Transition States for the Carboalumination of Alkenes and Alkynes

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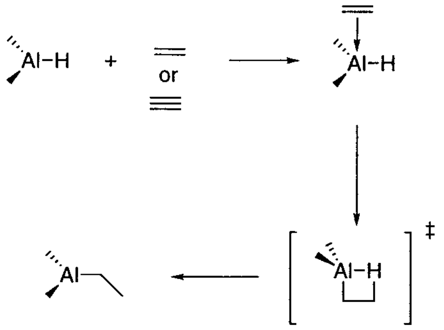
Ab initio molecular orbital theory was used to characterize stationary points on the potential energy surface for the carboalumination of alkenes and alkynes. Activation energies and entropies of activation were calculated and found to be in good agreement with experimental values. A π-complex between the alkyl aluminum and the substrate is a stable precursor to the transition structure. The transition structures are four-centered. Substituent effects on the transition structure geometries are small and predictable, suggesting that standard values for geometrical parameters for this and related reactions are reasonable. The anomalous relative reactivities of substrates can be explained by considering the reaction to essentially be a nucleophilic attack, rather than an electrophilic one.

Introduction

Carboalumination and hydroalumination were discovered by Ziegler[1] in the 1950s, thanks in part to his fortuitous choice of hydrocarbon solvents. Earlier workers had dismissed organoaluminum reagents as uninteresting, since the ether solvents that typically accelerated the analogous reactions with organolithium and -magnesium reagents rendered the aluminum reagents essentially inert. In 1972, on the basis of kinetic studies of the addition of propene to trimethylaluminum Egger[2] proposed that gas-phase carboalumination reactions proceed through a four-center transition state, without prior complexation of the substrate to the aluminum center, similar to that proposed for the hydroalumination reaction. Though there was evidence for stable intramolecular π-complexes of alkenes,[3] and other studies had implicated such intermediates in hydroalumination reactions,[4] Egger's interpretation of the kinetic data suggested that such complexes did not participate in carboalumination. He notes also that the relative reactivities of substrates, in particular the more rapid insertion of alkynes than alkenes, in these reactions is anomalous.

Scheme 1 depicts the accepted pathway for the addition of an alkene or alkyne to an aluminum−hydrogen bond. The reaction begins with formation of a π-complexed intermediate by electrophilic attack of the metal on the π-system of the target carbon−carbon multiple bond. These weakly bound intermediates intermediates[5] have previously been described theoretically by us.[6] A four-center planar transition structure connects the π-complexed intermediate with the insertion product. Such a transition state has been characterized using ab initio molecular orbital techniques by our group[7] and others.[8] As one might expect in these polar systems, the transition state exhibits asynchronous bond-breaking and bond-making between the four centers. The related hydroboration reaction has been theoretically studied by Houk[9] and others.[10]

Scheme 1



The more stringent requirements of the metal−carbon bond compared to the metal−hydrogen bond substantially limits the scope of carbometalation reactions in general. For example, simple alkylboranes do not typically add to alkenes and alkynes[11] (although there is evidence for allylboronation),[12] while hydroboration is facile. Products of reactions with alkylaluminum com-

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plexes are often affected by strongly competing hydroalumination reactions and, at least in the case of terminal alkynes, proton abstraction may dominate.

Sakai has theoretically characterized the insertion of ethylene into the AlC bond of H_2AlCH_3 at the 3-21G level as a model for the Ziegler−Natta reaction.[13] The reaction path is found to be analogous to that sketched above for hydroalumination, and contrary to Egger's proposal, included a π-complexed intermediate. A localized molecular orbital charge-center analysis was used to characterize the electronic structure of the critical points of the reaction, where the position of the charge centroid was taken to represent the "average" location of electrons.[14] Comparing this position in the π-complex, transition state, and product, Sakai suggested that AlC bond formation was more complete in the transition structure than either the breaking of the $AlCH_3$ or the making of the $C-CH_3$ bonds. A direct correlation was noted between activation energy and energy of the AlR bond into which the substrate inserts.

Related reactions have been studied theoretically, including multiple bond insertions into TiC and TiH bonds[15,16] and into LiC and LiH bonds.[17,18] A molecular orbital calculation characterizing the π-complex of MgH_2 with ethylene has been reported,[19] and we present below some our own preliminary results for the transition structure of the insertion that follows.

We have used ab initio molecular orbital theory to characterize the reaction path for addition of simple alkenes and alkynes into AlC bonds. Structures have been determined for critical points on the reaction surface, and statistical mechanics has been applied to compute the activation energy and the entropy of activation for the parent reactions. We find that a π-complexed intermediate is a stable minimum on the potential energy surface, albeit a shallow minimum that is unlikely to be important kinetically. Reaction barriers, both trends and absolute values, are in good agreement with experiment. Trends in entropies concur with those observed experimentally. We contend that the anomalies in relative reactivities can be explained in terms of a nucleophilic model for the reaction, instead of the more usual picture of an electrophilic attack.

Methods

The GAUSSIAN[20] and SPARTAN[21] program suites were used to perform all electron ab initio molecular orbital calculations. In general, no symmetry constraints were imposed on any of the structures, but care must be taken in the interpretation of Gaussian thermodynamic properties in these cases. The misassignment of the symmetry of the molecule, for example, when nominally symmetry equivalent bond lengths differ in later decimal places, can lead to large errors in the entropy computed by Gaussian. Normal-mode analysis was used to characterize the nature of critical points: structures having no imaginary frequencies are minima; structures having a single imaginary frequency correspond to transition structures.

