Why Is the Nickel(II) Diphenyldiimine Complex the Best Catalyst for Polymerization of Ethylene in Three Kinds of Cationic Nickel(II) Complexes, $[Ni(CH_3)L]^+$ (L = Diphenyldiimine, 2,2′-Bipyridine, or 1,2-Diphosphinoethane)? A Theoretical Study

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Ligand effects in the insertion of ethylene into the Ni(II)−CH_3 bond of $[Ni(CH_3)L]^+$ {L = diphenyldiimine (PhNCH═CHNPh; dpdiim), diimine (HNCH═CHNH; diim), 2,2′-bipyridine (bpy), 1,2-bis(dimethylphosphino)ethane ($Me_2PCH_2CH_2PMe_2$; dmdipe), or 1,2-diphosphinoethane ($H_2PCH_2CH_2PH_2$; dipe)} were theoretically investigated with the DFT method. Ethylene is easily inserted into the Ni(II)−CH_3 bond with a moderate activation barrier with L = diim, dpdiim, dipe, and dmdipe but with a larger activation barrier with L = bpy. This is reasonably interpreted in terms that the coordinate bond of bpy is less flexible than those of the others because of its well-conjugated electron system. Next, coordination of ethylene with the nickel(II) propyl complex $[Ni(CH_2CH_2CH_3)L]^+$ involving β-H agostic interaction takes place with a considerably large exothermicity with L = dpdiim, diim, bpy, and dipe but with much less exothermicity with L = dmdipe. Since the propagation process needs the next coordination of ethylene, the nickel(II) dmdipe complex is less favorable for the propagation than the nickel(II) dpdiim complex. These results suggest that the nickel(II) dpdiim complex is the best catalyst for polymerization of ethylene and that the nickel(II) dmdipe complex is less useful as a catalyst for polymerization of ethylene. However, we wish to propose that the chelate diphosphine complex would become useful as a polymerization catalyst if its ability for ethylene coordination was improved, since the ethylene insertion into the Ni(II)−CH_3 bond easily occurs with a similar E_a value in both the dmdipe and the dpdiim complexes. One of the worthwhile modifications is to introduce an electron-withdrawing group to chelate phosphine to lower the lone pair orbital in energy.

Introduction

Brookhart and his collaborators successfully developed nickel(II) and palladium(II) diimine catalysts for polymerization of α-olefin[1] and similar catalysts for copolymerization of ethylene and carbon monoxide.[2] These catalysts are of considerable interest and importance from both fundamental and practical points of view, since not the late transition-metal element but such early transition-metal elements as Ti and Zr had been used as a catalyst for polymerization of olefin before the imine catalyst. In this regard, the reaction mechanism and each elementary step have been experimentally investigated well by Brookhart and his collaborators.[3]

Also, many theoretical studies have been reported so far. Siegbahn and his collaborators theoretically investigated the insertion of ethylene into the M−CH_3 bond of nickel(II), palladium(II), and platinum(II) diimine complexes, $[M(CH_3)(HN{=}CH{-}CH{=}NH)]^+$ (M = Ni, Pd, or Pt), with the DFT method and reported that the nickel(II) complex is the best and the platinum(II) complex is the worst.[4] Ziegler's group theoretically investigated the dimerization of ethylene catalyzed by

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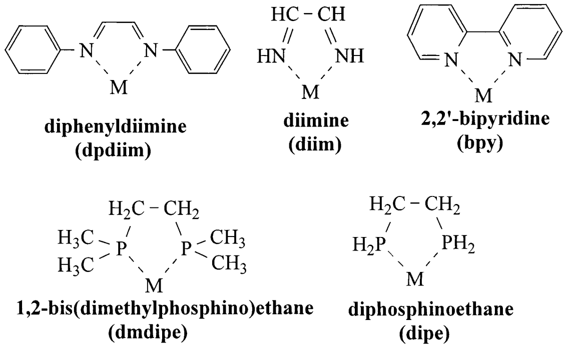
Ni(acac)H (acac = acetylacetonate),[5] the copolymerization of ethylene and carbon monoxide catalyzed by $[PdH(H_2PCH{=}CHPH_2)]^+$,[6] and the initiation, propagation, and termination processes of ethylene polymerization reaction catalyzed by a nickel(II) diimine complex, $[Ni(CH_3)(HN{=}CH{-}CH{=}NH)]^+$,[7] with the DFT method. Recently, they carried out a QM/MM study of the ethylene polymerization reaction catalyzed by a real nickel(II) diimine complex, $[Ni(CH_3)(ArN{=}CH{-}CH{=}NAr)]^+$ (Ar = 2,6-C_6H_3(i-Pr)$_2$).[8] Morokuma's group also theoretically investigated polymerization of ethylene catalyzed by nickel(II), palladium(II), and platinum(II) model diimine complexes with the DFT method[9,10] and polymerization of ethylene catalyzed by real nickel(II) and palladium(II) diimine complexes, $[M(CH_3)(ArN{=}CH{-}CH{=}NAr)]^+$ (M = Ni or Pd), with the ONIOM method.[11]

In the above-mentioned theoretical studies, they focused on the reaction mechanism[5−11] and differences in catalytic activity among nickel(II), palladium(II), and platinum(II) complexes.[4,10] However, ligand effects have not been investigated well, to our knowledge, despite the fundamental necessity for understanding the fact that diphenyldiimine with bulky substituents on the phenyl group is essential for the polymerization catalyst,[1] but the usual chelate diphosphine has been scarcely applied to the polymerization of olefin. For instance, nickel(II) and palladium(II) complexes with usual chelate diphosphine ligands were recently applied to the polymerization of ethylene, but a highly branched polymer was produced and its molecular weight (M_w) was not large.[12] Also, palladium(II) complexes of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) could not be applied to the polymerization of olefin, whereas they were successfully used as a catalyst for copolymerization of ethylene and carbon monoxide.[2] A previous theoretical study clearly explained the reason that these nickel(II) and palladium(II) complexes successfully catalyze not the polymerization of ethylene but copolymerization of ethylene and carbon monoxide. However, not the real bpy ligand but the simplest imine (HNCH=CHNH) was adopted as a model of bpy in the theoretical study. The simplest imine was adopted as a model of diphenyldiimine in theoretical studies of ethylene polymerization, too.[4,7,9,10] This means that we do not have any knowledge about differences between bpy and diphenyldiimine. It is worthwhile to compare the diimine ligand with bpy and chelate diphosphine and to find clear reasons that nickel(II) complexes of chelate diphosphine and bpy cannot catalyze efficiently the polymerization of olefin.

