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Effects of β-Substituents and Ancillary Ligands on the Structure and Stability of (η^3-Allyl)palladium Complexes. Implications for the Regioselectivity in Nucleophilic Addition Reactions

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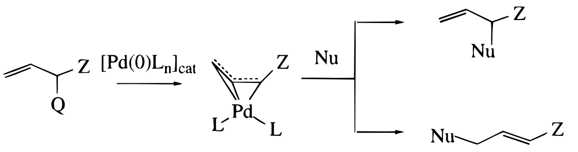
Abstract: (η^3-Allyl)palladium complexes possessing various allylic β-substituents ($X = Cl, OCH_3, H$) and ancillary ligands on palladium ($L = Cl^-, F^-, PH_3$) have been studied at the second-order Møller−Plesset (MP2) and fourth-order Møller−Plesset (MP4) perturbation theory level including single, double, and quadruple excitations (MP4SDQ). Interactions between the β-substituents and palladium have been analyzed as a function of the conformation and configuration of the complexes. Asymmetric polarization of the electron density by β-substituents leads to significant structural changes of the complexes. The β-substituent effects considerably increase the thermodynamic stability of the complexes and facilitate the heterolytic fission of the C−X bond. The intensity of these effects depends on the nature of the β-substituent, on the conformation and configuration of the complex, as well as on the σ-donor/π-acceptor character of the ancillary ligands on palladium. Since (η^3-allyl)palladium complexes are key intermediates of some important palladium catalyzed transformations, the β-substituent effects on the regiochemistry of the nucleophilic attack are also discussed. It was concluded that the regioselection is considerably enhanced in the presence of strong β-substituent effects.

1. Introduction

Catalytic transformations involving (η^3-allyl)palladium intermediates have found widespread utility in a number of important chemical processes, including allylic substitution reactions,[1−7] and bis-oxidation of conjugated dienes.[8−11] These two procedures (eqs 1 and 2) are considered as exceptionally useful preparative methods.[12,13] Palladium catalyzed allylic substitution reactions (eq 1) have recently been the subject of a great deal of interest from the synthetic community due to their potential for asymmetric synthesis through the use of chiral ligands.[3,5,6,14−21] A dual stereocontrol in palladium catalyzed bis-oxidation of conjugated dienes (eq 2) allows the preparation of a variety of stereodefined alkenes and heterocyclic compounds.[22−28]



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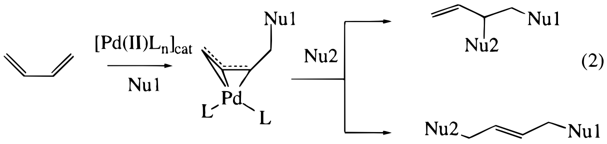

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When the substrates of the allylic substitution reactions have functionalities (Z) in an allylic position (eq 1), the nucleophile can attack either the more or the less substituted allylic termini of the allylpalladium intermediate. In bis-oxidation of conjugated dienes the asymmetrical (η^3-allyl)palladium intermediate is usually formed by the highly chemoselective attack of an O- or N-nucleophile (Nu1, eq 2) on a (η^4-diene)palladium com-

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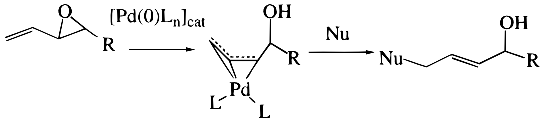
plex.[8] Addition of a second nucleophile (Nu2, eq 2) determines the regiochemistry of the reaction, which can give 1,2- or 1,4-substituted products. For both transformations (eqs 1−2) the synthetic value of a particular reaction is highly dependent on the degree of the regioselectivity. However, control of the regioselectivity, especially in allylic substitution reactions, represents one of the most difficult and challenging problems.

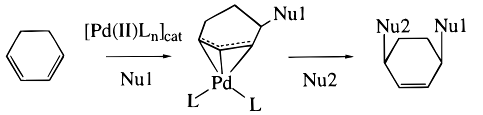
The factors that determine the regiochemistry of the addition of nucleophiles, which attack directly on the allyl moiety (Nu in eq 1, Nu2 in eq 2), can be partitioned between those based on steric and those based on electronic influences. Steric interactions between the incoming nucleophile and the allylic termini can be easily recognized by building molecular models or by doing force-field calculations. However, the influence of the electronic factors on the regiochemistry is not so obvious.

For example, one remarkable feature is that electronic effects created by certain functionalities, such as OH, OR, OAc, NR_2, or NO_2, are capable of being transmitted from positions even more remote to the allyl moiety. 1,3-Diene monoepoxides selectively undergo the addition of nucleophiles remote from the incipient CH_2OH group (eq 3).[2,29] Nitro,[30] methoxy,[31,32] and acetoxy[33−35] (Z = CH_2NO_2, CH_2OCH_3, CH_2OAc) functionalities show a similar control on the regioselectivity. This tendency is difficult to rationalize on steric grounds as isosteric alkyl groups do not exert nearly as effective regiocontrol. On the other hand, the observed regioselectivity cannot be explained simply by the electron withdrawing effects of β-substituent X (Scheme 1), since the electron deficiency is created at the more substituted terminus of the allyl moiety.



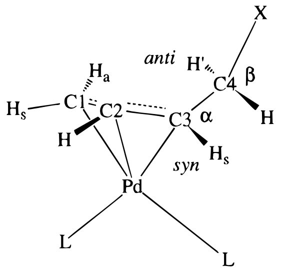
(3)

A further interesting observation is that the regioselectivity also depends on the molecular topology of the (η^3-allyl)-palladium intermediate. Thus in bis-oxidation reactions of conjugated dienes, where X is the OAc or OR functionality, the nucleophile (Nu2) exclusively attacks the less substituted terminus of the allyl moiety when C1−C4 is encompassed in a six- or seven-membered ring, giving the 1,4-product (eq 4). However, when the reaction involves acyclic intermediates a considerable amount (5−30%) of 1,2-adduct is formed (eq 2).[33,34]

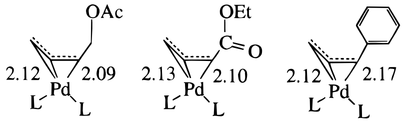


(4)

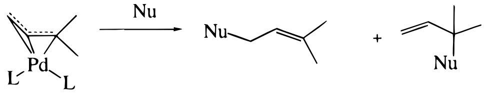
Scheme 1



Scheme 2



The nature of the ancillary ligands in the (η^3-allyl)palladium complexes can also influence the regioselectivity of the nucleophilic attack.[36−39] For example, Åkermark and co-workers[37] reported that σ-donor ligands (e.g. tmeda) give less reactive η^3-(3-methylbutenyl)palladium complexes, which react preferentially at the less substituted terminus, while π-acceptor ligands (such as COD and PPh_3) produce reactive complexes, which also react at the more substituted terminus (eq 5).



