Theoretical Studies on Coupling Reactions of Carbon Dioxide with Alkynes Mediated by Nickel(0) Complexes

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A computational study with the Becke3LYP DFT functional theory was carried out on Ni(0)-mediated coupling reactions of both terminal and internal alkynes with CO_2. We studied the mechanism for the formation of the five-membered metallacyclic intermediates in order to understand the regioselectivity. The steric and electronic factors that determine the regioselectivity have been discussed. The calculations indicate that electronic factors nicely explain the trend observed in the barriers calculated for the coupling reactions of CO_2 with the three terminal alkyne substrates having substituents with different electronic properties, but steric factors are dominant in the regioselectivity for the reaction of a given terminal alkyne substrate. For silyl-substituted internal alkynes, both electronic and steric effects favor the formation of compounds in which CO_2 couples with the silyl-substituted carbon.

Introduction

Carbon dioxide has been recognized as a greenhouse gas causing global warming. An effective chemical solution is to use it as a starting material in syntheses of new chemical products. Despite its chemical inertness, CO_2 can be transformed into other organic compounds mediated by various transition metals that are able to activate CO_2, resulting in the formation of new C−C, C−N, C−O, or C−H bonds.[1–5] Oxidative coupling of CO_2 and an unsaturated compound at a transition-metal center, one key step in CO_2 coupling reactions, has received much attention.

Reactions of alkenes and alkynes with carbon dioxide mediated by Ni(0) complexes were reported by Hoberg et al. as early as 1982.[6] Recent studies on the coupling reactions of terminal alkynes showed interesting regioselectivity. For example, reactions of terminal alkynes with CO_2, mediated by $Ni(DBU)_2$ complexes (DBU = diazabicycloundecene), give a mixture of α,*β*-unsaturated carboxylic acids (**III** + **IV**) with **IV** as the major products via the intermediate **II** (eq 1).[7] The preference for **IV** as the major products was also observed in the Ni(0) phosphine complex catalyzed cycloaddition of ethoxyethyne with CO_2.[8–10] The same regioselectivity was again seen when the cycloaddition reactions were expanded to involve an additional carbon−carbon bond formation via the addition of an organozinc reagent.[11] Interestingly, when 2,2′-bipyridine was used as the ligand, the expanded cycloaddition reactions did not take place.[7] It should be noted here that when electrode reactions were carried out using nickel(II), the opposite regioselectivity was reported and 2,2′-bipyridine was found as a good ligand.[12] In the electrode reactions, much more complicated reaction mechanisms are expected, and therefore, the mechanistic aspect is beyond the scope of the current study.

Various silyl-substituted internal alkynes reacted with Me_2Zn under CO_2 in the presence of a catalytic amount of $Ni(cod)_2$ to afford a variety of tetrasubstituted alkenes **VII** and **VIII** via oxanickelacyclopentenes **V** and **VI**, respectively, in good yields (eq 2).[13] In these reactions, the compounds **VIII**, where the carboxyl and TMS (TMS = $SiMe_3$) substituents are at the same carbon, are more favorably formed (eq 2).

In this paper, we are interested in understanding the regioselectivity observed in the Ni(0)-mediated coupling reactions of both terminal and internal alkynes with CO_2 summarized above. We will also address the question why a 2,2′-bipyridine ligand does not promote the reactions. We sought to study the reaction mechanism by employing density functional theory calculations

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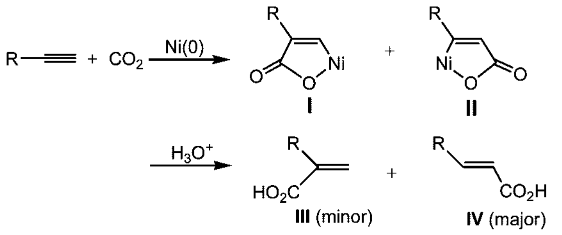
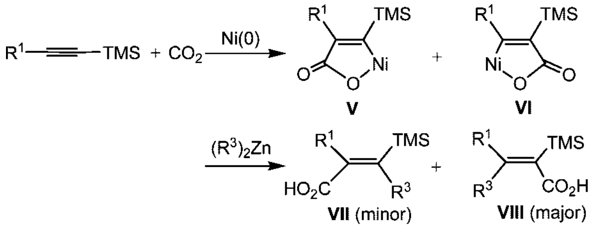


(1)

R = Ph, 4-MeOPh, 4-CF_3Ph, t-Bu, TMS, n-Hex



(2)

R^1 = $PhCH_2CH_2$, $BnOCH_2CH_2$, $BnOCH_2CH_2CH_2$, $BnOCH_2$, n-Hex

and hope that the insight provided through this study will help the effort in activating CO_2.

It should be noted here that in the past few years there have also been a few theoretical studies on transition-metal-mediated coupling reactions involving CO_2. For example, the mechanisms of metal-assisted CO_2/C_2H_4 reactions were recently studied by means of density functional calculations.[1,14–16] Ni(PH_3)-mediated coupling reaction of acetylene with carbon dioxide was investigated with the SD-CI method.[17,18] Using HC≡C(OH) and HC≡CMe as the model substrates and Ni(PH_3) as the metal fragment, Sakaki and co-workers studied the regioselectivity of the coupling reactions of terminal alkynes with CO_2.[17,18]

Computational Details

Molecular geometries of the complexes were optimized at the Becke3LYP level of density functional theory.[19] Frequency calculations at the same level of theory were also performed to identify all the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency) and to provide free energies at 298.15 K. Intrinsic reaction coordinate (IRC)[20] analysis was carried out to confirm that all stationary points are smoothly connected to each other. The Ni atom was described using the LANL2DZ basis set including a double-ζ valence basis set with the Hay and Wadt effective core potential (ECP).[21] The 6-31G* basis set[22] was used for the atoms in CO_2 and all of the alkyne substrates except MeC≡CSiMe$_3$ and for the N atoms coordinated to Ni in the DBU ligands. In MeC≡CSiMe$_3$, 6-31G was used for the three Me groups at Si and 6-31G* for the remaining atoms of the substrate. The The 6-31G basis set was used for all other atoms. Molecular orbitals obtained from the B3LYP calculations were plotted using the Molden 3.7 program written by Schaftenaar.[23] Partial atomic charges were calculated on the basis of natural bond orbital (NBO) analyses.[24] All calculations were performed with Gaussian 03 packages.[25]

