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Olefin Polymerization at Aluminum? A Theoretical Study

Giovanni Talarico* and Vincenzo Busico

Dipartimento di Chimica, Università degli Studi di Napoli, Federico II, Italy

Peter H. M. Budzelaar*

Department of Metal-Organic Chemistry, University of Nijmegen, Toernooiveld 1,
6525 ED Nijmegen, The Netherlands

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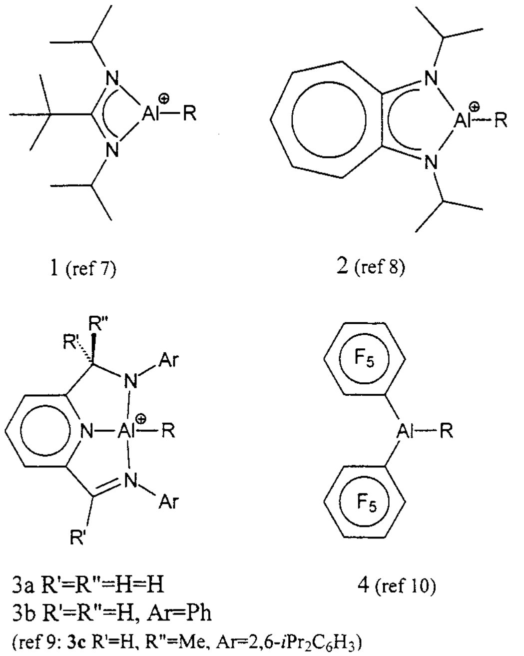
We have studied the balance between olefin insertion and β-hydrogen transfer to monomer for all "well-defined" aluminum polymerization catalysts reported to date. Consistently, the balance is predicted to be significantly worse than for Me_2AlEt, implying that *none* of the proposed active species should give a high-molecular-mass polymer. A more systematic analysis of ligand effects allows a rationalization of these results and shows that small modifications to the proposed active species are unlikely to solve the problem. We conclude that olefin polymerization at a single aluminum center is rather unlikely. Alternative interpretations of the experimental data are discussed.

Introduction

Olefin polymerization is traditionally associated with transition-metal catalysis: first classical Ziegler−Natta catalysts,[1] then metallocenes,[1,2] and more recently the Brookhart Ni and Pd α-diimine catalysts,[3] the Brookhart/Gibson pyridine-diimine Fe and Co systems,[4,5] and the Grubbs iminophenolate Ni catalysts.[6] Over the past few years, however, several reports have appeared describing ethene polymerization at apparently well-defined *aluminum* catalysts (Chart 1).[7−10] Obviously, such catalysts could be a very attractive alternative to those based on transition metals, because of catalyst cost and the simplicity of the ligands used (which would facilitate ligand tuning). Also, the fact that these catalysts do not require methylaluminoxane could be an important advantage. The possibly lower intrinsic activity of aluminum catalysts, compared to transition metals, might be acceptable under these circumstances.

Chart 1. Aluminum Polymerization Catalysts Studied



1 (ref 7)

2 (ref 8)

3a R'=R''=H=H
3b R'=R''=H, Ar=Ph
(ref 9: **3c** R'=H, R''=Me, Ar=2,6-iPr$_2$C$_6$H$_3$)

4 (ref 10)

After several years of intense study by a number of groups, however, there is still considerable doubt about the nature of the active species in each of the systems reported. In at least two cases (amidinates **1** and troponiminates **2**), the actual active species is *not* the three-coordinate $LArR^+$ species originally proposed.[11,12] Calculations also indicate that (amidinate)AlR^+ would not polymerize because chain transfer is too easy.[13,14]

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* To whom correspondence should be addressed. E-mail: G.T., talarico@chemistry.unina.it; P.H.M.B., budz@sci.kun.nl.

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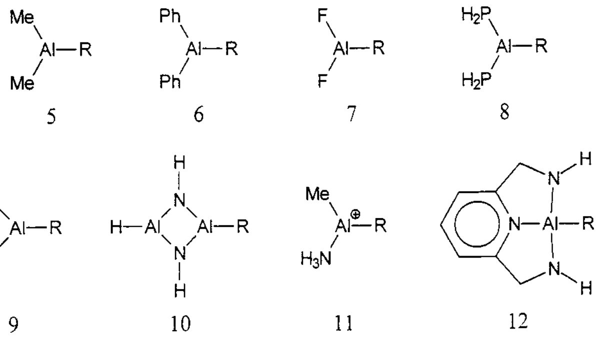
Chart 2. Aluminum Model Systems Studied



The group of Jordan, in particular, has gone to great lengths to rule out transition-metal contamination—the most obvious alternative explanation—but until the active species has been definitively pinned down, no possibility should be ruled out.

