DFT Study on the Mechanism of the Activation and Cleavage of CO₂ by (NHC)CuEPh₃ (E = Si, Ge, Sn)

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Supporting Information

ABSTRACT:

Density functional theory has been used to investigate the mechanism of the activation and cleavage of CO₂ by the complexes (NHC)CuEPh₃ (E = Si, Ge, Sn). Our results show that both the Cu–E and E–C(Ph) bonds are capable of activating and cleaving CO₂. The reactivity of the Cu–E bond toward CO₂ activation *decreases* as E becomes heavier, while the reactivity of the E–C(Ph) bond toward CO₂ activation *increases* as E becomes heavier. The higher electron-releasing capability of (NHC)Cu compared to the EPh₃ group causes the EPh₃ group to serve as a nucleophile (not an electrophile).

INTRODUCTION

Elevated CO₂ concentration in the atmosphere is mostly responsible for the increase in global temperature over recent decades.¹ To this end, numerous attempts have been made to reduce the atmospheric CO₂ concentration.² One approach is to use CO₂ as a precursor for the synthesis of useful organic chemicals.³ CO₂ activation through coupling of CO₂ with a transition metal-coordinated group has also attracted wide interest and has been investigated by both theoreticians^{4,5} and experimentalists.⁶ An alternative way of decreasing the CO₂ concentration is to reduce CO₂ to CO using transition metal complexes.⁷

In this regard, the organocopper complexes supported by N-heterocyclic carbene ligands have been found to be reactive toward either activation of CO₂ or the reductive C–O scission of CO₂ (Scheme 1).^{8–12,3j,3m} For R = Me, CO₂ inserts into a Cu–R bond to give (IPrⁱ)Cu(η¹-O₂CCH₃) (IPrⁱ = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), but this never extrudes CO.¹⁰ For the cases of R = Bpin⁹ (pin = pinacolate = OCMe₂CMe₂O) and SiPh₃,¹¹ the treatment of CO₂ with (IPrⁱ)CuR gives (IPrⁱ)CuOR, with concomitant CO expulsion. Interestingly, CO₂ in the reaction with (IPrⁱ)CuR (R = SnPh₃) reduces Sn(IV) to Sn(II), forming the benzoate complex (IPrⁱ)Cu(η¹-O₂CPh) + SnPh₂.⁸

In a DFT study, the mechanism of the reduction of CO₂ to CO promoted by the model complex (NHC)CuBeg (NHC = 1,3-dimethylimidazol-2-ylidene, eg = ethyleneglycolato =

OCH₂CH₂O) was investigated by Lin and co-workers.¹² They showed that the Cu–B bond has a nucleophilic character, consequently leading the boryl group to migrate to the carbon of CO₂ and not to one of the oxygen atoms of CO₂. Then, CO is eliminated through the subsequent migration of the boryl group from carbon to oxygen to give (NHC)CuOBeg + CO. Also, in agreement with the experimental results, the calculations showed that the elimination of CO from (NHC)Cu–OC(=O)–Me is highly endothermic, with an inaccessible activation barrier of 431.8 kJ/mol.¹²

Given this background, it seems timely to examine the reaction mechanism for the reductive cleavage of CO₂ by (IPrⁱ)CuSiPh₃. Accordingly, we wish to explore why the cleavage of CO₂ by (IPrⁱ)CuSnPh₃ could not be observed experimentally. In addition, the detailed mechanism of the reaction of (IPrⁱ)CuSnPh₃ with CO₂, leading to formation of (IPrⁱ)Cu(η¹-O₂CPh) + SnPh₂, is still unclear. Bhattacharyya et al.⁸ proposed two different pathways to account for the reaction of CO₂ + (IPrⁱ)CuSnPh₃: concerted and stepwise (Scheme 2). The concerted pathway is a process involving the nucleophilic attack of one of the Sn–Ph bonds to CO₂. In the stepwise pathway, (IPrⁱ)CuSnPh₃ is surmised to be in equilibrium with (IPrⁱ)CuPh + SnPh₂. Subsequently, the intermediate (IPrⁱ)CuPh interacts with CO₂, affording (IPrⁱ)Cu(η¹-O₂CPh). In this study, we compare

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Scheme 1

the calculated potential energy surfaces of these two pathways with the aid of density functional theory (DFT). This is the first time these two pathways have been explored in detail. We will also explore why $(\text{IPr})\text{CuSiPh}_3$ is inactive toward the formation of $(\text{IPr})\text{CuPh} + \text{SiPh}_2$. In addition, the DFT calculations are employed to predict the product of the reaction between $(\text{IPr})\text{CuGePh}_3$ and CO_2 .

