6.88 (m, 3 H, ArH), 7.02 (m, 6 H, ArH), 7.11 (m, 3 H, ArH), 7.32 (m, 6 H, ArH). ¹H-NMR (300 MHz, CD₂Cl₂, 25 °C): δ -1.82 (s, 6 H, AlC^aH₃), -1.11 (s, 6 H, ZnCH₃), -0.46 (s, 6 H, AlC^bH₃), 6.33 (m, 2 H, ArH), 6.68 (m, 4 H, ArH), 7.07 (m, 4 H, ArH), 7.15 (m, 6 H, ArH), 7.26 (m, 4 H, ArH), 7.41 (m, 10 H, ArH). ¹³C-NMR (75 MHz, C₆D₆, 25 °C): δ -14.8 (ZnCH₃), -9.8 (AlC^bH₃), -6.4 (AlC^bH₃), 88.8 (C), 122.0 (Ar), 122.2 (Ar), 125.6 (Ar), 126.5 (Ar), 128.2 (Ar), 128.5 (Ar), 129.3 (Ar), 130.5 (Ar), 132.6 (Ar), 133.3 (Ar), 142.8 (*ipso*-Ar), 149.1 (*ipso*-Ar), 149.5 (*ipso*-Ar), 169.5 (ZnNCN), 171.6 (AlNCNAl). ¹³C-NMR (75 MHz, CD₂Cl₂, 25 °C): δ -14.6 (ZnCH₃), -10.5 (AlC^bH₃), -7.3 (AlC^bH₃), 115.4 (C), 121.4 (Ar), 122.4 (Ar), 127.0 (Ar), 127.8 (Ar), 128.5 (Ar), 128.8 (Ar), 130.7 (Ar), 132.7 (Ar), 133.7 (Ar), 142.7 (*ipso*-Ar), 149.1 (*ipso*-Ar), 149.6 (*ipso*-Ar), 168.7 (ZnNCN), 169.7 (AlNCNAl). ATR-IR: ν 3055, 3019, 2916, 2878, 2813, 1589, 1545, 1486, 1450, 1433, 1397, 1336, 1262, 1233, 1177, 1088, 1068, 1024, 962, 909, 756, 729, 688, 638, 664, 561, 514, 497, 435 cm⁻¹.

{C[C(NPh)₂]₃[GaMe₂]₂[ZnMe]₂} **5b**. The synthesis of **5b** is similar to that of **5a**, using 0.5 g **3b** (0.63 mmol) and 2 mL of a 1.2 M ZnMe₂ solution in toluene (2.4 mmol). The reaction mixture was kept at 100 °C in a sealed pressure reactor for one day. Yield: 0.44 g (73.1%). Mp.: 220 °C (dec.). Elemental analysis calculated (%) for C₄₆H₄₈Ga₂N₆Zn₂ (955.14 g/mol): H 5.07, C 57.84, N 8.80; found: H 5.60, C 58.65, N 7.78. ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ -1.08 (s, 6 H, ZnCH₃), -0.78 (s, 6 H, GaC^aH₃), 0.46 (s, 6 H, GaC^bH₃), 6.27 (m, 6 H, ArH), 6.60 (m, 3 H, ArH), 6.75 (m, 3 H, ArH), 6.88 (m, 3 H, ArH), 7.02 (m, 6 H, ArH), 7.11 (m, 3 H, ArH), 7.32 (m, 6 H, ArH). ¹H-NMR (300 MHz, CD₂Cl₂, 25 °C): δ -1.82 (s, 6 H, AlC^aH₃), -1.11 (s, 6 H, ZnCH₃), -0.46 (s, 6 H, AlC^bH₃), 6.33 (m, 2 H, ArH), 6.68 (m, 4 H, ArH), 7.07 (m, 4 H, ArH), 7.15 (m, 6 H, ArH), 7.26 (m, 4 H, ArH), 7.41 (m, 10 H, ArH). ¹³C-NMR (75 MHz, C₆D₆, 25 °C): δ -14.7 (ZnCH₃), -8.3 (GaCH₃), -4.2 (GaCH₃), 88.9 (C), 121.4 (Ar), 121.7 (Ar), 125.7 (Ar), 126.2 (Ar), 127.5 (Ar), 128.6 (Ar), 129.4 (Ar), 130.5 (Ar), 132.3 (Ar), 133.1 (Ar), 144.2 (*ipso*-Ar), 149.9 (*ipso*-Ar), 151.0 (*ipso*-Ar), 168.6 (ZnNCN), 171.6 (GaNCNGa). ¹³C-NMR (75 MHz, CD₂Cl₂, 25 °C): δ -14.6 (ZnCH₃), -10.5 (AlCH₃), -7.3 (AlCH₃), 115.4 (C), 121.4 (Ar), 122.4 (Ar), 127.0 (Ar), 127.8 (Ar), 128.5 (Ar), 128.8 (Ar), 130.7 (Ar), 132.7 (Ar), 133.7 (Ar), 142.7 (*ipso*-Ar), 149.1 (*ipso*-Ar), 149.6 (*ipso*-Ar), 168.7 (ZnNCN), 169.7 (AlNCNAl). ATR-IR: ν 3058, 3021, 2958, 2921, 2854, 1652, 1592, 1483,

