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Bis(allyl)zinc Revisited: Sigma versus Pi Bonding of Allyl Coordination

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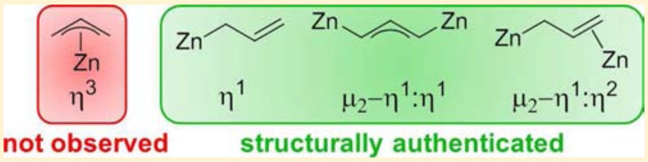
Supporting Information

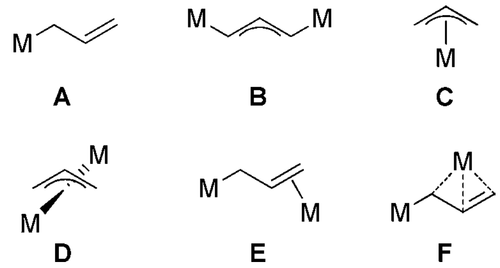
ABSTRACT: The reinvestigation of two allyl zinc compounds, parent bis(allyl)zinc $[Zn(C_3H_5)_2]$ (**1**) and 2-methallyl chloro zinc $[Zn(C_4H_7)Cl]$ (**2**), revealed two new coordination modes in the solid state for the allyl ligand, *viz cis-* and *trans-*μ_2-η^1:η^1. These results call for modification of the conventional interpretation of zinc−allyl interactions. Computational results indicate that the classical η^3-bonding mode of the allyl ligand is not favored in zinc compounds. A rare case of a zinc−olefin interaction in the dimer of $[Zn(\eta^1\text{-}C_3H_5)(OC(C_3H_5)Ph_2)]$ was found in the monoinsertion product of **1** with benzophenone.



1. INTRODUCTION

Understanding the interactions of delocalized π-electron systems with metal centers is of fundamental importance in organometallic chemistry.[1] The allyl group represents the simplest delocalized π-electron system, and allyl metal complexes are therefore ideal model systems. Six fundamentally different coordination modes of the allyl ligand have been structurally authenticated for main group and group 12 metals (**A**−**F**; Scheme 1).[2,3] Two of them show σ-type carbon metal interactions (**A**, **B**), two exhibit π-type carbon metal bonding (**C**, **D**), and two show possibly both types of carbon metal interactions (**E**, **F**). A precise discrimination is crucial for the understanding of the reactivity of such compounds. In palladium complexes, for instance, the allyl group reacts as a nucleophile when bonded in σ fashion (type **A**, **B**) but as an electrophile when bonded in π fashion (type **C**; Scheme 1).[1f−h,4,5] Recently, interactions of divalent, electropositive metals with allyl ligands have attracted some attention.[2b,c,f,6] For alkaline earth metal compounds, each element favors either σ-type interactions (Be, Mg) or π-type interactions (Ca, Sr, Ba).[7] In contrast, allyl zinc complexes have been reported to show a broader scope of coordination modes with examples of purely σ-type bonding (**A**), π-type bonding (**C**), as well as σ and possible π-type bonding (**E**).[8] We report here our findings on allyl zinc compounds, which disagree with earlier interpretations of experimental data. Our data suggest that purely π-type interactions in allyl zinc complexes are not favored. Rather, two σ-type bonding modes of allyl ligands, *cis*-**B** and *trans*-**B**, have been found as new bonding modes for the Lewis acidic divalent zinc centers.

Scheme 1. Coordination Modes of the Allyl Ligand Involving Carbon Metal Interactions of σ-Type (A: η^1; B: μ_2-η^1:η^1 (*cis* and *trans* Isomer Possible)), π-Type (C: η^3; D: μ_2-η^3:η^3), or σ- and Possibly π-Type (E: μ_2-η^1:η^2; F: μ_2-η^1:η^3)



2. RESULTS AND DISCUSSION

The parent allyl zinc compound, bis(allyl)zinc (**1**), was first reported in 1965[9a] and has been used as a nucleophilic allyl transfer reagent ever since.[10] Its properties and dynamics in solution were studied by Lehmkuhl and co-workers.[9] The allyl ligands in **1** are bonded to the metal center in an η^1 fashion in donor solvents at low temperature, but they exhibit fluxional behavior in solution at ambient temperature. On the basis of solid state CP MAS ^{13}C NMR measurements, it was suggested that **1** shows η^3 bound allyl ligands exclusively, i.e. π-type carbon−metal interactions (**C**, Scheme 1).[8c] However, the detailed solid state structure of **1** remained unknown for almost 50 years.

