

Comparing Nickel- and Palladium-Catalyzed Heck Reactions

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The possible use of Ni in Heck reactions was investigated with use of the density function theory method. It was found that the mechanisms of the Ni- and Pd-catalyzed Heck reactions are quite similar to each other. Nevertheless, oxidative addition and olefin insertion occur with lower energy barriers in the Ni system than in the Pd system. Because β -hydride elimination is more efficient in the Pd system than in the Ni system, there is a poorer selectivity to vinylation over Michael addition in the Ni system than in the Pd system. In addition, catalyst regeneration through HX removal is considerably harder to achieve with the Ni system than with the Pd system. Therefore, either a very strong base should be used for the Ni catalysis or a reductive pathway should be designed to remove HX from the Ni complex. Compared to the Pd system, oxidative addition of an alkenyl or aryl chloride is not much harder than oxidative addition of an alkenyl or aryl iodide in the Ni system. Therefore, the Ni-catalyzed Heck reaction may be applied to alkenyl or aryl chloride relatively easily. Also, because β -hydride elimination is more difficult in the Ni system than in the Pd system, the Ni-catalyzed Heck reaction may be applied to aliphatic halides. For an olefin with an electron-donating substituent, the Ni-catalyzed coupling should slightly favor the Markovnikov-type product, if the steric effect is not significant. For an olefin with an electron-withdrawing substituent, the Ni-catalyzed coupling should provide the anti-Markovnikov-type product as the major product. In addition, it was found that phosphine and pyridine ligands can reasonably well reduce the free energy in the HX removal step. Therefore, they appear to be promising ligands for the Ni-catalyzed Heck reactions. Finally, we found that the solvation effects, cation pathway, and anionic pathway in the Heck reactions did not change the general trends for the reactivities of the Ni and Pd catalysts.

Introduction

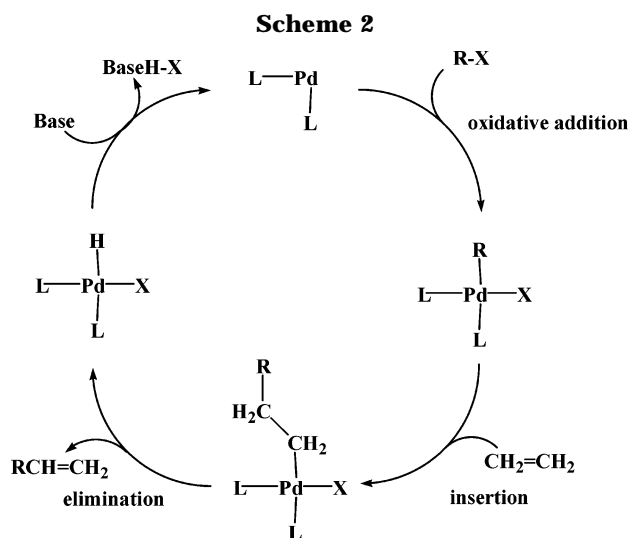
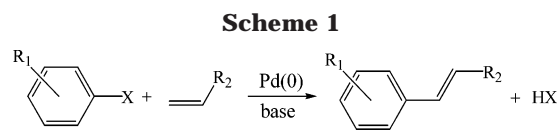
The transition metal catalyzed C–C coupling reaction of an aryl or alkenyl halide with an olefin is known as the Heck reaction¹ (Scheme 1). This reaction is one of the most powerful methods for the formation of C–C bonds.

The catalyst in the standard Heck reaction is a Pd(0) species stabilized by two phosphine ligands. The reaction mechanism includes four steps¹ (Scheme 2): (1) A σ -aryl–Pd(II) or σ -alkenyl–Pd(II) complex is formed via oxidative addition. (2) Either one of the phosphine ligands or the halide anion dissociates from the complex, leaving behind a vacant coordination site that is occupied by the olefin substrate. Insertion of the olefin at the aryl–Pd or alkenyl–Pd bond takes place subsequently. (3) An intramolecular β -hydride elimination occurs, which gives the coupling product. (4) PdL₂ catalyst is regenerated after the removal of HX from the complex mediated by the base.

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Because of the importance of the Heck reaction in organic synthesis, considerable effort has been devoted to the improvement of the efficiency and selectivity of the Pd-catalyzed Heck reactions. Due to the high cost

of Pd, researchers are also interested in the Heck reactions catalyzed by much cheaper transition metals such as Co,^{2,3} Cu,⁴ and Ni.⁵ These new Heck reactions may provide chemists opportunities to achieve novel reaction selectivities which cannot be accomplished with the Pd catalysts.

Among the inexpensive transition metals, Ni appears the most promising for the replacement of Pd. The earlier attempts to use the Ni(II) complexes such as NiCl₂(PPh₃)₂ to catalyze the coupling between activated olefins (e.g. ethyl acrylate) and aryl halides were moderately successful.⁵ Mixtures of addition and substitution products were obtained resulting in poor selectivity to the vinylation. In addition, stoichiometric amounts of a reductant such as Zn dust were required in the reaction to ensure the catalytic effect. Nevertheless, recently Iyer et al. found that some Ni(0) complexes such as Ni[P(OPh)₃]₄ and Ni[P(OEt)₃]₄ could catalyze the Heck reactions between aryl and vinyl halides with olefins and alkynes in the absence of any reductant.⁶ Furthermore, Arai et al. found that a catalyst system consisting of Ni/triphenylphosphine trisulfonate catalyst in ethylene glycol film supported on high surface area silica was effective in heterogenizing the Heck reaction.⁷

Although so far no Ni catalyst has been able to rival Pd for the Heck reaction, the Ni-catalyzed Heck reaction has one distinct advantage over the classic Pd-catalyzed reaction as it allows for the use of aliphatic halides (e.g., cyclohexyl bromide, secondary alkyl bromides) in addition to aryl and vinyl halides.⁵ The mild conditions of the reductive Ni-catalyzed Heck process are also worth noting. Furthermore, chlorobenzene was found to be reactive and gave a result very close to that obtained with bromobenzene in Ni-catalyzed Heck reactions, under very mild conditions and without any specific efforts of optimization.⁸ Therefore, Ni is very likely to have a huge but still largely hidden, due to scarce efforts given hitherto to this metal, potential for Heck chemistry.⁸

We recently initiated a project to study how to use inexpensive light transition metals (i.e., Fe, Co, Ni, Cu) to replace Pd in various catalytic reactions using both experimental and theoretical methods. We became quite interested in the probable application of Ni to Heck reactions. On the basis of the previous work,⁵⁻⁸ we envisioned that Ni must be able to participate in the Heck catalytic cycle, although with a different balance of individual steps and varied behavior of key intermediates compared to Pd. Detailed experimental studies

are ongoing now in our lab. A detailed theoretical study, which is reported herein, should also provide some important insights into the difference between Ni and Pd in catalyzing the Heck reaction.

