Metalloid Clusters

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The Intermetalloid Cluster $[(Cp^*AlCu)_6H_4]$, Embedding a Cu_6 Core Inside an Octahedral Al_6 Shell: Molecular Models of Hume–Rothery Nanophases**

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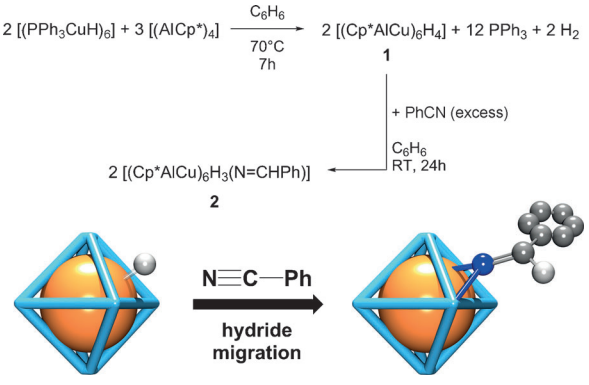
Abstract: *Defined molecular models for the surface chemistry of Hume–Rothery nanophases related to catalysis are very rare. The Al-Cu intermetalloid cluster $[(Cp^*AlCu)_6H_4]$ was selectively obtained from the clean reaction of $[(Cp^*Al)_4]$ and $[(Ph_3PCuH)_6]$. The stronger affinity of Cp*Al towards Cu sweeps the phosphine ligands from the copper hydride precursor and furnishes an octahedral Al_6 cage to encapsulate the Cu_6 core. The resulting hydrido cluster $M_{12}H_4$ reacts with benzonitrile to give the stoichiometric hydrometalation product $[(Cp^*AlCu)_6H_3(N{=}CHPh)]$.*

Nanoalloys and intermetallic clusters A_aB_b with control of size $(a+b)$ or composition (a/b) are an important avenue in materials science and hold promise for advanced applications (for example, selective catalysis), as the raised complexity of the mixed-metal systems allows going beyond the performance of homometallic parent species.[1] The development of synthetic methods for deriving mixed transition metal (A) main-group metal (B) clusters bottom-up by soft, wet chemistry is a particularly demanding challenge in this respect. For example, based on Zintl ion chemistry, fascinating binary and ternary intermetalloid molecular clusters with components B from Groups 14 and 15 have been demonstrated.[2] Motivated in this fashion and inspired by the vast diversity of compositions and structures of Hume–Rothery and Laves phases, our interest has focused on intermetallics left of the Zintl border with B elements from Groups 12 and 13 (i.e. B = Zn, Cd; Al, Ga, In), and we reported on the molecular access to nano-brass (Cu/Zn)[3] and related A/B phases (for example, NiAl).[4] Our synthesis strategy is routed in the coordination chemistry of low-valent organoelement species RB as ligands at transition-metal (A) centers (R = CH_3, bulky alkyl, aryl, and Cp* = C_5Me_5). Over the years, we obtained a library of metal-rich molecules of the general formula $[A_a(BR)_b]$.[5] Representative examples include the compounds $[Pd_3(AlCp^*)_6]$,[6] $[Mo(ZnMe)_9(ZnCp^*)_3]$,[7] and $[Pd_2Zn_6Ga_2(Cp^*)_5(Me)_3]$.[8] The intermetallic cores $M_n = A_aB_b$ $(b > a;\ n = a+b)$ are stabilized by wrapping the core structure M_n into an all-hydrocarbon shell R_c $(c < n)$. This feature is connecting $[A_a(BR)_b]$ to Schnöckel's famous family of ligand-stabilized metalloid Al_n and Ga_n clusters,[9] with $[Al_{50}Cp^*_{12}]$ as the most prominent example.[10] The analogy to the coordination chemistry of Cp*Al and Cp*Ga becomes intriguing when the Al_{50} system is written as $[Al_{38}(AlCp^*)_{12}]$. Thus, being a versatile and powerful donor ligand, the carbenoid Cp*Al should also be able to stabilize larger transition-metal cores A_a $(a > 3)$, which is quite similar to the role of CO in metal carbonyl clusters, and for many years we were working towards this goal. Herein, we present a breakthrough, the novel Al-Cu intermetalloid cluster $[(Cp^*AlCu)_6H_4]$ (**1**; Scheme 1). The molecular structure of **1** reveals a Cu_6 unit inside an octahedral Al_6 unit with the resulting M_{12} core being wrapped into a hydrocarbon shell of Cp* and H ligands only.

