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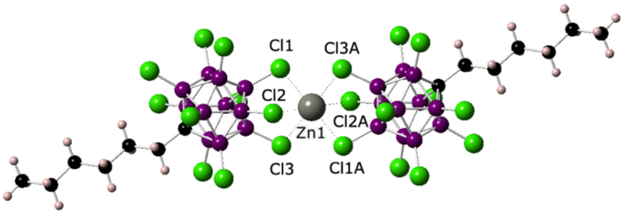

A salt compound containing a formal Zn^{2+} dication only stabilized by weakly coordinated carborate anions was first structurally characterized and shown to be soluble in low polarity solvents. Based on its reactivity with alkene, alkyne and in hydrosilylation catalysis, it is a strong Lewis acid, possibly the strongest Zn-based Lewis acid to date.

Keywords: Zinc – Lewis acid – cation – hydrosilylation – carborate

Towards “naked” Zn^{2+} in the condensed phase: synthesis, structure and reactivity of a highly Lewis acidic Zn(II) dication stabilized by weakly coordinating carborate anions

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Abstract. The employment of the hexyl-substituted anion $[HexCB_{11}Cl_{11}]^-$ allowed for the first time the synthesis of a Zn(II) species, $Zn[HexCB_{11}Cl_{11}]_2$, **3**, in which the Zn^{2+} cation is only weakly coordinated to two carborate counterions and that is soluble in low polarity organic solvents such as bromobenzene. DOSY NMR studies show the facile displacement of at least one of the counterions, and this near “nakedness” of the cation results in high catalytic activity in the hydrosilylation of 1-hexene and 1-methyl-1cyclohexene. Fluoride Ion Affinity (FIA) calculations reveal a solution Lewis acidity of **3** (FIA = 262.1 kJ·mol^{-1}) that is higher than that of the landmark Lewis acid $B(C_6F_5)_3$ (FIA = 220.5 kJ·mol^{-1}). This high Lewis acidity leads to a high activity in catalytic CO_2 and Ph_2CO reduction by Et_3SiH and hydrogenation of 1,1-diphenylethylene using 1,4-cyclohexadiene as the hydrogen source. Compound **3** was characterized by multinuclear NMR spectroscopy, mass spectrometry, single crystal X-ray diffraction and DFT studies.

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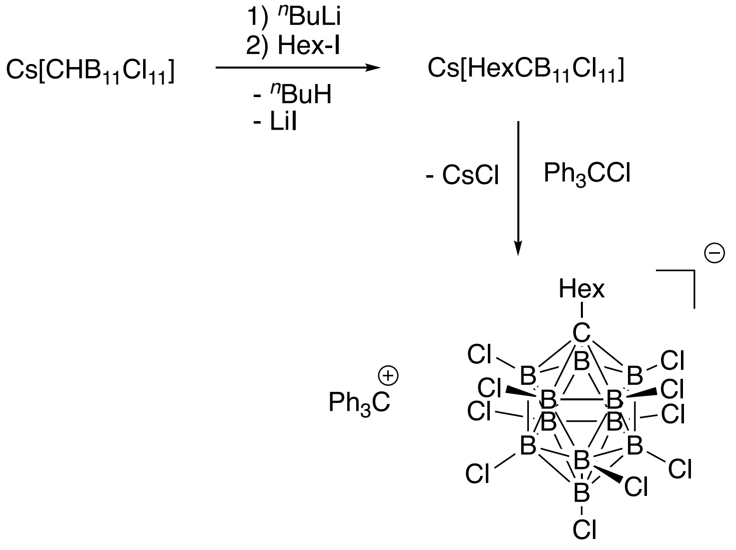
Metal-centered Lewis acids are widespread powerful and versatile reagents in all areas of chemistry, ranging from synthetic chemistry to material science, due to the utility of various Lewis acidic metal ions for substrate activation/functionalization.[1] In that regard, low-coordinate ligand-supported metal cations have attracted attention over the years to access electrophilic/reactive species for enhanced reactivity.[2] Ideally though, the simplest of all metal Lewis acids, *i.e.* ligand-free ("naked") or weakly coordinated metal cations, should be most reactive for chemical functionalization since direct "naked" metal cation/substrate activation should maximize electrophilic activation. However, access to stable ligand-free metal ions in the condensed phase has thus far remained a major challenge, which is due to their high electrophilicity, their instability and/or insolubility in common organic media. Over the past years, the use of modern weakly coordinating anions (WCAs) such as $[B(C_6F_5)_4]^-$, $[Al(OR^F)_4]^-$ and halogenated carborate ions (most notably $[CH_6B_6X_6]^-$ and $[CHB_{11}X_{11}]^-$; X = Cl, I) for minimal cation-anion interactions,[3] has led to the characterization of several mono-valent and M^+ Lewis acids only stabilized by a low basicity solvent and a WCA, including Li^+, Ag^+ and M^+ (M = group 13 metal) salts.[4,5,6,7,8,9,10] Such salts display enhanced reactivity due to weaker cation-anion interactions, including the acceleration of Diels-Alder reactions with $Li[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$,[4] carbonyl-ene reactions catalyzed by $Li[B(C_6F_5)_4]$,[5] and the polymerization of isobutene catalyzed by $[Ga(arene)_3][Al\{OC(CF_3)_3\}_4]$.[6] Also noteworthy, an Ag(I) complex with two P_4 molecules coordinated to one Ag^+ cation was characterized.[11]

