

Polar Copolymerization by a Palladium–Diimine-Based Catalyst. Influence of the Catalyst Charge and Polar Substituent on Catalyst Poisoning and Polymerization Activity. A Density Functional Theory Study

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Combined gradient-corrected density functional theory and molecular mechanics (QM/MM) has been used to investigate the copolymerization of ethylene with the $\text{CH}_2=\text{CHX}$ α -olefins, where $\text{X} = -\text{H}, -\text{Me}, -\text{CN}, -\text{COOMe}, -\text{OC(O)-Me}, -\text{Cl}$. The cationic $\text{N}\wedge\text{N}$ -Pd(II) diimine complex and its modified neutral and anionic derivatives have been used as catalysts, where $\text{N}\wedge\text{N} = -\text{NR}''\text{CR}^2\text{CR}^3\text{NR}''-$, $\text{R}'' = \text{aryl group}$, and $\text{R}^2, \text{R}^3 = \text{BH}_3^-, \text{H}$. The consecutive insertion steps of $\text{CH}_2=\text{CHX}$ into the Pd– CH_3 bond and of ethylene into the Pd– $\text{C(X)HCH}_2\text{CH}_3$ bond have been investigated. Focus has been put on the role of the X functional groups and the effect of the cationic, neutral, and anionic environments on the Pd(II)–diimine system. Calculations have been performed on the $\text{CH}_2=\text{CHX}$ monomers, model catalysts, precursor π -complexes, and σ -complexes of the monomers, as well as the chelate and H-agostic insertion products. The transition state of the insertion reaction and the corresponding activation energy was determined for both investigated insertion steps. The results show that the X group has only a minor effect on the insertion of the $\text{CH}_2=\text{CHX}$ monomers into the Pd– CH_3 bond. On the other hand, the barrier for insertion of ethylene into the Pd– CHXR bond revealed an increase with the electron-withdrawing ability of X. We predict that the application of neutral and anionic catalysts leads to a preference for π -complexation over σ -complexation of the polar monomers. Unfortunately, for an anionic model system the barriers for the first and second insertion are significantly increased for ethylene, whereas the first insertion barrier for the polar monomers only is moderately increased. Thus, while anionic catalysts are highly tolerant toward polar monomers, they are nearly inactive toward ethylene insertion.

Introduction

Copolymerization of ethylene with polar comonomers ($\text{CH}_2=\text{CHX}$) by late transition metals¹ is a very active research area. Coordination copolymerization of ethylene with vinyl ketones and acrylate^{2,3} has been explored using the Pd(II)- and Ni(II)-based cationic diimine catalysts introduced by Brookhart^{1,4} and co-workers. On the other hand, insertion copolymerization of ethylene with vinyl chloride has never been convincingly dem-

onstrated, due to difficulties recently analyzed by Jordan and co-workers.⁵ Acrylonitrile–ethylene copolymerization is one of the biggest challenges of recent polymer chemistry. Another family of catalysts that tolerate functional groups are the Ni(II) salicylaldimino complexes by Grubbs and co-workers.^{6a,b} Recently, by the additions of Al or $\text{B}(\text{C}_6\text{F}_5)_3$ to oxo-group-containing Ni(II) complexes, novel activations have been intro-

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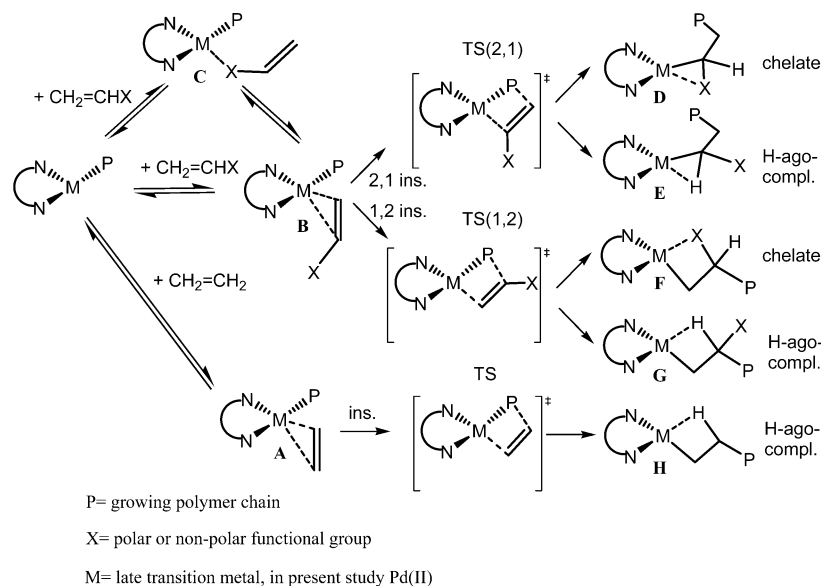
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Scheme 1. Elementary Reaction Steps in Copolymerization of Ethylene with CH₂=CHX Comonomers

duced by Bazan and co-workers.^{6c–g} Other zwitterionic complexes^{6h,i} are also active for dimerization, oligomerization, and polymerization of ethylene and other olefins.