Previous studies have shown the HF/3-21G(*)[22] level to be adequate for characterizing the geometry of trialkyl aluminum complexes[6,23] as well as hydroalumination transition structures.[7] It has proved less acceptable for the determination of the structures of the weakly bound π-complexes. This is not unexpected, given the generally poor performance of Hartree−Fock models in predicting the structures of donor−acceptor complexes. Hartree−Fock structures for these complexes are generally too weakly bound; the aluminum−substrate distances are roughly 0.1 Å too long when compared to results from correlated levels. Table 1 compares the HF/3-21G(*) bond-making and bond-breaking parameters for selected carboalumination transition structures with those from larger basis sets: 6-31G*,[24] 6-31G**, and 6-311+G*.[25] Changes in bond lengths relative to the HF/3-21G(*) model are all less than 0.01 Å, with the exception of the breaking AlC bond distance in the $H_2AlC_2H_5 + C_2H_4$ transition structure, which is 0.03 Å longer at HF/6-31G*. Changes in bond angles and dihedrals were also insignificant; the largest change in bond angle was less than 0.7° and that for dihedrals was 1.2°. Neither including polarization functions on hydrogen nor addition of diffuse functions significantly altered the calculated geometries in these systems. Including electron correlation in the model using second-order Møller−Plesset theory[26] resulted in somewhat larger changes in the calculated parameters relative to HF/3-21G(*). Differences in bond lengths between correlated and uncorrelated models for the transition states are substantially smaller than those seen in the π-complexes. For example, the forming AlC bond in the $H_2AlCH_3 + C_2H_4$ transition structure at the MP2/6-31G* level was 0.022 Å longer relative to the smaller uncorrelated HF/3-21G(*) model. The AlC bond in the corresponding intermediate is 0.136 Å shorter in the MP2/6-311+G* structure than in that from HF/3-21G(*). We therefore have chosen to use the HF/3-21G(*) model as our base for comparing geometries of transition structures, keeping in mind that the HF/3-21G(*) structures for the intermediates will be too weakly bound.

To determine whether the 3-21G(*) basis can be reasonably used to represent geometries of alkylmagnesium compounds, calculations on simple MgR_2 compounds were compared with the extant experimental data, and selected transition structures for hydro- and carbomagnesiation reactions were also

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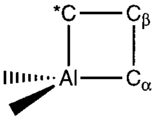
Table 1. Comparison of Carboalumination Transition-State Geometries Using Various Theoretical Models[a,b]

reaction	model	r(AlC*)	r(AlC$_\alpha$)	r(C$_\alpha$C$_\beta$)	r(C$_\beta$C*)	∠(AlC$_\alpha$C$_\beta$)	∠(C*AlC$_\alpha$)	d^c
$H_2AlCH_3 + C_2H_4$	3-21G(*)	2.184	2.050	1.434	2.156	82.6	93.7	8.1
	6-31G*	2.189	2.051	1.429	2.153	82.5	93.5	8.4
	6-31G**	2.189	2.050	1.429	2.152	82.5	93.5	8.2
	6-311+G*	2.185	2.049	1.428	2.149	82.4	93.5	8.7
	MP2/6-31G*	2.177	2.050	1.429	2.131	78.8	95.2	10.4
$H_2AlCH_3 + C_2H_2$	3-21G(*)	2.128	2.061	1.254	2.211	85.8	91.6	0.0
	6-31G*	2.124	2.056	1.250	2.219	85.3	92.3	0.0
	6-311+G*	2.120	2.055	1.247	2.216	85.2	92.3	0.0
$H_2AlCH_3 + C_3H_6$	3-21G(*)	2.175	2.033	1.445	2.173	84.8	93.7	3.9
	6-31G*	2.185	2.031	1.443	2.176	85.1	93.4	5.1
	6-31G**	2.185	2.030	1.443	2.175	85.2	93.4	5.1
$H_2AlC_2H_5 + C_2H_4$	3-21G(*)	2.212	2.042	1.438	2.157	81.8	93.8	11.4
	6-31G*	2.239	2.039	1.433	2.159	81.7	93.7	11.3

[a] Bond lengths in angstroms and angles in degrees. [b] Parameter labels are as shown below:



[c] Refers to the dihedral angle between AlC$_\alpha$C$_\beta$C*.

Table 2. Comparison of Calculated and Experimental Structures for Simple Magnesium Alkyls

molecule	basis set	r(MgC)[a]	∠(MgCC)
Mg(CH$_3$)	3-21G(*)	2.107	
	6-31G*	2.110	
HMgC$_2$H$_5$	3-21G(*)	2.111	113.3
	6-31G*	2.110	116.8
Mg(C$_2$H$_5$)$_2$	3-21G(*)	2.115	113.2
Mg(n-pentyl)$_2$[b]	expt	2.126	118.3

[a] Bond lengths in angstroms and angles in degrees. [b] Experimental structure from ref 28.

optimized at higher levels. At present, only the structures of four organomagnesium compounds have been determined using gas-phase electron diffraction methods.[27] Of these, dineopentylmagnesium is the simplest. Table 2 compares calculated HF/3-21G(*) geometrical parameters of small MgR$_2$ compounds with the calculated and experimental values from Mg(neopentyl)$_2$.[28] The HF/3-21G(*) calculated Mg−C bond length for dineopentylmagnesium agrees well with those for other small magnesium compounds and is 0.012 Å longer than the experimentally determined value. The MgCC bond angle is slightly smaller than the experimental value. At the HF/6-31G* level, the experimental structure is nearly exactly reproduced.

