Toward a Better Understanding of the Reactivity of Titanium and Zirconium Complexes with an Aryl-Substituted Tripodal Triamido Ligand Derived from *cis*,*cis*-1,3,5-Triaminocyclohexane: A Density Functional Study

Betty B. Coussens,*[,†] Els van Besien,[‡] Peter H. M. Budzelaar,[§] and Nic Friederichs[⊥]

DSM Research Technology & Analysis Geleen, SRU Industrial Chemicals, P.O. Box 18, 6160 MD Geleen, The Netherlands, University of Leuven, Quantum Chemistry and Physical Chemistry Section, Celestijnenlaan 200F, BE-3001 Heverlee, Belgium, Department of Chemistry, University of Manitoba, Winnipeg, MB R3T 2N2, Canada, and SABIC Europe, R&D, Department Chemistry & Catalysis, P.O. Box 319, 6160 AH Geleen, The Netherlands

Received October 25, 2007

Tilley and co-workers have shown that titanium and zirconium hydride complexes containing the triamido [*cis*,*cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]$^{3-}$ ligand (**L**) do not polymerize ethene. To get insight in this observation we have studied these systems and various modifications thereof using density functional theory. The reactivity toward ethene was investigated by computing the energy barriers for ethene insertion in the metal−hydride and metal−alkyl bonds of these compounds with the alkyl chain represented by a methyl or ethyl group. For titanium and zirconium complexes of **L**, the computational results agree with the experimental observation that insertion is possible in metal−hydride but not in metal−alkyl bonds. The energy barrier for insertion in the metal−alkyl bond can be lowered somewhat by reducing the steric bulk of the triamido ligand; however, even in the absence of any steric hindrance this barrier remains very high and no polymerization activity is expected. The ethene insertion barriers increase when reducing the rigidity of the triamido ligand by the introduction of methylene bridges between the coordinating nitrogen atoms and the cyclohexane backbone or replacing the cyclohexane-based ligand by three NH$_2$ groups. The effect of changing the four-coordinate ligand environment of titanium to a five-coordinate one by adding an additional donor molecule (NH$_3$) was found to be small. A significant lowering of the ethene insertion barriers in the metal−alkyl bonds was found only when creating a much more unsaturated metal center by removal of one of the −NR groups or replacement of one of these groups by a much weaker coordinating −OR group. Both the cationic d^0 and neutral d^1 variants of the latter compounds may be active polymerization catalysts. The calculated ease of ethene insertion is shown to be dominated by the electrophilicity of the metal center, quantified as the binding energy of the probe molecule ammonia, and roughly parallels the complexation energy of the ethene monomer.

Introduction

Since the discovery by Kaminsky in the early 1980s that the activation of metallocenes of group 4 metals by a suitable cocatalyst resulted in highly active catalysts for olefin polymerization,[1] metallocenes have attracted increased industrial interest. Compared to the traditional Ziegler–Natta systems they have several advantages. Whereas the former ones are heterogeneous in nature and contain a variety of active centers, which even today are not fully understood, the active species derived from metallocenes are well-characterized metallocene alkyl cations.[2] Furthermore, whereas the activity of traditional heterogeneous systems is due to a small fraction of Ti atoms only (usually less than 1%), a much larger fraction of metal atoms is active in metallocene-based systems.[3]

Fundamental studies on metallocenes revealed that both coordinative unsaturation and electrophilicity of the metal center contribute to their high reactivity. This knowledge has been exploited to develop viable alternatives to the cyclopentadienyl-based metallocenes. Of particular interest in this respect is the development of neutral systems that might not require a cocatalyst to generate the reactive species. Recent work by Turculet and Tilley is relevant in this context. They envisaged that highly reactive d^0 complexes would be obtained when using a triamido ligand based on a cyclohexane framework.[4] This ligand was expected to be particularly suitable because of the rigidity of the cyclohexane backbone and because the small chelate bite angles should enforce a relatively “open” coordination sphere, leaving the electrophilic metal center accessible to small reactants. To suppress dimerization while at the same time fostering the electrophilicity, their triamido ligand was decorated

---

[*] Corresponding author. E-mail: betty.coussens@dsm.com.

[†] DSM Research Technology & Analysis Geleen.

[‡] University of Leuven.

[§] University of Manitoba.

[⊥] SABIC Europe, R&D.

(1) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99–149.

