Mechanism of the $\eta^3-\eta^1-\eta^3$ Isomerization in Allylpalladium Complexes: Solvent Coordination, Ligand, and Substituent Effects

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Received August 31, 2001

The mechanism of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization of (η^3-allyl)palladium complexes occurring as catalytic intermediates in important synthetic transformations has been studied by applying density functional theory at the B3PW91(DZ+P) level. It was found that under catalytic conditions, in the condensed phase, the isomerization process involves tetracoordinated (η^1-allyl)palladium intermediates. In these intermediates a solvent molecule or another ancillary ligand coordinates to palladium. The stability of the (η^1-allyl)palladium intermediates critically depends on the electronic effects and on the coordination ability of the solvent molecules and the ancillary ligands. The theoretical calculations indicate a $d_\sigma \rightarrow \pi^*$ type hyperconjugative interaction occurring in the η^1-allyl moiety of the intermediary complexes. These hyperconjugative interactions influence the structure of the complexes and the activation barrier to rotation through the C1−C2 bond. Alkyl substitution of the metalated carbon leads to destabilization of the (η^1-allyl)palladium complexes, which increases the activation energy of the syn/anti isomerization process. This substituent effect arises from a dual steric and electronic destabilizing interaction between the methyl substituent and the metal atom.

1. Introduction

Allylpalladium chemistry is one of the most successful and innovative areas of organometallic catalysis. Catalytic transformations involving nucleophilic attack on (η^3-allyl)palladium intermediates have been widely applied in a number of important chemical processes,[1−5] including allylic substitution and the oxidation of alkenes and conjugated dienes. In particular, palladium-catalyzed allylic substitution reactions have been the subject of recent interest due to their synthetic potential for asymmetric carbon−carbon bond formation through the use of chiral ligands.[6−11] A great mechanistic advantage of the allylpalladium chemistry arises from the fact that the (η^3-allyl)palladium intermediates of the reactions are often isolable species, which can be directly studied by X-ray and NMR techniques.[11−25] Therefore the conformation, configuration, and isomerization processes of these catalytic intermediates can be directly observed. It is well-known by numerous structural studies that substituted (η^3-allyl)palladium complexes can undergo facile isomerization reactions under ambient conditions.[1,6,12,24,26−32]

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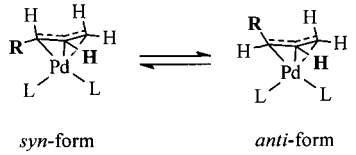
10.1021/om010793d CCC: $20.00
Publication on Web 11/13/2001

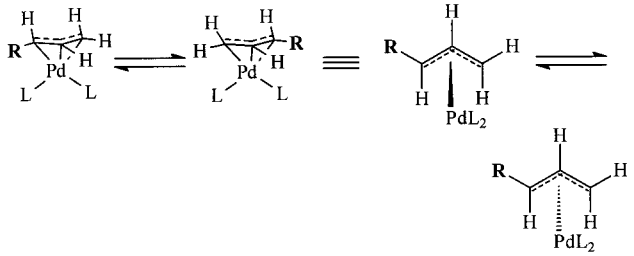
Two types of isomerization reactions of (η^3-allyl)-palladium complexes are of particular mechanistic and synthetic importance. The first type is the syn/anti isomerization involving the change of the geometry of

Scheme 1



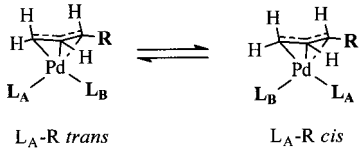
the allyl moiety (Scheme 1) or enantioface exchange of the allyl moiety (Scheme 2);[6,17,26] the other type is the

Scheme 2



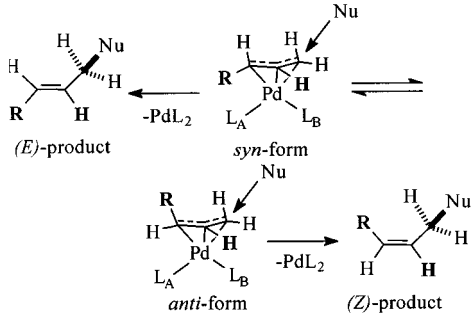
cis/trans isomerization changing the substituent positions with respect to the ligand disposition.[6] This latter process does not affect the geometry of the allyl moiety (Scheme 3). The isomerization processes are of great

Scheme 3



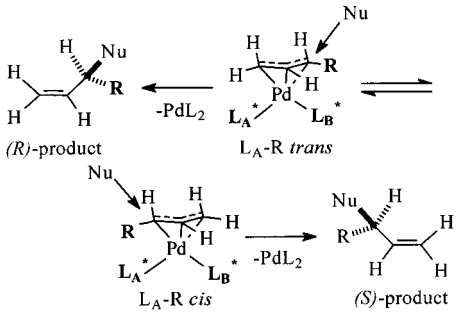
relevance for the selectivity of the catalytic transformations involving acyclic substrates. The syn/anti isomerization may affect the double-bond geometry in the product. Thus, a nucleophilic attack at the unsubstituted terminus of the syn form given in Scheme 4

Scheme 4



affords an *E* geometry in the product, while an attack at the same position of the anti form leads to *Z* geometry. The cis/trans isomerization and enantioface exchange influence the mechanism of the asymmetric induction process. An important strategy for chiral induction is the employment of the trans influence of a chiral ligand or one of the functionalities in a bidentate ligand.[6,9,33] In these cases a facile cis/trans isomerization accompanied by an enantioface exchange is a prerequisite for successful chiral induction (Scheme 5).

