Organometallics **2004,** *23,* 5252−5259

Mechanistic Details of Nickel(0)-Assisted Oxidative Coupling of CO_2 with C_2H_4

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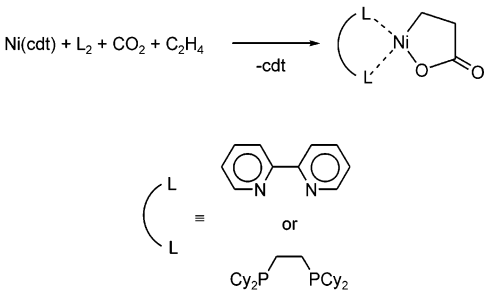
Received July 6, 2004

The mechanism of the experimentally observed formation of the five-membered nickela−carboxylate complex in the nickel(0)-assisted oxidative coupling of CO_2 and C_2H_4 is revealed by means of density functional calculations. The reliability of the applied DFT methodology has been first assessed by comparison to high-level coupled-cluster calculations on a relevant model reaction. The most important stationary points on the potential energy surface associated with the title reaction have been located, and low-energy reaction pathways have been identified. We show that the C−C bond formation occurs in a single step by the reaction of a nickel−ethylene complex with an incoming CO_2 molecule. The solvent effect and the influence of the ancillary ligands on the reaction energetics are examined, and both are shown to be important in these reactions.

Introduction

The direct carboxylation of alkenes with carbon dioxide plays a key role in developing CO_2-based synthetic methods.[1] A number of alkynes and alkenes have been shown to react with CO_2 using homogeneous transition-metal catalysts, affording a variety of esters and lactones.[2−4] C−C coupling reactions involving CO_2 and ethylene are of particular interest, because they may provide economic alternative routes to the synthesis of industrially valuable products. The $CO_2-C_2H_4$ coupling has been found to occur in several stoichiometric reactions in the presence of various transition-metal complexes;[5−14] however, the development of operating catalytic processes for these reactions is still lacking. A thorough understanding of the reaction mechanism is highly desired to facilitate the design of efficient catalysts.

Scheme 1



The first clear evidence for successful C−C bond formation between carbon dioxide and ethylene was provided by Hoberg et al. in 1983,[5] who reported that Ni(0) complexes of the NiL_2 type (with L_2 = 2,2′-bipyridine (bpy), 1,2-bis(dicyclohexylphosphino)ethane (dcpe)) produced in situ from Ni(cdt) (cdt = 1,5,9-cyclododecatriene) gave five-membered metallacycles in reactions with CO_2 and C_2H_4 (Scheme 1). The cyclic metalla−carboxylates could be isolated and further reacted with HCl to form saturated carboxylic acids.[5−7] In subsequent studies, ethylene complexes of several transition metals (Fe, Ti, Mo, W, Rh) were also shown to react with CO_2, yielding either metallacycles[8−10] or hydrido−acrylate species.[8,11−14] The latter reaction is of great interest, as it could be used for the synthesis of acrylic acid or its polymers from the direct coupling of two simple chemicals such as ethylene and CO_2 to great advantage with respect to existing synthetic methodologies.

In an attempt to reveal the mechanistic details of metal-assisted $CO_2-C_2H_4$ coupling reactions, we have recently identified the key elementary steps of the

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10.1021/om049496+ CCC: $27.50
Publication on Web 09/21/2004

formation of binuclear hydrido−acrylates via the reaction of the [*trans*-Mo$(C_2H_4)_2(PMe_3)_4$] complex with CO_2.[15] Our theoretical study has provided solid support for the reaction mechanism proposed by Carmona et al. from experimental observations.[11−14] We have confirmed that the C−C bond formation takes place via oxidative coupling between coordinated CO_2 and C_2H_4 ligands, resulting in a cyclic metalla−carboxylate intermediate, which can then undergo a β-hydrogen shift to yield the hydrido−acrylate species. We have found that the ancillary phosphine ligands play an important role in various phases of the reaction: their dissociation controls the coordination of CO_2, their presence facilitates the oxidative coupling, and some of the internal rearrangement processes are also associated with the nature of the phosphine ligands.

The basic question we address in the present theoretical study is whether the intermediacy of the carbon dioxide complex is a general requirement in $CO_2-C_2H_4$ coupling reactions. To this end, we have elucidated the mechanism of the Ni(0)-assisted oxidative coupling reactions depicted in Scheme 1 by identifying possible low-energy pathways from the reactants toward the cyclic metalla−carboxylate species. We show that the lowest energy pathway does not involve CO_2 coordination, as suggested in previous theoretical studies;[16,17] rather, it corresponds to a one-step C−C coupling process from $NiL_2(C_2H_4) + CO_2$, as already proposed on the basis of experimental observations.[10b] The possibility of controlling the relative stability of the metallacycle and the barrier of C−C coupling by modifying the ancillary ligands is also examined in the present work.

Computational Details

We assume that the reactions studied in the present work evolve on a single potential energy surface associated with the closed-shell singlet electronic ground states of the reactants and the cyclic metalla−carboxylate product. The relevance of this assumption was verified by the inspection of the HOMO−LUMO gap of the stationary points, which turned out to be always higher than 50 kcal/mol. The relative stability of the triplet states was explicitly checked for various stages of the reaction by carrying out single-point energy calculations for the triplet states as well, and these calculations indicated that the triplet states of the stationary points were always well above the corresponding singlet states.