To date, weakly coordinated or "naked" M^{2+} divalent cations that are stable at room temperature and soluble in low basicity/polarity solvents are unknown, despite their interest as strong Lewis acids/electrophiles. Compounds such as $M[BF_4]_2$ or $M[EF_6]_2$ (M = +2 cation, E = As, Sb), prepared by the reaction of MF_2 with BF_3 or EF_5 in anhydrous HF, are known but insoluble in most organic solvents.[12] Species $Hg[B_{12}H_{12}]$[13] and $Ni[B_{12}H_{12}]$,[14] were obtained from dehydration of hydrate salts $Hg(H_2O)_x[B_{12}H_{12}]$ and $Ni(H_2O)_6[B_{12}H_{12}]$, respectively. The solvent-free zinc salt $Zn[Al\{OCH(CF_3)_2\}_4]_2$ was also recently characterized, but the rather short $Zn\cdots O$ contacts (1.986 Å avg.) significantly quench the Lewis acidity of the Zn^{2+} center as deduced from solid state and solution data.[15] Zn(II) complexes of electron-rich arenes $Zn(SbF_6)_2\cdot C_6Me_6$ and $Zn(SbF_6)_2\cdot C_6HMe_5$ have only been characterized by NMR spectroscopy in SO_2 solution.[16] Only very recently, the structure of $Sr[Al\{OC(CF_3)_3\}_4]_2$ was reported, which features a partially "naked" large and therefore less Lewis acidic Sr^{2+} cation.[17]

Zn(II) salts, considered as borderline Lewis acids in Pearson's HSAB classification, are commonly used as Lewis acids for the mediation of various stoichiometric and catalytic transformations. Well-defined Zn organometallics such as arylzinc species $Zn(C_6F_5)_2$ are well-established Lewis acid catalysts, especially for the polymerization of various monomers.[18] Of particular interest, ligand-supported Zn(II)-based organocations are well-established electrophilic species but have attracted recent attention since Zn is an Earth-abundant and inexpensive metal source.[2a,19] Recent developments, including from our labs, have shown that a number of reactive low-coordinate (two- and three-coordinate) Zn(II) cations, all consisting of ligand-stabilized $[Zn–R]^+$ mono-cations (R = alkyl, aryl), may behave as Lewis acids for the mediation of various catalytic reactions ranging from alkyne hydroamination to alkyne, alkene and CO_2 hydrosilylation.[20] We herein report on the synthesis and structural characterization of the first weakly coordinated Zn^{2+} cation (isolated as $Zn[WCA]_2$) that is stable and soluble in low polarity organic solvents. We also provide preliminary reactivity studies indicating an unprecedentedly strong Lewis acidity for a Zn(II) species.