Scheme 1



In this theoretical study, we investigated the insertion of ethylene into the Ni(II)−CH_3 bond in $[Ni(CH_3)L]^+$ with the DFT method, where L is diimine (HN=CH−CH=NH; diim), diphenyldiimine (PhN=CH−CH=NPh; dpdiim), 2,2′-bipyridine (bpy), 1,2-bis(dimethylphosphino)ethane ($Me_2PCH_2CH_2PMe_2$; dmdipe), or 1,2-diphosphinoethane ($H_2PCH_2CH_2PH_2$; dipe), as shown in Scheme 1. We adopted these ligands, considering the following reasons: (1) diim was investigated in many previous theoretical works as the simplest model ligand,[4,7,9,10] (2) dpdiim is more realistic and a similar ligand was experimentally used,[1a] (3) bpy possesses π-conjugate orbitals such as dpdiim, but $[Ni(CH_3)(bpy)]^+$ has not been successfully applied to the polymerization of olefin (vide supra), and (4) the polymerization of ethylene by nickel(II) bpy and nickel(II) chelate diphosphine complexes has not been theoretically investigated yet. In the present study, we wish to clarify the ligand effects in the insertion of ethylene into the Ni(II)−CH_3 bond and the next coordination of ethylene with the nickel(II) propyl complex involving a β-H agostic interaction. Our purposes here are to clarify the reasons that diphenyldiimine is much better than chelate diphosphine and bpy, to explain why the nickel(II) bpy complex cannot be used for ethylene polymerization, and to present the proposal that chelate diphosphine is expected to become useful for a catalyst if its lone pair orbital becomes more stable in energy.

Computational Details

Geometries were optimized with the DFT method, where the B3LYP functional was used.[13,14] Two kinds of basis set systems were used here. Transition states were ascertained by frequency calculation. The smaller system (BS-I) was employed in geometry optimization. In BS-I, core electrons of Ni (up to 2p) and P (up to 2p) were replaced with effective core potentials (ECPs),[15,16] and their valence electrons were represented with (311/311/31) and (21/21) sets,[15,16] respectively, where a d-polarization function was added to the P atom.[17] For ligand atoms, 6-31G basis sets[18] were used. For ethylene and the methyl group, 6-31G(d) sets[19] were employed. The

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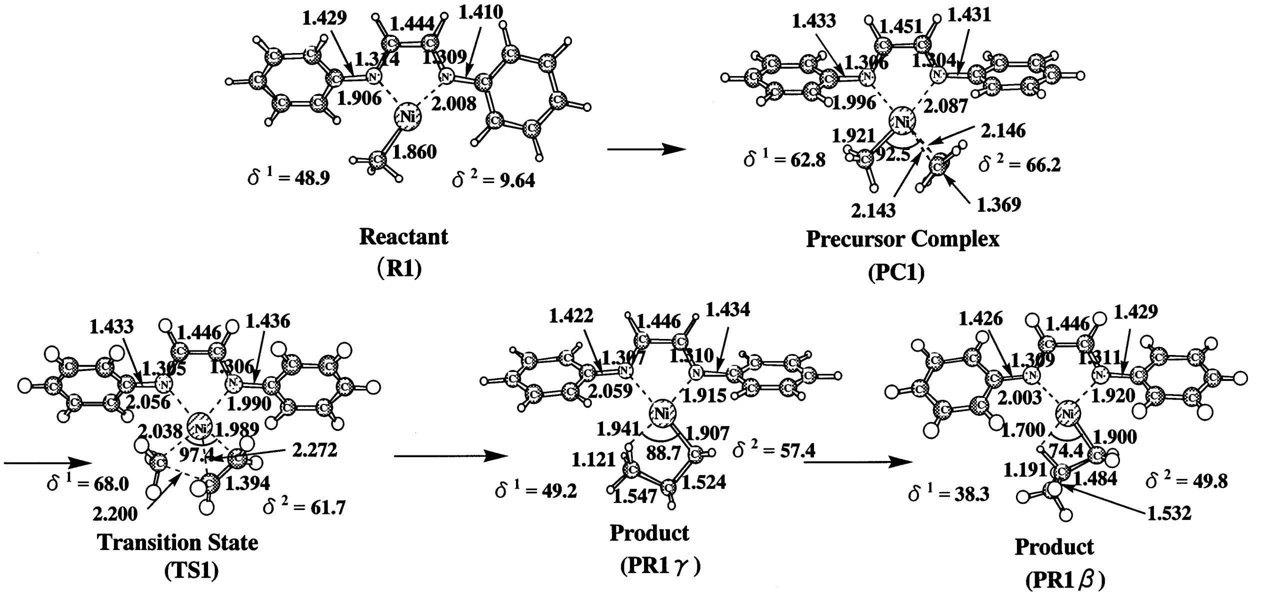

Figure 1. DFT-optimized geometry changes in ethylene insertion into the Ni(II)−CH_3 bond of $[Ni(CH_3)(dpdiim)]^+$ (dpdiim = diphenyldiimine). Bond distances in Å and bond angles in deg.

better basis set system (BS-II) was used in the evaluation of energy and population changes. In BS-II, a larger (541/541/211) set[20] was employed for Ni with the same ECPs as those of BS-I. For ethylene and the methyl group, 6-311G(d) sets were employed.[21]

Energy changes of the most simple reaction system were evaluated with DFT, MP2-MP4(SDQ), and CCSD(T) methods,[22] to examine the reliability of the DFT method. In the MP2-MP4(SDQ) and CCSD(T) calculations, core orbitals were excluded from the active space. In CCSD(T) calculations, the contribution of triple excitations was noniteratively incorporated with the CCSD wave function. Energy changes of the whole reaction systems were calculated with the DFT method, since the DFT method provides almost the same energy changes as those of the CCSD(T) method, as will be shown below. The Gaussian 98 program package was used for all these calculations.[23] Contour maps of Hartree−Fock orbitals and the Laplacian of electron density were drawn with the Molden program package.[24]