(2) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F *Chem. Rev.* **2000**, *100* (4), 1253–1345.

(3) Ciardelli, F.; Carlini, C. In *Comprehensive Polymer Science*, 1st Suppl.; Pergamon Press: New York, 1992; Chapter 4, pp 77–78.

(4) Turculet, L.; Tilley, T. D. *Organometallics* **2002**, *21* (19), 3961–3972.

10.1021/om7010744 CCC: $40.75

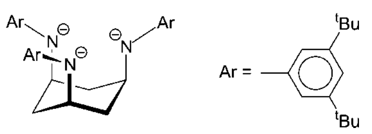

Figure 1. The triamido ligand [*cis*,*cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$-C$_6$H$_9$]$^{3-}$.

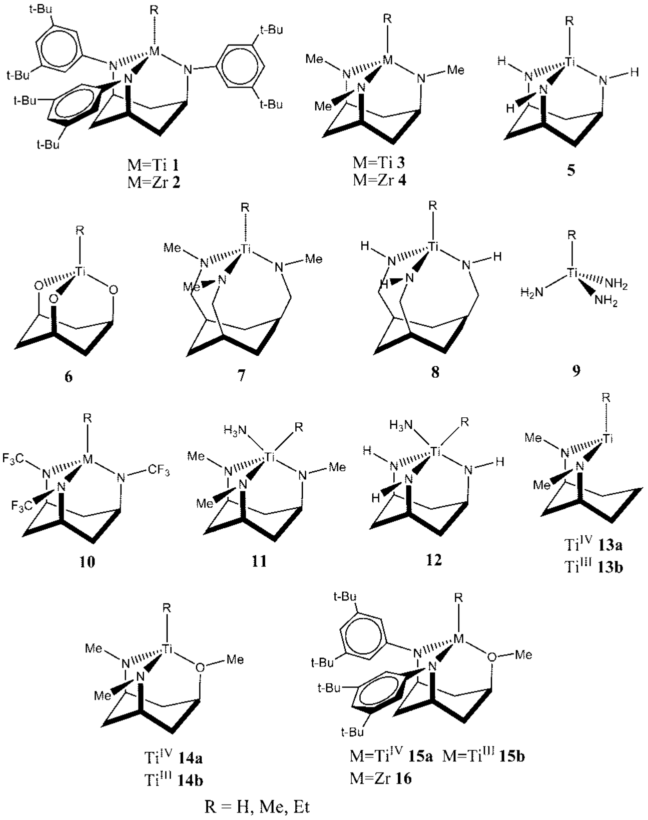

Figure 2. Investigated systems. R = H, Me, Et.

with sterically demanding, electron-withdrawing aryl substituents at the donor nitrogens. Ligands bearing fluorinated aryl groups at N (C_6F_5, 3,5-$(CF_3)_2C_6H_3$) were found to be prone to fluorine abstraction by the metal,[4] so most of the work was done with ligands having 3,5-^{t}Bu$_2$C$_6$H$_3$ groups at nitrogen (Figure 1).[5] Ti and Zr hydride complexes of the [*cis*,*cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$N)$_3$C$_6$H$_9$]$^{3-}$ ligand (**L**) were found to easily undergo 1-hexene insertion, forming the corresponding *n*-hexyl complexes. Remarkably, however, no subsequent 1-hexene insertions were observed. Also, the reaction of the Ti−H complex with ethene resulted in an insignificant amount of polyethylene. It thus seems that for these complexes insertion of olefins is possible in metal−hydrogen bonds, but *not* in metal−alkyl bonds.

In the present work, we aim at understanding the remarkable reluctance of the Ti and Zr complexes of **L** to catalyze olefin polymerization. We have computed the energy barriers for ethene insertion in the M−H and M−C bonds of Ti and Zr complexes of both the parent ligand **L** and a number of modifications thereof (Figure 2) using state-of-the-art density functional theory. The results allow us to disentangle the effects of steric bulk, coordination number, and electrophilicity of the metal center.

Computational Details

Density functional calculations were performed with the TURBOMOLE program[6] in combination with the OPTIMIZE routine of Baker and co-workers.[7] Minima and transition states were investigated at the b3-lyp level[8] in combination with the standard SV(P) basis sets[9] and an effective core potential with 28 core electrons for Zr.[10] For systems **3**, **5**, **13a**, and **14b**, b3-lyp single-point calculations on the SV(P) structures employing the larger TZVP basis sets[11] revealed that for describing *trends* in the ethene insertion barriers the b3-lyp/SV(P) method is adequate (Figure S1, Supporting Information).

