DFT Studies on the Copolymerization of α-Olefins with Polar Monomers: Comonomer Binding by Nickel- and Palladium-Based Catalysts with Brookhart and Grubbs Ligands

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Gradient-corrected density functional theory has been used to study the polar monomer binding mode in complexes with Ni- and Pd-based Brookhart-diimine (cationic) and Grubbs-salicylaldiminato (neutral) catalysts. Methyl acrylate and vinyl acrylate, as well as their fluorinated derivatives, have been studied as the comonomers in the copolymerization with α-olefins. Two binding modes have been considered: the π-complexes in which a polar monomer is bound by its olefinic functionality, and the O-complexes with a monomer bound by its carbonyl oxygen. The role of the electronic and the steric effects has been investigated, by considering the simplified (generic) models and the examples of the real catalysts. An energy decomposition of the contributions to the binding energies has been performed. The results show that for the Pd-based Brookhart system (active copolymerization catalyst) the π-complex is preferred, while for its Ni analogue (inactive) the O-complex is more stable. Further, the difference between Ni- and Pd-systems has mainly a steric (electrostatic + Pauli repulsion) origin: there is practically no difference in the orbital-interaction contribution to the binding energy between Ni- and Pd-based systems, as far as a comparison between the two binding modes is concerned. For the fluorinated monomers, the preference of the O-complex is decreased or reversed. However, the binding energies of both the π- and O-complexes are affected. In the complexes with Grubbs catalyst the π-complexes are strongly preferred for both the Ni- and Pd-based systems. The presence of bulky substituents on the catalysts results in a decrease in the binding energies of both the π- and O-complexes; the preference of the binding mode is not affected. Finally, the relative binding constants of the ethylene, propylene, and acrylate in the complexes involving the real Pd-Brookhart system agree with the experimental data for a similar catalyst: the ethylene complexes are most stable, followed by those of propylene and acrylate.

Introduction

The development of homogeneous catalysts for olefin polymerization in the 1980s has revolutionized the olefin polymerization field.[1−4] Since the structures of the single-site catalysts are well defined, they offer more control over the polymer properties than the heterogeneous Ziegler−Natta catalyst.[5−8] As such, they have provided chemists with the opportunity for rational catalyst engineering. The first single-site catalysts were group-4 metallocenes; the “metallocene revolution” period was followed by the development of new organometallic catalysts, involving almost all transition metals, some lanthanides, and a few main-group elements, as well as a great variety of ligands.[9−20]

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(1) Sinn, H.; Kaminsky, W.; Vollmer H. J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 380.

(2) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

(3) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233.

(4) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507.

(5) Ziegler, K.; Holtzkamp, E.; Martin, H.; Breil, H. *Angew. Chem.* **1955**, *67*, 541.

(6) Ziegler, K.; Holtzkamp, E.; Breil, H.; Martin, H. *Angew. Chem.* **1955**, *67*, 426.

(7) Natta, G. *J. Polym. Sci.* **1955**, *16*, 143.

(8) Natta, G. *Angew. Chem.* **1956**, *68*, 393.

(9) Togni, A.; Halterman, R. L. *Metallocenes*; Wiley: Weinheim, 1998.

(10) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymoth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143, and references therein.

(11) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587, and references therein.

(12) Alt, H. G.; Koppl, A. *Chem. Rev.* **2000**, *100*, 1205, and references therein.

(13) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223, and references therein.

(14) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253, and references therein.

(15) *Topics in Catalysis*; Marks, T. J., Stevens, J. C., Eds.; Baltzer: Amsterdam, 1999; Vol. 7, and references therein.

(16) *Metalorganic Catalysts for Synthesis and Polymerization: Recent Results by Ziegler-Natta and Metallocene Investigations*; Kaminsky, W., Ed.; Springer-Verlag: Berlin, 1999; and references therein.

(17) Mashima, K.; Nakayama, Y.; Nakamura, A. *Adv. Polym. Sci.* **1997**, *133*, 1.

(18) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428, and references therein.

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A new emerging frontier in olefin polymerization is the controlled copolymerization of α-olefins with monomers bearing a polar functional group.[21,22] The incorporation of even small amounts of polar monomers dramatically modifies the polymer properties compared to regular polyolefins in terms of toughness, adhesion, barrier properties, surface properties, solvent resistance, miscibility with other polymers, and rheology.[21,22] Of particular interest are the copolymers of monomers with oxygen-containing polar groups, such as vinyl alcohols, acids, and esters. Presently, available polar copolymers are produced in radical polymerization processes under high-temperature and high-pressure conditions.[23] A design of the single-site copolymerization catalyst would open new, less expensive routes to commercially available copolymers, but also it could lead to the synthesis of new materials, potentially possessing new properties.

Similarly to the traditional Ziegler−Natta system, the early-transition-metal-based catalysts are highly oxophilic and, as such, are poisoned by oxygen-containing compounds. Although some homopolymerizations[20,24−29] and block-copolymerizations[29−32] are possible, they involve mechanisms[20,24,25] different from Ziegler−Natta-type polymerization of ethylene/α-olefins.[33,34] Thus, the random copolymerizations cannot proceed. Hence, the attempts of incorporating polar groups into a polymer chain must employ alternative approaches, such as functional group protection and use of special monomers,[22,35−49] or chemical modifications of the polymer.[50−54] Design of an effective catalyst for controlled, direct copolymerizations still remains among the not yet achieved goals of organometallic chemistry. Here, the use of less oxophilic, late-transition-metal complexes has shown some promise, as demonstrated by some recent pioneering studies.[55−57] Unlike its Ni-based analogue, the Brookhart Pd-diimine catalyst[58−61] has been shown to copolymerize[55,56] ethylene and higher α-olefins with acrylates and vinyl ketones. Another family of catalysts that tolerate functional groups are the salicylaldiminato Ni-complexes by Grubbs et al.;[62] these neutral systems are highly active as homopolymerization catalysts even in the presence of polar compunds; they are also able to polymerize and copolymerize some polar monomers.[57] The most recent example of a late-transition-based catalyst that tolerates oxygen-containing functional groups has been presented by Sen et al.: the neutral palladium complex $[Pd(C_6F_5)Br(CH_3CN)_2]$, in the presence of 1 equiv of monodentate ligand, is capable of homopolymerizing acrylates via an insertion mechanism.[63]

To incorporate polar monomers into a polymer chain in a random copolymerization process, it is required that its insertion follows the same reaction mechanism as that of α-olefin Ziegler−Natta polymerization. Scheme 1 presents a rough outline of the elementary reaction steps involved in late-transition-metal-catalyzed olefin polymerization. This picture is based on both experimental[19,33,34] and theoretical studies.[64,65] The polymerization starts by the complexation of an olefin to the metal center to form the π-complex **A** where the monomer is bound to the metal through its olefin double bond. The π-complex **B** can react further by inserting the olefin into the $M-C_\alpha$ bond of **A**, leading to the propagation product **C**, where the growing chain has been extended with two carbon units. Alternatively, a

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(19) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169, and references therein.

(20) Yasuda, H.; Ihara, I. *Adv. Polym. Sci.* **1997**, *133*, 53, and references therein.

(21) *Functional Polymers: Modern Synthetic Methods and Novel Structures*; Patil, A. O., Schulz, D. N., Novak, B. M., Eds.; ACS Symposium Series 704; American Chemical Society: Washington, DC, 1998.

(22) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479, and references therein.

(23) Doak, K. W. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Ed.; John Wiley and Sons: New York, 1986; Vol. 6, pp 386-429.

(24) Li, Y.; Ward, D. G.; Reddy, S. S.; Collins, S. *Macromolecules* **1997**, *30*, 1875.

(25) Collins, S.; Ward, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 5461.

(26) Yasuda, H.; Yamamoto, H.; Yamashita, M.; Yokota, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, *26*, 7134.

(27) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908.

(28) Yamashita, M.; Takemoto, Y.; Ihara, E.; Yasuda, H. *Macromolecules* **1996**, *29*, 1798.

(29) Ihara, E.; Morimoto, M.; Yasuda, H. *Macromolecules* **1995**, *28*, 7886.

(30) Yasuda, H.; Furo, M.; Yamamoto, H.; Nakamura, A.; Miyake, S.; Kibino, N. *Macromolecules* **1992**, *25*, 5115.

(31) Boffa, L. S.; Novak, B. M. *Macromolecules* **1997**, *30*, 3494.

(32) Boffa, L. S.; Novak, B. M. *J. Mol. Catal. A* **1998**, *133*, 123.

(33) Coose, P. *J. Catal.* **1964**, *3*, 80.

(34) Arlman, E. J.; Coose, P. *J. Catal.* **1964**, *3*, 99.

(35) Purgett, M. D.; Vogl, O. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 677.

(36) Vogl, O. *J. Macromol. Sci., Chem.* **1985**, *A22*, 541.

(37) Vogl, O. *J. Macromol. Sci., Chem.* **1984**, *A21*, 1217.

(38) Purgett, M. D.; Vogl, O. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 2051.

(39) Purgett, M. D.; Vogl, O. *J. Macromol. Sci., Chem.* **1987**, *A24*, 1465.

(40) Aaltonen, P.; Löfgren, B. *Macromolecules* **1995**, *28*, 5353.

(41) Aaltonen, P.; Fink, G.; Löfgren, B.; Seppälä, J. *Macromolecules* **1996**, *29*, 5255.

(42) Wilén, C.-E.; Nasman, J. H. *Macromolecules* **1994**, *27*, 4051.

(43) Aaltonen, P.; Löfgren, B. *Eur. Polym. J.* **1997**, *33*, 1187.

