

## <sup>27</sup>Al NMR Spectroscopic Investigation of Aluminum(I) Compounds: Ab Initio Calculations and Experiment

Jürgen Gauss,<sup>†</sup> Uwe Schneider,<sup>†</sup> Reinhart Ahlrichs,<sup>\*†</sup> Carsten Dohmeier,<sup>‡</sup> and Hansgeorg Schnöckel<sup>‡</sup>

Contribution from the Lehrstuhl für Theoretische Chemie, Institut für Physikalische Chemie, Universität Karlsruhe, D-7500 Karlsruhe, Germany, and Institut für Anorganische Chemie, Universität München, D-8000 München 2, Germany. Received August 24, 1992

**Abstract:** We report ab initio calculations of <sup>27</sup>Al NMR chemical shifts for a variety of Al<sup>I</sup> compounds using the gauge-including atomic orbital method at the self-consistent-field and second-order Møller–Plesset perturbation theory levels. The calculated values, which include one of the most shielded (AlCp) and deshielded (AlSi<sup>t</sup>Bu<sub>3</sub>) NMR shifts known so far for aluminum compounds, are rationalized in terms of a molecular orbital picture of the bonding and compared to the available experimental data for Al<sup>I</sup> compounds. For AlCl, it is shown that solvation effects have to be included in order to reproduce the experimental NMR shift of +35 ppm of a AlCl/toluene/ether solution, while for AlCp and AlCp\* the <sup>27</sup>Al chemical shifts (−111 and −80.7 ppm, respectively) at low temperatures (<30 °C) can be assigned on the basis of the calculated values to the tetramers Al<sub>4</sub>Cp<sub>4</sub> and Al<sub>4</sub>Cp\*<sub>4</sub>. Increasing the temperature above 30 °C led in the case of the AlCp\* solution to a new NMR signal at −149 ppm, which is in good agreement with the theoretically predicted value of −143 ppm for the AlCp\* monomer. An analysis of the temperature-dependent NMR spectra yields an estimate of about 150 ± 20 kJ/mol for the dissociation energy of Al<sub>4</sub>Cp\*<sub>4</sub> into four AlCp\*. For AlCp, a similar analysis was, however, not possible due to the thermal instability of the AlCp solution, which decomposes above −60 °C. No assignment of the experimentally observed <sup>27</sup>Al NMR spectrum has been so far possible in the case of AlSi<sup>t</sup>Bu<sub>3</sub>, but the calculations show that both solvation and electron correlation effects have to be included in a reliable theoretical study of the <sup>27</sup>Al chemical shifts of AlSiR<sub>3</sub> compounds.

### I. Introduction

The recent synthesis and structural characterization of low-valent compounds of aluminum<sup>1–5</sup> in solution or as solids led to considerable interest in low-valent compounds of group III elements.<sup>6</sup> While such compounds have been known for some time for boron,<sup>7</sup> gallium,<sup>8</sup> and the heavier elements indium and thallium,<sup>8</sup> knowledge about low-valent aluminum compounds was until recently rather scarce. It was generally believed that such compounds would be stable only at high temperature and low pressure. For example, gaseous AlCl could be obtained by reaction of Cl<sub>2</sub> with Al at 1000 °C.<sup>9</sup> Later, AlCl was trapped in noble gas matrices and studied by IR spectroscopic means.<sup>10</sup> A systematic investigation of Al<sup>I</sup> compounds and their chemistry, however, was not possible until the more recent successful preparation of a metastable AlCl solution with a mixture of toluene and ether as solvent.<sup>1</sup> This AlCl solution opened new ways for exploring the chemistry of aluminum compounds. Besides the synthesis of some new and unusual Al<sup>III</sup> compounds,<sup>11</sup> the AlCl solution proved to be an ideal precursor for the synthesis of new Al<sup>I</sup> compounds. Reaction with MgCp\*<sub>2</sub> (Cp\* = C<sub>5</sub>Me<sub>5</sub> = pentamethyl cyclopentadienyl) yielded Al<sub>4</sub>Cp\*<sub>4</sub>,<sup>5</sup> a compound which is stable at room temperature. The structure of Al<sub>4</sub>Cp\*<sub>4</sub> was determined by X-ray diffraction<sup>5</sup> and shows an Al<sub>4</sub> tetrahedron similar to the tetrahedral cages found in analogous boron compounds (i.e., B<sub>4</sub>Cl<sub>4</sub><sup>12</sup> and B<sub>4</sub>Bu<sub>4</sub><sup>13</sup>). The Cp\* rings are η<sup>5</sup>-bonded to the aluminum in the same way as is found in a large number of transition-metal cyclopentadienyl complexes. Ab initio calculations of the monomer and tetramer of AlCp are in good agreement with the experimentally determined structure and led to an estimate for the tetramerization energy, i.e., the stabilization of the tetramer with respect to the monomer, of 150–160 kJ/mol.<sup>14</sup> By reaction of NaSi<sup>t</sup>Bu<sub>3</sub> with the AlCl solution, a compound which can be characterized as [Al(Si<sup>t</sup>Bu<sub>3</sub>)<sub>4</sub>]<sub>x</sub> has been obtained.<sup>15</sup> According to mass spectrometric results, it seems probable that AlSi<sup>t</sup>Bu<sub>3</sub> also forms tetramers. Ab initio calculations predict for Al<sub>4</sub>(Si<sup>t</sup>Bu<sub>3</sub>)<sub>4</sub> an even higher tetramerization energy of about 600–650 kJ/mol.<sup>16</sup>

On the other hand, not very much is known about the structure of Al<sup>I</sup> compounds in solution. The AlCl/toluene/ether solution was studied using IR and <sup>27</sup>Al NMR spectroscopy.<sup>1</sup> The observed IR band at 450 cm<sup>−1</sup>, which has to be compared to the corre-

sponding band at 477 cm<sup>−1</sup> for gaseous AlCl,<sup>17</sup> has been tentatively assigned to some adduct of AlCl with the solvent, denoted as AlCl·nEt<sub>2</sub>O. The observed <sup>27</sup>Al chemical shifts of 15 ppm for AlCl<sup>I</sup> and −80.8 ppm for a solution of Al<sub>4</sub>Cp\*<sub>4</sub><sup>5</sup> were difficult to interpret, in particular, since no experimental data were available for comparison. Thus, no conclusion with respect to the structure of Al<sup>I</sup> compounds in solution could be drawn so far from the measured <sup>27</sup>Al NMR chemical shifts.

In such a situation, theoretical calculations of spectroscopic properties can be very helpful and can provide the missing information. Within the self-consistent-field (SCF) approximation, efficient techniques for calculating NMR chemical shifts<sup>18–20</sup> have

- (1) Tacke, M.; Schnöckel, H. *Inorg. Chem.* **1989**, *28*, 2895.
- (2) Nesper, R.; Curda, J. *Z. Naturforsch.* **1987**, *B42*, 557.
- (3) Uhl, W. *Z. Naturforsch.* **1988**, *B43*, 1113.
- (4) Hiller, W.; Klinkhammer, K.-W.; Uhl, W.; Wagner, J. *Angew. Chem.* **1991**, *103*, 182; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 179.
- (5) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem.* **1991**, *103*, 594; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564.
- (6) Paetzold, P. *Angew. Chem.* **1991**, *103*, 559; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 544.
- (7) See, for example: Morrison, J. A. *Chem. Rev.* **1991**, *91*, 35.
- (8) See, for example: Schmidbauer, H. *Angew. Chem.* **1985**, *97*, 983; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 893.
- (9) Klemm, W.; Voss, E.; Geiersberger, K. *Z. Anorg. Allg. Chem.* **1948**, *256*, 15.
- (10) Schnöckel, H. *Z. Naturforsch.* **1976**, *B31*, 1291.
- (11) Schnöckel, H.; Leimkühler, M.; Lotz, R.; Mattes, R. *Angew. Chem.* **1986**, *98*, 929; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 921. Dohmeier, C.; Mattes, R.; Schnöckel, H. *J. Chem. Soc., Chem. Commun.* **1990**, 358.
- (12) Atoji, M.; Lipscomb, W. N. *Acta Crystallogr.* **1953**, *6*, 547.
- (13) Mennekes, T.; Paetzold, P.; Boese, R.; Bläser, D. *Angew. Chem.* **1991**, *103*, 199; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 173.
- (14) Ahlrichs, R.; Ehrig, M.; Horn, H. *Chem. Phys. Lett.* **1991**, *183*, 227.
- (15) Wiberg, N. In *Frontiers in Organosilicon Chemistry*; Bassindale, A. B., Gaspar, P. P., Eds.; The Royal Society of Chemistry: Cambridge, 1991; pp 263 ff.
- (16) Schneider, U.; Ahlrichs, R.; Horn, H.; Schäfer, A. *Angew. Chem.* **1992**, *104*, 327; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 353.
- (17) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.
- (18) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919.
- (19) Hansen, A. E.; Bouman, T. D. *J. Chem. Phys.* **1985**, *82*, 5035.
- (20) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.
- (21) For a review, see: Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Günther, H., Kosfeld, R., Seelig, J., Eds.; Springer: Berlin, 1991; pp 165 ff.

