DFT Study of Olefin versus Nitrogen Bonding in the Coordination of Nitrogen-Containing Polar Monomers to Diimine and Salicylaldiminato Nickel(II) and Palladium(II) Complexes. Implications for Copolymerization of Olefins with Nitrogen-Containing Polar Monomers

Dirk V. Deubel*,[1] and Tom Ziegler*,[1]

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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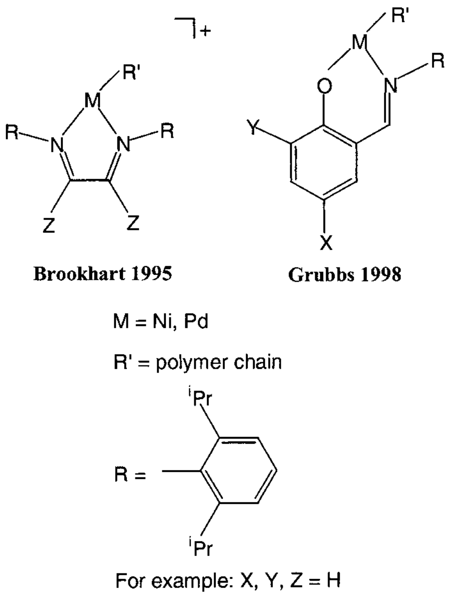
An initial screening of late-transition-metal catalysts and nitrogen-containing polar monomers toward an incorporation of amines or nitriles in the polymer chain of polyolefins has been performed using density functional theory. Substrates of the type $CH_2{=}CH(CH_2)_nX$ ($X =$ polar group) can bind either with the N-containing polar group or with the π moiety to the metal center of the catalyst. Monomer−catalyst combinations favoring the π complex over the N complex are promising, because the π-binding mode can subsequently lead to polymer growth. The stabilization energies for the π and N complexes of monomers of the type $CH_2{=}CH(CH_2)_nCN$, $CH_2{=}CH(CH_2)_nNH_2$, and $CH_2{=}CH(CH_2)_nN(CH_3)_2$ with generic models for the recently reported nickel(II) and palladium(II) catalysts with diimine ("Brookhart") and salicylaldiminato ("Grubbs") ligands have been calculated. While the investigated polar monomers have been shown to form very strong metal−nitrogen bonds with the Brookhart nickel catalysts, the enamine prefers the π binding mode in its complexes with all model catalysts. Promising results have also been obtained for the coordination of nitriles and amines with the Grubbs nickel catalysts. The palladium systems show an even larger preference for π coordination than their nickel counterparts. An energy-decomposition scheme has been used to rationalize the relative strength of the catalyst−monomer bonds.

Introduction

Objective. The development of catalysts for an efficient production of high-performance plastics remains an important goal in the chemical industry.[2] The random copolymerization of olefins with polar monomers is of particular interest, since the incorporation of polar functionalities in the polymer chain enables the control of polymer properties such as toughness and solubility.[2] Common copolymers such as polystyrene−acrylonitrile are still made via radical polymerization on a million-ton-per-year scale, despite the high energy cost and the environmental impact of this technique.[3]

Chart 1. Late-Transition-Metal Catalysts for Olefin Polymerization and Copolymerization Discovered by Brookhart and Co-Workers and Grubbs and Co-Workers



Promising catalysts for the copolymerization of olefins with *oxygen-containing* polar monomers were recently reported by Brookhart and co-workers[4] and Grubbs and co-workers[5] (Chart 1). These late-transition-metal catalysts are less oxophilic than their early-transition-metal counterparts and therefore potentially not poisoned by O-containing polar functionalities.[6,7] Despite the possible industrial importance, little is known about whether the copolymerization of olefins with *nitrogen-containing* polar monomers using late-transition-metal catalysts

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[1] E-mail: D.V.D., deubel@ucalgary.ca; T.Z., ziegler@ucalgary.ca. URL: D.V.D., http://staff-www.uni-marburg.de/~deubel; T.Z., http://www.cobalt.chem.ucalgary.ca/group/master.html.

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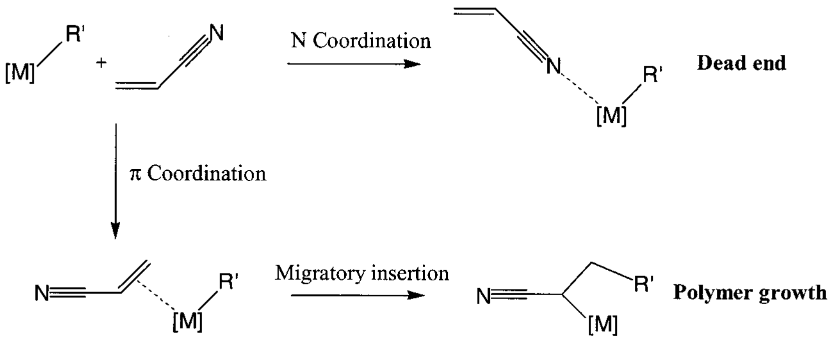
Scheme 1. π versus N Coordination of Nitrogen-Containing Polar Monomers with the Metal Center [M][a]



[a] While π binding subsequently leads to the growth of the polymer chain R′, the coordination of the polar site is a dead end.

can be achieved as well. The objective of this density functional theory (DFT) study at the BP86 level[8,9] is to perform an initial screening of late-transition-metal catalysts and N-containing polar monomers in order to reveal potential future directions of research into the copolymerization of olefins with amines or nitriles. DFT is today an important tool for computational investigations on group 10 complexes, as demonstrated by Dedieu.[10] DFT methods were already successfully used by the Morokuma/Musaev group[11] and others[12,13] to study olefin polymerization with Brookhart- and Grubbs-type catalysts (Chart 1). The π coordination energies for various monomers with Brookhart Pd complexes and the regioselectivity of subsequent olefin insertion into the Pd−methyl and Pd−phenyl bonds were analyzed by Svensson and co-workers.[14] A DFT study of the ethylene−methyl acrylate copolymerization using Brookhart Pd catalysts was recently reported.[35]