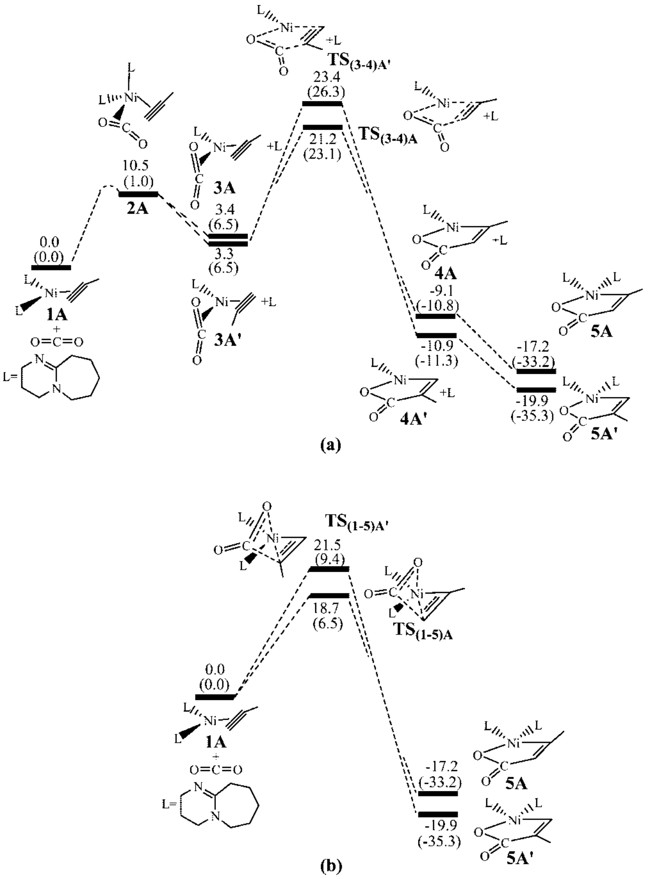


Figure 1. Energy profiles calculated for the coupling reaction of CO_2 with NiL_2(HC≡CMe) (L = DBU) via dissociative (a) and associative (b) pathways. The relative free energies (kcal/mol) and electronic energies (kcal/mol, in parentheses) are given.

Results and Discussion

Dissociative versus Associative Mechanism for the Coupling of Ni(DBU)$_2$(HC≡CMe) with CO_2. As mentioned in the Introduction, this paper mainly concerns the regioselectivity in Ni(0)-mediated coupling reactions of alkynes with CO_2. The crucial step that affects the regioselectivity is expected to be the coupling of a Ni(0)-alkyne species with CO_2 to give a five-membered metallacyclic intermediate as shown in eq 1. Therefore, we studied this step in detail in order to understand the regioselectivity summarized in the Introduction.

We first examined the coupling of Ni(DBU)$_2$(HC≡CMe) with CO_2, a reaction studied experimentally by Yamamoto and his co-workers.[7] Both the dissociative and associative mechanisms for the coupling reaction were calculated. The energy profiles are shown in Figure 1. In the figure, the relative free energies

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Table 1. Relative Free Energies (kcal/mol) of the Transition States in the Dissociative ($TS_{(3-4)}$) and Associative ($TS_{(1-5)}$) Mechanisms Calculated for the Coupling Reactions of CO_2 with $NiL_2(HC{\equiv}CX)$ (1: L = DBU; X = Me (A), CN (B), OMe (C))

	1 + CO_2	$TS_{(3-4)X}$ + L	$TS_{(3-4)X'}$ + L	$TS_{(1-5)X}$	$TS_{(1-5)X'}$
X = **A**	0.0	21.2	23.4	18.7	21.5
X = **B**	0.0	31.5	37.7	25.3	29.8
X = **C**	0.0	20.3	29.7	17.1	25.4

(ΔG) and electronic energies (ΔE, in parentheses) are given. Taking into account the effect of entropy, we use the free energies rather than the electronic energies for our discussion, since the reactions studied here involve gaseous molecules.

In the dissociative mechanism (Figure 1a), CO_2 first coordinates to the Ni center of $Ni(DBU)_2(HC{\equiv}CMe)$ to form the intermediate **2A**. $Ni(DBU)_2(HC{\equiv}CMe)$ is a 16e species and is therefore capable of taking one more ligand, CO_2 in this case, to form the η^2-O=C(O) intermediate **2A**. We were not able to locate the transition state connecting **1A** + CO_2 and **2A**, likely due to the fact that the barrier for the process, especially the reverse process, is very small. A relaxed potential energy surface scan along the Ni—C(CO_2) reaction coordinate indeed suggests that the barrier for the reverse process should be very small. Dissociation of one DBU ligand from the intermediate **2A** gives **3A** or **3A′**. Both **3A** and **3A′** can be considered as the precursor complexes for oxidative coupling of the CO_2 and HC≡CMe ligands. The oxidative couplings in **3A** and **3A′**, followed by recoordination of a DBU ligand, give the five-membered metallacyclic complexes **5A** and **5A′**, respectively, through the transiton states $\mathbf{TS_{(3-4)A}}$ and $\mathbf{TS_{(3-4)A'}}$. The overall free energy barriers for the formation of **5A** and **5A′** were calculated to be 21.2 and 23.4 kcal/mol, respectively. Figure 1a shows that **5A** is kinetically preferred over **5A′**, consistent with the regioselectivity observed experimentally.[7] **5A** and **5A′** are much more stable than the reactants **1A** + CO_2, implying that the formation of the five-membered metallacyclic complexes is irreversible. Therefore, the regioselectivity is kinetically controlled in this case.

In the associative mechanism, CO_2 directly attacks at the coordinated HC≡CMe. Interestingly, the overall free energy barriers for the formation of **5A** and **5A′** were calculated to be 18.7 and 21.5 kcal/mol, respectively: lower than those calculated for the dissociative mechanism. Again, **5A** is kinetically preferred over **5A′**. The results are also consistent with the regioselectivity observed experimentally.[7]

The results discussed above for the substrate HC≡CMe indicate that the associative mechanism is preferred. To examine if different substrates affect the preferred reaction mechanism, we studied the coupling reactions of the substrates HC≡CCN (**B**) and HC≡COMe (**C**). We calculated the relative free energies of the transition states in the two mechanisms discussed above, shown in Table 1. For the two substrates, the associative mechanism is still preferred. These results indicate that the preferred reaction mechanism is not substrate-dependent.

The reason that the associative mechanism is more favorable than the dissociative one can be explained as follows. As we will show later, in the coupling process, CO_2 attacks electrophilically one π bond of the coordinated alkyne substrate. In comparison with the dissociative mechanism, the associative mechanism has one more ligand in the transition state, making the coordinated alkyne substrate more electron-rich and promoting the electrophilic attack.

Factors That Affect the Regioselectivity. To study the factors that affect the regioselectivity, we consider the associative mechanism that is preferred for the coupling reactions. As mentioned in the Introduction, for reactions of terminal alkynes, CO_2 preferentially couples with the terminal carbon atom. The results of calculations on the three model substrates HC≡CMe, HC≡COMe, and HC≡CCN are consistent with the experimental observations. Figure 2 shows the energy profiles calculated for the coupling reactions of CO_2 with $NiL_2(HC{\equiv}CX)$ (L = DBU; X = Me (**A**), CN (**B**), OMe (**C**)). The five-membered metallacyclic complexes **5A**—**C**, in which CO_2 couples with the substrate terminal carbon, are preferentially formed. **5A** is kinetically preferred, while **5B**,**C** are both kinetically and thermodynamically preferred (Figure 2).