As an entry to $Zn[WCA]_2$, the fully chlorinated carborate anion $[CHB_{11}Cl_{11}]^-$, which is one of the least coordinating and least reactive anions known thus far,[21] was initially tested to access stable and characterizable $Zn[WCA]_2$ salts. To generate a formal Zn^{2+} di-cation in a low (Lewis) basicity medium, Et^- abstraction from $[EtZn(C_6H_6)][CHB_{11}Cl_{11}]$ (**1**),[20a] a formal source of the

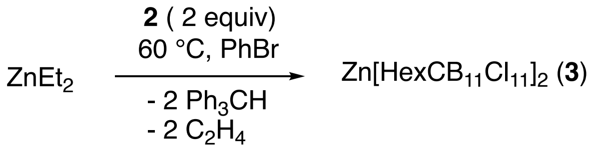
$[Zn{-}Et]^+$ mono-cation, with $[Ph_3C][CHB_{11}Cl_{11}]$ was first attempted. The reaction of a 1/1 **1**/$[Ph_3C][CHB_{11}Cl_{11}]$ mixture (C_6D_5Br, 24 h at RT and then 24 h at 95 °C) led to complete consumption of both reactants, the formation of Ph_3CH and ethylene (as deduced from NMR data) in line with Et^- abstraction from the $[Zn{-}Et]^+$ fragment, along with the precipitation of colorless solid, possibly $Zn[CHB_{11}Cl_{11}]_2$. However, poor solubility precluded structural identification whether in solution or in the solid state, prompting us towards the synthesis of a more soluble WCA as a Zn^{2+} counterion.[22] To this end, anion $[CHB_{11}Cl_{11}]^-$ was C-functionalized by a hexyl group to access the more soluble carborate anion $[HexCB_{11}Cl_{11}]^-$.[23] The C–*H* deprotonation of $Cs[CHB_{11}Cl_{11}]$ and subsequent hexyl functionalization afforded $Cs[HexCB_{11}Cl_{11}]$, isolated in 74% yield (Scheme 1). Salt metathesis between $Cs[HexCB_{11}Cl_{11}]$ and Ph_3CCl led to the corresponding trityl salt $[Ph_3C][HexCB_{11}Cl_{11}]$ (**2**, 73% yield), as confirmed by X-ray crystallographic analysis (see SI). IR data for salt $[HNOct_3][HexCB_{11}Cl_{11}]$ (see SI for its preparation) agree with a slightly more Lewis basic $[HexCB_{11}Cl_{11}]^-$ anion compared to $[CHB_{11}Cl_{11}]^-$ (ν_{NH} = 3176 and 3180 cm^{-1}, respectively) due to the better electron donor ability of the hexyl group (*vs.* hydrogen).[21]



$[Ph_3C][HexCB_{11}Cl_{11}]$ (**2**)

Scheme 1. Synthesis of trityl salt $[Ph_3C][HexCB_{11}Cl_{11}]$ (**2**)

The synthesis of Zn[HexCB$_{11}$Cl$_{11}$]$_2$ (**3**, Scheme 2) was achieved directly from ZnEt$_2$ and trityl salt **2**. Thus, the double ionization reaction of ZnEt$_2$ with 2 equiv of **2** (PhBr, 60 °C, 6 h) led to the quantitative formation of **3** along with Ph$_3$CH and ethylene, as deduced from NMR data. Species **3**, isolated in 71% yield, is soluble and stable for days in PhBr (RT) but decomposes within minutes in CH$_2$Cl$_2$ (RT) to unknown species.



$$\mathrm{ZnEt_2} \xrightarrow[\substack{-\,2\ \mathrm{Ph_3CH} \\ -\,2\ \mathrm{C_2H_4}}]{\substack{\mathbf{2}\ (2\ \text{equiv}) \\ 60\ ^\circ\mathrm{C,\ PhBr}}} \mathrm{Zn[HexCB_{11}Cl_{11}]_2}\ (\mathbf{3})$$

