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Ab Initio MO Study of the Geometry, $\eta^3 \rightleftarrows \eta^1$ Conversion, and Reductive Elimination of a Palladium(II) η^3-Allyl Hydride Complex and Its Platinum(II) Analogue

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The geometry, $\eta^3 \rightleftarrows \eta^1$ conversion, and reductive elimination of a palladium(II) η^3-allyl hydride complex and its platinum(II) analogue, $MH(\eta^3\text{-}C_3H_5)(PH_3)$ (**1**) (M = Pd, Pt), are theoretically investigated with ab initio MO/MP4, SD-CI, and coupled cluster double substitution (CCD) methods. In **1**, the M−C bond trans-positioned to H(hydride) is much longer than the other M−C bond, while the C−C bond trans-positioned to H is considerably shorter than the other C−C bond, due to the strong trans-influence of H. Nevertheless, the two C−C bonds of the allyl ligand are conjugated well with each other, and **1** is still considered as an η^3-allyl complex. The η^1-isomer, $MH(\eta^1\text{-}C_3H_5)(PH_3)$ (**2**), is less stable than **1** by 8.6 kcal/mol for M = Pd and 13.0 kcal/mol for M = Pt at the MP4SDQ level (MP4SDQ and SD-CI calculations yield similar energy differences). The C−H reductive elimination of $PdH(\eta^3\text{-}C_3H_5)(PH_3)$ proceeds with a much lower activation energy (E_a) of 5.4 kcal/mol and a significantly higher exothermicity (E_{exo}) of 29.4 kcal/mol than those of the Pt analogue (E_a = 20.9 kcal/mol and E_{exo} = 11.1 kcal/mol), where the MP4SDQ values are given. This C−H reductive elimination of **1** requires a somewhat higher E_a than that of $MH(CH_3)(PH_3)$. These results are interpreted in terms of bond energies. Changes in bonding characteristics caused by this reductive elimination are discussed in detail, on the basis of orbital mixing.

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Introduction

Transition metal η^3-allyl complexes, as well as transition metal σ-alkyl complexes, play important roles as active species and/or key intermediates in many reactions catalyzed by transition metal complexes.[1] For instance, a palladium(II) η^3-allyl hydride complex, $PdH(\eta^3\text{-}C_3H_5)(PR_3)$ (**1**), was postulated to serve as a key intermediate and to undergo C−H reductive elimination as an important elementary process in the palladium-catalyzed reductive cleavage of allyl compounds by formic acid.[2−6] In this regard, detailed knowledge such as geometries, bonding nature, and reactivities of transition metal η^3-allyl complexes is indispensable to understanding catalytic properties of transition metal complexes. However, it is not easy in general to obtain the above-mentioned, detailed knowledge. For instance, **1** has not been detected so far, and of course, its characterization has not been performed at all. Moreover, the reaction mechanism of the C−H reductive elimination of **1** is not clear. Considering the well-known $\eta^3 \rightleftarrows \eta^1$ interconversion (eq 1) of the palladium-

$$PdCl(PR_3)(\eta^3\text{-}C_3H_5) \rightleftarrows PdCl(PR_3)(\eta^1\text{-}C_3H_5) \quad (1)$$

(II) η^3-allyl complex,[7] we must take into consideration two possibilities in the reaction mechanism of C−H reductive elimination; one is the direct reductive elimination starting from **1**, and the other is the reductive elimination via the η^1-isomer, $PdH(\eta^1\text{-}C_3H_5)(PH_3)$. Although it has been ascertained experimentally that the reductive elimination of similar palladium η^3-allyl aryl complexes takes place directly from the η^3-form,[8,9] information has not been reported on the reductive elimination of **1**. The geometry of **1** is also worthy of investigation, since the η^3-allyl ligand is expected to distort toward the η^1-form due to the strong trans-influence of H. A similar distortion has been reported for $PdCl(PR_3)(\eta^3\text{-}C_3H_5)$.[7,10]

Theoretical methods should be useful for investigating the aforementioned issues, because theoretical calculations can provide meaningful information on short-lived reactive species and transition states. Nevertheless, only a few theoretical studies have been reported on

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Table 1. Comparisons of the Basis Sets and PH_3 Geometries in the C−H Reductive Elimination of $PdH(\eta^3\text{-}C_3H_5)(PH_3)$

method	PH_3 geometry	E_a (kcal/mol)	ΔE	bond dists (Å) in $PdH(\eta^3\text{-}C_3H_5)(PH_3)$			
				Pd−PH_3	Pd−$C^{(1)}$	Pd−$C^{(2)}$	Pd−H
MP2/BS-I[a]	fixed	5.7	−27.9	2.398	2.155	2.492	1.565
MP2/BS-II	fixed	5.0	−28.7	2.311	2.186	2.468	1.566
MP2/BS-I	opt	5.9	−27.7	2.401	2.157	2.489	1.565

[a] See text for discussion of BS-I and BS-II.

geometries and reactions of transition metal η^3-allyl complexes, except for theoretical work on photoelectron spectra of η^3-allyl complexes.[11] Some of the previous studies were semi-empirical MO studies on the geometry of the η^3-allyl complexes,[12] nucleophilic attack to the η^3-allyl ligand,[13,14] C−C reductive elimination of the palladium(II) η^3-allyl methyl complex,[9] and ab initio MO[15] and molecular mechanics studies[16] on geometries of palladium(II) and nickel(II) η^3-allyl complexes.

In this work, geometry, bonding, $\eta^3 \rightleftarrows \eta^1$ interconversion (eq 2), and C−H reductive elimination of MH-

$$MH(\eta^3\text{-}C_3H_5)(PH_3) \rightleftarrows MH(\eta^1\text{-}C_3H_5)(PH_3) \quad (2a)$$

$$MH(\eta^3\text{-}C_3H_5)(PH_3) + PH_3 \rightleftarrows MH(\eta^1\text{-}C_3H_5)(PH_3)_2 \quad (2b)$$

$$MH(\eta^3\text{-}C_3H_5)(PH_3) \rightarrow M(\eta^2\text{-}C_3H_6)(PH_3) \quad (3)$$

$(\eta^3\text{-}C_3H_5)(PH_3)$ (M = Pd, Pt; eq 3) are theoretically investigated, using ab initio MO/MP2-MP4, SD-CI, and coupled-cluster with double substitution (CCD) methods. We investigated eqs 2 and 3, because these are typical reactions of transition metal η^3-allyl complexes[7−9,17] and because detailed knowledge is not available on eq 3, which is important in palladium-catalyzed reductive cleavage of allyl compounds.[2−6] Our intention with this work is to present the first detailed study on the reductive elimination of eq 3 such as the transition-state (TS) structure, the activation energy (E_a), the reaction energy (ΔE), a comparison of reactivity between M = Pd and Pt, and a comparison of the C−H reductive elimination between $MH(\eta^3\text{-}C_3H_5)(PH_3)$ and a similar transition metal alkyl hydride complex, $MH(CH_3)(PH_3)$.