Scheme 5



For acyclic systems the syn/anti and cis/trans isomerizations are readily accomplished via an $\eta^3 \rightarrow \eta^1$ rearrangement, followed by rotation about the carbon−carbon σ-bond and/or the palladium−carbon σ-bond and then $\eta^1 \rightarrow \eta^3$ interconversion to regenerate the (η^3-allyl)-palladium complexes.[6,26,34,35] This process involving the intermediate formation of an (η^1-allyl)palladium species is the well-known $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ (also called $\pi \rightarrow \sigma \rightarrow \pi$) isomerization.[6,26,34,35] Despite the fact that the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization is commonly invoked in mechanistic studies on the development of the stereo- and enantioselectivity of the nucleophilic attack on acyclic (η^3-allyl)palladium complexes, many details of this important isomerization process are poorly understood. One important problem arises from the difficulties in observing the (η^1-allyl)palladium intermediates under the isomerization process.[28,29] Therefore, important properties of these (η^1-allyl)palladium intermediates, such as the coordination state, the preferred conformation, and the ligand and substituent effects are difficult to establish.

Direct observation of static (η^1-allyl)palladium complexes requires the presence of special ligand effects stabilizing the η^1-coordination state. Thus, Elsevier, van Leeuwen, Vrieze, and co-workers[27,36] have shown that (η^1-allyl)palladium complexes can be observed by ^{1}H NMR in the presence of terdentate NNN and PNN ligands. Osborn and co-workers[28] have studied the structure and reactivity of various (η^1-allyl)palladium complexes coordinated to terdentate ligands. In a very recent study Braunstein and Dedieu and co-workers[29] isolated and characterized an (η^1-allyl)palladium complex coordinated to a hemilabile bis(oxazoline)phenylphosphonite ligand and a chloride ligand. It was

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found that under appropriate conditions this complex is involved in an $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process. Furthermore, Jolly and co-workers[37] and Mayr and Kuhn[38] have demonstrated that one of the allyl moieties of bis(allyl)palladium complexes prefers the η^1 coordination state in the presence of phosphine type ligands.

The theoretical data available for (η^1-allyl)palladium complexes are rather limited. Sakaki and co-workers[39] have shown that the tricoordinated (η^1-allyl)PdH(PH_3) complex does not represent a minimum on the potential energy surface but this complex is converted to the corresponding η^3 form without an activation barrier. These authors have also shown that the tetracoordinated (η^1-allyl)PdH(PH_3)$_2$ complex is a minimum on the potential energy surface; however, this complex is still less stable than its η^3-coordinated counterpart.[39] In a very recent study Braunstein and Dedieu[29] have shown that in the case of a bidentate coordination of a P,N ligand to the (η^1-allyl)palladium fragment the nitrogen atom prefers to coordinate trans to the η^1-allyl moiety. Recently, a theoretical study was published on the structure and reactivity of bis(allyl)palladium complexes,[40] concluding also that the η^1,η^3 form of these species is particularly stable. It was established that in these complexes the η^1-allyl moiety has a very high reactivity toward electrophilic reagents.

Despite the considerable importance of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process for synthetic allylpalladium chemistry there has been a remarkable lack of theoretical studies published on the mechanistic aspects of this reaction. Therefore, the present study was undertaken to investigate the mechanism of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process with a special emphasis on the factors influencing the stability of the η^1 form of the complexes. In particular, we will study the following aspects.

(1) What is the preferred coordination state of the (η^1-allyl)palladium complexes in the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process?

(2) What electronic effects determine the conformation of the η^1-allyl moiety? How does these electronic effects influence the barrier to rotation through the carbon−carbon bond?

(3) How does the π-acceptor/σ-donor character of the ligands influence the stability of the η^1-species?

(4) How do the substituent effects stabilize the (η^1-allyl)palladium complexes? How do these effects depend on the location of the allylic substituents?

To answer these questions, density functional theory (DFT) calculations have been carried out for the η^3- and η^1-coordinated allylpalladium complexes **1**−**9**. These calculations also aim to provide specific help for the design and development of new selective catalytic transformations proceeding through acyclic allylpalladium complexes, and therefore, particular attention is paid to the synthetically important structural and reactivity features of these complexes.

2. Computational Methods

Unless otherwise stated, the geometries were fully optimized by employing a Becke-type[41] three-parameter density functional model, B3PW91. This so-called hybrid functional includes the exact (Hartree−Fock) exchange, the gradient-corrected exchange functional of Becke,[41] and the more recent correlation functional of Perdew and Wang.[42] All calculations have been carried out using a double-ζ(DZ)+P basis constructed from the LANL2DZ basis[43−45] by adding one set of d polarization functions to the heavy atoms (exponents: C, 0.63; N, 0.864; O, 1.154; P, 0.34) and one set of diffuse d functions on palladium (exponent 0.0628). Harmonic frequencies have been calculated at the level of optimization for all structures to characterize the calculated stationary points and to determine the zero-point energies (ZPE). The fully optimized transition state structures **1b**, **2b**,**d**, and **3c**−**9c** have been characterized by a single imaginary frequency, while the rest of the fully optimized structures possess only real frequencies. All calculations have been carried out by employing the Gaussian 98 program package.[46]

3. Results and Discussion

The B3PW91/LANL2DZ+P geometrical parameters for selected structures **1** and **2** are given in Figure 1, while energy diagrams for the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization of various allylpalladium complexes **1**−**9** are given in Figures 2−5. The theoretical calculations are restricted to cationic allylpalladium complexes, which are the immediate substrates of the nucleophilic attack in catalytic reactions.[1,2] Therefore, in most of the calculations PH_3 ligands are employed to model the phosphine ligands, such as PPh_3, routinely used in catalytic processes.