<sup>†</sup> Universität Karlsruhe.

<sup>‡</sup> Universität München.

been developed during the last decade, and numerous applications, in particular with the individual gauge for localized orbital (IGLO) method,<sup>18</sup> have shown that the results of such calculations are in most cases very reliable. A further improvement was recently achieved<sup>22</sup> by implementing the gauge-including atomic orbital (GIAO) method<sup>23</sup> for calculating chemical shifts within the direct SCF scheme,<sup>24</sup> thus making calculations with several hundred basis functions routinely possible. As is shown in the following, this development turns out to be crucial for our computational study, and it should be mentioned that the calculations presented in this paper would not have been possible with the more conventional implementations of ab initio methods for calculating NMR shifts.

However, the situation in the cases studied here is more complicated than usual. The electronic structure of Al<sup>I</sup> compounds involves low-lying unoccupied orbitals (i.e., the low-lying  $\pi$ -orbitals in case of the linear AlX compounds), which indicates that electron correlation effects might play an important role.<sup>14</sup> It is also well-known that an accurate theoretical description of analogous boron compounds requires explicitly correlated methods<sup>25</sup> and that SCF results are not always reliable. Second-order Møller–Plesset perturbation theory (MP2, also known as second-order many-body perturbation theory (MBPT(2)))<sup>26</sup> as the simplest approach for treating electron correlation effects in a systematic manner seems to be adequate for our purpose and will be used in this work. An MP2-based method for calculating chemical shifts within the gauge-invariant GIAO scheme has been recently formulated and implemented by one of us<sup>27</sup> and offers the possibility of studying the chemical shifts with explicit consideration of electron correlation effects.

We will report here on theoretical NMR shift calculations at SCF and MP2 levels for a variety of Al<sup>I</sup> compounds and will provide a theoretically sound basis for the interpretation of experimental <sup>27</sup>Al NMR shifts. The calculated chemical shifts will be used to analyze the available experimental data for Al<sup>I</sup> compounds. In addition, we will report on new experiments which were inspired by the calculations and which give first evidence for the existence of the AlCp\* monomer.

## II. Theoretical Methods

All calculations have been performed with the TURBOMOLE<sup>28</sup> and the ACES II<sup>29</sup> program packages. Equilibrium geometries have been first determined at the SCF level using semidirect methods and analytical gradients. Unless noted differently, the SCF calculations were followed by MP2 geometry optimizations to improve upon the SCF structure and to check the importance of electron correlation effects. The MP2 optimizations were carried out using a recently developed (semi)direct MP2 gradient program<sup>30</sup> which has been interfaced to TURBOMOLE. A split valence basis augmented by a single set of polarization functions (svp)<sup>31</sup> was used in all geometry calculations. The latter consists of a (7s3p1d/3s2p1d) contraction for carbon, an (8s4p1d/3s2p1d) contraction for fluorine, and a (10s7p1d/4s3p1d) contraction for second-row ele-

(22) Häser, M.; Ahlrichs, R.; Baron, H. P.; Weis, P.; Horn, H. *Theor. Chim. Acta* **1992**, *83*, 455.

(23) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.

(24) Almlöf, J.; Faegri, K., Jr.; Korsell, K. *J. Comput. Chem.* **1982**, *3*, 385. Cremer, D.; Gauss, J. *J. Comput. Chem.* **1986**, *7*, 274. Häser, M.; Ahlrichs, R. *J. Comput. Chem.* **1989**, *10*, 104.

(25) See, for example: Swanton, D.; Ahlrichs, R. *Theor. Chim. Acta* **1989**, *75*, 163. Chemical shift calculations for BH (Kutzelnigg, W.; van Wüllen, C.; Fleischer, U.; Franke, R. *The Calculation of NMR Shielding Constants and their Use in the Determination of the Geometric and Electronic Structure of Molecules and Solids*; in press.) and B<sub>2</sub>H<sub>2</sub> (Bühl, M.; Gauss, J.; Hofmann, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.*, submitted for publication.) show that correlation effects are, for these compounds, far from negligible.

(26) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(27) Gauss, J. *Chem. Phys. Lett.* **1992**, *191*, 614.

(28) TURBOMOLE: Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *154*, 165.

(29) ACES II (an ab initio program system): Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. University of Florida, Gainesville, FL, 1991.

(30) Haase, F.; Ahlrichs, R. *J. Comput. Chem.*, submitted for publication.

(31) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571. The exponents of the polarization functions are chosen as follows:  $d(\text{Al}) = 0.3$ ,  $d(\text{Si}) = 0.4$ ,  $d(\text{Cl}) = 0.65$ ,  $d(\text{O}) = 1.0$ ,  $d(\text{F}) = 1.2$ ,  $d(\text{H}) = 0.8$ . The optimized basis sets are available via FTP from host tchibm3.chemie.uni-karlsruhe.de (login id: anonymous).

Table I. Calculated Energies and Geometrical Parameters of Aluminum Compounds

compd	energies <sup>a,c</sup>	geometrical parameters <sup>b,c</sup>
AlH <sub>4</sub> <sup>-</sup>	-244.434 79	$r(\text{AlH}) = 163.8$
Al(CH <sub>3</sub> ) <sub>2</sub> Cl	(-780.428 54)	$r(\text{AlC}) = 197.0$ , $r(\text{AlCl}) = 212.5$ , $r(\text{CH}) = 109.4$
(Al(CH <sub>3</sub> ) <sub>2</sub> Cl) <sub>2</sub>	(-1561.395 50)	$r(\text{AlAl}) = 338.7$ , $r(\text{AlC}) = 196.9$ , $r(\text{AlCl}) = 235.6$
AlH	-242.430 89	$r(\text{AlH}) = 164.1$
AlF	-341.502 67	$r(\text{AlF}) = 167.9$
AlCl	-701.447 60	$r(\text{AlCl}) = 212.6$
AlSiH <sub>3</sub>	-532.544 09	$r(\text{AlSi}) = 256.9$ , $r(\text{SiH}) = 149.0$ , $\angle(\text{AlSiH}) = 112.4$
AlSi( <sup>t</sup> Bu) <sub>3</sub>	(-1000.443 89)	$r(\text{AlSi}) = 260.3$ , $r(\text{SiC}) = 197.1$
AlCp	-434.595 15	$r(\text{AlCp}) = 203.7$ , $r(\text{AlC}) = 236.8$ , $r(\text{CC}) = 142.0$ , $r(\text{CH}) = 107.9$
AlCp*	-630.313 98	$r(\text{AlCp}^*) = 198.9$ , $r(\text{AlC}) = 233.1$ , $r(\text{C}_{\text{Cp}}\text{C}_{\text{Cp}}) = 149.8$ , $r(\text{C}_{\text{Cp}}\text{C}_{\text{Me}}) = 142.8$ , $r(\text{CH}) = 109.8$
Al <sub>4</sub> H <sub>4</sub>	-969.940 16	$r(\text{AlAl}) = 258.3$ , $r(\text{AlH}) = 158.5$
Al <sub>4</sub> F <sub>4</sub>	-1366.133 13	$r(\text{AlAl}) = 260.5$ , $r(\text{AlF}) = 167.1$
Al <sub>4</sub> Cl <sub>4</sub>	-2805.934 63	$r(\text{AlAl}) = 259.8$ , $r(\text{AlCl}) = 209.8$
Al <sub>4</sub> (SiH <sub>3</sub> ) <sub>4</sub>	-2130.422 99	$r(\text{AlAl}) = 258.5$ , $r(\text{AlSi}) = 245.6$ , $\angle(\text{AlSiH}) = 110.9$
Al <sub>4</sub> Cp <sub>4</sub>		$r(\text{AlAl}) = 279.5$ , $r(\text{AlC}) = 237.9$ , $r(\text{CC}) = 140.8$

<sup>a</sup>Energies are given in hartrees. <sup>b</sup>Bond distances are given in picometers, and bond angles are in degrees. <sup>c</sup>Values given have been obtained at the MP2 level using the split valence plus polarization (svp) basis described in the text. SCF results are given in parentheses.

