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Diiminates and Diamides as Ligands in Polymerization Catalysts with M(III) (M = Ti, V, Cr) Metal Centers. A Theoretical Study

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A theoretical study has been carried out on two types of olefin polymerization catalysts based on the same M(III) centers (M = Ti, V, Cr) but different (mono) anionic ligand designs. The first system contains a mono-β-diiminato ligand that binds through the two imine nitrogens to the M(III) center and has the nitrogen lone-pairs perpendicular to the NMN coordination plane. It is shown that the generic mono-β-diiminato ligand system without bulky substituents on the nitrogen has barriers (kcal/mol) for insertion (Ti: 10.7; V: 12.2; Cr: 10.4) quite similar to the β-hydrogen transfer process (BHT) (Ti: 11.2; V: 9.8; Cr: 8.4), which serves as the chain-terminating step. The close proximity of the two barriers is in line with findings for other bidentate nitrogen ligands, where bulky aryl groups on the nitrogens were required in order to increase the BHT barrier relative to insertion and ensure acceptable molecular weights. The second system contains a bridged diamide ligand in which the ligand backbone forces the lone-pairs on the nitrogens into the NMN coordination plane and the bulk of the ligand to be below and above this plane. For this system barriers (kcal/mol) of insertion (Ti: 14.4; V: 9.7; Cr: 15.3) are calculated to be well below the barriers (Ti: 19.0; 18.7; 21.8) for the BTH process, as the BHT transition state is destabilized by the ligand backbone. Especially the V(III) system is predicted to be a good candidate as a high molecular weight polymerization catalyst.

Introduction

The discovery of active group IV *ansa*-bridged metallocene systems (**I**) by Kaminsky in 1976[1] has led to a range of homogeneous single-site polymerization catalysts. A further systematic modification of the substituents on the cyclopentadienyl rings (Cp) has resulted in significant improvements of both activity and selectivity toward isotactic and syndiotactic polymerization of propylene.[2] Single-site catalysts are not restricted to Cp ligands. Thus, the so-called "constrained geometry" catalysts (**II**) in which one *ansa*-bridged Cp ligand is replaced by an amide group exhibit unique catalytic properties,[3] and McConville et al. found a living polymerization system with a sterically demanding diamide ligand (**III**).[4] Meanwhile, a wide variety of active polymerization catalysts have emerged that contain group III/IV transition metals, lanthanides, and actinides stabilized with a broad range of auxiliary ligands.[5] These developments were accompanied by a large number of theoretical investigations on the principal reaction mechanism as well as specific ligand effects.[6] In a recent series of papers, a unified view of ethylene polymerization catalysis by d^0- and d^0f^n-metals was presented based on density functional theory (DFT) type calculations.[7]

Complexes of late transition metals have also shown promise as polymerization catalysts. Thus, Brookhart[8]

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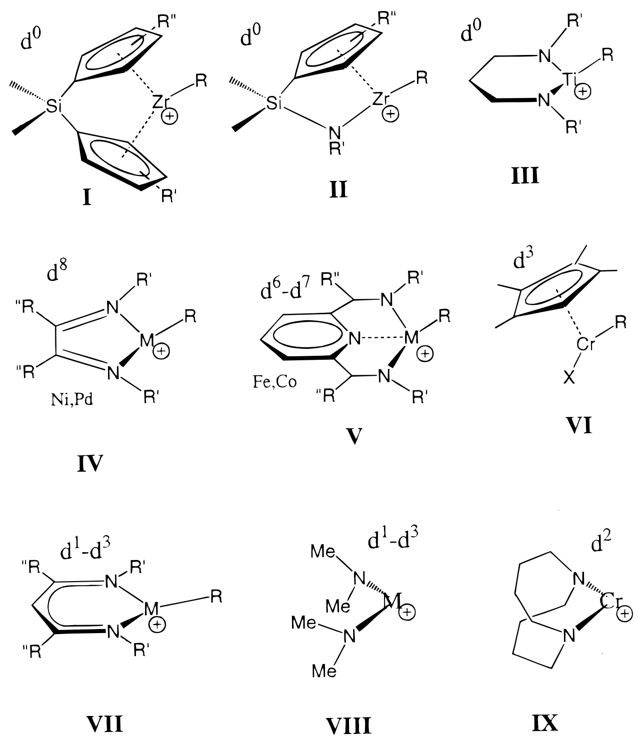
Scheme 1. Different Designs of Single-Site Olefin Polymerization Catalysts



et al. have demonstrated that Ni(II) and Pd(II) complexes (**IV**) with a d^8-electron count can be modified from olefin oligomerization catalysts to active polymerization catalysts by increasing the steric bulk of the auxiliary ligands.[8] This effect is based on a stronger inhibition of the chain termination reactions in comparison with chain propagation by steric strain, as verified by theoretical calculations.[9] Very recently, Brookhart et al. and Gibson et al. have shown that this concept can also be extended to Fe(II) and Co(II) complexes (**V**) with d^6- and d^7-electron configurations, respectively.[10a−d] These systems have also been the subject of theoretical invetigations.[10e−g]