Isomerization Proceeding through Tricoordinated η^1-Allyl Species. Cleavage of two of the three palladium−carbon bonds in the (η^3-allyl)Pd(PH_3)$_2$ complex[47] (**1a**) leads to a T-shaped tricoordinated complex (**1b**, Figure 1). In fact, the only stationary point found on the potential energy surface of the η^1-species is complex **1b**, which is characterized as a first-order saddle point by harmonic frequency analysis. Accordingly, the σ-coordinated (η^1-allyl)Pd(PH_3)$_2$ species is not a stable intermediate but a transition state (TS) structure of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process.

Since the η^1 species **1b** is considerably less stable (by 31.6 kcal mol^{-1}) than its η^3-coordinated counterpart, the activation barrier to isomerization is rather high. A particularly interesting structural feature in **1b** is that the allylic carbons are in the coordination plane of

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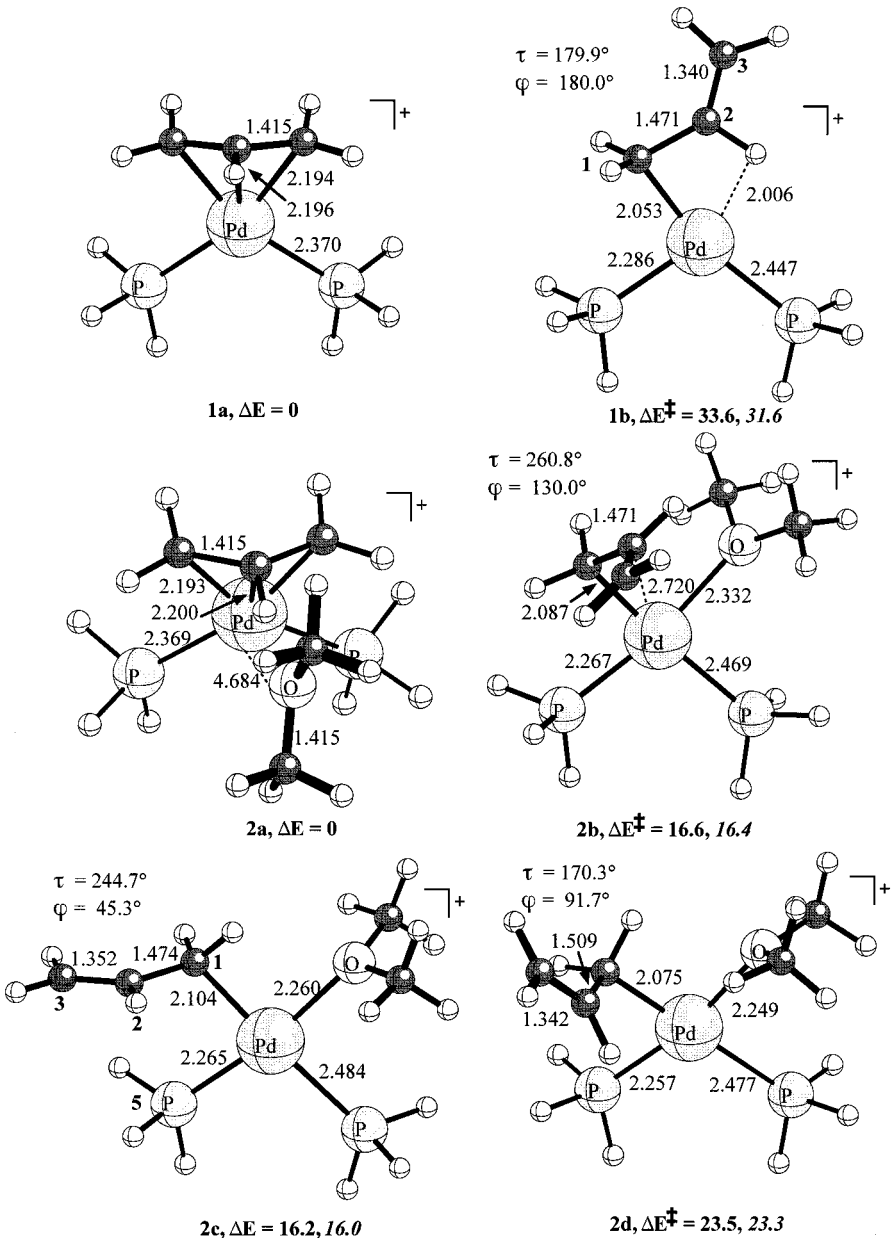

Figure 1. Selected B3PW91/LANL2DZ+P geometrical parameters of allylpalladium complexes **1** and **2** (bond lengths in Å, angles in deg, energies in kcal mol^{-1}). The dihedral angle τ is defined as Pd−C1−C2−C3, and the dihedral angle φ is defined as C2−C1−Pd−P5. The ZPE-corrected energies are given in italics.

palladium. This conformation allows an agostic coordination of the central C−H bond of the allyl group to the palladium atom. The short Pd−H distance (2.006 Å) indicates a high reactivity for the empty coordination site of the formally tricoordinated species. However, it is important to emphasize that the palladium-catalyzed transformations proceed in the condensed phase, where solvent molecules can also coordinate to the empty coordination site of palladium.