The reaction of $[(Cp^*Al)_4]$ with $[(Ph_3PCuH)_6]$ in a 3:2 molar ratio leads to the clean formation of $[(Cp^*AlCu)_6H_4]$ (**1**) as a brown-black crystalline solid in good, reproducible yields of about 80% (Scheme 1). Analogously, $[(Cp^*AlCu)_6D_4]$ ($\mathbf{1_D}$) was prepared from $[(Ph_3PCuD)_6]$. There are quite a few other examples of PR_3 substitution by ECp* (E = Al, Ga);[5b–d] however, only mononuclear complexes [M-



Scheme 1. Top: Synthesis of $[(Cp^*AlCu)_6H_4]$ (**1**) and $[(Cp^*AlCu)_6H_3(N{=}CHPh)]$ (**2**). Bottom: Conceptual scheme of the cluster surface reaction of benzonitrile with hydride migration (hydrometalation) to yield a Cu/Al-bonded aldiminate species. The structure of **2** serves as a molecular model of a catalytic surface hydrogenation reaction at Hume–Rothery nanophase materials.

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$(PR_3)_n(ECp^*)_m]$ are formed and higher nuclear clusters cannot be accessed in this way. Obviously in case of **1**, the critical step for aggregation is not just the PPh_3 substitution itself, but rather the elimination of H_2 as the ideal leaving group, and thus creating unsaturated Cu^0. This concept can be extended: Preliminary studies show that [(NHC)AuH] readily reacts with $[(AlCp^*)_4]$ to give the cluster $[(Au_nAl_{(8-n)})(AlCp^*)_6(H_x)]$, which features an M_8 cube (M = Au/Al) imbedded into an octahedral Al_6 shell (NHC = N-heterocyclic carbene). The characterization of this congener of **1** is still in progress. Single-crystal X-ray diffraction and analytical data support the cluster composition (see the Supporting Information).

Compounds **1** and $\mathbf{1_D}$ are moisture sensitive and instantly burn upon exposure to air. They are moderately soluble in common organic solvents, such as THF, hexane, benzene, and toluene. In the ^{1}H NMR spectrum the Cp* protons appear as a sharp singlet at $\delta = 2.01$ ppm, and the H ligands show a broad singlet at around $\delta = -2.86$ ppm (rel. int. 4H; see the Supporting Information). The ^{31}P NMR spectrum of isolated **1** clearly indicates the absence of triphenylphosphine ligands in the molecule. The ^{13}C NMR spectrum of **1** consists of two singlets at $\delta = 115.92$ and 12.15 ppm corresponding to the C-atoms of Cp*. Similar chemical shifts for Cp* were observed for $\mathbf{1_D}$ in ^{1}H and ^{13}C NMR spectra. Significant changes of the ^{1}H NMR spectral features of **1** were not observed at variable temperature; however, the low solubility of **1** prohibited the recording of NMR spectra below 0 °C. Liquid injection field desorption ionization mass spectrometry (LIFDI-MS) of **1** confirmed the composition $[(Cp^*AlCu)_6)H_n]$, and the molecular ion (MI) peak at m/z 1355.6 ($n = 1$: MI-3H; calc: 1355.2) was observed with the expected isotopic pattern. Accordingly, the tetra-deuterated $\mathbf{1_D}$ was confirmed by ^{2}H NMR and LIFDI-MS analysis. Compound $\mathbf{1_D}$ exhibits a peak at $\delta = -1.63$ ppm in its ^{2}H NMR spectrum, while LIFDI-MS analysis shows the full molecular-ion peak for $[(Cp^*AlCu)_6D_4]$ at m/z 1362.9 (MI; calc: 1362.2). The IR spectrum of compound **1** shows ν(C-H) stretching modes typical of Cp* units at $\tilde{\nu} = 2941$, 2879, and 2831 cm^{-1}. The most intense absorption band is found at $\tilde{\nu} = 426$ cm^{-1}. The UV/Vis spectrum of **1** shows an absorption at $\lambda = 488$ nm in toluene that is attributed to the interband electronic transition of the cluster owing to the discrete energy levels.[11] Single crystals of **1** suitable for X-ray diffraction analysis were grown from saturated benzene solutions at room temperature. Unfortunately, in the crystal the entire cluster is disordered about a 2/m special position, which generates four disorder sites. Owing to this severe disorder, precise structural parameters of **1** cannot be deduced from the refinement of the crystal structure. Nevertheless, the quality of the data allows unambiguous confirmation of the core composition Cu_aAl_b ($a = b = 6$) and the overall molecular structure (that is, Al-coordination sites of the Cp*).[12] Crystal data and details of the structure determination are presented in the Supporting Information.

