

The Exploration of Neutral Azoligand-Based Grubbs Type Palladium(II) Complex as Potential Catalyst for the Copolymerization of Ethylene with Acrylonitrile: A Theoretical Study Based on Density Functional Theory

Sheng-Yong Yang,[†] Miklos J. Szabo,[†] Artur Michalak,[‡] Thomas Weiss,[§]
Warren E. Piers,[†] Richard F. Jordan,[⊥] and Tom Ziegler^{*,†}

Department of Chemistry, University of Calgary, University Drive 2500, Calgary, Alberta, Canada T2N 1N4, Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland, Bayer AG, Bayer Polymers, BPO-IIS-INN-SYR-SPE, 51368 Leverkusen, Q18, Germany, and Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

Received December 12, 2004

A combined quantum-mechanical (QM) and molecular-mechanical (MM) method has been used to explore the potential of neutral azoligand-based Grubbs type Pd(II) complexes as catalysts for ethylene–acrylonitrile copolymerization. The first part of the investigation includes complexation of the monomers to the catalyst, the first insertion step, and isomerization of the first insertion product **1**. The results show that the π -complexation energies of acrylonitrile and ethylene are comparable, but the acrylonitrile insertion has a lower barrier over ethylene insertion by ca. 5 kcal/mol in the first step. The leading product **1** might conduct a series of isomerizations with a lower barrier to form different chelate structures. However, the most stable isomers have the CN group in the α -position. The second part explores the further role of the kinetic insertion product **1**. It is shown that **1** readily can complex another ethylene or acrylonitrile monomer. Unfortunately, it is even more favorable for **1** to coordinate its Pd(II) center to a nitrogen atom on a α -cyano-alkyl group of another **1** complex, leading to inert oligomers of **1** that do not further react with ethylene or acrylonitrile. Trimers of **1** are preferred over dimers because they allow for an optimal linear Pd–NC bonding mode with an angle of $\sim 180^\circ$. The preference for palladium coordination to the nitrogen on a α -cyano-alkyl group over N-coordination to acrylonitrile stems from the fact that the acrylonitrile nitrogen is less electron rich due to donation to the π^* orbital of the olefinic bond.

Introduction

Incorporation of polar monomers into the polyolefin chain can significantly improve the properties of a polymer in terms of its toughness and compatibility with other materials.^{1,2} Unfortunately, to date, polymers containing polar monomers are produced via expensive radical polymerization processes.^{3,4} Thus, finding alternative routes to polar copolymerization would be an important development.

One such attractive alternative route is transition metal catalyzed coordination copolymerization. Group

4 metallocenes, and other early transition metal single-site coordination polymerization catalysts, are unfortunately easily poisoned by polar reagents. On the other hand, late transition metal complexes are not as readily poisoned by polar groups containing oxygen or nitrogen. Indeed, recently some progress has been achieved in incorporating oxygen-containing polar groups into polyolefins by coordination polymerization.^{5–12} Thus, the cationic Brookhart^{5–7,13–15} Pd-diimine polymerization

* To whom correspondence should be addressed. E-mail: ziegler@ucalgary.ca.

[†] University of Calgary.

[‡] Jagiellonian University.

[§] Bayer AG.

[⊥] The University of Chicago.

(1) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479.

(2) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(3) Hagman, J. F.; Crary, J. W. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. W., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley: New York, 1985; Vol. 1, p 325.

(4) Hirai, H.; Gotah, H. In *Polymer Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, 1996; p 192.

(5) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

(6) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

(7) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.

(8) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.

(9) Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 534.

(10) Mecking, S. *Coord. Chem. Rev.* **2002**, *203*, 325.

(11) Drent, E.; Dijk, R. v.; Ginkel, R. v.; Oort, B. v.; Pugh, R. I. *Chem. Commun.* **2002**, 744.

(12) Stibrany, R. T.; Schulz, D. N.; Kacker, S.; Patil, A. O.; Baugh, L. S.; Rucker, S. P.; Zushma, S.; Berluche, E.; Sissano, J. A. *Macromolecules* **2003**, *36*, 8584.

(13) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664.

(14) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005.

Scheme 1

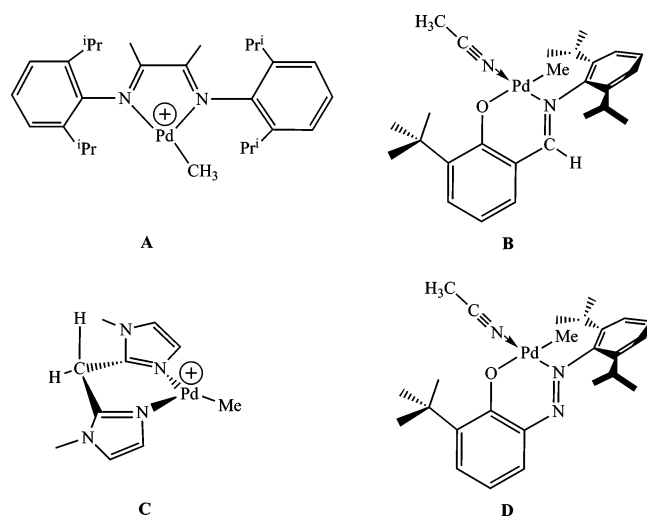
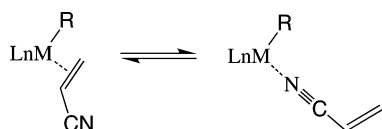


Chart 1



catalyst (**A** in Scheme 1) has been shown to copolymerize ethylene and higher α -olefins with acrylates and vinyl ketones.^{6,7} On the other hand incorporation of nitrogen-containing monomers has met with less success. This is especially the case for acrylonitrile,^{16–18} which will be the focal point of the present investigation.

Acrylonitrile can bind¹⁸ to the metal center of the catalyst using either the polar CN group (N-terminal) or the olefinic C=C π -functionality; see Chart 1. Generally, the π -complexation must be comparable with N-coordination in strength since only the π -binding mode subsequently can lead to chain propagation, whereas the coordination of the CN group is a dead end unless rearrangement to the π -isomer is energetically feasible. Deubel and Ziegler¹⁸ have reported that the N-complexation was strongly preferred over the π -complexation with a cationic Brookhart catalyst. However with the neutral Grubbs^{8,19,20} catalyst (**B** in Scheme 1), the two complexation energies are comparable.¹⁸ It would thus appear that neutral Grubbs (or Grubbs-like) catalyst systems might be used to incorporate acrylonitrile into a polyethylene chain.

