

An ab initio molecular orbital study of the reduction of carbonyls by alkylaluminum complexes

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Abstract

Semi-empirical and ab initio MO methods were used to explore mechanisms for the reduction of carbonyls by alkylaluminum reagents. Two distinct pathways have been observed experimentally, depending on the stoichiometric amounts of the reagents present. The corresponding intermediates and transition structures have been characterized. Alkylaluminum alkoxides are generally less reactive than the analogous alkylaluminum complexes. We suggest that the controlling factor here is not binding of the substrate, but the higher barrier to reaction of the alkoxide.

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1. Introduction

Dialkylaluminum hydrides, R_2AlH and trialkylaluminum compounds, in particular triethyl- and triisopropylaluminum, have proven to be effective reducing agents for carbonyl compounds. Their reactivities are similar to that of lithium aluminum hydride but under certain conditions they can offer improved selectivity. In addition, ease of preparation and handling, along with relatively low cost make these compounds a useful alternative to lithium aluminum hydride [1]. The principal drawback of these reagents is that in many cases, only one of the aluminum–carbon or aluminum–hydrogen bonds is utilized.

Organoaluminum compounds react with carbonyl compounds to give products resulting from addition, reduction and enolization reactions. The choice of pathway depends both on the substituents on the aluminum and the nature of the carbonyl compound as well as the stoichiometric ratio of the reagents. For example, reduction reactions predominate with alkyl aluminum hydrides, while some trialkylalumi-

num compounds and alkylaluminum halides can also serve as reducing agents via β -hydride elimination. We explore here mechanisms by which these two classes of aluminum reagents effect reduction of carbonyls.

Two distinct reaction pathways are observed in the reduction of carbonyls by aluminum hydrides. Pasykiewicz and Arabas [2] examined the reactions of propiophenone with trimethylaluminum and found that the yield and rate of the reaction was dependent on the trimethylaluminum:ketone stoichiometric ratio. Using a 2:1 molar ratio resulted in 100% yields of the reduced product, competing reactions reduced the yield significantly when a 1:1 ratio was used. The 2:1 systems also reacted much more rapidly than the 1:1 systems. They therefore proposed that the mechanism of the reaction depends on the molar ratio of the reactants.

Both of the proposed mechanisms proceed through initial complexation of the carbonyl to the aluminum center. In the 1:1 case, this intermediate proceeds directly to the transition structure. In systems where there is an excess of aluminum reagent present, a second monomer of the aluminum attacks the initially formed intermediate and this 2:1 complex moves through a different transition structure to product. Both proposed pathways are shown in Fig. 1. Several

