

Theoretical Characterizations of the Ring Expansion of a Metallacyclopropane to a Metallacyclopentane

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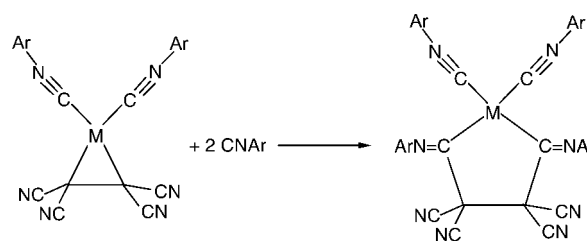
The potential energy surfaces for the ring expansion reactions of 16-valence-electron d^{10} metallacyclopropane species have been studied using density functional theory (B3LYP/LANL2DZ). Three metallacyclopropane species of the form $(\eta^2\text{-TCNE})\text{M}(\eta\text{-CNC}_6\text{H}_5)_2$, where M = Ni, Pd, and Pt, have been chosen as model reactants in this work. Also, the isocyanide with the form CNC_6H_5 has been used to study the ring expansion reactivities of these group 10 transition metal elements. Accordingly, this ring expansion reaction can be considered to proceed from metallacyclopropane to metallacyclopentane via the insertions of two isocyanide molecules. The present theoretical investigations suggest that the relative 16-valence-electron metallacyclopropane species' reactivity increases in the order nickelacyclopropane (**1**) < palladacyclopropane (**2**) \ll platinacyclopropane (**3**). That is, a less electronegative as well as a heavier group 10 atom center will lead to a smaller ΔE_{st} and, in turn, will facilitate the ring expansion reactions with isocyanides. Furthermore, the singlet–triplet energy splitting of the 16 valence-electron metallacyclopropane species, as described in the configuration mixing model attributed to the work of Pross and Shaik, can be used as a diagnostic tool to predict their ring expansion reactivities. The results obtained allow a number of predictions to be made.

I. Introduction

The principal motivation for this research is a remarkable recent experimental discovery in the laboratory of Nagashima.¹ Via a variable-temperature NMR spectroscopy and several other probe techniques, the Japanese group reported that the group 10 metal isocyanide complexes bearing a $\eta^2\text{-TCNE}$ ligand, $(\eta^2\text{-TCNE})\text{Ni}(\eta\text{-CNC}_6\text{H}_3\text{-2-6-Me}_2)_2$ (**1**), $(\eta^2\text{-TCNE})\text{Pd}(\eta\text{-CNC}_6\text{H}_3\text{-2-6-Me}_2)_2$ (**2**), and $(\eta^2\text{-TCNE})\text{Pt}(\eta\text{-CNC}_6\text{H}_3\text{-2-6-Me}_2)_2$ (**3**), were synthesized and characterized structurally.¹ In particular, they found that the coordination mode of the $\eta^2\text{-TCNE}$ ligand is a typical metallacyclopropane extreme, in which back-donation from Pt to TCNE contributes primarily to the stabilization of **3**.¹ Moreover, treatment of **3** with 2 equiv of $\text{CNC}_6\text{H}_3\text{-2,6-Me}_2$ resulted in ring expansion of the platinacyclopropane by insertion of $\text{CNC}_6\text{H}_3\text{-2,6-Me}_2$ into each platinum–carbon bond of the metallacycle, leading to formation of a new metal complex having a platinacyclopentane structure $(\text{TCNE})\text{-Pt}(\eta\text{-CNC}_6\text{H}_3\text{-2-6-Me}_2)_4$ (**4**). In spite of the molecular structures of nickel and palladium homologues of **3** being close to the corresponding platinacyclopropane, no metallacyclopentane complex was obtained under similar conditions.¹ Nagashima and co-workers proposed two possibilities for such a phenomena.¹ One is due to kinetic reasons. The insertion of an isocyanide requires a large contribution from back-donation, and only the platinum complex fits in this criterion. The other is due to thermodynamic reasons. The isocyanide undergoes a reversible insertion reaction with nickel and palladium homologues.

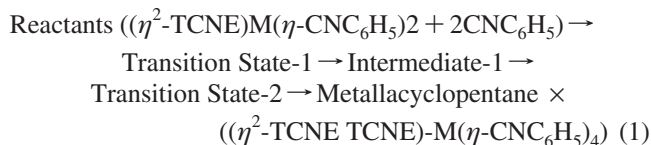
It is this fascinating experimental progress that has inspired this study. As far as we are aware, no theoretical study of such ring expansion reactions involving the group 10 compounds has

Scheme 1



been reported, even though two similar ring expansion reactions were investigated experimentally.^{2,3} Since the ring expansion reactions are both novel and useful, a detailed mechanistic knowledge would allow more control of their reactivity. In fact, a detailed understanding of ring expansion reactivity is of interest not only for the advancement of basic science but also for the continued development of their applications.

In this work we present the first density functional theory (DFT) study of the reaction potential surfaces of $(\eta^2\text{-TCNE})\text{M}(\eta\text{-CNC}_6\text{H}_5)_2$ with 2 isocyanide (CNC_6H_5) molecules. The metal, M, is nickel, palladium, or platinum. See Scheme 1. That is, the reaction process is as follows:



Through this theoretical study, we hope (a) to obtain a detailed understanding of the ring expansion mechanisms from metallacyclopropane to metallacyclopentane by way of 16-electron

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d^{10} ML_2 -type complexes, (b) to investigate the influence of different central metal atoms on the geometries and energies of the intermediates and transition states, and (c) to reveal the factors that control the activation barriers for these ring expansion reactions. It is our intention to show clearly that the singlet–triplet energy gap of the 16-electron d^{10} ML_2 species can be used as a guide to predict its reactivity for ring expansion reactions.