It is interesting to note that the couplings of CO_2 with three different substrates show the same regioselectivity, despite the fact they are very different in terms of their electronic properties. To understand this interesting result, we examine the transition-state structures calculated for the coupling reactions, shown in Figure 3. $\mathbf{TS_{(1-5)A}}$, $\mathbf{TS_{(1-5)B}}$, and $\mathbf{TS_{(1-5)C}}$ represent the transition states leading to the (kinetically) preferentially formed five-membered metallacyclic complexes **5A**—**C**, respectively, while $\mathbf{TS_{(1-5)A'}}$, $\mathbf{TS_{(1-5)B'}}$, and $\mathbf{TS_{(1-5)C'}}$ are the transition states leading to the formation of the five-membered metallacyclic complexes **5A′**—**C′**, respectively (structures for **5A**—**C** and **5A′**—**C′** are given in Figure 4). A common special structural feature can be found from examination of the transition-state structures shown in Figure 3. In the transition states, CO_2 approaches the coordinated alkyne from a direction out of the Ni—η^2-alkyne bonding plane. This special structural feature suggests that the $\pi_\perp$ orbital of the coordinated alkyne is likely to play the role during the oxidative coupling between CO_2 and the coordinated alkyne ligand. In view of the fact that the CO_2 carbon is an electron-deficient center, we can conveniently deduce that, in

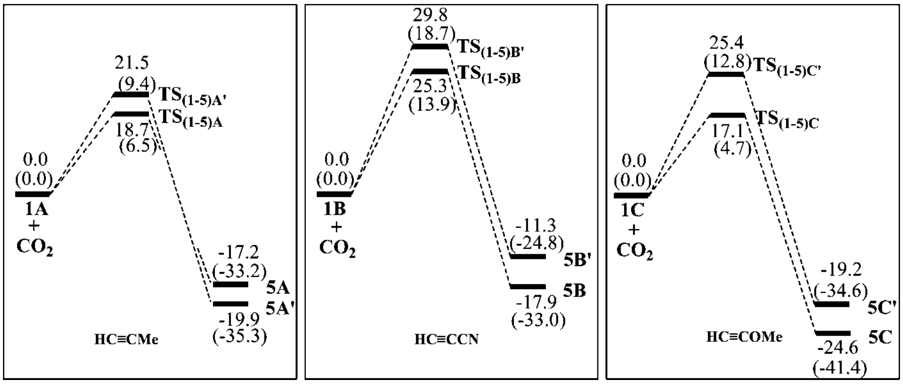
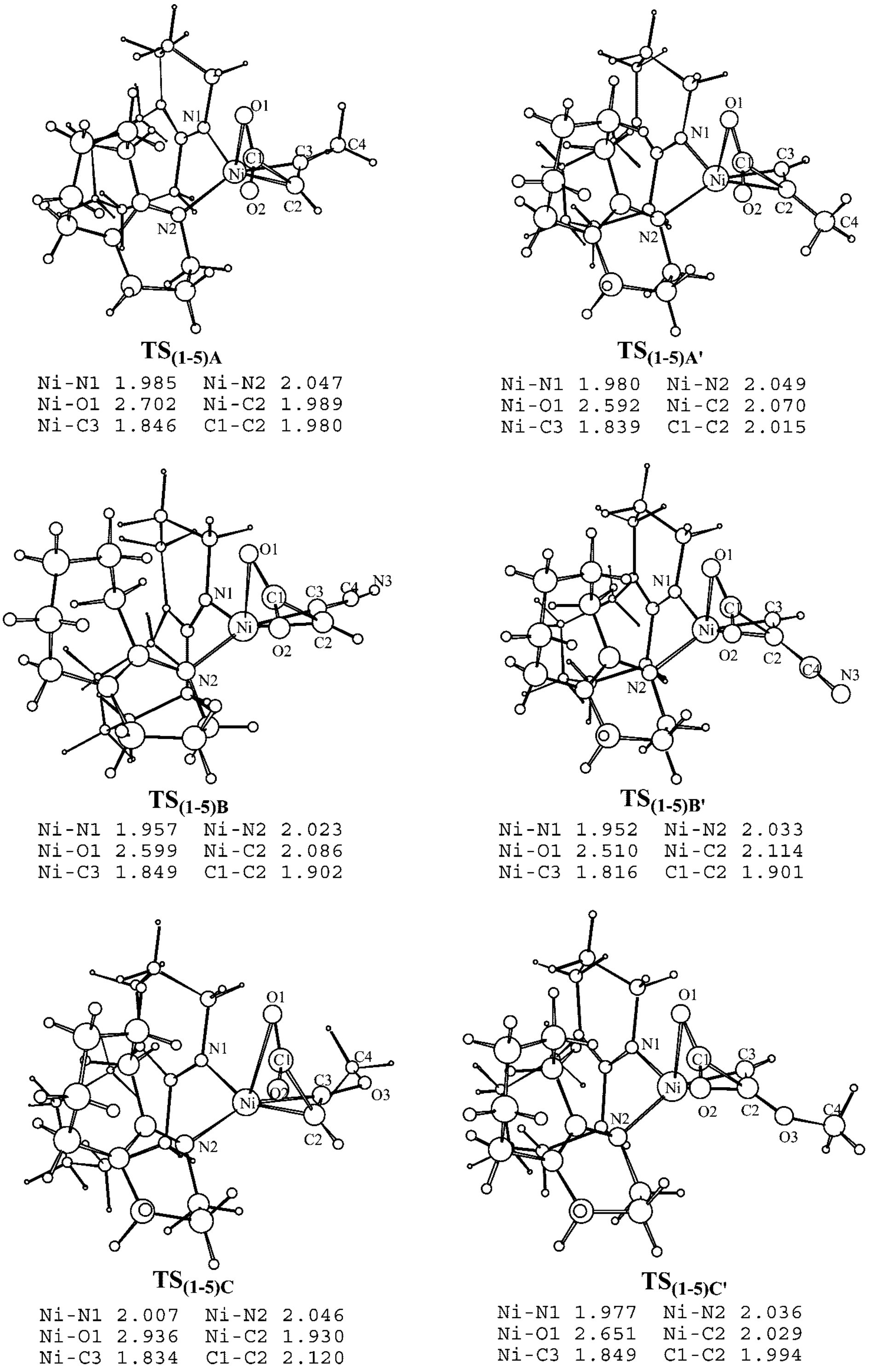


Figure 2. Energy profiles calculated for the coupling reactions of CO_2 with $NiL_2(HC{\equiv}CX)$ (L = DBU; X = Me (**A**), CN (**B**), OMe (**C**)) in an associative mechanism. The calculated relative free energies and electronic energies (in parentheses) are given in kcal/mol.