We obtained results from a single crystal X-ray analysis of **1** (Figure 1) which contradict the above-mentioned interpretation of solid state NMR data. Compound **1** crystallizes in the tetragonal space group $I4_1/a$ with $Z = 4$ and an asymmetric unit consisting of only three non-hydrogen atoms. The zinc atom occupies a special position of symmetry −4 with a tetrahedral coordination geometry ($C1{-}Zn1{-}C1'^{(\prime)}$, 103.86(12)° and 112.35(6)°). All Zn−C distances of 2.171(2) Å are equivalent by symmetry. They are elongated compared to corresponding values in zinc complexes with η^1 bonded allylic ligands (1.969(8)−2.031(12) Å).[8a,b] The elongated Zn−C bonds in **1** may also correlate with weaker intermolecular bonds, affecting the volatility of this compound: the 3D polymer **1** can be sublimed at 5×10^{-2} mbar and temperatures as low as 35 °C (see Experimental Section).[9a,c] Significant bonding

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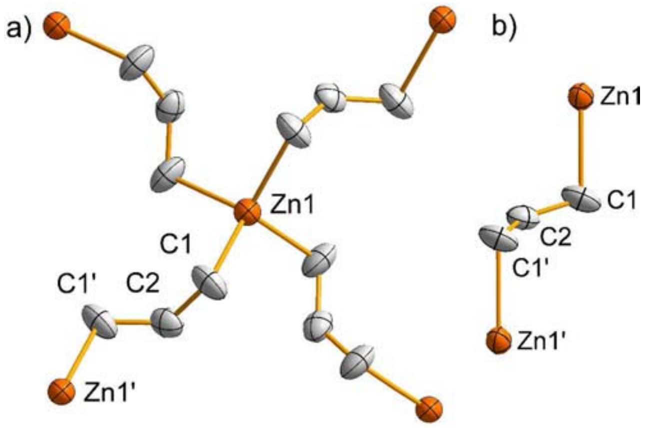


Figure 1. Cut-out of the solid state structure of bis(allyl)zinc (**1**): (a) three-dimensional network of **1**; (b) *trans* μ_2-η^1:η^1 coordination mode of the allyl ligand. Displacement ellipsoids are shown at the 50% probability level. Both symmetrically independent carbon atoms of the ligand occupy general positions; this implies 2-fold disorder for C2. Only one of the two split positions for C2 is shown. Hydrogen atoms are omitted for clarity. Bond lengths (Å) and angles (deg): Zn1−C1, 2.171(2); C1−C2, 1.423(4); C2−C1′, 1.333(5); C1−Zn1−C1′, 103.86(12); C1−Zn1−C1″, 112.36(8); C1−C2−C1′, 130.6(3). Primed atoms are related by symmetry code [$^3/_2 - x$, $^3/_2 - y$, $^1/_2 - z$].

interactions between Zn1 and C2 were ruled out.[11] Thus, the allyl ligands of **1** bind to the metal centers in a bridging *trans* μ_2-η^1:η^1 fashion (**B**, Scheme 1; Figure 1b), resulting in a three-dimensional network.[12] This is the first example of an allyl zinc compound showing a type **B** coordination mode.[13] In contrast to earlier interpretations, the metal−carbon bonds in **1** in the solid state are purely σ in nature without any significant π-type contributions.

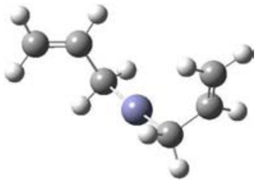


Figure 2. Structure of bis(η^1-allyl)zinc optimized at the MP2/aug-cc-pVDZ level of theory.

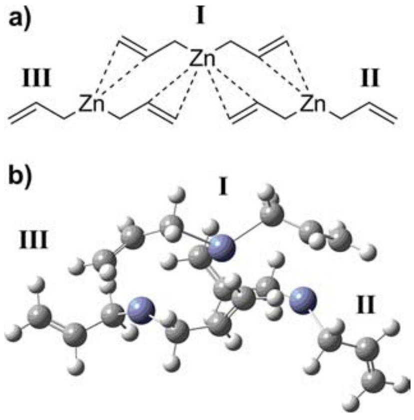


Figure 3. Lewis drawing (a) and calculated structure (b) of the bis(η^1-allyl)zinc trimer optimized at the MP2/aug-cc-pVDZ level of theory.