Recently experimental studies have appeared on copolymerization of acrylonitrile with ethylene. Jordan¹⁷ et al. found in agreement with the theoretical predictions by Deubel and Ziegler¹⁸ that palladium-based cationic Brookhart catalysts (**A** in Scheme 1) are poisoned by acrylonitrile. However, acrylonitrile was able

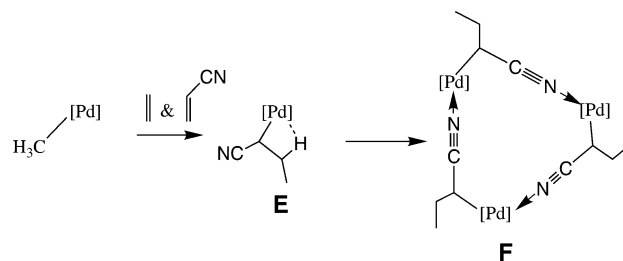


Figure 1. Insertion and trimerization.

to insert into the Pd–alkyl bond of a cationic palladium catalyst (**C** in Scheme 1) with a more electron-rich metal center to form the α -cyano-alkyl complex **E** in Figure 1. Unfortunately, the resulting α -cyano-alkyl complex **E** trimerizes to form a species (**F** in Figure 1) that is inert to further insertion under normal conditions. Similar trimerization reactions were observed by Piers¹⁶ et al. when they reacted acrylonitrile with respectively **B** and **D** in Scheme 1.

Our purpose here is to understand the detailed trimerization process of the neutral Grubbs type catalysts (**B**, **D**). As we have noted, structurally **B** and **D** are very similar. On the other hand, experimentally¹⁶ it was found that catalysts **B** and **D** had almost the same catalytic reactivity. Thus, we just chose the azoligand-based catalyst **D** as our model.

A proposed sequence of reaction steps leading to the trimerization of the α -cyano-alkyl complex is shown in Scheme 2. Initially, ethylene or acrylonitrile coordinates to the metal center of the catalyst by π -mode or in the case of acrylonitrile N-mode as well. Then the monomer inserts into the Pd–C bond. Because of the asymmetry of the azoligand and the insertion regioselectivity, ethylene insertion has two paths along a *trans* (alkyl ligand *trans* to the nitrogen) or *cis* (alkyl ligand *cis* to the nitrogen) pathway, respectively. However four paths may be possible for acrylonitrile, namely, *trans* 1,2-, 2,1- and *cis* 1,2-, 2,1-insertion. On the basis of our calculations, the acrylonitrile *trans* 2,1-insertion pathway, which produces the β -agostic *cis* complex **1**, is the most favorable insertion mode. Insertion product **1** (see Scheme 2) might conduct a series of isomerizations to form chelates with the CN group attached to the α -, β -, or γ -carbon. Ultimately, a trimerization of the α -cyano-alkyl complex **E** occurs.

We shall in the following present the results from an extensive computational study of all the processes described above, including the coordination of the monomers, the first insertion step, isomerization of the first insertion product **1** (Scheme 2), and examination of the trimerization reaction. We believe that a detailed understanding of all the reaction steps in Scheme 2 will ultimately help with the design of catalysts that can copolymerize ethylene and acrylonitrile.

Computational Details

All calculations were carried out with the Amsterdam Density Functional (ADF 2003) program package developed by Baerends et al.²¹ and vectorized by Ravenek.²² To model the real catalyst systems, the combined quantum mechanics and molecular mechanics (QM/MM) method implemented²³ into the ADF program was used. The partition scheme

(15) Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 10634.

(16) Groux, L. F.; Weiss, T.; Reddy, D. N.; Chase, P. A.; Piers, W. E.; Ziegler, T.; Parvez, M.; Benet-Buchholz, J. *J. Am. Chem. Soc.* Submitted.

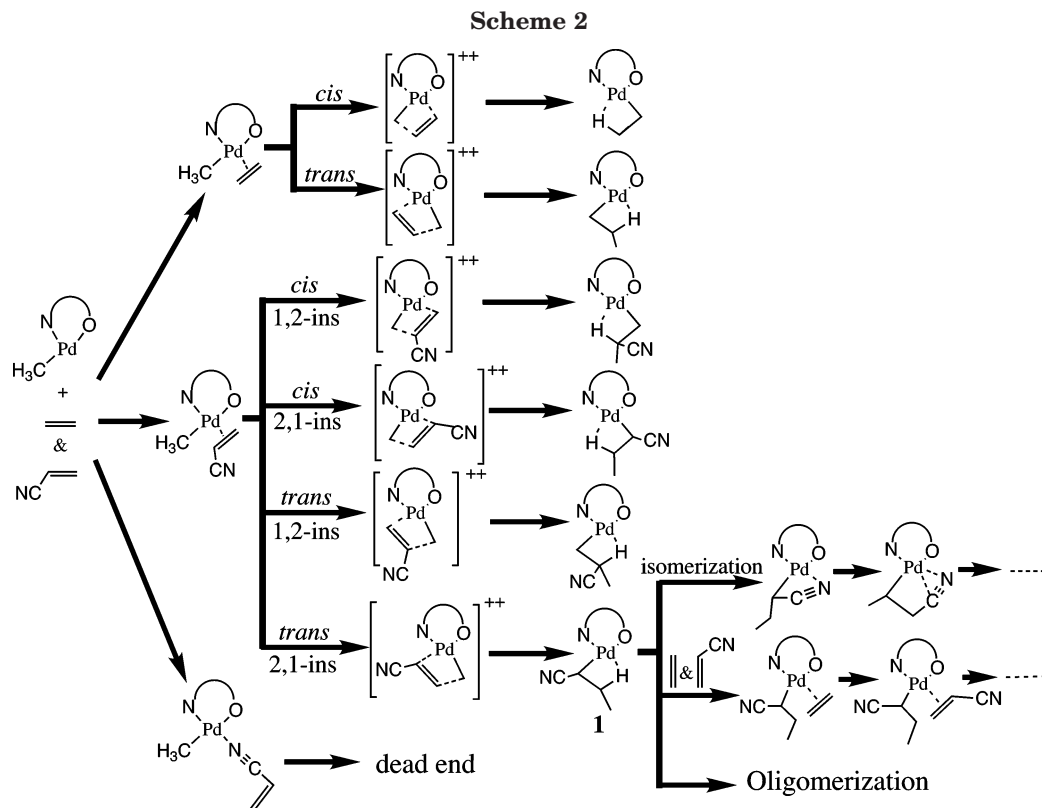
(17) Wu, F.; Foley, S. R.; Burns, C. T.; Jordan, R. F. *J. Am. Chem. Soc.* Submitted.

(18) (a) Deubel, D. V.; Ziegler, T. *Organometallics* **2002**, *21*, 1603.

(b) Deubel, D. V.; Ziegler, T. *Organometallics* **2002**, *21*, 4432.

(19) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149.

(20) Grubbs, R. H. Presentation at the 219th ACS National Meeting, San Francisco, March 27, 2000 (paper 230).



developed by Morokuma and Maseras²⁴ and augmented by Woo et al.²³ was used to couple the QM and the MM regions. Figure 2 depicts the QM/MM partitioning of the molecular system studied here. Hydrogens were used as capping atoms. A ratio, α , of 1.328 and 1.420 was adopted for the N(aryl)–C(aryl) and C(aryl)–C(aryl) link bonds, respectively, to reproduce the average experimental bond distances in related compounds.

