An Evaluation of Density Functional Theory and ab Initio Predictions for Bridge-Bonded Aluminum Compounds

Brian G. Willis and Klavs F. Jensen*

Department of Chemical Engineering, Massachusetts Institute of Technology Cambridge, Massachusetts 02139

Received: October 28, 1997; In Final Form: February 6, 1998

Ab initio and density functional methods have been employed to study bridge bonding of aluminum compounds. Results for geometry optimizations and vibrational frequency calculations are found to be consistent with the recent literature. Heats of formation for the aluminum compounds dimethylaluminum hydride and trimethylaluminum are poorly described with density functional theory (DFT) methods including the hybrid DFT method. G2 calculations are closer to experimental values with estimated errors of −1.0 to −2.0 kcal/mol per Al−CH_3 bond and −1.9 to −4.1 kcal/mol per Al−H bond. The major finding is that DFT methods poorly represent bridge bonding in aluminum compounds. While ab initio methods (represented by the MP2 method) reproduce experimental values within 2−3 kcal/mol, DFT methods, including the hybrid method, show errors of 5−12 kcal/mol. The DFT methods consistently under-bind the dimers of aluminum compounds with respect to two monomers. Exploration of the hybrid DFT functional shows that a better match between experiment and theory is provided by reducing the contribution of the Becke exchange correction. The binding energies are also found to be sensitive to the choice of correlation functional and the inclusion of "exact exchange". Results for associated units larger than dimers indicate it may be difficult to successfully describe all bridge-bonded aluminum compounds with existing DFT methods.

I. Introduction

Recent efforts have demonstrated the utility of density functional methods for studying molecular systems.[1] The rapid expansion in the number of papers employing density functional theory can be credited to the inclusion of electron correlation effects within a single configuration representation of the ground state of atoms and molecules. The implementation of electron correlation effects from density functional theory (DFT) methods allows useful thermodynamic data to be calculated for molecules of interest to many applications. Except for the lowest order accounting of electron correlation effects (Møller−Plesset perturbation theory on the Hartree−Fock wave function to second order), ab initio methods are typically impractical for routine application as quantum chemistry prediction tools. The tradeoff for the advantages offered by density functional theory is the loss of a convergent series for higher order treatments of correlation effects. In addition, there is currently no standard exchange correlation functional as evidenced by the many different implementations in the literature, (e.g., SVWN,[2,3] BVWN,[4,3] SLYP,[2,5] BLYP,[4,5] BP86,[4,6] BPW91,[4,7] B3LYP,[8] and B3PW91[8]).

Common experience has identified the hybrid functionals as the best density functional methods available for molecular calculations.[8,9] These hybrid functionals mix local exchange and correlation functionals with gradient corrections and some component of a Hartree−Fock like exchange calculation. Currently, the most popular methods (B3LYP, B3P86, and B3PW91, for example[3−8]) have their hybrid expansion parameters based upon a best fit to several properties of a large group of small molecules listed in ref 11. The mixing of DFT functionals with a Hartree−Fock-like exchange calculation

introduces a semiempirical component to these functionals. For small molecules, the hybrid functionals have been shown to give good results, comparable to or better than MP2 calculations, and in some cases close to the high-level G1 and G2 methods of calculation.[12−14] However, there is still a need to understand their behavior in more diverse molecular compounds. As more systems are encountered, we can expect varying performances for the hybrid methods.

In this paper, we report a computational study of "electron deficient" bridging aluminum compounds. These types of molecules have posed a challenge to computational chemistry methods in the past.[15−19] Electron correlation effects were found to be very important for obtaining the correct energetics. In general, complex bonding schemes have caused problems for even high level ab initio calculations as demonstrated by the G1 and G2 difficulties with SO_2.[12,13] Our results from the present study indicate that ab initio methods are capable of describing bridging aluminum compounds. However, contrary to what has generally been observed in the literature for "normal" single-bonded compounds,[9] we find large differences between DFT and ab initio calculated energetics. Also, in contrast to what has generally been reported, the few experimental results available suggest that for these bridge-bonded aluminum compounds MP2 calculations are superior to those from DFT methods. Although further studies are needed before any definite conclusions can be reached, our study suggests that current DFT methods introduce systematic errors into calculations of bridging aluminum compounds. These findings are unfortunate since the advantages of DFT methods would be particularly useful for the study of these types of systems.

The system of study includes the aluminum organometallic compounds dimethylaluminum hydride (DMAH) and trimethylaluminum (TMA). These compounds are useful for the chemical vapor deposition (CVD) of aluminum containing films

* To whom correspondence should be addressed. E-mail: bgw@mit.edu, kfjensen@mit.edu. Fax: 617 258−8224.
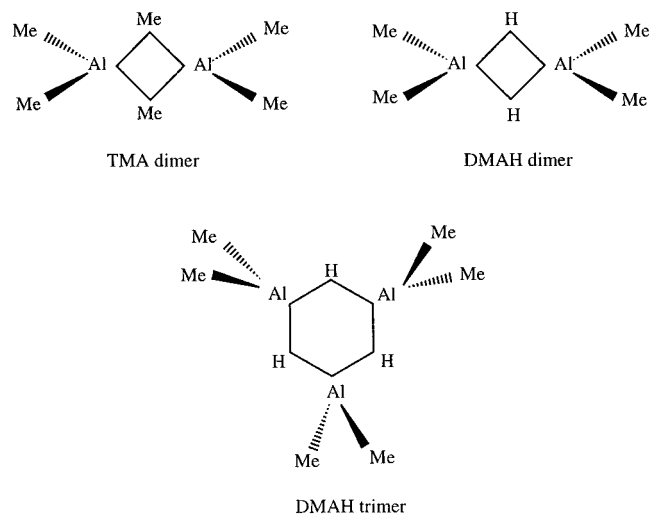
Figure 1. Bridge-bonded structures of dimethylaluminum hydride (DMAH) and trimethylaluminum (TMA).

including applications for semiconductor metallization and compound semiconductor devices.[20,21] DMAH, in particular, has been shown to grow extremely clean aluminum films.[22-24] Unlike DMAH, TMA chemical vapor deposition leads to unacceptably high levels of carbon contamination and is not useful for the deposition of high quality aluminum films. However, it has recently been confirmed that TMA is a surface reaction product of the growth reactions of DMAH, and thus its chemistry is important to understanding the growth of aluminum films from DMAH.[25,26] Characterizing the DMAH/TMA gas-phase system requires good thermodynamic data. Unfortunately, there are few data available for these chemical compounds, and those which are available are suspect of errors. Therefore, we have pursued a computational chemistry study of this reaction system. Because of the unexpected large errors in energy calculations with DFT methods, several other bridging aluminum compounds were included in the study to broaden the understanding of binding in these types of molecules.

As is common with aluminum compounds, DMAH and TMA form bridging bonds to create associated species (see Figure 1). In the case of DMAH, the monomer units form bridging hydrogen bonds to create dimer, trimer, and larger order associated units.[27-29] The monomer units of TMA form bridging bonds with methyl groups to create dimer units.[28,30,31] These ring-like structures involve three-centered, two-electron bonds which are termed "electron deficient".[32]

While we are not aware of any previous density functional theory studies of bridging aluminum compounds, there have been numerous theoretical studies of electron deficient bonding.[15-19] As mentioned above, these early studies discovered the importance of including electron correlation effects for obtaining accurate energetics. Whereas previously calculated dimerization enthalpies at the self-consistent field (SCF) level have been qualitatively successful for the alane molecule, they are completely wrong for methyl bridges. More recent studies of the dimers of alane, DMAH, and TMA have noted the importance of including polarization functions.[33-35] We have not been able to locate any geometric or energetic data on the DMAH trimer either from experiments or previous theoretical studies.

In addition to understanding the energetics of these bridging aluminum compounds, we are interested in exploring the calculated vibrational spectra as a function of method and basis set to better understand the utility of these calculations for bridge-

bonded aluminum compounds. Recent Hartree–Fock-based theoretical studies of the vibrational spectra of DMAH and TMA dimers employed simplified structures with hydrogen atoms replacing terminal CH_3 groups.[36] Comparison with experiment showed these simplified models were helpful for interpreting the experimental vibrational spectra. Here we include harmonic vibrational frequency calculations in our study of geometric structures, association enthalpies, and heats of formation of these complex bridging molecules to better understand the usefulness of density functional methods for predicting vibrational spectra of large molecules.

II. Methods of Calculation

Calculations were performed on standard workstations using the Gaussian 94 suite of programs.[10] The Gaussian 94 program was used to obtain minimum energy structures, total energies, harmonic vibrational frequencies, and thermodynamic corrections for temperature effects. Zero-point energy corrections to electronic energies were calculated from the harmonic vibrational frequencies and used unscaled. Analytic gradient techniques were used for both optimization and frequency calculations. Several DFT and ab initio methods were employed.