It is within this context that we embarked on a theoretical study of olefin polymerization at aluminum,[15] with a particular focus on the balance between insertion and chain transfer reactions. The aim was to elucidate the factors that determine this balance and, hence, help design new catalysts and possibly identify candidate active species in the existing catalytic systems. We naturally expected the study to agree with and aid the understanding of the experimental systems. In this particular case, however, we could not obtain a favorable balance between chain transfer and propagation for *any* of the “real” systems **1**−**4** (Scheme 1). This first led us to a more thorough investigation of the applicability of various ab initio and DFT methods (reported elsewhere[16,17]). Once we were satisfied that there was nothing wrong with our theoretical approach, we studied ligand effects in a more systematic fashion on the basis of selected, simple model systems (Chart 2). The results obtained for both model and real systems, reported here, form a consistent picture which does not, however, support the polymerization activity of any Al-containing active species proposed so far.

Methods

Geometries of all complexes were optimized at the MP2[18] or B3LYP[19] level[20] using the 6-31G(d) basis set.[21] Improved single-point energies were then calculated with the MP2/6-311G(d,p) basis set.[22] All calculations were carried with the GAUSSIAN-98[23] programs. All geometries were optimized as local minima or first-order saddle points (TS) without any symmetry restrictions, and the nature of each stationary point was checked by a frequency calculation. The reported energies include a zero-point energy correction (ZPE) but no thermal corrections.[24] Basis set superposition error (BSSE) was evaluated[25] at the olefin complex stage and assumed to be constant over the relevant reaction paths.

In earlier work, we used the following procedure to reproduce insertion and chain transfer barriers for Me_2AlEt to within ∼2 kcal/mol:[14,16] (a) optimize at either the MP2/6-31G(d) or B3LYP/6-31G(d) level;[20] (b) start with an MP2/6-311G(d,p) energy[26] at this geometry; (c) correct for contribution of higher excitations using CCSD(T)/6-31G(d);[27](d) correct for basis set extension using MP2/6-311+G(2df,2pd);[28,29] (e) correct for ZPE and thermal effects; (f) correct for chain extension from Et to *n*-Bu; (g) correct olefin complexation for BSSE.

For a number of other small model systems, we checked that the contributions of higher excitations, basis set extension, and chain extension are nearly constant relative to the MP2/6-311G(d,p) result, so that for *relative* values of the balance it suffices to compare insertion and hydrogen-transfer balance at the MP2/6-311G(d,p) level. In the present work, where we treat several rather large systems, we therefore used the following procedure: (a) optimize at either the MP2/6-31G(d) or the B3LYP/6-31G(d) level; (b) calculate MP2/6-311G(d,p) energy at this geometry; (c) correct for ZPE effects[24] at the B3LYP/6-31G(d) level; (d) correct olefin complexation for BSSE.

Of the factors left out, the largest is the Et to *n*-Bu chain extension, which favors β-hydrogen transfer to monomer (BHT) over insertion by ca. 2.5 kcal/mol. The other corrections also favor BHT slightly, so that one should subtract ca. 3 kcal/mol from our “balance” values to arrive at the $\Delta\Delta G^{\ddagger}$ values determining the molecular weight.

Results and Discussion

Coordination, Propagation, and Chain Transfer. The molecular weight of a polymer chain is generally determined by the balance between chain propagation and transfer. For polymerization at aluminum, the most important chain transfer mechanisms[13,14] are β-hydrogen transfer to monomer (BHT, bimolecular) and β-hy-

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(24) Thermal corrections depend on reaction conditions (temperature, concentrations, phases), and there is no single obvious set of appropriate conditions for all catalysts. Previous studies have shown that thermal corrections to the chain transfer/propagation balance are small (on the order of 1 kcal/mol) and favor β-hydrogen transfer.