Method

All the structures were completely optimized by using the gradient-corrected hybrid density function theory B3LYP method as implemented in the G98 set of programs.⁹ A basis set of valence double- ζ quality was used. Relativistic effects were addressed implicitly by the use of relativistic effective core potentials (RECPs) for I and Pd. For H and C the standard Dunning-Hay D95V basis was used. This basis set/RECP combination is usually denoted by the acronym "LANL2DZ".¹⁰

Harmonic vibrational frequencies were calculated with the B3LYP method for the optimized geometries. Zero-point vibrational energy corrections were obtained by using unscaled frequencies. The vibrational frequencies were also used to obtain thermodynamic corrections and entropies. All transition structures possessed one and only one imaginary frequency. They were further characterized by following the corresponding normal mode toward each product and reactant. In ambiguous cases for which an assignment by inspection of the corresponding imaginary eigenmode was not obvious, the correct topology of the potential energy hypersurface was verified by calculation of the intrinsic reaction coordinate (IRC) at the B3LYP/LANL2DZ level.

All species were treated as singlets. To obtain more reliable thermochemical data, additional single-point energy calculations were performed at the B3LYP/LANL2DZ+p level. The basis set LANL2DZ+p¹⁰ consists of the LANL2DZ basis set augmented by a single d polarization function for P, Cl, Br, and I. A single f polarization function is added for Ni and Pd. For H, C, and O the D95v(d) basis of Dunning was used. The single energy was used to calculate the free energy of each species at 298 K, 1 atm in the gas phase. The thermal corrections to the free energy were obtained from the B3LYP/LANL2DZ frequency calculations. It should be noted that the computation method used in this study is commonly more reliable in studying trends than providing absolute numbers for the reactions, although model calculations have been shown to afford remarkably accurate figures in absolute terms for migratory insertions.¹¹⁻¹³

In addition to the gas-phase energetics, the solvent effects on the Ni- and Pd-catalyzed Heck reactions were also considered. For this purpose, we used the continuum description of the solvent based on an SCRF method at the B3LYP/LANL2DZ+p level. The gas-phase geometry was used. The polarized continuum model (PCM) developed by Tomasi and co-workers¹⁴ was employed. Only the electrostatic contributions to the solvent effects were considered. Bondi radii were

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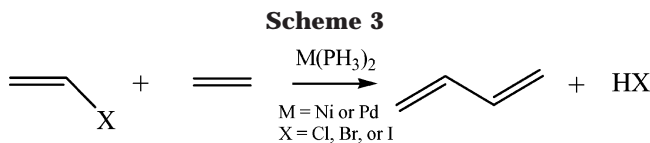
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used for the solvent effect calculations. It should be mentioned that all the free energies in the solution correspond to a standard state of 1 mol/L, 298 K.

Results and Discussion

1. A Catalytic Cycle. At first, we studied the full catalytic cycles of the Ni- and Pd-catalyzed Heck reactions, using the $\text{CH}_2=\text{CH}_2/\text{CH}_2=\text{CHCl}$ coupling as a model reaction and $\text{Ni}(\text{PH}_3)_2$ or $\text{Pd}(\text{PH}_3)_2$ as the catalyst (Scheme 3). Use of PH_3 as a phosphine ligand instead of some bulky ones (e.g., PPh_3) may lead to some unrealistic calculation results because the steric effects and some electronic effects may not be fully covered. However, the current computational resources make it necessary when the whole system is treated using the DFT theory.^{12,13}

1.a. The Catalysts. In Figure 1 are shown the structures of the Ni and Pd catalysts (**1** and **1'**). Both complexes are linearly coordinated. The calculated total binding free energy of both PH_3 ligands to the metal center is 87.2 kcal/mol for Ni and 41.7 kcal/mol for Pd. Clearly, metal–ligand interaction is considerably stronger in the bicoordinated Ni complex than in the bicoordinated Pd complex. In addition, the Ni–P bond length is 2.181 Å, which is smaller than the Pd–P bond length (2.374 Å). The shorter length of the Ni–P bond suggests that the steric effect in the Ni-catalyzed process should be more important than that in the Pd-catalyzed process.

The free energy changes for the binding between the Ni (or Pd) catalyst with some important species in the Heck reactions are shown in Table 1. According to Table 1, the binding strength decreases in the order alkene > alkenyl halide > phosphine > aryl halide for Ni and alkene > alkenyl halide > phosphine > aryl halide for Pd. (The same trends are also predicted by the CCSD(T)/LANL2DZ+P//B3LYP/LANL2DZ method, although



Figure 1. Optimized structures of $\text{Ni}(\text{PH}_3)_2$ and $\text{Pd}(\text{PH}_3)_2$.

Table 1. Free Energy Changes for the Reaction $\text{M}(\text{PH}_3)_2 + \text{L} \rightarrow \text{M}(\text{PH}_3)_2\text{L}$ (kcal/mol)

L	$\text{Ni}(\text{PH}_3)_2$		$\text{Pd}(\text{PH}_3)_2$	
	B3LYP ^a	CCSD(T) ^b	B3LYP ^a	CCSD(T) ^b
$\text{CH}_2=\text{CH}_2$ (² η)	-17.9	-30.3	-1.4	-8.7
$\text{CH}_2=\text{CH}_2-\text{Cl}$ (² η)	-17.3	-27.3	1.3	-8.2
$\text{Ph}-\text{Cl}$ (² η)	0.2	-7.9 ^c	16.5	0.9 ^c
PH_3	-9.3	-11.5	1.8	-2.0

^a Calculated with the B3LYP/LANL2DZ+P//B3LYP/LANL2DZ method. ^b Calculated with the CCSD(T)/LANL2DZ+P//B3LYP/LANL2DZ method. ^c Due to the size of the system, the energy was calculated with the B3LYP/LANL2DZ//B3LYP/LANL2DZ method.

the two methods provide different reaction energies. This suggests again that the DFT method used in this study should be more reliable in studying trends than providing absolute numbers.) Since the oxidative addition of aryl or alkenyl halide to the catalyst needs a vacant coordination site, one may expect to see serious inhibition effect of alkenes (or phosphine ligands) on the Heck reactions for both Ni and Pd. Indeed, the importance of ligand dissociation for the initiation of Heck reaction has been shown by experimental studies by Amatore and Jutand on the oxidative addition of PhI to $\text{Pd}(0)$ complexes with various ligands.¹⁵ Similar results have also been obtained in a recent theoretical study.¹³

1.b. Oxidative Addition. It is believed that before oxidative addition the catalyst should form a π complex with the halogenated alkene.¹⁶ Our results are in agreement with this theory. (See Figure 2.) The π complex (**2** or **2'**) formation decreases the system free energy by 17.3 kcal/mol for Ni but increases the system free energy by 1.3 kcal/mol for Pd. It is worthy to note that in 1972 Tolman et al. measured the equilibrium constants for $\text{ML}_3 + \text{C}_2\text{H}_4 \rightarrow \text{M}(\text{C}_2\text{H}_4)\text{L}_2 + \text{L}$ in benzene ($\text{L} = \text{PPh}_3$). They found that the equilibrium constant at 25 °C is 300 for $\text{M} = \text{Ni}$ and 0.013 for $\text{M} = \text{Pd}$.¹⁷ Therefore, both theoretical and experimental results show that the Ni–alkene complexation is much stronger than the Pd–alkene complexation.

