

Mono- and Dinuclear Olefin Reactions at Aluminum

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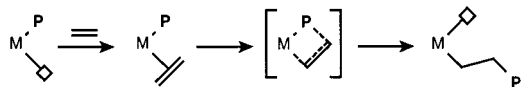
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As an alternative to the standard Cossee mechanism, in which olefin insertion involves two sites at a single metal center, we have investigated a true dinuclear alternative where the chain switches between two different metal centers at each insertion. The corresponding dinuclear variations of β -hydrogen elimination (BHE) and β -hydrogen transfer to monomer (BHT) were also investigated. Surprisingly, calculations indicate that the barriers for both insertion and BHT at two different metal centers are rather similar to those for the more usual mononuclear mechanisms. Dinuclear BHE is more competitive as a chain transfer mechanism, although it always has a higher barrier than BHT. In any system where polymerization at an unknown aluminum active species is believed to occur, dinuclear insertion should be considered as a real alternative to the "standard" mononuclear mechanism. However, from the systems we have studied the prospects for designing highly active, high-MW Al polymerization catalysts (i.e., significantly better than trialkylaluminum) appear just as dim for dinuclear as for mononuclear species.

Introduction

Just after the discovery of transition-metal-catalyzed olefin polymerization, there was a kind of "explosion" of mechanistic proposals for the path followed by this new and curious reaction. Today, the Cossee–Arlmann mechanism¹ seems well established, even though in some cases there may be doubt about the existence of a π -complex as a local minimum along the reaction path.²



Mononuclear "Cossee" insertion

In addition, there may be special cases where the Green carbene mechanism³ applies; none of the others seem to have withstood the test of time. In the early days of mechanistic proposals, however, many more exotic ideas were put forward, including several bimetallic variations (Figure 1).^{4–9}

Since they were conceived (and discarded) such a long time ago, they were never subjected to a more quantitative study that might establish just how (un)likely they are relative to the standard Cossee mechanism.

In our recent theoretical study of ethylene polymerization at aluminum centers,^{10–14} we encountered the problem that, according to calculations, mononuclear aluminum species are unlikely to produce polymers because chain transfer is too easy relative to propagation. Since several groups have reported experimental evidence that some aluminum systems do produce polyethylene,^{15–18} we started looking for alternative, possibly more exotic structures and mechanisms that might explain the polymerization activity. One of the mechanisms we studied is a true dinuclear mechanism