Concept. Substrates of the type $CH_2{=}CH(CH_2)_nX$ (X = nitrogen-containing polar group) can bind either with the polar group X or with the π moiety to the metal center of the catalyst. We have predicted the stabilization energies for the π and N complexes of the monomers $CH_2{=}CH(CH_2)_nX$ ($n \geq 0$; X = CN, NH_2, $N(CH_3)_2$), with generic models for the recently reported nickel(II) and palladium(II) catalysts with diimine ("Brookhart") and salicylaldiminato ("Grubbs") ligands. Catalyst−monomer combinations that prefer the π complex over the N complex are promising because the former binding mode can subsequently lead to polymer growth by migratory insertion of the C═C unit into the metal−C bond (Scheme 1).[11−15] Catalyst−monomer combinations that strongly favor the coordination of the polar site will be omitted in future studies, because the coordination of the polar site is a potential dead end. This concept was recently used by Michalak and Ziegler[16] to successfully reproduce experimental trends in the ability of different oxygen-containing polar monomers to undergo copolymerization using late-transition-metal catalysts.

We have been able to consider a large number of catalyst−monomer combinations by making the following approximations: *First*, the models **1**−**4** for the catalysts have been used, as shown in Figure 1.[17] *Second*, the conjugated monomers of the type $CH_2{=}CH(CH_2)_nX$ with $n = 0$ have been investigated explicitly,[18] while the nonconjugated systems with $n \geq 1$ have been studied using $CH_2{=}CHCH_3$ and CH_3X as models.[19] The model monomers and their coordination modes **a**−**i** are presented in Chart 2.

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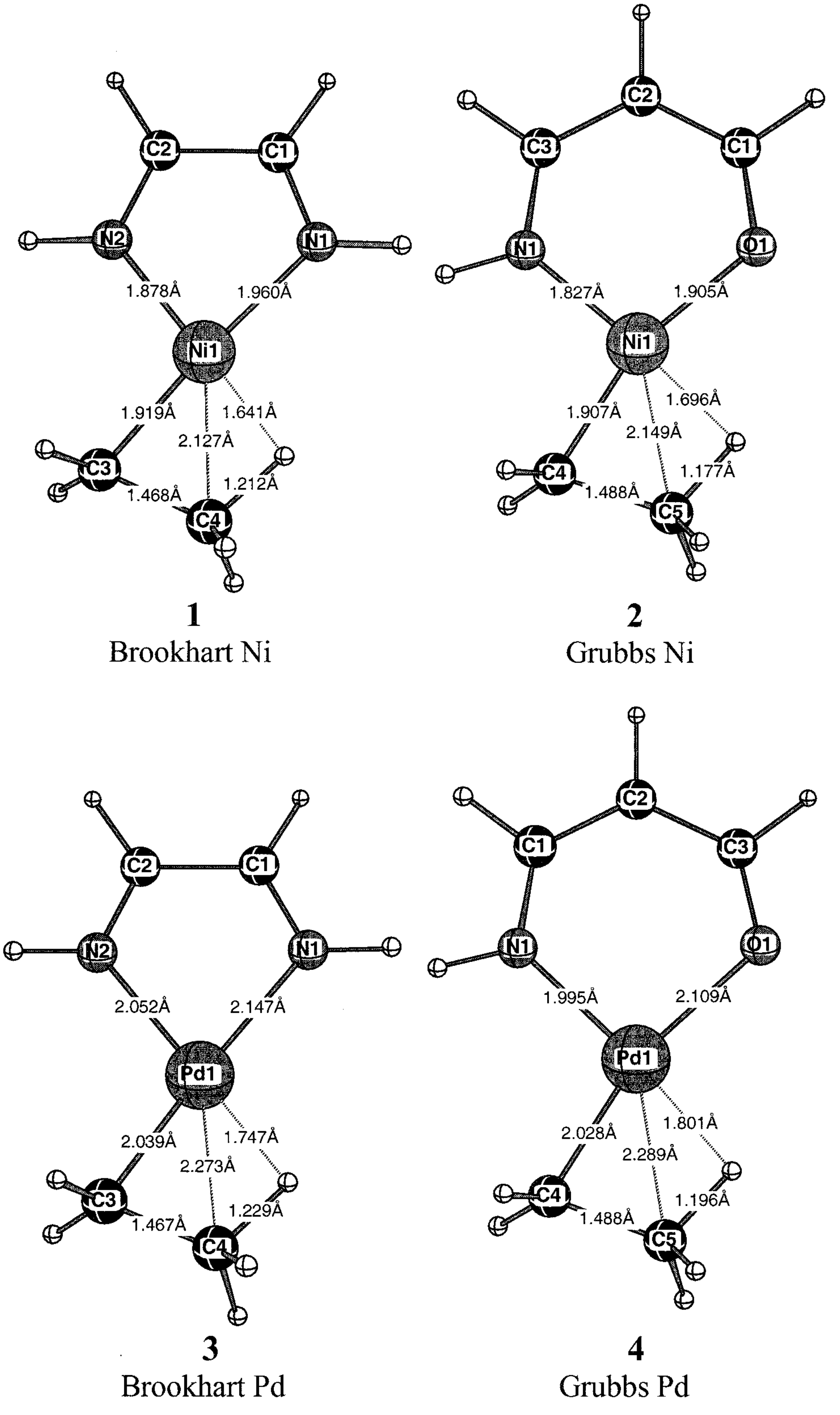
(17) The bulky *o,o*′-substituents at the imine nitrogen atoms have been replaced by H, since their main purpose is to prevent polymer-chain termination reactions via associative olefin exchange.[6] Their effect on the difference of π- and O-coordination energy for vinyl acetate and methyl acrylate with Brookhart-type catalysts is comparably small.[16] The benzo moiety of the Grubbs ligand has been replaced by a simple ethyno unit. Test calculations of the ethylene complex with the Grubbs nickel catalyst show that the change in the stabilization energy due to this simplification is only 1.2 kcal/mol.

