New Insights into Cinchonine–Aluminium Complexes and Their Application as Chiral Building Blocks: Unprecedented Ligand-Exchange Processes in the Presence of ZnR$_2$ Compounds

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Abstract: Previous studies have demonstrated that [(CN)$_2$AlCl] and [R$_2$Al-(μ-CN)]$_2$ (CN = deprotonated cinchonine) complexes can effectively act as chiral, semirigid, *N,N*-ditopic metalloligands for Zn-containing nodes, and provide viable means for constructing new, homochiral, heterometallic, coordination polymers of zigzag and helical topologies. These findings have prompted further investigations on the organometallic analogues of the formula [(CN)$_2$AlR], anticipating their utility as *N,N*-metalloligands for ZnR$_2$ units. Surprisingly, reactions of [(CN)$_2$AlMe]-type metalloligands with ZnR$_2$ compounds (R = Me or Et) revealed unprecedented ligand-exchange processes, including zinc-to-aluminium and aluminium-to-zinc transmetalations of alkyl groups. The molecular and crystal structure of the resulting compounds was determined by X-ray diffraction analysis. From the reaction of [(CN)$_2$AlMe] with ZnMe$_2$ a new pseudopolymorphic form of a noncovalent porous material based on [Me$_2$Al(μ-CN)]$_2$ molecules was isolated. Strikingly, the analogous reaction involving ZnEt$_2$ led to the generation of a new chiral 4*N*-tetratopic heterometalloligand [(CN)EtAl(μ-CN)$_2$ZnEt]. The latter unit was successfully connected by alkyl-exchanged ZnMe$_2$ nodes to give an original homochiral heterometallic {[(CN)EtAl(μ-CN)$_2$ZnEt]ZnMe$_2$}$_n$ coordination polymer adopting a snake 1D motif. The outcome of the revealed reactions indicates the complicated multistep reaction route that involves redistribution of cinchonine and alkyl ligands among the Al and Zn centers, and a general reaction scheme is proposed. The results are in strong contrast with the previously studied inorganic–organic [(CN)$_2$AlCl/ZnCl$_2$] system, which exclusively affords a helical coordination polymer based on ZnCl$_2$ nodes and (CN)$_2$AlCl metalloligands and lacks the exchange of CN ligands.

Keywords: alkoxides · aluminium · coordination polymers · transmetalation · zinc

Introduction

The last two decades have witnessed the fast development of metal–organic frameworks (MOFs) chemistry as a promising response to the limited tailorability of zeolitic materials.[1] Generally, MOFs are constructed in self-assembly processes of multifunctional organic ligands (linkers) and inorganic units (nodes).[2] In particular, the employment of optically pure chiral precursors affords homochiral MOFs, which proved to be promising substitutes of the long-sought-after chiral zeolites.[3] Among the vast library of building blocks, simple achiral bipyridines are one of the most commonly used linkers for the construction of MOFs,[4] unlike their less-numerous chiral derivatives for which the preparation is usually nontrivial and arduous.[5] Therefore, developing versatile strategies for facile generation of chiral bipyridines is the key challenge for advancing the surprisingly undeveloped field of homochiral MOFs. In this regard, the implementation of metal complexes with chiral auxiliary ligands as so-called metalloligands[6] creates a new level for the design and preparation methods of chiral bipyridine-type building units.

Recently, chiral biomolecules have emerged as particularly attractive building blocks for constructing MOFs.[7] Taking into account advantages, such as environmental and biological compatibility, in the application of biomolecules in the materials chemistry, we turned our attention toward readily available cinchona alkaloids and developed a new attractive route to chiral bipyridine-type linkers based on metal complexes of cinchona alkaloids.[8] This strategy appeared as an efficient method providing semirigid mononuclear and dinuclear chiral *N,N*-ditopic metalloligands, varying in angular disposition of N-donor centers. To our surprise, the resulting chiral aluminium complexes, with the following formulas [(CN)$_2$AlR][8a] and [R$_2$Al(μ-CN)]$_2$[8b] (CN = deprotonated cinchonine), exhibited intrinsic molecular