1455, 1438, 1386, 1333, 1261, 1237, 1171, 1091, 1069, 1024, 950, 906, 875, 797, 751, 689, 644, 620, 603, 565, 512, 481, 427, 399 cm⁻¹.

Supporting Information The crystallographic data (without structure factors) were deposited as "supplementary publication no. CCDC-943234 (**3a**), CCDC-943233 (**4b**) and CCDC-943232 (**5a**)" at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk). In addition, the structural data (bond lengths and angles) as well as detailed information on the NMR characterization are given in the electronic supplement.

Acknowledgments

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- [10] Detailed informations are given in the electronic supplement.
- [11] Bruker AXS D8 Kappa diffractometer with APEX2 detector (MoK α radiation, $\lambda = 0.71073$ Å; T = 180(1) K (**3a**), 100(1) K (**4b**, **4c**, **5c**)). The structures were solved by Direct Methods (SHELXS-97, G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473.) and refined by full-matrix least-squares on F². Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). All non-hydrogen atoms were refined anisotropically, methyl hydrogen atoms as rigid groups and others by a riding model. NH hydrogen atoms were taken from the difference fourier synthesis and refined freely with constrained U_{iso}. (SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, Universität Göttingen, 1997 and shelXle, *A Qt GUI for SHELXL*. See also: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122; C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* **2011**, *44*, 1281–1284.).
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- [15] The mean value of the Zn-N bond containing three-coordinated Zn atoms as found in the CSD database is 1.994 Å (304 structures). Cambridge Structural Database, Version 5.34, see also: F. H. Allen, *Acta Cryst.* **2002**, *B58*, 380–388. Then Zn-N bond was defined to be a "single bond".

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Table 1. Crystallographic data for **3a**, **4a**,^[8] **4b** and **5a**.

