Catch & Release of Al(I) at a Zinc Bis-Amide

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Abstract: [(HMDS)(Cp*)Al]₂Zn (1) is an intriguing trimetallic zinc aluminyl for which reactivity and quantum chemical studies remain elusive. Through a combined experimental and computational approach 1 is revisited showcasing its reversible formation and reaction chemistry. As revealed computationally, the compound is prone to eliminate and transfer monomeric [AICp*] - reminiscent of Schnöckels (AICp*)₄. Experimental validation is provided based on NMR studies which showcase the transfer of one and two equivalents of [AICp*] possible with suitable trapping reagents. Without trapping reagents and thermal treatment of 1, Cp* transfer, Al(HMDS) release and decomposition pathways are induced. Disclosing complementary reactivity, sequential insertion of carbodiimides into 1 vields a series of carbene complexes through one- and twofold insertions. All transformations are followed by state-of-the-art chemical calculations to understand the chemical bonding and bimetallic cooperation between the elements AI and Zn in-depth.

Introduction

The chemistry of Al(I)-derived heterometallic complexes including their synthesis, characterization and in-depth understanding through computational approaches has emerged significantly throughout the last years.^[1,2] Especially, aluminyl anions continuously serve as a platform for establishing heterobimetallic complexes and their bond activation chemistry.^[3,4] A landmark compound was published by Goicoechea and Aldridge, namely [(NON)AIK]₂ (NON = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tertbutyl-9,9-dimethyl-xanthene), which enabled the formation of [(NON)AIAuP^tBu₃] – a source of nucleophilic gold.^[5] The activation of various substrates proved bimetallic cooperation between both elements crucial for a range of chemical transformations attributable to metal-metal complementarity and tuneable activation pathways.^[6] In the realm of AI-based bimetallics, most investigated systems are installed in bimetallic [AI]-[M] fashion, and, their formation is due to the steric constraint of supporting ligand and/or salt metathesis routes in all cases irreversible. Lately, the field of heterometallic, low-valent aluminum complexes has further evolved and trimetallic species were characterized following a [AI]-[M]-[AI] motif.



Scheme 1: Known Al(I)-derived heterotrimetallic complexes, and the expansion as well as analogy to *Schnöckels* seminal Al(I) compound within this work.

[{(NON)AI}2Mg] (I)^[7] and K[{(NON)AI}2Cu] (II)^[8] were introduced by Aldridge and most recently, Lin & Yamashita introduced the first f-block metal complex including an X-type ligand, namely [Sm(THF)₄{AI(PDA)}₂]₂ (III) (PDA = N,N'-bis(2,6diisopropylphenyl)-1,3-propanediamide).^[9] The complexes I-III were all obtained via salt-metathesis and are hence irreversibly formed as well. Except computational efforts^[10] not much is known about the reversible formation of such or related heterometallic complexes including low-valent aluminum which is a general challenge due to the unfavourable, energetically costly reformation of an Al(I) precursor. Some homometallic versions which undergo reversible AI-AI bond formation processes are known but scarce. Most eminently, Schnöckel demonstrated that (AICp*)4 dissociates into a reactive monomer upon heating - upon gradually cooling down, however, AICp* tetramerizes back to (AICp*)₄.^[11] More elusive, Cowley, Krämer and co-workers demonstrate AI-AI bond formation processes with dialumenes species that possess a weak AI=AI double bond.[12] Upon dissolving, these compounds are (reversibly) cleaved into their respective monomers. Related to the formation of Al(I) centers from AI-AI bonds are Lewis-base induced disproportionation reactions. These were demonstrated by *Braunschweig* and coworkers which are again irreversible.^[13]

