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Calculation of the Change in ^{1}H NMR Spectrum of $Al(CH_3)_3$ (TMA) Produced by Complexation with C_4H_8O (THF)

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The commercial olefin polymerization cocatalyst methylaluminoxane (MAO) has a composition often described as $(AlOCH_3)_n$, but in fact it invariably shows an excess of CH_3 over Al on the order of 40−50 mol %. The ratio of CH_3 to Al can be determined in several ways. Determination using ^{1}H NMR is simple and efficient, but only if a base, such as tetrahydrofuran (THF), is added to complex all the trimethyl aluminum, $Al(CH_3)_3$ (TMA), and at the same time shift the ^{1}H NMR resonance of the TMA away from that of MAO, making a quantitative determination possible. We here calculate the structures and energetics of possible complexes between THF and TMA along with their ^{1}H, ^{13}C, ^{17}O, and ^{27}Al NMR shifts and (for O and Al) their quadrupole coupling constants. We find that TMA indeed bonds one THF strongly, even more strongly than it bonds to another TMA. The average ^{1}H NMR shift for the THF−TMA complex is calculated to be around −0.84 ppm (with respect to tetramethylsilane, TMS), while the experimental value is −1.07 ppm. The calculated energetics for complex formation indicate that THF bonds strongly enough with both TMA and with polyhedral methylaluminoxanes such as $(AlOCH_3)_6$ that it will decompose any aluminoxane−TMA complexes present within the MAO and complex all the TMA liberated.

Introduction

Homogeneous olefin polymerization by group 4 metallocene catalysts with methyaluminoxane (MAO) cocatalysts has been the object of intensive study, both experimental[1−5] and theoretical.[6−10] Nonetheless, the detailed structure of the MAO cocatalyst and the nature of the catalytically active structure within it remain unknown. Even the overall composition of commercial MAO is often unknown. Although MAO is sometimes formulated as $(AlOCH_3)_n$, most preparations of MAO seem to have a considerable excess of CH_3 over Al, and the activity of the MAO changes with the CH_3/Al ratio.[5] Several experimental methods have been developed to determine the CH_3/Al ratio. ^{1}H NMR was first used in the early 1990s, but the overlap of CH_3 resonances from MAO and those of free $Al(CH_3)_3$ (TMA) or $Al_2(CH_3)_6$ (TMA_2) made quantification difficult.[11,12] Recently a technique has been developed[13] in which a large excess of C_4H_8O (THF) is added to the MAO solution in toluene (in an approximate 4 THF:1 Al ratio) to form a complex with any liberated TMA as well as any TMA which was originally free in the MAO solution. The THF presumably forms a complex with the TMA, and the ^{1}H NMR signals in this complex are strongly shielded (by around 1 ppm) compared to that in the reference material $Si(CH_3)_4$ (TMS).

In this work we use quantum chemical methods to calculate the structures, stabilities, and NMR properties of the TMA−THF complex, as well as complexes of TMA with itself and with polyhedral methylaluminoxanes and complexes of THF with the methylaluminoxanes.

We first examine the computational methodology needed to accurately calculate the structure and stability of the $(TMA)_2$ complex. Our main goal is to establish the identity of the TMA−THF complex by matching its calculated average ^{1}H NMR shift with that observed experimentally. A second goal is to determine the magnitude of its stability and to determine if THF can be expected to dissociate complexes such as $(AlOCH_3)_6$-$Al(CH_3)_3$, in which TMA is bonded to a six-membered methylaluminoxane cage (which is often used as a

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simplified model of MAO). We also calculate a number of other properties of the TMA−THF complex to assist in its identification. A related complex, the dimer TMA_2, has been extensively studied computationally,[14] and we compare with those results.