Early first-row transition metals with a few d-electrons have also been shown to form compounds that are active polymerization catalysts. Key among these species are the chromium-based catalysts developed by Union Carbide[11a] and Phillips.[11b] To model the silica-supported active sites of the heterogeneous Union Carbide polymerization catalyst, a number of groups have investigated the corresponding Cr(III) model systems.[12] A Cr(III) complex of type **VI** with $X = OR_2$ was found to polymerize ethylene,[13] and a similar *ansa*-bridged system with $X = NR_3$ was shown to have quite remarkable activities.[14] The feasibility of direct ethylene insertion into the M−C bond for such d^3 Cr(III) systems has been investigated theoretically by Jensen and Børve[15] et al. from calculations on the model system $[CrCl(H_2O)CH_3]^+$. Very recently, Theopold et al. and Budzelaar et al. reported that M(III) complexes (M = Ti, Cr, V) with the so-called "nacnac" ligand (substituted β-diiminate) (**VII**) catalyze the homopolymerization of ethylene as well as the copolymerization of ethylene with α-olefins.[16]

We have in a previous study explored the ground rules for employing complexes of early first-row transition metals with a few d-electrons as olefin polymerization catalysts.[17] Our investigation revealed that diamide complexes (**VIII**) with a d^n ($n = 1-4$) metal center prefer the nitrogen lone-pairs of the NR_2 ligands to be in the N−M−N coordination plane during the insertion process, in contrast to d^0 complexes, where the lone-pairs prefer to be in a perpendicular position.[7] On the basis of this finding, we suggested a chelating diamide ligand (**IX**) in which a double link between the nitrogens forces their lone-pairs to be in the N−M−N plane.

It is the objective of the current study to broaden our understanding further of how one might use early first-row transition metals with a few d-electrons in olefin polymerization catalysis. Our starting point will be the recent work by the groups of Theopold and Budzelaar[16] on M(III) complexes (M = Ti, Cr, V) of the "nacnac" ligand **VII**, since it represents the first systematic experimental survey in this field. We shall to this end carry out density functional theory (DFT) calculations on the nacnac complexes and compare their electronic performance as polymerization catalysts to d^0 systems and late transition metal complexes.[18] The second part of our study explores an alternative monoanionic ligand, with a design similar to **IX** where the nitrogen lone-pairs are in the N−M−N plane rather than perpendicular to it as in the nacnac systems.

Computational Details

All calculations were performed with the Amsterdam density functional theory (DFT) program package ADF, developed by Baerends[19] et al., using the numerical integration scheme

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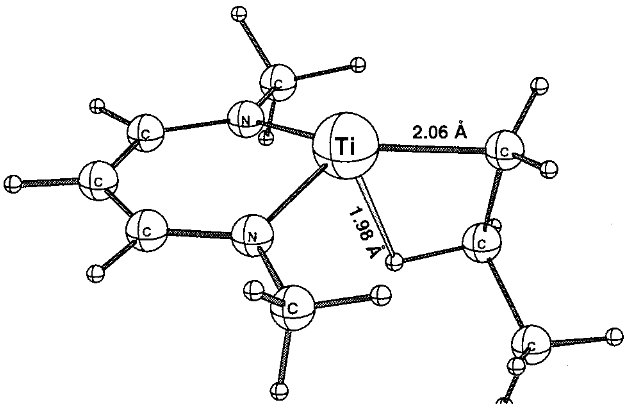
developed by te Velde[20] et al. The frozen core approximation was employed throughout. For the transition metal atoms (Ti, V, Cr) use was made of a triple-ζ Slater type basis set for the 3s, 3p, 3d, and 4s valence shells plus one 4p polarization function. Nonmetal atoms were described by a double-ζ STO basis with one 3d (C, N,P) or one 2p (H) polarization function.[21] A set of auxiliary s, p, d, f, and g STO functions, centered on all nuclei, was used in order to fit the molecular density and present Coulomb and exchange potentials accurately in each SCF cycle.[22] For all calculations, the local exchange−correlation potential by Vosko[23] et al. was augmented with gradient-corrected functionals for electron exchange according to Becke[24] and electron correlation according to Perdew[25] in a self-consistent fashion. This nonlocal density functional is usually termed BP86 in the literature, and it has proven to be reliable for both geometries and energetics of transition metal systems. Metal−ligand bond energies are usually overestimated by BP86 up to 5 kcal/mol,[26,27] whereas activation energies are underestimated (2−4 kcal/mol). Jensen and Børve have shown that the BP86 functional gives results in excellent agreement with the best wave function based methods available today, for the class of reactions investigated here.[28] All calculations were performed in a spin-unrestricted fashion except for the singlet vanadium species, for which spin-restricted calculations were carried out. First-order scalar relativistic corrections[29] were added to the total energy for all systems, since a perturbative relativistic approach is sufficient for first-row transition metals as shown by Deng[30] et al. All transition state structures were optimized fully.

