Theoretical Study of Cp_2Zr-, $(MeO)_2Zr$-, and $M(PH_3)$-Mediated Coupling Reactions of Acetylenes ($M = Ni, Pt$). Significant Differences between Early- and Late-Transition-Metal Complexes

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Theoretical calculations with DFT, MP2 to MP4(SDQ), and CCSD(T) methods clearly display that the Cp_2Zr-mediated coupling reaction of two acetylene molecules easily takes place through a nonsymmetrical transition state with nearly no barrier and significantly large exothermicity but the $M(PH_3)$-mediated reaction ($M = Ni, Pt$) takes place through a symmetrical transition state with either a considerably large activation barrier for $M = Pt$ or a moderately large activation barrier for $M = Ni$. The charge-transfer (CT) interaction between the d orbital of the transition-metal center and the $\pi^*-\pi^*$ bonding couple of two acetylene molecules plays an important role for the C−C bond formation in the $M(PH_3)$-mediated coupling reaction, which needs a symmetrical transition state structure. On the other hand, a CT interaction between the $d_\pi-\pi^*$ back-donation orbital of $Cp_2Zr(C_2H_2)$ and the π^* orbital of the second acetylene molecule is strongly formed in the Cp_2Zr-mediated coupling reaction, which leads to a nonsymmetrical transition state structure. These differences are reasonably interpreted by the $d_\pi-\pi^*$ back-donation of $Cp_2Zr(C_2H_2)$ being much stronger than that of $M(PH_3)(C_2H_2)$. This is because the early-transition-metal element has d orbitals at higher energy than does the late-transition-metal element. The $Ni(PH_3)$-mediated coupling reaction takes place with a smaller activation barrier than does the $Pt(PH_3)$-mediated reaction. This result is interpreted by noting that the 3d transition-metal element has d orbitals at higher energy than does the 5d transition-metal element. Also, $(MeO)_2Zr$-mediated coupling reaction proceeds with nearly no barrier, in spite of the fact that the d orbital is at lower energy in $(MeO)_2Zr(C_2H_2)$ than that in $Cp_2Zr(C_2H_2)$. This is because the MeO group is flexible and gives rise to little steric repulsion between ligands and substrates.

Introduction

Transition-metal-catalyzed coupling reactions of alkynes, which lead to syntheses of benzene and pyridine derivatives, have received considerable attention in organometallic chemistry and synthetic chemistry,[1] because syntheses of aromatic compounds are particularly important. Although this kind of transition-metal-catalyzed coupling reaction of alkynes was carried out a long time ago with low-valent nickel complexes by Reppe and his collaborators,[2] significant advancement has been achieved in the past decade not only with late-transition-metal complexes but also with early-transition-metal complexes such as $Cp_2ZrCl_2/2Bu^nLi$[1c,3] and $Ti(OPr^i)_4/2Pr^iMgCl$.[1g,4] Of these two species, $Cp_2ZrCl_2/2Bu^nLi$ is well-known as the Negishi reagent[5] and has been applied to many synthetic reactions such as syntheses of dienes, macrocycles, oligomers of acetylene, etc.[1c,5−10] Also, the $Ti(Pr^iO)_4/2Pr^iMgCl$ system is useful in similar synthetic reactions.[1g,4]

On the other hand, platinum(0) complexes are not very useful in the coupling reactions, except for a few

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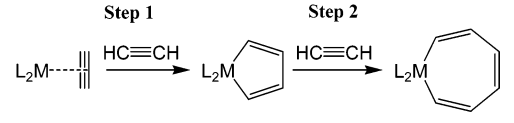
unexpected examples,[11−13] while transition-metal complexes such as Fe, Co, Ni, Ru, Rh, Pd, and Ir complexes are useful in the coupling reactions.[1a,b,d−f,h] Thus, it is worthwhile to theoretically investigate the reason Cp_2Zr and $Ti(OPr^i)_2$ species are reactive in the coupling reaction but the Pt(0) complex is not so reactive.

Scheme 1



$L_2M = Cp_2Zr, Ni(PH_3), \text{or } Pt(PH_3)$

However, only a few theoretical studies of transition-metal-catalyzed coupling reactions have been reported so far; for instance, acetylene trimerization by $CpCo(PH_3)$, CpCo, and CpRhCl complexes was theoretically investigated with the Hartree−Fock and DFT methods,[14−16] and the similar $Ni(PH_3)$-mediated coupling reaction of acetylene and carbon dioxide was investigated with the SD-CI method.[17] Also, the regioselectivity of the reaction between Cp_2Zr(alkyne) and alkyne was recently investigated with the DFT method.[18] Interestingly, the transition state is symmetrical in the CpCoL- and CpRhCl-catalyzed trimerization of acetylenes (L = none, PH_3)[14−16] and it is nearly symmetrical in the $Ni(PH_3)$-mediated coupling reaction between acetylene and carbon dioxide,[17] while the transition state is not symmetrical in the Cp_2Zr-mediated coupling reaction of acetylenes.[18] In 1980, Hoffmann and his collaborator discussed the orbital interaction in the transition-metal-mediated coupling reaction of two alkenes on the basis of the extended Hückel MO method[19] and clearly showed that the transition-metal-catalyzed coupling reaction of two alkenes proceeds through a symmetrical transition state. Thus, it is of considerable importance to clarify the reason that the transition state is not symmetrical in the Cp_2Zr-mediated coupling reaction.

In the present work, we have theoretically investigated Cp_2Zr-, $(MeO)_2Zr$-, and $M(PH_3)$-mediated coupling reactions of two acetylene molecules (M = Ni, Pt)[20] to afford metallacyclopentadienyl species (step 1 of Scheme 1) with DFT, MP2 to MP4(SDQ), and CCSD(T) methods. We selected these reactions because the Cp_2Zr-mediated coupling reaction of two acetylene molecules is involved as a key step in the aforementioned syntheses of aromatic compounds and similar coupling reactions. Our intentions here are to show how much different the reactivity is between early- and late-transition-metal complexes, to clarify the reason for the nonsymmetrical transition state of the Cp_2Zr-mediated coupling reaction, and to discuss important orbital interactions in the nonsymmetrical transition state. Also, the $(MeO)_2Zr$-mediated coupling reaction was investigated here to show whether $Zr(OR)_4/2R'MgCl$ is useful for a coupling reaction such as $Ti(OPr^i)_4/2Pr^iMgCl$.

Computations

Geometries were optimized with the DFT method, where the B3LYP functional was used for the exchange-correlation

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(20) (a) Although PH_3 is small and simple relative to real phosphines used experimentally, we employed here $M(PH_3)$ as a model of late-transition-metal complexes, because $M(PH_3)$ is considered enough to make the clear comparison between the early- and late-transition-metal complexes, which is one of our main purposes here. We examined the $Pt(PMe_3)$-mediated coupling reaction of acetylenes but did not observe significant differences between $Pt(PMe_3)$ and $Pt(PH_3)$ (see Table S1 in the Supporting Information). (b) The Ni(dppe)-mediated coupling reaction of acetylenes was reported experimentally,[20c] where dppe represents diphenylphosphinoethane. Although this experimental report suggests the possibility that two coordination sites are occupied by the chelate phosphine, we employed $Ni(PH_3)$ here. This is because $Ni(PH_3)$ was investigated here to compare $Pt(PH_3)$ with $Ni(PH_3)$. Also, Ni(0) complexes with monodentate phosphines were used for these types of coupling reactions. In such cases, it is likely that one phosphine dissociates from the Ni canter. Thus, $Ni(PH_3)$ is considered a reasonable model. (c) Stekling, L.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 496. (d) The transition state of the Cp_2Zr-mediated coupling reaction of diphenylacetylene molecules[18] is much less reactantlike than that of the Cp_2Zr-mediated coupling reaction of acetylenes, because of the large substituents. Although this difference exists between acetylene and diphenylacetylene, we employed C_2H_2 as a substrate because our main purpose is to make clear comparisons in the reaction behavior and reactivity between early- and late-transition-metal complexes. It is likely that the bulky substituents increase the activation barrier of both early- and late-transition-metal-mediated coupling reactions.

term.[21,22] Transition states were ascertained by calculating vibration frequencies and examining geometry changes that were involved in each imaginary frequency; see Table S2 in the Supporting Information for Cartesian coordinates of important species, including all the transition states.

Two kinds of basis set systems were used. The smaller system (BS-I) was employed in geometry optimization. In BS-I, core electrons of Ni (up to 2p), Zr (up to 3d), and Pt (up to 4f) were replaced with effective core potentials (ECPs) and their valence electrons were represented with (341/321/41), (341/321/31), and (341/321/21) basis sets, respectively.[23] For valence electrons of P, a (21/21/1) basis set was used with the ECPs.[24,25] For C and O atoms, 6-31G(d) basis sets were employed,[26] while the d polarization function was excluded from the basis set for the C atoms of Cp and methyl groups. A better basis set system (BS-II) was employed in the evaluation of energy and population changes. In BS-II, (541/541/311/1), (541/541/211/1), and (541/541/111/1) basis sets[23,27,28] were used for valence electrons of Ni, Zr, and Pt, respectively, with the ECPs being the same as those of BS-I. For C and O, 6-311G-(d) basis sets were employed,[29] while the d polarization function was excluded from the C atoms of Cp and methyl groups. The same basis sets and ECPs as in BS-I were used for P. To check the reliability of the basis sets used here, cc-pvdz, cc-pvtz,[30] and 6-311G(d)[31] were used for H, C, and P atoms in the $Pt(PH_3)$-mediated coupling reaction. However, significant basis set effects were not observed, as shown in Table S3 in the Supporting Information.