Effects of Coordination of a Solvent Molecule in the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ Isomerization. A more realistic model for description of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization in the condensed phase involves a dimethyl ether molecule (**2a**−**d**). Dimethyl ether is used to approximate tetrahydrofuran, which is a commonly applied solvent in allylic substitution reactions.[1,2] The long Pd−O(Me_2) distance (4.684 Å) clearly indicates that the dimethyl ether molecule does not coordinate to the central atom of the (η^3-allyl)palladium complexes in **2a**. This also involves that the dimethyl ether molecule does not form a pentacoordinated adduct with **1a**; instead, the monomers are kept together by electrostatic interactions. Because of these electrostatic interactions complex **2a** is more stable (by 6 kcal mol^{-1}) than the corresponding separated monomers (**1a** and Me_2O). According to the counterpoise estimate[48] the basis set superposition error for the dimer **2a** is insignificantly small (0.6 kcal mol^{-1}).

It is also important to emphasize that the palladium−carbon and palladium−phosphorus bonds are practically unchanged by the dimethyl ether association (cf. **1a** and **2a**), suggesting that structural studies on (η^3-allyl)-palladium complexes do not require explicit treatment of the solvent effects.

Breaking two of the palladium−carbon bonds in the η^3-coordinated complex **2a** leads to the η^1 complex **2c**.

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In contrast to **1b**, complex **2c** represents a minimum on the potential energy surface according to harmonic vibration analysis. Probably the most important structural feature of **2c** is that the dimethyl ether molecule is strongly bound to the fourth coordination site of palladium (Pd−O = 2.260 Å). Coordination of dimethyl ether to **1b** is a strongly exothermic process, evolving 21.6 kcal mol^{-1}. The above stability and structural features clearly indicate that the properties of the η^1 intermediates occurring in the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process in condensed phase cannot be discussed without accounting for coordination of a solvent molecule or other ligands to the fourth coordination site of palladium.

The η^1 moiety exerts a strong trans influence to the phosphine ligand. As one goes from **2a** to **2c**, the palladium−phosphorus bond trans to the palladium−carbon bond is elongated by 0.12 Å. This bond elongation is a direct consequence of the carbanion-like coordination of the allyl moiety, resulting in a pure σ-type palladium−carbon bond. In contrast to **1b**, the carbon atoms of the allyl moiety in **2c** do not lie in the coordination plane of palladium. The Pd−C1−C2−C3 dihedral angle (referred as τ) is 244.7° (−115.3°) in **2c**, a structural feature which is persistent in all calculated η^1-allyl intermediates in this study.

The **2a** → **2c** isomerization is a highly endothermic process, indicating a low stability for the η^1 form compared to the η^3 form. The low thermodynamic stability of the η^1 form represents an obvious hindrance to the experimental studies. A further reason for the difficult observation of the η^1 form **2c,** and its analogues, is the low activation barrier (0.4 kcal mol^{-1}) to the formation of the η^3-coordinated counterpart (**2a**). The transition state structure **2b** is very similar to the η^1 intermediate **2c**. The main structural difference between **2b** and **2c** is related to the variation of the C2−C1−Pd−P5 dihedral angle (referred as φ). Since the rotation through the Pd−C σ-bond is practically unhindered, the energy difference between **2b** and **2c** is very small.

Rotation through the Carbon−Carbon σ-Bond of the η^1 Moiety. Complex **2c** can undergo isomerization of the η^1 moiety by rotation through the C1−C2 σ-bond. In substituted complexes this isomerization forms the basis of the syn/anti isomerization (Schemes 1 and 4). The isomerization of the η^1 moiety in **2c** proceeds through the TS structure **2d**. The activation barrier (7.3 kcal mol^{-1}) is surprisingly high for a vinyl rotation process (vide infra). Structure **2d** also represents the highest stationary point on the potential energy surface of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process for **2a**.

Comparison of the energy profiles obtained for the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization of **1a** and **2a** (Figure 2) reveals two important differences: (1) the coordination of the solvent molecule considerably (by 8.3 kcal mol^{-1}) decreases the activation energy of the isomerization and (2) the solvent participation leads to a more complicated potential energy surface involving three TS structures and two η^1 intermediates, while without solvent coordination there is only one TS structure corresponding to the η^1 form. Because of (1), it can be concluded that the high-energy process involving the tricoordinated species **1b** is not relevant for the description of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process under realistic catalytic conditions.