Table 3 reports the parameters derived from various theoretical models describing the MgCCC and MgCCH core for transition structures for the insertion of substrates into MgC and MgH bonds. The deviations from HF/3-21G(*) values in the parameters describing the transition structure core are at most 0.02 Å for bond lengths and 0.9° for bond angles. At the 6-31G* level the forming and breaking Mg−C bonds lengthened by an average of 0.01 Å. Addition of polarization functions to the hydrogen basis set did not affect the core parameters significantly. Including correlation effects at the MP2/6-31G* level resulted in geometrical changes similar to those observed in the corresponding aluminum structures. The forming CH bond is shortened by 0.07 Å. The MgCC angle decreases by 4.2°, while the CCH angle increases by 4.8°. Similar shifts are noted in the MP2/6-31G* geometry of the HMgCH$_3$ + ethylene transition structure. Differences from the 3-21G(*) values were less than 0.01 Å for lengths and 3.1° for angles. We will also use the HF/3-21G(*) as our basis for the description of the structures of magnesium compounds.

As the Hartree−Fock model is known to do a poor job of describing the absolute energies of bond-making and -breaking processes, we have used correlated models to compute these energy differences. Single-point energy calculations at the MP2/6-311+G**//HF/3-21G(*) geometry were used to compute barriers for a subset of reactions. Trends in reaction barriers seem to be well predicted using only HF/3-21G(*)//HF/3-21G(*); we have used this model to survey the reactivity of the larger set of reactions. Corrections for zero-point vibrational energies and to higher temperatures for comparison to experimental work were computed where indicated along with entropies of activation.[29]

A modified version of CHELP was used to calculate atomic charges.[30]

Results and Discussion

Intermediate π-Complexes. π-bound alkyl aluminum halide complexes of alkenes and alkynes are found to be stable intermediates on the carboalumination

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$$RT^2\left(\frac{1}{q_{\rm tors}}\right)\left(\frac{\partial q_{\rm tors}}{\partial T}\right)$$

At high temperatures, typically greater than 300 K, the rotations are essentially free, and $q_{\rm tors}$ for an m-fold barrier can be computed from

$$q_{\rm tors,free} = \frac{1}{m}\left(\frac{8\pi^3 IkT}{h^2}\right)^{1/2}$$

Terms in $S_{\rm vib}$ which arise from low-frequency torsional modes were replaced by

$$R \ln q_{\rm tors} + \frac{RT}{q_{\rm tors}}\left(\frac{\partial q_{\rm tors}}{\partial T}\right)$$

where $q_{\rm tors}$ must be explicitly constructed for rotations that are not free, but may be calculated using the expression given above for $q_{\rm tors,free}$.

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Table 3. Comparison of HMgR + Alkene/Alkyne Transition-State Geometries Using Various Theoretical Models[a,b]

reaction	model	r(MgR*)	r(MgC$_\alpha$)	r(C$_\alpha$C$_\beta$)	r(C$_\beta$R*)	∠(MgC$_\alpha$C$_\beta$)	∠(C*MgC$_\alpha$)
$MgH_2 + C_2H_4$	3-21G(*)	1.844	2.241	1.404	1.721	80.8	79.1
	6-31G*	1.845	2.252	1.402	1.703	80.7	78.2
$MgH_2 + C_2H_2$	3-21G(*)	1.803	2.246	1.240	1.866	83.6	79.8
	6-31G*	1.799	2.257	1.238	1.870	83.6	79.5
	6-31G**	1.793	2.259	1.238	1.869	83.3	79.6
	MP2/6-31G*	1.800	2.244	1.255	1.797	79.4	80.4
$HMgCH_3 + C_2H_4$	3-21G(*)	2.224	2.186	1.413	2.209	82.3	91.4
	6-31G*	2.236	2.195	1.411	2.202	82.5	90.6
	6-31G**	2.238	2.195	1.412	2.200	82.6	90.5
	MP2/6-31G*	2.217	2.199	1.413	2.199	79.2	92.7

[a] Bond lengths in angstroms and angles in degrees. [b] Parameter labels are as shown below:

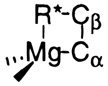

Table 4. Selected HF/3-21G(*) Geometrical Parameters for π-Complexes[a]

molecule	r(AlC)	r(CC)
$H_2AlCH_3\cdots C_2H_4$	2.760	1.327
$H_2AlCH_3\cdots C_3H_6$	2.805	1.329
$H_2AlC_2H_5\cdots C_2H_4$	2.755	1.327
$HAl(CH_3)_2\cdots C_2H_4$	2.862	1.325
$Al(CH_3)_3\cdots C_2H_4$	2.965	1.323
$HClAlCH_3\cdots C_2H_4$	2.730	1.328
$Cl_2AlCH_3\cdots C_2H_4$	2.654	1.330
$H_2AlCH_3\cdots C_2H_2$	2.813	1.193
$H_2AlC_2H_5\cdots C_2H_2$	2.803	1.193
$Al(CH_3)_3\cdots C_2H_4$	3.000	1.191
$Cl_2AlCH_3\cdots C_2H_4$	2.768	1.194

[a] Bond lengths in angstroms.

pathway, as expected. Aluminum−carbon and carbon−carbon bond distances for these intermediates are collected in Table 4. The CC bond lengths in the substrates are not markedly affected by binding to the aluminum; the largest difference is seen in the ethylene complex of Cl_2AlCH_3, where the CC bond is 1.327 Å compared to 1.315 Å for uncomplexed ethylene at the same level. The CC bond in acetylene is shortened by less than 0.01 Å upon complexation. As in the corresponding intermediates on the hydroalumination pathway, alkynes are somewhat more weakly bound than alkenes due to the lower energy of the bonding π-orbitals. The complexes are not as strongly bound as the hydroalumination intermediates; the predicted AlC distance in the complex of AlH_3 with ethylene is 2.700 Å, while that for H_2AlCH_3 is 2.760 Å. The HF/3-21G(*) structures provide an upper limit to the binding of these substrates. Binding is substantially tighter at the MP2/6-311+G** level; the AlC distance in $H_2AlCH_3\cdots C_2H_4$ is reduced to 2.623 Å and the CC distance is 1.348 Å. The trends in binding are as expected, with the stronger Lewis acids having shorter AlC distances.[31]

