Insertion Aptitudes and Insertion Regiochemistry of Various Alkenes Coordinated to Cationic (σ-R)(diimine)palladium(II) (R = $-CH_3$, $-C_6H_5$). A Theoretical Study

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The coordination of a range of substituted alkenes (C_2H_3X; X = H, CH_3, t-Bu, CN, CO_2CH_3, CF_3, OCH_3, $CHCH_2$, C_6H_5, F, Cl, Br) to a cationic methyl- or phenylpalladium(II)-diimine complex and the subsequent migratory insertion into the methyl−palladium and phenyl−palladium bonds are studied using DFT calculations at the B3LYP level of theory. The focus of this investigation is on monitoring the insertion barrier and the regiochemical outcome as a function of alkene properties, with special attention to the functionalized alkene as a potential comonomer in polymerization. In general, electron-rich alkenes coordinate more strongly, whereas electron poor alkenes insert more readily. The barriers of insertion range from 4.7 to 26.5 kcal/mol, and mostly the 2,1-insertion is favored. In all cases the alkenes have a weaker coordination to the phenylpalladium(II)diimine compared to the methylpalladium(II)diimine complex and, as expected, a lower insertion barrier.

Introduction

Metal−alkyl and −aryl complexes are intermediates in a number of important metal-catalyzed reactions. The transition-metal-catalyzed polymerization of alkenes provides a wide variety of polymeric materials. The different qualities are accomplished by change of catalysts, process parameters, and comonomers. Unfortunately, the commercial catalysts of today are incompatible with functionalized comonomers. A considerable effort is therefore devoted to developing new transition-metal catalysts that tolerate functionalized alkenes with the ultimate goal of affording materials with new and highly desirable properties with respect to toughness, wetting, adhesion, blendability, and biodegradation.[1] A reason for the restriction is that most of the catalyst metals, standing to the left in the periodic table, are very oxophilic and suffer from catalyst poisoning in the presence of oxygen-containing comonomers. In this regard the less electrophilic metals to the right in the periodic table may appear more promising. Owing to recent breakthroughs, some transition metals that previously were considered unsuitable for polymerization purposes have entered the field, e.g., palladium, rhodium, and iron.[1,2] It was also shown by Brookhart that cationic diimine palladium(II) is actually able to slowly copolymerize ethylene or propylene with methyl acrylate.[3]

To elucidate the potential for copolymerization with some functionalized comonomers, we have calculated the association energy of the comonomers to a cationic (σ-R)palladium(II)diimine complex **1a** (R = $-CH_3$) and the transition barrier for either of the two possible subsequent insertion steps (Figure 1).

Complex **1a** is closely related to Brookhart's catalysts, the main difference being that the latter are carrying bulky aryl substituents at the diimine nitrogens.

We have also made calculations on the related complex **1b** (R = $-C_6H_5$), which is a model for the intermediate in the Heck reaction. The comparison with the Heck reaction is interesting for several reasons. In this reaction, β-hydrogen elimination, which must be suppressed in polymerization, is usually facile. As in polymerization, the control of regiochemistry in the Heck reaction is also of importance.[4] An understanding

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(4) See for example: Brown, J. M.; Hii, K. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 679. Ludwig, M.; Strömberg, S.; Svensson, M.; Åkermark, B. *Organometallics* **1999**, *18*, 970, and references therein.

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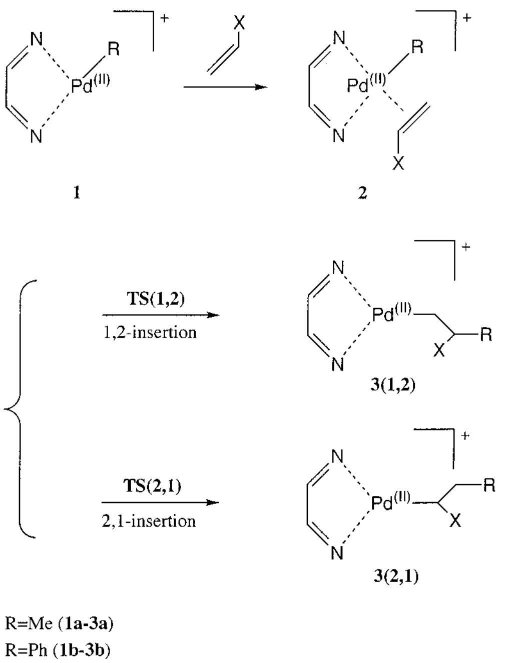

Figure 1. Regiochemical possibilities in the coordination−insertion pathway.

of the relevant factors governing the selectivity therefore deserves attention.