COMPUTATIONAL DETAILS

Gaussian 09¹³ was used to fully optimize all the structures reported in this paper at the B3LYP level^{14–16} of density functional theory. The effective core potentials of Hay and Wadt with double- ζ valence basis sets (LanL2DZ)^{17–19} were chosen to describe Cu, Sn, Ge, and Si. The 6-31G(d) basis set was used for other atoms.²⁰ Polarization functions were also added for Cu ($\zeta_d = 3.525$), Si ($\zeta_d = 0.284$), Ge ($\zeta_d = 0.230$), and Sn ($\zeta_d = 0.180$).^{21,22} This basis set combination will be referred to as BS1. Frequency calculations were carried out at the same level of theory used for structural optimization. IRC calculations were used to confirm the connectivity between transition structures and minima. To further refine the energies obtained from the B3LYP/BS1 calculations, we carried out single-point energy calculations for all the structures with a larger basis set (BS2). BS2 utilizes the quadruple- ζ valence def2-QZVP²³ basis set on Cu, Si, Ge, and Sn with the corresponding ECP on Sn and the 6-311+G(2d,p) basis set on other atoms. To estimate the corresponding Gibbs free energies, ΔG , the entropy corrections were calculated at the B3LYP/BS1 level, adjusted by the method proposed by Okuno²⁴ and finally added to the B3LYP/BS2 total energies. We have used these B3LYP/BS2//B3LYP/BS1 free energies throughout the paper unless otherwise stated. The Okuno method uses the following equations to estimate the relative enthalpies (ΔH_{liq}), entropies (ΔS_{liq}), and Gibbs free energies (ΔG_{liq}) in nonpolar solvents where R , T , and m are the gas constant, the absolute temperature, and the overall orders of reaction, respectively.

$$\Delta H_{\text{liq}} = \Delta H_{\text{gas}} - (1 - m)RT \quad (\text{a})$$

$$\Delta S_{\text{liq}} = \Delta S_{\text{gas}} + R \ln(10^{2m-2}m) \quad (\text{b})$$

$$\Delta G_{\text{liq}} = \Delta H_{\text{liq}} - T\Delta S_{\text{liq}} \quad (\text{c})$$

RESULTS AND DISCUSSION

Activation and Reduction of CO_2 through Insertion into the Cu–E Bond. The overall energy profiles for the reductive C–O scission of CO_2 using model complex $(\text{NHC})\text{CuEPh}_3$ ($\text{E} = \text{Si, Ge, Sn}$; $\text{NHC} = 1,3\text{-dimethylimidazol-2-ylidene}$) are outlined in Figure 1.²⁵ According to our calculation, the reaction

Scheme 2

starts with the approach of CO_2 to the Cu center. The presence of long distances between Cu and the oxygen atom of CO_2 in the intermediates **2E** ($\text{E} = \text{Si, Ge, Sn}$) indicates that CO_2 has only a van der Waals interaction with the Cu metal center (Figure 2). This result suggests that the Cu–E bonds are much less nucleophilic than the Cu–B π bond; the higher nucleophilicity of the Cu–B π bond results in the formation of a CO_2 π -coordinated intermediate in the reaction of $(\text{NHC})\text{CuB}\pi$ with CO_2 .¹² The next step of the reaction is surmised to be the insertion of CO_2 into the Cu–E bond. Our calculations show that the EPh_3 group in **1E** preferentially acts as a nucleophile and migrates to the carbon atom of the bound CO_2 . The attack of the EPh_3 group to CO_2 via transition structure **1E_TS** gives **3E**, which has a single Cu–O bond. **3E** can easily isomerize to the more stable intermediate **4E** via transition structure **2E_TS** (Figures 1 and 2). The barrier for this process is calculated to be very small. The higher stability of **4E** compared to **3E** can likely be explained by a steric argument. As can be seen from Figure 2, in **3E** the bulky EPh_3 group is pointing toward the $(\text{NHC})\text{Cu}$ fragment, while in **4E** the bulky group is pointing away from it. The increased steric demand is reflected in the larger angle of C1–O–Cu in **3E** than in **4E** (Figure 2).

