Probing the Reactivity of Aluminum(I) Compounds: The Reaction of Pentamethylcyclopentadienyl-Aluminum, Al[$C_5(CH_3)_5$], Monomers with Dihydrogen in a Solid Ar Matrix to Give the New Aluminum Hydride Molecule $H_2Al[C_5(CH_3)_5]$

Hans-Jörg Himmel* and Jean Vollet

Institut für Anorganische Chemie der Universität Karlsruhe,
Engesserstrasse, Geb. 30.45, 76128 Karlsruhe, Germany

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The photoinduced reaction of AlCp* [Cp* = $C_5(CH_3)_5$] monomers with H_2 in an Ar matrix at 12 K was followed with IR spectroscopy. The experimental results allied with detailed quantum chemical calculations show that the product of this reaction is the new aluminum hydride species H_2AlCp*. The properties of this species are investigated and compared with those of related known monomeric hydrides such as AlH_3, H_2AlNH_2, and $HAlCl_2$. The comparison between the reactivities of species such as AlCl and AlCp* is of importance for a better understanding of the bonding properties in AlCp*. The possibility for π-back-donation in the product of the reaction between AlCp* and H_2, H_2AlCp*, certainly affects chemical properties such as the Lewis acidity. The differences between the wavenumbers for the ν(Al−H) stretching modes of H_2AlCp* and H_2AlCl show that the influence of the Cp* group is significant.

1. Introduction

There is not much known about the reactivity of Al(I) compounds in their monomeric forms because under normal conditions these molecules generally form oligomers.[1] Hence AlCp* [Cp* = $C_5(CH_3)_5$] exists as a [AlCp*]$_4$ tetramer with a tetrahedral structure in the solid state and also in solution at room temperature.[2] From temperature-dependent ^{27}Al NMR studies of solutions the tetramerization energy was estimated to be about −150 kJ mol^{-1}.[3] Thus, even at temperatures as high as 120 °C, there is a large proportion of [AlCp*]$_4$ tetrameric units left in the solution. Some reactions of AlCp* (monomeric or oligomeric) in solution were studied and shown to lead to products in which the AlCp* unit occupies either a terminal or a bridging position. For example, AlCp* was shown to react with $Cr(CO)_5C_8H_{14}$ (C_8H_{14} = *cis*-cyclooctene) in toluene at 60 °C to give Cp*Al−Cr(CO)$_5$ featuring a terminal Cp*Al unit.[4] Another example is provided by the compound Cp*AlFe(CO)$_4$.[5] Bridging AlCp* units were found in (AlCp*)$_2$(NiCp)$_2$[6] and (AlCp*)$_2$[Co(CO)$_3$]$_2$.[7] However, the reactivity of isolated Cp*Al molecules has so far not been studied in detail.

It has also been shown that AlCp* can be evaporated at temperatures above 100 °C (estimated vapor pressure at 140 °C about 0.05 Torr).[8] However, the compound cannot be kept for more than a few hours at this temperature because decomposition slowly occurs. In the vapor phase, AlCp* is a monomer, the dimensions of which were determined from electron diffraction studies,[8] revealing an Al−C distance of 2.388 Å. The physical properties of AlCp and AlCp* were also examined in quantum chemical studies.[9] The calculated dipole moment of AlCp amounts to 1.37 D, but, in contrast to AlF and AlCl, the negative pole is apparently located at the Al center. This has been explained by the extended Al lone pair in combination with a reduced charge transfer from the Al atom to the Cp unit. The computed gross charge at the aluminum amounts to +0.33 e. The calculations also showed that there is a significant amount of π-back-donation in the direction Cp → Al.[9]

The subvalent halides of aluminum, AlX (X = Cl, Br, or I), also form tetrameric units, which are stabilized by donor molecules. Thus, the structure of $Al_4Br_4(NEt_3)_4$ was studied in the solid state, and in this case the Al atoms form a square four-membered ring.[10] Metastable

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* To whom correspondence should be addressed.