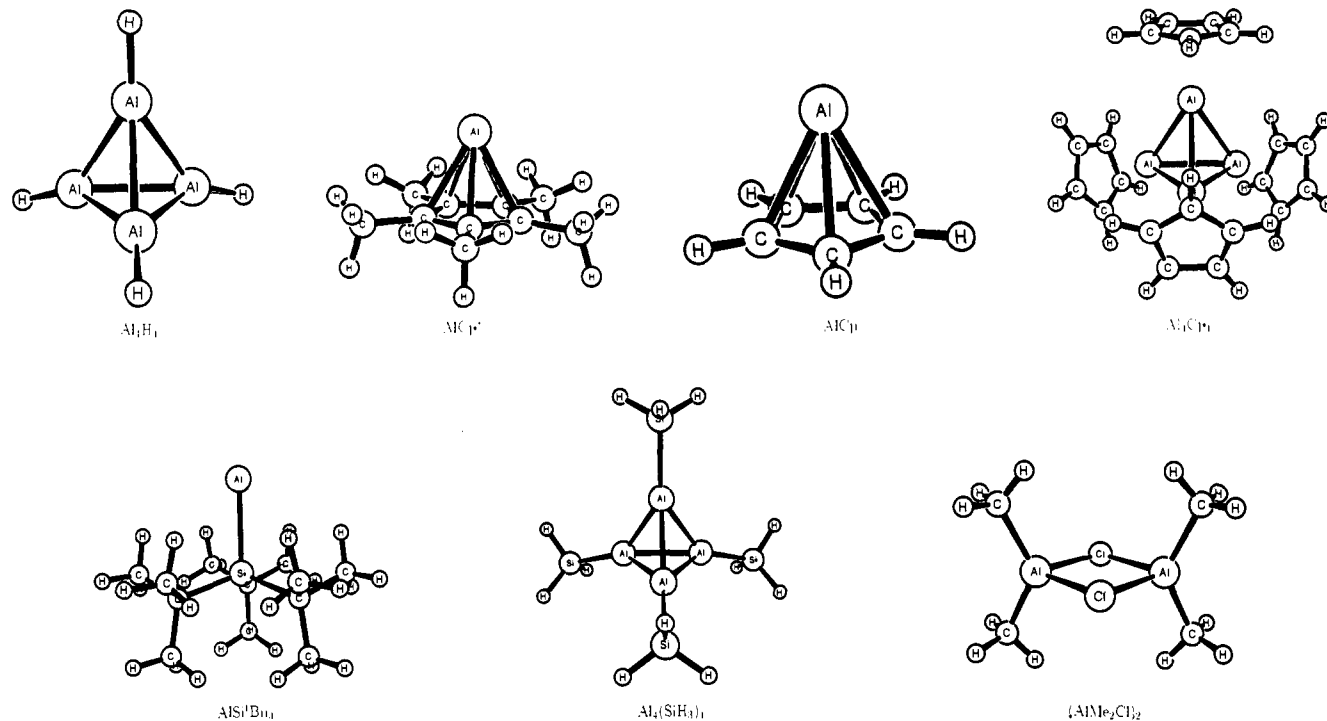
Table II. Calculated <sup>27</sup>Al Chemical Shifts at SCF and MP2 Levels Using the dzp and dzpcs Basis Sets Described in the Text

compd	basis	$\sigma^a$		$\delta^a$	
		SCF	MP2	SCF	MP2
AlH <sub>4</sub> <sup>-</sup>	dzp	514.7	509.1	101 <sup>b</sup>	101 <sup>b</sup>
	dzpcs	518.5	512.2	101 <sup>b</sup>	101 <sup>b</sup>
Al(CH <sub>3</sub> ) <sub>2</sub> Cl <sup>c</sup>	dzpcs	361.7		257	
	dzpcs	430.0		189	
AlH	dzp	126.8	137.0	489	473
	dzpcs	131.5	136.6	488	476
AlF	dzp	571.9	563.3	44	47
	dzpcs	574.2	565.5	45	48
AlCl	dzp	466.0	463.5	150	147
	dzpcs	469.1	464.7	150	149
AlSiH <sub>3</sub>	dzp	-135.0	-62.8	751	673
	dzpcs	-132.4	-67.0	752	680
AlSi <sup>t</sup> Bu <sub>3</sub>	dzpcs	-234.8		854	
	dzp	784.3	782.0	-169	-172 <sup>d</sup>
AlCp	dzpcs	782.5		-163	
	dzpcs	761.1		-143	
AlCp*	dzp	158.5	195.2	457	414
	dzpcs	162.3		457	
Al <sub>4</sub> H <sub>4</sub>	dzp	470.1	471.9	146	138
	dzpcs	471.1		148	
Al <sub>4</sub> F <sub>4</sub>	dzpcs	384.3		235	
	dzpcs	-9.1		629	
Al <sub>4</sub> Cp <sub>4</sub> <sup>c</sup>	dzpcs	724.5		-105	
	Al <sub>4</sub> Cp <sub>4</sub> <sup>e</sup>			estimated to -85 <sup>e</sup>	

<sup>a</sup>Absolute shieldings  $\sigma$  and relative shifts  $\delta$  with Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> as standard are given in ppm. <sup>b</sup>Reference 34. <sup>c</sup>Calculated at SCF/svp optimized geometry. <sup>d</sup>Calculation has been performed with the dzp basis for aluminum and carbon and a dz basis for hydrogen. <sup>e</sup>The estimate is obtained by adding to the  $\delta$  value of Al<sub>4</sub>Cp<sub>4</sub> the difference between the chemical shifts of AlCp\* and AlCp.

ments. For hydrogen, a (4s1p/2s1p) contraction was used. In all calculations, the s-component of the full set of six Cartesian d-functions was deleted.

To overcome the gauge-origin problem inherent to all calculations of magnetic properties, NMR shift calculations have been performed with the gauge-including atomic orbital (GIAO) method. Exact gauge invariance is here ensured by using explicitly field-dependent basis functions. The latter are obtained by multiplying the standard atomic orbitals (Cartesian Gaussian functions) by the additional phase factor  $\exp(-i/2c)(\mathbf{B} \times \mathbf{r})$  with  $\mathbf{B}$  the magnetic field strength,  $\mathbf{r}$  the center of the basis function, and  $\mathbf{r}$  the electron coordinate. At the SCF level, the



**Figure 1.** Calculated structures of some of the aluminum compounds considered in this study. For a complete list of all considered aluminum compounds as well as the calculated geometrical parameters, see Table I.

GIAO calculations have been performed with the semidirect GIAO-SCF program developed by Häser et al.<sup>22</sup> The correlated chemical shift calculations were carried out with the GIAO-MP2 program implemented in ACES II. A double-zeta plus polarization (dzp)<sup>32</sup> and a dzp basis improved by uncontracting the inner p-functions of the valence shell (dzpcs) have been used in the GIAO calculations. The latter consists of an (8s4p1d/4s3p1d) contraction for the first-row elements and an (11s7p1d/6s5p1d) contraction for second-row elements, while for hydrogen the same contraction as for the svp basis has been chosen. Note that due to program restrictions, the full set of six Cartesian d-functions was included in the GIAO-MP2 calculations.