Anionic complexes of late transition metals have also been considered as polymerization catalysts. The greater functional group tolerance of late-transition-metal complexes⁷ relative to early metals makes them the likely targets for the development of catalysts for the copolymerization of ethylene with polar comonomers under mild conditions.^{8,9}

The mechanism of copolymerization involves a competition between olefin and the polar monomer (see Scheme 1). The incorporation of the polar and nonpolar monomers into a polymer chain by coordination polymerization is likely to be possible if the polar monomer insertion follows the same Cossee–Arman mechanism¹⁰ as the nonpolar monomer (Scheme 1). Thus, before insertion, the polar monomer must be bound^{4,8,11} to the metal center by its C=C bond (**B**) rather than by its polar functionality (**C**) (Scheme 1). There are two major alternative insertion routes for CH₂=CHX olefins, where X is a functional group. The insertion step can follow a 1,2- and a 2,1-pathway in which the nonsubstituted or the substituted carbon atom forms the bond with the metal atom, respectively (see Scheme 1). In most of the cases the 2,1-insertion has a lower barrier than the 1,2-insertion.^{13e,f} This preference has been rationalized by Michalak et al.^{13e}

The insertion of ethene or propene gives rise to the agostic complexes **E** and **G** of Scheme 1. These products can insert another monomer, or they can isomerize into other agostic complexes. In contrast, the insertion mechanism of polar monomers is more complicated because of the formation of chelate structures (**D** and **F**). In a chelate structure, the polar group sitting on the alkyl chain in α -, β -, γ -positions etc. can bind to the metal atom, thus forming a chelate ring structure. Further, smaller chelate rings can isomerize to higher member chelate structures. The incorporation of the next monomer unit requires an opening of the chelates for the catalytic cycle to repeat itself. Thus, an understanding of the copolymerization processes requires knowledge of the relative stabilities of all the reaction intermediates as well as the energy barriers for all the elementary steps.

We shall in the following consider copolymerization between ethylene and the CH₂=CHX monomers propene (**2b**), acrylonitrile (**2c**), methyl acrylate (**2d**), vinyl acetate (**2e**), and vinyl chloride (**2f**), with the X groups given by –Me, –CN, –COOMe, –OC(O)Me, and –Cl, respectively (Chart 1). The process will be catalyzed by the cationic Pd–diimine Brookhart complex **1** with bulky aryl substituents on the N-heteroatoms (see Chart 1).

It is a prerequisite for a good polar copolymerization catalyst that the π -complexation (**1** \rightarrow **4**) be equal in strength to the σ -binding (**1** \rightarrow **3**) (Scheme 2), so that the catalyst is not poisoned. Recent experimental¹² and computational^{13,14} works have revealed that cationic

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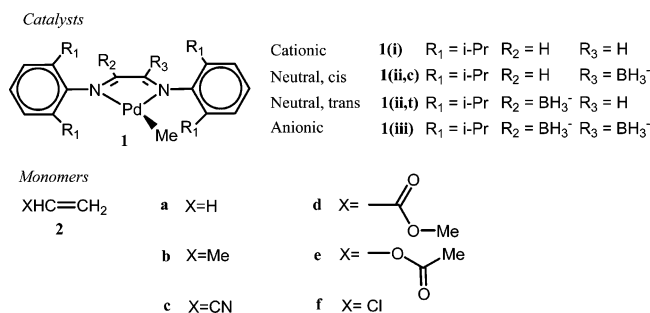
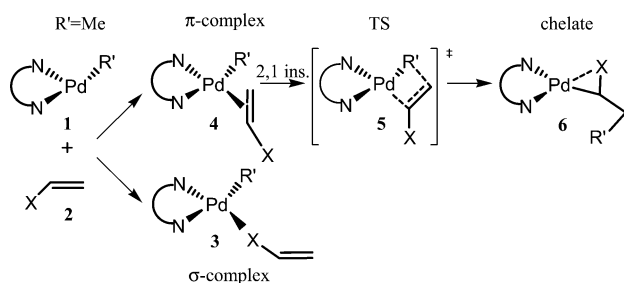
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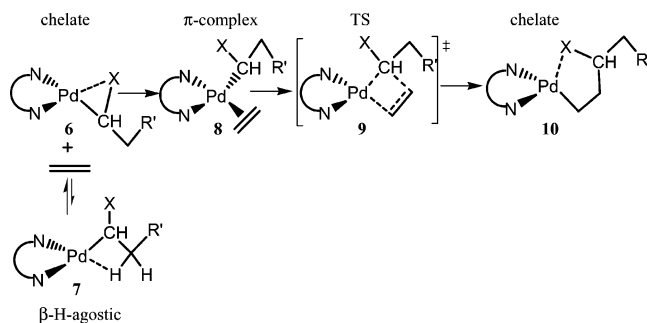
Chart 1. Scope of the Investigated Monomers and the Pd(II) Diimine Complex**Scheme 2. Incorporation of the CHX=CH₂ Monomers**

Pd(II) and Ni(II) diimine complexes in many cases exhibit a preference for σ -complexation. Fortunately, computational work has also demonstrated that the application of a neutral or anionic environment can promote the π -coordination mode over the σ -mode.^{13a,c,15} Therefore, we have also investigated the modification of the cationic Brookhart complex by replacing one or more hydrogen atoms by anionic BH₃⁻ substituents on the backbone of the Pd–diimine ring (Chart 1). Thus, the first objective has been to gauge the relation between catalyst charge and catalyst poisoning.