For the transition state optimizations, reasonable starting Hessians were obtained from PM3(tm) computations with the Spartan Pro package of Wavefunction Inc.[12] Except for the titanium and zirconium complexes with the complete ligand **L** and the OMe variants thereof (**15** and **16**), all optimized geometries were subjected to analytical (closed shell systems) or numerical (open shell systems) frequency calculations. Only real frequencies were obtained for the minima whereas a single imaginary frequency corresponding to the correct reaction coordinate was found for the transition states as required. Thermal corrections (enthalpy and entropy) were calculated at 273 K, 1 bar, using the standard formulas of statistical thermodynamics.[13] For some of the investigated systems (**11**, **13a/b**, and **14a/b**) various conformations were considered. Cp_2ZrX^+ systems, calculated at the same level of theory, were included here for comparison.

Results and Discussion

Table 1 collects the (free) energies of the ethene complexes and transition states for ethene insertion relative to the free reactants.

General Trends. In most cases the ethene π-adducts were unstable to ligand dissociation and only weak Van der Waals complexes (not included in Table 1) were obtained. Even in cases where an ethene π-complex could be identified, entropy effects caused most of these to be higher in free energy than the separated reactants. The most notable exceptions in this respect are the cationic systems **13a** with a highly unsaturated Ti center due to the removal of one amido donor group. For the much less electrophilic neutral Ti^{III} analogues a stable

---

(5) Turculet, L.; Tilley, T. D. *Organometallics* **2004**, *23* (7), 1542–1553.

(6) (a) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162* (3), 165–169. (b) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102* (1), 346–354. (c) Ahlrichs, R.; Bär, M.; Baron, H.-P.; Bauernschmitt, R.; Böcker, S.; Ehrig, M.; Eichkorn; K.; Elliott, S.; Furche, F.; Haase, F.; Häser, M.; Hättig, C.; Horn, H.; Huber, C.; Huniar, U.; Kattannek, M.; Köhn, A.; Kölmel, C.; Kollwitz, M.; May, K.; Ochsenfeld, C.; Öhm, H.; Schäfer, A.; Schneider, U.; Treutler, O.; Tsereteli, K.; Unterreiner, B.; von Arnim, M.; Weigend, F.; Weis, P.; Weiss, H. *Turbomole*, Version 5; Theoretical Chemistry Group: University of Karlsruhe, Jan. 2002.

(7) (a) *PQS*, version 2.4; Parallel Quantum Solutions: Fayetteville, AK, 2001 (the Baker optimizer is available separately from PQS upon request). (b) Baker, J. *J. Comput. Chem.* **1986**, *7* (4), 385–395.

(8) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37* (2), 785–789. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98* (2), 1372–1377. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98* (7), 5648–5652. (d) All calculations were performed with the Turbomole functional “b3-lyp”, which is not identical with the Gaussian “B3LYP” functional.

(9) Schäfer, A.; Horn, H.; Ahlrichs, R *J. Chem. Phys.* **1992**, *97* (4), 2571–2577.

(10) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123–141.

(11) Schäfer, A.; Huber, C.; Ahlrichs, R *J. Chem. Phys.* **1994**, *100* (8), 5829–5835.

(12) *PC Spartan Pro*, version 1.0.3; Wavefunction Inc.: 18401 Von Karman Ave., Suite 370, Ivrine, CA 92612, Jan. 2000.

(13) Frequencies below a threshold of 11 cm^{-1} were smoothly adjusted to a value remaining above 10 cm^{-1} to avoid artificial “blow-up” of the entropic correction for very low frequencies, for which the harmonic oscillator model is no longer appropriate.