Computational Details

Geometries of reactants, TS, and products were optimized at the MP2 level with the energy gradient method, where the geometry of PH_3 was taken to be the same as that of the free PH_3 molecule.[18] Then, MP2 ∼ MP4SDQ, SD-CI, and coupled-cluster with double substitution (CCD) calculations were carried out on those optimized geometries, to evaluate more reliable energy changes. In CCD calculations, the contribution of single and triple excitations was estimated through the fourth order using the CCD wave function.[19] Core orbitals were excluded from the active space in all these correlated calculations. The Gaussian 92[20] program was used for these calculations.

Three kinds of basis sets were used, where the core electrons of Pd (up to 3d) and Pt (up to 4f) were replaced with effective core potentials[21] in all the basis sets. In the smallest basis set (BS-I), (5s 5p 4d)/[3s 3p 2d] and (5s 5p 3d)/[3s 3p 2d] sets were used for the valence electrons of Pd and Pt, and MIDI4[22] and (4s)/[2s][23] sets were employed for C, P, and H, respectively. In the second basis set (BS-II), a d-polarization function[22] was added to P without any other modification of BS-I. In the largest basis set (BS-III), (5s 5p 4d)/[3s 3p 3d],[21] (5s 5p 3d)/[3s 3p 3d],[21] (9s 5p 1d)/[3s 2p 1d],[23] and (5s)/[3s][24] sets were used for the valence electrons of Pd, Pt, C, and H, respectively, where basis sets for PH_3 were taken to be the same as those in BS-II. In all of the basis sets, a p-polarization function (ζ = 1.0)[23] was added to the basis set for the active H atom, where the active H atom was the hydride ligand.

First, we optimized geometries, using BS-I. However, the Pd−PH_3 distance appears to be too long; the Pd−P distance is 2.492 Å and the Pt−P distance is 2.372 Å in $MH(\eta^3\text{-}C_3H_5)(PH_3)$ (M = Pd, Pt). When BS-II was used, the Pd−PH_3 distance dramatically changed to a reasonable value, as shown in Table 1. Then, the activation energy (E_a) and the exothermicity (E_{exo}) are compared between BS-I and BS-II (Table 1). It is noted that BS-I and BS-II yield similar E_a and E_{exo} values, whereas the optimized geometries are somewhat different between the two basis sets. This means that the energy change would be reliably evaluated even if BS-I were used and the optimized Pd−PH_3 distance is too long. Nevertheless, BS-II was adopted here for geometry optimization. The geometry relaxation of PH_3 was also examined, using the BS-I basis set. The P−H distances change only a little in the reaction: the averaged P−H distance is 1.443 Å in $PdH(\eta^3\text{-}C_3H_5)(PH_3)$, 1.445 Å in the TS, and 1.445 Å in $Pd(PH_3)(C_3H_6)$. Also, it is noted that the E_a and ΔE values calculated for the experimental geometry of PH_3 are little changed by taking into consideration the geometry relaxation of PH_3 (Table 1). These results provide support that E_a and ΔE are reliably evaluated with the experimental geometry of PH_3.

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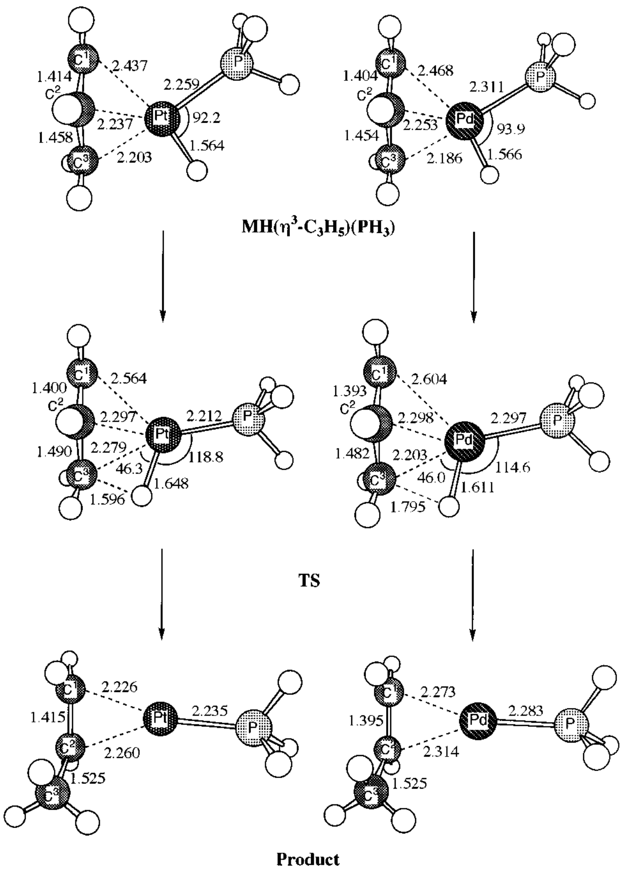

Figure 1. Geometry changes in the C−H reductive elimination of MH(η^3-C_3H_5)(PH_3) (M = Pd, Pt). Bond lengths are in Å, and bond angles are in deg. MP2/BS-II optimization was used.

Energy changes were calculated with MP4SDQ, SD-CI, and CCD methods using BS-III. In the SD-CI calculation, the contribution of higher order excited configurations was estimated with the methods proposed by Davidson,[25] Davidson−Silver,[26] and Pople.[27] In all the correlated calculations, core orbitals were excluded from the active space.