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solutions of AlX were used extensively for the preparation of new aluminum cluster compounds with interesting physical properties.[11] Matrix isolation has proved to be extremely useful, on the other hand, to study the reactivity of monomeric subvalent halides of group 13 elements. For example, the photoactivated reactions of AlCl with HCl,[12] HBr,[13] and O_2,[14] of GaCl with HCl[15] and H_2,[16] and of InCl with HCl and H_2[17] in solid Ar matrixes at 12 K have been shown to give new interesting molecular compounds. Recently we have shown for the reaction of GaCl or InCl with H_2 that photolysis causes excitation of the subhalide molecule from its $^1\Sigma$ electronic ground state to its $^3\Pi$ excited state.[18] The dipole moment of the AlCl monomer was calculated to be 1.75 D, but this time, as anticipated, the negative pole is at the Cl. There exist then some clear differences between AlCl and AlCp*, which should also affect the reactivity of these molecules.

Herein we report on the results of the matrix reaction between AlCp* and H_2. To our knowledge, this is not only the first study of the reactivity of monomeric matrix-isolated AlCp*, but also the first report of the IR properties of monomeric AlCp* on its own. It will be shown that AlCp* reacts under photoactivation ($\lambda_{max} =$ 254 nm) with H_2 to give the new monomeric aluminum hydride species Cp^*AlH_2. Volatile molecular hydrides of group 13 elements are of importance not only because of their potential to act as precursor to metal or semiconductor materials but also because of their structural richness.[19] Cp^*AlH_2 will be examined on the basis of our experimental as well as quantum chemical results, and its properties compared with those of known monomeric hydrides such as AlH_3,[20] H_2AlNH_2,[21] and $HAlCl_2$.[12]

2. Experimental Section

The preparation of AlCp* followed the description given in the literature (see eq 1).[2] Briefly, 2.4 g of $MgCp^*_2$ (8.14 mmol) was dissolved in a nitrogen atmosphere in 40 mL of toluene, and the mixture was then cooled to −78 °C. Then 36 mL of a 0.264 M metastable solution of AlCl in a toluene/Et_2O mixture, kept also at −78 °C, was slowly added. The deeply red-colored reaction mixture was stirred for a period of 12 h at ca. −70 °C. Then the mixture was allowed to warm over a period of 3 h to a temperature of −20 °C, at which the ether was pumped off, leaving behind a solution of AlCp* in toluene. Over a period of 7 days at −28 °C, yellow, octahedral crystals of $[AlCp^*]_4$ precipitated.

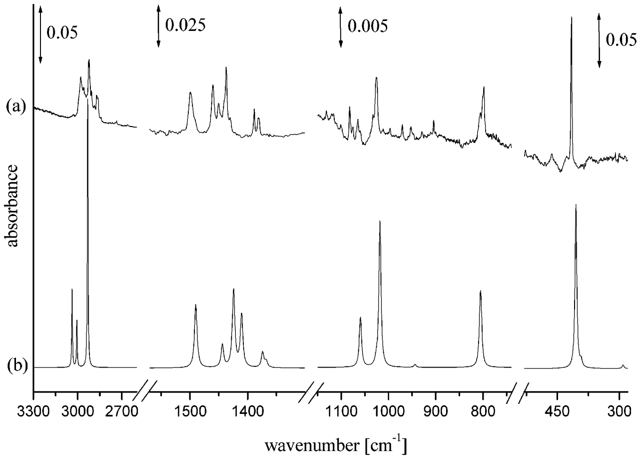

Figure 1. Comparison between the IR spectra of AlCp* (a) measured in an Ar matrix at 12 K and (b) calculated using quantum chemical methods.

$$MgCp^*_2 + \text{“AlCl”} \xrightarrow[-78\ °C]{Tol} {}^1/_4[AlCp^*]_4 + MgCp^*Cl\cdot Et_2O \quad (1)$$

For the matrix experiments, AlCp* was heated in a glass container to 133 °C and the vapor sprayed slowly together with Ar doped with up to 5% of H_2 [Messer, 5.0 (99.999 vol %], D_2 [Messer, 2.7 (99.7 mass %)], or HD (Aldrich, 96 mol %) onto a freshly polished copper block kept at 12 K by means of a closed-cycle refrigerator (Leybold LB510). Details of the relevant procedures and experimental techniques can be found elsewhere.[22]

Infrared spectra of the matrix samples were recorded on a Bruker 113v FTIR instrument. A DTGS and a MCT detector were used to measure IR spectra in the region 4000−200 cm^{-1} with a resolution of 0.5−1 cm^{-1}. Photolysis was achieved with the aid of a low-pressure Hg lamp (λ_{max} = 254 nm, Graentzel, Karlsruhe) operating at 200 W.

