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Ethene Polymerization at Cationic Aluminum Amidinate and Neutral Aluminum Alkyl. A Theoretical Study

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The effect of substituent variation on olefin insertion and chain transfer in cationic aluminum amidinate alkyls $[R^1C(NR^2)_2AlEt]^+$ was studied by theoretical methods. Introduction of bulky substituents at C (*t*-Bu) and N (*i*-Pr) favors insertion more than chain transfer, but the system still keeps a clear preference for chain transfer, and even the full system $[t\text{-BuC}(Ni\text{-Pr})_2AlEt]^+$ is predicted *not* to polymerize ethene. Changing to a neutral analogue (as in $H_2C(NH)_2AlEt$) and relieving the geometric constraints (in Me_2AlEt) favor insertion even more, so that trialkylaluminum is finally predicted to have a clear preference for oligomerization.

Introduction

There has always been a close relationship between ethene oligomerization at aluminum and polymerization at transition metals. Ethene oligomerization at Al (the "Aufbau" reaction) has been known for a long time.[1] In fact, transition metal (TM) catalyzed olefin polymerization was discovered serendipitously as a result of a systematic study of the Aufbau reaction.[2] In TM catalyzed polymerization, aluminum alkyls continue to play a prominent role as activators and scavengers.[3] Even though TM polymerization and oligomerization have far outgrown the Al process in importance, the latter continues to be used for the preparation of medium-sized alcohols.

Although aluminum compounds are usually assumed to produce ethene *oligomers* only, there have also been reports of formation of high-MW *polymers* at aluminum. One early report mentions polymerization with simple aluminum trialkyls.[4] Recently, Jordan proposed cationic aluminum amidinate species as well-defined ethene polymerization catalysts,[5] although later the reaction of the aluminum dialkyl precursor with the borane activator was shown to be more complicated,[6] and the nature of the active species remains unclear. Cationic troponiminate aluminum alkyls were also shown to polymerize ethene.[7] Very recently, Sen reported polymerization with aluminum alkyls activated with $B(C_6F_5)_3$.[8] The prospect of using simple and inexpensive aluminum compounds as polymerization catalysts has led to a revival of interest in aluminum alkyls.[9−11]

We have recently reported[12−15] on the competition between chain transfer and propagation in a prototypical "Jordan" catalyst, $[HC(NH)_2AlEt]^+$ (**1a**). The results were found to be rather sensitive to the theoretical method used, but *all methods* agree that chain transfer is much easier than propagation in this system

This would seem to argue against the involvement of **1** as the active species in the Jordan system. However, studies by Ziegler on transition metal systems have demonstrated that substituents can play a crucial role in changing the balance between chain transfer and propagation.[16,17] The substituents in the real Jordan system (**1c**) are rather bulky, so it is conceivable that

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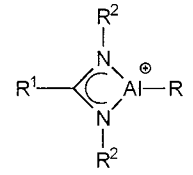
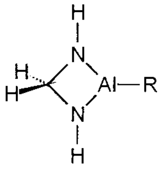


$R^1 = R^2 = H$ **1a**
$R^1 = H, R^2 = i\text{-Pr}$ **1b**
$R^1 = t\text{-Bu}, R^2 = i\text{-Pr}$ **1c**



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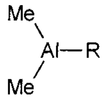

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they play an important role in this system too. Therefore, we decided to extend our earlier work to include the complete "catalyst" **1c**. This provides us with a clear picture of the importance of substituent effects. In addition, we studied two neutral analogues of **1**, viz., **2** and **3**. This allows an assessment of the effects of charge and geometry on the insertion and chain-transfer steps. Surprisingly, and in contrast to the suggestions reported in the literature,[5,18] we find that the positive charge in **1** does *not* lead to a better polymerization catalyst.

Methods

All calculations were carried out with the GAMESS−UK[19] and Gaussian 94/98 series of programs.[20] Geometries for species derived from **1a**, **2,** and **3** were fully optimized at the MP2[21] and B3LYP levels[22] using the 6-31G(d) basis set.[23] Improved single-point energies were then calculated at the same level with the 6-311G-(d,p) basis set. For the larger systems **1b** and **1c**, geometries were optimized at the B3LYP level, using the 3-21G basis for the *i*-Pr and *t*-Bu substituents and 6-31G(d) for the remaining atoms; single-point MP2 and B3LYP energies were then calculated with the 6-311G-(d,p) basis. All energies reported in the text have been corrected for BSSE. The nature of all optimized transition states was checked by a vibrational analysis. Geometries and energies for **1b**,**c** and **2** are given in the Supporting Information; the corresponding data for **1a** are taken from ref 12; geometrical details for **3** will be reported separately.[25]