Results and Discussion

Geometry Changes in Ethylene Insertion into the Ni(II)−CH_3 Bond. Geometry changes in ethylene insertion into the Ni(II)−CH_3 bond of $[Ni(CH_3)(dpdiim)]^+$ are shown in Figure 1, where those of ethylene insertion in $[Ni(CH_3)(diim)]^+$ are omitted to save space because the geometry changes of this system have been reported previously[7,9,10] (see Supporting Information, Figure S-1). In Figure 1, we found several interesting geometrical changes, as follows: Phenyl groups of dpdiim are almost coplanar to the molecular plane in $[Ni(CH_3)(dpdiim)]^+$ **R1**, but they become almost perpendicular to the molecular plane upon coordination of ethylene (see $[Ni(CH_3)(dpdiim)(C_2H_4)]^+$ **PC1**) and again return to a nearly coplanar structure in the product, $[Ni(CH_2CH_2CH_3)(dpdiim)]^+$ ***PR1β***, which involves a β-H agostic interaction (see Figure 1). Ziegler et al. theoretically reported that the phenyl plane of diphenyldiimine, ArN═CH−CH═NHAr, fluctuated when ethylene approached the Ni(II) center.[8b] However, fluctuation of the phenyl plane has not been noticed yet in the insertion of ethylene into the Ni(II)−CH_3 bond, to our knowledge. The coplanar structure of dpdiim in **R1** is easily interpreted in terms of π-conjugation in dpdiim. In **PC1**, however, coordination of ethylene gives rise to direct steric repulsion with one of phenyl groups. At the same time, ethylene pushes away the methyl ligand toward the other phenyl group, which increases the steric repulsion between the methyl and phenyl groups. As a result, both phenyl groups become almost perpendicular to the molecular plane, to reduce the steric repulsion between dpdiim and ethylene. In the transition state **TS1**, the Ni−C^α distance of 1.989 Å is almost the same as that of the product, while the Ni−CH_3 distance slightly lengthens to 2.038 Å and the C^β−CH_3 distance (2.200 Å) is still much longer than the usual C−C single bond (1.54 Å). Consistent with the long C^β−CH_3 distance, the C^α−C^β bond of ethylene slightly lengthens by only 0.025 Å. These geometrical features are essentially the same as those reported by Morokuma et al. with the ONIOM method,[11] except for the slightly longer Ni−N distances here than their value. From these features, the transition state is characterized as

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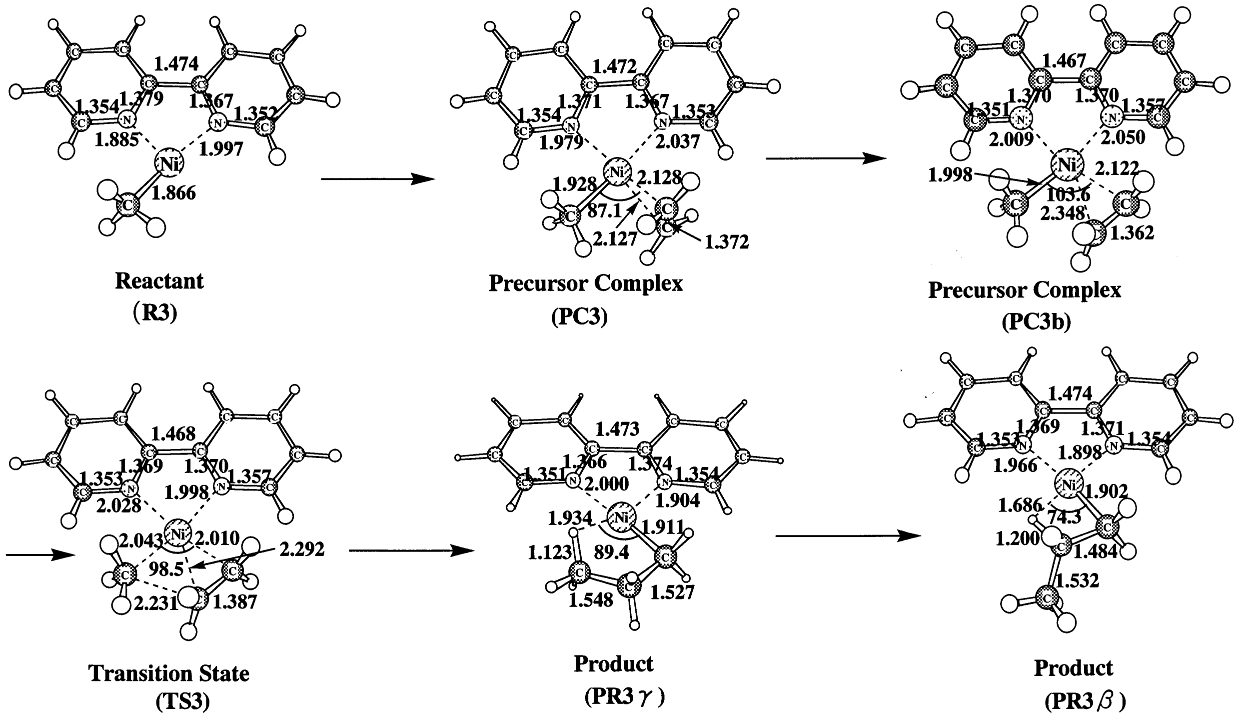

Reactant (R3)

Precursor Complex (PC3)

Precursor Complex (PC3b)

Transition State (TS3)

Product (PR3γ)

Product (PR3β)

Figure 2. DFT-optimized geometry changes in ethylene insertion into the Ni(II)$-$CH$_3$ bond of [Ni(CH$_3$)(bpy)]$^+$ (bpy = 2,2′-bipyridine). Bond distances in Å and bond angles in deg.

follows: The nickel$-$alkyl bond has been already formed in the transition state, while the C$^\beta-$CH$_3$ interaction has not been completely formed and the Ni$-$CH$_3$ bond has not been completely broken yet. The C$^\alpha-$C$^\beta$ bond still maintains double-bond character in the transition state. The formation of the metal$-$alkyl bond at the transition state has been observed in the insertion of ethylene into the metal$-$hydride, metal$-$alkyl, and metal$-$silyl bonds, too.[25] This is a common feature of the ethylene insertion reaction.

The product **PR1γ** just after the ethylene insertion involves an agostic interaction between γ-H and Ni atoms. However, **PR1γ** is less stable than the different form **PR1β**, which involves a β-H agostic interaction, as has been reported previously.[11] In **PR1β**, the H$^\beta-$Ni$-$C angle is much smaller than the H$^\gamma-$Ni$-$C angle in **PR1γ**, as shown in Figure 1. This small H$^\beta-$Ni$-$C angle leads to small steric repulsion between the propyl group and phenyl planes. As a result, two phenyl planes of dpdiim again become nearly coplanar to the molecular plane in **PR1β**.