(5)

L			
L = TMEDA	>95	:	1
COD	7	:	1
PPh_3	2.7	:	1

The electronic factors in determining regiochemistry are based on the ability of substituents on the allyl moiety and/or ancillary ligands on the palladium to induce an asymmetric electron distribution, thereby making one of the termini more reactive toward nucleophilic attack. Manchand and co-workers[35] and Grant and co-workers[40,41] reported X-ray structures for some substituted (η^3-allyl)palladium complexes (Scheme 2). These authors found that the allylic terminus which is closer to the O-functionality is “hinging toward” the metal.[41] However, when a bulky phenyl group is attached to the allyl moiety, the more substituted terminus is “hinging away” from palladium.[40] From the analysis of the contacts within and between molecules, Grant and co-workers[41] concluded that the asymmetrical metal−allyl bonding in the oxygen containing complexes was electronically induced and not simply a consequence of steric effects. However, the X-ray structure determination did not provide enough information for characterization of these peculiar electronic interactions, which are believed to be responsible for the control of regioselectivity in nucleophilic additions.[7]

Despite the considerable synthetic and mechanistic importance of palladium−allyl chemistry there has been a remarkable lack of high level theoretical studies published in this field. The majority of theoretical calculations on (η^3-allyl)palladium complexes have been carried out on a semiempirical level[42−45] but very recently two ab initio studies have also appeared.[46,47]

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The scope of these theoretical works was the investigation of the structure[45,46] and reactivity[42,43,47] of the parent, unsubstituted (η^3-allyl)PdL_2 complex. However, the electronic effects induced by the functional groups and ancillary ligands on the structure and stability of the allyl−palladium complexes remained largely unstudied. The above experimental findings show that electronegative β-substituents exert peculiar electronic effects on the structure of the allyl−palladium complexes and can also govern the regiochemistry in the nucleophilic addition reactions. The present study was undertaken to investigate these electronic effects by discussing the following questions:

(1) What conformational and stereoelectronic requirements have to be fulfilled to have the most effective interactions between the C4−X bond and palladium?

(2) What is the relationship between the intensity of the interactions and electronic properties of X?

(3) How do the interactions between the C4−X bond and palladium influence the geometry and the thermodynamic and kinetic stability of the complexes?

(4) How does the π-acceptor/σ-donor character of the ancillary ligands modify the interactions between the C4−X bond and palladium?

(5) What predictions can be made for the regiochemistry of the nucleophilic attack?

In order to answer these questions, ab initio calculations were carried out for simple model systems **1**−**7** (Figure 1) in which the β-substituents (X = Cl, OCH$_3$, H) have the basic electronic effects of those functionalities that usually occur in the allyl−palladium intermediates of palladium catalyzed transformations. The effects of the ancillary ligands on the structure and stability of substituted (η^3-allyl)palladium complexes were studied by employing σ-donor (L = Cl$^-$, F$^-$) and π-acceptor (L = PH$_3$) ligands on palladium. It should also be mentioned that alkyl- and aryl-substituted derivatives of **1-5** and **7** are actual intermediates of palladium-catalyzed allylic substitutions and bis-oxidation of conjugated dienes.

2. Computational Methods

The geometries of **1-7** were optimized employing second order Møller−Plesset (MP2) perturbation theory.[48] All electrons, for which the MOs are described by basis functions, were correlated. For hydrogens the primitive (4s)[49] basis was used contracted to [2s]. For carbon, fluorine, phosphorus, and chlorine atoms the (9s,5p) basis of Huzinaga[49] was used, augmented with one d-function[50] and contracted to [3s,2p,1d], with the phosphorus and chlorine core replaced by an ECP.[51] For palladium a relativistic ECP according to Hay and Wadt[52] was used; the semicore 4s and 4p orbitals were described by a single-ζ contraction; the valence 5s and 5p orbitals were described by a double-ζ basis; and the 4d orbital by a triple-ζ basis that finally gave a LANL2DZ basis augmented with a diffuse d-function. The whole basis set is referred to as basis set A.[53] Single-point calculations with MP2/A geometries have been carried out at a higher level of theory, namely at third-order MP (MP3) and fourth-order MP (MP4), where in the later case single (S), double (D), and quadruple (Q) excitations have been included (MP4SDQ). In the single-point calculations the inner shells were excluded from the correlation energy calculations and basis set A was extended. For phosphorus and chlorine the (11s, 7p, 1d)/[4s, 3p, 1d] basis set from Huzinaga[50,54,55] was used and the basis set of palladium was augmented with a (3f)/[1f] polarization function. This basis set is referred to as basis set B,[56] and the single point calculations are denoted by MP3/B//MP2/A and MP4SDQ/B//MP2/A.

3. Results and Discussion

The MP2/A geometrical parameters and C−Cl force constants of molecules **1**−**7** calculated in this work are summarized in Figure 1. In Tables 1 and 2 the conformational energies and the Mulliken analysis of the MP2/A response density are given.

Geometry and Conformational Energy of Chloro Complex 1a. Full geometry optimization of the β-chloro substituted complex leads to equilibrium structure **1a**, which shows some remarkable geometrical features. The C4−Cl bond (1.83 Å), which is antiperiplanar to the Pd−C3 bond ($\tau = 170°$), is longer by 0.04 Å than the calculated C−Cl bond length in CH$_3$Cl (1.79 Å, MP2/A). Bonding between palladium and the allylic carbons is also influenced by the chloro substituent. The Pd−C1 and Pd−C2 bond lengths in **1a** and in the unsubstituted[46] [(η^3-allyl)-PdCl$_2$]$^-$ complex are similar; however, the Pd−C3 bond is somewhat shorter, i.e., the more substituted allylic terminus is closer to the palladium than the less substituted one. This is surprising in view of the fact that in allyl−metal complexes there is a considerable repulsion between the metal atom and the *anti* functionality.[46,57] Furthermore, there is another steric factor that is expected to destabilize the antiperiplanar conformation. The nonbonding distance between the *anti* hydrogen on C1 (H1$_a$) and one of the hydrogen atoms on C4 (H4′) is 2.18 Å (Figure 1, Scheme 1), which is shorter than the sum of the van der Waals radii of hydrogen atoms[58] (2.40 Å).