Carboalumination Transition Structures. Table 5 summarizes the key structural parameters for the 17 carboalumination reactions we consider here. Table 6 contains the corresponding data for seven carbomagnesiation reactions. Scanning the tables quickly reveals the similarity of the structures. All the structures are much tighter than the corresponding intermediate π-complexes. The forming AlC bonds average 2.04 Å for the ethylene insertion structures, compared to an average value of 2.78 Å in the corresponding π-complexes. The AlCCC core is planar in the transition structures, or nearly so, as opposed to the perpendicular arrangement of the substrate relative to the active AlC bond found in the intermediates. The differences in the distances between the aluminum center and the two substrate carbons are sufficiently different to warrant calling these four-center transition structures (2.346 and 2.050 Å in the $H_2AlCH_3 + C_2H_4$ transition structure). The angle between the axis connecting the aluminum to the centroid of the CC double bond and the breaking AlC bond is 73.8°, compared to 90° expected for a three-center structure.[32] The analogous angle in the $HMgCH_2CH_3 + C_2H_4$ transition structure is comparable, 73.3°. We note that Hommes and Schleyer[33] have shown that post-Hartree−Fock methods are necessary to properly discriminate between three- and four-center transition states in insertion reactions with boron; however, we did not find that to be the case for the hydroalumination reaction. The MP2/6-31G* structure for the $H_2AlCH_3 + C_2H_4$ transition structure is not substantially different than the HF/3-21G(*) geometry; the two AlC distances are 2.260 and 2.050 Å and the CC centroid−aluminum axis makes an angle of 75.3° with the breaking AlC bond.

Figure 1 shows the HOMO for the transition structure for the reaction of H_2AlCH_3 with C_2H_4, compared to the HOMO for the intermediate. Note that while the π-system is intact in the intermediate, there has been visible degradation in the transition structure. Similar alterations in the π-bond were seen in the hydroalumination transition structure.[7]

These reactions are highly exothermic (>20 kcal mol^{-1}), and one would therefore expect the transition structures to be early. However, most of the parameters suggest otherwise. The forming AlC bond is roughly 2.04 Å compared to an average value of 1.99 Å in the products, suggesting it is nearly completely formed. Similarly, the CC double bond in the alkene insertion transition structures with an average value of 1.44 Å is very nearly midway between a double and a single bond. The CC triple bond in the alkyne transition structures has a mean value of 1.26 Å, also suggesting

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(31) The trends in Lewis acidities are $AlCl_3 > AlRCl_2 > AlR_2Cl > AlR_3$. The π-donating capability of chlorine does not greatly influence the orbital energy of the LUMO. See refs 6 and 35b.

(32) This angle in a perfect four-center structure with all bonds the same length would be 63°.

(33) Hommes, N. J. R. v. E.; Schleyer, P. v. R. *J. Org. Chem.* **1991**, *56*, 4074.

Table 5. Selected Parameters for Carboalumination Transition Structures Optimized at HF/3-21G(*)[a]

reaction	r(AlC*)	r(AlC$_\alpha$)	r(C$_{\alpha C\beta}$)	r(C$_{\beta C*}$)	∠(AlC$_\alpha$C$_\beta$)	∠(C*AlC$_\alpha$)	d[c]
$H_2AlCH_3 + C_2H_4$	2.184	2.050	1.434	2.156	82.6	93.7	8.1
$H_2AlCH_3 + C_3H_6$	2.175	2.033	1.445	2.173	84.8	93.7	3.9
$H_2AlCH_3 + C_3H_6$[b]	2.185	2.048	1.436	2.152	82.0	93.5	13.3
H_2AlCH_3 + isobutene	2.164	2.022	1.458	2.191	86.2	93.3	10.3
H_2AlCH_3 + isobutene[b]	2.185	2.046	1.440	2.157	82.1	94.1	10.1
$HAl(CH_3)_2 + C_2H_4$	2.187	2.058	1.431	2.159	82.7	93.5	7.1
$Al(CH_3)_3 + C_2H_4$	2.187	2.066	1.428	2.161	82.7	93.3	7.7
$H(Cl)AlCH_3 + C_2H_4$	2.147	2.029	1.437	2.160	82.8	94.6	9.5
$Cl_2AlCH_3 + C_2H_4$	2.120	2.008	1.443	2.159	83.2	95.6	6.5
$H_2AlC_2H_5 + C_2H_4$	2.212	2.042	1.438	2.157	81.8	93.8	11.4
$H_2AlC_2H_5 + C_3H_6$[b]	2.211	2.021	1.453	2.164	84.2	93.8	5.1
$H_2AlC_2H_5 + C_3H_6$	2.196	2.030	1.447	2.179	83.4	93.5	15.9
$H(CH_3)AlC_2H_5 + C_2H_4$	2.212	2.042	1.438	2.157	81.8	93.9	11.4
$H_2AlCH_3 + C_2H_2$	2.128	2.061	1.254	2.211	85.8	91.6	0.0
$H_2AlCH_3 + C_3H_4$	2.125	2.028	1.262	2.244	89.5	91.5	0.0
$H_2AlC_2H_5 + C_2H_2$	2.161	2.048	1.257	2.191	84.7	91.6	0.0
$H_2AlC_2H_5 + C_3H_4$[b]	2.161	2.048	1.257	2.191	84.7	91.0	0.0

[a] Bond lengths in angstroms and angles in degrees. See Table 1 for parameter labels. [b] Transition structure leading to Markovnikov addition. [c] Refers to the dihedral angle between AlC$_\alpha$C$_\beta$C*.