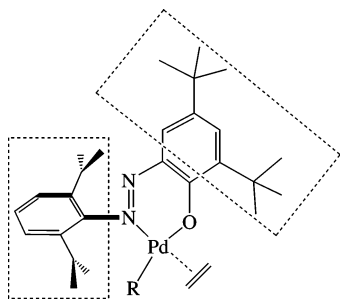


Figure 2. Partitioning of catalyst into MM region (inside dotted squares) and QM region (outside dotted squares).

Density functional theory was used for the QM part. In the QM calculations, the electronic configurations of the atoms were described by a triple- ζ basis set on palladium (4s, 4p, 4d, and 5s) and augmented with a single 5p polarization function. Double- ζ STO basis sets were used for carbon (2s, 2p), hydrogen (1s), and nitrogen (2s, 2p), augmented with a

single 3d polarization function, except for hydrogen, where a 2p polarization function was used. The $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$ on Pd and $1s^2$ for C, N, and O were treated with the frozen-core approximation. A set of auxiliary s, p, d, f, and g STO functions centered on all nuclei was used to fit the molecular density and represent Coulomb and exchange potentials accurately in each SCF cycle.²⁵ The energy differences were calculated by augmenting the local density approximation energy with Perdew and Wang's nonlocal correlation correction and Becke's exchange corrections (PWB91).^{26–29} An augmented Sybyl³⁰ molecular mechanics force field was utilized to describe the molecular mechanics potential, which includes van der Waals parameters for palladium from the universal force field (UFF) due to Rappé.³¹

In this study, full optimization was applied to the minima (reactants, products, and intermediates). The insertion transition states were obtained from linear transit^{32,33} calculations with the distance between one olefin carbon and the methyl carbon as the reaction coordinate. The transition states for the isomerization by a series of hydrogen transfers were got from linear transit calculations where the difference between the C_β –H distance and Pd–H distance was taken as the reaction coordinate.

Results and Discussions

We shall now provide a discussion of the first insertion of both ethylene and acrylonitrile into the metal–

(21) (a) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41. (b) Baerends, E. J.; Ros, P. *Chem. Phys.* **1973**, *2*, 52. (c) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84. (d) Fonseca, C. G.; Visser, O.; Snijders, J. G.; te Velde, G.; Baerends, E. J. In *Methods and Techniques in Computational Chemistry*, METECC-95; Clementi, E., Corongiu, G., Eds.; STEF: Cagliari, Italy, 1995; p 305.

(22) Ravenek, W. In *Algorithms and Applications on Vector and Parallel Computers*; te Riele, H. J. J., Dekker: T. J., vand de Horst, H. A., Eds.; Elsevier: Amsterdam, 1987.

(23) Woo, T. K.; Cavallo, L.; Ziegler, T. *Theor. Chem. Acc.* **1998**, *100*, 307.

(24) Maseras, F.; Morokuma, K. *J. Comput. Chem.* **1995**, *16*, 1170.

(25) Krijn, J.; Baerends, E. J. *Fit Functions in the HFS-Method*; Free University of Amsterdam: Amsterdam, 1984.

(26) Perdew, J. P. *Phys. Rev. B* **1992**, *46*, 6671.

(27) Becke, A. *Phys. Rev. A* **1988**, *38*, 3098.

(28) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.

(29) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(30) Clark, M.; Cramer, R. D., III; van Opdenbosch, N. *J. Comput. Chem.* **1989**, *10*, 982.

(31) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024.

(32) Banerjee, A.; Adams, N.; Simons, J.; Shepard, R. *J. Phys. Chem.* **1985**, *89*, 52.

(33) Fan, L.; Ziegler, T. *J. Chem. Phys.* **1990**, *92*, 3645.

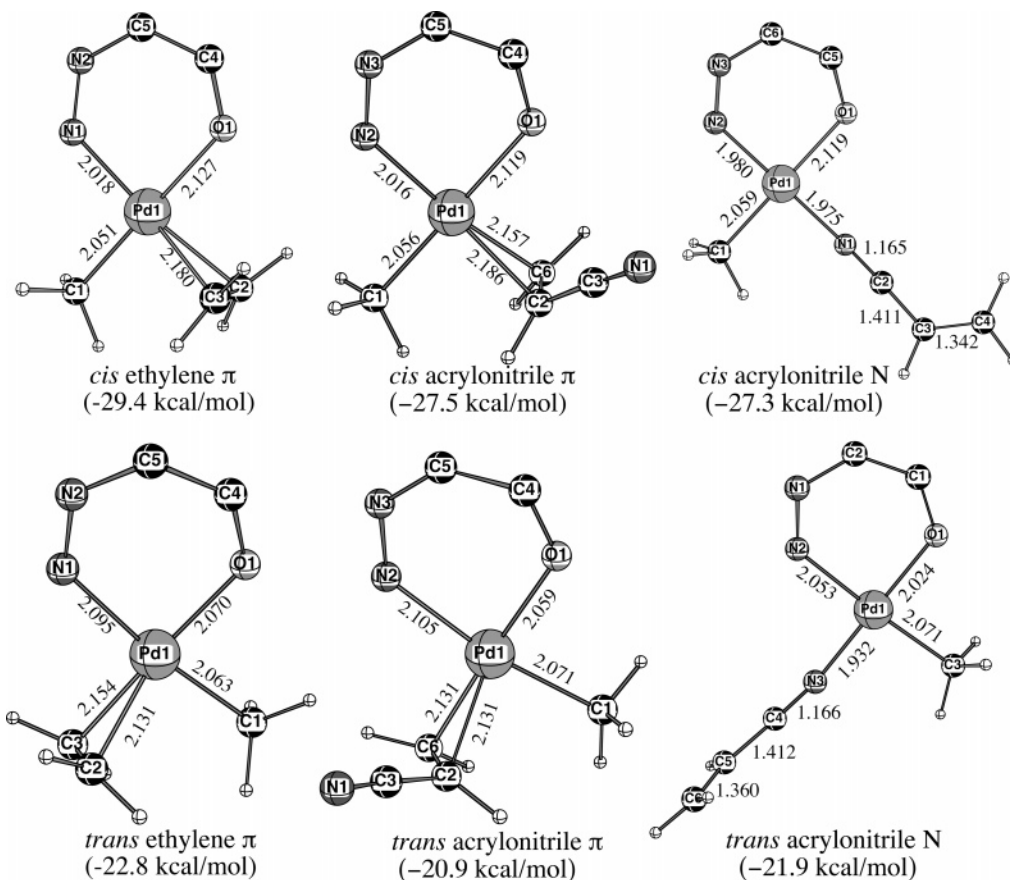


Figure 3. Optimized structures of *cis* and *trans* ethylene and acrylonitrile complexes together with the relative energies. Bond distances are in Å.

methyl bond as well as the subsequent isomerization and oligomerization processes (see Scheme 2). Our discussion will initially be based on the azo-type Grubbs catalyst **D** in Scheme 1 due to Piers et al.¹⁶ We shall organize our discussion based on the possible reaction process, i.e., starting from the coordination of monomers, the first insertion step, isomerization of the first insertion product **1** (see Scheme 2), and finally ending at the catalyst trimerization.