Results and Discussion

General. In a previous paper,[12] we showed that the two most important reactions of the system **1a** + ethene are hydrogen transfer (from ethyl to ethene) and ethene insertion in the Al−Et bond. Alternative chain-transfer mechanisms (β-elimination, σ-bond metathesis) are much more difficult and cannot compete. A high tendency to β-hydrogen transfer in cationic aluminum alkyls has also been observed experimentally. We found the same preference, though less pronounced, for the neutral systems studied in the present work.[26] Since β-elimination is unimolecular, while both propagation and β-hydrogen transfer are bimolecular, it is still possible that β-elimination becomes the dominant chain-transfer mechanism under conditions of low monomer concentration and high temperature. We will return to this point at the end of the discussion. Until then, we will only discuss the balance between propagation and β-hydrogen transfer, precisely because this does not depend on the reaction conditions and thus sets an upper limit for the average molecular weight.

Propagation (insertion) follows the standard path via a π-complex and a four-center transition state, similar to that observed with transition metal compounds. Hydrogen transfer to monomer proceeds via a six-center cyclic transition state in which there is no direct interaction between the metal and the hydrogen being transferred; this is very different from the situation in transition metal systems, where the transition state has a short metal−hydrogen distance.[16,17] These factors were all found to be similar for the three systems **1**−**3**.

Calculated barriers for the aluminum system are rather sensitive to the theoretical method employed and—to a lesser extent—to the size of the basis set.[12,13] The MP2/6-31G(d) barriers were found to be too high by 3−4 kcal/mol, relative to the estimated CCSD(T)/6-311+G(2df,2pd) values; the B3LYP/6-31G(d) value for the insertion barrier is very close to the best estimate, while the B3LYP chain-transfer barrier is too low by 5 kcal/mol. Density functional theory (DFT) methods in general tend to underestimate the barriers for hydrogen transfer.[27] In the present work, we give both MP2/6-311G(d,p) and B3LYP/6-311G(d,p) barriers. The MP2 values should give the most reliable *relative* barriers, while on average the B3LYP values might be better in *absolute* terms.

Substituent Effects in 1. Table 1 compares calculated insertion and chain-transfer barriers for three systems **1a**−**c** of increasing steric bulk. Ligand bulk is expected to destabilize the olefin complex, thus lowering the barriers for both reactions. The C−Al−C angle in the TS for chain transfer is slightly larger than that in the propagation TS, and the large Al−C−C angles in the chain-transfer TS also cause more steric interaction of the ethene α hydrogens with substituents at N, so

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[26] β-Elimination *does* become easier for neutral systems. The reaction remains highly endothermic because of the unfavorable formation of a terminal Al−H bond, but this would be trapped by free olefin or stabilized by dimer formation. More complicated dinuclear elimination mechanisms, in which a more favorable bridging hydride is directly formed, are also conceivable. We decided not to include such mechanisms in the present study.

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Table 1. Energy Profiles (kcal/mol) for Ethene Insertion and Chain Transfer in 1a–1c[a]

	1a		**1b**		**1c**	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
reactants	18.4	15.9	16.3	13.1	14.0	9.2
π-complex	0	0	0	0	0	0
chain-transfer TS	21.6	16.2	24.2	18.6	25.1	18.9
insertion TS	29.1	27.6	27.7	26.5	28.9	27.7
insertion Product	11.2	7.9	11.6	9.3	16.5	12.8
ΔE (transfer/prop)	7.5	11.4	3.5	7.9	3.8	8.8

[a] For details of the calculations, see Methods.