II. Methodology

All the geometries were fully optimized without imposing any symmetry constraints, although in some instances the resulting structure showed various elements of symmetry. For our DFT calculations, we used the hybrid gradient-corrected exchange functional proposed by Becke,⁴ combined with the gradient-corrected correlation functional of Lee, Yang, and Parr.⁵ This functional is commonly known as B3LYP and has been shown to be quite reliable for both geometries and energies.⁶ These B3LYP calculations were carried out using relativistic effective core potentials on the group 10 transition elements modeled using the double- ζ (DZ) basis sets⁷ augmented by a set of d-type polarization functions.^{7c} Accordingly, we denote our B3LYP calculations by B3LYP/LANL2DZ. The spin-unrestricted (UB3LYP) formalism was used for the open-shell (triplet) species. The computed expectation values of the spin-squared operator $\langle S^2 \rangle$ were in the range 2.001–2.005 for all of the triplet species considered here. They were therefore very close to the correct value of 2.0 for pure triplets, so that their geometries and energetics are reliable for this study. Frequency calculations were performed on all the structures to confirm that the reactants and products had no imaginary frequencies and that the transition states possessed only one imaginary frequency. The relative energies were thus corrected for vibrational zero-point energies (ZPE, not scaled). Thermodynamic corrections to 298 K, ZPE corrections, heat capacity corrections, and entropy corrections (ΔS) obtained were applied at the B3LYP/LANL2DZ level. Thus, the relative free energy (ΔG) at 298 K was also calculated at the same level of theory. All of the theoretical calculations were performed using the GAUSSIAN 03 package of programs.⁸

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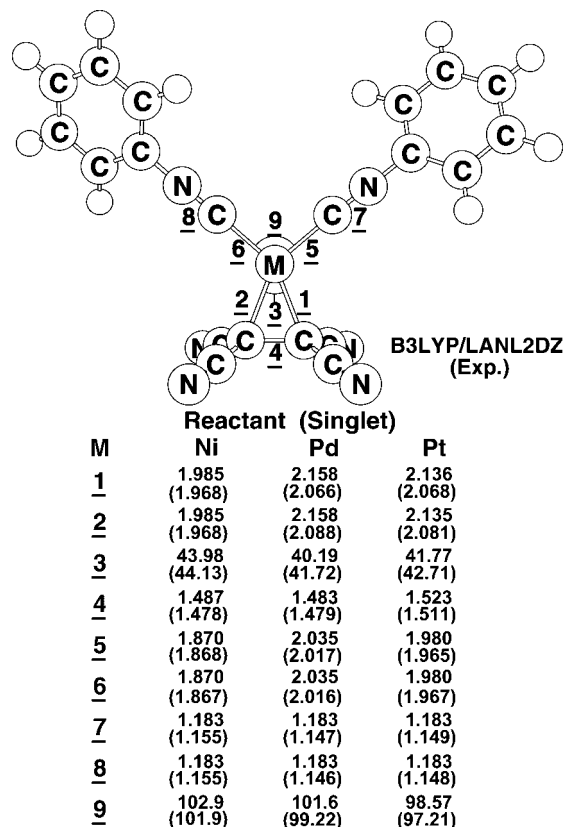
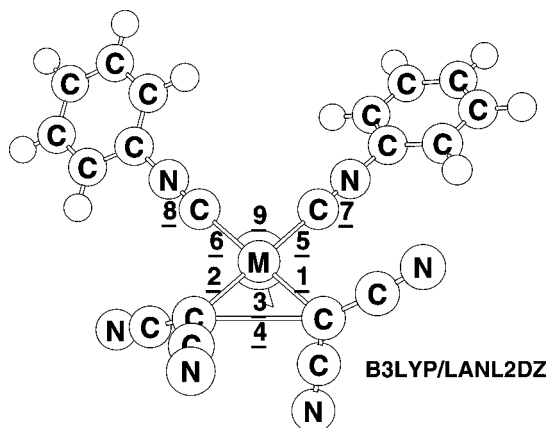


Figure 1. B3LYP/LANL2DZ-optimized geometries (in Å and deg) of the reactants (singlet) $(\eta^2\text{-TCNE})M(\eta\text{-CNC}_6\text{H}_5)_2$ ($M = \text{Ni, Pd, and Pt}$). The experimental values (see ref 1) are in parentheses. The relative energies for each species are shown in Table 1. Hydrogens are omitted for clarity.

III. Results and Discussion

1. Geometries and Electronic Structures of Metallacyclopropane and Metallacyclopentanes. Before discussing the geometrical optimizations and the potential energy surfaces for the chemical reactions of metallacyclopropane to metallacyclopentane with the group 10 transition elements, we shall first examine the geometries and electronic structures of the reactants and final products, i.e., $(\eta^2\text{-TCNE})M(\eta\text{-CNC}_6\text{H}_5)_2$ and $(\eta^2\text{-TCNE})M(\eta\text{-CNC}_6\text{H}_5)_4$ ($M = \text{Ni, Pd, and Pt}$), respectively. The optimized geometries for these transition metal complexes were calculated at the B3LYP/LANL2DZ level of theory, and their selected geometrical parameters are collected in Figures 1 and 2, where they are compared with some available experimental data.¹ Also, experimentally measured geometrical parameters of platinacyclopentane (TCNE)-Pt($\eta\text{-CNC}_6\text{H}_5$)₄ (**Pt-Pro**) are given in Figure 3 for comparison with our B3LYP results. The relative energies obtained from the B3LYP calculations are summarized in Table 1. Their Cartesian coordinates are included in the Supporting Information.