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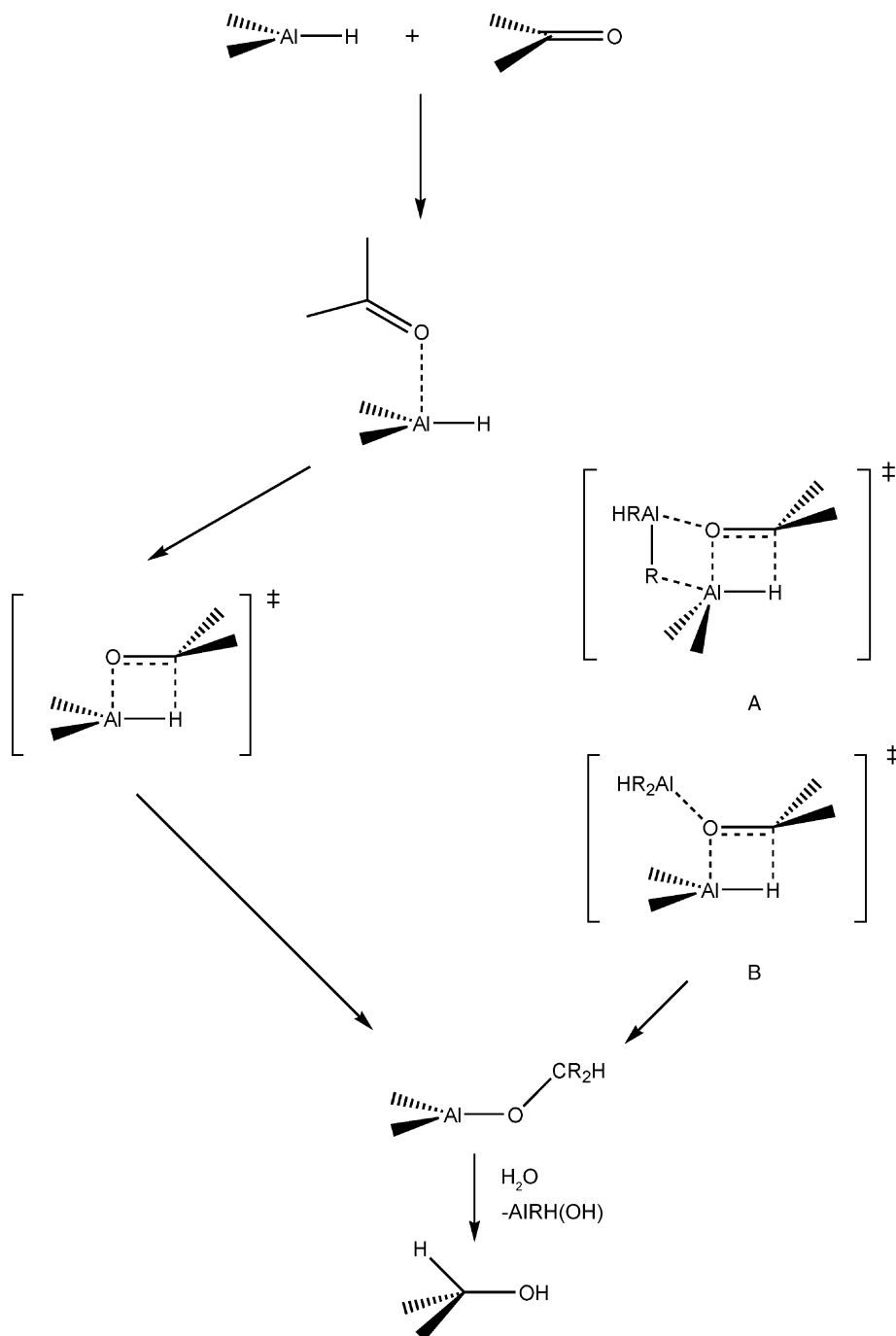


Fig. 1. Proposed 1:1 and 2:1 reaction pathways.

possible motifs have been suggested for the 2:1 transition state, including **A**, a structure consisting of two fused four-membered rings where the oxygen interacts with both aluminum atoms [3] and **B**, a structure with a four-membered ring, analogous to the 1:1 transition state, with the second aluminum monomer coordinated to the oxygen [4]. The major difference between the two is the presence of the bridging alkyl group in **A**.

We have used semi-empirical and ab initio MO methods to characterize the reactions of formaldehyde with a series of

methyl- and chloro-substituted aluminum monomers. The effects of substitution at both the aluminum and the carbonyl substrate on the structures and energies of the intermediates and transition states were explored. We determine a structure for the 2:1 transition state, and address the relative rates of the 2:1 and 1:1 reaction pathways.

Wittig and Bub [5] proposed the mechanism shown in Fig. 2 for the reduction of carbonyls by AlEt₃. The carbonyl initially coordinates to the aluminum through the oxygen, followed by transfer of the hydrogen from the β -carbon of

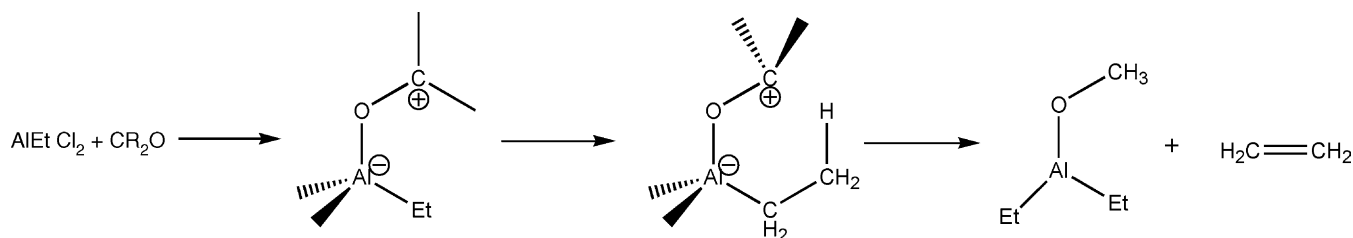


Fig. 2. Proposed mechanism for reduction of carbonyls by AlEt_3 .

the ethyl group to the carbonyl carbon with elimination of ethylene via a six-membered cyclic transition state. We have also determined the structure and energies of the intermediate and transition state for this reaction.