As will be shown below, either the precursor complex or the transition state is formed from two molecules in the coupling reactions investigated here. Thus, the entropy effects should be considered in the discussion. Entropy and thermal energy were evaluated in the usual way, where translation, rotation, and vibration movements were taken into consideration and all substrates were treated as ideal gases. The free energy change evaluated in the usual way is called $\Delta G°$. The $\Delta G°$ value tends to overestimate the entropy change in the solution reaction, because translational and rotational movements are considerably suppressed in the solution reaction. We also evaluated the entropy and the thermal energy with exclusion of the contribution of translational and rotational movements. The free energy change evaluated in this way is called $\Delta G_v°$ hereafter. The $\Delta G_v°$ value tends to underestimate the free energy change, because translation and rotation are not completely frozen in the solution. The DFT/BS-I method was adopted to calculate vibrational frequencies without a scaling factor. The comparison of all the reactions investigated here is presented with these two kinds of free energy changes.

The Gaussian 98 program package was used for all calculations.[32] Population analysis was carried out with the method proposed by Weinhold et al.[33] A contour map of the molecular orbital was drawn with the Molden program package.[34]

Results and Discussion

Comparison of Reaction Energy between Cp_2Zr- and $M(PH_3)$-Mediated Coupling Reactions (M = Ni, Pt).

First, we briefly compared the reaction energy among Cp_2Zr-, $Ni(PH_3)$-, and $Pt(PH_3)$-mediated coupling reactions. In the coupling reaction leading to metallacyclopentadienyl species (step 1 in Scheme 1), the Cp_2Zr-mediated reaction is much more exothermic than the $Pt(PH_3)$- and $Ni(PH_3)$-mediated reactions, as shown in Table 1. The energies of the coupling reaction of the metallacyclopentadienyl species with the third acetylene, leading to the metallacycloheptatrienyl species (step 2 in Scheme 1), are, however, larger in $Ni(PH_3)$- and $Pt(PH_3)$-mediated reactions than in the Cp_2Zr-mediated reaction; see Figure S1 in the Supporting Information for the geometries of metallacycloheptatrienyl species. This result suggests that the reason for the good reactivity of the Cp_2Zr species should be observed in the first step, in which the metallacyclopentadienyl species is formed from two acetylene molecules. Also, it is likely that step 2 occurs with difficulty in the Cp_2Zr-mediated coupling reaction, as will be discussed below.[35] Thus, we will investigate step 1 in detail below.

Table 1. Reaction Energy (ΔE in kcal/mol)[a] of the Coupling Reaction of Acetylenes Shown in Scheme 1

	step 1	step 2
Cp_2Zr	−50.5 (−52.4)[b]	−45.8
$Ni(PH_3)$	−8.4 (−33.6)	−61.0
$Pt(PH_3)$	−29.6 (−40.2)	−57.7

[a] The DFT/BS-II method. [b] The reaction energies relative to the sum of $ML_2(C_2H_2)$ and C_2H_2 are given in parentheses. The values not in parentheses are the reaction energies relative to the precursor complex, $ML_2(C_2H_2)_2$.

Although we will concentrate on the coupling reaction of two acetylene molecules (step 1 in Scheme 1) hereafter, we wish to mention the results on the formation of metallacycloheptatriene species (step 2 in Scheme 1). Interestingly, the reaction energy of step 2 is greater in $Ni(PH_3)$- and $Pt(PH_3)$-mediated reactions than in the Cp_2Zr-mediated reaction.[35] These results clearly indicate that the platinum and nickel complexes are useful in syntheses of aromatic compounds from acetylenes when the nickelacyclopentadienyl and platinacyclopen-

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[35] Although the exothemicity of step 2 suggests that the conversion of metallacyclopentadienyl species to metallacycloheptatrienyl species can occur in Cp_2Zr-mediated coupling reactions, approach of the third acetylene to the Zr center of $Cp_2Zr(CH{=}CHCH{=}CH)$ is considered difficult because the zirconacyclopentadienyl moiety is not flexible. Actually, the reaction system of $Cp_2Zr(CH{=}CHCH{=}CH) + C_2H_2$ becomes less stable in energy by 18.4 kcal/mol (DFT/BS-II calculation) relative to the precursor complex, when the C atom of the third acetylene approaches the Zr center at 2.5 Å (see Figure S5 in the Supporting Information). The transition state could not be optimized at this moment, but it should be less stable than this geometry.

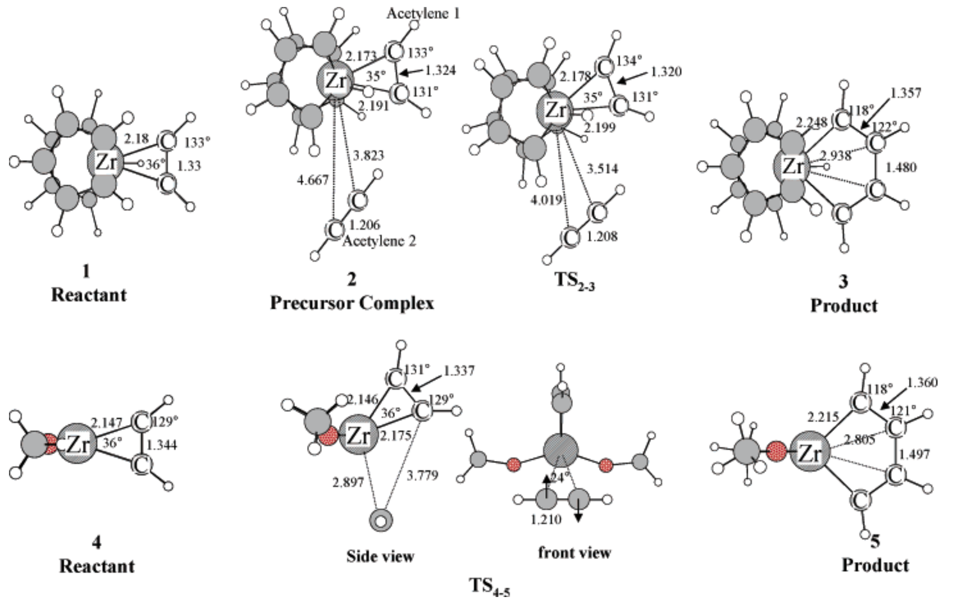
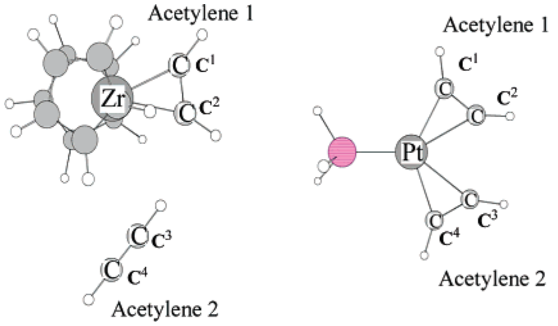


Figure 1. Geometry changes in the coupling reactions of $\mathrm{Cp_2Zr(C_2H_2)}$ and $\mathrm{(MeO)_2Zr(C_2H_2)}$ with $\mathrm{C_2H_2}$. Bond distances are given in angstroms and bond angles in degrees.

Chart 1



tadienyl species are first produced by a reaction such as transmetalation, as experimentally reported.[3c]