Coordination of Ethylene and Acrylonitrile. The first crucial step in coordination polymerization is the uptake of the monomers by the catalyst. Compared to ethylene, acrylonitrile has two possible coordination modes (π - and N-mode). Figure 3 displays the calculated structures and complexation energies corresponding to the possible coordination modes and geometric isomers. It follows from Figure 3 that the *cis* isomers (methyl ligand *cis* to the imine) are more stable than the corresponding *trans* isomers (methyl ligand *trans* to the imine) by ~ 7 kcal/mol. This is due to the fact that the imine moiety of the chelate azoligand is a stronger donor than the enolate moiety.³⁴ Thus, the methyl group, which is a stronger donor than the C=C ligand, prefers to coordinate *trans* to the weaker enolate moiety.

Considering first the more stable *cis* isomers, the calculated π -complexation energies are -29.4 kcal/mol for ethylene and -27.5 kcal/mol for acrylonitrile, whereas the N-complexation energy is -27.3 kcal/mol for acrylonitrile. The small energy difference between the two

π -complexes stems from the steric effect. One may argue that it possibly originates from electronic reasons. Actually the electron-withdrawing CN substituent decreases both the π (HOMO) and π^* (LUMO) levels of the monomer. The calculated π and π^* orbital energies are respectively -7.16 and -1.35 eV for ethylene and -7.83 and -3.27 eV for acrylonitrile. That is to say, the ability of acrylonitrile to donate electrons to the catalysts is weakened. However, at the same time, the back-donation is also enhanced relative to the parent ethylene complex. Indeed, a full QM calculation to the QM part (without the bulky MM part) gives almost the same π -complexation energies.

First Insertion Step of Ethylene and Acrylonitrile. The calculated π -complexation energies do not preclude the possible insertion of either ethylene or acrylonitrile. The energy profiles for the insertion of ethylene and acrylonitrile are given in Figures 4 and 5, respectively. It is shown in Figure 4 that the lowest barrier for ethylene insertion corresponds to the *trans* insertion pathway with an activation energy of 22.5 kcal/mol relative to the most stable π -complex. For the acrylonitrile insertion, the lowest insertion barrier of 17.6 kcal/mol corresponds to the *trans* 2,1-insertion (see Figure 5), leading to the β -agostic *cis* product **1** in Scheme 2.

We note in Figures 4 and 5 a crossover in the preferred reaction mode from the *cis* pathway in the initial π -complexation stage to the *trans* pathway at the insertion transition state. Thus, for the ethylene insertion the *cis* π -complex is more stable than the *trans*

(34) Shriver, D. F.; Atkins, P. W.; Laangford, C. H. *Inorganic Chemistry*; Oxford, 1992.

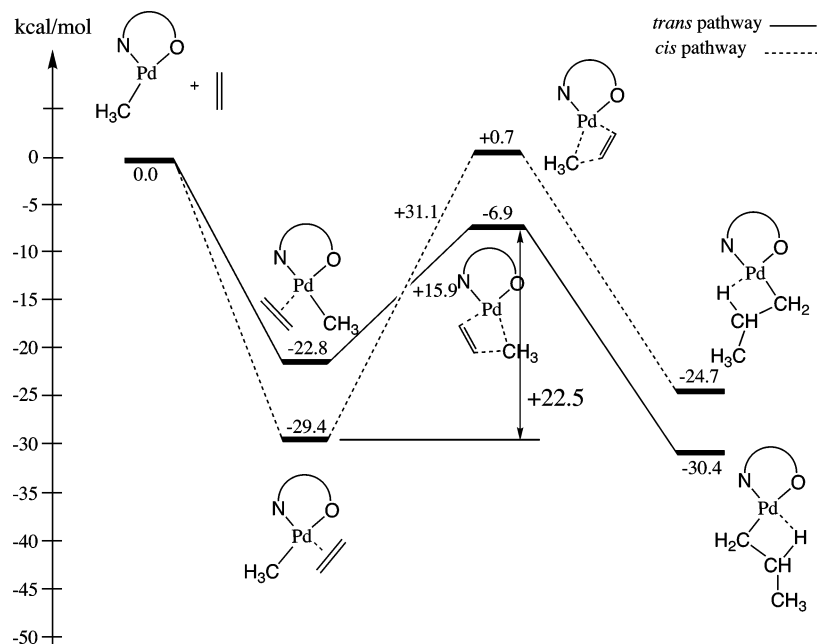


Figure 4. Energy profile of ethylene insertion into a Pd-CH₃ bond.

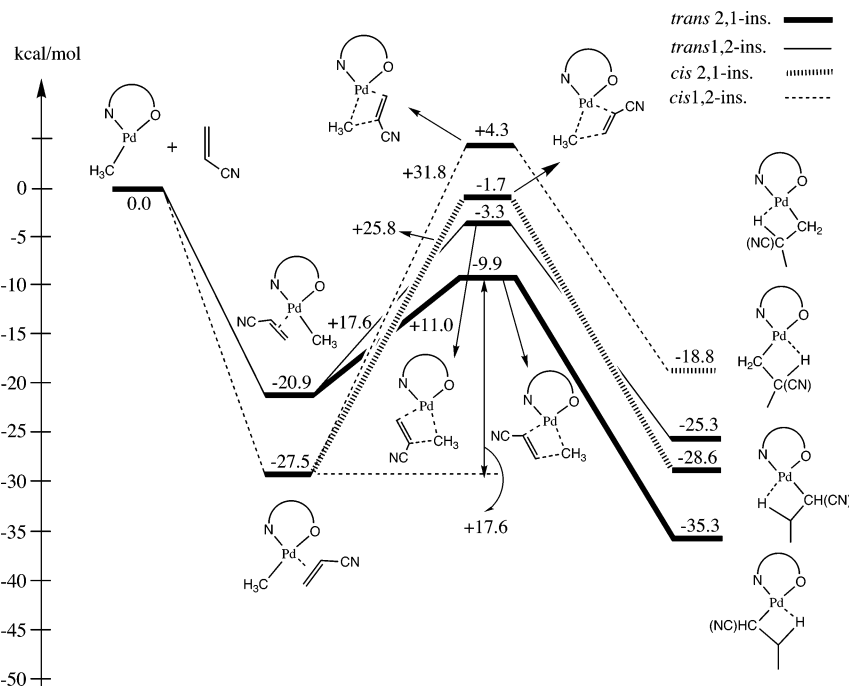


Figure 5. Energy profile of acrylonitrile insertion into a Pd-CH₃ bond.

isomer by ~ 7 kcal/mol, whereas the *trans* transition state is lower than the *cis* transition state by ~ 7 kcal/mol, Figure 4. We can rationalize the *trans* (to imine) preference for the methyl ligand in the transition state by observing that the initial ethylene π -ligand here is transformed into a σ -donor with a M-C bond that is stronger than the weakened M-methyl linkage, Figure 6. The overall reaction profile can be associated with a Curtin-Hammett mechanism,^{35,36} in which the *cis* π -complex rearranges to the *trans* isomer, after which the *trans* pathway is followed to produce a *cis* product.³⁷ Support can be found from the calculated *cis*-to-*trans*

isomerization barrier, ca. 15 kcal/mol, which is lower than the insertion barrier. The *cis*-to-*trans* isomerization is just a ligand rearrangement procedure through a tetrahedral transition state. For the acrylonitrile insertion a similar Curtin-Hammett mechanism is followed now involving an insertion regioselectivity (2,1- vs 1,2-insertion). We have found that the 2,1-insertion is preferred over the 1,2-insertion since the transition state energy for the 2,1-insertion is lower than the 1,2-insertion by ca. 6 kcal/mol.