The second objective has been to examine how the X group influences the activation barrier for the insertion of the CH₂=CHX monomer into the M–CH₃ bond (Scheme 2). This examination will again be carried out for the cationic Pd(II) Brookhart complex, as well as its neutral and anionic derivatives, in order to gauge the influence of the catalyst charge.

It is generally believed that a polar substituent at the α -position of the growing polymer chain might inhibit the second insertion because (i) the polar groups are able to form a very stable chelate **6** with the metal atom, (ii) polar groups can bind to the metal atom of the neighboring molecule, forming oligomers, or (iii) they can act with their electronic or steric influence, which might inhibit the next monomer insertion. Therefore, as the third objective of our study, we have investigated the next step of the polymerization when a prior polar comonomer insertion is followed by the ethylene insertion **8** → **9** (Scheme 3), with the polar group X in the α -position. Again special emphasis will be given to the influence of the catalyst charge. The situation in which the growing chain isomerizes^{8a,14b} to a chelate with the polar group X in a β -, γ -, or δ -position prior to insertion will be considered elsewhere.^{15b}

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Scheme 3. Ethylene Insertion into a Pd–CHXCH₂R' Bond**Computational Details**

Molecular geometries have been optimized at the level of gradient-corrected density functional theory using the Becke–Perdew exchange–correlation functional.^{16–18} The calculations have been carried out with the Amsterdam Density Functional (ADF 2000) program package developed by Baerends et al.^{19,20} and vectorized by Ravenek.^{21,22} The numerical integration scheme applied for the calculations was developed by te Velde et al.²³ The geometry optimization procedure was based on the method of Versluis and Ziegler.²⁴ For the palladium atom the standard triple- ζ STO basis set, from the ADF database IV, was employed with 1s–3d electrons treated as a frozen core. For the nonmetal elements a standard double- ζ basis set with one set of polarization functions (ADF database III) was applied, with frozen cores including 1s electrons for B, C, N, and O and 1s2s2p for Cl.^{25,26} Auxiliary²⁷ s, p, d, f, and g STO functions centered on all nuclei were used to fit the Coulomb and exchange potentials during the SCF process. The reported relative energies include scalar relativistic corrections,^{28–30} since it was shown that such an approach is sufficient for the systems containing the 4d transition metals.³¹ All structures shown correspond to minimum points on the potential surface, except those prefixed by TS, which represent transition states. Transition states were fully optimized using the algorithm of Banerjee et al.,^{32,33} starting from the structures obtained by linear transit calculations. No symmetry constraints were used.

The combined DFT and molecular mechanics calculations were performed using the quantum mechanics/molecular

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mechanics (QM/MM) implementation in the ADF program.³⁴ An augmented Sybyl molecular mechanics force field³⁵ was utilized to describe the molecular mechanics potential, which includes van der Waals parameters from the UFF force field³⁶ for palladium and boron. In the combined QM/MM calculations, the QM part consisted of the generic complex, in which the 2,6-diisopropylphenyl substituents on the nitrogen atoms were replaced by hydrogen atoms. The actual bulky aryl groups attached to the nitrogens were treated by the pure MM method. QM(DFT) and MM parts are coupled self-consistently according to the method prescribed by Maseras and Morokuma^{37a} and implemented into the ADF program by Woo et al.^{37b} The geometry optimization on the entire system was carried out with coupling between QM and MM atoms. In the optimization of the MM part, the N–C(aryl) distances were constrained to be 0.33 Å longer than the optimized N–H(generic) distance. Electrostatic interactions were not included in the molecular mechanics potential. A similar approach has been applied successfully in previous studies of the Brookhart diimine systems.^{38a–d} The density functional theory methodology we use has become a reliable tool for understanding the chemistry of group 10 transition-metal complexes and for their polymerization catalysts.^{38,39}

We should finally note that the energetics discussed below are missing zero-point vibrational energy and entropy corrections, since it was impractical to perform a vibrational analysis on systems of the size considered here. Also, at this stage of our work, we did not carry out investigation of the solvent and counterion effects. From our experience with the Brookhart catalyst, counterion effects are not important for the late transition metals.^{38a–d} Also, we do not expect solvation effects to be important as long as no charge separation is involved.^{38e,h}