Table 6. Selected Parameters for Carbomagnesiation Transition States Optimized at HF/3-21G(*)[a]

reaction	r(MgR*)	r(MgC$_\alpha$)	r(C$_\alpha$C$_\beta$)	r(C$_\beta$R*)	∠(MgC$_\alpha$C$_\beta$)	∠(C*MgC$_\alpha$)
$HMgCH_3 + C_2H_4$	2.224	2.186	1.413	2.208	82.5	91.4
$HMgCH_3 + C_3H_6$	2.220	2.168	1.422	2.224	84.0	91.3
$ClMgCH_3 + C_2H_4$	2.191	2.164	1.416	2.221	82.1	92.8
$HMgC_2H_5 + C_2H_4$	2.225	2.197	1.406	2.250	80.8	93.0
$HMgCH_3 + C_2H_2$	2.219	2.192	1.248	2.277	84.1	89.8
$ClMgCH_3 + C_2H_2$	2.190	2.168	1.250	2.286	84.1	91.1
$HMgC_2H_5 + C_2H_2$	2.239	2.191	1.249	2.273	83.1	90.0

[a] Bond lengths in angstroms and angles in degrees. See Table 3 for parameter labels.

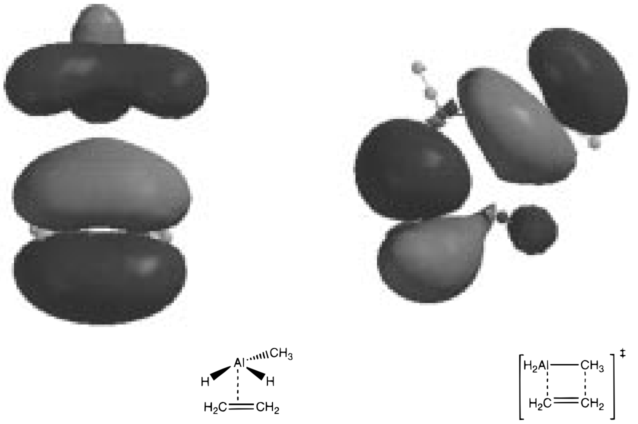

Figure 1. HOMO of π-complex between H_2AlCH_3 and ethylene (left) compared with HOMO of the transition structure for reaction of ethylene with H_2AlCH_3 (right).

it is halfway to a double bond. Both these values indicate a later transition state than the Hammond postulate might predict. If one instead uses the forming CC bond as a measure, which has a mean value of 2.16 Å, the transition state appears to be much earlier. Though this CC bond is substantially shorter than the 3.6 Å typical of the intermediates, it is still more than 0.5 Å longer than the usual CC single bond. The asynchronous nature of these transition structures, late in some senses, early in others, allows them to sidestep the Woodward−Hoffmann rules, which forbid this 2+2 addition.

The reduced binding affinity of alkynes relative to alkenes does not appear to play a major role in the geometry of the alkyne transition structures. The forming AlC distances are not much different than those in the corresponding alkene structures and exhibit no particular trend with regard to those structures. The breaking AlC bond distances are all slightly shorter than those in alkene insertions, and the forming CC bonds are longer, suggesting a slightly earlier transition structure. Overall, the alkyne insertion transition structures appear no tighter than those leading to alkene insertion for either aluminum or magnesium systems. Computed absolute entropies for the $H_2AlCH_3 + C_2H_4$ and $H_2AlCH_3 + C_2H_2$ transition structures support this: the difference in $S_{298.15}$ is less than 0.01 cal mol^{-1} K^{-1}. Differences in the absolute entropies for the corresponding carbomagnesiation transition structures are somewhat larger, 2.16 cal mol^{-1} K^{-1}.

We do find that while the alkyne carboalumination transition structures are planar, as are all the hydroalumination transition structures, alkene carboalumination transition structures are slightly twisted. Morokuma et al. observed a similar nonplanarity in the transition structure for insertion of ethylene into the TiC bond of $CH_3TiCl_2^+$, which they attribute to the need to avoid interactions between CH bonds on the methyl group attached to the titanium and the CH bonds on the substrate.[15] Alternatively, the twist could alleviate F-strain[34] between the AlR bonds and the CH bonds on the substrate. Comparison of the AlC=CC dihedral angle in the anti-Markovnikov and Markovnikov transition structures suggests the latter. Substitution at the substrate carbon alpha to the aluminum results in a dihedral of 13.3° compared to 3.9° for the preferred orientation. Carbomagnesiation transition structures are also all planar, again suggesting alleviation of F-strain as the source of the twist in the alkene carboalumination structures.

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(34) Brown, H. C.; Davidson, N. *J. Am. Chem. Soc.* **1942**, *64*, 316. Buhr, G.; Muller, G. E. *Chem. Ber.* **1955**, *88*, 251.

Structurally, the transition states for carboalumination are considerably tighter than those for the corresponding hydroalumination reactions. Typical forming AlC bonds are 2.04 Å for carboalumination compared to 2.13 Å for hydroalumination; the substrate bond has slightly more double-bond character, 1.41 Å compared to 1.44 Å. Sterically one might expect that the transition structure involving the less demanding ligand, H, be tighter. The closer approach required to form a CH rather than a CC bond should also promote a tighter structure. Experimental kinetic isotope effects support the assignment of a looser transition structure for insertion into the AlH bond.[35]

Egger[36] proposes a quadrupolar transition structure, while Eisch argues for less charge separation based on Hammet σ,ρ relationships.[35] Charges on the key atoms are summarized in Table 7. The data suggest that while indeed there is substantial charge separation in the transition structure, it would not be best described as quadrupolar. The breaking AlC bond is quite polar, with the metal bearing a charge of roughly $+0.5e$ and the carbon completing the dipole with a corresponding charge of approximately $-0.5e$. The alkene or alkyne substrates are not complete polarized, though the carbon proximate to the metal (C_α) is more negatively charged than in the free molecules, $-0.6e$ compared to $-0.3e$ for ethylene and $-0.5e$ compared to $-0.3e$ for acetylene. Substitution at the carbon which is transferring to the substrate with an electron-donating group not surprisingly results in a less polar AlC bond.