When the Cl substituent of **1a** is replaced by a H (**2a**) the Pd−C3 bond is lengthened by 0.01 Å. Changing the Pd−C4 distance is also interesting. As one goes from **2a** (2.98 Å) to **1a** (2.89 Å) the Pd−C4 distance decreases by 0.09 Å. The C3−C4 distance is also shorter by 0.016 Å in **1a** (1.500 Å) than in **2a** (1.516 Å). These geometrical features are indicative of electronic interactions between C4(−Cl) and Pd, which thermodynamically stabilize the antiperiplanar conformation in **1a**.

Rotational potential of **1a** is obtained by freezing the Pd−C3−C4−Cl dihedral angle (τ) to different values ($\tau = n\cdot30°$, n = 1, 2, ..., 12) and reoptimizing all the other geometrical parameters at the MP2/A level (Figure 2). Since MP2 tends to overestimate[59] the stabilization energy of those types of electronic interactions, which are effective between C4−Cl bond and palladium (*vide infra*), the energies have also been checked at the MP3 and MP4SDQ levels of theory. However, the conformational energies calculated at the different levels of theory are rather similar (cf. Table 1), and they do not show oscillating values at different orders of perturbation theory, as do for example the bond dissociation energies of first row transition metal complexes.[60−62] The rotation potential shows

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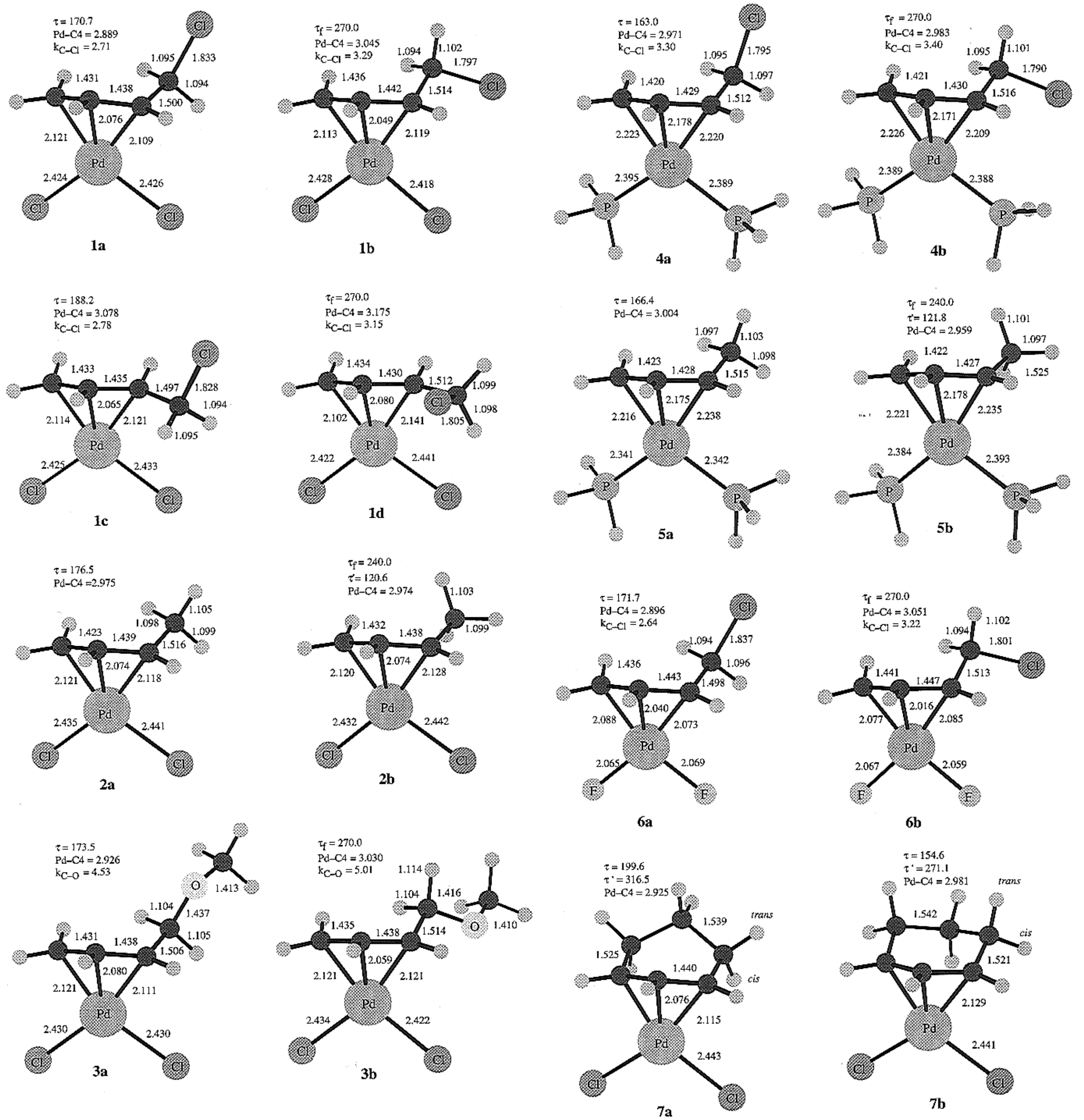


Figure 1. MP2/A geometries and C4−X force constants (k_{C-X}) of **1**−**7** (bond lengths in Å, angles in deg, force constants in mdyn/Å); τ denotes the Pd−C3−C4−X dihedral angle (see also Newman projection in Figure 2); τ_f indicates that this dihedral angle is frozen; k_{C-X} values are calculated at the MP2/A level of theory and scaled by 0.9.

a deep minimum around $\tau = 170°$, plateaus in regions of $60° < \tau < 90°$ and $240° < \tau < 300°$ ($-120° < \tau < -60°$), and a slight increase in the region of $60° < \tau < 300°$ ($60° < \tau < -60°$). The plateau in the region of $60° < \tau < 90°$, when Cl is on the Pd−C2 side, is lower by about 1 kcal/mol than in the $240° < \tau < 300°$ region. When Cl approaches the metal ($60° < \tau < -60°$), the energy further rises indicating that direct complexation of the chloro substituent by the palladium is thermodynamically destabilizing. The overall rotational barrier is about 10 kcal/mol, which is certainly not enough to effectively hinder the rotation through the C3−C4 bond, but it can be assumed that the antiperiplanar form would be the most populated conformation at room temperature.