The transition state for the oxidative addition (**TS1** or **TS1'**) is shown in Figure 2. The activation free energy for the oxidative addition is +20.1 kcal/mol for Ni and

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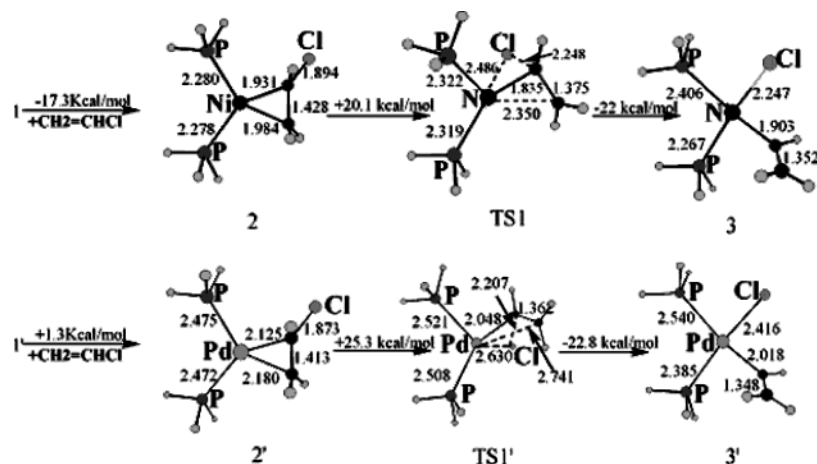


Figure 2. Oxidative addition of $\text{CH}_2=\text{CHCl}$ to $\text{Ni}(\text{PH}_3)_2$ and $\text{Pd}(\text{PH}_3)_2$.

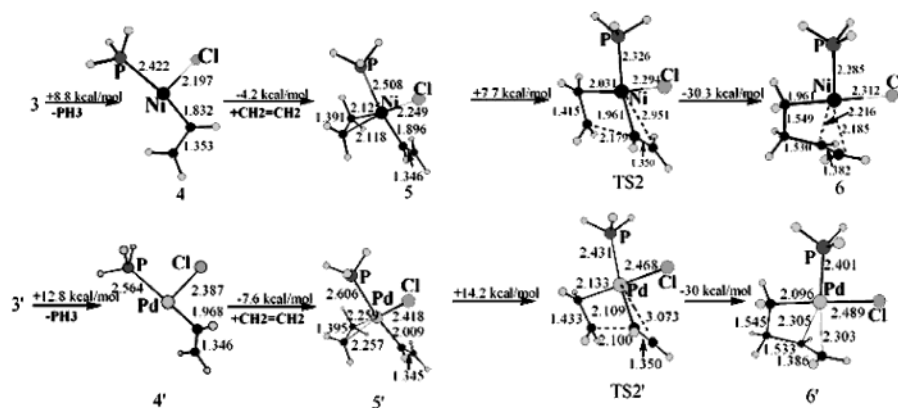


Figure 3. Insertion of $\text{CH}_2=\text{CH}_2$ into the metal-carbon bond.

+25.3 kcal/mol for Pd. Therefore, the Ni catalyst triggers a faster oxidative addition.

The initial product of the oxidative addition is a cis complex (**3** or **3'**).¹⁸ The total reaction free energy of the oxidative addition is -1.9 kcal/mol for Ni and $+2.5$ kcal/mol for Pd. Presumably, Ni is easier to oxidize than Pd because Ni is less electronegative than Pd.

1.c. Insertion. Thorn and Hoffmann found that insertion from a five-coordinate intermediate is usually hard.¹⁹ Therefore, a vacant coordination site is required to allow for a coordination of $\text{CH}_2=\text{CH}_2$ to the metal center. Since the chloride anion binds more strongly than PH_3 to the metal center, we propose that one PH_3 ligand should dissociate from the complex providing complex **4** or **4'** as shown in Figure 3. This dissociation step increases the system free energy by $+8.8$ kcal/mol for Ni and $+12.8$ kcal/mol for Pd. A positive free energy change here means that the phosphine ligand may retard the reaction (as shown later, the cationic pathway does not have this phosphine retardation problem).

Addition of $\text{CH}_2=\text{CH}_2$ to **4** (or **4'**) leads to complex **5** (or **5'**). This step decreases the system free energy by 4.2 kcal/mol for Ni and 7.6 kcal/mol for Pd. Notably, the metal-alkene interaction for Pd is stronger than that for Ni in these tetracoordinated complexes. This result contradicts the former observation for the bicoordinated complexes, presumably due to the larger steric effect

in the tetracoordinated Ni complex. The different polarizability and back-bonding ability in the Pd and Ni complexes may also play a role here.

Rotation of the ethylene ligand initiates the insertion into the metal- C_2H_3 bond. The transition state for this transformation (**TS2** or **TS2'**) is shown in Figure 3. The activation free energy for this step is $+7.7$ kcal/mol for Ni and $+12.8$ kcal/mol for Pd. Thus, Ni also triggers a faster insertion than Pd.

The immediate product from the insertion (**6** or **6'**) is a four-coordinate complex. There is a metal- $\text{C}=\text{C}$ π -interaction in the complex. Due to the formation of a C-C bond, the total free energy change for the insertion step is highly negative, i.e., -22.6 kcal/mol for Ni and -19.5 kcal/mol for Pd.

1.d. β -Elimination.²⁰ β -Hydride elimination (Figure 4) is initiated by a rotation of the $\text{CH}_\alpha-\text{CH}_\beta-\text{CH}=\text{CH}_2$ moiety around the $\text{C}_\alpha-\text{C}_\beta$ bond leading to the β -agostic complex **7** or **7'**. A transition state (**TS3** or **TS3'**) for this $\text{C}_\alpha-\text{C}_\beta$ bond rotation is found. The rotation barrier is calculated to be $+8.7$ kcal/mol for Ni and $+10.8$ kcal/mol for Pd.

(18) The product of oxidative addition could isomerize to a trans complex. However, we only considered the cis complex in this study to simplify the calculations.

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(20) Deeth et al. proposed that β -hydrogen elimination did not occur in the Heck reactions because the agostic hydrogen is kinetically the more acidic one and hence preferentially deprotonated. (See: (a) Deeth, R. J.; Smith, A.; Hii, K. K.; Brown, J. M. *Tetrahedron Lett.* **1998**, *39*, 3229. (b) Hii, K. K.; Claridge, T. D. W.; Brown, J. M.; Smith, A.; Deeth, R. J. *Helv. Chim. Acta* **2002**, *84*, 3043.) In disagreement with Deeth's proposal, our results suggest that β -elimination is the preferential pathway. It is noteworthy that others have also proposed the β -hydrogen elimination pathway in related reactions. Some also found that β -hydrogen elimination occurs more easily in the Pd complex than in the Ni complex (see: Musaev, D. G.; Morokuma, K. *Top. Catal.* **1999**, *7*, 107).