Following the recent interest in [AI]-[M] heterometallic (covalent) bonds,^[7,8,14–26] we have previously reported commodity amides for the design of Al-Zn bonds.^[27] This concept was noteworthy briefly employed by *R. Fischer* already in 2017. The group synthesized [(HMDS)Cp*AI]₂Zn (1)^[28] – a trimetallic compound including low-valent Al (and/or Zn) but had not employed for reactivity studies yet. Also, its nature was not yet discussed. In here, we demonstrate that this compound can astonishingly be formed fully reversible. Suitable transfer experiments, backed up by state-of-the-art quantum chemical calculations reveal **1** as an undiscovered heterometallic Al(I), namely [AICp*], source reminiscent of *Schnöckel's* homometallic (AICp*)₄. In other words, we reveal Zn(HMDS)₂ as a platform for the catch and release of low-valent aluminum.

Results and Discussion

Catch and Release of Al(I) at Zn(HMDS)₂: Theory and Experiment

Our initial efforts focused on to which extent **1** can be formed. Numerous NMR experiments for reaction of $(AlCp^*)_4$ with $Zn(HMDS)_2$ gave us a best yield for the formation of *in-situ* generated **1** of 83%. Low concentrations (c ~ 0.035 mmoL/mL), slight substoichiometric amounts of "AlCp*" and a temperature not exceeding 50°C were key (see ESI: section 4.1). Calculations at the DLPNO-CCSD(T)/def2-TZVPP//r²SCAN-3c level of theory with implicit solvation in benzene have been performed to illustrate the twofold insertion of monomeric AlCp* into Zn(HMDS)₂ (Scheme 2). Following a previous study of ours,^[27] AlCp* barrierlessly coordinates to Zn(HMDS)₂ to form adduct [Cp*Al-Zn(HMDS)₂] slightly endergonic (**IM1**; $\Delta G = +22 \text{ kJ} \cdot \text{mol}^{-1}$). The next step is the insertion into one of the Zn-N bonds *via* **TS1** (ΔG^{\neq} = +62 kJ mol⁻¹). The formation of bimetallic compound *pre-1* then yields –41 kJ mol⁻¹.