Figures 2 and 3 show geometry changes in the ethylene insertion into the Ni$-$CH$_3$ bond of [Ni(CH$_3$)(bpy)]$^+$ **R3** and [Ni(CH$_3$)(dmdipe)]$^+$ **R4**, respectively. These geometry changes are essentially the same as those of the insertion reaction of **R1** except that the in-plane ethylene complex **PC3b** could be optimized in the reaction of **R3**. This in-plane ethylene complex was optimized in the reaction of [Ni(CH$_3$)(diim)]$^+$ **R2**, too (see Supporting Information, Figure S-1). Since ethylene seems to suffer much smaller steric repulsion with diim and bpy ligands in **PC2b** and **PC3b**, the steric repulsion is considered a key factor to destabilize the in-plane ethylene complex. One important difference among these ethylene complexes is found in the Ni$-$C$_2$H$_4$ distance. The Ni$-$C$_2$H$_4$ distances of **PC4** and **PC5** are much longer than those of the other complexes by 0.08$-$0.12 Å. The longer Ni$-$C$_2$H$_4$ distance indicates that the coordinate bond of ethylene is weak in these complexes, which will be discussed below in more detail. Though the Ni$-$C$_2$H$_4$ distances of **PC4** and **PC5** are much longer than those of the other ethylene complexes, the geometries of **TS4** and **TS5** are almost the same as those of the other transition states. This feature comes from the fact that the sp^3 orbital of CH$_3$, the π and π^* orbitals of ethylene, and the d orbital of Ni must take the best position and the best orientation in the transition state so as to induce C$-$C bond formation between ethylene and the methyl group in a concerted manner with the Ni$-$CH$_3$ bond breaking. In other words, they cannot afford to take flexible positions and orientations. Thus, the geometry of the transition state depends little on these kinds of ligand. In the products **PR4γ**, **PR5γ**, **PR4β**, and **PR5β**, which involve γ-H or β-H agostic interaction, the Ni$-$H$^\gamma$ and Ni$-$H$^\beta$ distances are somewhat longer than those of the other products. Since the agostic interaction is formed by the charge transfer from the C$-$H bonding orbital to the empty d orbital of the central metal,[26] these longer Ni$-$H$^\gamma$ and Ni$-$H$^\beta$ distances suggest that the charge transfer is suppressed by dipe and dmdipe ligands because of the strong donating interaction of these ligands. We will discuss this below in more detail.

Energy Changes by Ethylene Insertion Reaction. The DFT method has been employed in almost all theoretical studies of ethylene polymerization catalyzed by nickel(II) and palladium(II) diimine complexes,[4-11] but the reliability of the method has not been

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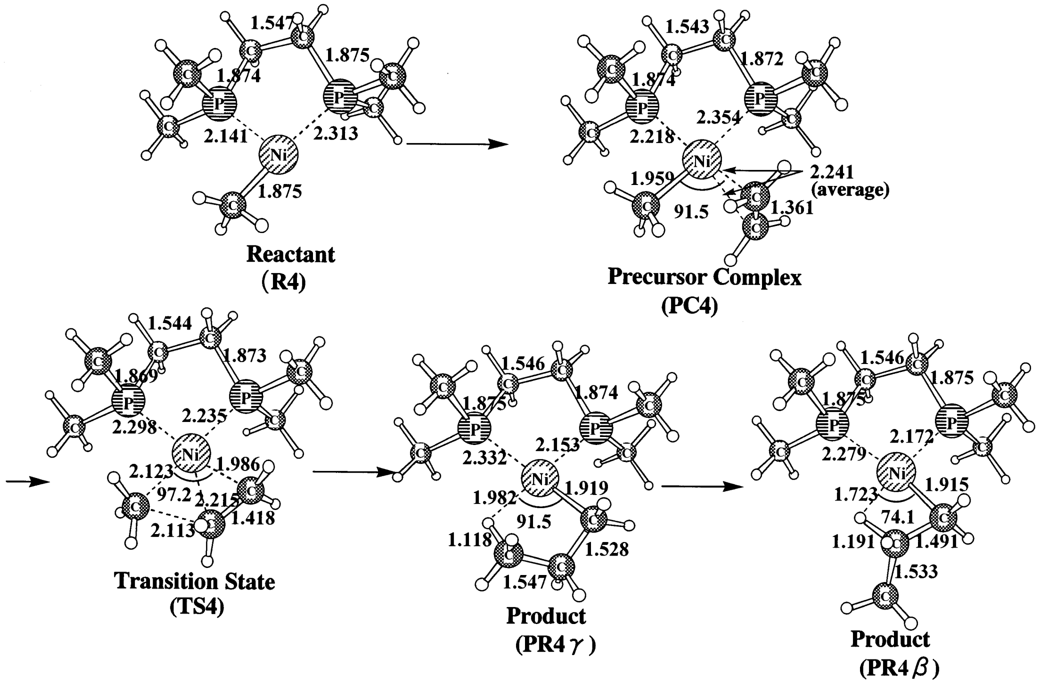


Figure 3. DFT-optimized geometry changes in ethylene insertion into the Ni(II)−CH_3 bond of $[Ni(CH_3)(dmdipe)]^+$ (dmdipe = 1,2-bis(dimethylphosphino)ethane). Bond distances in Å and bond angles in deg.

Table 1. Energy Changes (kcal/mol) by Ethylene Insertion into the Ni(II)−CH_3 Bond of $[Ni(CH_3)(HNCHCHNH)]^+$

	R2	PC2	PC2b	TS2	PR2γ	PR2β
DFT	34.4	0.0	5.7	10.7	−4.1	−11.8
MP2	36.2	0.0	9.7	10.2	−4.3	−15.9
MP3	25.0	0.0	5.7	12.7	−8.7	−12.9
MP4(DQ)	30.6	0.0	8.6	13.0	−5.4	−14.5
MP4(SDQ)	35.9	0.0	9.9	12.5	−3.0	−14.8
CCSD(T)	32.9	0.0	6.0	11.8	−5.7	−11.4