(44) Hakala, K.; Löfgren, B.; Helaja, T. *Eur. Polym. J.* **1998**, *34*, 1093.

(45) Marques, M. M.; Correia, S. G.; Ascenso, J. R.; Ribeiro, A. F. G.; Gomes, P. T.; Dias, A. R.; Foster, P.; Rausch, M. D.; Chien, J. C. W. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2457.

(46) Correia, S. G.; Marques, M. M.; Ascenzo, J. R.; Ribeiro, A. F. G.; Gomes, P. T.; Dias, A. R.; Blais, M.; Rausch, M. D.; Chien, J. C. W. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2471.

(47) Marques, M. M.; Correia, S. G.; Fernandez, S.; Chien, J. C. W. *J. Proceedings of "Organometallics Catalyst and Polymerization. New Millenium International Conference"*; Oslo, Norway, June 18−22, 2000.

(48) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123.

(49) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679.

(50) Chung, T. C. *Macromolecules* **1988**, *21*, 865.

(51) Chung, T. C.; Rhubright, D. *Macromolecules* **1994**, *27*, 1313.

(52) Chung, T. C.; Rhubright, D. *Macromolecules* **1993**, *26*, 3019.

(53) Chung, T. C.; Rhubright, D. *Macromolecules* **1991**, *24*, 970.

(54) Chung, T. C.; Janvikul, W. *J. Organomet. Chem.* **1999**, *581*, 176.

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

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

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

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

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

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

(61) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686.

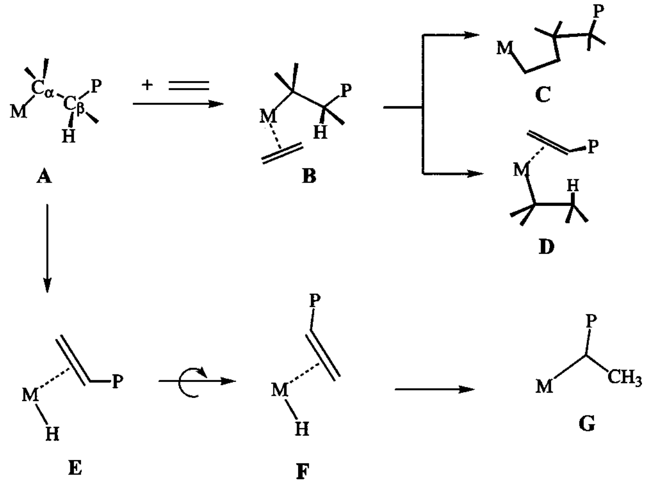
(62) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149.

(63) Elia, C. N.; Sen, A.; Albeniz, A. C.; Espinet, P. Proceedings of the ACS National Meeting, Washington, Aug 20−24, 2000.

(64) Rappe, A. K.; Skiff, W. M.; Casewit, C. J. *Chem. Rev.* **2000**, *100*, 1435, and references therein.

(65) Angermund, K.; Fink, G.; Jensen, V. R.; Kleinschmidt, R. *Chem. Rev.* **2000**, *100*, 1457, and references therein.

Scheme 1. Mechanism for the Ethylene Polymerization Catalyzed by Late-Transition-Metal-Complexes



hydrogen on C_β can migrate to the olefinic monomer leading to **D**, where the old growing chain now is an olefin that can be eliminated, whereas the olefinic monomer now has been converted into a new growing chain. The reaction **B** → **C** represents a possible termination of polymer growth. It is also possible for the linear polymer **A** to isomerize to the branched chain **G** through the sequence **A** → **E** → **F** → **G**.

Thus, the polar monomer must also be bound to the metal center by its double C=C bond rather than by the oxygen atom of the polar group. The initial steps in the copolymerization processes involve the competition between the π-complexes of olefin and polar monomer, the complexes with the latter being bound by its polar group (Scheme 2). Thus, it seems reasonable to assume that potential catalysts can initially be screened, by determining the preferred bonding mode: the model systems with a strong preference of the O-bound coordination mode can be excluded as less promising catalysts.

In the present study we have computationally investigated the binding mode of the oxygen-containing monomers (methyl acrylate and vinyl acetate) in the complexes involving cationic and neutral Ni- and Pd-based catalysts with the Brookhart and Grubbs ligands. The main purpose of this study was to understand the origin of the difference in the behavior of the Brookhart systems based on Pd (active copolymerization catalyst) and Ni (inactive). The role of the electronic and steric factors will be discussed, on the basis of the DFT calculations for simplified model systems as well as a selection of real catalysts. Also discussed are the effects of the reduced basicity of the carbonyl oxygen on the monomer (in the fluorinated compounds) as well as of the reduced oxophilicity of the catalyst (in the neutral Grubbs system).

Computational Details and the Model Systems

The molecular systems studied in the present work are shown in Scheme 3. We have considered complexes in which the polar monomer is bound to the metal by either its olefinic functionality (π-complexes) or by the oxygen atom of the polar group (O-complexes). Both the Pd- and Ni-based catalysts with Brookhart and Grubbs ligands have been considered. With methyl acrylate (MA) and vinyl acetate (VA) as comonomers, the calculations have been performed for the generic catalyst models (**1a**,**b** and **3a**,**b**), in which the bulky substituents of the real systems have been replaced by hydrogen atoms. In addition, in the generic Brookhart Pd- and Ni-based catalysts, the complexes with fluorinated monomers (FMA and FVA) have also been studied, to obtain insight into the influence of the basicity of the carbonyl oxygen on the complexation energies and the preference of the bonding mode. Finally, calculations have also been performed on the complexes involving methyl acrylate and the larger models for Ni- and Pd-based Brookhart (**2a**,**b**) and Ni-based Grubbs (**4a**, **5a**, **6a**) systems, with the bulky substituents corresponding to the real catalysts; in the following we will refer to those complexes as "real" systems. This set of complexes allows us to discuss the role of both the electronic and the steric factors, as well as to compare the results with the previous studies[66-75] on the ethylene and propylene homopolymerizations with Brookhart and Grubbs catalysts.

All the results were obtained from the DFT calculations based on the Becke–Perdew exchange–correlation functional,[76-78] using the Amsterdam Density Functional (ADF) program.[79-83] The standard double-ζ STO basis with one set of polarization functions was applied for H, C, N, O, and F atoms, while the standard triple-ζ basis sets were employed for Ni and Pd atoms.[84,85] The 1s electrons of C, N, O, and F, as well as the 1s–2p electrons of Ni and the 1s–3d electrons of Pd, were treated as frozen core. The auxiliary s, p, d, f, and g STO functions,[86] centered on all nuclei, were used to fit the electron density and the Coulomb and exchange potentials in each SCF cycle. The reported energy differences include first-order scalar relativistic correction,[87-89] since it has been shown that such an approach is sufficient for 4d transition-metal atoms.[90]

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

(67) Michalak, A.; Ziegler, T. *Organometallics* **2000**, *19*, 1850.

(68) Deng L.; Woo, T. K.; Cavallo, L.; Margl, P M.; Ziegler T. *J. Am. Chem. Soc.* **1997**, *119*, 6177.

(69) Deng, L.; Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 1094.

(70) Musaev, D. G.; Svensson, M.; Morokuma, K.; Strömberg, S.; Zetterberg, K.; Siegbahn, P. E. M. *Organometallics* **1997**, *16*, 1933.

(71) Froese, R. D. J.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 1581.

(72) Musaev, D. G.; Froese, R. D. J.; Morokuma, K. *Organometallics* **1998**, *17*, 1850.

(73) Margl, P.; Deng, L.; Ziegler, T. *J. Am. Chem. Soc.* **1999**, *121*, 154.

(74) Woo, T. K.; Blöchl, P. E.; Ziegler, T. *J. Phys. Chem. A* **2000**, *104*, 121.

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

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

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

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

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

(80) Boerrigter, P. M.; te Velde, G.; Baerends, E. J. *Int. J. Quantum Chem.* **1988**, *33*, 87.

(81) Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322.

(82) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84.

(83) Fonesca Geurra, C.; Visser, O.; Snijders, J. G.; te Velde, G.; Baerends, E. J. In *Methods and Techniques in Computational Chemistry METACC-95*; Clementi, E., Corongiu, G., Eds.; STEF: Cagliari, 1995.

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

(85) Vernoijs, P.; Snijders, J. G.; Baerends, E. J. *Slater Type Basis Functions for the Whole Periodic System*; Internal report (in Dutch); Department of Theoretical Chemistry, Free University: Amsterdam, The Netherlands, 1981.

(86) Krijn, J.; Baerends, E. J. *Fit Functions in the HFS Method*; Internal Report (in Dutch); Department of Theoretical Chemistry, Free University: Amsterdam, The Netherlands, 1984.

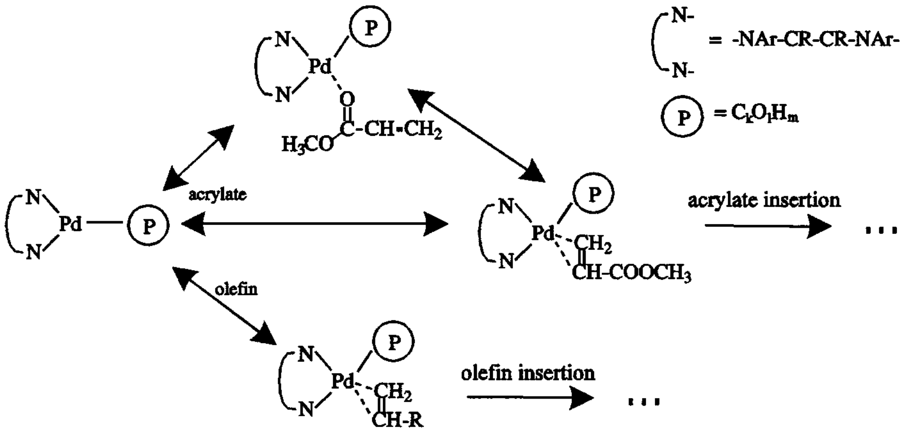
(87) Ziegler, T.; Tschinke, V.; Baerends, E. J.; Snijders, J. G.; Ravenek, W. *J. Phys. Chem.* **1989**, *93*, 3050.