After coordination of a second equivalent of AICp* (IM2; $\Delta G = -5$ kJ mol⁻¹, ΔG^{\neq} = +36 kJ mol⁻¹) a second transition state follows (**TS2**; ΔG = +20 kJ mol⁻¹, ΔG^{\neq} = +61 kJ mol⁻¹). The formation of **1** is overall favoured by -51 kJ mol⁻¹. Notably, the formation of 1 compared to **pre-1** is only favoured by $\Delta \Delta_{\rm R} G = -10 \text{ kJ mol}^{-1}$. Hence, the barrier for the formation of 1 is almost the same for the back-reaction due to near thermo-neutrality. The provided thermodynamic picture thus predicts the formation of 1 via pre-1 to be fully reversible. Accordingly, 1 and pre-1 are in an equilibrium as the reaction is pushed to maximum consumption of (AICp*)₄. We emphasize that combining Zn(HMDS)₂ and (AICp*)₄ delivers a peculiar system as we could not obtain further compounds with [Al]-Zn-[Al] core when using various zinc bis amides (e.g. Zn(N(TMS)*t*Bu)₂, Zn(N(TMS)Dipp)2, $Zn(N(TMS)Mes)_2$ or also $Zn(TMP)_2$; TMS = SiMe₃). The DFTcalculated HOMO of 1 represents the sigma bonding between the two metal centers (Scheme 3: bottom; see also Figure S57 for intrinsic bond orbitals). The WBI (Wiberg bond index) shows values of 0.52 and 0.51. The LUMO represents a fully delocalized π-symmetric orbital across the Al-Zn-Al unit. Reaction chemistry is therefore overall expected to proceed through both Al-Zn bonds. We note that 1 has broad absorption in the purple-to-blue visible region and a maximum in the UV/VIS spectrum can be observed at around 395 nm. TD-DFT calculations revealed that the absorption can be attributed to HOMO→LUMO and HOMO→LUMO+1 transitions derived from different conformers (see 1 and e.g. 1^{twisted}; Scheme 3: bottom). Upon reaction of a freshly prepared, and instantly converted solution of 1 with initial reactant Zn(HMDS)₂, we noticed the rapid and quantitative formation of pre-1 which can also be visually followed by eye through fading of the yellow colour. ¹H NMR studies (see Figure S1) revealed that the single CH_3 resonance of 1 (0.31 ppm) splits into the two single resonances of pre-1 (0.23 and 0.29 ppm) as well as a shift of the CH₃ resonance of Cp* (2.07 ppm in 1 vs. 1.96 ppm in pre-1). The thermodynamic considerations (Figure 1 and Figure S62) in combination with this successful back-reaction to pre-1 can potentially identify 1 as a surrogate for monomeric AICp*. To investigate the plausibility of an AICp* transfer we performed control reactions to rule out the reaction proceeds solely through scrambling between 1 and Zn(HMDS)₂ via [(HMDS)(Cp*)Al]⁻ / [HMDS]⁻ exchange. We created a scenario that showcases the jump of monomeric AICp* from 1. For this purpose, Zn(N(TMS)^tBu)₂ was employed. First, we rationally synthesized [^tBu(TMS)N-ZnAI(Cp*)N(TMS)^tBu] (pre-1^{N-TMS-tBu}). The reaction of Zn(N(TMS)^tBu)₂ with 0.25 eq (AICp*)₄ leads to its selective formation as two sets of singlets for the ^tBu (1.37 and 1.28 ppm) and TMS (0.32 and 0.28 ppm) groups are observed in the ¹H NMR (see ESI for further characterization). Among *pre-1*, pre-1^{N-TMS-tBu} is indeed found in the ¹H NMR spectrum when trimetallic 1 is converted with Zn(N(TMS)^tBu)₂ (>35%; Figure S2 and Scheme 4: bottom). We also obtained suitable crystals of pre-1^{N-TMS-tBu} for SC-XRD (Scheme 4: middle). The Al-Zn atom distance of 2.3995(5) Å is among the shortest ones observed so far (see Table S1). With an angle of 178.19(4)°, the Al-Zn-N unit is near linear. As evident from disorder around the [N(TMS)^tBu] fragment, various isomers are observed in the crystal. Overall, the AICp* transfer from 1 proofs reasonable for this example.



Scheme 3: Closed synthetic cycle for the reversible formation of 1 (top left) and QTAIM analysis (top right) with the Laplacian distribution $\nabla^2 \rho(r)$ for **pre-1** and 1. Red dashed areas show regions of charge concentration ($\nabla^2 \rho(r) < 0$) and blue dashed areas are region of charge depletion ($\nabla^2 \rho(r) > 0$). Black spheres correspond to the bond critical points (BCP). QTAIM, NPA charges and WBI were calculated at the PBE1PBE/def2-TZVPP//r²SCAN-3c level of theory. Frontier orbitals and predicted UV Vis spectra (bottom) are depicted at the O3LYP D3/def2-TZVPP//r²SCAN-3c level of theory. Yields marked with * are NMR acquired against naphthalene as internal standard.



Scheme 4: Thermodynamic considerations for aluminylene and aluminyl transfer (top) and experimental findings (bottom) for reaction of **1** with two different zinc bis amides. Energies determined at the DLPNO-CCSD(T) CPCM(C_6H_6)/def2-TZVPP//r²SCAN-3c level of theory. Yields marked with * are NMR acquired against naphthalene as internal standard and refer to the maximum amount of "AICp*" transferable from **1**. Thermal ellipsoids in X-ray structure set at 50% probability level. For X-ray crystallographic details see ESI.