There are two factors responsible for the insertion regioselectivity. The first stems from the fact that the ethylene carbon that is forming the new carbon-carbon

(35) Curin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 111.

(36) Adam, W.; Bach, R. D.; Dmitrenko, O.; Saha-Moller, C. R. *J. Org. Chem.* **2000**, *65*, 6715.

(37) Chan, M. S. W.; Deng, L.; Ziegler, T. *Organometallics* **2000**, *19*, 2741-2750.

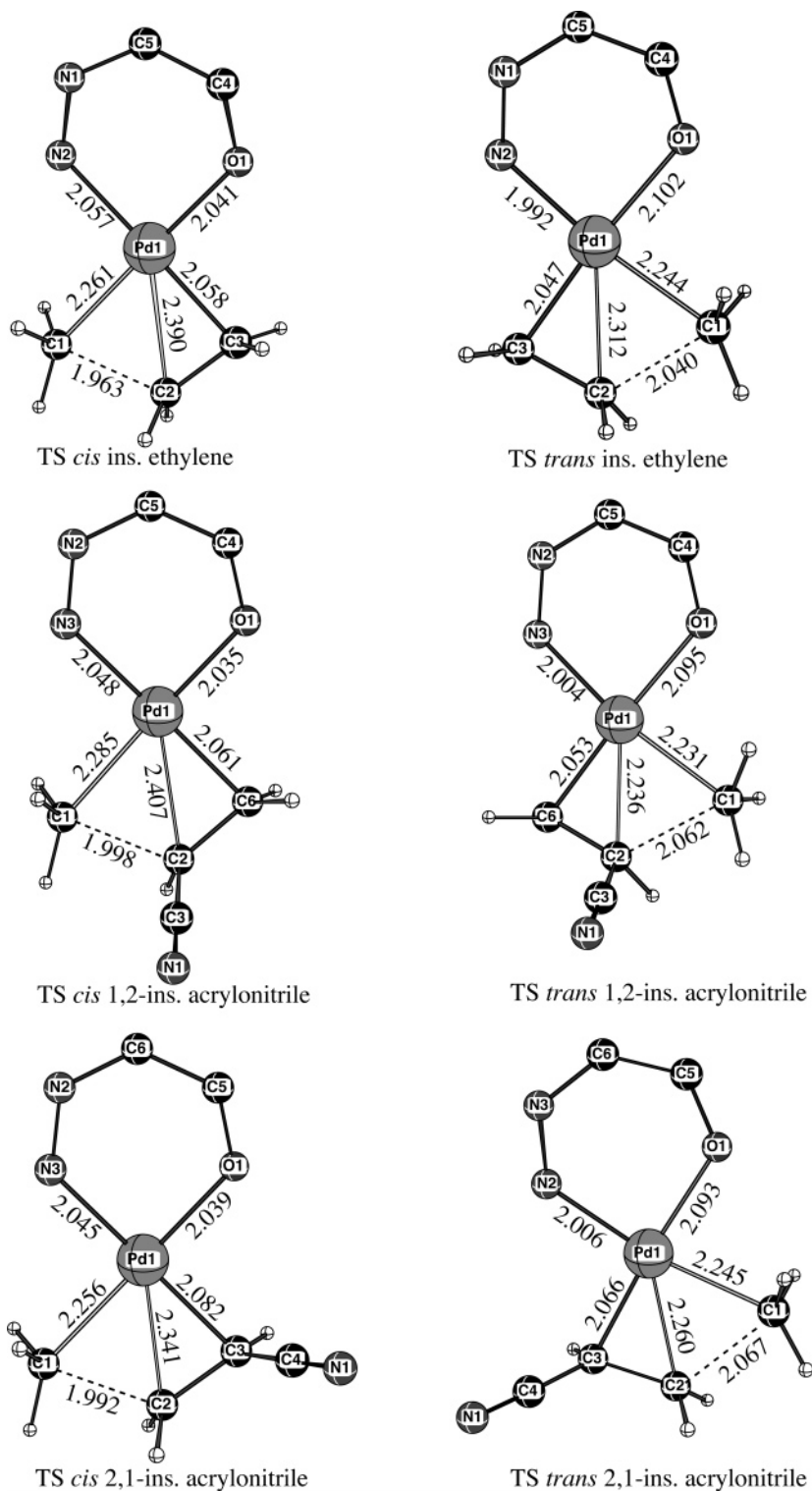


Figure 6. Optimized structures of the insertion transition states of ethylene and acrylonitrile. Bond distances are in Å.

bond undergoes a substantial angular distortion to become sp^3 hybridized in the transition state. However, the angular distortion of two C–H bonds (as it would happen for 2,1-insertion) requires less energy than the distortion of one C–H and one C–X bond (as in the case of 1,2-insertion with $X = CN$).³⁸ One may notice that the angular distortions of C–H and C–X bonds occur even in 2,1-insertion, whose purpose is to form the C–Pd bond. However, the hybridization change of the

C atom that interacts with the methyl group is more critical to the transition state than that of the C atom that interacts with the metal center. That is because the transition state corresponds to a structure with an almost formed C(ethylene)–Pd bond and a new forming C–C bond, Figure 6. The second factor is related to the electronic properties of the monomers, which has been discussed by Deubel.¹⁸ Thus, the p_z coefficients in HOMO and LUMO of the monomers with a CN-substituted C=C bond are larger at the terminal carbon atom than at the vicinal carbon atom. The 2,1-insertion,

(38) Michalak, A.; Ziegler, T. *Organometallics* **1999**, *18*, 3998.