Density functional theory applied at the B3LYP/SDDP level has been used to locate the stationary points on the singlet state potential energy surfaces. Here, B3LYP refers to the hybrid-type exchange-correlation functional[18−20] and SDDP denotes a basis set that involves the Stuttgart−Dresden quasi-relativistic small-core ECP basis set for Ni[21] and the Dunning/Huzinaga DZP all-electron basis set for the lighter atoms.[22−24] The relative energies of the located minima and transition states have been estimated at the B3LYP/6-311++G(d,p) level by carrying out single-point energy calculations for the B3LYP/SDDP stationary points. The accuracy of this methodology has been assessed on a model reaction relevant to the investigated systems by performing calculations at increasing levels of theory (see next section). First, the B3LYP limit has been approximated by employing the extended 6-311++G(3df,3pd) basis set,[25] and the results have also been compared with those of CCSD(T)/6-311++G(3df,3pd) calculations, which is considered to be a fairly reliable reference level. The applied basis sets will also be referred to as B_1 (SDDP), B_2 (6-311++G(d,p)), and B_3 (6-311++G(3df,3pd)).

Normal-coordinate analysis has been carried out for each optimized structure to characterize the nature of the located stationary point. For transition-state structures, we have calculated the intrinsic reaction coordinate (IRC) routes in both directions defined by the normal coordinate corresponding to the imaginary vibrational frequency. For some of the transition states, the IRC calculations failed to reach the energy minima on the potential energy surface; therefore, in those cases we performed full geometry optimizations from various points of the IRC path using either the steepest descent or the Berny optimization algorithm (pseudo-IRC calculations).

To estimate the effect of the solvent medium on the energetics of the reactions, the self-consistent reaction field approach with the polarized continuum model (PCM)[26] has been used at the B3LYP/SDDP level to calculate the Gibbs free energy of solvation for the gas-phase stationary points. The dielectric constant of the polarizable medium has been set to $\epsilon = 2.83$, corresponding to toluene, which is one of the solvents used in related experiments.

All these calculations have been carried out by using the Gaussian98 program package.[27]

Results and Discussion

A. Test Calculations for $Ni(C_2H_4)(CO_2) \rightarrow Ni(CH_2CH_2COO)$. Although density functional theory, particularly when applied using the so-called hybrid energy functionals, is considered to provide reasonable energetics for organometallic reactions,[28] it is always recommended to estimate the errors one may expect for a given type of reaction. Since the key step of the

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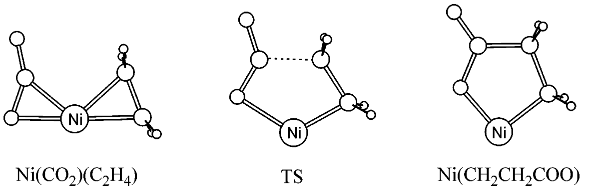

Figure 1. Three stationary points on the Ni + CO_2 + C_2H_4 potential energy surface.

Table 1. Relative Energies (in kcal/mol) of $Ni(CH_2CH_2COO)$ and TS Structures with Respect to $Ni(CO_2)(C_2H_4)$ Obtained at Various Levels of Theory[a]

energy	geometry	$Ni(CH_2CH_2COO)$	TS
$B3LYP/B_1$	$B3LYP/B_1$	12.6	45.0
$B3LYP/B_2$	$B3LYP/B_1$	18.5	49.0
$B3LYP/B_2$	$B3LYP/B_2$	18.7	49.1
$B3LYP/B_3$	$B3LYP/B_2$	19.4	49.7
$CCSD(T)/B_2$	$B3LYP/B_2$	17.0	39.9
$CCSD(T)/B_3$	$B3LYP/B_2$	18.1	41.2

[a] The first column of the table refers to the level of energy calculations carried out on structures optimized at the level shown in the second column. Notation for the basis sets: B_1 = SDDP, B_2 = 6-311++G(d,p), B_3 = 6-311++G(3df,3pd).

reactions investigated in the present work is the C−C bond formation between CO_2 and C_2H_4, the simplest model that may describe the structural changes along this elementary step of the nickel-assisted oxidative CO_2−C_2H_4 coupling includes a single Ni atom and the reacting molecules. Although the omission of the ancillary ligands (here, bpy or dcpe) introduces a drastic simplification in modeling the electronic structure of the metal center, this model may provide a reasonable estimate for the accuracy of the applied density functional methodology concerning the energy predictions.

The three stationary points relevant to the CO_2−C_2H_4 coupling on the Ni + CO_2 + C_2H_4 potential energy surface are illustrated in Figure 1, and they correspond to the $Ni(CO_2)(C_2H_4)$ coordination complex, the transition state (TS) related to the C−C bond formation, and the $Ni(CH_2CH_2COO)$ metallacycle. We mention here that, in our calculations, the structure of these species has been constrained to be planar (i.e. kept in C_s symmetry), so as to be able to carry out the calculations at higher levels of theory.[29] The results of our test calculations are compiled in Table 1.

It is worth noting that the methodology used as a standard level in our work (i.e. the $B3LYP/B_2//B3LYP/B_1$ method) approaches the quality of the B3LYP limit ($B3LYP/B_3//B3LYP/B_2$ calculations) to within 1 kcal/mol. The comparison with the most accurate results (the reference level is $CCSD(T)/B_3//B3LYP/B_2$) indicates that the standard method gives accurate prediction for the relative stability of the two minima; however, the barrier height represented by the transition state is overestimated by about 20%. This latter finding is somewhat surprising, given that DFT methodologies usually tend to provide lower energy barriers than do wave function based correlated methods. Of course, the presence of the ancillary ligands has a significant effect on the relative energies of these stationary points, but it is reasonable to assume that our observations here can be extrapolated to the realistic models as well. Thus, we expect to provide rather reliable energetics for the reaction intermediates presented in the next sections; however, the calculated barriers for the C−C coupling step should be considered as overestimations to the barrier heights.