Compound **1** offers the perspective to investigate the stability and surface reactivity of the hydrogenated $M_{12}H_4$ core by treatment with various unsaturated organic functional groups. Isolation of specific compounds and/or intermediate species from such homogeneous reactions suggests indirect hints and conceptual understanding of chemical processes happening at the surface of catalytically active bimetallic nanoparticles/alloys in hydrogenation reactions.[1,13] In fact, **1** reacts well with small unsaturated organic molecules, such as R–C≡C–H (R = H, Ph) and PhCN. However, defined complexes have been isolated only in rare cases. For example, treatment of **1** with an excess of benzonitrile in benzene at room temperature over 24 h gives $[(Cp^*AlCu)_6H_3(N{=}CHPh)]$ (**2**) in quantitative yield as the 1:1 stoichiometric insertion product (Scheme 1). In analogy to the hydrometalation reactions of nitriles, for example, with $AlH_3{\cdot}NMe_3$,[14] the reaction apparently proceeds through the interaction of benzonitrile with one hydride at the $M_{12}H_4$ surface of **1** followed by the migration of the hydride to the nitrilic carbon. The ^{1}H NMR spectrum of compound **2** at room temperature in C_6D_6 displays four sharp singlets at $\delta = 1.83$, 1.93, 2.00, and 2.20 ppm with an integral ratio of 2:2:1:1, representing the four distinct AlCp* ligands. A very broad hydride peak was observed at around $\delta = -2.50$ ppm (rel. int. 3H; see the Supporting Information). Furthermore, the phenyl group shows a multiplet and a doublet centered at $\delta = 7.24$ and 8.06 ppm, whereas the aldimine carbon atom of the group PhC*H*=$N_{surface}$ exhibits a characteristic sharp singlet at $\delta = 7.70$ ppm. The ^{13}C NMR spectrum of **2** consists of the expected four singlets at $\delta = 12.07$, 12.11, 12.62, and 13.47 ppm corresponding to methyl carbons of the Cp* rings, whereas the cyclopentadienyl carbons show signals in the downfield region at $\delta = 116.00$, 116.02, 117.24, and 118.26 ppm. The ATR-IR spectrum of **2** shows vibrational bands characteristic of Cp* ($\tilde{\nu} = 2885$, 2824, 1414, and 1364 cm^{-1}) along with a weak symmetric stretching band for the –C=N functional group at $\tilde{\nu} = 1600$ cm^{-1}. No absorptions assigned to ν(Cu-H) or ν(Al-H) vibrational modes were observed in the IR spectra of **1** and **2**. Similar anomalies were also seen in compounds such as $[(R_3PCuH)_6]$ (R = Ph, NMe_2) and polymeric CuH.[15] The spectroscopic and analytical data are consistent with the proposed composition and structure of **2**, and the molecular structure was unambiguously determined by single-crystal X-ray diffraction analysis (Figure 1). Crystal data, the details of the structure determination, and selected bond lengths and angles are given in the Supporting Information, Table S1 and S2. Crystals of **2** suitable for X-ray diffraction analysis were grown from a saturated benzene solution, and **2** was isolated as a closely related derivative of **1**. As **2** does not show any disorder, the detailed structural discussion given below is justified and the results are transferable to **1**.