### III. Theoretical Results

Table I lists all aluminum compounds considered in this study and summarizes their optimized geometrical parameters. In addition, Figure 1 displays the structure for some of the more complicated aluminum compounds. The calculated <sup>27</sup>Al NMR chemical shifts are given in Table II. Before discussing the results in detail, it is necessary to comment on two points, namely the conversion of the theoretical absolute shieldings  $\sigma$  to the experimentally used relative shifts  $\delta$  and the expected accuracy of the theoretical calculations.

The usually chosen reference for <sup>27</sup>Al NMR shifts is Al-(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup><sup>33</sup> which is better described as a solvated Al<sup>3+</sup> ion in aqueous solution. Theoretical calculations for this ion are not feasible, in particular due to the difficulties in incorporating solvation effects in a proper way. However, the conversion from the calculated absolute shieldings to the relative shifts and vice versa is always possible using an arbitrary reference compound for which a theoretical value of  $\sigma$  and a reliable experimental  $\delta$  value are available. Since the <sup>27</sup>Al chemical shift of the anion AlH<sub>4</sub><sup>-</sup> has been measured several times<sup>34</sup> and turns out to be nearly

**Table III.** Basis Set Dependence of the Calculated <sup>27</sup>Al Chemical Shifts of the Monomers AlH, AlF, AlCl, and AlSiH<sub>3</sub>

compd	basis	$\sigma^a$		$\delta^a$	
		SCF	MP2	SCF	MP2
AlH <sub>4</sub> <sup>-</sup>	dzp	514.7	509.1	101 <sup>b</sup>	101 <sup>b</sup>
	tzp	514.5	508.9	101 <sup>b</sup>	101 <sup>b</sup>
	tz2p	512.9	508.1	101 <sup>b</sup>	101 <sup>b</sup>
AlH	dzp	126.8	137.0	489	473
	tzp	123.5	131.3	492	479
	tz2p	128.4	131.0	486	478
AlF	dzp	571.9	563.3	44	47
	tzp	575.6	568.1	40	42
	tz2p	577.5	569.9	36	39
AlCl	dzp	466.0	463.5	150	147
	tzp	467.3	465.2	148	145
	tz2p	470.9	469.7	143	139
AlSiH <sub>3</sub>	dzp	-135.0	-62.8	751	673
	tzp	-143.4	-75.1	759	685
	tz2p	-137.7	-76.3	752	685

<sup>a</sup> Absolute shieldings  $\sigma$  and relative shifts  $\delta$  with Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> as standard are given in ppm. The GIAO calculations with the tzp and tz2p basis sets have been performed with the full set of six Cartesian d-functions. <sup>b</sup> Reference 34.

independent of solvation and concentration effects, we have decided to use AlH<sub>4</sub><sup>-</sup> as our reference with  $\delta$  equal to 101 ppm.<sup>34</sup> The theoretical absolute shieldings for AlH<sub>4</sub><sup>-</sup> are 515 (SCF/dzp), 518 (SCF/dzpcs), 509 (MP2/dzp), and 512 ppm (MP2/dzpcs) and show a strong dependence neither on basis set nor on electron correlation. Thus, contrary to the analogous anion AlCl<sub>4</sub><sup>-</sup>, for which correlation effects are more important,<sup>36</sup> AlH<sub>4</sub><sup>-</sup> is a suitable standard for both SCF and MP2 calculations.

To check the reliability of our NMR shift calculations, we included in our study the monomer and dimer of AlMe<sub>2</sub>Cl. The structure of the dimer (optimized at the SCF/svp level, see Figure 1 and Table I) shows two Al-Cl-Al bridges and tetracoordinated aluminum. The calculated shift of 189 ppm is in good agreement with the experimental value of 180 ppm,<sup>33</sup> while the calculated value of 257 ppm for the monomer falls in the typical range of

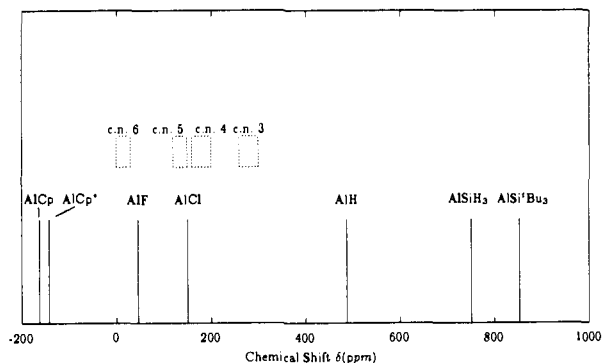
(32) Huzinaga, S. *Approximate Atomic Functions*. Technical Report; University of Alberta: Canada, 1971. For the exponents of the polarization functions, see ref 31.

(33) Benn, R.; Rufinska, A. *Angew. Chem.* **1986**, *98*, 851; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861.

(34) Nöth, H. Z. *Naturforsch.* **1980**, *B35*, 119 and references therein.

(35) The triple-zeta basis set consists of a (13s10p/8s6p) contraction for second-row elements, a (10s6p/6s3p) contraction for first-row elements, and a (6s/3s) contraction for hydrogen (see ref 31). The polarization exponents for the 1z2p basis are chosen as follows:  $d(\text{Al}) = 0.52$  and  $0.17$ ,  $d(\text{Si}) = 0.69$  and  $0.23$ ,  $d(\text{Cl}) = 1.13$  and  $0.38$ ,  $d(\text{F}) = 2.42$  and  $0.81$ , and  $p(\text{H}) = 0.8$ . For the polarization exponents of the 1zp basis, see ref 31.

(36) The calculated values for AlCl<sub>4</sub><sup>-</sup> are 493.8 (SCF/dzp) and 473.6 ppm (MP2/dzp).

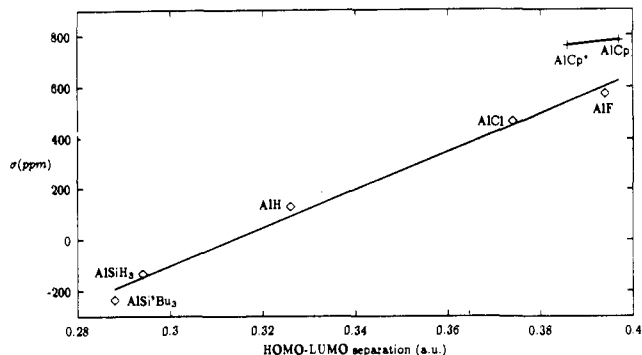


**Figure 2.** Comparison of the <sup>27</sup>Al chemical shifts calculated for the Al<sup>I</sup> compounds with those of Al<sup>III</sup> compounds (dashed boxes). The latter are taken from ref 33 and grouped together according to the coordination number (cn) of the aluminum atom.

three-coordinated aluminum.<sup>33</sup> Furthermore, to check convergence of the calculated chemical shifts with respect to the chosen basis set, we repeated for some of the monomers (AlH, AlF, AlCl, and AlSiH<sub>3</sub>) the NMR shift calculations with larger basis sets of triple-zeta plus (double) polarization quality (tzp and tz2p).<sup>35</sup> As the results summarized in Table III show, the remaining error due to basis set incompleteness can be estimated to about 10–20 ppm and is therefore less than the accuracy required for a comparison with experiment (20–30 ppm). For the correlated calculations, the error is slightly larger (see, for example, the results for AlSiH<sub>3</sub> which show the largest correlation correction) but still small (12 ppm for MP2/dzp and 4 ppm for MP2/dzpc compared to the MP2/tz2p result). As these test calculations and the example (AlMe<sub>2</sub>Cl) given above demonstrate, GIAO calculations using basis sets of dzp (or triple-zeta plus polarization (tzp)) quality are capable of providing accurate and reliable chemical shifts for aluminum compounds. As an upper bound for the error in the relative shifts due to remaining basis set and correlation effects, 20–30 ppm might be a conservative estimate.

