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Accessing two-coordinate Zn(II) Organocations *via* NHC coordination: synthesis, structure and use as π-Lewis acids in alkene, alkyne, and CO_2 hydrosilylation

David Specklin,[a] Frédéric Hild,[a] Christophe Fliedel,[a] Christophe Gourlaouen,[a] Luis. F. Veiros[b] and Samuel Dagorne*[a]

Dedication ((optional))

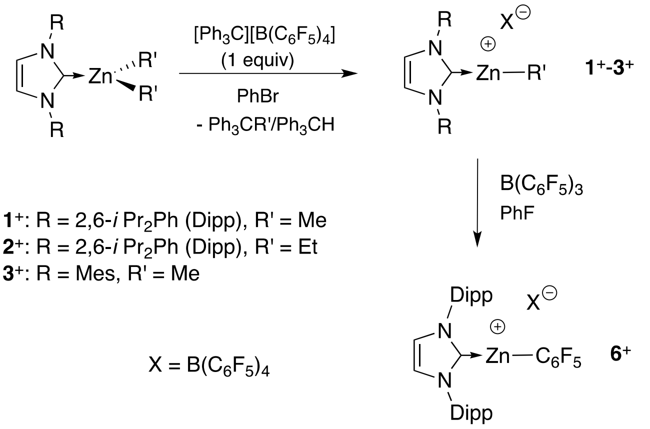
Abstract: Discrete two-coordinate Zn(II) organocations are first reported, presently of the type (NHC)Zn–R$^+$, thanks to NHC stabilization. In preliminary reactivity studies, such entities, which are direct cationic analogues of long-known ZnR_2 species, act as effective and tunable π-Lewis acid catalysts in alkene, alkyne and CO_2 hydrosilylation.

Neutral diorganozinc species, first prepared by Frankland in 1849, have long been established as useful reagents in organic synthesis and catalysis, most notably for the fonctionalization of unsaturated substrates.[1] Structurally, such species are typically monomeric, display a linear C-Zn-C array and bears a two-coordinate *sp*-hybridized Zn(II) center with two low-lying vacant π orbitals available for coordination. Since Zn(II) is only moderately Lewis acidic (HSAB scale), Zn(II) organocations are of particular interest for enhanced Lewis acidity at Zn(II) to improve substrate activation in Lewis-acid stoichiometric/catalytic processes. In this area, a number of structurally characterized three- and four-coordinate Zn(II) supported by various *N*-/*O*-/*P*-/*C*-based supporting ligands have been reported over the past twenty years and successfully exploited in polymerization, alkene/alkyne hydroamination and CO_2 functionalisation catalysis.[2-5] Such ligand-stabilized Zn(II) organocations are usually stable but typically display moderate catalytic performances. For more Lewis acidic Zn-based organocations, challenging studies were recently performed by the groups of Wehmschulte and Krossing to access thus-far-unknown "free" mono-coordinate cation $[EtZn]^+$ *via* direct ionization of $ZnEt_2$ in the presence of a weakly coordinating anion, such as perfluorinated aluminate anions of the type $[Al(OR)_4]^-$ or the carborane anion $[CHB_{11}Cl_{11}]^-$.[4a,6] Ion-like species such as $EtZn(\eta^3\text{-}C_6H_6)(CHB_{11}Cl_{11})$ and $EtZn[Al(OR)_4]$ display weak anion-Zn(II) bonding interactions leading, for instance, to a three-coordinate Zn(II) center in $EtZn(Al(OR)_4$. Discrete $[EtZn(arene)_2]^+$ Zn(II) cations, with arene π-coordination to the Zn(II) center, were also recently characterized.[6]

Structurally characterized and isolable two-coordinate Zn(II) organocations of the type $[(L)Zn–R]^+$ (L monodentate) are unknown thus far. To date, (DMF)Zn–alkyl$^+$ cations have been observed in the gas phase and a two-coordinate phenalenyl-based Zn(II) cation was proposed to exist in solution.[7] In principle, in addition to their fundamental interest, such electrophilic entities may represent a better reactivity/stability balance when compared to, on the one hand, more robust but less Lewis acidic three-/four-coordinate cationic analogues and, on the other hand, elusive mono-coordinate $[RZn]^+$ cations.