Table 1. Electronic Energies (*E*) and Free Energies (*G*) for Ethene Complexes and Insertion Transition States (kJ/mol), Relative to the Separated Reactants

system	$\Delta E(C_2H_4)$	ΔE(TS)	$\Delta G(C_2H_4)$	ΔG(TS)
1-H	*a*	17.2	*b*	*b*
2-H	*a*	18.4	*b*	*b*
3-H	2.3	22.9	32.8	67.6
4-H	−10.4	19.8	28.0	65.6
5-H	*a*	17.0	*a*	61.5
6-H	−7.3	26.1	25.7	72.2
7-H	*a*	54.1	*a*	107.2
8-H	*a*	29.0	*a*	78.1
9-H	*a*	36.7	*a*	84.1
10-H	−20.6	−12.3	26.3	39.6
11-H	*a*	38.9	*a*	91.7
12-H	*a*	13.7	*a*	69.3
13a-H	−101.5	−80.7	−57.1	−34.8
13b-H	−70.5	−40.9	−8.0	6.1
14a-H	−46.5	−42.3	−2.5	7.8
14b-H	−50.0	−21.0	−6.9	21.4
1-Me	*a*	117.8	*b*	*b*
2-Me	*a*	112.1	*b*	*b*
3-Et	*a*	113.1	*a*	171.0
4-Et	−6.5	83.5	30.5	139.0
5-Et	*a*	79.7	*a*	143.4
6-Et	*a*	95.0	*a*	151.3
7-Et	*a*	130.5	*a*	190.9
8-Et	*a*	96.5	*a*	157.3
9-Et	*a*	99.6	*a*	161.5
10-Et	*a*	110.5	*a*	168.7
11-Et	*a*	110.3	*a*	169.3
12-Et	*a*	70.7	*a*	136.2
13a-Et	−78.4	−34.2	−31.5	25.2
13b-Et	−60.1	33.6	5.4	86.7
14a-Et	−13.5	39.9	36.3	101.9
14b-Et	−39.0[c]	41.5	4.7	95.6
15a-Et	*b*	58.2	*b*	*b*
15b-Et	*b*	27.0	*b*	*b*
16-Et	*b*	31.5	*b*	*b*
$\mathbf{Cp_2Zr}$-H	−87.9	−87.6	−42.1	−38.4
$\mathbf{Cp_2Zr}$-Et	−38.0	−1.2	17.5	65.9

[a] No ethene π-complex found. [b] Not calculated. [c] OMe dissociated from Ti.

Table 2. Energy Barriers for Ethene Insertion (kJ/mol)

insertion in M−H			insertion in M−C		
system	$\Delta E^{\ddagger}$(ins)	$\Delta G^{\ddagger}$(ins)	system	$\Delta E^{\ddagger}$(ins)	$\Delta G^{\ddagger}$(ins)
1-H	17.2	*a*	**1**-Me	117.8	*a*
2-H	18.4	*a*	**2**-Me	112.1	*a*
3-H	22.9	67.6	**3**-Et	113.1	171.0
4-H	30.2	65.6	**4**-Et	90.0	139.0
5-H	17.0	61.5	**5**-Et	79.7	143.4
6-H	33.4	72.2	**6**-Et	95.0	151.3
7-H	54.1	107.2	**7**-Et	130.5	190.9
8-H	29.0	78.1	**8**-Et	96.5	157.3
9-H	36.7	84.5	**9**-Et	99.6	161.5
10-H	8.3	39.6	**10**-Et	110.5	168.7
11-H	38.9	91.7	**11**-Et	110.3	169.3
12-H	13.7	69.3	**12**-Et	70.7	136.2
13a-H	20.8	22.3	**13a**-Et	44.2	56.7
13b-H	29.6	14.1	**13b**-Et	93.7	86.7
14a-H	4.2	10.3	**14a**-Et	53.4	101.9
14b-H	29.0	28.3	**14b**-Et	80.5	95.6
			15a-Et	58.2	*a*
			15b-Et	27.0	*a*
			16-Et	31.5	*a*
Cp_2Zr−H	0.3	3.7	Cp_2Zr-Et	36.8	65.9

[a] Not calculated.

π-adduct is found only for the hydride **13b**-H; even here, the free energy is computed to be only 8 kJ/mol lower than that of the separated reactants (cf. 57.1 kJ/mol for the π-complex of cationic **13a**-H). The only other modifications for which stable but weak π-complexes are found are **14a** and **14b** in which the electrophilicity of the Ti center is increased by replacing one of the NMe groups by a much more weakly coordinating OMe group. Table S1 in the Supporting Information shows that the remaining N−Ti−N angle significantly increases as a result of the NMe → OMe substitution, creating a much more open metal center opposite to the OMe group. It is therefore not surprising that the most stable conformations of the π-complexes of **14a** and **14b** have a trigonal bipyramidal structure with the OMe group in the apical position, trans to the ethene ligand.