To further explore the nature of zinc−allyl interactions, quantum-chemical *ab initio* calculations were performed on two model systems: (a) monomeric bis(allyl)zinc (Figure 2) and (b) a cluster of three monomers (Figure 3). The structure of bis(allyl)zinc obtained at the MP2/aug-cc-pVDZ level of theory exhibits two η^1 bonded allyl ligands (Figure 2). The optimized structure has an approximate C_2-symmetry with a Zn−C bond length of 1.958 Å, which falls into the range of the corresponding values obtained for dialkylzinc compounds by rotational spectroscopy[14] and electron diffraction (1.930(2)−1.974(3) Å).[15] The C−Zn−C angle amounts to 175.7°, and an NBO analysis shows that the Zn atom binds to the alkyl groups via sp-type hybrids. The average distances between the zinc atom and the doubly bonded carbon atoms are 2.806 and 3.707 Å, respectively. According to the NBO analysis, there are no bonding interactions between the allyl π-bonds and the metal atom. Moreover, within the framework of the NBO analysis, neither the metal 3d-like orbitals nor those of higher principal quantum number contribute significantly to the Zn−C σ-bonds in bis(η^1-allyl)zinc. The metal−carbon bonds are strongly polarized toward the carbon atom (≈85%) and involve almost exclusively the 2s- and 2p-orbitals of carbon and the 4s- and 4p-orbitals of the zinc atom. This is different from the case for bis(allyl)nickel, where the partly filled 3d-valence orbitals participate to a significant degree in metal−carbon bonding, resulting in an η^3-coordination of the metal atom.[16] Both the first and the second steps of the formation of bis(η^1-allyl)zinc from Zn^{2+} and two allyl anions are highly exergonic. Addition of the first allyl anion to Zn^{2+} is associated with a reaction energy of −444.7 kcal·mol^{-1}, while addition of the second allyl anion yields further −206.3 kcal·mol^{-1} (MP2/aug-cc-pVDZ). The trimer of bis(allyl)zinc was chosen as a model system to study the intermolecular interactions between bis(allyl)zinc units. In contrast to the high reaction energies mentioned above, trimerization results in a reaction energy of only −42.3 kcal·mol^{-1} (MP2/aug-cc-pVDZ), corresponding to −14.1 kcal·mol^{-1} per molecular unit (Figure 3). Intramolecular zinc−allyl interactions in the trimer are purely σ in nature. Intermolecular interactions are realized by coordination of the olefinic moieties of the allyl ligands to zinc centers of the neighboring $[Zn(C_3H_5)_2]$ molecules. The trimer shows two different types of bis(allyl)zinc units (**I** vs **II** and **III**; cf. Figure 3). In addition to the two intramolecular Zn−C σ bonds, the zinc atom in **I** undergoes intermolecular interactions with two C═C units (belonging to the allyl ligands of **II** and **III**). It adopts a distorted tetrahedral coordination geometry with angles around Zn(I) ranging from 99.6° to 122.6°. The zinc atoms in **II** and **III** show only one intermolecular interaction each: they are coordinated by the olefinic functionalities of the allyl ligands in **I**. A strongly distorted trigonal planar coordination geometry was assigned to Zn(**II**) and Zn(**III**) (angle sums around Zn: 358°).[17] Covalent Zn−C bonds in the trimer are elongated compared to corresponding bonds in monomeric bis(allyl)zinc. This effect is more pronounced for allyl ligands that are involved in intermolecular interactions (2.006−2.057 Å) than for "dangling" allyl ligands (1.985 Å, 1.990 Å). Accordingly, C═C bonds which coordinate to zinc centers are elongated compared to noncoordinating olefinic groups (1.375 Å vs 1.358 Å). Zn−C^{olefin} bond lengths range from 2.393 Å to 2.591 Å. As in the case of the monomer (Figure 2), Zn−C σ-bonding is accomplished by approximate *sp* hybrids. These bonds are strongly polarized to the carbon atoms (~89%), with average natural charges of about −1.0 at the carbons and +1.3 at the metal atoms. The second order interaction energies between the bonding orbitals of the allylic C=C bonds and lone pair type orbitals at the metal atom (Lp*) range from −36.3 kcal·mol^{-1} (Zn(I)···C=C(II,III)) to −27.0 kcal·mol^{-1} (Zn(II)···C=C(I)). In contrast, interactions of the antibonding MOs of these C=C bonds and occupied metal orbitals can be neglected; that is, there is no significant d(Zn) → π^*(C=C) back-donation.