As mentioned above, the C4−Cl bond is remarkably long in the equilibrium conformation of **1a**. Weakening of the C4−Cl bond is also reflected by its low stretching force constant ($k_{C-Cl} = 2.71$ mdyn/Å), which is smaller than the C-Cl stretching force constant in CH_3Cl ($k_{C-Cl} = 3.48$ mdyn/Å, MP2/A) by about 22%. The C4−Cl bond strength is also a function of τ (Figure 3). The C4−Cl force constant is the smallest in the antiperiplanar conformation (**1a**) and largest when $\tau = 270°$ (−90°, 3.29 mdyn/Å, **1b**). Interestingly, the C4−Cl bond is the weakest in the equilibrium conformation, hence the electronic interactions thermodynamically stabilize the kinetically least stable conformation. As one goes from $\tau = 270°$ to 330° the C4−Cl force constant decreases again indicating direct coordination of the Cl substituent by Pd, which, however, raises the total energy. Clearly, the intensity of the interactions between palladium and the C4−Cl bond in **1a** is determined by stereoelectronic effects. These interactions are strongest in the antiperiplanar equilibrium

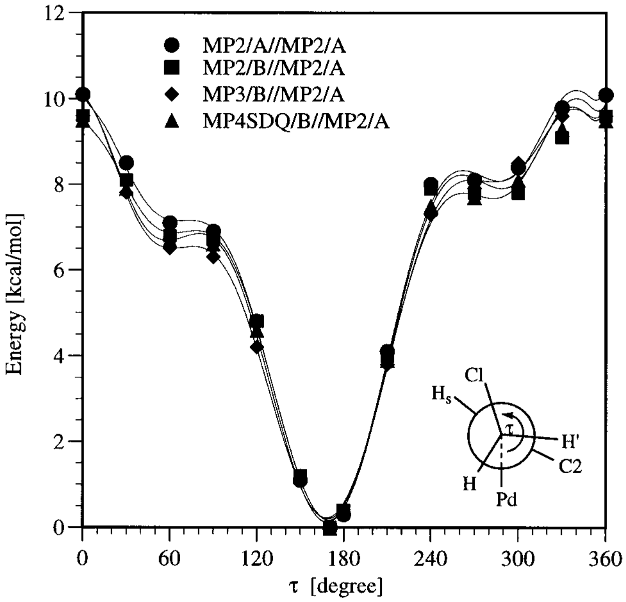


Figure 2. Rotation potential of **1a** as a function of τ.

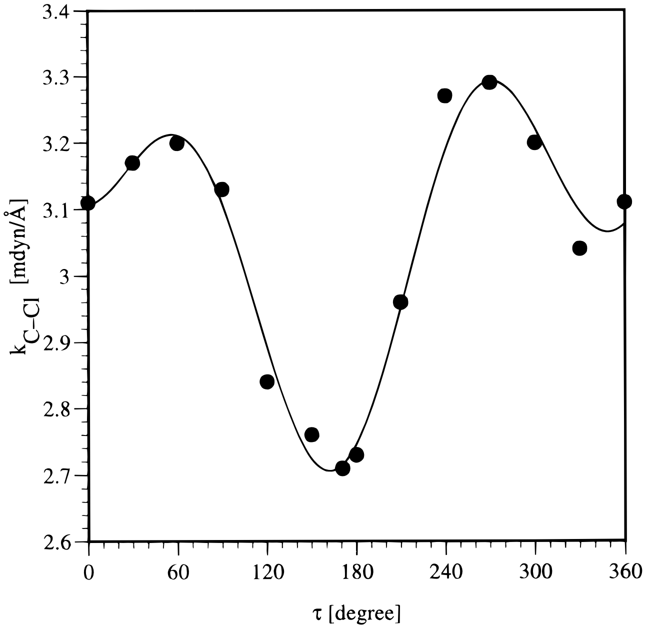
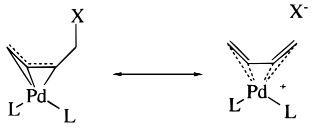


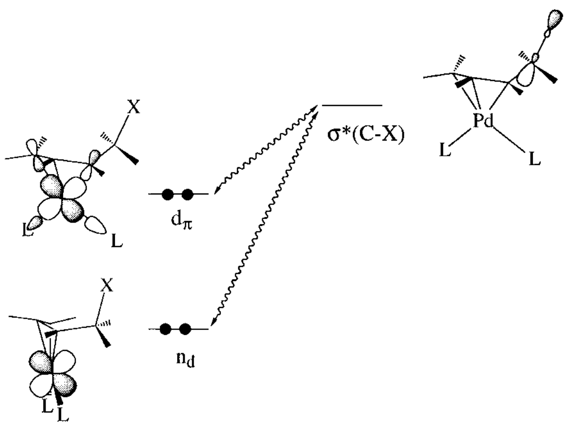
Figure 3. Stretching force constant (k_{C-Cl}) of **1a** as a function of τ.

Scheme 3



conformation (**1a**) and weakest when $\tau = 270°$ (**1b**). When τ is changed from 170° (**1a**) to 270° (**1b**) the C3−C4 bond is elongated by 0.014 Å, Pd−C1 and Pd−C3 bonds are equalized, the Pd−C4 distance is lengthened by 0.16 Å, and the C4−Cl distance is shortened by 0.04 Å.