(88) Snijders, J. G.; Baerends, E. J. *Mol. Phys.* **1978**, *36*, 1789.

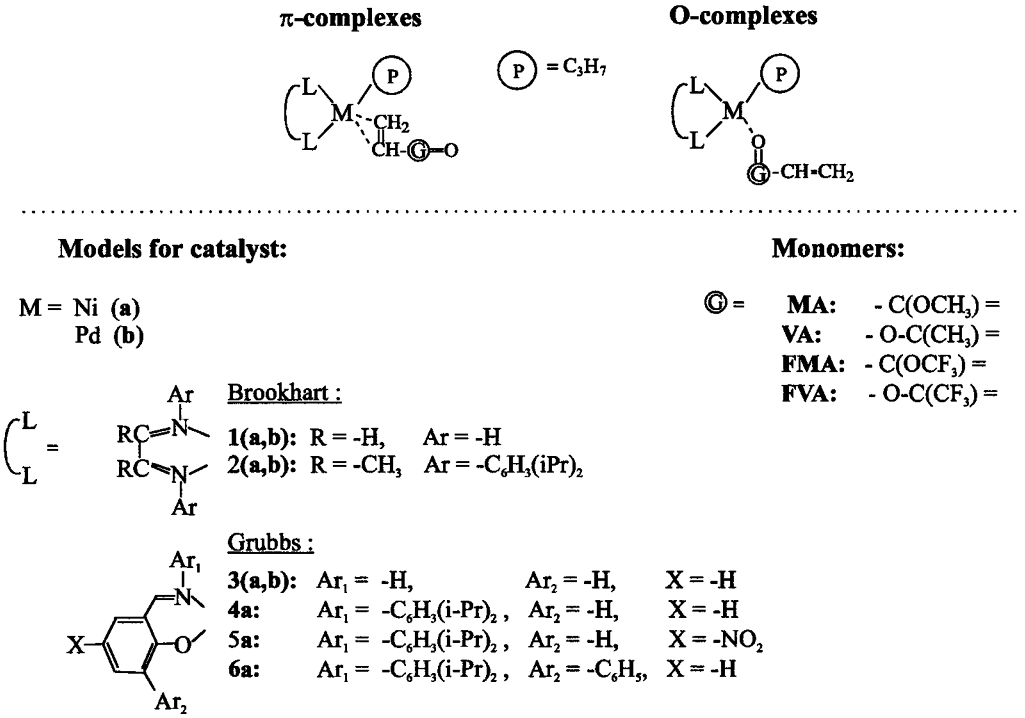
(89) Snijders, J. G.; Baerends, E. J.; Ros, P. *Mol. Phys.* **1979**, *38*, 1909.

(90) Deng, L.; Ziegler, T.; Woo, T. K.; Margl, P.; Fan, T. *Organometallics* **1998**, *17*, 3240.

Scheme 2. Initial Steps in the Copopymerization of α-Olefins with Polar Monomers (Here, Methyl Acrylate and Brookhart Pd-Diimine Catalysts Are Used as an Example)



Scheme 3. Complexes Studied in the Present Work



Results and Discussion

The complexation energies for all the monomers for the generic models of the Ni- and Pd-based Brookhart and Grubbs catalysts are collected in Table 1. The results show that all the complexes are stable, with binding energies varying between −8.1 and −21.7 kcal/mol. Here, it can be seen that the change of the transition metal, the catalyst ligands, or the monomer can strongly affect the complexation energies as well as the preferred binding mode. In the following, we will first discuss the methyl acrylate and vinyl acetate complexes with the Brookhart catalysts (Ni- and Pd-based), then the corresponding complexes with fluorinated monomers, and the methyl acrylate and vinyl acetate complexes with Ni- and Pd-based catalysts with Grubbs ligands. Finally, the effect of the electronic and steric factors in the real Brookhart and Grubbs catalysts will be discussed.

Table 1. Monomer Binding Energies for the Generic Models for the Ni- and Pd-Based Brookhart and Grubbs Catalysts

catalyst[a]	monomer[a]	ΔE(C=C)[b]	ΔE(O)[c]	E(C=C) − E(O)[d]
1a. Brookhart/Ni	MA	−17.10	−21.10	+4.00
1b. Brookhart/Pd	MA	−20.70	−17.30	−3.40
1a. Brookhart/Ni	VA	−17.07	−17.75	+0.68
1b. Brookhart/Pd	VA	−20.12	−14.96	−5.16
1a. Brookhart/Ni	FMA	−13.93	−16.25	+2.32
1b. Brookhart/Pd	FMA	−17.95	−12.92	−5.03
1a. Brookhart/Ni	FVA	−11.41	−9.99	−1.42
1b. Brookhart/Pd	FVA	−14.76	−8.10	−6.66
3a. Grubbs/Ni	MA	−17.74	−10.18	−7.56
3b. Grubbs/Pd	MA	−24.34	−10.17	−14.17
3a. Grubbs/Ni	VA	−16.09	−9.72	−7.18
3b. Grubbs/Pd	VA	−21.72	−9.56	−12.16

[a] See Scheme 3. [b] π-Complex stabilization energy, in kcal/mol. [c] Stabilization energy of the O-complex, in kcal/mol. [d] The difference in the energies of the π-complex and O-complex.

Acrylate Complexes with the Generic Ni- and Pd-Based Brookhart Catalysts. The geometries of the most stable π- and O-bound acrylate complexes with Ni- and Pd-based Brookhart catalysts are shown in Figure 1. As in the propylene case,[66,67] the two carbon–

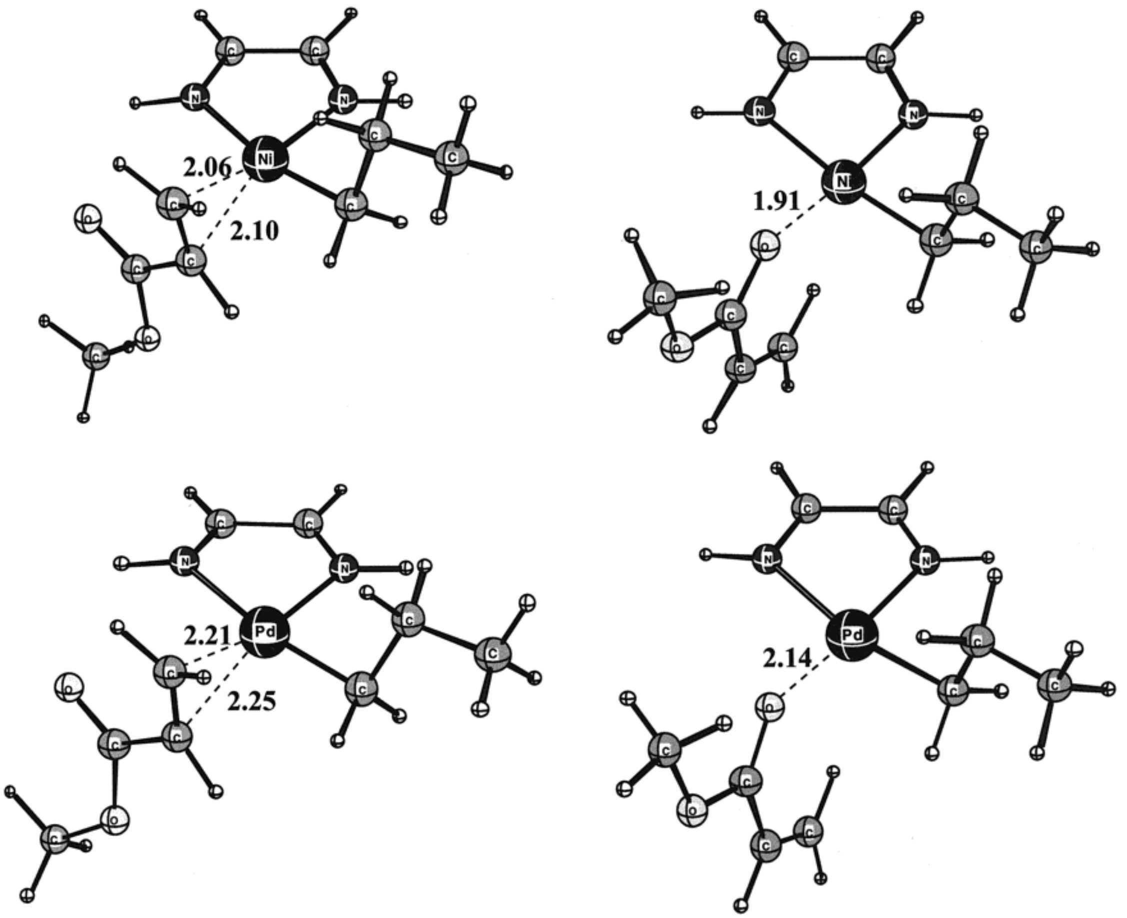


Figure 1. Geometries of the methyl acrylate π- (left) and O-complexes (right) with the Ni- (top) and Pd-based (bottom) Brookhart catalysts.

metal bonds in the π-complexes are not equivalent: for both Ni- and Pd-based catalysts the C−M bonds involving the unsubstituted carbon are shorter, due to the polarization of the monomer π-orbital toward the CH_2 group. For the generic catalyst models, the acrylate bonding energies for the π-complexes (−17.10 and −20.70 kcal/mol for Ni- and Pd-catalyst, respectively) are larger than those of ethylene (−15.53 and −18.82 kcal/mol), but slightly smaller than those of propylene (−18.01 and −20.85 kcal/mol).[66] It should be emphasized, however, that this order of the binding energies for a model catalysts does not agree with the experimentally determined relative binding constants for these monomers,[56] as experiments found the strongest stabilization for ethylene complexes, followed by propylene and finally acrylates. As we demonstrated in previous studies for ethylene and propylene, the electronic factors that determine relative binding constants for a generic catalyst are overridden by steric factors in the real systems.[67] For acrylate complexes we will discuss this later (see Table 5).