B. Ni(cdt) + bpy + CO_2 + C_2H_4 System. Both reactions corresponding to L_2 = bpy, dcpe chelating ligands have been considered in this work. We examine first the L_2 = bpy case in detail, and in the next section, we present the results obtained for L_2 = dcpe as well. The possible intermediates involved in the reaction of Ni(cdt) with bpy, CO_2, and C_2H_4 to afford $Ni(bpy)(CH_2CH_2COO)$ plus cdt are depicted in Scheme 2.

1. Ligand Exchange Processes. Relying upon the assumption that the active form of the metal center in the Ni(0)-induced CO_2−C_2H_4 coupling reactions includes a coordinated L_2 ligand,[5−7] the initial step of the present reaction is likely the addition of bpy to Ni(cdt) (**1**) to form a ternary Ni(η^2-cdt)(bpy) complex (**2**), in which the cdt ligand is attached to the metal atom via only one olefinic bond (see Figure 2). Our calculations indicate that this step is thermodynamically allowed, because complex **2** is predicted to lie 12.0 kcal/mol below **1** + bpy. Closely related reactions, namely the addition of a chelating $(t\text{-}Bu)_2PCH_2CH_2P(t\text{-}Bu)_2$ phosphine to **1**[31] or the addition of bpy to $Ni(cod)_2$ (cod = cyclooctadiene),[32] have been observed experimentally, underlying the feasibility of this reaction step.

In their original work,[5,6] Hoberg et al. assumed that the C−C coupling between CO_2 and C_2H_4 occurs via the 18e $Ni(bpy)(CO_2)(C_2H_4)$ intermediate (**5**), which might be produced either from $Ni(bpy)(C_2H_4)$ (**3**) + CO_2, or from $Ni(bpy)(CO_2)$ (**4**) + C_2H_4, as shown in Scheme 2. We have therefore optimized the structures of these complexes and calculated their relative stabilities with respect to **2** + CO_2 + C_2H_4.

We found that the two 16e nickel complexes (**3** and **4**) have distorted-trigonal-planar structures (see Figure 3), which is in agreement with the experimental structural data available for analogous compounds such as $Ni(PCy_3)_2(CO_2)$[33] and $Ni(PPh_3)_2(C_2H_4)$.[34] In fact, the $Ni(bpy)(C_2H_4)$ complex has also been isolated and its single-crystal structure has been analyzed,[35] but as far as we are aware, the structural data have not been published. The calculations reveal that the formation of the ethylene complex **3** via the replacement of the η^2-coordinated cdt ligand in **2** is favored energetically by 8.4 kcal/mol. The ligand exchange for CO_2 to give complex **4** is, however, quite unlikely, since the **2** + CO_2 → **4** + cdt substitution is predicted to be endothermic by 1.4 kcal/mol. The difference found for the stability of these complexes is consistent with the result of our previous theoretical study on 1:1 complexes of Ni with C_2H_4 and CO_2[36] and also with the experimental obser-

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[29] The fully optimized TS and $Ni(CH_2CH_2COO)$ structures are only slightly distorted from the planar arrangement, whereas the global minimum of $Ni(CO_2)(C_2H_4)$ is characterized by a perpendicular arrangement of the coordinated CO_2 and C_2H_4 ligands.