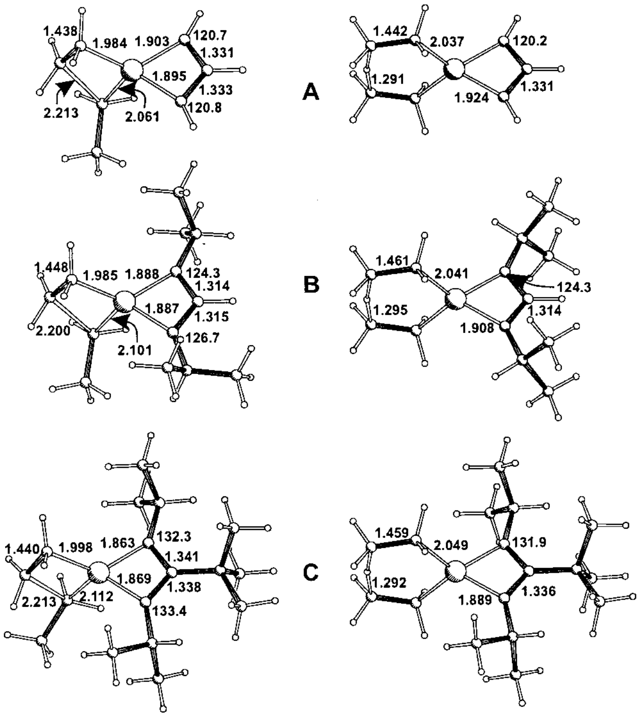

Figure 1. Ethene insertion (left) and chain-transfer (right) transition states for (A) **1a** (MP2/6-31G(d) optimized), (B) **1b**, and (C) **1c** (B3LYP/3-21G,6-31G(d) optimized). Bond lengths, Å; angles, deg.

ligand bulk should selectively favor propagation. Indeed, we find that, on going from **1a** to **1b**, the barrier for chain transfer *increases*, while that for propagation *decreases*. The net result is a shift of 3–4 kcal/mol in the direction of propagation, which is significant but not enough to tip the balance toward propagation. Going from **1b** to **1c**, the complexation energy decreases even more, but the barriers for insertion and chain transfer hardly change. Apparently, the effect of adding the *t*-Bu group is rather indiscriminate. In any case, we arrive at the definite prediction that **1c** is *not* a polymerization catalyst.

The effect of increasing steric bulk is clearly illustrated in the insertion transition states shown in Figure 1. Going from **1a** to **1b**, the isopropyl substituents cause an opening of the C–N–(H/C) angles at the amidinate ligand from 121 to 125°; the latter value is close to that reported for $MeC(NCy)_2AlMe_2$ (125°) and $MeC(N\textit{i}\text{-}Pr)_2AlCl_2$ (126°).[9] Since the ethyl and ethene moieties at Al need so little space, the only possible steric hindrance in the insertion TS is between the ethyl CH_3 group and one *i*-Pr group; Figure 1B shows how this is avoided by rotation of the *i*-Pr group. Introduction of the *t*-Bu group at carbon opens the C–N–C angles even more to 133°, similar to the values reported for $t\text{-}BuC(NCy)_2AlMe_2$ (132° average) and $t\text{-}BuC(N\,\textit{i}\text{-}Pr)_2AlCl_2$ (133°). This enforces an orientation of the *i*-Pr groups such that all methyl groups point toward the other substituents at Al. Thus, repulsion between the *i*-Pr group and the ethyl CH_3 group can no longer be avoided. As Figure 1C shows, this results in a rotation of the whole ethyl group to a less favorable orientation, and this is probably the main reason for the higher insertion barrier. The increased steric hindrance in **1c** is most clearly illustrated by the shortest nonbonded Me(Et)–Me(*i*-Pr) C–C distance, which decreases from 4.94 Å in **1b** to 4.44 Å in **1c**, even though the Et group has rotated to avoid the *i*-Pr group.

Neutral vs Cationic Systems. To assess the importance of the positive charge in **1**, we have also carried out a series of calculations on neutral analogue **2**. The calculated insertion barrier (see Table 2) is somewhat higher (≈4 kcal/mol) for this system than for **1a**. Surprisingly, the calculated chain-transfer barrier is *much* higher (by ≈12 kcal/mol)! For this system, chain transfer and propagation are close in energy, and the inclusion of substituent effects might result in a (small) preference for poly- or at least oligomerization. So, in contrast to the suggestion by Jordan, the positive charge in **1** is not beneficial to polymerization: it lowers the barrier for chain transfer more than for propagation. It should be noted that the β-elimination reaction is indeed more difficult in charged species **1** than in neutral **2**. Since, however, β-elimination is not the dominant chain-transfer process with either **1** or **2**, this is not relevant here.