Results and Discussion

σ - vs π -Complexation. The calculated complexation energies for the various comonomers (**2a–f**) in the σ -mode (**3c–f**) or the π -conformation (**4a–f**) (Scheme 2) are given in Table 1. All binding energies are with respect to the separated cationic (**1(i)**), neutral (**1(ii,c)**), or anionic (**1(iii)**) [Pd]–Me complexes and the monomers (**2a–f**). The results for the cationic complexes presented in this paper compared well (to within a few kcal mol⁻¹) with estimates from previous calculations by Goddard et al.,^{14b} Svensson et al.,^{14a} and Ziegler et al.¹³

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Table 1. Relative Energies (ΔE , kcal mol⁻¹) and Insertion Barriers (ΔE^\ddagger) of the Studied Complexes for Ethylene (2a**) and Comonomers (**2b–f**)**

monomer CHX=CH ₂		catalyst charge	$\Delta E(\mathbf{n})$			
X group	2a–f		σ -compl ^a 3	π -compl ^a 4	TS 5 ^a	$\Delta E^\ddagger(\mathbf{5})^b$
–H	2a	cationic 1(i)		–40.2	–23.9	16.3
–H	2a	neutral ^c 1(ii)		–33.8	–12.2	21.6
–H	2a	anionic 1(iii)		–30.7	–6.3	24.4
–Me	2b	cationic 1(i)		–44.8	–25.9	18.9
–CN	2c	cationic 1(i)	–47.5	–34.4	–18.1	16.3
–CN	2c	neutral ^c 1(ii)	–34.2	–34.2	–13.8	20.5
–CN	2c	anionic 1(iii)	–29.6	–36.8	–17.5	19.3
–COOMe	2d	cationic 1(i)	–40.8	–41.2	–26.0	15.1
–COOMe	2d	anionic 1(iii)	–19.7	–33.5	–15.6	17.9
–OC(O)Me	2e	cationic 1(i)	–38.6	–43.4	–24.9	18.6
–Cl	2f	cationic 1(i)	–26.9	–38.5	–21.2	17.3
–Cl	2f	anionic 1(iii)	–12.5	–31.3	–10.1	21.2

^a Relative energies $\Delta E(\mathbf{n})$ (kcal mol⁻¹) of the compounds (**n** = **3–5**) are with respect to the separated [Pd]–Me complex and the monomer. ^b $\Delta E^\ddagger(\mathbf{5}) = \Delta E(\mathbf{5}) - \Delta E(\mathbf{4})$. ^c The energy of the thermodynamically most stable isomer is shown.

Among the polar monomers acrylonitrile is an extreme case. For the cationic Pd-based Brookhart catalyst **1(i)**, acrylonitrile **2c** forms the most stable σ -complex among the polar monomers with a relative energy relative to **1** and **2** of $\Delta E(\mathbf{3}) = -47.5$ kcal mol⁻¹ (Table 1). For the CN group the typical binding mode is the end-on mode over the side-on coordination mode.^{14b} The oxygen-containing methyl acrylate (**2d**) and vinyl acetate (**2e**) are next, with binding energies of –40.8 and –38.6 kcal mol⁻¹, respectively. The oxygen-containing (**2d,e**) polar groups form O-complex binding with their lone pair. Other binding modes are thermodynamically less stable.^{13,14b} The vinyl chloride **2f** forms the weakest bond, with an energy of –26.9 kcal mol⁻¹. The heteroatom on the X group carries a negative charge that is attractive to the positive metal charge and follows the order N > O > Cl. This order accounts for the stability of the σ -complex.

We note in turning to the π -complexation that trends in the binding energies $\Delta E(\mathbf{4})$ here can be rationalized in terms of the π/π^* -frontier orbitals^{13,14} of the monomers **2a–f** (Figure 1). A monomer with an electron-donating X group, e.g. a methyl group, has a destabilizing effect on the frontier orbitals; therefore, propene is a better donor and poorer acceptor than ethylene. A monomer with a strongly electron withdrawing substituent, e.g. the CN group, has a stabilizing effect on the frontier orbitals; therefore, acrylonitrile (**2c**) is a poorer electron donor and better acceptor than ethylene (**2a**). For the oxygen-containing polar monomers and vinyl chloride the relative energies of the π -donor and π^* -acceptor orbitals are between those of propylene and acrylonitrile. It follows from Table 1 that π -complexation is more favorable than σ -coordination for all monomers, except acrylonitrile (**2c**), bound to the cationic complex **1(i)**. Further, the dominating bonding mode for π -complexation to the cationic complex **1(i)** must be π -donation to the metal. It is thus not surprising that π -complexation is strongest for propylene and weakest for acrylonitrile, with the oxygen-containing polar monomers and vinyl chloride in between.