Table 2. Key Catalyst−Monomer Interatomic Distances in the π- and O-Complexes with the Generic Models for the Ni- and Pd-Based Brookhart and Grubbs Catalysts

catalyst[a]	monomer[a]	M−C[b]	M−O[c]
1a. Brookhart/Ni	MA	2.06, 2.10	1.91
1b. Brookhart/Pd	MA	2.21, 2.25	2.14
1a. Brookhart/Ni	VA	2.03, 2.16	1.92
1b. Brookhart/Pd	VA	2.19, 2.30	2.15
1a. Brookhart/Ni	FMA	2.05, 2.09	1.91
1b. Brookhart/Pd	FMA	2.21, 2.25	2.16
1a. Brookhart/Ni	FVA	2.03, 2.10	1.95
1b. Brookhart/Pd	FVA	2.20, 2.26	2.20
3a. Grubbs/Ni	MA	2.02, 2.04	1.95
3b. Grubbs/Pd	MA	2.17, 2.20	2.18
3a. Grubbs/Ni	VA	2.03, 2.06	1.97
3b. Grubbs/Pd	VA	2.19, 2.24	2.19

[a] See Scheme 3. [b] Metal−carbon distances in the π-complex; in Å. [c] Metal−oxygen distance in the O-complex; in Å.

In a recent paper[66] we explained the difference in the ethylene and propylene complexation energies in terms of their HOMO (π C═C bonding orbital) energies: a destabilization of the propylene HOMO facilitates the monomer-to-metal charge transfer. The energies of the frontier orbitals for the monomers studied in the present work are presented in Figure 2. The HOMO of methyl acrylate has different character; it describes the lone pair of the carbonyl oxygen. The C═C π-orbital (HOMO-1) has lower energy (−7.30 eV) than the HOMO of ethylene (−7.16 eV) and propylene (−6.65 eV). Therefore, it could be expected that substantially weaker carbon−metal π-bonds would be formed in the acrylate case. However, the acrylate LUMO (of the C═C π*-character) is strongly stabilized (−2.81 eV) in comparison to the LUMO of ethylene (−1.35 eV) and propylene (−1.01 eV); this facilitates back-donation from the catalyst. As a result of these opposing factors, the acrylate binding energy is located between those of ethylene and propylene.

In the O-complexes, the acrylate molecule adapts an orientation in which its coordination plane is roughly perpendicular to the plane of the Pd−C−N−N−C ring,

Table 3. Contributions to the Methyl Acrylate Binding Energy (see Eq 1) in the π- and O-Complexes with the Generic Models for the Ni- and Pd-Based Brookhart and Grubbs Catalysts

catalyst[a]	complex	ΔE_{el}[b]	ΔE_{Pauli}[b]	ΔE_{steric}[b,c]	$\Delta E_{orb.int.}$[b]	$\Delta E_{tot.}$[b,d]	$\Delta E_{geom.}$[b]
1a. Brookhart/Ni	π	−91.48	+115.13	+23.65	−69.23	−45.58	+28.48
1a. Brookhart/Ni	O	−62.75	+61.95	−0.80	−40.81	−41.61	+20.50
1b. Brookhart/Pd	π	−99.63	+120.60	+20.97	−60.40	−39.43	+18.73
1b. Brookhart/Pd	O	−49.54	+50.27	+0.73	−32.06	−31.33	+13.03
3a. Grubbs/Ni	π	−106.4	+141.39	+34.99	−82.82	−47.83	+30.09
3a. Grubbs/Ni	O	−50.9	+58.53	+7.63	−30.03	−22.40	+12.22
3b. Grubbs/Pd	π	−114.03	+144.69	+30.66	−70.39	−39.73	+15.39
3b. Grubbs/Pd	O	−40.4	+47.17	+6.77	−24.39	−17.63	+7.33

[a] See Scheme 3. [b] In kcal/mol. [c] $\Delta E_{steric} = \Delta E_{el.} + \Delta E_{Pauli}$. [d] $\Delta E_{tot.} = \Delta E_{steric} + \Delta E_{orb.int.}$.

Table 4. Contributions to the Vinyl Acetate Binding Energy (see Eq 1) in the π- and O-Complexes with the Generic Models for the Ni- and Pd-Based Brookhart and Grubbs Catalysts

catalyst[a]	complex	ΔE_{el}[b]	ΔE_{Pauli}[b]	ΔE_{steric}[b]	$\Delta E_{orb.int.}$[b]	$\Delta E_{tot.}$[b]	$\Delta E_{geom.}$[b]
1a. Brookhart/Ni	π	−90.31	+109.74	+19.43	−65.18	−45.75	+28.68
1a. Brookhart/Ni	O	−58.6	+56.65	−1.95	−37.50	−39.45	+21.70
1b. Brookhart/Pd	π	−97.29	+116.21	+18.92	−57.54	−38.62	+18.50
1b. Brookhart/Pd	O	−47.42	+47.70	+0.28	−30.27	−29.99	+15.03
3a. Grubbs/Ni	π	−101.15	+134.35	+33.20	−69.35	−36.15	+20.06
3a. Grubbs/Ni	O	−50.41	+55.52	+5.11	−27.67	−22.56	+12.84
3b. Grubbs/Pd	π	−101.65	+127.97	+26.32	−58.14	−31.82	+10.10
3b. Grubbs/Pd	O	−38.56	+42.51	+3.95	−21.42	−17.46	+7.90

[a] See Scheme 3. [b] In kcal/mol. [c] $\Delta E_{steric} = \Delta E_{el.} + \Delta E_{Pauli}$. [d] $\Delta E_{tot.} = \Delta E_{steric} + \Delta E_{orb.int.}$.

Table 5. Binding Energies for Methyl Acrylate Complexes with the Real Brookhart and Grubbs Catalysts

catalyst[a]	ΔE(C=C)[b]	ΔE(O)[c]	E(C=C) − E(O)[d]
2a. Brookhart/Ni	−10.10	−13.09	+2.99
2b. Brookhart/Pd	−13.65	−10.64	−3.01
4a. Grubbs/Ni	−12.82	−6.49	−6.33
5a. Grubbs/Ni	−12.50	−7.51	−4.99
6a. Grubbs/Ni	−13.15	−7.31	−5.84

[a] See Scheme 3. [b] π-Complex stabilization energy, in kcal/mol. [c] Stabilization energy of the O-complex, in kcal/mol. [d] The difference in the energies of the π-complex and O-complex, in kcal/mol.

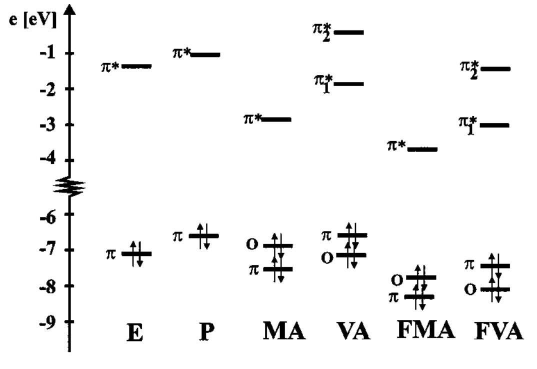


Figure 2. Frontier-orbital energies for the monomers studied in the present work.

with the C=O−Pd=N torsion angle of 96° and 106° for the Ni- and Pd-system, respectively. The C=O−Pd bond angles of 135° and 136° (for Ni and Pd) indicate that the monomer is bound by a lone pair of the oxygen atom.

A comparison of the first two rows of Table 1 shows that for the Brookhart Ni-based catalyst the acrylate O-complex is preferred by 4.0 kcal/mol, while for the analogous Pd-system, the π-complex is more stable by 3.4 kcal/mol. In comparison to the Ni-system, in the Pd-case the stabilization energy is increased by 3.6 kcal/mol for the π-complex and decreased by 3.8 kcal/mol for the O-complex. The preference of the binding mode is reflected in the metal−monomer bonding distances (Figure 1 and Table 2). Although for both catalysts the oxygen−metal bond in the O-complexes is shorter than the carbon−metal bonds in the π-complexes, it can be seen that the difference becomes smaller in the Pd-case. Namely, while the Ni−O bond (1.91 Å) is shorter then the Ni−C bonds (2.06 and 2.10 Å) by 0.14−0.19 Å, the corresponding differences in the Pd-case are only 0.07−0.11 Å.