Results and Discussion

Geometry of MH(η^3-C_3H_5)(PH_3) (1) (M = Pd, Pt) and Geometry Changes in Reductive Elimination. In **1** (Figure 1), the M−C^1 distance is much longer than the M−C^3 distance.[28] This feature is not surprising, because the H(hydride) ligand exhibits a much stronger trans-influence than PH_3. Consistent with this geometrical feature, the C^1−C^2 distance is shorter than the C^2−C^3 distance by 0.05 Å, indicating that the C^1−C^2 bond has greater double-bond character than the C^2−C^3 bond. A similar distortion of the η^3-allyl ligand was previously reported in PdCl(η^3-C_3H_5)(PR_3),[10] in which the Pd−C bond trans-positioned to PR_3 is longer than the other Pd−C bond, and the C−C bond trans-positioned to PR_3 is shorter than the other C−C bond, because PR_3 exhibits a stronger trans influence than Cl. Of course, the C^1−C^2 bond is conjugated well with the C^2−C^3 bond in MH(η^3-C_3H_5)(PH_3), which is reflected in the geometrical feature that the C^1−C^2 distance of **1** is only 0.05 Å different from the C^2−C^3 distance, in contrast to the significant difference between the C^1−C^2 and C^2−C^3 distances in $C^1H_2{=}C^2HC^3H_3$ ($R(C^1{-}C^2)$ = 1.356 Å and $R(C^2{-}C^3)$ = 1.527 Å). These features indicate that the allyl group of **1** is somewhat distorted toward an η^1-allyl structure but can be still considered to be a π-allyl group.

At the TS of Pd and Pt reaction systems, the M−C^1 distance considerably lengthens, but the M−C^3 distance slightly shortens. Corresponding to these geometrical changes, the C^1−C^2 bond shortens and the C^2−C^3 bond lengthens. This allyl geometry resembles well the η^1-allyl group in MH(PH_3)(η^1-C_3H_5), which will be shown below (Figure 3). The hydride ligand has substantially changed its position with respect to the allyl group. Furthermore, the M−H bond slightly lengthens and the C^3−H distance is still long in both reaction systems. Although the geometry changes occur similarly in both the Pd and Pt reaction systems, the TS of the Pt reaction system involves the shorter C^3−H distance and the longer Pt−H distance compared to those of the Pd reaction system. From the above results, the characteristic profile of the TS can be summarized as follows: (1) The hydride ligand can easily move toward the allyl ligand with a slight lengthening of the M−H bond. (2) The C−H bond between hydride and allyl ligands has not been formed yet, and the M−H bond is still intact at the TS. (3) The allyl group has mostly evolved to an η^1-allyl structure at the TS. (4) The $C^1{=}C^2$ bond of the allyl group only weakly interacts with the central metal. (5) The TS of the Pt reaction system is more productlike than that of the Pd reaction system.

The product, M(PH_3)(C_3H_6), has a linear structure, in which the Pt−C^1 and Pt−C^2 distances are somewhat shorter than Pd−C^1 and Pd−C^2 distances, respectively, and the $C^1{=}C^2$ double bond distance (1.415 Å for M = Pt and 1.395 Å for M = Pd) is longer than the C=C double bond (1.356 Å) of free C_3H_6. The shorter Pt−C^1 and Pt−C^2 bonds and longer C=C bond in Pt(PH_3)(C_3H_6) would arise from the stronger σ-donation and π-back-donation interactions in this complex than in Pd(PH_3)(C_3H_6). This bonding feature is consistent with the electron distribution; the C_3H_6 electron population (23.788 e) in Pt(PH_3)(C_3H_6) is smaller than that (23.878 e) in Pd(PH_3)(C_3H_6), and the Pt 5d orbital population (9.799 e) is smaller than the Pd 4d orbital population (9.873 e), indicating that both σ-donation and π-back-donation are stronger in Pt(C_3H_6)(PH_3) than in Pd(C_3H_6)(PH_3). These bonding features are easily interpreted in terms of the orbital energies of M(PH_3): since the occupied d_π orbital (−9.07 eV) of Pt is at a higher energy than the occupied d_π orbital (−9.29 eV) of Pd and the unoccupied sp orbital of Pt (1.00 eV) is at a lower energy than that (1.28 eV) of Pd, Pt(PH_3) engages in stronger σ-donation and π-back-donation than does Pd(PH_3). These orbital energy differences between Pt(PH_3)

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(28) To certify that this geometrical feature is correct, we reoptimized PdH(η^3-C_3H_5)(PH_3) at the MP2 level, using BS-II augumented with a d-polarization function on C (named as BS-II*). Pd−C^1 becomes less long, but it is still very long (ca. 2.39 A), compared to the Pd−C^3 bond (2.14 A), and the difference between Pd−C^1 and Pd−C^3 bond distances is similar to that calculated with the original BS-II. The geometry of the C_3H_5 group changes little by the MP2/BS-II* optimization. Moreover, the E_a value at the MP2/BS-II* level is almost the same as that calculated for geometries optimized with BS-II. Thus, the geometrical feature of this complex is correct, and the energy change is reliable, while the Pd−C^1 distance is a little bit overestimated.

Table 2. Activation Energies (E_a, kcal/mol) and Reaction Energies (ΔE) of the C−H Reductive Elimination of MH(η^3-C_3H_5)(PH_3) (M = Pd, Pt)

	Pd		Pt	
	E_a	ΔE^a	E_a	ΔE^a
HF	9.3	−40.5	25.9	−17.4
MP2	6.1	−24.8	20.6	−7.4
MP3	9.4	−27.4	24.2	−9.8
MP4DQ	7.2	−28.1	22.3	−10.2
MP4SDQ	5.4	−29.4	20.9	−11.1
SD-CI(D)[b]	8.4	−29.7	23.9	−10.7
SD-CI(DS)[c]	8.3	−26.5	23.1	−9.3
SD-CI(P)[d]	8.3	−27.3	23.3	−9.6
CCD	8.1	−28.2		
CCD(ST4)	5.6	−27.9		

[a] A negative value represents energy stabilization. [b] Davidson correction[30] for higher order excitation. [c] Davidson−Silver correction[31] for higher order excitation. [d] Pople correction[32] for higher order excitation.

and Pd(PH_3) apparently originate from the well-known fact that Pt has a d^9s^1 electron configuration but Pd has the d^{10} electron configuration.