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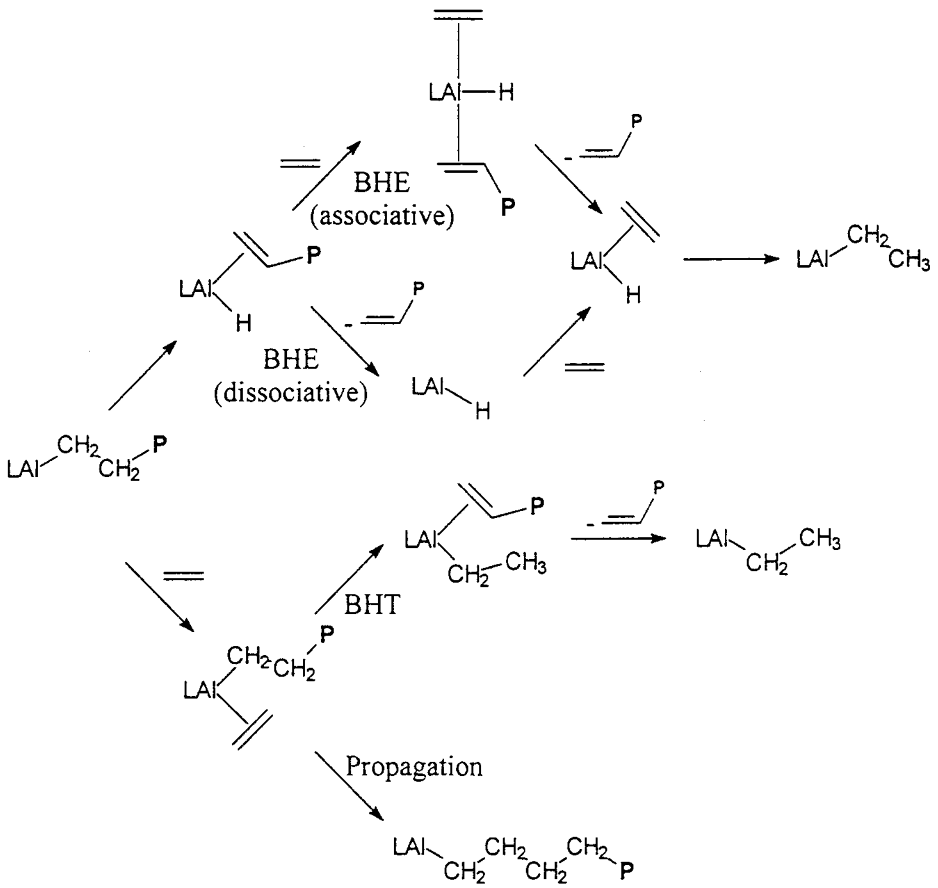
Scheme 1. Propagation and Chain Transfer in Polymerization at Al



dride elimination (dissociative BHE, unimolecular), illustrated in Scheme 1.[30]

As we have shown earlier, BHT usually has a lower activation energy than BHE, although under conditions of low monomer concentration and high temperature BHE might still be the dominant chain transfer process. However, BHT and propagation (which is also bimolecular) have similar dependencies on reaction conditions (solvent, temperature, monomer concentration); thus, their balance sets a more or less absolute upper limit on the molecular weight. Therefore, in this paper we concentrate on the balance between propagation and BHT.

Table 1 lists the final MP2/6-311G(d,p) olefin coordination energies and barriers for ethene insertion and BHT of LAlEt complexes. Figure 1 shows calculated transition state geometries for troponiminate, pyridine–imine–amide, and pentafluorophenyl systems.

Olefin insertion at Al follows the standard Cossee mechanism[31] involving an olefin π-complex and a four-membered-ring transition state.[13,15] Neutral three-coordinate Al complexes (**4**–**10**) form weak bonds to olefins. We calculate binding energies of 1–6 kcal/mol, with more electronegative substituents at Al resulting in stronger bonding. Cationic systems (**1**, **2**, and **11**) form stronger bonds (6–17 kcal/mol for the systems studied). Olefin complexation by four-coordinate aluminum complexes (**3** and **12**) is much weaker than by three-coordinate species. In general, the interaction appears to be mainly electrostatic, since the Al–olefin distances are quite large (2.5–3 Å) and the C=C bond is not much elongated relative to the free olefin.