The general strategy was to optimize molecules with the 6-31G(d,p) split-valence basis set and then expand the basis set for single-point energy calculations. Owing to the different computational burdens of DFT versus ab initio methods, larger basis sets could be used with DFT calculations. The basis sets used for single point energy calculations by DFT and MP2-(Full) methods were respectively 6-311++G(2df,pd) and 6-311+G(d,p). The choice of the 6-311+G(d,p) basis set for MP2 calculations is supported by other successful MP2/6-311+G(d,p) calculations on bridging aluminum compounds.[37]

For geometry optimizations and frequency calculations, the different DFT exchange correlation functionals are expected to perform similarly and the BLYP and B3LYP methods were chosen to represent the pure and hybrid methods. Heats of formation were also computed with the BLYP and B3LYP methods again representing the pure and hybrid DFT methods. For the DMAH and TMA monomers, the resulting heats of formation are compared with those from the more demanding G1 and G2 methods. DFT calculations of heats of reaction were found to be very sensitive to the choice of exchange correlation functional. Therefore, several combinations of exchange and correlation functionals were used to characterize dimerization enthalpies: SVWN, BVWN, SLYP, BLYP, B3LYP, B3P86, and a modified B3PW91.

Harmonic vibrational frequencies were calculated with the BLYP density functional method using the 6-31G(d,p) as well as with larger, modified basis sets. The first of the modified basis sets uses a 6-311G(df,pd) basis for the heavy atoms and bridging hydrogen atoms (including hydrogen atoms on bridging methyl groups), and a 6-31G basis for all remaining (nonbridging) hydrogen atoms. The second modified basis set is similar to the first, but adds diffuse s and p functions to the heavy atoms and a diffuse s function on each bridging hydrogen atom (a 6-311++G(df,pd) basis). Again, a 6-31G basis set was used for all nonbridging hydrogen atoms. B3LYP/6-31G(d,p) harmonic frequency calculations were also performed for comparison purposes. For both DFT methods, only the infrared values are reported.

III. Results & Discussion

A. Structure. The general features of the structures considered in this study are shown in Figure 1. The compounds

TABLE 1: Selected Geometrical Parameters for the Dimethylaluminum Hydride (DMAH) and Trimethylaluminum (TMA) Gas-Phase Compounds Studied[f]

	BLYP/ 6-31G(d,p)	BLYP/ modified[e]	B3LYP/ 6-31G(d,p)	MP2(Full)/ 6-31G(d,p)	expt
AlH(CH$_3$)$_2$ (DMAH monomer)					
r(Al$-$H)	1.61	1.60	1.60	1.59	
r(Al$-$C)	1.98	1.98	1.97	1.96	
a(C$-$Al$-$C)	123.7	123.7	123.6	123.4	
[AlH(CH$_3$)$_2$]$_2$ (DMAH dimer)					
r(Al$-$H$_b$)	1.77	1.76	1.76	1.74	1.676 ± 0.19[a]
r(Al$-$C)	1.98	1.98	1.97	1.96	1.947 ± 0.003[a]
r(Al$-$Al)	2.68	2.66	2.65	2.62	2.617 ± 0.006[a]
a(Al$-$H$_b$$-$Al)	98.4	98.2	98.1	97.8	102.6 ± 1.6[a]
a(C$_t$$-Al-C_t$)	125.8	126.0	126.1	126.8	118.5 ± 0.9[a]
[Al(CH$_3$)$_2$]$_3$ (DMAH trimer)					
r(Al$-$H$_b$)	1.72	1.72	1.71	1.69	
r(Al$-$C)	1.98	1.98	1.97	1.96	
r(Al$-$Al)	3.27	3.28	3.25	3.20	
a(Al$-$H$_b$$-$Al)	143.5	144.1	143.1	142.2	
a(C$-$Al$-$C)	126.4	126.4	126.8	128.2	
Al(CH$_3$)$_3$ (TMA monomer)					
r(Al$-$C)	1.99		1.97	1.97	1.957 ± 0.003[b,c]
[Al(CH$_3$)$_3$]$_2$ (TMA dimer)					
r(Al$-$C$_b$)	2.19	2.18	2.17	2.14	2.140 ± 0.004[b,d,g]
r(Al$-$C$_t$)	1.98	1.98	1.97	1.96	1.97[d*]
					1.957 ± 0.003[b]
r(Al$-$Al)	2.65	2.65	2.63	2.60	2.600 ± 0.004[d]
					2.619 ± 0.005[b]
a(Al$-$C$_b$$-$Al)	74.8	74.9	74.9	74.7	74.7 ± 0.4[d]
					75.5 ± 0.1[b]
a(C$_t$$-Al-C_t$)	122.0	122.4	122.3	123.9	123.1 ± 0.4[d]
					117.3 ± 1.5[b]
[(Al(CH$_3$)$_3$)(AlH(CH$_3$)$_2$)] (pentamethyldialane)					
r(Al$-$C$_b$)	2.19		2.17	2.15	
r(Al$-$H$_b$)	1.75		1.74	1.73	
r(Al$-$C$_t$)	1.98		1.97	1.96	
r(Al$-$Al)	2.66		2.64	2.61	
a(C$_t$$-Al-C_t$)	124.0		124.3	125.6	
a(Al$-$C$_b$$-$Al)	74.7		74.8	74.6	
a(Al$-$H$_b$$-$Al)	98.7		98.5	98.1	

[a] Reference 27. [b] Reference 31. [c] Compare with a previous study at HF/3-21G* and HF/6-31G*: rAl$-$C = 1.98, 1.98, respectively (ref 35). [d] Reference 41. [e] 6-311G(df,pd) basis set for heavy atoms and bridging hydrogen atoms (including hydrogen atoms on bridging methyl groups), 6-31G basis for all terminal methyl hydrogens. [f] Bond lengths are given in angstroms and bond angles in degrees. [g] Average of their two values.

of interest are monomer, dimer, and trimer of DMAH; monomer and dimer of TMA; and the DMAH$-$TMA cross species (pentamethyldialane). The optimized geometrical parameters of these species are listed in Table 1. The table includes BLYP-, B3LYP-, and MP2(Full)-optimized structures. Geometry optimizations were performed for each method with a 6-31G(d,p) split-valence basis set. This basis set was found to adequately represent the structures and energetics of these compounds. In addition, optimized structures for the BLYP method with a larger, modified basis set are included. As can be seen in the table, the significant increase in basis set size has little effect on the BLYP-optimized structures.

For the cases of the DMAH dimer and TMA monomer and dimer where experimental data are available, the hybrid DFT and MP2 geometries agree fairly well with the expected accuracy of approximately 0.01 angstroms for bond lengths and 1 degree for bond angles.[38] Exceptions are noted for the DMAH terminal C$-$Al$-$C and bridging Al$-$H$-$Al bond angles. The seven plus degree difference between the calculated value and experiment for the terminal bond angle is abnormally large and inconsistent with the good agreement among the other geometrical parameters. The calculated structural features of DMAH are consistent with previous theoretical studies of alane where the terminal groups are hydrogen atoms but the optimized

geometrical parameters are similar.[34,39] In the case of alane, the SCF calculated Al$-$H$-$Al bridge angle is reported as 97.9° and the H$-$Al$-$H terminal bond angle is 127.3°, very similar to those calculated for DMAH.

The larger terminal angle of the dimer with bridging hydrogen atoms as opposed to methyl groups can be rationalized with previous arguments founded on the donating ability of the bridging group.[40] On the basis of arguments of coupling constants, the previous work qualitatively predicts that the same Me-Al-Me terminal bond should be larger for halogen than OR or NR$_2$ bridge units. Our calculations (not tabulated) agree, with B3LYP/6-31G(d,p) calculations predicting 127.7°, 122.9°, and 121.0° angles for bridging Cl, NH$_2$, and OCH$_3$ units. The same logic can be used to explain the large C$-$Al$-$C terminal angle in DMAH. These arguments rationalize the differences in calculated terminal C$-$Al$-$C bond angles for DMAH and TMA, but still do not explain the gas phase electron diffraction results. The error in the bridge angle is similarly difficult to explain. The consistent disagreement for all methods with experiment for these two structural features combined with the good agreement of all methods for the same structural features of TMA suggests the experimental value may need reevaluation. However, the poor agreement with experiment does also leave

TABLE 2: Association Enthalpies (298.15K) for the Dimethylaluminum Hydride (DMAH) and Trimethylaluminum (TMA) Gas Phase System[g]