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shape-derived properties for noncovalent-interactions-driven self-assembly into chiral microporous supramolecular architectures prone to racemate separation[8a] or selective gas sorption.[8b] Furthermore, we demonstrated that [(CN)$_2$AlCl][8a] and [R$_2$Al(μ-CN)]$_2$[8c] complexes can effectively act as chiral, semirigid N,N-ditopic metalloligands for Zn-containing nodes, and provide viable means for constructing new homochiral heterometallic coordination polymers of zigzag and helical topologies. These findings have prompted our investigations on the organometallic analogues of the formula [(CN)$_2$AlR], anticipating that their utilization as N,N-metalloligands for ZnR$_2$ units could unveil new, original polymeric structures, as well as provide more profound insight into asymmetric catalytic processes effectively mediated by metal complexes with cinchona alkaloid scaffolds.[9] We report here the results of reactions of [(CN)$_2$AlR]-type metalloligands with ZnR$_2$ compounds (R = Me or Et), which revealed unexpected and unprecedented ligand-exchange processes, including zinc-to-aluminium and aluminium-to-zinc transmetalations of alkyl groups, leading to the generation of both a new chiral 4N-tetratopic heterometalloligand and an original Al,Zn-coordination polymer.

Results and Discussion

The reaction of [(CN)$_2$AlMe] with equimolar amounts of ZnMe$_2$ in toluene led to a pale-yellow solution and single colorless crystals were obtained as a result of crystallization from a toluene/hexane solution at −10°C (Scheme 1a). Strikingly, the X-ray studies revealed that instead of the ex-

pected heterometallic coordination polymer compound the isolated product was identified as a noncovalent solid constructed from discrete dimeric units of the formula [Me$_2$Al-(μ-CN)]$_2$ (1).[10] The structural characterization of the [Me$_2$Al(μ-CN)]$_2$ complex as a solvate with THF (1(α)·THF) was reported in our previous paper,[8b] and in this regard we were surprised to reveal that the resulted solid is a new solvent-free pseudopolymorphic β form of complex 1 (Figure 3, see below). The unexpected isolation of the dimethylaluminium compound 1 as the main product from the above reaction suggests a complex reaction course that involves ligand exchange between various organozinc and organoaluminium species. Formally, one can depict this process as the alkylation of the parent five-coordinate [(CN)$_2$AlMe] complex by ZnMe$_2$, leading to [Me$_2$Al(μ-CN)]$_2$, which is accompanied by transfer of one CN ligand to the zinc species and likely the formation of a [MeZn(CN)] moiety. This type of transformation did not occur in the previously studied [(CN)$_2$AlCl/ZnCl$_2$] system, which afforded a helical coordination polymer based on ZnCl$_2$ nodes and the [(CN)$_2$AlCl] metalloligand.[8a] Moreover, to the best of our knowledge, this type of ligand-exchange between dialkylzincs and organoaluminium alkoxides has no precedent in the literature. The cinchona alkaloid/AlEt$_3$/ZnEt$_2$ system was successfully examined for alkynylzinc asymmetric addition to carbonyl compounds, however neither the nature of catalytic center nor transmetalation events were considered by the authors.[9a]