Compound **2** crystallizes in the triclinic space group $P\bar{1}$, along with three benzene molecules per asymmetric unit.[12] Compounds **1** and **2** consist of discrete $M_{12} = Cu_6Al_6$ units entrapped into a spherical capsule of six Cp* with a mean inner diameter of 9.85 Å. The Cu_6 core adopts a bicapped tetrahedral cluster structure and this unit is incarnated into an octahedral Al_6 shell. Interestingly, the arrangement of atoms in the M_{12} units can be correlated to the nested polyhedra of well-known intermetallic phases, such as Cu_9Al_4, $MgCu_2$ (the cubic Laves phase), Be_5Au, α-Mn (the χ-phase), which are all structurally closely related to Cu_5Zn_8 (γ-brass). The 26-atom

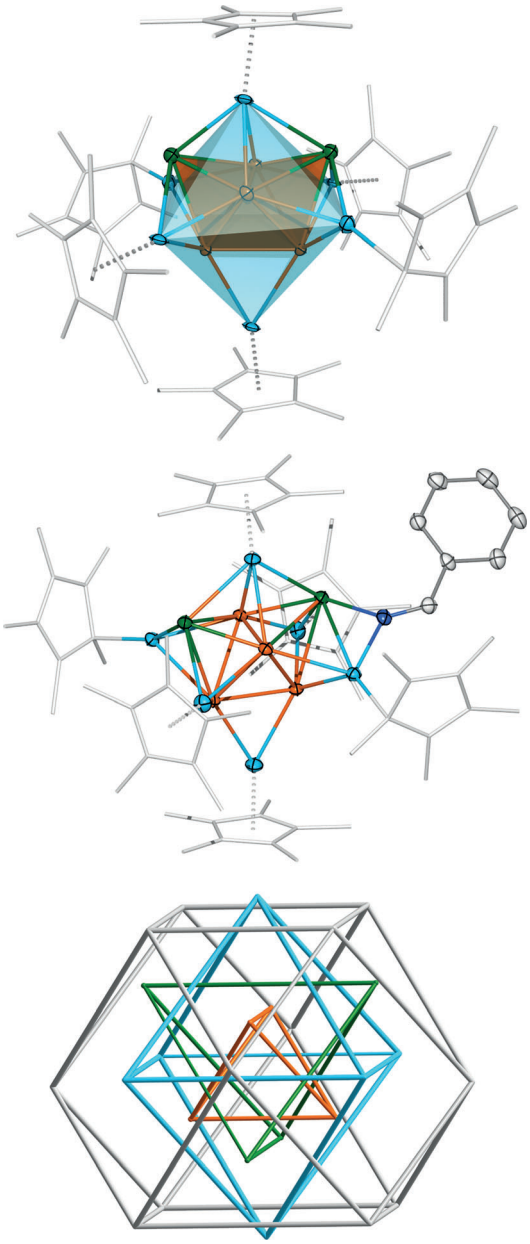

Figure 1. Top: Molecular structures of $[(Cp^*AlCu)_6H_4]$ (**1**) and $[(Cp^*AlCu)_6H_3(N{=}CHPh)]$ (**2**) (Cu orange, green; Al blue; N dark blue; C gray). Note that clusters **1** and **2** share the same Cu_6Al_6 core structure. H-atoms have been omitted for clarity, and ellipsoids are drawn at 30% probability. Atom numbering and selected bond lengths and angles are given in the Supporting Information. Bottom: Model of the 26-atom nested polyhedra of γ-brass Cu_5Zn_8 for comparison with the 12-atom nested polyhedra of **1** and **2**.