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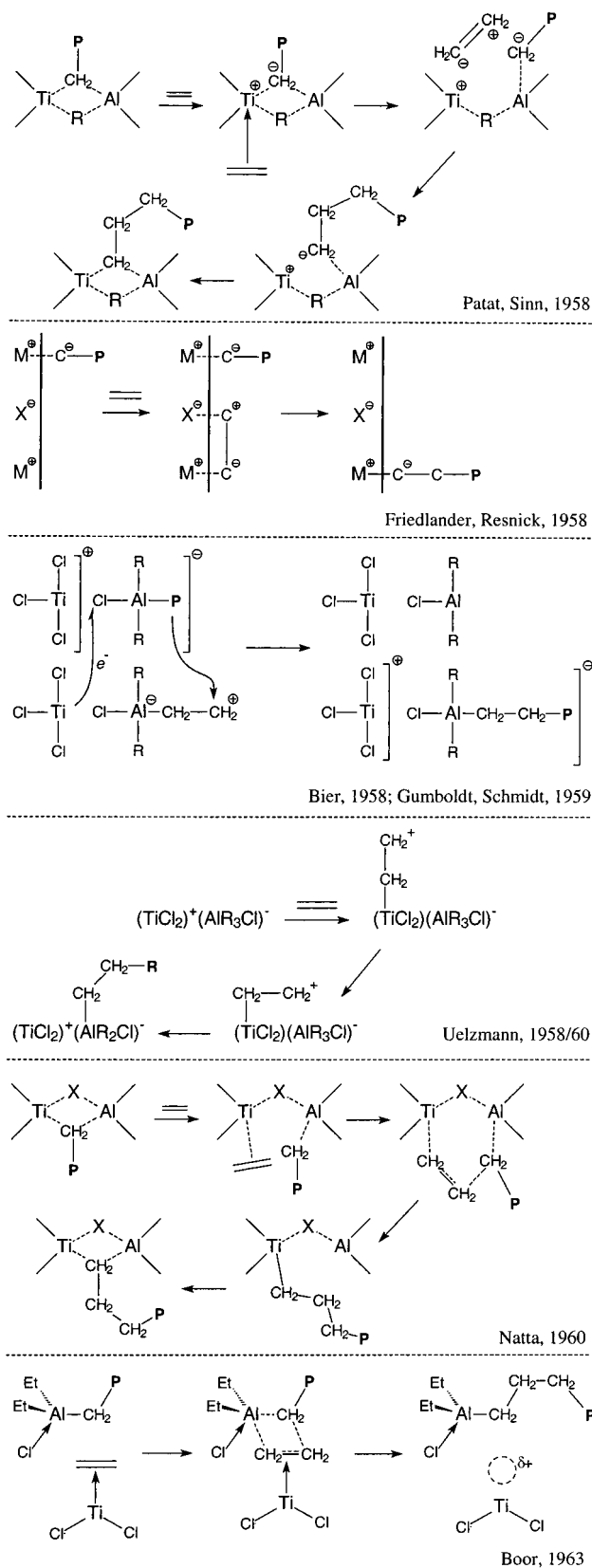
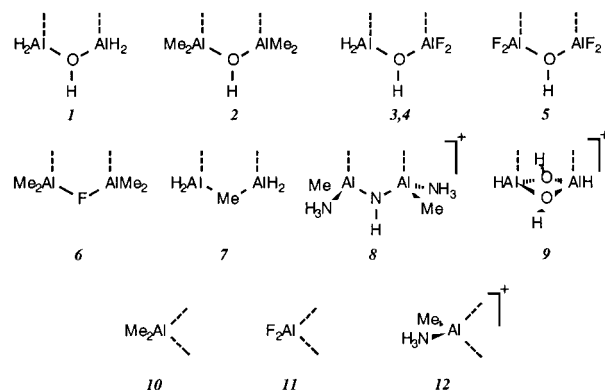


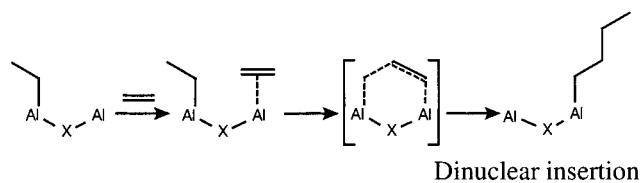
Figure 1. A selection of dinuclear olefin polymerization mechanisms proposed between 1955 and 1965.⁴⁻⁹

where the chain migrates between sites at two different metal centers (instead of between two sites at the same metal center) with each insertion, rather similar to some of the mechanisms in Figure 1. Dinuclear aluminum sites have been studied theoretically by Meier, but he

Scheme 1. Dinuclear Systems and Mononuclear Reference Systems Studied



only considered the “classical” insertion at a single metal center, the other metal simply acting as part of a large “metalloligand”.¹⁹



To our surprise, initial indications were²⁰ that dinuclear insertion is not much more difficult than insertion at a single center, nor did it have a worse balance between propagation and chain transfer. Thus, dinuclear systems deserved some consideration as candidate “active species” in Al polymerization. However, dinuclear systems are intrinsically more complicated than mononuclear ones because of the occurrence of monomer–dimer equilibria and various possibilities for bridge formation. In the present work, we report on a more detailed study of the reactivity of several dinuclear systems (Scheme 1) and assess the likelihood that dinuclear species could indeed be involved in observed Al polymerization.

