

Challenge of the Copolymerization of Olefins with N-Containing Polar Monomers. Systematic Screening of Nickel(II) and Palladium(II) Catalysts with Brookhart and Grubbs Ligands. 2. Chain-Propagation Barriers, Intrinsic Regioselectivity, and Curtin-Hammett Reactivity[†]

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The second level of a computational screening of late-transition-metal catalysts and nitrogen-containing polar monomers toward an incorporation of amines and nitriles in the polymer chain of polyolefins is reported. The structures and energies of the transition states for the insertion of the C=C bond of ethylene, propylene, acrylonitrile, and vinylamine into the metal–carbon bond of generic models for Ni(II) and Pd(II) complexes with diimine (Brookhart) and salicylaldiminato (Grubbs) ligands have been calculated using density functional theory. The calculations reveal the general trend that the activation energies for the ethylene, propylene, and acrylonitrile insertion in the Brookhart systems are similar, whereas the activation energies for the vinylamine insertion are much higher. The nickel systems show lower insertion barriers than do their palladium counterparts. For the chain propagation with the Grubbs catalysts, a Curtin–Hammett-type energy profile involving cis–trans isomerization and subsequent C–C insertion is predicted. The regioselectivity of the propylene, acrylonitrile, and vinylamine insertion is rationalized by the analysis of the frontier orbitals of the free monomers.

Introduction

Copolymers of olefins and nitrogen-containing polar monomers such as poly(styrene–acrylonitrile) are still produced via an expensive radical polymerization process, and current research efforts have focused on the development of alternative copolymerization methods using single-site catalysts.^{2,3} Since Brookhart and co-workers,⁴ Grubbs and co-workers,⁵ and others^{6,7} recently reported novel late-transition-metal catalysts which tolerate a variety of functional groups and enable the

incorporation of *O*-containing polar monomers in the polymer chain of polyolefins, we started a purely computational and very systematic screening of Ni(II) and Pd(II) catalysts toward the copolymerization of olefins with *N*-containing polar monomers such as amines and nitriles. The density functional theory (DFT) methodology we use (see Computational Details) has become a reliable tool for an understanding of the chemistry of group 10 metal complexes⁸ and, in particular, of polymerization catalysis.^{9–13}

In our first study,¹⁴ we investigated the relative stabilization energies for the coordination of the π and

[†] Part 1: Reference 14.

(1) D.V.D.: Academia Sinica, CSCS, and University of Calgary. T.Z.: University of Calgary.

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

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

(4) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (c) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (d) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686. (e) Held, A.; Mecking, S. *Chem. Eur. J.* **2000**, *6*, 4623. (f) Shultz, L. H.; Brookhart, M. *Organometallics* **2001**, *20*, 3975. (g) Shultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539.

(5) (a) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149. (b) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.

(6) Recent reviews: (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 428. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (c) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325. (d) Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 534.

(7) Novel nickel(II) catalysts were recently reported by Bazan and co-workers and by Brookhart and co-workers: (a) Lee, B. Y.; Bazan, G. C.; Vela, J.; Komon, Z. J. A.; Bu, X. *J. Am. Chem. Soc.* **2001**, *123*, 5352. (b) Hicks, F. A.; Brookhart, M. *Organometallics* **2001**, *20*, 3217. (c) Lee, B. Y.; Bu, X.; Bazan, G. C. *Organometallics* **2001**, *20*, 5425.

(8) Dedieu, A. *Chem. Rev.* **2000**, *100*, 543.

(9) (a) Musaev, D. G.; Froese, R. D. J.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 367. (b) Musaev, D. G.; Svensson, M.; Morokuma, K.; Strömberg, S.; Zetterberg, K.; Siegbahn, P. *Organometallics* **1997**, *16*, 1933. (c) Musaev, D. G.; Froese, R. D. J.; Morokuma, K. *New J. Chem.* **1997**, *22*, 1265. (d) Froese, R. D. J.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 1581. (e) Musaev, D. G.; Froese, R. D. J.; Morokuma, K. *Organometallics* **1998**, *17*, 1850. (f) Musaev, D. G.; Morokuma, K. *Top. Catal.* **1999**, *7*, 107.

N moieties of the ω -unsaturated amines $\text{CH}_2=\text{CH}(\text{CH}_2)_n(\text{NH}_2)$ and the nitriles $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CN}$ ($n \geq 0$) to the metal center of generic models for Ni(II) and Pd(II) catalysts with diimine (Brookhart) and salicylaldiminato (Grubbs) ligands.^{15,16} The calculations indicated similar stabilization energies for the π and N complexation of the neutral Grubbs Ni(II) and Pd(II) complexes, whereas the cationic Brookhart Ni(II) and Pd(II) catalysts strongly prefer the N coordination of acrylonitrile, $\text{CH}_2=\text{CHCN}$, nonconjugated nitriles $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CN}$ ($n > 0$), and nonconjugated amines, $\text{CH}_2=\text{CH}(\text{CH}_2)_n(\text{NH}_2)$ ($n > 0$), over their π -binding mode. In contrast, vinylamine, $\text{CH}_2=\text{CH}(\text{NH}_2)$, was found to favor π coordination with all model catalysts. The palladium catalysts showed a larger relative preference for the π mode, in comparison with the nickel counterparts.

A strong stability of the π complex, formed from the free monomer and the β -agostic catalyst complex, was considered promising,¹⁴ since π complexes are intermediates in the chain propagation process, while the N complexation is a potential dead end. However, if the π complexes are too stable with respect to the transition states (TS), it might be difficult to achieve copolymerization with these systems. Consequently, we have now explored the reactivity of the π complexes by calculating the energy profile of chain propagation for the four model catalysts and the four model monomers given in Figure 1. Intermediates and transition states that have been considered are shown in Figure 2 for the Brookhart catalysts.

Two additional aspects in the chain propagation mediated by group 10 complexes are important. First, the intrinsic regioselectivity of olefin insertion is one of the factors that determine the polymer or copolymer microstructure.¹⁷ The pathway with a bond formation between the metal-coordinated carbon atom of the polymer chain and the terminal carbon of the monomer is denoted 2,1-insertion and the regioisomeric pathway is denoted 1,2-insertion (Figure 3). Hence, we have studied both pathways (2,1 and 1,2) in each case. Second, the mechanism of chain propagation with the Grubbs-type complexes is more complicated due to the potential presence of geometric isomers (Figure 4).¹¹ The exploration of possible reaction pathways is of current

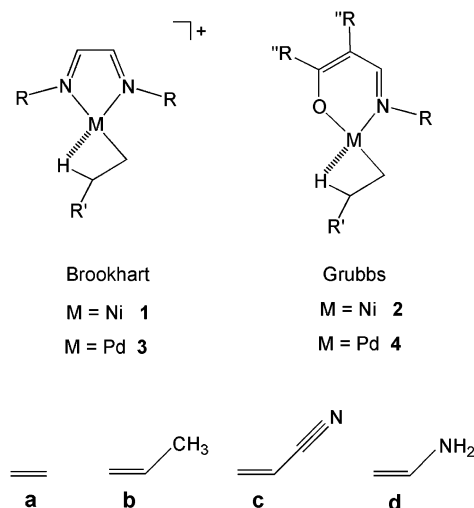


Figure 1. Model substrates ethylene (a), propylene (b), acrylonitrile (c), and vinylamine (d) and model catalysts 1–4. Legend: R = 2,6-bis(1-methylethyl)phenyl; R' = polymer chain; (R'')₂ = benzo group with additional substituents. Computational screening was performed using R = R' = R'' = H.

interest,¹⁸ including a comparison of the isomerization barriers for the β -agostic and π complexes as well as an investigation of the insertion reactivity of the different π complexes.