nested polyhedral clusters of γ-brass (Figure 1) consist of successive layers of an inner tetrahedron (*IT*, orange), an outer tetrahedron (*OT*, green), an octahedron (*OH*, pale blue), and a distorted cuboctahedron (*CO*, gray).[16] The polyhedron formed by combination of the tetrahedra *IT* and *OT* is also known as "stella-quadrangula". In Cu_5Zn_8, *OT* and *OH* are occupied by Cu atoms, while *IT* and *CO* represent Zn positions. In Cu_9Al_4 two types of individual clusters are found.[17] In one cluster only *IT* is occupied by Al atoms, while *OT*, *OH*, and *CO* represent Cu atoms, in the second cluster the Cu atoms are found in *IT*, *OT*, and *OH*, while *CO* is occupied by Al atoms. Most interestingly, the metal core structures of **1** and **2** are structurally closely related to the above described nested cluster structure of γ-brass (Figure 1). Cu(1), Cu(2), Cu(4), and Cu(5) (for **1**) and Cu(1), Cu(2), Cu(3), and Cu(5) atoms (for **2**) form *IT* (orange), while the remaining two Cu atoms (green) represent *OT* with two vacant vertices. While no *CO* shell is present in **1** and **2**, *OH* positions are occupied by Al atoms (blue) in both molecules (for detailed numbering of the atoms, see the Supporting Information).

The Cu–Cu distances in the *IT* of **2** vary from 2.4178(9) to 2.6022(8) Å with a mean value of 2.531 Å. The dihedral angle produced by the Cu(4) and Cu(6) atoms with the *IT* is 8.71° (Cu(4)-Cu(2)-Cu(5)-Cu-(6)). The capping Cu(4) and Cu(6) atoms make two successive long (2.6062(9) and 2.6210(8) for Cu(4), 2.6408(9) and 2.7027(9) for Cu(6)) and a short (2.3289(9) for Cu(4), 2.3419(9) for Cu(6)) bond to the *IT* vertices. All Cu–Cu distances are significantly shorter than the sum of the van der Waals radii (2.8 Å)[18] and are comparable with those found in the copper clusters stabilized by dichalcogenophosph(in)ato ligands ($[E_2P(OR)_2]^-$, $[E_2PR_2]^-$; E = S, Se).[19] The Cu_6 core exhibits the characteristic acute and obtuse angles ranging from 52.73(2)° to 66.70(3)° and 104.50(3)° to 112.67(3)°, respectively. The *OH* plane Al(1), Al(2), Al(3), and Al(6) is almost planar with an Al(1)-Al(2)-Al(3)-Al(6) dihedral angle of −9.38°. The distances between adjacent Al···Al atoms in the *OH* shell vary from 4.040 to 4.434 Å. In compound **2**, the Al–Cu distances vary from 2.4027(14) to 2.7189(14) Å, the shorter of which even falls below the shortest Cu–Al distance found in the Cu_9Al_4 phase (2.473(5) Å).

The Cp* ligands in **1** and **2** adopt η^1 as well as η^5 coordination modes. The geometry around the aldiminate nitrogen center that bridges the Al(1) and Cu(6) atoms is trigonal planar, with a sum of angles around the nitrogen close to 360°. Note that Cu(6) is one of the two more exposed Cu atoms (*OT*, marked in green, see Figure 1) of the nested Cu_6 unit of **1**. Also note the η^1 coordination of the Cp* attached to Al(1), which gives space for binding to the N-atom. The N(20)–Al(1) and N(20)–Cu(6) distances are 1.897(4) Å and 1.958(4) Å, respectively, while the Al(1)-N(20)-Cu(6) angle is 89.70(16)°. It should be noted that hydrides could not be localized and refined in either **1** or **2**. However, the presence of hydrides is unequivocally clear from the respective signals in the ^1H NMR spectra of both compounds.

The compounds **1** and **2** are the first examples for Hume–Rothery-type intermetallic molecular clusters approaching the limit for classification as "metalloid" M_nR_c ($n = 12$; $c = 10$; $c < n$). Hume–Rothery nanophases, for example, Fe_4Al_{13},[20] PdGa,[21] and NiGa,[22] attracted attention as selective semihydrogenation catalysts of alkynes to alkenes (active site isolation concept). These findings suggest inexpensive and abundant alternatives for established but rare and precious noble metal catalysts (for example, Pt,[23] Pd,[24] Ru,[25] Rh,[26] or Au[27]). The insertion of a nitrile into the M–H bonds of **1** leading to **2** in a clean reaction provides a first study case (molecular model) for surface reactions on hydrogenated