(18) 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.



1
Brookhart Ni

2
Grubbs Ni

3
Brookhart Pd

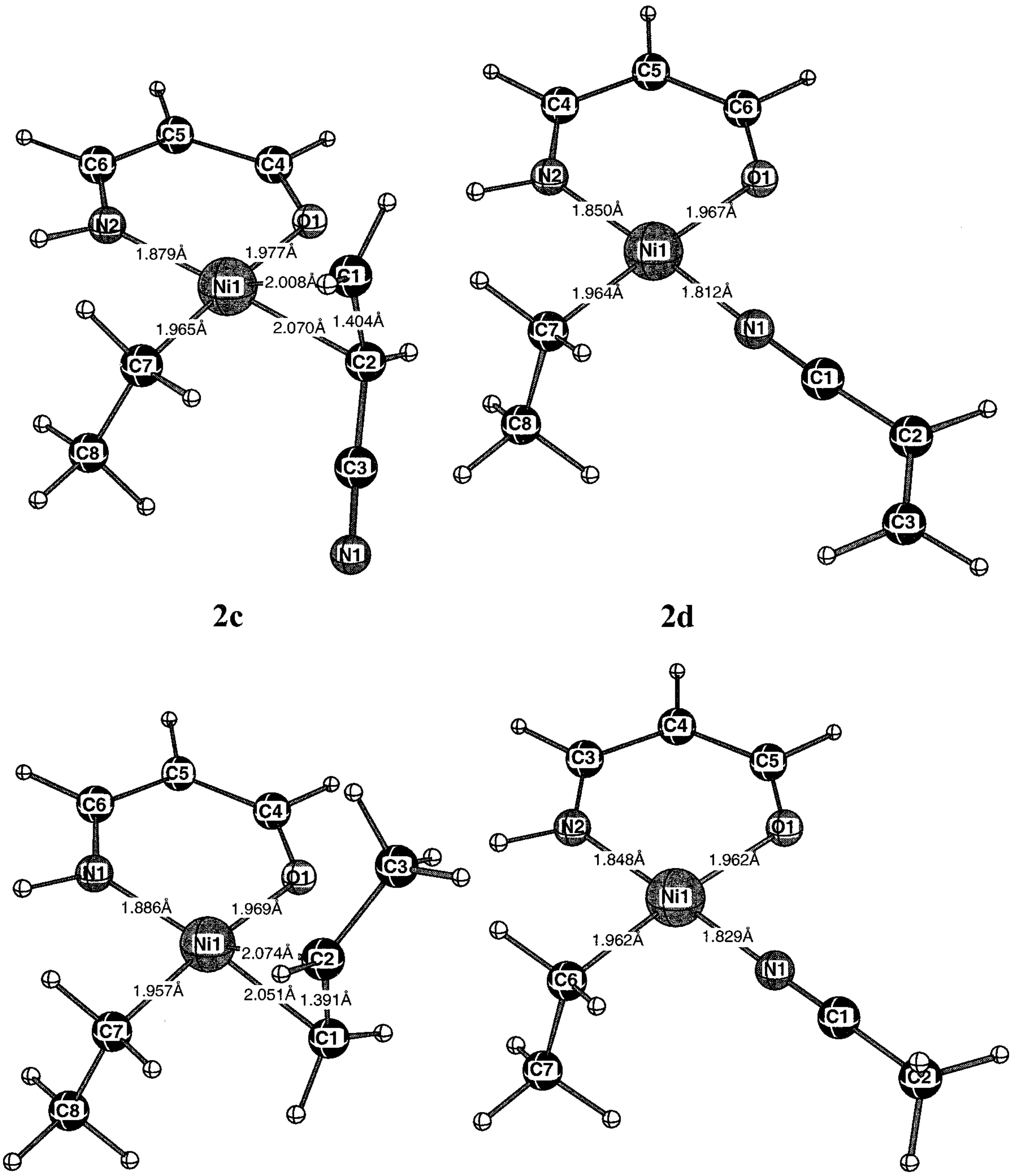
4
Grubbs Pd

Figure 1. Calculated structures of the model catalysts **1**−**4**.

Results

All complexes of the catalysts **1**−**4** and the model monomers with the coordination modes **a**−**i** have been investigated.[20] Figure 2 displays the optimized structures for the Grubbs nickel complexes with acrylonitrile (**2c**,**d**) and with propylene (**2b**) and acetonitrile (**2g**) as model ligands for nitriles of the type $CH_2{=}CH(CH_2)_nCN$ with $n \geq 1$. The most important bond distances in all complexes **1a**−**i** to **4a**−**i** are given in Table 1 and will be rationalized in the discussion section. Theoretically predicted monomer coordination energies of the complexes **1a**−**i** to **4a**−**i** are reported in Table 2. These stabilization energies for the target monomers are visualized in Figure 3.

We first focus on the *nickel π complexes* **1a**−**c**,**e** and **2a**−**c**,**e** (Table 2). The coordination of ethylene with the



2c **2d**

2b **2g**

Figure 2. Calculated structures of the complexes **2b**−**d**,**g**. The $CH_2{=}CHCH_3$ and CH_3CN complexes **2b** and **2g** have been used as models for the complexes of $CH_2{=}CH(CH_2)_nCN$.

metal center leads to a stabilization of −16.2 kcal/mol (Brookhart catalyst, **1a**) and −18.3 kcal/mol (Grubbs catalyst, **2a**). The formal substitution of ethylene by propylene (**a** → **b**) is slightly exothermic for **1** and slightly endothermic for **2**. The π conjugation in the polar monomer has a strong effect on the complexes of the Brookhart catalyst, with a destabilization by the electron-withdrawing nitrile (**1c**: −11.5 kcal/mol) and a stabilization by the electron-donating amino moiety (**1e**: −28.4 kcal/mol). In contrast, the Grubbs complexes are scarcely affected by conjugation at the C=C bond; both acetonitrile and vinylamine form slightly more stable complexes with **2** (−19.0 and −20.2 kcal/mol, respectively) than does propylene.