Results and Discussion

Brookhart Catalysts. The geometries of the π complexes of the catalysts 1–4 with the model monomers a–d were previously reported.¹⁴ We now briefly discuss the calculated transition structures for the insertion of the C=C bond into the metal–C(ethyl) bond of the diimine catalysts.¹⁹ Figure 5 displays the optimized TS geometries for the 1,2-insertion (left) and the 2,1-insertion (right) in the Brookhart nickel systems. The calculated C2–C3 distance in the TS for 2,1-insertion (right) reveals that the acrylonitrile insertion has an earlier transition state (C2–C3 = 2.149 Å) than the ethylene (2.104 Å) and propylene (2.076 Å) insertion, whereas the vinylamine insertion has a later transition state (2.026 Å). This trend is confirmed by comparing the Ni–C1, Ni–C3, and C1–C2 distances in the 2,1-TS. Furthermore, the 2,1-TS species are earlier than the 1,2-TS (Figure 5).

Qualitative relations among the extent of reaction at the TS, activation energy, and reaction energy belong to the tools of every chemist:²⁰ (i) more exothermic reactions usually have earlier transition states, known as the Hammond postulate;²¹ (ii) more exothermic reactions are usually faster, known as the Bell–Evans–Polanyi principle;²² (iii) faster reactions have earlier transition states, concluded from (i) and (ii). Applying

(18) Younkin, T. R.; Grubbs, R. H.; Henling, L. M.; Day, M. W. *Abstr. Pap. Am. Chem. Soc.* **2001**, 221, INOR 253.

(19) For each of the 16 catalyst-monomer pairs, 1a–d, 2a–d, 3a–d, and 4a–d, up to 8 isomeric transition states for insertion have been optimized. Only the isomers lowest in energy are reported.

(20) Marcus theory connects the three parameters quantitatively: Marcus, R. A. *J. Phys. Chem.* **1968**, 72, 891.

(21) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, 77, 334.

(22) (a) Bell, R. P. *Proc. R. Soc. London, Ser. A* **1936**, 154, 414. (b) Evans, M. G.; Polanyi, M. *J. Chem. Soc., Faraday Trans.* **1936**, 32, 1340.

(10) (a) Deng, L.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, 119, 1094. (b) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, 119, 6177. (c) Michalak, A.; Ziegler, T. *Organometallics* **1999**, 18, 3998. (d) Woo, T. K.; Ziegler, T. *J. Organomet. Chem.* **1999**, 591, 204. (e) Woo, T. K.; Blöchl, P. E.; Ziegler, T. *J. Phys. Chem. A* **2000**, 104, 121. (f) Michalak, A.; Ziegler, T. *Organometallics* **2000**, 19, 1850.

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

(12) (a) Michalak, A.; Ziegler, T. *Organometallics* **2001**, 20, 1521. (b) Michalak, A.; Ziegler, T. *J. Am. Chem. Soc.* **2001**, 123, 12266.

(13) Von Schenck, H.; Strömberg, S.; Zetterberg, K.; Ludwig, M.; Åkermark, B.; Svensson, M. *Organometallics* **2001**, 20, 2813.

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

(15) Vinylamine has been used as a model for enamines. Note that the tautomeric enamine–imine equilibrium lies for simple systems in the imine form: (a) De Savignac, A.; Bon, M. M.; Lattes, A. *Bull. Soc. Chim. Fr.* **1972**, 3167. (b) Shainyan, B. A.; Mirskova, A. N. *Russ. Chem. Rev. (Engl. Transl.)* **1979**, 48, 107. (c) Cook, A. G. *Enamines*; Marcel Dekker: New York, 1988.

(16) To reduce the number of conformational degrees of freedom which were considered in our computational study, the nonconjugated molecules ($n > 0$) were modeled using propylene as the olefin moiety and methylamine and acetonitrile, respectively, as polar functionalities.

(17) Other important factors are steric effects of the bulky substituents at the imine nitrogen atoms and pathways of polymer-chain isomerization via β -hydride elimination and β -hydrogen transfer.

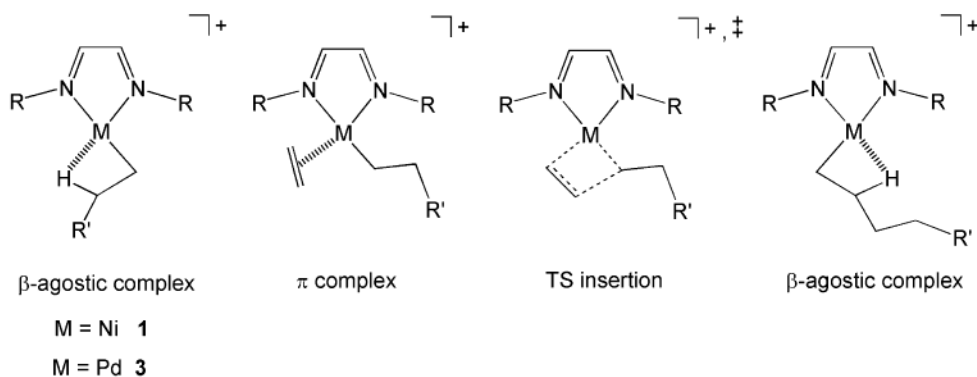


Figure 2. Intermediates and transition states (TS) of the ethylene polymerization with Brookhart's catalysts via a β -agostic complex (Ni, **1**; Pd, **3**), a π complex of the monomer, TS for insertion, and a β -agostic complex with an extended polymer chain.