**A. AlX with X = H, F, Cl, Cp, Cp\*, SiH<sub>3</sub>, and Si<sup>t</sup>Bu<sub>3</sub>.** Inspecting the calculated chemical shifts for the AlX monomers in Table II, it is surprising at first sight that the calculated shifts cover such a large range on the <sup>27</sup>Al NMR scale and depend so strongly on the nature of X. While for AlCp a shift of –163 ppm is calculated, a value which represents one of the highest upfield shifts observed/calculated for aluminum compounds so far, the calculated value of 854 ppm for AlSi<sup>t</sup>Bu<sub>3</sub> represents the highest known downfield shift. The calculated values for X = H, F, and Cl are between these two extreme values. To illustrate the large range of <sup>27</sup>Al shifts predicted for the monomer AlX compounds, Figure 2 displays the calculated values together with the typical ranges for Al<sup>III</sup> compounds.<sup>33</sup> While the shifts of the latter are restricted to rather narrow regions and can be satisfactorily correlated with the coordination number of the aluminum atom as indicated in Figure 2, the calculated shifts for the Al<sup>I</sup> compounds are solely determined by electronic effects.

A detailed analysis shows that the variation of the <sup>27</sup>Al chemical shifts originates in the paramagnetic contribution (using the gauge-independent decomposition suggested by Ditchfield<sup>23</sup>) to  $\sigma$  and that the diamagnetic part of  $\sigma$  is more or less constant, varying only by a few ppm. As it is well known from the theory of magnetic properties, calculation of the paramagnetic part of  $\sigma$  involves an energy denominator containing the excitation energies of the considered molecule (for example, see the sum-over-states approach for calculating molecular properties<sup>37</sup>). In CPHF theory,<sup>38</sup> this denominator is approximated by an expression which involves the difference of the orbital energies of occupied and virtual orbitals.<sup>39</sup> Therefore, the HOMO–LUMO energy gap



**Figure 3.** Plot of the NMR shielding constants  $\sigma$  calculated for the AlX compounds with X = H, F, Cl, Cp, Cp\*, SiH<sub>3</sub>, and Si<sup>t</sup>Bu<sub>3</sub> as a function of the HOMO–LUMO energy gap.

**Table IV.** Calculated Mulliken Charges and Populations for the AlX Compounds (X = H, F, Cl, Cp, Cp\*, SiH<sub>3</sub>, and Si<sup>t</sup>Bu<sub>3</sub>)

compd	q(Al)	q(3p <sub>x</sub> )
AlH	0.33	0.00
AlF	0.50	0.12
AlCl	0.46	0.10
AlSiH <sub>3</sub>	0.29	0.01
AlSi <sup>t</sup> Bu <sub>3</sub>	0.26	0.02
AlCp	0.32	0.38
AlCp*	0.33	0.38

should provide a rough measure for the size of the paramagnetic contribution to  $\sigma$ , and we therefore plot in Figure 3 the calculated shieldings as a function of the latter. As the figure shows, there is indeed a correlation between these two quantities; in particular, the paramagnetic contribution increases as the HOMO–LUMO gap decreases. It is also evident from Figure 3 that there is a significant difference between the bonding in AlCp and AlCp\* on one side and AlF, AlCl, AlH, and AlSiR<sub>3</sub> on the other side. To explain these differences and to give a rationale for the calculated shieldings, two electronic effects have to be discussed.<sup>14,16</sup> First, due to the higher electronegativity of all considered X compared to Al, there is a charge transfer from Al to X, leaving a positive charge at the aluminum. Second, since there are empty p-orbitals at Al (p<sub>x</sub> and p<sub>y</sub>, assuming that AlX is oriented parallel to the z-axis),  $\pi$ -(back-)bonding from X to Al might occur and be important. The first effect is dominant for X = H, F, Cl, and SiR<sub>3</sub>, though  $\pi$ -back-bonding is certainly not negligible for X = F and Cl.<sup>14</sup> The orbital energy of the HOMO which can be described as an sp hybrid lone-pair orbital at Al is lowered with increasing positive charge of Al, i.e., with increasing electronegativity of X, while the orbital energy of the LUMO can be considered in a first approximation as constant. Thus, with increasing electronegativity of X, the paramagnetic contribution to  $\sigma$  is reduced and the calculated shieldings are shifted to higher field.

Hence, the largest values for  $\sigma$  can be expected for SiR<sub>3</sub> and the smallest for F and Cl, as it is also found in the calculations, not considering the somewhat special cases AlCp and AlCp\*. For these,  $\pi$ -bonding between Al and the Cp ring is the dominant feature and the source of stability.<sup>14</sup> Due to these strong  $\pi$ -interactions, the energy of the LUMO is shifted toward higher values, thus yielding a large HOMO–LUMO gap. The calculated paramagnetic contributions to  $\sigma$  are therefore for AlCp and AlCp\* very small and are the origin of the high upfield shifts predicted for these two compounds. It should be noted that similar upfield shifts have been observed for Cp complexes of other elements, such

(39) We are well aware of the fact that orbital energies have no real physical meaning and have to be discussed with some care. In addition, it should be noted that the notation of the lowest unoccupied molecular orbital (LUMO) is somewhat questionable, in particular, since the latter has in an infinite basis calculation an orbital energy of less than or equal to 0 and corresponds in cases without a stable electron attached state to a free electron orbital. However, for a qualitative discussion using a finite basis set calculation, the HOMO–LUMO energy gap might be used as long as the limitations mentioned above are kept in mind.

(37) See, for example, the formula of NMR chemical shifts given by Ramsey (Ramsey, N. F. *Phys. Rev.* **1952**, *86*, 243).

(38) McWeeny, R. *Rev. Mod. Phys.* **1960**, *32*, 335; *Phys. Rev.* **1961**, *126*, 1028. Stevens, R. M.; Pitzer, R. M.; Lipscomb, W. N. *J. Chem. Phys.* **1963**, *38*, 550. Gerratt, J.; Mills, I. M. *J. Chem. Phys.* **1968**, *49*, 1719.

**Table V.** Calculated Changes (in ppm) in the  $^{27}\text{Al}$  Chemical Shifts upon Tetramerization

	SCF	MP2
$\text{AlH} \rightarrow \text{Al}_4\text{H}_4$	-31	-59
$\text{AlF} \rightarrow \text{Al}_4\text{F}_4$	103	91
$\text{AlCl} \rightarrow \text{Al}_4\text{Cl}_4$	85	
$\text{AlSiH}_3 \rightarrow \text{Al}_4(\text{SiH}_3)_4$	-123	
$\text{AlCp} \rightarrow \text{Al}_4\text{Cp}_4$	58	

**Table VI.** Calculated "Solvent" Effects on the  $^{27}\text{Al}$  Chemical Shifts of  $\text{AlCl}^a$ 

<i>n</i>	$\text{H}_2\text{O}$		$\text{Me}_2\text{O}$	
	$\Delta\delta$	$\Delta E$	$\Delta\delta$	$\Delta E$
1	-32.9	25		
2	-63.3	48	-50.4	30
3	-76.6	65	-65.1	40
4	-97.5	80		

<sup>a</sup> Calculations have been carried out at the SCF level for various complexes of  $\text{AlCl}$  with  $\text{H}_2\text{O}$  and  $\text{Me}_2\text{O}$ .  $\Delta\delta$  gives the changes for the  $^{27}\text{Al}$  chemical shifts relative to gaseous  $\text{AlCl}$  in ppm,  $\Delta E$  denotes the interaction energy in kJ/mol, and *n* is the number of "solvent" molecules attached to  $\text{AlCl}$ .

as  $\text{SnCp}_2$ ,<sup>40</sup>  $\text{SiCp}^*$ ,<sup>41</sup>  $\text{TiCp}$ ,<sup>42</sup>  $\text{GaCp}$ ,<sup>43</sup> or substituted  $\text{LiCp}$  derivatives.<sup>44</sup>

To present further evidence for the two electronic effects, Table IV displays the calculated Mulliken charges and populations<sup>45</sup> for the  $\text{AlX}$  monomers. The computed charges at Al are in agreement with our arguments given in the previous paragraph and increase in the order  $\text{Si}^+\text{Bu}_3$ ,  $\text{SiH}_3$ ,  $\text{H}$ ,  $\text{Cl}$ ,  $\text{F}$ . The population of the  $3p_x$  and  $3p_y$  orbitals at Al which are responsible for the  $\pi$ -(back)-bonding are for H and  $\text{SiR}_3$  0 or close to 0, but are also for F and Cl rather small. For Cp and  $\text{Cp}^*$ , on the other hand, the  $3p_x$  and  $3p_y$  populations are significant ( $q(3p_x) \approx 0.19$ ), thus underlining the importance of  $\pi$ -interaction in these two Cp complexes.