investigated yet in the case of the ethylene polymerization reaction. We evaluated the energy changes with various computational methods such as DFT, MP2-MP4(SDQ), and CCSD(T), to investigate whether the DFT method is reliable in the theoretical study of the insertion of ethylene into the Ni(II)−CH_3 bond. Here, we adopted the simplest system, $[Ni(CH_3)(diim)]^+$ (**R2**), to save CPU time in the CCSD(T) calculations. As shown in Table 1, the ethylene complex $[Ni(CH_3)(diim)(C_2H_4)]^+$ (**PC2**) is about 33−36 kcal/mol more stable than **R2** in all the computational methods except for the MP3 and MP4(DQ) methods, which yield much smaller stabilization energy than the others. The activation barrier, which is defined as an energy difference between the transition state and the precursor complex ($E_a = E_t(\mathbf{TS2}) - E_t(\mathbf{PC2})$), moderately fluctuates upon going to MP4(SDQ) from MP2 but converges to about 12 kcal/mol upon going to CCSD(T) from MP4(SDQ). The DFT-calculated activation barrier is almost the same as this value. The relative stability of **PR2γ** with respect to **PC2** is calculated to be −3.0 to −5.4 kcal/mol with the MP2−MP4(SDQ), CCSD(T), and DFT methods and that of **PR2β** is calculated to be −11 to −12 kcal/mol with the DFT and CCSD(T) methods, whereas the MP2, MP4(DQ), and MP4(SDQ) methods overestimate this relative stability. From these results, it should be concluded that the DFT method is reliable for the ethylene insertion reaction. We adopted the DFT method hereafter.

Table 2. Energy Changes (kcal/mol)[a] by Ethylene Insertion into the Ni(II)−CH_3 Bond of $[Ni(CH_3)(L)]^+$ (L = dpdiim, diim, bpy, dipe, or dmdipe)

	Rn[b]	PCn	PCnb	TSn	PRnγ	PRnβ
dpdiim	26.6	0.0		12.5	−7.0	−16.4
diim	34.4	0.0	5.7	10.7	−4.1	−11.8
bpy	29.2	0.0	13.4	14.0	−5.8	−14.6
dmdipe	22.9	0.0		12.0	−9.0	−18.3
dipe	26.8	0.0		11.9	−7.8	−17.2

[a] The DFT/BS-II method was used. [b] n = 1−5 for L = dpdiim, diim, bpy, dmdipe, and dipe, respectively.

In Table 2, DFT-calculated energy changes are compared among various reaction systems. The activation barrier (E_a) is the largest in L = bpy, the smallest in L = diim, and intermediate in the others. The product **PRnγ** (n = 1−5) just after the insertion reaction is considerably more stable in L = dipe, dmdipe, and dpdiim, while this is the least stable in L = diim. Similar relative stabilities are observed in the final product **PRnβ**. From these results, the following conclusions are presented: (1) the diim, dpdiim, dmdipe, and dipe complexes are useful for ethylene insertion reaction, (2) the bpy complex is not useful for the ethylene insertion, and (3) not the reactivity for ethylene insertion but the other factor is responsible for the fact that the nickel(II) chelate diphosphine complex is not useful as a catalyst for the polymerization of olefin.

We will inspect here the relation between the E_a value of ethylene insertion and the coordinate bond of ethylene with the Ni(II) center, since the stabilization energy by the ethylene coordination would be related to the reactivity for the ethylene insertion reaction, as follows:[4] In the insertion of ethylene into the metal−alkyl bond, both the metal−ethylene coordinate bond and the

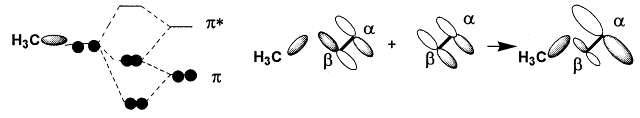
Table 3. Population Changes[a] upon Going to Transition State from Precursor Complex

	dpdiim	diim	bpy	dmdipe	dipe
Ni	0.015	0.005	0.022	0.023	0.034
CH_3	−0.098	−0.121	−0.092	−0.139	−0.175
C_2H_4	0.070	0.098	0.070	0.105	0.151
C^{α}	0.149	0.171	0.179	0.170	0.203
C^{β}	−0.071	−0.060	−0.103	−0.040	−0.047
L	0.012	0.017	0.0	0.004	−0.010
N^1 (or P^1)	0.022	0.033	0.024	0.110	0.115
N^2 (or P^2)	−0.016	−0.032	−0.006	−0.101	−0.093
ΔR(Ni−N^1 (or P^1))[d]	0.117	0.076	0.019	0.080	0.115
ΔR(Ni−N^2 (or P^2))[d]	−0.157	−0.082	−0.052	−0.119	−0.132

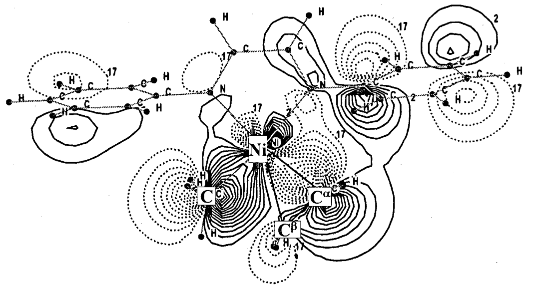
[a] A positive value represents an increase in population upon going to transition state from precursor complex (vice versa). [b] The C^{α} atom becomes the C atom that directly interacts with the Ni(II) center, and the C^{β} atom starts to interact with the CH_3 group. [c] The N^1 (or P^1) atom is at a position trans to ethylene, and the N^2 (or P^2) atom is at a position trans to the CH_3 ligand. [d] The change in the bond length upon going to TS atom PC (in Å).

metal−alkyl bond are broken, while the C=C double bond is converted to the C−C single bond and the metal−alkyl bond is newly formed. The newly formed metal−alkyl bond is considered to be as strong as that of the reactant, if we neglect the difference in steric repulsion. The conversion of the C=C double bond to the C−C single bond is common in all the reaction systems. The above discussion leads us to the suggestion that the reactivity for ethylene insertion depends on the metal−ethylene coordinate bond; in other words, ethylene is easily inserted into the metal−alkyl bond when the coordinate bond of ethylene is weak. However, this suggestion is not consistent with the results here, as follows: The stabilization energy is the largest in L = diim, the next is in L = bpy, the smallest in L = dmdipe, and intermediate in L = realistic dpdiim. Apparently, neither the stabilization energy by the coordination of ethylene nor the reaction energy (i.e., the stabilization energy of the product relative to the reactant) is related to the activation barrier for the ethylene insertion. This indicates that the ligand effects in the ethylene insertion reaction arise from the bonding feature in the transition state.