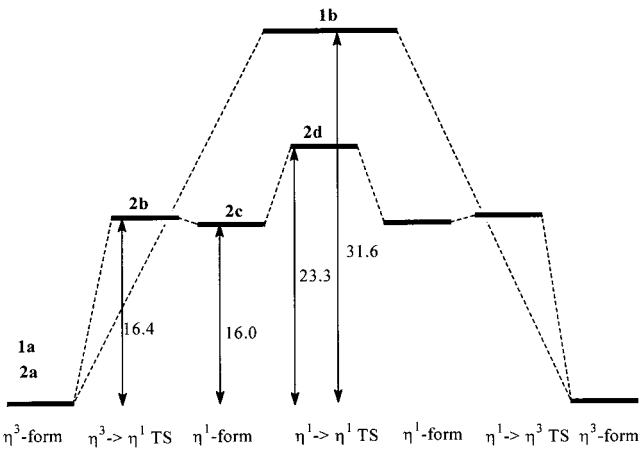

Figure 2. Reaction profile of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process for complexes **1** and **2** (energies in kcal mol^{-1}). All energies are ZPE-corrected.

In **2c** the value of the Pd−C1−C2−C3 dihedral angle (designated as τ) is 244.7°, indicating that the C1−C2 double bond and the palladium−carbon σ-bond are close to an orthogonal (270°) conformation. Conversion of the η^1 intermediate **2c** to the TS structure **2d** involves a substantial change of the dihedral angle τ, leading to a conformation in which the C1−C2 double bond and the Pd−C σ-bond are in the same plane (τ = 170.3°). The isomerization also involves significant changes in the bond lengths of the allyl moiety. As one goes from **2c** to **2d**, the Pd−C bond is shortened, the C1−C2 single bond is elongated, and the C2−C3 double bond is slightly shortened. These structural changes are consistent with a hyperconjugative interaction between the d_σ(PdC1) and the π^*(C2C3) MO's in the allyl moiety in **2c**. A similar interaction was reported for the η^1 moiety in η^1,η^3 bis(allyl)palladium species.[40] The hyperconjugative interaction in **2c** involves transfer of the electron density from the d_σ(Pd−C) MO to the antibonding π^*(C=C) orbital, and therefore the Pd−C1 and C2−C3 bonds are weakened and elongated. A partial π interaction between C1 and C2 leads to strengthening of the single bond. In the TS **2d** the d_σ and π^* MO's are orthogonal, and therefore, the hyperconjugative interactions are shut down.

Solvent and Ligand Effects on the Activation Energy of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ Isomerization. Variation of the coordination ability of the ligands and solvent molecule leads to substantial changes in the stability of the η^1 intermediate and the activation barrier to the isomerization of the η^1-allyl moiety.

Change of the dimethyl ether molecule in **2a**,**b** to a more weakly coordinating dichloromethane molecule (**3a**,**b**) leads to a substantial destabilization of the η^1 species **3b** (Figure 3). Thus, the η^1 complex **3b** containing dichloromethane (22.8 kcal mol^{-1}) is less stable by 6.8 kcal mol^{-1} than its dimethyl ether coordinated counterpart **2c** (16.0 kcal mol^{-1}). However, **3b** is still much more stable (by 8.8 kcal mol^{-1}) than the tricoordinated complex **1b**. Because of the flatness of the potential energy surface in the vicinity of the η^1 complexes (cf. **2b**,**c**), it is rather difficult to localize the TS's (such as **2b**) of the $\eta^3 \rightarrow \eta^1$ processes. Therefore, in the

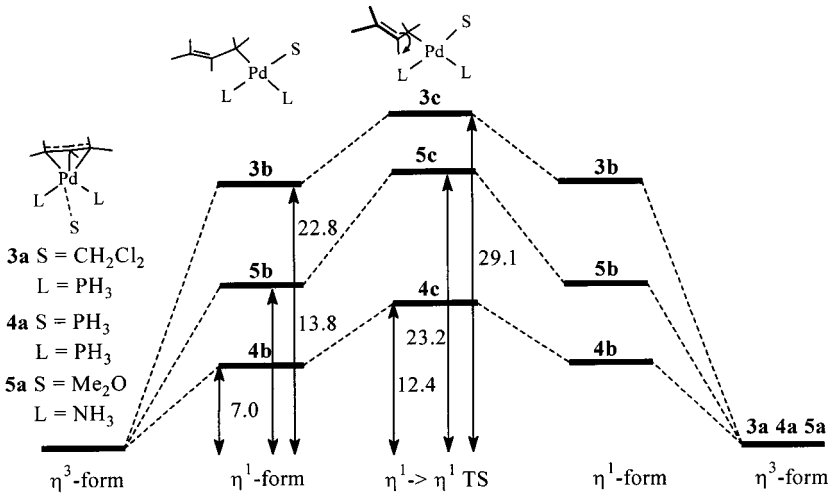

Figure 3. Solvent and ligand effects on the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization (energies in kcal mol^{-1}). All energies are ZPE-corrected. For the sake of clarity the hydrogens are represented by sticks.

subsequent studies the TS structures for formation of the η^1 complexes **3b**−**8b** were not determined. However, it is important to emphasize that these TS structures are very similar to the corresponding η^1 complexes (**3b**−**9b**) and that the activation barrier to formation to the corresponding η^3 forms is very low.