Geometry Changes in $\mathrm{Cp_2Zr}$- and $\mathrm{(MeO)_2Zr}$-Mediated Coupling Reactions of Acetylenes. Geometry changes in the coupling reactions of $\mathrm{Cp_2Zr(C_2H_2)}$ with the second acetylene are shown in Figure 1. In the reactant $\mathrm{Cp_2Zr(C_2H_2)}$ (**1**), the C−C distance is much longer than that of free acetylene by about 0.12 Å. This distance is almost the same as that of ethylene (1.339 Å). Consistent with this long C−C distance, the H−C−C angle (133°) is much smaller than that of free acetylene. These results suggest that the $\mathrm{Zr(C_2H_2)}$ moiety is considered to take a zirconacyclopropene structure which contains the Zr−C single bond. In the precursor complex **2**, the second acetylene molecule 2 is very distant from the Zr center and its geometry is almost the same as that of free acetylene,[36] where acetylene 1, acetylene 2, and C^1−C^4 are defined in Chart 1. These geometrical features indicate that this precursor complex is not very stable. Interestingly, the transition state ($\mathbf{TS_{2-3}}$) of the $\mathrm{Cp_2Zr}$-mediated reaction is considerably reactant-like; for instance, acetylene 2 is distant from the Zr center and both geometries of $\mathrm{Cp_2Zr(C_2H_2)}$ and acetylene 2 change little, except that acetylene 1 coordinated with the Zr center moves somewhat from its original position. It should be noted that the transition state is not symmetrical, as reported,[18] and that this transition state is much more reactant-like than the recently reported transition state of the $\mathrm{Cp_2Zr}$-mediated coupling reaction between methylacetylene and phenyl(pentafluorophenyl)acetylene.[18] This is probably because the coupling reaction takes place more easily in the present system than in the previous one, due to steric repulsion in the present system being much less than in the previous system. The product **3** has a symmetrical structure, as reported.[18] The Zr−C^1 and Zr−C^4 distances (2.25 Å) of **3** are about 0.03 Å shorter than the experimental values of $\mathrm{Cp_2Zr[C(C_6H_5){=}C(C_6F_5)\text{-}C(C_6F_5){=}CC_6H_5]}$,[18] because of the absence of a bulky substitutent in **3**. On the other hand, the geometry of the butadienyl moiety (−HC═CHCH═CH−) of **3** is almost the same as that of the experimental structure of $\mathrm{Cp_2Zr[C(C_6H_5){=}C(C_6F_5)C(C_6F_5){=}CC_6H_5]}$,[18] while the substituents on the butadienyl group are quite different between them. These results suggest that the geometry of the butadienyl moiety is mainly determined by the electronic factors of π orbitals; note that substituents mainly influence the σ-electronic frame.

In $\mathrm{(MeO)_2Zr(C_2H_2)}$ (**4**), the Zr−C distance is much shorter than that of **1**, while the C−C distance of acetylene 1 is almost the same as that of **1**. The precursor complex could not be optimized, unlike the case for **2**. In the transition state $\mathbf{TS_{4-5}}$, acetylene 2 is perpendicular to acetylene 1, which coordinates with the Zr center. This transition state is not symmetrical, but it is much different from $\mathbf{TS_{2-3}}$. The geometry change that is mainly observed in the imaginary frequency is the rotation of acetylene 2. This result suggests that the C−C bond formation easily occurs when acetylene 2

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(36) (a) A symmetrical dialkyne complex of $\mathrm{Cp_2Zr}$ was previously reported.[36b] The nonsymmetrical dialkyne complex of $\mathrm{Cp_2Zr}$ was not optimized in the present work. This result is not consistent with the previous experimental result, seemingly. However, it is likely that the dialkyne complex of $\mathrm{Cp_2Zr}$ can exist as a stable species when the coupling reaction cannot take place. Actually, the coupling reaction could not take place in the experimentally reported dialkyne complex of $\mathrm{Cp_2Zr}$, probably because the coupling product contains a very strained cyclobutene ring. (b) Warner, B. P.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 5471.

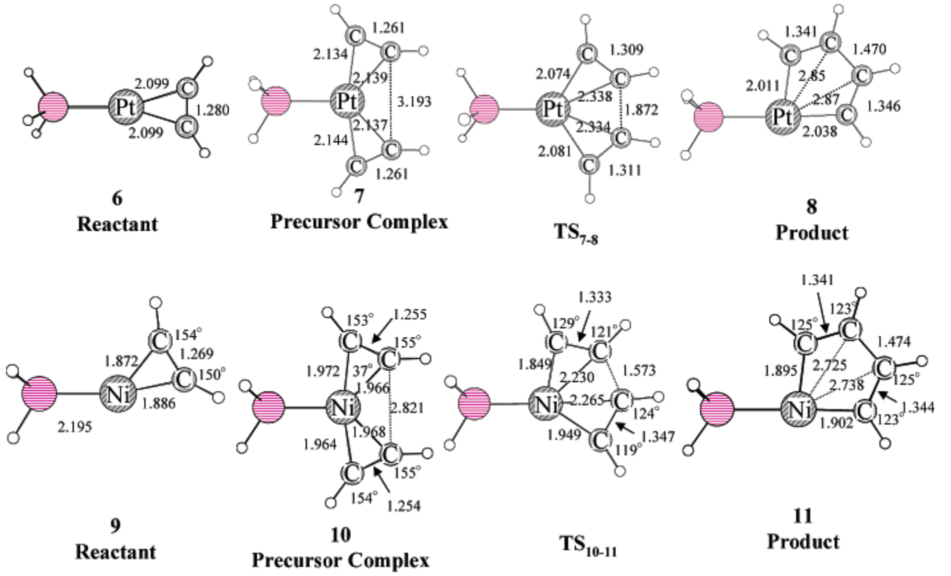

Figure 2. Geometry changes in the coupling reactions of $M(PH_3)(C_2H_2)$ ($M = Ni, Pt$) with C_2H_2. Bond distances are given in angstroms and bond angles in degrees.

takes an orientation coplanar with acetylene **1**.[37] The geometry of the product **5** is essentially the same as that of **3**, while the Zr−C distance is moderately shorter than that of **3**. The shorter Zr−C distances of **4** and **5** as compared to those of **1** and **3** are reasonably interpreted in terms of the steric repulsion with the MeO ligand being less than that with the Cp ligand.

Geometry Changes in the M(PH_3)-Mediated Coupling Reaction of Acetylenes (M = Ni, Pt). Because a recent experiment reported that the active species of the Pt-mediated coupling reaction of acetylenes was a platinum(0) monophosphine complex,[13] we adopted here $Pt(PH_3)(C_2H_2)$ (**6**) as a model of the active species. Because this complex is coordinatively unsaturated, one more acetylene easily coordinates with the Pt center, to afford $Pt(PH_3)(C_2H_2)_2$ (**7**), as shown in Figure 2.

The precursor complex **7** takes a typical C_3-like geometry. Similar three-coordinate platinum(0) alkene complexes were found experimentally.[38] Because the C_3-like geometry and the bonding nature have been theoretically discussed previously,[39,40] the discussion is omitted in this work. However, we wish to mention here that the C−C distance of each acetylene in **7** is considerably shorter than that of ethylene, unlike the case for **2**. This means that the C−C bond of acetylene is still characterized as a triple bond in **7**. It should be noted that the transition state $\mathbf{TS_{7-8}}$ is almost symmetrical, as reported previously.[14−16,19] In $\mathbf{TS_{7-8}}$, the C−C distance between two acetylene molecules is still 1.87 Å, which is considerably longer than the usual C−C bond distance. On the other hand, the Pt−C^1 and Pt−C^4 distances are slightly longer than those of the product **8** by 0.05−0.06 Å. Also, the C−C bond distances of acetylenes are 1.33−1.34 Å, which are almost the same as those of the product **8**. These geometrical features indicate that the C≡C triple bond of acetylene changes to a C=C double bond and both Pt−C^1 and Pt−C^4 bonds are almost formed in $\mathbf{TS_{7-8}}$, while the C−C bond formation between two acetylene molecules is still in progress in $\mathbf{TS_{7-8}}$. The product **8** takes a T-shaped three-coordinate structure. The reason that the three-coordinate complex of the d^8 transition-metal element takes a T-shaped structure was previously discussed in theoretical works.[41,42] The geometry of the butadienyl moiety in **8** is almost the same as those of **3** and **5**.

The geometry changes of the $Ni(PH_3)$-mediated coupling reaction are different from those of the $Pt(PH_3)$-mediated reaction in several ways. One of them is the geometry of the reactant $Ni(PH_3)(C_2H_2)$ (**9**). Complex **9** is not symmetrical, unlike **6**. The symmetrical structure is slightly less stable than **9** by 1.7 kcal/mol (the DFT/BS-II calculation). The reason for the nonsymmetrical structure of **9** is easily interpreted in terms of the π-back-donation.[43] However, a detailed discussion is omitted here, because it does not directly relate to the coupling reaction. The precursor complex **10** has a symmetrical three-coordinate structure like that of the platinum analogue, while the Ni−C distance is somewhat shorter than the Pt−C distance of **7**. However, the transition state $\mathbf{TS_{10-11}}$ is not perfectly symmetrical but slightly distorted, unlike $\mathbf{TS_{7-8}}$ of the Pt system. In $\mathbf{TS_{10-11}}$, the C−C distance between two acetylene molecules is 1.573 Å, which is only 0.1 Å longer than that of the product **11**. Also, the Ni−C^1 and Ni−C^4 distances are 0.05 Å longer than those of **11**. Thus,

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[37] We tried to find the coplanar transition state but finally obtained the transition state $\mathbf{TS_{4-5}}$.

[38] Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 6, p 471.

[39] Rösch, N.; Hoffmann, R. *Inorg. Chem.* **1974**, *13*, 2656.

[40] (a) Sakaki, S.; Tsuru, N.; Ohkubo, K. *J. Phys. Chem.* **1980**, *84*, 3390. (b) Kitaura, K.; Sakaki, S.; Morokuma, K. *Inorg. Chem.* **1981**, *20*, 2292.

[41] Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255.

[42] Sakaki, S.; Kitaura, K.; Morokuma, K. Ohkubo, K. *J. Am. Chem. Soc.* **1983**, *105*, 2280.