The stabilization energies for the *nickel N complexes* are also given in Table 2 (**1d**,**f**−**i** and **2d**,**f**−**i**). The

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(19) This approach significantly reduces the number of conformational degrees of freedom which have been considered in our computational study. We have investigated one case with a real nonconjugated monomer (X = CN, $n = 1$, with the Brookhart Ni catalyst, **1**) to show that our approximation is justified. The calculated energy for π coordination is −18.7 kcal/mol, and the calculated energy for N coordination is −30.4 kcal/mol. The corresponding values with the abbreviated models are −18.3 kcal/mol (**1b**) and −28.3 kcal/mol (**1g**), respectively (Table 1). The results demonstrate that the differences are relatively small and our approach is warranted.

(20) For each of the 36 complexes **1a**−**i** to **4a**−**i**, up to 8 stereoisomers have been optimized. Only the isomers lowest in energy are reported. Note that the isomers of the Grubbs complexes with a monomer coordinated trans to the oxygen are less stable than the cis isomers by about 4 kcal/mol.[16]

Chart 2. N-Containing Polar Monomers of Industrial Interest and Model Monomers with Binding Modes a–i

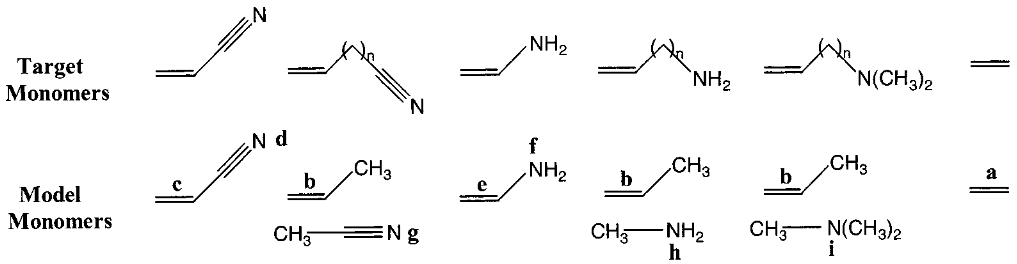

Table 1. Calculated Metal–Carbon Distances (M–C1 and M–C2), Carbon–Carbon Distances (C1–C2), and Metal–Nitrogen Distances (M–N) in the Complexes 1a–i to 4a–i[a]

monomer	binding mode	bond	**1**	**2**	**3**	**4**	free monomer
$\mathrm{CH_2{=}CH_2}$ (**a**)	π	M–C1	2.065	2.039	2.168	2.159	
		M–C2	2.072	2.061	2.183	2.163	
		C1–C2	1.384	1.387	1.387	1.389	1.332
$\mathrm{CH_2{=}CHCH_3}$ (**b**)	π	M–C1	2.049	2.051	2.174	2.150	
		M–C2	2.123	2.074	2.210	2.191	
		C1–C2	1.388	1.391	1.389	1.392	1.334
$\mathrm{CH_2{=}CH_2CN}$ (**c**)	π	M–C1	2.044	2.008	2.170	2.136	
		M–C2	2.069	2.070	2.168	2.165	
		C1–C2	1.400	1.404	1.401	1.403	1.339
$\mathrm{CH_2{=}CH_2CN}$ (**d**)	N	M–N	1.835	1.812	1.984	1.961	
$\mathrm{CH_2{=}CH_2NH_2}$ (**e**)	π	M–C1	2.004	2.018	2.115	2.130	
		M–C2	2.318	2.141	2.477	2.268	
		C1–C2	1.405	1.398	1.406	1.397	1.341
$\mathrm{CH_2{=}CH_2NH_2}$ (**f**)	N	M–N	1.968	1.992	2.113	2.125	
$\mathrm{CH_3CN}$ (**g**)	N	M–N	1.847	1.829	1.992	1.979	
$\mathrm{CH_3NH_2}$ (**h**)	N	M–N	1.957	1.966	2.099	2.104	
$\mathrm{N(CH_3)_3}$ (**i**)	N	M–N	2.023	2.080	2.142	2.171	

[a] The terminal carbon atom of the C=C bond is denoted C1. All distances are given in Å.

Table 2. Calculated Stabilization Energies (kcal/mol) for the Coordination Modes a–i of the Polar Monomers with the Model Catalysts 1–4

monomer	binding mode	**1**	**2**	**3**	**4**
$\mathrm{CH_2{=}CH_2}$ (**a**)	π	−16.2	−18.0	−20.0	−24.7
$\mathrm{CH_2{=}CHCH_3}$ (**b**)	π	−18.3	−16.8	−22.4	−24.2
$\mathrm{CH_2{=}CH_2CN}$ (**c**)	π	−11.5	−19.0	−14.6	−24.8
$\mathrm{CH_2{=}CH_2CN}$ (**d**)	N	−28.4	−20.2	−27.4	−21.9
$\mathrm{CH_2{=}CH_2NH_2}$ (**e**)	π	−27.0	−21.0	−30.2	−27.4
$\mathrm{CH_2{=}CH_2NH_2}$ (**f**)	N	−23.1	−17.5	−23.9	−20.8
$\mathrm{CH_3CN}$ (**g**)	N	−28.3	−17.5	−27.5	−20.0
$\mathrm{CH_3NH_2}$ (**h**)	N	−31.2	−23.2	−31.8	−26.6
$\mathrm{N(CH_3)_3}$ (**i**)	N	−28.3	−16.1	−28.9	−23.7

calculations show that the cationic Brookhart model catalyst forms very strong bonds to the polar sites. The smallest and largest stabilization energies, respectively, have been predicted for vinylamine (−23.1 kcal/mol) and methylamine (−31.2 kcal/mol), while the calculated coordination energies for nitrile binding are within this range (−28.4 kcal/mol). Trimethylamine forms a slightly weaker bond (−28.3 kcal/mol) to the metal than methylamine (−31.2 kcal/mol). The metal–N bonds in the Grubbs system are much weaker than in the Brookhart system; stabilization energies not larger than −23.2 kcal/mol (methylamine) have been calculated for the N complexes with the Grubbs catalyst **2**.

