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Intrinsic Aptitude of Cationic Methyl- and Ethylpalladium To Associate Ethylene and To Further Undergo Subsequent Migratory Insertion. A Theoretical Study

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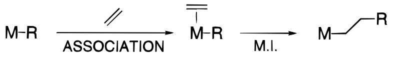
Density Functional Theory (DFT) calculations at the B3LYP level and PCI-80 calculations have been carried out for the following reaction sequence: (a) association of ethylene to cationic (σ-alkyl)palladium(II) complexes, forming a π-ethylene σ-alkyl intermediate, (b) subsequent migratory insertion, and (c) β-hydride elimination of the insertion product. Ethylene coordinates strongly to the "naked" complexes $PdCH_3^+$ and $PdC_2H_5^+$ (43.9 kcal/mol and 36.0 kcal/mol respectively). Nitrogen ligands modify association exothermicity (or conversely dissociation endothermicity): $Pd(NH_3)_2CH_3^+$ (27.3 kcal/mol), $Pd(NH_3)_2C_2H_5^+$ (14.9 kcal/mol) and $Pd(CHNH)_2CH_3^+$ (29.8 kcal/mol), where $(CHNH)_2$ is chelating diimine. Substantial agostic interaction between metal and β-hydrogens and differences in charge on palladium account for the differences. The migratory insertion step is endothermic for naked 12-electron (π-ethylene)(σ-alkyl)palladium complexes and exothermic for 16-electron complexes with two nitrogen ligands. Calculated values for the barriers of migratory insertion agree remarkably with reported values experimentally found. Thus, the barrier for migratory insertion of $PdCH_3^+(C_2H_4)$ is calculated to 18.3 kcal/mol and 18.0 kcal/mol for the bisamine complex, whereas Brookhart recently found a value of 18.5 kcal/mol for corresponding phenanthroline complex (see ref 1). The lowest value (16.4 kcal/mol) is calculated for $Pd(CHNH)_2CH_3^+(C_2H_4)$ and the lowest found (17.2 kcal/mol) experimentally is for the diimine complex $Pd(HCN[2,6\text{-}C_6H_3(i\text{-}Pr)_2])_2CH_3^+(C_2H_4)$ (see ref 2). The product of the insertion reaction readily undergoes β-hydride elimination, which is thermoneutral for "naked" complexes and slightly endothermic (3.2−4.8 kcal/mol) for 16-electron complexes. The results suggest that (a) DFT calculations at the B3LYP level seem to provide values close to experimentally found energetics for this type of organometallic chemistry and (b) alkene coordination is sensitive to coordinated ligands but insertion kinetics are less so.

Introduction

In its simplicity the straightforward association of an alkene to a transition-metal σ-alkyl complex and the following migratory insertion (MI) represent a part in common for some, in all respects, very productive organic reactions catalyzed by transition metals (eq 1).



(1)

Consequently, this two-step sequence describes the progression for both strategic scale Ziegler−Natta polymerization[3] of simple olefins as well as the nickel-catalyzed oligomerization of ethylene (the SHOP process).[4] On the more modest laboratory scale, the sequence may represent the crucial part of the catalytic cycle responsible for synthetically useful Heck arylation (Scheme 1).[5]

These few, rather diverse examples of carbon−carbon bond-forming reactions serve to illustrate a generality. In spite of the obvious significance of these steps several issues remain to be settled. In contrast to transition-metal π-alkene hydride complexes, which readily insert, the corresponding transition-metal π-alkene σ-alkyl species are generally reluctant to undergo migratory

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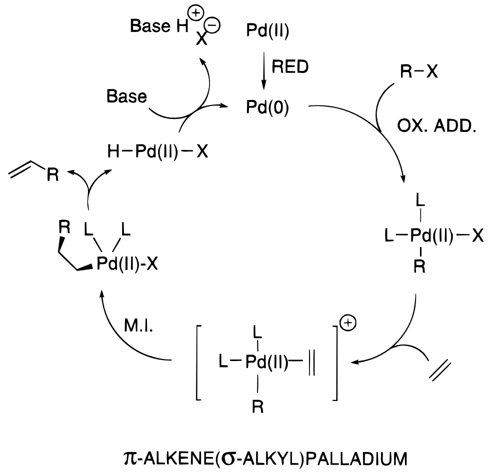
Scheme 1. Principal Steps of the Heck Reaction



insertion.[6,7] However, this latter migratory insertion is usually extremely facile in polymerization reactions. As a matter of fact, under polymerization conditions detection of this crucial intermediate is rare.[8] Also in the Heck reaction the crucial π-alkene σ-alkyl intermediate defies detection.[5c,d]

In short, it is difficult to deal with a reaction that proceeds very fast via elusive intermediates, whereas model compounds, i.e. isolated (π-alkene)(σ-alkyl)metals, for the same type of intermediates are mostly unreactive. We have recently suggested a partial solution: models and intermediates representing (π-alkene)-metals of two different kinds. The model compounds are characterized by strong π-alkene coordination and, conversely, the hard to detect intermediates by weak coordination. This dissimilarity relates not only to a superficial difference in bond strength but also to a difference in predisposition to undergo insertion.[9a,10,11] Accordingly, polymerization catalysts, with few exceptions, only tolerate noncoordinating solvents and are extremely sensitive to poisoning.

A correlation between weak alkene coordination and polymerization is also suggested from a look at the periodic table. Commercial polymerization metals can be found to the left and up the triads. In contrast, among the transition metals capable of strong coordination, e.g. to the right and down the triads, polymerization is scarce.[9a] The consistency of this pattern has just recently been altered, as both rhodium and palladium have been shown to be able to polymerize simple alkenes.[12]

The main issue of this study is the intrinsic inclination for cationic (σ-alkyl)palladium complexes to (a) associate an alkene and (b) promote the subsequent migratory insertion and ultimately act as polymerization catalysts. Furthermore, we will discuss the potential of stabilization by agostic interactions and the energetics of β-hydride elimination from the product of the migratory insertion.