A number of labeling conventions have been adopted throughout this paper. Thus, species of the nacnac system will be referred to by numerals attached to lower-case letters (e.g., **1a**, **1b**, **1c**), whereas numerals attached to upper-case letters (e.g., **2A**, **1B**, **3C**) refer to structures of the alternative ligand based on **IX**. Further, the numeric-alphabetic labels may have the suffix t or q for species with respectively a triplet and quartet spin state. On the other hand, labels without the suffix refer to species with a doublet spin state. All transition states have prefix TS followed by the direct (kinetic) reactant and product within square brackets. Finally, **1a**(M) or **1A**(M) indicate the specific metal (M) used in the calculations.

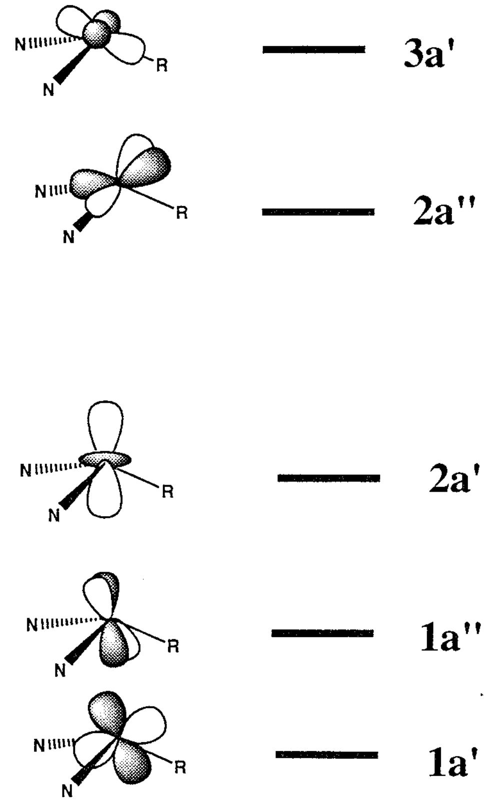
Results and Discussion

a. (Mono-β-diiminato)M(III) Cations (M = Ti, V, Cr). The structure of the alkyl (mono) cation (**1a**) $LMC_3H_7^+$ (L = R′N(R″)CHC(R″)NR′$^-$; M = Ti, V, Cr; R′ = CH_3; R″ = H) has the two imine nitrogens and the α-carbon of the propyl chain in a trigonal conformation with a β-hydrogen on the alkyl group bound in an axial position to the metal center. The basic orbital interaction diagram for **1a** is shown in Scheme 2. The three d-based orbitals (1a′, 1a″, and 2a″) of lowest energy are only weakly interacting with the σ-orbitals of the ligands, whereas the two remaining d-based orbitals of higher energy (2a″ and 3a′) interact out-of-phase with the σ-orbitals of the ligands. For **1a**(Ti), **1a**(V)_t, and **1a**(Cr)_q, electrons are subsequently added to 1a′, 1a″, and 2a′, respectively, to obtain the high-spin electron conformation. The low-spin states for the vanadium and chromium species were much higher in energy than **1a**(V)_t and **1a**(Cr)_q, respectively. Schematic energy profiles for the elementary steps of the polymerization cycles starting with **1a** are shown in Figure 1. Table 1 displays the relative energies of all species involved for the three metals M = Ti, V, and Cr, respectively The groups of Theopold and Budzelaar have characterized the related species $LMCl_2(THF)_2$ (M = Ti, V, Cr)[16a] and $LMCl_2$ (M = Ti, V). They found these to be high-spin, and the geometrical parameters from the X-ray structures compare well (where applicable) with those calculated for $LMC_3H_7^+$.



1a(Ti)

Scheme 2. Schematic Energy Diagram for the d-Based Orbitals in the Cationic Alkyl Complexes 1a and 1A



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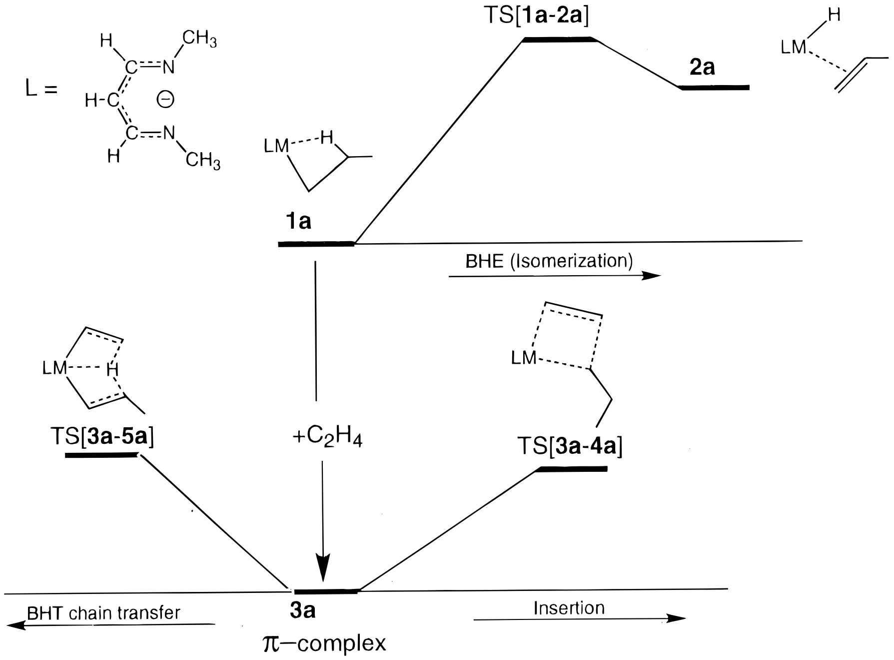
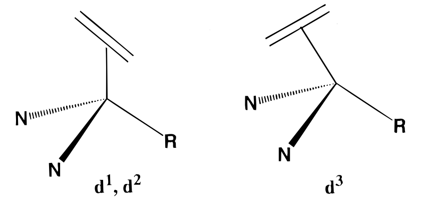