A theoretical approach is specifically well suited for screening and studies of trends, since calculations are not restricted by the normal limitations in the laboratory such as tedious preparations or faltering stabilities. In a calculation we can quite easily vary the substituents of ligands to measure the electronic and steric effects in a particular step in a catalytic cycle. Within this context it should be noted that calculations are commonly more reliable in studying trends than providing absolute numbers for a specific reaction, although modern calculations have shown to afford remarkably accurate figures also in absolute terms for migratory insertions.[5] Ligand effects have been studied for cationic palladium(II)diimine complexes using gradient-corrected density functional theory.[6] The main purpose of the work presented here is to monitor the transition barriers for the insertion of functionalized alkenes, coordinated to cationic methyl- or phenylpalladium(II)-diimine complexes.

Computational Details

Geometries and energies of all intermediates and transition states were fully optimized using the gradient-corrected hybrid density functional method B3LYP.[7] Stationary points have been validated by normal-mode analysis for the reaction of ethylene, methylacrylate, and methoxyethylene. The effects of zero-point corrections (ZPC) on the relative energies are less than 0.5 kcal/mol for the activation barriers and less than 0.3 kcal/mol for the regioselectivity. The absolute π-complexation energy is reduced by approximately 2 kcal/mol, but the difference between different alkenes is less than 0.8 kcal/mol. We have not included ZPC in our reported relative energies, since it does not influence the trends central to this study. We used a basis set of double-ζ valence quality labeled LANL2DZ in the Gaussian98 program.[8] For Pd the core electrons were replaced by a relativistic electron core potential (ECP) developed by Hay and Wadt.[9] For nonmetal atoms the double-ζ basis sets of Huzinaga and Dunning were assigned.[10] All relative energies were recalculated using a valence triple-ζ quality basis set at the B3LYP level. For all nonmetal atoms the 6-311G(d,p) basis set[11] was employed, and for Pd the LANL2DZ basis set was recontracted to 4s4p3d and a set of f-functions was added.[12] The atomic charges were calculated using the Merz−Singh−Kollman[13] scheme as implemented in Gaussian98.

The calculated energetics at this chosen level of approximation appear to be reliable compared to experiments. Brookhart et al. observed an enthalpy of activation for methylacrylate, 12.1 ± 1.2 kcal/mol, which compares well with our calculated energy of activation, 13.3 kcal/mol. In addition, the difference in coordination strength between ethylene and methylacrylate was experimentally measured as 4.9 ± 0.2 kcal/mol, and our calculated value is 4.5 kcal/mol. We recalculated this difference in coordination strength to 4.2 kcal/mol for the palladium(II)-diimine complex used by Brookhart et al.[14]

Results and Discussion

The relative complexation energies for 12 different alkenes coordinating to a cationic methylpalladium(II)-diimine, **1a**, and the activation energies for the subsequent insertion into the methyl−palladium bond are presented in Table 1. The corresponding energies for the phenylpalladium(II)diimine, **1b**, system are given in Table 2. The choice of the alkenes is made to span the electron-donating capacity from strongly donating (C_2H_3-OCH_3) to electron-withdrawing ($C_2H_3CF_3$). Representative structures of the π-coordinated alkenes and the two possible transition states are given in Figure 2.

π-Complexation. From Table 1 it is seen that ethylene (entry 1), propylene (entry 2), and 3,3-dimethylbutene (*tert*-butylethylene) (entry 3) differ very little in coordination ability to cationic palladium species **1a**. A parallel result is obtained for the alkene π-complexes with **1b** (Table 2; entries 13, 14, and 15). Similar