Computational Details

Most of the present calculations have been done using an empirically parametrized density functional theory (DFT) method, hereafter termed B3LYP. The B3LYP functional can be written as

$$F^{\mathrm{B3LYP}} = (1 - A)F_{\mathrm{x}}^{\mathrm{Slater}} + AF_{\mathrm{x}}^{\mathrm{HF}} + BF_{\mathrm{x}}^{\mathrm{Becke}} + CF_{\mathrm{c}}^{\mathrm{LYP}} + (1 - C)F_{\mathrm{c}}^{\mathrm{VWN}}$$

where $F_{\mathrm{x}}^{\mathrm{Slater}}$ is the Slater exchange, $F_{\mathrm{x}}^{\mathrm{HF}}$ is the Hartree−Fock exchange, $F_{\mathrm{x}}^{\mathrm{Becke}}$ is the exchange functional of Becke,[13] $F_{\mathrm{c}}^{\mathrm{LYP}}$ is the correlation functional of Lee, Yang, and Parr,[14] and $F_{\mathrm{c}}^{\mathrm{VWN}}$ is the correlation functional of Vosko, Wilk, and Nusair.[15] However, it should be noted that Becke did not use $F_{\mathrm{c}}^{\mathrm{LYP}}$ in the expression above when the coefficients were determined but used the correlation functional of Perdew and Wang instead.[16] *A*, *B*, and *C* are the coefficients determined by Becke[13] using a fit to experimental heats of formation for a common benchmark test[17] consisting of 55 first- and second-row molecules. The introduction of gradient corrections, Hartree−Fock exchange, and empirical parameters has made this type of hybrid DFT approach highly competitive in accuracy with the most accurate standard quantum-chemical methods.[18] The B3LYP calculations were carried out using the GAUSSIAN92/DFT package.[19]

For some of the present cationic palladium systems comparative calculations were performed using the recently developed PCI-80 scheme.[20] This parametrized scheme is based on calculations performed using the modified coupled

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(8) (a) A (π-alkene)(σ-alkyl)cobalt species has been detected in a living homogeneous polymerization catalyst: Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634. (b) The resting states represented by (π-alkene)(σ-alkyl)palladium complexes have been detected.[2]

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(10) Recent calculations show polymerization with weak precoordination of ethylene to Ti: (a) Weiss, H.; Ehrig, M.; Ahlrichs, R. *J. Am. Chem. Soc.* **1994**, *116*, 4919. (b) Jensen, R. V.; Børve, K. J.; Ystenes, M. *J. Am. Chem. Soc.* **1995**, *117*, 4109. Stronger precoordination has also been calculated: (c) Yoshida, T.; Koga, N.; Morokuma, K. *Organometallics* **1995**, *14*, 746.

(11) It is well accepted that π-back-donation to an alkene is unfavorable for alkyl insertion. However, this circumstance does not suffice to discriminate against the transition metals to the right in the periodic table, as π-back-contribution is less important for *e.g.* palladium(II) and silver(I): (a) Ban, E. M.; Hughes, R. P.; Powell, J. *J. Chem. Soc., Chem. Commun.* **1973**, *16*, 591. (b) Partenheimer, W.; Durham, B. *J. Am. Chem. Soc.* **1974**, *96*, 3800. (c) Isolated cationic alkene complexes of *e.g.* Ni(II), Pd(II), Pt(II), Rh(III), Fe(II), Ru(II), and Os(II) undergo nucleophilic attack. In these cases there is not "any significant back donation". Bäckvall, J. E. In *Reaction of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, p 679.

(12) For rhodium see: (a) Wang, L.; Flood, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 3169. (b) Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999. For palladium see: (c) Reference 2.

(13) (a) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

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pair functional (MCPF) method,[21] which is a standard quantum-chemical, size-consistent, single-reference-state method. The zeroth-order wave functions were determined at the SCF level. All valence electrons were correlated, including the 4d and 5s electrons on the palladium atom. If standard double-ζ plus polarization (DZP) basis sets are used, it can be shown that about 80% of the correlation effects on bond strengths are obtained, irrespective of the system studied. A good estimate of a bond strength is thus obtained by simply adding 20% of the correlation effects, and this is what is done in the PCI-80 scheme.[20a] The parameter 80 is thus an empirical parameter, which is not fitted but still chosen to give agreement with experiment for a benchmark test similar to that used for the B3LYP method. There are thus clear similarities between these methods in this respect. For several first-row systems it was shown in ref 20a that a Hartree–Fock limit correction is also strictly needed in the PCI-80 scheme. However, this correction is usually small for transition-metal systems and a useful procedure is to consider these effects together with basis set superposition errors and 4s, 4p correlation effects as included in the parametrization. This procedure has been used in the present study. In the PCI-80 calculations relativistic effects were added using perturbation theory for the mass–velocity and Darwin terms.[22] The PCI-80 calculations were performed using the STOCKHOLM set of programs.[23]

Essentially the same standard DZP basis sets were used for both the B3LYP and the PCI-80 calculations. For first row atoms the primitive (9s, 5p) basis from ref 24 was used in the PCI-80 calculations, augmented with one d function and contracted to [3s, 2p, 1d]. For hydrogen the primitive (5s) basis from ref 24 was used in the PCI-80 calculations, augmented with one p function and contracted to [3s, 1p]. For the B3LYP calculations a primitive (4s, 1p) basis contracted to [2s, 1p] was used instead. In the PCI-80 calculations an all-electron description was used for the palladium atom using the Huzinaga primitive basis[25] extended by adding one diffuse d function, two p functions in the 5p region, and three f functions, yielding a (17s, 13p, 9d, 3f) primitive basis. The core orbitals were totally contracted except for the 4s and 4p orbitals, which have to be described by at least two functions each to properly reproduce the relativistic effects. The 5s and 5p orbitals were described by a double-ζ contraction, and the 4d orbital was described by a triple-ζ contraction. The f functions were contracted to one function, giving a [7s, 6p, 4d, 1f] contracted basis. For the B3LYP calculations, on the other hand, the relativistic ECP (RECP) according to Hay and Wadt[26] was used for palladium (the standard contraction for LANL2DZ[19] was used).

All the geometries of the present study have been optimized at the B3LYP level using the above basis sets without polarization functions. In most cases all degrees of freedom were optimized. However, for some model systems the angle between the ammonia ligands was frozen at various values to study the effect of a constraint on this angle similar to the one present for bidentate ligands (*vide infra*). Zero-point vibrational effects were finally added on the basis of SCF calculations for the reactions between $PdCH_3^+$ and ethylene and between $Pd(NH_3)_2CH_3^+$ and ethylene.

Results and Discussion

Table 1. Reaction Energies (kcal/mol) for the Reaction between $PdCH_3^+$ and Ethylene[a]

system	descripn	energy
$PdCH_3^+ + C_2H_4$	reactant	0.0
$PdCH_3(C_2H_4)^+$	π-equilibrium	−43.9
$PdCH_3^+ + C_2H_4$	migration TS	−25.6
$PdC_3H_7^+$	inserted equilibrium	−40.8
$PdHC_3H_6^+$	β-el TS	−37.7
$PdH(C_3H_6)^+$	π-equilibrium	−41.0

[a] In this and all subsequent tables, TS = transition state and β-el = β-elimination.