Our systematic investigation shows that the thermodynamic feasibility of the insertion reaction $\mathbf{1E} \rightarrow \mathbf{4E}$ mainly depends on the nature of the E group; the reaction is exergonic for $\text{E} = \text{Si}$ (Figure 1a), roughly thermoneutral for $\text{E} = \text{Ge}$ (Figure 1b), and endergonic for $\text{E} = \text{Sn}$ (Figure 1c). To obtain a detailed insight into why the heavier EPh_3 groups disfavor the insertion reaction, we employed the reactions shown in eqs 1 and 2, calculated at B3LYP/BS2//B3LYP/BS1. During the course of the insertion reaction, one of the CO_2 π bonds and the Cu–E bond in **1E** are broken, while the two new bonds of $(\text{CO}_2)\text{C–E}$ and Cu–O(CO_2) in **4E** are formed. Thus, the difference between the bond strengths of Cu–E and $(\text{CO}_2)\text{C–E}$ can rationalize the trend observed in the insertion reaction energy. Through eqs 1 and 2, we can obtain an estimation of the bond strengths of Cu–E in **1E** and $(\text{CO}_2)\text{C–E}$ in **4E**. From eq 1, we can see that all three bonds of Cu–E have nearly the same strength. In contrast, our results show a decreasing trend for the bond strength of $(\text{CO}_2)\text{C–E}$, $\text{E} = \text{Si} > \text{Ge} > \text{Sn}$ (eq 2). Thus, the thermodynamic driving force for the insertion reaction is provided only by the formation of a strong $(\text{CO}_2)\text{C–E}$ bond. For instance, the reaction $\mathbf{1Sn} \rightarrow \mathbf{4Sn}$ is endothermic because the $(\text{CO}_2)\text{C–Sn}$ bond in **4Sn** is not strong enough to stabilize **4Sn** with respect to $\mathbf{1Sn} + \text{CO}_2$.

The insertion activation barrier from **1E** is $\Delta G^\ddagger = 113.0, 131.0$, and 134.3 kJ/mol for $\text{E} = \text{Si, Ge, and Sn}$, respectively (Figure 1). The lower activation barrier for $\text{E} = \text{Si}$ can be partly related to the relative stability of **3Si**. Also, the bonding of CO_2 to $(\text{NHC})\text{CuE}$

Figure 1. Energy profiles calculated for the activation and reduction of CO₂ through insertion into (a) Cu-Si, (b) Cu-Ge, and (c) Cu-Sn. The relative free energies and electronic energies (in parentheses) obtained from the B3LYP/BS2//B3LYP/BS1 calculations are given in kJ/mol.

in 1E_TS is dominated by the interaction between the HOMO of 1E, which has significant Cu-E σ character, and the CO₂ LUMO (Figure 3).¹² 1Si is more susceptible to interact with the CO₂ than 1Ge and 1Sn because 1Si has the highest lying HOMO; the HOMO energies for E = Si, Ge, and Sn are -5.1, -5.3, and -5.4 eV, respectively. In such a case an earlier transition state is anticipated for 1Si_TS than for 1Ge_TS and 1Sn_TS. The Cu-Si bond in 1Si_TS is elongated by only 0.144 Å from 1Si. A larger elongation is calculated for the bonds of Cu-Ge (0.211 Å) and Cu-Sn (0.212 Å), which further supports the argument that 1Si_TS is an earlier transition state than 1Ge_TS and 1Sn_TS.

Figure 2. Calculated structures for species **1E**, **2E**, **1E_TS**, **3E**, **4E**, **3E_TS**, and **5E** ($E = \text{Si, Ge, Sn}$). Selected structural parameters are given in Å and deg. Data for $E = \text{Si}$ are in plain text, for $E = \text{Ge}$ in italics, and for $E = \text{Sn}$ in bold.