Our computational results concur with the experimental findings mentioned above in that Zn−C σ-bonding is energetically strongly favored over Zn···C π-bonding. η^2-Coordination of the metal atom to the localized double bonds of the allyl ligands was observed as a secondary effect. Further calculations at the HF level were carried out for model compounds involving coordination modes such as **C** and **D** (cf. Scheme 1). The results of these calculations are not discussed here in detail, but suffice it to mention that the model compounds collapse to structures featured by Zn−C σ-bonding when all structural constraints are lifted in the optimization process (see Experimental Section).

Apart from bis(allyl)zinc (**1**), (2-methylallyl)zinc chloride (**2**) has also previously been studied by solid state CP MAS ^{13}C NMR analysis. On the basis of this data, **2** was reported to exhibit an η^3-bonding mode in the solid state.[8c] In light of our new data on **1**, we set out to reinvestigate the solid state structure of **2**. Single crystal X-ray analysis revealed that **2** crystallizes in the monoclinic space group $C2/c$ with Z = 4. It arranges as a cyclic hexamer in the solid state with one formula unit of **2** corresponding to a monomeric unit (Figure 4).[18] Monomeric units form six membered rings which adopt slightly distorted chair conformations and are linked via zinc atoms in a spiro fashion. The six zinc atoms of a hexamer are located in one plane (largest deviation: 0.0998(2) Å). The chlorine atoms are found on top of and below this plane in an alternating manner. The same holds for the methyl groups of the 2-methylallyl ligands. The zinc atoms in **2** show a slightly distorted tetrahedral coordination geometry, each interacting with two chlorine and two allyl ligands (C/Cl−Zn−C/Cl, 104.11(2)−117.66(8)°). Each chlorine atom and each 2-methylallyl ligand bridge two zinc centers. Notably, the 2-methylallyl ligand adopts a *cis* μ_2-η^1:η^1 coordination mode. This is the first example of an allyl zinc complex showing a type **B** bonding mode of *cis* configuration. Thus, as in the case of bis(allyl)zinc (**1**), Zn−C interactions in compound **2** are also exclusively of σ-type. Taken together, the results obtained for **1** and **2** represent a rare case of two closely related compounds to exhibit a *cis* and a *trans* configuration of a type **B** coordination mode.[19] The Zn−C bond lengths in **2** are all very similar, ranging from 2.071(2) Å to 2.143(2) Å, which is slightly longer than the corresponding values reported for zinc compounds with allylic ligands in η^1-coordination modes.[8a,b] C−C distances in the allylic part of the 2-methylallyl ligand (1.380(3)−1.421(3) Å) are between those expected for C−C single and double bonds. All these parameters are in good agreement with the μ_2-η^1:η^1-coordination mode.

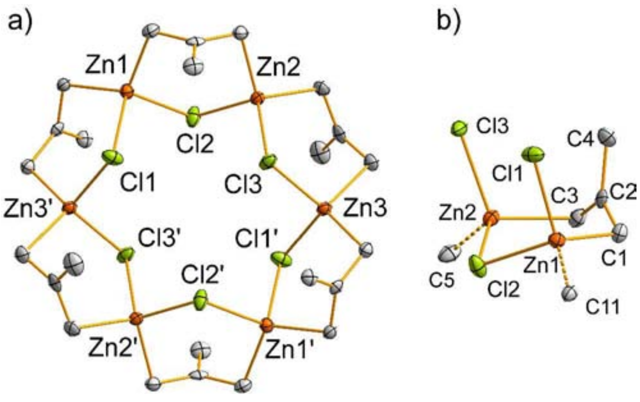


Figure 4. Molecular structure of (2-methylallyl)zinc chloride (**2**): (a) top view on cyclic hexameric arrangement; (b) side view on monomeric unit. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and a molecule of Et_2O which is found per hexamer and does not interact with **2** are omitted for clarity. Three monomeric units of **2** are crystallographically independent. Selected bond lengths (Å) and angles (deg): Zn1−C1, 2.071(2); Zn1−C11, 2.103(2); Zn2−C3, 2.141(2); Zn2−C5, 2.071(2); Zn1−Cl2, 2.3597(5); Zn2−Cl2, 2.3127(6); C1−C2, 1.419(3); C2−C3, 1.381(3); C2−C4, 1.507(3); C1−C2−C3, 124.3(2). Primed atoms are related by symmetry code [−x, −y, −z].