Geometry Effects. Both **1** and **2** are strained systems, with an N–Al–N angle constrained to ca. 70–80°. For comparison, we have studied insertion in unstrained Me_2AlEt (**3**), a model for the original “Aufbau” reaction. The release of steric constraints in **3** results in a significant lowering of the insertion barrier by ca. 11 kcal/mol relative to **2** (7 kcal/mol relative to **1a**). Surprisingly, the chain-transfer barrier hardly changes from its value in **2**, and so remains much higher than in **1**. This can be rationalized as follows. The opening of the L–Al–L angle in the series **1a** (≈70°), **2** (≈80°), **3** (≈120°) is accompanied by a compensating *decrease* of the C–Al–C angle at the transition states. This appears to have a beneficial effect for the insertion TS, since a smaller C–Al–C angle is more easily accommodated in the four-center TS. For the six-center hydrogen-transfer TS, however, a smaller C–Al–C angle is not favorable. A clear correlation between the C–Al–C angle at the insertion TS and the chain-transfer/insertion barrier difference ΔE is seen in Figure

Table 2. Energy Profiles (kcal/mol) for Ethene Insertion and Chain Transfer in 1a, 2 and 3[a]

	1a		2		3	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
reactants	18.4	15.9	2.7	0.2	5.2	2.0
π-complex	0	0	0	0	0	0
chain-transfer TS	21.6	16.2	31.9	29.1	30.5	28.2
insertion TS	29.1	27.6	33.1	33.3	21.9	23.2
insertion Product	11.2	7.9	23.3	22.6	21.5	19.1
ΔE (transfer/prop)	7.5	11.4	1.2	4.2	8.6	5.0

[a] For details of the calculations, see Methods.

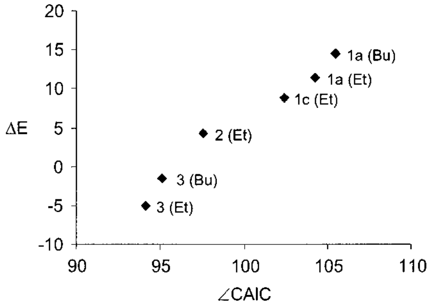

Figure 2. Dependence of the ethene chain-transfer/propagation barrier difference (ΔE, kcal/mol) on the C−Al−C angle (deg) at the insertion TS.

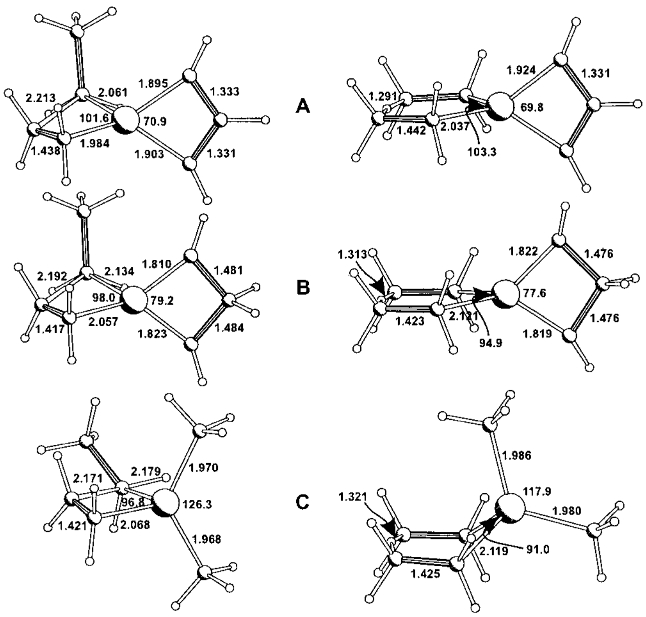

Figure 3. Propagation (left) and chain-transfer (right) transition states for (A) **1a**, (B) **2**, and (C) **3**. Bond lengths (Å) and angles (deg) are for MP2/6-31G(d) optimized geometries.

2. We stress this almost linear correlation must in part be fortuitous; electronic factors should also be important.

The chain-transfer TS derived from **1** and **2** has a planar, C_{2v}-symmetric Al(C−C)$_2$H skeleton, as shown in Figure 3A,B. The smaller C−Al−C angle in the TS for **3** results in a nonplanar structure in which the Al-(C−C)$_2$H ring adopts an envelope conformation (Figure 3C). In this way the nearly linear C−H−C arrangement of **1a** and **2** can be preserved, but only at the expense of a twisted H−C−C−Al fragment.

Comparison with Experimental Aufbau Reaction Data.[25] Me$_2$AlEt is predicted to have a clear preference for insertion over hydrogen transfer (see Table 2), in agreement with the observation of olefin oligomerization in the Aufbau reaction. Comparison of our results with experimental data is complicated by the occurrence of monomer−dimer equilibria for R$_3$Al species, differences between solution and gas-phase chemistry, and the (possible) competition of β-elimination as a chain-transfer process.