The activation barrier (**3c**) to the rotation of the η^1-allyl moiety in **3b** is somewhat lower (6.3 kcal mol^{-1}) than the corresponding activation barrier in **2c** (7.3 kcal mol^{-1}). However, because of the poor stability of the η^1 species **3b** the overall $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process (**3a** → **3c**) requires much higher activation energy than the corresponding process assisted by a dimethyl ether molecule (**2a** → **2d**).

When excess ligand is employed, a ligand molecule can also coordinate to the free coordination site in the η^1 intermediate. Change of the dimethyl ether molecule to a phosphine molecule in **2c** affords the unusually stable η^1 species **4b**. The third phosphine molecule apparently coordinates more strongly to palladium than the dimethyl ether molecule, stabilizing the η^1 form (**4b**) by 9.0 kcal mol^{-1}. The rotation barrier through the C2−C3 bond is also somewhat lower (5.4 kcal mol^{-1}) than the corresponding barrier for **2c**. Therefore, the overall barrier for the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization is substantially lower (by 11−17 kcal mol^{-1}) for the **4a** → **4c** process than for the isomerization involving **2d** or **3c**.

Exchange of the phosphine ligands in **2c** with σ-donor ammonia ligands leads to an interesting change of the stability of the η^1 species. The η^1 species **5b** is more stable (by 2.2 kcal mol^{-1}) than the phosphine complex **2c**. Interestingly, the rotation barrier of the η^1-allyl moiety in **5b** (9.4 kcal mol^{-1}) is significantly higher than in **2c** (7.3 kcal mol^{-1}) and it is also much higher than in **4b** (5.4 kcal mol^{-1}). Increase of the activation barrier can be explained by the stronger hyperconjugative interactions in **5b** than in phosphine complexes **2c** and **4b**. The ammonia ligands supply electrons to palladium, which lead to an increase of the d_σ(Pd−C) orbital energy. Lowering the gap between d_σ(Pd−C) and π^*(C═C) MOs enhances the hyperconjugative interactions, increasing the activation barrier to rotation. Since the electronic effects, determining the stability of the η^1 intermediate and the activation barrier to the η^1 rotation, work in opposite directions, the overall barrier of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process is practically the same for the **2a** → **2d** (23.3 kcal mol^{-1}) and for the **5a** → **5c** (23.2 kcal mol^{-1}) conversions.

Substituent Effects. Alkyl substituents commonly occur in preparatively important (η^3-allyl)palladium intermediates, and therefore, the substituent effects for the syn/anti and cis/trans isomerizations of these complexes are particularly interesting.

Complex **6a** is substituted with a terminal methyl group ($R^1 = CH_3$) which has a syn configuration. Formation of the η^1 form **6b** is more endothermic (by 6.0 kcal mol^{-1}) than the corresponding process for the unsubstituted analogue (**2a** → **2c**). Clearly, methyl substitution of the metal-bonded carbon strongly destabilizes the η^1 complex. Complex **6b** may undergo two different processes. Rotation through the palladium−carbon bond is practically barrierless and leads to recovery of the η^3 form **6a**. When the two ancillary ligands are different, regeneration of the η^3 form may also involve a cis/trans isomerization (Scheme 3). As was indicated above, the $\eta^1 \rightarrow \eta^3$ conversion requires a very low activation barrier. The alternative process is a rotation through the C1−C2 single bond, which requires an activation energy of 6.5 kcal mol^{-1}. This activation energy has to be invested to overcome the hyperconjugative stabilization of the η^1-allyl moiety in **6b**. The η^1 rotation changes the relationship between H2 and the methyl group (R^1), which leads to a change of the initial syn configuration of the methyl substituent (**6a**) to an anti configuration in the resulting η^3-coordinated complex **6e**. The **6c** → **6e** conversion proceeds through another η^1 intermediate (**6d**), which is about as stable as **6b**. The anti η^3 form **6e** (2.2 kcal mol^{-1}) is somewhat less stable than the syn η^3 form **6a**.[49] Because of the low stability of the η^1 complex **6b** the overall activation barrier of the syn/anti isomerization of **6a** is much higher (by 5.2 kcal mol^{-1}) than the analogous isomerization of the unsubstituted analogue **2a**.

In complex **7a**, which is isoenergetic with **6a**, the R^1 substituent is a hydrogen atom, while the other allylic terminus is methyl substituted (R^2 = Me). The η^1 complex (**7b**) formed from **7a** bears the methyl group on the terminal alkenyl carbon. Complex **7b** is remark-

(49) Szabó, K. J. *J. Am. Chem. Soc.* **1996**, *118*, 7818.