The *differences* in the energies of π and N coordination are of particular importance. These data are listed in Table 3 and visualized in Figure 3 for the target monomers. The coordination of the polar site of nitriles and amines with the Brookhart nickel catalyst **1** is favored over the π mode by at least 10.0 kcal/mol. There is one exception: vinylamine prefers π coordination by 3.9 kcal/mol. The Grubbs nickel system **2** is much more promising than the Brookhart catalyst **1**. The nitriles favor N coordination only slightly (1.2 kcal/mol), while vinylamine again prefers π binding by more than 3 kcal/mol. Surprisingly, trimethylamine (as a model for monomers of the type $\mathrm{CH_2{=}CH(CH_2)_nN(CH_3)_2}$) forms a weaker bond to the metal than methylamine, indicating that steric effects are already present in the generic systems to a certain extent. These effects are stronger in **2** than in **1**, since the former catalyst has a larger bite angle.

A comparison between the *nickel and palladium* systems is presented in Figure 3. The calculations reveal that the Brookhart palladium catalyst **3** and the target monomers form π complexes which are in general more stable than their nickel counterparts **1** by approximately 3 kcal/mol (Figure 3). The same systematic trend is present in the complexes with the Grubbs catalysts; the π complexes of the palladium compound **4** are stabilized by about 6 kcal/mol in comparison with the corresponding nickel systems **2**. There are slight differences in the energies for the coordination of the polar site to the Ni and Pd Brookhart catalysts **1** and **3**. The Pd Grubbs catalyst **4** forms slightly more stable N complexes than the corresponding Ni catalyst **2**; the energy difference has been predicted to be about 3 kcal/mol (Figure 3).

Discussion

We focus the discussion on the following points: (i) rationalization of the theoretically predicted monomer–catalyst bond strength, (ii) brief comparison to the results for oxygen-containing monomers,[16] (iii) rationalization of the bond distances in the calculated structures **1a–i** to **4a–i**, and (iv) proposal of subsequent studies.

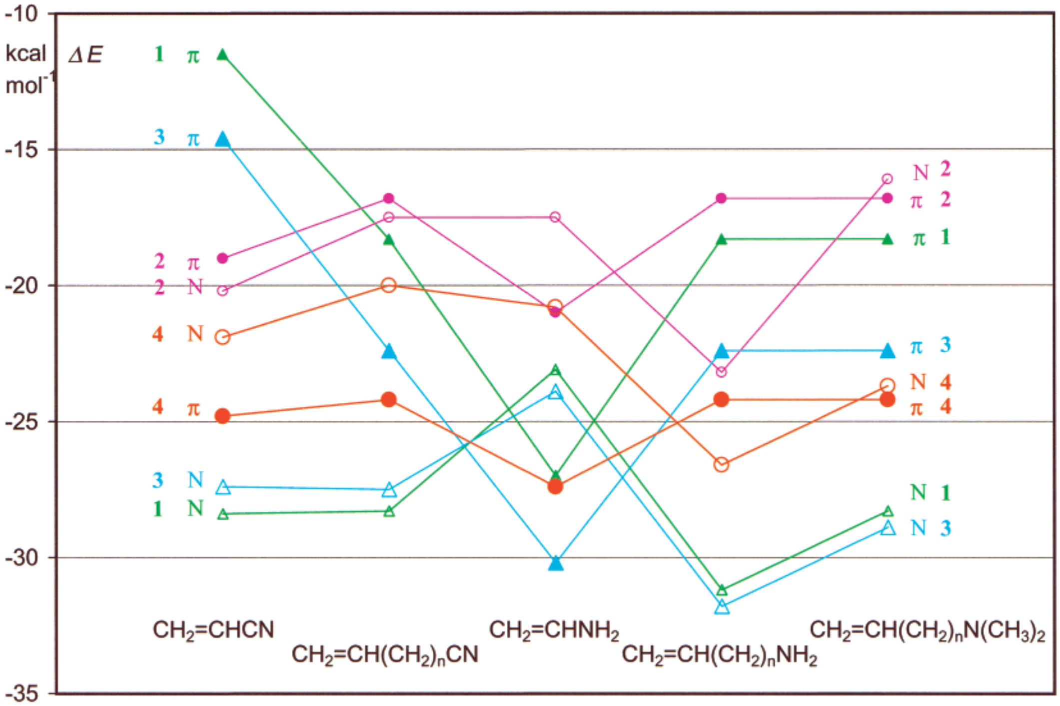

Figure 3. Calculated stabilization energies for the coordination of polar monomers with the nickel catalysts **1** and **2** and the palladium catalysts **3** and **4**.