The quantum chemical (DFT) calculations relied on the TURBOMOLE program package.[23] The BP method in combination of the TZVPP basis set for Al with the SVP basis set for all other elements was used in all calculations. For the visualization of the IR spectra Lorentz-type functions with a fixed half-width of 5 cm^{-1} were used.

3. Results

AlCp*. Figure 1a displays the IR spectrum of AlCp* in a solid Ar matrix at 12 K. A very strong and sharp absorption appears at 417.6 cm^{-1}. Absorption maxima were also detected at 2977.8, 2921.0, and 2864.2 cm^{-1}, positions characteristic of ν(C−H) stretching modes of CH_3 groups. Six clear maxima were detected in the region 1500−1380 cm^{-1}, being located at 1497.8, 1459.2, 1451.0, 1438.0, 1387.7, and 1380.4 cm^{-1}. Finally, two sharp absorptions occurred at 1026.2 and 799.0 cm^{-1}.

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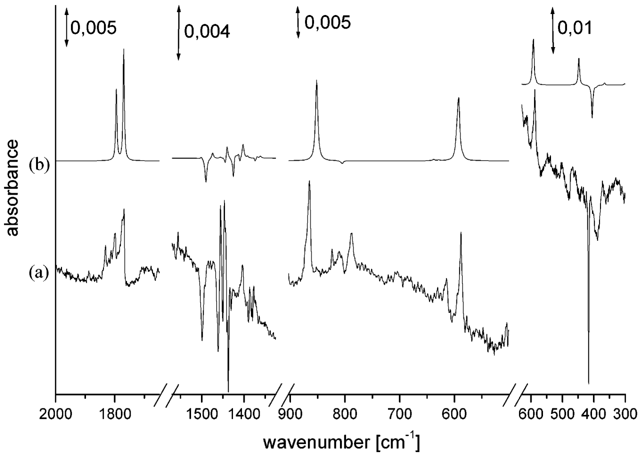

Figure 2. (a) IR difference spectra after minus before 10 min of photolysis (λ_{max} = 254 nm) of an Ar matrix containing AlCp* and H_2 at 12 K. (b) Calculated IR spectrum of H_2AlCp^* minus the calculated IR spectrum of AlCp*.

AlCp*/H_2. The IR spectrum taken upon deposition of AlCp* together with H_2 in an excess of Ar showed no sign of a spontaneously formed reaction product. Photolysis was needed to initiate a reaction. A period of 10 min of photolysis at λ_{max} = 254 nm caused all the absorptions due to AlCp* to decrease significantly. At the same time several new absorptions were observed to grow in. A typical difference spectrum (after 10 min of photolysis at λ_{max} = 254 nm minus before photolysis) is displayed in Figure 2a. The new bands were located at 2944.9, 1801.5, 1773.7, 1445.6, 1405.1, 864.6, 588.7, and 464.1 cm^{-1}.[24] Experiments with different concentrations of H_2 in the matrix indicate that all the bands belong to the same absorber. The two bands at 1801.5 and 1773.7 cm^{-1} appear in a region characteristic of ν(Al−H) stretching fundamentals (cf. AlH_3 1882.7 cm^{-1},[20] AlH_2 1806.3/1769.5 cm^{-1} [25]), while that at 588.7 cm^{-1} occurs in a region in which AlH_2 wagging modes are expected to show (cf. H_2AlNH_2 608.7,[21] H_2AlPH 569.0 cm^{-1} [26]).

The experiment was repeated but now with D_2 in place of H_2. Again, no absorption attributable to a reaction product could be detected upon deposition. Photolysis again caused all absorptions belonging to AlCp* to decrease and new bands to develop. These new absorptions were now located at 2989.5, 2942.9, 1445.6, 1404.4, 1304.4 (shoulder), 1296.3, 645.1, 610.6, 582.0, and 461.8 cm^{-1} (see Figure 3a). Thus some of the product absorptions were *red*-shifted with respect to their positions in the experiment with H_2. The absorptions at 1304.4 and 1296.3 cm^{-1} appear in a region characteristic of ν(Al−D) stretching modes.