In retrospect, earlier misinterpretations regarding the coordination modes in **1** and **2** in the solid state can be rationalized, as the formerly postulated η^3 and the newly detected μ_2-η^1:η^1 bonding mode are indistinguishable by means of solid state CP MAS ^{13}C NMR analysis.[20]

Reaction of bis(allyl)zinc (**1**) with 1 equiv of benzophenone led to the selective formation of the monoinsertion product $[Zn(C_3H_5)(OC(C_3H_5)Ph_2)]$ (**3**). Allyl alkoxide **3** offers the possibility to investigate the bonding mode of the allyl ligand at a zinc center in the presence of an anionic ligand with olefin and aryl groups as additional donors. NMR spectroscopic analysis of THF solutions of **3** revealed an η^1-coordination of the allyl ligand at ambient temperature. In contrast, allyl ligands without substituents in the α- and γ-positions usually show fluxional behavior in solution at ambient temperature, when bonded to zinc centers, as shown for **1**, $[Zn(CH_2C(CH_3)CH_2)_2]$,[9d] and **2** (see the Experimental Section). In compound **3**, the bulky, strong σ-donor $(OC(C_3H_5)Ph_2)^-$ significantly slows down the dynamic process which the allyl ligands undergo in solution. The solid state structure of compound **3** was investigated by means of single crystal X-ray analysis. **3** crystallizes in the monoclinic space group $C2/c$ with Z = 4. It arranges as a dimer in the solid state with two Zn and two O atoms forming an essentially planar, rhomboidal unit (Figure 5). This arrangement causes severe distortions of the tetrahedral coordination geometry around the Zn centers (C/O−Zn1−C/O, 82.2(7)−135.2(1)°). The allyl ligand in **3** exhibits localized C−C bonds and coordinates to the zinc center in an η^1 fashion. The Zn1−C1 distance compares well to corresponding values in other zinc complexes bearing η^1 bound allylic ligands.[8a,b] The most important point concerning the molecular structure of **3** centers around the question which ligand occupies the fourth coordination site of the zinc atom. Hypothetically, an η^3-bonding mode of the allyl ligand would have increased the coordination number of the zinc center to four. However, coordination of the olefinic moiety of the $(OC(C_3H_5)Ph_2)^-$ ligand is realized instead. This is only the second structurally authenticated example of a zinc atom interacting with a nonconjugated C=C double bond.[21] In compound **3**, a rare case of a Zn−C$^{\text{olefin}}$ interaction is preferred over an η^3-coordination mode of the allyl ligand to increase the coordination number of the metal center to four. Zn−C$^{\text{olefin}}$ distances of 2.619(4) Å and 2.741(4) Å are found in **3**, which compares well to values in $[Zn(C(Me)=CH_2)_2]_\infty$.[22]

Coordination modes of the allyl ligand in organozinc compounds may be compared to those in the related allyl

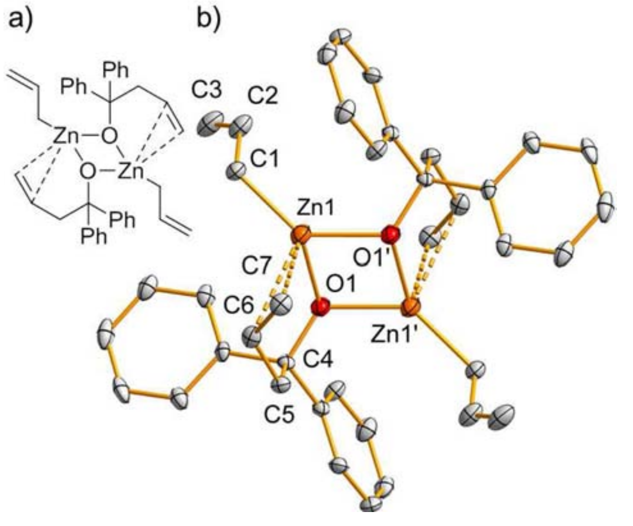
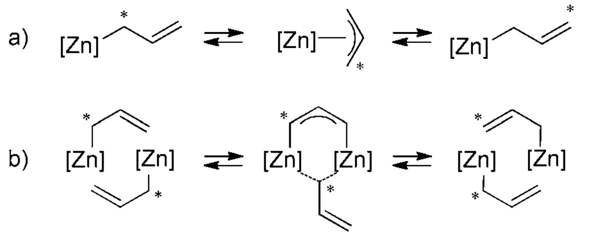