We shall next gauge the influence of the overall catalyst charge on the relative stability of π - and σ -complexation by substituting one or two hydrogen

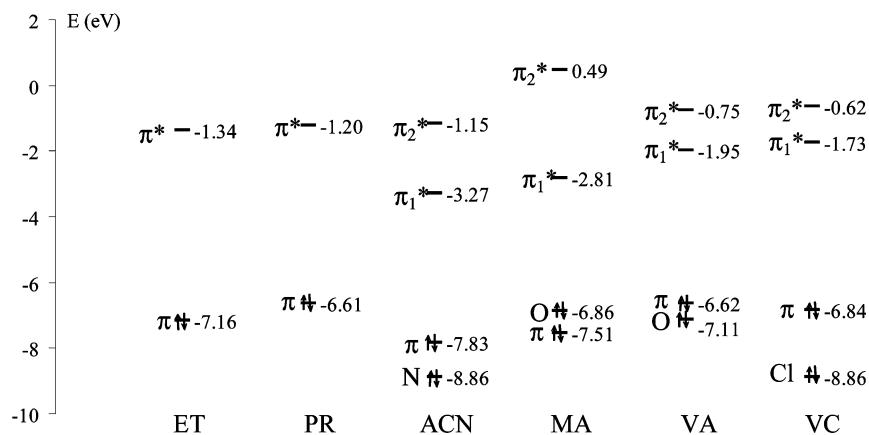


Figure 1. Frontier orbitals of the monomers studied.

Table 2. Relative Energies (ΔE , kcal mol⁻¹) of the Species, Complexation Energies, and Insertion Barriers (ΔE^\ddagger) of Ethylene Insertion after a Prior 2,1-Insertion of Comonomers

[Pd]–CXR		β -H agostic complex 7		$\Delta E(n)$			
X group	charge	charge	chelate ^a 6	π -compd ^b 8	TS ^c 9	π -compd ^d $\Delta E'$ (8)	TS ^e ΔE^\ddagger (9)
–Me	b	cationic	(i)	–16.3	2.4	–16.3	18.7
–CN	c	cationic	(i)	–5.4	–24.7	–1.0	23.7
–CN	c	neutral ^f	(ii)	–3.4	–23.1	4.0	27.1
–CN	c	anionic	(iii)	–1.9	–21.9	10.5	32.4
–COOMe	d	cationic	(i)	–6.9	–19.4	1.8	21.2
–OC(O)Me	e	cationic	(i)	–15.6	–24.6	0.0	24.6
–Cl	f	cationic	(i)	–5.6	–25.3	0.2	25.6

^a Energy of chelate complex **6** relative to β -agostic complex **7** of Scheme 3. ^b Energy of π -complex **8** relative to free ethylene and β -agostic alkyl complex **7**. ^c Energy of transition state **9** relative to β -agostic complex **7** and free ethylene. ^d Energy of π -complex **8** relative to free ethylene and chelate complex **6**. ^e Energy of transition state **9** relative to ΔE (**8**). ^f The energy of the thermodynamically most stable isomer is shown.

atoms on the backbone of the cationic Pd Brookhart complex (see Chart 1) with BH₃[–] ligands to generate the cis and trans neutral (**1(ii,c)** and **1(ii,t)**) and anionic (**1(iii)**) model catalysts, respectively. The cis neutral alkyl complex **1(ii,c)** is more stable than the trans neutral complex **1(ii,t)** by 1.7 kcal mol⁻¹. Therefore, in Tables 1 and 2, only the relative energies of the thermodynamically more stable isomers are shown, with respect to the separated monomer and the cis neutral alkyl complex. Considering first acrylonitrile with the strongest σ -complexation in the cationic case (–47.5 kcal mol⁻¹), we note that the σ -bond strength has declined to –34.2 kcal mol⁻¹ (**1(ii)**) for the neutral system and –29.6 kcal mol⁻¹ (**1(iii)**) for the anionic complex (Table 1). The trend is easily rationalized when we note that the interaction between the negative nitrogen on acrylonitrile and the metal complex **1** is weakened as the charge on **1** goes from positive to negative (Table 1). The same destabilization is seen for X = –COOMe, –Cl when we go from the cationic to the anionic complex (Table 1).

The influence of the overall catalyst charge on the π -complexation can be studied by comparing π -bonding energies for acrylonitrile and ethylene. The strength of the π -bond is seen to decrease as we go from the cationic to the anionic system for ethylene (Table 1). This is understandable, since the predominating bonding mode is switching from π -donation to π^* -back-donation and ethylene is a better donor than acceptor. On the other hand, acrylonitrile with the electron-withdrawing group is a better acceptor, for which the π -bond strength increases from positive to negative catalyst charge (Table 1). For methyl acrylate (**2d**) and vinyl chloride (**2f**) we see a decrease in the π -bond strength as in the

case of ethylene. However, the decrease is smaller due to the (moderately) electron-withdrawing substituents –COOMe and –Cl. It follows from our study that the relative strength of σ - and π -complexation is strongly influenced by the catalyst charge. Thus, in going from a cationic to a neutral or anionic system, one is able to switch from σ - to π -complexation as the preferred bonding mode and thus avoid any poisoning of the catalyst.