More pronounced, though, is the transfer of the whole [AI(Cp*)HMDS]⁻ unit. The bimetallic compound [^tBu(SiMe₃)N-ZnAl(Cp*)(HMDS)] can be unambiguously observed in the same ¹H NMR as well (>58%; Figure S2). Hence, we note that 1 operates as both, aluminylene and aluminyl transfer reagent here. This is most likely due to similar steric demand of the [HMDS]and [^tBu(SiMe₃)N]⁻ groups. A completely different picture is observed, when 1 is converted with bulkier Zn(TMP)₂. Bimetallic (*pre-*1[™]) [(TMP)ZnAI(Cp*)TMP] is selectively formed concomitantly with *pre-1*. The formation of bimetallic *pre-1*^{™P} can most indicatively be identified in the ¹H NMR through chemical shifts of the CH₃ resonances of TMP (1.36 and 1.27 ppm) and of Cp* (2.03 ppm) (see Figure S7).[27] Through the higher steric constraint, selective aluminylene transfer is initiated here. From a computational viewpoint all transformations can be rationalized (Scheme 4). As computationally determined, the reaction of 1 with Zn(HMDS)₂ yields -32 kJ mol⁻¹. Experimentally observed is the rapid and clean formation to two equivalents of pre-1 (Figure S62). Reaction of 1 with Zn(N(TMS)^tBu)₂ was experimentally shown to have two different outcomes. Calculations prove this possible as the two different transfer motifs (aluminyl vs. aluminylene) are only separated by $\Delta\Delta G = +6$ kJ mol⁻¹ in energy. A different picture is obtained in case of Zn(TMP)2. As can be seen here, the aluminyl transfer is disfavored by $\Delta\Delta G = +30 \text{ kJ mol}^{-1}$ compared to aluminylene transfer which is why there is only aluminylene transfer observed experimentally. The conversion of trimetallic 1 into various bimetallic species is illustrated. To showcase AICp* transfer is fully reversible, we employed a boron Lewis acid as a trapping reagent.^[29,30] Upon heating a solution of pre-1 and $B(C_6F_5)_3$, a new resonance appears in the ¹H NMR at 1.39 ppm, which is in perfect agreement with previously reported [(Cp*)Al- $B(C_6F_5)_3$] (2) (see ESI section 3.4 for NMR studies).^[30] Concomitantly, equimolar amounts of Zn(HMDS)₂ are formed as evidenced by a resonance appearing at 0.20 ppm. The integration nicely proves this assumption by a 15:36 ratio (Figure S10). Consumption of pre-1 was time-framed with ¹H NMR spectroscopy in 40 min. intervals (Figure S9). Conversion stagnates at around 160 min. Further NMR screening reveals slow decomposition into various unidentified species and formation of significant amounts of metallic precipitates. Nevertheless, the NMR yield of 2 is around 70% at the point of stagnation. Reacting pre-1^{N(TMS)/tBu} with B(C₆F₅)₃ leads to a similar result, the conversion is faster, though (see ESI section 3.5 for NMR studies). As computationally determined, the simple AICp* coordination towards B(C₆F₅)₃ affords -60 kJ mol⁻¹. Transfer of AICp* from **pre-1** onto $B(C_6F_5)_3$ in conjunction with the formation of Zn(HMDS)₂ yields –18 kJ mol⁻¹ (detailed view see Figure S63). Our results at this stage not only provide more insights into lowvalent heterobimetallics of Al and Zn, but also showcase their firsttime reversible formation.

On the Nature of AI/Zn Heterometallic Compounds

The experimental results motivated us to investigate the nature of the AlZn bonds in depth. Figure 1 depicts the Laplacian of the density on the Al-Zn-Al plane and additional descriptors derived from the topological analysis of the density according to the Quantum Theory of Atoms in Molecules (QTAIM) for **1** and *pre-1*.