Finally, another experiment was conducted with HD. As in the experiments using H_2 and D_2, absorptions assignable to a reaction product appeared only if the matrix was subjected to photolysis. Then bands at 1785.9, 1288.8, and 785.5 cm^{-1} showed and clearly belonged to a common reaction product.

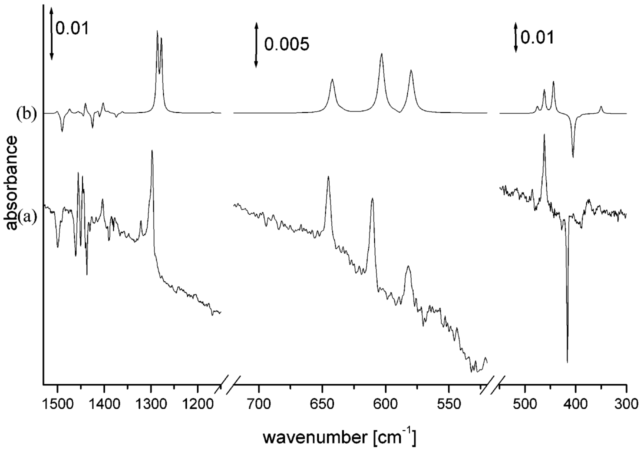

Figure 3. (a) IR difference spectra after minus before 10 min of photolysis (λ_{max} = 254 nm) of an Ar matrix containing AlCp* and D_2 at 12 K. (b) Calculated IR spectrum of D_2AlCp^* minus the calculated IR spectrum of AlCp*.

Table 1. Observed Wavenumbers (in cm^{-1}) for AlCp* in a Solid Ar Matrix at 12 K

obsd[a]	calcd	approximately description of molecular motion
2977.8 (s)	3040	ν(C−H)
2921.0 (s)	3002	ν(C−H)
2864.2 (s)	2933	ν(C−H)
1497.8 (s)	1490	CH_3, antisymmetric bend
1459.2 (s)	1444	
1451.0 (w)	1425	
1438.0 (s)	1411	symmetric ν(C−C) + ν(C−CH_3)
1387.7 (w)	1375	CH_3, symmetric bend
1380.4 (w)	1370	
1082/1063 (w)	1060	CH_3 rock
1026.2 (w)	1017	
799.0 (w)	805	antisymmetric ν(C−C)
417.6 (vs)	393	symmetric ν(Al−Cp*)

[a] vs: very strong, s: strong, w: weak, vw: very weak.

4. Discussion

It will be shown in the following that the product of the reaction of AlCp* with H_2 is the new aluminum hydride species H_2AlCp^*. A combination of experimental and calculational results will be used to explore the properties of this new aluminum hydride species. Another possibility, the formation of the dimer $[AlCp^*]_2$ and its photoproduct with H_2, $[HAlCp^*]_2$, can be ruled out.

AlCp*. To our knowledge, this is the first detailed study of the IR properties of the AlCp* molecule in its monomeric form. The most intense absorption in the spectrum of AlCp* at 417.6 cm^{-1} can be assigned to the symmetric ν(Al−C) stretching mode. For comparison, the symmetric and antisymmetric ν(M−C) stretching modes in CpLi, CpNa, and CpK molecules in solution were detected at 426/154, 232/137, and 213/133 cm^{-1}, respectively.[27] The relatively high wavenumber of the ν(Al−C) stretching mode in AlCp* might indicate a significant degree of Cp* → Al back-donation, in line with the results of quantum chemical calculations.[9] Table 1 compares the experimentally observed wavenumbers with those calculated using DFT methods. It also contains an attempt to describe the molecular motion of these vibrations, although an adequate de-

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[24] An additional weak absorption at 1831.9 cm^{-1} can be assigned to the ν(Al−H) stretching vibration of Cp*AlH(OH), the reaction product of Cp*Al with H_2O.