Stable two-coordinate $[(L)Zn–R]^+$ cations (L monodentate) are expected to require a strong σ-donating L ligand (for a robust L–Zn–R$^+$ array) providing a significant steric protection of the Lewis acidic Zn(II) center, ligand properties for which *N*-heterocyclic carbenes (NHCs) are so priviledged and widely used.[8] As part of our studies on NHC-stabilized Zn(II) organocations,[5d,9] we herein report on the synthesis and structure of two-coordinate Zn(II) di-organyl cations (NHC)Zn–R$^+$ (R = alkyl, aryl), as stable and robust entities thanks to NHC stabilization. Such entities, which are the first direct cationic analogues of long-known ZnR_2 species, are shown to act as effective and tunable π-Lewis acid catalysts in alkene, alkyne and CO_2 hydrosilylation.

Two-coordinate cations (NHC)Zn–R$^+$ may be prepared *via* alkyde (R$^-$) abstraction reaction from the corresponding neutral dialkyl precursors with an electrophile such as Ph_3C^+, an approach successfully used by Bochmann to access three-/four-coordinate Zn(II)–alkyl cations.[2c-e] Thus, the reaction of adducts $(IDipp)ZnR_2$ (R = Me, Et) with 1 equiv $[Ph_3C][B(C_6F_5)_4]$ (RT, 30 min, PhBr) led to the high yield formation and isolation of the corresponding two-coordinate cations $[(IDipp)Zn–R]^+$ (as $B(C_6F_5)_4^-$ salts; R = Me, [**1**][$B(C_6F_5)_4$]; R = Et, [**2**][$B(C_6F_5)_4$]; Scheme 1), as deduced from solution and solid state data.



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Scheme 1. Synthesis of Zn(II) cations **1**$^+$-**3**$^+$ and **6**$^+$.

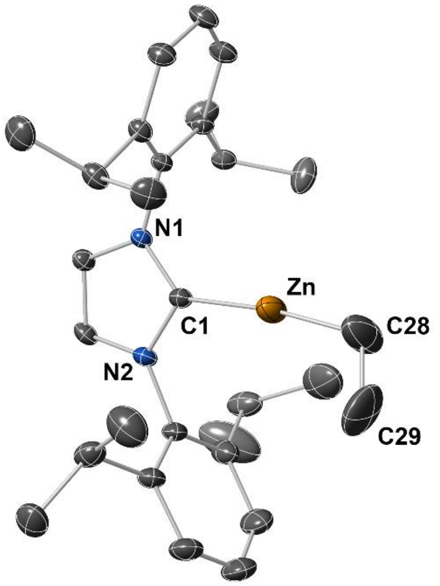


Figure 1. Molecular structure of cation **2**$^+$ (H atoms are omitted for clarity). Selected bond distances (Å) and angles (°): Zn-Et = 1.909(5), Zn-NHC = 1.961(3), C-Zn-C = 173.0(3).