	3a	4b	4c ^[d]	5a ^[e]
Empirical formula	C ₄₄ H ₄₄ Al ₂ N ₆	C ₄₈ H ₅₄ Ga ₄ N ₆	C ₄₄ H ₄₂ N ₆ Zn ₄	C ₅₃ H ₅₆ Al ₂ N ₆ Zn ₂
<i>M</i>	710.81	993.85	916.32	961.74
Crystal size [mm]	0.18 × 0.15 × 0.12	0.32 × 0.12 × 0.10	0.27 × 0.12 × 0.10	0.38 × 0.32 × 0.26
<i>T</i> [K]	180(1)	100(1)	100(2)	100(1)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	C2/c	P2 ₁ /c	C2
<i>a</i> [Å]	18.787(5)	17.527(4)	13.643(2)	18.0425(14)
<i>b</i> [Å]	13.925(4)	15.401(3)	13.432(3)	18.1801(14)
<i>c</i> [Å]	15.707(5)	18.607(4)	22.182(4)	23.2870(18)
α [°]	90	90	90	90
β [°]	96.166(12)	116.848(8)	100.325(7)	95.991(2)
γ [°]	90	90	90	90
<i>V</i> [Å ³]	4085(2)	4481.5(16)	3999.0(13)	7596.8(10)
<i>Z</i>	4	4	4	6
<i>D</i> _{calc} [g·cm ⁻³]	1.156	1.473	1.522	1.261
μ (MoK α [mm ⁻¹])	0.109	2.419	2.410	1.022
Transmissions	0.75/0.65	0.75/0.48	0.75/0.36	0.75/0.66
<i>F</i> (000)	1504	2032	1872	3012
Index ranges	-24 ≤ <i>h</i> ≤ 24 -18 ≤ <i>k</i> ≤ 18 -20 ≤ <i>l</i> ≤ 18	-23 ≤ <i>h</i> ≤ 23 -20 ≤ <i>k</i> ≤ 20 -24 ≤ <i>l</i> ≤ 24	-11 ≤ <i>h</i> ≤ 16 -9 ≤ <i>k</i> ≤ 15 -25 ≤ <i>l</i> ≤ 25	-25 ≤ <i>h</i> ≤ 24 -25 ≤ <i>k</i> ≤ 24 0 ≤ <i>l</i> ≤ 33
$\theta_{\max}$ [°]	27.64	28.42	25.02	30.66
Reflections collected	67524	42079	20652	78914
Independent reflections	9274	5594	6544	22149
<i>R</i> _{int}	0.0290	0.0344	0.1747	0.0302
Refined parameter	475	263	149	835
Completeness	97.3%	98.9%	92.8%	97.2%

[a] $R_I = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ (for $I > 2\sigma(I)$). - [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. - [c] Goodness of fit = $\{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_{\text{observns}} - N_{\text{params}})\}^{1/2}$. $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ with $P = [F_o^2 + 2F_c^2]/3$, *a* and *b* are constants chosen by the programme. - [d] Because of the poor quality of the crystal only the connectivity of the atoms should be regarded reliable. Any atoms were refined isotropically since an anisotropic refinement did not yield a reasonable description of a thermal movement and several atoms showed non-positively defined ellipsoids. - [e] The toluene molecule on the two-fold axis could not be refined with anisotropic displacement parameters in a satisfactory manner. Moreover, the C-C bond lengths in the phenyl rings of the solvent were restraint to 1.390(2) Å. In the difference Fourier synthesis remained several peaks with 1.2 - 1.8 e/Å³ corresponding to a highly disordered toluene molecule, which could not be modeled properly. Consequently, the final refinement was performed with solvent-free reflection data following PLATON/squeeze run.

Table 2. Selected bond lengths (Å) of **3a**, **4a**,^[8] **4b** and **5a**.