Scheme 2. Synthesis of Zn[HexCB$_{11}$Cl$_{11}$]$_2$ (**3**)

The solid state molecular structure of **3** was determined through XRD studies (Figure 1). It crystallizes as an ion pair with a central Zn^{2+} cation in a slightly distorted octahedral environment since surrounded by two [HexCB$_{11}$Cl$_{11}$]$^-$ anions coordinated in a κ^3-*Cl$_3$* fashion. The Zn···Cl contacts (2.495 Å average) are shorter than those in compound [EtZn(C$_6$H$_6$)][CHB$_{11}$Cl$_{11}$] (2.613 Å average), reflecting the higher charge at Zn in **3** and thus stronger electrostatic interactions. As has been observed previously,[20a, 31b] the coordination to the Zn^{2+} cation results in a slight elongation of the involved B-Cl bonds (1.801 Å average *versus* 1.763 Å average).

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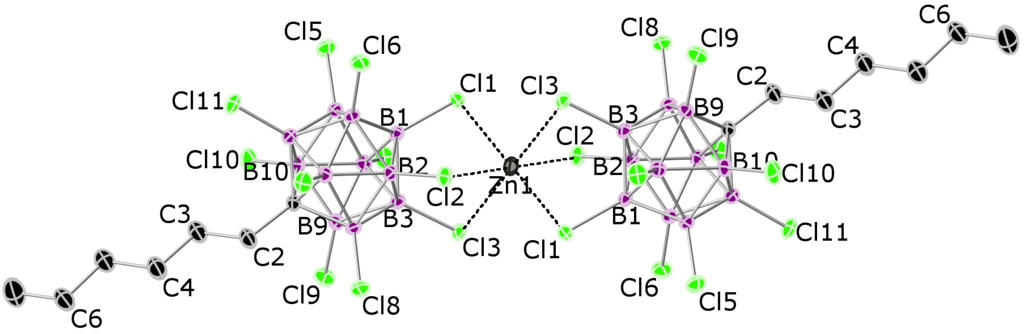


Figure 1. Molecular structure (ORTEP view, 50% probability) of Zn[HexCB$_{11}$Cl$_{11}$]$_2$ (**3**). H atoms have been omitted for clarity. Selected distances (Å) and angles (°): Zn(1)···Cl(1) 2.4544(7), Zn(1)···Cl(2) 2.4905(7), Zn(1)···Cl(3) 2.5456(7), B-Cl(···Zn) 1.810(avg.), B-Cl 1.763(avg.), Cl(1)-Zn-Cl(1A) 180, Cl(1)-Zn-Cl(2) 90.85(2), Cl(1)-Zn-Cl(3) 86.94(2).