The theoretical findings based on the B3LYP calculations indicate that they all possess a singlet ground state. As can be seen in Figure 1, the agreement for both bond lengths and bond angles in the rings ($M = \text{Ni, Pd, and Pt}$) between the B3LYP results and experiments¹ for the singlet metallacyclopropane is quite good, with the bond lengths and angles in agreement to within 0.092 Å and 2.4°, respectively. Again, as can be seen in Figure 3, the molecular parameters of platinacyclopentane (**Pt-Pro**) for our B3LYP calculations compare well with the experimental results.¹ The bond lengths and bond angles are in agreement to within 0.064 Å and 2.5°, respectively. As a result

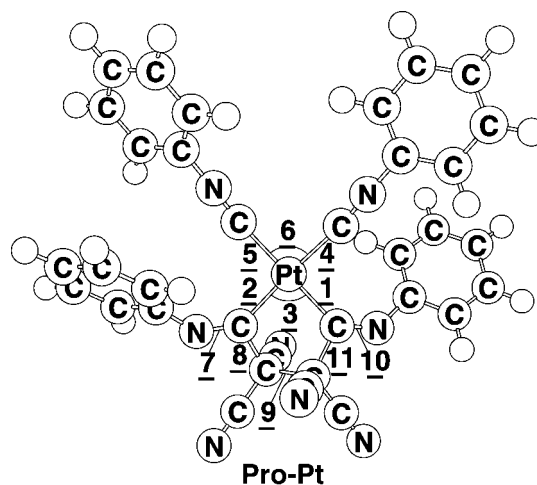


X	Reactant (Triplet)		
	Ni	Pd	Pt
<u>1</u>	1.939	2.072	2.071
<u>2</u>	1.942	2.073	2.071
<u>3</u>	90.31	89.58	90.03
<u>4</u>	2.752	2.920	2.930
<u>5</u>	1.885	2.033	1.995
<u>6</u>	1.887	2.034	1.996
<u>7</u>	1.179	1.178	1.178
<u>8</u>	1.178	1.178	1.178
<u>9</u>	92.27	93.94	93.54

Figure 2. B3LYP/LANL2DZ-optimized geometries (in Å and deg) of the reactants (triplet) $(\eta^2\text{-TCNE})\text{M}(\eta\text{-CNC}_6\text{H}_5)_2$ (M = Ni, Pd, and Pt). The relative energies for each species are shown in Table 1. Hydrogens are omitted for clarity.

of these good agreements on the known singlet-state features, we are confident that the computational methods used in this study are reliable and useful for comparison with possible future experimental studies.

An interesting trend that can be observed in Figures 1 and 2 is the increase in the bond distances (i.e., M–TCNE) and the decrease in the bond angles (i.e., $\angle\text{CMC}$) on going from the singlet to the triplet state. The reason for this phenomenon could be due to the occupation of antibonding orbitals.¹² Furthermore, according to the Dewar–Chatt–Duncanson model,⁹ the nature of the bonding in an olefin transition metal complex is described by the synergistic σ -bonding and π -back-bonding interactions using olefinic π -type and metal d orbitals. In a resonance formulation, the structure is depicted as a combination of two resonance hybrids, a π -complex and a metallacyclopropane, while the relative importance of the two structures depends on the electronic nature of both the metal and the olefin.¹⁰ See Figure 4. On one hand, in the “ π -complex” species, interaction of the ethylene HOMO with unoccupied orbitals of a weakly π -basic transition metal fragment can make the carbon–carbon bond distance slightly longer than that of uncoordinated ethylene



X	B3LYP/LANL2DZ		EXP.
	B3LYP/LANL2DZ	EXP.	
<u>1</u>	2.089	2.028	
<u>2</u>	2.081	2.017	
<u>3</u>	83.40	83.23	
<u>4</u>	2.022	2.008	
<u>5</u>	2.017	1.998	
<u>6</u>	87.79	85.30	
<u>7</u>	1.279	1.283	
<u>8</u>	1.592	1.583	
<u>9</u>	1.579	1.535	
<u>10</u>	1.277	1.271	
<u>11</u>	1.600	1.581	

Figure 3. B3LYP/LANL2DZ-optimized geometries (in Å and deg) of the insertion product of $(\eta^2\text{-TCNE})\text{Pt}(\eta\text{-CNC}_6\text{H}_5)_4$. The relative energies for each species are shown in Table 1. Hydrogens are omitted for clarity.

(1.337 Å).^{10,11} On the other hand, in the “metallacyclopropane” species, interaction of occupied orbitals of the transition metal fragment with the LUMO of ethylene contributes to significant elongation of the carbon–carbon bond and a change in the hybridization of the olefinic carbons of ethylene from sp^2 to sp^3 on coordination. From the above discussion, it is evident that the carbon–carbon bond distance and the planarity of the coordinated TCNE are key indications of a combination of donation and back-donation.¹ Stalick and Ibers¹³ define the α angle for discussing the deviation from planarity of the alkene by coordination to the transition metal center as given in Scheme 2. As a result, a longer carbon–carbon bond distance and a larger α angle indicate an increased contribution from back-donation, which can give a typical metallacyclopropane extreme. As one can see in Figure 1, the C–C bond distance in TCNE of the metallacyclopropane increases in the order Ni (1.478 Å) < Pd (1.479 Å) < Pt (1.511 Å).¹ This compares well with the B3LYP results: Ni (1.487 Å) < Pd (1.488 Å) < Pt (1.523 Å). That is to say, the carbon–carbon distance of the coordinated C=C moiety for 1–3 is significantly longer than that of the uncoordinated TCNE molecule by 0.134 Å (Ni), 0.137 Å (Pd), and 0.167 Å (Pt), respectively. Similarly, our theoretical