Table 1. Calculated Energies (in kcal/mol) of the π Complexes of the Monomers a–d with the Brookhart Ni and Pd Catalysts **1** and **3** and Transition States for 2,1- and 1,2-Insertion of the C–C Unit into the Metal–C Bond^a

monomer	1				3			
	β -agostic complex + monomer	π complex	TS 2,1-insertion	TS 1,2-insertion	β -agostic complex + monomer	π complex	TS 2,1-insertion	TS 1,2-insertion
a ethylene	0.0 (–7.1) ^b	–16.2 ^c (0.0)	–2.7 (13.5)	<i>d</i>	0.0 (–3.3) ^b	–20.0 ^c (0.0)	0.9 (20.9)	<i>d</i>
b propylene	0.0 (–5.0) ^b	–18.3 ^c (0.0)	–2.8 (15.5)	–1.9 (16.4)	0.0 (–0.9) ^b	–22.4 ^c (0.0)	0.3 (22.7)	1.4 (23.8)
c acrylonitrile	0.0 (–11.8) ^b	–11.5 ^c (0.0)	3.9 (15.4)	9.8 (21.3)	0.0 (–6.7) ^b	–14.6 ^c (0.0)	7.3 (21.9)	11.9 (26.5)
d vinylamine	0.0 (3.7) ^b	–27.0 ^c (0.0)	–4.6 (22.4)	0.2 (27.2)	0.0 (6.9) ^b	–30.2 ^c (0.0)	–2.2 (28.0)	2.7 (32.9)

^a Energies relative to the β -agostic complexes; in parentheses are given energies relative to the π complexes. ^b Energies relative to the π complex of the previous insertion step. The reaction energy of one insertion step is estimated by the reaction $C_2H_4 + C_2H_6 \rightarrow C_4H_{10}$ (–23.3 kcal/mol). ^c Energies taken from: Deubel, D. V.; Ziegler, T. *Organometallics* **2002**, *21*, 1603. ^d No 2,1- versus 1,2-regioselectivity.

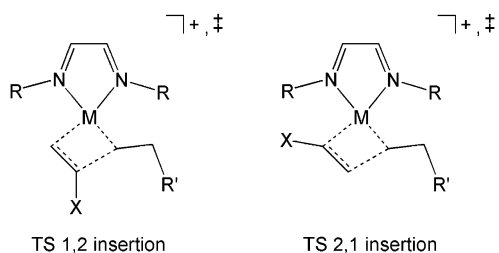


Figure 3. 1,2- versus 2,1-regioselectivity of the insertion of substituted C=C bonds, $CH_2=CHX$: X = H (**a**, no regioselectivity), CH_3 (**b**), CN (**c**), and NH_2 (**d**).

(iii) to the transition structures, we predict the activation energies for the insertion with Brookhart's nickel catalyst, **1**, to be in the order acrylonitrile < propylene < vinylamine and the transition states for 1,2-insertion to be higher in energy than the 2,1-TS. These qualitative trends will be confirmed by the calculated relative energies.

The computed energy profile of an insertion step with the Brookhart Ni systems, **1**, is listed in Table 1 and displayed in Figure 6. In this figure, the energies are given relative to those of the π complexes. We first focus the discussion on the 2,1-insertion (solid lines in Figure 6). The calculations reveal that the barrier for the acrylonitrile insertion (14.4 kcal/mol) is slightly lower than the propylene insertion barrier (14.5 kcal/mol), while vinylamine has a much higher activation barrier (21.3 kcal/mol). Note that the insertion step is endothermic for vinylamine, while it is exothermic for the other monomers. As predicted from the transition structures, the 2,1-insertion (solid lines in Figure 6) has a lower barrier than the 1,2-insertion (dashed lines).

The calculated energy profile of one insertion step with the Brookhart Pd systems is presented in Table 1; the transition structures for the 1,2- and 2,1-insertion of acrylonitrile are shown in Figure 7. Most of the transition states of the palladium system are later than those of the nickel counterparts. The energy profile is qualitatively very similar to the results for the nickel catalysts, but the activation energies of the Pd(II) complexes are larger than the barriers for the Ni(II) complexes by approximately 6–7 kcal/mol. Consideration of the energies relative to the β -agostic complex (Table 1) shows that half of the activation-energy difference, approximately 3–4 kcal/mol, is due to the larger stability of the palladium π complexes.

Grubbs Catalysts. The reaction mechanism of the chain propagation with the salicylaldiminato catalysts is more complicated, since geometric cis and trans isomers might be involved (Figure 4).^{11,18} Note that the cis pathway leads to the trans product and vice versa (Figure 4). We have calculated the structures and energies of the isomers and transition states which are potentially important. Optimized geometries for the Grubbs Ni system are presented in Figure 8; the corresponding energies are given in Table 2 and Figure 9. The cis isomer of the β -agostic complex is more stable than the trans isomer, since the imine moiety of the chelate ligand is a stronger ligand than the enolate moiety. The alkyl ligand is stronger than the β -hydrogen and prefers the coordination trans to the enolate moiety. The same trend holds for the π complexes, because the C=C ligand is weaker than the alkyl ligand. Isomerization of the β -agostic complexes or of the π complexes or both might occur. Tetrahedral transition states have