The energetic preference of the O-complex for the Ni-based catalyst and the π-complex for the Pd-system do reflect their activity in the copolymerization processes: while the Ni-system is inactive, the Pd-based catalyst can copolymerize ethylene and α-olefins with methyl acrylate.[55,56] These results confirm that the prospective candidates for a random copolymerization catalyst can be initially screened by theoretical determination of the preferred comonomer binding mode: the systems with the preference for the O-complex can be excluded from further studies.

Let us now examine the origin of the difference between the Ni- and Pd-based systems. In Table 3 the results of the fragment-based energy decomposition of the acrylate binding energy are presented for the O- and π-complexes. In this analysis, the monomer complexation energy is decomposed as[91]

$$\Delta E = \Delta E_{geom.} + \Delta E_{tot.} = \Delta E_{geom.} + [\Delta E_{steric} + \Delta E_{orb.int.}] = \Delta E_{geom.} + [(\Delta E_{el.} + \Delta E_{Pauli}) + \Delta E_{orb.int.}] \tag{1}$$

where $\Delta E_{geom.}$ is a geometry distortion term, comprising the contributions from both reactants (monomer, with respect to the free molecule geometry, and the catalyst-alkyl fragment, with respect to the most stable, β-agostic complex geometry), and $\Delta E_{tot.}$ is the total interaction energy between the distorted reactants. The latter can be further decomposed into the orbital interaction term (stabilizing, two-orbital, two-electron interactions), $\Delta E_{orb.int.}$, and the steric contribution consisting of the electrostatic interaction (stabilizing or destabilizing) and

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[91] Ziegler, T.; Rauk, A. *Theor. Chim. Acta (Berlin)* **1978**, *46*, 1.

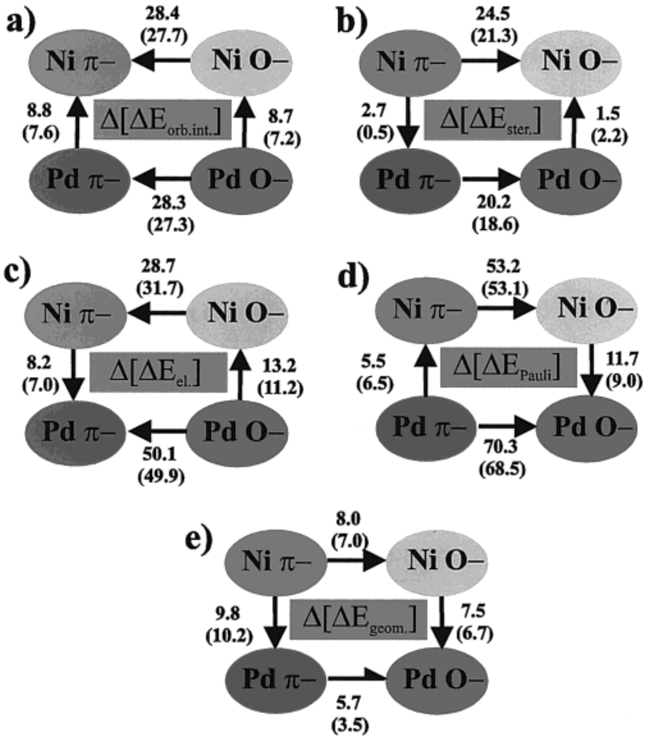

Figure 3. Schematic representation of the differences in the contributions to the bonding energies between the O- and π-complexes of the methyl acrylate and vinyl acetate with the Ni- and Pd-based Brookhart catalysts. Panels a–e display the differences in the orbital interaction, steric, electrostatic, Pauli repulsion, and geometry distortion contributions, respectively. The arrows point to the preferred complex of the respective pair. The numbers correspond to the differences in respective contributions (for vinyl acatate in parantheses).

the Pauli repulsion (destabilizing, two orbital, four-electron interaction), $\Delta E_{\text{steric}} = \Delta E_{\text{el.}} + \Delta E_{\text{Pauli.}}$ To facilitate the discussion, in Figure 3 we schematically present the differences in these contributions between Ni- and Pd-based complexes and the two binding modes (π and O).

An analysis of the data presented in Table 3 and Figure 3 indicates two major conclusions. Namely, there is practically no difference between Ni- and Pd-catalysts in the orbital interaction terms, as far as the comparison between the two binding modes is concerned. There are, however, qualitative differences in the steric contribution, i.e., in both the electrostatic and Pauli repulsion terms, accompanied by the quantitative differences in the geometry distortion part of the binding energy.

Let us now have a look at the orbital interaction terms. Comparing the π- and O-complexes, it can be seen that for both Ni and Pd the values for the π-complexes are more negative (stabilizing) by ca. 28 kcal/mol. Similarly, a comparison between the Ni- and Pd-complexes shows that for both the π- and O-complexes the Ni $\Delta E_{\text{orb.int.}}$ values are lower by ca. 9 kcal/mol. The change of the transition metal in the Brookhart catalyst does not introduce any differences between the π- and O-complexes; for both of them the stabilization energy coming from orbital interaction changes by the same amount. This is further qualitatively confirmed by the results of the Mulliken population analysis. Namely, for both the Ni- and Pd-catalysts there is a strong donation/back-donation from/to the acrylate π/π^*-orbitals in the π-complexes, as indicated by changes in the Mulliken populations of the catalyst and acrylate occupied and virtual orbitals. For example, in the Ni-complex the acrylate occupied orbitals lose 0.42 electron, and its virtual orbitals gain 0.27 electron; for the catalyst the changes in the populations of its occupied and virtual orbitals are −0.33 and +0.48 electron, respectively. For the O-complexes, however, there is practically no back-donation: the changes in the populations of acrylate occupied and virtual orbitals are −0.30 and +0.05; the corresponding values for the catalyst are −0.05 and +0.29.

In the case of the steric contribution to the acrylate bonding energies there is a qualitative difference between the Ni- and Pd-based complexes. Namely, for the π-complex the steric repulsion is lower for Pd than for Ni by 2.7 kcal/mol, while in the O-complexes the steric term is lower for Ni by 1.5 kcal/mol (attractive for Ni and repulsive for Pd). The diagrams in Figure 3 and the values of Table 3 show that the electrostatic and Pauli repusion terms change in opposite directions, with the electrostatic term dominating when comparing the Ni- and Pd-complexes. As a result, for Ni the steric contribution in the O-complex is lower by 24.5 kcal/mol than in the π-complex; for Pd the steric preference for the O-complex is only 20.2 kcal/mol.

Finally, the geometry distortion terms are substantially larger in the case of the π-complexes than for the systems with O-bound monomer. It should be pointed out that for both orientations the absolute values of catalyst−alkyl distortion energies are much larger than the acrylate contributions, mainly due to a breaking of the agostic bond. The acrylate distortion, however, is equally important when considering the difference between the $\Delta E_{\text{geom.}}$ values for the two orientations: the distortion energies of both reactants to the π-complex geometry are similarly increased in comparison to the O-complex. For example, in the Ni-system the acrylate distortion costs +5.22 kcal/mol for the π-complex and only +1.54 kcal/mol for the O-complex; the corresponding values for the catalyst are +23.26 and +18.96 kcal/mol. For the Pd-system the acrylate (catalyst−alkyl) distortion energies are +4.88 (+13.85) and +1.17 (+11.86) kcal/mol for the π- and O-complexes, respectively.

Vinyl Acetate Complexes with the Generic Ni- and Pd-Based Brookhart Catalysts. In the π- and O-complexes the geometrical arrangements of vinyl acetate (VA) are similar to those of methyl acrylate (MA) in the corresponding complexes. The catalyst−monomer distances of Table 2 show an increased asymmetry of the two metal−carbon bonds in the π-complexes. In comparison to acrylate one of the bonds is slightly shortened (from 2.06 to 2.03 Å in the Ni-case and from 2.21 to 2.19 Å in the Pd-case), and the other is lengthened (from 2.10 to 2.16 Å and from 2.25 to 2.30 Å). This comes as a result of stronger polarization of the vinyl acetate π/π^*-orbitals. In the O-complexes of vinyl acetate the metal−oxygen bond is slightly longer than in the corresponding acrylate complexes.

The vinyl acetate binding energies presented in Table 1 show that for the Ni-catalyst the O-complex is slightly preferred (by 0.68 kcal/mol), while for the Pd-system the

π-complex is more stable by 5.16 kcal/mol. For both catalysts the π-complexation energies are close to those of acrylate. For O-complexes, however, the binding energies are decreased in comparison to the acrylate case. This can be qualitatively explained in terms of the energies of the vinyl acetate frontier orbitals. Namely, the energetic order of the vinyl acetate orbitals is different than that of acrylate; here, the HOMO is the bonding C═C π-orbital and the HOMO-1 corresponds to the lone pair of the carbonyl oxygen. The vinyl acetate π-orbital is destabilized compared to the acrylate one, which facilitates the electron transfer to the metal. Two vinyl acetate antibonding orbitals (π_1* and π_2*) act as electron acceptor; both of them comprise contributions from C═C and C═O, with π_1* being polarized toward C═O and π_2* toward the C═C bond. They are higher in energy than the acrylate acceptor orbital, which makes back-donation more difficult. As a result of the two opposing factors, the π-complexation energies of methyl acrylate and vinyl acetate become similar. The destabilization of the vinyl acetate O-complexes comes as a result of the stabilization of its lone pair orbital, which implies lower charge transfer from the monomer to the metal, compared to the acrylate O-complex. As in the acrylate case, in the vinyl acetate O-complexes there is practically no back-donation from the catalyst. Thus, the stabilization of the donor orbital directly results in a decrease in the O-complex binding energies.