Table 1. Olefin Coordination Energies and Insertion and Chain Transfer Barriers[a] for Aluminum–Ethyl Complexes (kcal/mol)

no.	system	E(coord)	$E^\ddagger$(insertion)	$E^\ddagger$(BHT)	balance
5	$(CH_3)_2AlEt$ (reference)[c]	3.6	23.0	28.6	5.6
	$HC(NH)_2AlEt^+$ [b,c]	16.9	29.5	19.7	−9.8
	$HC(N\text{-}i\text{-}Pr)_2AlEt^+$ [c]	14.1	27.7	22.1	−5.6
1	$t\text{-}BuC(N\text{-}i\text{-}Pr)_2AlEt^+$ [c]	11.6	29.1	22.9	−6.2
	$C_7H_5(NH)_2AlEt^+$	8.2	30.1	21.6	−8.5
2	$C_7H_5(N\text{-}i\text{-}Pr)_2AlEt^+$	6.0	28.8	21.6	−7.2
3a	$C_5H_3N(CHNH)$-$(CH_2NH)AlEt^+$	5.6	28.0	26.0	−2.0
3b	$C_5H_3N(CHNPh)$-$(CH_2NPh)AlEt^+$	5.1	30.2	28.9	−1.3
4	$(C_6F_5)_2AlEt$	6.3	25.1	27.3	2.2
6	$(C_6H_5)_2AlEt$	4.8	25.4	30.5	5.1
7	F_2AlEt	4.6	27.0	27.3	0.3
8	$(PH_2)_2AlEt$	3.7	24.2	27.5	3.3
9	$H_2C(NH)_2AlEt$[c]	1.9	33.9	30.4	−3.5
10	$HAl(NH)_2AlEt$	1.2	31.9	30.2	−1.7
11	$(CH_3)(NH_3)AlEt^+$	12.3	24.5	21.1	−3.4
12	$C_5H_3N(CH_2NH)_2AlEt$[d]		26.3	26.2	−0.1

[a] Barriers relative to the olefin complex. [b] See also ref 13. [c] See also ref 14. [d] No π-complex formed; barriers relative to free reactants.

The reported insertion and chain transfer (BHT) barriers in Table 1 are counted from the olefin complex stage. Depending on the reaction conditions, this might not be the most appropriate choice. For example, in the

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(30) In principle, associative BHE could also occur, as shown in Scheme 1. However, this variant combines the high activation of BHE with the concentration dependence of BHT and will therefore always be less favorable than BHT or dissociative BHE.

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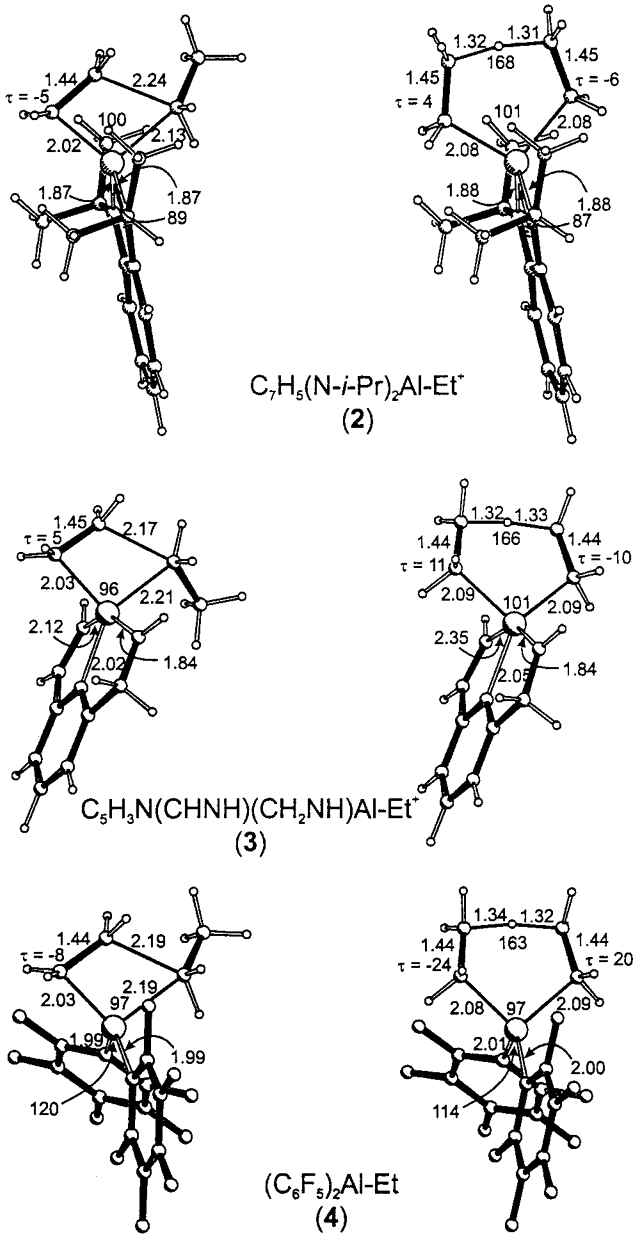