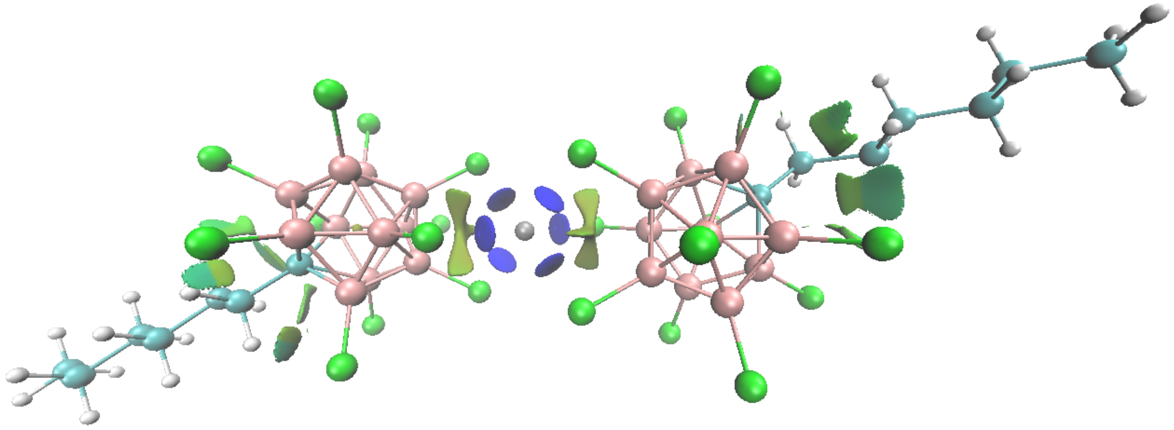


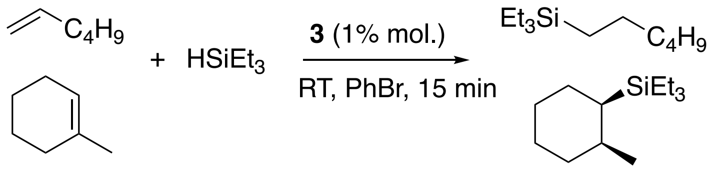
Figure 2. DFT-estimated (B3LYP/6-31+G**) Non-Covalent Interaction (NCI) analysis of a model species for **3**. Attractive electrostatic interactions appear in blue areas and attractive dispersion forces appear in green areas.

Computations on the electronic structure of species **3** using Electron Localization Function (ELF, see SI) and Non-Covalent Interactions (NCI, Figure 2) analysis agree with purely electrostatic interactions (and no covalence) between the central Zn^{2+} cation and the surrounding chlorines. Importantly, species **3** is clearly dynamic in solution as deduced by

NMR data indicating a ready cation/anion dissociation at room temperature in C_6D_5Br. Thus, DOSY NMR measurements for **3** led to an estimated hydrodynamic volume of 1100 Å, *i.e.* lying between those of free $[HexCB_{11}Cl_{11}]^-$ anion (around 850 Å) and solid-state characterized **3** (around 1650 Å). This is consistent with fast cation/anion dissociation in **3** on the NMR timescale with stabilization of the Zn^{2+} by PhBr coordination.[24] This is corroborated by DFT calculations (B3LYP/6-31+G**, PhBr as solvent, modelled in the presence of one PhBr molecule) with the dissociation of **3** to $[Zn(HexCB_{11}Cl_{11})(PhBr)]^+$ and free $[HexCB_{11}Cl_{11}]^-$ anion computed to occur at little energy cost ($\Delta G = 28.4\ kJ\cdot mol^{-1}$).[25] Furthermore, to assess the Lewis acidity of species **3**, its Fluoride Ion Affinity (FIA) was DFT-estimated (B3LYP/6-31+G**, PhBr, see SI).[26,27] In agreement with a highly electrophilic Zn(II) center, FIA calculations are consistent with **3** (FIA = 262.1 $kJ\cdot mol^{-1}$) being significantly more Lewis acidic than the ion-pair $[EtZn(C_6H_6)][CHB_{11}Cl_{11}]$ (FIA = 224.3 $kJ\cdot mol^{-1}$), the two-coordinate $(NHC)Zn–C_6F_5^+$ cation (NHC = IDipp, FIA = 185.5 $kJ\cdot mol^{-1}$) and the landmark Lewis acid $B(C_6F_5)_3$ (FIA = 220.5 $kJ\cdot mol^{-1}$).