$TS_{(1-5)A}$
Ni-N1 1.985 Ni-N2 2.047
Ni-O1 2.702 Ni-C2 1.989
Ni-C3 1.846 C1-C2 1.980

$TS_{(1-5)A'}$
Ni-N1 1.980 Ni-N2 2.049
Ni-O1 2.592 Ni-C2 2.070
Ni-C3 1.839 C1-C2 2.015

$TS_{(1-5)B}$
Ni-N1 1.957 Ni-N2 2.023
Ni-O1 2.599 Ni-C2 2.086
Ni-C3 1.849 C1-C2 1.902

$TS_{(1-5)B'}$
Ni-N1 1.952 Ni-N2 2.033
Ni-O1 2.510 Ni-C2 2.114
Ni-C3 1.816 C1-C2 1.901

$TS_{(1-5)C}$
Ni-N1 2.007 Ni-N2 2.046
Ni-O1 2.936 Ni-C2 1.930
Ni-C3 1.834 C1-C2 2.120

$TS_{(1-5)C'}$
Ni-N1 1.977 Ni-N2 2.036
Ni-O1 2.651 Ni-C2 2.029
Ni-C3 1.849 C1-C2 1.994

Figure 3. Transition-state structures calculated for the coupling reactions of CO_2 with $NiL_2(HC{\equiv}CX)$ (L = DBU; X = Me (**A**), CN (**B**), OMe (**C**)). Selected bond distances are given in Å.

the coupling process, the CO_2 carbon is the electrophilic center and the coordinated alkyne ligand acts as a nucleophile by providing the $\pi_\perp$ bonding electrons. Indeed, $HC{\equiv}CCN$ gives the highest barrier, while $HC{\equiv}C(OMe)$ gives the lowest barrier among the six pathways shown in Figure 2, further supporting the argument that the coordinated alkyne ligand acts as a nucleophile. The OMe substituent makes the π bonds more electron-rich, increasing the nucleophilicity of the alkyne and reducing the coupling barrier. In contrast, the CN substituent makes the π bonds electron-poor, decreasing the nucleophilicity of the alkyne and increasing the coupling barrier. The structural parameters calculated for the transition states also support the electronic argument here. The transition states (**$TS_{(1-5)B}$** and **$TS_{(1-5)B'}$**) calculated for the $HC{\equiv}CCN$ substrate have shorter C1−C2 bonds (see Figure 3) than those (**$TS_{(1-5)C}$** and **$TS_{(1-5)C'}$**) calculated for the $HC{\equiv}C(OMe)$ substrate. Coupling of electron-poorer π bonds with CO_2 requires closer C−C contacts in order to achieve the transition states. To further support the argument that the coordinated alkyne ligand acts as a nucleophile and CO_2 as an electrophile, we performed an NBO charge analysis to obtain the charges associated with the CO_2 moieties in the transition states **$TS_{(1-5)A}$**, **$TS_{(1-5)B}$**, **$TS_{(1-5)C}$**, **$TS_{(1-5)A'}$**, **$TS_{(1-5)B'}$**,

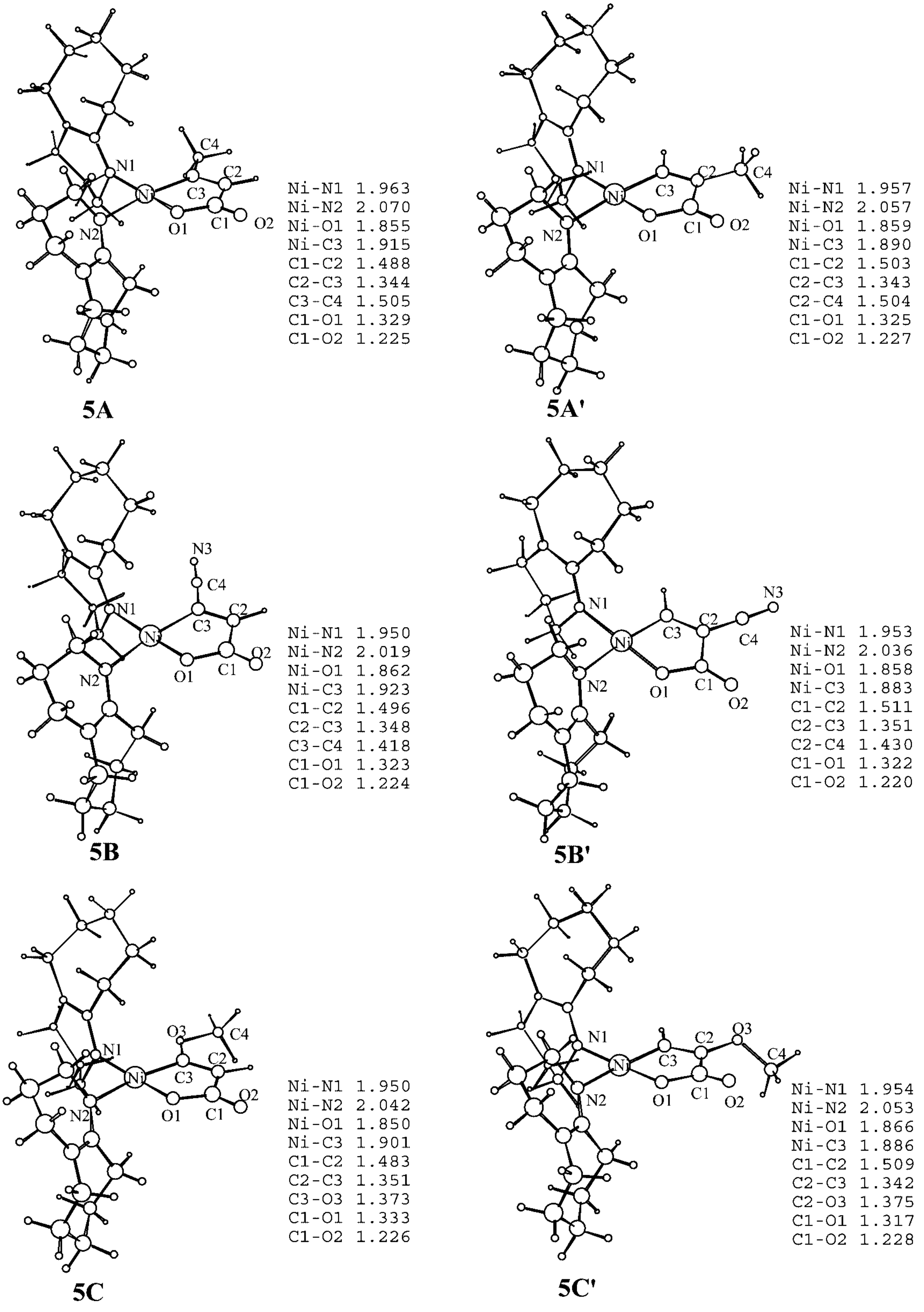


Figure 4. Calculated structures for the five-membered metallacyclic complexes formed from the coupling reactions of CO_2 with $NiL_2(HC{\equiv}CX)$ (L = DBU; X = Me (**A**), CN (**B**), OMe (**C**)). Selected bond distances are given in Å.

and $\mathbf{TS}_{(1-5)C'}$. The results show that the charges associated with the CO_2 moieties in the transition states $\mathbf{TS}_{(1-5)A}$, $\mathbf{TS}_{(1-5)B}$, $\mathbf{TS}_{(1-5)C}$, $\mathbf{TS}_{(1-5)A'}$, $\mathbf{TS}_{(1-5)B'}$, and $\mathbf{TS}_{(1-5)C'}$ are −0.43, −0.46, −0.62, −0.47, −0.46, and −0.43, respectively, suggesting that CO_2 receives electrons and acts as an electrophile in the reactions.