Figure 1. Energy profiles for insertion, β-hydrogen elimination (BHE), and β-hydrogen transfer for the generic nacnac system. Energies in kcal mol^{-1}.

Table 1. Relative Energies[a] and Barriers[b] for Nacnac-Based Catalysts

species	metal center				
	Ti_d	V_s	V_t	Cr_d	Cr_q
1a	0.0[a]	12.5[a]	0.0[a]	20.3[a]	0.0[a]
TS[**1a**−**2a**]	16.7 (16.7)[b]	28.8 (28.8)[b]	6.8 (6.8)[b]	31.3 (31.2)[b]	14.3 (14.3)[b]
2a	13.6		3.1	22.6	13.6
3a	−23.0	−29.7	−30.1	−15.8	−12.5
TS[**3a**−**4a**]	−12.3 (10.7)		−17.9 (12.2)	9.7 (25.5)	−5.4 (10.4)
TS[**3a**−**5a**]	−11.8 (11.2)	−18.6 (10.4)	−20.3 (9.8)	−7.4 (8.4)	3.2 (19.0)

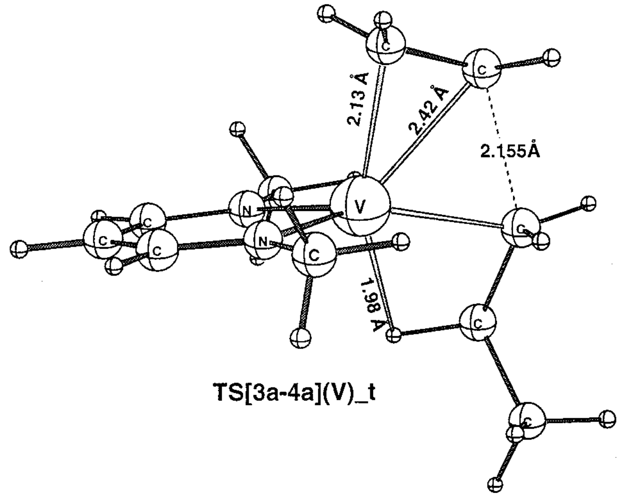
[a] All energies (kcal mol^{-1}) are relative to the alkyl complex **1a** of highest spin multiplicity. [b] Barriers (kcal mol^{-1}) are shown in parentheses. They are all relative to most stable reactant.



3a

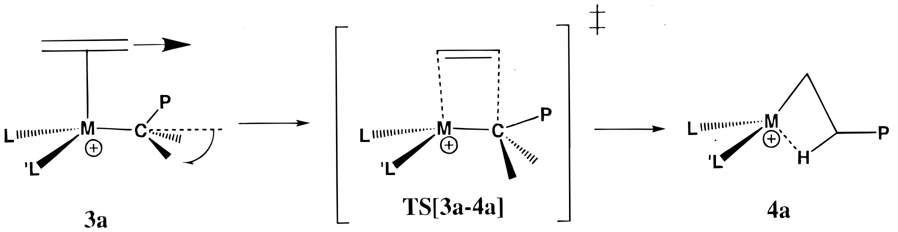
The addition of ethylene to **1a** leads to the olefin π-complex **3a** with a high-spin ground state configuration for all three metals. For the d^1- and d^2-systems 2a′ (Scheme 1) is used as acceptor orbital for the π-olefin density, whereas density is back-donated from a single electron in 1a″ to π* of ethylene. This bonding is optimal for M = V, where **1a**(V)_t already has a single electron in 1a″. For this reason **1a**(V)_t has a large ethylene uptake energy of 30.1 kcal/mol (Figure 1 and Table 1). For titanium the uptake energy is somewhat less at 23.0 kcal/mol since an electron has to be promoted from 1a′ in **1a**(Ti) to 1a″ in **3a**(Ti). In the case of **1a**(Cr)_q the suitable acceptor orbital 2a′ (Scheme 2) is occupied by one electron; hence use must be made of the unoccupied orbital 3a′ of higher energy. As a result, the uptake energy in **3a**(Cr)_q is reduced to 15.8 kcal/mol (Table 1). The olefin complex **3a** (or one of its isomers; see later) is seen to represent the resting state for the polymerization cycle.