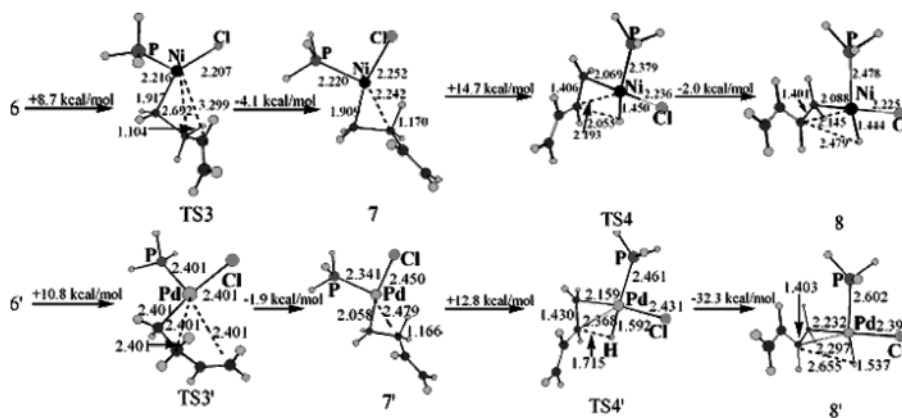


Figure 4. β -Hydride elimination.

mol for Pd. The free energy change of the C_{α} – C_{β} bond rotation is +4.6 kcal/mol for Ni and +8.9 kcal/mol for Pd.

The C_{β} –H bond of the β -agostic complex **7** (or **7'**) is then broken and a metal–H bond is formed leading to complex **8** (or **8'**). The transition state for this step is **TS4** or **TS4'**. The activation free energy for this step is calculated to be +14.7 kcal/mol for Ni and +8.5 kcal/mol for Pd. The reaction free energy for this step is +12.7 kcal/mol for Ni and +4.0 kcal/mol for Pd. Clearly, β -hydride elimination in the Ni system is harder than that in the Pd system.²⁰

1.e. Regeneration of Catalyst. After losing the product $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, complex **8** or **8'** changes into complex **9** or **9'**. The free energy of the system increases in this step by 13.3 kcal/mol for both Ni and Pd.

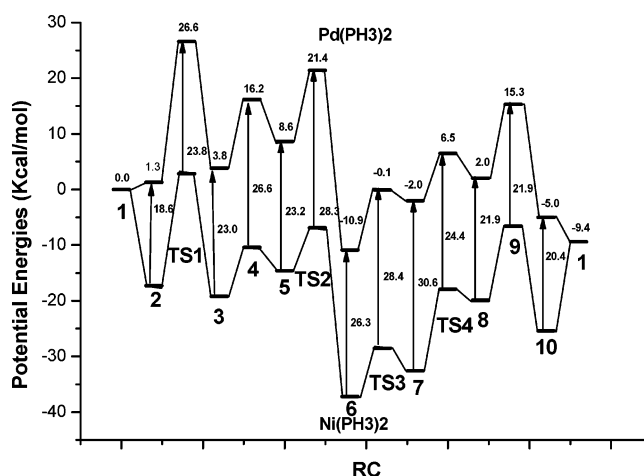
Complex **9** or **9'** has a vacant coordination site, which could be occupied by PH_3 . This step decreases the system free energy by 18.8 kcal/mol for Ni and by 20.3 kcal/mol for Pd. The product is complex **10** or **10'**.

Reductive elimination of HCl from **10** or **10'** increases the system free energy by +16.0 kcal/mol for Ni but decreases the system free energy by 4.4 kcal/mol for Pd. Clearly, HCl elimination in the Ni system is much harder than that in the Pd system.

1.f. Comparison between Ni- and Pd-Catalyzed Heck Reaction. From the above calculations, we can see that Ni causes a faster oxidative addition and insertion than Pd (Chart 1). It is worthy to note that in a recent theoretical study on the copolymerization of olefins with N-containing polar monomers¹¹⁷ Deubel and Ziegler also found that the Ni systems have lower insertion barriers than do their Pd counterparts. However, we find that β -hydride elimination in the Ni system is less efficient than that in the Pd system. This explains the observation of mixtures of addition and substitution products in the original studies on Ni-catalyzed Heck reactions.⁵ The difficulty in β -hydride elimination for the Ni system may also explain why aliphatic halides (e.g., cyclohexyl bromide and secondary alkyl bromides) in addition to aryl and vinyl halides can be used in Ni-catalyzed Heck reactions.⁵

The elimination of HCl to regenerate the catalyst in the last step is considerably easier with the Pd catalyst than with the Ni catalyst. This observation indicates that Ni(0) species cannot be effectively regenerated by the mechanism common to the Pd-catalyzed Heck

Chart 1. Free Energy of Each Stage (in kcal/mol) Relative to the Reactants Involved in $\text{Ni}(\text{PH}_3)_2$ and $\text{Pd}(\text{PH}_3)_2$ -Catalyzed Heck Reactions between $\text{CH}_2=\text{CH}_2$ and $\text{CH}_2=\text{CHCl}$



reaction through deprotonation of hydride complex by base. In the earlier experiments, it was found that stoichiometric amounts of a reductant such as Zn dust were required in the Ni-catalyzed reaction to ensure the catalytic effect.⁵

2. Comparison between Aryl Halide and Alkenyl Halide. Due to the CPU limitation, in the present study we will focus on the Heck reaction between alkenyl halide and alkene. Nevertheless, in this section we would like to briefly compare the aryl halide coupling with the alkenyl halide coupling (Table 2).

According to Table 2, the major difference between aryl coupling and alkenyl coupling arises in the breaking of the aryl or alkenyl chloride bond. The complexation between the metal and alkenyl halide is much stronger than that between the metal and aryl halide. As a result, the energy barrier for the oxidative addition is much lower in the aryl coupling than that in the alkenyl coupling.

The activation barrier in the insertion step does not vary significantly from the alkenyl coupling to the aryl coupling. The β -hydride elimination is slightly easier in the alkenyl coupling than that in the aryl coupling. Therefore, as long as we bear in mind the difference between the oxidative addition step, we can focus on the alkenyl coupling to study the Heck reaction in general.

Table 2. Comparison between Aryl and Alkenyl Coupling^a

reaction coord	Ni(PH ₃) ₂		Pd(PH ₃) ₂	
	CH ₂ =CH-Cl	Ph-Cl	CH ₂ =CH-Cl	Ph-Cl
1	0	0	0	0
2	-17.3	0.2	1.3	16.5
TS1	2.8	9.1	26.6	29.9
3	-19.2	-19.1	3.8	4.0
4	-10.4	-10.0	16.2	16.8
5	-14.6	-14.5	8.6	8.8
TS2	-6.9	-5.6	21.4	22.6
6	-37.2	-31.0	-10.9	-4.0
TS3	-28.5	-27.8	-0.1	0.1
7	-32.6	-33.3	-2.0	-2.9
TS4	-17.9	-16.6	6.5	8.6
8	-19.9	-19.1	2.0	3.1
9	-6.6	-5.9	15.3	16.0
10	-25.4	-24.7	-5.0	-4.3
1	-9.4	-8.7	-9.4	-8.7

^a Values in kcal/mol. In each row of the table we used the metal complex to show the stage in the catalytic cycle. The free energy was calculated for all the species at each particular stage. For example, in the first row the free energy was calculated for **1** + RCl + CH₂=CH₂. In the last row, the free energy was calculated for **1** + R-CH=CH₂ + HCl.