Table 2. Reaction Energies (kcal/mol) for the Reaction between $PdC_2H_5^+$ and Ethylene

system	descripn	energy
$PdC_2H_5^+ + C_2H_4$	reactant	0.0
$PdC_2H_5(C_2H_4)^+$	π-equilibrium	−36.0
$PdC_2H_5^+ + C_2H_4$	migration TS	−10.9
$PdC_4H_9^+$	inserted equilibrium	−25.7
$PdHC_4H_8^+$	β-el TS	−22.5
$PdH(C_4H_8)^+$	π-equilibrium	−25.8

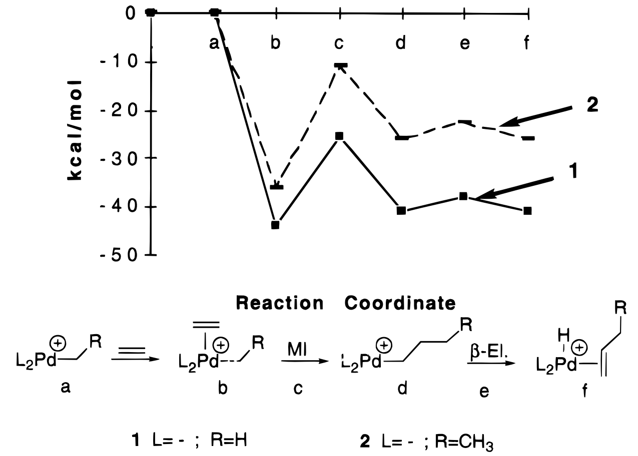

Figure 1. Energetics for the reaction between PdR^+ and ethylene.

a. Intrinsic Bond Strengths: Reactions of Naked PdR^+. It was indicated in the Introduction that from experimental results there appears to be a correlation between the ability to polymerize and the weakness of the olefin–metal bond. In order to investigate this point further, calculations were performed for the reactions between naked, formally 10-electron PdR^+ and ethylene. The results for $PdCH_3^+$ are shown in Table 1 and for $PdC_2H_5^+$ in Table 2. Both reaction paths are displayed in Figure 1.

Since cationic palladium complexes have been shown to effectively perform at least the first step in the polymerization of ethylene, it could be expected that this type of cationic complex should have weak bonds to olefins. As seen in Tables 1 and 2, this is not the case for a naked metal atom. On the contrary, the bond between $PdCH_3^+$ and ethylene is as strong as 43.9 kcal/mol and the corresponding bond for $PdC_2H_5^+$ amounts to 36.0 kcal/mol. These interactions represent unusually strong coordination between palladium and alkene. A rough estimate is that a palladium–alkene bond may often be in the area of 25 kcal/mol for isolated complexes.[27] A consequence of this strong coordination is that the thermodynamics for the subsequent migratory insertion are unfavorable. Furthermore, for $PdC_2H_5^+$ the transition barrier is substantial (25.1 kcal/mol). The origin of this increased bond strength is a large effect from a charge-induced dipole interaction from the very polarizable ethylene ligand. This effect more than

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(21) Chong, D. P.; Langhoff, S. R. *J. Chem. Phys.* **1986**, *84*, 5606.

(22) Martin, R. L. *J. Phys. Chem.* **1983**, *87*, 750. See also: Cowan, R. D.; Griffin, D. C. *J. Opt. Soc. Am.* **1976**, *66*, 1010.

(23) STOCKHOLM is a general purpose quantum-chemical set of programs written by: P. E. M. Siegbahn, M. R. A. Blomberg, L. G. M. Pettersson, B. O. Roos, and J. Almlöf.

(24) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

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compensates for the reduced ability of a cationic palladium to afford a stabilizing π-back-donation which in any event is present to some extent.

The strength of the Pd−olefin bond is reduced by 7.9 kcal/mol for $PdC_2H_5^+$ compared to $PdCH_3^+$. The reason for the decrease is that the charge on palladium is partially delocalized onto the larger ethyl group and the metal is consequently less effective in polarizing the ethylene ligand.

When the reaction for $PdCH_3^+$ is examined (Table 1 and Figure 1), the following features can be identified. First there is a barrier for olefin migration of 18.3 kcal/mol, which is in remarkably good agreement with the value of 18.5 kcal/mol measured by Rix and Brookhart for a corresponding cationic (phenanthroline)palladium complex.[1] However, the insertion step for naked $PdCH_3^+$ is endothermic by 3.1 kcal/mol, in obvious disagreement with the observed facile first polymerization step for some cationic palladium complexes. Apparently, ligands are of considerable importance in this context. After the insertion, a thermodynamically close to thermoneutral β-hydride elimination can occur with an extremely low barrier of 3.1 kcal/mol.

The reaction for $PdC_2H_5^+$ and ethylene (Table 2) displays some rather striking differences compared to the analogous reaction with $PdCH_3^+$ (Table 1). The weakening of the Pd−olefin bond strength has already been mentioned. Intuitively such a weakening would be expected to imply a decrease of the migratory insertion barrier. However, the barrier has increased by 6.8 kcal/mol to 25.1 kcal/mol. This value is in rather poor agreement with the value measured by Rix and Brookhart of 19.4 kcal/mol for the ethyl case.[1] This circumstance further indicates that ligands may affect this step in a profound way (*vide infra*). The origin of the increased barrier for the naked cationic (ethyl)palladium species compared to the corresponding methyl reaction can be seen in the calculated endothermicity of the migration step. For ethyl this step is endothermic by 10.3 kcal/mol, which is 7.2 kcal/mol more than for the methyl reaction. This increase of the endothermicity is apparently carried over almost entirely to an increase of the barrier for the migration. The origin of the increased endothermicity is also due to agostic interactions (*vide infra*) and the decreased π-bond strength of the olefin in the ethyl case, as discussed above. The remaining part of the reaction, the β-hydride elimination, is quite similar for methyl and ethyl species with a barrier for ethyl of 3.2 kcal/mol, again in an almost thermoneutral reaction.

It is interesting to compare the computed thermodynamics of the polymerization step with that obtained from the calculations on the gas-phase reaction without the metal. In this case, when a methyl radical and ethylene form a propyl radical, the reaction is exothermic by 20.4 kcal/mol, including a large zero-point vibrational effect of −5.9 kcal/mol. For the formation of a butyl radical from an ethyl radical the calculated value is 18.0 kcal/mol. The ethyl value is thus only slightly smaller than the value of 25.7 kcal/mol obtained for this step for $PdC_2H_5^+$ (see Table 2), while the methyl value is much smaller than the value of 40.8 kcal/mol in Table 1. The origin of the increased exothermicity for the $PdCH_3^+$ reaction is easy to understand when the structures of the PdR^+ complexes are studied (see Figures 2 and 3).

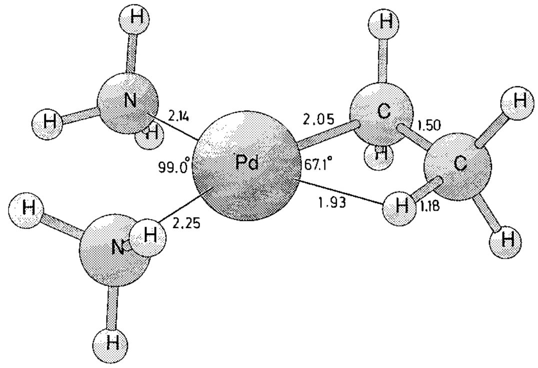

Figure 2. β-Agostic interaction in $Pd(NH_3)_2C_2H_5^+$.