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Table 2. Observed and Calculated Wavenumbers (in cm^{-1}) for H_2AlCp^*, D_2AlCp^*, and $H(D)AlCp^*$[a]

H_2AlCp^*		D_2AlCp^*		$H(D)AlCp^*$		
obsd	calcd	obsd	calcd	obsd	calcd	approximate description
		2989.5	3039			ν(C−H)
2944.9	2938	2942.9	2933			ν(C−H)
1801.5	1794.8	1304.4	1285.9	1785.9	1786.7	antisymmetric ν(Al−H)
1773.7	1769.9	1296.3	1277.5	1288.8	1278.5	symmetric ν(Al−H)
1445.6	1439.5	1445.6	1437.7			symmetric ν(C−C) + ν(C−CH_3)
1405.1	1403.3	1404.4	1400.5			
864.6	851.8	645.1	642.1	785.5	768.7	AlH_2 bend
		610.6	603.2			
588.7	592.2	461.8	462.0			AlH_2 wag
		582.0	579.8			
(464.1)	447.5					ν(Al−Cp*)

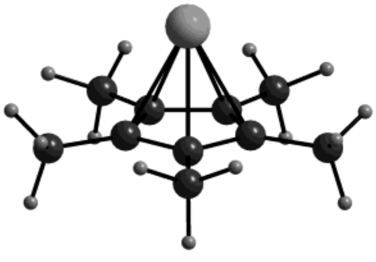
[a] The wavenumber in parentheses relates to a band of very low intensity.

Table 3. Calculated Al−H Bond Distances (in Å), H−Al−H Bond Angles (in deg), and Wavenumbers of the ν(Al−H) Stretching Modes (in cm^{-1}) for Several Aluminum Hydrides

compound	Al−H	H−Al−H	ν(Al−H)
H_2AlCl	1.590	124.9	1910.5/1890.1
H_2AlNH_2	1.596	124.6	1881.7/1871.5
AlH_3	1.599	120.0	1878.0/1863.8
H_2AlCH_3	1.604	118.4	1851.4/1846.1
$H_3Al{\cdot}NH_3$	1.615	117.3	1809.9/1797.9
H_2AlCp^*	1.613/1.616	113.3	1794.8/1769.9

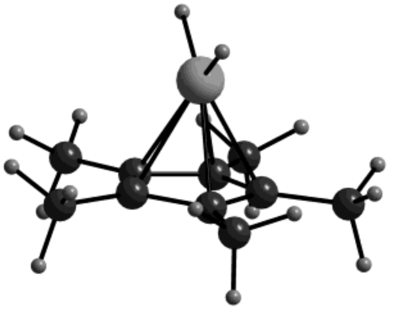
scription proved complicated because of the inevitable presence of heavy mode coupling. Figure 1 compares the experimentally obtained IR spectra with the calculated one. The calculated wavenumbers are free from any scaling, and it can be seen that the general level of agreement between the calculated and experimental results is very pleasing.

As already mentioned, the structure of this molecule was determined experimentally from gas-phase electron diffraction studies.[8] Our calculations indicated Al−C, C−C (C atoms within the C_5 ring), C−CH_3, and C−H bond distances of 2.348, 1.439, 1.507, and 1.111 Å, dimensions in good agreement with the experimentally derived ones (2.388, 1.414, 1.529, and 1.110 Å, respectively).[8]



AlCp*

H_2AlCp^*. As already mentioned, the observed intense product absorptions at 1801.5 and 1773.7 cm^{-1} in the experiments with H_2, at 1304.4 and 1296.3 cm^{-1} in the experiments with D_2, and at 1785.9 and 1288.8 cm^{-1} in the experiments with HD indicate the presence of terminal Al−H bonds in the product of the photoinduced reaction between AlCp* and dihydrogen. Together with the band at 588.7 or 461.8 cm^{-1} in the experiments with H_2 or D_2, respectively, the experimental data suggest that the product is the aluminum hydride species H_2AlCp^*. Table 2 lists the calculated wavenumbers for such a molecule along with a description. Figures 2 and 3 contain a comparison of the experimental spectra with those derived from quantum chemical calculations for H_2AlCp^* and D_2AlCp^*, respectively. Hence it is obvious that the match between experiment and theory is perfectly convincing.