2. Methods

Ab initio molecular orbital calculations were performed using the Gaussian [6] and SPARTAN [7] suites of programs. All structures were fully optimized at the AM1 [8], HF/3-21G^(*)//HF/3-21G^(*) [9] and HF/6-31G^{*}//HF/6-31G^{*} [10] levels. Intermediates were confirmed to be minima on the potential energy surface by normal mode analysis. Transition states, characterized one and only one imaginary frequency, were followed to the appropriate products and reactants using IRC [11]. Energies were calculated at MP2/6-31G^{*}//HF/6-31G^{*} [12] and were corrected to 298 K and for zero-point vibrational energies [13]. Applying the corrections to the calculated energy of binding of the intermediates changes the values computed based on E_{pot} alone by roughly 1 kcal mol⁻¹ on average. Some systems are found to be more strongly binding after the correction is applied, others less binding. The computed barrier to reaction using H_{298} is generally about 1 kcal mol⁻¹ lower than that calculated from the simple ΔE . We did not correct for the BSSE in computing the binding energies for the intermediates, as it would be unlikely to affect the trends [14], and even at MP2/6-31G^{*} the absolute binding energies are so reliable as to warrant the attempt [15].

Optimized geometries for selected intermediate structures using AM1 leads to notably more loosely bound geometries than that from either of the Hartree–Fock methods. Al–O distances were considerably shorter, by 0.16–0.26 Å relative to HF/6-31G^{*}. The transition state structures were generally early. AM1 predicts Al–O distances for transition structures to be shorter by 0.01–0.15 Å than those from HF/6-31G^{*}. In addition, the AM1 geometries were less sensitive to substitution. For example, the Al–O distance varied at most by 0.02 Å in both intermediates and transition structures across the set considered here. The AM1 structures are grossly correct, but the method appears to severely underestimate the binding of aluminum to the oxygen. The smaller 3-21G^(*) basis set has previously been shown [16] to adequately describe the structures of many organoaluminum compounds.

In this study, however, the HF/6-31G^{*} optimized geometries differed significantly from the HF/3-21G^(*) geometries in both the intermediates and the transition structures. Differences in the Al–O distances for both the intermediates and the transition states ranged between 0.05 and 0.15 Å. We conclude that polarization functions on the oxygen atoms are necessary for proper description of the bonding in these carbonyl complexes. We suspect that the relatively poor description of the Al–O binding by AM1 is a result of the minimal basis set employed in that approach.

3. Results and discussion

3.1. Aluminum hydrides

3.1.1. 1:1 Intermediate: structure and energetics

The initial step of both the proposed 1:1 and 2:1 mechanisms is complexation of the carbonyl to the aluminum compound, through donation of an oxygen lone pair into the empty p-orbital on the aluminum. Table 1 shows the Al–O bond lengths and complexation energies for each of the complexes studied. As expected, there is a good correlation between the Lewis acidity of the aluminum compound or the basicity of the carbonyl with the HF/3-21G^(*) and HF/6-31G^{*} Al–O bond lengths in the intermediates. Better Lewis acids, AlH_2Cl and AlHCl_2 , show shorter Al–O distances; 0.04 and 0.07 Å shorter at HF/6-31G^{*}, respectively, than the 2.05 Å Al–O bond in the complex with AlH_3 . These shorter Al–O distances are reflected in the corresponding increases in the magnitude of the complexation energy. Formation of the chloroaluminum hydride intermediates is more favorable than formation of the aluminum trihydride intermediates: –19.7 kcal/mol and –21.1 kcal/mol at MP2/6-31G^{*} for AlH_2Cl and AlHCl_2 , respectively, compared to –16.4 kcal/mol for complexation to AlH_3 . Poorer Lewis acids, AlH_2Me and AlHMe_2 , exhibit slightly longer Al–O distances, by 0.01 and 0.02 Å, respectively, compared to the parent AlH_3 complex. Similarly, the complexation energies of the methylaluminum hydride complexes are reduced relative to that of AlH_3 . Substitution of electron-donating methyl groups at the carbonyl, as expected, results in tighter complexation in the intermediates, as seen in the shorter Al–O distances and increased complexation energies. In contrast, substitution of electron-withdrawing trifluoromethyl groups at the carbonyl