The free energies of the transition states for ethene insertion (relative to the separated reactants) reveal a similar trend as the complexation energies. Much lower ΔG(TS) values are obtained for the highly unsaturated systems **13a/13b** and for modifications **14a/b** bearing a weakly coordinating OMe group.

Table 2 gives the energy barriers for ethene insertion. As most of the ethene π-complexes were found to be unstable this barrier is mostly given by the difference in (free) energy between the transition state for ethene insertion and the separated reactants, i.e. $\Delta E^{\ddagger}(\text{ins}) = \Delta E(\text{TS})$ and $\Delta G^{\ddagger}(\text{ins}) = \Delta G(\text{TS})$. In those cases where the ethene complex is stable to dissociation, $\Delta E^{\ddagger}$(ins) and $\Delta G^{\ddagger}$(ins) are respectively given by $\Delta E(\text{TS}) - \Delta E(C_2H_4)$ and $\Delta G(\text{TS}) - \Delta G(C_2H_4)$.

Ti- and Zr-Complexes with the [*cis,cis*-1,3,5-(3,5-^{t}Bu$_2$C$_6$H$_3$-N)$_3$C$_6$H$_9$]$^{3-}$ Ligand (1, 2). For the Ti- and Zr-complexes with the complete ligand **L**, our b3-lyp/SV(P) calculations reveal a much higher barrier for ethene insertion in the M−C than in the M−H bond. This difference is consistent with literature results for metallocenes and other polymerization catalysts, where uniformly insertion in M−H is easier than in M−C.[14,15] However, the *absolute* barriers for both insertion reactions are remarkably high in the present case. For active polymerization catalysts, calculated barriers for insertion in the gas phase are so low that other elementary reaction steps than insertion were suggested to be rate determining.[16] For such systems, the *real* propagation barriers may be affected strongly by the presence of solvent and counterions and no clear correlation between gas-phase barriers and observed activity can be expected. However, when gas-phase insertion barriers are already prohibitive ($\Delta G^{\ddagger}(\text{ins}) > 100$ kJ/mol) it seems very likely that the rate of propagation will be determined by the insertion step itself and the system will not be active in polymerization regardless of solvent and counterion effects. Our b3-lyp/SV(P) results for systems **1** and **2** thus seem to agree with the experimental fact that ethene insertion is observed in the M−H but not in the M−C bonds of these complexes.

Tilley and co-workers invoked steric crowding at the metal center as a result of dimer formation or coordination of additional donor functionalities as a possible explanation for the low reactivity of complexes **1** and **2**.[5] Although this is probably a contributing factor, the results of Table 1 indicate that low reactivities are also expected when these effects are negligible.

---

(14) Thorshaug, K.; Støvneng; J, A.; Rytter, E.; Ystenes, M. *Macromolecules* **1998**, *31* (21), 7149–7165.

(15) Yoshida, T.; Koga, N.; Morokuma, K. *Organometallics* **1995**, *14* (2), 746–758.

(16) See e.g.: (a) Nifant'ev, I. E.; Ustynyuk, L. Y.; Laikov, D. N. *Russ. Chem. Bull.* **2000**, *49*, 1735. (b) Vanka, K.; Xu, Z.; Seth, M.; Ziegler, T. *Top. Catal.* **2005**, *34* (1–4), 143–164.

Complexes with the Smaller Ligands [*cis*,*cis*-1,3,5-(MeN)$_3$-C$_6$H$_9$]$^{3-}$ (3, 4), [*cis*,*cis*-1,3,5-(HN)$_3$C$_6$H$_9$]$^{3-}$ (5), and [*cis*,*cis*-1,3,5-O$_3$C$_6$H$_9$]$^{3-}$ (6). When reducing the steric hindrance in **1** and **2** by replacing the bulky aryl groups by much smaller methyl groups (**3** and **4**) or hydrogen atoms (**5**) the energy barrier for insertion in the M−H bond is hardly affected whereas the barrier for insertion in the M−C bond is lowered somewhat (by ca. 20 kJ/mol). However, even for the all-hydrogen ligand **5** the M−C insertion barrier remains significantly larger than for metallocenes ($\Delta G^{\ddagger}$(ins) = 143.4 kJ/mol versus only 65.9 kJ/mol for Cp$_2$Zr). The complete removal of the substituents by going to trisalkoxide **6** even leads to a small *increase* of the free energy barrier to 151.3 kJ/mol. It is thus clear that the experimentally observed low reactivity of complexes **1** and **2** cannot simply be explained by steric hindrance.