The above conclusions are further qualitatively confirmed by the results of the Mulliken population analysis. For example, in the case of the VA π-complexes with the Ni-catalyst the net charge transfer from the monomer to the catalyst of 0.24 electron is larger than that from MA (0.15 electron). Values of the changes in the populations of the catalyst and monomer occupied and virtual orbitals reveal an increased donation accompanied by a decreased back-donation in the VA case. The changes in the populations of the occupied/virtual orbitals are −0.24/+0.48 and −0.44/+0.21 for the catalyst and the monomer, respectively. The corresponding changes in the MA complexes are −0.33/+0.48 and −0.42/+0.27. Also in the case of O-complexes, the changes in the Mulliken populations confirm the conclusions drawn from the monomer orbital energies. For the VA O-complexes, the net charge transfer of 0.21 electron is lower than that of MA (0.24 electron). The changes in the populations of occupied/virtual orbitals of the catalyst and VA are −0.04/+0.25 and −0.25/+0.04. The corresponding values for the MA O-complex are −0.05/ +0.29 and −0.30/+0.06.

The analysis of the contributions to the monomer binding energies (according to eq 1) presented in Table 4 further indicates that in the case of the π-complexes both the geometry distortion terms ($\Delta E_{\mathrm{geom.}}$; +28.68 and +18.50 kcal/mol for Ni and Pd, respectively) and the binding energies of distorted reactants ($\Delta E_{\mathrm{tot.}}$; −45.75 and −38.62 kcal/mol) remain similar to those of acrylate ($\Delta E_{\mathrm{geom.}}$; +28.48 and +18.73; $\Delta E_{\mathrm{tot.}}$; −45.58 and −39.43 kcal/mol). In the case of the O-complexes, a decrease in the stabilization in the $\Delta E_{\mathrm{tot.}}$ term (from −41.46/−31.33 kcal/mol for acrylate Ni-/Pd-complexes to −37.50/−30.27 kcal/mol for vinyl acetate) is accompanied by an increase in the geometry distortion contribution (from +20.5/ +13.03 kcal/mol for acrylate Ni-/Pd-complexes to +21.70/ +15.03 kcal/mol for vinyl acetate).

Although the binding energies for the O-complexes are decreased for the vinyl acetate, in the Ni-case the O-complex still remains slightly preferred. As for the acrylate, there is a qualitative difference between the Ni- and Pd-based systems: the stabilization energy of the π-complex is increased for Pd (from −17.07 in Ni- to −20.12 in Pd-system), while that of the O-complex is decreased (from −17.75 to −14.96). A comparison of the contribution to the binding energies of the vinyl acetate Ni- and Pd-based π- and O-complexes (Table 4 and Figure 3, values in parantheses) leads to conclusions similar to those in the acrylate case. There is no major difference between Ni- and Pd-systems in the orbital interaction terms. Namely, the Ni/Pd π-complex is preferred by 27.7/27.3 kcal/mol over the O-complex; at the same time the $\Delta E_{\mathrm{orb.int.}}$ term for the Ni π-complex/ O-complex is more stabilizing than for the Pd-systems by 7.6/7.2 kcal/mol. The preference for the O-complex in the Ni-case and for the π-complex in the Pd-case comes as a result of differences in the steric and geometry distortion contributions. The steric term favors the Pd π-complex over the Ni π-complex (by 0.5 kcal/ mol), but the Ni O-complex over the Pd O-complex (by 2.2 kcal/mol). Comparing further, the Ni O-complex is preferred over the Ni π-complex by 21.3 kcal/mol, and the Pd O-complex is preferred over the Pd π-complex by only 18.6 kcal/mol. As in the methyl acrylate case, the differences in the Ni and Pd steric terms reflect the trend in the electrostatic contributions dominating over the Pauli repulsion terms. Finally, the trends in the differences of the geometry distortion terms are also similar to those of acrylate: for both the Ni- and Pd-systems the geometry distortion costs less in the O-complexes than in the π-complexes (by 7.0 and 3.5 kcal/ mol); for both the π- and O-complexes the $\Delta E_{\mathrm{geom.}}$ term favors the Pd- over the Ni-complexes (by 10.2 and 6.7 kcal/mol).

The above analysis indicates that the difference in the methyl acrylate and vinyl acetate bonding between the Ni- and Pd-based Brookhart catalyst has mainly a steric (electrostatic + Pauli repulsion) origin. Thus, the incorporation of polar comonomers can be facilitated by either the choice of monomers with reduced basicity of carbonyl oxygen (e.g., fluorinated vinyl compounds) or the use of catalysts with reduced oxophilicity, e.g., the neutral complexes (such as a Grubbs Ni-based catalyst) instead of the cationic ones. In the following we will compare the polar comonomer binding modes for the model systems corresponding to these two options.

Fluorinated Monomer Complexes with the Generic Ni- and Pd-Based Brookhart Catalysts. The results of Table 1 demonstrate that for both catalysts the bonding energies of fluorinated monomers are lower than for methyl acrylate and vinyl acetate. This is true for both the π- and O-binding mode. However, as could be expected, the decrease in bonding energies is larger in the O-complexes. For the Ni-/Pd-based system, the stabilization energies of the O-complexes decrease by 4.85/4.38 kcal/mol for FMA (from −21.10/−17.30 kcal/ mol for MA to −16.25/−12.92 kcal/mol for FMA) and by 7.76/6.86 kcal/mol for FVA (from −17.75/−14.96 kcal/ mol for VA to −9.99/−8.10 kcal/mol for FVA). The corresponding π-complexation energies for the Ni-/Pd-based catalyst decrease by 3.17/2.75 kcal/mol for FMA (from −17.10/−20.70 kcal/mol for MA to −13.93/−17.95 kcal/mol for FMA) and by 5.66/5.36 kcal/mol for FVA (from −17.07/−20.12 kcal/mol for VA to −11.41/−14.76 kcal/mol for FVA). Thus, for FMA the preference for the O-binding mode in the Ni-system is reduced to 2.32 kcal/mol (from 4.00 kcal/mol for MA), and the preference of the π-complex for the Pd-catalyst is enhanced to 5.03 (from 3.40 kcal/mol). For FVA, in both the Ni- and Pd-based systems, the π-complexes become preferred over the O-complexes, by 1.42 and 6.66 kcal/mol, respectively.

The trends in the binding energies can again be explained in terms of the monomer donor/acceptor orbital energies. The frontier orbital energies of both FMA and FVA are shifted down in comparison to MA and VA (Figure 2). It should be pointed out, however, that the energetic order and the character of these orbitals remain similar: in the VMA case the HOMO corresponds to the oxygen lone pair orbital and the HOMO-1 to the π C=C orbital. In the VFA case the order of these two orbitals is reversed; as in vinyl acetate, there are two antibonding orbitals acting as the electron acceptors when the π-complex is formed. The FVA orbitals are slightly destabilized in comparison to FMA orbitals, similarly to the VA compared to the MA orbitals. The strong stabilization of the donor orbitals (π and O) of fluorinated monomers leads to the decrease in the bonding energies of the corresponding complexes. In the case of the π-complexes, this effect is partially compensated by a stabilization of the monomer acceptor orbital(s) (facilitating back-donation); therefore, the O-complexes are destabilized more than the π-complexes.

From the above results, it can be concluded that, indeed, in the case of fluorinated monomers the stabilization of the O-complexes is strongly decreased, and the preference of the binding mode can be reversed even for the Ni-based system. However, not only the O-complex binding energies but also the stabilization of the π-complexes are affected. As a result, one can expect a lower incorporation of the polar comonomer. Therefore, the prospective copolymerization of the α-olefins with fluorinated monomers seems to be less attractive than the use of less oxophilic catalysts, as will be demonstrated in the next section.

MA and VA Complexes with the Generic Ni- and Pd-Based Grubbs Catalysts. The geometries of the four alternative methyl acrylate complexes with Ni-based Grubbs catalyst are shown in Figure 4. Due to an asymmetry of the catalyst, two pairs of the π- and O-complexes are possible. Namely, the monomer can be coordinated in the position either cis or trans with respect to the position of the nitrogen atom. For both the Ni- and Pd-catalyst and for both of the monomers (MA and VA) we have found that the trans-O-complex is always more stable (by ca. 5−6 kcal/mol) than the cis-O-complex. In the case of the π-complexes, the cis position of the polar monomer is always slightly preferred (by ca. 1.5−3 kcal/mol). Therefore, the binding energies presented in Table 1 refer to the cis-π- and trans-O-complexes, i.e., the most stable species.

It should be noted that for ethylene and propylene, the trans-π-complexes are more stable by ca. 3 kcal/mol.[75] This follows the preference of the mother alkyl complexes: the precursors of the trans-π-complexes, the alkyl β-agostic complexes with the alkyl in the position cis to nitrogen, are more stable by 4.3 and 2.7 kcal/mol for Ni- and Pd-based systems, respectively. The stability of the MA and VA O-complexes also follows the alkyl pattern. In the π-complexes, however, this trend is reversed, most likely due to the repulsive interaction between the catalyst oxygen atom and the pending carbonyl oxygen of the polar monomer, destabilizing the trans-π-complex.