After activation of CO_2 , the reduction of CO_2 to CO can occur via the migration of the EPh_3 group from carbon to the Cu-bound oxygen atom through transition structure **3E_TS**. The overall reaction $\mathbf{1E} + \text{CO}_2 \rightarrow \mathbf{5E} + \text{CO}$ is highly exergonic for $E = \text{Si}$ (Figure 1a), nearly thermoneutral for $E = \text{Ge}$ (Figure 1b), and extremely endergonic for $E = \text{Sn}$ (Figure 1c). This result is a direct reflection of the bond energy of $\text{E}-\text{O}$ in **5E**. As shown in eq 3, the $\text{E}-\text{O}$ bond becomes weaker as the E group becomes heavier. The activation barrier relative to **4E** increases in the order $E = \text{Si}$ (102.9) < Sn (120.1) < Ge (146.4) (kJ/mol). The calculated activation barrier of 102.9 kJ/mol for $E = \text{Si}$ can be compared to the value experimentally measured by Laitar ($\Delta H^\ddagger = 87.9 \pm 3.3$ kJ/mol).¹¹ The lower activation barrier for the case of $E = \text{Si}$ can be attributed

to the high exergonicity of the reaction $4\text{Si} \rightarrow 5\text{Si} + \text{CO}$ ($\Delta G = -87.0$ kJ/mol). The hypervalency of the E groups can also play an important role in stabilizing the transition structure **3E_TS**. The smaller activation barrier for $E = \text{Sn}$, as compared to that of $E = \text{Ge}$, can be explained in terms of the stronger Lewis acidity of Sn . The Lewis acidity of group 14 compounds increases upon going from Si to Sn .^{26,27} The geometry around the E atom in **3E_TS** can be described as a highly distorted trigonal bipyramid with two Ph groups and one oxygen atom at the equatorial positions (**3E_TS** in Figure 2). A comparison of the structural parameters of **4E**, **3E_TS**, and **5E** shows that, due to the hypervalency of the E atoms, in transition structure **3E_TS** the $\text{E}-\text{C}$ bonds are slightly weakened, while the $\text{E}-\text{O}$ bonds are nearly completely formed (Figure 2). In contrast, Lin et al. showed that the absence of the hypervalency of the carbon atom causes the Me migration in the reaction of $\text{LCu}-\text{O}-\text{C}(\text{O})-\text{Me} \rightarrow \text{LCu}-\text{O}-\text{Me} + \text{CO}$ to occur with an activation barrier as high as 433.5 kJ/mol.¹² The high barrier calculated for the Me migration was attributed to the weak interaction of the Me group with both the oxygen and carbon atoms in the transition structure; in the transition structure for the Me migration, the $\text{Me}-\text{C}$ bond (2.117 Å) is 0.596 Å longer than that (1.521 Å) in

Figure 3. Contour plots showing (a) the HOMO for **1E**, (b) the LUMO for CO_2 , and (c) the HOMO for **1E**_TS.

Figure 4. Profiles relevant to the energetics of the interconversion of **3E** $\rightarrow$ **6E** for (a) $E = \text{Si}$ and (b) $E = \text{Ge}$, and the conversion of **1E** + $\text{CO}_2 \rightarrow$ **6E** (c) for $E = \text{Sn}$. The relative free energies and electronic energies (in parentheses) obtained from the B3LYP/BS2//B3LYP/BS1 calculations are given in kJ/mol.

$\text{LCu}-\text{O}-\text{C}(\text{O})-\text{Me}$ and the $\text{Me}-\text{O}$ bond ($1.867 \text{ \AA}$) is $0.485 \text{ \AA}$ longer than that ($1.382 \text{ \AA}$) in $\text{LCu}-\text{O}-\text{Me}$.¹²

In summary, our calculations show that the activation and reduction of CO_2 by insertion into $\text{Cu}-\text{SiPh}_3$ is possible in terms of both the activation energy and relative energies of the reactants and products. Calculations predict that, in accordance with experiment, the rate-limiting step in this process is the insertion of CO_2 into the $\text{Cu}-\text{Si}$ bond; the activation barrier for the reaction $\mathbf{1Si} + \text{CO}_2 \rightarrow \mathbf{3Si}$ (113.0 kJ/mol) is higher in energy than the reaction $\mathbf{4Si} \rightarrow \mathbf{5Si} + \text{CO}$ (102.9 kJ/mol) by 10.0 kJ/mol . For $E = \text{Sn}$, the sequence $\mathbf{1E} \rightarrow \mathbf{4E} \rightarrow \mathbf{5E}$ occurs with a significant barrier and a high endothermicity, indicating that $(\text{NHC})\text{Cu}(\text{SnPh}_3)$ is not capable of activating and cleaving CO_2 through the insertion reaction into the $\text{Cu}-\text{Sn}$ bond. For $E = \text{GePh}_3$, the lesser stability of $\mathbf{5Ge} + \text{CO}$ and $\mathbf{3Ge}$ relative to