Insertion of the CH₂=CHX Monomer into the Pd–CH₃ Bond. The calculated energies ΔE (**5**) of the transition states **5** relative to the monomer **2** and the methyl complex **1** are given in Table 1 along with the 2,1-insertion barriers ΔE^\ddagger (**5**) = ΔE (**5**) – ΔE (**4**). It follows from Table 1 that the relative energies ΔE (**5**) of the cationic transition states **5(i)** are correlating with the relative energy of the corresponding π -complexes, ΔE (**4**). Thus, the lower the relative energy of the π -complex ΔE (**4**) for one particular monomer, the lower the relative energy of the transition state, ΔE (**5**). Therefore, the calculated internal barriers of the 2,1-insertion step ΔE^\ddagger (**5**) = ΔE (**5**) – ΔE (**4**) are within the range from 15.1 to 18.9 kcal mol⁻¹ and exhibit only a minor influence from the X group (**a–f**).

It is well-known that the geometric structures of the π -complexes and transition states are substantially different (Scheme 1). In the π -complex the orientation of the monomer C=C bond is perpendicular to the plane of the Pd–diimine ring (Scheme 1). Moreover, in an insertion step, the inserting olefin must turn into the plane of the Pd–diimine ring (Scheme 1). With this motion the attacking olefin also elongates the [Pd]–Me bond, but of course it is not completely broken in the transition state.

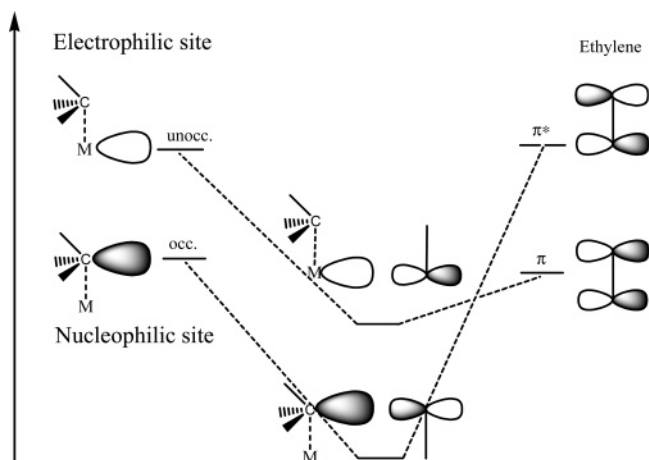


Figure 2. Schematic representation of the donor–acceptor interaction in the transition state of the ethylene insertion.

The key interactions between the (distorted) metal fragment and the (distorted) monomer in the transition state involves two electron pairs, the first of which participates in a ligand to metal donation and the other in a metal to ligand back-donation just as in the π -complexation (Figure 2). The donation is a charge transfer from the occupied π -orbital of the olefin (polarized toward the substituted carbon) to an unoccupied orbital of the metal fragments. The unoccupied orbital has mainly metal d character. On the other hand, the back-donation is a charge transfer from the metal fragment orbital to the π^* of olefin (polarized toward the unsubstituted carbon). The donor orbital (mainly HOMO) of the metal fragment has a large contribution from the methyl carbon atom (41% carbon p character), because of the partially broken Pd–Me bond (Figure 2). For the cationic metal fragment the donor mode is the most important. It is not surprising for the cationic metal fragments where donation is predominant that good donor monomers (such as ethylene) are able to stabilize not only the π -complex but also the transition state **5**, whereas poor donors (such as acrylonitrile) give rise to a much weaker π -complex and a less stable transition state (Table 1). As a result in the cationic case, the 2,1-insertion barriers are nearly the same for all the monomers whether they are poor or good π -donors.

We apply the Curtin–Hammett reactivity rules to calculate the insertion barriers of the neutral systems.^{13b} Moreover, all neutral data are located between the cationic and anionic values. Therefore we carried out studies only for the X = H and X = CN cases with the neutral catalyst. Changing now the catalyst charge from cationic to neutral and anionic, we note for ethylene a destabilization of the transition state **5**, as one would expect for a poor acceptor monomer such as ethylene. The destabilization is larger than for the π -complex, with the result that the insertion barrier increases substantially. For the good electron acceptor acrylonitrile we notice that the substantial decrease in the TS stability observed for ethylene is turned into a marginal destabilization, due to the good acceptor ability of the –CN group. As a result the increase in the 2,1-insertion barrier is modest. For methyl acrylate (**2d**) and vinyl chloride (**2f**), which are intermediate π -acceptors, we observe an increase in the 2,1-insertion barrier $\Delta E^\ddagger(\mathbf{5})$

that is larger than for ethylene but more modest than for acrylonitrile. Thus, going from a cationic to a neutral or anionic Pd–CH₃ polymerization catalyst is likely to decrease the rate of insertion of CH₂=CHX into the Pd–CH₃ bond. The decrease is large for good π -donors (X = –H, –CH₃) and only modest for good π -acceptors (X = –CN).