	3a		4a ^[8]		4b		5a ^[a]
Al(1)-N(1)	1.9220(14)	Al(1)-N(2)	1.9984(11)	Ga(1)-N(2)	2.0694(12)	Al(1)-N(6)	1.9146(17)
Al(1)-N(6)	1.8956(14)	Al(1)-N(1)	1.9199(11)	Ga(1)-N(1)	1.9972(12)	Al(1)-N(1)	1.8822(17)
Al(2)-N(4)	1.9272(14)	Al(1)#1-N(2)#1	1.9984(11)	Ga(1)#1-N(2)#1	2.0694(12)	Al(2)-N(3)	1.9187(17)
Al(2)-N(5)	1.9015(14)	Al(1)#1-N(1)#1	1.9199(11)	Ga(1)#1-N(1)#1	1.9972(12)	Al(2)-N(2)	1.8901(17)
		Al(2)-N(2)	1.9967(11)	Ga(2)-N(2)	2.0741(13)	Zn(2)-C(61)	2.514(2)
		Al(2)-N(3)	1.9268(11)	Ga(2)-N(3)	1.9989(13)	Zn(2)-N(4)	1.9159(16)
		Al(2)#1-N(2)#1	1.9967(11)	Ga(2)#1-N(2)#1	2.0741(13)	Zn(1)-C(31)	2.551(2)
		Al(2)#1-N(3)#1	1.9268(11)	Ga(2)#1-N(3)#1	1.9989(13)	Zn(1)-N(5)	1.9067(16)
C(1)-C(2)	1.4564(19)	C(1)-C(3)	1.4191(15)	C(1)-C(3)	1.4208(17)	C(1)-C(3)	1.456(2)
C(1)-C(3)	1.453(2)	C(1)-C(3)#1	1.4191(15)	C(1)-C(3)#1	1.4208(17)	C(1)-C(4)	1.464(2)
C(1)-C(4)	1.446(2)	C(1)-C(2)	1.506(2)	C(1)-C(2)	1.504(3)	C(1)-C(2)	1.434(2)
N(1)-C(2)	1.3295(19)	N(3)-C(3)	1.3257(16)	N(3)-C(3)	1.3269(18)	N(3)-C(3)	1.338(2)
N(2)-C(2)	1.3667(19)	N(2)-C(3)	1.4470(15)	N(2)-C(3)	1.4385(18)	N(5)-C(3)	1.364(2)
N(4)-C(3)	1.3254(18)	N(3)#1-C(3)#1	1.3257(16)	N(3)#1-C(3)#1	1.3269(18)	N(6)-C(4)	1.333(2)
N(3)-C(3)	1.3694(19)	N(2)#1-C(3)#1	1.4470(15)	N(2)#1-C(3)#1	1.4385(18)	N(4)-C(4)	1.359(2)
N(6)-C(4)	1.3601(19)	N(1)-C(2)	1.3404(13)	N(1)-C(2)	1.3415(15)	N(2)-C(2)	1.352(2)
N(5)-C(4)	1.3605(18)	N(1)-C(2)#1	1.3404(13)	N(1)-C(2)#1	1.3415(15)	N(1)-C(2)	1.366(2)

^[a] Only the bond lengths of molecule **1** are given.Table 3. Selected bond angles (°) of **3a**, **4a**,^[8] **4b** and **5a**.

	3a		4a ^[8]		4b		5a ^[a]
N(6)-Al(1)-N(1)	92.39(6)	N(1)-Al(1)-N(2)	90.67(5)	N(1)-Ga(1)-N(2)	88.08(5)	N(2)-Al(2)-N(3)	92.82(7)
N(5)-Al(2)-N(4)	91.45(5)	N(1)#1-Al(1)#1-N(2)#1	90.67(5)	N(1)#1-Ga(1)#1-N(2)#1	88.08(5)	N(1)-Al(1)-N(6)	91.22(7)
		N(3)-Al(2)-N(2)	68.46(4)	N(3)-Ga(2)-N(2)	65.45(5)	N(4)-Zn(2)-C(61)	73.27(7)
		N(3)#1-Al(2)#1-N(2)#1	68.46(4)	N(3)#1-Ga(2)#1-N(2)#1	65.45(5)	N(5)-Zn(1)-C(31)	71.97(7)
C(4)-N(6)-Al(1)	123.49(10)	C(2)-N(1)-Al(1)	125.64(9)	C(2)-N(1)-Ga(1)	125.67(11)	C(2)-N(2)-Al(2)	122.83(13)
C(4)-N(5)-Al(2)	121.84(10)	C(2)-N(1)#1-Al(1)#1	125.64(9)	C(2)-N(1)#1-Ga(1)#1	125.67(11)	C(2)-N(1)-Al(1)	119.93(12)
C(2)-N(1)-Al(1)	122.76(10)	C(3)-N(2)-Al(1)	101.14(7)	C(3)-N(2)-Ga(1)	100.61(8)	C(3)-N(3)-Al(2)	124.82(13)
C(3)-N(4)-Al(2)	122.50(10)	C(3)#1-N(2)#1-Al(1)#1	101.14(7)	C(3)#1-N(2)#1-Ga(1)#1	100.61(8)	C(4)-N(6)-Al(1)	123.91(13)
		C(3)-N(2)-Al(2)	89.32(7)	C(3)-N(2)-Ga(2)	90.83(8)		
		C(3)#1-N(2)#1-Al(2)#1	89.32(7)	C(3)#1-N(2)#1-Ga(2)#1	90.83(8)		
		C(3)-N(3)-Al(2)	96.09(8)	C(3)-N(3)-Ga(2)	97.60(9)	C(3)-N(5)-Zn(1)	121.88(13)
		C(3)#1-N(3)#1-	96.09(8)	C(3)#1-N(3)#1-	97.60(9)	C(4)-N(4)-Zn(2)	120.27(13)