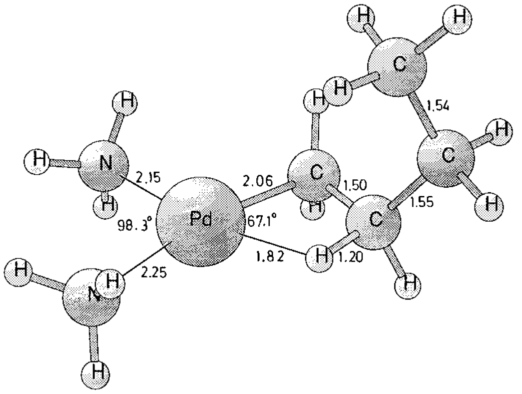

Figure 3. β-Agostic interaction in $Pd(NH_3)_2C_4H_9^+$, the insertion product of $Pd(NH_3)_2C_2H_5^+(C_2H_4)$.

The figures visualize typical agostic interactions for the R ligands with β-hydrogens. However, $PdCH_3^+$ lacks β-hydrogens. Therefore, the exothermicity of the $PdCH_3^+$ reaction is larger than that for the $PdC_2H_5^+$ reaction by an amount that equals the strength of the agostic bonding. From these calculations it is thus possible to directly obtain the agostic bond strength as the difference between these reaction energies, which leads to the considerable value of 15.1 kcal/mol.

Another, perhaps even more direct, way of obtaining an estimate of the agostic bond strength is to compare the $Pd^+{-}R$ bond strength for methyl and ethyl. The calculated values for these bond strengths are 51.6 and 66.2 kcal/mol, respectively, leading to an agostic bond strength of 14.6 kcal/mol, in good agreement with the above estimate of 15.1 kcal/mol. The $Pd^+{-}R$ bond strength for propyl is still somewhat larger with a value of 69.9 kcal/mol, showing that the chain length also affects the bond strength to some extent. The origin of this effect can be attributed to the greater polarizability of the alkyl group.

From the above results it is now possible to understand why the olefin migration is more endothermic by 7.2 kcal/mol in the ethyl case. If the agostic interactions were the only differences between the methyl and ethyl

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(27) Data of measured bond strengths for bonds between metal and alkene is scarce. The lower limit for BDE in $[Rh(P\text{-}i\text{-}Pr_3)_2Cl(L)$ (L = ethylene) is estimated to be −15.9 ± 0.6 kcal/mol. Wang, K.; Goldman, A. S.; Li, C.; Nolan, S. P. *Organometallics* **1995**, *14*, 4010. The relatively stable (η^5-Cp)Pd(PR_3)(ethylene) shows no exchange with free ethylene in solution on the NMR time scale at 23 °C as reported by: Kurosawa, H.; Majima, T.; Asada, N. *J. Am. Chem. Soc.* **1980**, *102*, 6996. This suggests a bond dissociation energy above ~15.0 kcal/mol. The solution of the same complex tolerates storage at room temperature for days but decomposes rapidly at +50 °C. If the decomposition is initiated by loss of ethylene, this would correspond to a bond dissociation energy in the area suggested.

Table 3. Reaction Energies (kcal/mol) for the Reaction between $Pd(NH_3)_2CH_3^+$ and Ethylene[a]

system	descripn	∠(N−Pd−N)	energy
$Pd(NH_3)_2CH_3^+ + C_2H_4$	reactant	105.6	0.0
$Pd(NH_3)_2CH_3(C_2H_4)^+$	π-equilibrium	94.0	−27.3
$Pd(NH_3)_2CH_3^+ + C_2H_4$	migration TS	93.4	− 9.3
$Pd(NH_3)_2C_3H_7^+$	inserted equilibrium	98.8	−34.8
$Pd(NH_3)_2HC_3H_6^+$	β-el TS	94.2	−29.4
$Pd(NH_3)_2H(C_3H_6)^+$	π-equilibrium	95.4	−31.1

[a] In this table and Table 4, ∠(N−Pd−N) is the angle between the two ammonia ligands (in deg).

Table 4. Reaction Energies (kcal/mol) for the Reaction between $Pd(NH_3)_2C_2H_5^+$ and Ethylene

system	descripn	∠(N−Pd−N)	energy
$Pd(NH_3)_2C_2H_5^+ + C_2H_4$	reactant	99.0	0.0
$Pd(NH_3)_2C_2H_5(C_2H_4)^+$	π-equilibrium	91.8	−14.9
$Pd(NH_3)_2C_2H_5^+ + C_2H_4$	migration TS	92.7	+4.4
$Pd(NH_3)_2C_4H_9^+$	inserted equilibrium	98.3	−22.5
$Pd(NH_3)_2HC_4H_8^+$	β-el TS	93.7	−14.8
$Pd(NH_3)_2H(C_4H_8)^+$	π-equilibrium	94.8	−18.5

reactions, a difference in the endothermicity of 15.1 kcal/mol should be expected. However, due to the greater charge delocalization in the ethyl case, the interaction between olefin and metal is 7.9 kcal/mol weaker for ethyl. Once again, subtraction of these two effects leads to a difference in endothermicity for the migration of 7.2 kcal/mol.

The final issue addressed in this section concerns the accuracy of the calculations. The above results were all obtained using the B3LYP method. In order to test the accuracy of these calculations, some calculations were also performed using the PCI-80 scheme. This scheme has been demonstrated to perform very well compared to experiments for second-row transition-metal complexes.[20a] For the exothermicity of the first polymerization step for $PdCH_3^+$ the PCI-80 value is 40.8 kcal/mol, in perfect agreement with the B3LYP value. The individual $Pd^+{-}R$ bond strengths differ a little bit more, with PCI-80 values for methyl of 57.4 kcal/mol (B3LYP value 51.6 kcal/mol), for ethyl of 70.5 kcal/mol (66.2 kcal/mol), and for propyl of 74.0 kcal/mol (69.9 kcal/mol). However, the trends of these bond strengths are well-reproduced. The PCI-80 energy for the olefin migration transition state for the methyl reaction is −24.3 kcal/mol (−25.6 kcal/mol) and for the β-elimination transition state −36.3 kcal/mol (−37.7 kcal/mol). Overall, the agreement between the two methods must be considered quite satisfactory, and in the following only the B3LYP values will be discussed.

b. Effects of Ligands: Reactions of $PdR^+(NH_3)_2$. The results of the reaction between $Pd(NH_3)_2CH_3^+$ and ethylene are shown in Table 3. The corresponding results for $Pd(NH_3)_2C_2H_5^+$ are given in Table 4, and both reactions are displayed in Figure 4.