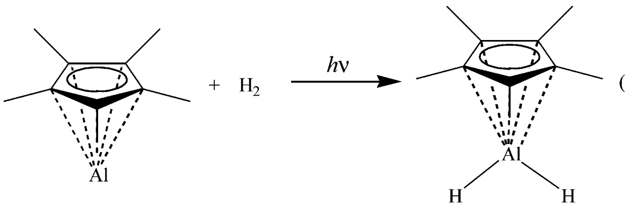
H_2AlCp^*

Our DFT calculations yielded the following dimensions (bond distances in Å) for H_2AlCp^*: Al−H 1.613/1.616, Al−C 2.257−2.324, C−C 1.426−1.453 (C atoms within the C5 ring), C−CH_3 1.503−1.509, H−Al−H 113.3°. Thus the Al−C distances in H_2AlCp^* are only slightly (but significantly) shorter than those in AlCp*. This can be explained, at least partially, by the increased formal positive charge on the Al in H_2AlCp^* in comparison with AlCp*. However, it might come as a surprise that the Al−C distances in $(AlCp^*)_4$ were also found to be slightly shorter than in the monomer AlCp*. The contributions of the s and p (and apparently also d)[9] orbitals at the Al to the bonding undergo changes with consequences for the Al−C bond lengths.

Comparison of H_2AlCp^* with Related Hydrides. Among the most interesting features in the IR spectrum of H_2AlCp^* are the relatively low wavenumbers of the symmetric and antisymmetric ν(Al−H) stretching modes, which give indirect information also about the properties of the Al−Cp* bond interaction. We have calculated the IR properties of several related species, namely, AlH_3, H_2AlCl, H_2AlCH_3, H_2AlNH_2, and $AlH_3{\cdot}NH_3$. Of these, H_2AlNH_2[21] and AlH_3[20] were already sighted experimentally in matrix isolation studies. Our calculations gave the following trends of the wavenumbers (in cm^{-1}) of the ν(Al−H) stretching modes: H_2AlCl 1910.5/1890.1 > H_2AlNH_2 1881.7/1871.5 > AlH_3 1878.0/1863.8 > H_2AlCH_3 1851.4/1846.1 > $H_3Al{\cdot}NH_3$ 1809.9/1797.9 > Cp^*AlH_2 1794.8/1769.9.

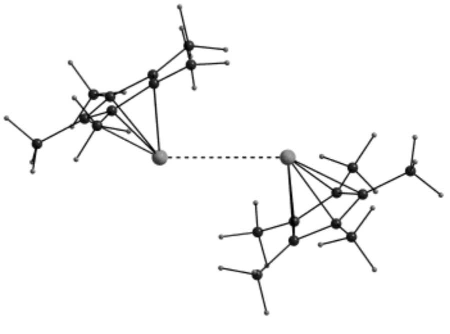
Table 3 compares the Al−H distance, the H−Al−H bond angle, and the wavenumbers of the symmetric and antisymmetric ν(Al−H) stretching modes with those deduced for other related aluminum hydrides of the general formula H_2AlX ($X = Cl, NH_2, H, CH_3, Cp^*$) and of $H_3Al{\cdot}NH_3$. The Al−H distance increases in the order $H_2AlCl < H_2AlNH_2 < AlH_3 < H_2AlCH_3 < H_3Al{\cdot}NH_3 < H_2AlCp^*$. The reasons for these changes can be found in differences of the substituents X in electronegativity and ability for back-donation into empty orbitals at the Al. In the same order, the H−Al−H bond angle decreases. This is generally in line with what is expected on the basis of the VSEPR theory.[28] The trends are well reflected in the wavenumbers of the symmetric and antisymmetric ν(Al−H) stretching modes.

With a reaction energy of -18.5 kJ mol^{-1} and a reaction enthalpy at 0 K of -9.5 kJ mol^{-1}, reaction 2 is calculated to be weakly exothermic. The effect of photolysis in all probability is the excitation of an electron from the lone pair at the Al to molecular orbitals with a high contribution from the empty p-orbitals at the Al, resulting in a mainly metal-centered electronic transition. In the case of TlCp in methanol solutions, the corresponding metal-centered $a_1 \rightarrow (a_1^*, e_1^*)$ transition was observed at $\lambda_{max} = 280$ nm.[29] In this respect, the effect of photolysis resembles also that observed in the case of GaCl or InCl.[18]



(2)