The argument above based on electronic factors nicely explains the trend observed in the barriers calculated for the coupling reactions of CO_2 with the three alkyne substrates having very different electronic properties. The results indicate that the electronic factors indeed govern the relative coupling barriers among the different substrates. However, when we come to the regioselectivity issue, in which the relative stabilities of $\mathbf{TS}_{(1-5)}$ and $\mathbf{TS}_{(1-5)'}$ for a given substrate need to be considered, it becomes problematic if we do not invoke steric factors. If only electronic factors determine the regioselectivity for a given

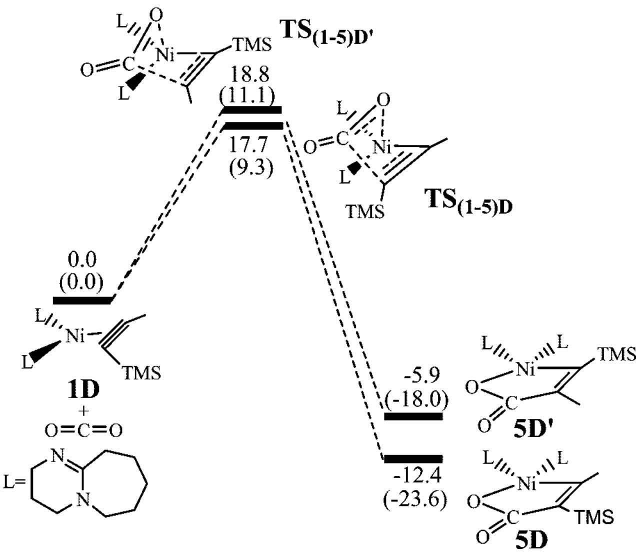


Figure 5. Energy profiles calculated for the coupling reactions of CO_2 with $NiL_2(MeC{\equiv}CTMS)$ (L = DBU) in an associative mechanism. The calculated relative free energies and electronic energies (in parentheses) are given in kcal/mol.

substrate, we would have expected a switch in the regioselectivity from the coupling reaction of $HC{\equiv}CCN$ to that of $HC{\equiv}C(OMe)$, because the π-electron-rich carbon is the internal carbon in the former but the terminal carbon in the latter. The results of calculations show no switch in the regioselectivity (Figure 2). Therefore, we can conclude that the difference in the π-electron density between the two alkyne atoms of a given terminal alkyne substrate caused by the electronic properties of the substituent is not the main reason for the observed regioselectivity.

In the coupling reactions, a new carbon−carbon bond is formed between the CO_2 carbon and one alkyne carbon. Therefore, we expect that there is a steric repulsive interaction between the substituent at the alkyne carbon, which forms the new carbon−carbon bond with the CO_2 carbon, and the non-reacted C═O group of CO_2 (see C1═O2 in Figure 3). The fact that $\mathbf{TS_{(1-5)A'}}$, $\mathbf{TS_{(1-5)B'}}$, and $\mathbf{TS_{(1-5)C'}}$ lie higher in energy than $\mathbf{TS_{(1-5)A}}$, $\mathbf{TS_{(1-5)B}}$, and $\mathbf{TS_{(1-5)C}}$, respectively, suggests that the steric repulsion is significant because the substituent at the alkyne carbon is non-hydrogen in $\mathbf{TS_{(1-5)A'}}$, $\mathbf{TS_{(1-5)B'}}$, and $\mathbf{TS_{(1-5)C'}}$ but is hydrogen in $\mathbf{TS_{(1-5)A}}$, $\mathbf{TS_{(1-5)B}}$, and $\mathbf{TS_{(1-5)C}}$ (see C2 in Figure 3). In $\mathbf{TS_{(1-5)A'}}$, $\mathbf{TS_{(1-5)B'}}$, and $\mathbf{TS_{(1-5)C'}}$, the nonbonded distances between the nonreacted C═O oxygen and the atom bonded to C2 in the non-hydrogen substituent are calculated to be 2.839, 2.849, and 2.719 Å, respectively. The nonbonded contacts are significantly shorter than the sum of the van der Waals radii of the relevant elements (3.31 Å for C−C and 3.12 Å for C−O),[26] supporting the steric argument put forth above. In $\mathbf{TS_{(1-5)A}}$, $\mathbf{TS_{(1-5)B}}$, and $\mathbf{TS_{(1-5)C}}$, the distances between the nonreacted C═O oxygen and the hydrogen H atom bonded to C2 are calculated to be 2.605, 2.587, and 2.631Å, respectively, only slightly shorter than the sum of the van der Waals radii of the relevant elements (2.65 Å for C−H).

When the alkyne substrate is $HC{\equiv}C(OMe)$, both the electronic and steric factors favor $\mathbf{TS_{(1-5)C}}$ over $\mathbf{TS_{(1-5)C'}}$ because the electron-donating OMe substituent makes the terminal carbon (the hydrogen-substituted carbon) more electron-rich and more nucleophilic. Here, the electronic and steric factors reinforce each other, leading to a large energy difference between $\mathbf{TS_{(1-5)C'}}$ and $\mathbf{TS_{(1-5)C}}$, 8.3 kcal/mol (Figure 2). When the alkyne substrate is $HC{\equiv}CCN$, electronic factors favor $\mathbf{TS_{(1-5)B'}}$ over $\mathbf{TS_{(1-5)B}}$. However, steric factors favor $\mathbf{TS_{(1-5)B}}$ over $\mathbf{TS_{(1-5)B'}}$. The calculation results suggest that steric factors are more important. Because the steric and electronic factors have opposite effects here, the energy difference between $\mathbf{TS_{(1-5)B'}}$ and $\mathbf{TS_{(1-5)B}}$ is much smaller, 4.5 kcal/mol (Figure 2). For the substrate $HC{\equiv}CMe$, the Me substituent is σ-donating and has limited electronic effect on the $\pi_\perp$ bonding electrons. Therefore, the energy difference between $\mathbf{TS_{(1-5)A'}}$ and $\mathbf{TS_{(1-5)A}}$ can be considered mainly due to steric factors.

The relative stabilities of **5B** and **5B′** parallel those of $\mathbf{TS_{(1-5)B}}$ and $\mathbf{TS_{(1-5)B'}}$. The same is true for the relative stabilities of **5C** and **5C′**. These results suggest that the steric factors discussed above for the transition states are still dominant in the relative stabilities of the two isomeric five-membered metallacyclic complexes formed from the coupling reaction of CO_2 with $NiL_2(HC{\equiv}CCN)$ (L = DBU) or $NiL_2(HC{\equiv}COMe)$. For **5A** and **5A′**, **5A** is less stable than **5A′**. Although we do not have a good explanation for this result, the relative stabilities of **5A** and **5A′** are closely related to the relative stabilities of the organic moieties in the two metallacycles. HOOCCH═CHMe was calculated to be less stable by ca. 1 kcal/mol than $HOOCCMe{=}CH_2$.