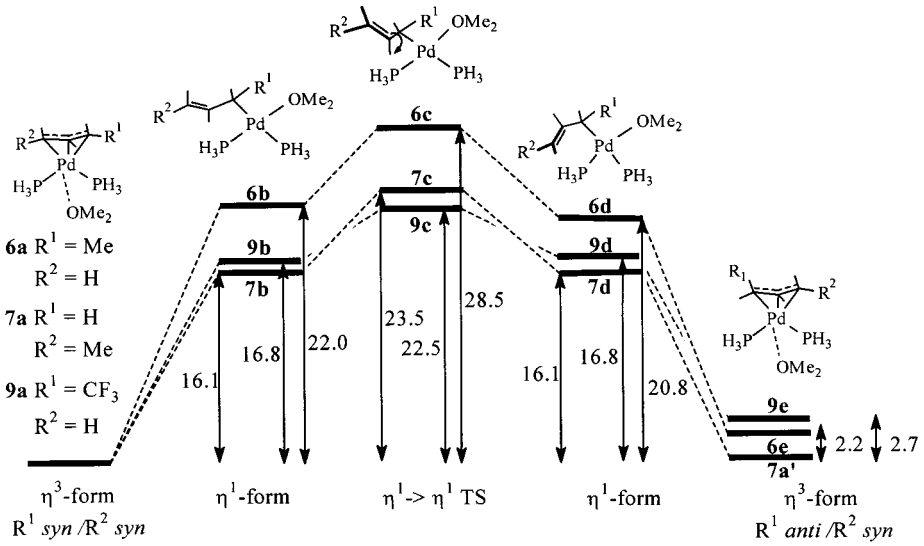

Figure 4. Effects of monosubstitution of the allyl moiety (energies in kcal mol^{-1}). All energies are ZPE-corrected. For the sake of clarity the hydrogens are represented by sticks.

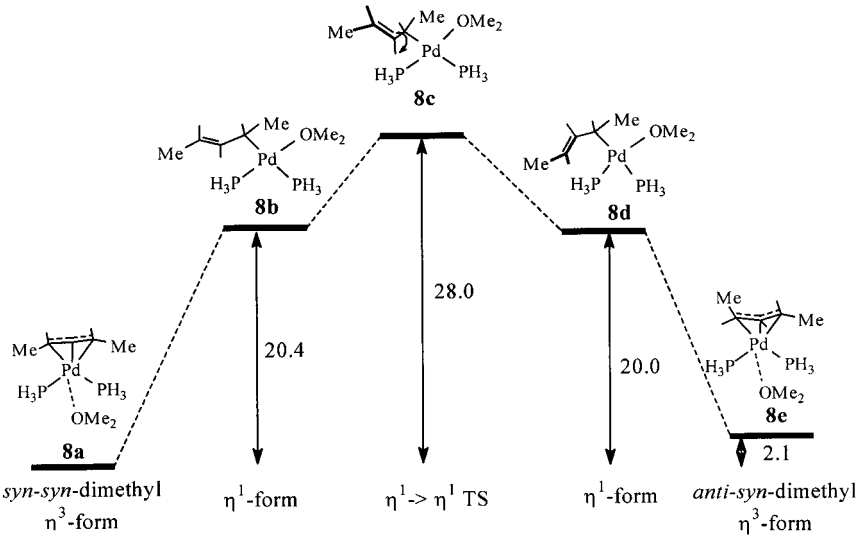

Figure 5. Effects of disubstitution of the allyl moiety (energies in kcal mol^{-1}). All energies are ZPE-corrected. For the sake of clarity the hydrogens are represented by sticks.

ably (by 5.9 kcal mol^{-1}) more stable than the isodesmic η^1 complex **6b**, confirming the above conclusion that the alkyl substitution of the metalated allyl terminus of the η^1-allyl moiety is thermodynamically destabilizing. Complex **7b** may undergo allyl rotation through the palladium−carbon bond, followed by regeneration of the η^3 form **7a**. Another possibility is the rotation of the allyl moiety through the C1−C2 σ-bond, which does not alter the relationship between H2 and R^2. Accordingly, this rotation does not lead to syn/anti isomerization of the methyl substituent R^2; however, this process involves enantioface exchange of the allyl ligand (Scheme 2).[17,26] The TS structure **7c** (23.5 kcal mol^{-1}) has a substantially lower energy than the TS structure calculated for **6c**. This energy difference arises from the destabilizing effect of the methyl substitution of the metalated carbon in **6c**.

When both terminal allyl positions are methyl-substituted, the reaction profile (Figure 5) of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process (**8a** → **8e**) resembles the reaction profile of the **6a** → **6e** interconversion. Because of symmetry reasons the metalated terminal carbon is methyl substituted in the η^1 forms (**8b** and **8d**) and in the TS structure (**8c**), which leads to a high activation barrier (28.0 kcal mol^{-1}) to the syn/anti isomerization process. The η^1 intermediate **8b** is less stable (by 4.3 kcal mol^{-1}) than its monomethylated analogue **7b**.

Electronic Nature of the Substituent Effects. The above results clearly indicate that the methyl substitution of the allylic termini higher the activation barrier of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process. An obvious explanation of the low stability of **6b** (or **8b**) arises from the steric interactions between the R^1 methyl group and the palladium atom in the η^1 form.[28] However, it is well-known that alkyl groups destabilize electron-rich carbons, such as carbanions,[50] suggesting that the alkyl group has also an electronic destabilizing effect. Replacement of the methyl functionality (R^1) of **6a** with the closely isosteric (in fact, somewhat bulkier) trifluoromethyl (CF_3) group leads to the η^3 complex **9a** (Figure 4). Interestingly, the η^1 form (**9b**) is much more

(50) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 152.

stable (by 5.2 kcal mol^{-1}) than its methyl-substituted analogue (**6b**). Despite the steric interactions between the trifluoromethyl group and palladium, complex **9b** (16.8 kcal mol^{-1}) is about as stable as its unsubstituted analogue **2c** (16.0 kcal mol^{-1}). Furthermore, the activation barrier to the syn/anti isomerization **9a** → **9e** is about as high as the analogous process involving the unsubstituted species (**2a**−**d**). These results clearly indicate that electron-withdrawing substituents on the metalated carbon thermodynamically stabilize the η^1 forms of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process. Accordingly, an electron-donor methyl (or alkyl) substituent at the C1 carbon (R^1) destabilizes the (η^1-allyl)palladium complexes by both its steric and electronic effects.