	HF/ 6-311+G(d,p)	BLYP/ 6-31G(d,p)	B3LYP/ 6-31G(d,p)	MP2(Full)/ 6-31G(d,p)	BLYP/ 6-311++G(2df,pd)
$[AlH(CH_3)_2]_2 \rightleftharpoons 2\ AlH(CH_3)_2$	23.7	26.3	28.0	33.2	25.9
$2\ [AlH(CH_3)_2]_3 \rightleftharpoons 3\ [AlH(CH_3)_2]_2$	8.3	12.1	11.9	15.1	9.0
$[Al(CH_3)_3]_2 \rightleftharpoons 2\ Al(CH_3)_3$	0.3	6.5	9.0	19.5	3.5
$[(CH_3)_2AlH(CH_3)Al(CH_3)_2] \rightleftharpoons AlH(CH_3)_2 + Al(CH_3)_3$	12.1	16.4	18.6	26.4	14.8

	B3LYP/ 6-311++G(2df,pd)	MP2(Full)/ 6-311+G(d,p)	MP4	G2MP2	expt
$[AlH(CH_3)_2]_2 \rightleftharpoons 2\ AlH(CH_3)_2$	28.2	33.6	32.5[d]	34.9	30.0−40.0[a]
$2\ [AlH(CH_3)_2]_3 \rightleftharpoons 3\ [AlH(CH_3)_2]_2$	9.0	14.7		12.0[f]	15.0 − 20.0 per bridge[a]
$[Al(CH_3)_3]_2 \rightleftharpoons 2\ Al(CH_3)_3$	7.0	18.5	16.6[e]		20.40 ± 0.34[b] 19.8[c]
$[(CH_3)_2AlH(CH_3)Al(CH_3)_2] \rightleftharpoons AlH(CH_3)_2 + Al(CH_3)_3$	17.7	26.1			

[a] Referemce 44. [b] Reference 45. [c] Reference 32b. [d] MP4(SDQ)/6-311G(d,p). [e] MP4(SDTQ)/6-31G(d). [f] QCISD step without triples contribution. [g] Each method uses its own optimized geometry with a 6-31G(d,p) Basis except the MP4 and HF (Hartree−Fock) calculations which use the MP2(Full)/6-31G(d,p)-optimized geometry. Zero-point energies and thermal energy corrections to 298.15 K are based on B3LYP harmonic frequencies for all calculations except G2MP2. All values are given in kcal/mol.

open the possibility that higher order corrections are needed to correctly describe the DMAH dimer.

For all methods used, the TMA-optimized geometry is consistent with the symmetric bridge bond observed in experimental gas-phase electron diffraction studies,[41] rather than the asymmetric structure computed in ref 33. Due to the many CH_3 groups, our optimized TMA structure has C_i symmetry rather than the D_{2h} symmetry of the aluminum carbon skeleton or the C_{2h} symmetry possible with the bridging methyl groups. Long-range H−H interactions aggravate the search for a true minimum (no imaginary frequencies) with the higher symmetries. The H−H interaction problem can be dealt with by either reducing the basis functions on the H atoms (to reduce the interactions) or by increasing the basis functions on the H atoms and allowing them to interact more strongly. The later method was used to rotate the methyl groups into optimized positions at the higher basis set level. Once such a minimum was found, the calculation was repeated at the appropriate basis set level with the new geometry. With this approach we were able to find minimas with no imaginary modes. However, the high symmetry of gas-phase molecules with freely rotating methyl groups could not always be maintained. Constraining the molecule to C_{2h} (the highest symmetry possible in a calculation of the TMA dimer) gives an energy which differs from the C_i structure by less than a microhartree. Geometries are similarly identical except for a 0.1° decrease in the terminal C−Al−C bond angle caused by the change in steric interactions.

Experimental gas-phase electron diffraction studies of the TMA structure have found D_{2h} symmetry (freely rotating methyl groups) as opposed to the solid-state measurements which indicated an offset/distortion between the two planes of the dimer defined by each Al atom and its two terminal carbon atoms.[31,41] Although the symmetry of the DFT- and MP2-optimized structures compare better with the gas-phase studies, the bond lengths and angles compare better with the solid-state measuremcts. Therefore, the solid-state geometric values for TMA are listed in the table along with the gas-phase measurements. Whether the difference between the solid state and gas-phase determinations is due to actual physical differences or measurement technique is unclear. Table 1 shows that all methods give reasonable dimer structures, the best being the MP2(full) method, and the second best being the hybrid functional.
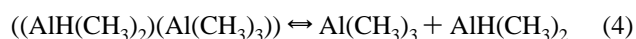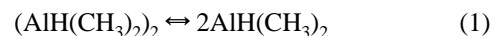
Unfortunately, there are no experimental results to compare with the DMAH−TMA cross species (pentamethyldialane) data.

Compared with the Al−H bridge bond of DMAH, the Al−H bridge bond length in the mixed DMAH−TMA species shows a slight contraction. This structural effect does not appear to show up in the energy calculations (see below). There is also a slight opening of the Al−H_b−Al angle compared with DMAH. The other structural parameters, such as the Al−Al distance, appear to be averages of the parent molecules. The enlargement of the terminal C−Al−C bonds compared with TMA is consistent with either reduced bridge-terminal steric interactions due to the replacement of one bridging methyl group with a hydrogen atom and/or the reduced electron donating ability of the hydride bridge as discussed above.

There are no published structures for the DMAH trimer either, but there are some related structures for comparison such as those of the AlF_3 tetramer and the $(CH_3)_2AlN(CH_3)_2$ trimer.[42] The DMAH trimer is found to have a six-membered ring structure as is consistent with the related compounds, but the planarity of the ring is unique (D_{3h} symmetry). The terminal Al−CH_3 geometric parameters are similar to those of the DMAH dimer but with an even larger terminal C−Al−C angle. The shortening of the aluminum−hydrogen bridge bond is consistent with a more linear bond and the need to decrease the bond length to maintain overlap.[28] The larger Al−Al lengths would preclude any Al−Al bonding in the trimer, but the heat of association per bridge actually increases.[43]

Comparison of geometrical structures between methods shows the same trends which have generally been observed in the literature. BLYP bond lengths are too long, and B3LYP partially corrects this behavior. Increasing the basis set for BLYP calculations has very little effect. Comparison with experiment and MP2 results shows that B3LYP bond lengths are still too long. Overall, the MP2 numbers are closest to experiment with the hybrid DFT method second.

B. Heats of Association. Heats of association for the dimer and trimer structures are listed in Table 2. The important reactions are:

$$(AlH(CH_3)_2)_2 \rightleftharpoons 2AlH(CH_3)_2 \qquad (1)$$

$$(Al(CH_3)_3)_2 \rightleftharpoons 2Al(CH_3)_3 \qquad (2)$$

$$2(AlH(CH_3)_2)_3 \rightleftharpoons 3(AlH(CH_3)_2)_2 \qquad (3)$$

$$((AlH(CH_3)_2)(Al(CH_3)_3)) \rightleftharpoons Al(CH_3)_3 + AlH(CH_3)_2 \qquad (4)$$

Reactions 1, 2, 3, and 4 correspond to the binding of the DMAH

TABLE 3: Association Enthalpies (298.15 K) of Several Bridging Aluminum Compounds[l]

	HF/6-31G(d,p)	MP2(Full)/6-31G(d,p)	B3LYP/6-31G(d,p)	expt
$[AlH_3]_2{}^{a,b} \rightleftharpoons 2\ AlH_3$	24.3	32.9	29.8	
$[Al(NH_2)(CH_3)_2]_2 \rightleftharpoons 2\ Al(NH_2)(CH_3)_2$	54.9/48.9[e]	64.7/57.8[e]	53.8/46.0[f]	
$[AlOH(CH_3)_2]_2 \rightleftharpoons 2\ AlOH(CH_3)_2$	56.6/53.2[e]	63.8/57.8[e]	54.0/46.9[f]	
$[AlF_3]_2{}^c \rightleftharpoons 2\ AlF_3$	57.0/48.1[e]	64.2/48.8[e]	58.7/43.9[f]	52.2[g], 50.7 ± 4.02[h,i]
$[AlCl(CH_3)_2]_2 \rightleftharpoons 2\ AlCl(CH_3)_2$	18.6/19.1[e]	29.1/32.3[e]	22.7/22.0[f]	
$[AlCl_3]_2{}^{d,k} \rightleftharpoons 2\ AlCl_3$	17.1/18.2[e]	28.3/32.1[e]	21.9/21.6[f]	30.3[g], 29.6[j]

[a] Compare with (scaled ZPE) 31.5 [MP4/6-31G**], ref 34. [b] Compare with (at 298 K) 27 [HF/3-21G*//HF/3-21G*], 24 [HF/6-31G*//HF/6-31G*], 27 [MP2/6-31G*//HF/6-31G*)] (with no ZPE or ΔE corrections) 33 [MP2/6-311+G*//HF/6-31G*], ref 35. [c] Compare with (ΔH(0 K)) 47.6 [MP2/6-311+G(d)//RHF/6-311+G(d)], ref 37. [d] Compare with (no ZPE or ΔE corrections) 25 [HF/3-21G*//HF/3-21G*], 18 [HF/6-31G*//HF/6-31G*], ref 37. [e] 6-311+G(d,p) basis set for single point energy calculation. [f] 6-311++G(2df,pd) basis set for single-point energy calculation. [g] NBS Technical Note 270−3, Washington, DC, 1968. [h] Porter, R. F.; Zeller, E. E. *J. Chem. Phys.* **1960**, *33*, 858. [i] Adjusted from 1000 to 298 K via calculated differences in thermal energy. [j] Reference 32. [k] Compare with (ΔH(0 K)) 31.5 [MP2/6-311+G(d)//RHF/6-311+G(d)], ref 37. [l] All calculations were performed with B3LYP/6-31G(d,p) optimized geometries. Zero-point energies and thermal energy corrections were also calculated with B3LYP/6-31G(d,p) harmonic frequencies. All values are given in kcal/mol.

and TMA dimer, DMAH trimer, and the DMAH−TMA cross species (pentamethyldialane), respectively. The association enthalpies were calculated with several different computational chemistry methods (Table 2). The compounds are discussed in turn below.