Regioselectivity in the Coupling Reactions of Silyl-Substituted Internal Alkynes. In this section, we will examine the regioselectivity in the coupling reactions of silyl-substituted internal alkynes shown in eq 2. The experiments by Shimizu et al. showed that CO_2 preferentially couples with the silyl-substituted carbon (eq 2). To study the factors that affect the regioselectivity, we again consider the associative mechanism that is preferred for the coupling reactions.[27] We used $MeC{\equiv}CTMS$ as the model substrate in the calculations. Figure 5 shows the energy profiles calculated for the coupling reactions of CO_2 with $NiL_2(MeC{\equiv}CTMS)$ (L = DBU). The five-membered metallacyclic complex **5D**, in which CO_2 couples with the substrate carbon atom bearing a silyl group, is preferentially formed both kinetically and thermodynamicallly, consistent with the regioselectivity observed experimentally.[13]

For the substrate $MeC{\equiv}CTMS$, the TMS substituent can be considered to be π accepting.[28] The electronic factor favors the transition state $\mathbf{TS_{(1-5)D}}$, because the TMS substituent makes the TMS-substituted carbon π electron richer in comparison with the Me-substituted carbon. However, the steric repulsion between the TMS substituent and the nonreacted C═O group of CO_2 disfavors the transition state. Therefore, $\mathbf{TS_{(1-5)D}}$ would be expected to be less favorable than $\mathbf{TS_{(1-5)D'}}$, because in the coupling reactions of terminal alkynes discussed in the preceding section, we have seen that the effect from the steric repulsion is greater than the effect from electronic factors. The result (Figure 5) is opposite to what we expected. We believe that additional steric repulsive interaction between the sterically demanding TMS substituent and the DBU ligand at the metal center needs to be considered. In $\mathbf{TS_{(1-5)D}}$, the additional steric repulsion is smaller than that in $\mathbf{TS_{(1-5)D'}}$ because $\mathbf{TS_{(1-5)D}}$ has a longer Ni−C2 bond (Figure 6). In comparison with $\mathbf{TS_{(1-5)D'}}$,

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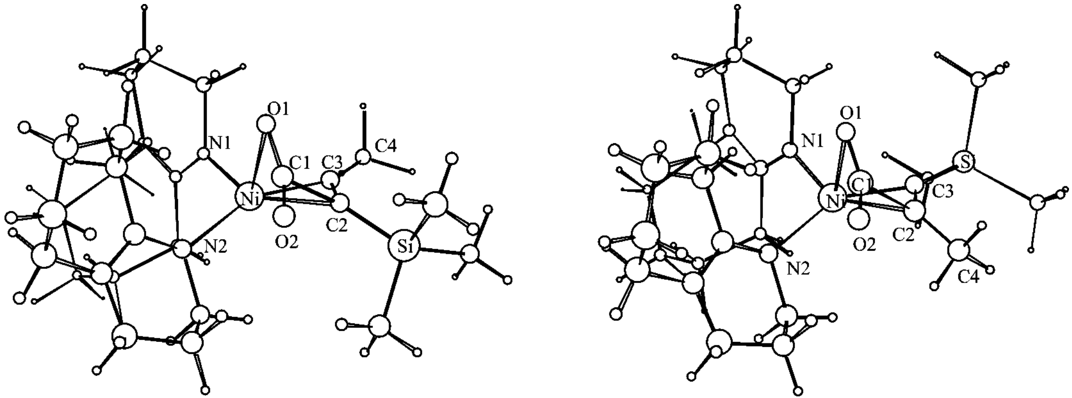
(26) Rowland, R. S.; Taylor, R. *J. Phys. Chem.* **1996**, *100*, 7384.

(27) The overall free energy barriers for the formation of **5D** and **5D′** in the dissociative pathway were calculated to be 21.0 and 23.4 kcal/mol, respectively.

(28) (a) Choi, S.-H.; Lin, Z.; Xue, X.-L. *Organometallics* **1999**, *18*, 5488. (b) Yang, S. Y.; Wen, T. B.; Jia, G.; Lin, Z. *Organometallics* **2000**, *19*, 5477.

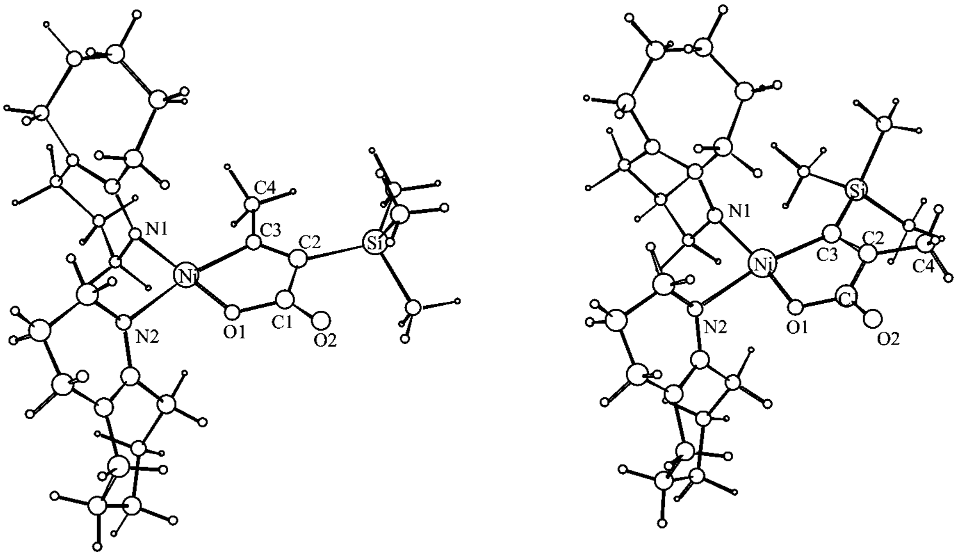


$TS_{(1\text{-}5)D}$

Ni-N1 1.981 Ni-N2 2.059
Ni-O1 2.574 Ni-C2 2.095
Ni-C3 1.834 C1-C2 1.981
C3-Si 1.873

$TS_{(1\text{-}5)D'}$

Ni-N1 1.986 Ni-N2 2.051
Ni-O1 2.540 Ni-C2 2.057
Ni-C3 1.876 C1-C2 1.934
C3-Si 1.853



5D

Ni-N1 1.964 Ni-N2 2.082
Ni-O1 1.844 Ni-C3 1.920
C1-C2 1.507 C2-C3 1.356
C3-C4 1.507 C1-O1 1.322
C1-O2 1.232 C3-Si 1.900

5D′

Ni-N1 1.979 Ni-N2 2.093
Ni-O1 1.848 Ni-C3 1.961
C1-C2 1.505 C2-C3 1.358
C3-C4 1.512 C1-O1 1.318
C1-O2 1.227 C3-Si 1.890

Figure 6. Calculated structures for the transition state and five-membered metallacyclic complexes formed from the coupling reactions of CO_2 with $NiL_2(MeC{\equiv}CTMS)$. Selected bond distances are given in Å.

$\mathbf{TS_{(1-5)D}}$ has smaller additional steric repulsion and more favored electronic factors but greater repulsion between the TMS substituent and the nonreacted C=O group of CO_2. $\mathbf{TS_{(1-5)D}}$ is only slightly more favorable, by 1.1 kcal/mol, than $\mathbf{TS_{(1-5)D'}}$, suggesting that the favorable factors offset slightly the unfavorable factors. Supporting the notion that the TMS substituent is π accepting, we performed an NBO charge analysis on $\mathbf{TS_{(1-5)D'}}$ and $\mathbf{TS_{(1-5)D}}$. The silyl-substituted alkyne carbon atom indeed carries more negative charge (−0.65 and −0.79 for $\mathbf{TS_{(1-5)D'}}$ and $\mathbf{TS_{(1-5)D}}$, respectively) than the methyl-substituted carbon atom (−0.25 and −0.09 for $\mathbf{TS_{(1-5)D'}}$ and $\mathbf{TS_{(1-5)D}}$, respectively).