Figure 5. Lewis drawing (a) and molecular structure (b) of the dimer of [Zn(η^1-C_3H_5)(OC(C_3H_5)Ph_2)] (**3**). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1−C1, 1.976(4); Zn1−C6, 2.741(4); Zn1−C7, 2.619(4); Zn1−O1, 1.975(2); C1−C2, 1.485(7); C2−C3, 1.280(8); C4−O1, 1.429(5); C4−C5, 1.544(6); C5−C6, 1.502(6); C6−C7, 1.325(6); C1−Zn1−center-(C6−C7), 107.0(1); C1−Zn1−O1, 134.9(1); C1−Zn1−O1′, 135.2(1); center(C6−C7)−Zn1−O1, 82.2(7); center(C6−C7)−Zn1−O1′, 101.0(8); O1−Zn1−O1′, 82.7(1); Zn1−O1−Zn1′, 97.3(1); C1−C2−C3, 129.9(5); C5−C6−C7, 124.9(4). Primed atoms are related by symmetry code [−*x*, −*y*, −*z*].

compounds [KR], [CaR_2], [ScR_2]$^+$, and [GaR_2]$^+$ (R = $(C_3H_5)^-$, $(C_3H_3(SiMe_3)_2)^-$). For such compounds containing group 1−3 metals, η^3 bound allyl groups are found predominantly.[6d,e,f,23] In contrast, no η^3-coordination of the allyl ligand to a zinc or a gallium center has been structurally authenticated to date.[24] These differences are most likely due to a significant stabilization of the η^3-bonding mode of the allyl ligand by $\pi^{\text{allyl}} \rightarrow d^{\text{metal}}$ interactions and the strongly electropositive nature of group 1−3 metals.

The insights we gained from the coordination chemistry of allyl zinc compounds also contribute to a better description of the dynamic solution behavior of these complexes. The allyl ligands of allylzinc (halide) compounds undergo rapid exchange in solution at ambient temperature. An intramolecular mechanism involving an η^3 bonded allyl ligand and an intermolecular mechanism without allyl ligands in an η^3-coordination mode has been discussed in the literature for this exchange (Scheme 2).[8c,9f] Although an intramolecular reaction can be expected to proceed faster, kinetic studies revealed an intermolecular mechanism for the allyl exchange of [Zn(C_3H_5)$_2$] (**1**) in THF.[9f] Our results now offer an explanation for these experimental observations: as the η^3-coordination mode of the allyl ligand should be disfavored in allylzinc compounds, the allyl exchange probably proceeds in an intermolecular fashion. For this type of exchange process, we suggest a transition state involving a μ_2-η^1:η^1-coordination mode resembling the solid state structure of **1**. A transition state with two (μ_2-η^1:η^1-C_3H_5)$^-$ groups would be symmetry forbidden.[25]

Scheme 2. (a) Intramolecular Allyl Exchange Mechanism via the η^3 Transition State; (b) Intermolecular Allyl Exchange Mechanism via the μ_2-η^1:η^1 Transition State



3. CONCLUSION

Allyl zinc compounds exhibit zinc−allyl bonding modes with σ-type contributions in the solid state, in solution, and in the gas phase. Notably, no indications for π-type zinc−allyl interactions have been detected. Instead, two new bonding modes of the allyl ligand in the coordination chemistry of zinc (*cis* and *trans* μ_2-η^1:η^1) have been authenticated. This suggests modifications of earlier interpretations[8c,9f] and revises the conventional picture of interactions of zinc centers with small π-electron systems. Our results could contribute to the understanding of the differences in reactivity, chemoselectivity, and stereoselectivity between allyl zinc compounds and allylation reagents based on other Lewis-acidic metals such as Li, Mg, Al, or Cu.