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Table 1. Relative Energies for Singlet and Triplet Group 10 Metallacyclopropane, (η^2 -TCNE) $M(\eta$ -CNC₆H₅)₂, (ΔE_{st}) and for the Ring Expansion Process: Reactants ($(\eta^2$ -TCNE) $M(\eta$ -CNC₆H₅)₂ + 2CNC₆H₅) \rightarrow Transition State-1 (ΔE_1^\ddagger) \rightarrow Intermediate-1 (ΔH_1) \rightarrow Transition State-2 (ΔE_2^\ddagger) \rightarrow Metallacyclopentane ($(\eta^2$ -TCNE)- $M(\eta$ -CNC₆H₅)₄) (ΔH_2^{ab})

system ^c	ΔE_{st}^d (kcal mol ⁻¹)	$\Delta E_1^{\ddagger e}$ (kcal mol ⁻¹)	ΔH_1^e (kcal mol ⁻¹)	$\Delta E_2^{\ddagger e}$ (kcal mol ⁻¹)	ΔH_2^e (kcal mol ⁻¹)
M = Ni	51.42	20.31	6.203	24.65	11.68
M = Pd	46.26	19.50	4.222	20.08	-2.590
M = Pt	31.26	7.671	-5.462	13.12	-14.27

^a All were calculated at the B3LYP/LANL2DZ level of theory. For the B3LYP-optimized structures of the stationary points see Figures 2–8. ^b Energy differences have been zero-point corrected. See the text. ^c The dipole moments for nickelacyclopropane (1), palladacyclopropane (2), and platinumacyclopropane (3) are calculated to be 15.34, 15.29, and 16.49 D, respectively. ^d A positive value means the singlet is the ground state. ^e All energies relative to the corresponding singlet state.

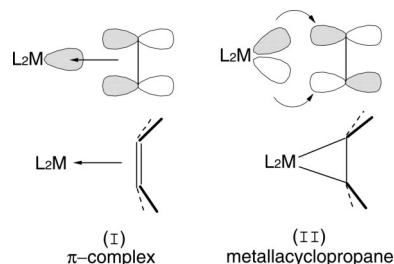
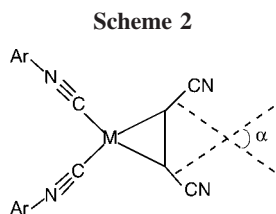


Figure 4. Comparisons of transition metal–olefin interaction: (I) σ -donation and (II) π -back-donation.



calculations indicate that the C=C bond length is greater than that of the uncoordinated TCNE compound by 0.106 Å (Ni), 0.107 Å (Pd), and 0.142 Å (Pt), respectively [B3LYP/LANL2DZ uncoordinated TCNE: C=C 1.381 Å]. Besides this, the experimental α angle decreases in the order 61.0° (Ni) > 54.5° (Pt) > 53.1° (Pd), while the theoretical α angle decreases in the order 54.1° (Ni) > 52.9° (Pt) > 38.2° (Pd). As a consequence, all the above evidence strongly suggests that back-donation favorably contributes to the coordination of TCNE in the nickel, palladium, and platinum homologues. As a result, our theoretical findings are consistent with the experimental observations.¹

Furthermore, the other intriguing feature is the singlet–triplet splitting ($\Delta E_{st} = E_{\text{triplet}} - E_{\text{singlet}}$) of the metallacyclopropane. As shown in Table 1, our DFT calculations indicate that the singlet–triplet splittings for **Rea-1**, **Rea-2**, and **Rea-3** are 51 (Ni), 46 (Pd), and 31 (Pt) kcal/mol, respectively. That is, ΔE_{st} decreases in the order Ni > Pd > Pt, following the same trend as the electronegativity of the central atom M. Apparently, the group 10 transition metal elements are pivotal atoms in this regard. Finally, as shown in Table 1, all the metallacyclopropane species are predicted to have singlet ground states according to the B3LYP computational results. This indicates that all the chemical reactions (eq 1) studied in the work should proceed on the singlet surface. We shall thus focus on the singlet surface from now on.

2. First Transition State of One Isocyanide Insertion Reactions. As stated earlier, the reaction from metallacyclopropane to metallacyclopentane can be considered as a ring expansion of the three-membered ring species to the five-membered complex by incorporation of two molecules of CNC₆H₅-2-6-Me₂. One may thus predict that the insertion mechanism should be like that illustrated in eq 1. That is, one isocyanide molecule (CNC₆H₅) is inserted into one M–C bond

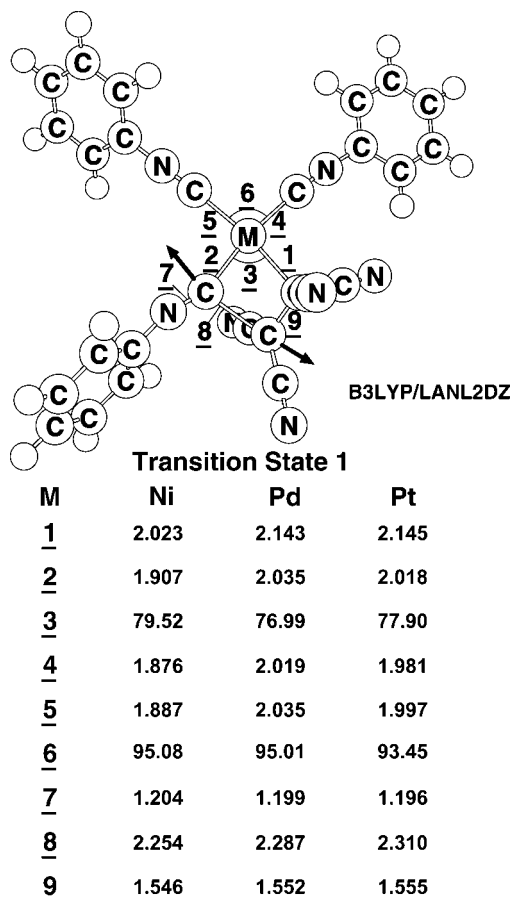
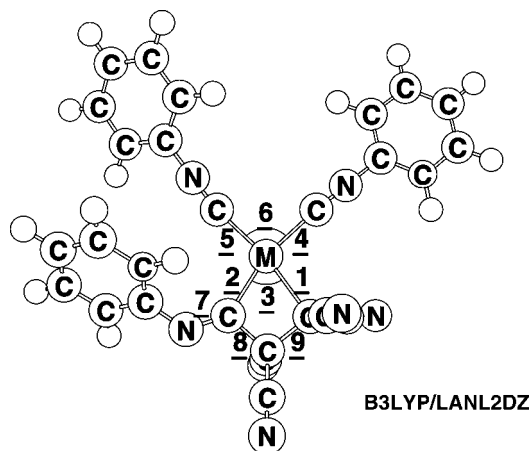