To substantiate the electrophilicity of the Zn(II) center in **3**, it was first reacted with unsaturated substrates such as 1-hexene and 1-octyne, as well as H_2. ^1H NMR data of a 1/1 **3**/1-hexene mixture (RT, C_6D_5Br) agree with immediate reaction, but a ready polymerization of 1-hexene precluded any adduct characterization. This was further confirmed by the reaction of a 1/100 **3**/1-hexene mixture (RT, C_6D_5Br) leading to a 61% conversion of 1-hexene to poorly defined poly(1-hexene) oligomers within 3 h, as deduced from GPC data ($M_n = 924$ g. mol^{-1}, $Đ = 1.76$). DFT (B3LYP/6-31+G**, PhBr) calculations predict that the formation of π-adduct $[(HexCB_{11}Cl_{11})Zn(propene)]^+$ (along with free carborate) from **3** and propene should occur under the reaction conditions ($\Delta G = 5.9\ kJ\cdot mol^{-1}$), reflecting the strong Lewis acidity of Zn(II) center.[28] Alkene oligo-/poly-merization mediated by Lewis acidic metal complexes is well-established.[2a] Likewise, 1-octyne immediately reacts with 1 equiv of **3** (RT, C_6D_5Br) according to ^1H NMR data, provoking a significant downfield of the alkynyl proton ^1H NMR shift (s, br, $\delta = 4.40$ ppm) *vs.* that of free 1-octyne (t, $\delta = 1.92$ ppm), in line with an enhanced vinylic character. Though the latter suggests the formation of a Zn–alkyne adduct, further characterization was precluded due its decomposition within a couple of hours to unknown species. According to DFT (B3LYP/6-31+G**, PhBr) calculations with propyne as the modelled alkyne, the formation of π-adduct $[(HexCB_{11}Cl_{11})Zn(propyne)]^+$ (along with free carborate) from **3** and propyne also occurs at little energy cost ($\Delta G = 7.9\ kJ\cdot mol^{-1}$), in agreement with a labile Zn–alkyne adduct at RT. The reactivity of salt **3** with H_2 was also probed: no apparent reaction was observed between **3** under H_2 (3 bar) at RT or 90 °C in C_6D_5Br for 2 h.

Next, species **3** was evaluated in hydrosilylation catalysis (alkene and CO_2) to probe the ability of **3** for Si-H activation.[29] In the presence of $HSiEt_3$, species **3** (1 mol%) catalyzes fast 1-hexene hydrosilylation at room temperature (C_6D_5Br) with a quantitative conversion to **4** within 15 min (Scheme 3). As a comparison, $[EtZn(C_6H_6)][CHB_{11}Cl_{11}]$ is an inactive catalyst at room temperature while cation $[(IDipp)Zn–C_6F_5]^+$ and $B(C_6F_5)_3$ proceed much more slowly.[20a,20c,30] A similar high activity was observed for the hydrosilylation of 1-methylcyclohexene catalyzed by **3** (1 mol%, C_6D_5Br, RT, 15 min) and selectively led to the *cis*-hydrosilylated product **5**, consistent with a selective *anti*-1,2-addition of Si–H to the C=C bond. Though species **3** remains intact after olefin hydrosilylation catalysis, an NMR control experiment of a $HSiEt_3$/**3** mixture showed that species **3** interacts with $HSiEt_3$ (2 equiv, PhBr, RT) with an immediate broadening of the Si-*H* ^1H NMR resonance, in line with Si-H activation by the Zn(II) cationic center (see SI).



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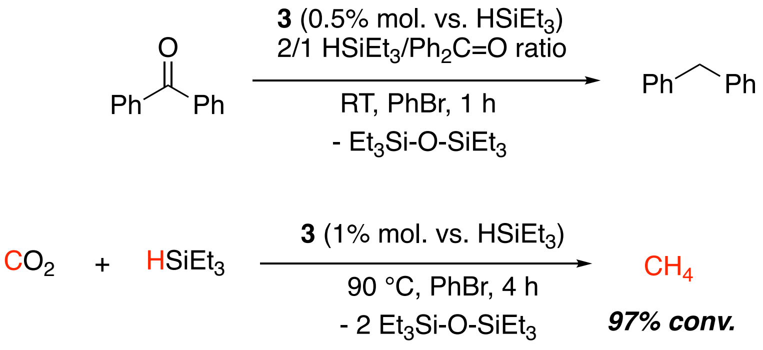
Scheme 3. Olefin hydrosilylation catalyzed by Zn(II) species **3**.