Energy Changes in Reductive Elimination. The activation barrier (E_a) and the reaction energy (ΔE) were calculated with the various computational methods to examine electron correlation effects on E_a and ΔE. As shown in Table 2, introduction of correlation effects slightly decreases the E_a value but considerably increases the exothermicity (E_{exo}) in both the Pd and Pt reaction systems. Although E_a and E_{exo} values fluctuate somewhat upon going to MP4SDQ from MP2, the MP4SDQ value is similar to the CCD(ST4) value. On the other hand, the SD-CI calculations yield slightly different E_a and E_{exo} values. Thus, the discussion presented here is based on E_a and ΔE values at both MP4SDQ and SD-CI levels.

The most important result to be noted here is that the C−H reductive elimination of PdH(η^3-C_3H_5)(PH_3) takes place very easily with a much lower E_a (5−8 kcal/mol) and a much higher E_{exo} (26−29 kcal/mol) than those of the Pt analogue (E_a = 20−24 kcal/mol and E_{exo} = 9−11 kcal/mol).

In an attempt to clarify the characteristic features of the C−H reductive elimination of MH(η^3-C_3H_5)(PH_3), the similar C−H reductive elimination (eq 4) of MH(CH_3)(PH_3) was investigated theoretically, as shown in Figure 2 and Table 3.

$$MH(CH_3)(PH_3) \rightarrow M(PH_3) + CH_4 \qquad (4)$$

In the case of M = Pd, this reductive elimination proceeds with no barrier at the MP2 level, and therefore, the geometry of PdH(CH_3)(PH_3) was optimized under a constraint that the HPd(CH_3) angle was fixed to be the same as it in PtH(CH_3)(PH_3). In the case of M = Pt, this reductive elimination is endothermic (E_{endo} = ca. 7 kcal/mol) but proceeds with a much lower E_a of 9 kcal/mol than the C−H reductive elimination of PtH(η^3-C_3H_5)(PH_3), where MP4SDQ values are given here. From these results, two important conclusions are extracted: (1) Both C−H reductive eliminations of PdH(η^3-C_3H_5)(PH_3) and PdH(CH_3)(PH_3) more easily occur than those of the Pt analogues, and (2) the C−H reductive elimination of MH(η^3-C_3H_5)(PH_3) requires a higher E_a than that of MH(CH_3)(PH_3).

The above-described differences in reactivity between the Pd and Pt reaction systems might be interpreted in terms of ground-state electron configurations of naked Pt and Pd atoms; since the ground-state electron configuration is d^{10} for Pd and d^9s^1 for Pt, the Pd d orbital is considered to be at a lower energy than the Pt d orbital. Thus, the Pd(II) complex tends to convert to the Pd(0) complex more easily than the Pt(II) complex.

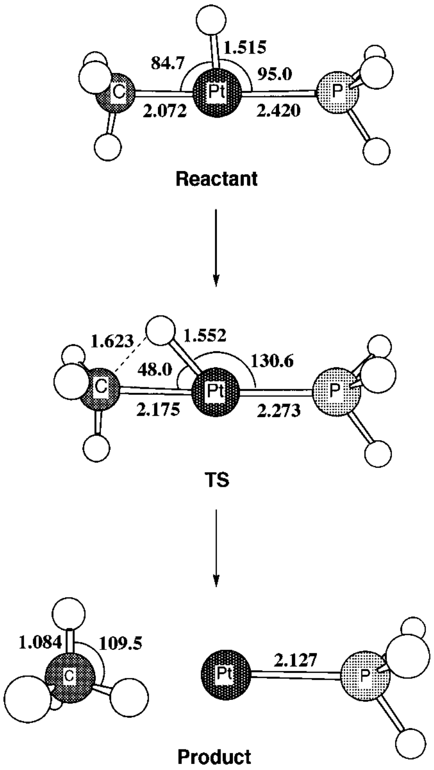

Figure 2. Geometry changes in the C−H reductive elimination of PtH(CH_3)(PH_3). Bond lengths are in Å, and bond angles are in deg. MP2/BS-II optimization was used.

Table 3. Activation Energies (E_a kcal/mol) and Reaction Energies (ΔE) of the C−H Reductive Elimination of PtH(CH_3)(PH_3)

	E_a	ΔE		E_a	ΔE
HF	14.2	−9.4	MP4SDQ	9.1	7.2
MP2	7.8	9.0	SDCI(D)	11.3	1.1
MP3	11.6	8.4	SDCI(DS)	11.0	7.1
MP4DQ	10.2	7.6	SDCI(P)	11.1	6.7

Reductive elimination easily occurs when the M(II)−R (R = H, CH_3, C_3H_5, etc.) bond energy is small. This means that the M(II)−R bond energy is considered to be a measure of the reactivity for the C−H reductive elimination. Consequently, we discuss here the difference in reactivity between Pt and Pd reactions using bond energies. Previously, we estimated the M−H and M−CH_3 bond energies, by considering eq 5.[29] Although

$$M(PH_3)_2 + H_2 \rightarrow cis\text{-}MH_2(PH_3)_2 \qquad (5a)$$

$$M(PH_3)_2 + H_3C{-}CH_3 \rightarrow cis\text{-}M(CH_3)_2(PH_3)_2 \qquad (5b)$$

M−H and M−CH_3 bond energies would be different between MH(CH_3)(PH_3) and MH(CH_3)(PH_3)$_2$, the bond energy difference, DE(Pt−R) − DE(Pd−R), of MH(R)(PH_3) (R = H, CH_3) should differ little from that of MH(CH_3)(PH_3)$_2$. As previously estimated,[29] the Pt−H and Pt−CH_3 bond energies are greater than the Pd−H and

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(29) (a) Sakaki, S.; Ogawa, M.; Musashi, Y.; Arai, T. *Inorg. Chem.* **1994**, *33*, 1660. (b) Sakaki, S.; Ogawa, M.; Kinoshita, M. *J. Phys. Chem.* **1995**, *99*, 9933.