Scheme 4



Considering the structural differences between **1a**, **1b**, and **2a**, the electronic interactions induced by the chloro substituent in **1a** can be attributed to a partial coordination of C4 to the palladium atom. A qualitative description of these interactions is given in Scheme 3 in terms of resonance structures and in Scheme 4 using MO formalism. Accordingly, partial coordination of C4 to palladium lends C1−C4 similarity to the *s-cis* butadiene (Scheme 3). Charge transfer from a high-lying palladium−allyl bonding orbital (d_π) and a properly positioned lone pair orbital of palladium (n_d) into the σ^*(C−Cl) orbital leads to weakening and elongation of the C−Cl single bond in **1a** (Scheme 4, X = Cl). Overlap between σ^*(C−Cl) and d_π increases C3−C4 bonding, which leads to shortening of the C3−C4 bond. Interaction between n_d and σ^*(C−X) leads to partial coordination of C4 to palladium (cf. orbital interactions in (η^4-butadiene)palladium complexes[63]), and therefore shortening of the Pd−C4 distance. Shortening of the Pd−C3 bond is the result of conflicting steric and electronic interactions. Electronic interactions between σ^*(C−Cl) and d_π, as well as steric repulsion between H4, H4′, and palladium, would weaken the Pd−C3 bond, but these effects are compensated by the attractive interactions between σ^*(C−Cl) and n_d. In Scheme 4 the interacting lone-pair orbital of palladium is represented by a d_{yz} type of orbital, which is most favorably situated for overlap with the σ^*(C−X) level. However, when the conjugated diene character of C1−C4 is considerably increased due to enhanced β-substituent effects, the orbital overlap between σ^*(C−X) and other types of lone pair orbitals, such as d_{z^2}, will be significantly improved[63] leading to additional thermodynamic stabilization.

The conjugative interactions can be completely shut off upon rotation to the **1b** form in which d_π, n_d, and σ^*(C−Cl) are orthogonal. This conformational change rises the total energy by 8 kcal/mol; however, this energy difference is only a lower limit for the overall interaction energy, since on rotation of the CH_2Cl group (**1b**) the C−H′ bond occupies a favorable position for interaction with palladium (Pd−C3−C4−H′ = 153.4°). This is reflected by the slight lengthening of the C−H′ bond. A similar effect can be observed in **2a**, where the C4−H bond (1.105 Å), which is antiperiplanar to the Pd−C3 bond, is slightly longer than the other two C4−H bonds (1.098 and 1.099 Å).

***β*-Substituent Effects.** When the methyl group of **2a** is rotated by 60° (**2b**) the total energy rises by 2.7 kcal/mol. Accordingly, **2b** is destabilized, despite the fact that upon rotation, the H1s-H4' distance in **2a** (2.2 Å) is increased by 0.5 Å (H1s−H4′ = 2.72 Å in **2b**), which relieves the nonbonding strain. Although interactions between d_π, n_d, and σ^*(C−H) are considerably weakened in **2b**, due to unfavorable orbital overlap, they do not vanish completely, which is indicated by a slightly elongated C4−H bond (1.103 Å). Recognition of the weak electronic interactions between the C4−H bond and palladium in **2a** is of relevance for a better understanding of the regiochemistry of the nucleophilic addition to alkyl-substituted (η^3-allyl)Pd complexes, since in these reactions methyl and alkyl groups have usually been considered as solely "steric factors".

The CH_2OCH_3 and CH_2OR functionalities frequently occur in (η^3-allyl)palladium intermediates of synthetically useful

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[63] Sautet, P.; Eisenstein, O.; Nicholas, K. M. *Organometallics* **1987**, *6*, 1845.

Table 1. Calculated Energies of Molecules **1**−**7**[a]

	L	X	MP2/A// MP2/A	MP2/B// MP2/A	MP3/B// MP2/A	MP4SDQ/B// MP2/A
1a	Cl^-	Cl	0	0	0	0
1b	Cl^-	Cl	8.1	7.8	7.9	7.7
1c	Cl^-	Cl	−1.7	−1.5	−1.5	−1.5
1d	Cl^-	Cl	2.7	3.0	2.3	2.7
2a	Cl^-	H	0	0	0	0
2b	Cl^-	H	2.5	2.6	2.2	2.4
3a	Cl^-	OCH_3	0	0	0	0
3b	Cl^-	OCH_3	6.8	6.9	6.8	6.7
4a	PH_3	Cl	0	0	0	0
4b	PH_3	Cl	−1.7	−1.9	−2.1	−1.9
5a	PH_3	H	0	0	0	0
5b	PH_3	H	1.3	1.3	1.3	1.4
6a	F^-	Cl	0	0	0	0
6b	F^-	Cl	7.2	7.0	7.2	7.0
7a	Cl^-	H	0			
7b	Cl^-	H	0.3			

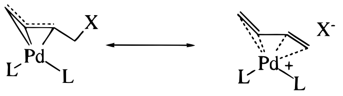
[a] All energies in kcal/mol.

transformations.[27,32,64,65] Similar to **1a**, the geometry of **3a** shows some peculiar features: (a) antiperiplanar Pd−C3−C4−O conformation; (b) asymmetric allyl−palladium bonding; (c) a short C3−C4 bond (1.506 Å); (d) a long C4−O bond (1.437 Å); and (e) a relatively short Pd−C4 distance (2.93 Å). When τ is locked at 270° (**3b**), the allyl−palladium bonding is symmetrized, C3−C4 (1.514 Å) and Pd−C4 (3.03 Å) are elongated, and the C−O (1.416 Å) bond is shortened. As one goes from **3a** to **3b** the total energy rises by 6.7 kcal/mol and the C4−O force constant is increased by 11%. These structural features in **3a** can be attributed to conjugative interactions between the C4−O bond and palladium, which are apparently of the same character, as was described for the C4−Cl−palladium interactions in **1a**.

From the above examples (X = Cl, H, OCH_3) it appears that the intensity of the electronic interactions between C4−X and Pd also depends on the nature of the β-substituent X. Since the σ*(C−X) energy level is diminished upon β-substitution by Cl and OCH_3,[66] the energy gap between n_d, d_π, and σ*(C−X) levels is reduced (Scheme 4), thereby the stabilizing MO interactions are enhanced.