We shall end this section by making a few comments about the preference for 1,2- vs 2,1-insertion. The insertion barrier has two contributions. The first is a deformation of the monomer and the Pd–Me complex from the geometries in the π -complex to the structures in the transition states. The second is the difference in interaction energy between the two fragments in the TS state and the π -complex. We find the second term to be nearly (~ 0.5 kcal mol^{–1}) the same for the two insertion processes, although one might have expected the polarization^{12a,b,40} of the π^* -orbitals toward the substituted carbon to favor 1,2-insertion. On the other hand, the deformation term is largest for the 1,2-insertion. The reason for this is that the carbon forming the new C–C bond is sp³ hybridized and that such a hybridization is more difficult for a substituted carbon.^{13e}

Ethylene Insertion into the Pd–C(X)HCH₂CH₃ Bond. We considered in the previous section the 2,1-insertion of the CH₂=CHX monomer into the Pd–CH₃ bond. We shall now discuss the subsequent insertion of ethylene into the Pd–C(X)HCH₂CH₃ bond (see Scheme 3).

The cationic complex Pd–C(X)HCH₂CH₃ can, prior to ethylene uptake, adopt a conformation where the chain is bound to the metal either through a β -agostic interaction involving a β -hydrogen (**7**) or through a chelate interaction involving a heteroatom on the X group (**6**). It follows from Table 2 that the chelate conformation for all the X groups is preferred, since the energy $\Delta E(\mathbf{6})$ of **6** relative to **7** in all the cases is negative. The most stable chelate **6(i)–2f** is formed by the vinyl acetate with a relative energy of -15.6 kcal mol^{–1}, with respect to the β -H agostic complex. The stability of the acetate chelate is very high because of the formation of a five-membered ring. Other chelate structures were found to be less stable.^{12d,13a} After 2,1-insertion, acrylonitrile and methyl acrylate form four-membered chelate rings with relative energies of -5.4 and -6.9 kcal mol^{–1}, respectively. However, according to earlier computational studies^{8,14b} these two chelates can isomerize to six- and eight-membered rings by isomerization (chain walking). However, in our work we are primarily interested in how the X group at the α -position influences the ethylene insertion barrier. We shall as a consequence postpone a discussion of chain walking to a later study.^{15b} The influence of the catalyst charge on the preference for chelate formation, $\Delta E(\mathbf{6})$, was examined for acrylonitrile (Table 2). As one could expect, the preference decreases in going from the cationic to the anionic complex, as the interaction between the negative charge on nitrogen and the total charge on the complex becomes less favorable. We expect a similar trend for the other X groups.

The trend in the stability $\Delta E(\mathbf{8})$ of the π -complex (**8**) relative to ethylene and the β -agostic alkyl complex **7** with the –C(X)HCH₂CH₃ chain is a good measure of

(40) Deubel, D. V. *J. Org. Chem.* **2001**, *66*, 3790.

how the X group influences ethylene complexation (Table 2). We note for the cationic systems that the two strongly electron withdrawing substituents X = –CN, –Cl give rise to the most stable π -complexes, whereas the electron-donating substituent X = –CH₃ affords the least stable complex (Table 2). This trend is in line with the fact that ethylene is a better donor than acceptor, as discussed previously. One would expect the two substituents X = –COOMe, –OC(O)Me of intermediate electron-withdrawing strength to afford π -complexes of intermediate strength. This is also the case for X = –COOMe. However, for X = –OC(O)Me the π -complex acquires some extra strength by forming a Pd–O chelate bond in the axial position, which makes this π -complex equal in strength to those with X = –CN, –Cl. The other X groups do not form chelate bonds in the π -complex. Changing the metal complex from cationic to neutral and anionic reduces the stability $\Delta E(\mathbf{8})$ of the ethylene π -complex, as is shown for acrylonitrile in Table 2. This is to be expected, since the important bonding mode changes from donation to back-donation, and ethylene is a better donor than acceptor. We expect a similar trend for the other X substituents. In reality the most stable conformation for the alkyl complex has a chelate bond (**6**) rather than a β -agostic interaction (**7**). Thus, one should give the stability of the π -complex relative to **6**, as is done in Table 2 under the heading $\Delta E'(\mathbf{8})$. Now the regularity observed for $\Delta E(\mathbf{8})$ is to some degree masked by the fact that the X substituents form chelate bonds of different strengths.