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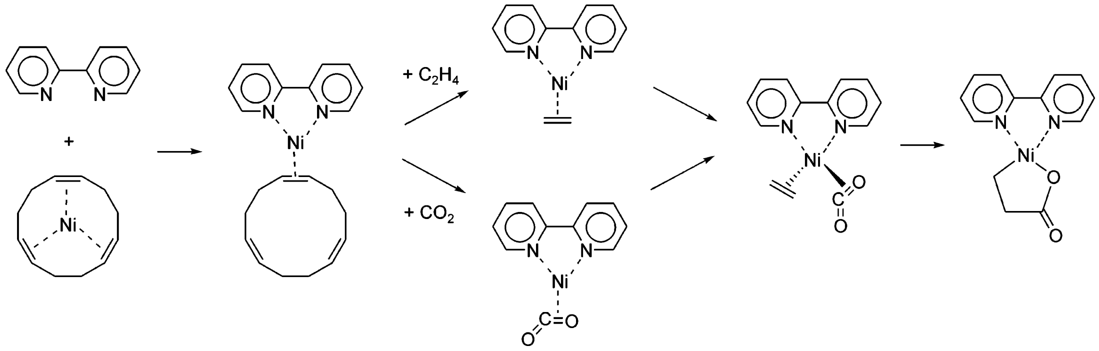
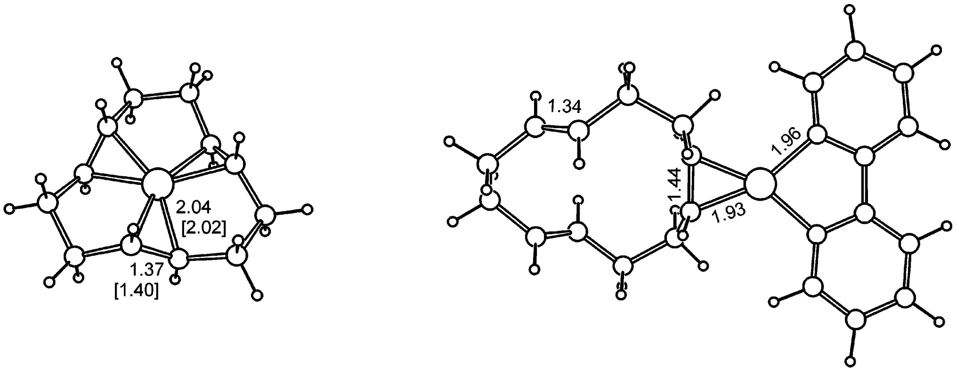
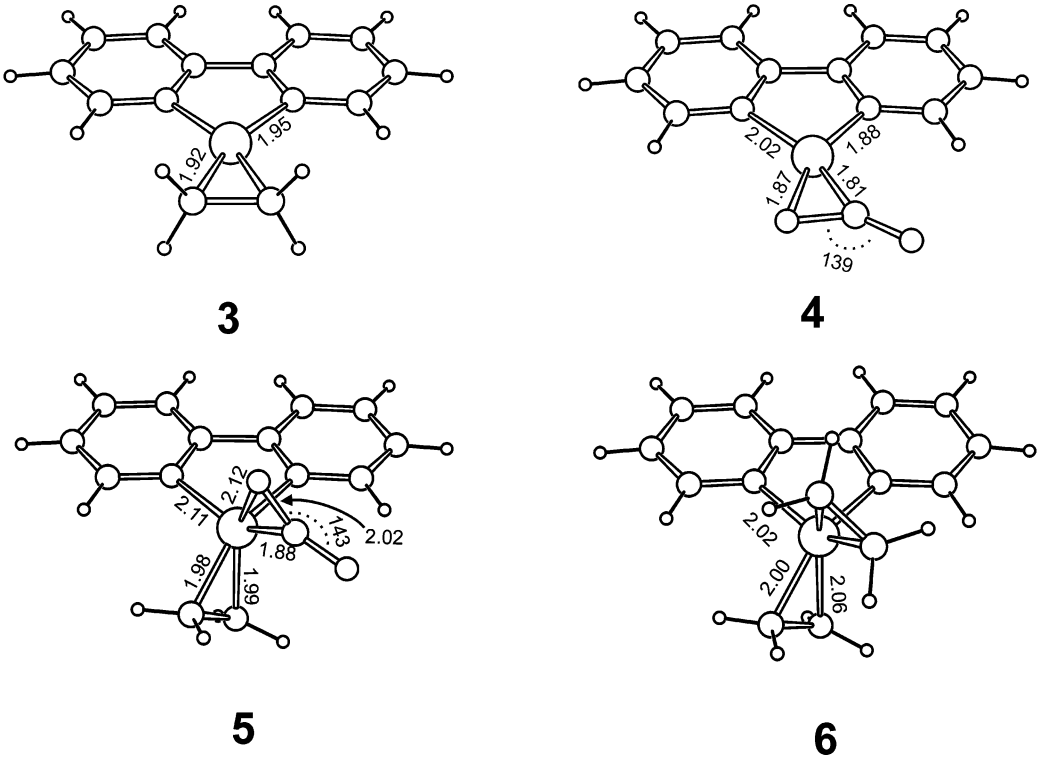
Scheme 2





1 **2**

Figure 2. Optimized structures and selected geometric parameters of the Ni(cdt) and Ni(η^2-cdt)(bpy) complexes. Relevant data from X-ray measurements[30] are given in brackets.



3 **4** **5** **6**

Figure 3. Optimized structures and selected geometric parameters of the complexes Ni(bpy)(C_2H_4) (**3**), Ni(bpy)(CO_2) (**4**), Ni(bpy)(CO_2)(C_2H_4) (**5**), and Ni(bpy)(C_2H_4)$_2$ (**6**).

vation that nickel–CO_2 complexes can easily undergo exchange reactions with olefins.[37]

The saturated 18e Ni(bpy)(CO_2)(C_2H_4) complex (**5**) that was assumed to act as a precursor for the C–C

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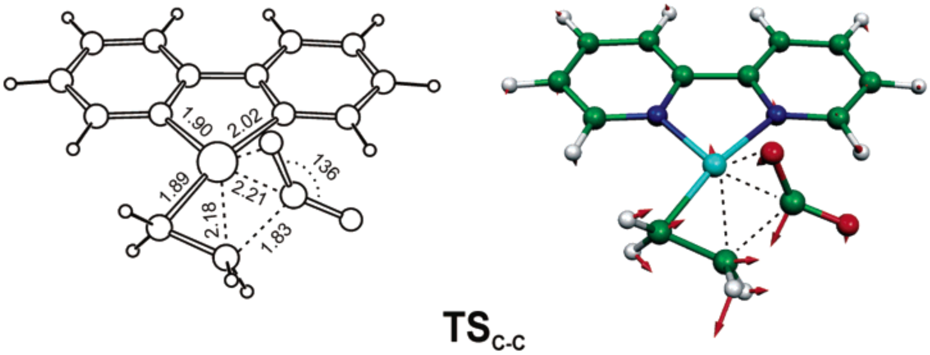


TS_{C-C}

Figure 4. Structure of the C−C coupling transition state and the vector representation of the normal coordinate associated with the imaginary vibrational frequency of **TS_{C-C}**.

bond formation[6] was also identified as a local minimum in our calculations. This complex, however, appears to be a fairly labile species, as it lies 7.1 kcal/mol higher in energy than **3** + CO_2; moreover, the barrier toward this dissociation is calculated to be only 0.8 kcal/mol. It is therefore quite unlikely that complex **5** is an intermediate in the investigated reaction. In principle, another saturated species, the bis(ethylene) complex Ni(bpy)$(C_2H_4)_2$, can be formed in the reaction. This molecule is very close in energy to **3** + C_2H_4 (the stabilization introduced by the coordination of the second C_2H_4 molecule is only 0.9 kcal/mol), which means that the mono- and bis(ethylene) complexes are probably in equilibrium in the solution.