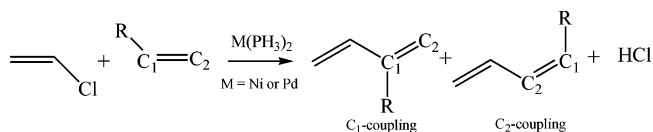
Table 3. Comparison between Alkenyl Chloride, Bromide, and Iodide in the Coupling of CH₂=CHX with CH₂=CH₂^a

reaction coord	Ni(PH ₃) ₂			Pd(PH ₃) ₂		
	Cl	Br	I	Cl	Br	I
1	0	0	0	0	0	0
2	-17.3	-18.6	-19.4	1.3	0.4	0.9
TS1	2.8	-2.9	-8.0	26.6	20.1	14.0
3	-19.2	-21.3	-22.4	3.8	-0.0	-2.9
4	-10.4	-13.7	-16.1	16.2	10.2	4.9
5	-14.6	-16.3	-17.2	8.6	4.8	2.1
TS2	-6.9	-8.6	-8.9	21.4	17.8	15.8
6	-37.2	-39	-39.3	-10.9	-14.7	-16.7
TS3	-28.5	-30.4	-31.0	-0.1	-4.1	-6.4
7	-32.6	-34.7	-35.6	-2.0	-6.1	-8.8
TS4	-17.9	-21.1	-23.6	6.5	1.6	-2.3
8	-19.9	-22.9	-25.2	2.0	-3.0	-7.1
9	-6.6	-10.0	-13.5	15.3	7.7	0.8
10	-25.4	-28.4	-30.6	-5.0	-10.1	-14.1
1	-9.4	-9.3	-9.2	-9.4	-9.3	-9.2

^a Values in kcal/mol. In each row of the table we used the metal complex to show the stage in the catalytic cycle. The free energy was calculated for all the species at each particular stage. For example, in the first row the free energy was calculated for **1** + RX + CH₂=CH₂. In the last row, the free energy was calculated for **1** + R-CH=CH₂ + HX.

It is worthy to note again that in the aryl coupling, Ni again triggers a faster oxidative addition and insertion than Pd. However, β -hydride elimination in the Ni system is less efficient than that in the Pd system. Finally, regeneration of the Ni catalyst is considerably more difficult than regeneration of the Pd catalyst.

3. Comparison between Alkenyl Chloride, Bromide, and Iodide. Table 3 shows the free energy changes in the coupling of alkenyl chloride, bromide, and iodide. According to Table 3, the energy barriers for the oxidative additions of alkenyl chloride, bromide, and iodide are +20.1, +15.7, and +11.4 kcal/mol in the Ni system. In comparison, the energy barriers for the oxidative additions of alkenyl chloride, bromide, and iodide are +25.3, +19.7, and +13.1 kcal/mol in the Pd system. These results indicate that the efficiency of the oxidative addition decreases in the order alkenyl iodide > alkenyl bromide > alkenyl chloride for both Ni and

Scheme 4. Regiochemistry in Heck Reactions

Pd systems. Also, oxidative addition is always less efficient in the Pd system than in the Ni system.

For the Pd system, the energy barrier of oxidative addition for alkenyl chloride is 12.2 kcal/mol higher than that for alkenyl iodide. For the Ni system, the energy barrier of oxidative addition for alkenyl chloride is only 8.7 kcal/mol higher than that for alkenyl iodide. Therefore, compared to the Pd-catalyzed Heck reactions, Ni catalysts may exhibit higher reactivity with alkenyl or aryl chloride. This prediction is in agreement with the experimental observation, i.e., chlorobenzene is reactive and gives a result very close to that obtained with bromobenzene in Ni-catalyzed Heck reactions.⁵

The energy barriers for the insertion step are +7.7, +7.7, and +8.3 kcal/mol for alkenyl chloride, bromide, and iodide in the Ni system. In comparison, the energy barriers for the insertion step are +12.8, +13.0, and +13.7 kcal/mol for alkenyl chloride, bromide, and iodide in the Pd system. Therefore, the change of halide does not affect the insertion step significantly. Also, insertion is always more efficient in the Ni system than in the Pd system.

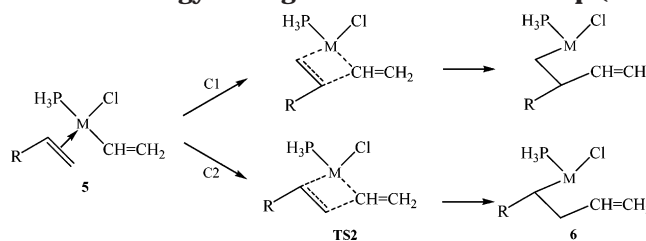
The energy barriers for the β -hydride elimination are +14.7, +13.6, and +12.0 kcal/mol for alkenyl chloride, bromide, and iodide in the Ni system. The same energy barriers in the Pd system are +8.5, +7.7, and +6.5 kcal/mol for alkenyl chloride, bromide, and iodide. Therefore, the efficiency of β -hydride elimination decreases in the order alkenyl iodide > alkenyl bromide > alkenyl chloride. Also, the elimination energy barriers for the Ni systems are always significantly larger than those for the Pd systems.

Removal of HX from the catalyst to regenerate the catalyst leads to a free energy increase of +16.0, +19.1, or +21.4 kcal/mol for alkenyl chloride, bromide, or iodide in the Ni systems. These values are significantly larger than the corresponding values for the Pd system, which are -4.4, +0.8, and +4.9 kcal/mol, respectively.

4. Substitution on Olefins. In this section the effect of olefin substitution on the Heck reaction is examined. An important issue here is the regiochemistry (see Scheme 4). The detailed free energy changes for the catalytic cycle can be found in the Supporting Information. Herein, to focus on the regiochemistry problem we show in Table 4 the free energy changes in the insertion step.

According to Table 4, CH₃ substitution on the olefin slightly increases the energy barrier of insertion for both the Ni and Pd systems. C1 coupling is slightly favored over C2 coupling in both the Ni and Pd system, in accordance with the Markovnikov rule. Similar results were obtained in recent elegant studies by von Schenck et al.²¹

(21) (a) von Schenck, H.; Stroemberg, S.; Zetterberg, K.; Ludwig, M.; Akermark, B.; Svensson, M. *Organometallics* **2001**, *20*, 2813. (b) von Schenck, H.; Kermark, B.; Svensson, M. *Organometallics* **2002**, *21*, 2248. (c) von Schenck, H.; Kermark, B.; Svensson, M. *J. Am. Chem. Soc.* **2003**, *125*, 3503.