After optimization, there are bond critical points (BCP), and bond paths detectable with both Zn-Al contacts. The values of the density and the Laplacian at the BCPs are consistent with covalent bonding interactions (Scheme 3). The BCPs are shifted towards the AI centres so that the basin of Zn is significantly larger than that of the AI. Consequently, the QTAIM partial charge on Zn is -0.57 while that of the AI centers is +1.89 (averaged). This result is somewhat surprising considering that the covalent radii of Zn and Al are very similar (118 pm vs 126 pm),^[31] also regarding their sum which is close to the Zn-Al distance in 1 (2.4482(6) Å [X-ray at 113K];^[28] 2.488 and 2.4539 [r²SCAN-3c]^[32]). However, the natural population analysis (see Scheme 3: right) reveals partial atomic charges of +0.78 for Zn and +0.98 for Al, much more in line with the covalent nature of the bond and with the small difference in electronegativity of Zn and Al (see Table S10). Partial atomic charges though only represent the average number of electrons and are not directly related to formal oxidation states (OS).[33] For that purpose, specific wavefunction analysis tools have been devised, such as the effective oxidation state (EOS)^[34] analysis, which relies on the so-called spinresolved effective fragment orbitals (EFOs)[35] and their occupations. The EFOs can be seen as the spin natural orbitals of a fragment (e.g. metal or ligand) within a molecular system. Oxidation states are obtained by sorting the EFOs by decreasing occupation number and assigning integer electrons (electron pairs in the case of restricted closed-shell species) to the most occupied EFOs. A reliability index (R) for the overall assignment is derived from the occupations of the frontier EFOs, i.e. the last occupied (LO) and the first unoccupied (FU) among all fragments (see eq 1). The closer R to 50% is, the more ambiguous the overall OS assignment is. An atom-in-molecule (AIM) definition is required to obtain the EFOs and their occupations. We have used both real-space QTAIM and TFVC (topological fuzzy Voronoi cells) and Hilbert-space NAO schemes. In all calculations, we defined each metal and each ligand as individual fragments. The results of EOS analysis for 1 are summarized in Table 1. According to EOS, all the ligands (i.e. each Cp* and HMDS) are clearly pictured with a -1 formal charge in all cases. The assigned OS of Zn, however, depends on the particular AIM used. With NAO, the method yields formal Zn (+2) and Al (+1), with a reliability of R(%)=63. Contrarily, using real-space schemes the assignment is Zn (-2) and Al(+3), with R(%)=61 and R(%)=55 for QTAIM and TFVC, respectively.

$$R(\%) = 100 \cdot \min\left(1, \max\left(0, \lambda_{LO}^{\sigma} - \lambda_{FU}^{\sigma} + \frac{1}{2}\right)\right) \quad \sigma = \alpha, \beta \quad (eq 1)$$

Table 1: Reliability index (R(%), partial charges (Q, in a.u.), oxidation states(OS), and occupation number of relevant EFOs from Hilbert-space (NAO) andreal-space (QTAIM and TFVC) analyses.

AIM	R(%)	Al (average)		Zn				
		Q	λ3s	OS	Q	λ4s	λ 4p	OS
NAO	63.1	+0.98	0.70	+1	+0.78	0.57	0.04	+2
			(occ)			(unocc)	(unocc)	
QTAIM	61.2	+1.89	0.34	+3	-0.57	0.71	0.46	-2
			(unocc)			(occ)	(occ)	
TFVC	54.6	+1.73	0.36	+3	-0.29	0.66	0.41	-2
			(unocc)			(occ)	(occ)	