Calculations

Geometries of all complexes were optimized at the B3LYP²¹ or MP2²² level²³ using the 6-31G(d) basis set.²⁴ Improved single-point energies were then calculated with the MP2/6-311G(d,p) basis set.²⁵ We have shown earlier that this level is adequate to assess *relative* barriers for insertion and chain transfer, although *absolute* barriers require a somewhat more sophisticated treatment.^{13,14} For representative systems stud-

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Table 1. Energies (kcal/mol) for Stationary Points on the Reaction Path Relative to the Most Relevant Reference Point (in bold)

system	BHE TS	(μ -)Et	π -cplx	insn TS	BHT TS	$\Delta E_{\text{insn/BHT}}$	
1	H ₂ Al(μ -OH)AlH ₂	+37.8	0	+2.5	+29.5	+33.5	+4.0
2	Me ₂ Al(μ -OH)AlMe ₂	+38.6	0	+4.4	+31.5	+37.6	+6.1
3	H ₂ Al(μ -OH)AlF ₂ ^a	+42.6	+3.7	+12.6	+35.4	+36.5 ^c	+1.1
4	F ₂ Al(μ -OH)AlH ₂ ^b	+43.8	0	<i>d</i>	+32.1	+35.8	+3.7
5	F ₂ Al(μ -OH)AlF ₂	+40.6	0	<i>d</i>	+27.4 ^e	+27.4 ^e	0.0
6	Me ₂ Al(μ -F)AlMe ₂	+40.2	0	+5.6	+32.7	+37.9	+5.2
7	H ₂ Al(μ -Me)AlH ₂	+47.0	0	<i>d</i>	+40.3 ^f	+48.1 ^f	+7.8
8	(Me)(NH ₃)Al(μ -NH)Al(Me)(NH ₃) ⁺	+35.9	+2.0	0	+25.7	+30.0	+4.4
9	HAl(μ -OH) ₂ AlH ⁺	+40.5	+17.6	0	+31.7	+23.7	-8.0
10	Me ₂ Al	+38.6	+3.6	0	+23.0	+28.6	+5.6
11	F ₂ Al	+49.2	+4.6	0	+27.0	+27.3	+0.3
12	(Me)(NH ₃)Al ⁺	+44.1	+12.3	0	+24.5	+21.1	-3.4

^a Ethene on AlF₂ side of complex. ^b Ethene on AlH₂ side of complex. ^c Using average BSSE of the two isomeric ethene complexes. ^d π -complex is not a local minimum. ^e BSSE estimated at 6 kcal/mol. ^f BSSE estimated at 4 kcal/mol.

ied here (**1**, **9**), we also carried out CCSD(T)²⁶/6-31G(d) single-point calculations, but these did not significantly change the results. All calculations were carried out with the GAUSSIAN-98²⁷ 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.²⁸ Basis set superposition error (BSSE) was evaluated²⁹ at the olefin complex stage and assumed to be constant over the relevant reaction paths. For the two cases where no stable π -complex is formed (**5** and **7**), BSSE was estimated from the values for closely related complexes (see Table 1 and Table S1); note that BSSE does not affect the balance between propagation and chain transfer.

Table 1 contains olefin complexation energies and insertion/chain transfer barriers for dinuclear systems **1–9**; in addition, we have included data for monomeric systems **10–12** for comparison. The corresponding total energies are given in Table S1. The barriers in Table 1 do not correspond directly to energies for propagation and chain transfer. The most important contribution that is missing from the numbers is the correction for chain extension from Et to *n*-Bu, which favors β -hydrogen transfer to monomer (BHT) over insertion by ca. 2.5 kcal/mol. Various 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.¹⁴

Results and Discussion

Reaction Paths. In the present work, we are considering three elementary reactions, as illustrated in