Dimethylaluminum Hydride. The calculated association enthalpies of DMAH for all methods which treat electron correlation are in rough agreement with the experimental estimate of 15−20 kcal/mol per hydrogen bridge.[44] Even the Hartree−Fock value has the correct qualitative (binding) behavior. The hybrid DFT and MP2 methods differ by approximately 5 kcal/mol. The B3LYP association enthalpy values are approximately 2 kcal more binding than those from the BLYP method. Compared with the MP2 numbers, the implementation of the MP4 method shows no significant effects of higher order corrections for electron correlation. A G2MP2[13] calculation of the association enthalpy for the DMAH dimer gives the most binding value of 34.9 kcal/mol. Overall, the ab initio methods bind the dimer (with respect to two monomers) more than the DFT methods with differences of approximately 5−7 kcal/mol. Comparison with the estimate based on experimental observation favors the ab initio values.

For the association of DMAH to trimer, the discussion parallels that for the dimer. The experimental estimate is very approximate and not useful for extensive discussion. The calculated enthalpy per H bridge is actually larger for the trimer than the dimer, 19.3 vs 16.8 kcal/mol at the MP2(Full)/6-311+G(d,p) level. This effect could be due to greater binding of the hydrogen atoms with the shorter bond distance or reduced repulsion between Al atoms.[43]

Trimethylaluminum. Results for the TMA association reaction reveal even larger differences between DFT and ab initio calculations than those for DMAH. Trimethylaluminum is generally accepted to exist in the vapor phase as a dimer with an experimental binding value of 20.4 ± 0.34 kcal/mol.[45] The ab initio methods are consistent with the experimental value but the DFT methods, including the hybrid B3LYP method, show striking disagreement. Errors are within 2 kcal/mol for the ab initio methods, but greater than 10 kcal/mol for the DFT based calculations. In comparisons of B3LYP and MP2 energy calculations for "normal" single-bonded molecules, it is generally the MP2 numbers which are inferior.[9] In this case, the experimental value is firm and the conclusion must be that DFT methods are in substantial error. Observation of the large error for the Hartree−Fock dimerization enthalpy gives some indication of the importance of electron correlation for the dimer structure. The DFT under binding of the TMA dimer complex with respect to monomers is similar in direction to the errors discussed above for DMAH. The under-binding of dimer units

(with respect to monomer units) is a trend which continues for several other bridging aluminum structures. This observation will be discussed in detail below after mention of the results for the cross species (pentamethyldialane).

Pentamethyldialane. The computed binding enthalpy of the DMAH−TMA cross compound (pentamethyldialane) is intermediate between DMAH and TMA values for all methods. The association strength is very nearly the summation of one-half the dimerization enthalpy of DMAH and one-half that of TMA. In contrast to an earlier report which suggested hydrogen bridging in the DMAH−TMA complex is stronger than DMAH hydrogen bridges, these results show no significant strengthening or weakening interaction for the two different bridging bonds.[36] Although there are no experimental values to compare, we suggest the MP2 calculated energies are the best listed here.

Reports of poor performance for the hybrid DFT methods in ground state systems (especially in comparison with MP2 numbers) are uncommon, and the present results (Table 2) must be related to this particular system of study. For purposes of discussion, the dimerization enthalpies of several other bridging aluminum compounds are given in Table 3. Both "electron deficient" and "normal" two-center two-electron bridge bonds are represented. All bridging systems show significant differences between DFT (including the hybrid method) and ab initio values for calculated association enthalpies. Although good experimental data is sparse, the data which are available favor MP2 over DFT numbers. The differences between methods increase as the bridging species changes loosely in the order H, F, Cl, OH, CH_3, and NH_2. The DFT errors are not confined to the electron deficient bonds, but are also exhibited with "normal" bridge bonds. In all cases, the hybrid DFT methods underbind the dimer unit with respect to monomers.

Calculations of association enthalpies of bridging structures with different combinations of exchange and correlation functionals (Table 4) provide additional insight into DFT results. Table 4 shows large (>20 kcal/mol) variations in the association enthalpies calculated by different methods. The values range from both over-binding of the dimers (SVWN and SLYP) to strongly underbinding (BVWN). Although each method uses its own converged density, the geometry is the same for all calculations on each bridging compound. These calculations do not rigorously decouple the electron density and functional evaluations, but they do offer some indications of the tendencies of the methods for the same geometrical structures. Given that the hybrid method underbinds the dimer (with respect to two monomers) and that all combinations of the Becke exchange functional with a correlation functional under-bind as well, it is suggested that for these systems the Becke gradient corrected exchange term overcompensates the over-binding of the local

TABLE 4: Association Enthalpies (298.15 K) of Several Bridging Aluminum Compounds Evaluated with Various Combinations of Local and Gradient Corrected DFT Functionals[a]

	SVWN/6-31G(d,p)	BVWN/6-31G(d,p)	SLYP/6-31G(d,p)	BLYP/6-31G(d,p)	B3LYP/6-31G(d,p)
$[AlH_3]_2 \rightleftharpoons 2 \ AlH_3$	43.9	24.7	47.9	28.2	29.8
$[AlH(CH_3)_2]_2 \rightleftharpoons 2 \ AlH(CH_3)_2$	41.6	22.6	45.6	26.3	28.0
$[Al(CH_3)_3]_2 \rightleftharpoons 2 \ Al(CH_3)_3$	30.5	−0.4	38.0	6.5	9.0
$[Al(NH_2)(CH_3)_2]_2 \rightleftharpoons 2 \ Al(NH_2)(CH_3)_2$	68.9	44.4	74.9	49.5	53.8
$[AlOH(CH_3)_2]_2 \rightleftharpoons 2 \ AlOH(CH_3)_2$	67.1	43.6	73.4	49.1	54.0
$[AlF_3]_2 \rightleftharpoons 2 \ AlF_3$	70.2	49.1	77.8	55.9	58.7
$[AlCl(CH_3)_2]_2 \rightleftharpoons 2 \ AlCl(CH_3)_2$	37.6	15.9	43.0	20.6	22.7
$[AlCl_3]_2 \rightleftharpoons 2 \ AlCl_3$	38.3	14.6	44.1	19.7	21.9

[a] All energy calculations were carried out on B3LYP/6-31G(d,p) optimized geometries. Zero-point energies and thermal energy corrections were also calculated with B3LYP/6-31G(d,p) harmonic frequencies. All values are given in kcal/mol. [Note: Some calculations presented here are basis set deficient. However, the binding trends are not expected to be affected by basis set limitations. See Table 3 for larger basis set calculations with the B3LYP method.]

TABLE 5: Association Enthalpies (298.15 K) of Bridging Aluminum Compounds for B3P86 and a Modified B3PW91 Hybrid Functional[c]

	B3P86/6-31G(d,p)	[a]modified B3PW91/6-31G(d,p)
$[AlH_3]_2 \rightleftharpoons 2 \ AlH_3$	33.9	37.0
$[AlH(CH_3)_2]_2 \rightleftharpoons 2 \ AlH(CH_3)_2$	31.9	34.9
$[Al(CH_3)_3]_2 \rightleftharpoons 2 \ Al(CH_3)_3$	14.9	20.1
$2 \ [AlH(CH_3)_2]_3 \rightleftharpoons 3 \ [AlH(CH_3)_2]_2$	10.5	9.2
$[(CH_3)_2Al(CH_3)(H)Al(CH_3)_2] \rightleftharpoons Al(CH_3)_3 + AlH(CH_3)_2$	23.5	27.6
$[Al(NH_2)(CH_3)_2]_2 \rightleftharpoons 2 \ Al(NH_2)(CH_3)_2$	59.2/51.9[b]	62.4/55.1[b]
$[AlOH(CH_3)_2]_2 \rightleftharpoons 2 \ AlOH(CH_3)_2$	56.9/50.5[b]	59.9/53.4[b]
$[AlF_3]_2 \rightleftharpoons 2 \ AlF_3$	59.0/46.0[b]	61.7/48.4[b]
$[AlCl(CH_3)_2]_2 \rightleftharpoons 2 \ AlCl(CH_3)_2$	26.6	29.7
$[AlCl_3]_2 \rightleftharpoons 2 \ AlCl_3$	26.4	29.8