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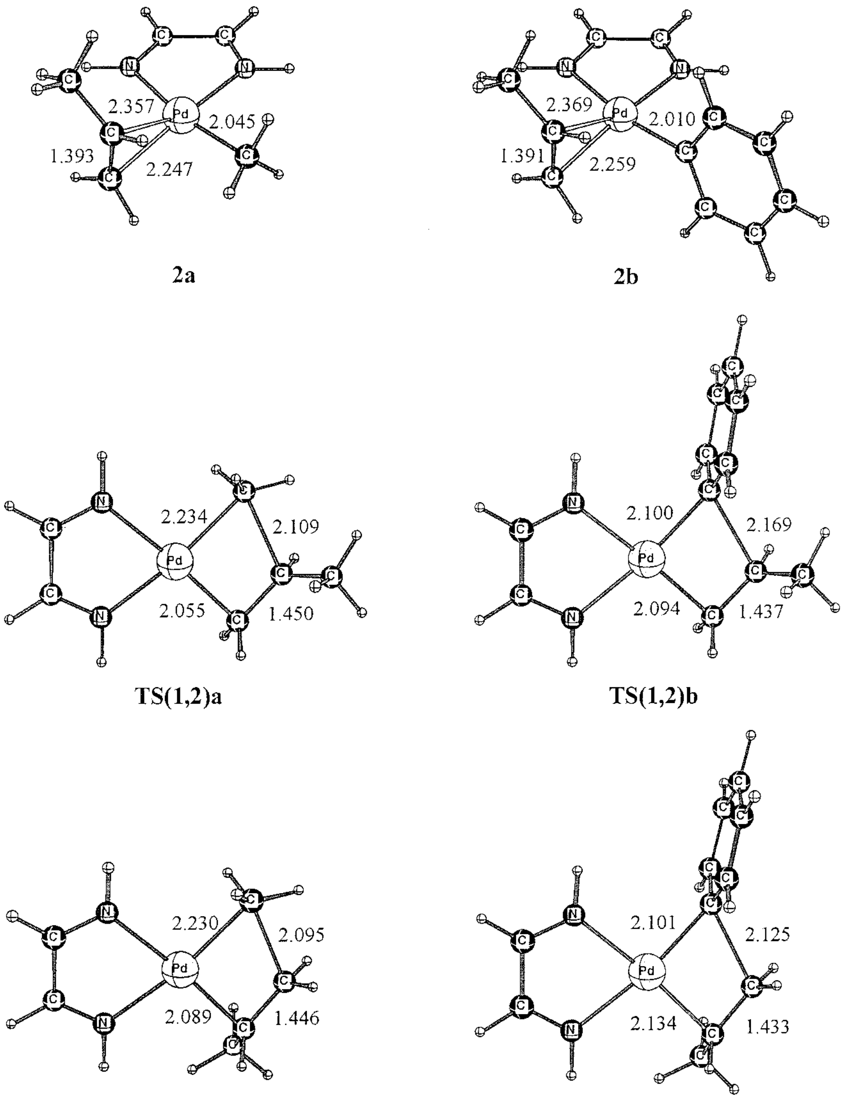

2a **2b**

TS(1,2)a **TS(1,2)b**

TS(2,1)a **TS(2,1)b**

Figure 2. Representative structures of the π-coordinated olefin species (**2**) and the two possible transition state geometries (**TS(1,2)** and **TS(2,1)**).

Table 1. Relative Energies (kcal/mol) of the Complexation and Activation Energy of Insertion of Alkenes into the Pd−Me Bond

subst.	entry	$\Delta E(\pi)^a$	$\Delta E^*(2,1)^b$	$\Delta E^*(1,2)^c$	$\Delta\Delta E^d$
H	1	−33.1	17.8	17.8	0.0
CH_3	2	−33.5	20.1	19.9	0.2
t-Bu	3	−32.8	20.4	21.4	−1.0
CN	4	−24.2	17.2	22.7	−5.4
CO_2CH_3	5	−29.3	13.3	19.7	−6.4
CF_3	6	−27.5	16.6	21.4	−4.8
OCH_3	7	−39.3	26.5	24.2	2.3
$CHCH_2$	8	−33.4	19.9	23.1	−3.2
C_6H_5	9	−36.4	20.7	23.9	−3.2
F	10	−30.2	20.0	20.0	0.0
Cl	11	−28.1	17.9	22.0	−4.1
Br	12	−28.8	17.7	22.4	−4.7

[a] $\Delta E(\pi)$ is the π-complexation energy of alkenes, forming **2a**. [b] $\Delta E^*(2,1)$ is the reaction activation energy, forming **TS(2,1)a**. [c] $\Delta E^*(1,2)$ is the reaction activation energy, forming **TS(1,2)a**. [d] $\Delta\Delta E = \Delta E^*(2,1) - \Delta E^*(1,2)$.