Table 3. Calculated Differences in the Stabilization Energies (kcal/mol) for π Coordination and N Coordination of the Polar Monomers with the Model Catalysts 1−4[a]

target monomer	model monomers	1	2	3	4
$CH_2{=}CH_2CN$	$CH_2{=}CH_2CN$	16.9	1.2	12.9	−3.2
$CH_2{=}CH(CH_2)_nCN$	$CH_2{=}CHCH_3$ and CH_3CN	10.0	1.1	5.2	−4.0
$CH_2{=}CH_2NH_2$	$CH_2{=}CH_2NH_2$	−3.9	−3.5	−6.3	−6.6
$CH_2{=}CH(CH_2)_nNH_2$	$CH_2{=}CHCH_3$ and CH_3NH_2	12.9	6.4	9.5	2.6
$CH_2{=}CH(CH_2)_nN(CH_3)_2$	$CH_2{=}CHCH_3$ and $CH_3N(CH_3)_2$	10.0	−0.7	6.0	−0.9

[a] Negative values indicate that the π complexes are favored, while positive values indicate that N binding is preferred.

Our calculations have revealed a significant stabilization of the Pd π complexes relative to the corresponding Ni complexes. First-row transition metals have *n*s, *n*p, and *n*d ($n = 3$) orbitals of the same radial extent. This makes it difficult for ligand orbitals to acquire overlaps with the 3d set without at the same time incurring repulsive interactions with 3s and 3p. On the other hand, for second- and third-row transition metals, the *n*s and *n*p orbitals are much more contracted than *n*d ($n = 4, 5$), and the ligands are able to obtain much larger overlaps with 4d and 5d.[21,22] Thus, the 4d set of palladium is able to overlap much more efficiently with π^* of olefins than the corresponding 3d set on nickel, with the result that the Pd−olefin bond for each monomer is stronger than the Ni−olefin bond. Note that the stabilization of the Pd π complexes relative to the Ni congeners is largest in the Grubbs systems. In the neutral Grubbs complexes, electron back-donation from metal d orbitals into π^* is expected to be larger than in the cationic Brookhart systems (see discussion below).

To understand the effect of substituents at the C=C bond on the stability of the Brookhart and Grubbs π complexes, we have reoptimized the complexes **1a** and **2a** in C_s symmetry and analyzed them using the energy-decomposition scheme of Ziegler and Rauk;[23] these C_s-symmetric complexes are denoted **1j** and **2j**.[24] In **1j** and **2j**, the olefin HOMO belongs to the a′ irreducible representation and the LUMO belongs to a″ (Figure 4). Hence, the analysis reveals the role of electron donation from the olefin HOMO to empty orbitals of the metal fragment in comparison to back-donation from occupied metal orbitals to the olefin LUMO. The results clearly show that donation (a′) in the ethylene complex of the Brookhart catalyst is much more important than back-donation (a″), as visualized in Figures 4 and 5 (**1** + ethylene).[25,26] This is due to the overall positive charge of the catalyst. The electron-withdrawing CN substitu-

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[21] Frenking, G.; Fröhlich, N. *Chem. Rev.* **2000**, *100*, 717.

[22] We have investigated the overlap integrals between the Slater-type metal d (triple-ζ) and ethylene carbon p (double-ζ) basis functions in the ethylene complexes of the Brookhart catalyst. The analysis shows that the largest overlap integrals are $\langle C{-}p_y^{l}|Ni\text{-}d_{x^2-y^2}^{s}\rangle = 0.168$ and $\langle C{-}p_y^{s}|Pd\text{-}d_{x^2-y^2}^{m}\rangle = 0.384$, respectively, indicating a stronger overlap of Pd 4d with ethylene p orbitals than of Ni 3d with ethylene p orbitals (l = large exponent, m = middle exponent, s = small exponent).

[23] (a) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1. (b) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558. (c) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755.

[24] The C_s-symmetric ethylene complexes **1j** and **2j** are higher in energy than the C_1-symmetric complexes **1a** and **2a** by 3.0 and 2.5 kcal/mol, respectively.

[25] Besides stabilizing orbital interactions, ΔE_{orb}, there are additional contributions to the bond energy ΔE, such as Pauli repulsion, ΔE_{Pauli}, electrostatics, ΔE_{elst}, and strain energy, ΔE_{str}. The last contribution, ΔE_{str}, reflects the strength of the β-agostic interaction being present in the catalysts **1** (19.9 kcal/mol) and **2** (14.3 kcal/mol) rather than in their π and N complexes with monomers. For details, see Table 4.

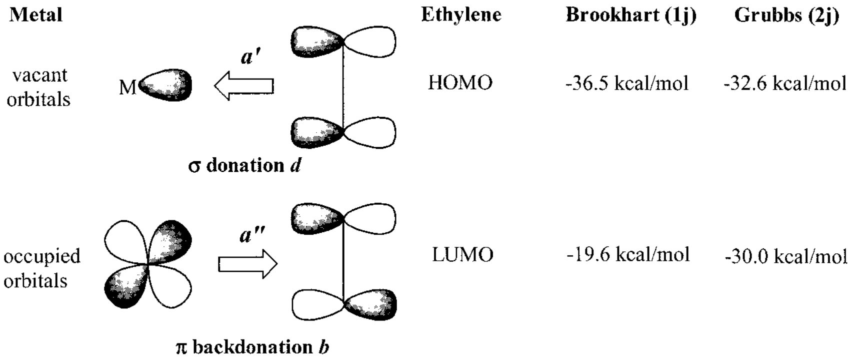

Figure 4. Contributions of the irreducible representations a′ and a″ to the orbital interactions between the metal and the monomer in the ethylene complexes of the Brookhart and Grubbs catalysts.