[43] The electron population of C_2H_2 is 14.32e and the Ni atomic population is 27.78e in **9**, while the electron population of C_2H_2 is 14.26e and the Ni atomic population is 27.85e in the linear structure of $Ni(PH_3)(C_2H_2)$. These electron populations clearly show that the π-back-donation is stronger in **9** than in the linear structure of $Ni(PH_3)(C_2H_2)$. This means that **9** has a slightly bent structure because of the strong π-back-donation interaction. This is due to the fact that the d orbital that is destabilized in energy by PH_3 interacts with the π^* orbital of acetylene in **9**.

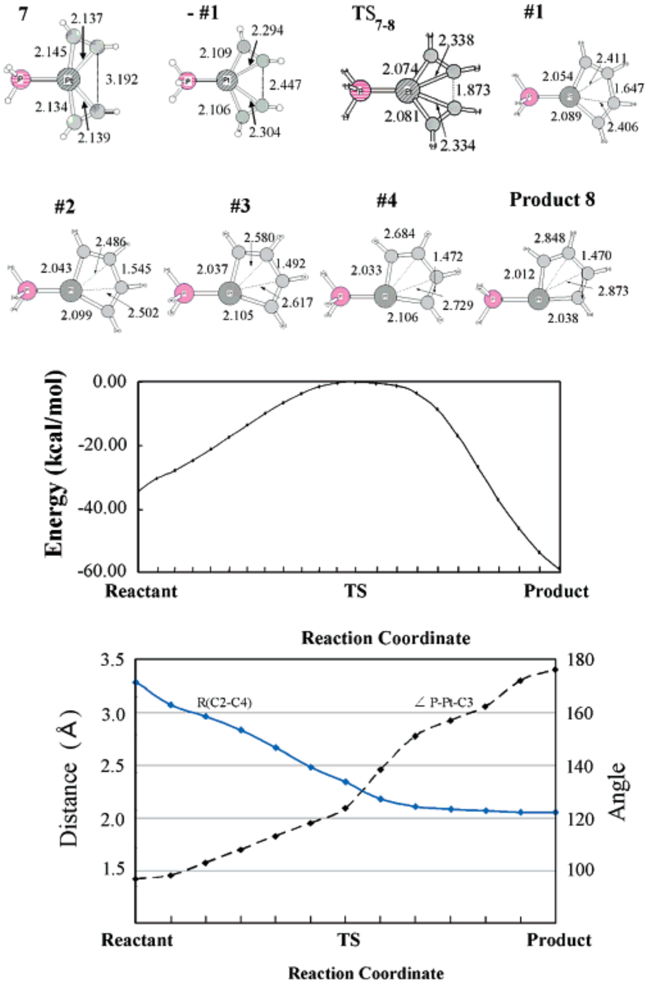

Figure 3. IRC calculation of the coupling reactions of Pt(PH_3)(C_2H_2) with C_2H_2. Bond distances are given in angstroms and bond angles in degrees.

TS_{10-11} is somewhat more productlike than **TS_{7-8}**, and as a result, it becomes nonsymmetrical; remember that the product is nonsymmetrical. In other words, the reason that **TS_{10-11}** is nonsymmetrical is not the same as that for the nonsymmetrical **TS_{2-3}** of the Cp_2Zr-mediated reaction. The product **11** takes a T-shaped three-coordinate structure like that of **8**. Again, the geometry of the butadienyl moiety of **11** is essentially the same as that of **8**.

IRC Calculation of the Pt(PH_3)-Mediated Coupling Reaction and Pseudo-IRC Calculation of the Cp_2Zr-Mediated Coupling Reaction. Interestingly, the symmetrical product **3** is produced through the nonsymmetrical transition state **TS_{2-3}** in the Cp_2Zr-mediated coupling reaction, while the nonsymmetrical product **8** is produced through the symmetrical transition state **TS_{7-8}** in the Pt(PH_3)-mediated reaction. We carried out an IRC calculation of the Pt(PH_3)-mediated reaction to ascertain that the symmetrical transition state leads to the nonsymmetrical product. As shown in Figure 3, the geometry gradually changes to the nonsymmetrical product **8** from the symmetrical transition state **TS_{7-8}**.

Apparently, **#1**, which is the geometry at the reaction coordinate of 0.3,[44] is not symmetrical but the energy

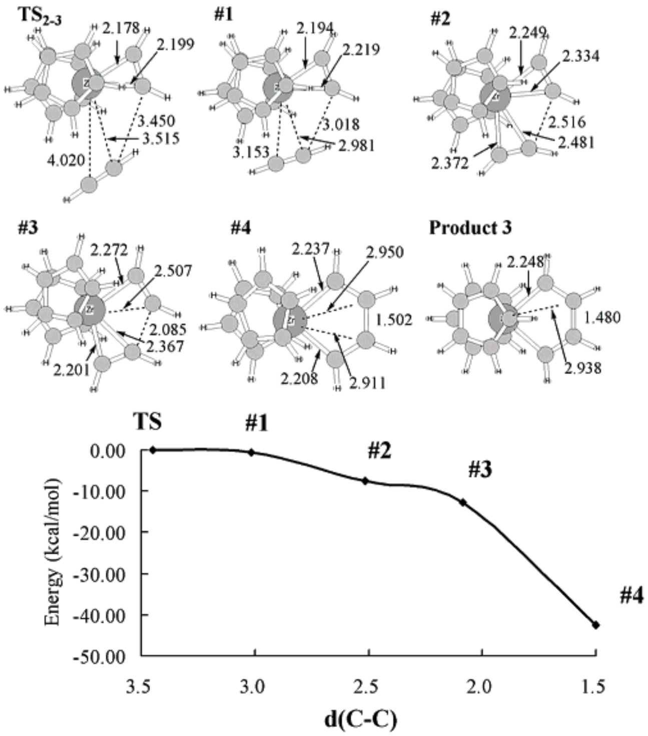

Figure 4. Pseudo-IRC calculation of the coupling reactions of $Cp_2Zr(C_2H_2)$ with C_2H_2. Bond distances are given in angstroms and bond angles in degrees.

difference between **#1** and **TS_{7-8}** is negligibly small; in other words, the potential energy surface is considerably flat around the transition state. Also, it is noted that the C−C distance between two acetylene molecules is 1.647 Å in **#1** and 1.545 Å in **#2**, but these two structures are much different from that of **8** and they are much less stable in energy than **8**. These results clearly indicate that the C−C bond is almost formed between two acetylene molecules in **#1** and **#2** but the geometry significantly changes upon going to **8** from **#2**. This means that the C−C bond formation takes place before the geometry change to the T-shaped structure.

In the Cp_2Zr-mediated coupling reaction, we failed to perform an IRC calculation, probably because the potential energy surface is too flat; remember that the transition state is reactantlike. Therefore, we carried out the geometry optimization starting from **TS_{2-3}** and show the geometry and energy changes in Figure 4. In this figure, the energy changes are shown as a function of the C−C distance between two acetylene molecules.[45] Apparently, the geometry gradually changes to the symmetrical product **3** from the nonsymmetrical transition state **TS_{2-3}**. It is noted that the geometry becomes nearly symmetrical in **#3**, in which the C−C distance between two acetylene molecules is 2.08 Å. This distance is not very different from that of **TS_{7-8}** of the Pt(PH_3)-mediated coupling reaction; in other words, the geometry becomes symmetrical when the C−C bond formation occurs such as that of the Pt(PH_3)-mediated reaction, which will be discussed below in detail.

In conclusion, these IRC and pseudo-IRC calculations clearly show that the nonsymmetrical transition state

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(44) This value of 0.3 means that the reaction proceeds by 30% from the transition state to the product.

(45) The C−C distance is not a good reaction coordinate in the late stage of the reaction, as clearly shown by the IRC calculation of the Pt(PH_3)-mediated coupling reaction (see Figure 3). As a result, the energy change is not smoothly presented in Figure 4.

Table 2. Binding Energies (*BE*),[a] Activation Barriers (E_a),[b] and Reaction Energies (ΔE)[c] of Cp_2Zr- and $Pt(PH_3)$-Mediated Coupling Reactions of Acetylenes

		BE	E_a	ΔE
Cp_2Zr	DFT	−1.8	0.6	−52.0
	MP2	−5.9	−0.9	−56.8
	MP3	−4.4	−0.1	−56.6
	MP4(DQ)	−4.4	−0.2	−55.6
	MP4(SDQ)	−4.7	−0.3	−56.2
$(MeO)_2Zr$	DFT	–[d]	−6.5	−56.7
	MP2		−12.5	−57.6
	MP3		−10.9	−58.8
	MP4(DQ)		−13.3	−57.7
	MP4(SDQ)		−10.7	−58.0
$Pt(PH_3)$	DFT	−13.4	31.0	−42.8
	MP2	−31.9	45.4	−41.8
	MP3	−19.5	35.6	−47.9
	MP4(DQ)	−22.6	39.7	−44.5
	MP4(SDQ)	−22.4	37.9	−45.5
	CCSD	−20.8	35.4	−47.7
	CCSD(T)	−24.1	34.8	−49.0
$Ni(PH_3)$	DFT	−25.5	20.0	−33.9
	CCSD	−25.1	12.0	−38.7
	CCSD(T)	−30.6	16.1	−39.5

[a] *BE* is the stabilization energy of the reactant complex relative to the sum of reactants. [b] E_a is the difference energy between the transition state and the precursor complex. [c] ΔE is the energy difference between the product and the sum of reactants. [d] The precursor complex could not be optimized.