The insertion process leads from **3a** through the transition state TS[**3a**−**4a**] to the new alkyl chain **4a** with two more carbon units (Scheme 3). The barrier of insertion in d^1−d^3 complexes stems from the slippage of the olefin unit toward the α-carbon of the growing chain (Scheme 3) whereby the back-donation from the



TS[3a-4a](V)_t

Scheme 3. Schematic Representation of Olefin Slippage in the Insertion Process

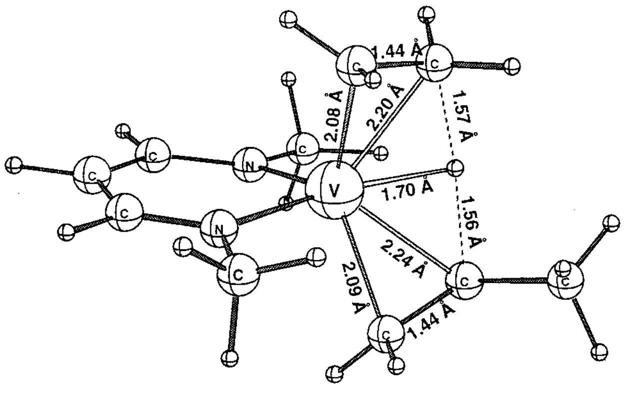


Insertion

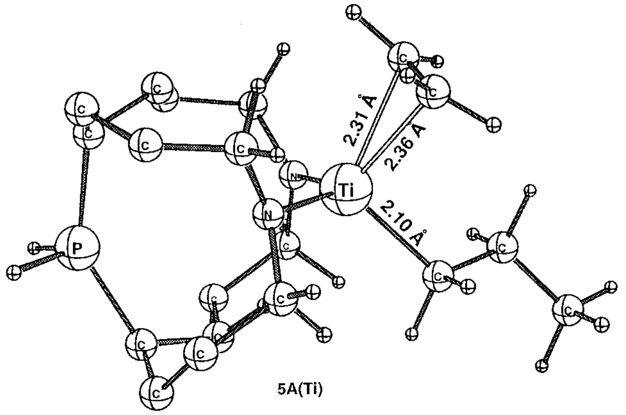
metal to π^* of ethylene is lost. The barrier of insertion is essentially the same (12.2−10.4 kcal/mol) for all three metals as much the same back-donation interaction is lost. The insertion process takes place on the high-spin potential surfaces for all the metals.

An often implied, the chain termination route involves β-hydrogen elimination (BHE) from **1a** over the transition state TS[**1a**−**2a**] to produce the hydrido-olefin complex **2a**, from which the growing chain with the olefinic end-group can dissociate. The β-hydrogen elimination step takes place on the high-spin surface. It has a larger barrier than insertion for titanium (16.7 kcal/mol) and chromium (14.2 kcal/mol), whereas the opposite is the case for vanadium (6.8 kcal/mol), Table 1. The high olefin ethylene uptake energies will make the concentrations of **1a** exceedingly small in comparison to the olefin complex **3a** under normal monomer pressures. Thus, it is not likely that the nacnac systems studied here will exhibit isomerization (branching) or termination by β-hydrogen elimination (BHE). Even if BHE took place, the strong metal−olefin bonds in **2a** (>30 kcal/mol) would make it difficult to release the growing chain with the olefinic end-group attached to the metal by dissociation or associative replacement.

An alternative chain termination step is represented by β-hydrogen transfer (BHT). In this process a hydrogen migrates from the growing chain in **3a** to the ethylene monomer (Scheme 4) over the transition state TS[**3a**−**5a**]. The result is a new olefin complex **5a** (similar to **3a**), in which the growing chain is an ethyl group and the complexed monomer an olefin unit with the former growing chain attached, Scheme 4. The barrier is essentially caused by the same slippage of ethylene (Scheme 4) as in the case of the insertion, and the activation energies are in the same range (11.2−8.3 kcal/mol). We note that TS[**3a**−**5a**] can be viewed as a six-membered metallacycle with the ring in a plane perpendicular to the NMN coordination plane. A similar arrangement is also seen for the BHT transition states[9] involving the systems **III**−**V**.