2. C−C Bond Formation. The structure we located as a transition state describing the C−C bond formation between CO_2 + C_2H_4 is depicted in Figure 4, along with the normal vector associated with the imaginary vibrational frequency. The nature of this transition state is rather similar to those found previously for the Mo-assisted CO_2−C_2H_4 coupling reactions,[15] in that it can also be characterized as a five-center transition state, where the formation of the C−C bond is strongly coupled with the cleavage of the related metal−carbon bonds.

To identify the two energy minima corresponding to the transition state, we initiated intrinsic reaction coordinate (IRC) calculations from **TS_{C-C}** in both directions. Similar to our previous experience,[15] the reaction path following the algorithm failed to reach the two minima; therefore, the remaining part of the reaction path was monitored via standard geometry optimizations. These calculations revealed that the located transition state is indeed associated with the Ni(bpy)-(CH_2CH_2COO) metallacycle (**7**). We found, however, that the reaction path in the other direction does not correspond to the ethylene−carbon dioxide complex but rather to the dissociation of CO_2 from the metal center: i.e., to the **3** + CO_2 asymptote. The results of the reaction path following calculations in this direction are summarized in Figure 5. Notice that all routes mapped by the Berny optimization algorithm starting from various points on the IRC or steepest descent paths approach a rather flat region on the potential energy surface before converging to the **3** + CO_2 minimum. This region, which is only about 5 kcal/mol above **3** + CO_2, corresponds to a structure that involves a bent CO_2 molecule linked in an η^1(C) manner to the Ni atom (see Figure 6).

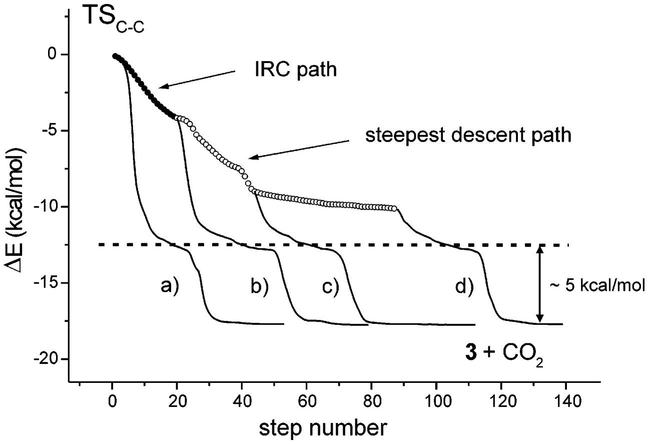


Figure 5. Energy variation along the routes followed from the **TS_{C-C}** transition state toward the **3** + CO_2 minimum. The IRC and the steepest descent geometry optimization steps are shown by circles. Energy curves indicated by lines refer to geometry optimizations using the Berny algorithm. Labels a−d denote the four different routes from **TS_{C-C}** to **3** + CO_2.

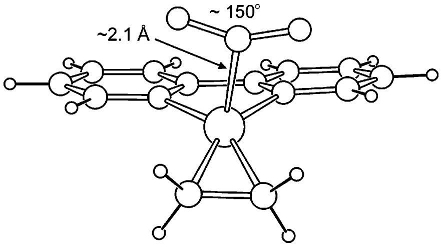


Figure 6. Structure representing the flat region of the energy curves shown in Figure 5.

These results thus indicate that the C−C coupling in the present reaction does not proceed from an intermediate that involves coordinated CO_2 and C_2H_4 molecules but occurs in a single elementary step from the **3** + CO_2 minimum. This conclusion is at variance with that of a previous theoretical study reported by Dedieu et al.,[16,17] who suggested that the CO_2−C_2H_4 coupling at the NiL_2 centers involves a coordinated CO_2 attacked by an incoming C_2H_4 molecule. It should be mentioned, however, that no transition state optimization was carried out by these authors; moreover, only the planar arrangement of the reacting molecules was examined, making their conclusions only tentative. It is also relevant to note here that CISD calculations carried out by Sakaki et al. for the NiL_2 + CO_2 + C_2H_2 →