To acquire a better view of the observed ligand-exchange processes, we also examined a mixed-alkyl reaction system composed of [(CN)$_2$AlMe] and ZnEt$_2$ as substrates. The addition of [(CN)$_2$AlMe] to equimolar amounts of ZnEt$_2$ in toluene at 20°C leads to a pale-yellow solution from which yellow monocrystals were obtained at −10°C (Scheme 1b). In this case, the X-ray studies allowed for the identification of the crystalline product as a new coordination polymer with the unexpected composition of {[(CN)EtAl(μ-CN)$_2$ZnEt]ZnMe$_2$}$_n$ (2; Scheme 1b and Figure 1). Formally, the resulting homochiral coordination polymer can be considered as being based on Me$_2$Zn nodes connected by the new heterometalloligand [(CN)EtAl(μ-CN)$_2$ZnEt]. The revealed reaction outcome confirms the complex multistep reaction route that involves the redistribution of cinchonine and alkyl ligands among the Al and Zn centers. The most striking observation is the presence of ZnMe$_2$ molecules, undoubtedly resulting from transmetalation of the methyl group of the parent five-coordinate alkylaluminium complex to the zinc atom. This process is accompanied by the transfer of the ethyl group to aluminium and formally only one ethyl group stays bound to the same zinc atom. Taking into consideration the results from both the [(CN)$_2$AlMe/ZnMe$_2$] and the [(CN)$_2$AlMe/ZnEt$_2$] reaction systems, we propose a general reaction scheme (Scheme 1). It is reasonable to assume that the crystallization product of each reaction is determined by the relative solubility of both [R'$_2$Al(μ-CN)]$_2$ and {[(CN)R'Al(μ-CN)$_2$ZnR']ZnR$_2$}$_n$ in the employed solvent, and that the redistribution equilibria of the crystalliza-
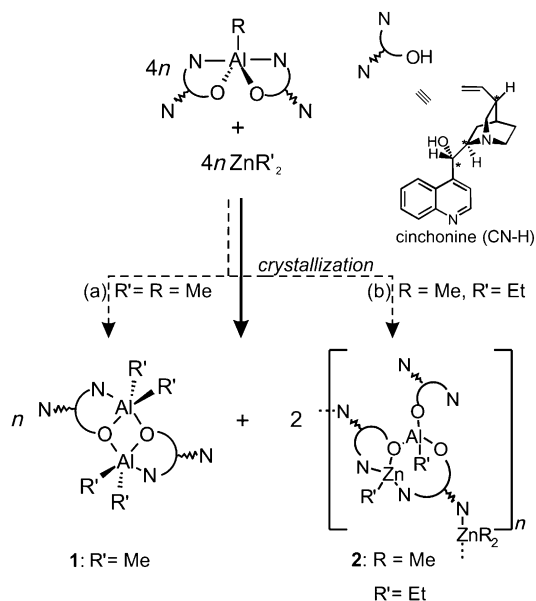
Scheme 1. Proposed general reaction scheme (bold arrow) for the [(CN)$_2$AlR/ZnR'$_2$] system. Dashed arrows point at the corresponding products of crystallization of a) [(CN)$_2$AlMe/ZnMe$_2$] and b) [(CN)$_2$AlMe/ZnEt$_2$].
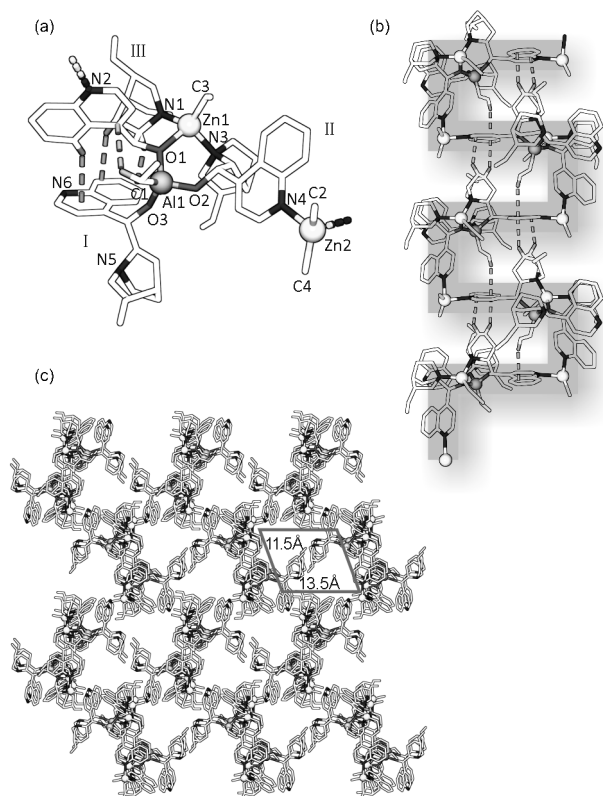
Figure 1. a) The asymmetric unit of **2**. b) The snake motif adopted by the 1D coordination polymer **2**; intrachain C−H···π interactions are marked by dashed lines. c) View along the *a* axis of the structure of **2**, revealing parallelogram-shaped 1D open channels decorated with free N-donor centers of the pendant quinuclidine group.

tions shift completely to the side of the less-soluble compound. We cannot, however, rule out the possibility of formation of other products from the [(CN)$_2$AlMe/ZnEt$_2$] reaction system, such as [Me$_2$Al(μ-CN)]$_2$ and [MeEt$_2$Al(μ-CN)]$_2$; this is difficult to clarify due to the complex ^{1}H NMR spectra of the postcrystallization filtrate. Nevertheless, it is not likely that [Me$_2$Al(μ-CN)]$_2$ is generated in significant yield as, consequently, its preferential crystallization over **2** would be the expected result.