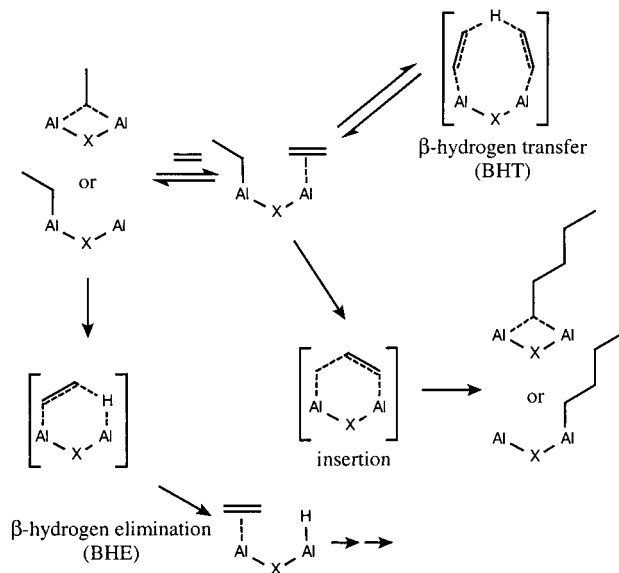
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(28) Thermal corrections depend on reaction conditions (temperature, concentrations, phases), and there is no single obvious set of appropriate conditions for all catalysts. Previous studies^{10,12} have shown that thermal corrections to the chain transfer/propagation balance are small (on the order of 1 kcal/mol) and favor β -hydrogen transfer.

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Scheme 2. Model Reactions for Dinuclear Propagation and Chain Transfer



Scheme 2. The first is insertion (propagation), which is seen to be similar to some of the earlier bimetallic mechanisms of Figure 1. The other two reactions are chain transfer steps: β -hydrogen transfer to monomer (BHT, bimolecular chain termination) and β -hydrogen elimination (BHE, monomolecular chain termination). For mononuclear systems, we reported earlier that BHT always has a lower barrier than BHE (although BHE might still prevail under conditions of high temperature and low monomer concentration), so that for an evaluation of polymerization potential a comparison of insertion and BHT suffices.^{10,11} In the case of dinuclear systems, it is not immediately obvious that the same trend holds; therefore, we also included BHE explicitly in the present work.

Reactants, Complexes, and Products. Dinuclear species have many more opportunities for forming alternative structures (e.g., singly, doubly, or triply bridged; different choices of bridging groups) than mononuclear ones. This is not directly relevant when we only want to compare insertion and BHT, since they start from a common reference point. If, however, we are interested in the real activation energy, the question of the most stable structures of reactants and π -complexes becomes important. In the present work, we are considering various simple dinuclear structures as

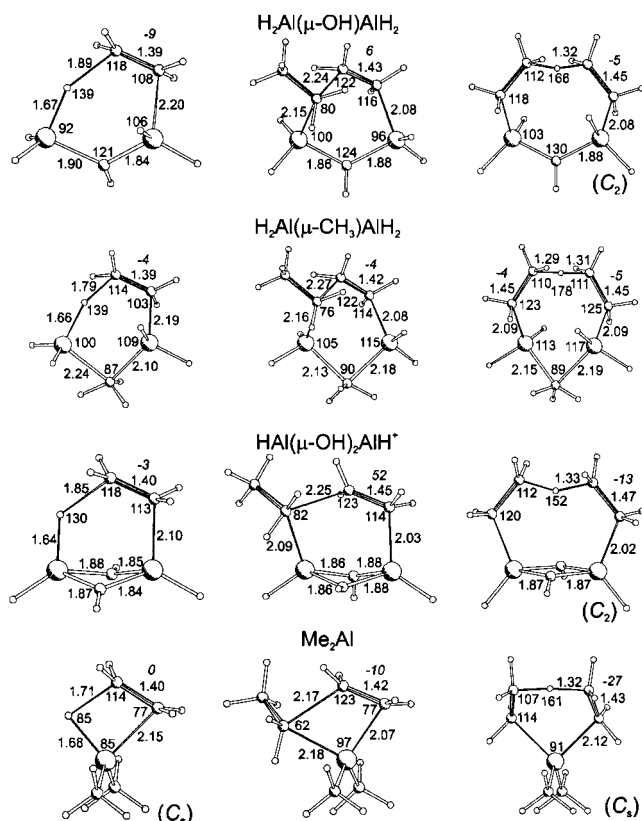


Figure 2. Optimized transition state geometries for representative mono- and dinuclear propagation and chain transfer models. Distances in Å, angles in deg; the torsion angle about the C=C bond is given in *italics*.

models for potential, more complicated *real* catalysts. This means that the terminating groups will be artificial and simplified; structures in which these “terminating groups” have moved into bridging positions are not relevant because presumably such a reaction could not happen in the corresponding *real* system. However, structures in which the alkyl group (of the reactant or product) has moved into a bridging position *are* relevant, since that would also happen in any *real* catalyst.