[a]See text. [b] 6-311++G(2df,pd) basis set. [c] Table entries are single-point energy calculations with B3LYP/6-31G(d,p) optimized geometries. Zero-point energies and thermal energy corrections are calculated with B3LYP/6-31G(d,p) harmonic frequencies. All values are given in kcal/mol.

exchange term. The under-binding of dimers for methods which include the Becke gradient corrected exchange term is consistent for all bridging aluminum compounds studied. The relative effects of the several combinations of exchange and correlation functionals appear to be typical.[46]

The observed disparity between the results of ab initio and density functional methods is consistent with a recent study on another "electron deficient" molecule, beryllium borohydride (BeB$_2$H$_8$).[47] In that study, the relative stability of two conformers which differed in the number of bridge bonds was compared. It was found that both BLYP and B3LYP calculations favor the conformer with less bridge bonds, whereas both ab initio methods and experiment favor the structure with more bridge bonds. These results are consistent with the current observation of underprediction of dimerization enthalpies for the BLYP and B3LYP methods. In the paper, it was found that the hybrid method with the Perdew 86[6] (P86) correlation functional replacing the Lee−Yang−Parr[5] functional correctly predicted the order of stability. Motivated by these similarities, dimerization enthalpies were re-computed with the B3P86 functional. The results are tabulated in Table 5.

The B3P86 calculations in Table 5 represent a sizable improvement over the B3LYP and BLYP methods. The errors are reduced considerably, but the consistent under-prediction of binding energies remains. Greater improvement is obtained by modifying the hybrid expansion to reduce the contribution of the Becke exchange correction. On the basis of the data in Table 4 and the suggested overcompensation of the exchange correction, the modified functional adjusts the expansion recommended in ref 8 by decreasing the contribution of the exchange correction from 0.72 to 0.5:[48]

$$E_{xc} = E_{xc}^{LSDA} + a_o(E_x^{HF} - E_x^{LSDA}) + a_x\Delta E_x^{B88} + a_c\Delta E_c^{PW91}$$

The computed dimerization enthalpies for this modified B3PW91 functional are listed in the second column of Table 5. All dimerization enthalpies are shifted to more binding values. The dimerization enthalpy for alane is now possibly too large (a G2 calculation gives a binding energy of 34.5 kcal/mol at 298 K), but for the methyl, chlorine, and fluorine bridges, the values are now in better agreement with experiment. The uniform improvement is somewhat surprising given the fundamental physical differences between "electron deficient" and "normal" bonds. The observation of improvement for both adjustments in the correlation (B3P86 vs B3LYP) and exchange functionals (modified hybrid method) illustrates a compensation effect between exchange and correlation for the hybrid methods. The lack of a fixed functional for either exchange or correlation introduces a semiempirical element to these calculations.

Given that DFT errors for dimerization enthalpies are not restricted to "electron deficient" bonds, it might seem reasonable to associate the error with the long, stretched, and bent bonds of the dimer units. This analysis is consistent with Wade's partitioning of the dimerization energy into bonding and reorganization terms.[32] Figures 2 and 3 compare B3LYP, MP2-(Full), and Hartree−Fock energy changes accompanying the stretching and bending of a TMA monomer Al−CH$_3$ bond. The hybrid DFT method shows no abnormal behavior for the extended bonds. Rather, the hybrid DFT method shows a lower energetic cost of bending and stretching the bond than either Hartree−Fock or MP2 calculations. The errors in dimerization enthalpies can be narrowed to an incomplete treatment of bridge bonding.

Another aspect of the bridge bonds concerns the parallels of dimerization reactions to transition states (Figure 4). The exchange of methyl groups through the dimer may be compared to a transition state. The bond lengths and angles are distorted and the density is spread over an extended area. From this point of view it would be interesting to explore the analogy between
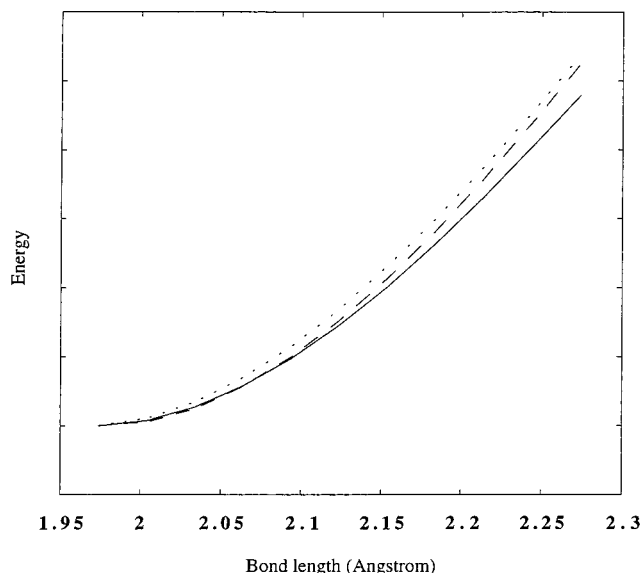
Bridge-Bonded Aluminum Compounds

J. Phys. Chem. A, Vol. 102, No. 15, 1998 **2619**

Figure 2. B3LYP (—), MP2(Full) (···), and HF (− − −) energy evaluated with a 6-31G(d,p) basis set as a function of the Al−CH$_3$ bond length for the TMA monomer. B3LYP has the lowest energy rise in response to the bond extension.
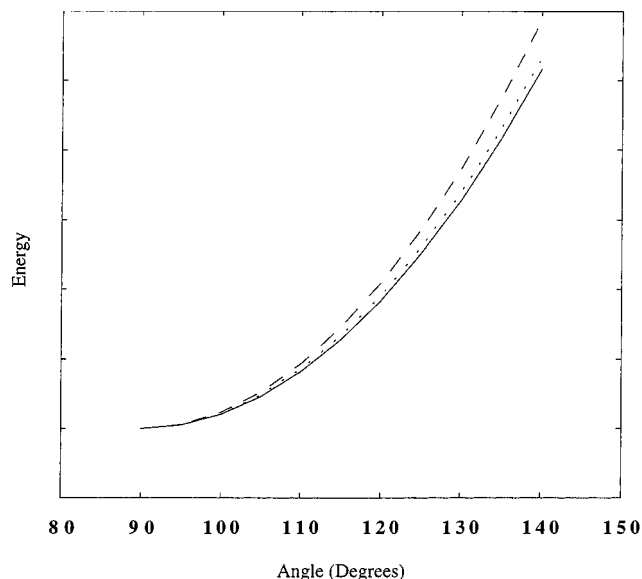

Figure 3. B3LYP (—), MP2(Full) (···), and HF (− − −) energy evaluated with a 6-31G(d,p) basis set as a function of the out of plane angle of a single Al−CH$_3$ bond in the TMA monomer. B3LYP has the lowest energy rise in response to the angle distortion.

the under-predicted well depth of these dimers to the reported under-prediction of transition state barriers with DFT methods.[49] Previous studies[50] have identified "exact" exchange as important to obtaining accurate transition state barriers. In these studies of hybrid DFT methods for bridging aluminum compounds, the Hartree−Fock like exchange calculation also has a strong effect on binding enthalpies. Decreasing the ratio of Hartree−Fock to Slater exchange in the hybrid functional gives more binding values for the dimer structures. Eliminating the HF contribution to exchange in the hybrid DFT expansion ($a_o = 0$) gives a TMA dimer binding enthalpy (298.15 K) of 18.1 kcal/mol. Increasing the Hartree−Fock component decreases the stability of the "transition state"-like dimer.

To summarize the effects of the components in the hybrid DFT expansion, we note that increasing the Hartree−Fock exchange component or the Becke gradient correction leads to
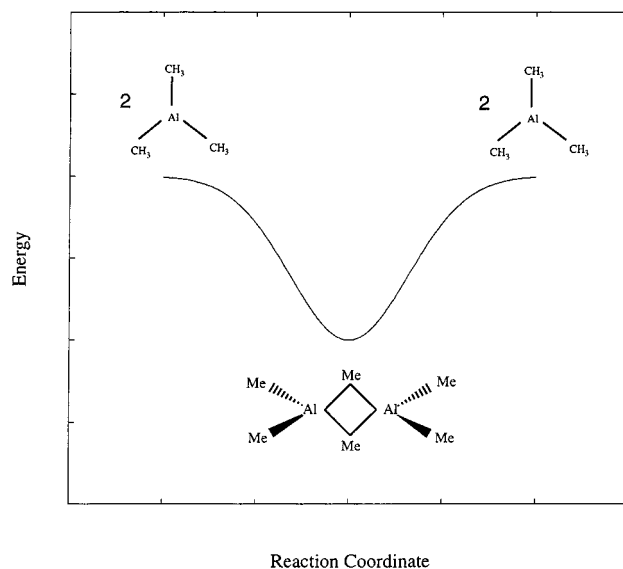

Figure 4. Aluminum dimerization reactions pictured as an "inverse" transition state.

underbinding of the dimers. Increasing the correlation gradient correction from $a_c = 0.81$ results in stronger binding. In addition, the binding is sensitive to the type of correlation functional.