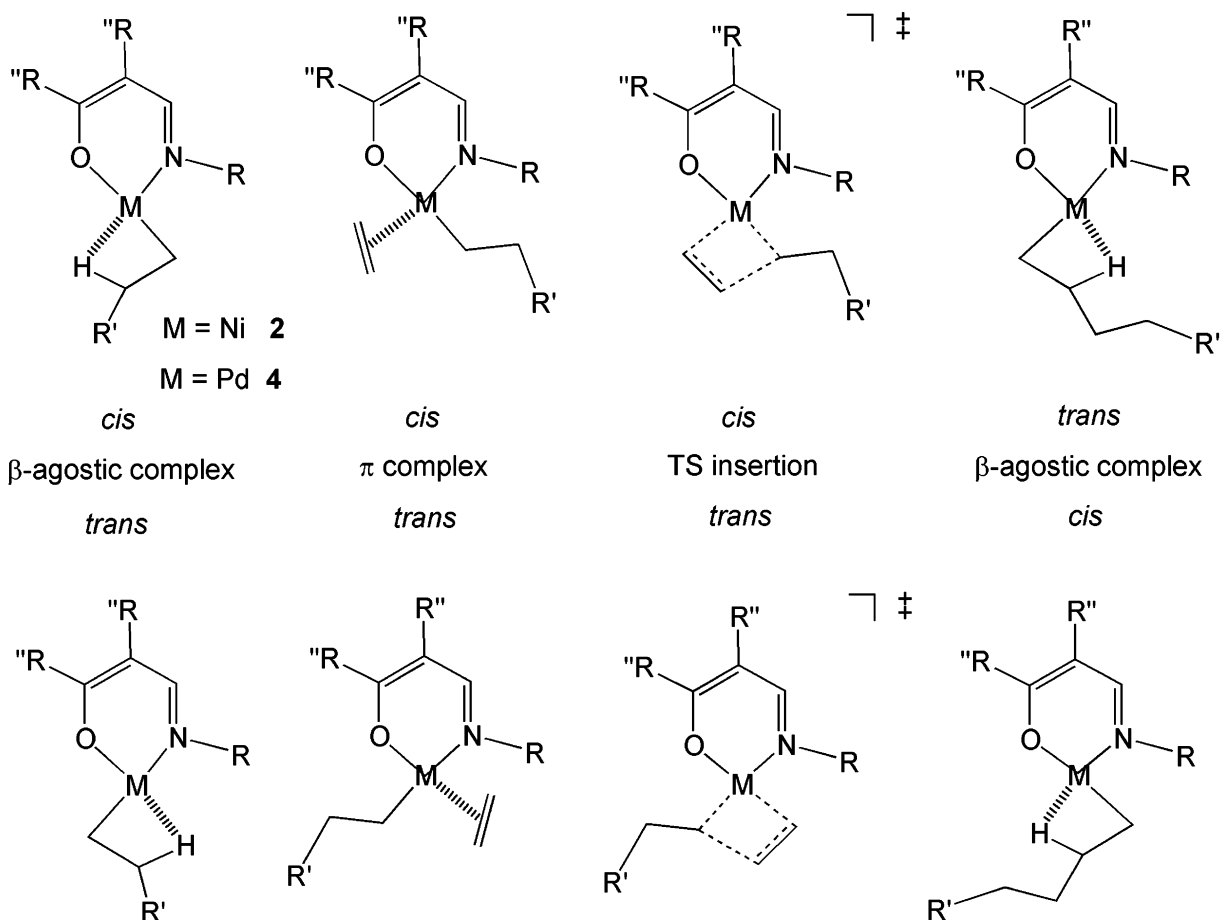


Figure 4. Intermediates and transition states (TS) of the ethylene polymerization with Grubbs catalysts (Ni, **2**; Pd, **4**). The cis pathway (top) leads to the trans isomer and vice versa; interconversion of geometric isomers might occur.

Table 2. Calculated Energies (in kcal/mol) of the π Complexes (Cis and Trans Isomers) of the Monomers a–d with the Grubbs Ni Catalyst **2, Transition States for Cis–Trans Isomerization of the π Complexes, and Transition States (Cis and Trans Isomers) for 2,1- and 1,2-Insertion of the C–C Unit into the Metal–C Bond^a**

monomer	β -agostic complex ^b + monomer	π complex cis	π complex trans	TS isomerizn	TS 2,1-insertion cis	TS 2,1-insertion trans	TS 1,2-insertion cis	TS 1,2-insertion trans
a ethylene	0.0 (–5.3) ^c	–18.0 ^d (0.0)	–13.7 (4.3)	–2.8 (15.2)	10.2 (28.2)	3.3 (21.3)	<i>e</i>	<i>e</i>
b propylene	0.0 (–6.5) ^c	–16.8 ^d (0.0)	–12.3 (4.5)	–1.7 (15.1)	11.1 (27.9)	5.4 (22.2)	12.4 (29.2)	5.9 (22.7)
c acrylonitrile	0.0 (–4.3) ^c	–19.0 ^d (0.0)	–15.6 (3.4)	–5.5 (13.5)	7.2 (26.1)	0.6 (19.6)	13.9 (32.9)	6.6 (25.6)
d vinylamine	0.0 (–2.3) ^c	–21.0 ^d (0.0)	–15.4 (5.6)	–0.8 (20.2)	12.4 (33.4)	8.3 (29.3)	15.3 (36.3)	8.4 (29.4)

^a Energies relative to the β -agostic complexes; in parentheses are given energies relative to the π complexes. ^b Cis isomer. The trans isomer is higher in energy by 4.5 kcal/mol; the isomerization barrier is 32.7 kcal/mol. ^c Energies relative to the π complex of the previous insertion step. Reaction energy of one insertion step estimated by the reaction $C_2H_4 + C_2H_6 \rightarrow C_4H_{10}$ (–23.3 kcal/mol). ^d Energies taken from: Deubel, D. V.; Ziegler, T. *Organometallics* **2002**, *21*, 1603. ^e No regioselectivity.

been found in both cases. The calculations reveal that the barrier of isomerization of the β -agostic complex is very high (32.7 kcal/mol). In contrast, the barriers of isomerization of the π complexes are between 13.5 kcal/mol (acrylonitrile) and 20.2 kcal/mol (vinylamine) and are lower than the insertion barriers (Figure 9). A typical Curtin–Hammett profile²³ with two reactive structures which are connected by a low isomerization barrier has been found. In contrast to the π complexes, the trans transition states are lower in energy than the cis transition states by approximately 7 kcal/mol (Figure 9). The π ligand, which is transformed into a σ ligand,

now competes with the metal–C(alkyl) bond being cleaved and favors the coordination site trans to the enolate moiety. We conclude that chain propagation follows the mechanism π cis \rightarrow TS isomerization \rightarrow π trans \rightarrow TS insertion trans \rightarrow β cis \rightarrow π cis rather than the direct insertion pathway (Figure 9). The Grubbs nickel complexes of the four monomers show a reactivity trend similar to that of the Brookhart analogues: i.e., the acrylonitrile complex has a low insertion barrier, while the enamine complex has a much higher barrier. 2,1-Insertion is again preferred over 1,2-insertion, with one exception: the energies of the two regioisomeric transition states for the insertion of vinylamine into the Ni–C bond of the Grubbs catalyst are equal. This surprising result will be discussed below.

(23) (a) Curtin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 111. (b) Adam, W.; Bach, R. D.; Dmitrenko, O.; Saha-Möllner, C. R. *J. Org. Chem.* **2000**, *65*, 6715.