Figure 1. Transition state geometries for ethene insertion and β-hydrogen transfer to monomer in $C_7H_5(N\text{-}i\text{-}Pr)_2$-$AlEt^+$, $C_5H_3N(CHNH)(CH_2NH)AlEt^+$, and $(C_6F_5)_2AlEt$. Distances are given in Å and angles in deg. τ is the torsion angle along the double bond.

gas-phase Aufbau process,[32] where the olefin complex would be fully dissociated, the separated reactants would provide a more suitable reference. However, this does not affect the *balance* between insertion and BHT, since both start from the same olefin complex.

Evaluation of Insertion/Chain Transfer Balance. As a reference point for all other systems, we use Me_2-$AlEt$ (**5**), a model for trialkylaluminum, which is the only system for which accurate kinetic parameters are available. We have studied this system in detail and showed[14] that it is possible to reproduce its propagation/chain-transfer balance to satisfactory accuracy (within ~2 kcal/mol) as described in Methods. However, several of these factors are virtually constant for different Al systems, and therefore we used a simpler procedure here (also described in Methods) which should still give reliable *relative* balance values. The actual balance values (for a real chain) should be ca. 3 kcal/mol lower than those reported here for Al−Et species. In the present context, systems having a worse balance (higher preference for chain transfer) than Me_2AlEt (which is an *oligo*merization catalyst) are then assumed to be unsuitable as polymerization catalysts.

Real Systems. (a) (amidinate)AlR$^+$. $[t\text{-BuC(N-}i\text{-Pr)}_2AlR]^+$ (**1**) was the first "well-defined" aluminum catalyst to be reported,[7] although later work showed that this species was not actually being formed from the two catalyst components and that the real system was more complex.[11] Calculations on the simple model system $[HC(NH)_2AlR]^+$ showed that this cation has a very strong preference for chain transfer over insertion.[13] Later work, extending the model to the "real" amidinate cation, demonstrated that the bulky substituents have little influence on the balance, which for **1** is predicted to be nearly 12 kcal/mol *worse* than that of Me_2AlEt.[14] Since the steric requirements of the two competing transition states are so similar, this should come as no surprise. It does, however, illustrate one of the important differences with transition-metal systems, where ligand bulk is frequently essential to prevent "associative displacement" of olefin.

(b) (troponiminate)AlR$^+$. In contrast to the above-mentioned amidinate cations, well-defined (nearly) three-coordinate (troponiminate)Al(alkyl) cations (e.g., **2**) have been prepared, isolated, and characterized by X-ray diffraction.[8] These species were originally thought to be active in polymerization, but recent work by Jordan showed that—though the polymerization definitely happens in this system—the active species is *not* the three-coordinated cation. Indeed, the experimental results obtained demonstrated the high tendency of the aluminum-bound alkyls to undergo β-hydrogen transfer not only to olefins but also to ketones and acetylenes.[12] This is in perfect agreement with our theoretical results, which show that, like the amidinate system, the troponiminate system (with or without the isopropyl substituents) strongly favors chain transfer. The calculated transition state geometries (Figure 1) are also very similar to the ones found earlier for amidinates.

(c) (pyridine−imine−amide)AlR$^+$. This species (**3**) was proposed by Gibson et al. as an olefin polymerization catalyst.[10] Reaction of $AlMe_3$ with a pyridine−diimine ligand produces the anionic ligand via addition to an imine bond. The resulting $LAlMe_2$ complex has two strongly coordinated nitrogens and a third one at a much longer distance, resulting in a situation intermediate between 4- and 5-coordination. Methyl abstraction with $B(C_6F_5)_3$ was said to produce $LAlMe^+$ cations which polymerized ethene to rather low molecular weight. However, the rather large M_w/M_n values of 2.9−6.3 reported for this system do not support a well-defined single-site catalyst; again, the situation appears to be more complex.