For most neutral systems, we find that the ethyl-bridged reactant is more stable than the olefin π -complex (by 2–6 kcal/mol). For cationic systems, and for the asymmetric system **4**, the π -complex is lower in energy. In two cases, we find no stable structure for the olefin π -complex because it dissociates spontaneously (**7**) or because the preference for having the “terminating groups” in bridging position is too strong (**5**). In Table 1, the nature of the most stable “relevant” reference point is indicated, and all energies are given relative to this point.

Geometries. Figure 2 compares calculated geometries for three dinuclear systems: **1**, bridged by a 4-e-donor OH group; **7**, bridged by a 2-e-donor CH₃ group; and **9**, bridged by two OH groups. The mononuclear system **10** has been included for comparison.

Insertion over two metal centers does not appear to be very different from insertion at a single metal center. The bond lengths in the 6-center dinuclear transition states are rather similar to those in the 4-center mononuclear ones. The transition states for dinuclear BHT (8-center vs 6-center) and BHE (6-center vs

4-center) are also quite similar. One clear change on going from mono- to dinuclear systems is the opening of the angle Al \cdots H \cdots C for the BHE transition state, from $<90^\circ$ to $130\text{--}140^\circ$. Hydrogen, which uses mainly its 1s orbital in this reaction, does not seem to have a strong preference for a particular angle, although a linear arrangement would probably be optimal. The corresponding Al \cdots C \cdots C angle for the insertion TS, on the other hand, opens up much less (from $<65^\circ$ to $75\text{--}85^\circ$), because of the strong directionality of the carbon sp³ orbital involved. The dinuclear transition states are all far from planar, since in planar transition states the angles at most atoms would become too large. In the rigid doubly bridged system **9**, where the backbone forces a nearly coplanar orientation of the two Al–C bonds, the torsion is concentrated in the alkyl/olefin part of the transition state. For the other dinuclear systems, deviations from planarity are spread out over the ring.

Energies. Here we encounter what is probably the largest surprise of the present study. Activation energies for dinuclear insertion are higher than for mononuclear ones (see Table 1), but the difference is not large, with barriers for most systems between 25 and 35 kcal/mol. In our earlier studies on mononuclear insertion,^{10,11,14} we found that most barriers were in the same range. The lowest mononuclear one, for Me₂AlEt **10** (23 kcal/mol), is indeed lower than all dinuclear barriers. Part of this difference is, however, artificial, because we take as a reference point for the dinuclear system an ethyl-bridged species, whereas for the mononuclear reaction we start from a monomeric aluminum trialkyl-olefin complex. One could argue that the proper reference point for **10**, at least for solution polymerization, would also be the alkyl-bridged dimer, in which case the difference in barrier with, for example, **5** or **8** would almost vanish. In any case, it is clear that dinuclear insertion is not prohibitively more difficult than mononuclear insertion.

The same appears to hold for the dinuclear variations of β -hydrogen transfer to monomer and β -elimination. BHE is consistently more difficult than BHT, although the differences are not as large as in the mononuclear systems: given the entropy differences between BHE (monomolecular) and BHT (bimolecular), BHE might well prevail even in solution, depending on reaction conditions. All barriers are relatively insensitive to the nature of the substituents at Al. Table 1 illustrates the effect of changing the nature of the bridging atom (**2**→**6**), changing the terminal atoms (**2**→**1**, **2**→**5**), and changing the charge of the complex (**2**→**8**). None of these changes has a dramatic effect. If the dinuclear system is made asymmetric (**4/5**: two fluorides on one Al atom, two hydrides on the other), the two alternative BHE and insertion states differ by only 1 and 3 kcal/mol, respectively (although the two alternative π -complexes differ by 13 kcal/mol). The only really large substituent effect we have found is caused by the change from a singly bridged to a doubly bridged structure (**1**→**9**), which is accompanied by a large drop of the BHT barrier.