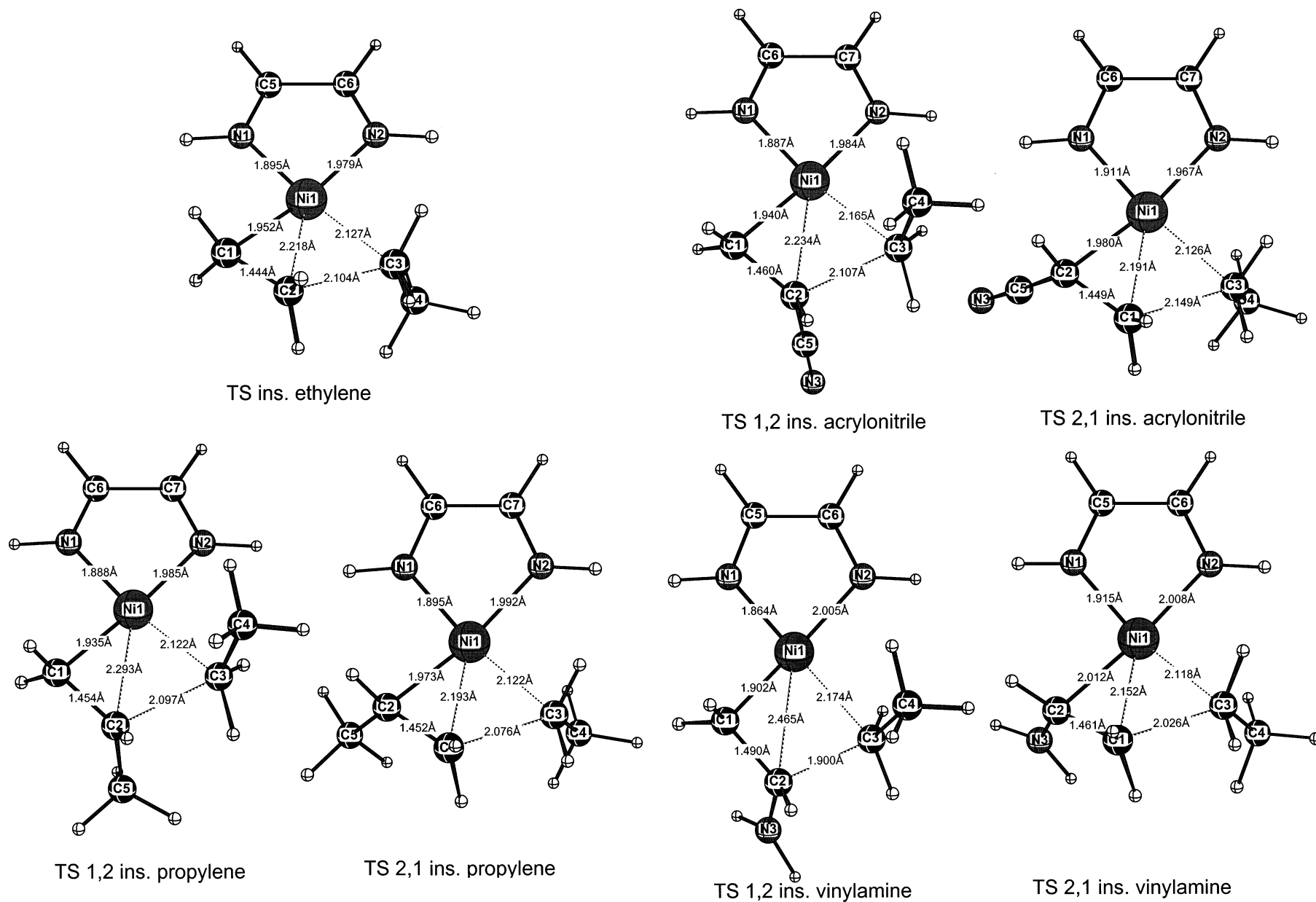


Figure 5. Calculated transition structures for the insertion of the C=C moiety of ethylene into the metal-C bond of the Brookhart Ni catalyst 1, and for the 1,2- and 2,1-insertions of propylene, acrylonitrile, and vinylamine.

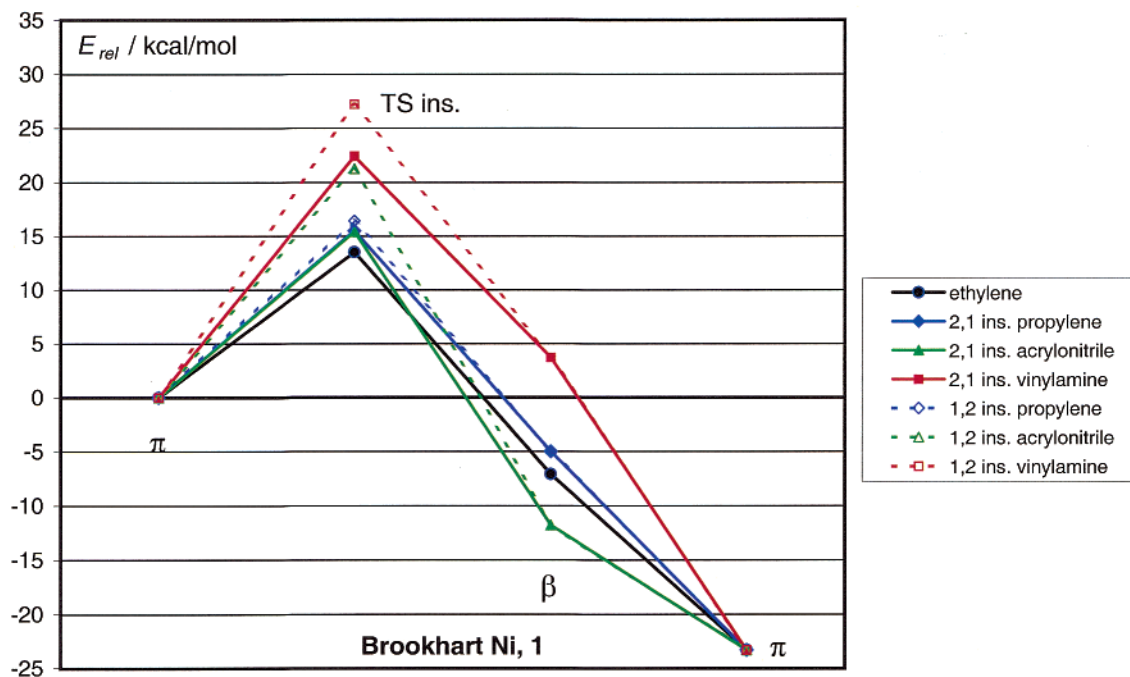


Figure 6. Calculated energy profile for a chain propagation step with the Brookhart Ni catalyst **1** and the four monomers. Energies are given relative to those of the π complexes.