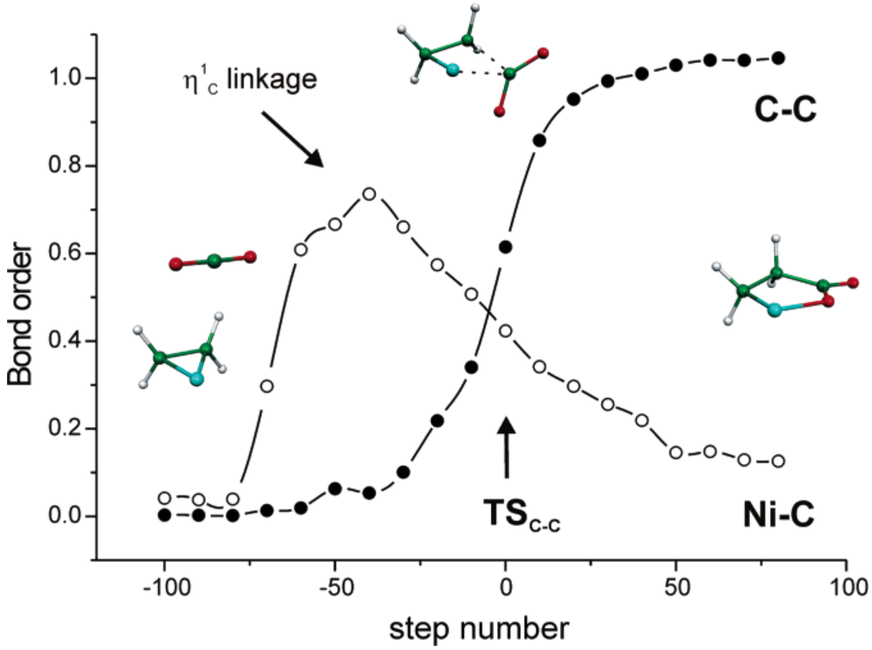


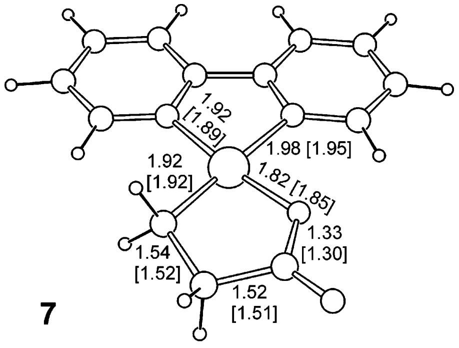
Figure 7. Calculated Ni−C and C−C bond orders along the single-step $\mathbf{3} + CO_2 \rightarrow \mathbf{7}$ reaction route. The $\mathbf{TS_{C-C}} \rightarrow \mathbf{7}$ part of this route corresponds to pathway c in Figure 5. The bpy ligands in the depicted structures are omitted for clarity.

oxanickelacyclopentene coupling reaction[38] indicated that the C−C coupling proceeds via the approach of CO_2 to the $NiL_2(C_2H_2)$ complex.

It is evident, however, that the Ni(0) center has a prominent role in the title reaction, because the C−C coupling is initiated by the metal-induced activation of CO_2 that allows the oxidative coupling with the coordinated ethylene. To characterize the evolution of Ni−CO_2 and CO_2−C_2H_4 linkages along the reaction pathway from $\mathbf{3} + CO_2$ to **7** via $\mathbf{TS_{C-C}}$, we plotted the Ni−CO_2-related Ni−C and CO_2−C_2H_4 related C−C bond orders calculated with the “Fuzzy” algorithm developed recently by Mayer and Salvador.[39] Figure 7 illustrates clearly the development of the bonding Ni−CO_2 interaction prior to the formation of the new C−C bond.

The energy barrier represented by $\mathbf{TS_{C-C}}$ when going from $\mathbf{3} + CO_2$ to the metallacycle is predicted to be 22.7 kcal/mol, but we recall that the present density functional methodology is expected to overestimate the barrier by about 20%. We also mention that the inclusion of the solvation energies in terms of the PCM model reduces the barrier by 3.6 kcal/mol. Taking into account these corrections, we estimate that the energy barrier of the C−C coupling from $\mathbf{3} + CO_2$ should be about 15 kcal/mol.

After passing $\mathbf{TS_{C-C}}$, the system is stabilized significantly by the formation of the five-membered metallacycle. Our calculations show that the final product lies 12.8 kcal/mol below the $\mathbf{3} + CO_2$ level. Complex **7** is characterized as a square-planar Ni(II) species, and Figure 8 illustrates well that the structural parameters provided by the B3LYP/SDDP methodology are reasonably close to those from X-ray measurements.[40]



7

Figure 8. Calculated equilibrium structure of the reaction product **7** with selected structural parameters. Experimental data from ref 40 are shown in brackets.

Table 2. Summary of Relative Energies (in kcal/mol) along the Entire Reaction Path[a]

	ΔE_g	δE_s	ΔE_s
$Ni(cdt) + bpy + CO_2 + C_2H_4$	0.0	−1.6	0.0
$Ni(\eta^2\text{-}cdt)(bpy) + CO_2 + C_2H_4$	−12.0	−0.4	−7.4
$Ni(bpy)(C_2H_4) + cdt + CO_2$	−20.4	−2.4	−19.6
$Ni(bpy)(CO_2) + cdt + C_2H_4$	−10.6	−5.5	−12.9
$Ni(bpy)(C_2H_4)(CO_2) + cdt$	−13.3	−2.7	−13.6
$Ni(bpy)(C_2H_4)_2 + cdt$	−21.3	+0.5	−18.4
$TS_{C-C} + cdt$	+2.3	−5.3	−0.6
$Ni(bpy)(CH_2CH_2COO) + cdt$	−32.8	−5.8	−36.2

[a] The reference level corresponds to $Ni(cdt) + bpy + CO_2 + C_2H_4$. Notation: ΔE_g= relative energies in gas phase; δE_s = solvation free energy of the involved Ni complex as obtained from PCM calculations with $\epsilon = 2.83$ (the solvation free energies for cdt, bpy, CO_2 and C_2H_4 ligands are −1.0, −3.4, +0.8, and +0.8 kcal/mol, respectively); ΔE_s = relative energies including the solvent effects.