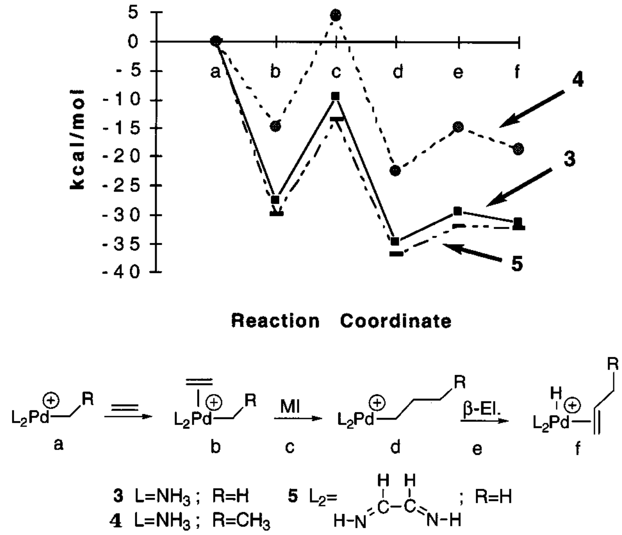

Figure 4. Energetics for the reaction between L_2PdR^+ and ethylene.

Table 5. Mulliken Charges for the Pd−(alkyl)$^+$ and the π-Bonded Olefin Complexes with and without Ammonia Ligands Present

system	*q*(Pd)	*q*(R)	*q*(C_2H_4)	*q*(NH_3)
$PdCH_3^+$	+0.68	+0.32		
$PdC_2H_5^+$	+0.48	+0.52		
$PdC_3H_7^+$	+0.44	+0.56		
$PdC_4H_9^+$	+0.41	+0.59		
$PdCH_3(C_2H_4)^+$	+0.42	+0.20	+0.38	
$PdC_2H_5(C_2H_4)^+$	+0.26	+0.41	+0.33	
$Pd(NH_3)_2CH_3^+$	+0.37	+0.06		+0.29
$Pd(NH_3)_2C_2H_5^+$	+0.20	+0.26		+0.27
$Pd(NH_3)_2C_3H_7^+$	+0.17	+0.31		+0.26
$Pd(NH_3)_2C_4H_9^+$	+0.15	+0.34		+0.26
$Pd(NH_3)_2CH_3^+(C_2H_4)$	+0.21	−0.01	+0.28	+0.26
$Pd(NH_3)_2C_2H_5^+(C_2H_4)$	+0.18	+0.07	+0.26	+0.24

There are several interesting differences between the results in Tables 3 and 4 and the results without ammonia ligands discussed above. Perhaps the most striking difference concerns the coordination strength. The energy released upon coordination to $Pd(NH_3)_2CH_3^+$ is 27.3 kcal/mol, as compared to 43.9 kcal/mol without ammonia ligands. For $Pd(NH_3)_2C_2H_5^+$ this energy is as small as 14.9 kcal/mol, compared to 36.0 kcal/mol without ammonia ligands. The calculations show that ammonia coordinates more strongly to the metal than ethylene. The values are 31.0 kcal/mol for $Pd(NH_3)_2CH_3(C_2H_4)^+$ and 26.7 kcal/mol for $Pd(NH_3)_2C_2H_5(C_2H_4)^+$. This circumstance lends support to the calculations, as amine ligands may irreversibly replace alkenes coordinated to palladium(II).[28] The weak coordination between olefin and metal in $Pd(NH_3)_2C_2H_5(C_2H_4)^+$ makes this 16-electron complex vulnerable to dissociative displacement of the olefin ligand at room temperature. Actually, dissociation is faster than migratory insertion.

The reduced binding energy of the olefin when ligands are added is a result of a positive charge delocalization over to the ammonia ligands. As seen in Table 5, the ammonia ligands reduce the charge on palladium from +0.68 to +0.37 for the methyl case. The charge polarization contribution of the Pd−olefin bonding is therefore also reduced. For the ethyl case the palladium charge is further reduced down to +0.20 but is then only marginally reduced for the longer alkyl chains down to +0.15. Some invariability of the Pd−olefin bond strength is therefore achieved already for an alkyl chain as short as ethyl. The major effect introduced as one goes from methyl to ethyl is, as mentioned above, the agostic interaction, which is effective in reducing the metal charge.

Overall, the quite dramatic effects due to the positive charge, as noticed in the preceding subsection, are

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(28) Åkermark, B.; Bäckvall, J.-E.; Hegedus, L. S.; Siirala-Hanse'n, K.; Sjöberg, K.; Zetterberg, K. *J. Organomet. Chem.* **1974**, *72*, 127.

Table 6. Reaction Energies (kcal/mol) for the Reaction between $PdCH_3^+(CHNH)_2$ and Ethylene[a]

system	descripn	∠(N−Pd−N)	energy
$Pd(CHNH)_2CH_3^+ + C_2H_4$	reactant	77.4	0.0
$Pd(CHNH)_2CH_3(C_2H_4)^+$	π-equilibrium	76.1	−29.8
$Pd(CHNH)_2CH_3^+ + C_2H_4$	migration TS	76.2	−13.4
$Pd(CHNH)_2C_3H_7^+$	inserted equilibrium	76.7	−36.8
$Pd(CHNH)_2HC_3H_6^+$	β-el TS	76.5	−31.8
$Pd(CHNH)_2H(C_3H_6)^+$	π-equilibrium	76.4	−32.0

[a] ∠(N−Pd−N) is the bidentate angle (in deg).

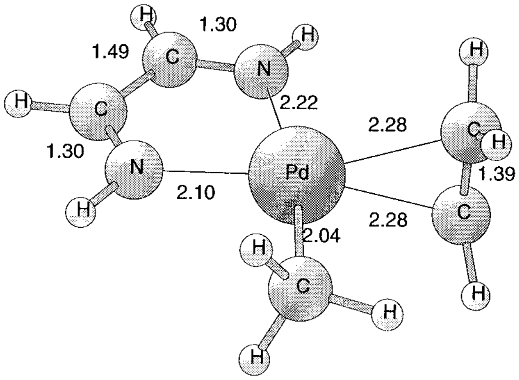

Figure 5. Optimized geometry of the (π-alkene)methyl(diimine)palladium complex.

strongly suppressed when the ammonia ligands are added. For example, the total reaction exothermicity of the olefin addition and subsequent insertion step of the polymerization is reduced from 40.8 kcal/mol for $PdCH_3^+$ down to 34.8 kcal/mol for $Pd(NH_3)_2CH_3^+$ and further down to 22.5 kcal/mol for $Pd(NH_3)_2C_2H_5^+$. The value 22.5 kcal/mol is actually not much larger than the gas-phase value for the addition of ethylene to the ethyl radical, yielding the butyl radical, which is 18.0 kcal/mol. Accordingly, the energetics of the polymerization reaction is therefore not going to change very much as the chain length increases from butyl.