The activation energy for insertion of ethene in monomeric R$_3$Al in the gas phase has been estimated by Egger as 17.6 ± 1.4 kcal/mol (R = Et) or 22.5 ± 0.5 kcal/mol (R = Me).[28] However, Egger also states that he believes the difference between these values to be too large. Therefore, it is probably more realistic to use an experimental value of 20 ± 2.5 kcal/mol (R = Me or Et).

Given the low R$_3$Al-olefin complexation energy of 2.0 (B3LYP) or 5.2 (MP2) kcal/mol, formation of the olefin complex will be uphill in the gas phase for entropy reasons. Therefore, the activation energy has to be calculated relative to the free reactants, which gives 16.7 (MP2) or 21.2 (B3LYP) kcal/mol. Extrapolation of the MP2 results to a better basis set, CCSD(T), and correction for zero point energy effects produces a “best estimate” 18.7 kcal/mol.[29] In view of the uncertainty in the experimental data, the agreement is satisfactory.

Experimentally, the molecular weight of the growing chain does not exceed 3000 (M_n; 100 bar, 100 °C),[30] which corresponds to a maximum chain length of slightly over 100 units. Under the conditions of the Aufbau process, two types of chain-transfer processes have to be considered: β-hydride elimination (unimolecular) and the β-hydrogen-transfer reaction we have concentrated on so far (bimolecular). Experimental results indicate that chain transfer (or “olefin displacement”) is unimolecular for β-branched aluminum alkyls in combination with substituted olefins,[31] suggesting that β-elimination is easier than hydrogen transfer. However, this combination of alkyl and olefin is the least favorable case for β-hydrogen transfer. For the combination of linear alkyls with ethene, which is the most favorable case, no direct mechanistic information is available. This means we cannot say a priori what the dominant chain-transfer step is under process conditions.

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[28] Egger, K. W. *J. Am. Chem. Soc.* **1969**, *91*, 2867. Egger, K. W. *J. Chem. Soc., Faraday Trans.* **1972**, *68*, 1017.

[29] Details of the extrapolation to CCSD(T)/6-311+G(2df, 2pd), ZPE corrections and the Et→Bu correction for system **3** are given in Table S1 of the Supporting Information.

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It is still useful to estimate the average molecular weight predicted for β-hydrogen transfer only, because this sets the upper limit for the average MW attainable in the Aufbau reaction. Since both propagation and hydrogen transfer pass through the same olefin complex, the choice of reference state (reactants or complex) does not affect the barrier difference. The most reliable value from our work for the difference between the two reactions should be the MP2/6-311G(d,p) value from Table 2 (8.6 kcal/mol). This has to be corrected for a number of factors studied in detail in our previous work on the cationic system:[12,29] zero point energy and thermal corrections (−3.3 kcal/mol at 100 °C); Bu vs Et chain (−2.9 kcal/mol); extrapolation to CCSD(T)/6-311+G(2df,2pd) (+0.7 kcal/mol).

Combination of these numbers produces a best estimate for $\Delta G^{\ddagger}_{373}$ of 3.1 kcal/mol, which would correspond to an average degree of polymerization of 70 units. Considering the nature of the approximations made, the agreement is excellent. It might still be that under the conditions of the Aufbau reaction β-elimination also contributes, but our results indicate that even if it could be suppressed (e.g. by going to higher ethylene pressures), the molecular weight could not get much higher because it would be limited by β-hydrogen transfer.

Conclusions

On the basis of our calculations, it seems unlikely that a species such as **1c** could be active in ethene polymerization. The insertion barrier is not prohibitively high, but chain transfer is always too fast, resulting in a dimerization catalyst at best. This is true even when ignoring zero point energy effects,[32] entropy contributions, and the effect of having a larger alkyl chain, all of which have been shown in this and earlier[12,13] work to favor chain transfer over propagation.

Both the positive charge and the geometric constraints in **1** contribute to this preference for chain transfer. Neutral, unstrained, monomeric aluminum alkyls should have both a clear preference for oligo-/polymerization and an insertion barrier that is lower than that of **1**.

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Supporting Information Available: Tables listing details of the energy corrections for insertion in **3** (Table S1), optimized geometries of the structures **1b**, **1c**, **2**, and energies for **1b**, **1c**, **2,** and **3** at various levels. This material is available free of charge via the Internet at http://pubs.acs.org.

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[32] Zero point energy corrections calculated for system **1b** further favor the chain termination vs insertion by 2.5 kcal/mol.