Finally, it is necessary to comment on the importance of electron correlation effects. Somewhat unexpectedly, they are rather small, and we obtain a larger correction of about 70 ppm only for  $\text{AlSiH}_3$  (and presumably also for  $\text{AlSi}^+\text{Bu}_3$ , which we could not study by the GIAO-MP2 method). Again, it is possible to explain this result by correlating the MP2 corrections to the shieldings with the HOMO-LUMO energy gap which can be considered as a rough measure for the importance of electron correlation.

**B.  $(\text{AlX})_4$  with X = H, F, Cl, Cp, and  $\text{SiH}_3$ .** Table V gives the differences in the calculated  $^{27}\text{Al}$  NMR chemical shifts between monomers and the corresponding tetramers (for the calculated relative shifts of the tetramers, see Table II). The influence of correlation effects have been checked for the two smallest tetramers,  $\text{Al}_4\text{H}_4$  and  $\text{Al}_4\text{F}_4$ , and have been found to be, within 10–20 ppm, rather small. They are presumably larger for the  $\text{Al}_4(\text{SiR}_3)_4$  compounds, as can be expected from the calculated MP2 corrections for the monomers. Somewhat unexpectedly, the changes  $\Delta\delta$  ( $\Delta\delta = \delta(\text{tetramer}) - \delta(\text{monomer})$ ) strongly depend on the substituent X and even have different signs. While for  $\text{Al}_4\text{H}_4$  and  $\text{Al}_4(\text{SiR}_3)_4$   $\Delta\delta$  is negative, i.e., the chemical shifts are moved toward higher field, the opposite is found for  $\text{Al}_4\text{F}_4$ ,  $\text{Al}_4\text{Cl}_4$ , and  $\text{Al}_4\text{Cp}_4$ . To rationalize these differences, it is important to understand the nature of the bonding in the tetramers. A thorough discussion on this topic has already been given in refs 14 and 16,

**Table VII.** Experimental  $^{27}\text{Al}$  NMR Shifts of  $\text{Al}^I$  Compounds<sup>a</sup>

compd	<i>T</i> /°C	$W_{1/2}$ /Hz	$\delta$	solvent
$\text{AlCl}$	-80	1800	+35	toluene/ether (3:1)
$(\text{AlSi}^+\text{Bu}_3)_x$	25	100	+64.5	benzene
$\text{Al}_4\text{Cp}^*_4$	-80	1225	-80.7	toluene
	25	140	-80.9	toluene
$\text{AlCp}^*$	100	100	-149.5	toluene
$\text{Al}_4\text{Cp}_4$	-80	1250	-111	toluene/ether (3:1)

<sup>a</sup>  $^{27}\text{Al}$  NMR: 70.4 MHz, external standard  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ .

and, therefore, we will only recapitulate the most important aspects and try to relate these findings with the calculated  $\Delta\delta$  values.

Bonding in the tetramers and their stabilization with respect to the monomers is a result of " $\sigma$ - $\pi$ " orbital interactions (for simplicity, we are using the orbital notation for the linear  $\text{AlX}$  compounds). The main feature is explained in Figure 1 of ref 14. The four lone-pair orbitals at the aluminum atoms of the tetrahedral cage form in  $T_d$  symmetry (the symmetry group of all simple  $\text{Al}_4\text{X}_4$  compounds,  $\text{Al}_4\text{Cp}_4$  possesses  $D_{2d}$  symmetry) a low-lying  $a_1$  orbital and a high-lying set of  $t_2$  orbitals. The latter are stabilized by interaction with the low-lying unoccupied  $t_2$  orbitals formed from the empty  $\pi$  orbitals of the monomers.<sup>14</sup> The strength of the  $\sigma$ - $\pi$  interactions depends on the HOMO-LUMO gap of the monomer and is reflected in the calculated tetramerization energies.<sup>14,16</sup>

What are the consequences for the chemical shifts? Based on the arguments given in the previous section for the monomers, it is clear that increased  $\pi$ -bonding leads to an upfield shift in the chemical shieldings. In complete analogy, one might therefore expect that the  $\sigma$ - $\pi$  interactions in the tetramers should induce the same changes, namely a shift to lower  $\delta$  values. This effect seems to be dominant in  $\text{Al}_4\text{H}_4$  and  $\text{Al}_4(\text{SiR}_3)_4$ , where strong  $\sigma$ - $\pi$  mixing leads to large tetramerization energies.<sup>16</sup> However, the same argument does not apply to the other tetramers, where the changes are in the opposite direction, namely to lower field. Here, one has to consider in addition the effects of the tetramerization on the  $\text{AlX}$  bonding. As explained in ref 14, tetramerization reduces the charge transfer from Al to X and furthermore diminishes the  $\pi$ -back-bonding from X to Al. These two effects should lead to a downfield shift of the  $^{27}\text{Al}$  NMR signal as it is calculated for  $\text{Al}_4\text{F}_4$  and  $\text{Al}_4\text{Cl}_4$ . Apparently, the two latter effects are for X = F and Cl more important than the  $\sigma$ - $\pi$  interactions, which is also supported by the fact that the calculated tetramerization energies are much smaller than for  $\text{Al}_4\text{H}_4$  and  $\text{Al}_4(\text{SiR}_3)_4$ . For the tetramers of  $\text{AlCp}$  and  $\text{AlCp}^*$ , weakening of the  $\pi$ -bonding between Al and Cp, which is also reflected by the slightly larger Al-Cp distances found for the tetramers, seems to be the cause of the downfield shift of the  $^{27}\text{Al}$  NMR signal upon tetramerization.

However, the main conclusion of the calculations is certainly that the tetramers can be unambiguously identified by their  $^{27}\text{Al}$  chemical shifts, which are in all considered cases significantly different from the chemical shifts of the corresponding monomer. In particular, for the experimentally known  $\text{Al}_4\text{Cp}^*_4$ , a conclusive answer regarding the structure in solution should be possible. A more thorough discussion of this topic and a comparison with experimental results for these systems is given in the next section.

#### IV. Discussion and Comparison with Experiment

In this section, we will compare our calculated  $^{27}\text{Al}$  chemical shifts with available experimental data for  $\text{Al}^I$  compounds and report, in addition, new experiments carried out for  $\text{AlCp}$  and  $\text{AlCp}^*$ . Let us first consider  $\text{AlCl}$ , for which Tacke and Schnöckel<sup>1</sup> reported three years ago  $^{27}\text{Al}$  NMR spectroscopic results.

**A.  $\text{AlCl}$ .** Figure 4 compares the calculated chemical shifts for  $\text{AlCl}$  monomer and tetramer with the experimental results. The experimental value for  $\text{AlCl}$  in solution with toluene/ether as solvent is +35 ppm (see ref 1 and Table VII for more recent experimental results). Neither our calculated value for the monomer ( $\delta = 150$  ppm) nor the computed shift for the tetramer ( $\delta = 235$  ppm) agrees with the experimentally observed  $^{27}\text{Al}$  NMR chemical shift (cf. Figure 4). However, since solvation effects

(40) Kennedy, J. D.; McFarlane, W. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; pp 342 ff.

(41) Jutzi, P.; Holtmann, U.; Kanne, D.; Krüger, C.; Blom, R.; Gleiter, R.; Hyla-Krypsin, I. *Chem. Ber.* **1989**, *122*, 1629.

(42) Köppel, H.; Dallorso, J.; Walther, B. *Z. Anorg. Allg. Chem.* **1976**, *427*, 24.

(43) Loos, D.; Schnöckel, H.; Gauss, J.; Schneider, U. *Angew. Chem.* **1992**, *104*, 1376; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1362.