In some cases the presence of the ammonia ligands modifies also the other steps of the reaction path shown in Figure 4. Even though the $Pd(NH_3)_2CH_3^+$ migration barrier hardly changes (from 18.0 kcal/mol with and 18.3 kcal/mol without ammonia ligands), in the case of $Pd(NH_3)_2C_2H_5^+$ the barrier changes significantly down to 19.3 kcal/mol (from 25.1 kcal/mol). Once again the calculated barriers with ammonia ligands present are in noticeable agreement with the barriers measured by Rix and Brookhart for corresponding phenanthroline complexes.[1] In this case the values are 18.5 kcal/mol for methyl and 19.4 kcal/mol for ethyl. Part of this agreement has to be fortuitous, but the general features of the experiment and the calculations are clearly the same, showing the adequacy of the present model systems. It is noteworthy that the lowest barrier, 16.4 kcal/mol (see Table 6), is calculated for the bidentate diimine ligand, and again a value is obtained which is reasonably close to the observed value of 17.2 kcal/mol for a methyl(diimine)palladium catalyst inserting ethylene.[2] Some significant geometries are illustrated in the case with diimine as auxiliary ligand for the π-ethylene methyl complex (Figure 5), the transition state of insertion (Figure 6), and the final product, the propyl complex (Figure 7).

The origin of the lowering of the barrier in the ethyl case warrants some discussion.

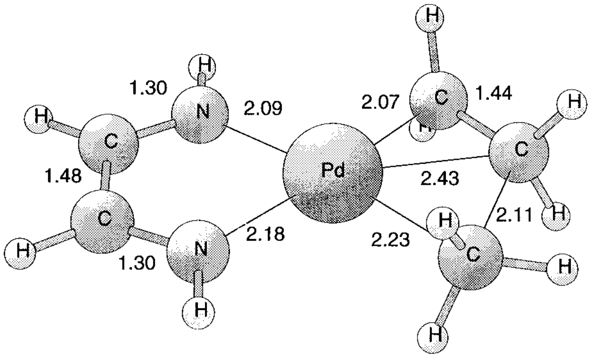

Figure 6. Optimized geometry of the transition state for insertion of (π-alkene)methyl(diimine)palladium.

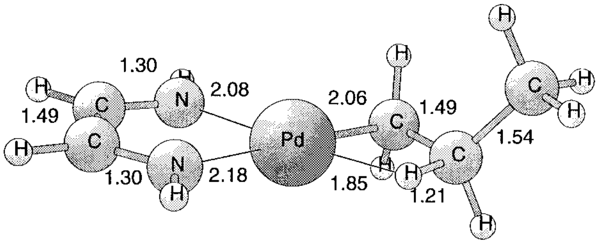

Figure 7. Optimized geometry of the insertion product propyl(diimine)palladium.

An apparent explanation is that the bond strength between metal and alkene (21.1 kcal/mol) has remarkably decreased. This explanation is in harmony with the general idea that a weak metal−olefin bond correlates with a low migration barrier. However, it is equally obvious that $PdC_2H_5(C_2H_4)^+$, in contrast to the other π-alkene complexes, may lose β-agostic interaction in the transition state of the insertion. These two tentative explanations may be less divergent than is immediately apparent. At least in part, the reason for the weak interaction between alkene and metal in $Pd(NH_3)_2C_2H_5^+(C_2H_4)$ is the lack of β-agostic interaction. This complex will gain a β-agostic interaction both upon dissociation of alkene and upon insertion. We also suggest that a charge effect may be worth consideration. Addition of ammonia ligands to the palladium atom decreases substantially the charge at the alkyl group, and we notice a small decrease for the migratory insertion barrier of $Pd(NH_3)_2CH_3(C_2H_4)^+$ (compared to $PdCH_3(C_2H_4)^+$) and a large decrease for the barrier of $Pd(NH_3)_2C_2H_5(C_2H_4)^+$ (compared to $PdC_2H_5(C_2H_4)^+$). Furthermore, the highest barrier by far, 25.1 kcal/mol (for naked $PdC_2H_5(C_2H_4)^+$), is correlated to the absolutely highest positive charge at the alkyl group (+0.41). Charges for the other (π-alkene)(σ-alkyl)palladium compounds are +0.20 or lower. A discussion relating a moderate positive, or even better a negative charge, on the alkyl group with a low migratory insertion barrier is compatible with a suggestion, proposed in ref 9a, about a balanced electrophilicity being optimal for this reaction step (Figure 8).

A further aspect is worth consideration. The migration barriers are, with the exception of $PdC_2H_5(C_2H_4)^+$, fairly close and calculated values agree well with those experimentally found. A conceivable interpretation of this observation is that solvent and counterion have only minor influences on the migratory insertion barrier. Moreover, for 16-electron complexes perhaps also the choices within a group of similar ligands are of rather small importance; i.e., the height of the migration

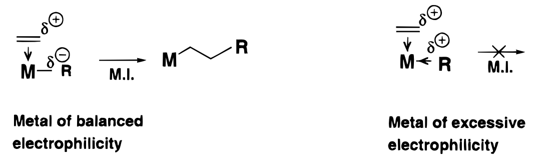

Figure 8. Role of positive charge on the alkyl group in impeding migratory insertion.

barrier is intrinsic to the metal. A suggestion such as this may seem speculative, but an early transition state, rather likely for an exothermic process, would be compatible with the above suggestion.

The amount of agostic bonding is only slightly reduced by the presence of the ammonia ligands. Following the procedure in the preceding subsection, an estimate of the agostic bond strength is obtained as the reaction energy difference between the ethyl- and methylpalladium reactions. With ammonia ligands present, this leads to an agostic bond strength of 12.3 kcal/mol, compared to 15.1 kcal/mol without ammonia ligands. The effect of the ligands is thus a reduction by 2.8 kcal/mol. A slightly different estimate is obtained by directly comparing the Pd−R bond strengths for methyl and ethyl. This leads to an agostic bond strength of 10.3 kcal/mol with ammonia ligands compared to 14.6 kcal/mol without these ligands. In this case the effect of the ligands is a reduction by 4.3 kcal/mol. Again, the origin of the reduction of the agostic bond strength is that the positive charge originally on the metal is more delocalized over to the ammonia ligands, thus diminishing the important charge polarization contribution of agostic bonding.

The β-elimination step is affected to a minor but not insignificant extent by the ammonia ligands, with respect to both kinetics and thermodynamics. In the methyl case (affording a propyl ligand) the ammonia ligands raise the barrier from 3.1 to 5.4 kcal/mol, and in the ethyl case the increase is larger, from 3.2 to 7.7 kcal/mol. Furthermore, this reaction is no longer thermoneutral but slightly endothermic. Both effects may in part be ascribed to reduced positive charge on palladium.

An important effect when the ammonia ligands are added is that the migration step becomes exothermic. Without the ammonia ligands the migration is endothermic by 3.1 kcal/mol in the methyl case and by 10.3 kcal/mol in the ethyl case (*vide supra*). With these ligands the migration becomes exothermic, by 7.5 kcal/mol in the methyl case and by 7.6 kcal/mol in the ethyl case. This ligand effect is clearly connected with the reduced binding energy of the olefin, and again the reduced metal charge is critical in this context.