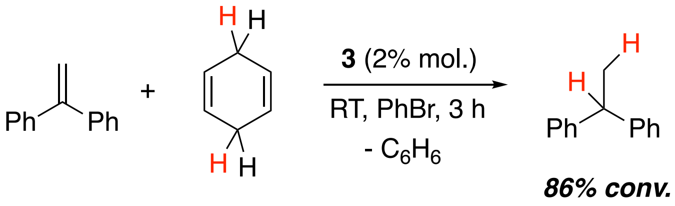
Consistent with **3**/$HSiEt_3$ interactions, $HSiEt_3$ redistribution was observed over time in the presence of a catalytic amount of **3** (1 mol% *vs.* $HSiEt_3$), with the formation of a mixture of $SiEt_4$ (38% conv. of initial $HSiEt_3$), $HSiEt_3$, H_2SiEt_2 and H_3SiEt after 16 h at room temperature, as indicated by ^1H, ^{13}C, ^{29}Si and 2D NMR analysis (see SI). Interestingly, according to DFT computation (B3LYP/6-31+G**, PhBr), the formation of the $[Et_3Si\cdots H\cdots SiEt_3]^+$ silylium cation and the Zn–H species $[(HexCB_{11}Cl_{11})Zn–H]$ from strong Lewis acid **3** and 2 equiv of $HSiEt_3$ is possible at low energy cost ($\Delta G = 25.9\ kJ\cdot mol^{-1}$), though such products were not experimentally observed.[31,32] Besides, as DFT-computed, $HSiEt_3$ cleavage mediated by **3** is even more accessible in the presence of an alkene (propene as model) to afford $[(HexCB_{11}Cl_{11})Zn–H]$ and cation $[(propyl)SiEt_3]^+$ ($\Delta G = 9.2\ kJ\cdot mol^{-1}$). In view of the latter and for comparison with **3**, hydrosilylation of methylcyclohexene catalyzed by $[Ph_3C][HexCB_{11}Cl_{11}]$ (1% mol vs. $HSiEt_3$, RT, C_6D_5Br),[33] was studied: it was found to proceed with a similar rate (quantitative within 15 min) and selectivity with the formation of the *cis*-product **5**, as typically observed in silylium-catalyzed alkene hydrosilylation.[30,34,35] Altogether, though no clear-cut mechanism may be proposed at this stage, DFT and experimental data strongly suggest the involvement of a transient silylium cation, generated from the reaction of **3** with $HSiEt_3$, to account for the observed catalytic activity and selectivity in alkene hydrosilylation.



Scheme 4. Hydrosilylation of C=O substrates catalyzed by species **3**.