Figure 5. B3LYP/LANL2DZ-optimized geometries (in Å and deg) of the transition states of (η^2 -TCNE) $M(\eta$ -CNC₆H₅)₂ (M = Ni, Pd, and Pt) and an isocyanide (CNC₆H₅) molecules. The relative energies for each species are shown in Table 1. The heavy arrows indicate the main atomic motions in the transition-state eigenvector. Hydrogens are omitted for clarity.

in (η^2 -TCNE) $M(\eta$ -CNC₆H₅)₂ to form a four-membered-ring species. Then, the second isocyanide molecule is again inserted into the other M–C bond in (η^2 -TCNE) $M(\eta$ -CNC₆H₅)₂ to form a five-membered-ring complex. The optimized transition-state structures (**Ni-TS-1**, **Pd-TS-1**, and **Pt-TS-1**) along with the calculated transition vectors are given in Figure 5, respectively. Also, the relative energies of these stationary points based on the B3LYP method are summarized in Table 1. The arrows in Figure 5 indicate the directions in which the atoms move in the normal coordinate corresponding to the imaginary frequency. It is apparent that these transition states connect the reactant molecules to the corresponding insertion intermediates (metallacyclobutane). Examination of the single imaginary frequency for each transition state (188i cm⁻¹ for **Ni-TS-1**, 207i cm⁻¹ for **Pd-TS-1**, and 191i cm⁻¹ for **Pt-TS-1**) provides an excellent



Intermediate			
M	Ni	Pd	Pt
<u>1</u>	2.024	2.159	2.149
<u>2</u>	1.934	2.056	2.057
<u>3</u>	71.66	68.33	68.80
<u>4</u>	1.911	2.079	2.026
<u>5</u>	1.867	2.017	1.974
<u>6</u>	93.95	92.90	91.31
<u>7</u>	1.274	1.272	1.278
<u>8</u>	1.560	1.556	1.569
<u>9</u>	1.588	1.601	1.611

Figure 6. B3LYP/LANL2DZ-optimized geometries (in Å and deg) of the intermediate of $(\eta^2\text{-TCNE})\text{M}(\eta\text{-CNC}_6\text{H}_5)_2$ ($\text{M} = \text{Ni}, \text{Pd},$ and Pt) and an isocyanide (CNC_6H_5) molecule. The relative energies for each species are shown in Table 1. Hydrogens are omitted for clarity.

confirmation of the concept of an insertion process. That is, an isocyanide molecule attacks one $\text{M}-\text{C}$ bond to form the metallacyclobutane complex.

3. Metallacyclobutane Intermediates of One Isocyanide Insertion Reactions. The geometries and energetics of the metallacyclobutane intermediate points (**Int-Ni**, **Int-Pd**, and **Int-Pt**) for an isocyanide insertion reaction (i.e., eq 1) have been calculated using the B3LYP method. The fully optimized geometries for these four-membered-ring intermediates calculated at the B3LYP/LANL2DZ level are given in Figure 6. Their relative energies are also collected in Table 2. Cartesian coordinates calculated for these points at the DFT level are included in the Supporting Information. As expected, these metallacyclobutanes all display four-membered-ring bonding characteristics. Unfortunately, according to the experimental observations,¹ so far no metallacyclobutane has been found. Nevertheless, such a species is possibly involved as a reaction intermediate.

4. Second Transition State of Two Isocyanide Insertion Reactions. Again, the optimized transition-state structures (**Ni-TS-2**, **Pd-TS-2**, and **Pt-TS-2**) together with arrows indicating the main atom motion in the transition-state eigenvector are shown in Figure 7. Examination of the single imaginary frequency for each transition state ($108i \text{ cm}^{-1}$ for **Ni-TS-2**, $106i \text{ cm}^{-1}$ for **Pd-TS-2**, and $130i \text{ cm}^{-1}$ for **Pt-TS-2**) provides an excellent confirmation of the concept of the second isocyanide insertion process. That is, the reactants approach each other with

their molecular planes perpendicular, and two new bonds are formed at the same time.

All these transition-state structures show the same three-center pattern involving metal, carbon, and carbon atoms. The transition-state vectors represented by the heavy arrows in the transition-state structures all are in accordance with the insertion process, primarily the $\text{M}-\text{C}$ bond stretching with a isocyanide molecule migrating to the metal center.

5. Metallacyclopentanes from Two Isocyanide Insertion Reactions. Finally, the optimized product geometries (**Ni-Pro**, **Pd-Pro**, and **Pt-Pro**) are collected in Figure 8. Examining these product conformations, it is obvious that the product structure contains a five-membered-ring form. Also, the relative energies of these stationary points based on the B3LYP/LANL2DZ method are summarized in Table 1. The Cartesian coordinates and energies calculated for these points at the B3LYP level are available as Supporting Information.

IV. Overview of Metallacyclopropane Ring Expansion Reaction

The potential energy profiles based on the data in Table 1 are summarized in Figure 9. Five intriguing results can be drawn from this figure.¹⁶

(1) Starting from the reactants, metallacyclopropane, and two isocyanides, there are three reaction paths for **Rea-1** (Ni), **Rea-2** (Pd), and **Rea-3** (Pt), respectively. As shown in Figure 9, the interaction between one isocyanide and the metallacyclopropane, resulting in the first ring expansion, is the first step (**TS1**) in all three paths, producing the metallacyclobutane (**Int**). Then, an intermolecular insertion of the second isocyanide into the other $\text{M}-\text{C}$ bond of the metallacyclobutane occurs, completing the formation of the five-membered-ring product, metallacyclopentane (**Pro**).