Configurational Effects. In **1a**, **2a**, and **3a** the CH_2X functionalities are in the *anti* position that occurs in cyclic (η^3-allyl)palladium complexes (eg. eq 4). In acyclic systems, however, the *syn* configuration is also possible. Although the *syn* configuration (**1c**) is sterically more favorable than the *anti* configuration (**1a**), since in **1c** the H1s−H4′ nonbonding strain is absent, **1c** is only 1.5 kcal/mol more stable than **1a**. Some structural features of **1c** are similar to those of **1a**: (a) the Pd−C3 and C−Cl bonds are in an antiperiplanar position; (b) the C3−C4 bond is short (1.497 Å); and (c) the C4−Cl bond (1.828 Å) is relatively long. However, the PdC3 bond and PdC4 distance are longer by 0.01 and 0.19 Å, respectively, also k_{C-Cl} is somewhat larger in **1c** (2.78 mdyn/Å) than in **1a** (2.71 mdyn/Å). When the CH_2Cl group in **1d** is rotated to $\tau = 270°$, PdC3, PdC4, and C3C4 are lengthened, while C4−Cl is shortened, as was the case for the **1a** → **1b** rotation. However, the conformational energy change for the *syn* complex (4.2 kcal/mol) is lower by 40% than that for the *anti* complex (7.7 kcal/mol). These findings indicate that in the *syn* complex (**1c**) the β-substituent effects are considerably weaker than in the *anti* complex (**1a**).

Scheme 5



Conjugative interactions between the C−Cl bond and Pd can be described by the resonance structures given in Scheme 5. Accordingly, partial coordination of C4 to palladium lends C1−C4 similarity to the *s-trans* butadiene. The interaction between the d_π and σ*(C−Cl) orbitals is probably as effective as in the *anti* complex (**1a**). However, due to the twisted structure of the allyl moiety,[45,46,57] the palladium−C4 distance is longer, and therefore, the overlap between n_d and σ*(C−Cl) is less favorable in a *syn* than in an *anti* configuration. As a consequence, the structure and stability of the antiperiplanar *syn* complex is less affected by the β-substituent effects than the antiperiplanar *anti* complex.

The nonbonding strain in the η^3-coordinated *anti* complexes could also be relieved by migration of the PdL_2 fragment on the allyl moiety leading to a stable η^1-coordinated species. However, such an $\eta^3 \rightarrow \eta^1$ conversion is unlikely in the investigated complexes, since it implies breaking of two Pd−C bonds, which is more destabilizing than a H1s−H4′ type nonbonding strain.[67] According to a very recent study by Sakaki and co-workers[47] an (η^1-allyl)PdL_2 complex is converted to its (η^3-allyl)PdL_2 counterpart without an activation barrier even in such cases when the ligand effects are expected to facilitate the $\eta^3 \rightarrow \eta^1$ conversion. Furthermore, so far solely the η^3-coordinated form of the parent or substituted **1**−**5** and **7** complexes has been directly detected by X-ray and NMR measurements.[32,35−37,41,68−75]

Ligand Effects. Phosphine ligands are often used to activate (η^3-allyl)palladium complexes toward nucleophilic attack. The σ-donor/π-acceptor character of a phosphine ligand is determined by the nature of substituents attached to the phosphorus atom.[76−78] In **4** and **5** the phosphine ligands are modeled by PH_3, which is considered as a fairly strong π-acceptor.[77,78] Replacement of chloride ligands with phosphines (**4a**) leads to lengthening of the palladium−carbon bonds, which can be attributed to the π-acceptor character of PH_3.[46] Although the antiperiplanar conformation represents a minimum on the potential energy surface, its geometry reflects very weak (if any) interactions between the β-chloro substituent and palladium. The C3−C4 bond and Pd−C4 distance are longer, while the C4−Cl bond is considerably shorter in **4a** than in **1a**. The C−Cl stretching force constants in **4a** (3.30 mdyn/Å) and in CH_3Cl (3.48 mdyn/Å) are rather similar. Rotation of the CH_2Cl group to $\tau = 270°$ decreases the total energy by 1.9 kcal/mol. This shows that in **4b** loss of the weak conjugative interactions is

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Table 2. Mulliken Charges Calculated from the MP2/A Density[a]

	X	q_{total}	q(C1H$_2$)	q(C2H)	q(C3H)	q(C$_4$H2)	q(X)	q(allyl)[b]
1a	Cl	−1.000	−0.024	0.049	0.109	0.098	−0.194	0.134
1b	Cl	−1.000	−0.036	0.021	0.091	0.057	−0.130	0.076
1c	Cl	−1.000	−0.012	0.035	0.125	0.082	−0.198	0.148
1d	Cl	−1.000	−0.018	0.041	0.084	0.094	−0.169	0.107
2a	H	−1.000	−0.040	0.025	0.104	−0.227	0.204	0.089
2b	H	−1.000	−0.020	0.008	0.106	−0.247	0.231	0.094
3a	OCH$_3$	−1.000	−0.035	0.044	0.057	0.169	−0.158	0.066
3b	OCH$_3$	−1.000	−0.040	0.014	0.057	0.139	−0.121	0.031
4a	Cl	1.000	0.065	0.194	0.111	−0.059	−0.060	0.370
4b	Cl	1.000	0.061	0.164	0.106	0.135	−0.080	0.331
5a	H	1.000	0.051	0.173	0.111	−0.203	0.283	0.335
5b	H	1.000	0.071	0.159	0.123	−0.189	0.270	0.353
6a	Cl	−1.000	−0.064	0.014	0.088	0.083	−0.203	0.038
6b	Cl	−1.000	−0.076	−0.016	0.066	0.051	−0.143	−0.026

[a] Charges in electron. [b] Group charge on the C1H$_2$−C2H−C3H fragment.

overruled by the steric stabilization due to relief of the H1s−H4′ nonbonding strain. Coordination of π-acceptors, such as in **4a**, involves charge transfer from the metal to the ligand through back-donation that leads to orbital contraction and therefore lowering of the n$_{\mathrm{d}}$ level. Decreasing the energy of n$_{\mathrm{d}}$ causes the energy gap between n$_{\mathrm{d}}$ and σ*(C−Cl) to increase, which leads to weakening of the orbital interactions.

Since the nonbonding distances between the ligands and the chloro substituents in **1b** (**1a**) and **4b** (**4a**) are rather long (>4.0 Å), the steric environment of the chloro substituent is about the same. Consequently, the difference between the conformational energy changes for **1a** → **1b** (7.7 kcal/mol) and **4a** → **4b** (−1.9 kcal/mol) processes can be attributed to the variation of the electronic interactions. Accordingly, the electronic interactions induced by the antiperiplanar β-chloro substituent provide a stabilization energy that is larger by 9.6 kcal/mol in **1a** than in **4a**. A much weaker but similar tendency can be observed for the methyl−allyl complexes **2a** and **5a**. Rotation of the methyl functionality by 60° destabilizes **2a** (2.4 kcal/mol) more than **5a** (1.4 kcal/mol) by 1 kcal/mol.