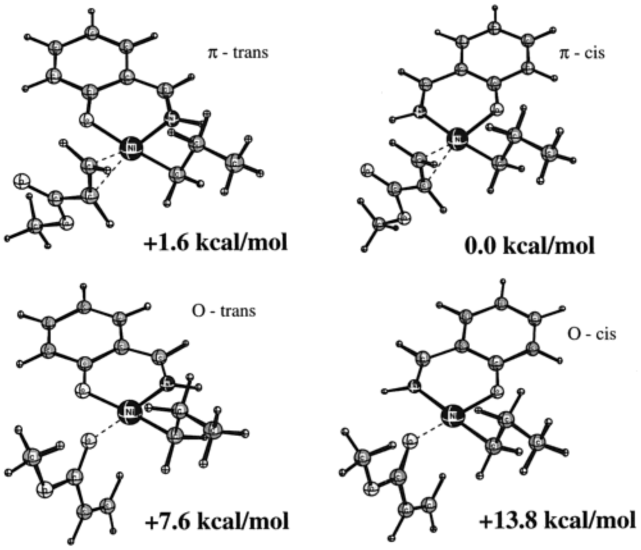

Figure 4. Geometries of the alternative cis (right) and trans (left) methyl acrylate π- (top) and O-complexes (bottom) with the Ni-based Grubbs catalyst, together with their energies, relative to the most stable complex.

An analysis of the polar monomer binding energies of Table 1 indicates that despite their neutral character, the Ni- and Pd-based catalysts with Grubbs ligands strongly bind MA and VA. The π-complexation energies are relatively close to those of the Brookhart systems: the Ni-catalyst binds methyl acrylate slightly stronger and vinyl acetate slightly weaker than the Ni−Brookhart complex (by ca. 0.7/1 kcal/mol). The π-complexation energies for the Pd-based analogue of the Grubbs catalyst exceed those of the Brookhart Pd-catalyst by 3.6 and 1.6 kcal/mol, for MA and VA, respectively.

Unlike for the Brookhart systems, for both Grubbs catalysts (Ni- and Pd-based) the O-complexes of both MA and VA are substantially less stable than the π-complexes. The MA/VA π-complex is preferred by 7.56/7.18 kcal/mol for the Ni-based and by 14.17 and 12.16 kcal/mol for the Pd-based catalyst. Interestingly, the absolute values of the binding energies for the Ni- and Pd-catalysts practically remain unchanged (10.17/10.18 kcal/mol for MA and 9.72/9.56 kcal/mol for VA).

The weakening of the catalyst−monomer bonds in the O-complexes with Grubbs catalysts is also reflected in the metal−oxygen bond lengths (see Table 2): for all the complexes the M−O bonds are longer by 0.04−0.05 Å than in the corresponding Brookhart systems. In the π-complexes the bonding metal−carbon distances are usually slightly shorter for the Grubbs catalysts.

Let us now analyze the origin of the similarities and differences between Grubbs and Brookhart systems. A weakening of the catalyst−monomer bond in the O-complexes for the Grubbs catalysts can be intuitively expected. The neutral character of the catalyst must result in a substantial increase in the steric repuslion term, coming from a decrease in the electrostatic stabilization and/or an increase in the Pauli repulsion term, compared to the cationic Brookhart systems. One could expect, however, that this effect should also be pronounced for the π-complexes. As we have already mentioned, in comparison to the Brookhart systems, the binding energies for the complexes involving the Grubbs catalysts are noticeably decreased only for the O-complexes, while those for the π-complexes stay similar. Thus, in the case of the Grubbs π-complexes the steric (electrostatic + Pauli repulsion) destabilization must be compensated by an extra stabilization coming from the orbital interaction term.

The above conclusion is confirmed by the result of the fragment analysis of the contributions to MA and VA binding energies, presented in Tables 3 and 4, respectively. Here, both effects can be observed: the increase in steric repulsion for the Grubbs system compared to the corresponding Brookhart complexes, for both π- and O-coordination modes, as well as an increase in the orbital-interaction stabilization terms for the π-complexes. Moreover, the orbital-interaction terms decrease for the O-coordinated Grubbs systems, compared to the correspondng Brookhart complexes. For example, in the MA case the steric terms (electrostatic + Pauli repulsion) increase from +23.6/+21.0 for the π-complexes and −0.8/+0.7 kcal/mol for the O-complexes with Ni/Pd Brookhart catalyst to +35.0/+30.7 and +7.6/6.8 kcal/mol for the corresponding complexes with the Ni/Pd-based Grubbs catalysts. Similar effects can be observed for the VA complexes. For the MA π-complexes, the orbital interaction terms change from −69.2/−60.4 kcal/mol for the Ni/Pd Brookhart catalyst to −82.8/−70.3 kcal/mol for the Ni/Pd-based Grubbs systems. For the MA O-complexes, however, the orbital-interaction stabilization decreases from −40.8/−32.6 kcal/mol for the Brookhart Ni/Pd-based catalysts to −30.0/−24.4 kcal/mol for the Grubbs systems. For VA, an extra stabilization from the orbital-interaction terms for the Grubbs π-complexes, compared to the Brookhart catalyst, is much smaller than for MA. Here, the $\Delta E_{\mathrm{orb.int.}}$ contribution changes from −65.2/−57.5 kcal/mol for the Ni/Pd Brookhart catalyst to −69.4/−58.1 kcal/mol for the Ni/Pd-based Grubbs system. A destabilization of the Grubbs VA O-complexes on the orbital-interaction level, however, is comparable to that of MA. Here, the orbital-interaction term changes from −37.5/−30.3 kcal/mol for the Ni/Pd Brookhart catalyst to −27.7/−21.4 kcal/mol for the Ni/Pd-based Grubbs system.

A stabilization/destabilization of the Grubbs π-/O-complexes, compared to the corresponding Brookhart systems, coming from the orbital-interaction term can be qualitatively explained in terms of the frontier-orbital energies of the catalysts. The frontier orbitals of the cationic Brookhart systems are strongly stabilized compared to those of the nuetral Grubbs catalysts, due to a positive charge. For example, the HOMO/LUMO energies of the Ni-based Grubbs catalyst (in the geometry of the π-complex) are −4.98/−3.81 eV, while the orbital energies for the corresponding Brookhart catalyst are −9.83/−8.82 eV. Thus, one can expect a decreased monomer-to-catalyst charge transfer and an increased catalyst-to-monomer back-donation in the Grubbs complexes compared to the Brookhart catalyst. In the Grubbs π-complexes, an extra stabilization coming from an increased back-donation overrides a destabilization from a suppressed monomer-to-catalyst charge transfer. This is not the case for the O-binding mode: here, as in the complexes with the Brookhart catalyst, there is practically no back-donation, and a destabilization of the catalyst acceptor orbital directly results in a decrease in the binding energies of the O-complexes.

Again, the above explanation is qualitatively supported by the results of the Mulliken population analysis. For the Ni-based Grubbs MA π-complex, the net charge transfer is 0.07 electron, directed from the catalyst to the monomer, while for the O-complex 0.15 electron flows from the monomer to the catalyst. The corresponding values for the Brookhart Ni-complexes are 0.15 and 0.24, with the direction from MA to the catalyst in both (π and O) cases. For the Ni-based Grubbs MA π-complex the changes in the populations of occupied/virtual orbitals of the catalyst and the monomer are −0.50/+0.43 and −0.40/+0.45, respectively; the corresponding values for the Brookhart catalyst are −0.33/+0.48 and −0.42/+0.27. These values clearly indicate a decreased donation and an enhanced back-donation in the Grubbs catalyst case. For the Ni-based Grubbs O-complexes the changes in the populations of occupied/virtual orbitals of the catalyst and the monomer are −0.08/+0.23 and −0.22/+0.07, respectively; the corresponding values for the Brookhart catalyst are −0.05/+0.29 and −0.30/+0.06. We would like to point out here that the absolute values of the changes in Mulliken population have no physical meaning (including the direction of the net charge flow); the above results can be used only to qualitatively analyze the observed trends in a series of catalysts or monomers.

Finally, conclusions from a comparison of the Grubbs MA and VA complexes are similar to those for the Brookhart catalysts and follow from a comparison of the frontier-orbital energies of the two monomers (Figure 2). As in the case of the Brookhart catalysts, in the Grubbs VA π-complexes a destabilization of the VA π- and π*-orbitals, compared to that of MA, results in an increased monomer-to-catalyst charge transfer and in a decreased back-donation. As we argued above, an increased back-donation in the case of Grubbs catalyst is responsible for an extra stabilization at the orbital-interaction level, compared to the Brookhart catalyst. Therefore, it is not surprising that this extra stabilization is much smaller in the VA complexes compared to the MA complexes.

The above results for the Ni- and Pd-based systems with Grubbs ligands lead to the conclusion that the use of the neutral catalyst in the copolymerization of α-olefins with polar monomers is promising. With reduced oxophilicity of the catalyst, the polar monomer is bound by its olefinic functionality rather than by the carbonyl oxygen atom.