Table 1
Al–O distances and complexation energies in 1:1 and 2:1 intermediates

Compound	Substrate	Al–O distance ^a			Complexation energy ^b			
		AM1	HF/3-21G ^(*)	HF/6-31G [*]	AM1	HF/3-21G ^(*)	HF/6-31G [*]	MP2/6-31G [*]
AlHCl ₂	CH ₂ O	1.84	1.92	1.98	–5.2	–34.0	–20.6	–21.1
AlH ₂ Cl	CH ₂ O	1.85	1.93	2.01	–7.2	–31.9	–18.4	–19.7
AlH ₂ (OMe)	CH ₂ O		1.95	2.01		–27.4	–15.3	–16.5
AlH ₃	CH ₂ O	1.83	1.97	2.05	–15.0	–26.0	–14.1	–16.4
AlH(OMe) ₂	CH ₂ O		1.95	2.00		–26.1	–14.8	–16.3
AlH ₂ Me	CH ₂ O	1.84	1.98	2.06	–9.3	–23.9	–12.2	–14.6
AlHMe ₂	CH ₂ O	1.85	1.99	2.07	–3.9	–19.8	–8.1	–10.7
AlH ₃	(CH ₃) ₂ CO		1.93	2.00		–28.7	–15.6	–18.2
AlH ₃	CH ₃ CHO	1.83	1.95	2.02	–17.2	–27.9	–15.8	–18.1
AlH ₃	CF ₃ CHO	1.84	2.02	2.10	–7.3	–16.7	–7.9	–10.9
AlH ₃	(CF ₃) ₂ CO		2.08	2.23		–10.7	–2.1	–5.6

^a Distances in Å.

^b Energies in kcal mol^{–1}, corrected for zero point energies and to 298 K.

results in the longer Al–O bond distances and significantly reduced complexation energies observed in these intermediates.

Trends in the MP2 binding energies are reproduced at the HF/3-21G^(*) and HF/6-31G^{*} levels, though HF/3-21G^(*) tends to overestimate the binding, while HF/6-31G^{*} slightly underestimates it. AM1 significantly underestimates the binding to the strongest Lewis acids, AlHCl₂ and AlH₂Cl.

3.1.2. 1:1 and 2:1 Transition states: structures

The 1:1 transition state is found to be a four-membered ring as originally suggested by Ashby. The structure is analogous to the transition state found for the hydroalumi-

nation of alkenes by aluminum hydride reagents [12]. Table 2 shows the bond lengths and angles of the four membered ring in the 1:1 transition state for a series of substituted aluminum reagents and carbonyls. The same trend in Al–O bond lengths observed in the intermediate structures is found here, increased Lewis acidity in the aluminum catalyst or the electron-rich carbonyls leads to shorter Al–O distances. The Al–O distances in the transition state are shorter than those found in the intermediate by 0.07–0.13 Å. The C–H bond distances follow the same trend as the Al–O distances. The O–C and Al–H distances are fairly insensitive to changes in substituents at the aluminum or the carbonyl, differing from the values in the parent

Table 2
AM1 and HF/6-31G^{*} optimized parameters^a for 1:1 aluminum hydride-carbonyl transition structures

Method	Compound	Substrate	rAlO	rOC	rCH	rAlH	∠HAIO	∠AlOC	∠CHAl	∠OCH	ωHAIOC
AM1	AlH ₃	CH ₂ O	1.87	1.31	1.81	1.54	85.8	91.6	86.8	95.8	0.0
	AlH ₂ Me		1.88	1.30	1.82	1.54	85.3	92.2	87.2	95.0	–2.4
	AlHMe ₂		1.89	1.30	1.83	1.54	84.9	92.7	87.5	94.9	0.0
	AlH ₂ Cl		1.88	1.30	1.79	1.56	83.4	93.2	88.5	94.5	4.9
	AlHCl ₂		1.88	1.30	1.78	1.56	82.0	94.2	89.8	93.9	0.0
	AlH ₃	CH ₃ CHO	1.86	1.30	1.75	1.56	83.8	92.1	88.5	95.5	1.9
		CF ₃ CHO	1.89	1.29	1.86	1.54	85.8	92.6	86.4	94.7	6.3
HF/6-31G [*]	AlH ₃	CH ₂ O	1.96	1.24	1.94	1.68	84.0	94.8	83.0	98.2	0.0
	AlH ₂ Me		1.97	1.24	1.95	1.68	83.8	94.9	83.1	98.2	–1.5
	AlHMe ₂		1.99	1.23	1.96	1.69	83.5	95.0	83.3	98.2	0.0
	AlH ₂ Cl		1.91	1.25	1.90	1.67	84.0	95.1	82.9	97.5	6.1
	AlHCl ₂		1.87	1.25	1.87	1.67	84.3	95.3	83.0	97.3	0.0
	AlH ₂ (OMe)		1.94	1.24	1.90	1.68	83.5	94.3	83.1	98.3	7.5
	AlH(OMe) ₂		1.93	1.24	1.89	1.68	83.4	94.6	83.3	98.1	6.6
	AlH ₃	CH ₃ CHO	1.90	1.26	1.84	1.70	82.3	95.3	84.3	98.1	1.4
		(CH ₃) ₂ CO	1.87	1.27	1.79	1.70	81.1	95.7	85.4	97.8	0.0
		CF ₃ CHO	2.02	1.22	1.98	1.67	83.2	95.0	84.0	97.5	5.1