Whereas the alkylation of Zn moieties by homoleptic aluminium alkyls is well recognized,[11] the processes involving alkylaluminium alkoxides have, to the best of our knowledge, not been reported. Due to both the limited data and unprecedented character of these processes, it is premature to discuss the observed complex transmetalation equilibria in detail. Nevertheless, our results suggest that the outcome of the alkyl exchange reactions, involving zinc and aluminium in these systems, is a subtle balance between various affecting factors, such as mediation by O- and N-donor sites, charge influence of the alkoxide groups, the semirigidity of cinchonine–aluminium complexes and crystal-packing forces. There is continuing interest in the development of various useful reaction systems that feature transmetalation of alkyl groups from or to zinc,[12] including systems involving cinchona alkaloid metal complexes,[9a,d] and in our opin-

ion, the revealed transmetalation equilibria that involves alkylaluminium alkoxides and zinc alkyls open new frontiers in this chemistry.

The molecular and crystal-structure analysis of the resulting crystalline materials from the reaction of [(CN)$_2$AlR]-type metalloligands with ZnR$_2$ compounds provides new insights into cinchonine–aluminium complexes and their propensity for the formation of extended inorganic–organic frameworks by noncovalent-interaction- and coordination-driven self-assembly. Compound **2** crystallizes in the $P2_12_12_1$ space group. The asymmetric unit contains two chemically inequivalent tetrahedral Zn centers and one tetrahedral Al center coordinated by alkyl groups and three deprotonated cinchonine ligands (Figure 1a). The latter demonstrate different modes of coordination to metal sites. One of the three CN ligands (type **I**, Figure 1a) features a terminal coordination to an Al(1) center through the alkoxide O(3) atom and acts as a spectator in the construction of the 1D polymeric chain. Simultaneously the Al center is linked to the Zn(1) center by another CN ligand (**II**) through its alkoxide O(2) atom and quinuclidine N(3) atom. The remaining CN unit (**III**) also bridges the two metal centers through double coordination of its alkoxide O(1) atom, closing a central seven-membered metallacyclic ring ZnOAlOCCN. The bond distances Al(1)−O(2) and Al(1)−O(3) are approximately 0.1 Å shorter than the bridging Al(1)−O(1) bond (1.840(4) Å). The latter bond is 0.2 Å shorter than the bridging Zn(1)−O(1) bond. As noted before, we were surprised to discover that the alkyl groups coordinated to the Al(1) and Zn(2) centers differ from those in the parent compounds [(CN)$_2$AlMe] and ZnEt$_2$, in which the Al(1) atom is coordinated by an Et group and Zn(2) is coordinated by two Me groups. Thus, formally, the ligand-exchange processes between the parent metalloligand [(CN)$_2$AlMe] and ZnEt$_2$ afforded a new heterometalloligand, [(CN)EtAl(μ-CN)$_2$ZnEt]. The latter building unit may potentially act as a 4*N*-tetratopic chiral metalloligand, possessing three terminal quinoline and one quinuclidine amine donor centers.

A more detailed analysis of the supramolecular structure of **2** shows that the single polymeric chain of **2** adopts a unique snake structural motif, which is supported by C−H···π interactions (2.66 Å) between quinoline rings and quinuclidine hydrogen atoms of the neighboring **II** units (Figure 1b). Interestingly, an inspection into the crystal lattice along the *a* axis reveals a 1D open-channel system (Figure 1c) with the framework being stabilized by interchain C−H···π interactions. The 1D nanopores are parallelogram-shaped (ca. 13.5×11.5 Å) with quinuclidine moieties protruding alternately from the opposite corners of the parallelogram. The presence of flexible amine groups within the open-channel network of the chiral crystalline solid is a very attractive feature, which provides opportunities for designing selective processes that involve Lewis acid guests.[13]