$\mathbf{1Ge} + \text{CO}_2$ and the very high barrier calculated for $\mathbf{3Ge_TS}$ predict that $\mathbf{3Ge}$ and $\mathbf{5Ge}$ should be present only under very severe reaction conditions and even then in only small concentrations.

Migration of EPh_3 to One of the Oxygen Atoms of CO_2 . For the case of $E = \text{Sn}$, the transition structure $\mathbf{4'Sn_TS}$ connecting $\mathbf{1Sn}$ to $\mathbf{6Sn}$ lies 27.6 kJ/mol higher in energy than the transition structure $\mathbf{1Sn_TS}$ connecting $\mathbf{1Sn}$ to $\mathbf{3Sn}$ (see Figures 4c and 1c). For the cases of $E = \text{Ge}$ and Si , all efforts to locate a transition structure for the EPh_3 migration to one of the oxygen atoms of CO_2 failed and led to the formation of transition structure $\mathbf{4'E_TS}$ (Figure 4). The IRC calculations show that $\mathbf{4'E_TS}$ connects $\mathbf{3E}$ to $\mathbf{6E}$.¹² These results suggest that the direct migration of EPh_3 to one of the oxygen atoms of CO_2 is less favorable than the migration of EPh_3 to the carbon atom of CO_2 .

The formation of **6Si** from **1Si** is exergonic (-48.1 kJ/mol) and requires a large activation energy (132.2 kJ/mol, Figure 4a). The higher energy of transition structure **4Si_TS** compared to **3Si_TS** suggests that the reaction $\mathbf{1Si} + \text{CO}_2 \rightarrow \mathbf{6Si}$ is unlikely to occur. The DFT calculation also predicts that the formation of **6Ge** and **6Sn** should be impossible from both kinetic and thermodynamic points of view (Figure 4b and c).

Mechanism of the CO₂ Insertion into the Cu–E Bond. To understand why the E group preferentially migrates to the carbon atom of CO₂, the NBO population analyses for species **1E** and **1E_TS** were investigated. The NBO charge on E in **1Si**, **1Ge**, and **1Sn** is calculated to be -0.458 , -0.434 , and -0.364 , respectively. This indicates that the electron-releasing capability of the Cu(I) fragment is higher than the EPh₃ group, polarizing the

electron density toward the EPh₃ group, causing it to serve as a nucleophile (not an electrophile).²⁸ The higher electron-releasing capability of the Cu(I) fragment can be explained in terms of the orbital energies in that the energy of the singly occupied molecular orbital (SOMO) of (NHC)Cu[•] (-2.9 eV) lies much higher in energy than that of the [•]EPh₃ radicals; the calculated SOMO energies for [•]SiPh₃, [•]GePh₃, and [•]SnPh₃ are -4.7 , -4.9 , and -5.1 eV, respectively.

In the insertion transition structure **1E_TS**, the NBO population of the EPh₃ group is reduced to -0.034 , $+0.011$, and $+0.065$ for E = Si, Ge, and Sn, respectively. The NBO population of CO₂ changes from zero, in the free species, to -0.575 in **1Si_TS**, -0.626 in **1Ge_TS**, and -0.655 in **1Sn_TS**. The charge on (NHC)Cu is less positive in **1E** than in **1E_TS**: $+0.458$ in **1Si** vs $+0.609$ in **1Si_TS**, $+0.434$ in **1Ge** vs $+0.614$ in **1Ge_TS**, $+0.364$ in **1Sn** vs $+0.590$ in **1Sn_TS**. This means that the charge transfer process occurs from the EPh₃ groups to CO₂ by receiving electron population from the Cu fragment. A similar situation for charge transfer was proposed by Sakaki et al. for the insertion of CO₂ into Cu–CH₃ and Cu–H bonds.^{5d} If the EPh₃ group migrates to one of the oxygen atoms of CO₂, the charge transfer should occur in the opposite direction, that is, from Cu to CO₂, by receiving electron density from EPh₃. Such a process is electronically unfavorable because the electron-releasing capability of the Cu(I) fragment is higher than the EPh₃ group (Scheme 3a).