Computational Methods

We use standard methods of molecular quantum mechanics, which are descibed in several monographs. The simplest method used for the calculation of equilibrium geometries and energies was the Hartree−Fock method,[15,16] using an effective core potential valence double-ζ basis set[17] with d polarization functions on all the non-H atoms (designated polarized SBK). For the evaluation of the NMR shieldings the simplest method employed was the coupled Hartree−Fock perturbation theory method in its GIAO implementation,[18] with an all-electron 6-31G** basis.[15] The computer requirements are only slightly greater for a 6-31G** than for a 6-31G* basis, and the results were considerably better for species with many $-CH_3$ groups. We have also calculated equilibrium geometries using the all-electron 6-31G* basis and HF, gradient-corrected density functional BLYP[19] and Moller−Plesset second order perturbation theory (MP2),[20] which we expect to be more accurate than the polarized SBK HF results. For each of these calculated geometries we have then used the GIAO method with the 6-31G** basis to calculate NMR parameters. In some cases we have also used the larger 6-311G(2d,p) basis and we have tried both HF and BLYP methods for calculating the NMR shieldings, to test the stability of our calculated ^{1}H NMR shifts toward changes in method. We used GAMESS[21] and GAUSSIAN94[22] quantum chemical software.

In addition to our evaluation of ^{1}H NMR shieldings, we have examined the energetics of complex formation. Vibrational frequencies have been calculated, and all translational, rotational, and vibrational contributions to ΔH and ΔG have been evaluated for the formation in the gas phase of both TMA_2 and TMA−THF. We use the 6-31G* Hartree−Fock values of the frequencies (unscaled) to estimate these quantities for all the methods considered. For TMA_2 evaluation of basis set superposition error (BSSE) using the counterpoise method[23a] is problematic[14] since the dimer is so much different in structure from the monomer. For TMA−THF, where the two parts of the complex are fairly similar to the original reactants, we have evaluated BSSE using the counterpoise method, using the 6-31G* basis at both the HF and MP2 level, although MP2 estimates of BSSE are somewhat controversial.[23b] Although the calculation of such gas-phase energies is straightforward, evaluation of the effect of solvation on the energies of reactants and products is more difficult. We have estimated solvation energies in toluene (dielectric constant 2.438) using the polarized continuum method[24] (PCM). We have also examined the NMR shieldings of other nuclei, including ^{27}Al and ^{13}C and the electric field gradients (EFG) at Al and O.

Table 1. Calculated Energies (in kcal/mol) for Dimerization of $Al(CH_3)_3$ and R(Al−Al) (in Å) Reaction: $2\ Al(CH_3)_3 \Rightarrow Al_2(CH_3)_6$

basis, method	ΔE	ΔH	ΔG	R(Al−Al)
		Present Work		
Pol. SBK HF	−2.1	1.6	12.7	2.616
6-31G* HF	−1.6	2.1	13.2	2.629
6-31G* BLYP	−6.1	−2.4	8.7	2.638
Pol. SBK MP2	−21.8	−18.1	−7.0	2.587
6-31G* MP2	−24.6	−20.9	−9.8	2.595
		Previous Work		
DZP, BP86[a]			0.4	
DZP, DPW91[b]	−12.0	−9.5	7.5	2.642
6-31G** MP2[c]	−20.0	−17.4		2.60
		Experiment		
		−20.2, −20.4[d]	−7.6[d]	2.619[e]
				2.606[f]
				2.700[g]

[a] Ref 10. [b] Ref 7. [c] Ref 14. [d] Ref 25. [e] Gas-phase electron diffraction, $T = 333$ K, ref 26b. [f] X-ray diffraction, $T = 103$ K, ref 26a. [g] Neutron diffraction, $T = 4.5$ K, ref 26c.

Table 2. Calculated Energies (in kcal/mol) for Complexation of C_4H_8O with $Al(CH_3)_3$ and R(O−Al) (in Å) Reaction: $C_4H_8O + Al(CH_3)_3 \Rightarrow C_4H_8OAl(CH_3)_3$ (values in parentheses corrected for basis set superposition error using the counterpoise method)

basis, method	ΔE	ΔH	ΔG	R(O−Al)
Pol. SBK HF	−14.1	−15.7	−3.8	2.112
6-31G* HF	−18.1 (−15.8)	−19.7	−7.8	2.040
6-311+G(d,p) HF	−16.5	−18.1	−6.2	2.030
6-31G* BLYP	−15.8	−17.4	−5.5	2.090
Pol. SBK MP2	−23.0	−24.6	−12.7	2.089
6-31G* MP2	−24.0 (−17.5)	−25.6	−13.7	2.044

Results and Discussion

Properties calculated for $(TMA)_2$ at a number of different quantum mechanical levels are shown in Table 1. Such a comparison helps us to determine what level of rigor might be needed for accurate study of the TMA−THF complex. Our results are similar to those recently reported by Berthomieu et al.[14] We find that a HF level description gives accurate bond distances but dimerization energies that are substantially underestimated. Density functional methods seem to give some improvement in dimerization energy, but with results that are strongly dependent upon the particular functional used. Calculations at the MP2 level seem to give much more accurate dimerization energies, although the bond distances are little affected. Augmentation of the SBK basis by inclusion of two d polarization functions on each Al and C, p polarization functions on H, and diffuse s and p functions on Al and C changed the dimerization energy by only 0.1 kcal/mol.