Table 2. Relative Energies (kcal/mol) of the Complexation and Activation Energy of Insertion of Alkenes into the Pd−Ph Bond

subst.	entry	$\Delta E(\pi)^a$	$\Delta E^*(2,1)^b$	$\Delta E^*(1,2)^c$	$\Delta\Delta E^d$
H	13	−29.1	8.8	8.8	0.0
CH_3	14	−30.1	11.6	10.9	0.7
t-Bu	15	−29.5	12.3	14.2	−1.9
CN	16	−21.9	9.1	13.6	−4.5
CO_2CH_3	17	−24.6	4.7	12.0	−7.3
CF_3	18	−24.4	7.8	13.7	−5.9
OCH_3	19	−35.8	18.1	11.5	6.6
$CHCH_2$	20	−29.9	11.2	13.9	−2.7
C_6H_5	21	−32.7	12.1	14.0	−1.9
F	22	−26.9	11.6	10.3	1.3
Cl	23	−25.0	9.7	12.8	−3.2
Br	24	−25.7	10.1	13.8	−3.7

[a] $\Delta E(\pi)$ is the π-complexation energy of alkenes, forming **2b**. [b] $\Delta E^*(2,1)$ is the reaction activation energy, forming **TS(2,1)b**. [c] $\Delta E^*(1,2)$ is the reaction activation energy, forming **TS(1,2)b**. [d] $\Delta\Delta E = \Delta E^*(2,1) - \Delta E^*(1,2)$.

observations are made for anionic trichloro palladium alkene complexes.[15] These trends suggest that steric effects are of minor importance for the palladium(II) alkene π-complexes. Of course, bulky spectator ligands may change the situation. This effect has been studied in a recent theoretical work, with various substituents (R′) at the nitrogen positions of a cationic Pd(II) diimine catalyst. For propylene, it was found that the steric

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interactions between the methyl group and R′ destabilized the π-complex significantly as the size of R′ increased.[6] For our flat diimine complexes the steric repulsion between the diimine ligand and the substituents of the π-coordinated alkene is rather small since the geometry of the π-coordination is perpendicular to the ligand plane; see Figure 2.[16]

If a metal is electron-deficient, we anticipate electron-rich alkenes to coordinate more strongly than electron-poor. Such a tendency can be observed for both complexes **1a** and **1b**. In the case of methylpalladium(II)-diimine, acrylonitrile (entry 4), methylacrylate (entry 5), and 3,3,3-trifluoropropene (entry 6) are much more weakly coordinated than ethylene (8.9, 3.8, and 5.6 kcal/mol, respectively). Conversely, electron-rich methoxyethylene (methyl vinyl ether) (entry 7) is 6.2 kcal/mol more strongly coordinated than ethylene to palladium. For phenylpalladium(II)diimine, acrylonitrile (entry 16), methylacrylate (entry 17), and 3,3,3-trifluoropropene (entry 18) coordinate more weakly than ethylene by 7.2, 4.5, and 4.7 kcal/mol, respectively. Methyl vinyl ether (entry 19) coordinates more strongly than ethylene by 6.7 kcal/mol. Hence, the relative coordinating capacity of electronically different types of alkenes is similar for **1a** and **1b**.

This tendency for different types of alkenes is in accordance with σ-donation being more important than π-back-donation in the coordination. In such a case it is reasonable to expect a relation between the energy of the π-orbital (HOMO) of the alkenes and the complexation energy; that is, the higher the HOMO, the better the bonding. Figure 3a shows this correlation clearly. For the conjugated alkenes, styrene and butadiene (entries 8 and 9), the less stable π-orbital of styrene results in a 3 kcal/mol stronger alkene−metal bond. Deviations from linearity in Figure 3a may be explained ad hoc in terms of changed conjugation between the olefinic and functional parts of the alkene and changed polarizations in the alkene upon coordination. In the π-complexes of methyl acrylate and 3,3,3-trifluoropropene a hydrogen bond to one of the imine protons stabilizes these structures a few kcal/mol. Consequently, these two alkenes bind stronger than alkenes without this hydrogen-bonding capacity (see Figure 4a). In Figure 3b the alkene complexation energy is plotted against the energy of the of the alkene π^*-orbital (LUMO). No clear correlation is observed between the two energies for these cationic palladium complexes.