We find that the transition structure geometries for insertion into either AlC or MgC bonds are relatively insensitive to substitution with alkyl groups at various position. Houk and co-workers have noted a similar lack of sensitivity to alkyl substitution in the transition structures for hydroboration.[9b] Substitution by electron-withdrawing chlorine gives rise to larger changes in the core parameters for the carboalumination reactions. Replacement of hydrogen with an electron donor at the aluminum leads to an increase in the length of the forming AlC bond, as the electrophilicity of the aluminum is reduced. The forming AlC distance increases by 0.008 Å when a single methyl group is substituted, by twice that when two methyl groups are used. Substantial shortening is observed when chlorine is substituted instead, 0.021 and 0.042 Å, respectively. The forming MgC bond is also shortened by substitution of chlorine at the metal center. Replacing the transferring methyl group with ethyl leads to slight increases in the breaking AlC bond distance (roughly 0.03 Å). The remaining parameters are virtually unchanged.

Comparing the transition structures for Markovnikov and anti-Markovnikov additions, we again find only small differences. The trends are as expected. The distance between the slightly positive β-carbon and the more negative carbon in the alkyl group being transferred should therefore be longer in the Markovnikov structure; the lengthening should be less pronounced in those structures with greater stabilization of the δ positive charge on the β-carbon. The forming CC single bond is generally longer in the preferred anti-Markovnikov structures. It is 0.03 Å longer in the transition structure for the anti-Markovnikov addition of an AlC bond to isobutene in which two electron-donating groups are attached at the β-carbon and 0.05 longer in the transition structure for the preferred addition orientation to propyne.

Table 7. Charges for Transition Structures Optimized at HF/3-21G(*)[a,b]

reaction	Al	C*	C_α	C_β
$H_2AlCH_3 + C_2H_4$	0.73	−0.50	−0.58	0.03
$H_2AlC_2H_5 + C_2H_4$	0.64	−0.13	−0.57	0.03
$H_2AlCH_3 + C_2H_2$	0.70	−0.58	−0.46	−0.02
$H_2AlC_2H_5 + C_2H_2$	0.57	−0.19	−0.40	−0.10

[a] Aluminum and magnesium radii were determined by best fit to HF/3-21G(*) electron density surfaces using SPHERE (Francl, M. M.; Hout, R. F., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 563). Al = 2.1 Å, Mg = 1.7 Å, C = 1.8 Å, Al−H = 1.4 Å, C−H = 1.2 Å. [b] For parameter labels refer to Table 1.

Table 8. Relative Energies for Critical Points at HF/3-21G(*)//HF/3-21G(*) for Carboalumination Reactions

reaction	structure	relative energy (kcal mol^{-1})
$H_2AlCH_3 + C_2H_4$	reactants	0.0
	π-complex	−8.4
	TS	+27.1
	product	−19.9
$H_2AlCH_3 + C_3H_6$	reactants	0.0
	TS I	+26.7
	TS II[a]	+31.4
H_2AlCH_3 + isobutene	reactants	0.0
	TS I	+27.1
	TS II[a]	+35.6
$HAl(CH_3)_2 + C_2H_4$	reactants	0.0
	TS	+28.2
$Al(CH_3)_3 + C_2H_4$	reactants	0.0
	TS	+29.1
$Cl_2AlCH_3 + C_2H_4$	reactants	0.0
	TS	+25.7
$H_2AlC_2H_5 + C_2H_4$	reactants	0.0
	TS	+28.5
$H_2AlC_2H_5 + C_3H_6$	reactants	0.0
	TS II	+30.0
$H(CH_3)AlC_2H_5 + C_2H_4$	reactants	0.0
	TS	+29.8
$H_2AlCH_3 + C_2H_2$	reactants	0.0
	π-complex	−6.7
	TS	+23.7
	product	−36.1
$H_2AlCH_3 + C_3H_4$	reactants	0.0
	TS	+24.7
$H_2AlC_2H_5 + C_2H_2$	reactants	0.0
	TS	+25.2
$H_2AlC_2H_5 + C_3H_4$	reactants	0.0
	TS[a]	+28.4

[a] Transition state leading to Markovnikov addition.

Reactivity. Tables 8 and 9 summarize the barriers to reaction for carbometalation reactions of aluminum and magnesium complexes, respectively. In all cases the π-complexed intermediates are more stable than the reactants. The barriers to carboalumination are all found to be higher than those for the corresponding hydroalumination reaction. The calculated barriers toward insertion into AlC bonds at HF/3-21G(*) are all on the order of 25−30 kcal mol^{-1}; those for insertion into MgC are comparable. Our experience with comput-

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(35) (a) Eisch, J. J. Aluminum. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, England, 1995; Vol. 11, McKillop, A., Ed.; Chapter 6, pp 277−311. (b) Esich, J. J. Aluminum. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, England, 1995; Vol. 1, Housecroft, C., Ed.; Chapter 10, pp 431−502.

(36) (a) Egger, K. W. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1017. (b) Egger, K. W. *J. Am. Chem. Soc.* **1969**, *91*, 2867.