3. Overall Energetics. The relative energies calculated for the species discussed above are collected in Table 2, where we also show the results of PCM calculations that were carried out to estimate the solvent effects on the energetics. The solvation free energies (δE_s) of the structures identified in the reaction vary between +0.5 and −5.8 kcal/mol, and these cor-

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(38) Sakaki, S.; Mine, K.; Taguchi, D.; Arai, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3289.

(39) (a) Mayer, I.; Salvador, P. *Chem. Phys. Lett.* **2004**, *383*, 368. (b) Mayer, I.; Salvador, P. *Program “FUZZY”*, Version 1.00; Girona, October 2003.

(40) Hipler, B.; Döring, M.; Dubs, C.; Görls, H.; Hübler, T.; Uhlig, E. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1329.

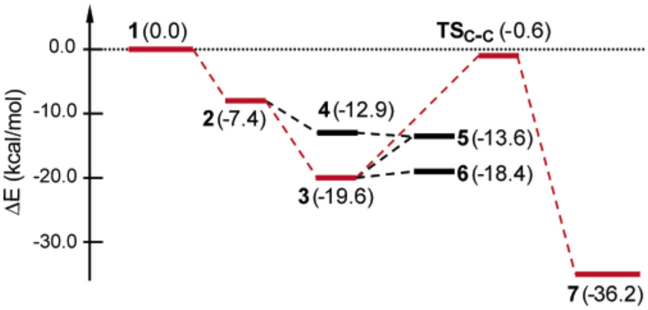


Figure 9. Energy profile for the Ni(cdt) + bpy + CO_2 + C_2H_4 reaction corresponding to the solvated model (ΔE_s values are from Table 2). Note that only the Ni complexes involved in the reaction are indicated; the correct stoichiometry of the elementary steps is provided in Table 2. The minimum energy pathway is shown in red; complexes that are not involved directly in the reaction are indicated in black.

rections slightly alter the energy profile of the entire reaction path. For instance, due to the charge flow taking place from the metal center toward the reacting molecules in the oxidative C−C coupling step, the metallacycle and the $\mathbf{TS_{C-C}}$ transition state become more polarized than the Ni(bpy)(C_2H_4) intermediate; therefore, the inclusion of solvent effects reduces the barrier and the exothermicity of this step.

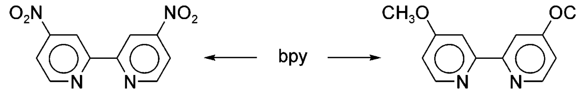
The energy diagram of the entire reaction path as calculated with the solvated model is plotted in Figure 9. This energy profile clearly indicates that the global minimum on the Ni(cdt) + bpy + CO_2 + C_2H_4 potential energy surface corresponds to the metalla−carboxylate species that lies well below the reaction intermediates. Although we have not estimated the energy barriers for the ligand exchange reactions occurring prior to the formation of the ethylene complex **3**, experimental observations for related systems[41] indicate that these exchange reactions occur already below 0 °C; therefore, it is quite likely that the $\mathbf{TS_{C-C}}$ transition state represents the highest energy barrier in the entire reaction. The remarkably large thermodynamic stability of the cyclic Ni(bpy)(CH_2CH_2COO) complex might be one of the main reasons that the reaction does not proceed further via a β-hydrogen shift toward the formation of the hydrido−acrylate species, as observed in the reaction of bis(ethylene) complexes of Mo.[6] A transition state corresponding to the β-hydrogen transfer connecting complex **7** with the NiH(bpy)($CH_2{=}CHCOO$) hydrido−acrylate species was located on the Ni(cdt) + L_2 + CO_2 + C_2H_4 potential energy surface, but the barrier of this step is about 50 kcal/mol. This energy gap for the Mo-assisted reaction was estimated to be only 10 kcal/mol.[15] For this latter reaction, we have found[15] that the five-membered metallacycle is only 5.8 kcal/mol more stable than the initial ethylene complex (+CO_2), which is quite different from the situation discussed in this paper, where the energy difference between **7** and **3** + CO_2 is 16.6 kcal/mol.

Table 3. Calculated Gas-Phase Relative Energies (in kcal/mol) for Selected Species Involved in the Ni(cdt) + L_2 + CO_2 + C_2H_4 → Ni(L_2)(CH_2CH_2COO) + cdt Reaction[a]

	L_2			
	bpy	dcpe	mbpy	nbpy
Ni(L_2)(C_2H_4) + cdt + CO_2	−20.4	−23.8	−19.6	−20.9
Ni(L_2)(CO_2) + cdt + C_2H_4	−10.6	−12.9		
Ni(L_2)(C_2H_4)(CO_2) + cdt	−13.3	−11.4		
$\mathbf{TS_{C-C}}$ + cdt	+2.3	−0.9	+1.0	+6.3
Ni(L_2)(CH_2CH_2COO) + cdt	−32.8	−28.3	−34.3	−27.4

[a] The reference level corresponds to Ni(cdt) + L_2 + CO_2 + C_2H_4.

Scheme 3



4,4'-dinitro-2,2'-bipyridine
(nbpy)

4,4'-dimethoxy-2,2'-bipyridine
(mbpy)

Since the metal atom acts as a nucleophile in the oxidative C−C coupling processes, the relative stability of the two minima associated with the C−C bond formation (the cyclic species and the ethylene complex, in the present case) is expected to be sensitive to the choice of the coligands involved in the reaction. We have therefore undertaken further investigations on this issue.