To further support the argument above, we also investigated the CO₂ insertion into the Pd–Sn bond of the model complex *cis*-Pd(PH₃)₂(Me)(SnPh₃) (**1Pd**). Unlike (NHC)CuSnPh₃, **1Pd** preferentially undergoes the insertion reaction through the SnPh₃

Scheme 3

Figure 5. Comparison of the energy profiles of the concerted and stepwise mechanisms for the activation of CO₂ through nucleophilic attack of a Ph group of SnPh₃. The relative free energies and electronic energies (in parentheses) obtained from the B3LYP/BS2//B3LYP/BS1 calculations are given in kJ/mol.

Scheme 4

migration into one of the oxygen atoms of CO₂ (Scheme 4). Our calculations show that, regardless of the type of mechanism,²⁹ the CO₂ insertion pathways that lead to the formation of the Pd-C(O)-O-Sn linkage (pathways 1 and 4) have barriers considerably lower than the CO₂ insertion pathways giving the Pd-O-C(O)-Sn linkage (pathways 2 and 3). Unlike in (NHC)CuSnPh₃, the NBO charge carried by SnPh₃ in *cis*-Pd(PH₃)₂(Me)(SnPh₃) is positive (+0.146), implying that the electron-releasing capability of the *cis*-(PH₃)₂(Me)Pd is poorer than the (NHC)Cu fragment. The SOMO energy for the *cis*-(PH₃)₂(Me)Pd* fragment is calculated to be -4.5 eV. In such a case, the Pd-Sn bond can be easily polarized toward Pd, enhancing the oxophilicity of the Sn center, thus favoring the SnPh₃ migration into one of the oxygen atoms of CO₂ (Scheme 3b).

Activation of CO₂ through Nucleophilic Attack of a Ph Group of SnPh₃. Now we turn our attention to the reaction leading to activation of CO₂ through the migration of a Ph group from SnPh₃ to CO₂. As mentioned in the Introduction, two major mechanistic possibilities were proposed for this reaction (Scheme 2): concerted and stepwise. Here, both possible reaction mechanisms are computationally investigated (Figure 5).

In the concerted pathway, a Ph group from SnPh₃ is transferred via transition structure **5Sn_TS** to CO₂, affording intermediate **7Sn**. Then, product **8** is formed by dissociation of SnPh₂ from **7Sn**. The reaction of CO₂ + (NHC)CuSnPh₃ → (NHC)Cu(η¹-O₂CPh) + SnPh₂ is calculated to be very slightly exergonic, the products lying 0.4 kJ/mol below the reactants (Figure 5).³⁰

The stepwise pathway starts with α-phenyl elimination through the transition structure **6Sn_TS** and leads to the formation of the intermediate **9Sn**. This intermediate is 56.1 kJ/mol higher in energy than **1Sn**. **9Sn** subsequently undergoes Cu-SnPh₂ bond dissociation to produce **10**. CO₂ can now insert into the Cu-Ph bond to give product **8**. The insertion step is predicted to be rate determining for the stepwise pathway with an activation free energy of 158.2 kJ/mol. Our calculations also showed that the CO₂ insertion into the Cu-Ph bond of **9Sn** is energetically less favorable than that of **8**; **7Sn_TS** is 23.4 kJ/mol higher in energy than **8_TS** (Figure 5).

Comparing the two calculated energy profiles shown in Figure 5, it is obvious that the relative energy surface for the concerted pathway is kinetically more favorable than the stepwise pathway. Given the potential for functional dependence in the prediction of bond energies, the energies of the highest points on the concerted and stepwise pathways were calculated by using different functionals (B97D,³¹ M06,³² BP86,³³ PBE1PBE,³⁴ and MP2³⁵), as shown in Table 1. All the calculations are unanimous

Table 1. Comparison of the Energies of the Highest Points on the Concerted and Stepwise Pathways Using Different Functionals (kJ/mol)

method	5Sn_TS	8_TS
B97D	97.5 (59.4)	155.6 (158.6)
M06	109.2 (71.1)	173.2 (176.1)
BP86	119.7 (81.6)	144.8 (147.7)
PBE1PBE	121.8 (82.4)	171.1 (174.1)
MP2	104.2 (66.1)	222.2 (225.1)

in favoring the concerted mechanism over the alternative stepwise mechanism.