Al(2)#1				Ga(2)#1			
C(3)-C(1)-C(2)	116.91(12)	C(3)#1-C(1)-C(3)	120.55(16)	C(3)#1-C(1)-C(3)	120.58(18)	C(3)-C(1)-C(4)	116.12(15)
C(4)-C(1)-C(2)	121.76(12)	C(3)-C(1)-C(2)	119.73(8)	C(3)-C(1)-C(2)	119.71(9)	C(2)-C(1)-C(3)	122.85(15)
C(4)-C(1)-C(3)	121.30(12)	C(3)#1-C(1)-C(2)	119.73(8)	C(3)#1-C(1)-C(2)	119.71(9)	C(2)-C(1)-C(4)	121.02(16)
N(1)-C(2)-N(2)	118.46(13)	N(3)-C(3)-N(2)	105.46(10)	N(3)-C(3)-N(2)	105.53(12)	N(3)-C(3)-N(5)	117.89(16)
N(1)-C(2)-C(1)	122.86(13)	N(3)-C(3)-C(1)	132.19(12)	N(3)-C(3)-C(1)	131.37(14)	N(5)-C(3)-C(1)	121.69(16)
N(2)-C(2)-C(1)	118.63(13)	C(1)-C(3)-N(2)	122.29(11)	C(1)-C(3)-N(2)	123.06(13)	N(3)-C(3)-C(1)	120.26(16)
N(4)-C(3)-N(3)	117.83(13)	N(3)#1-C(3)#1-N(2)#1	105.46(10)	N(3)#1-C(3)#1-N(2)#1	105.53(12)	N(6)-C(4)-N(4)	118.89(16)
N(4)-C(3)-C(1)	122.51(13)	N(3)#1-C(3)#1-C(1)#1	132.19(12)	N(3)#1-C(3)#1-C(1)#1	131.37(14)	N(4)-C(4)-C(1)	121.55(16)
N(3)-C(3)-C(1)	119.65(12)	C(1)#1-C(3)#1-N(2)#1	122.29(11)	C(1)#1-C(3)#1-N(2)#1	123.06(13)	N(6)-C(4)-C(1)	119.44(16)
N(6)-C(4)-N(5)	121.59(13)	N(1)-C(2)-N(1)#1	125.02(16)	N(1)-C(2)-N(1)#1	124.47(18)	N(2)-C(2)-N(1)	119.87(16)
N(5)-C(4)-C(1)	119.55(12)	N(1)-C(2)-C(1)	117.49(8)	N(1)-C(2)-C(1)	117.76(9)	N(2)-C(2)-C(1)	120.59(16)
N(6)-C(4)-C(1)	118.86(12)	N(1)#1-C(2)-C(1)	117.49(8)	N(1)#1-C(2)-C(1)	117.76(9)	N(1)-C(2)-C(1)	119.54(16)

^[a] Only the bond lengths of molecule 1 are given.

Methanetrisamidines can be twofold and fourfold metalated by different metal organic complexes with formation of dinuclear and tetranuclear homometallic complexes. Moreover, the different acidity of the N-H groups also allows stepwise deprotonation by different organometallic reagents with subsequent formation of heterobimetallic complexes.

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Heterobimetallic Metal-Amidinate Complexes by Stepwise Metalation of Methanetrisamidines

Keywords: Heterobimetallic / Zinc / Aluminum / X-ray diffraction

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