Variation of the stabilization energy as a function of the ligands and the antiperiplanar β-substituents can also be calculated by isodesmic and isosteric eq 6. Accordingly, replacement of PH$_3$ ligands in the chloromethyl substituted **4a** with chloride ligands of the methyl substituted complex **2a** is an exothermic process with $\Delta E = -10.1$ kcal/mol (MP4SDQ/B//MP2/A calculations) ($\Delta E = -10.4$ kcal/mol, MP2/A; −10.0 kcal/mol, MP2/B//MP2/A; −9.9 kcal/mol, MP3/B//MP2/A).

$$E(\mathbf{2a}) + E(\mathbf{4a}) = E(\mathbf{1a}) + E(\mathbf{5a}) + \Delta E \qquad (6)$$

The isodesmic energy (eq 7) calculated for the corresponding complexes, in which the interactions between C−X and palladium are suppressed, is considerably lower: $\Delta E = -1.6$ kcal/mol (MP4SDQ/B//MP2/A calculations) ($\Delta E = -1.7$ kcal/mol, MP2/A; −1.6 kcal/mol, MP2/B//MP2/A; −0.6 kcal/mol, MP3/B//MP2/A).

$$E(\mathbf{2b}) + E(\mathbf{4b}) = E(\mathbf{1b}) + E(\mathbf{5b}) + \Delta E \qquad (7)$$

The above discussion also illustrates an important feature of allyl−palladium chemistry, namely that activation of (η^3-allyl)palladium complexes toward nucleophilic attack, by replacement of both σ-donor ligands with π-acceptors on palladium, also implies a substantial reduction of the β-substituent effects on the asymmetric electron distribution of the allyl moiety.

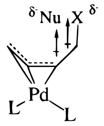
The presence of fluoride ligands on palladium (**6a**) leads to strong and relatively short bonds between the allyl moiety and the metal.[46] Increase of the σ-donor ability of the ligands leads to small but significant weakening of the C4−Cl bond as shown by the C4−Cl bond lengths and C4−Cl stretching force constants in **6a** (1.837 Å, 2.64 mdyn/Å) and in **1a** (1.833 Å, 2.71 mdyn/Å). However, on rotation of the CH$_2$Cl group to $\tau = 270°$ (**6b**) the total energy rises only by 7 kcal/mol, which is less by 0.7 kcal/mol than the conformational energy change in the **1a** → **1b** process. Due to the shorter Pd−allyl distances, the non-bonding repulsion between H4 , H4′, and the metal is probably stronger in **6a** than in **1a**. Consequently, replacement of chloride ligands by fluoride ligands leads to a slight decrease of both the thermodynamic and the kinetic stability of β-chloro substituted (η^3-allyl)palladium complexes.

Mulliken Analysis of the Electron Density. Inspection of the data in Table 2 reveals that the more substituted allyl terminus (C3) always bears more positive charge than the less substituted one (C1), which is due to the electron withdrawing character of the CH$_2$X functionalities. The β-substituent effects in **1a**, **1c**, **3a**, and **6a** lead to accumulation of the negative charge on the X substituent and increase of the positive charge on the allylic fragment, which can be attributed to the charge transfer from the d$_\pi$ and n$_{\mathrm{d}}$ orbitals to σ*(C−Cl). In the methyl−allyl complex **2a** the antiperiplanar H atom ($\tau = 177°$) bears less positive charge than the corresponding H atom in **2b** ($\tau = 240°$). When chloride ligands are replaced by phosphines the charge on the antiperiplanar Cl and H substituents drops by 0.13 electrons (q(Cl) = −0.19 in **1a**, and −0.06 in **4a**) and by 0.08 electrons (q(H) = 0.20 in **2a**, and 0.28 in **5a**), respectively. This also indicates that in the presence of π-acceptor ligands the charge transfer from the palladium and allyl fragment to the C−X bond is considerably diminished.

4. Relevance of This Study in the Chemistry of *β*-Substituted (*η*^{3}-Allyl)palladium Complexes

Displacement of the X Substituent. The structure and properties of the chloro dimer of **1a** (bis[4-Cl-(1−3-η^3)-butenyl)-PdCl]) were first reported by Robinson and Shaw.[68] These authors observed a remarkable high reactivity for the β-chloro substituent, which could be replaced by a methoxy group, providing the chloro dimer of **3a**, simply by dissolving the complex in methanol. This finding can be easily explained on the basis of the above theoretical results. Because of the β-substituent effects, negative charge is transferred from palladium to the antibonding σ*(C4−Cl) orbital, which facilitates the heterolytic cleavage of the C−Cl bond. The methoxy substituent is also involved in β-substituent interactions; however, the C4−O bond is weakened to a smaller extent than the C−Cl bond (cf. $k_{\mathrm{C-Cl}} = 2.71$ mdyn/Å in **1a**, and $k_{\mathrm{C-O}} = 4.53$ mdyn/Å in **3a**), and therefore the methoxy-substituted complex is kinetically more stable than the chloro-substituted complex.

Scheme 6



Kinetic instability of the β-chloro substituted allyl−palladium complexes is the reason for the high chemoselectivity in the palladium catalyzed acetoxychlorination[27,33] and oxychlorination[8,64] of conjugated dienes. In these bis-oxidation reactions (eqs 2 and 4) O-substituted (η^3-allyl)palladium complexes are formed preferentially in the first addition step, even in the presence of a chloride nucleophile.

Regioselectivity of the Nucleophilic Attack. Partial coordination of C4 to the palladium is an important structural consequence of the β-substituent effects. The presence of somewhat similar interactions has previously been suggested for certain allyl−molybdenum complexes[79,80] but not for allyl−palladium complexes, and probably therefore, these effects have not received enough attention in allyl−palladium chemistry. In the absence of β-substituent and sizable steric effects the (η^3-allyl)palladium fragment possesses local C_s symmetry and, therefore, in an orbital-controlled process the external nucleophile will attack one of the allylic termini with a relatively low regiopreference. However, in the presence of strong β-substituent effects, such as in **1a**, **3a**, and **6a**, the π-electron acceptor MO σ^*(C4−X) polarizes the electron distribution of the allyl fragment in such a way that the electronic structure of the complex lends similarity to that of a (η^4-butadiene)palladium complex.[63] As a consequence, the more substituted allylic terminus will resemble the C2 (internal) position of a diene−palladium complex, which is unreactive toward an initial nucleophilic attack.[63,81,82] Because of the accumulation of the negative charge on X (Table 2) another effect will emerge, namely repulsive electrostatic interactions between the polarized antiperiplanar C−X bond and the incoming electron-rich nucleophile (Scheme 6). These electrostatic interactions are weaker when the remote allylic terminus (C1) is attacked by the nucleophile.