TS[3a-5a](V)_s

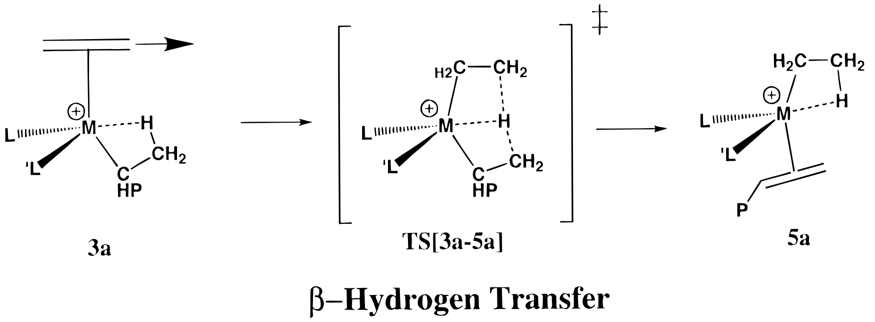


5A(Ti)

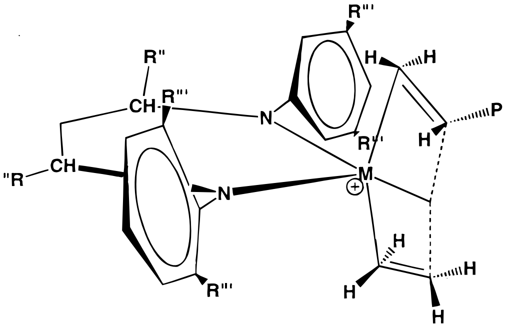
We have found that the generic nacnac systems **VII** with $R' = CH_3$ and $R'' = H$ have quite similar propagation and termination (BHT) barriers. This finding is not unique; in fact the same has been demonstrated theoretically—and in some cases also experimentally—for the systems **III**−**V**. The close proximity of the two barriers clearly makes the generic systems **III**−**V** oligomerization catalysts at best. However, for **III**−**V** the introduction of bulky substituents on the nitrogens—such as substituted aryls—increases[4,8,10] the barrier for the BHT compared to insertion. This has been rationalized[9] in terms of increasing steric interactions between the emerging six-membered metallacycle perpendicular to the NMN plane of the transition state for the BHT process and the substituents on the nitrogens. This is illustrated in Scheme 5, where the aryl groups are kept perpendicular to the NMN plane by the R″ substituents (mostly methyl) on the neighboring carbons.

Bulky aryl substituents (R′) have also been employed by the groups of Theopold and Budzelaar[16] for the nacnac system **VII**. Theopold[16a] et al. made use of $R' = C_6H_5$ to obtain nacnac-based olefin polymerization catalysts with modest activity and molecular weights in the range of 10^6. However, when Budzelaar[16b] et al. increased the steric bulk of the aryl substituents moderately to $R' = 2,4,6\text{-}Me_3C_6H_2$, the polymerization activity of the nacnac system was reduced considerably. We shall not pursue the role of steric bulk in nacnac system **VII** computationally here since we already[9] have examined the analogous role of large aryl groups (R′) for the systems **III**−**V**. We shall instead in the next section introduce a new and alternative strategy for

Scheme 4. Schematic Representation of Olefin Slippage in the *β*-Hydrogen Transfer Process



Scheme 5. Destabilization of Transition State for the *β*-Hydrogen Transfer Process by Arene Substituents in III−V and VII



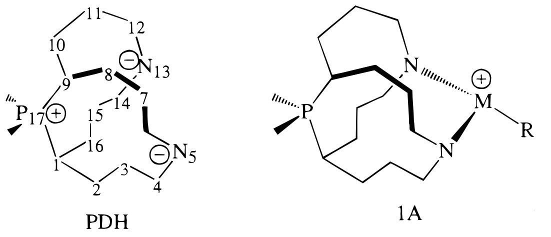
increasing the barrier of termination (BHT) compared to insertion.

Before closing this section it should be pointed out that the BHT process is only the first step toward chain termination. The final step requires a dissociation (or associative substitution) from **5a** of the growing chain with the olefinic end-group attached to the metal. The required dissociation energies are high and similar to the corresponding dissociation energies (30−15 kcal/mol) obtained for **3a**. Thus for the generic nacnac system **VII** with high olefin dissociation energies the olefinic end-group has a good chance to reinsert with a barrier similar to that found for TS[**3a**−**4a**] (12−10 kcal/mol). As a result, even the generic nacnac system might work as polymerization catalysts.

b. [(DPH)MR]$^+$ (M = Ti, V, Cr) Systems. The nacnac ligand **VI** as well as the catalyst designs **III**−**V** have the nitrogen lone-pairs perpendicular to the NMN plane. Further, for the generic systems (R′ = R″ = H) the steric bulk of the ligands is confined to that same plane and unable to destabilize the BHT transition state. For such a destabiliztion to take place aryl groups must be attached to the nitrogens, Scheme 5.

We shall now introduce a ligand design similar to **IX** in which the nitrogen lone-pairs are perpendicular to the NMN plane. This design is introduced since we have shown in a previous study[17] that the in-plane orientation electronically lowers the insertion barrier for d^1−d^3-metals. Of equal importance in the present context is the fact that the in-plane orientation forces the bulk of the ligand (**IX**) above and below the NMN plane, where it can destabilize the BHT transition state sterically.