Although the experimental energetics[24] seems well established, there is a disturbing discrepancy of about 0.1 Å between the X-ray and neutron values for the Al−Al distance.[25] Although the experimental X-ray and neutron structure determinations were done in different phases and at different temperatures, such a large variation in Al−Al distance is still unusual.

A similar set of computational results for the TMA−THF complex is given in Table 2. Here we see the same trend in energetics as for $(TMA)_2$, with the MP2 dimer-

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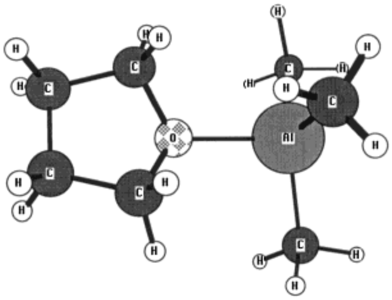
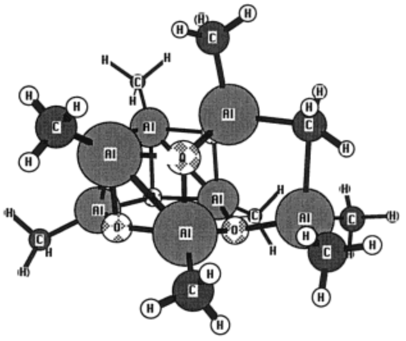
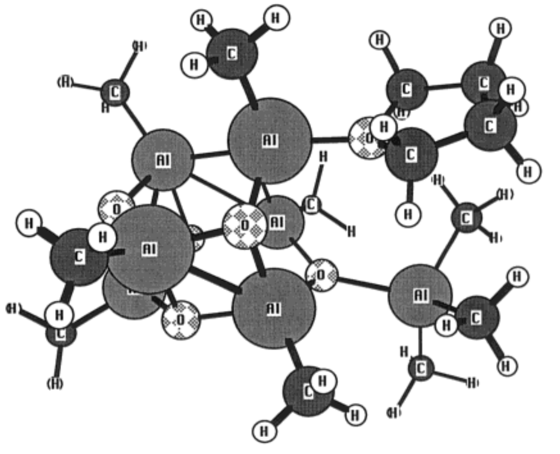


$C_4H_8OAl(CH_3)_3$



$(AlOCH_3)_6Al(CH_3)_3$



$(AlOCH_3)_6Al(CH_3)_3C_4H_8O$

Figure 1. Geometries calculated at the 6-31G* BLYP level for $C_4H_8OAl(CH_3)_3$ (TMA−THF), $(AlOCH_3)_6Al(CH_3)_3$, and $(AlOCH_3)_6Al(CH_3)_3C_4H_8O$.

ization energies being consistently more negative. There is also a substantial variation in the O−Al distance. A picture of the TMA−THF complex, calculated at the 6-31G* BLYP level, is given in Figure 1. For this complex we have also evaluated the basis set superposition error at the 6-31G* HF and MP2 levels using the counterpoise method, obtaining values of +2.3 and +6.5 kcal/mol for the counterpoise corrections, respectively, somewhat reducing the calculated stability and bringing the HF and MP2 results closer together. We have not considered how the BSSE might change the equilibrium geometry of the complex, as in more sophisticated studies of smaller complexes.[15b]

Calculated NMR properties for the heavy atoms O, C, and Al in THF and TMA and in the TMA−THF complex are given in Table 3 (based on 6-31G* BLYP geometries and 6-31G** GIAO calculations). We see that the Al is strongly shielded by formation of the complex, as expected since its coordination number increases from 3 to 4. Nonetheless, it is still deshielded by about 60 ppm compared to the Al of $(AlOCH_3)_6$, calculated at the same level. The O and C of THF are slightly deshielded by complex formation, while the C of the TMA is slightly shielded. The electric field gradient at Al is strongly reduced by complex formation, while that of O is almost unaffected.