4. EXPERIMENTAL SECTION

General Considerations. All operations were carried out under argon using standard Schlenk-line and glovebox techniques. Starting materials were purchased from ABCR Chemicals or Sigma Aldrich and purified following standard laboratory procedures. Nondeuterated solvents were purified using an MB SPS-800 solvent purification system. THF-d_8 was distilled from sodium benzophenone ketyl. All NMR spectra were recorded at ambient temperature using a Bruker Avance II 400 MHz spectrometer. The chemical shifts of ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and are reported relative to the chemical shift of tetramethylsilane. The resonances in ^{1}H and ^{13}C NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HMQC, HMBC).

[Zn(η^1-C_3H_5)$_2$] (1). **1** can be prepared according to the literature[9a,c] or following an alternative route: $ZnBr_2$ (1.380 g, 6.13 mmol) was suspended in diethyl ether (20 mL). Allyl potassium (982 mg, 12.25 mmol) was slowly added at ambient temperature to give a suspension. The liquid phase was separated by centrifugation and decantation after 30 min. The residue was extracted with diethyl ether (20 mL). All volatiles were removed from the combined liquid phases under reduced pressure to give a yellow solid which was dried in vacuo for 3.5 h. Yield: 774 mg (525 mmol), 86%. NMR data was consistent with the literature. Anal. Calcd for $C_6H_{10}Zn$ (147.55 g/mol): Zn, 44.33. Found: Zn, 44.06. A test for halides was negative. The crude product can be further purified by sublimation. Single crystals were obtained by sublimation at 35 °C under a dynamic vacuum of 5×10^{-2} mbar.

[Zn(C_4H_7)Cl(Et_2O)$_{0.3}$]·2(Et_2O)$_{0.3}$. The compound was synthesized following a procedure slightly modified from that in the literature.[9f] No analytical data for **2** was reported in the literature. A solution of Zn($CH_2C(CH_3)CH_2$)$_2$ (131 mg, 0.75 mmol) in diethyl ether (1.0 mL) was added to a solution of $ZnCl_2$ (102 mg, 0.75 mmol) in diethyl ether (2.0 mL). All volatiles were removed from the reaction mixture under reduced pressure to give a pale yellow solid which was washed with pentane (3 × 1 mL) and dried in vacuo. Substoichiometric amounts of diethyl ether could not be removed by recrystallization or prolonged drying in vacuo.[26] Yield: 240 mg (0.60 mmol), 81%. Single crystals were obtained by cooling a saturated solution of **2** in diethyl ether/pentane (1:1) to −30 °C.

^{1}H NMR (400.1 MHz, THF-d_8). δ = 1.11 (t, $^3J_{\text{HH}}$ = 7.0 Hz, 0.3 × 6H, O($CH_2$$CH_3$)$_2$), 1.71 (s, 3H, $CH_2C(CH_3)CH_2$), 2.71 (br s, 4H, $CH_2C(CH_3)CH_2$), 3.38 (q, $^3J_{\text{HH}}$ = 7.0 Hz, 0.3 × 4H, O(CH_2CH_3)$_2$)

ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 15.79 (s, $O(CH_2CH_3)_2$), 26.41 (s, $CH_2C(CH_3)CH_2$), 66.42 (s, $O(CH_2CH_3)_2$), 116.20 (br s, $CH_2C(CH_3)CH_2$), 152.46 (s, $CH_2C(CH_3)CH_2$) ppm. Anal. Calcd for $C_4H_7OClZn\cdot(C_4H_{10}O)_{0.3}$ (178.17 g/mol): Zn, 36.70. Found: Zn, 36.75.

[Zn(C_3H_5)(OC(C_3H_5)Ph_2)] (3). A solution of benzophenone (32 mg, 0.18 mmol) in diethyl ether (1 mL) was added to a solution of **1** (26 mg, 0.18 mmol) in diethyl ether (1 mL). All volatiles were removed from the reaction mixture under reduced pressure to give a colorless solid which was washed with pentane (2 × 1 mL) and dried in vacuo. Yield: 48 mg (0.15 mmol), 83%. Single crystals were obtained by cooling a saturated solution of **3** in diethyl ether/pentane (1:1) to −30 °C.