Table 4. Free Energy Changes in the Insertion Step (kcal/mol)

coupling position	Ni(PH ₃) ₂				Pd(PH ₃) ₂					
	H	CH ₃		COOH		H	CH ₃		COOH	
	–	C ₁	C ₂	C ₁	C ₂	–	C ₁	C ₂	C ₁	C ₂
$\Delta G^\ddagger(5 \rightarrow \text{TS2})$	+7.7	+8.2	+9.7	+10.5	+5.6	+12.8	+14.0	+14.7	+16.2	+10.6
$\Delta G(5 \rightarrow 6)$	-22.6	-20.7	-18.3	-20.0	-26.4	-19.5	-17.6	-16.3	-17.5	-23.3

COOH substitution on the olefin changes the regiochemistry considerably. In this case, C2 coupling is significantly more efficient than C1 coupling. This behavior should be due to the electron-withdrawing property of COOH. The insertion energy barrier for C2 coupling of CH₂=CHCOOH is lower than that for CH₂=CH₂ coupling. Therefore, electron-poor olefins should be better substrates than electron-rich olefins in both Ni- and Pd-catalyzed Heck reactions. This prediction is in agreement with the experimental results.^{5,8}

β -Hydride elimination is another step where the olefin substitution has significant effects. According to Table 3, the energy barriers of β -hydride elimination for CH₂=CH₂, CH₃-CH=CH₂ (C1 coupling), and CH₂=CH-COOH (C2 coupling) are +14.7, +14.3, and +18.0 kcal/mol in the Ni systems. The same barriers are +8.5, +7.1, and +10.1 kcal/mol in the Pd systems. Therefore, electron-poor olefins tend to provide more (Michael) addition products than electron-rich olefins in both Ni- and Pd-catalyzed Heck reactions.

5. Effects of Ligands on Ni-Catalyzed Heck Reactions. According to the above results, there are two major problems for the Ni-catalyzed Heck reactions. First, the energy barrier for β -hydride elimination is too high resulting in poor selectivity to the vinylation. Second, removal of HX from the Ni(II) complex to regenerate the Ni(0) catalyst is highly endothermic.

An appropriate choice of ligands may solve the above two problems. Because the last step, i.e., removal of HX, appears to be the most serious problem for the Ni-catalyzed Heck reactions, we first attempt to decrease the free energy change of this step by changing the ligands. The results are shown in Table 5.

According to Table 5, without any ligand removal of HCl from Ni(0) increases the system free energy by +79.2 kcal/mol. Neutral monodentate ligands including NH₃, H₂O, PH₃, and H₂S decrease this free energy change. Since PH₃ is the most effective in these ligands, use of NR₃, R₂O, PR₃, and R₂S ligands will not solve the problem in catalyst regeneration. Use of bidentate phosphine ligands may not solve the problem either. In fact, the free energy of HCl removal with H₂P-CH₂-CH₂-PH₂ or H₂P-(CH₂)₃-PH₂ is higher than that with PH₃.

As expected, PMe₃ is a worse ligand than PH₃ for the HCl removal because of the electron-donating property of Me. However, despite the fact that OR groups are σ -withdrawing, the free energy of the HCl removal with P(OH)₃ and P(OMe)₃ is 21.0 and 28.3 kcal/mol, which

Table 5. Ligand Effects on the Reaction Free Energy of HCl Removal (kcal/mol)

ligands	ΔG	E_{HOMO} (au) ^a	E_{LUMO} (au) ^a
none	79.2		
NH ₃	27.1	-0.252	0.079
H ₂ O	32.6	-0.291	0.063
PH ₃	16.0	-0.276	0.032
H ₂ S	19.7	-0.262	0.020
H ₂ P-CH ₂ -CH ₂ -PH ₂	26.6	-0.240	0.024
H ₂ P-(CH ₂) ₃ -PH ₂	24.6	-0.242	0.021
H ₂ P-O-CH ₂ -O-PH ₂	23.1	-0.254	-0.012
PMe ₃	21.9	-0.220	0.064
P(OMe) ₃	28.3	-0.232	0.038
P(OH) ₃	21.0	-0.266	0.021
OH ⁻	58.7	0.161	0.413
SCN ⁻	43.8	-0.015	0.272
CN ⁻	42.8	0.018	0.354
H ₂ C=NH	16.4	-0.268	-0.009
(NH ₂) ₂ C:	27.0	-0.188	0.062
CO	-6.8	-0.371	-0.022
CH ₂ =CH ₂	-6.0	-0.267	0.019

^a E_{HOMO} and E_{LUMO} were calculated with the B3LYP/6-31G(d) method.

is higher than that with PH₃. Therefore, it appears that use of P(OR)₃ may not improve the HX removal reaction. Nevertheless, recently Iyer et al. reported that Ni-[P(OPh)₃]₄ and Ni[P(OEt)₃]₄ could catalyze the Heck reactions between aryl and vinyl halides with olefins and alkynes in the absence of any reductant.⁶

Use of anionic ligands (e.g., OH⁻, SCN⁻, CN⁻) does not effectively decrease the free energy of HCl removal. Therefore, more serious problems in catalyst regeneration are expected for these types of ligands. A carbene-type ligand, (NH₂)₂C:, provides a free energy of +27.0 kcal/mol for HCl removal. Clearly, it does not solve the problem either.

H₂C=NH (a model compound for pyridines) provides a free energy of +16.4 kcal/mol for HCl removal. It should be mentioned in this system that H₂C=NH coordinates to Ni via the lone pair electrons on the nitrogen (i.e., end-on geometry). Since this energy is very close to that for PH₃, pyridines may be an interesting type of ligands for Ni-catalyzed Heck reactions.

Strikingly, CO provides a free energy of -6.8 kcal/mol for HCl removal. This particular value should be caused by the fact that CO is a strong π acid. A strong back-bonding between the ligand π^* orbital and the d-orbital of Ni is expected, which removes some electron density from Ni. As a result, this Ni complex (i.e., Ni(CO)₂HCl) can lose HCl readily through reductive elimination.

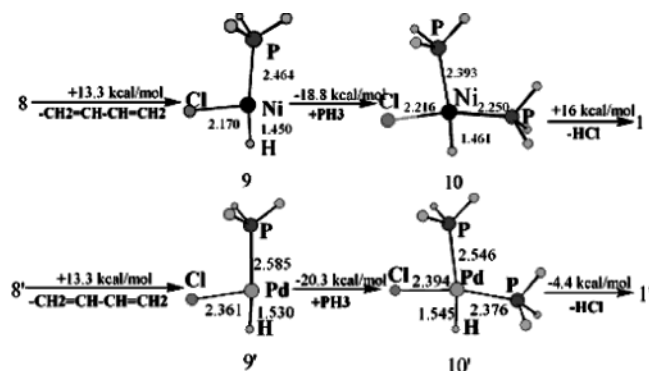


Figure 5. Catalyst regeneration.