Table 3. Calculated ^{13}C, ^{17}O, and ^{27}Al NMR Shieldings (in ppm) and ^{17}O and ^{27}Al EFGs (in au) for C_4H_8O, $Al(CH_3)_3$, and the $C_4H_8OAl(CH_3)_3$ Complex (using 6-31G* BLYP geometries and the 6-31G basis)[a]**

	property				
molecule	σ^{Al}	σ^{O}	σ^{C}	q^{Al}	q^{O}
C_4H_8O		295.7	137.5, 175.3		1.992
$Al(CH_3)_3$	374.4		204.1	1.168	
$C_4H_8OAl(CH_3)_3$	469.0	292.0	135.9, 176.7, 205.9 (C−Al)	0.865	1.887

[a] Shift reference for C is TMS (σ^{C} = 199.7) and that for Al is $Al(OH_2)_6^{+3}$ (σ^{Al} = 638.5).

Table 4. Average ^{1}H NMR Shifts (vs TMS) for Various Compounds (using 6-31G* BLYP geometries and the GIAO method with a 6-31G basis)**

molecule	average calcd ^{1}H shift[a]	(apparent) exptl ^{1}H shift[b]
TMS[a]	0	
TMA	−0.34	−0.37
$(TMA)_2$		
$C_{bridging}$	+0.14	0.02
$C_{nonbridging}$	−0.57	−0.53
average	−0.33	−0.36
TMA−THF	−0.84	−1.07
$(TMA)_2$−THF	−0.90	
$(AlOCH_3)_6$	−0.33	max. around −0.3
$(AlOCH_3)_6$−THF most strongly perturbed ^{1}H	−0.78	max. around −0.8
$(AlOCH_3)_6$−TMA	−0.50	
CH_3 groups from $(AlOCH_3)_6$	−0.50	
CH_3 groups from TMA	−0.20	
nonbridging $-CH_3$		
bridging $-CH_3$		

[a] Calculated ^{1}H NMR shielding in TMS at this level of theory is 31.76 ppm; shifts are averaged over all protons related by rotations about single bonds. [b] Ref 13.

Calculated average ^{1}H NMR shifts (vs TMS) are shown for a number of compounds in Table 4, calculated at the 6-31G* BLYP geometry, with the GIAO method and a 6-31G** basis (the polyhedral $(AlOCH_3)_6$ complexes are too big for MP2 geometry optimzations so we employed BLYP in an attempt to partially incorporate electron correlation effects upon the geometries). The experimental shifts from ref 13 with their assignments are also given. It is apparent that the average ^{1}H shift value for TMA−THF is in fairly good agreement with experiment (−0.84 ppm calculated at this level vs −1.07 ppm exptl). The shift difference between the bridging C protons and the nonbridging C protons in $(TMA)_2$ (which appear separately in low-temperature spectra, but are averaged at room temperature) is also well reproduced, as is the average ^{1}H shift of $(TMA)_2$. The $(AlOCH_3)_6$−THF complex, in which a single THF is coordinated to one of the Al atoms of the cage, shows a range of ^{1}H shifts, with the protons closest to the THF shielded by about 0.45 ppm, compared to those farthest away. In the presence of excess THF we anticipate that

Table 5. Variation in Average ^{1}H Shieldings and Shifts (in ppm) for the TMA−THF Complex, vs TMS, Using Various Methods (for TMA−THF only CH_3 protons of TMA part are included in average)

geometry	basis for GIAO calculation	$\sigma^H{}_{TMS}$	$\sigma^H{}_{TMA-THF}$	$\delta^H{}_{TMA-THF}$
6-31G* BLYP	6-31G**	31.76	32.60	−0.84
Pol. SBK MP2	6-31G**	31.46	32.17	−0.71
Pol. SBK MP2	6-311+G(2d,p)	31.52	32.27	−0.75
Pol. SBK MP2	6-31G** BLYP	31.78	32.56	−0.78

all the protons of the $(AlOCH_3)_6$ would be close to added THF and so would be shielded by about this amount, in agreement with experiment, which shows the broad MAO peak to be more shielded by about 0.5 ppm when excess THF is added.