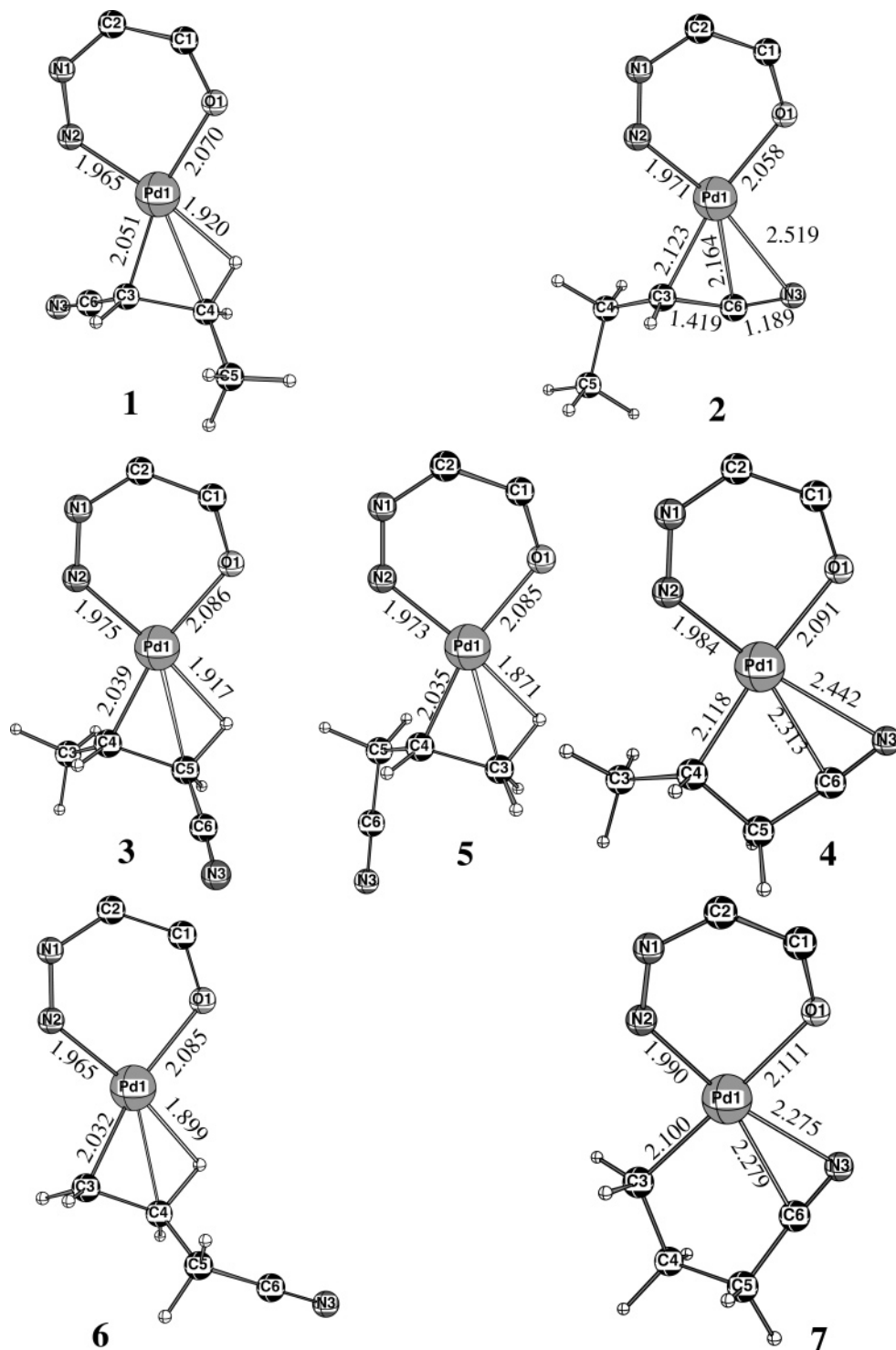


Figure 7. Optimized structures of the intermediates from isomerization of complex **1**. Bond distances are in Å.

which involves the formation of the new C–C bond to the terminal carbon, is therefore favored.

Isomerization of the First Insertion Product **1**.

The kinetic product from the first insertion of acrylonitrile is the β -agostic α -cyano alkyl complex **1**, which can isomerize to form the four-membered chelate structure **2**; see Figures 7 and 8. In addition the CN group on **1** might shift from the α -position to the β - or γ -carbon in a chain walking mechanism involving β -hydrogen elimination and a hydride intermediate (see Figure 8). Each of the new chelates could potentially be sufficiently stable to prevent further insertion by blocking coordina-

tion of a new monomer. It is thus important to explore the potential energy surface connecting the various isomers related to **1**.

Optimized structures for some of the possible isomers are shown in Figure 7. The energy profile for the isomerization is presented in Figure 8. This surface contains β -agostic alkyl-cyano complexes with the CN group in the α -, β -, or γ -position. Of these species the α -cyano alkyl isomer is the most stable. We can understand this by observing that the corresponding α -cyano alkyl radical is more stable than the β -, γ -counterparts since the π^*_{CN} orbital in the former species can have a

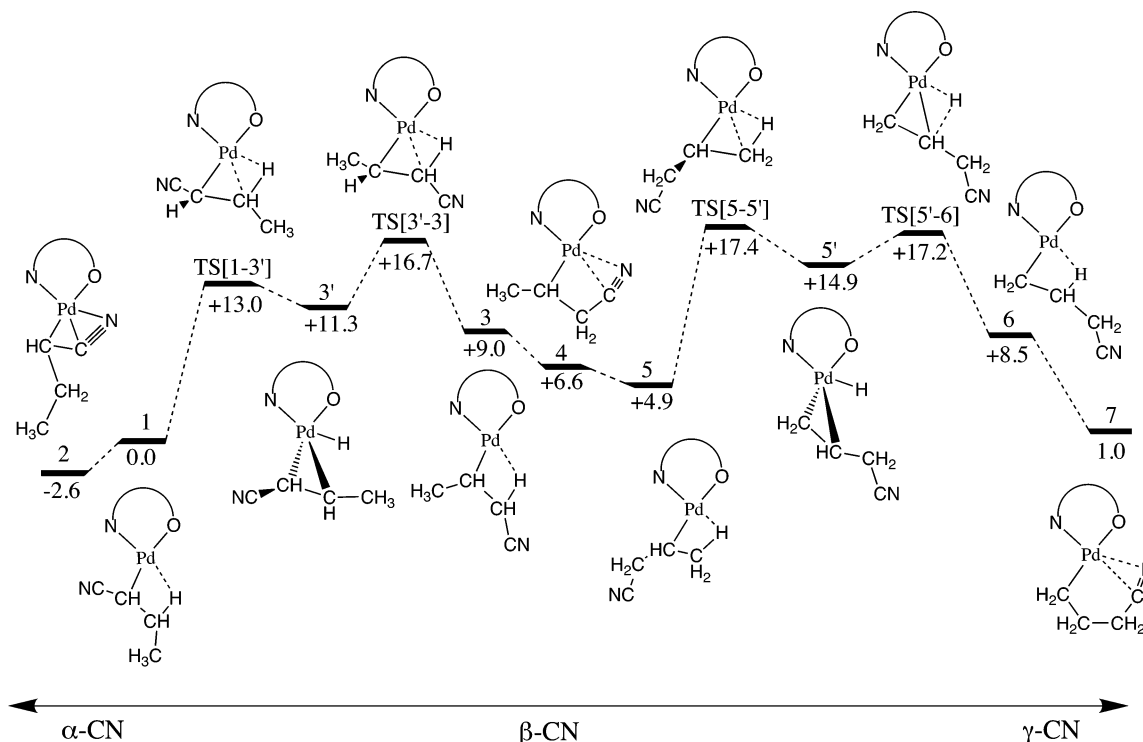
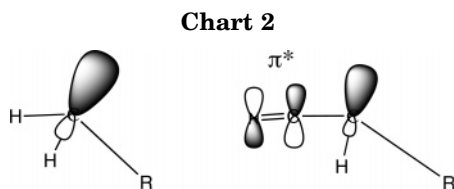