(2) In the first step (**Rea** \rightarrow **TS1**), the energy barrier was calculated to decrease in the order **Ni-TS-1** (20.3 kcal/mol) > **Pd-TS-1** (19.5 kcal/mol) > **Pt-TS-1** (7.67 kcal/mol). In the second step (**TS1** \rightarrow **Int**), the enthalpy with respect to the reactant molecules was determined to decrease in the order **Ni-Int** (6.20 kcal/mol) > **Pd-Int** (4.22 kcal/mol) > **Pt-Int** (-5.46 kcal/mol). In particular, the energy of **Pt-Int** is lower than that of its corresponding reactant **Rea-3**. Again, in the third step (**Int** \rightarrow **TS2**), the barrier height was computed to decrease in the order **Ni-TS-2** (24.7 kcal/mol) > **Pd-TS-2** (20.1 kcal/mol) > **Pt-TS-2** (13.1 kcal/mol). This is the rate-determining step for the whole reaction. Finally, the entire reaction enthalpy decreases in the order **Ni-Pro** (11.7 kcal/mol) > **Pd-Pro** (-2.59 kcal/mol) > **Pt-Pro** (-14.3 kcal/mol). This strongly indicates that the ring expansion reactions by nickelacyclopropane (**Rea-1**) and palladacyclopropane (**Rea-2**) are energetically unfavorable and would be endothermic.

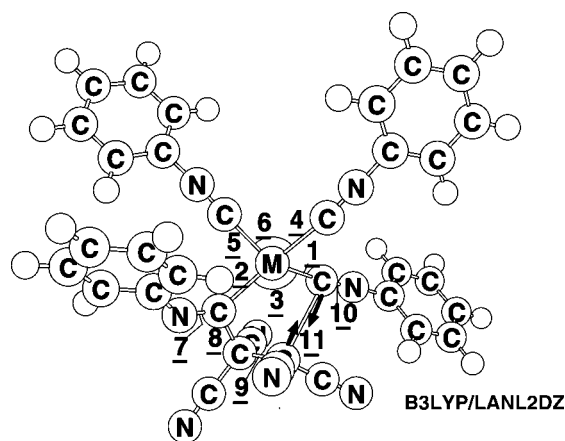
(3) As mentioned in the Introduction, according to Nagashima and co-workers' paper,¹ the insertion of $\text{CNC}_6\text{H}_3\text{-2-6-Me}_2$ should also take place in nickelacyclopropane (**Rea-1**) and palladacyclopropane (**Rea-2**), but it is essentially reversible. However, our model results, as demonstrated in Figure 9, suggest that these two compounds cannot undergo reversible reactions from an energetic viewpoint.

(4) Considering both the activation barrier and reaction enthalpy based on the model calculations presented here, we conclude that the metallacyclopropane reactivity order is as follows: **Rea-1** (Ni) < **Rea-2** (Pd) \ll **Rea-3** (Pt). In other words, a metallacyclopropane with a heavier but less electronegative central atom will undergo a more rapid and more exothermic ring expansion reaction with isocyanide. Our conclusions are

Table 2. Relative Gibbs Free Energies for Singlet and Triplet Group 10 Metallacyclopropane, (η^2 -TCNE)M(η -CNC₆H₅)₂, (ΔE_{st}) and for the Ring Expansion Process: Reactants ($(\eta^2$ -TCNE)M(η -CNC₆H₅)₂ + 2CNC₆H₅) \rightarrow Transition State-1 (ΔG_1^\ddagger) \rightarrow Intermediate-1 (ΔG_1) \rightarrow Transition State-2 (ΔG_2^\ddagger) \rightarrow Metallacyclopentane ($(\eta^2$ -TCNE)-M(η -CNC₆H₅)₄) (ΔG_2^{ab})

system	ΔE_{st}^c (kcal mol ⁻¹)	G_1^{*d} (kcal mol ⁻¹)	ΔG_1^d (kcal mol ⁻¹)	ΔG_2^{*d} (kcal mol ⁻¹)	ΔG_2^d (kcal mol ⁻¹)
M = Ni	47.56	33.96	21.43	53.70	38.33
M = Pd	44.28	33.15	20.74	34.70	27.33
M = Pt	29.58	20.35	7.801	24.27	-4.295

^a All were calculated at the B3LYP/LANL2DZ level of theory. For the B3LYP-optimized structures of the stationary points see Figures 2–8. ^b All energies relative to the corresponding singlet state. ^c A positive value means the singlet is the ground state. ^d All energies relative to the corresponding singlet state.

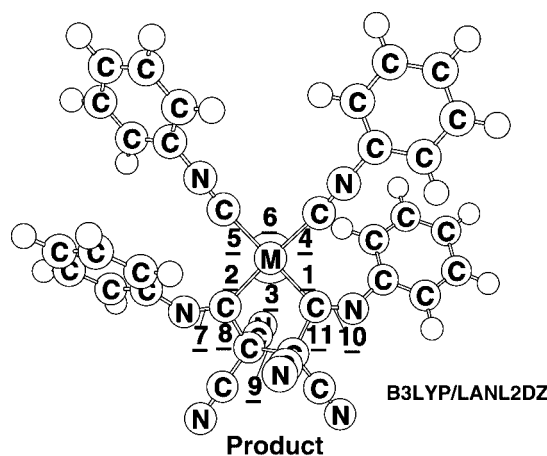


M	Transition State 2		
	Ni	Pd	Pt
<u>1</u>	2.069	2.321	2.232
<u>2</u>	1.971	2.087	2.085
<u>3</u>	111.5	108.4	106.3
<u>4</u>	1.963	2.135	2.054
<u>5</u>	1.842	1.983	1.935
<u>6</u>	93.28	92.60	91.36
<u>7</u>	1.267	1.264	1.274
<u>8</u>	1.547	1.548	1.559
<u>9</u>	1.561	1.566	1.582
<u>10</u>	1.186	1.185	1.184
<u>11</u>	2.972	3.153	3.055