As can be seen in Table 3, the geometrical variations in the C1−C2 double bond distance in the π-complex are small. The overall tendency is also consistent with complexation energies for ethylene binding to palladium displaying the general order cationic complexes > neutral complexes > anionic complexes.[17]

For clarity of presentation, Figures 3a and 3b show only the complexation energies for the cationic methylpalladium(II)diimine species. The trend for phenylpalladium(II)diimine is parallel. However, comparing values of $\Delta E(\pi)$ in Tables 1 and 2, it is seen that alkenes coordinate somewhat weaker (3−4 kcal/mol) to complex **1b** compared to **1a**. This is explained by the fact that the accepting unoccupied MO (a 5s4d-hybrid) of **1a** lies 0.4 eV lower than the corresponding MO of **1b**.[18]

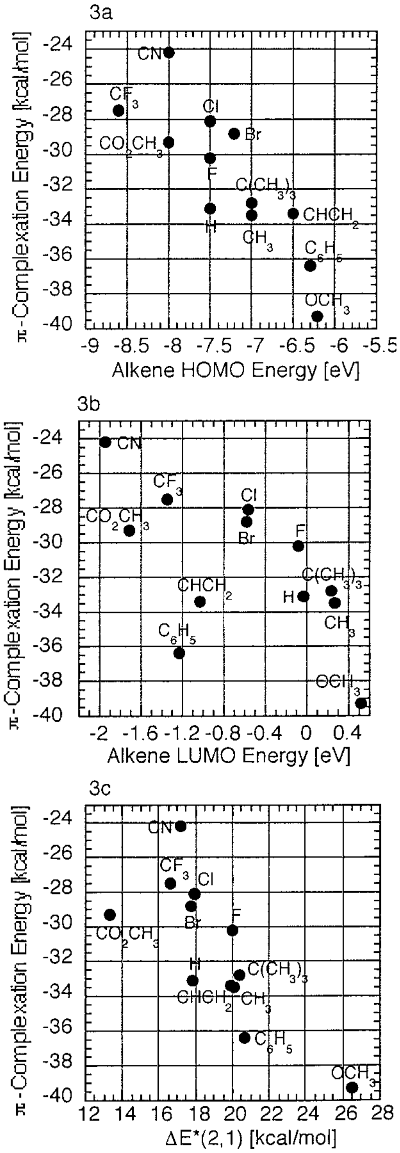

Figure 3. (a) HOMO energy of the free olefin (eV) vs π-complexation energy forming complex **2a** (kcal/mol). (b) LUMO energy of the free olefin (eV) vs π-complexation energy forming complex **2a** (kcal/mol). (c) Transition state barrier of **TS(2,1)a** (kcal/mol) vs π-complexation energy of forming species **2a** (kcal/mol).

Migratory Insertion. There are two regiochemical outcomes of insertion as depicted in Figure 1.[19] Tables 1 and 2 show that 2,1-insertion is usually favored. A

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[15] The stability constants for complexes of ethylene, propylene, and 1-butene in anionic $[Pd(olefin)Cl_3]^-$ are very similar. Hartly, F. R. *The Chemistry of Platinum and Palladium*; Applied Science Publichers Ltd: London, U.K., 1973; p 377.

[16] In a theoretical study of the insertion of propene into the Pd−Ph bond for a series of different types of diimine ligands, steric factors dominate the regioselectivity. von Schenck, H.; Svensson, M. Unpublished results.

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[18] The LUMO of both **1a** and **1b** is in essence a π^* MO located on the diimine ligand. The LUMO+1, involved in the binding with the alkenes, is a 5s4d-hybrid centered on the metal.

[19] In the case of butadiene as monomer the final product is a η^3-allylpalladium. (a) Stromberg, S.; Oksman, M.; Zhang, L.; Zetterberg, K. *Acta Chem. Scand.* **1995**, *49*, 689. (b) De Felice, V.; Cucciolito, M. E.; De Renzi, A.; Ruffo, F.; Tesauro, D. J. *J. Organomet. Chem.* **1995**, *493*, 269. In the case of styrene the final product is a η^3-benzylpalladium. (c) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436.