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Table 4. Differences in M−H and M−(η^3-C_3H_5) Bond Energies[a] between Pt and Pd

	ΔE_{r-1}(eq 6)				
	Pd	Pt	DE(Pd−H)	DE(Pt−H)	DE(Pt−(η^3-C_3H_5)) − DE(Pd−(η^3-C_3H_5))
MP2	−24.8	−7.4	49.4	56.7	10.1
MP3	−27.4	−9.8	50.1	59.3	8.4
MP4DQ	−28.1	−10.2	51.1	59.1	9.9
MP4SDQ	−29.4	−11.1	52.1	58.7	11.7

[a] kcal/mol units.

Table 5. Differences[a] between M−(η^3-C_3H_5) and M−CH_3 Bond Energies[a]

	Pd	Pt
MP2	28.4	30.8
MP3	19.1	20.8
MP4DQ	20.7	22.5
MP4SDQ	22.1	23.6

[a] DE(M−(η^3-C_3H_5)) − DE(M−CH_3) (kcal/mol units).

Pd−CH_3 bond energies by 10−13 kcal/mol (MP4SDQ). From these bond energies, the M−(η^3-C_3H_5) bond energy can be related to eq 6 as follows:

$$\mathrm{MH}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{PH_3}) \rightarrow \mathrm{M}(\mathrm{PH_3}) + \mathrm{C_3H_6} \tag{6}$$

$$\Delta E_{r-1} = E_t(\text{right-hand side of eq 6}) - E_t(\text{left-hand side of eq 6}) = \mathrm{DE}(\mathrm{M{-}H}) + \mathrm{DE}(\mathrm{M}{-}(\eta^3\text{-}\mathrm{C_3H_5})) - \mathrm{DE}(\mathrm{C{-}H\ of\ C_3H_6}) \tag{7}$$

Taking the difference between Pt and Pd, eq 8 is obtained. Using this eq 8, the Pt−(η^3-C_3H_5) bond is

$$\mathrm{DE}(\mathrm{Pt}{-}(\eta^3\text{-}\mathrm{C_3H_5})) - \mathrm{DE}(\mathrm{Pd}{-}(\eta^3\text{-}\mathrm{C_3H_5})) = \Delta E_{r-1}(\mathrm{M = Pt}) - \Delta E_{r-1}(\mathrm{M = Pd}) + \mathrm{DE}(\mathrm{Pd{-}H}) - \mathrm{DE}(\mathrm{Pt{-}H}) \tag{8}$$

estimated to be about 10 kcal/mol stronger than the Pd−(η^3-C_3H_5) bond (Table 4). This difference is similar to the difference between the Pt−CH_3 and Pd−CH_3 bonds (Table 4). Thus, it is reasonably suggested that the reactivity difference between Pd and Pt is similar in both MH(η^3-C_3H_5)(PH_3) and MH(CH_3)(PH_3).

The next issue to be discussed is the difference in reactivity between η^3-allyl and η^1-alkyl complexes. The difference between DE(M−CH_3) and DE(M−(η^3-C_3H_5)) is similarly estimated with eq 10, considering eq 9. As

$$\mathrm{MH}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{PH_3}) + \mathrm{CH_4} \rightarrow \mathrm{MH}(\mathrm{CH_3})(\mathrm{PH_3}) + \mathrm{C_3H_6} \tag{9}$$

$$\mathrm{DE}(\mathrm{M}{-}(\eta^3\text{-}\mathrm{C_3H_5})) - \mathrm{DE}(\mathrm{M\text{-}CH_3}) = E_t(\mathrm{C_3H_6}) - E_t(\mathrm{CH_4}) + E_t(\mathrm{MH}(\mathrm{CH_3})(\mathrm{PH_3})) - E_t(\mathrm{MH}(\eta^3\text{-}\mathrm{C_3H_5})(\mathrm{PH_3})) + \mathrm{DE}(\mathrm{C{-}H})_{\mathrm{allyl}} - \mathrm{DE}(\mathrm{C{-}H})_{\mathrm{alkyl}} \tag{10}$$

shown in Table 5, the M−(η^3-C_3H_5) bond is stronger than the M−CH_3 bond by 22 kcal/mol for M = Pd and 24 kcal/mol for M = Pt. The stronger M−(η^3-C_3H_5) bond should arise from the η^3-coordination of the allyl ligand. Therefore, the reductive elimination of MH(η^3-C_3H_5)(PH_3) requires a higher E_a than that of MH(CH_3)(PH_3).

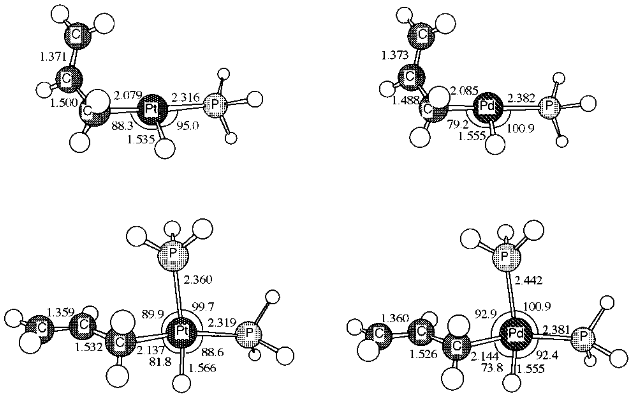

Figure 3. Optimized geometries of the η^1-allyl complexes, MH(η^1-C_3H_5)(PH_3) and MH(η^1-C_3H_5)(PH_3)$_2$. Bond lengths are in Å, and bond angles are in deg. MP2/BS-II optimization was used.

Table 6. Relative Stabilities[a] of MH(η^3-C_3H_5)(PH_3)$_n$ and MH(η^1-C_3H_5)(PH_3)$_n$ (n = 1, 2)

	$n = 1$		$n = 2$	
	Pd	Pt	Pd	Pt
MP2	8.8	16.8	1.9	−7.8
MP3	6.7	10.7	1.6	−7.8
MP4DQ	7.8	12.3	2.5	−8.1
MP4SDQ	8.6	13.0	3.1	−8.6
SD-CI(D)	7.5		6.2	
SD-CI(DS)	7.9		1.5	
SD-CI(P)	7.8		1.2	

[a] E_t(MH(η^1-C_3H_5)(PH_3)$_n$) − E_t(MH(η^3-C_3H_5)(PH_3)$_n$) (kcal/mol units).