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In all cases the reliability index is low, indicating a rather closecall situation typical of covalent systems.[36] The respective shapes of the most relevant frontier EFOs are depicted in Figure S58. They correspond, irrespective of the AIM used, to Zn's 4sand 4p- and Al's 3s-type orbitals, polarized by the molecular environment. With both QTAIM and TFVC, the occupation of the Zn's 4p-type EFO is larger than that of the 3s-type EFO of each of the AI centers, thus leading to a formal 3d¹⁰4s²4p² electron configuration for Zn, which appears unfeasible. In light of these rather unexpected results, we decided to extend our study to the pre-1,[27] bimetallic Al-Zn systems and bulkier [(NacNacMes)ZnAI(NON)].^[16] The topological analysis of the density for the former and the results of EOS analysis are shown in Figures S59 and S60 and Tables S10 and S11. The situation is very similar to trimetallic species 1. Again, the QTAIM descriptors indicate a covalent Zn-Al bond but the position of the corresponding BCP, which dictates the size of the atomic basins, leads to exaggerated partial charges, compared to those derived from NPA (+1.15 and +1.04 for AI and Zn, respectively). Consequently, NAO and QTAIM lead to different OS assignations for the metals. While NAO yields again Zn (+2) and Al (+1) with a quite high reliability index of 73%, with QTAIM the occupation of the 4s-type EFO of Zn is larger than the 3s-type EFO of Al, leading to the formal Zn (0) and Al (3+) picture with an even higher reliability index (R=94%). Such large deviations between NAO and QTAIM have also been recently discussed in rather simple systems like AeF⁻ with Ae = Be-Ba.^[37] In this case, the discrepancy is rooted in the fact that the (n)p AOs of the alkaline earth atoms are not properly weighted as valence orbitals in the NAO scheme. A similar situation was also reported for the set ENi(CO)3⁻ with E=Li-Cs,^[38] where using NBO3 or NBO7 produced totally different partial atomic charges due to the different treatment of the Ni's 4p shell in both implementations. Here, we also tested the NAOs from NBO3 (which includes the 4p shell of Zn as valence). The differences observed with the results obtained with NBO7 are minimal, indicating that the 4p orbitals of Zn should not play a significant role in these systems, contrary to what stems from QTAIM analyses. In this regard, we envision the trimetallic and bimetallic complexes 1 and pre-1 as an accessible Al (+1) (and Zn (+2) source), comparable to more sterically crowded aluminyl complexes.

Thermally Induced AI(I)-Release

1 was NMR spectroscopically screened upon prolonged heating without reaction partner. The investigations revealed a series of different compounds which can only form due to Al(I)-transfer which aligns with the calculations (*vide supra*). Heating of **1** rapidly forms a new species which shows a CH₃ resonance for a Cp^{*} moiety at 2.09 in the ¹H NMR. This resonance corresponds to a CH₃ unit of HMDS at 0.30 ppm. The ratio of Cp^{*}:HMDS is 1:2 (Figure S26). Thus, [(Cp^{*})Zn-Al(HMDS)₂] (**3**) can tentatively be assigned. Another species (2.11, 1.87 and 0.23 ppm; Figure S27) is found possessing a Cp^{*}:Cp^{*}:HMDS ratio of 1:1:1. A suitable structure representation is [(Cp^{*})Zn-Al(Cp^{*})(HMDS)] (**4**). This species could be crystallized in tiny amounts and the molecular structure was determined by SC-XRD (Scheme 5: bottom).



Scheme 5: Zinc templated Al(I) transfer and decomposition pathways upon thermal treatment of **1**. Thermal ellipsoids in X-ray structure set at 50% probability level. For crystallographic details see ESI.

We assume that species 3 and 4 can only form upon release (see 3) and catch (see 4) of AI(HMDS). Note that AI(HMDS) has recently been proposed by us to be crucial for the formation of a hexametallic copper aluminylene aluminyl.^[39] Keeping in mind that our initial quantum chemical calculations prove the release of AlCp* from 1 possible, a prolonged heating should increase the amount of AICp*. Indeed, this can be observed throughout the NMR screening due to an increase of the characteristic resonance of AICp* at 1.90 ppm (Figure S25). Hence, we propose pre-1 to be fleetingly formed as well. This species cannot be observed upon our NMR screenings though. As Al(HMDS) is expected to be exceptionally reactive, it will potentially swiftly insert into the Zn-N bond of pre-1. Upon simultaneous release of another equivalent of AI(I)HMDS and Cp* transfer 3 may eventually form. AI(HMDS) as a building block was first reported by Schnöckel upon reaction of LiHMDS with (AICp*)₄ which furnishes [(HMDS)AI(AICp*)₃] **(5)**.^[40] The NMR spectroscopic characterization of this compound revealed the CH₃ groups of Cp* at 1.93 ppm and those of HMDS at 0.42 ppm. Strikingly, this species can be obtained upon prolonged heating of 1 as well (Figure S28) which undoubtedly proves monomeric Al(HMDS) to be present in these solutions. Here, this species is captured by monomeric AICp* to form 5. Finally, we note that AI(III)HMDS is present in the ¹H NMR spectrum at 0.36 ppm^[41] which most likely forms through disproportionation of AI(I) precursors. Conveniently, these NMR studies substantiate the interpretation of 1 being an accessible AI (+1) source.