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Table 3. Selected Geometrical Parameters for the Complexes 2a and TS(2,1)a (Entries 1–12), 2b, and TS(2,1)b (Entries 13–24) (Distances in Å)

subst.	entry	C_1–Pd(π)[a]	C_2–Pd(π)[b]	C_1–C_2(π)[c]	C_2–R(2,1)[d]	C_1–Pd(2,1)[e]
H	1	2.278	2.278	1.390	2.111	2.071
CH_3	2	2.357	2.247	1.393	2.095	2.089
t-Bu	3	2.440	2.248	1.391	2.087	2.095
CN	4	2.278	2.267	1.402	2.134	2.092
CO_2CH_3	5	2.275	2.274	1.393	2.137	2.076
CF_3	6	2.250	2.279	1.390	2.152	2.081
OCH_3	7	2.423	2.204	1.395	2.115	2.106
$CHCH_2$	8	2.372	2.240	1.398	2.086	2.103
C_6H_5	9	2.365	2.235	1.400	2.097	2.108
F	10	2.275	2.262	1.382	2.150	2.053
Cl	11	2.276	2.256	1.386	2.156	2.054
Br	12	2.279	2.258	1.388	2.149	2.057
H	13	2.295	2.295	1.387	2.159	2.120
CH_3	14	2.369	2.259	1.391	2.125	2.134
t-Bu	15	2.436	2.243	1.390	2.137	2.164
CN	16	2.303	2.300	1.395	2.222	2.154
CO_2CH_3	17	2.293	2.294	1.390	2.208	2.130
CF_3	18	2.265	2.294	1.388	2.229	2.142
OCH_3	19	2.423	2.220	1.393	2.135	2.146
$CHCH_2$	20	2.388	2.252	1.397	2.127	2.152
C_6H_5	21	2.373	2.250	1.397	2.125	2.152
F	22	2.291	2.281	1.379	2.187	2.101
Cl	23	2.283	2.279	1.382	2.210	2.106
Br	24	2.285	2.274	1.385	2.210	2.110

[a] The distance between substituted carbon of the monomer and the metal in the π-complex. [b] The distance between nonsubstituted carbon of the monomer and the metal in the π-complex. [c] The distance between the monomer carbons in the π-complex. [d] The distance between nonsubstituted carbon of the monomer and the migrating methyl or phenyl group in **TS(2,1)**. [e] The distance between substituted carbon of the monomer and the metal in **TS(2,1)**.

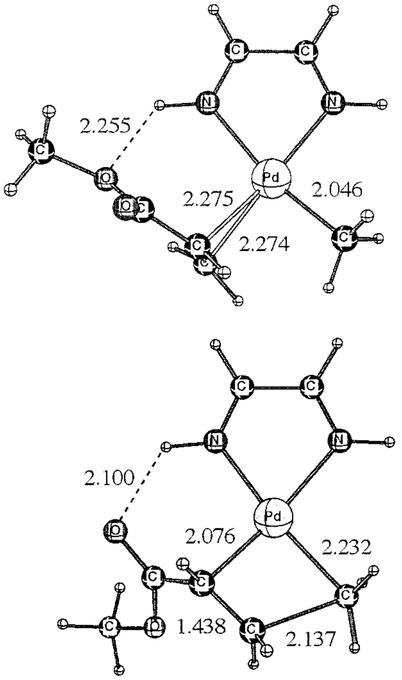

Figure 4. In the case of methylacrylate, hydrogen bonding lowers the energy of both the π-complex **2a** and the transition state **TS(2,1)a**.

significant exception for complex **1a** is noted for the electron-rich methyl vinyl ether preferring 1,2-insertion. This functionalized olefin is at the same time the only one where the lowest barrier of insertion for complex **1a** is prohibitively high, 24.2 kcal/mol, i.e., more than 6 kcal/mol higher than the barrier for ethylene. None of the other barriers for 2,1-insertion are more than 3 kcal/mol higher than the barrier for ethylene, and actually, some alkenes insert faster than ethylene. These reasonably low barriers suggest that, in general, the inability of functionalized comonomers to participate in a palladium-catalyzed polymerization with ethylene is not found in the insertion step. Actually, Brookhart has shown that a relatively stable resting state in the case of palladium-catalyzed copolymerization of ethylene and methyl acrylate is the reason for a slow reaction compared to a homopolymerization of ethylene.[3] For the phenylpalladium analogue, **1b**, 2,1-insertion is also generally preferred, but in addition to methoxy ethylene, flouroethylene prefers 1,2-insertion. The reason for the general preference of 2,1-insertion over the 1,2-insertion path seems to be due to less steric repulsion between the migrating group (methyl or phenyl) and the substituent on the alkene. Electronic effects in electron-deficient alkenes may strengthen this preference; that is, the methyl or phenyl group migrates in a pattern similar to a nucleophile in a Michael addition. Electronic effects induced by the substituents will only in some cases, e.g., in electron-rich methyl vinyl ether, override this inherent 2,1-selectivity.