C. Effect of Coligands on the Energetics. First, we considered the reaction with L_2 = dcpe, which was also studied experimentally by Hoberg and co-workers.[5,6] The gas-phase energetics calculated for the most important species involved in the reaction are given in Table 3. The relative stability of these species is quite similar to that of their L_2 = bpy analogues, but there are a few interesting points to be mentioned. For example, the calculations predict the Ni(dcpe)(CO_2)(C_2H_4) complex to lie even above the Ni(dcpe)(CO_2) + C_2H_4 level, indicating that the Ni(dcpe)(CO_2)(C_2H_4) complex is not expected to be an intermediate in the C−C bond formation for the Ni(cdt) + dcpe + CO_2 + C_2H_4 → Ni(dcpe)(CH_2CH_2COO) + cdt reaction either, and the oxidative coupling should also occur in a single step, as we found for L_2 = bpy.

It is also worth mentioning that despite the similarity in the calculated C−C coupling energy barriers (the calculated gas-phase values are 22.7 and 22.9 kcal/mol for L_2 = bpy, dcpe, respectively), the metalla−carboxylate species in the latter reaction is not separated so clearly in energy from the Ni(dcpe)(C_2H_4) + CO_2 intermediate. The calculated exothermicity of the oxidative coupling step is 12.4 kcal/mol for L_2 = bpy, whereas this energy difference reduces to 4.5 kcal/mol when using L_2 = dcpe. These findings are consistent with the experimental observation that, for L_2 = dcpe, the C−C bond formation is reversible.[6]

To monitor the effect emerging from the presence of electron-donating and electron-withdrawing groups on the bpy ligand, we investigated the effect of methoxy and nitro substituents at the 4- and 4′-positions in bpy (Scheme 3) and estimated the relative stability of the three stationary points associated with the C−C coupling (see Table 3). As is expected from the charge-transfer mechanism of the oxidative C−C coupling, the exothermicity of the Ni(L_2)(C_2H_4) + CO_2 → Ni(L_2)(CH_2CH_2COO) elementary step decreases on going from L_2 = bpy to L_2 = nbpy (the exothermicities are −12.4 and

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(41) (a) Dinjus, E.; Langbein, H.; Walther, D. *J. Organomet. Chem.* **1978**, *152*, 229. (b) Schröder, W.; Pörschke, K. R. *J. Organomet. Chem.* **1987**, *322*, 385.

−6.5 kcal/mol, respectively), because the electron-withdrawing $-NO_2$ groups reduce the σ-donating ability of the chelating ligand, resulting in the reduction of charge density on the metal center. On the other hand, the methoxy substitution facilitates the $Ni \rightarrow CO_2$ and $Ni \rightarrow C_2H_4$ electron donation; thus, the stability of the $Ni(L_2)(CH_2CH_2COO)$ species is enhanced with L_2 = mbpy (the exothermicity of this step is calculated to be −14.7 kcal/mol). Consistent with this trend, the calculated activation barriers vary in the following order: nbpy (27.2 kcal/mol) > bpy (22.7 kcal/mol) > mbpy (20.6 kcal/mol).

All these results indicate that the energetics of the metal-induced $CO_2-C_2H_4$ coupling reactions are rather sensitive to the choice of ancillary ligands and demonstrate their importance in these processes.

Concluding Remarks

Density functional theory has been applied to elucidate the mechanism of Ni(0)-assisted $CO_2-C_2H_4$ coupling reactions that were previously shown to produce cyclic metalla−carboxylate species. As a prelude to our mechanistic study, we have estimated the accuracy of the applied DFT methodology on a model reaction and found that the B3LYP/6-311++G(d,p) level gives very accurate relative energies for the located minima, but it overestimates the barrier of the C−C bond formation by about 20%.

We have shown that the $Ni(cdt) + bpy + CO_2 + C_2H_4 \rightarrow Ni(bpy)(CH_2CH_2COO) + cdt$ reaction is initiated by the addition of chelating bpy to Ni(cdt), which is followed by an olefin exchange that gives the $Ni(bpy)(C_2H_4)$ intermediate. The main conclusion of our work is that the coordination of the reacting CO_2 molecule, i.e., the formation of a “mixed” ethylene−carbon dioxide complex, is not a prerequisite for the $CO_2-C_2H_4$ coupling reactions, because the C−C bond formation in the present reaction is shown to occur in a single step from the reaction of the $Ni(bpy)(C_2H_4)$ intermediate with an incoming CO_2. Although the $Ni(bpy)(CO_2)(C_2H_4)$ complex has been identified as a minimum on the potential energy surface, the barrier to $Ni(bpy)(C_2H_4) + CO_2$ dissociation is extremely low; therefore, its presence in the reaction mixture is quite unlikely.

We have also examined the coligand effect on the calculated energetics and found that the relative stability of the two minima associated with the C−C bond formation and the related activation barrier are sensitive to the nature of the chelating ligands. Theoretical studies to elucidate possible reaction pathways from the metallacycle toward the formation of acrylic acid in systems involving other transition metals and a wide variety of coligands are in progress in our group.

Acknowledgment. This work has been supported in part by the Hungarian Research Foundation (OTKA grants: T037345 and T034547). Computer facilities provided by the NIIF Supercomputer Center in Budapest are greatly acknowledged.

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