Similarly, the $(AlOCH_3)_6$−TMA complex, whose structure is shown in Figure 1, shows a range of shieldings. The protons on the C atoms of the original $(AlOCH_3)_6$ group have shifts averaging −0.50 ppm. The protons derived from the TMA component of $(AlOCH_3)_6$−TMA have somewhat different shifts depending upon whether they are nonbriding (−0.50 ppm) or bridging (−0.20), probably contributing to the width of the original MAO peak. Note that there is a CH_3 group (from the TMA component) bridging between two Al atoms. The bonding of this group is quite sensitive to the level of quantum mechanical treatment, Hartree−Fock level calculations give a nonbridging geometry for this group, that is, it is coordinated to only one Al atom.

The calculated shift for TMA−THF vs the reference TMS seems to be reasonably stable with respect to theoretical level, as shown in Table 5. As we descend this table, the computational level improves, finally reaching polarized SBK MP2 for the geometries and 6-311+G(2d,p) for the Hartree−Fock level GIAO calculations. The use of the BLYP approach rather than HF in the GIAO calculation may also improve the results, although there is some controversy about this.[27] However, the calculated ^{1}H shifts do not improve compared to experiment, even deteriorating slightly.

It is not clear what changes in methodology would be necessary to get improved agreement with experiment. Certainly a higher level calculation of the shieldings, e.g., at the MP2 level, would be desirable. It may also be that the equlibrium geometry needs to be determined with a higher level method. Other possible sources of error are neglect of the effect of solvent (toluene) on the geometry and/or the shielding and failure to vibrationally average the shieldings, particularly those for the TMA−THF complex. Qualitatively, we can relate the increased shielding of protons within the TMA−THF complex to the elimination of low-energy unoccupied orbitals when the coordinatively unsaturated three-coordinate Al of TMA is converted to the four-coordinate Al of the TMA−THF complex.

Table 6. Calculated Energies (in kcal/mol) for the Addition of C_4H_8O (THF) to $Al(CH_3)_3$ (TMA) or $(AlOCH_3)_6$ and for the Reaction of TMA with $(AlOCH_3)_6$ (using the polarized SBK basis)

reaction	Δ*E*(HF)	Δ*E*(MP2@HF)
$C_4H_8O + Al(CH_3)_3 \Rightarrow C_4H_8OAl(CH_3)_3$ (1)	−14.1	−21.5
$C_4H_8O + C_4H_8OAl(CH_3)_3 \Rightarrow (C_4H_8O)_2Al(CH_3)_3$ (2)	+1.6	−6.2
$C_4H_8O + (AlOCH_3)_6 \Rightarrow (AlOCH_3)_6C_4H_8O$ (3)	−8.0	−16.2
$Al(CH_3)_3 + (AlOCH_3)_6 \Rightarrow (AlOCH_3)_6Al(CH_3)_3$ (4)	−13.6	−30.2
$C_4H_8O + (AlOCH_3)_6Al(CH_3)_3 \Rightarrow (AlOCH_3)_6Al(CH_3)_3C_4H_8O$ (5)	−7.7	−16.1
$2\ C_4H_8O + (AlOCH_3)_6Al(CH_3)_3 \Rightarrow (AlOCH_3)_6C_4H_8O + C_4H_8OAl(CH_3)_3$ (6)	−8.5	−7.5
$C_4H_8O + (AlOCH_3)_6Al(CH_3)_3 \Rightarrow (AlOCH_3)_6 + C_4H_8OAl(CH_3)_3$(7)	−0.4	+8.8
$C_4H_8O + (AlOCH_3)_6Al(CH_3)_3C_4H_8O \Rightarrow (AlOCH_3)_6C_4H_8O + C_4H_8OAl(CH_3)_3$ (8)	−0.8	+8.6