It is clear from the above results that the improvement of calculated binding enthalpies for bridging compounds from the modified hybrid functional is due to a recalibration of the hybrid expansion. Although originally intended to be universally applicable, the hybrid functional does not satisfactorily represent bridge bonding. This is not surprising, perhaps, given that these types of compounds were not included in the original param-etrization.[8] As more chemical systems are studied, we can expect more troubled areas for the hybrid methods.[51] Recent studies of high reduced density gradients suggest the exchange term bears the larger portion of the error.[52]

A final note concerns the extension of the above arguments to other types of bridge bonding, the trimer for example. Table 5 shows that the same corrections which increase the binding of the dimer decrease the relative binding of the trimer. Therefore, the above arguments may not be generally applicable for all bridging aluminum compounds. It may be difficult (if at all possible) to describe all bridging aluminum compounds with a single modification of existing functionals. The current lack of data for the higher order associated units precludes a detailed investigation.

Heats of Formation. Fortunately, systematic errors of DFT methods encountered with heats of association of bridging aluminum compounds should not interfere with the calculation of heats of formation (of monomer units). The problems experienced with DFT methods for describing enthalpies of association of aluminum compounds are rooted in the bridge bonds. For calculated properties of the monomers, such as heats of reaction and heats of formation, we might expect good results from DFT calculations.[53]

Heats of formation for the components of the TMA and DMAH system are reported in Table 6. Calculations are based on atomization enthalpies and experimental data for heats of formation of H(g), Al(g), and C(g) at 298.15 K. No special procedures such as isogyric or isodesmic reactions were employed. Results show G2 calculations are close to experi-mental data with errors of approximately 3−6 kcal/mol. G2MP2 calculations are close to the full G2 results, but G1

TABLE 6: Heats of Formation (298.15 K) for the Dimethylaluminum Hydride (DMAH) and Trimethylaluminum (TMA) Gas-Phase System[i]

	BLYP/ 6-31G(d,p)	BLYP/ 6-311++ G(2df,pd)	B3LYP/ 6-311++ G(2df,pd)	G2MP2	G1	G2[f]	expt
$AlH(CH_3)_2(g)$	9.3	14.7	6.2	0.9	3.2	−0.4	−6.4[a]
$[AlH(CH_3)_2]_2(g)$	−7.7	3.5	−15.9	−31.7[g]	−27.2[g]	−34.5[g] (−38.4 to −42.6)	h
$[AlH(CH_3)_2]_3(g)$	−17.6	0.7	−28.3	−55.0[g]	−48.2[g]	−59.0[g] (−64.8 to −71.2)	h
$Al(CH_3)_3(g)$	−2.6	5.2	−5.6	−13.1	−9.8	−14.8	−17.7[c] to −20.9[b]
$[Al(CH_3)_3]_2(g)$	−11.7	6.9	−18.2	−44.6[g]	−38.1[g]	−48.0[g] (−51.8 to −56.1)	−55 to −60[d], −55.2[e]
$[(CH_3)_2Al(H)(CH_3)Al(CH_3)_2](g)$	−9.7	5.1	−17.1	−38.2[g]	−32.7[g]	−41.3[g] (−45.2 to −49.4)	h

[a] Estimated in Smith, M. B. *J. Organometal. Chem.* **1974**, *76*, 171. [b] There is some variability in the literature between −13 and −21 kcal/mol; this number was selected on the advice of the above reference. [c] Wagman, D. D. *J. Phys. Chem. Ref. Data* **1982**. [d] Based upon reported heats of formation of monomer and the experimental enthalpy of association. [e] NBS Technical Note 270−3, Washington, DC, 1968. [f] Values in parentheses are corrected for the estimated Al−CH$_3$ bond error, see text. [g] Based upon *G#* values for monomer units and MP2(Full)/6-311+G(d,p) association enthalpies. [h] A best estimate based on calculated and experimental monomer heats of formation and G2MP2 or MP2/6-311+G(d,p) association enthalpies gives −47.7, −77.6, and −53.4 for DMAH dimer and trimer and DMAH/TMA cross species, respectively. [i] Each method uses its own harmonic frequencies for calculation of zero-point energies and thermal energy corrections. For the BLYP and B3LYP frequency calculations, the 6-31G(d,p) basis was employed. All values are given in kcal/mol.

calculations have about twice the error (8−11 kcal/mol). DFT calculations have significantly greater errors of approximately 12−15 kcal/mol for the B3LYP method, and >15 kcal/mol for the BLYP method. The BLYP/6-311++G(2df,pd) heats of formation are inferior to the smaller basis set calculations due to a fortuitous basis set error for the smaller basis set calculations. Further increasing the basis set to 6-311++G-(3df,3pd) gives +12.9 and +2.8 kcal/mol for the heats of formation of DMAH and TMA, respectively. At least a portion of the error is due to underbinding of H$_2$(g) with the large basis set BLYP calculations. In this sense, the G2 values are over-rated since their slight over-binding of H$_2$(g) results in more favorable heats of formation.[54] Both DFT methods yield poor heats of formation, but the hybrid method is a substantial improvement to pure DFT methods (8−10 kcal/mol).

Heats of formation for the dimers and trimer based upon the calculated heats of formation of the monomers and MP2/6-311+G(d,p) dimerization enthalpies are included in Table 6. The lack of sufficient experimental data makes these numbers difficult to asses, but the combination of errors from heats of formation of monomer units and dimerization enthalpies suggest the likelihood of considerable errors. The general behavior of the different methods for these aluminum compounds implies the table values are lower limits to actual heats of formation.

A crude partitioning of the errors for the DMAH and TMA monomer heats of formation can be used as a consistency check with the alane compound. Assignment of a G2 Al−CH$_3$ bond error of −1.0 to −2.0 kcal/mol (per bond) leaves an estimate for the aluminum hydrogen bond error of −1.9 to −4.1 kcal/mol. The combination of these estimates with a G2 heat of formation for alane (AlH$_{3(g)}$) of +28.2 kcal/mol (not tabulated) suggests an improved heat of formation of +16.0 to +22.4 kcal/mol. These heats of formation for alane compare reasonably well with the +18 kcal/mol estimate from ref 55. Unfortunately, the bond error estimates cannot be used to help localize the dimerization enthalpies since bridge Al−CH$_3$ and Al−H bonds are completely different from monomer bonds. They can, however, be used to improve the heats of formation for the dimers and trimer by at least compensating for the error in the terminal Al−CH$_3$ bonds. These values are listed in Table 6 in parentheses next to the uncorrected values, for the G2 calculations only.

The general observations from the heat of formation data suggest that while the pure DFT method is only modestly in error for geometry optimizations, vibrational frequencies (see below), and general reaction enthalpies, the method is significantly in error for the calculation of heats of formation of these aluminum compounds. The hybrid DFT method is an improvement, but still yields poor heats of formation. The observed comparison between G2 calculations and the DFT methods are in contrast with a recent study on silicon compounds.[14,54]

IR Vibrational Frequency Calculations. Infrared spectroscopy is a major tool for experimental studies of aluminum organometallic compounds. Previous ab initio IR studies have been performed on model compounds of DMAH and TMA and the cross-bridged species DMAH−TMA (pentamethyldi-alane).[36] The complex bridging modes provide a test for the abilities of the various computational chemistry methods to predict harmonic vibrational frequencies. Unfortunately, MP2 vibrational frequency calculations on the herein studied molecules are impractical for workstation calculations. In contrast, DFT methods are currently practical for vibrational frequency calculations on molecules as large as the DMAH trimer. Experimental and DFT calculated values of selected infrared modes are shown in Table 7. Given the constraints that the calculations do not account for Fermi resonances or anharmonic affects, the predicted spectra are quite successful at capturing the essence of the experimental spectra, including the complex bridging modes. For example, for the largest basis set used, the symmetric Al−H stretch of the DMAH trimer (which has a very broad experimental feature) is predicted within 40 cm^{-1}.