Table 9. Relative Energies for Critical Points at HF/3-21G(*)//HF/3-21G(*) for Carbomagnesiation Reactions

reaction	structure	relative energy (kcal mol^{-1})
$HMgCH_3 + C_2H_4$	reactants	0.0
	π-complex	−8.0
	TS	+25.4
$HMgCH_3 + C_3H_6$	reactants	0.0
	TS	+26.2
$ClMgCH_3 + C_2H_4$	reactants	0.0
	TS	+24.3
$HMgC_2H_5 + C_2H_4$	reactants	0.0
	TS	+24.0
$ClMgH + C_2H_2$	reactants	0.0
	TS	+14.2
$HMgCH_3 + C_2H_2$	reactants	0.0
	TS	+21.5
$ClMgCH_3 + C_2H_2$	reactants	0.0
	TS	+20.5
$HMgC_2H_5 + C_2H_2$	reactants	0.0
	TS	+21.2

ing barriers to hydroalumination suggests the HF/3-21G(*) values will be too high relative to experiment.[7] Using the MP2/6-311+G**//HF/3-21G(*) model, we find the predicted barriers to be lower, on the order of 15−20 kcal mol^{-1}.

The MP2/6-311+G**//HF/3-21G(*) barriers in Table 10 compare well to experimental values when corrected for zero-point vibrational energy and thermal effects. At 500 K we compute an enthalpy of activation for the reaction of H_2AlCH_3 and C_2H_4 of 22.2 kcal mol^{-1}, which matches within experimental error Egger's measured value of 22.5 ± 0.45 kcal mol^{-1} [36b] for the reaction of $Al(CH_3)_3$ and C_2H_4. We also correctly find that the enthalpy of activation is smaller for the insertion of propene into the AlC bond of H_2AlCH_3 than for the insertion of ethylene. Note that while the "barrier" to reaction is lower, the reaction with propene actually proceeds more slowly due to a smaller Arrhenius pre-exponential factor. Experimentally $\Delta G^‡$ for the propene insertion is 36.2 kcal mol^{-1} compared to 34.5 kcal mol^{-1} for ethylene.[36a] Our results parallel these. Propene insertion has a calculated $\Delta G^‡$ of 47.0 kcal mol^{-1} at MP2/6-311+G**//HF/3-21G(*), while ethylene insertion is a somewhat lower 43.4 kcal mol^{-1}. Calculated values for the entropy of activation are larger than those derived experimentally, probably as a result of the relatively poor description of the low-frequency modes of vibration at HF/3-21G(*). Our results underscore the importance of considering more than the simple quantum mechanical ΔE of reaction and correcting for thermal effects as well as computing entropies of activation in assessing relative reactivities in these reaction. Since experimentally the relative reactivity of these compounds is anomalous, and since the order provides some insight into the characteristics of the transition structure, predicting the correct order is critical.

In agreement with experiment, we find alkynes to be more reactive than the corresponding alkenes. Generally, alkenes are expected to have a higher reactivity toward electrophilic attack than alkynes.[37] For example, though steric factors play a significant role in the relative rate of hydroboration, it appears that alkenes are more reactive.[9b,38] Eisch attributes the unexpectedly higher reactivity of the alkynes in both hydroalumination and carboalumination to a tighter transition structure for alkene insertion which would lead to an increase in F-strain, arguing that the ensuing relative destabilization of the transition structure would raise the barrier to reaction. We find that neither the structural evidence (vide supra) nor the absolute entropies support this. $S_{298.15}$ of the acetylene and ethylene carboalumination transition states are similar, 73.9 and 73.8 cal mol^{-1} K^{-1}, respectively.[39] However, the observed order of reactivity would be expected if this were considered a *nucleophilic attack*. Indeed, if one looks at the HOMO of the four-center carboalumination transition structure (Figure 2), it strongly resembles that for nucleophilic attack of methyl anion on an alkene with an AlR_2 "spectator". We suggest that the heightened nucleophilic character of the transition structure leads to an expectation of higher reactivity for alkynes. Conversely, the HOMO for the three-center hydroboration transition structure (Figure 2) is more reminiscent of those seen for electrophilic attack; hence one expects (as indeed one finds) the preference to be for alkenes.

Comparing the relative reactivity of propene and ethylene offers further support for a nucleophilic model for these reactions. Here the expectations based on an electrophilic attack model are that the more highly substituted (and therefore electron-rich) alkenes would be more reactive. Again, the relative barriers are as anticipated for the hydroboration reactions. Of propene and ethylene, propene is the more reactive. The so-called "inverse olefin" effect for carboalumination has been well documented; for example, the relative rates of reaction are $H_2C{=}CH_2 > H_2C{=}CHR > RCH{=}CHR > H_2C{=}CR_2$.[35] Dialkylmagnesium compounds exhibit similar reactivity patterns. For example, they are known to add more easily to $H_2C{=}CH_2$ than to $H_2C{=}CHR$.[40] Morokuma calculated propene to be less reactive than ethylene with $CH_3TiCl_2^+$.[16] Egger and others have attributed the higher reactivity of less substituted substrates to steric effects which overwhelm the expected stabilization of the transition structure expected from increasing substitution. Again, considering this to be a nucleophilic reaction changes the expectations: substrates that are electron rich, e.g., those with alkyl substituents, will be less reactive. Similarly, increasing the Lewis acidity of the aluminum, resulting in an electron-deficient substrate, should lower the barrier. We find the HF/3-21G(*) barrier to insertion to be about 2 kcal mol^{-1} lower for Cl_2AlCH_3 than for H_2AlCH_3. Decreasing the Lewis acidity of aluminum, as expected, raises the barrier. The HF/3-21G(*) barrier for the reaction of $Al(CH_3)_3$ and C_2H_4 is roughly 2 kcal mol^{-1} higher than that in the parent.

Hay et al. found the addition of 1-octene to be more reactive by 2 ± 2 kcal mol^{-1} with triethyl than trimethylaluminum (18.3 ± 1.0 to 20.3 ± 1.0 kcal mol^{-1}).[41] Egger measured the rate of insertion of ethylene into triethylaluminum and found the reaction to be faster

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[37] March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley and Sons: New York, 1985.

[38] Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 3834.

[39] For comparison, $S_{298.15}$ of the transition state for the insertion of ethylene into AlH_3 is 74.1 cal mol^{-1} K^{-1}.