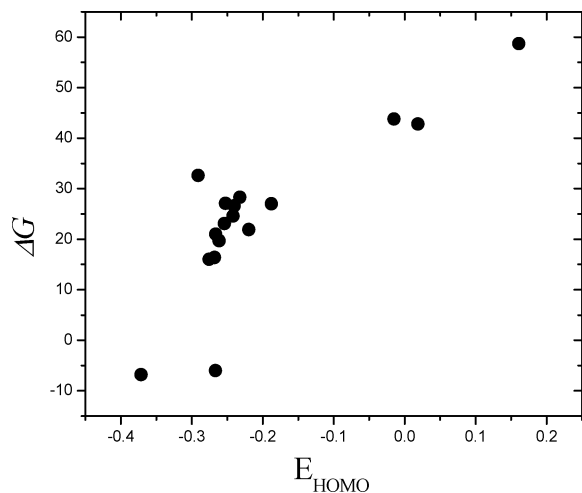


Figure 6. The correlation between the reaction free energies of HX removal and the HOMO energies of the ligands.

Unfortunately, a low HCl removal energy associated with CO does not mean that CO is a desirable ligand for the Ni-catalyzed Heck reaction. By using CO as the ligand for Ni-catalyzed coupling between $\text{CH}_2=\text{CHCl}$ and $\text{CH}_2=\text{CH}_2$, the energy barrier for oxidative addition becomes +21.2 kcal/mol, a value significantly higher than that for PH_3 (+14.8 kcal/mol). This is to be expected, because a complex easy to reduce must be a complex hard to oxidize. Besides, in addition to olefin insertion CO may also insert into the Ni–C bond. This reactivity may complicate the whole reaction.

Another interesting ligand is $\text{CH}_2=\text{CH}_2$. It also leads to a negative free energy change in HCl removal (–6.0 kcal/mol). This behavior should also be caused by the fact that alkenes are π -acceptors. However, use of alkene ligands in the Heck reaction may lead to undesirable ligand insertion into the M–C bond. Therefore, we are not certain whether an olefin-type ligand can be developed for the Ni-catalyzed Heck reactions.

At this point, it is worthy mentioning that there is an interesting correlation between the reaction free energies of HX removal and the HOMO energies of the ligands (see Figure 6). Generally, a higher HOMO energy corresponds to a higher HX removal free energy. Therefore, using the HOMO energies we may predict the reactivities of some ligands. A similar correlation was observed in the previous studies between the HOMO energies and reaction barriers.²¹ Nonetheless,

Table 6. Gas-Phase Free Energy Changes in the Coupling of $\text{CH}_2=\text{CHOTf}$ with $\text{CH}_2=\text{CH}_2$ through a Cationic Pathway (kcal/mol)

	Ni(PH_3) ₂	Pd(PH_3) ₂
$\Delta G^\ddagger(\text{insertion, gas})$	5.6	9.3
$\Delta G(\text{insertion, gas})$	–21.2	–20.1
$\Delta G^\ddagger(\beta\text{-H-elimination, gas})$	9.6	5.7
$\Delta G(\beta\text{-H-elimination, gas})$	8.3	2.9
$\Delta G(\text{catalyst regeneration, gas})^a$	210.8	197.3

^a The catalyst regeneration step of the cationic pathway is $[\text{HML}_2]^+ \rightarrow \text{ML}_2 + \text{H}^+$. The electronic energy of proton is treated as 0. It is worthy to note that because the solvation effects have not been considered for proton, the absolute energy changes in this step are not realistic. Only the relative value between Ni and Pd is meaningful.

it is clear from Figure 6 that the correlation is not perfect. The same problem is noticeable in the previous studies.²¹

6. Solvent Effect. The above calculations are conducted in the gas phase. To examine whether the solvent effects may significantly change the results from the above calculations, we calculated the solution-phase free energy changes in the coupling of $\text{CH}_2=\text{CHCl}$ with $\text{CH}_2=\text{CH}_2$. We considered THF (dielectric constant = 5.78) and DMF (dielectric constant = 36.71). These two solvents represent the nonpolar and polar solvents, respectively.

The detailed calculation results for the solvent effects can be found in the Supporting Information. According to the results, there are some solvent effects on the Heck reaction. In the oxidative addition step, the activation free energies are +20.1 (vacuum), +19.5 (THF), and +17.5 (DMF) kcal/mol for the Ni catalyst and +27.9 (vacuum), +24.2 (THF), and +22.2 (DMF) kcal/mol for Pd. Clearly, a more polar medium favors the oxidative addition step because of the charge separation in the addition.

For the olefin insertion step, the activation free energies are +7.7 (vacuum), +7.4 (THF), and +6.9 (DMF) kcal/mol for the Ni catalyst and +12.8 (vacuum), +12.0 (THF), and +11.3 (DMF) kcal/mol for Pd. For the β -hydride elimination step, the activation free energies are +14.7 (vacuum), +14.2 (THF), and +11.0 (DMF) kcal/mol for the Ni catalyst and +8.5 (vacuum), +7.8 (THF), and +5.2 (DMF) kcal/mol for Pd. Therefore, a more polar medium slightly favors these two steps.

For the HCl removal step, the reaction free energies are +16.0 (vacuum), +21.6 (THF), and +22.8 (DMF) kcal/mol for the Ni catalyst and –4.4 (vacuum), +1.0 (THF), and +2.7 (DMF) kcal/mol for Pd. A more polar solvent disfavors this step because the metal center is reduced from M(II) to M(0) in this step.

On the basis of the above results, it is clear that the solvent effects do not significantly affect the trends in the Ni- or Pd-catalyzed Heck reactions. All the conclusions drawn from the gas-phase calculations are still qualitatively valid for the solution-phase Heck reactions.

7. Cationic Pathway. In the previous sections we mentioned that for alkenyl or aryl halide, before the coordination of $\text{CH}_2=\text{CH}_2$ it must be the phosphine but not the halide ligand that leaves the metal center. This is the so-called neutral pathway. It occurs because halide binds more strongly with the metal center than phosphines. Nevertheless, for the Heck reaction of alkenyl or aryl triflate one may expect a cationic

Table 7. Gas-Phase and Solution-Phase (THF or DMF) Free Energy Changes in the Oxidative Addition of CH₂=CHCl to Ni(PH₃)Cl⁻ and Pd(PH₃)Cl⁻ (kcal/mol)^a

	Ni(PH ₃)Cl			Pd(PH ₃)Cl		
	in a vacuum	in THF	in DMF	in a vacuum	in THF	in DMF
M(PH ₃)Cl ⁻	0.0	0.0	0.0	0.0	0.0	0.0
(CH ₂ =CHCl)M(PH ₃)Cl ⁻	-17.2	-13.5	-12.6	0.1	4.6	6.4
TS	2.7	4.5	4.6	18.6	22.6	25.2
(CH ₂ =CH)M(PH ₃)Cl ₂ ⁻	-31.6	-29.9	-29.3	-11.5	-8.0	-6.7

	Ni(PH ₃) ₂			Pd(PH ₃) ₂		
	in a vacuum	in THF	in DMF	in a vacuum	in THF	in DMF
M(PH ₃) ₂	0.0	0.0	0.0	0.0	0.0	0.0
(CH ₂ =CHCl)M(PH ₃) ₂	-17.3	-19.6	-19.5	1.3	-0.5	0.1
TS	2.8	-0.1	-2.0	26.6	23.7	22.3
(CH ₂ =CH)M(PH ₃) ₂ Cl	-19.2	-24.3	-26.6	3.8	-1.4	-3.1

pathway. In this pathway, it is the triflate anion but not the phosphine ligand that leaves the metal center as the metal–triflate interaction is very weak.²² Herein we briefly examined if the cationic pathway may change the conclusions we have drawn for the difference between Ni- and Pd-catalyzed Heck reactions. Therefore, we calculated the gas-phase free energy changes in the coupling of CH₂=CHOTf with CH₂=CH₂ through a cationic pathway. The results show that the insertion step is faster in the Ni case than in the Pd case. The β-hydride elimination and the catalyst regeneration steps are much easier in the Pd case than in the Ni case. Therefore, the basic conclusions drawn from the neutral pathway can also apply to the cationic pathway.