We shall finally turn to the barrier for ethylene insertion into the Pd=C(X)HCH₂CH₃ bond. It will again prove informative initially to consider the cationic systems with the β -agostic alkyl complex **7** as the reference state. Table 2 gives under the heading $\Delta E(\mathbf{9})$ the energy of the transition state **9** relative to **7** and free ethylene. We note the same trends as for the ethylene complexes. Thus, **9** is least stable for X = –CH₃ and most stable for X = –CN, –Cl, –OC(O)–Me, with the last group again entering due to an axial chelate interaction. X = –COOMe is intermediate. However, the variation in $\Delta E(\mathbf{9})$ for different X groups is much smaller than for $\Delta E(\mathbf{8})$. We see as a consequence that the barrier $\Delta E^+(\mathbf{9}) = \Delta E(\mathbf{9}) - \Delta E(\mathbf{8})$ primarily is set by the stability of the π -complex. Thus, the three-electron-withdrawing substituents X = –CN, –Cl give rise to stable π -complexes and high barriers, whereas X = –CH₃ is responsible for a weaker π -complex and a lower barrier. Again, X = –COOMe is seen to be intermediate, whereas X = –OC(O)Me is off with a higher than expected barrier due to chelate formation. Changing from the cationic to the neutral and anionic systems for X = –CN destabilizes both the π -complex ($\Delta E(\mathbf{8})$) and the transition state ($\Delta E(\mathbf{9})$), again because ethylene is a better donor than acceptor. However, the transition state is destabilized more than the π -complex and the barrier is therefore seen to increase from the cationic to the anionic system (Table 2). We expect a similar trend for the other X groups.

It should be pointed out that the most stable conformation for the alkyl complex has a chelate bond (**6**) rather than a β -agostic interaction (**7**). Thus, one should give the stability of the π -complex **8** and the transition state **9** relative to **6**, as is done in Table 2 under the

headings $\Delta E'(\mathbf{8})$ and $\Delta E'(\mathbf{9})$. However, such a change of reference does not affect the magnitude of the insertion barrier, since $\Delta E^+(\mathbf{9}) = \Delta E(\mathbf{9}) - \Delta E(\mathbf{8}) = \Delta E'(\mathbf{9}) - \Delta E'(\mathbf{8})$.

Conclusion

We have considered copolymerization between ethylene and the CH₂=CHX monomers propene (**2b**), acrylonitrile (**2c**), methyl acrylate (**2d**), vinyl acetate (**2e**), and vinyl chloride (**2f**), with the X groups given by –Me, –CN, –COOMe, –OC(O)Me and –Cl, respectively (Chart 1), with the cationic Pd–diimine Brookhart complex (**1(i)**) and its neutral (**1(ii)**) and anionic derivatives (**1(iii)**) as the catalysts.

It is a prerequisite for a good polar copolymerization catalyst that the π -complexation (**1** \rightarrow **4**) at least is competitive in strength with the σ -binding (**1** \rightarrow **3**) (Scheme 2), so that the catalyst is not poisoned. We have shown that it is possible for all the monomers to turn the preference from σ -binding (**1** \rightarrow **3**) in the cationic system (**1(i)**) to π -complexation (**1** \rightarrow **4**) by going to the neutral or anionic Brookhart catalyst. Thus, direct poisoning of the catalyst by the polar monomer can always be prevented by making the catalyst neutral or negative.

The second part of the study investigated how the X group influences the activation barrier for the insertion of the CH₂=CHX monomer into the M–CH₃ bond (Scheme 2). For the cationic system, it was shown that the X group destabilized the π -complex and the insertion transition state as it became more electron withdrawing (relative to X = –CH₃). However, the destabilization was quite similar for the two systems, so that the barrier of insertion remained constant within the narrow range of 15.1–18.9 kcal mol^{–1}. On the other hand, going to neutral and negative complexes raised the insertion barriers. The increase was only modest for the more electron-withdrawing substituents such as X = –CN but substantial for X = –H. Thus, for the anionic system the barrier of insertion for X = –H is 24.4 kcal mol^{–1}, compared to 19.3 kcal mol^{–1} for X = –CN, whereas the corresponding values were 16.3 and 16.4 kcal mol^{–1}, respectively, for the cationic systems. It is thus clear that the change of the catalyst from cationic to anionic might solve the problem of poisoning only to introduce a reduced polymerization activity toward the nonpolar monomer.

We have finally studied the second propagation step in which ethylene inserts into the Pd–C(X)HCH₂CH₃ bond. The barrier for this process was found to increase with the electron-withdrawing ability of the X substituents as well as the total electron charge on the catalyst. Thus, the barrier of insertion for X = –H (cationic) is 18.7 kcal mol^{–1}, compared to 23.7 kcal mol^{–1} (cationic) and 32.4 kcal mol^{–1} (anionic), respectively, for X = –CN. It is apparent for the second insertion step as well that the change of the catalyst from cationic to anionic might solve the problem of poisoning only to introduce a reduced polymerization activity toward the nonpolar monomer. Thus, while anionic Pd(II) catalysts are highly tolerant toward polar monomers, they are nearly inactive toward ethylene insertion.

It is generally believed^{8,13,14c} that a polar substituent at the α -position of the growing polymer chain might

inhibit the second insertion, because the polar groups are able to form a very stable chelate with the metal atom or polar groups can bind to the metal atom of the neighboring molecule, forming oligomers. Experimental and theoretical studies based on our idea of using anionic substituents such as BF_3^- to reduce the poisoning of the catalyst by the polar group will appear later.¹⁵

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Supporting Information Available: Tables giving the optimized geometries of the crucial structures reported in the paper (the atomic symbols followed by three Cartesian coordinates, in Å). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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