The molecular structures of salts [**1**-**2**][B(C_6F_5)$_4$] were determined through single-crystal X-ray diffraction studies (XRD) and both display similar features (Table S1; Figures 1, S20-21). Taking the example of [**2**][B(C_6F_5)$_4$], it crystallizes from PhBr as discrete two-coordinate (IDipp)Zn–Et$^+$ cations and B(C_6F_5)$_4^-$ anions with no cation/anion short contacts (Figure S22). Cation **2**$^+$ contains a central *sp*-hybridized two-coordinate Zn(II) center, with a nearly linear C_{NHC}-Zn-C_{Et} array [173.0(3)°]. The Zn–C_{Et} bond distance in **2**$^+$ [1.909(5) Å] is significant shorter than that in higher coordinate Zn(II)–alkyl cations [1.964(6) and 1.964(3) Å in Et–Zn(η^3-toluene)(κ^2-CHB$_{11}$Cl$_{11}$)] and Et–Zn(OEt$_2$)$_3^+$, respectively,[4a,10] and in ZnEt$_2$ [1.948(5) Å],[11] reflecting an enhanced electrophilicity at Zn(II). The NMR data for [**1**-**2**][B(C_6F_5)$_4$] (CD$_2$Cl$_2$, RT) are consistent with weakly interacting anions and cations in solution. The ^{1}H and ^{19}F DOSY NMR data for salt [**1**][B(C_6F_5)$_4$] suggests the presence of contact ion pairs (RT, CD$_2$Cl$_2$).[12] In line with their ionic nature, cations **1**$^+$ and **2**$^+$ are only sparingly soluble in benzene and toluene while they are soluble and stable (for days) in CD$_2$Cl$_2$ and C$_6$D$_5$Br (RT, under N$_2$). Steric protection at Zn(II) by the NHC ligand may matter for stability. Thus, the less sterically bulky cation (IMes)Zn–Me$^+$ (**3**$^+$, Scheme 1), generated by ionization of (IMes)ZnMe$_2$ with [Ph$_3$C][B(C_6F_5)$_4$], is unstable at room temperature and decomposes within a few hours to unknown species, precluding its isolation and further use. Expectedly, cation **1**$^+$ reacts fast and irreversibly with Lewis bases (L) such as THF and benzaldehyde to form the corresponding (IDipp)Zn(Me)(L)$^+$ adducts (**4**$^+$ and **5**$^+$, respectively). The Zn-PhCHO cation **5**$^+$ is however stable for hours in C$_6$D$_5$Br (90 °C, 12h) or THF (70 °C, 12h) with no C=O insertion reactivity (into the Zn–Me bond), unlike the typical behavior of ZnR$_2$ towards carbonyl substrates.

Cations **1**$^+$ and **2**$^+$ may be further derivatized for enhanced Lewis acidity at Zn(II). Thus, **1**$^+$ cleanly reacts with 1 equiv B(C_6F_5)$_3$ (RT, PhF) *via* a Me/C_6F_5 exchange reaction to quantitatively afford two-coordinate cation (IDipp)Zn–$C_6F_5^+$ (**6**$^+$), isolated as [**6**][B(C_6F_5)$_4$] (Scheme 1).[13] From CH$_2$Cl$_2$, it crystallizes as discrete (IDipp)Zn–$C_6F_5^+$ and B(C_6F_5)$_4^-$ ions as determined from XRD studies (Figure 2a). Two-coordinate cation **6**$^+$ is structurally similar to **1**$^+$ and **2**$^+$, albeit with a shorter Zn-C_{NHC} bond distance [1.938(3) *vs.* 1.961(3) Å in **2**$^+$], indicative of a more electrophilic Zn(II) center. DOSY ^{1}H and ^{19}F NMR data for [**6**][B(C_6F_5)$_4$] agree with separated ions in solution (CD$_2$Cl$_2$, RT; Figures S17-20). From PhBr, cation **6**$^+$ crystallizes as adduct (IDipp)Zn–$C_6F_5^+$·PhBr (Figure 2b) with a side-on position of PhBr and a Zn···Br distance [2.6909(5) Å] well below the sum of VdW radii of Zn and Br (3.24 Å). π-interactions between the *Ph*Br and Zn-*C_6F_5*$^+$ aromatic rings may also stabilize such an arrangement in the solid state. Similar M···BrPh interactions were observed with the strong Lewis acid Al(C_6F_5)$_3$ and may account for the excellent thermal stability of cation **6**$^+$ in PhBr.[14]