The relative stabilities of **5D** and **5D′** parallel those of $\mathbf{TS_{(1-5)D}}$ and $\mathbf{TS_{(1-5)D'}}$. However, the energy difference between them is greater than that between $\mathbf{TS_{(1-5)D}}$ and $\mathbf{TS_{(1-5)D'}}$, a result of an increase in the additional steric repulsion between the TMS subsituent and the DBU ligand from $\mathbf{TS_{(1-5)D'}}$ to **5D′**.

It is worth commenting more on the relative stabilities of **5D** and **5D′**. In a few early-transition-metal complexes containing a silyl-substituted vinyl ligand, the silyl substituent is found to be preferred at the vinyl α-carbon over the vinyl β-carbon.[29] Interestingly, the nickel complex **5D** is more stable than **5D′**, although the former has the TMS substituent at the β-carbon. We put forward our explanation for the difference as follows. The early-transition-metal complexes have formally a d^0 metal center, which is capable of accepting π electrons from the vinyl ligand and prefers to have a more electron-rich α-carbon. In contrast, back-donation is expected from the metal center to the vinyl ligand π^* in late-transition-metal complexes. A π-accepting substituent, such as TMS, at the vinyl β-carbon is

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(29) (a) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870. (b) Takahashi, T.; Suzuki, N.; Kageyama, M.; Kondakov, D. Y.; Hara, R. *Tetrahedron Lett.* **1993**, *34*, 4811.

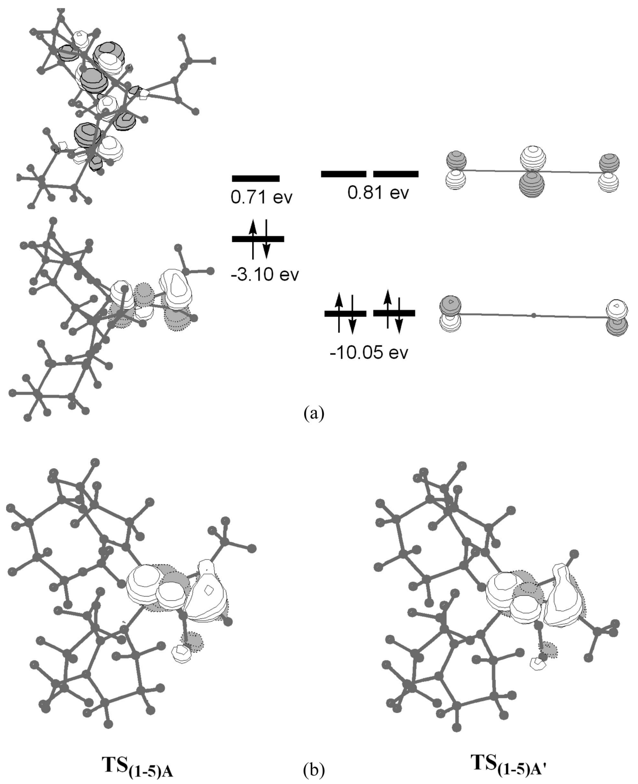

Figure 7. Spatial plots of the frontier orbitals for CO_2 and $Ni(DBU)_2(HC{\equiv}CMe)$ (**1A**) (a) and the highest occupied molecular orbitals for the transition states $\mathbf{TS_{(1-5)A}}$ and $\mathbf{TS_{(1-5)A'}}$ (b).

able to enhance the back-donation interaction by creating a push−pull scenario.

Nature of the Ni-Mediated Coupling of CO_2 with Alkynes. To probe the nature of the Ni-mediated coupling of CO_2 with alkynes, we analyzed the frontier molecular orbitals calculated for CO_2 and $Ni(DBU)_2(HC{\equiv}CMe)$ (**1A**) (Figure 7a). In **1A**, the highest occupied molecular orbital (HOMO) corresponds to the $\pi_\perp$ orbital of the coordinated alkyne. For CO_2, the HOMO can be considered as nonbonding and the lowest unoccupied molecular orbitals (LUMOs) are a pair of degenerate MOs that are π^* antibonding among the three atoms with a dominant contribution from the carbon atom. The energy gap between the LUMOs of CO_2 and the HOMO of **1A** is much smaller than that between the HOMOs of CO_2 and the LUMO of **1A**. Therefore, the CO_2−alkyne coupling is expected to be through the orbital interaction between the $\pi_\perp$ orbital of the η^2-coordinated alkyne and the CO_2 π^* orbitals. Indeed, the highest occupied molecular orbital (HOMO) of the transition state $\mathbf{TS_{(1-5)A}}$ or $\mathbf{TS_{(1-5)A'}}$ (Figure 7b) displays a bonding interaction between the $\pi_\perp$ orbital of the coordinated alkyne and one of the CO_2 π^* orbitals, although the orbital contribution from the C atom of the CO_2 moiety is less obvious because of the extensive orbital mixings. These results further support the notion put forward above that during the coupling process the CO_2 carbon is the electrophilic center and the coordinated alkyne ligand acts as a nucleophile by providing the $\pi_\perp$ bonding electrons.

Use of 2,2′-Bipyridine as the Ligand. In the Introduction, we mentioned that the coupling reaction did not take place when 2,2′-bipyridine (bipy) was used as the ligand.[7] Figure 8 shows the energy profiles calculated for the coupling reactions of CO_2 with $Ni(bipy)(HC{\equiv}CMe)$. The overall free energy barriers for the formation of **5E** and **5E′** were calculated to be 28.2 and 30.4 kcal/mol, respectively. The barriers are much higher than those calculated for the coupling reactions of CO_2 with $NiL_2(HC{\equiv}CMe)$ (L = DBU). The results are consistent with the experimental observation that 2,2′-bipyridine is not a good ligand for the coupling reactions. Examination of the transition state structures shown in Figure 9 leads us to believe that the bipy ligand is much less electron-donating than the DBU ligand, making the coordinated alkyne less electron-rich, decreasing the nucleophilicity of the coordinated alkyne and increasing the coupling barriers. As shown in Figure 9, the C1−C2 bonds in the transition states $\mathbf{TS_{(1-5)E}}$ and $\mathbf{TS_{(1-5)E'}}$ are noticeably shorter than those in $\mathbf{TS_{(1-5)A}}$ and $\mathbf{TS_{(1-5)A'}}$. As discussed above, coupling of electron-poorer π bonds with CO_2 requires closer C−C contacts in order to achieve the transition states. The results discussed here have the following significant implication. Strongly electron-donating ligands should be used to promote the coupling reactions of CO_2 with alkynes.