Table 3. Free Energy Changes[a] in the Cp_2Zr-, $(MeO)_2Zr$-, and $M(PH_3)$-Mediated Coupling Reactions

	reactant complex	TS	product
	Cp_2Zr		
ΔG° [b]	6.8	8.7	−34.3
ΔG_v° [c]	−3.7	−1.8	−44.9
	$(MeO)_2Zr$		
ΔG°	–[d]	3.8	−42.4
ΔG_v°		−6.7	−52.9
	$Pt(PH_3)$		
ΔG°	−2.2	31.1	−27.6
ΔG_v°	−12.3	20.9	−37.7
	$Ni(PH_3)$		
ΔG°	−14.4	8.9	−19.5
ΔG_v°	−24.6	−1.3	−29.6

[a] Electronic energy was calculated with the DFT/BS-II method. [b] ΔG°: translational, rotational, and vibrational movements were considered in the estimation of thermal energy and entropy, where all substrates were treated as ideal gases. [c] ΔG_v°: vibrational movements were considered in the estimation of thermal energy and entropy, while translational and rotational movements were neglected. [d] The precursor complex could not be optimized.

$\mathbf{TS_{2-3}}$ leads to the symmetrical product **3** in the Cp_2Zr-mediated reaction and the symmetrical transition state $\mathbf{TS_{7-8}}$ leads to the nonsymmetrical product **8** in the $Pt(PH_3)$-mediated coupling reaction.

Energy Changes in the Cp_2Zr-, $(MeO)_2Zr$-, and $M(PH_3)$-Mediated Coupling Reactions of Acetylenes (M = Ni, Pt). The binding energy (*BE*), activation barrier (E_a), and reaction energy (ΔE) of these coupling reactions are listed in Table 2, where *BE* is the stabilization energy of the precursor complex relative to the sum of reactants, E_a is the energy difference between the transition state and the precursor complex, and ΔE is the energy difference between the product and the sum of reactants. In the $Pt(PH_3)$-mediated coupling reaction, the DFT method gives a considerably smaller *BE* value and somewhat smaller E_a value than the other computational methods. Although the *BE*, E_a, and ΔE values somewhat fluctuate around the MP2 level, they fluctuate much less on going to MP4(SDQ) from MP3. Moreover, the CCSD(T) method gives BE, E_a, and ΔE values similar to those calculated with the MP4(SDQ) method. In the $Ni(PH_3)$-mediated reaction, however, the *BE*, E_a, and ΔE values change considerably on going from MP2 to MP4(SDQ); see Table S4 in the Supporting Information. This is because Møller−Plesset perturbation theory is not useful for 3d transition-metal complexes in general.[46] On the other hand, the *BE*, E_a, and ΔE values calculated with the CCSD(T) method are similar to those of the DFT method in this reaction. Thus, we present a discussion based on the BE, E_a, and ΔE values calculated with the CCSD(T) method in the $Ni(PH_3)$- and $Pt(PH_3)$-mediated coupling reactions.

Not only the CCSD(T) method but also all the computational methods here indicate that the $Pt(PH_3)$-mediated coupling reaction takes place with a very large activation barrier, despite considerably large exothermicity. The $Ni(PH_3)$-mediated reaction takes place with a much smaller activation barrier than does the $Pt(PH_3)$-mediated reaction. These results agree with the experimental results that the nickel(0) complexes are useful for the coupling reaction of acetylenes but the platinum(0) complexes are not very useful.

In the Cp_2Zr- and $(MeO)_2Zr$-mediated reactions, the discussion is presented on the basis of the MP4(SDQ) method, because this reaction system is too large to be calculated with the CCSD(T) method. We believe that a discussion based on the MP4(SDQ) calculations is reliable, considering that all the computational methods give similar E_a and ΔE values, except that the DFT method somewhat underestimates the *BE* value compared with MP2 to MP4(SDQ) methods. Interestingly, the Cp_2Zr- and $(MeO)_2Zr$-mediated reactions occur with nearly no barrier and very large exothermicity. These results indicate that the Cp_2Zr species is very reactive for this type of coupling reaction and the $(MeO)_2Zr$ species is useful as a reactive reagent, like the Negishi reagent.

The above conclusions of the relative reactivity do not change on incorporation of entropy effects. As shown in Table 3, the ΔG_v° values are similar to those of potential energy changes which are listed in Table 2. This is because the ΔG_v° value does not contain the contribution by translational and rotational movements. On the other hand, the ΔG° values are much different from the potential energy changes, as shown in Table 3, because the ΔG° value contains the contributions from translational, rotational, and vibrational movements and the entropy from translational and rotational movements considerably decreases on adduct formation. Although the ΔG° value is much different from the ΔG_v° value, the activation free energy change $\Delta G^{\circ\ddagger}$ is the smallest in the coupling reaction of $(MeO)_2Zr(C_2H_2)$ with C_2H_2 and increases in the order $(MeO)_2Zr(C_2H_2)$ (3.8) < $Cp_2Zr(C_2H_2)$ (8.7) < $Ni(PH_3)(C_2H_2)$ (23.3) < $Pt(PH_3)(C_2H_2)$ (33.3), like the $\Delta G_v^{\circ\ddagger}$ value, where the $\Delta G^{\circ\ddagger}$ values are given in parentheses (in kcal/mol). From these results, it should be concluded that the reactivity for this coupling reaction increases in the order $Pt(PH_3)(C_2H_2)$ < $Ni(PH_3)(C_2H_2)$ < $Cp_2Zr(C_2H_2)$ < $(MeO)_2Zr(C_2H_2)$.

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(46) Sakaki, S.; Ohkubo, K. *J. Phys. Chem.* **1989**, *93*, 5655.

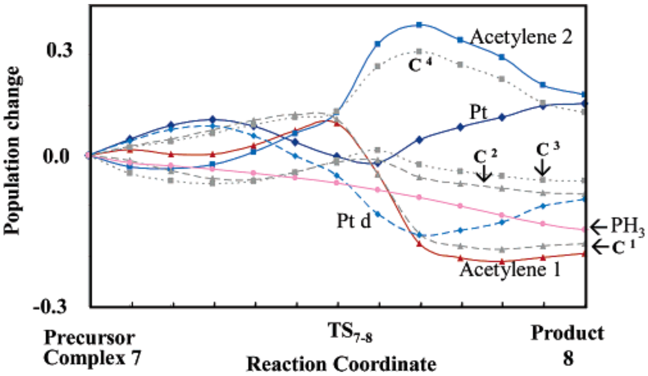

Figure 5. Population changes along the reaction course of the coupling reactions of $Pt(PH_3)(C_2H_2)$ with C_2H_2. Positive values represent increases in the electron population and vice versa.

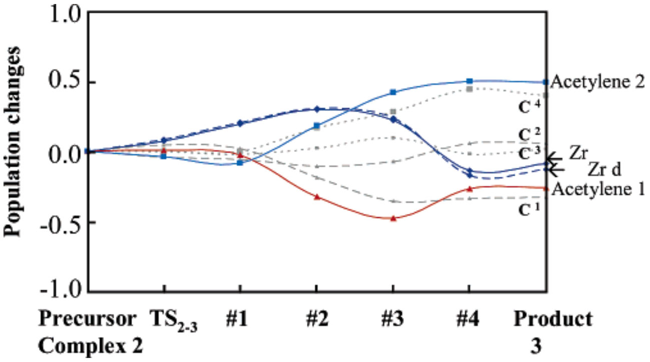

Figure 6. Population changes along the reaction course of the coupling reactions of $Cp_2Zr(C_2H_2)$ with C_2H_2. Positive values represent increases in the electron population and vice versa.

Population Changes and Orbital Interactions in the Coupling Reaction. The next issue is to clarify the reasons that the Cp_2Zr and $(MeO)_2Zr$ species are extremely reactive and $Ni(PH_3)$ is considerably reactive but $Pt(PH_3)$ is not reactive. To investigate this, it is necessary to know the electronic process of this coupling reaction on the basis of population changes and orbital interactions.