Hume–Rothery type intermetallic nanophases showing cooperative interaction of A and B sites. This opens a new perspective for gaining insight into reaction mechanisms and adsorbed intermediate species possibly present at the surfaces of such novel kind of heterogeneous mixed-metal catalysts. It should be noted that preliminary investigations point to the possibility of a thermally induced, controlled cluster growth using **1** as a precursor: in situ ^{1}H NMR spectroscopy shows gradual elimination of Cp*H on heating a [D$_8$]toluene solution of **1** to 110 °C over a period of 24 h (see the Supporting Information). Further investigations on the possible formation of larger clusters, presumably with an alloyed Al-Cu core are currently underway. Accordingly, we are extending the concept to other Hume–Rothery-type intermetallics, which have been shown to be useful in catalytic hydrogenation reactions.[20–22] The challenge for the synthesis of other metalloid clusters (for example, Al-Fe) related to **1** and **2** will be identifying the right transition metal (hydride) precursors for the A-component similar to [(Ph$_3$PCuH)$_6$] or [(NHC)AuH]. These studies are based on a profound knowledge on the coordination chemistry of low-valent Group 12/13 metal (B) species at transition-metal centers.[5] In particular, the Al-Fe compound [Fe(AlCp*)$_5$] is already known.[28] Thus, more examples of the general type [A$_a$B$_b$]R$_c$, and even larger clusters ($a+b \gg c$), may be discovered in the future.

Experimental Section

Synthesis of **1**: A mixture of [(Cp*Al)$_4$] (0.500 g, 0.77 mmol) and [(Ph$_3$PCuH)$_6$] (1.007 g, 0.51 mmol) was heated to 70 °C in benzene (7 mL) for 7 h with constant stirring. It was then cooled to room temperature, filtered, and the brown-black crystalline material was washed with a minimum amount of benzene (2 mL). Yield: 0.547 g (0.40 mmol, 78 %). Anal. calcd. for $C_{60}H_{94}Al_6Cu_6$: C 53.04, H 6.97, Al 11.92, Cu 28.06; found: C 53.14, H 6.48, Al 11.69, Cu 28.22 %. IR (neat): $\tilde{\nu}$ = 2941 (w), 2879 (m), 2831 (m), 2695 (w), 1466 (w), 1409 (m), 1361 (m), 1020 (w), 789 (w), 668 (m), 578 (w), 426 cm^{-1} (s). UV/Vis [(nm)]: λ_{max} = 488, 652. ^{1}H NMR (C$_6$D$_6$, 250 MHz): δ = 2.01 (s, 90 H, C$_5$(CH$_3$)$_5$), −2.86 ppm (br s, 4 H, hydride). ^{13}C NMR (C$_6$D$_6$, 63 MHz): δ = 12.15 (C$_5$*Me*$_5$), 115.92 ppm (*C*$_5$Me$_5$). MS (LIFDI, toluene): *m*/*z* 1355.64 (MI-3 H).

Synthesis of **1$_D$**: This was synthesized by a procedure similar to that of **1** using [(Cp*Al)$_4$] (0.148 g, 0.23 mmol) and [(Ph$_3$PCuD)$_6$] (0.300 g, 0.15 mmol) in benzene (3 mL). Yield: 0.145 g (0.106 mmol, 70 %). IR (neat): $\tilde{\nu}$ = 2941 (w), 2885 (m), 2827 (m), 2698 (w), 1462 (w), 1415 (m), 1363 (m), 1063 (w), 1016 (m), 787 (m), 668 (m), 580 (m), 440 cm^{-1} (s). ^{1}H NMR (C$_6$D$_6$, 250 MHz): δ = 2.01 ppm (s, 90 H, C$_5$(CH$_3$)$_5$). ^{2}H NMR (*n*-hexane, 38 MHz): δ = −1.63 ppm (s, 4D, deuteride). ^{13}C NMR (C$_6$D$_6$, 63 MHz): δ = 12.13 (C$_5$*Me*$_5$), 115.97 ppm (*C*$_5$Me$_5$). MS (LIFDI, toluene): *m*/*z* 1362.9 (MI$^+$).