Relative Stability of the η^1-C_3H_5 Isomer. The geometries of MH(η^1-C_3H_5)(PH_3) and MH(η^1-C_3H_5)(PH_3)$_2$ (M = Pd, Pt) are given in Figure 3.[30] MH(η^1-C_3H_5)(PH_3) has a T-shaped structure, because this is a three-coordinate d^8 complex.[31] MH(η^1-C_3H_5)(PH_3)$_2$ has a distorted square planar structure, in which the HMC angle is smaller than 90° but the CM(PH_3) angle is larger than 90° due to the steric repulsion between allyl and PH_3 ligands. The η^1-C_3H_5 form, MH(η^1-C_3H_5)(PH_3), is calculated to be less stable than the η^3-C_3H_5 form by 8.6 kcal/mol for M = Pd and by 13.0 kcal/mol for M = Pt at the MP4SDQ level, as shown in Table 6. These energy changes are consistent with the fact that the $\eta^3 \rightleftarrows \eta^1$ interconversion of MH(η^3-C_3H_5)(PH_3) occurs thermally, as experimentally observed.[7]

MH(η^1-C_3H_5)(PH_3) complexes can undergo additional coordination of PH_3 because MH(η^1-C_3H_5)(PH_3) is a coordinatively unsaturated three-coordinate complex. PdH(η^1-C_3H_5)(PH_3)$_2$ is only slightly less stable than PdH(η^3-C_3H_5)(PH_3) + PH_3, as shown in Table 6. On the other hand, PtH(η^1-C_3H_5)(PH_3)$_2$ is ca. 8 kcal/mol more stable than PtH(η^3-C_3H_5)(PH_3) + PH_3. These results indicate that the coordinating species accelerates the $\eta^3 \rightleftarrows \eta^1$ interconversion.

Now, we have made all the preparation for discussing the possibility that the reductive elimination proceeds via the η^1-form. In the Pd reaction system, the η^1-form is much less stable than the η^3-form. However, the C−H reductive elimination of PdH(η^1-C_3H_5)(PH_3) should occur with no barrier as in PdH(CH_3)(PH_3) (vide su-

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(30) Because geometry optimization of MH(η^1-C_3H_5)(PH_3) leads to MH(η^3-C_3H_5)(PH_3), the geometry of MH(η^1-C_3H_5)(PH_3) was optimized under a constraint that the bond angle around the C$^\alpha$ atom was fixed to be the same as it in MH(η^1-C_3H_5)(PH_3)$_2$.

(31) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255.

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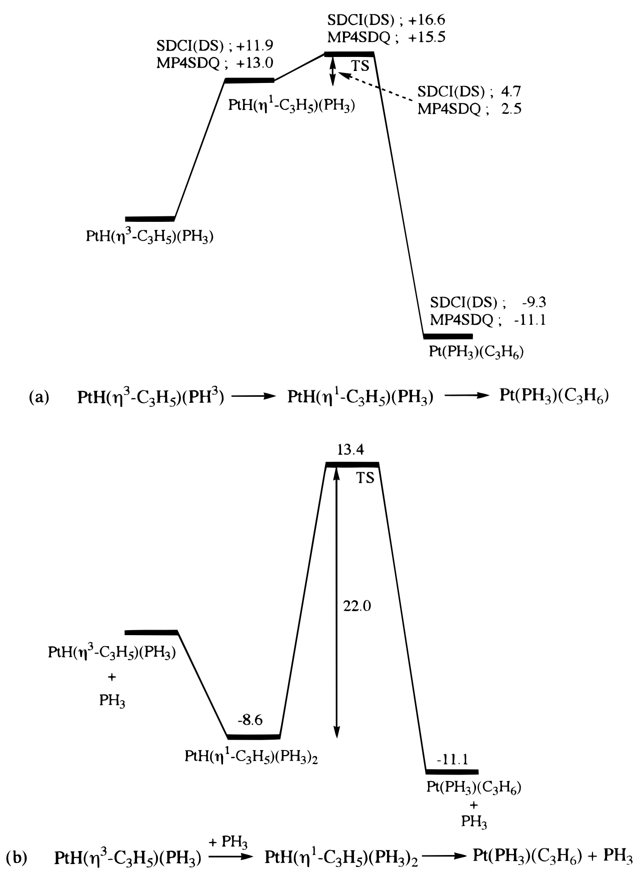
Scheme 1



pra).[32] Thus, the C−H reductive elimination via PdH($(\eta^1\text{-}C_3H_5)(PH_3)$) would proceed with an energy destabilization of about 9 kcal/mol, and this energy destabilization is similar to E_a of the C−H reductive elimination of PdH($(\eta^3\text{-}C_3H_5)(PH_3)$); E_a = 5.4 kcal/mol at the MP4SDQ, 8.3 kcal/mol at the SD-CI, and 5.6 kcal/mol at the CCD(ST4) level. Even if we adopt the lowest E_a value (5.4 kcal/mol), PdH($(\eta^1\text{-}C_3H_5)(PH_3)$) can be formed in thermal equilibrium with PdH($(\eta^3\text{-}C_3H_5)(PH_3)$) at temperatures sufficient to drive a reaction with E_a = 5−6 kcal/mol. In the Pt reaction system, a similar situation is observed. The transformation of PtH($(\eta^3\text{-}C_3H_5)(PH_3)$) to its η^1-isomer requires an energy destabilization of about 13 kcal/mol, and then the C−H reductive elimination of PtH($(\eta^1$-allyl$)(PH_3)$) proceeds with E_a of 9−11 kcal/mol,[32] as shown in Scheme 1a. The sum of 13 and 9−11 (=22−25) kcal/mol roughly corresponds to the E_a (21 kcal/mol) of the direct C−H reductive elimination of PtH($(\eta^3\text{-}C_3H_5)(PH_3)$). From these results, it is reasonably concluded that the C−H reductive elimination of MH($(\eta^3\text{-}C_3H_5)(PH_3)$) proceeds through two reaction courses; one is the direct reaction without conversion to the $\eta^1\text{-}C_3H_5$ isomer, and the other is the reaction via an $\eta^1\text{-}C_3H_5$ isomer. In PdH($(\eta^3\text{-}C_3H_5)(PH_3)$), the direct reaction seems slightly more favorable than the other.