Activation of CO₂ through Nucleophilic Attack of a Ph Group of SiPh₃ and GePh₃. The results of the calculations for the concerted pathway³⁶ show that the Ph migration from SiPh₃ and GePh₃ occurs with higher barriers than from SnPh₃ (Figure 6). The activation barrier was found to follow the order E = Sn < Ge < Si. The migration reaction was also found to be endergonic for both E = Si and Ge (Figure 6). The reaction is most endergonic for E = Si with the product **8** + SiPh₂ lying 110.9 kJ/mol above the reactants **1Si** + CO₂. The product for E = Ge (**8** + GePh₂) lies 52.7 kJ/mol above **1Ge** + CO₂. From these results we can conclude that **1Ge** and **1Si** are not capable of undergoing the Ph migration reaction. In other words, the reactions **1Ge** + CO₂ → **8** + GePh₂ and **1Si** + CO₂ → **8** + SiPh₂ are unlikely to occur.

The activation barrier associated with the Ph migration from EPh₃ to CO₂ follows the trends in thermodynamics. The pattern computed for the thermodynamic and kinetic data of the Ph migration correlates well with the strength of the E-Ph bond in the EPh₃ fragment. The E-Ph bond strength was found to decrease as the size of E increases (eq 4). The weaker the E-Ph bond, the stronger the driving force for the reaction of **1E** + CO₂ → **8** + EPh₂. In addition, the differences in the reactivity of **1E** toward the Ph migration reaction can also be explained in terms of the Cu-E bond strengths. Since the nucleophilic attack of a Ph group of EPh₃ to CO₂ results in significant weakening of the Cu-E bond in **7E**, the **1E** complex having the weaker Cu-E bond is able to undergo the Ph migration reaction more successfully. Thus, another driving force for the favorability of the reaction of **1Sn** + CO₂ → **8** + SnPh₂ over the analogous reactions for the lighter elements is the weaker Cu-Sn bond in **1Sn**. The nucleophilicity of the Ph groups in the **1E** complexes can be attributed to the ionic character of the E-Ph bonds; the

Figure 6. Energy profiles calculated for the activation of CO₂ through nucleophilic attack of a Ph group of (a) GePh₃ and (b) SiPh₃. The relative free energies and electronic energies (in parentheses) obtained from the B3LYP/BS2//B3LYP/BS1 calculations are given in kJ/mol.

NBO population on a Ph ring of **1E** is calculated to be -0.485 , -0.480 , and -0.523 for E = Si, Ge, and Sn, respectively.

$\cdot\text{EPh}_3 \xrightarrow{\Delta E_4} \cdot\text{Ph} + \text{EPh}_2$	(4)		
E	Si	Ge	Sn
ΔE_4 (kJ/mol)	283.7	220.1	166.9

CONCLUSIONS

Density functional theory was applied to investigate the mechanism of the activating and cleaving of CO₂ by the complexes (NHC)CuEPh₃ (E = Si, Ge, Sn). The results show that both the Cu–E and E–C(Ph) bonds play a role in the activating and cleaving of CO₂.

The reactivity of the Cu–E bond toward the activation and cleavage of CO₂ decreases as E becomes heavier. The Cu–E interaction with CO₂ is via a shift in electron density from Cu to EPh₃, which in turn is transferred to the carbon of incoming CO₂, forming a C–E bond. It is the strength of this bond that controls the energetics of the CO₂ insertion reaction. If E becomes heavier (as in Ge or Sn), the newly formed C–E bond strength decreases and hence the thermodynamic driving force necessary for the insertion reaction decreases. Elimination of CO, after CO₂ insertion, follows the same pattern, except here it is the E–O bond strength that becomes relevant.

The E–C(Ph) bond was found to have the reverse trend in reactivity toward CO₂ activation; that is, the reactivity of the E–C(Ph) bond toward CO₂ activation increases as E becomes heavier. Again this trend can be rationalized in terms of bond strengths. The weaker the E–C(Ph) bond, the more easily the bond interacts with CO₂. Our calculations also showed that the

concerted pathway for CO₂ activation by the Sn–C(Ph) bond of (NHC)CuSnPh₃ is kinetically more favorable than the stepwise pathway.