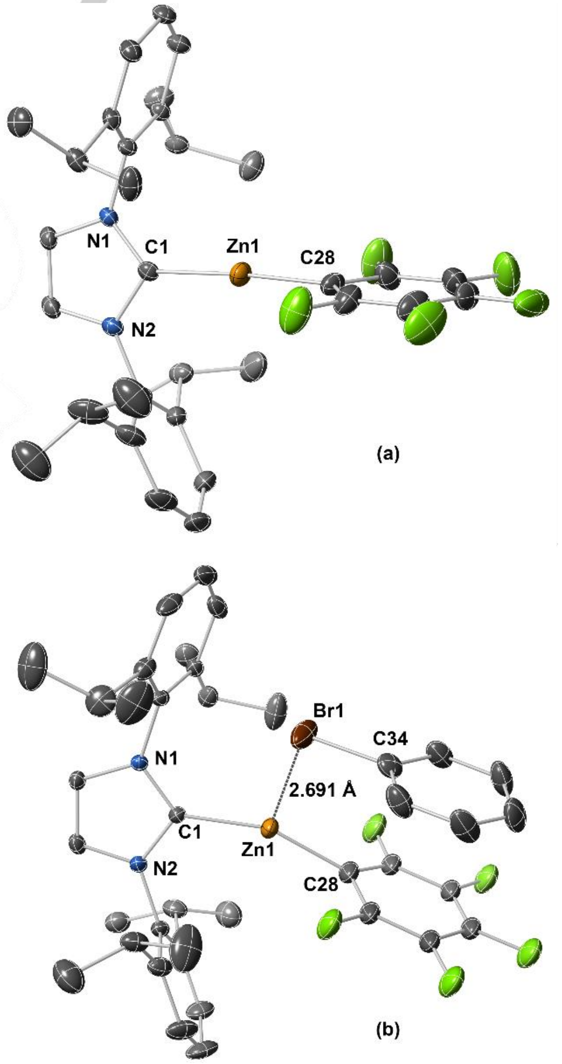


Figure 2. Molecular structures of cation 6^+ (a) and 6^+·PhBr (b). Selected bond distances (Å) and angles (°): for 6^+; Zn-C6F5 = 1.919(3), Zn-NHC = 1.938(3), C-Zn-C = 175.4(1). For 6^+·PhBr; Zn···Br = 2.6909(5), C-Zn-C = 155.8(1).

To gain further insight on cations $\mathbf{1}^+$, $\mathbf{2}^+$ and $\mathbf{6}^+$ as π-Lewis acids, their Lewis acidity was experimentally estimated with the Gutmann-Beckett method, where the ^{31}P NMR chemical shift of $Et_3P{=}O$ (acting as a Lewis base) is used to probe Lewis acidity.[15] According to these measurements, the Lewis acidity of $\mathbf{6}^+$ is comparable to that of $B(C_6F_5)_3$ and higher than that of $\mathbf{1}^+$ and $Zn(C_6F_5)_2$ [$\Delta\delta^{31}$P (CD_2Cl_2) = 26.4, 24.7, 17.2 and 14.5 ppm for $B(C_6F_5)_3$, $\mathbf{6}^+$, $Zn(C_6F_5)_2$ and $\mathbf{1}^+$, respectively], albeit within the limit of validity of such a method.[16] Since best suited for HSAB hard Lewis acid/base interactions, the Fluoride Ion Affinity (FIA), which also correlates to Lewis acidity (the higher the FIA, the stronger the Lewis acid), was also calculated for cations $\mathbf{1}^+$ and $\mathbf{6}^+$ using a known methodology (see Supporting Information).[17] FIA calculations agree with $\mathbf{6}^+$ and $\mathbf{1}^+$ being more Lewis acidic than $B(C_6F_5)_3$ [FIA = 156, 146, 106 and 86 kcal/mol for $\mathbf{6}^+$, $\mathbf{1}^+$, $B(C_6F_5)_3$ and $Zn(C_6F_5)_2$, respectively]. In any case, the latter estimations establish $\mathbf{6}^+$ and, to a lesser extent, $\mathbf{1}^+$ as potent π-Lewis acids. Furthermore, as DFT-estimated (BLYP/def2-SVP), it is interesting to note that the LUMOs of $\mathbf{1}^+$ and $\mathbf{6}^+$ both exhibit a significant π-bonding interaction between the $C_{carbene}$ and Zn(II), which suggests that the NHC π-Lewis acid character may further enhance the Lewis acidity of these cations (for $\mathbf{1}^+$ and $\mathbf{6}^+$, see Figures 3 and S35, respectively).