4. Relevance of These Studies in Allylpalladium Chemistry

The above study clearly indicates that the intermediate of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process in the condensed phase proceeds through a tetracoordinated (η^1-allyl)palladium intermediate, such as **2c** and **3b**−**9b**. This complex is formed from the corresponding (η^3-allyl)palladium complex by coordination of a solvent molecule or other ligand to palladium. The isomerization process involving tricoordinated (η^1-allyl)palladium species (such as **1b**) has a very high activation energy (Figure 2), and this process has probably only relevance in gas-phase mechanistic studies. In addition, a tricoordinated (η^1-allyl)palladium species represents a first-order saddle point on the potential energy surface, and therefore, it is not an isolable intermediate.

The tetracoordinated (η^1-allyl)palladium species are stabilized by hyperconjugative interactions between the d_σ(Pd−C1) MO and the π^*(C2−C3) orbital. This interaction determines the conformation of the η^1-allyl moiety, which indicates that the C2−C3 double bond and the Pd−C1 bond are close to an orthogonal arrangement ($\tau \approx -90°$). The activation barrier to the rotation through the C1−C2 bond is raised by the hyperconjugative interactions. In the TS of the C1−C2 rotation the Pd−C1 and C2−C3 bonds are approximately in the same plane ($\tau \approx 180°$), and therefore the hyperconjugative interactions are shut off. In the presence of σ-donor ligands (**5b** → **5c**) the activation barrier of the C1−C2 rotation is significantly higher than for π-acceptors (**2c** → **2d**).

Strongly coordinating solvent molecules stabilize the (η^1-allyl)palladium species and, therefore, lower the activation energy of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process. This result is in line with the experimental observation that the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization is accelerated in strongly coordinating solvents.[51] Ancillary ligands with σ-donor character (e.g. NH_3, in **5b**) stabilize the (η^1-allyl)palladium species more than do π-acceptor ligands (e.g. PH_3, in **2c**). This stabilization is due to the enhanced hyperconjugative interactions provided by σ-donor ligands. In place of solvent molecules, additives, such as excess ancillary ligands, can also coordinate to palladium. A significant stabilization of the (η^1-allyl)palladium intermediates can be achieved by employment of excess phosphine ligand (**4b**). Furthermore, because of their electron-withdrawing character, π-acceptor ligands, such as PH_3, also decrease the activation barrier of the C1−C2 rotation (**4b** → **4c**). Acceleration of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process by addition of excess phosphine ligands has also been observed in NMR studies by Powell and Shaw.[52]

Alkyl substitution at the metalated carbon C1 (R^1 = Me) decreases the stability of the (η^1-allyl)palladium intermediate (**6b**), and therefore it increases the overall activation barrier of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process involving syn/anti isomerization (Scheme 1). This effect has also been observed by dynamic NMR studies.[28] On the other hand, the alkyl substitution at the C3 position (R^2 = Me) does not change significantly the stability of the (η^1-allyl)palladium intermediate (**7b**) and the activation barrier of the C1−C2 rotation (**7b** → **7c**). This important substituent effect explains the observation that the syn/anti isomerization (**6a** → **6b** → **6c** → **6d** → **6e**) is slower than the enantioface exchange (**7a** → **7b** → **7c** → **7d** → **7a′**) in (η^3-allyl)palladium complexes, which are monoalkyl substituted at one of the allylic termini.[26,28]

The destabilizing effect of the alkyl substituent at the metalated carbon arises from its steric bulk and from its electronic interaction with the electron-rich carbon (C1). Replacement of the methyl group with an electron-withdrawing substituent (CF_3) leads to a significant stabilization of the substituted (η^1-allyl)palladium intermediate (**9b**) and decrease of the overall activation barrier of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process. Accordingly, it can be predicted that the syn/anti isomerization of (η^3-allyl)palladium complexes with electron-withdrawing terminal functionalities has a lower activation barrier than that of their alkyl-substituted analogues.

5. Conclusion

This theoretical study describes the mechanism of the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ isomerization process in the condensed phase. This isomerization proceeds through tetracoordinated (η^1-allyl)palladium intermediates and involves a TS for the C1−C2 rotation. The coordination ability of the solvent molecule and the ancillary ligands has a very important effect on the stability of the η^1 intermediate. The η^1-allyl moiety is involved in hyperconjugative interactions by the d_σ(Pd−C1) and the π^*(C2−C3) MOs. This hyperconjugation determines the conformation (τ) of the allyl moiety and influences the activation barrier of the C1−C2 rotation. Alkyl substitution of the C1 position leads to a steric and electronic destabilization effect of the η^1-intermediate involved in the syn/anti isomerization process.

Acknowledgment. This work was supported by the Swedish Natural Science Research Council (NFR). The calculations were done at the IBM SP2 parallel computer facility of the Parallelldatorcentrum (PDC) at the Royal Institute of Technology in Sweden. We thank the PDC for a generous allotment of computer time.

OM010793D

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(52) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1839.