The higher electron-releasing capability of (NHC)Cu compared to the EPh₃ group causes the EPh₃ group to serve as a nucleophile (not an electrophile). An opposite trend was observed for the *cis*-Pd(PH₃)₂(Me)(SnPh₃) structure. The low electron-releasing capability of the *cis*-Pd(PH₃)₂(Me) fragment increases the oxophilicity of Sn, resulting in the migration of SnPh₃ onto one of the oxygen atoms of CO₂.

ASSOCIATED CONTENT

S Supporting Information. Total energies and Cartesian coordinates of all structures, complete ref 13, and a detailed discussion of the mechanism of CO₂ insertion into the Pd–Sn bond. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (26) The heavier E centers give lower lying unoccupied orbitals in $\cdot\text{ER}_3$; for example, the LUMO energy in $\cdot\text{EMe}_3$ is calculated to be 0.057, 0.053, and -0.033 eV for E = Si, Ge, and Sn, respectively. Therefore, the stronger Lewis acidity of the heavier group 14 compounds can be related to the lower lying unoccupied orbitals, mainly located on the E center.
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- (28) As stated in the text, the CO₂ insertion into the Cu–E bond of **1E** is promoted by the interaction of the HOMO of **1E** and the CO₂ LUMO. It is expected that the observed regioselectivity of the CO₂ insertion can be explained by the larger contribution of the EPH₃ orbital to the HOMO of **1E**. Although this is the case for E = Si and Ge, it does not hold true for E = Sn. The calculations carried out with the AOMix program showed that the percentage contribution of Cu and E in the HOMO of **1E** is 26.1% and 30.9% for E = Si, 24.5% and 30.2% for E = Ge, and 29.0% and 26.4% for E = Sn. Therefore, the regioselectivity for the CO₂ insertion can be explained more reasonably by the charge distribution calculated in **1E**. For AOMix see: Gorelsky, S. I. *AOMix: Program for Molecular Orbital Analysis*; York University: Toronto, Canada, 1997; <http://www.sf-chem.net/>.
- (29) For the CO₂ insertion into the Pd–Sn bond, two different mechanisms, direct and dissociative, were considered. In the direct mechanism, CO₂ inserts directly into the Pd–Sn bond of *cis*-Pd(PH₃)₂–(Me)(SnPh₃). In the dissociative mechanism, one of the PH₃ ligands in the Pd complex is substituted by CO₂ followed by CO₂ insertion and subsequent PH₃ recoordination. Of the pathways investigated, pathway 4 is the most favorable. In pathway 4, the approach of CO₂ to the Pd complex leads to a strong donation of electron density from the filled d_{z²} orbital of palladium to the π^* orbital of CO₂. This interaction that leads to the formation of the Pd–C(CO₂) bond is accompanied by the coordination of one of the oxygen atoms of CO₂ to the hypervalent Sn center. As a result, the favorability for the formation of the Pd–C(O)–O–Sn linkage over the Pd–O–C(O)–Sn linkage can be mainly attributed to the stronger electron-releasing capability of SnPh₃ relative to the Pd fragment as well as to the hypervalency of the Sn center. A more detailed picture for the CO₂ insertion into the Pd–Sn bond is given in the Supporting Information.

(30) The low exergonicity calculated for the reaction of $\text{CO}_2 + (\text{NHC})\text{CuSnPh}_3 \rightarrow (\text{NHC})\text{Cu}(\eta^1\text{-O}_2\text{CPh}) + \text{SnPh}_2$ suggests that this reaction should be in equilibrium, a result that is not consistent with the high yield observed experimentally (90%) (see ref 8). This apparent inconsistency can be related to the experimental final product composition, which is ambiguous based on the SnPh_2 moiety. The formation of an unknown compound produced from the SnPh_2 moiety most likely provides the additional driving force behind the high yield.

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(36) Similar to the case for $\text{E} = \text{Sn}$, the stepwise pathway for $\text{E} = \text{Si}$ and Ge is calculated to be less favorable than the concerted pathway; the energy of 8_TS is 269.6 (277.3) and 211.5 (218.1) kJ/mol for $\text{E} = \text{Si}$ and Ge , respectively.