8. Anionic Pathway. Usually it is postulated that the effective catalyst in the Heck reaction is Pd(0)L₂, which is used in the above sections. However, recent studies by Amatore and Jutand have shown that the ligand on the palladium precatalyst can profoundly influence the mechanism of Heck reactions.²³ Amatore and Jutand proposed that halide and acetate anions coordinate Pd(0)L₂ to form anionic tricoordinated complexes Pd(0)L₂Cl⁻ or Pd(0)L₂(OAc)⁻, which undergo oxidative addition to aryl halide. Thus, the tricoordinated anionic complex Pd(0)L₂X⁻ was suggested to be the effective catalyst instead of the usually postulated Pd(0)L₂ complex in Heck reactions.

To test if this anionic pathway may change the conclusions drawn in the above sections, we have also studied the possibility of using Ni(PH₃)₂Cl⁻ and Pd(PH₃)₂Cl⁻ as the effective catalysts. However, we cannot find any stable form of the tetracoordinated complex (CH₂=CHCl)PdCl(PH₃)₂⁻, which always automatically decomposes into Pd(PH₃)₂(CH₂=CHCl) and a free Cl⁻ ion. For the Ni case, although the tetracoordinated complex is stable, the pentacoordinated complex (CH₂=CH)Ni(PH₃)₂Cl₂⁻ is not found to be a stable species. Therefore, our theoretical results do not support the proposed anionic pathway through which oxidative addition of RX to MCIL₂⁻ gives a pentacoordinated anionic complex RMXCIL₂⁻.

It is worthy to note that in Amatore and Jutand's study Pd(0)L₂Cl⁻ or Pd(0)L₂(OAc)⁻ was found to be the reactive species²³ but there is no evidence that they are the real catalyst. An alternative anionic catalyst is the

14-electron complex Pd(0)LCl⁻ or Pd(0)L(OAc)⁻ that is a perfectly reasonable species in equilibrium with Pd(0)L₂Cl⁻ or Pd(0)L₂(OAc)⁻ in the solution. Herein, we test the possibility of using Ni(PH₃)Cl⁻ and Pd(PH₃)Cl⁻ as the catalyst. We find that oxidative addition of CH₂=CHCl to Ni(PH₃)Cl⁻ and Pd(PH₃)Cl⁻ can give (CH₂=CH)Ni(PH₃)Cl₂⁻ and (CH₂=CH)Pd(PH₃)Cl₂⁻. All the intermediates and transition states in these oxidative reactions are successfully modeled by the theoretical methods. The results are shown in Table 7.

According to Table 7 it can be seen that in the gas phase the free energy barrier for the oxidative addition is +19.9 and +18.5 kcal/mol for Ni(PH₃)Cl⁻ and Pd(PH₃)Cl⁻, respectively. These values are smaller than the corresponding values for Ni(PH₃)₂ and Pd(PH₃)₂ (neutral pathway), which are +20.1 and +25.3 kcal/mol. Clearly the anionic pathway causes a faster oxidative addition because the metal center is more electron rich in an anionic complex. This effect is much larger for Pd than for Ni, possibly because more negative charge is located at the metal center in the Pd complex than in the Ni complex.

The above results also indicate that using the anionic pathway Ni causes a slower oxidative addition than Pd in the gas phase. This trend is different from that observed for the neutral pathway. Nevertheless, in THF the free energy barrier for the oxidative addition is +18.0 and +18.0 kcal/mol for Ni(PH₃)Cl⁻ and Pd(PH₃)Cl⁻, respectively. In DMF the free energy barrier for the oxidative addition is +17.2 and +18.8 kcal/mol for Ni(PH₃)Cl⁻ and Pd(PH₃)Cl⁻, respectively. Therefore, in solution it is possible that Ni still causes a slightly faster oxidative addition than Pd with use of the anionic pathway.

4. Conclusion

In the present study we investigated the possible use of Ni in Heck reactions. On the basis of detailed comparisons, we can draw the following conclusions.

(1) The mechanism of the Ni-catalyzed Heck reaction is quite similar to that of the Pd-catalyzed Heck reaction. There are four major steps in a catalytic cycle. (a) A σ-aryl–M(II) or σ-alkenyl–M(II) (M = Ni or Pd) complex is formed via oxidative addition. (b) An olefin substrate coordinates to the metal, followed by the insertion of the olefin at the C–M bond. (c) An intramolecular β-hydride elimination occurs, providing the coupling product. (d) M(0) catalyst is regenerated after the removal of HX from the complex.

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(2) Oxidative addition and olefin insertion occur with lower energy barriers in the Ni system than in the Pd system. However, β -hydride elimination is more efficient in the Pd system than in the Ni system. This leads to poorer selectivity to vinylation over Michael addition in the Ni system than in the Pd system. More importantly, catalyst regeneration through HX removal is considerably harder to achieve with the Ni system than with the Pd system. Either a very strong base should be used for the Ni catalyst or a reduction method should be designed to remove HX from the Ni complex.

(3) Compared to the Pd system, oxidative addition of an alkenyl or aryl chloride is not much harder than oxidative addition of an alkenyl or aryl iodide in the Ni system. Therefore, the Ni-catalyzed Heck reaction may be applied to alkenyl or aryl chloride relatively easily. Also, because β -hydride elimination is more difficult in the Ni system than in the Pd system, the Ni-catalyzed Heck reaction may be applied to aliphatic halides.

(4) For an olefin with an electron-donating substituent, the Ni-catalyzed coupling should slightly favor the

Markovnikov-type product, if the steric effect is not significant. For an olefin with an electron-withdrawing substituent, the Ni-catalyzed coupling should provide the anti-Markovnikov-type product as the major product.

(5) Phosphine and pyridine ligands can reasonably well reduce the free energy in the HX removal step. Therefore, they appear to be promising ligands for the Ni-catalyzed Heck reactions.

(6) Solvation effects, cation pathway, and anionic pathway do not change the general trends for the reactivities of the Ni and Pd catalysts in Heck reactions.

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Supporting Information Available: Structures and energies for all the species discussed in the study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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