It is interesting to note that the reverse reaction of a migratory insertion, i.e. a β-carbon−carbon bond cleavage, is thermodynamically more favorable than a β-hydride elimination for complexes void of nitrogen ligands. As the transition barriers for these β-carbon−carbon bond cleavages are rather low (15.2 kcal/mol for $PdC_3H_7^+$ and 14.8 kcal/mol for $PdC_4H_9^+$), the hypothetical (π-alkene)hydridopalladium complexes $PdH(C_3H_6)^+$ and $PdH(C_4H_8)^+$ would readily revert to (π-alkene)(σ-alkyl)palladium compounds. This is astonishing, as such a reaction would exchange a hydride−metal bond for an alkyl−metal bond. It is generally agreed that hydrides are more strongly bonded than methyl groups to the late transition metals.[29] This unusual retro migratory insertion demonstrates the importance of the greater polarizability of an alkyl group compared to a hydride in a highly unsaturated, cationic palladium. The results are in accordance with the statements concerning early transition metals and lanthanides that "β-methyl elimination may be more thermodynamically favored over β-hydride elimination for strongly electron-deficient metal centers"[30] and that "chain transfer by β-methyl elimination may be competitive with β-hydride elimination" in polymerization of propylene.[31] Increased unsaturation and/or increased positive charge on palladium appear to make palladium in some respect more like an early transition metal. In all, the coordination of ammonia or diimine thermodynamically and kinetically disfavor β-carbon−carbon bond cleavages and to a lesser extent β-hydride elimination. This result seems very reasonable, as spectator ligands tend to make the metal more willing to compress (MI) and more reluctant to increase (β-el) its coordination sphere, respectively.

Still, these barriers are very low and allow facile β-hydride elimination as well as the reverse, i.e. hydride readdition. Consequently, palladium catalysis would be expected to afford a branched polyethylene. Indeed, this is also what is observed by Brookhart, Johnson, and Killian for diimine palladium catalysts.[2] The bulkiness in these systems prevents associative displacement.

In contrast, unhindered phenanthroline catalysts do not accomplish polymerization, but merely dimerization and partially oligomerization.[1,9] This is consistent with associative displacements by ethylene and low-molecular-weight oligomers, or possibly by counterion, efficiently competing with chain propagation. Such displacements are fast for square-planar complexes and seem to accelerate with increased positive charge on the metal.[32] Readdition of low-molecular-weight oligomers will eventually promote chain growth, but this growth will gradually turn slower as the proceeding reaction yields oligomers with internal double bonds and more branched carbon skeletons.

An interesting structural parameter is the optimized angle between the ammonia ligands, and this angle is therefore given in Tables 3 and 4. Experimentally, bidentate ligands where the N−Pd−N angle is essentially fixed are often used and it is not entirely clear from the experiments what the effects of this geometrical constraint are. The largest N−Pd−N angles are found, as expected, for the three-coordinated situations, with an angle of 105.6° for methyl, of 99.0° for ethyl, of 98.8° for propyl, and of 98.3° for butyl. The monotonic decrease of this angle is in conformity with increased steric repulsion. The largest effect appears in turning from methyl to ethyl, which is the step introducing a sterically more demanding agostic interaction. For olefin complexes (for ethylene, propene, and butene) the N−Pd−N angle is 94−96°, except when the alkyl group is ethyl. Since the ethyl ligand has agostic bonding, the N−Pd−N angle is now decreased to 91.8°. The steric effect on the N−Pd−N angle of going from

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[29] Ziegler, T.; Tschinke, V. *Bonding Energetics in Organometallic Compounds*; ACS Symposium Series 428; Marks, T. J., Ed.; American Chemical Society: Washington, DC, 1990; p 284.

[30] Sini, G.; Macgregor, S. A.; Eisenstein, O.; Teuben, J. H. *Organometallics* **1994**, *13*, 1049.

[31] Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147.

[32] Åkermark, B.; Glaser, J.; Öhrström, L.; Zetterberg, K. *Organometallics* **1991**, *10*, 733.

Table 7. Reaction Energies (kcal/mol) for the Reaction between $Pd(NH_3)_2CH_3^+$ and Ethylene with a Constraint on ∠(N−Pd−N) (deg) between the Ammonia Ligands

∠(N−Pd−N)	π-equilibrium	inserted equilibrium
unconstrained	−27.3	−34.8
80	−30.9	−37.2
70	−33.5	−38.3
60	−30.8	−34.6

propene to butene is quite small, in accordance with the previous discussion; chain buildup has only a minor effect, and the conditions for agostic interaction are not changed.

c. Effects of a Constraint on the N−Pd−N Angle. Two types of models were used to study the effects on the polymerization reaction from a constraint on the N−Pd−N angle. First, the olefin bond strength and the energy of the polymerization step were studied as a function of the N−Pd−N angle. Full geometry optimizations were performed as before, but with the the N−Pd−N angle locked at 80, 70, and 60°. The results are given in Table 7.

The second model for constraining the N−Pd−N angle is the same as that used experimentally, that is to use a bidentate ligand.[33] The ligand used was $(CHNH)_2$, which has an optimized N−Pd−N angle of 76°. The results for the polymerization reaction in the methyl case are given in Table 6.

The strength of the coordination of ethylene to $Pd(NH_3)_2CH_3^+$ is 27.3 kcal/mol in the unconstrained case, where the N−Pd−N angle is 105.6° before the binding and 94° when the olefin is bound. Clearly, the olefin exerts some steric repulsion on the ligands when it is bound, which reduces the ligand bond angle. Therefore, when the ligand bond angle is constrained at a small value it is expected that this will reduce steric repulsion and thus increase the Pd−olefin bond strength. This is also what happens initially. For an N−Pd−N angle of 80° the π-bond strength increases from 27.3 to 30.9 kcal/mol, and for a still smaller angle of 70° the coordination strength increases up to 33.5 kcal/mol. For a ligand bond angle of 60° something different happens. This bond angle is so small that the Pd cation does not want to bind both ligands. Instead, one of the ammonia ligands moves away from palladium. For the ammonia ligand that is still bound to palladium, the Pd−N distance is 2.07 Å, while the other Pd−N distance is as long as 3.35 Å. This effect is actually seen to some extent already for an N−Pd−N angle of 70°, where the two Pd−N distances are 2.17 and 2.41 Å. The loss of one of the ammonia ligands for the N−Pd−N angle of 60° leads to a change of trend for the Pd−olefin bond strength, which now is reduced from the value 33.5 kcal/mol for an N−Pd−N angle of 70° down to 30.8 kcal/mol for an angle of 60°. It is not easy to find an obvious reason for this reduction of the π-bond strength. One reason could be that when only one ammonia is bound to palladium, there is no longer any steric repulsion toward the olefin and therefore no longer any gain of bond strength by a reduction of steric repulsion. This effect could have been counterbalanced by a change in the charge distribution. However, the charge distribution is very similar to the unconstrained case, even when one ammonia is no longer bound to palladium. For the unconstrained case the charge on palladium (see Table 5) changes from +0.37 to +0.21 as the olefin is bound, while for the N−Pd−N angle of 60° the change is from +0.40 to +0.23. The intermediate angles are quite similar to this. Also, the charge on the alkyl group stays rather similar, independent of the constraint on the angle. For the unconstrained case the alkyl charge changes from +0.06 to −0.01 when the olefin is added, while for the N−Pd−N angle of 60° the change is from +0.13 to +0.11. However, it should be noted that when one of the ammonia ligands is no longer directly bound to palladium but the N−Pd−N angle is still fixed, the situation is somewhat artificial and probably does not have too much bearing on actual situations. Instead, the results for 60° in Table 7 mainly serve to show the limitations of this model. For the initial polymerization step (i.e. the sum of the first ethylene addition and concomitant migratory insertion) from methyl to propyl the trend of the energy change as a function of N−Pd−N angle is quite similar to that of the olefin bond strength. However, this result is mainly due to a dominant trend of the addition step. The migratory insertion is, as seen from Table 7, disfavored on closing of the N−Pd−N angle.