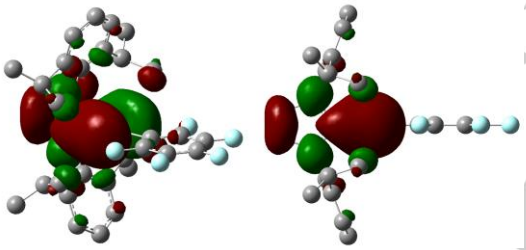
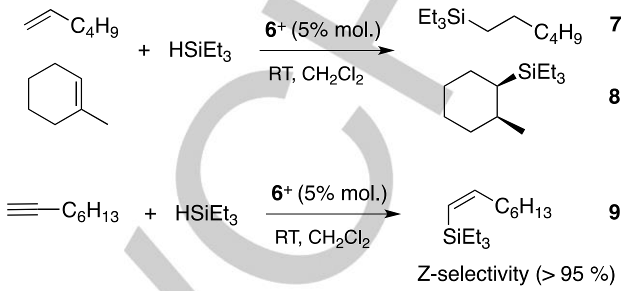


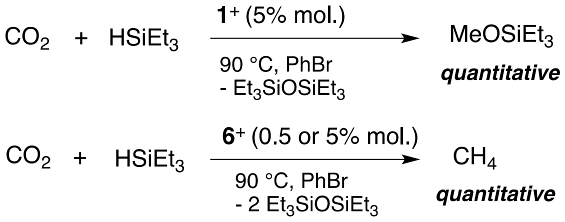
Figure 3. Front (left) and side (right) view of the DFT-computed (BLYP/def2-SVP) LUMO of cation $\mathbf{6}^+$ (-4.756 eV).

Cations $\mathbf{1}^+$, $\mathbf{2}^+$ and $\mathbf{6}^+$ were evaluated in alkene, alkyne and CO_2 hydrosilylation catalysis and their performance compared to $B(C_6F_5)_3$.[18] Thus, in the presence of $HSiEt_3$, cation $\mathbf{6}^+$ (5% mol.) catalyzes 1-hexene hydrosilylation at room temperature (CD_2Cl_2, quantitative conv. to **7** within 18h, Scheme 2) while less Lewis acidic cations $\mathbf{1}^+$ and $\mathbf{2}^+$ are inactive under these conditions (Figures S25). Hydrosilylation of methylcyclohexene mediated by $\mathbf{6}^+$ (5% mol., CD_2Cl_2, RT, 14h) only led to hydrosilylated product **8**, thus consistent with a selective *anti*-1,2-addition of Si–H to the C=C bond (Figures S26). Cation $\mathbf{6}^+$ retains its integrity during catalysis with no apparent catalyst/substrates interactions, as monitored by ^{1}H NMR (CD_2Cl_2, RT). Altogether, these data are consistent a Lewis-acid-catalyzed process, as observed with strong group 13 Lewis acids $E(C_6F_5)_3$ (E = B, Al).[19] Also, cation $\mathbf{6}^+$ is highly active and selective in 1-octyne hydrosilylation to afford the Z-selective product **9** (5% mol. of $\mathbf{6}^+$, quantitative conv. to **9** within 15 min, RT, CD_2Cl_2, Scheme 2, Figure S27). This contrasts with the absence of any catalytic activity when using $B(C_6F_5)_3$ as 1-octyne hydrosilylation catalyst under identical conditions (< 5% conv. to **9**, 24h, CD_2Cl_2). A Lewis-acid-mediated reaction is likely operating based on experimental data, with a hydrosilylation proceeding an *anti*-1,2-addition of Si–H to the C-C triple bond.[20]