Figure 8. Energy profile for isomerization of complex **1**. Energies are in kcal/mol.



stabilizing interaction with the σ orbital on the α -carbon; see Chart 2. In the actual complexes the Pd–C bond will be somewhat weakest for the α -cyano alkyl ligand with the electron-withdrawing CN group in the α -position due to the reduced donor ability. This can be seen by comparing the Pd–C $_{\alpha}$ bond distance of 2.051 Å in **1** (α -CN) with the Pd–C $_{\alpha}$ bond lengths of 2.039 and 2.032 Å for **3** (β -CN) and **6** (γ -CN), respectively; see Figure 7. This destabilization is, however, compensated for by a stronger Pd–O bond in the *trans* position for α -CN (**1**: 2.070 Å) compared to β -CN (**3**: 2.086 Å) and γ -CN (**6**: 2.085 Å); see Figure 7. All-in-all the most stable β -agostic cyano-alkyl isomer has the CN group in the α -position due to the special electronic property of the CN group.

Also presented in Figure 8 are chelates with the CN group in the α (**2**), β (**4**), and γ (**7**) positions. One could have envisioned that the reduced strain in the five-membered β -CN chelate **4** or six-membered γ -CN chelate **7** would have prompted a migration of the CN group from the preferred α -position in the very strained α -CN chelate **2**. However, this is not the case and **2** remains the most stable chelate isomer.

We note finally that the α -CN to β -CN and β -CN to γ -CN isomerizations take place by a β -hydrogen elimination process with the olefin hydrides **3'** and **5'** as intermediates. Each isomerization process has a β -hydrogen elimination transition state (TS[1–3'] and TS[5–5']) leading to the olefin hydride and another representing the reinsertion of the olefin into the Pd–H

bond (TS[3'–3] and TS[5'–6]). The highest barrier of the isomerization is ~ 17 kcal/mol relative to the β -agostic α -CN isomer **1**. From the fact that the higher member chelates are not stable over complex **1** (Figure 8), we can conclude for the neutral catalysts that the higher member chelate ring structures such as **3** and **6** (Figure 8) are unlikely to be a problem in blocking further coordination of a new monomer to the metal center.

Isomerization of the α -Cyano-propyl Group in the Cationic Pd(II)-Based Brookhart Catalyst.

While the α -cyano-alkyl isomer is the most stable for neutral complexes, this might not be the case for cationic systems where the Pd(II)–nitrogen bonding interaction is much stronger.¹⁸ This is illustrated in Figure 9, where we give the isomerization profile for the α -cyano-propyl group in the cationic Pd(II)-based Brookhart catalyst **A** in Scheme 1. Here the β - and γ -agostic α -cyano-propyl conformations are the isomers of highest energy, whereas the chelated six-membered γ -cyano-propyl isomer is lowest in energy with the four-membered chelated α -cyano-propyl and five-membered chelated β -cyano-propyl between in energy, Figure 9. Thus, for these systems where the Pd(II)–nitrogen interaction is much stronger than in the neutral complexes,¹⁸ an unstrained chelate interaction is preferred over an α -position for the CN group.

Catalyst Trimerization. From the analysis of the neutral catalyst **D** (Scheme 1) above, we conclude that the first insertion product **1** might conduct a series of isomerizations, but the most stable isomer for the neutral species is the α -CN chelate **2** (see Figure 8). In order for the polymerization to proceed, **1** must undergo further monomer complexation and insertion. The calculated monomer binding energies to **1** are -21.3 kcal/mol for ethylene compared to -18.2 kcal/mol (π -bonding) and -22.0 kcal/mol (N-bonding) for acrylonitrile. Compared to the first step (see Figure 3), the complexation

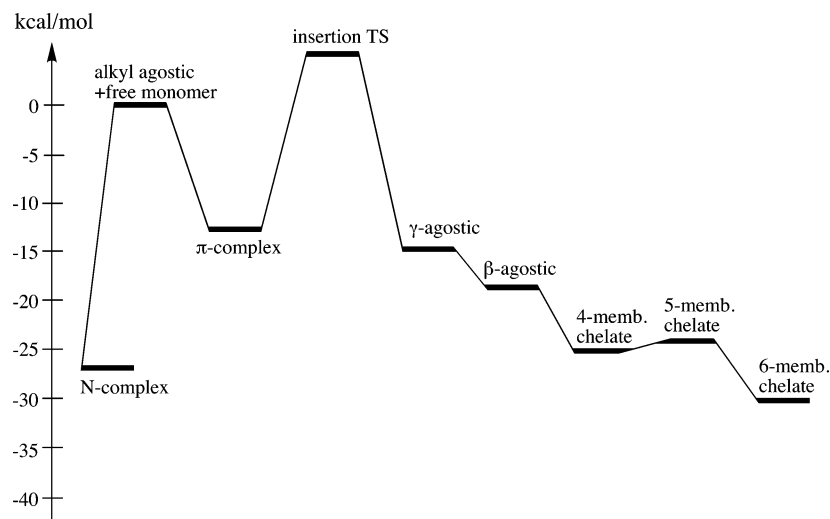


Figure 9. Isomerization profile for the α -cyano-propyl group in the cationic Pd(II)-based Brookhart catalyst **A** of Scheme 1.

energies are lower by several kcal/mol. This can be rationalized by noting that the $\text{C}_2\text{H}_5(\text{CN})\text{HC}$ group has a larger steric bulk than CH_3 . Further, the $\text{C}_2\text{H}_5(\text{CN})\text{-HC}$ complex is stabilized by a β -agostic bond.

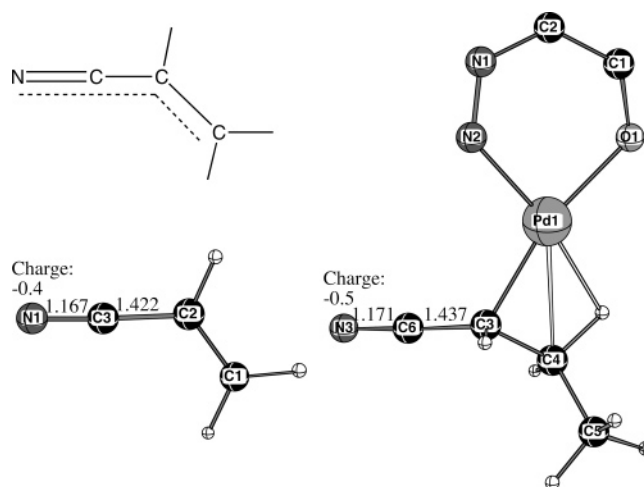
Unfortunately, **1** can undergo an even more favorable reaction by binding the Pd(II) metal center to the nitrogen of an α -cyano-alkyl group of another complex **1**, thus forming oligomers of **1**. We find that the trimerization of **1** is especially favorable, with a formation energy per monomer of -31 kcal/mol, whereas the dimerization affords only -18 kcal/mol per monomer. Taking into account the entropic effect by assuming a penalty of 12 kcal/mol³⁹ in free energy for each mole lost of free species in the bi- and trimolecular reactions, one still finds trimerization to be favored with a free energy of formation per monomer of -23 kcal/mol compared to -10 kcal/mol for N-complexation of acrylonitrile to **1**. It is thus understandable why several experimental studies^{16,17} have observed the formation of inert catalyst trimers made up of α -cyano-alkyl Pd(II) complexes in reacting acrylonitrile with Pd(II) methyl complexes.