^a Distances in Å, angles in degrees. Core structure of the TS is

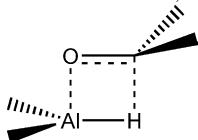
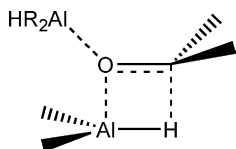


Table 3
HF/6-31G^{*} optimized parameters^a for 2:1 aluminum hydride-carbonyl transition structures

Compound	Substrate	<i>r</i> AlO	<i>r</i> OC	<i>r</i> CH	<i>r</i> AlH	∠ HAlO	∠ AlOC	∠ CHAl	∠ OCH	ωHAlOC	ωHAlOAl
AlH ₃	CH ₂ O	2.19	1.24	2.05	1.64	81.3	92.6	87.2	97.6	9.6	−120.1
AlH ₂ Me		2.20	1.24	2.05	1.65	81.0	92.5	87.6	98.0	8.6	−120.2
AlHMe ₂		2.20	1.24	2.06	1.66	80.5	92.9	87.3	97.0	13.4	−123.5
AlH ₂ Cl		2.08	1.25	2.00	1.64	81.8	94.0	86.0	95.2	15.2	−117.1
AlHCl ₂		2.14	1.25	2.00	1.62	81.2	92.9	87.9	96.3	11.6	−130.5
AlH ₃	CH ₃ CHO	2.04	1.26	1.97	1.66	81.4	95.7	86.8	95.0	9.3	−138.7
	(CH ₃) ₂ CO	1.99	1.28	1.95	1.66	81.3	97.8	87.5	93.2	3.1	−156.1
	CF ₃ CHO	2.34	1.23	2.02	1.63	77.0	90.7	92.5	99.8	−0.9	−128.4

^a Distances in Å, angles in degrees. Core structure of the TS is



transition state by at most 0.03 and 0.02 Å, respectively, over the entire series. None of the bond angles in the ring are particularly sensitive to changes in substituents at either the aluminum or the carbonyl, with deviations from the AlH₃ bond angles of less than 3°. The four-membered ring in the transition state exhibits small, presumably sterically induced, deviations from planarity of approximately 1–8°.

The primary difference between **A** and **B** is the presence of a bridging ligand in **A**, and the resulting second four-membered ring. Structure **A** was proposed by Neumann et al. [3] based on models of the proposed six-centered cyclic transition state. Bridging ligands are common in aluminum compounds and chlorine bridges are particularly stable, so attempts to model structure **A** were made with the chloroaluminum hydrides. All attempts to optimize a structure of this form opened up to the non-bridging form, **B**. Previous work [17] in this group indicates that alkoxyaluminum complexes are disinclined to have non-oxo bridges between aluminum centers. The determination of the 2:1 transition structure to be structure **B** is in accord with this observation.

Structural parameters for the 2:1 transition state are summarized in Table 3. As in the 1:1 intermediate and transition state, there is a correlation between the Al–O distance and the Lewis acidity of the aluminum reagent and the electron-donating ability of substituents on the carbonyl. With two equivalents of aluminum present in this structure, sterics play a larger role than in the 1:1 complexes. The structural parameters are relatively insensitive to substituent effects, deviations from the parent transition state are on the order of 0.01 Å for distances and less than 5° for critical angles. The four-membered rings in these structures show substantially larger deviations from planarity than those in the 1:1 transition structure, ranging from 4 to 21°. The second aluminum group coordinated to the oxygen is positioned between 130 and 140° clockwise about the Al–O axis from the “plane” of the four-membered ring. The

largest dihedral of this type observed in this study is the nearly 160° angle found in the acetone complex. The second aluminum group in this structure moves away to minimize steric interactions with the methyl group on the carbonyl.