Population changes in the $Pt(PH_3)$-mediated coupling reaction are shown in Figure 5. Electron populations of two acetylene molecules slightly decrease and then increase upon going to $\mathbf{TS_{7-8}}$ from the precursor complex **7**. Consistent with these population decreases, the Pt atomic population increases in the early stage of the step on going to $\mathbf{TS_{7-8}}$ from **7**. These population changes are interpreted in terms of the position changes of two acetylene molecules, as follows: in **7**, two acetylene molecules take the best positions to form the π-back-donation interaction with the Pt(0) center.[47] However, two acetylene molecules are changing their positions to approach each other upon going to $\mathbf{TS_{7-8}}$ from **7**, which induces weakening of the π-back-donation interaction. As a result, the electron populations of two acetylene molecules decrease but the Pt atomic population increases first. In the later stages of the step going to $\mathbf{TS_{7-8}}$ from **7**, however, electron populations of two acetylene molecules increase and both electron populations of the Pt center and PH_3 decrease. These population changes indicate that the charge transfer from the Pt center to two acetylene molecules becomes stronger again and the Pt center is provided electron density by the PH_3 ligand. This charge transfer relates to the C−C bond formation between two acetylene molecules, as will be discussed below. After $\mathbf{TS_{7-8}}$, acetylene 2 receives a great deal of electron density but acetylene 1 loses electron density. These population changes are consistent with the geometry changes shown in Figure 3, as follows: because acetylene 2 moves to a position trans to PH_3, its electron donation to the Pt center becomes weaker, while the electron donation of acetylene 1 to the Pt center becomes stronger because it moves to a position trans to an empty coordination site during the geometry change on going to **8** from $\mathbf{TS_{7-8}}$. In particular, the C^4 atomic population considerably increases, because this atom moves to a position trans to PH_3, and the C^1 atomic population considerably decreases, because it moves to a position trans to an empty coordination site on going to **8** from $\mathbf{TS_{7-8}}$. The Pt atomic population and the d orbital population gradually increase on going to **8** from $\mathbf{TS_{7-8}}$, unexpectedly. This is because the charge transfer from the Pt center to two acetylene molecules occurs considerably around the transition state to induce the C−C bond formation, as will be discussed below in detail, but the butadienyl moiety which is gradually formed after $\mathbf{TS_{7-8}}$ donates electron density to the Pt center in the later stage of the reaction.

Population changes in the Cp_2Zr-mediated coupling reaction are shown in Figure 6. Consistent with the reactantlike transition state $\mathbf{TS_{2-3}}$, the electron populations change little upon going to $\mathbf{TS_{2-3}}$ from the precursor complex **2**. On going to the geometries **#2** and **#3** from $\mathbf{TS_{2-3}}$, the electron population of acetylene 2 considerably increases but that of acetylene 1 considerably decreases, where **#2, #3**, etc. are shown in Figure 4. The d orbital population of Zr changes little. These population changes indicate that the charge transfer occurs mainly from acetylene 1 to acetylene 2. Because the C−C bond formation starts around **#3**, it is likely that the charge transfer from acetylene 1 to acetylene 2 plays an important role in the C−C bond formation, as will be discussed below in terms of the orbital overlap in the HOMO.

The HOMO of the Pt reaction system was examined along the reaction course, as shown in Figure 7. Apparently, the doubly occupied d orbital of $Pt(PH_3)$ overlaps in a bonding way with the $\pi^*-\pi^*$ bonding couple of two acetylene molecules in $\mathbf{TS_{7-8}}$. This CT interaction contributes to the C−C bonding interaction between two acetylene molecules, as shown in Scheme 2. Because of this CT interaction, the Pt atomic population decreases and electron populations of two acetylene molecules increase in the latter half of the step from **7** to $\mathbf{TS_{7-8}}$, as was described above. In $\mathbf{TS_{7-8}}$, PH_3 takes the best position to push up the d orbital in energy that participates in the CT interaction with the $\pi^*-\pi^*$ bonding couple of two acetylene molecules. As a result, the symmetrical transition state is favorable to the C−C bond formation between two acetylene molecules.[19]

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[47] In the precursor complexes **7** and **10**, the PH_3 ligand destabilizes the d orbital that interacts in a bonding way with the π* orbitals of two acetylene molecules. This means that PH_3 takes the best position for the π-back-donation interaction with two acetylene molecules in **7** and **10**.

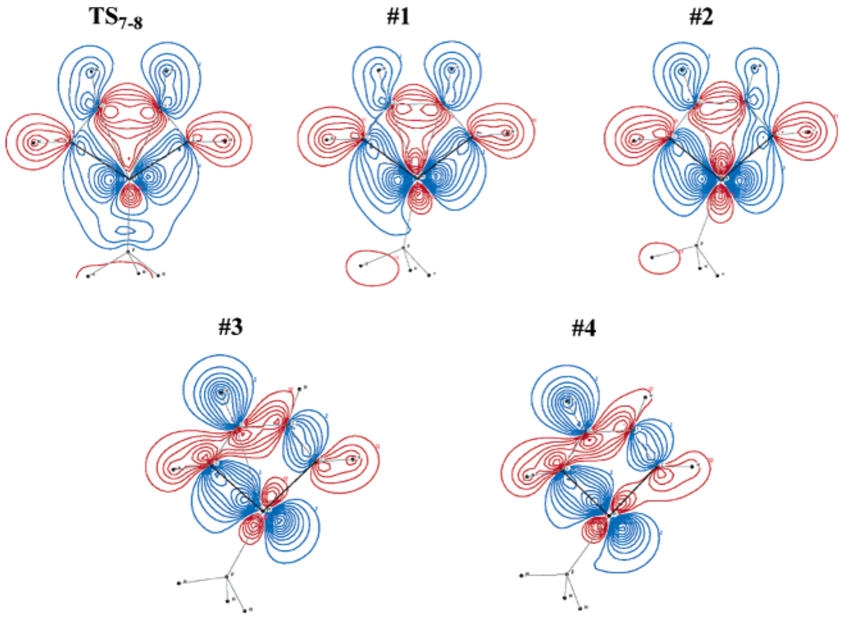
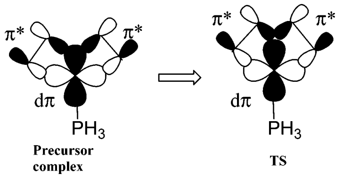


Figure 7. Changes in HOMO in the coupling reactions of $Pt(PH_3)(C_2H_2)$ with C_2H_2. Contour values are ±0.025, ±0.050, ±0.075, ...

Scheme 2



In the Cp_2Zr-mediated reaction, on the other hand, somewhat different orbital interactions are observed in $\mathbf{TS_{2-3}}$. As shown in Figure 8, the HOMO of $\mathbf{TS_{2-3}}$ involves very large bonding overlap between the d_π orbital of Zr and the π^* orbital of acetylene 1, which clearly indicates that a very strong π-back-donation interaction is formed in $Cp_2Zr(C_2H_2)$. However, the π^* orbital of acetylene 2 mixes little with this π-back-donation orbital in $\mathbf{TS_{2-3}}$, where the frontier orbital is in the b_2 representation, as shown in Scheme 3. This is not surprising, because this transition state is reactant-like. After the transition state, the π^* orbital of acetylene 2 starts to mix with the $d_\pi-\pi^*$ back-donation orbital of $Cp_2Zr(C_2H_2)$, as shown by the HOMO of **#2** (see Figure 8). Interestingly, the HOMO becomes almost symmetrical in **#3**, in which the C−C bond formation occurs; in other words, the HOMO of **#3** is characterized to be the a_1 representation of the C_{2v} symmetry. This change in the HOMO is shown in Scheme 3. Note that the HOMO of **#3** is similar to those observed in transition states of the $Pt(PH_3)$-mediated coupling reaction of acetylene molecules and the Cp_2Zr-mediated coupling reaction of phenylacetylenes.[18] These results can be summarized as follows: (1) the C−C bond formation occurs after the transition state, (2) the frontier orbital becomes symmetrical when the C−C bond formation occurs, and (3) the reaction system has become more stable than the transition state before the C−C bond formation occurs. Thus, the next issue is to investigate why the reaction system becomes stable before the C−C bond formation, which will be discussed below.

Reasons for the Differences between Cp_2Zr and $M(PH_3)$ Species. In this section, we wish to discuss the reasons for differences between Cp_2Zr- and $M(PH_3)$-mediated coupling reactions. The first issue to be discussed is the nonsymmetrical transition state of the Cp_2Zr-mediated coupling reaction. Although orbital mixing hardly occurs between $Cp_2Zr(C_2H_2)$ and acetylene 2 in $\mathbf{TS_{2-3}}$, the π^* orbital of acetylene 2 overlaps in a bonding way with the $d_\pi-\pi^*$ back-donation orbital of $Cp_2Zr(C_2H_2)$ in **#2**, which is the geometry slightly after $\mathbf{TS_{2-3}}$, as shown in Figure 8. This CT interaction contributes considerably to stabilization of the reaction system, concomitant with the considerable decrease in the electron population of acetylene 1 and the considerable increase in the population of acetylene 2, as discussed above. To induce C−C bond formation, the $Cp_2Zr(C_2H_2)$ moiety distorts and acetylene 2 must approach acetylene 1 of the $Cp_2Zr(C_2H_2)$ moiety, which gives rise to the distortion energy of the $Cp_2Zr(C_2H_2)$ moiety and the steric repulsion between acetylene 2 and $Cp_2Zr(C_2H_2)$. However, the destabilization energy by distortion and steric repulsion is compensated well by the aforementioned CT interaction. As a result, the reaction system becomes stable before the C−C bond formation; in other words, the C−C bond formation occurs after the transition state. Because the C−C bond formation does not occur in the transition state, the transition state does not necessarily have a symmetrical structure. Thus, it is important to clarify the reason that acetylene 2 can form the strong CT interaction with the $d_\pi-\pi^*$ back-donation orbital of $Cp_2Zr(C_2H_2)$. As shown in Table 4, the electron population of the C_2H_2 moiety of $Cp_2Zr(C_2H_2)$ is much larger than those of $Pt(PH_3)(C_2H_2)$ and $Ni(PH_3)(C_2H_2)$, which clearly shows that the $d_\pi-\pi^*$ back-donation interaction is much stronger in $Cp_2Zr(C_2H_2)$ than in $Pt(PH_3)(C_2H_2)$ and $Ni(PH_3)(C_2H_2)$. This means that the π^* orbital of acetylene 1 largely contributes to the $d_\pi-\pi^*$ back-donation orbital of $Cp_2Zr(C_2H_2)$, as shown in Scheme 3. As a result, the π^* orbital of acetylene 2 overlaps well with the π^* orbital of acetylene 1 as well as with the d_π orbital of the Zr center, as shown in Scheme 3, to form the significantly strong CT interaction mentioned above. A similar