Sequential Insertion Reactions

It is a common feature for [AI]-[Zn] systems to insert heterocumulenes into their Al-Zn bonds.[16,27] Preferentially, zinc acts as a nucleophilic and aluminum as an electrophilic site. Similar reactivity can be observed for 1 which demonstrates how versatile this reagent is. Treating 1 with one equivalent of DIC diisopropylcarbodiimide) or DCC (DIC (DCC dicyclohexylcarbodiimide) rapidly yields insertion products. NMR spectroscopy reveals both, [(HMDS)(Cp*)AI{(NⁱPr)₂C}Zn-AI(HMDS)(Cp*)] (6a) and [(HMDS)(Cp*)Al{(NCy)₂C}Zn-AI(HMDS)(Cp*)] (6b). The formation of one-fold insertion product 6a, however, is accompanied with significant amounts of the double insertion product [(HMDS)(Cp*)Al{(NⁱPr)₂C}]₂Zn (7a), though. Whereas this neglects the isolation of 6a, things are different for 6b utilizing the bulkier substrate DCC. 6b could be isolated in 60% yield after a thorough workup. Both compounds reveal an exceptionally low-field shifted ¹³C{¹H} resonance for the R'NCNR' unit at 204.1 (6a) and 204.5 ppm (6b), respectively, yet compare well with previously reported metal complexes containing such carbene ligands.^[16,22-24,27] The presence of two adjacent metal-metal bonds enables the insertion of also a second equivalent of carbodiimide. This furnishes the respective bis-carbene complexes. 1 readily reacts with DIC to 7a whereas DCC yields [(HMDS)(Cp*)Al{(NCy)₂C}]₂Zn (7b). Crystal structure determination was possible for 7b (Scheme 6). The central Zn atom is almost perfectly linearly coordinated by the two carbene ligands (4C-Zn-C = 176.77(8)°). The Al-N-C-N mean planes spanned by the inserted carbodiimides are almost perpendicular to each other as the angle between the planes is 89.5° attributable to the steric constraint of the cyclohexyl groups. The Zn-C atom distances are with 1.957(2) and 1.966(2) slightly shorter than Zn-C distances found in various NHC-Zn(II) adducts (cf $[Zn(Cp^{Me4})_2(ItBu)]; d(Zn-C) = 2.062(2)Å).^{[42]}$ Through successful handling of mono-inserted product 6b, we converted an in-situ generated solution of 6b with one equivalent of DIC. This affords the the heteroleptic zinc complex $[(HMDS)(Cp^*)Al\{(NCy)_2C\}]Zn[Al\{(N'Pr)_2C\}(Cp^*)(HMDS)] (\textbf{7c}) as$ its TMS solvate in 49% yield after workup (see ESI). Different from 7a and 7b the compound possesses two indicative ¹³C{¹H} NMR resonances for the {(RN)₂C} units at 192.8 and 193.4 ppm, respectively. The power of covalent Al-Zn bonds could thus be used to also generate a heteroleptic zinc carbene complex. Little is known about the interplay of Al and Zn facilitating such insertions. We thus thoroughly studied the insertion mechanism of DIC into trimetallic 1 computationally. Calculations at the at the DLPNO-CCSD(T)/def2-TZVPP//r²SCAN-3c level of theory including an implicit solvation in benzene were performed (see Figure 1). The coordination of DIC proceeds endergonically with +57 kJ mol⁻¹ (IM3) and follows insertion into the Al-Zn bond via **TS3** (ΔG^{\neq} = +89 kJ mol⁻¹). The N-C-Al-Zn four-membered cycle **IM4** is obtained as a very labile intermediate ($\Delta G = +12 \text{ kJ mol}^{-1}$). Two possible pathways follow from hereon. Kinetically, the formation of species IM5 is slightly favored here (see TS4a (ΔG^{\neq} = +27 kJ mol⁻¹)). Notably, IM5 shows an alternative insertion mode of the carbodiimide that follows Al-nucleophilic and Znelectrophilic behavior. The reason why this product cannot be observed experimentally is probably its reversible formation