Overall, the carbonyl is more loosely bound to the aluminum effecting the reduction in the 2:1 transition state than in the 1:1. Both the Al–O and nascent C–H bonds are significantly longer (0.12–0.32 Å and 0.04–0.16 Å longer, respectively) in the 2:1 structure than in the 1:1. This is partly steric, particularly in the case of AlHCl₂ where the steric crowding is the worst, worse even than in the dimethylaluminum hydride because the Al–O distance is shorter. It is primarily due, however, to the electronic effects of the complexation of carbonyl to a second aluminum monomer. By coordinating a second aluminum monomer, the carbonyl oxygen reduces its capacity to donate to the primary aluminum and the resulting complex is looser. It is interesting to note that the Al–O distances in the 1:1 transition state are typically about 0.1 Å shorter than those in the intermediate, while the Al–O distances in the 2:1 transition state are typically about 0.1 Å longer than those in the intermediate.

3.1.3. Activation energies

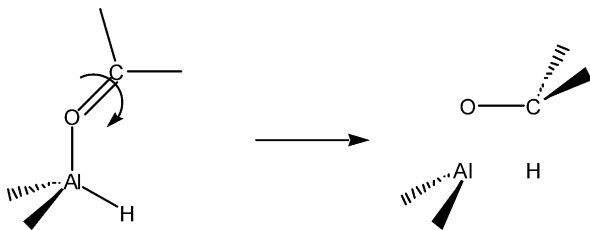
What is the source of the rate increase in the 2:1 pathway? Initial complexation of the carbonyl by the aluminum reagent is highly favorable and should occur immediately upon mixing of the reagents experimentally [18]. Since these reactions take place in solution, the energy of complexation is rapidly lost to solvent molecules. As a result, activation energies have been calculated from the intermediate rather than the reactants. Table 4 gives the activation energies for the 1:1 and 2:1 reaction pathways for the various substituted aluminum complexes and carbonyl substrates. At the MP2/6-31G^{*} level, all of the systems except the dimethylaluminum hydride show a lower activation energy for the 2:1 pathway than the 1:1 pathway. The small decrease observed

Table 4
Activation energies for 1:1 and 2:1 carbonyl reduction mechanisms

Al compound	Carbonyl	Activation energies ^a				
		AM1	6-31G*		MP2/6-31G*	
		1:1	1:1	2:1	1:1	2:1
AlH ₃	CH ₂ O	17.0	13.4	8.7	11.9	4.5
AlH ₂ Me		16.8	11.2	14.2	9.6	9.3
AlHMe ₂		13.7	12.4	24.4	10.6	18.7
AlH ₂ Cl		17.4	17.8	8.9	15.9	4.4
AlHCl ₂		22.4	19.6	14.4	17.8	9.0
AlH ₂ (OMe)			18.1		16.3	
AlH(OMe) ₂			19.4		18.6	
AlH ₃	CH ₃ CHO	19.3	16.6	8.7	13.8	3.5
	CF ₃ CHO	17.4	12.5	12.7	8.9	6.4

^a Energies in kcal mol⁻¹, corrected for zero point energies and to 298 K.

for methylaluminum hydride and the increase observed for dimethylaluminum hydride are most likely due to steric considerations. In all of the other reactions listed in Table 4, the 2:1 activation energy is between 2.5 and 11.5 kcal/mol lower than the corresponding 1:1 activation energy. This lower barrier to reaction is a result of the coordination of the second aluminum to the carbonyl oxygen. To progress from the initially formed intermediate to either of the four-membered ring transition structures found for this reaction, the carbonyl has to rotate 90° about the O=C bond.



The coordination of the second aluminum to the carbonyl oxygen weakens the binding of the oxygen by the aluminum and facilitates rearrangement to the transition state, thus lowering the activation energy relative to the unfacilitated rearrangement that must occur in the 1:1 pathway.

3.2. Alkylaluminum reagents with β -hydrides

The reaction mechanism for the reduction of carbonyls by alkylaluminum reagents possessing β -hydrides is shown in Fig. 3. This mechanism, like the aluminum hydride mechanism, begins with initial formation of an intermediate

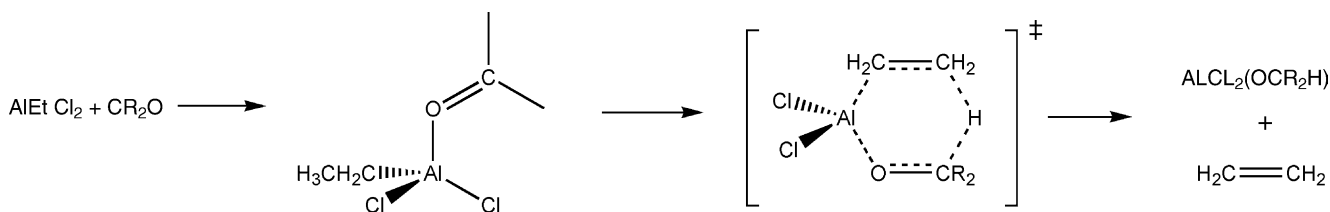


Fig. 3. Proposed mechanism for β -hydride reduction of carbonyls.