Bonding Feature of the Transition State in the Ethylene Insertion Reaction. To shed some light on the bonding feature in the transition state, population changes upon going to **TSn** from **PCn** are investigated, as shown in Table 3, where natural bond orbital (NBO) population analysis was employed to evaluate the electron population.[27] In all the reaction systems, electron populations of the ethylene moiety and Ni increase, while the electron population of the CH_3 moiety decreases. These changes suggest that ethylene insertion is understood in terms of nucleophilic attack of the CH_3 moiety to ethylene. It is also noted that the C^{α} atomic population considerably increases but the C^{β} atomic population considerably decreases. This electron redistribution seems not to be directly related to the charge transfer from CH_3 to the π* orbital of ethylene, since such charge-transfer interaction increases both C^{α} and C^{β} atomic populations. Not the simple charge transfer but orbital mixing coupled with the charge transfer yields this electron redistribution,[25] as follows: The sp^3 orbital of CH_3 overlaps with the π* orbital of ethylene in a bonding way, as shown in Figure 4A, which corresponds to the charge transfer from the sp^3 orbital of CH_3 to the π* orbital of ethylene. The π orbital of ethylene mixes into this orbital overlap in an antibonding way with the sp^3 orbital of CH_3, since the sp^3 orbital of the anionic CH_3 ligand is at a higher energy than the π orbital of ethylene. This mixing increases the contribution of the C^{α} p_{π} orbital but decreases the contribution of the C^{β} p_{π} orbital in the HOMO of the transition state.[28] Actually, the HOMO consists of a larger p_{π} orbital of C^{α} and a smaller p_{π} orbital of C^{β}, as shown in Figure 4B. This HOMO yields the electron redistribution mentioned above.



(A) Important orbital interaction



(B) Contour map of the next HOMO[a)] of the ethylene insertion into the Ni(II)-CH_3 bond

Figure 4. Contour map of the HOMO in the transition state of ethylene insertion reaction of $[Ni(CH_3)(dpdiim)]^+$ and the schematic representation of orbital mixing in the next HOMO[a)]. Contour values are 0.0, ±0.0125, ±0.025, ±0.0375, ±0.0500, and so on. (a) Hartree−Fock orbital.

Though the charge transfer coupled with the orbital mixing is an important interaction in the transition state, as discussed above, the quantity of charge transfer is not related to the E_a value, as follows: the electron population of CH_3 decreases in the order dipe > dmdipe > diim > dpdiim ≈ bpy, which is different from the increasing order of E_a, diim < dipe ≈ dmdipe ≈ dpdiim < bpy. This result suggests that not the charger transfer but the other interaction determines the E_a value of the insertion reaction.

To find what is a determining factor of the activation barrier, we inspected the transition state in detail with the Laplacian of electron density.[29] Here, the most simple system, $[Ni(CH_3)(diim)(C_2H_4)]^+$, is investigated as an example in Figure 5, because the Laplacian of the diim complex is less complicated than that of the dpdiim complex but essentially the same as that of the dpdiim complex (see Supporting Information, Figure S-4 for the Laplacian of the dpdiim complex). Apparently, the

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(27) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 849, and references therein.

(28) This orbital mixing is observed in the HOMO when L is diim, dmdipe, and dipe, but in the next HOMO when L is dpdiim and bpy in which the HOMO is the π orbital of the phenyl and pyridyl groups, respectively.

(29) (a) Bader, R. F. W.; Gillespie, R. J.; MacDougall, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7329. (b) Gillespie, R. J.; Bytheway, I.; MacDougall, P. J.; Bader, R. F. W. *Inorg. Chem.* **1994**, *33*, 2115. (c) Gillespie, R. J.; Bytheway, I.; Tang, T.-H.; Bader, R. F. W. *Inorg. Chem.* **1995**, *35*, 2407.

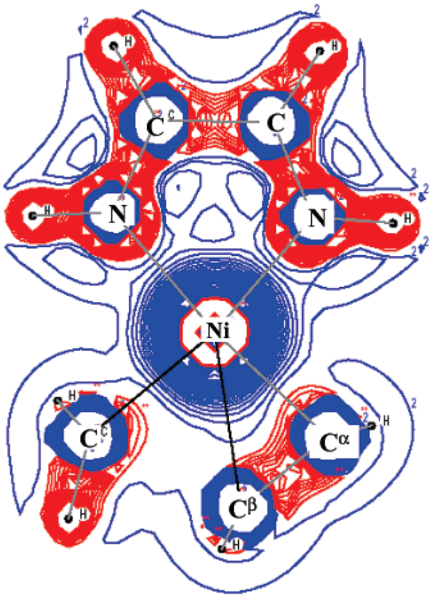
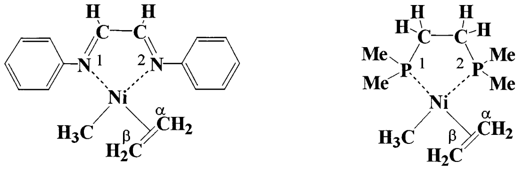


Figure 5. Laplacian of electron density in the transition state of ethylene insertion reaction of $[Ni(CH_3)(diim)]^+$. Contour values are 0.0, ±0.1, ±0.2, ±0.3, and so on. Red lines represent negative value and blue ones positive value.

Scheme 2



negative zone (red lines) around the $C^{\alpha}-C^{\beta}$ bond is polarizing toward the Ni(II) atom, and interestingly, the negative zone expands toward the Ni atom from the C^{α} atom, which indicates that the $Ni-C^{\alpha}$ bond has been almost formed. At the same time, the negative zone near the CH_3 ligand is moving toward the C^{β} atom of ethylene. However, this negative zone has not reached the intermediate region between CH_3 and the C^{β} atom, which suggests that the C−C bond formation between CH_3 and ethylene has not been completed yet in the transition state. These features are consistent with the above-discussed geometry changes that the M−alkyl bond distance is almost the same as that of the product but the $C^{\beta}-CH_3$ distance is still much longer than the usual C−C single bond.