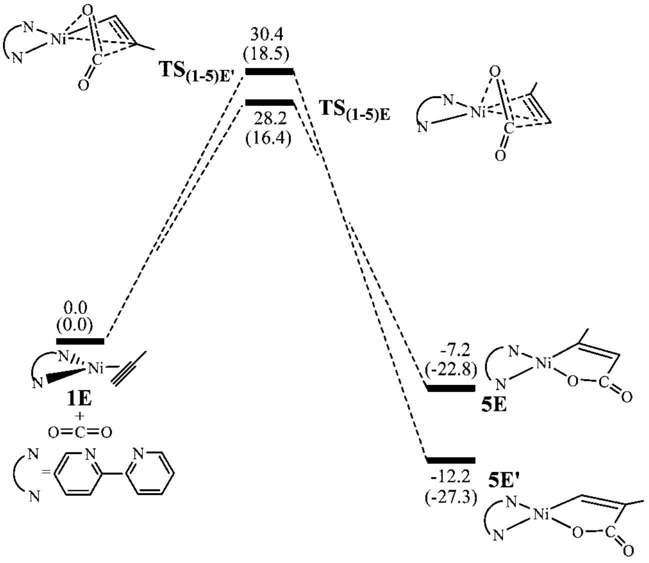

Figure 8. Energy profiles calculated for the coupling reaction of CO_2 with $Ni(bipy)(HC{\equiv}CMe)$. The calculated relative free energies and electronic energies (in parentheses) are given in kcal/mol.

While 2,2′-bipyridine is a relatively poorer ligand, bidentate bis(amidine) ligands were recently found to be good ligands for nickel(0)-mediated coupling of CO_2 with both terminal and internal alkynes,[30] likely due to the fact that these ligands are more electron-rich and less rigid than 2,2′-bipyridine. The regioselectivity observed in the coupling reactions mediated by these nickel bis(amidine) complexes seems much more complicated and requires further study.

Conclusions

The mechanism of the coupling reactions of alkynes with CO_2 mediated by a nickel(0) DBU complex was theoretically studied with the aid of DFT calculations at the B3LYP level. The calculations show that the coupling reactions mainly proceed through an associative mechanism in which a direct electrophilic attack of CO_2 at the $\pi_\perp$ bond of an η^2-coordinated alkyne substrate occurs. The associative mechanism is preferred, because more ligands in the transition state make the coordinated alkyne substrate more electron-rich and promote the electrophilic attack.

The results of calculations indicate that the coupling reactions of CO_2 with the three model terminal alkynes $HC{\equiv}CMe$,

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(30) Aoki, M.; Kaneko, M.; Izumi, S.; Ukai, K.; Iwasawa, N. *Chem. Commun.* **2004**, 2568.

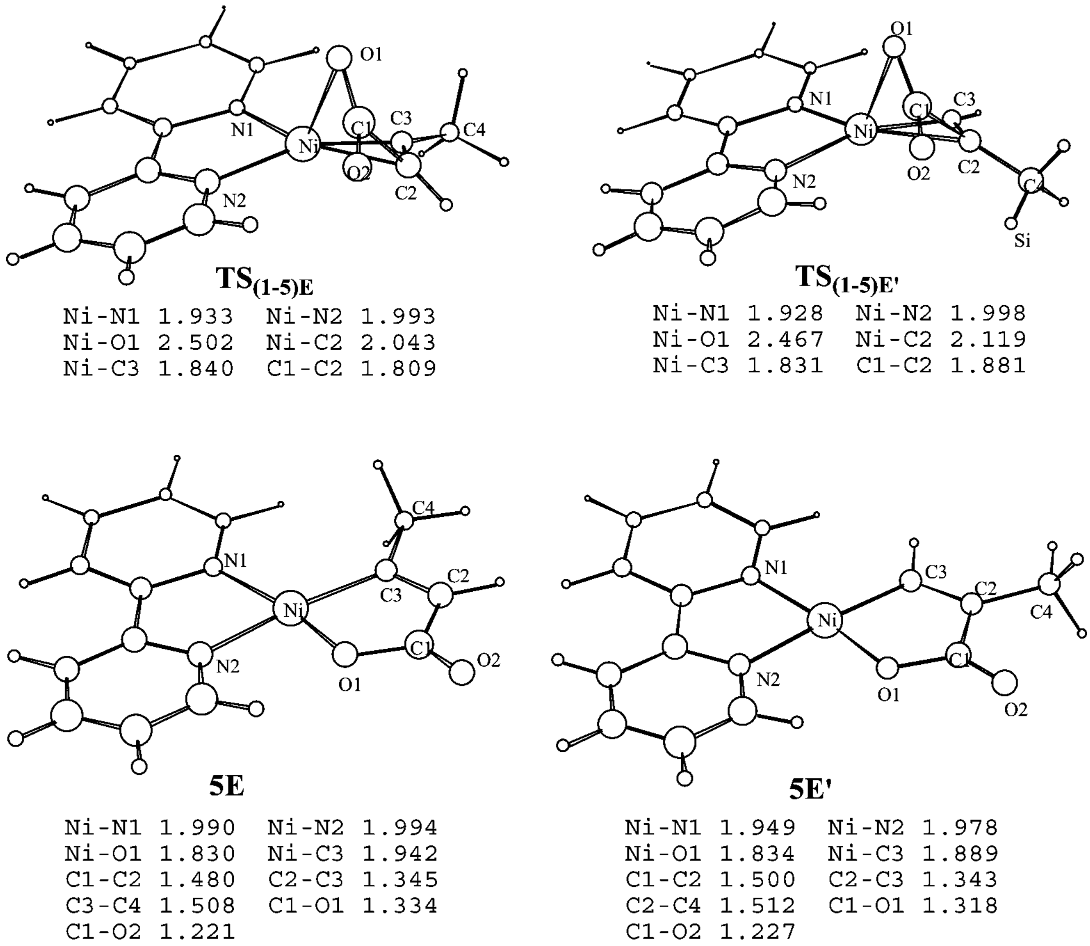

Figure 9. Calculated structures for the transition states and the five-membered metallacyclic complexes formed from the coupling reaction of CO_2 with Ni(bipy)(HC≡CMe). Selected bond distances are given in Å.

HC≡COMe, and HC≡CCN give the same regioselectivity, although the three alkynes are very different in terms of their electronic properties. The analysis of the frontier molecular orbitals suggest that the coupling is through the orbital interaction between the $\pi_\perp$ orbital of the η^2-coordinated alkyne and the CO_2 π^* orbitals. Electronic factors nicely explain the results that HC≡CCN gives the highest barrier, while HC≡C(OMe) gives the lowest barrier. The OMe substituent makes the π bonds more electron-rich, while the CN substituent makes the π bonds electron-poor. Regarding the regioselectivity observed in coupling reactions of CO_2 with a given terminal alkyne substrate, steric repulsive interactions between the substituent at the alkyne carbon, which forms the new carbon−carbon bond with the CO_2 carbon, and the nonreacted C=O group of CO_2 were found to dominate.

For the coupling reactions of CO_2 with the TMS-substituted internal alkynes, the additional steric repulsive interaction between the sterically demanding TMS substituent and the DBU ligand at the metal center also needs to be considered when the regioselectivity is considered. We found that both the additional steric factors and the electronic factors favor the coupling between CO_2 and the TMS-subsituted carbon.

We have also examined why the bipy ligand is not a good ligand for the Ni-mediated coupling reactions. The bipy ligand is much less electron-donating than the DBU ligand. As a result, the coordinated alkyne is not electron-rich enough and has poorer nucleophilicity, leading to high coupling barriers.

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Supporting Information Available: Text giving the complete ref 25 and tables giving Cartesian coordinates and electronic energies for all of the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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