Table 5
HF/6-31G* optimized Al–O distances and complexation energies for β -hydride aluminum–carbonyl intermediates

Compound	Substrate	AlO distance ^a	Complexation energy ^b	
			HF/6-31G*	MP2/6-31G*//HF/6-31G*
AlEtCl ₂	CH ₂ O	1.99	–20.1	–21.0
Al(iPr)Cl ₂		1.99	–20.3	–21.4
AlEt ₂ Cl		2.02	–15.8	–18.1
AlEtCl(OMe)		2.01	–17.5	–18.9
AlEtCl ₂	CH ₃ CHO	1.96	–20.4	–21.2
	CF ₃ CHO	2.03	–10.0	–12.3

^a Distances in Å.

^b Energies in kcal mol⁻¹, corrected for zero point energies and to 298 K.

carbonyl–aluminum donor–acceptor complex. The Al–O distances and complexation energies of the carbonyl–alkylaluminum intermediates studied are summarized in Table 5. As in the aluminum hydride intermediates, the Al–O distances and complexation energies correlate well with the Lewis acidity of the aluminum compound and the electron donating ability of the carbonyl substrates. The alkylaluminum compounds with two strongly electron-withdrawing chlorine substituents (AlEtCl₂ and Al(iPr)Cl₂) have shorter Al–O distances and larger complexation energies than those with only one chloro substituent (AlEt₂Cl and AlEtCl(OMe)). Similarly, the dichloroethylaluminum complex with the stronger Lewis base, CH₃CHO, has a shorter Al–O distance than the analogous CH₂O complex. However, steric interactions between the ethyl substituent on the aluminum and the methyl group on the carbonyl counter the increase in stability due to the increased electron-donating ability of the carbonyl, resulting in essentially no change in complexation energy relative to the parent. The dichloroethylaluminum intermediate with CF₃CHO has a longer Al–O distance and lower complexation energy than the CH₂O intermediate, as expected for such an electron-poor substrate.

The transition state for this reaction is a six-membered cyclohexane-like ring. Selected ring parameters are summarized in Table 6. The ring is somewhat distorted due to the partial C–C and O–C double bonds present in the ring, i.e. the C–C and O–C bonds are not coplanar. This distortion from planarity, approximately 9°, is not as severe as that seen in cyclohexene, where it is approximately 26°. Taking the

non-coplanarity of the C–C and O–C bonds into account, the ring structure is a distorted chair configuration. The ring parameters listed in Table 6 are quite insensitive to substituent changes at the aluminum. The maximum deviation of any of the parameters from the AlEtCl₂ parameters is 0.01 Å. The bond distances listed are slightly more sensitive to changes in the carbonyl, with the C_β–H and C_O–H distances being the most sensitive.

Table 7 shows the activation energies for the various reactions examined. As in the aluminum hydride reactions, initial complexation of the carbonyl to the aluminum in these systems is highly favorable (complexation energies of approximately –12 to –21 kcal/mol) and excess energy in the intermediates would be rapidly lost to solvent molecules. As a result, activation energies are calculated from the intermediate. MP2/6-31G* energies show the diethylaluminum chloride to be more reactive than the monoethylaluminum dichloride. They also show the isopropylaluminum chloride to be less reactive than the ethylaluminum chloride.

Table 8 addresses the question of the reduced reactivity of the aluminum alkoxides relative to their alkyl counterparts. Although the complexation energies of the diethylaluminum chloride and the methoxyethylaluminum chloride are the same, the activation energy of the methoxy compound is 2.2 kcal/mol greater. Given the lower activation barrier for the alkylaluminum intermediate to proceed on to product and that the activation barrier for dissociation back to reactants is 4.2 kcal/mol lower than that to proceed forward to product, we posit that it is more favorable for the methoxy intermediate to dissociate and for the carbonyl to complex with an alkylaluminum monomer than to continue on to product.