Figure 7. B3LYP/LANL2DZ-optimized geometries (in Å and deg) of the transition states of (η^2 -TCNE)M(η -CNC₆H₅)₂ (M = Ni, Pd, and Pt) and two isocyanide (CNC₆H₅) molecules. The relative energies for each species are shown in Table 1. The heavy arrows indicate the main atomic motions in the transition-state eigenvector. Hydrogens are omitted for clarity.

in good agreement with the experimental observations.¹ That is, only the platinum–TCNE complex reacts with CNC₆H₅-2-6-Me₂, and the palladium and nickel homologues do not.

(5) We have also calculated the free energy differences (ΔG) for eq 1 at 298 K, which are also given in Table 2. As shown there, in contrast to platinacyclopropane (**Rea-3**), our theoretical results indicate that, after considering the thermodynamic factors, the energies of stationary points of nickelacyclopropane (**Rea-1**) and palladacyclopropane (**Rea-2**) are still above that of the corresponding reactants. Our theoretical investigations therefore strongly suggest that the ring expansion reaction should occur only during the formation of the platinacyclopentane species (**Pt-Pro**). Indeed, our theoretical conclusions are in good agreement with the available experimental observations.¹



M	Product		
	Ni	Pd	Pt
<u>1</u>	1.988	2.100	2.089
<u>2</u>	1.970	2.086	2.081
<u>3</u>	86.72	83.07	83.40
<u>4</u>	1.902	2.075	2.022
<u>5</u>	1.905	2.068	2.017
<u>6</u>	88.42	87.71	87.79
<u>7</u>	1.275	1.274	1.279
<u>8</u>	1.602	1.591	1.592
<u>9</u>	1.567	1.579	1.579
<u>10</u>	1.268	1.273	1.277
<u>11</u>	1.618	1.600	1.600

Figure 8. B3LYP/LANL2DZ-optimized geometries (in Å and deg) of the final products of (η^2 -TCNE)M(η -CNC₆H₅)₂ (M = Ni, Pd, and Pt) and two isocyanide (CNC₆H₅) molecules. The relative energies for each species are shown in Table 1. Hydrogens are omitted for clarity.

V. Configuration Mixing Model

In this section, an intriguing model for interpreting the relative reactivity of the reactants is provided by the configuration mixing (CM) model, which is based on Pross and Shaik's work.^{14,15}

In this approach, it was suggested that the barrier for the reaction between metallacyclopropane and isocyanide is a result of a crossing between two surfaces, one associated with the

(14) For details, see: (a) Shaik, S.; Schlegel, H. B.; Wolfe, S. In *Theoretical Aspects of Physical Organic Chemistry*; John Wiley & Sons Inc.: New York, 1992. (b) Pross, A. In *Theoretical and Physical Principles of Organic Reactivity*; John Wiley & Sons Inc.: New York, 1995. (c) Shaik, S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197.

(15) The first paper that originated the CM model: (a) Shaik, S. *J. Am. Chem. Soc.* **1981**, *103*, 3692. About the most updated review of the CM model, one can see: (b) Shaik, S.; Shurki, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 586.

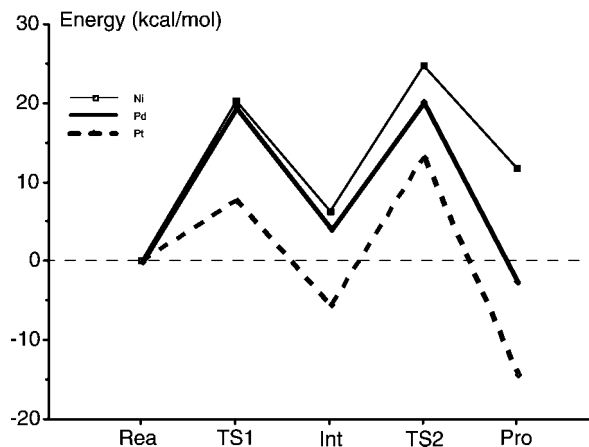


Figure 9. Potential energy profiles for the ring expansion process: reactants $((\eta^2\text{-TCNE})\text{M}(\eta\text{-CNC}_6\text{H}_5)_2 + 2\text{CNC}_6\text{H}_5) \rightarrow$ transition state-1 \rightarrow intermediate-1 \rightarrow transition state-2 \rightarrow metallacyclopentane $((\eta^2\text{-TCNE TCNE})\text{-M}(\eta\text{-CNC}_6\text{H}_5)_4)$. The relative energies for each species are shown in Table 1.

reactant spin-coupling (A) and the other with the product spin-coupling (B). In other words, configuration A, labeled $^1[\text{MC}_2]^1[\text{ArNC}]$, is termed the reactant configuration, in which the two electrons on the metallacyclopropane (MC_2) moiety are spin-paired to form the M–C bond, while the two electrons on the isocyanide (ArNC) moiety are spin-paired as well. On the other hand, configuration B is the product configuration. Note that the spin arrangement is now different. The electron pairs are coupled to allow both M–CNAr bond formation and simultaneous M–C ring bond breaking. In order to obtain this configuration from the reactant configuration A, each of the two original electron pairs needs to be uncoupled. Namely, those two electron pairs require excitation from the singlet state to the triplet state. Hence, this configuration is labeled $^3[\text{MC}_2]^3\text{-}[\text{ArNC}]$. It should be noted that there is no actual spin change here because, despite the fact that $^3[\text{MC}_2]^3[\text{ArNC}]$ appears to contain two triplet pairs, the overall spin state of $^3[\text{MC}_2]^3[\text{ArNC}]$ remains a singlet. Moreover, it is a doubly excited configuration only in the reactant geometry. In terms of the product geometry, it is not an excited configuration at all, just the configuration that describes the ground-state metallacyclobutane products. Consequently, it is the avoided crossing of these two configurations that leads to the simplest description of the ground-state energy profiles for the ring expansion.