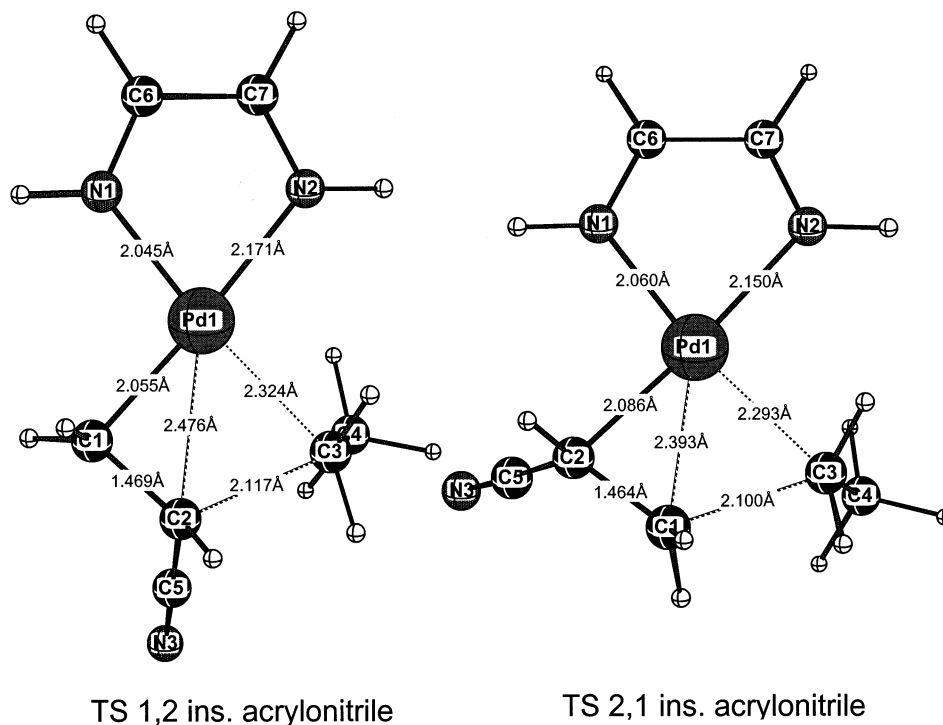


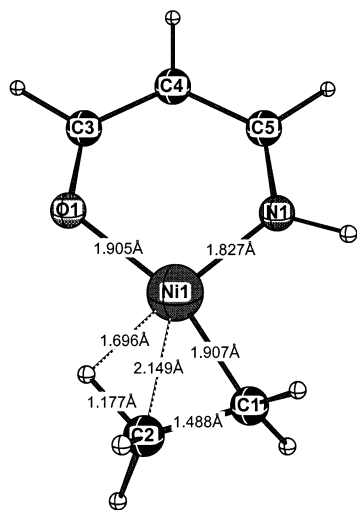
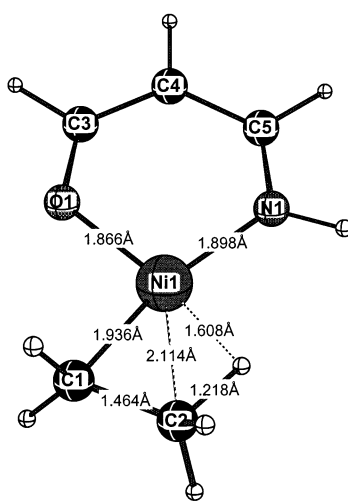
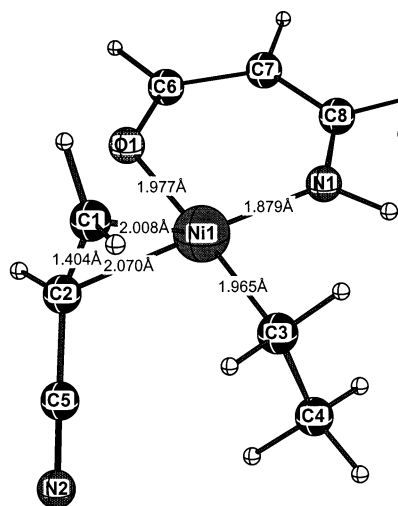
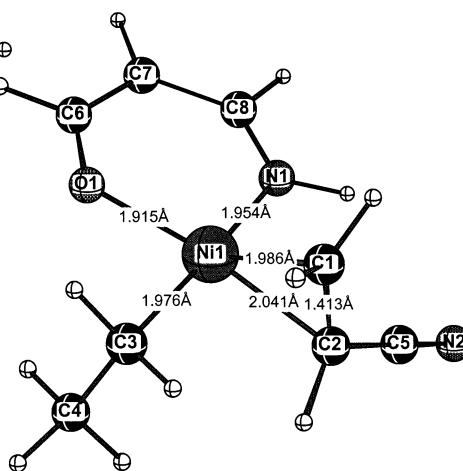
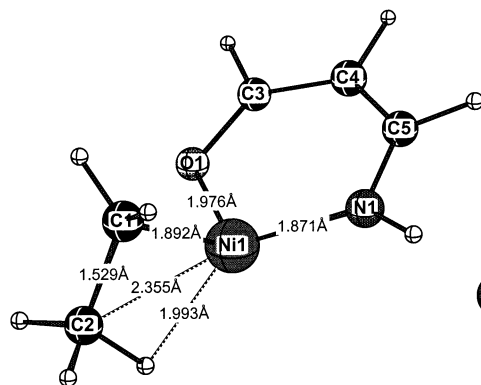
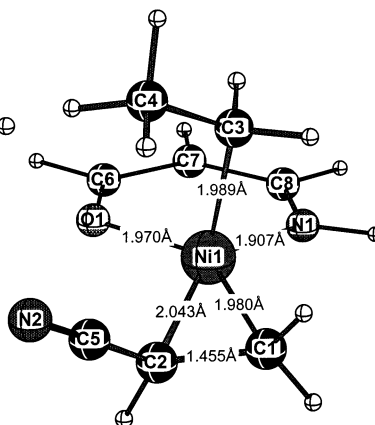
Figure 7. Calculated transition structures for the 1,2- and 2,1-insertions of the C=C moiety of acrylonitrile into the metal-C bond of the Brookhart Pd catalyst **3**.

The relative energies of the chain propagation with the Grubbs Pd catalyst, **4**, are presented in Table 3. The most significant difference between the Ni and Pd systems is the height of the barrier for π -complex isomerization via the tetrahedral transition state, which is as much as 9 kcal/mol higher in the palladium systems. Palladium(II) clearly favors a square-planar coordination environment, while the coordination environment in the complexes of nickel(II) is much more variable.²⁴ The Grubbs Pd complexes of the four mono-

mers show a reactivity trend similar to that of the nickel counterparts.

Origin of the Insertion Regioselectivity. The intrinsic regioselectivity of olefin insertion is one of the factors governing the microstructure of the polymer or copolymer.¹⁷ We have found that the 2,1-insertion is preferred over the 1,2-insertion, with the two equal

(24) Huheey, J. E.; Keiter, R. L.; Keiter, E. A.; *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper-Collins College: New York, 1993.

 β cis β trans π cis π transTS β isom.TS π isom.