4. Conclusions

4.1. Aluminum hydrides

The mechanism of reduction of carbonyls by aluminum hydrides has been characterized theoretically. Two distinct pathways exist for this reduction, depending on the molar ratio of aluminum reagent to carbonyl complex. The two pathways share a common intermediate, a donor–acceptor complex formed by donation of a lone-pair from the carbonyl oxygen into the empty 3p of the aluminum. The Al–O distance in the intermediate decreases with increasing Lewis acidity of the aluminum complex and increasing Lewis basicity of the carbonyl.

In systems with a molar ratio of 1:1, the initially formed intermediate rearranges to form a hydrogen transfer transition state involving a nearly planar four-membered ring, similar to those found for hydroalumination and carbalumination. In systems with an excess of aluminum reagent, a second aluminum monomer attacks the intermediate and facilitates the rearrangement to the transition state by reducing the electron-donating ability of the carbonyl oxygen and loosening up the complex. This “looser” complex is more

Table 6
HF/6-31G* optimized parameters^a for β-hydride aluminum-carbonyl transition structures

Compound	Substrate	r _{CC}	r _{C_βH}	r _{OC}	r _{C_OH}
AlEtCl ₂	CH ₂ O	1.44	1.37	1.29	1.28
Al(iPr)Cl ₂		1.44	1.37	1.30	1.28
AlEt ₂ Cl		1.44	1.36	1.29	1.29
AlEtCl(OMe)		1.44	1.37	1.29	1.29
AlEtCl ₂	CH ₃ CHO	1.43	1.40	1.31	1.26
	CF ₃ CHO	1.46	1.31	1.27	1.33
	(CF ₃) ₂ CO	1.47	1.25	1.25	1.39

^a Distances in Å.

Table 7
Activation energies for β-hydride mechanisms

Compound	Substrate	Activation energies ^a	
		HF/6-31G*	MP2/6-31G*//HF/6-31G*
AlEtCl ₂	CH ₂ O	33.7	20.9
Al(iPr)Cl ₂		35.6	22.6
AlEt ₂ Cl		33.0	19.7
AlEtCl(OMe)		34.7	21.9
AlEtCl ₂	CH ₃ CHO	39.2	24.7
	CF ₃ CHO	31.2	

^a Activation energies in kcal mol^{–1}, corrected for zero point energies and to 298 K.

Table 8
Complexation and activation energies^a for reduction of carbonyls by alkyl- and alkoxyaluminum reagents with β-hydrides

Compound	Complexation Energy		Activation Energy	
	HF/6-31G*//	MP2/6-31G*//	HF/6-31G*//	MP2/6-31G*//
	HF/6-31G*	HF/6-31G*	HF/6-31G*	HF/6-31G*
AlEt ₂ Cl	–15.5	–17.7	33.0	19.7
AlEtCl(OMe)	–16.3	–17.7	34.7	21.9

^a Energies in kcal mol^{–1}, corrected for zero point energies and to 298 K.

easily able to rearrange, for both steric and electronic reasons, to the hydrogen-transfer transition state. This weakening of the complexation in the intermediate by the second aluminum monomer results in a lowering of the activation energy for the hydrogen transfer and accounts for the increased rate of the 2:1 pathway over the 1:1 pathway. The 2:1 transition state contains a four-membered ring very similar in structure to the 1:1 transition state with the second aluminum coordinated to the carbonyl oxygen. The Al–O and nascent C–H distances in the 2:1 ring are longer than the corresponding distances in the 1:1 structure, indicative of the looser binding of the carbonyl to the aluminum in this structure.

4.2. Alkylaluminum reagents with β-hydrides

The mechanism of reduction of carbonyls by alkylaluminum reagents with β-hydrides has been examined. The

first step in this reaction is complexation of the carbonyl to the aluminum reagent via donation of a carbonyl-oxygen lone-pair into the empty 3p orbital of the aluminum. Formation of this complex is rapid and the intermediate formed is very stable. Complexation energies range from –12 to –21 kcal/mol. The transition state for hydrogen transfer consists of a six-membered cyclohexane-like ring in a slightly distorted chair configuration. The activation barrier for this reaction is calculated from the intermediate and ranges between 16 and 23 kcal/mol for the aluminum reagents and carbonyls studied. The reduced reactivity of the alkylalkoxyaluminum reaction products towards reduction of further carbonyls was found to be due to a larger activation barrier from intermediate to dialkoxy product than from the alkylaluminum intermediate to monoalkoxy product. The complexation energies of both aluminum reagents are the same and the activation energy to dissociation of the alkoxyaluminum intermediate is lower than the activation energy for forward reaction to product, making dissociation of the alkoxyaluminum intermediate more favorable than reduction of the carbonyl by the alkoxy reagent.

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