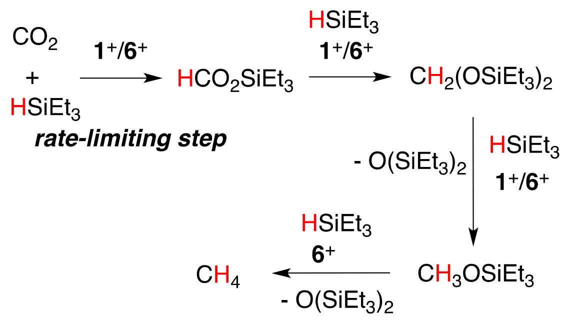
Scheme 2. Alkene and alkyne hydrosilylation catalysis by cation $\mathbf{6}^+$

There are a number of metal-based catalysts able to efficiently hydrosilylate CO_2 to the formate level (HCO_2SiR_3). However, effective and selective systems for CO_2 reduction to aldehyde-, methanol-equivalent and methane (*i.e.* $R_3SiOCH_2OSiR_3$, CH_3OSiR_3 and CH_4) remain challenging.[21,22] As recently shown, strong group 13 Lewis acids, such as ion pair $Et_2Al(CHB_{11}Cl_{11})$ and mixed $Al(C_6F_5)_3/B(C_6F_5)_3$ catalytic systems, may convert CO_2 to CH_4.[5a,23] Satisfyingly, Zn(II) cation $\mathbf{1}^+$ (5% mol.) catalyzes CO_2 hydrosilylation in the presence of $HSiEt_3$ to quantitatively and selectively yield methanol-equivalent $MeOSiEt_3$ (1.5 bar of CO_2, C_6D_5Br, 90 °C, 12h), along with $Et_3SiOSiEt_3$ as a side-product (Scheme 3, Figures S28-S29). Instead, when using more Lewis acidic $\mathbf{6}^+$ (5% mol.), CO_2 is completely converted to CH_4 within 6h under identical reaction conditions (Scheme 3, Figures S30-S31). As a comparison, benchmark Lewis acids $Zn(C_6F_5)_2$, $B(C_6F_5)_3$ and $EtZn(OEt_2)_3^+$ are inactive in CO_2 hydrosilylation under such conditions. In line with the robustness of $\mathbf{6}^+$, decreasing catalyst loading by ten (0.5% mol. in $\mathbf{6}^+$) led to a 95% conv. of the $CO_2/HSiEt_3$ mixture to CH_4 within 23h (C_6D_5Br, 90 °C; Figure S32).



Scheme 3. CO_2 hydrosilylation catalyzed by cations $\mathbf{1}^+$ and $\mathbf{6}^+$.

According to ^{1}H NMR control experiments, both $\mathbf{2}^+$ and $\mathbf{6}^+$ are unreactive under CO_2 alone (1.5 bar, C_6D_5Br, 90 °C, 24h), and, likewise, do not react with $HSiEt_3$ on its own (5 equiv, C_6D_5Br, 90 °C, 24h). Also, while CO_2 hydrosilylation is neglectable at room temperature (< 5% conv. to CH_4 after 24h), $\mathbf{6}^+$ reacts at room temperature with silyl formate HCO_2SiEt_3 (7 equiv) in the presence of $HSiEt_3$ (21 equiv) to quantitatively afford a mixture of $MeOSiEt_3$ and CH_4 (15 and 85% conv., respectively; 24h, C_6D_5Br), with catalyst **6**$^+$ retaining its integrity (Figure S33). Under identical conditions, the stoichiometric reaction of **6**$^+$ with a 1/1 $HCO_2SiEt_3/HSiEt_3$ mixture leads to the fast formation of a 1/5 $CH_2(OSiEt_3)_2/MeOSiEt_3$ mixture (15 min, 50% conv. of $HSiEt_3$) along with unreacted HCO_2SiEt_3 (Figure S34). Altogether, these observations suggest a Lewis-acid-mediated CO_2 reduction catalysis with the initial CO_2 functionalisation (*i.e.* formation of HCO_2SiEt_3) being rate-limiting, followed by faster sequential hydrosilylation of HCO_2SiEt_3 to $CH_2(OSiEt_3)_2$, $MeOSiEt_3$ and finally CH_4 (Scheme 4).