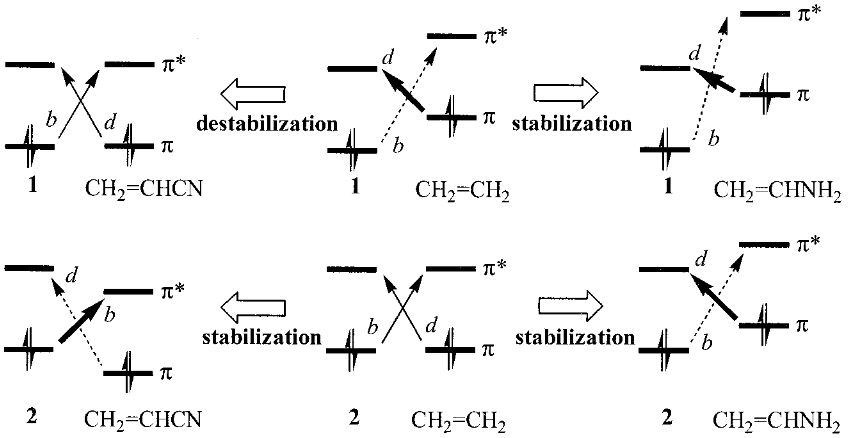

Figure 5. Donor−acceptor interactions in the catalyst−monomer *π* complexes and their effect on the stabilization energy. *d* is defined as the donation from the monomer to the catalyst and *b* the back-donation from the catalyst to the monomer.

Table 4. Results of the Fragment Analysis of the C_s-Symmetric Ethylene Complexes 1j and 2j[a]

	ΔE_{str}					ΔE_{orb}				
complex	catalyst	ethylene	total	ΔE_{Pauli}	ΔE_{elst}	a′	a″	total	ΔE_{int}	ΔE
1j	19.9	2.8	22.7	101.8	−81.5	−36.5	−19.6	−56.1	−35.8	−13.2
2j	14.3	3.8	18.1	123.2	−94.2	−32.6	−30.0	−62.6	−33.6	−15.5

[a] Definitions: strain energy, ΔE_{str}; Pauli repulsion, ΔE_{Pauli}; electrostatic interaction energy, ΔE_{elst}; orbital interaction energy, ΔE_{orb}, for contributions of the a′ and a″ irreducible representations to ΔE_{orb}; interaction energy, $\Delta E_{int} = \Delta E_{Pauli} + \Delta E_{elst} + \Delta E_{orb}$; activation energy, $\Delta E = \Delta E_{str} + \Delta E_{int}$. All values are given in units of kcal/mol.

Table 5. Energies (in eV) of the π(C=C) and π^*(C=C) Orbitals and of the Nitrogen Lone Pair

monomer		π(C=C) (HOMO)	π^*(C=C) (LUMO)	n(N)
CH_2=CH_2	D_{2h}	b_{1u} −7.16	b_{2g} −1.35	
CH_2=$CHCH_3$	C_s	a″ −6.65	a″ −1.01	
CH_2=CH_2CN	C_s	a″ −7.83	a″ −3.27	HOMO-1 a′ −8.86
CH_2=CH_2NH_2	C_1	a −5.32	a −0.37	HOMO a −5.32
CH_3CN	C_{3v}			HOMO a_1 −8.48
CH_3NH_2	C_s			HOMO a′ −5.69
$N(CH_3)_3$	C_{3v}			HOMO a_1 −5.16

ent decreases the HOMO level of the monomer (Table 5). The ability of acrylonitrile to donate electrons to the catalyst is therefore weakened, resulting in a destabilization relative to the parent ethylene complex (Figure 5, **1** + acrylonitrile). The electron-releasing amino substituent has a strong stabilizing effect on the Brookhart *π* complexes, since the NH_2 group increases the olefin HOMO level (Figure 5, **1** + vinylamine). In contrast, donation and back-donation are of equal strength in the neutral Grubbs complex **2j** (Figure 4). The electron-withdrawing CN substituent at the C=C bond therefore leads to a slight stabilization of the *π* complex by favoring back-donation from the catalyst, while electron-releasing groups such as NH_2 induce a slight stabilization due to increased donation (Figure 5).[27]

In comparing nitrogen- and oxygen-containing polar monomers, one should note that the energies of the *π* complexes of the investigated N- and O-containing monomers are similar.[16] However, the metal−nitrogen bonds are stronger than the metal−oxygen(carbonyl) bonds by about 15 kcal/mol.[16] This result can be elucidated by the fact that oxygen is a poorer donor than nitrogen.[28]

The theoretically predicted bond distances in the complexes **1a**−**i** to **4a**−**i** are listed in Table 1 and can now be rationalized as follows. (i) The Ni−N and Ni−C bonds in **1a**−**i** to **2a**−**i** are shorter than the correspond-

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(26) Note that Figure 5 oversimplifies the nature of the chemical bond. In complexes and chemical reactions of transition-metal compounds, there are several orbitals of the metal fragment that contribute to the interactions. For example, see: Deubel, D. V.; Frenking, G. *J. Am. Chem. Soc.* **1999**, *121*, 2021.

ing bonds to the palladium catalysts **3a**−**i** to **4a**−**i**, which is due to different metal radii. (ii) The metal−N bonds in the amine complexes of the Brookhart catalysts **1f**,**h**,**i** and **3f**,**h**,**i** are shorter than the corresponding bonds in the Grubbs systems **2f**,**h**,**i** and **4f**,**h**,**i**, since the Brookhart catalysts are cationic. (iii) The metal−N bonds in the trimethylamine complexes **1i**−**4i** are longer than the corresponding bonds in the methylamine complexes **1h**−**4h**, indicating that steric effects are already present in our model systems to a certain extent. (iv) The metal−C bonds in the π complexes of the Brookhart catalysts **1a**−**c**,**e** and **3a**−**c**,**e** are longer than the corresponding bonds in the Grubbs systems **2a**−**c**,**e** and **4a**−**c**,**e**, although some of the bonds to the Brookhart catalysts are stronger. (v) The metal−N bonds in the nitrile complexes of the Brookhart catalysts **1d**,**g** and **3d**,**g** are longer than the corresponding bonds in the Grubbs systems **2d**,**g** and **4d**,**g**, although all metal−N(nitrile) bonds in the Brookhart complexes are stronger. The interesting findings (iv) and (v) can be rationalized by the fact that there is a considerable amount of π back-donation in the olefin and nitrile complexes of the Grubbs catalyst (Figure 4). This type of interaction requires shorter interatomic distances than σ donation but contributes less to the bond energy.[29] (vi) The metal−C1 bonds to the terminal carbon C1 in the π complexes **1**−**4b**,**c**,**e** are shorter than the metal−C2 bonds to the vicinal carbon C2, since the p_z coefficient at the terminal carbon in the HOMO of propylene and of the π-conjugated systems is larger than at the vicinal carbon.[30] (vii) The relative differences of the C1−C2 distances in the complexes are comparably small. The double bonds are elongated by electron back-donation from the metal into π^* C═C orbitals and by a strong donation from π C═C orbitals to vacant metal orbitals.