According to the conclusions of this model (see Figure 10), the energy barriers governing processes as well as the reaction enthalpies are proportional to the energy gaps for both metallacyclopropane and isocyanide, that is, $\Delta E_{\text{st}} (= E_{\text{triplet}} - E_{\text{singlet}}$ for metallacyclopropane) $+ \Delta E_{\pi\pi^*} (= E_{\text{triplet}} - E_{\text{singlet}}$ for isocyanide). We therefore conclude that both the order of the singlet and triplet states and their energy separation are responsible for the existence and the height of the energy barrier.^{14,15} Bearing these analyses in mind, we shall now explain the origin of the following observed trends:

Why is the Pt reaction more favorable than the Ni and Pd reactions in the ring expansion by double insertion of isocyanides into M–C bonds?

(16) We have evaluated an alternative reaction mechanism in which insertion of a bound isocyanide and coordination of an additional one to the metal occur in this sequence, opposite that considered currently, via the intermediacy of three-coordinate M^{II} metallacyclobutane and -pentane structures. However, after about several weeks' search, it always failed. We thus think the mechanism proposed in the present work should be trustful.

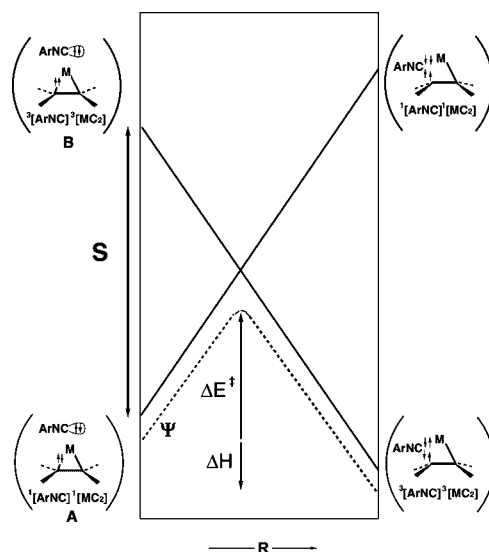


Figure 10. Energy diagram for a ring expansion reaction showing the formation of a state curve (Ψ) by mixing two configurations: the reactant configuration (A) and the product configuration (B). In the reactants, they are separated by an energy gap S . $S = \Delta E_{\text{st}}$ (i.e., the metallacyclopropane singlet–triplet splitting) $+ \Delta E_{\pi\pi^*}$ (i.e., the triplet excitation energy for isocyanide). Configuration mixing near the crossing point causes an avoided crossing (dotted line).

The reason for this can be traced back to the singlet–triplet gap (ΔE_{st}) of the 16-electron $d^{10}\text{ML}_2$ species. According to the available experiments,¹⁷ on one hand, Ni and Pd atoms have a triplet d^8s^2 and singlet d^{10} ground state with excitation energies of 9.8 and 22 kcal/mol, respectively, to the triplet d^9s^1 state. On the other hand, the ground state of the Pt atom is triplet d^8s^2 , but with an excitation energy of 11 kcal/mol to the singlet d^{10} state. This strongly implies that Pt would prefer to remain in a high-spin state, whereas both Ni and Pd favor a low-spin state. Indeed, our B3LYP/LANL2DZ results given in Table 1 indicate that the singlet–triplet energy splitting ΔE_{st} should be 51, 46, and 31 for **Rea-1**, **Rea-2**, and **Rea-3**, respectively. That is, ΔE_{st} of the Pt (**Rea-3**) complex is smaller than that of the Ni (**Rea-1**) and Pd (**Rea-2**) complexes. This suggests that the ring expansion reaction of isocyanides to a metallacyclopropane is easier and more exothermic for the Pt system than for either its Ni or Pd counterparts. This is what we observed in the 16-electron $d^{10}\text{ML}_2$ ($\text{M} = \text{Ni}, \text{Pd}, \text{and Pt}$) systems in the present work and in the experimental observations.¹ Accordingly, our theoretical findings are in good accordance with the CM model.

VI. Conclusion

Our DFT investigations present the first theoretical evidence that the ring expansion reactivity of 16-valence-electron d^{10} metallacyclopropane species with isocyanides increases in the order nickelacyclopropane (**Rea-1**) $<$ palladacyclopropane (**Rea-2**) \ll platinumacyclopropane (**Rea-3**).

Also, our study has shown that the singlet–triplet gap ΔE_{st} ($= E_{\text{triplet}} - E_{\text{singlet}}$) based on the CM model can provide a useful basis for understanding and rationalizing the relative magnitude of the activation barriers as well as the reaction enthalpies for the same ring expansion reaction. We are confident in predicting that, for the 16-valence-electron metallacyclopropane species

(17) Moore, C. E. In *Atomic Energy Levels*; NBS: Washington, D.C., 1971; Vol. III. (These state splittings were averaged over j states to cancel out spin–orbit coupling).

system, a less electronegative as well as a heavier transition metal atom center will lead to a smaller ΔE_{st} and, in turn, will facilitate the ring expansion reactions with isocyanides. Despite the fact that the estimated magnitude of the energy barriers and the predicted geometries of the transition states for such reactions may appear to be dependent on the level of calculation applied, our qualitative predictions are consistent with the computational results presented here as well as experimental findings.

It is hoped that this study can stimulate further research into the subject.

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