Furthermore, the analysis of the crystal structure of the new β phase of **1**, isolated from the [(CN)$_2$AlMe/ZnMe$_2$] system, contributes to the investigations on the nature of the [Me$_2$Al(μ-CN)]$_2$ building block. The β phase is characterized

by the orthorhombic $P2_12_12$ space group symmetry, whereas the polymorph α phase[8b] belongs to the monoclinic $C2$ space group. The asymmetric unit of **1**(β) consists of a single five-coordinate dimeric complex [Me$_2$Al(μ-CN)]$_2$ for which the molecular structure corresponds to that of the α form (Figure 2a). Although most distances and angles around the
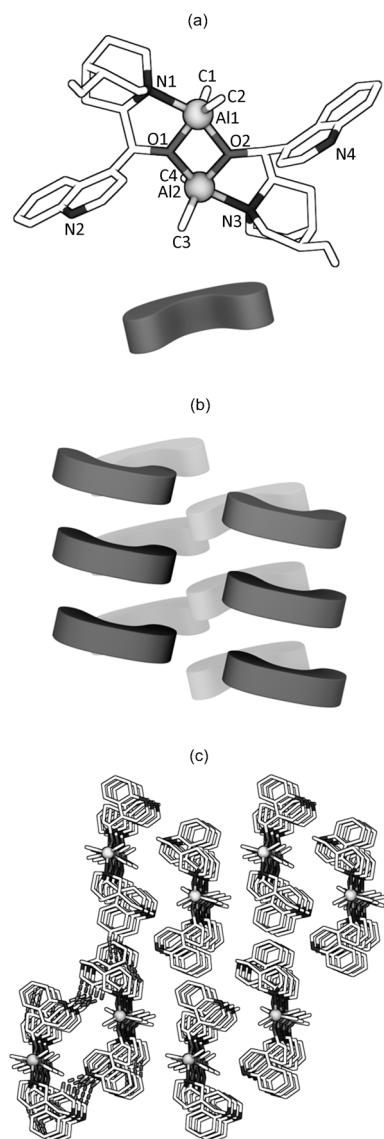

Figure 2. Self-organization process of metalloligand **1** into the new non-porous crystalline β phase.

Al atoms in **1**(β) are roughly the same as for **1**(α), certain parameters differ slightly in the two polymorphs. For example, in **1**(β), the two Al−N bond lengths are 2.200(6) and 2.173(5) Å, whereas in **1**(α), the distances are both 2.216(5) Å. Most notably, the angle between the binding directions of the uncoordinated quinoline N centers (Ω) is significantly widened, from 49.3° in **1**(α) to 83.7° in **1**(β). It is also interesting to compare the geometric parameters of **1**(α) and **1**(β) with those in the structure of a previously re-

ported coordination polymer {[Me$_2$Al(μ-CN)]$_2$ZnMe$_2$}$_n$ (**3a**),[8c] which contains two conformationally different metalloligand [Me$_2$Al(μ-CN)]$_2$ units: **A** and **B**. We found out that the bond lengths of **1**(α) and the angle Ω generally match with the corresponding values of the metalloligand unit **B** in **3a**, whereas the same parameters in **1**(β) are roughly the same as those in unit **A**. This finding, not only substantiates the flexible and adaptive nature of the metalloligand [R$_2$Al(μ-CN)]$_2$ skeleton, but indicates its two preferred conformations (with two characteristic binding angles Ω) and suggests bistability of this building block.