Methyl Acrylate Complexes with the Real Brookhart and Grubbs Catalysts. Finally, we would like to examine the influence of the steric effects, introduced by bulky substituents of the real catalysts, on the binding mode of the polar monomer. In Table 5 the

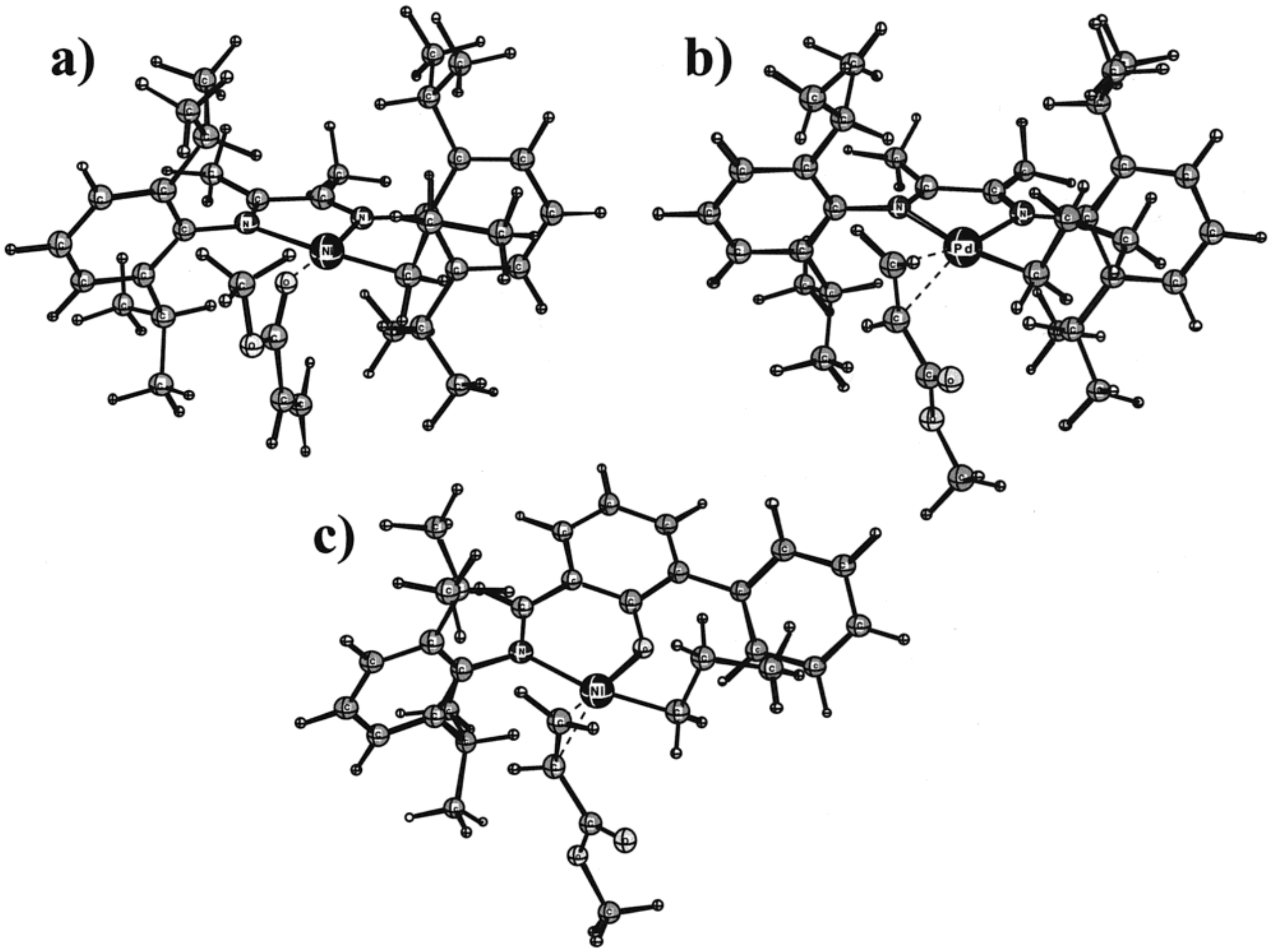

Figure 5. Geometries of the most stable methyl acrylate complexes with the real Ni- (panel a; O-complex) and Pd-based (panel b; π-complex) Brookhart and the Ni-based Grubbs (panel c; π-complex) catalysts.

binding energies are presented for the methyl acrylate π- and O-complexes, involving the real Ni- and Pd-based Brookhart catalysts (**2a** and **2b**, see Scheme 3) and the real Ni-based Grubbs catalysts with substituents of different character (**4a**, **5a**, **6a**). The examples of the geometries for the preferred complexes (O with **2a**, π with **2b** and **6a**) are shown in Figure 5.

The results of Table 5 show that in all the real complexes the binding energies are substantially decreased in comparison to the generic systems (Table 1), as a result of the steric repulsion between the monomer and the bulky substituents of the catalyst. A similar effect has been observed and discussed in detail for ethylene and propylene complexes with Ni- and Pd-based Brookhart catalysts.[66−75] The presence of the large substituents on the catalyst influences also the preferred orientation of the monomer in the π-complexes. As in the propylene case, in all the complexes with a generic catalyst, the $-(C{=}O){-}O{-}CH_3$ group is located "on the opposite side" of both the catalyst ring and the C═C bond, relative to the position of the alkyl chain (see Figures 1 and 4). In such an orientation the steric repulsion between the polar group and the alkyl is minimized. In the real systems, the $(C{=}O){-}O{-}CH_3$ group is located "on the same side" of the C═C bond as the alkyl group (see Figure 5b,c), to minimize the repulsion between the polar group and the bulky catalyst substituents, which is now more pronounced than the corresponding repulsion with the alkyl chain.

However, the major conclusions from the results obtained for the generic catalyst models remain unchanged: in the real Ni-Brookhart system the O-complex has a lower energy by 2.99 kcal/mol, while in the corresponding Pd-based system the π-complex is preferred by 3.01 kcal/mol. The presence of the catalyst bulky substituents results in a decrease of the absolute values of the binding energies and practically does not influence the difference between the two binding modes. Similarly, in the case of all of the real Ni-Grubbs catalysts, the π-complexes are preferred over the O-complexes by ca. 5−6.3 kcal/mol. As in the Brookhart systems, the presence of the isopropyl-substituted aryl group results in a substantial decrease in the complexation energies for both binding modes, compared to the generic catalysts. Further introduction of the $-C_6H_5$ or the $-NO_2$ groups has only a minor effect on the binding energies of the π-complexes (−0.3 kcal/mol) and results in a slight increase in the O-complex binding energies (by ca. 0.8−1.0 kcal/mol).

Finally, we would like to point out that for the Pd-based real catalyst **2b** the calculated acrylate π-complex stabilization (−13.6 kcal/mol) is smaller than in the case of propylene and ethylene (−16.3 and −16.4 kcal/mol, respectively).[67] This is in agreement with the experimental results; the relative binding constants by Brookhart suggest the strongest stabilization of the ethylene and the weakest of the acrylate π-complex.[56] The difference in the calculated binding energies of ethylene and acrylate (2.8 kcal/mol) is lower than the experimental value of 4.9 kcal/mol; so is the difference between propylene and ethylene (0.1 kcal/mol calculated vs 0.9 kcal/mol experimental). However, these experimental data were obtained for the catalyst with the hydrogens as backbone substituents (R = H), and the methyl groups were used in our calculations (R = CH_3, see Scheme 3); also, the entropic effects are not taken into account in our calculations, while experiments give the differences in the free energies.

Concluding Remarks

We have carried out DFT studies on the binding of the oxygen-containing polar comonomer in the complexes involving Ni- and Pd-based Brookhart (cationic) and Grubbs (neutral) olefin polymerization catalysts. The primary objective has been to identify the factors that are responsible for the different behavior of the Ni- and Pd-based Brookhart catalyst in the polar copolymerizations: the Ni-system is inactive, while the Pd-complexes can catalyze copolymerization of the α-olefin with some polar comonomers. We have studied the methyl acrylate (MA) and vinyl acetate (VA) complexes in which the monomer is bound by its olefinic functionalty (π-complexes) or by the carbonyl oxygen atom (O-complexes). Further, we have examined the complexes with monomers containing a fluorinated methyl group and, thus, the carbonyl oxygen of less basic character, as well as the complexes with the neutral Grubbs catalyst, of less oxophilic character. Besides the studies on the electronic effects in simplified (generic) models for the catalysts, the role of the steric effects in the real systems has also been examined.

The results clearly indicate that in the case of the Ni-based Brookhart catalyst the polar monomers are bound by the carbonyl oxygen atom, while in the Pd-systems the π-complexes are preferred. The difference between the Ni- and Pd-systems has mainly a steric (electrostatic + Pauli repulsion) origin; there is practically no difference in the orbital-interaction contribution to the binding energy between Ni- and Pd-based systems, as far as a comparison between the two binding modes is concerned. In the case of the fluorinated polar monomers (FMA and FVA), the complexation energies of both the π- and O-complexes are decreased in comparison to methyl acrylate and vinyl acetate. Thus, in a prospective copolymerization with fluorinated compounds, the incorporation of the polar monomer into a polyolefin chain would be relatively small. The use of neutral catalysts seems to be more promising. The results for Ni- and Pd-based systems with Grubbs ligands show that for both metals the π-complexes are strongly preferred over the O-complexes; the binding energies of the π-complexes are comparable with the corresponding systems involving the Brookhart catalysts.

Further, the results show that an introduction of the steric bulk in the real catalysts does not affect the preference of the comonomer binding mode; the absolute values for the binding energies of the π- and O-complexes are decreased, while the differences between them remain qualitatively similar. Also, the relative binding energies of acrylate, propylene, and ethylene, calculated for the real catalyst **2b**, are in qualitative agreement with the experimental data obtained for a similar system:[56] both the calculations and experimental data show the strongest stabilization for the ethylene π-complexes and the weakest for acrylate.

A comparison of Ni- and Pd-based Brookhart systems leads to the conclusion that the analysis of the polar comonomer binding mode can be used as a screening test to select the best prospective catalytic candidates for the copolymerization; the complexes with a relatively strong preference of the O-complexes can be excluded from further studies. Here, the use of theoretical methods can be very useful. Obviously, the monomer binding is only an initial step in the complex mechanism of the copolymerization processes. Therefore, the studies on the polar comonomer binding mode can be used only for a negative selection. To get more definitive answers about the catalyst activities, a full mechanistic study is needed, involving evaluation of the barriers of all the elementary reactions and the relative stabilities of the reaction intermediates.

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

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