Synthesis of **2**: A mixture of **1** (0.200 g, 0.15 mmol) and benzonitrile (0.091 g, 0.88 mmol) was stirred at room temperature in benzene (4 mL) for 24 h. It was then filtered and the brown crystalline material was washed with a minimum amount of benzene (1 mL) to give an analytically pure form of **2**. The combined filtrates were dried under reduced pressure to give an additional amount of pure **2**. Yield: 0.200 g (0.14 mmol, 93 %). Anal. calcd. for $C_{67}H_{99}NAl_6Cu_6$: C 55.05, H 6.83, N 0.96, Al 11.08, Cu 26.08; found: C 52.93, H 7.22, N 0.94, Al 10.89, C 25.73 %. IR (neat): $\tilde{\nu}$ = 2885 (m), 2824 (m), 1600 (w), 1414 (m), 1364 (m), 1188 (w), 1024 (w), 788 (w), 743 (m), 672 (m), 639 (m), 579 (m), 425 cm^{-1} (s). ^{1}H NMR (C$_6$D$_6$, 250 MHz): δ = 8.06 (m, 2 H, C$_6$*H*$_5$), 7.70 (s, 1 H, N = C*H*Ph), 7.29 (m, 3 H, C$_6$*H*$_5$), 2.20 (s, 30 H, C$_5$(C*H*$_3$)$_5$), 2.00 (s, 30 H, C$_5$(C*H*$_3$)$_5$), 1.93 (s, 15 H, C$_5$(C*H*$_3$)$_5$), 1.83 (s, 15 H, C$_5$(C*H*$_3$)$_5$), −2.50 ppm (br s, 3 H, hydride). ^{13}C NMR (C$_6$D$_6$, 63 MHz): δ = 12.07 (C$_5$*Me*$_5$), 12.11 (C$_5$*Me*$_5$), 12.62 (C$_5$*Me*$_5$), 13.47 (C$_5$*Me*$_5$), 116.00 (*C*$_5$Me$_5$), 116.02 (*C*$_5$Me$_5$), 117.24 (*C*$_5$Me$_5$), 118.26 (*C*$_5$Me$_5$), 128.92 (*C*$_6$H$_5$), 131.93 (*C*$_6$H$_5$), 137.68 (*C*$_6$H$_5$), 164.55 ppm (*C*$_6$H$_5$).

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[12] Crystal data for **1** and **2** were obtained at 113(2) K with an Oxford Supernova diffractometer and Cu-K_α radiation (λ = 1.54184 Å). **1**·C$_6$H$_6$: $C_{66}H_{100}Al_6Cu_6$; M_r = 1436.58; monoclinic; space group *I*2*m*; *Z* = 2; *a* = 12.7283(2), *b* = 18.1126(3), *c* = 15.2699(3) Å; β = 91.013(1)°; *V* = 3519.81(11) Å^3; $\rho_{calc.}$ = 1.355 mg m^{-1} m^3; μ = 2.963 mm^{-1}; *T* = 100(2) K; $2\theta_{max}$ = 148.50°; 54154 reflections measured of which 3686 were independent, R_{int} = 0.0697; The final values for *R*1 and *wR*2 were 0.0635 and 0.1613 [$I > 2\sigma(I)$]; Largest diff. peak/hole 0.794/−0.682 e Å^{-3}. **2**·**3**·C$_6$H$_6$: $C_{85}H_{117}NAl_6Cu_6$; M_r = 1695.92; triclinic; space group $P\bar{1}$; *Z* = 2; *a* = 13.6197(4), *b* = 13.7220(3), *c* = 22.7748(5) Å; α = 92.374(2), β = 94.753(2), γ = 95.926(2)°; *V* = 4213.70(18) Å^3; $\rho_{calc.}$ = 1.337 mg m^{-1} m^3; μ = 2.565 mm^{-1}; *T* = 100(2) K; $2\theta_{max}$ = 148.74°; 28897 reflections measured of which 28897 were independent, R_{int} = 0.0730; The final values for *R*1 and *wR*2 were 0.0635 and 0.1867 [$I > 2\sigma(I)$]; Largest diff. peak/hole 1.225/−0.939 e Å^{-3}.For both structures **1** and **2**, full-matrix least-

squares on F^2 was used as the refinement method. CCDC 985105 (**1**) and CCDC 985106 (**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.

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