(44) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776. Jutzi, P.; Leffers, W.; Pohl, S.; Saak, W. *Chem. Ber.* **1989**, *122*, 1449.

(45) Mulliken, R. *J. Chem. Phys.* **1955**, *23*, 1833.

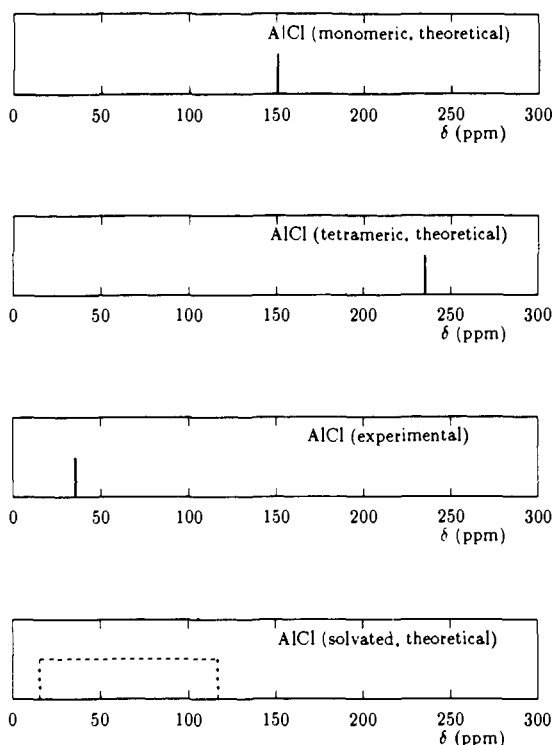


Figure 4. Comparison of the calculated  $^{27}\text{Al}$  chemical shifts for  $\text{AlCl}_3$ ,  $\text{Al}_4\text{Cl}_{12}$ , and "solvated  $\text{AlCl}_3$ " with the experimental spectrum of a  $\text{AlCl}_3$ /toluene/ether solution.

play an essential role in stabilizing  $\text{AlCl}_3$ , it is certainly not justified to use isolated  $\text{AlCl}_3$  as a model to compute spectroscopic properties of the solution of  $\text{AlCl}_3$  in toluene/ether.

To investigate solvation effects we performed model calculations on complexes of  $\text{AlCl}_3$  with one, two, three, and four water molecules. In addition, we carried out calculations on complexes of  $\text{AlCl}_3$  with two and three dimethyl ether molecules, which are probably slightly more realistic model compounds. In all calculations, the solvent molecules were oriented in a way that allows efficient interaction between the lone-pair orbitals at oxygen and the empty  $\pi$ -orbitals of  $\text{AlCl}_3$ . The structures of these complexes were optimized at the SCF level, assuming the highest chemically reasonable symmetry ( $C_3$  for  $\text{AlCl}_3\cdot\text{H}_2\text{O}$ ,  $C_{2v}$  for  $\text{AlCl}_3\cdot 2\text{H}_2\text{O}$ ,  $C_{3v}$  for  $\text{AlCl}_3\cdot 3\text{H}_2\text{O}$ , and  $C_{4v}$  for  $\text{AlCl}_3\cdot 4\text{H}_2\text{O}$ ).<sup>46</sup> The computed "solvent shifts" on the  $^{27}\text{Al}$  shieldings are given in Table VI together with the calculated complexation energies.

The calculated interaction energies of 20–60 kJ/mol per solvent molecule clearly show that  $\text{AlCl}_3$  strongly interacts with the solvent. Furthermore, the computed solvent shifts of 50 to more than 100 ppm are in complete agreement with our hypothesis that the spectroscopic properties of isolated (gaseous)  $\text{AlCl}_3$  and solvated  $\text{AlCl}_3$  are very different. Taking the largest calculated shift of 103 ppm, one obtains for solvated  $\text{AlCl}_3$  a  $^{27}\text{Al}$  chemical shift of 48 ppm, which is close to the experimental value of 35 ppm (cf. Figure 4). However, though our results provide a qualitative explanation for the experimentally observed shift, one has to realize that we are using a very crude model to account for solvation effects. In particular, the situation is much more complicated and it is not possible to assign the observed broad signal to a specific  $\text{AlCl}_3$  solvent complex. Furthermore, we have so far not considered the other constituent of the solvent, toluene. Preliminary calculations on  $\text{AlH}$  benzene complexes indicate that these interactions could cause similar upfield shifts, i.e., in the range of 50–100 ppm.

**B.  $\text{AlSi}^i\text{Bu}_3$ .**  $(\text{AlSi}^i\text{Bu}_3)_x$  is obtained by reaction of an  $\text{AlCl}_3$ /toluene/ether solution with  $^i\text{Bu}_3\text{SiNa}$ .<sup>15</sup> Sublimation in

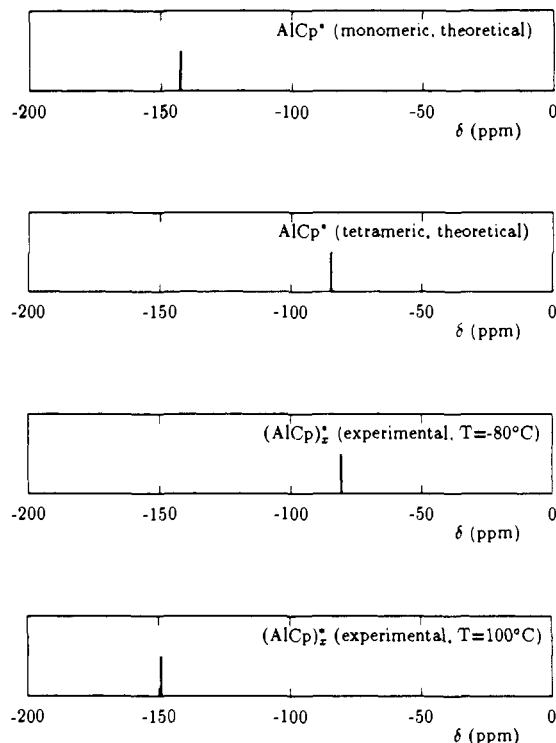


Figure 5. Comparison of the calculated  $^{27}\text{Al}$  chemical shifts for  $\text{AlCp}^*$  and  $\text{Al}_4\text{Cp}^*_4$  with the experimental spectra of a solution of  $\text{Al}_4\text{Cp}^*_4$  crystals in toluene at  $-80$  and  $100^\circ\text{C}$ .

vacuum at  $180^\circ\text{C}$  yields violet crystals which, unfortunately, were not suitable for an X-ray analysis. There is some evidence from the mass spectra that  $\text{AlSi}^i\text{Bu}_3$  forms tetramers. The observed sharp  $^{27}\text{Al}$  NMR signal at 64.5 ppm<sup>47</sup> of a solution of  $(\text{AlSi}^i\text{Bu}_3)_x$  in benzene supports a well-defined molecular structure, though it could not be assigned to a specific value of  $x$ , since no data for comparison were available.

Our calculated  $^{27}\text{Al}$  chemical shifts for monomers and tetramers of  $\text{AlSiH}_3$  and  $\text{AlSi}^i\text{Bu}_3$  are, however, not in agreement with the experimentally observed value. Though correlation effects (cf. Table II) are important and therefore our results for the various  $\text{AlSiR}_3$  compounds are somewhat less accurate than the results obtained for the other  $\text{Al}^I$  compounds, the discrepancy between experiment and theory (about 300 ppm) is so large that one can safely conclude that the experimental NMR signal is due neither to isolated  $\text{AlSi}^i\text{Bu}_3$  nor to  $\text{Al}_4(\text{Si}^i\text{Bu}_3)_4$ . However, as for  $\text{AlCl}_3$ , the main explanation for the large discrepancy between experiment and theory might be due to the importance of solvation effects. Some preliminary calculations on  $\text{AlSiH}_3\cdot n\text{H}_2\text{O}$  complexes indicate that the latter are even larger than for  $\text{AlCl}_3$  and probably in the range of several hundred ppm. Certainly, our calculations and the underlying simple model used to account for solvation effects are not sufficient to provide a clear interpretation of the experimental data and in particular a specific value for  $x$ . More sophisticated calculations and further experimental studies are required to obtain a more detailed picture of the structure of  $\text{AlSi}^i\text{Bu}_3$  in solution.