Propagation/Chain Transfer Balance. Interestingly, even though we are comparing rather dissimilar reaction types (insertion and hydrogen shift), the balance between insertion and BHT for dinuclear systems is fairly similar to that for mononuclear systems.

Neutral, singly bridged systems such as **1**, **2**, and **6** have a balance comparable with that for Me₂AlEt, the “best” mononuclear system. Electron-withdrawing substituents facilitate BHT (**5** vs **2**), just as in mononuclear systems (**11** vs **10**). Even the monocationic system **8** does not have a poor balance. This is interesting, since for mononuclear systems we have not been able to find a single cationic example having a reasonable balance.¹⁴ For example, the related cationic system **12** is 9 kcal/mol worse than neutral **10**, whereas cationic **8** is less than 2 kcal/mol worse than neutral **2**. On the other hand, the doubly bridged system **9** has a very poor balance, presumably for geometrical reasons. So far, we have not found an example of a dinuclear system with a significantly *better* balance than aluminum trialkyl, nor with a lower barrier for propagation.³⁰ In that sense, dinuclear systems do not appear to be the “improved” catalysts we were searching for.

Conclusions

Counting from the relevant reference point, insertion and BHT reactions at various dinuclear Al systems are not much more difficult than at mononuclear systems.³¹ Also, the balance between the two is rather similar. Dinuclear systems have different geometric requirements, and these will have their influence on the insertion/chain transfer balance. Apart from that, it appears that—surprisingly—dinuclear insertion cannot immediately be discarded as an unrealistic idea. What, then, are the implications for aluminum polymerization?

In the first place, our results indicate that dinuclear systems are unlikely to provide a big *improvement* over mononuclear trialkylaluminum, neither in terms of

activation energy nor for molecular weight. One should be cautious here, since the number of possible dinuclear species is large, and we have only selected a few simple cases. However, the results obtained so far do not provide much hope for the “next generation of cheap polymerization catalysts”. We drew the same conclusion earlier for mononuclear Al species;¹⁴ it seems remarkably difficult to improve on the ancient trialkylaluminum system.

In the second place, could dinuclear species be involved in any of the Al polymerizations reported to date? It is important to note here that all of these “catalysts” have rather low productivities, compatible with the activation energies of ≈25 kcal/mol calculated for some of the best mononuclear (e.g., R₃Al) and dinuclear systems. In that sense, they cannot be ruled out. Interestingly, whereas we could definitely exclude *cationic mononuclear* catalysts, because they would always give a low molecular weight, for dinuclear species the presence of a positive charge does not have to be a problem (e.g., **8**), so cationic dinuclear species also remain possible. If one assumes that the reported catalysis is indeed due to aluminum species, the possibility of these species being dimers and following a dinuclear insertion mechanism deserves serious attention.

Finally, there is the intriguing question of whether at *other* metals, where insertion is easier and the insertion/chain transfer balance is more favorable, dinuclear insertion would still be as easy as the mononuclear variation. If so, this would certainly open up new possibilities for “rational catalyst design”.

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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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(30) The only system that *does* clearly have a better balance is **7**, but this has very high *absolute* barriers. Since the single alkyl bridge is rather weak, **7** would dissociate and undergo mononuclear reactions in preference to following the dinuclear paths studied here.

(31) Thermal (entropy) corrections are very similar for mono- and dinuclear systems and hence do not change the conclusions. Of course, there will be a large entropy difference in cases where the system has a choice between propagating as a binuclear system or dissociating first and then propagating as a mononuclear system. Since, as mentioned in the text, we regard our systems as models for more complicated “real” catalysts, where presumably such dissociation is prevented by ligand constraints, we do not consider this possibility here.