Next, we consider the case where excess PH_3 exists in the reaction system. In this case, PdH($(\eta^1\text{-}C_3H_5)(PH_3)_2$) is stable similarly to PdH($(\eta^3\text{-}C_3H_5)(PH_3)$) + PH_3, and the C−H reductive elimination of PdH($(\eta^1\text{-}C_3H_5)(PH_3)_2$) should occur with little barrier like PdH($(CH_3)(PH_3)_2$).[33] PtH($(\eta^1\text{-}C_3H_5)(PH_3)_2$) is 8 kcal/mol more stable than PtH($(\eta^3\text{-}C_3H_5)(PH_3)$) + PH_3, and the C−H reductive elimination of PtH($(\eta^1\text{-}C_3H_5)(PH_3)_2$) should proceed with an E_a of about 22 kcal/mol,[32] as schematically shown in Scheme 1b. Apparently, it is likely that PdH($(\eta^3\text{-}C_3H_5)(PH_3)$) and the Pt analogue convert to the $\eta^1\text{-}C_3H_5$ isomer, followed by the C−H reductive elimination to yield M($(PH_3)_2(C_3H_6)$), when excess phosphine exists.

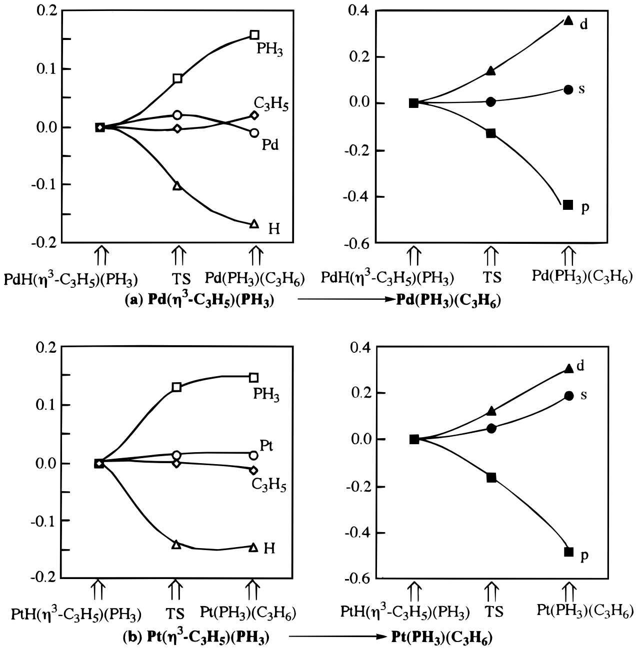


Figure 4. Population changes in the C−H reductive elimination of MH($(\eta^3\text{-}C_3H_5)(PH_3)$). A positive value represents an increase in population relative to the reactant and vice verse.

Changes in Electron Distribution and Orbital Interactions in the C−H Reductive Elimination. In the C−H reductive elimination of PdH($(\eta^3\text{-}C_3H_5)(PH_3)$), the electron populations of C_3H_5 and H decrease, and those of Pd and PH_3 increase, as shown in Figure 4a. In particular, the Pd d orbital population significantly increases in the reaction. These changes are in accordance with our expectation. On the other hand, the Pd p orbital population unexpectedly decreases. Its decrease is easily interpreted in terms of rehybridization as follows: The dsp^2 hybridization of the reactant (square planar structure) changes into sp hybridization in the product (linear structure). Since this rehybridization leads to a decrease in the p-nature, the p orbital population decreases considerably.

In the reductive elimination of PtH($(\eta^3\text{-}C_3H_5)(PH_3)$), the electron distribution changes in a slightly different manner, as shown in Figure 4b: (1) The H atomic population considerably decreases and the PH_3 electron population considerably increases at the TS, and they are almost the same as in the product. These results are consistent with the productlike TS of the Pt reaction system. (2) The Pt d orbital population increases less than the Pd d orbital. This result would arise from the well-known fact that the Pd d orbital lies at a lower energy than the Pt d orbital (recall the d orbital energy

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[32] (a) It is reasonably assumed that E_a of the C−H reductive elimination differs little between MH($(\eta^3\text{-}C_3H_5)(PH_3)_n$) and MH($(CH_3)(PH_3)_n$), since the C=C bond would only weakly coordinate to the central metal around the TS (see Figure 2). E_a was estimated to be 9−11 kcal/mol for the C−H reductive elimination of PtH($(CH_3)(PH_3)$) (this work) and to be 22 kcal/mol for that of PtH($(CH_3)(PH_3)_2$).[31b] (b) Sakaki, S.; Ieki, M. *J. Am. Chem. Soc.* **1993**, *115*, 2373.

[33] Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 6115.

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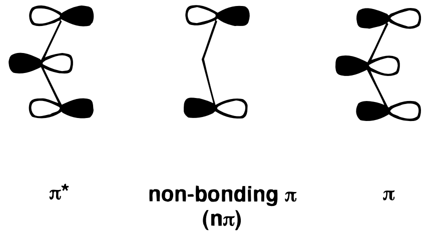
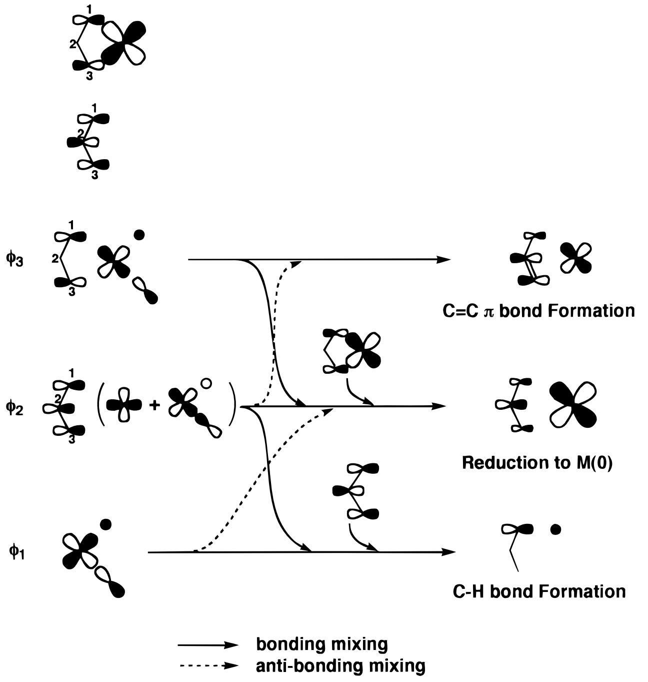
Chart 1



Scheme 2



of M(PH$_3$) (M = Pd, Pt) and the ground-state electron configuration of Pt and Pd (vide supra)).