A general error analysis was performed using the modes with available experimental data. For both BLYP and B3LYP, there is a general trend (with exceptions) to overestimate modes above approximately 600 cm^{-1} and underestimate the lower wavenumber modes. These results are consistent with the general observations in the literature.[58] The average absolute errors for the predicted modes are 29, 53, 25, and 25 cm^{-1} for BLYP/6-31G(d,p), B3LYP/6-31G(d,p), BLYP/mod1, and BLYP/mod2, respectively. The larger error of the B3LYP method is due to the greater overestimation of the higher wavenumber modes. Below approximately 600 cm^{-1}, the B3LYP method is closer to experiment than all BLYP calculations. The better match with experiment at low wavenumbers for the B3LYP method may give it an advantage with respect to thermal energy corrections. The average absolute percent deviations are 2.9, 3.7, 2.4, and 2.5% for the same ordering as above. Due to over and under prediction, a single linear scaling factor is not helpful for either the BLYP or B3LYP calculated frequencies. Applying both the high and low scale factors recommended in ref 58 with a dividing line of 600 cm^{-1} improves the mean absolute errors to 21 and 17 cm^{-1} for the BLYP/6-31G(d,p) and B3LYP methods, respectively. After scaling, the errors are distributed

Bridge-Bonded Aluminum Compounds

J. Phys. Chem. A, Vol. 102, No. 15, 1998 **2621**

TABLE 7: Selected Infrared Harmonic Vibrational Frequencies for Associated Aluminum Compounds[h]

	BLYP/ 6-31G(d,p)	B3LYP/ 6-31G(d,p)	BLYP/ 6-311G(df,pd)[c]	BLYP/ 6-311++G(df,pd)[c]	expt
DMAH dimer[d] (D_{2h})					
CH_3 ν_{as}	3023−3038	3102−3115	2995−3010	2988−3004	2950−2955
CH_3 ν_s	2957	3031	2941	2936	2902−2905
CH_3 δ_{as}	1437−1446	1473−1480	1433−1442	1428−1437	1444
CH_3 δ_s	1222−1228	1259−1264	1222	1217	1206
CH_3 ρ	732	747	723	721	709
CH_3 ω	714	728	706	703	692
AlH ν_{as}	1388	1442	1401	1399	1368[a]
AlH ν_s	1206	1245	1220	1220	1215
AlC_2 ν_{as}	654	675	658	656	690
AlC_2 ν_s	541	558	543	542	570−571
Me_2Al ρ_s	846	871	850	845	851
DMAH trimer[d] (D_{3h})					
AlH ν_{as}	1828	1899	1827		1785−1789
AlH in plane asymmetric motion	867	891	864		934−940[b]
AlH out of plane symmetric motion	798	819	796		792
TMA dimer[e]					
CH_3 ν_{as}	3011	3090	2984	2986	2941
CH_3 ν_s	2986, 2945	3068, 3020	2972, 2932	2934, 2926	2899, 2837
CH_3 δ_{as}	1456	1490	1450	1446	1437
CH_{3t} δ_s	1234	1268	1226	1221	1201
CH_{3b} δ_s	1262	1298	1253	1252	1255
CH_{3t} ρ	725	742	715	715	697
CH_{3b} ρ	778, 599	800, 618	770, 591	768, 585	768, 608
AlC_t ν_{as}	625	645	626	626	
AlC_t ν_s	542	559	544	542	564
AlC_b ν_s	463	482	461	461	480
AlC_b ν_{as}	340	356	342	340	367
ν_{14}, ν_{18}[g]	159, 155	163, 158	162, 155	162, 156	175
DMAH−TMA complex[f] (pentamethyldialane)					
AlH ν_{as}	1388	1436			1416
AlH ν_s	1342	1382			1339
AlC_b ν_{as}	302	320			326
AlC_b ν_s	444	463			468
Me_2Al ρ	810	834			815

[a] Perturbed by Fermi resonance, estimated. [b] There is some uncertainty as to the assignment of this mode. The experimental assignment is to symmetric AlH vibrations of the trimer. The closest calculated mode is a symmetric, in plane motion of the H atoms moving in and out of the ring at ∼998 cm^{-1}. However, this mode is of A1′ symmetry and not IR active for the D_{3h} point group. There exists a doubly degenerate mode calculated at ∼860−870 wavenumbers of the correct symmetry and with significant intensity which is not assigned experimentally. The mode corresponds to in-plane, asymmetric AlH motion. We tentatively assign this calculated mode to the observed mode at 934−940 cm^{-1}. However, it is unlikely that the harmonic mode should appear below the actual vibration. This inconsistency suggests some complications in the experimental spectrum. (Note: the mode was not included in our error analysis). [c] Modified basis sets. A 6-31G basis set is used for each hydrogen atom in a terminal methyl group. All other atoms have the basis set listed in the table. [d] Experimental assignments: ref 56. [e] Experimental assignments: ref 57. [f] Experimental assignments: ref 36. [g] See ref 59 for mode description. [h] All values are in wavenumbers (cm^{-1}).

with both positive and negative deviations, indicating a limit to the application of linear scaling factors.

The modified basis sets were used to explore the sensitivity of vibrational modes to basis set size. The data show the effect of increasing basis set size to be modest. The average corrections to the BLYP/6-31G(d,p) predicted modes are 9 and 11 wavenumbers for modified basis sets 1 and 2, respectively. When compared with experiments, though, the corrections of the modified basis sets lead to an average improvement of only about 4 cm^{-1}. The greatest improvement seems to come from the high wavenumber vibrations which are reduced in magnitude and brought closer to experiment. Since the primary effect of the larger basis sets is to reduce these high wavenumber frequencies, their corrections can largely be captured in scaling factors. It is interesting to note that, although the modified basis sets actually reduce the number of basis functions on the hydrogen atoms of the terminal methyl groups, the terminal CH_3 stretching, bending, and rocking modes are better represented than with the 6-31G(d,p) basis set. The overall better match between experiment and theory for BLYP versus B3LYP is probably a favorable consequence of the over prediction of bond lengths by BLYP. Applying the recommended scaling factors appears to reduce the advantage of the BLYP calculated spectra.

In addition, even considering the complicated bridging modes it does not seem worthwhile to use oversized basis sets for frequency calculations.

Conclusion

Consistent with many recently reported computational chemistry studies, we find the hybrid DFT method (here represented by B3LYP, B3P86, and B3PW91) is the best DFT method available for these aluminum compounds and gives good results for geometry optimizations and harmonic vibrational frequency calculations. Heats of formation are significantly in error, but are an improvement to "pure" DFT methods. The "pure" gradient corrected DFT method (BLYP) provides reasonable structures and good vibrational modes, but is not useful for calculating heats of formation of the studied compounds.

Results show that DFT methods under-bind the dimers of bridge-bonded aluminum compounds. The underprediction of binding enthalpies occurs for weak (10 kcal/mol/bridge) to moderate (29 kcal/mol/bridge) bond strengths. For the B3LYP hybrid DFT method, errors range from 5 to 12 kcal/mol for the various bridging arrangements. A compensation effect between exchange and correlation functionals makes the identification

of the error difficult. Differences between experiment and theory can be reduced both by using a different correlation functional or by changing the coefficient for the contribution of the exchange correction in the hybrid functional. The systematic under-binding of the aluminum bridge bonded dimers with respect to monomers is not limited to "electron deficient" bonds, but also appears for "normal" two-center two-electron bridge bonds. Ab initio calculations at the MP2 level are found to provide enthalpies of association close to experimental values, but there are insufficient data for a rigorous measurement of the accuracy. Given the prevalence of bridge-bonding in aluminum organometallic chemistry the poor performance of DFT methods for the compounds studied is unfortunate. Unless the errors can be systematically corrected or new functionals derived, DFT methods may be of limited use for this class of compounds.

Calculation of heats of formation of DMAH and TMA monomers with the G2 method gives errors reasonably close to the proposed target accuracy of 2 kcal/mol.[13] G2MP2 calculations are close to the G2 calculations, but G1 calculations yield errors twice as large. Absolute errors of 1.0−2.0 kcal/mol per Al−CH$_3$ bond and 1.9−4.1 kcal/mol per Al−H bond are estimated for the G2 calculations.

Infrared vibrational frequencies, including the complex bridge modes, are reproduced well by both pure and hybrid DFT methods. The match between experiment theory is better for the pure BLYP method due to a fortuitous effect of the over prediction of bond lengths. Both methods tend to overestimate the vibrational frequencies at high wavenumber, but the error is not consistent throughout the frequency range, and a single linear scale factor is insufficient. Applying recommended scaling factors for both high and low frequencies leads to average absolute errors of less than 20 cm^{-1} for the BLYP and B3LYP methods with a 6-31G(d,p) basis set. The scaling factors also appear to offset the advantages of the pure DFT method relative to the hybrid method for vibrational frequency calculations with these compounds.

References and Notes

(1) Ziegler, T.; *Chem. Rev.* **1991**, *91*, 651.

(2) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. 4 (*The Self-Consistent Field for Molecules and Solids*).

(3) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(4) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(5) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(6) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 4524.