Scheme 6. PDH Ligand Design



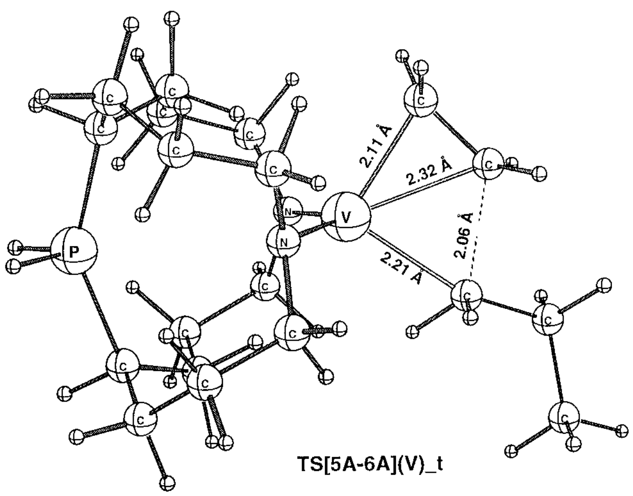
17-phosphonium-5,13,diazabicyclo[7,7,1]heptadecane(-)

We have chosen as a possible ligand for the new design 17-phosphonium-5,13-diazabicyclo[7,7,1]heptadecane(−) (Scheme 6)—for short called PDH—which can bind to the metal center through the two amide groups, **1A**. To keep a close analogy with the nacnac system, we have further made the ligand (mono) anionic by introducing a phosphonium ion.

The electronic structure of **1A** is quite similar to that of the **1a** alkyl cation. Thus, the vanadium and chromium **1A** species are both high-spin. A schematic energy profile for the elementary steps of the polymerization cycles starting with **1A** is shown in Figure 2. Table 2 displays activation barriers and relative energies of all species involved.

The uptake of ethylene by **1A** results in the olefin *π*-complex **5A**. As for the nacnac system **3a**, the chromium center forms for much the same reason the weakest ethylene−metal bond. The olefin uptake energies (Table 2) are in general reduced by 10−15 kcal/mol compared to **3a** due to the steric bulk of the PDF ligand. For vanadium and chromium the high- and low-spin configurations for **5A** are very close in energy (Table 2).

Both the insertion step, **5A** → TS[**5A**−**6A**] → 6A , and the termination process, **5A** → TS[**5A**−**7A**] → 7A



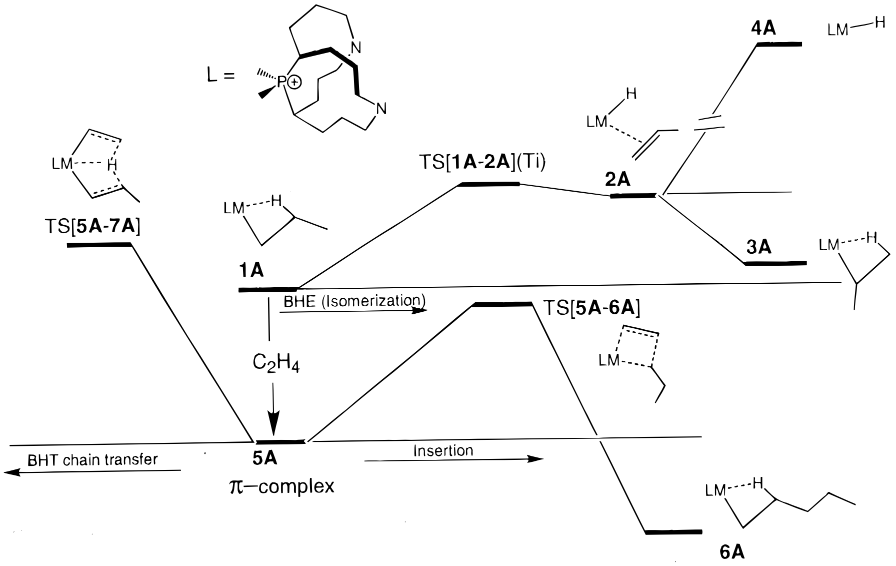


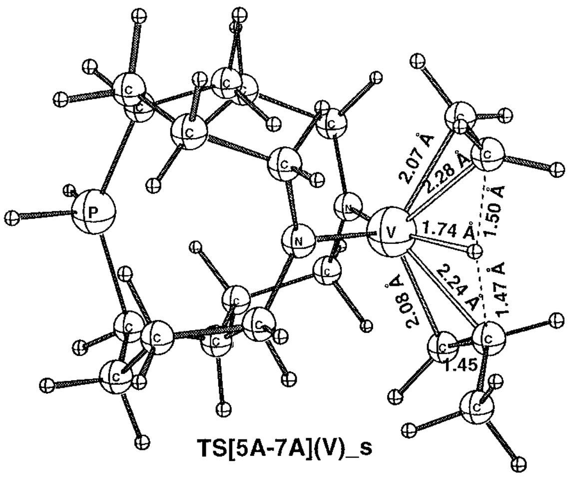
Figure 2. Energy profiles for insertion, β-hydrogen elimination (BHE), and β-hydrogen transfer for the PDH system. Energies in kcal mol^{-1}.