The supramolecular structure of **1**(β) consists of tightly packed columns that run along the c direction (Figure 2b and S3 in the Supporting Information). Each column is constructed from two C_2-symmetric "walls" of the translationally equivalent unit **1**. These units pack closely together along the axis of the column, which is supported by the effective utilization of the molecular shape of complex **1** (Figure S3 in the Supporting Information). The two walls interdigitate such that a quinoline arm of **1** from one wall is inserted into a cavity in the central part of the neighboring molecule **1** from the other wall, and the resulting column can be described by an elliptic cylinder geometry (Figure 2c). The cylindrical double-wall structure is stabilized by a group of intermolecular noncovalent bonds: C−H⋯π interactions within a single wall, involving several quinuclidine hydrogen atoms as acceptors of π electrons from a single quinoline moiety of a neighboring **1** unit, and another C−H⋯π interaction that involves vinyl hydrogen atom as well as C−H⋯N hydrogen bond between the quinoline arms of the oppositely arranged molecule **1**, linking the pair of walls into the interdigitated walls motif (Figure 2c and S3 in the Supporting Information). It is interesting to compare the arrangement of **1** molecules in the elliptic column in **1**(β) with two other structures described previously constructed from the same type of metallotecton [R$_2$Al(μ-CN)]$_2$: the "virtual helix" in **1**(α)[8b] and the helical coordination polymer {[Et$_2$Al(μ-CN)]$_2$ZnEt$_2$}$_n$ (the "real helix", **3b**;[8c] Figure 3). Compared with the structural motif of **1**(α), the **1** units in **1**(β) were moved closer along the c direction to the close-fitting positions forming the wall. Interestingly, this double-wall ar-

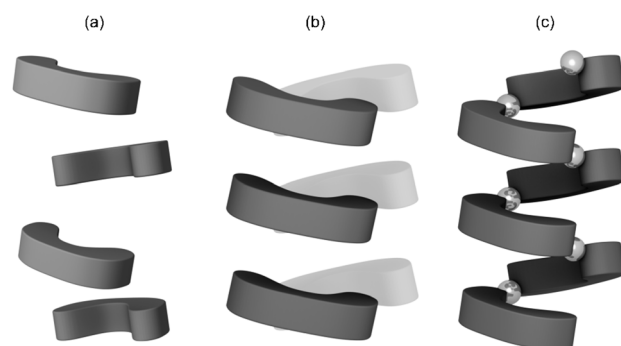Figure 3. Arrangement of the [R$_2$Al(μ-CN)]$_2$ building blocks in the structures of: a) "virtual helix" of **1**(α); b) double-wall structure of **1**(β); c) "real helix" of **3b**.

rangement of the **1**-type metalloligands can also be observed in the structure of **3b**. The noticeable difference, however, is the shift in positions of the two walls, from the frontal arrangement in the circular helical tube in **3b** to the interdigitated walls in the elliptic column in **1(β)**. Evidently, the replacement of **1** by ZnR₂ nodes results in "destabilization" of the tubular arrangement of **3b** and generation of the more dense architecture of the elliptic column in **1(β)**. In this regard, it is surprising that THF evolution from the open-channel network of **1(α)** does not result in a solid-state transformation to the nonporous **1(β)** (no traces of **1(β)** were detected by PXRD up to 70 °C—the temperature of **1(α)** amorphization[8b]), in spite of the generally high propensity of noncovalent solids to form architectures of maximal density.

Conclusion

In summary, the reported studies on reactions between the potentially *N,N*-ditopic, chiral metalloligand of the formula [(CN)₂AlMe] with ZnR₂ compounds (R=Me, Et) demonstrate an unprecedented ligand-exchange processes, including zinc-to-aluminium and aluminium-to-zinc transmetalations of the alkyl groups. Strikingly, the [(CN)₂AlMe/ ZnMe₂] system gives rise to a unique, homochiral, snake-shaped, coordination polymer based on the new 4*N*-topic heterometalloligand {[(CN)EtAl(μ-CN)₂ZnEt]ZnMe₂}ₙ. This result is in strong contrast with the previously studied inorganic–organic [(CN)₂AlCl/ZnCl₂] system, which exclusively affords a helical coordination polymer based on ZnCl₂ nodes and the [(CN)₂AlCl] metalloligand, lacking the exchange of CN ligands.[8a] Thus, the results, not only significantly contribute to crystal engineering of homochiral extended architectures based on multitopic heterometallic building blocks derived from metal complexes of cinchona alkaloids, but also open new frontiers in the transmetalation chemistry of catalytic processes that involve zinc alkyl reagents and metal alkoxides.

Experimental Section

General experimental procedure: All operations were carried out under dry nitrogen by using standard Schlenk techniques. Solvents were dried and distilled prior to use. Commercial cinchonine was purified by column chromatography with Merck silica gel 60 (230–400 mesh) and 2-metoxyethanol as eluent; column output was monitored on TLC plates (0.25 mm, Merck silica gel 60 F254 on aluminium). Pure cinchonine ($R_f = 0.47$ in methoxyethanol) was recrystallized in toluene and dried in a vacuum desiccator. NMR spectra were recorded on a Varian Mercury 400 spectrometer.