Complexes with the Flexible Ligands [*cis*,*cis*-1,3,5-(MeNCH$_2$)$_3$C$_6$H$_9$]$^{3-}$ (7), [*cis*,*cis*-1,3,5-(HNCH$_2$)$_3$C$_6$H$_9$]$^{3-}$ (8), and (NH$_2$)$_3$$^{3-}$ (9). Tilley and co-workers indicated the importance of a rigid cyclohexane backbone to create a sufficiently "open" coordination sphere, leaving the electrophilic metal center accessible to small reactants.[5] The introduction of methylene bridges between the coordinating nitrogen atoms and the cyclohexane backbone (**3** → **7**, **5** → **8**) and the complete removal of the cyclohexane backbone (**5** → **9**) demonstrate the importance of this rigidity: insertion barriers increase by ca. 20 kJ/mol for these more flexible systems. Table S1 in the Supporting Information reveals that both modifications have a significant effect on the N−Ti−N angles of the Ti−H and Ti−Et starting complexes. These increase from ca. 96° to ca. 103° for modifications **7** and **8** and to ca. 113° for modification **9**. Consequently, in accordance with the suggestion by Tilley and co-workers,[5] the Ti center of the Ti−H and Ti−Et complexes of variants **7**−**9** is less easily accessible for the ethene monomer than the Ti center of modifications **3** and **5**.

Complexes with the Less Donating Ligand [*cis*,*cis*-1,3,5-(CF$_3$N)$_3$C$_6$H$_9$]$^{3-}$(10). Increasing the electrophilicity of the metal center by replacing the methyl groups in modification **3** by electron-withdrawing CF$_3$ groups (**10**) leads to a decrease of the energy barrier for insertion in the Ti−H bond by ca. 30 kJ/mol but has a negligible effect on the barrier for insertion in the Ti−Et bond. For the latter case, partial compensation of increased electrophilicity by simultaneously increased steric hindrance might have occurred. In any case, a significant lowering of the barrier for insertion in the metal−alkyl bond requires more than simple steric effects or addition of electron-withdrawing substituents.

Addition of an NH$_3$ Ligand (11, 12). We speculated that the requirement in complexes **1–10** to form a 5-coordinate intermediate might be a reason for the high insertion barriers. Both Ti and Zr typically prefer 4- or 6-coordination to a 5-coordinate environment. Therefore, we added an extra donor molecule (NH$_3$) to **3** (to give **11**) and **5** (to give **12**). In this way, the metal center starts out in a 5-coordinate geometry and achieves its (presumably more favorable) coordination number of six upon coordination of ethene. As shown by Table 2, however, this does not result in a strong binding of the olefin, or in significant reduction of the barrier heights for ethene insertion.

Removal of One of the NMe Groups (13a, 13b). Instead of *adding* a ligand to obtain a less favorable ligand environment around Ti, we also investigated the effect of *removing* one of the Ti−N bonds, thereby obtaining a three-coordinated starting complex (**13**), which could be either cationic (d^0 Ti^{IV}) or neutral (d^1 Ti^{III}).

The effect of the increased electrophilicity in **13a**-Et is clearly indicated by the presence of a Ti−H$_\beta$-agostic interaction, similar to that commonly observed in metallocene alkyl cations; such interactions are not seen in any of the neutral complexes studied here. Moreover, this cationic modification leads to a dramatic reduction of the ethene insertion barriers. On going from variant **3** to variant **13a** we find a reduction from 67.6 to 22.3 kJ/mol for insertion in Ti−H, and from 171.0 to only 56.7 kJ/mol for insertion in Ti−Et. This is not just a charge effect, as a significant reduction of the insertion barriers is also obtained for the neutral variant **13b**. Creating an unsaturated Ti center is thus more important than making this Ti center positively charged.