Formation of the Ni−alkyl bond in the transition state induces several important changes in electron distribution and geometry, as follows: The electron population of the N^1 (or P^1) atom, which is at a position trans to ethylene, increases upon going to **TS** from **PC**, as shown in Table 3 (see Scheme 2 for N^1 and P^1). Consistent with this electron redistribution, the $Ni-N^1$ (or $Ni-P^1$) bond becomes longer upon going to **TS** from **PC** (see Table 3). This is interpreted in terms that formation of the Ni−alkyl bond at a position trans to the N^1 (or P^1) atom suppresses the charge transfer from the N^1 (or P^1) atom to Ni in the transition state because of the strong trans-influence of the alkyl ligand. In other words, the newly formed Ni−alkyl bond is stabilized by the weakening of the $Ni-N^1$ (or $Ni-P^1$) bond. On the other hand, the electron population of the N^2 (or P^2) atom which is at a position trans to the CH_3 ligand decreases and the $Ni-N^2$ (or $Ni-P^2$) bond shortens upon going to **TS** from **PC** because the charge transfer from the N^2 (or P^2) atom to Ni is enhanced by weakening of the $Ni-CH_3$ bond. This means that destabilization by the $Ni-CH_3$ bond breaking is compensated by the strengthening of the $Ni-N^2$ (or $Ni-P^2$) bond. The decrease of the N^2 (or P^2) atomic population takes place to a similar extent to the increase of the N^1 (or P^1) atomic population in diim, dpdiim, dmdipe, and dipe complexes. In the bpy complex, however, the N^2 atomic population increases little unlike those of the other complexes, whereas the N^1 atomic population decreases to a similar extent to those of dpdiim and diim complexes. Also, the $Ni-N^1$ and $Ni-N^2$ bond distances of the bpy complex change to a much lesser extent than those of the other complexes (see Table 3). All these results indicate that the coordinate bond of bpy is much less flexible than those of the others. As a result, the $Ni-CH_3$ bond weakening in the TS is not compensated well by the strengthening of the $Ni-N^2$ bond and the formation of the Ni−alkyl bond is suppressed by weakening of the $Ni-N^1$ bond. This would be the main reason that the E_a value is largest in the bpy complex.

Table 4. Energy Changes[a] (kcal/mol) by Ethylene Coordination with the Ni(II) Center in $[Ni(CH_3)(L)]^+$ and $[Ni(CH_2CH_2CH_3)(L)]^+$

	ethylene coordination to	
	$[Ni(CH_3)(L)]^+$	$[Ni(CH_2CH_2CH_3)(L)]^+$
dpdiim	−26.6	−8.5
diim	−34.4	−10.9
bpy	−29.2	−9.1
dmdipe	−22.9	−6.1
dipe	−26.8	−9.0

[a] DFT(B3LYP)/BS-II.

Coordination of Ethylene with the Ni(II) Center. To cause the propagation, one more ethylene must coordinate with the Ni(II) center of $[Ni(C_3H_7)L]^+$. This coordination of ethylene occurs with large exothermicity in diim, bpy, dpdiim, and dipe complexes but with much less exothermicity in the dmdipe complex, as shown in Table 4. Consistent with the smallest stabilization energy of the dmdipe complex, its $Ni-C_2H_4$ distance is considerably long, as mentioned above. This result suggests that the dmdipe complex is less favorable for the propagation reaction than the others.

Since the ethylene insertion into the $Ni(II)-CH_3$ bond easily occurs in the nickel(II) dmdipe complex, we can expect that the dmdipe complex will become useful as a catalyst for polymerization if we could improve the ability of the complex for ethylene coordination. Thus, it is of considerable importance to investigate the reason that the ethylene coordination with the Ni(II) center is weak in the dmdipe complex. We investigate here the ethylene coordination with the Ni(II) center in $[Ni(CH_3)L]^+$, since the stabilization energy (BE) by the coordination of ethylene decreases in the order diim > bpy > dipe ≈ dpdiim > dmdipe in both $[Ni(CH_3)L]^+$ and $[Ni(C_3H_7)L]^+$. Population changes caused by the ethylene coordination are listed in Table 5. Apparently, the electron population of ethylene considerably decreases in all the complexes. Consistent with this population change, the Ni atomic population increases in the dpdiim, diim, and bpy complexes, whereas it slightly

Table 5. Changes in Electron Population[a] and NBO Occupancies by Ethylene Coordination with the Ni(II) Center of $[Ni(CH_3)(L)]^+$

	dpdiim	diim	bpy	dmdipe	dipe
BE (kcal/mol)	26.6	34.4	29.2	22.9	26.8
Ni	0.111	0.120	0.105	−0.007	0.023
CH_3	−0.045	0.009	−0.039	0.046	0.059
C_2H_4	−0.146	−0.161	−0.128	−0.115	−0.133
N^1 (or P^1)	0.023	0.023	0.039	0.074	0.053
N^2 (or P^2)	−0.029	−0.025	−0.032	−0.032	−0.023
π	1.735	1.744	1.736	1.803	1.792
π*	0.119	0.098	0.137	0.083	0.071
R(Ni−C)	2.127 (2.124)[b]	2.161 (2.156)	2.127 (2.126)	2.240 (2.223)	2.250 (2.221)
energy of a lone pair orbital[c]	−11.1	−10.6	−11.7	−8.4	−9.4

[a] A positive value represents an increase in population by coordination of ethylene. [b] The Ni−C distance (in Å) in $[Ni(C_3H_7)L(C_2H_4)]^+$. [c] The lone pair orbital energy (in eV) of the free ligand. The Hartree−Fock/BS-II method was employed.

increases in the dipe complex and it slightly decreases in the dmdipe complex. These results lead us to the suggestion that the σ-donation participates in the coordinate bond to a greater extent than does the π-back-donation. However, the decreasing order of electron population of ethylene, diim > dpdiim > dipe > bpy > dmdipe, is different from the increasing order of the stabilization energy by the ethylene coordination. This is not surprising because not only σ-donation but also π-back-donation participates in the coordinate bond of ethylene even though the π-back-donation is weak. The occupancy number[27] of the π orbital, which reflects the strength of σ-donation, decreases in the order dmdipe > dipe > diim > dpdiim ≈ bpy, and the occupancy number of the π* orbital, which reflects the strength of π-back-donation, increases in the order dipe < dmdipe < diim < dpdiim < bpy, as shown in Table 5. These occupancy numbers suggest that the coordinate bond of ethylene becomes weak in the order bpy > dpdiim > diim > dipe > dmdipe, which is slightly different from the decreasing order of BE; for instance, the BE value of the diim complex is larger and the BE value of the dmdipe complex is smaller than those expected from the occupancy numbers. This discrepancy results from steric factors, as follows: Ethylene coordination with the Ni(II) center gives rise to smaller steric repulsion from diim than that from bpy and dpdiim, which leads to the strong coordinate bond of ethylene in the diim complex despite the less favorable situation from electronic factors. In the dmdipe complex, ethylene causes steric repulsion with the phenyl groups, which leads to the smaller BE value than that expected from the occupation numbers.