Synthesis of 1(β): A slurry of cinchonine (0.30 g, 1.02 mmol) in toluene (7 mL) was cooled to −78 °C, and Me₃Al (0.34 mL of a 1.5 M solution in toluene, 0.51 mmol) was added dropwise. After stirring for 4 h at room temperature, the reaction mixture became clear colorless, and then Me₂Zn (0.34 mL of a 1.5 M solution in toluene, 0.51 mmol) was added to give a yellow-colored solution. Compound **1(β)** was obtained as colorless single crystals from a toluene/hexane solution at −10 °C, isolated yield

about 73 %. Elemental analysis (%) calcd for C₄₆H₅₄N₄O₂Al₂: C 71.98, H 7.77, N 7.99, O 4.57; found: C 71.93, H 7.86, N 8.01, O 4.60; the ¹H NMR (C₆D₆, 400 MHz) spectrum is consistent with the corresponding data found in ref. [8b].

Synthesis of 2: A slurry of cinchonine (0.30 g, 1.02 mmol) in toluene (7 mL) was cooled to −78 °C, and Me₃Al (0.34 mL of a 1.5 M solution in toluene, 0.51 mmol) was added dropwise. After stirring for 4 h at room temperature, the reaction mixture became clear colorless, and then Et₂Zn (0.34 mL of a 1.5 M solution in toluene, 0.51 mmol) was added to a give yellow-colored solution. Compound **2** was obtained as yellow single crystals from a toluene/hexane solution at −10 °C, isolated yield about 88 %. Elemental analysis (%) calcd for C₄₆H₅₄N₄O₂Al₂: C 71.98, H 7.77, N 7.99, O 4.57; found: C 71.93, H 7.86, N 8.01, O 4.60; compound **2** was not characterized by ¹H NMR due to the insolubility in popular deuterated solvents.

Crystallographic data: The data were collected at 100(2) K on a Nonius Kappa CCD diffractometer by using graphite monochromated Mo$_{Kα}$ radiation ($λ = 0.71073$ Å). The crystal was mounted in a nylon loop in a drop of silicon oil to prevent the possibility of decay of the crystal during data collection. The unit-cell parameters were determined from ten frames, then refined on all data. The structure was solved by direct methods with the SHELXS97[14] program and was refined by full-matrix least-squares on F^2 with the program SHELXL97.[15] All non-hydrogen atoms were refined with anisotropic displacement parameters. CCDC-882091 (**1(β)**) and CCDC-882092 (**2**) 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. For selected bond distances see Table S1 and S2 in the Supporting Information.

Crystal data for 1(β): C₄₂H₅₄Al₂N₄O₂: $M = 700.85$, crystal dimensions $0.44 \times 0.36 \times 0.20$ mm³, orthorhombic, space group $P2_12_12$ (no. 18), $a = 14.1770(8)$ Å, $b = 29.6210(13)$ Å $c = 9.126(3)$ Å, $U = 3832.3(12)$ Å³, $Z = 4$, $F(000) = 2384$, $ρ_{cald} = 1.215$ g m³, $T = 100(2)$ K, $μ(Mo_{Kα}) = 0.117$ mm⁻¹, $θ_{max} = 22.96°$, $R1 = 0.0622$, $wR2 = 0.1143$ for 2408 reflections with $I_o > 2σ(I_o)$.

Crystal data for 2: C₆₃H₇₉AlN₆O₃Zn₂: $M = 1126.09$, crystal dimensions $0.46 \times 0.34 \times 0.22$ mm³, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 14.9601(5)$ Å, $b = 18.7102(11)$ Å $c = 28.3131(19)$ Å, $U = 7925.0(8)$ Å³, $Z = 4$, $F(000) = 2384$, $ρ_{cald} = 0.944$ g m³, $T = 100(2$ K, $μ(Mo_{Kα}) = 0.653$ mm⁻¹, $θ_{max} = 21.97°$, $R1 = 0.0616$, $wR2 = 0.1579$ for 5881 reflections with $I_o > 2σ(I_o)$.

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