The increased regioselectivity of the nucleophilic attack on (η^3-allyl)palladium intermediates, in which OH, OR, OAc, OCOR, NR_2, or NO_2 β-substituents are present,[2,30−35] can be explained on the basis of the above discussion. Lowering the energy of the σ^*(C4−X) MO by these electron withdrawing X substituents diminishes the energy gap between d_π, n_d, and σ^*(C4−X) levels, thereby the β-substituent interactions are amplified. The β-substituent effects in (η^3-allyl)palladium complexes are related to other well-known electronic interactions, which determine the structure and reactivity of certain carbohydrates, steroids, and other natural products. The d_π−σ^*(C4−X) interactions are basically similar to the anomeric effects,[66,83−86] while the n_d−σ^*(C4−X) interactions can be regarded as homoconjugation.[59,66,87,88] A high selectivity in the palladium-catalyzed allylic substitution and bis-oxidation of conjugated dienes can be attributed to the simultaneous action of these electronic effects provided by the (η^3-allyl)palladium framework of the reaction intermediate.

When C1−C4 is encompassed in a six membered ring, the CH_2X functionality is in an *anti* position, while in acyclic systems it is preferentially in a *syn* position. The higher regioselectivity found[33,34] for β-substituted cyclic (η^3-allyl)palladium intermediates can also be explained by the fact that the β-substituent effects are more extensive for *anti* complexes, such as **1a**, than *syn* complexes, such as **1c**. However, there is a further important effect, which is encountered for cyclic systems. Because of the conformational rigidity of the cyclohexenyl−allyl moiety the six-membered ring can only adopt boat and chair conformations,[73,89] such as in **7a** and in **7b**, respectively. The energy difference between the two conformers is rather small (0.3 kcal/mol). The *trans* H4 atom is positioned at the face opposite to the palladium with Pd−C3−C4−H4(*trans*) dihedral angles (τ) of 200° (**7a**) and 155° (**7b**). Consequently, in cyclic intermediates the *trans* β-substituent is biased into a conformation ($150° > \tau > 200°$) in which strong electronic interactions with palladium are expected (cf. Figure 2). On the contrary, the *cis* β-substituent is less available for such interactions, since Pd−C3−C4−H4(*cis*) dihedral angles (τ') are 317° and 271° in **7a** and in **7b**, respectively (cf. Figure 2). Bäckvall and coworkers[27] provided direct experimental evidence for the presence of a *trans* β-substituent in the cyclic allyl−palladium intermediate of the bis-oxidation of conjugated dienes. In view of the theoretical calculations, it is easy to understand the high regioselectivity, which is observed in these reactions (eq 4). In fact, because of the remarkable high degree of regioselectivity, these transformations are usually called 1,4-oxidation of conjugated dienes.

Replacement of σ-donor ligands with π-acceptors reduces the intensity of the β-substituent effects, and therefore the regioselectivity is also decreased. This can explain the dependence of the regiochemistry on the ligand effects observed for nucleophilic additions to η^3-(3-methylbutenyl)palladium complexes (eq 5).[37] There are also several examples for the decrease of regioselectivity in bis-oxidation of conjugated dienes, which is probably due to ligand effects.[22,31,33,34,65] Since those ancillary ligands (i.e. π-acceptors) that activate the (η^3-allyl)palladium complexes toward nucleophilic attack also decrease the intensity of the β-substituent effects, the reaction conditions have to be chosen carefully when a high degree of regioselectivity is desired. The best compromise is to employ bidentate ligands with a σ-donor and a π-acceptor functionality. If β-substituent effects apply, the σ-donor functionality would preferentially occupy a *trans* position to the more substituted allylic terminus in order to maximize the stabilization effects. Such combined β-substituent−ancillary ligand effects can be exploited to enhance the enantioselection in asymmetric catalysis. In fact, in a recent publication Pfaltz and Pregosin and co-workers[90] postulated a new mechanism which suggests that the enantioselectivity in the allylic substitution reactions is determined by the regioselectivity of the nucleophilic attack at the (η^3-allyl)palladium intermediate.

5. Conclusions

This study describes and characterizes a new type of electronic interaction, which occurs between the allylic β-sub-

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stituents (X) and palladium atom in allyl−palladium complexes. These interactions influence (a) the structure of (η^3-allyl)-palladium complexes, (b) the kinetic and thermodynamic stability of these species, and (c) the regiochemistry of the nucleophilic attack on the allyl moiety.

The structural changes can be summarized as follows: (1) antiperiplanar Pd−C3 and C4−X bonds; (2) elongation of the C4−X bond; (3) shortening of the C3−C4 bond; (4) shortening of the Pd−C3 bond; (5) shortening of the Pd−C4 distance; and (6) charge accumulation on the X substituent.

The β-substituent effects thermodynamically stabilize the (η^3-allyl)palladium complexes by up to 8−10 kcal/mol. Weakening of the C−X bond, as shown by the C−X stretching force constants, facilitates its heterolytic fission, and therefore the β-substituent effects lead to a decrease of the kinetic stability of the complexes.

The β-substituent effects induce asymmetric electron distribution on both the allylic fragment and the C−X bond, which makes the less substituted allylic terminus more reactive toward nucleophilic attack.

The β-substituent effects can be enhanced by (1) employing such X substituents that effectively lower the energy of the σ^*(C−X) orbital (e.g., OR, OCOR, NR_2, NO_2, etc.), (2) enforcing the C4−X and Pd−C3 bonds to an antiperiplanar position, (3) enforcing an *anti* configuration for the CH_2X functionality, and (4) employing at least one σ-donor or two moderately π-acceptor ligands on palladium.

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Supporting Information Available: Tables of calculated geometries for **1a**−**d**, **3a**,**b**, **4a**,**b**, **5a**,**b**, **6a**,**b**, and **7a**,**b** (12 pages). See any current masthead page for ordering and Internet access instructions.

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