In our calculations, we had to simplify the ligand by omitting the bulky aryl substituents at the imine and amide nitrogens. Inspection of the calculated insertion and chain transfer transition states for **3a** (Figure 1)

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indicates that neither should be affected much by the presence of these groups. Thus, the main effect of the substituents would probably be on the olefin complexation energy, which does not affect the balance. To verify this, we also optimized transition states for insertion and BHT for a model bearing phenyl groups at the imine and amide nitrogens (**3b**). The phenyls have different conformations in the insertion and BHT transition states, but the effect on the balance is negligible; we see no reason to expect significant effects of adding substituents to the phenyl groups.

A new feature in this system is the presence of an “extra” donor group in the molecule, the dangling imine. This could be expected to partially saturate the cationic Al alkyl and hence impede both insertion and hydrogen transfer. In fact, we see little evidence for this in the energies, calculated barriers being roughly similar to those predicted for amidinates and troponiminates. The balance is shifted somewhat in favor of insertion, but not enough by far to make this an efficient polymerization catalyst: it is still nearly 7 kcal/mol *worse* than Me_2AlEt. The calculated geometries show that the imine group is bound more tightly in the insertion TS (Al−N = 2.12 Å) than in the hydrogen transfer TS (Al−N = 2.35 Å), in accord with the more open geometry of the insertion TS, but the energetic consequences of this appear to be minor.

(d) $(C_6F_5)_2AlR$. This neutral aluminum alkyl (**4**), formed e.g. from R_3Al and $B(C_6F_5)_3$ or $Al(C_6F_5)_3$, was proposed by Sen to polymerize not only ethene but also propene. Moreover, it was reported to be active in ethene/propene *co*polymerization.[9] Our calculations do not support this: $(C_6F_5)_2AlEt$ is predicted to have a *worse* balance than Me_2AlEt by 3.4 kcal/mol. The transition-state geometries, shown in Figure 1, are unremarkable and rather similar to those calculated for Me_2AlEt. Even if the balance would be the same as for aluminum trialkyls, that could not explain the observed copolymerization, since β-hydrogen transfer from a β-branched alkyl (as formed after a propene insertion) to ethene should be even easier than from a linear alkyl. We conclude that it is unlikely that monomeric $(C_6F_5)_2AlR$ is the species responsible for the observed (co)polymerization activity.

Ligand Effects. At this point we are in an embarrassing situation: we apparently “prove” that *none* of the active species proposed so far should behave as a polymerization catalyst and no other obvious explanation of the experimental fact that a polymer does form appears from the calculations. To complete the picture, we engaged in a more systematic study of ligand effects.

(a) Substituent Electronegativity. We first studied the effect of ligand electronegativity in neutral systems, using the series X_2AlEt with X = CH_3 (**5**), C_6H_5 (**6**), C_6F_5 (**4**), F (**7**). The results show a clear and unambiguous trend: more electron-withdrawing groups result in *easier* chain transfer, with C_6F_5 closer to F than to CH_3. The differences in steric properties do not appear to be important here, probably because none of these groups is particularly bulky. Phosphorus has nearly the same electronegativity as carbon, and indeed $(PH_2)_2AlEt$ (**8**) shows nearly the same balance. One could expect that less electron-withdrawing groups would result in a more favorable balance. However, it is not easy to think of realistic substituents that are more electron-donating than alkyl yet would not become involved in reactions with olefins themselves. One possibility we considered was $HAl(NH)_2AlEt$ (**10**), where the aluminum atom bound to the amides should increase their donor character relative to those in $H_2C(NH)_2AlEt$ (**9**). Indeed, the $H_2C \rightarrow HAl$ substitution does improve the balance somewhat, but the four-membered ring constraints work in the opposite direction relative to acyclic systems (see below), so that the end result is still a poor catalyst.

(b) Overall Charge. The next effect, one that has been exploited with success in transition-metal chemistry, is the change to a cationic system. We modeled that in a simple system by going from $(CH_3)_2AlEt$ to $(CH_3)(NH_3)AlEt^+$ (**11**). As could have been expected, this has the same effect as the introduction of a very electronegative substituent: it favors chain transfer over insertion, shifting the balance by ca. 8 kcal/mol. The balance calculated for the “Gibson” model **3a** is very similar to that for **11**. Our interpretation is that the additional ligand group in the pyridine−imine−amide ligand has little influence, apart from letting the ligand behave as one with a larger “bite angle” than expected for a five-membered chelate ring, and that the presence of the positive charge is the main effect here. The much stronger chain-transfer preferences calculated for amidinate **1** and troponiminate **2** are also partly caused by the charge effect.