Table 2. Relative Energies[a] and Barriers[b] for PDH-Based Catalysts

species	metal center Ti_d	V_s	V_t	Cr_d	Cr_q
1A	0.0		0.0		0.0
2A	8.0		9.2		22.3
3A	1.4		−0.6		0.2
4A	34.8		40.0		30.9
5A	−15.2	−11.7	−11.8	−2.2	−0.9
6A			−26.2		−24.0
7A	−25.1				
TS[**1A**−**2A**]	10.0 (10.0)		9.5 (9.5)		22.4 (22.4)
TS[5A−6A]	−1.0 (14.2)		−2.1 (9.7)		13.2 (15.4)
TS[5A−7A]	3.8 (19.0)	6.9 (18.7)	13.0 (24.8)	23.8 (26.0)	19.6 (21.8)

[a] All energies (kcal mol^{-1}) are relative to the alkyl complex **1A** of highest spin multiplicity. [b] Barriers (kcal mol^{-1}) are shown in parentheses. They are all relative to most stable reactant.

(Schemes 4−6), are influenced by the steric bulk on the PDH ligand. The congestion in the axial positions is especially felt for the BHT reaction where the corresponding transition state TS[**5A**−**7A**] has the six-membered ring perpendicular to the NMN plane. The barrier of activation for BHT has, as a result, been increased by some 10 kcal/mol compared to the nacnac systems TS[**3a**−**5a**]. The insertion transition state TS-[**5A**−**6A**] is, on the other hand, less encumbered with the monomer and the α-carbon of the growing chain close to each other and to the NMN plane. Compared with the nacnac system, the insertion barrier has been raised by 2−5 kcal/mol. In the overall picture the catalysts based on the PDH ligand are seen to have a much lower barrier for insertion compared to BHT, in contrast with the nacnac systems. Especially promising is the vanadium PDH catalyst, with an insertion barrier of 9.7 kcal/mol and a BHT barrier of 18.7 kcal/mol. On the basis of these two numbers alone, one would predict molecular weights in the range of 10^8.



TS[5A-7A](V)_s

The β-hydrogen elimination path (BHE) was excluded as an important process in the case of the generic nacnac system due to the high ethylene uptake energy of **1a**, which would make the concentration of **1a** exceedingly small in comparison to the olefin complex **3a** under normal monomer pressures. However, the same argument cannot be used for the PDH ligand since the uptake energy of **1A** is reduced considerably, Table 2. For this process we find barriers (8−10 kcal/mol) comparable to that of the insertion in the case of titanium and vanadium, whereas the BHE barrier is much higher (24 kcal/mol) for chromium. We shall in the following restrict our discussion to the first two metals.

The BHE process leads from the alkyl complex **1A** over the transition state TS[**1A**−**2A**] to the hydrido-olefin complex **2A**. For titanium and vanadium the strong metal−olefin bonds in **2A** (∼30 kcal/mol) would make it difficult to release the growing chain with the olefinic end-group attached to the metal by dissociation or associative replacement. Instead the olefinic end-group is likely to reinsert into the M−H bond with a barrier of ∼2 kcal/mol, Table 2. Such a reinsertion might be preceded by rotations of the olefin unit around the bond vector to the metal center. In this case reinsertion will result in isomerization of the polymer in a way previously observed by Brookhart[8] et al. in their Ni(II)/Pd(II) diimine systems.

Summary

We have presented a theoretical study on two types of olefin polymerization catalysts based on the same M(III) centers (M = Ti, V, Cr) but different (mono) anionic ligand designs. The first system contains a generic mono-β-diiminato ligand (**VIII**: R′ = Me, R″ = H) that binds through the two imine nitrogens to the M(III) center and have the nitrogen lone-pairs perpendicular to the NMN coordination plane. This system is very similar to other generic designs (**IV**, **V**, **VI**: R′ = H, R″ = H) in that the insertion process and the potential chain termination step (BHT) have similar barriers of activation. Thus—as for **IV**, **V**, **VI**—bulky aryl substituents[16] (R′) have to be added to the nitrogens in order to increase the barrier for the termination (see Scheme 5) and produce polymers of reasonable molecular weights. The second catalyst was based on the PDH ligand (Scheme 6). It has the lone-pairs of the chelating nitrogens in the NMN plane and the steric bulk above and below the same plane. This design ensures—without the use of aryl substituents—a much higher barrier for the termination (BHT) than for the insertion. Especially promising was the V(III) PDH complex, with an insertion barrier of 9.7 kcal/mol compared to an activation enthalpy for the termination step (BHT) of 18.7 kcal/mol. Such a difference could be consistent with molecular weights of 10^8 amu. The V(III) PDH catalyst was also predicted to exhibit potential for branching through β-hydrogen elimination and olefin reinsertion.

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Supporting Information Available: Table of force field parameters used for the QM/MM calculations as well as tables of gas-phase energies and Cartesian coordinates of DFT optimized structures of **a**−**e** and **h**,**i** for all six catalyst systems and **f**,**g** for systems **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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