 $(\Delta G_{\rm IM5} = -64 \text{ kJ mol}^{-1}; \Delta G^{\pm}_{\rm IM5 \rightarrow IM4} = +91 \text{ kJ mol}^{-1}).$ *Thermodynamically*, ^{*cis*}**6a** ($\Delta G = -135 \text{ kJ mol}^{-1}$) is significantly favoured and drives the reaction to completion. The barrier to form this species *via* **TS4** ($\Delta G^{\pm} = 45 \text{ kJ mol}^{-1}$) is similarly low in energy. A final isomerization of ^{*cis*}**6a** occurs to give **6a** ($\Delta G = -146 \text{ kJ mol}^{-1}$). Our computationally explored ambiphilic coordination behavior of the carbodiimide aligns perfectly with the experimentally observations in related silver and copper complexes.^[23,24] An insertion of a second equivalent of DIC is similarly exergonic to also furnish **7a** ($\Delta G = -277 \text{ kJ mol}^{-1}$).



Scheme 6: Stepwise insertion of carbodiimides into the trimetallic zinc aluminyl **1** (top). Isolated, crystalline yields provided includes TMS solvation (see ESI). Molecular structure of **7b** in the crystal (bottom) with thermal ellipsoids set at 50% probability level.

Conclusion

To conclude, we have demonstrated the trimetallic zinc aluminyl **1** as a versatile reagent. It acts as a surrogate for monomeric AlCp^{*}, can be fully reversibly formed in the presence of suitable trapping reagents and sequentially inserts carbodiimides. State-of-the-art quantum chemical calculations proved the lability of **1** with respect to AlCp^{*}-loss as well as possibilities in AlCp^{*}-transfer and unveiled bimetallic cooperation upon insertion reactions. QTAIM analysis of **1** in combination with EOS assignments indicate that the Al/Zn bonds are highly covalent in nature, yet are best described as Al(I) and Zn(II). Even though **1** has been known for a couple of years, we point out that it is a first congener of a heterometallic AlCp^{*} source reminiscent of *Schnöckel's* homometallic (AlCp^{*})₄.



Figure 1: Computed energy pathway for the insertion of DIC into 1 according to the DLPNO-CCSD(T) CPCM(C₆H₆)/def2-TZVPP//r²SCAN-3c level of theory (bottom) including relevant transition states (top) and the optimized structure of kinetic product **IM5** (r²SCAN-3c). Depiction of bond lengths given in Å. The purple pathway indicates an alternative pathway to reversible formation of a kinetic product.

Supporting Information

The authors have cited additional references within the Supporting Information.^[43–76] For deposited X-ray data please see the reference section.^[77]

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Entry for the Table of Contents



The trimetallic zinc aluminyl $[(HMDS)(Cp^*)Al]_2Zn$ (1) is revisited. A combined experimental and computational approach was used to thoroughly characterize 1 which unlocked it to be a heterometallic Al(I) transfer reagent reminiscent of *Schnöckel's* (AlCp^{*})₄. The reversible formation of this system, reactivity studies, bimetallic cooperation and nature of its AlZn bonds are demonstrated.

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