^{1}H NMR (400.1 MHz, THF-d_8). δ = 0.72 (d, $^3J_{HH}$ = 8.8 Hz, 2H, $Zn{-}C\mathit{H}_2{-}CH{=}CH_2$), 3.15 (d, $^3J_{HH}$ = 7.1 Hz, 2H, $C{-}C\mathit{H}_2{-}CH{=}CH_2$), 4.11 (dd, $^2J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 9.8 Hz, 1H, $Zn{-}CH_2{-}CH{=}C\mathit{H}^{cis}H^{trans}$), 4.23 (ddm, $^2J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 16.8 Hz, 1H, $Zn{-}CH_2{-}CH{=}CH^{cis}\mathit{H}^{trans}$), 4.92 (dm, $^3J_{HH}$ = 17.0 Hz, 1H, $C{-}CH_2{-}CH{=}CH^{cis}\mathit{H}^{trans}$), 4.95 (dm, $^3J_{HH}$ = 17.0 Hz, 1H, $C{-}CH_2{-}CH{=}C\mathit{H}^{cis}H^{trans}$), 5.50 (ddt, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 9.8 Hz, $^3J_{HH}$ = 16.8 Hz, 1H, $Zn{-}CH_2{-}C\mathit{H}{=}CH_2$), 5.67 (ddt, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 17.0 Hz, 1H, $C{-}CH_2{-}C\mathit{H}{=}CH_2$), 7.14 (tm, $^3J_{HH}$ = 7.3 Hz, 2H, *p*-Ph), 7.22–7.26 (m, 4H, *m*-Ph), 7.40–7.43 (m, 4H, *o*-Ph) ppm. ^{13}C NMR (100.6 MHz, THF-d_8): δ = 20.61 (s, $Zn{-}CH_2{-}CH{=}CH_2$), 48.70 (s, $C{-}CH_2{-}CH{=}CH_2$), 80.81 (s, $C{-}CH_2{-}CH{=}CH_2$), 103.38 (s, $Zn{-}CH_2{-}CH{=}CH_2$), 119.48 (s, $C{-}CH_2{-}CH{=}CH_2$), 127.08 (s, *p*-Ph), 127.82 (s, *o*-Ph), 128.54 (s, *m*-Ph), 137.86 (s, $C{-}CH_2{-}CH{=}CH_2$), 144.26 (s, $Zn{-}CH_2{-}CH{=}CH_2$), 150.20 (s, *ipso*-Ph) ppm. Anal. Calcd for $C_{19}H_{20}OZn$ (329.77 g/mol): Zn, 19.83. Found: Zn, 19.97.

Single Crystal X-ray Crystallography. Diffraction measurements were performed on a Bruker AXS diffractometer equipped with an Incoatec microsource and an APEX area detector using Mo Kα radiation. Data reductions were performed with the Bruker SAINT software. Structure solution (SIR-92) and refinement (SHELXL-97 as implemented in the WinGX program[27] system) for **2** and **3** were unexceptional. **1** crystallizes as a merohedral twin as indicated by a very low $\langle E^2 - 1\rangle$ value of ca. 0.6.

Theoretical Calculations. All quantum-chemical calculations were carried out with the Gaussian09 suite of quantum-chemical routines[28] running on the facilities of the Computing and Communication Center of the RWTH Aachen University. All model compounds under consideration were preoptimized at the Hartree−Fock level (HF) with the split valence 3-21G[29] set of contracted Gaussian functions. Since this basis set contains neither polarization nor diffuse functions for some of the elements contained in the molecules under study, we considered the resulting structures merely as starting points for further optimization at higher levels of theory. Thus, additional HF calculations were performed by employing the correlation-consistent aug-cc-pVDZ basis set,[30] which is also doubly split in the valence orbitals but which also has polarization and diffuse functions for all the elements of our model compounds. Final geometry optimizations for the model compounds were performed including correlation energy with Møller−Plesset perturbation theory to the second order (MP2).[31] Attempts have also been made to optimize structures of $Zn(C_3H_5)_2$ monomers featured by metal−π interactions (e.g., in an η^3 fashion) at the MP2/aug-cc-pVDZ level of *ab initio* theory without previous optimization at the HF/3-21G level. Initial optimizations were performed under the constraint that all four distances between the terminal carbon atoms of the two allyl moieties and the Zn atom are equal. However, normal coordinate analyses revealed that the resulting structures were not local minima but saddle points of higher order. These structures collapsed, resulting in the structure shown in Figure 2 when the constraints were lifted. To arrive at a better understanding of bonding between the metal atom and the allyl ligands, we also performed natural bond orbital analyses (NBO)[32] for the optimized structures, employing the NBO method as implemented in the Gaussian09 program.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information files (cif) for compounds 1, 2, and 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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