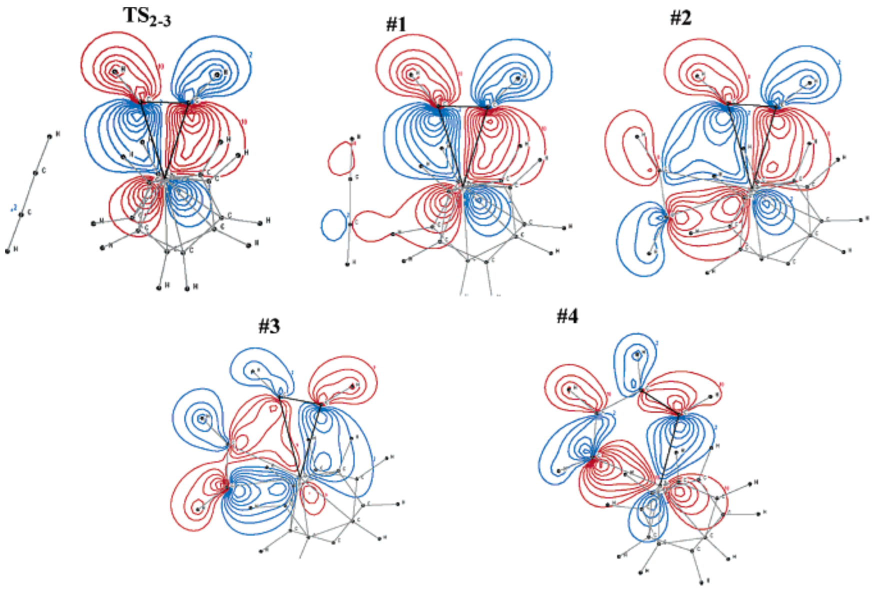


Figure 8. Changes in HOMO in the coupling reactions of $Cp_2Zr(C_2H_2)$ with C_2H_2. Contour values are ±0.025, ±0.050, ±0.075, ...

Scheme 3

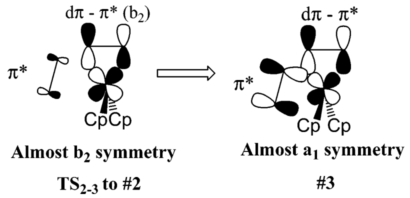


Table 4. Electron Distribution in $Cp_2Zr(C_2H_2)$, $(MeO)_2Zr(C_2H_2)$, $Ni(PH_3)(C_2H_2)$, and $Pt(PH_3)(C_2H_2)$ and the d Orbital Energy of Cp_2Zr, $(MeO)_2Zr$, $Ni(PH_3)$, and $Pt(PH_3)$ Species

	Cp_2Zr-(C_2H_2)	$(MeO)_2Zr$-(C_2H_2)	$Ni(PH_3)$-(C_2H_2)	$Pt(PH_3)$-(C_2H_2)
M	38.380	37.929	27.775	78.140
C_2H_2	14.757	14.861	14.316	14.101
Cp or PH_3	35.433	11.422	17.908	17.759
ε(d) (eV)	−2.99	–[a)]	−4.64	−6.24

[a] The Hartree−Fock calculation of $(MeO)_2Zr$ failed, probably because the d orbital is at too high energy and the Hartree−Fock wave function is not stable.

interaction was observed in the coupling reaction of silane with $Cp_2Zr(C_2H_4)$, which is involved as an important elementary step in the Cp_2Zr-catalyzed hydrosilylation of alkene.[49] These results indicate that the very strong $d_\pi-\pi^*$ back-donation interaction of Cp_2Zr(alkyne) and Cp_2Zr(alkene) plays a key role in their reactions and is an origin of the interesting reaction behavior of these species.

In the $Pt(PH_3)$- and $Ni(PH_3)$-mediated coupling reactions, on the other hand, the precursor complexes, **7** and **10**, and transition states, $\mathbf{TS_{7-8}}$ and $\mathbf{TS_{10-11}}$, are symmetrical, as shown in Figure 2. In the precursor complexes, the π^* orbital of acetylene 2 tends to interact with the d orbital of the M center in a bonding way, as shown in Scheme 2. This is because the π^* orbital of acetylene 1 is not sufficiently large in the $d_\pi-\pi^*$ back-donation orbital of $Pt(PH_3)(C_2H_2)$ and $Ni(PH_3)(C_2H_2)$, unlike that of $Cp_2Zr(C_2H_2)$, as shown by the electron population of acetylene 1 in these complexes being smaller than that of $Cp_2Zr(C_2H_2)$. As a result, acetylene 2 must necessarily approach the M center to afford a symmetrical precursor complex in which acetylene 1 is considerably distant from acetylene 2 (see Scheme 2). The mutual approach of two acetylene molecules must occur to form the C−C bond, which induces destabilization energy. When the stabilization energy by the C−C bond formation starts to compensate for the destabilization energy, the reaction system starts to become stable. Thus, the C−C bond formation occurs around the transition state, which requires a symmetrical transition state; remember that the symmetrical transition state is necessary for the C−C bond formation.[19]

It is of considerable importance to elucidate the reason that the π^* orbital of acetylene contributes to the $d_\pi-\pi^*$ back-donation orbital in $Cp_2Zr(C_2H_2)$ to a much greater extent than in $M(PH_3)(C_2H_2)$. The $d_\pi-\pi^*$ back-donation becomes stronger and the contribution of the π^* orbital of acetylene increases as the occupied d orbital of the metal center rises in energy. Because the d orbital of Cp_2Zr is at much high energy than that of $M(PH_3)$, as shown in Table 4, a much stronger $d_\pi-\pi^*$ back-donation is formed in $Cp_2Zr(C_2H_2)$, in which the π^* orbital of acetylene 1 largely participates. This feature of the d orbital energy comes from the general trend that the d orbital becomes lower in energy upon going to the right-hand side from the left-hand side in the periodic table.[50]

The next issue is the significant difference in the activation barrier among Cp_2Zr-, $(MeO)_2Zr$-, and $M(PH_3)$-

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(48) In the early stage of the reaction ($\mathbf{TS_{2-3}}$ to **#2**), the π-back-donation b_2 orbital of $Cp_2Zr(C_2H_2)$ moderately mixes with the π^* orbital of the second acetylene to form a nonsymmetrical frontier orbital, as shown in Scheme 3 and Figure 8. In the late stage of the reaction (after **#3**) in which the C−C bond formation occurs, the component of the π^* orbital of the second acetylene considerably increases in the frontier orbital, to lead to an almost symmetrical frontier orbital (see Scheme 3 and Figure 8). This orbital is essentially the same as the a_1 orbital, in which the $\pi^*-\pi^*$ bonding couple of two acetylene molecules overlaps in a bonding way with the d orbital of the Zr center, as was reported previously.[18,19]

(49) Sakaki, S.; Takayama, T.; Sumimoto, M.; Sugimoto, M. *J. Am. Chem. Soc.* **2004**, *126*, 3332.