Substitution of One of the NMe Groups by OMe (14a, 14b, 15a, 15b, 16). A less draconian way of creating a more unsaturated Ti center than complete removal of a donor group is replacement of one of the amido groups by a more weakly coordinating OMe group (**3** → **14**). Again, the result of this substitution is a cationic d^0 Ti^{IV} complex (**14a**) or a neutral d^1 Ti^{III} system (**14b**). As indicated above, this substitution results in a more easily accessible Ti center opposite to the OMe group, as the remaining N−Ti−N angle significantly increases. Except for the **14b**-Et system, this also appears to be the most favorable side for the incoming ethene, i.e., the transition state for ethene insertion is more stable when the ethene monomer is opposite the OMe group than opposite one of the NMe groups. As the Ti−OMe bond is weaker than the Ti−NMe bond it can also more easily respond to the incoming ethene. This can clearly be seen from the change of the Ti−OMe and Ti−NMe distances during the insertion process. For both **14a** and **14b**, going from the hydride or ethyl starting complex to the corresponding transition state results in larger changes in the Ti−O than in the Ti−N distances. It is thus not surprising that modifications **14a** and **14b** result in lower insertion barriers than those for system **3** but higher than those for the cationic and neutral modifications **13**. For insertion in the Ti−C bond the $\Delta G^{\ddagger}$(ins) values are calculated to be 171.0, 101.9, 95.6, 56.7, and 86.7 kJ/mol for **3**, **14a**, **14b**, **13a**, and **13b** respectively (Table 2). The $\Delta E^{\ddagger}$(ins) values indicate a similar energetic effect for the original Tilley systems, i.e., on going from **1** to **15** or **2** to **16**.

Analysis of the Ligand Effects. To transform the original Tilley systems **1** and **2** into an active polymerization catalyst a significant lowering of the ethene insertion barrier in the M−alkyl bond would be required. On the basis of our DFT results described above, neither reducing the steric bulk nor adding electron-withdrawing substituents at nitrogen is predicted to have a large impact. Rather, it seems essential to increase the electrophilicity of the metal center by removing one amide donor completely (**13a/b**) or replacing it by a much weaker donor (e.g., an ether group as in **14a/b**, **15a/b**, and **16**). Using as a quantitative measure of the electrophilicity of the metal center the complexation energy of the probe molecule ammonia (as in our previous work on the hydrogen sensitivity of olefin polymerization catalysts[17]), we indeed find that the metal center of modifications **13–16** is significantly more electrophilic than in any of the other variants (Table 3). For the cationic complex **13a**-Et an even larger NH$_3$ complexation energy is obtained than for the Cp$_2$Zr system. Furthermore, the NH$_3$ complexation energy shows a clear correlation with the energy barriers for ethene insertion (Figure 3): with increasing electrophilicity insertion becomes easier. It can thus be concluded that the ethene

---

[17] Friederichs, N.; Wang, B.; Budzelaar, P. H. M.; Coussens, B. B. *J. Mol. Catal. A* **2005**, *242* (1–2), 91–104.

Table 3. Binding Energies, $\Delta E_b(NH_3)$, and Free Energies, $\Delta G_b(NH_3)$, for the Probe Molecule Ammonia (kJ/mol)

	$\Delta E_b(NH_3)$	$\Delta G_b(NH_3)$
1-Me	81.9	*a*
2-Me	73.7	*a*
3-Et	49.4	−3.8
4-Et	73.6	24.5
5-Et	62.2	8.8
6-Et	69.0	17.4
7-Et	28.9	−24.8
8-Et	48.2	−4.1
9-Et	36.8	−16.2
10-Et	80.9	26.3
11-Et	32.4	−19.6
12-Et	49.7	−6.2
13a-Et	185.5	137.8
13b-Et	93.7	49.6
14a-Et	123.3	66.4
14b-Et	95.5	40.9
15a-Et	122.7	*a*
15b-Et	151.3	*a*
16-Et	138.9	*a*
Cp_2Zr-Et	153.9	94.8

[a] Not calculated.