Calculated energies for a number of complexation reactions are shown in Table 6, obtained using both the polarized SBK HF method and the polarized SBK MP2 method at the HF optimized geometries. As noted above, going to the more accurate MP2 level for geometry optimizations for those reactions involving $(AlOCH_3)_6$ would be prohibitively expensive computationally, but we have performed single-point polarized SBK MP2 calculations at the polarized SBK HF geometries. For the TMA−THF complex such single-point MP2 calculations at the HF geometries give a Δ*E* value of −21.5 kcal/mol, while the full MP2 optimization gives −23.0 kcal/mol. For $(TMA)_2$ the single-point MP2 dimerization energy is −20.5 kcal/mol, while the reoptimized MP2 result is −21.8 kcal/mol. Therefore our results for the systems containing $(AlOCH_3)_6$ units should be of almost the same accuracy as obtained from a full MP2 optimization. Recall that the Δ*G* values for the formation of the complexes $(TMA)_2$ and TMA−THF, given in Tables 1 and 2, were less negative than the Δ*H* values by about 12 kcal/mol, a simple consequence of the reduction in number of moles in the reaction for formation of the complex. We can anticipate that other reactions in which the number of moles decreases by 1 will be similarly disfavored by the $-T\Delta S$ term in the free energy. Therefore, reactions 1−6 in Table 6 are all chosen to have a reduction of 1 in number of moles of material. Reactions 7 and 8 have no change in number of moles of material, so the entropic contribution should be fairly small.

We have not calculated solvation energies for all these reactions, but we have performed PCM solvation energy calculations for TMA, THF, $(TMA)_2$, and TMA−THF in toluene. Our results indicate that the TMA dimerization energy and the TMA−THF complex formation energy are changed by less than 1 kcal/mol by solvation in toluene, an energy change that is much smaller than the error in the gas-phase energies at the HF level.

Even with the limitations described above some interesting results emerge from our calculations. Remember that for reactions 1−6 we should add around +12 kcal/mol to obtain Δ*G* values. We find that the formation of the larger complex TMA−$(THF)_2$ is *not* favored vs TMA−THF. We see as well that the interaction energy of THF with the $(AlOCH_3)_6$ cage is significant, but substantially weaker than that with TMA (−16.2 kcal/mol vs −21.5 kcal/mol at the MP2 level). The interaction energy of TMA with the $(AlOCH_3)_6$ cage

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is substantially larger (−30.2 kcal/mol at the MP2 level) than its interaction with THF. The reaction energy for adding THF to $(AlOCH_3)_6Al(CH_3)_3$ is −16.1 kcal/mol, essentially the same as its interaction energy with $(AlOCH_3)_6$. The geometry of this complex is shown in Figure 1. For reaction 6, in which two C_4H_8O molecules decompose the $(AlOCH_3)_6Al(CH_3)_3$ complex, the MP2 interaction energy is −7.5 kcal/mol, but the ΔG value will be considerably more positive for the reasons described above. For reactions 7 and 8, in which TMA is removed from $(AlOCH_3)_6Al(CH_3)_3$ or $(AlOCH_3)_6Al(CH_3)_3C_4H_8O$ and complexed with THF (with no change in number of moles from reactant to product side), the interaction energy is actually positive.

Our calculated reaction energies at the polarized SBK HF level are actually similar to those obtained using DFT in ref 10. For example, those researchers obtained interaction energies of about −14 kcal/mol for the formation of the TMA−THF complex and about −7 kcal/mol for the formation of the complex of THF with the $(AlOCH_3)_6$ cage. However, our MP2 results are considerably different, indicating much greater stability for each of the complexes.

In reaction 6 the complexation of THF with the $(AlOCH_3)_6$ essentially provides the driving force for displacing the TMA from the aluminoxane cage. This supports the analysis of ref 13, which rested upon the idea that excess THF would dissociate any complex of TMA with the MAO cage and coordinate the TMA. However, to substantiate this argument, it would be necessary to accurately calculate the entropic and solvation contributions to the energetics of this reaction. It may also be that in the simple model of MAO that we have used, with TMA complexed to a $(AlOCH_3)_6$ cage, the TMA is bound more tightly than it is in real MAO.

Conclusions

Fairly good agreement of calculated and experimental ^1H NMR shifts confirms that the species with δ^H = −1.07 ppm (calc δ^H = −0.84 ppm) is almost certainly the TMA−THF complex. Calculated energetics indicate that excess THF will abstract TMA from its complexes with $(AlOCH_3)_6$ (and presumably other polyhedral cage aluminoxanes), although it would certainly be desirable to calculate these energetics at a higher quantum chemical level than the present polarized SBK MP2 and include entropic and solvation corrections.

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