(50) Fraga, S.; Saxena, K. M. S.; Karwowski, J. *Physical Science Data 5 Handbook of Atomic Data*; Elsevier: Amsterdam, 1976.

mediated coupling reactions. In the Cp_2Zr-mediated coupling reaction, the π^* orbital of acetylene 2 can overlap well with the π^* orbital of acetylene 1, which is largely involved in the $d_\pi-\pi^*$ back-donation orbital of $Cp_2Zr(C_2H_2)$. This CT interaction smoothly leads to the C−C bond formation between two acetylenes and at the same time considerably stabilizes the reaction system. Thus, the Cp_2Zr-mediated coupling reaction very easily takes place with nearly no barrier. These features come from the fact that Cp_2Zr has an occupied d orbital at high energy, as discussed above. Also, it is noted that $(MeO)_2Zr$ is more reactive than Cp_2Zr. The d orbital of $Cp_2Zr(C_2H_2)$ is somewhat higher in energy than that of $(MeO)_2Zr(C_2H_2)$.[51] Thus, not the d orbital energy but the other factor is responsible for the high reactivity of $(MeO)_2Zr$. Such a factor is the steric repulsion; because the MeO ligand flexibly rotates about the coordinate bond,[52] the steric repulsion between the MeO ligands and acetylene 2 is much smaller than that between the Cp ligands and acetylene 2. As a result, the $(MeO)_2Zr$ species is very reactive. In the $M(PH_3)$-mediated coupling reaction, on the other hand, acetylene 2 tends to interact with the M center in the precursor complex, in which acetylene 2 is distant from acetylene 1. This is because the π^* orbital of acetylene 1 is small in the $d_\pi-\pi^*$ back-donation orbital in $M(PH_3)(C_2H_2)$, due to the d orbital at low energy (vide supra). The mutual approach of two acetylene molecules must occur for the C−C bond formation, but this mutual approach gives rise to the destabilization energy by the steric repulsion and the weakening of the π-back-donation interaction of $Pt(PH_3)(C_2H_2)$, as discussed above. The destabilization energy is the origin of the activation barrier. Thus, the occupied d orbitals at lower energy of $M(PH_3)$ is the reason for the reactivity of $M(PH_3)$ being lower than that of Cp_2Zr and $(MeO)_2Zr$. The higher reactivity of $Ni(PH_3)$ as compared to that of $Pt(PH_3)$ is easily interpreted by $Ni(PH_3)$ having its occupied d orbitals at higher energy than those of $Pt(PH_3)$, as shown in Table 4.

Summarizing the above discussion, we reach the conclusions that the very small activation barrier and nonsymmetrical transition state of the Cp_2Zr-mediated coupling reaction arise from the presence of the occupied d orbital at high energy.

Also, one can easily understand the reason that the catalytic trimerization of acetylenes can be successfully carried out with the cobalt and rhodium complexes such as CpCoL and CpRhCl, as follows: as mentioned above, the d orbital becomes lower in energy upon going to the right-hand side from the left-hand side of the periodic table.[50] This means that the d orbitals of the Co(I) and Rh(I) complexes are at lower energy than that of Cp_2Zr but at higher energy than that of $Pt(PH_3)$. As a result, the cobalt- and rhodium-mediated coupling reactions of acetylenes take place more easily than the platinum-mediated reaction, and their reductive eliminations take place more easily than the zirconium-mediated reaction. In general, the early-transition-metal complex is very reactive for the formation of metallacyclopendadienyl species but not favorable for the reductive elimination from metallacycloheptatrienyl species because of the d orbital at high energy. Also, we wish to mention the possibility that the third acetylene is inserted into the Zr−C bond of $Cp_2\overline{Zr(CH{=}CHCH{=}C}H)$ with difficulty, because of the large steric repulsion with two Cp ligands and nonflexible metallacyclopentadienyl moiety;[35] in other words, it is likely that the formation of metallacycloheptatrienyl species is difficult in the Cp_2Zr-mediated coupling reaction. On the other hand, the late-transition-metal complex is reactive for the reductive elimination but not reactive for the formation of metallacyclopentadienyl species. Thus, transition-metal complexes in intermediate position of the periodic table is useful as a catalyst for this kind of trimerization reaction of acetylene. An early-transition-metal complex is, on the other hand, useful for the formation of metallacyclopentadienyl species, while the transmetalation step is necessary to complete the syntheses of aromatic compounds, as reported experimentally.[3c] A late-transition-metal complex is useful for syntheses of aromatic compounds and oligomers of acetylenes, if the metallacyclopentadienyl species is produced by transmetalation.

Conclusions

Cp_2Zr-, $(MeO)_2Zr$-, and $M(PH_3)$-mediated coupling reactions (M = Ni, Pt) of acetylenes were theoretically investigated with the DFT, MP2 to MP4(SDQ), and CCSD(T) methods. Some of the important results can be summarized as follows. (1) The transition states of the Cp_2Zr- and $(MeO)_2Zr$-mediated reactions are not symmetrical, as reported experimentally and theoretically,[18] while that of the $Pt(PH_3)$-mediated reaction is symmetrical and that of the $Ni(PH_3)$-mediated reaction is nearly symmetrical, as expected. IRC and pseudo-IRC calculations clearly show that the nonsymmetrical transition state of the Cp_2Zr-mediated reaction leads to a symmetrical product and that the symmetrical transition state of the $Pt(PH_3)$-mediated reaction leads to a nonsymmetrical product. (2) The Cp_2Zr- and $(MeO)_2Zr$-mediated reactions take place with nearly no barrier and substantially large exothermicity. (3) The $Pt(PH_3)$-mediated reaction needs a considerably large activation barrier. (4) The activation barrier of the $Ni(PH_3)$-mediated reaction is smaller than that of the $Pt(PH_3)$-mediated reaction but larger than those of Cp_2Zr- and $(MeO)_2Zr$-mediated reactions. (5) Computational results of the reactivities of Cp_2Zr, $Pt(PH_3)$, and $Ni(PH_3)$ are consistent with the experimental results that the Cp_2Zr-mediated coupling reaction of acetylene easily takes place but the $Pt(PH_3)$-mediated reaction occurs with more difficulty than the $Ni(PH_3)$-mediated reaction. (6) The DFT method presents reliable results in these coupling reactions, except that this method moderately underestimates the activation barrier (E_a) of the $Pt(PH_3)$-mediated reaction and considerably underestimates the binding energy (BE) of the precursor complex in Cp_2Zr- and $Pt(PH_3)$-mediated reactions. The MP4(SDQ) and CCSD(T) methods are considered reliable in the $Pt(PH_3)$-mediated reaction. (7) In the $Ni(PH_3)$-mediated coupling reaction, the DFT and CCSD(T)

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(51) The HOMO of $Cp_2Zr(C_2H_2)$ is at −8.23 eV, and that of $(MeO)_2Zr(C_2H_2)$ is at −9.20 eV. The Hartree−Fock calculation of $(MeO)_2Zr$ failed, probably because the singlet electronic state is very unstable. Thus, we present the discussion on the basis of the d orbital energies of $(MeO)_2Zr(C_2H_2)$ and $Cp_2Zr(C_2H_2)$.

(52) The MeO ligand changes its orientation upon going from the reactant to the transition state and the product, as shown in Figure 1. It is likely that the MeO group easily rotates around the Zr−O bond.

methods present reliable results but the MP2 to MP4(SDQ) methods do not.

The HOMO of the $M(PH_3)$ reaction system shows that the CT interaction between the d orbital of the transition-metal center and the $\pi^*-\pi^*$ bonding couple of two acetylene molecules plays an important role in the C−C bond formation. As a result, the transition state is symmetrical, which is favorable for the CT interaction. On the other hand, a CT interaction between the $d_\pi-\pi^*$ back-donation orbital of $Cp_2Zr(C_2H_2)$ and the π^* orbital of acetylene 2 is strongly formed in the Cp_2Zr-mediated coupling reaction. This CT interaction smoothly leads to the C−C bond formation, concomitant with the stabilization of the reaction system. As a result, the coupling reaction takes place easily through nonsymmetrical transition state. These differences are reasonably interpreted in terms that the d orbital of Cp_2Zr is at a much higher energy than that of $M(PH_3)$. The greater reactivity of $Ni(PH_3)$ compared to that of the Pt analogue is also interpreted in terms that the d orbital of $Ni(PH_3)$ is at higher energy than that of $Pt(PH_3)$. The $(MeO)_2Zr$ species is more reactive than the Cp_2Zr species, in spite of the fact that its d orbital is at moderately lower energy than that of the Cp_2Zr species. It is likely that $(MeO)_2Zr$ is very reactive because the MeO group is flexible and gives rise to little steric repulsion with substrates.

In conclusion, this theoretical study clearly shows the reason that early-transition-metal complexes such as Cp_2Zr and similar Zr complexes are reactive in the alkyne coupling reactions to form metallacyclopentadienyl species. Also, we wish to mention here that the transition-metal complexes in the intermediate region of the periodic table are useful as catalysts for the trimerization of alkynes and that the late-transition-metal complexes are useful for the syntheses of benzene and pyridine derivatives, once the metallacyclopentadienyl species are produced through trans metalation, as reported experimentally.[3c]

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Supporting Information Available: Tables giving activation barriers and reaction energies of $Pt(PMe_3)$-mediated coupling reaction of acetylene, Cartesian coordinates of important species, including transition states, basis set effects, and MP2-MP4(SDQ) computational results of the $Ni(PH_3)$-mediated coupling reaction and figures giving geometries of zirconacycloheptatrienyl species, $Cp_2Zr(CH{=}CHCH{=}CHCH{=}CH)$, and platinacycloheptatrienyl species, $Pt(CH{=}CHCH{=}CHCH{=}CH)(PH_3)$, population changes of $(MeO)_2Zr$- and $Ni(PH_3)$-mediated coupling reactions of two acetylenes, frontier orbitals of Cp_2Zr, $Pt(PH_3)$, and $Ni(PH_3)$, and the geometry of $Cp_2Zr(CH{=}CHCH{=}CH) + C_2H_2$, when the third acetylene approaches the Zr center. This material is available free of charge via the Internet at http://pubs.acs.org.

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