It has been suggested that within a series of similar σ-alkyl(π-olefin) complexes coordination strengths and insertion barriers correlate.[5b,c,17] This is experimentally demonstrated within a limited series of styrene complexes.[19c] A reasonable rationale is that a significant part of the coordination is lost in the transition state. Figure 3c lends support to the hypothesis that a stronger coordination will result in a higher insertion barrier. However, methyl acrylate presents a deviation from a linear trend and thereby suggests that other factors in some cases can be of importance. A possible explanation may be that this complex experiences a hydrogen-bonding situation both in the ground state and in the transition state (see Figure 4). It should be kept in mind that this is an effect of the chosen catalyst model.

The trend shown in Figure 3c for **1a** is parallel for the **1b** systems. The important difference between the

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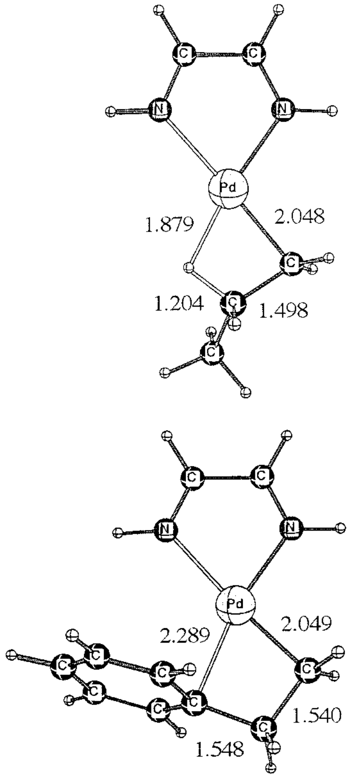

Figure 5. Products for the coordination−insertion of ethylene. Complex **3a** is stabilized by β-agostic interaction, while complex **3b** is stabilized by aryl−palladium π-interaction.

two cases is easily noted from Tables 1 and 2, where it is clear that the phenyl migrating barriers are substantially lower than the methyl migrating barriers. The reason for this is the larger driving force from the π-complex to the alkyl−palladium product in the phenyl case. This argument comes in two parts. First of all, as mentioned above, the alkene π-complexation is less stable for **1b**. Second, the product formed from phenyl insertion is more stable than for methyl insertion. Products **3a** form β-agostic species, while **3b** products display an ipso-bonding situation toward the phenyl ring (see Figure 5).

Structure **3b** is considerably stabilized through the aryl−palladium π-interaction. For example, when ethylene is the monomer, the energy difference for step **2a** to **3a** is −5.4 kcal/mol and −13.5 kcal/mol for the step **2b** to **3b**. The phenyl−palladium insertion is thus 8.1 kcal/mol more exothermic. Therefore, the TS for phenyl−palladium insertion is expected to be early compared to methyl−palladium insertion. Selected bond lengths of the π-complexes and transition states are given in Table 3.

It can be noted that C_1−Pd and C_2−R, i.e., the bonds formed in the transition state, are longer for **TS(2,1)b** compared to **TS(2,1)a** (on the average 0.06 and 0.05 Å, respectively). This confirms the notion of an earlier TS in the case of phenyl−palladium insertion.

The regiochemical outcome of the migratory insertion deserves some further comments. It is plausible that a tilted π-complexation of the alkene could be connected to regiochemical preference, i.e., that the methyl or phenyl group would migrate to the monomer carbon with the weakest (longest) bond to Pd. However, from distances presented in Table 3, no clear correlation is observed. In fact, the Pd−C_1 distance is longer than Pd−C_2 for nearly all alkenes. Only 3,3,3-trifluoropropene has a notable reverse tilting. Still, the 2,1-insertion, where the migrating group ends up on the nonsubstituted carbon of the monomer, is generally preferred.