(c) Geometric Constraints. Finally, we looked at the effect of geometric constraints by comparing $(CH_3)_2AlEt$, $CH_2(NH)_2AlEt$, and $CH(NH)_2AlEt^+$. Going from $(CH_3)_2AlEt$ to $CH_2(NH)_2AlEt$, one would expect 2−3 kcal/mol due to the electronegativity difference between C and N; the remainder should be caused by the geometric constraints of the four-membered ring. Then going from $CH_2(NH)_2AlEt$ to $CH(NH)_2AlEt^+$, we should (and do) see the more or less “pure” effect of introducing the positive charge (similar to going from $(CH_3)_2AlEt$ to $(CH_3)(NH_3)AlEt^+$). From this comparison, we estimate the effect of reducing the intraligand angle at Al from 120° to ca. 80° to be 5−6 kcal/mol, in favor of chain transfer. This trend is reasonable, given that the ideal C−Al−C angle for the six-membered hydrogen transfer TS is larger than the corresponding angle for the four-membered insertion TS. The magnitude of the “constraint effect” is thus comparable to that of the positive charge. The constrained N−Al−N angle (ca. 89°) probably also contributes to the strong hydrogen-transfer tendency of the troponiminate system. Thus, to improve the balance by geometric constraints one would need to design ligands that prefer “bite angles” larger than 120°, which is probably not easy.

As an extension of the “Gibson” pyridine−imine−amide system, we considered a system **12** containing the pyridine−diamide ligand $C_5H_3N(CH_2NH)_2^{2-}$. Complex **12** is overall neutral, has a large angle between the two amide donor groups[33] at Al (142°), and has substituents at Al with only slightly higher electronegativity than Me_2AlEt. This neutral, four-coordinate aluminum complex does not form an olefin π-complex: thus, the activation energies in Table 1 are calculated relative to the free reactants. The improvement relative to the cationic Gibson system is only about 2 kcal/mol,

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[33] Ignoring the more weakly bound pyridine donor.

however; we still find a balance that is worse than that for Me_2AlEt by nearly 6 kcal/mol.

Conclusions

Previous calculations on trialkylaluminum give us confidence that we can use theoretical methods to predict the balance between propagation and chain transfer at aluminum with reasonable accuracy. If we accept this, our results force us to conclude that *none* of the "well-defined" aluminum systems reported recently in the literature[7−10] has as its active species the one proposed originally. Moreover, trends in ligand effects are such that it is hard to imagine any mononuclear aluminum species, *neutral or otherwise*, that would have a balance more favorable than trialkylaluminum. In addition, although it is not the main focus of the paper, we also note here that none of the systems studied has a calculated insertion barrier lower than trialkylaluminum. We believe that all reported systems are indeed more complex than initially thought.

As far as we can see, two reasonable possibilities remain. One is polymerization at a dinuclear or polynuclear species, following a real "dinuclear mechanism".[34,35] According to our calculations, barriers for chain transfer and insertion can be comparable to those for mononuclear systems. We have not yet found such a species with a balance *better* than that of Me_2AlEt, but the number of possible structural types is so large that such species might exist. We do not think this is a likely possibility, but it cannot be ruled out at this stage. The other possibility is the more trivial one of transition-metal contamination. Only time will tell whether one of these is true or whether another, hitherto overlooked explanation applies.

Regardless of the explanations for experimental Al polymerization systems, our work indicates that the prospects for high-activity, high-molecular-weight polymerization catalysts based on aluminum are not very promising. The remarkable ease with which Al alkyls undergo β-hydrogen transfer need not, however, be considered solely as an undesirable chemical feature. The reaction can also be exploited deliberately, as in reductions of ketones by aluminum alkyls or in Meerwein−Pondorf−Verley reduction of ketones by alcohols. Using Al species with improved β-hydrogen transfer tendencies, e.g. based on the Jordan troponiminates,[8] it might well be possible to derive efficient chiral transfer hydrogenation catalysts.

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Supporting Information Available: Relevant total energies for all species mentioned in the text (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org. Optimized geometrical parameters for these species are available on request from one of the authors (G.T.).

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(35) Here we mean a mechanism in which the chain switches metal in each insertion step: i.e., fundamentally different from the "standard" Cossee mechanism. We do not think mechanisms in which an Al dimer is involved but where the polymerization still happens at a single metal center according to the normal Cossee mechanism[36] could be a solution, since in that case the second Al center is just part of a larger, more complicated metalloligand and would therefore not change the balance much.

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