[40] Richey, H. G., Jr. In *Inorganic Reactions and Methods*; Hagen, A. P., Ed.; VCH: New York, 1989; Vol. 10, Section 5.4.2.5.1.

[41] Hay, J. N.; Hooper, P. G.; Robb, J. C. *Trans. Faraday Soc.* **1970**, *66*, 280.

Table 10. Reaction Barriers Computed at MP2/6-311+G//HF/3-21G(*)**[a]

reaction	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger\,b}$	$\Delta H^{\ddagger}{}_{500K}{}^{c}$	$\Delta S^{\ddagger}{}_{500K}{}^{c,d}$	$\Delta G^{\ddagger}{}_{500K}{}^{c}$	$\Delta G^{\ddagger}{}_{500K(expt)}{}^{e}$
$H_2AlCH_3 + C_2H_4$	20.6	23.5	22.2	−42.4	43.4	34.5
$H_2AlCH_3 + C_2H_2$	17.3	19.2	17.9	−39.2	37.5	
$H_2AlCH_3 + C_3H_6$	17.3	20.1	19.3	−55.3	47.0	36.2
$H_2AlC_2H_5 + C_2H_4$	17.8	20.6	19.6	−45.0	42.1	31.9

[a] All values in kcal/mol unless otherwise noted. [b] Corrected for zero-point vibrational energy. [c] Corrected for thermal effects. See Appendix for details. [d] Values in cal/(mol K). [e] Experimental data from ref 34a.

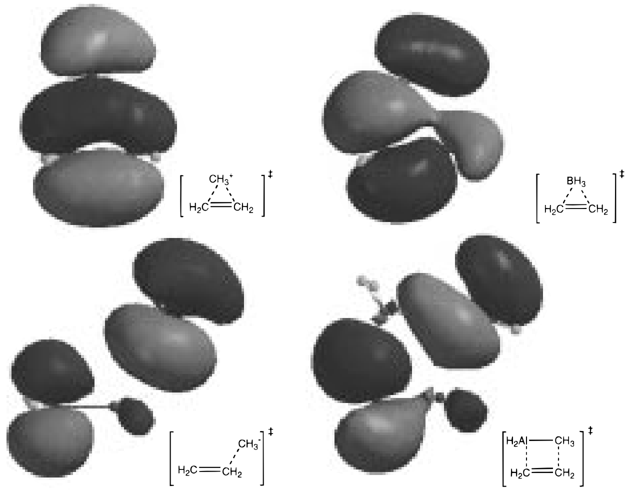

Figure 2. HOMO of the transition structure for the electrophilic attack of CH_3^+ on ethylene (top left) compared with the HOMO for the transition structure for the hydroboration of ethylene (top right). HOMO of the transition structure for the nucleophilic attack of CH_3^- on ethylene (bottom left) compared with the HOMO for the transition structure for the carboalumination of ethylene (bottom right).

than that with trimethylaluminum.[42] It has been suggested that the lower reactivity of trimethylaluminum reagents reflects the higher dissociation energy of the dimer due to the better bridging capabilities of CH_3 (ΔH_d = 20.2 kcal mol^{-1} for $Al(CH_3)_3$ and 10.2 kcal mol^{-1} for $Al(C_2H_5)_3$)[43] in a preliminary step of the reaction. However, it is unlikely that this step dominates the kinetics at high temperatures in the gas phase, yet the higher lability of the ethyl persists. Alternatively, Sakai has suggested in related reactions[13] that the barriers are related to the MC bond strength. We note, however, that while the AlC bond in Cl_2AlCH_3 is stronger than that in H_2AlCH_3, the barrier to reaction is lower. Again, a nucleophilic model of the reaction provides a better explanation, suggesting that reactivity should increase as the nucleophilicity of the transferring group increases. We find, in accord with experiment, $H_2AlCH_2CH_3$ to be more reactive than H_2AlCH_3, as expected from the relative nucleophilicities of CH_3^- and $CH_2CH_3^-$. Similarly, reaction of $HMgCH_2CH_3$ with ethylene is more facile than $HMgCH_3$. In the electrophilic (and fictional) corresponding carboboration reactions, the boron methyl bond is more reactive.[44]

We thus argue that considering these reactions as electrophilic attack by the metal on the multiple bond is misleading. At their essence, carboalumination and other similar metalation reactions are assisted nucleophilic attacks by an alkyl anion on the multiple bond.

Conclusions

(1) π-complexes between substrate and alkyl aluminum complex are stable intermediates on the potential energy surface. They are lower in energy that the reactants, suggesting they would be kinetically unimportant.

(2) The transition structures are four-centered, in contrast to the three-centered transition structures observed in the first-row congeners.

(3) These reactions are essentially nucleophilic attacks by alkyl anions on substrates activated by a Lewis acid substituent. The "inverse olefin" effect can easily be understood using this rubric, as can the higher reactivity of alkynes relative to alkenes.

(4) While this work focuses on the pathway for a specific reaction, we are interested more generally in gathering sufficient information regarding transition structures for organometallic reactions to permit chemists to apply general structural principles to transitions states. Substitutent effects on the geometries of the transition structures are small. As for ground states, it is possible to collect a set of standard geometries for these and related reactions.

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Supporting Information Available: Coordinates and total energies for optimized geometries of transition structures and intermediates are available. The material can be obtained free of charge at http://pubs.acs.org.

OM990350Y

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[42] Egger, K. W. *Int. J. Chem. Kinet.* **1969**, *1*, 459. Egger, K. W. *Trans. Faraday Soc.* **1971**, *67*, 2638.

[43] Hay, J. N.; Hooper, P. G.; Robb, J. C. *J. Organomet. Chem.* **1971**, *28*, 193.

[44] Bundens, J. W.; Francl, M. M. Unpublished work.