**C.  $\text{AlCp}$  and  $\text{AlCp}^*$ .** The structural characterization of  $\text{AlCp}^*$  crystals by X-ray analysis shows that solid  $\text{AlCp}^*$  forms tetramers.<sup>5</sup> Whether these tetramers are preserved in solution or fall apart in monomers could not be answered so far. The observation of one sharp signal at  $-80$  ppm in the  $^{27}\text{Al}$  NMR spectrum indicates that only one species exists in solution, but because of the lack of data for comparison, it was not possible to assign this NMR signal to a specific value of  $x$ . On the other side, reliable determinations of the molecular mass were hampered by the low

(46) Since the considered  $\text{AlCl}_3\cdot n\text{H}_2\text{O}$  are only model complexes, we did not check whether the calculated structures represent local minima on the corresponding potential surfaces; neither do we claim that these complexes really exist in solution.

(47) Dohmeier, C.; Passler, T.; Schnöckel, H.; Wiberg, N., manuscript in preparation.

solubility of AlCp\* in benzene and its extreme sensitivity to moisture and air.

The theoretical  $^{27}\text{Al}$  NMR chemical shifts for the monomer and tetramer of AlCp\* allow an assignment of the NMR signal at  $-80$  ppm to the tetramer (cf. Figure 5). The estimated value of  $-85$  ppm for the tetramer, which is obtained by adding the difference between the chemical shifts of AlCp\* and AlCp to the  $\delta$  value of  $\text{Al}_4\text{Cp}_4$  (cf. Table II), agrees very well with the experimental value, while for the monomer an even more shielded value of  $-143$  ppm is obtained in the calculations. Therefore, the tetrameric units of the solid phase are preserved in solution and, at least at low temperature, no experimental evidence for the monomer of AlCp\* exists.

Since the calculated tetramerization energy of AlCp (about  $150$ – $160$  kJ/mol<sup>14</sup>) is rather low and since a similar value can be expected for AlCp\*, we have tried to observe the dissociation of  $\text{Al}_4\text{Cp}_4$  by increasing the temperature and monitoring the  $^{27}\text{Al}$  NMR spectrum. Indeed, above  $30$  °C a new signal at  $-149.5$  ppm is observed, which, according to the quantum chemical calculations (cf. Figure 5 and Table II; the calculated value is  $-143$  ppm), can be attributed to the AlCp\* monomer.

By further increasing the temperature, the new peak at  $-149.5$  ppm is growing in intensity, while at the same time the intensity of the original peak is more and more decreased. An analysis of the intensity ratios at  $60$ ,  $80$ , and  $100$  °C yields for the tetramerization energy ( $\Delta H^\circ$ ) an estimate of about  $150 \pm 20$  kJ/mol, which is of same magnitude as the value predicted for AlCp by ab initio calculations.<sup>14</sup>

In the case of AlCp\*, the combination of  $^{27}\text{Al}$  NMR spectroscopy with quantum chemical ab initio calculations of chemical shifts leads to a detailed characterization of the solution of  $\text{Al}_4\text{Cp}_4$  crystals in toluene and provides for the first time evidence for the existence of monomeric AlCp\*. Finally, it should be noted that solvation effects turn out to be negligible for AlCp\*. Test calculations of AlCp-H<sub>2</sub>O complexes showed that the latter are only weakly bonded and that the chemical shifts are at most affected by  $5$ – $10$  ppm, as expected by the  $\sigma$ - $\pi$  model, much less than the estimated accuracy of our calculations.

Using the same procedure as we have just described for AlCp\*, it should be possible to investigate the structure of a solution of AlCp in toluene/ether. The latter can be prepared in the same way as AlCp\*,<sup>5</sup> by reaction of AlCl in a mixture of toluene and ether as solvent with MgCp<sub>2</sub>. However, AlCp is only stable up to  $-60$  °C and disproportionates at higher temperatures. Therefore, it was not possible to carry out a temperature-dependent NMR study, and we could only obtain the  $^{27}\text{Al}$  NMR spectrum at  $-80$  °C. The latter shows one signal at  $-111$  ppm, which, according to the quantum chemical calculations (cf. Table II), can be assigned to the tetramer. The calculated value for  $\text{Al}_4\text{Cp}_4$  is  $-105$  ppm, while the corresponding value for the monomer is predicted to be  $-172$  ppm. Due to the thermal instability of AlCp, no experimental evidence for the existence of the monomer of AlCp could be obtained so far.

## V. Conclusions

We have shown that experimental NMR spectra of Al<sup>I</sup> compounds in solution can be interpreted on the basis of theoretical calculation of  $^{27}\text{Al}$  chemical shifts. This approach has been proven particularly successful in the case of AlCp\*, where theoretical calculations allowed an unambiguous identification of tetrameric and monomeric species in solution. Theoretical calculations were furthermore the basis of a thorough investigation of the dissociation of  $\text{Al}_4\text{Cp}_4$  into  $4\text{AlCp}^*$ . In addition, first evidence for the existence of the AlCp\* monomer in solution has been obtained on the basis of the theoretical predictions.

The given examples add further support to the power of theoretical NMR shift calculations concerning the interpretation of experimental spectra of hitherto unknown compounds. In particular, chemical shift calculations are an invaluable tool for the interpretation of experimental spectra if there are no other experimental NMR data available for comparison, as in the case of the Al<sup>I</sup> compounds.

**Acknowledgment.** This work was supported by the Fonds der Chemischen Industrie, in particular through a "Liebig-Stipendium" to J.G. which is gratefully acknowledged.

## Molecular Modeling of the Kinetic Isotope Effect for the [1,5] Sigmatropic Rearrangement of *cis*-1,3-Pentadiene

Yi-Ping Liu,<sup>†</sup> Gillian C. Lynch,<sup>†</sup> Thanh N. Truong,<sup>†</sup> Da-hong Lu,<sup>†</sup> Donald G. Truhlar,<sup>\*,†</sup> and Bruce C. Garrett<sup>‡</sup>

Contribution from the Department of Chemistry and Supercomputer Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, and Molecular Sciences Research Center, Pacific Northwest Laboratory, Richland, Washington 99352. Received June 8, 1992

**Abstract:** The primary kinetic isotope effect for the [1,5] sigmatropic rearrangement reaction of *cis*-1,3-pentadiene is studied by the direct dynamics method. The calculations are carried out with the computer code MORATE, which combines the semiempirical molecular orbital package, MOPAC, and the polyatomic dynamics code, POLYRATE, developed previously by our research group. Dynamics calculations are based on canonical variational transition-state theory including multidimensional tunneling corrections. The force field is obtained by molecular orbital theory with the AM1, PM3, and MINDO/3 parameterizations. The kinetic isotope effects calculated with the MINDO/3 and PM3 Hamiltonians agree with those calculated by AM1 within 13%, and the latter agree with experiment within 13%. The tunneling contributions to the kinetic isotope effects are analyzed, and the nature of the vibrationally assisted tunneling process is discussed. General features of the dynamics from all three parameterizations are similar, and the quantitative differences in the predictions of the three calculations can be understood in terms of global characteristics of the potential energy functions that they predict.

## Introduction

Reactions involving transfer or migration of hydrogen atoms, protons, and hydride ions often involve tunneling,<sup>1</sup> and realistic calculations of tunneling processes require at least a semiglobal

potential energy function (PEF).<sup>2</sup> Analytic representation of PEFs (i.e., potential surface fitting)<sup>3</sup> is a difficult, time-consuming,

<sup>†</sup> University of Minnesota.

<sup>‡</sup> Molecular Sciences Research Center.

(1) (a) Skodje, R. T.; Truhlar, D. G.; Garrett, B. C. *J. Chem. Phys.* **1982**, *77*, 5955. (b) Kreevoy, M. M.; Truhlar, D. G. In *Investigation of Rates and Mechanisms of Reaction* ("Techniques of Chemistry", 4th ed.); Bernasconi, C. F., Ed.; John Wiley & Sons: New York, 1986; Part I, p 13.