The orbital interaction diagram in the C−H reductive elimination of η^3-allyl hydride complexes is expected to be much different and perhaps more complicated than that in the C−C and C−H reductive eliminations of transition metal alkyl complexes,[34] since two conjugated C−C bonds change into C=C double and C−C single bonds in addition to the M−H and M−(η^3-C$_3$H$_5$) bond breaking and the C−H bond formation. Thus, it is worthwhile to discuss the orbital interaction diagram in the C−H reductive elimination of an η^3-allyl hydride complex. Here, frontier orbitals are π, nonbonding π (nπ), and π^* orbitals of the η^3-allyl ligand (Chart 1), donor orbitals of H(hydride) and PH$_3$, and d orbitals of the central metal.

In MH(η^3-C$_3$H$_5$)(PH$_3$), the most stable ϕ_1 orbital involves the bonding interaction between metal d$_\sigma$ and H(hydride) 1s orbitals, as shown in Scheme 2. The ϕ_2 orbital mainly involves the π-orbital into which metal d and H 1s orbitals mix in a bonding way. In the HOMO (ϕ_3), the nπ orbital is a main contributor into which the metal d$_\sigma$ orbital slightly mixes in a bonding manner. Approach of H(hydride) to η^3-C$_3$H$_5$ causes orbital mixing among them. The ϕ_1 orbital undergoes bonding mixing of ϕ_2, ϕ_3, and π^* of η^3-C$_3$H$_5$, which considerably decreases the p$_\pi$ components on C^2 and C^3 because their phases are reversed in the ϕ_2, ϕ_3, and π^* orbitals. On the other hand, the C^1 p$_\pi$ component increases by this orbital mixing. These orbital mixings correspond to C−H bond formation. Although the ϕ_2 orbital involves the C^1−H antibonding interaction, the bonding mixing of the virtual d$_\sigma$ orbital increases the d$_\sigma$ contribution but decreases the C p$_\pi$ contribution, which leads to the doubly occupied d$_\sigma$ orbital, i.e., the zero-valent Pt and Pd complexes. The ϕ_2 orbital mixes into the ϕ_3 orbital in an antibonding way with the H 1s orbital, which reduces the p$_\pi$ component of C^1 and enhances the p$_\pi$ components of C^2 and C^3 in the ϕ_3 orbital. As a result, the ϕ_3 orbital changes into the C^2=C^3 π-orbital. Thus, the bond breaking and bond formation can be reasonably understood in terms of this orbital mixing. From this orbital mixing, we can easily understand the reason that the C−H reductive elimination of PtH(η^3-C$_3$H$_5$)(PH$_3$) is difficult, unlike that of the Pd analogue. Since the Pt d$_\sigma$ orbital lies at a higher energy than the Pd d$_\sigma$ orbital, the d$_\sigma$ orbital mixes into ϕ_2 less easily in the Pt reaction system than in the Pd reaction system, which makes difficult the C−H reductive elimination of the Pt reaction system.

Concluding Remarks

The C−H reductive elimination of MH(η^3-C$_3$H$_5$)(PH$_3$) (M = Pd, Pt) was theoretically investigated, where geometries of reactant, transition state, and product were optimized at the MP2 level. MH(η^3-C$_3$H$_5$)(PH$_3$) exhibits interesting geometrical features: (1) the M−C^1 bond trans-positioned to H(hydride) is longer than the other M−C^3 bond, and (2) the C^1−C^2 bond trans-positioned to H is shorter than the other C^2−C^3 bond. These features arise from the strong trans influence of H. Although the geometry of allyl group somewhat resembles the η^1-allyl form, the C^1−C^2 and C^2−C^3 bonds are conjugated well with each other and the allyl group is still considered as a π-allyl ligand. The following characteristic features are observed at the TS of the C−H reductive elimination of MH(η^3-C$_3$H$_5$)(PH$_3$): the H ligand considerably moves toward the allyl ligand, but the C−H bond between H and allyl is not formed yet and the M−H bond is still maintained. The TS of the Pt reaction system is more productlike than that of the Pd reaction system. The activation energy (E_a) slightly decreases but the exothermicity (E_{exo}) considerably increases upon introducing correlation effects. This reductive elimination of PdH(η^3-C$_3$H$_5$)(PH$_3$) proceeds with a much lower E_a (ca. 5 kcal/mol) and higher E_{exo} (ca. 29 kcal/mol) than those of the Pt analogue (E_a = ca. 21 kcal/mol and E_{exo} = ca. 11 kcal/mol). In both the Pd and Pt reaction systems, the C−H reductive elimination of the η^3-allyl hydride complex requires a higher E_a than that of the alkyl hydride complex. These results are easily interpreted in terms of bond energies as follows: Pd−(η^3-C$_3$H$_5$) and Pt−(η^3-C$_3$H$_5$) bonds are stronger than Pd−CH$_3$ and Pt−CH$_3$ bonds by 22 and 24 kcal/mol, respectively, and the Pt−(η^3-C$_3$H$_5$) bond is stronger than the Pd−(η^3-C$_3$H$_5$) bond by ca. 10 kcal/mol.

The C−H reductive elimination of the η^3-allyl hydride complex is more complicated than that of the alkyl hydride complex. Bond breaking and bond formation

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(34) For instance: (a) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Still, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857. (b) Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 6115; *Organometallics* **1986**, *5*, 609. (c) Siegbahn, P. E. M.; Blomberg, M. R. A. *Organometallics* **1994**, *13*, 354, 2833 and references therein.

in this reaction are, however, easily interpreted in terms of the orbital mixing diagram presented here.

These results provide meaningful suggestions concerning the palladium-catalyzed reductive cleavage of allyl compounds,[2−6] as follows: (1) It is very difficult to detect $PdH(\eta^3\text{-}C_3H_5)(PR_3)$, and (2) an attempt to detect such an η^3-allyl hydride complex should be made by using the Pt analogue since C−H reductive elimination is more difficult in $PtH(\eta^3\text{-}C_3H_5)(PR_3)$.

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