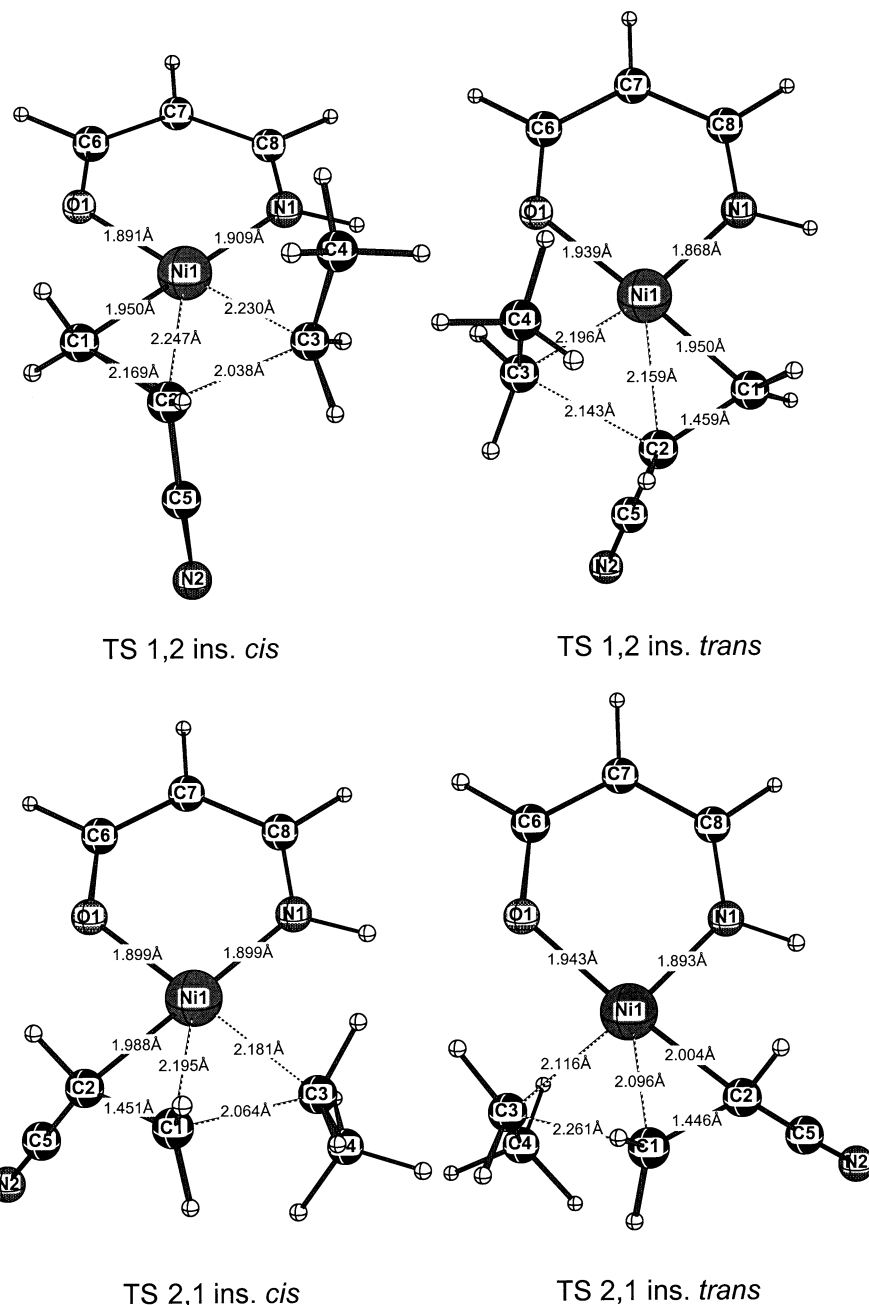


Figure 8. Calculated structures of the β -agostic complexes, π complexes, and transition states for the 1,2- and 2,1-insertions with the Grubbs Ni catalyst **2** and acrylonitrile.

Table 3. Calculated Energies (in kcal/mol) of the π Complexes (Cis and Trans Isomers) of the Monomers a–d with the Grubbs Pd Catalyst **4**, Transition States for Cis–Trans Isomerization of the π Complexes, and Transition States (Cis and Trans Isomers) for 2,1- and 1,2-Insertion of the C–C Unit into the Metal–C Bond^a

monomer	β -agostic complex ^b + monomer	π complex cis	π complex trans	TS isomerizn	TS 2,1-insertion cis	TS 2,1-insertion trans	TS 1,2-insertion cis	TS 1,2-insertion trans
a ethylene	0.0 (1.4) ^c	–24.0 ^d (0.0)	–20.1 (4.6)	–0.5 (24.2)	8.1 (32.8)	2.8 (27.5)	<i>e</i>	<i>e</i>
b propylene	0.0 (0.9) ^c	–24.2 ^d (0.0)	–19.3 (4.9)	0.4 (24.6)	8.9 (33.1)	5.8 (30.0)	10.5 (34.7)	6.9 (31.1)
c acrylonitrile	0.0 (1.5) ^c	–24.8 ^d (0.0)	–20.5 (4.3)	–2.2 (22.6)	6.2 (31.0)	0.8 (25.6)	11.9 (36.7)	6.2 (31.0)
d vinylamine	0.0 (4.1) ^c	–27.4 ^d (0.0)	–21.0 (6.4)	1.4 (28.8)	9.6 (37.0)	7.1 (34.5)	11.9 (39.3)	7.2 (34.6)

^a Energies relative to the β -agostic complexes; in parentheses are given energies relative to the π complexes. ^b Cis isomer. The trans isomer is higher in energy by 3.8 kcal/mol; the isomerization barrier is 30.6 kcal/mol. ^c Energies relative to the π complex of the previous insertion step. The reaction energy of one insertion step is estimated by the reaction $C_2H_4 + C_2H_6 \rightarrow C_4H_{10}$ (–23.3 kcal/mol). ^d Energies taken from: Deubel, D. V.; Ziegler, T. *Organometallics* **2002**, *21*, 1603. ^e No regioselectivity.

barriers for the 2,1- and 1,2-insertion of vinylamine in the Grubbs systems being an exception. Since the electronic structure of transition-metal complexes is

rather complicated, a rationalization of the regioselectivity based on electronic properties of the monomers would be useful. We concluded in our study¹⁴ that, in

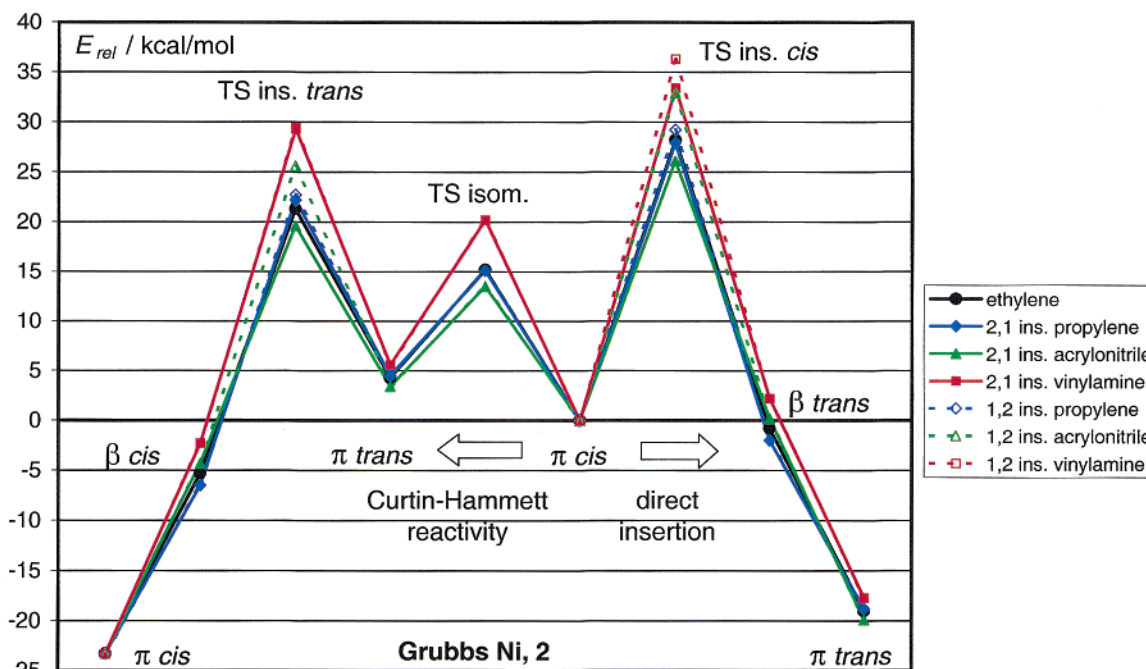


Figure 9. Calculated energy profile for a chain propagation step with the Grubbs Ni catalyst **2**, and the four monomers: Curtin–Hammett reactivity versus direct insertion. Energies are given relative to the cis π complexes.