(7) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(8) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(9) Baker, J.; Muir, M.; Andzelm, J.; Scheiner, A. In *Chemical Applications of Density Functional Theory*; Laird, B. B., Ross, R. B., Ziegler, T. Eds.; ACS Symposium Series 629; American Chemical Society: Washington, DC, 1996.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. Gaussian 94, Revision B.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(11) Gill, P. M. W.; Johnson, B. G.; Pople, J. A.; Frisch, M. J. In *Int. J. Quantum Chem., Quantum Chem. Symp.* Löwdin, P.-O., Öhrn, N. Y., Sabin, J. R., Zerner, M. C., Eds.; Wiley: New York, 1992; Vol. 26, p 319.

(12) Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1990**, *93*, 2537.

(13) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(14) Hay, J. P. *J. Phys. Chem.* **1996**, *100*, 5.

(15) Ahlrics, R. *Theor. Chim. Acta* **1974**, *35*, 59.

(16) Levinson, K. A.; Perkins, P. G. *Theor. Chim. Acta* **1970**, *17*, 1.

(17) Levinson, K. A.; Perkins, P. G. *Theor. Chim. Acta* **1970**, *17*, 15.

(18) Lappert, M. F.; Pedley, J. B.; Sharp, G. J.; Guest, M. F. *J. Chem. Soc., Faraday Trans. 2* **1976**, 539.

(19) Gropen, O.; Johansen, R. *J. Organomet. Chem.* **1975**, *92*, 147.

(20) Bhat, R.; Koza, M. A.; Chang, C. C.; Schwarz, S. A. *J. Cryst. Growth* **1986**, *77*, 7.

(21) Biswas, D. R.; Ghosh, C.; Layman, R. L. *J. Electrochem. Soc.* **1983**, *130*, 234.

(22) Kondoh, E.; Ohta, T. *J. Vac. Sci. Technol., A* **1995,** *13*, 2863.

(23) Zhu, N.; Cacouris, T.; Scarmozzino, R.; Osgood, J., Jr. *J. Vac. Sci. Technol., B* **1992**, *10*, 1167.

(24) Fiordalice, R. W.; Ong, T.; Garcia, S.; Farkas, J.; Fernandes, M.; Freeman, M.; Gall, M.; Jain, A.; Jawarani, D.; Kawasaki, H.; Klein, J.; Roman, B.; Sparks, T.; Venkatraman, R.; Vuong, T.; Weitzman, E.; Pintchovski, F. In *Advanced Metallization and Interconnect Systems for ULSI Applications in 1996*; Havemann, R., Schmitz, J., Komiyama, H., Tsubouchi, K. Eds.; Materials Research Society: Pittsburgh, PA, 1996; p 13.

(25) Willis, B. G.; Jensen, K. F. In *Advanced Metallization and Interconnect Systems for ULSI Applications in 1996*; Havemann, R., Schmitz, J., Komiyama, H., Tsubouchi, K. Eds.; Materials Research Society: Pittsburgh, PA, 1996; p 29.

(26) Strongin, D. R.; Commita, P. B. *J. Phys. Chem.* **1991**, *95*, 1329.

(27) Almenningen, A.; Anderson, G. A.; Forgaard, F. R.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 2315.

(28) Tanaka, J.; Smith, S. R. *Inorg. Chem.* **1969**, *8*, 265.

(29) Wartick, T.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1953**, *75*, 835.

(30) Lewis, P. H.; Rundle, R. E. *J. Chem. Phys.* **1953**, *21*, 986.

(31) Vranka R. G.; Amma, E. L. *J. Am. Chem. Soc.* **1967**, *89*, 3121.

(32) Wade, K. *Electron Deficient Compounds*; Nelson: London, 1971. (b) Wade, K., *J. Chem. Educ.* **1972**, *49*, 502.

(33) Hiraoka, Y. S.; Mashita, M. *J. Cryst. Growth* **1994**, *145*, 473.

(34) Lammertsma, K.; Leszczynski, J. *J. Phys. Chem.* **1990**, *94*, 2806.

(35) Chey, J.; Choe, H. S.; Chook, Y. M.; Jensen, E.; Seida, P. R.; Francl, M. M. *Organometallics* **1990**, *9*, 2430.

(36) Russell, D. K.; Claxton, T. A.; Grady, A. S.; Linney, R. E.; Mahmood, Z.; Markwell, R. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3015.

(37) Williams, S. D.; Harper, W.; Mamantov, G.; Tortorelli, L. J.; Shankle, G. *J. Comput. Chem.* **1996**, *17*, 1696.

(38) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

(39) Liang, C.; Davy, R. D.; Schaefer, H. F., III *Chem. Phys. Lett.* **1989**, *159*, 393.

(40) Dewar, M. J. S.; Patterson, D. B.; Simpson, W. I. *J. Chem. Soc., Dalton Trans.* **1973**, 2381.

(41) Almenningen, A.; Halvorsen, S.; Haaland, A. *Acta Chem. Scan.* **1971**, *25*, 1937.

(42) Oliver, J. P. In *Advances in Organometallic Chemistry*; Academic Press: New York, 1977; Vol. 235.

(43) It has been noted [30, 31, 34, 41, 42] that the Al−Al distance is close to the sum of the van der Waal radii of the two aluminum atoms and argued that Al−Al bonding is important for stabilizing dimer structures. Regarding this idea, it is interesting to note that DMAH and TMA have similar Al−Al distances. Rather than lengthen the Al−Al distance, the bonding in TMA dimer decreases the Al−C−Al bridging angle. These geometrical features may be linked to the optimal configurations for Al−C bonding and repulsion between Al atoms at small distances rather than to Al−Al bonding.

(44) Hoffmann, Von E. G.; Schomburg, G. *Z. Elektrochem.* **1964**, *68*, 1101.

(45) Henrickson, C. H.; Eyman, D. P. *Inorg. Chem.* **1967**, *6*, 1461.

(46) Mohr, M.; Zipse, H.; Marx, D.; Parrinello, M. *J. Phys. Chem. A.* **1997**, *101*, 8942.

(47) Derecskei-Kovacs, A.; Marynick, D. S. *Chem. Phys. Lett.* **1994**, *228*, 252.

(48) The modified B3PW91 functional is not suggested as a new functional for any other system. Its purpose is only to demonstrate the compensation effect for the exchange and correlation functionals and the abnormal behavior of the bridging aluminum compounds. Calculations on other systems with this functional would not be expected to give quality results. However, the general approach may have implications for understanding corrections to systematic errors in DFT calculations.

(49) Baker, A. S.; Muir, M.; Andzelm, J. *J Chem. Phys.* **1995**, *102*, 2063.

(50) Baker, J.; Andzelm, J.; Muir, M.; Taylor, P. R. *Chem. Phys. Lett.* **1995**, *237*, 53.

(51) Wesolowski, T. A.; Parisel, O.; Ellinger, Y.; Weber, J. *J. Phys. Chem. A.* **1997**, *101*, 7818.

Bridge-Bonded Aluminum Compounds

J. Phys. Chem. A, Vol. 102, No. 15, 1998 **2623**

(52) Ruiz, E.; Salahub, D. R.; Vela, A. *J. Am. Chem. Soc.* **1995**, *117*, 1141.

(53) Here, heats of reaction is meant to include nonassociative reactions. This excludes a large portion of aluminum organometallic chemistry.

(54) This statement deserves some comment. The fortuitous effect comes from the difference between the experimental and G2 measurement of the $H_2(g)$ binding enthalpy. The procedure of calculating heats of formation via atomization enthalpies and using the experimental heat of formation for H(g) artificially improves the calculated heats of formation of DMAH and TMA. When using the experimental heat of formation of H(g), the difference between this number and the G2 value is multiplied by the number of hydrogen atoms in the molecule and added to the calculated heats of formation. In the case of TMA with 9 hydrogen atoms, the effect is almost 5 kcal/mol. If instead the heats of formation are calculated through a reaction with hydrogen in its standard state ($H_2(g)$) or, equivalently, using the G2 heat of formation of H(g), the favorable effect is not present and the G2

values are only slightly (~1 kcal/mol) better than the G1 numbers. This effect is not present for the G1 calculations because in the G1 method the higher level correction is specifically designed to make the electronic energy exact for the H atom and hydrogen molecule.[13] The choice of using the experimental heat of formation for the H atom to calculate heats of formation has a small favorable effect on B3LYP computed values and an unfavorable effect on BLYP calculations. Note that, without this effect, G1 and G2 heats of formation are only ~4 kcal/mol superior to B3LYP calculations.

(55) Tirtowidjojo, M.; Pollard, R. *J. Cryst. Growth* **1986**, *77*, 200.

(56) Grady, A. S.; Puntambekar, S. G.; Russell, D.K., *Spectrochim. Acta* **1991**, *47a*, 47.

(57) Ogawa, T. *Spectrochim. Acta* **1968**, *24A*, 15.

(58) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(59) Mole, T.; Jeffery, E. A. *Organoaluminum Compounds*; Elsevier: New York, 1972; p 56.