Species **3** was also tested in hydrosilylation/deoxygenation catalysis of C=O substrates (Scheme 4). In the presence of **3** (1 mol%), a 1/1 mixture of benzophenone/$HSiEt_3$ (C_6D_5Br, RT, 5 h, not optimized) led to the formation of doubly reduced product Ph_2CH_2 (50 % conv) along with side-product $Et_3SiOSiEt_3$ and 50% of unreacted $Ph_2C=O$, based on ^1H NMR data. Starting from a 1/100/200 **3**/$Ph_2C=O$/$HSiEt_3$ mixture led to an 80% conversion of $Ph_2C=O$ to reduction products $PhCH-OSiEt_3$/Ph_2CH_2 in a 1/15 ratio within 15 min at RT. A complete formation of $PhCH_2Ph$ (along with equimolar amount of $Et_3SiOSiEt_3$) occurred within 1 h at room temperature in C_6D_5Br. Interestingly, CO_2, a more challenging C=O substrate, may also be reduced by $HSiEt_3$ in the presence of **3** as catalyst. An initial run at room temperature (10 mol% of **3**, 1.5 atm CO_2, C_6D_5Br) showed slow CO_2 hydrosilylation (15% silane conversion after 60 h) with the observation of reduction products $Et_3SiOCH_2OSiEt_3$, $MeOSiEt_3$ and eventually CH_4 as the reduction reaction proceeds.[36] However, satisfyingly, species **3** (1 mol% vs. $HSiEt_3$) efficiently and selectively catalyzed CO_2 hydrosilylation upon heating (1.5 atm CO_2, C_6D_5Br, 90 °C) with a nearly quantitative conversion of $HSiEt_3$ (97%) to methane and $SiEt_4$/siloxanes by-products within 4 h, as deduced from NMR and GC-MS data (SI). Remarkably, as a Lewis acid catalyst in CO_2 hydrosilylation, species **3** is considerably more active than any other Zn(II) cations such as $[EtZn(C_6H_6)][CHB_{11}Cl_{11}]$, two-coordinate $[(NHC)Zn–R]^+$ systems and even group 13 metal cations of the type $[MR_2]^+$ (M = Al, Ga) thus far reported.[20a,20c,37] No adduct formation was observed between **3** and CO_2 at various temperatures (1.5 atm CO_2, C_6D_5Br) according to ^{13}C data recorded from -20 °C to 90 °C. Under the studies' conditions and given the reactivity of **3** with $HSiEt_3$ (*vide supra*), CO_2 hydrosilylation catalysis by **3** is likely to proceed through the initial involvement of cation $[Et_3Si\cdots H\cdots SiEt_3]^+$ cation and/or $[(HexCB_{11}Cl_{11})Zn–H]$. To gain additional insight, the relative performances of **3** *vs.* $[Et_3Si\cdots H\cdots SiEt_3]^+$ were contrasted. Thus, CO_2 hydrosilylation initiated by $[Ph_3C][HexCB_{11}Cl_{11}]$ (1% mol vs. $HSiEt_3$, 70 °C, 2.5 h, C_6D_5Br) proceeded twice as fast as that mediated by **3** (1% mol) under identical conditions (61% vs. 30% conversion of $HSiEt_3$, respectively), both catalysis yielding methane as the only reduction product.[38] The latter could be consistent with cation $[Et_3Si\cdots H\cdots SiEt_3]^+$ being the catalytically active component upon associating **3** and $HSiEt_3$, with a lower activity due to a smaller concentration in silylium as the catalysis proceeds. Though a few ligand-supported $Zn–H^+$ cations are known to effectively reduce CO_2 under similar reaction conditions to ours,[39] the possible inactivity of a nearly "naked" Zn–H moiety such as $[(HexCB_{11}Cl_{11})Zn–H]$ could be due to its decomposition under such conditions.

Finally, in preliminary studies, highly Lewis acidic species **3** was also tested in transfer hydrogenation of alkenes using 1,4-cyclohexadiene (CHD) as hydrogen source, a very convenient and safe H_2 surrogate. Such hydrogenations may be catalyzed by gallium or boron Lewis acidic complexes, though heating and long reaction times are frequently required.[40] A Zn(II) cation was also recently reported to catalyze hydrogenation transfer of 1,1-diphenylethylene at 80 °C with 24 h using 10 mol% of catalyst.[41] Satisfyingly, species **3** (2 mol% *vs.* substrates) performed much better and efficiently catalyzed 1,1-diphenylethylene hydrogenation to Ph_2CH-CH_3 at room temperature in the presence of CHD within 3 h (Scheme 5), further illustrating the strong Lewis acidity of the Zn^{2+} center of **3**.



Scheme 5. Transfer hydrogenation of 1,1-diphenylethylene catalyzed by species **3**.

In conclusion, we synthesized and characterized the first example of a compound incorporating a formal Zn^{2+} cation only stabilized by weakly coordinating anions, that is stable at room temperature and soluble in low polarity organic solvents. Based on its reactivity with various substrates, it stands as a strong (perhaps the strongest) Zn-based Lewis acid in solution thanks to ready anion dissociation even in a low-basicity solvent such as PhBr. It constitutes an important step forward towards a "naked" Zn(II) dication in the condensed phase, i.e. a compound in which cation···anion interactions are minimized as far as possible. Further reactivity studies of such Zn(II) dications for the activation of various small molecules as well as access to other "naked" metal cations are currently underway in our labs.

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