Since one of the important results here is that the coordinate bond of ethylene is the weakest in the dmdipe complex, we will focus here on the coordinate bond of ethylene in the dmdipe complex. As shown in Table 5, the occupancy number of the π orbital is considerably large in **PC4**, which shows that the σ-donation is weak. The σ-donation of ethylene is considered to be influenced very much by the trans-influence of the ligand that is at a position trans to ethylene. Since the trans-influence is related to the donor orbital of the ligand, the energies of the lone pair orbital of the ligands are examined here, as listed in Table 5. Apparently, the lone pair orbital of dmdipe is at the highest energy in these ligands and that of dipe is the next highest.[30] Thus, dmdipe is the most donating and most suppresses the electron donation from ethylene to the Ni(II) center. This feature is also reflected in the Ni−H^β distance in **PR4*β***; since the agostic interaction is formed through charge transfer from the C−H bonding orbital to the empty d orbital of the metal center,[26] the donating dmdipe ligand suppresses the charge transfer, which leads to the weak agostic interaction and the longest Ni−H^β distance in **PR4*β***. On the other hand, the lone pair orbital of bpy is the most stable in energy and that of dpdiim is the next. Thus, the coordinate bond of ethylene is stronger and the Ni−H^β distance is shorter in the dpdiim and bpy complexes than those of the dmdipe complex, as shown in Table 5.

We will mention here the coordination of ethylene with $[Ni(C_3H_7)L]^+$. The stabilization energy by this coordination is much smaller than that by the coordination of ethylene with $[Ni(CH_3)L]^+$, as shown in Table 4. This is because the agostic interaction of $[Ni(C_3H_7)L]^+$ is broken by the coordination of ethylene and also ethylene suffers larger steric repulsion from the propyl group than that from the methyl group. Consistent with these results, the Ni−C_2H_4 distance of $[Ni(C_3H_7)L(C_2H_4)]^+$ is longer than that of $[Ni(CH_3)L(C_2H_4)]^+$ (see Table 5). Since the coordinate bond of ethylene in $[Ni(C_3H_7)L(C_2H_4)]^+$ is essentially the same as that of $[Ni(CH_3)L(C_2H_4)]^+$, we will stop further discussion.

Conclusions and Some Predictions

In this work, insertion of ethylene into the Ni(II)−CH_3 bond of $[Ni(CH_3)L]^+$ (L = dpdiim, diim, bpy, dmdipe, or dipe) was theoretically investigated with the DFT method. This insertion reaction occurs with the smallest activation barrier in the diim complex, with moderate activation barriers in the dpdiim, dmdipe, and dipe complexes, and with the largest activation barrier in the bpy complex. The largest activation barrier of the bpy complex is interpreted in terms that bpy is a good chelating ligand with a well-conjugated electron system, as follows: Since the Ni−N coordinate bond of the bpy complex is not flexible, the Ni−N^1 bond becomes weaker by formation of the Ni−alkyl bond and the Ni−N^2 bond becomes stronger by the Ni−CH_3 bond weakening to a much lesser extent than those of the other complexes. As a result, the formation of an alkyl group at a position trans to the N^1 atom less easily occurs and the Ni−CH_3 bond breaking is not compensated well by the Ni−N^2 bond strengthening, which leads to the large activation barrier.

In the dpdiim complex, ethylene is easily inserted into the Ni−alkyl bond, since the coordinate bond of dpdiim is flexible unlike that of bpy. Also, the next coordination of ethylene with the Ni(II) center takes place with considerably large exothermicity, since the lone pair orbital of dpdiim is at a low energy. As a result, the propagation reaction easily proceeds in the dpdiim complex.

Though the activation barrier for the ethylene insertion is not large in the dmdipe complex, the second

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(30) The slightly different orbital energies were calculated with the DFT(B3LYP) method, as follows: −5.93 eV for dpdiim, −7.11 eV for diim, −6.21 eV for bpy, −5.65 eV for dmdipe, and −6.51 eV for dipe. In these results, however, the lone pair orbital of dmdipe is at a higher energy than those of dpdiim and bpy.

ethylene less easily coordinates with the Ni(II) center in this complex than that in the other complexes. This means that the chelate diphosphine complex is as favorable as the dpdiim complexes for ethylene insertion but less favorable than the dpdiim complex for the propagation process.

Though there are several differences between dpdiim and dmdipe complexes, those differences are not significantly large. Thus, one can expect that the chelate diphosphine complex would become useful as a catalyt for polymerization of alkene if we succeeded in improving the chelate diphosphine. One worthwhile modification is to introduce the electron-withdrawing group to phosphine, since dmdipe has the lone pair orbital at a higher energy than that of dpdiim and it is unfavorable for the coordination of alkene. Chelate diphosphite with bulky substituents would be a good candidates because phosphite is more electron-withdrawing than phosphine.

The other interesting result is that the phenyl planes of dpdiim considerably rotate in the ethylene insertion, which decreases the steric repulsion. For instance, the dihedral angle between the phenyl plane and the NCCN plane increases upon the coordination of ethylene and gradually decreases upon going to **PR1β** from **PC1**. This means that the π-conjugation of dpdiim is broken by the coordination of ethylene, but it recovers during the ethylene insertion. This leads to significantly larger exothermicity in the dpdiim complex than that in the diim complex. In the diphenyldiimine ligand ArNC-(CH$_3$)=C(CH$_3$)NAr used experimentally, six *i*-Pr and two methyl substituents are introduced to two phenyl groups and the bridging carbon atoms, respectively. Because of these geometrical features, the phenyl groups fluctuate less easily in ArNC(CH$_3$)=C(CH$_3$)NAr. However, the fluctuation occurs in the real diphenyldiimine ligand, ArNC(CH$_3$)=C(CH$_3$)NAr, too, as reported in the ethylene coordination process by Ziegler et al.[6] This would be one of the strong points of the diphenyldiimine ligand for the polymerization catalytst. We believe that the results of diphenyldiimine and chelate diphosphine provide us with new points of view which are useful in finding a new catalyst.

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Supporting Information Available: Figures of geometry changes in ethylene insertion into the Ni−CH$_3$ bond of [Ni(CH$_3$)(L)]$^+$ (L = diim or dipe). Three-dimensional picture of the HOMO and the Laplacian of electron density in the transition state of the ethylene insertion into the Ni(II)−CH$_3$ bond of [Ni(CH$_3$)(dpdiim)]$^+$. Tables of all the geometries examined here. This material is available free of charge via the Internet at http://pubs.acs.org.

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