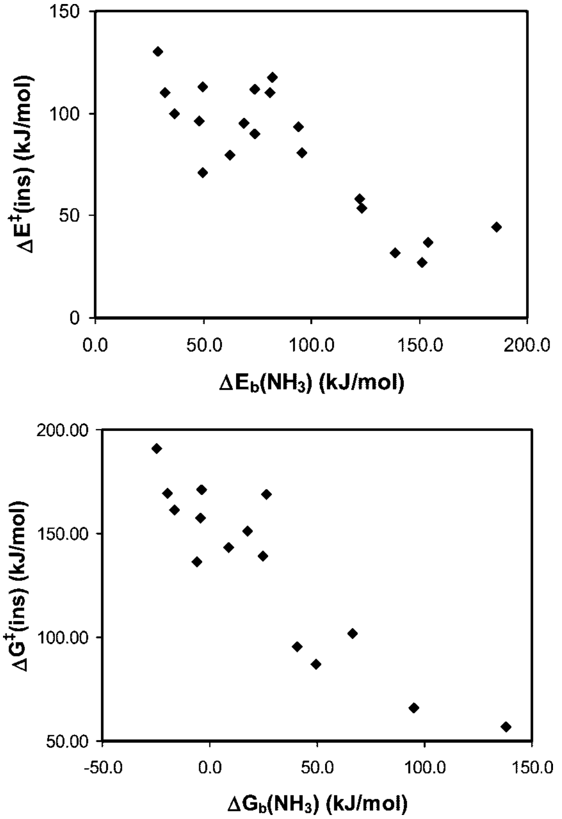

Figure 3. Ethene insertion barriers versus ammonia binding energies.

insertion barriers are dominated by the electrophilicity of the metal center, steric effects playing only a secondary role. The $\Delta E_b(NH_3)$ values of Table 3 also parallel the ethene complexation energies of Table 1 (where these could be calculated). Roughly speaking, the ethene insertion barriers thus decrease with increasing complexation energy of the ethene monomer.

Interestingly, the olefin polymerization activity of complexes similar to system **13a** has been investigated by MConville and co-workers.[18] They found that complexes of the type $[ArN(CH_2)_3NR]TiMe_2$ (Ar = 2,6-$^i Pr_2C_6H_3$ or 2,6-$Me_2C_6H_3$), when activated with methyl aluminoxane (MAO), form highly active catalysts for the polymerization of 1-hexene. Also, a mixture of equimolar amounts of these Ti dimethyl complexes and $B(C_6F_5)_3$ catalyzes the living aspecific polymerization of α-olefins at room temperature.[19] Donor group removal thus seems to be a viable strategy for increasing the activity of metal alkyls.

Conclusions

The reactivity toward ethene insertion of Ti and Zr complexes with the aryl-substituted tripodal triamido ligand derived from *cis*,*cis*-1,3,5-triaminocyclohexane (Figure 1) as reported by Tilley and co-workers[5] and various modifications thereof has been investigated by means of density functional computations. For the Ti- and Zr-complexes with the $[cis,cis\text{-}1,3,5\text{-}(3,5\text{-}^tBu_2C_6H_3N)_3C_6H_9]^{3-}$ ligand the computational results agree with the experimental observation that insertion is possible in the metal−hydride but not in the metal–carbon bonds. The barriers for ethene insertion become even higher when reducing the rigidity of the triamido ligand by the introduction of methylene bridges between the coordinating nitrogen atoms and the cyclohexane backbone or replacing the cyclohexane-based ligand by three NH_2 groups. They can be lowered somewhat by reducing the steric bulk of the triamido ligand; however, even in the absence of any steric hindrance the barrier for insertion in the metal–carbon bond remains very high and no polymerization activity is expected. A significant reduction of this ethene insertion barrier was obtained only when removing one of the coordinating nitrogen atoms (leading to a chelating *di*amide) or replacing it by a more weakly coordinating –OMe group. Both the cationic d^0 and neutral d^1 variants of the latter compounds may be active polymerization catalysts. The ethene insertion barrier appears to be dominated by the electrophilicity of the metal center, quantified as the binding energy of the probe molecule ammonia, and roughly parallels the complexation energy of the ethene monomer.

Acknowledgment. The authors thank the management of Sabic and DSM for their permission to publish this work.

Supporting Information Available: A table giving relevant bond distances, bond angles, and torsion angles of M−H and M−Et (M = Ti, Zr) starting complexes, tables giving electronic energies, zero point vibrational energies, enthalpy, and entropy corrections (273.15 K, 1 bar), Cartesian coordinates of minima and transition states, and a figure comparing calculated free energy barriers for ethene insertion at the b3-lyp/SV(P) and b3-lyp/TZVP//SV(P) level. This material is available free of charge via the Internet at http://pubs.acs.org.

OM7010744

---

(18) Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29* (15), 5241–5243.

(19) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118* (41), 10008–10009.