For the methylpalladium(II)diimine species, the 2,1-regioselectivity varies between 6.4 and 3.2 kcal/mol for methyl acrylate, acrylonitrile, 3,3,3-trifluoropropylene, bromoethylene, chloroethylene, and 1,3-butadiene. In the situation where the reacting olefins have low lying π^* LUMOs, it is reasonable to expect orbital-driven selectivity, where the migrating group ends up at the carbon with the largest orbital ($2p_z$) coefficient. In the group just mentioned, the olefins all have stable π^* LUMOs (≤ -0.6 eV).[20] However, the orbital ($2p_z$) coefficients of the sp^2 carbons are approximately the same. The other possibility is that charge separation effects govern the regiochemistry. Once again, for these alkenes, the charge differences for the sp^2 carbons are small (<0.1 electron). The selectivity is thus biased by steric effects, leaving the migrating group on the unsubstituted carbon.

In contrast, alkenes with less stable π^* LUMOs (≥ -0.1 eV),[20] such as fluoroethylene, propylene, and methyl vinyl ether, are less prone to 2,1-insertion. In these olefins, the charge separation between the alkene carbons is considerable (0.6−0.8 electron), with the substituted sp^2 carbon being more positively charged. This charge effect negates the intrinsic 2,1-preference, leading to virtually no regiochemical preference (flouroethylene and propylene), or a moderate 1,2-selectivity (methyl vinyl ether). The steric effect is further exemplified by *tert*-butylethylene, with electronic properties similar to propylene, but with a 2,1-preference of 1.0 kcal/mol. The regiochemistry of phenylpalladium(II)diimine shows the same trends as methylpalladium(II)diimine. As expected, the steric bias is even more pronounced when bulky alkene substituents are involved (e.g., *tert*-butylethylene prefers 2,1-insertion by 1.9 kcal/mol versus 1.0 kcal/mol for methylpalladium(II)diimine).

The regiochemical outcome is thus due to both electronic and steric properties of the monomers. In the model catalyst used in this study, the steric interactions between the monomers and the diimine substituents at the nitrogen positions are minimized. It has been shown, however, that interactions with bulky ligand substituents can be used to control the regioselectivity, e.g., in the polymerization of propylene.[6]

Conclusions

Electron-rich functionalized alkenes coordinate more strongly than ethylene to cationic methylpalladium(II)diimine **1a**, whereas electron-poor coordinate more weakly. The resulting cationic π-alkene(methyl)palladium(II)diimine, **2a**, undergoes migratory insertion more readily if the alkene−metal coordination is weak. The same trends are observed for the phenylpalladium(II)diimine complex **1b**. The average reaction barrier

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(20) The calculated π^*-orbital energies, in eV, of the free alkenes: CN −1.95, CO_2CH_3 −1.71, CF_3 −1.35, C_6H_5 −1.24, $CHCH_2$ −1.04, Br −0.58, Cl −0.57, F −0.09, H −0.04, *t*-Bu 0.24, CH_3 0.27, and OCH_3 0.51.

(related to the preferred regiochemical outcome) is about 9 kcal/mol lower for **2b** than **2a**. The π-coordination of alkenes to **1b** is weaker since the accepting unoccupied MO of this species is 0.4 eV higher in energy than for **1a**. Furthermore, the reaction product, **3b**, is more stable. These properties together account for the lower insertion barrier seen for the phenyl−palladium species. There is a general preference for a 2,1-insertion pathway, due to lower steric repulsion between the alkene substituent and the migrating group. However, there are examples where the electronically induced effects of the alkene substituent overcome this inherent selectivity, e.g., propylene and methyl vinyl ether for both **1a** and **1b**. In general, the relative selectivities of complexes methylpalladium(II)diimine and phenylpalladium(II)diimine are the same.

All functionalized alkenes, with the exception of methyl vinyl ether, have reasonably low barriers to insertion into the methyl−palladium or phenyl−palladium bond; that is, this step does not seem to be prohibitive in a copolymerization process.

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Supporting Information Available: Optimized geometries of the all structures reported (Cartesian coordinates, in Å). This material is available free of charge via the Internet at http://pubs.acs.org.

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