It follows from the discussion above that the Pd(II) center prefers to complex a nitrogen atom of an α -cyano-alkyl group of another complex **1** rather than the nitrogen of the original acrylonitrile monomer. This can be understood by observing that the acrylonitrile nitrogen is less electron rich than the nitrogen of the α -cyano-alkyl group since it can donate some of its density to the π^* orbital of the olefinic bond, Chart 3.⁴⁰ It is also found in the discussion above that trimerization is

(39) For a bimolecular reaction $\text{A} + \text{B} \rightarrow \text{C}$, the entropy contribution to the free energy change from reactants to product comes from (1) the loss of the translational and rotational freedoms, which can be calculated easily from the translational and rotational partition functions (totally, it loses 3 translational and 3 rotational freedoms); (2) vibration and other contributions, which can be calculated approximately by some static methods, or accurately by some dynamic methods. Recently we have studied the free energy changes for a lot of bimolecular reactions dynamically. See: Kelly, E.; Seth, M.; Ziegler, T. *J. Phys. Chem. A* **2004**, *108*, 2176. Yang, S. Y.; Hristov, I.; Fleurat-Lessard, P.; Ziegler, T. *J. Phys. Chem. A* ASAP. Based on our studies, the entropy contribution for a bimolecular reaction $\text{A} + \text{B} \rightarrow \text{C}$ is about $8\text{--}12$ kcal/mol.

(40) There is another explanation that was suggested by one of the reviewers. In the monomer case a more "electronegative" sp^2 carbon is connected to the nitrile functionality and, in accordance, the electron-donating properties will increase when a sp^3 carbon is attached to the nitrile.

Chart 3



preferred over dimerization. This is readily understood by observing that an optimal linear Pd–NC coordination with an Pd–N–C angle of $\sim 180^\circ$ is possible in the trimer, whereas ring strain in the dimer dictates a less optimal Pd–N–C angle of only 157° , Figure 10.

Conclusions

We have examined the neutral azoligand-based Grubbs type Pd(II) complex **D** (Scheme 1) due to Piers et al.¹⁶ as a potential catalyst for copolymerization of ethylene and acrylonitrile. The investigation was based on a combined quantum-mechanical (DFT) and molecular-mechanical (MM) approach.

The first part of the investigation focused on the complexation of either of the two monomers to the Pd(II) center followed by insertion into the Pd– CH_3 bond. The study revealed that the π -complexation energies for ethylene and acrylonitrile are comparable. Further, the catalyst is not poisoned by acrylonitrile due to a strong N-coordination, as the N- and π -complexation energies are quite similar. Insertion of acrylonitrile has a barrier that is 5 kcal/mol lower than that of ethylene insertion. Thus, in an equal mixture of the two monomers one is most likely to observe acrylonitrile insertion in agreement with experiment.¹⁶

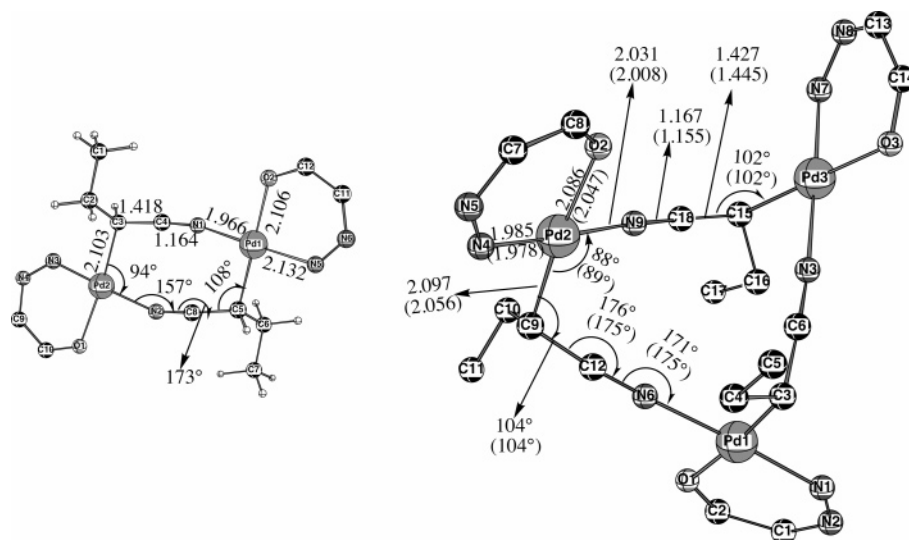


Figure 10. Optimized structure parameters of catalyst dimer (left) and trimer (right) together with the experimental values (in parentheses) for the trimer. Bond distances are in Å, angles in deg.

The kinetic product from the insertion of acrylonitrile into the Pd(II)–CH₃ bond is the β -agostic α -cyano-alkyl complex **1** of Scheme 2. This system can isomerize to β - or γ -cyano complexes that have an additional bond to the metal center through a β -agostic or N-chelate interaction. The isomerization takes place through a low-barrier β -hydrogen elimination mechanism. However, the cyano group prefers to be in an α -position for electronic reasons, although the β - or γ -cyano isomers experience less ring strain.

For **D** of Scheme 1 to be a successful polymerization catalyst, **1** must coordinate another monomer to the Pd(II) center. Unfortunately, **1** prefers instead to coordinate its Pd(II) center to a nitrogen atom on a α -cyano-alkyl group of another **1** complex, leading to inert oligomers of **1** that do not further react with ethylene or acrylonitrile. Trimers of **1** are preferred over dimers

because they allow for an optimal linear Pd–NC bonding mode with an angle of $\sim 180^\circ$. The preference for palladium coordination to the nitrogen on a α -cyano-alkyl group over N-coordination to acrylonitrile stems from the fact that the acrylonitrile nitrogen is less electron rich due to electron donation to the π^* orbital of the olefinic bond.

Acknowledgment. An important part of the calculations has been performed on the Westgrid and MACI cluster (Multimedia Advanced Computational Infrastructure) at the University of Calgary. This work has been supported by the National Sciences and Engineering Research Council of Canada (NSERC), as well as Bayer Polymers. T.Z. thanks the Canadian government for a Canada Research Chair.

OM049015M