The results in Table 6 for the bidentate $(CHNH)_2$ ligand illustrate trends similar to those discussed above for the constrained N−Pd−N angle with two ammonia ligands. Both the (π-alkene)metal bond strength and the exothermicity of the migratory insertion are increased when a bidentate ligand is used. For the unconstrained case the bond strength is 27.3 kcal/mol, which increases to 29.8 kcal/mol for the bidentate ligand. This effect of 2.5 kcal/mol, with an N−Pd−N angle of 76−77°, is somewhat smaller than the effect of 3.6 kcal/mol found for the N−Pd−N angle of 80° in Table 7. There is a combination of three different, partially antagonistic effects that accounts for the overall increase of the bond strength for the case with the bidentate ligand. First, as a dominating effect, there is a reduction of the steric repulsion compared to the case with two unconstrained ammonia ligands. Second, the palladium charge is greater for the case with the bidentate ligand, +0.46 compared to +0.37 for the ammonia ligands, which should also lead to a greater strength of the olefin−metal bond, but also a strengthened agostic interaction with the propyl formed. Third, there is some back-donation present with the π-orbitals of the bidentate ligand which competes with the same type of bonding for the olefin, and this effect should reduce the olefin bond strength. For a fixed N−Pd−N angle of 76° for $Pd(NH_3)_2CH_3^+$ the exothermicity of the migratory insertion step can be estimated as 5.7 kcal/mol. As this value is 7.0 for $Pd(CHNH)_2CH_3^+$, the "diimine" effect would correspond to a modest 1.3 kcal/mol.

In Table 6 the effects of constraining the N−Pd−N angle on the migration transition state and on the β-elimination step can also be seen. For the migration step the effect is a lowering of the barrier from 18.0 kcal/mol with two unconstrained ammonia ligands down to 16.4 kcal/mol for the bidentate ligand. It can be noted that this decrease occurs even though the olefin is more

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[33] Examples of N−Pd−N angles: (a) De Felice, V.; Albano, V. G.; Castellari, C.; Cucciolito, M. E.; De Renzi, A. *J. Organomet. Chem.* **1991**, *403*, 269. (b) Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitagliano, A. *Organometallics* **1990**, *9*, 1269.

strongly bound in the bidentate case. A correlation between the olefin bond strength and the barrier height does therefore not exist in this case. Instead, the origin of the lowering of the barrier is a combined result of the three different effects mentioned above, where the reduced steric repulsion is probably most important. The unconstrained bond angle at the migration transition state is 93.4° (see Table 3), which is significantly smaller than the angle for the product of 98.8° but only slightly smaller than 94.0° for the π-bound olefin. The loss of π-back-donation may also contribute to the lowering of the migration barrier. The increased charge on palladium is probably also important for reducing the barrier, since the binding becomes more ionic and therefore less sensitive to the change of direction of the bonds that occurs at the transition state.

Finally, true poly- or oligomerization catalysts based on palladium[2,9] or nickel[4] have one condition in common. The metal and a bidentate ligand form a medium-sized *nonflexible* metallacycle (five- or six-membered). Consistent with this, the calculations show the insertion barrier to be slightly lower and β-hydride elimination (from three-coordinate species) to be slightly more unfavorable in the case of a bidentate diimine ligand. It is also known that four-coordinate (σ-alkyl)palladium(II) complexes are thermally more stable and less prone to undergo β-hydride elimination if a bidentate ligand ensures "geometrical rigidity around the metal center".[34] This circumstance in common may be worth consideration.

Conclusion

Theoretical calculations afford thermodynamic and kinetic values inherent to a system unaffected by its surroundings. Sometimes such intrinsic values are close to the corresponding observed values and hence, calculations may successfully be used to obtain reliable results without the eventual need of difficult experiments. In cases where calculated and observed values differ, calculations are still of importance. Thus, information about the influence of surroundings, i.e. solvent, counterion, specially designed substituents, may be deduced. We have studied the energetics of association of ethylene to cationic (σ-alkyl)palladium complexes, subsequent migratory insertion (MI), and β-hydride elimination as seen in Figures 1 and 4.

1. The calculated strengths of the bonds between metal and alkene vary substantially with different ligand patterns. The differences are ascribed to polarization phenomena and existing β-agostic interactions of the alkyl ligand. Accordingly, coordination of alkenes to palladium is most likely sensitive to solvent and counterion, as these may alter the strength of the polarization and interfere with β-agostic interactions. It is conceivable that estimates of the strength of intrinsic coordination will differ from experimentally obtained values.

2. Migratory insertion is endothermic for naked cationic (σ-alkyl)palladium complexes. Additional nitrogen ligands turn the insertion exothermic.

3. Calculated and observed barriers of migratory insertions are pleasantly similar. This particular step therefore seem to be rather independent of solvent and counterion. Although ligands seem to be of somewhat more importance to the barrier, the variations are surprisingly small. An exception is noted for highly unsaturated $PdC_2H_5^+(C_2H_4)$. This complex has an unusually high barrier (25.1 kcal/mol). A comparatively high positive charge on the ethyl group may be responsible. The lowest barrier (16.4 kcal/mol) is obtained for a diimine complex.

4. If one looks merely at calculated values for the migratory insertion step, it would appear that a manifold of cationic (σ-alkyl)palladium complexes should be able to polymerize ethylene. Still, very few palladium complexes perform in this respect.[2] The low barrier for β-hydride elimination and following associative displacement may account for poor polymerization in most cases. The calculations show a β-hydride elimination from the three-coordinate primary insertion intermediate to be very facile.

5. The calculated ease of β-hydride elimination compared to migratory insertion is consistent with a sole insertion step in the Heck arylation. Facile β-hydride elimination is also responsible for branching in the palladium-catalyzed polymerization of ethylene.

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Supporting Information Available: A table of binding energies of ammonia to some cationic (σ-alkyl)palladium compounds (1 page). Ordering information is given on any current masthead page.

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