Scheme 4. Stepwise hydrosilylation of CO_2 to methanol-equivalent and CH_4 catalyzed by cations **1**$^+$and **6**$^+$

For the initial functionalisation of CO_2, DFT calculations (BLYP/def2-SVP, Figure 4) agree with an initial CO_2 activation/coordination by **VI**$^+$ (**VI-CO2**, Figures 4 and S36), followed by Et_3Si-*H* attack at *C*=O (reactant complex **A**, Figures 4 and S37) to afford the hydrosilylated thermodynamic product **C** through transition state **B** (ΔG = 21.6 kcal/mol, Figure 4). The reaction energy barrier (22.8 kcal/mol) for CO_2 functionalisation by **VI**$^+$ is compatible with experimental observations.

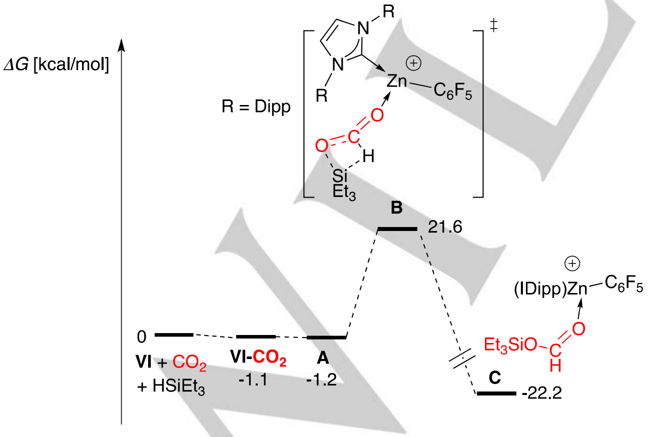


Figure 4. DFT-computed (BLYP/def2-SVP, gas phase) Gibbs free energy (kcal/mol) reaction of CO_2 with $HSiEt_3$ mediated by **VI**$^+$ (model of **6**$^+$)

In summary, we first reported on discrete two-coordinate Zn(II) organocations, presently of the type (NHC)Zn–R$^+$, thanks to NHC stabilization. Structurally analogous to ZnR_2 compounds, preliminary reactivity studies show such cations behave as effective and selective π-Lewis acid catalysts for a number of organic transformations of current interest, outperforming classical Lewis acids such as $B(C_6F_5)_3$ in some instances. These cations benefit from several attractive features which should promote their further use and development, including: i) stability, ii) possible tunability of the Lewis acidity (*via* the nature of the NHC and Zn–*R*$^+$ moieties) and iii) straightforward synthesis from commonly used reagents. With Zn being a cheap and low toxic metal source, this may lead to new developments in fundamental and applied reactivity.

Acknowledgements ((optional))

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Keywords: Zinc • organocation • carbene • Lewis acid • hydrosilylation

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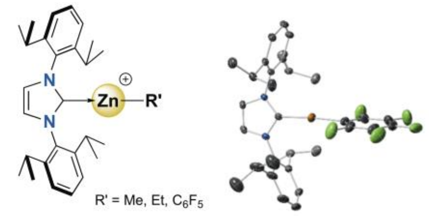

Two-coordinate Zn(II) organocations

Discrete two-coordinate Zn(II) organocations, presently of the type (NHC)Zn–R^+, are first structurally characterized thanks to NHC stabilization. Such entities, which are direct cationic analogues of long-known ZnR_2 species, act as effective and tunable *π*-Lewis acid as effective and tunable *π*-Lewis acid catalysts in alkene, alkyne and CO_2 hydrosilylation.

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