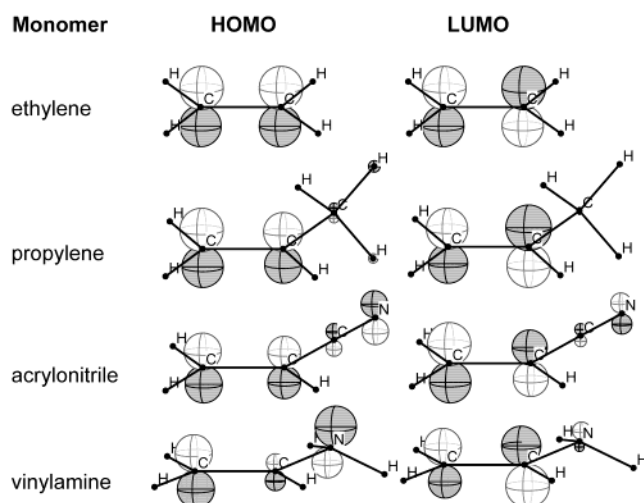


Figure 10. Schematic representation of the frontier orbitals of the four monomers.

the π complexes, predominantly the HOMO of the monomer interacts with the cationic Brookhart catalysts. The frontier orbitals of the monomers are plotted in Figure 10. The p_z coefficients in the HOMO of all monomers with a substituted C=C bond are larger at the terminal carbon atom than at the vicinal carbon atom.²⁵ The 2,1-insertion, which involves the formation of the new C–C bond to the terminal carbon, is therefore favored. In contrast, both the HOMO and LUMO of the monomer interact with the neutral Grubbs catalyst.¹⁴ The p_z coefficient in the LUMO of acrylonitrile is also larger at the terminal carbon than at the vicinal carbon, and the 2,1-pathway is also preferred. The LUMO of vinylamine, which is an analogue of the allyl anion, however, has a large coefficient at the central carbon. The interaction of the vinylamine LUMO with occupied

Grubbs catalyst orbitals favors 1,2-insertion, while the HOMO with vacant catalyst orbitals favors 2,1-insertion. As a result, both barriers were found to be equal.

Conclusions

We have completed the first two levels of a computational screening of four group 10 catalysts and nitrogen-containing polar monomers toward an incorporation of amines and nitriles in the polymer chain of polyolefins. The initial study was the investigation of the relative energies of π and N binding of nitrogen-containing monomers with the metal center of the catalysts.¹⁴ The calculations revealed similar stabilization energies for π and N coordination to the salicylaldiminato (Grubbs) Ni(II) and Pd(II) complexes, while the cationic diimine (Brookhart) Ni(II) and Pd(II) catalysts strongly prefer N coordination of acrylonitrile, $\text{CH}_2=\text{CHCN}$, nonconjugated nitriles, $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CN}$ ($n > 0$), and nonconjugated amines, $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{NH}_2$ ($n > 0$), over π binding. Vinylamine, $\text{CH}_2=\text{CH}(\text{NH}_2)$, was found to favor π coordination with the Brookhart complexes. The palladium catalysts showed a stronger preference for the π mode than do the nickel counterparts.

We have now reported the structures and energies of the transition states for insertion of acrylonitrile and vinylamine into the metal–C bond of the four catalysts. The calculations show that the activation energies for the vinylamine insertion are much higher than for the ethylene and propylene insertion, making a copolymerization with these monomers difficult. In contrast, the energies for acrylonitrile have been predicted to have insertion barriers similar to those of ethylene and propylene. Qualitatively equivalent results have been found with both metal centers, with the nickel π complexes showing a greater reactivity than their palladium counterparts.

Furthermore, it has been demonstrated that chain propagation with the Grubbs catalysts follows a Curtin–

(25) For quantitative data of the frontier orbitals of the monomers, see: Deubel, D. V. *J. Org. Chem.* **2001**, *66*, 3790.

Hammett mechanism with a cis–trans isomerization of the π complexes via a tetrahedral transition state. The trans isomer is less stable than the cis isomer, but much more reactive. Isomerization of the β -agostic complexes does not occur, since the activation energies are too large. Investigation of the insertion regioselectivity revealed that the 2,1-insertion is usually favored over the regioisomeric pathway, with equal barriers for the 2,1- and 1,2-insertion of vinylamine in the Grubbs systems being an exception. This unexpected exception is elucidated by the relative importance of electron back-donation from the neutral Grubbs catalyst to the monomer and by the large p_z coefficient at the central carbon in the LUMO of the allyl anion analogue, in contrast to the other monomers.

Computational Details

Quantum-chemical calculations were performed at the gradient-corrected density functional theory (DFT) level using Becke's exchange functional²⁶ and Perdew's correlation functional²⁷ (BP86). Uncontracted Slater-type orbitals (STOs) were used as basis functions in the SCF calculations.²⁸ The basis functions at the metals have triple- ζ quality, augmented with a set of p functions. The basis set at the other atoms has double- ζ quality, augmented with a set of d-type polarization functions. The (1s)² core electrons of C, N, and O, the (1s2s2p)¹⁰ core electrons of Ni, and the (1s2s2p3s3p3d)²⁸ core electrons of Pd were treated within the frozen-core approximation.²⁹ An auxiliary basis set of s, p, d, f, and g STOs was utilized to fit the molecular densities and to represent the Coulomb and exchange potentials in each SCF cycle. Relativistic effects were considered using the zeroth-order regular approximation (ZORA).³⁰ In view of the fact that the compounds studied in this work show a large HOMO–LUMO gap, a spin-restricted formalism was used for all calculations. The calculations were carried out with the ADF 2000 program package.³¹ The transition structures were optimized at the BP86/LANL2DZ level using Gaussian 98³² before calculating the energies with the methods described above. Vibrational frequencies were also

computed at the BP86/LANL2DZ level. For selected transition states in the present work and other metalla-analogous cycloadditions,³³ geometries and relative energies calculated at the BP86 level with the two programs were found to be very similar to each other. This procedure allowed us to perform (i) a systematic study of the insertion TS and π -complex-isomerization TS for 16 catalyst–monomer combinations with up to 8 stereoisomers for each TS, (ii) the characterization of all transition states by exactly one imaginary frequency and by inspection of the corresponding eigenvector, and (iii) a comparison to related systems by employing our standard methodology for energy calculations.

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(31) (a) Fonseca Guerra, C.; Snijders, J. G.; Te Felde, G.; Baerends, E. J. *Theor. Chem. Acta* **1998**, *99*, 391. (b) Bickelhaupt, F. M.; Baerends, E. J. *Rev. Comput. Chem.* **2000**, *15*, 1. (c) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(33) (a) Deubel, D. V.; Schlecht, S.; Frenking, G. *J. Am. Chem. Soc.* **2001**, *123*, 10085. (b) Deubel, D. V. *J. Phys. Chem. A* **2002**, *106*, 431.

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

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

(28) Snijders, J. G.; Baerends, E. J.; Vernooijs, P. *At. Data Nucl. Tables* **1982**, *26*, 483.

(29) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.

(30) Van Lenthe, E.; Ehlers, A. E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943 and references cited therein.