Although the computational results reported seem promising for some of the systems, this does not necessarily imply that a copolymerization with the investigated catalyst−substrate combinations can easily be achieved. The study of the olefin insertion barriers is required to finally determine the copolymerization activity. Furthermore, the insertion of polar monomers can yield chelates. Since the β-hydrogen atoms in alkyl complexes of late transition metals are comparably labile, isomerization of the chelates can subsequently lead to the most stable rings. Six-membered chelates are known to be resting states in the copolymerization of ethylene with Brookhart palladium catalysts,[4b] but this situation might be different in the nitrogen-containing systems. These aspects will be addressed in subsequent studies.

Conclusions

We have calculated and compared the energies for the π and N coordination of the nitrogen-containing polar monomers $CH_2{=}CH(CH_2)_nX$ ($n \geq 0$; X = CN, NH_2, $N(CH_3)_2$) with generic models for the recently reported nickel(II) and palladium(II) catalysts with diimine ("Brookhart") and salicylaldiminato ("Grubbs") ligands. The results can be summarized as follows. (i) The enamine is the only monomer which prefers π binding over N binding in its complexes with all four model catalysts **1**−**4**. (ii) The copolymerization of the other monomers and olefins using the Brookhart catalysts **1** (Ni) and **3** (Pd) will require different techniques such as functional-group protection.[2] (iii) The results for the Grubbs model catalysts **2** (Ni) and **4** (Pd) are very promising, because π complexation can compete with N coordination. (iv) Alkyl-substituted amines show a larger relative preference for π binding due to the steric destabilization of the N complexes. (v) A relative stabilization of the π-coordination mode in the Pd systems **3** and **4** by about 3 kcal/mol in comparison with the Ni systems has been found. The energies for the coordination of polar monomers with the model catalysts can be rationalized by investigating the role of electron donation from the polar monomer to the metal and vice versa.

Computational Details

Molecular geometries have been optimized at the gradient-corrected density-functional-theory (DFT) level using Becke's exchange functional[8] and Perdew's correlation functional[9] (BP86). Uncontracted Slater-type orbitals (STOs) have been used as basis functions for the SCF calculations.[31] 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 have been treated within the frozen-core approximation.[32] An auxiliary basis set of s, p, d, f, and g STOs has been utilized to fit the molecular densities and to represent the Coulomb and exchange potentials in each SCF cycle. Relativistic effects have been considered using the zeroth-order regular approximation (ZORA).[33] The calculations have been

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(27) We have performed a fragment-based population analysis of the complexes **1a**,**c**,**e** and **2a**,**c**,**e** to demonstrate the interactions shown in Figure 5. The formation of the ethylene complex **1a** from ethylene and the catalyst **1** leads to an electron loss in the occupied orbitals of ethylene (−0.44 e) and to an electron gain in the vacant orbitals of **1** (+0.49 e). These values are a measure of donation *d* from ethylene to the catalyst. The occupied orbitals of **1** lose fewer electrons (−0.30 e) and the vacant orbitals of ethylene gain a similar amount (+0.24 e), indicating that back-donation *b* from the Brookhart catalyst to the olefin is much weaker than donation. In contrast, donation and back-donation in the Grubbs ethylene complex **2a** are of same strength (d = −0.37, +0.42; b = −0.36, +0.32). The population analysis also reflects the electron-withdrawing effect of the nitrile substituent in the complexes **1c** (d = −0.39, +0.45; b = −0.40, +0.33) and **2c** (d = −0.31, +0.37; b = −0.50, +0.43) as well as the electron-releasing effect of the amine moieties in **1e** (d = −0.49, +0.51; b = −0.16, +0.15) and **2e** (d = −0.42, +0.45; b = −0.33, +0.27).

(28) The energy of the oxygen lone pairs of methyl acrylate (−6.8 eV) is given in ref 16 and can be compared to the lone pairs of the nitrogen-containing systems (Table 5). It is interesting to note that the lone-pair energy of the nitriles is lower and the lone-pair energy of the amines is higher than the value of methyl acrylate. Since both N-containing monomers form stronger bonds with the Brookhart catalyst than does the O-containing system, lone-pair energies are unsuitable to elucidate the stabilization energies. We have performed additional energy-decomposition analyses of the complexes **1g**,**h**,**j**−**4g**,**h**,**j** for comparison with the analyses of the methyl acrylate complexes in ref 16. The results are given in the Supporting Information. The analysis reveals that the Pauli repulsion between the nitrogen-containing monomer and the catalyst are larger. This contribution is overcompensated by stronger electrostatic and orbital-interaction terms, indicating that the nitrogen-containing functionalities are much better donors than the O ligand.

(29) Another example is the influence of π interactions on the transition structures for olefin epoxidation: Deubel, D. V.; Frenking, G.; Senn, H. M.; Sundermeyer, J. *Chem. Commun.* **2000**, 2469.

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carried out with the ADF 2000 program package.[34] For electronic-structure analyses, Ziegler and Rauk's[23] energy-decomposition scheme has been employed.

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Supporting Information Available: A table giving fragment analyses of the complexes of ethylene, acetonitrile, and methylamine with the catalysts **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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