$[AlCp^*]_2$ and $[HAlCp^*]_2$. As already mentioned, with 1801.5 and 1773.7 cm^{-1}, the wavenumbers of the ν(Al−H) stretching fundamentals in H_2AlCp^* are significantly lower than the ones found in Al(III) species such as AlH_3, H_2AlNH_2, and $HAlCl_2$ (see Table 3). On the other hand, they are close to the wavenumbers observed for known matrix-isolated Al(II) species such as AlH_2,[25] $HAlNH_2$,[21] and $HAlPH_2$[26] (1806.3/1769.5, 1761.1, and 1768.2 cm^{-1}). Therefore we have thought about the possibility of the formation of Cp*(H)AlAl(H)Cp*, representing the product of the reaction between two moieties of AlCp* and H_2. The two moieties of AlCp* might first form a dimer $[AlCp^*]_2$, which then reacts upon photoactivation with H_2. In the following, we are discussing the calculated geometries and IR properties of these species. The calculated IR properties are then compared with the experimentally observed spectra. It will be shown that the experimental results clearly indicate that neither the dimer $[AlCp^*]_2$ nor $[HAlCp^*]_2$ is formed in detectable yields in our experiments.



$[AlCp^*]_2$

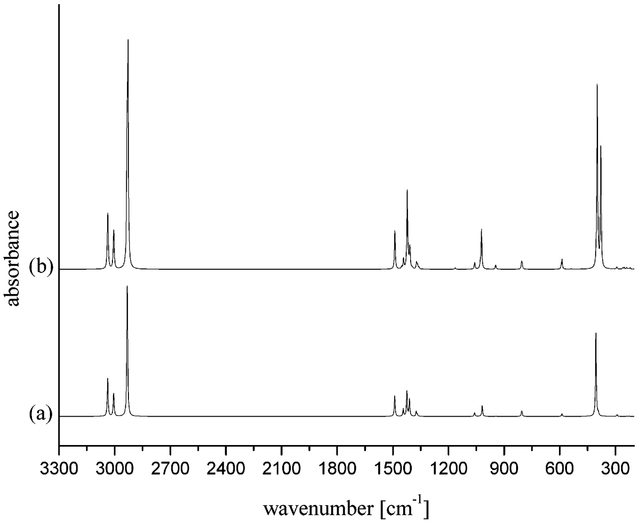


Figure 4. Comparison between the calculated IR spectra of (a) AlCp* and (b) $[AlCp^*]_2$.

As expected, it turned out that the interaction between the two AlCp* units in a "dimer" $[AlCp^*]_2$, if it exists at all, is very small. According to our calculations, the "dimerization" of two molecules of AlCp* to give $[AlCp^*]_2$ is associated with an energy gain of only 4.5 kJ mol^{-1}, meaning that the interaction between the two AlCp* units in the "dimer" is next to zero. The very large Al−Al distance of 3.565 Å (0.7 Å more than the Al−Al distance in solid Al metal) also indicates that there is almost no interaction between the AlCp* molecules. Nevertheless it is interesting that the two Cp* rings are oriented to each other in a well-defined way. Certainly our simple DFT methods are not apt to describe accurately the interaction in such a loosely bound dimer. However, it is noteworthy that compounds such as $[GaCp^*]_6$[30] or $[InCp^*]_6$,[31] for which crystal structures are known, exhibit Ga⋯Ga and In⋯In distances (4.073−4.173 and 3.942−3.963 Å, respectively) that exceed by far the distances between the atoms in the solid elements. Again, the oligomerization of GaCp* is associated with a (very small, but apparently significant) decrease of the Ga−C bond lengths,[32] analogous to that observed for the tetramerization of AlCp*. For $[AlCp^*]_2$, we calculated Al−C bond distances between 2.337 and 2.367 Å, some distances being slightly longer than in the monomer AlCp*, and others slightly shorter. Figure 4 shows the calculated IR spectrum of the dimer $[AlCp^*]_2$ together with that calculated for the monomer AlCp*. The most obvious difference between the two is the presence of two intense absorptions near 400 cm^{-1} in the spectrum of the dimer. Because of the small dimerization energy, it is unlikely that the dimer is stable under normal conditions. In this respect, AlCp*

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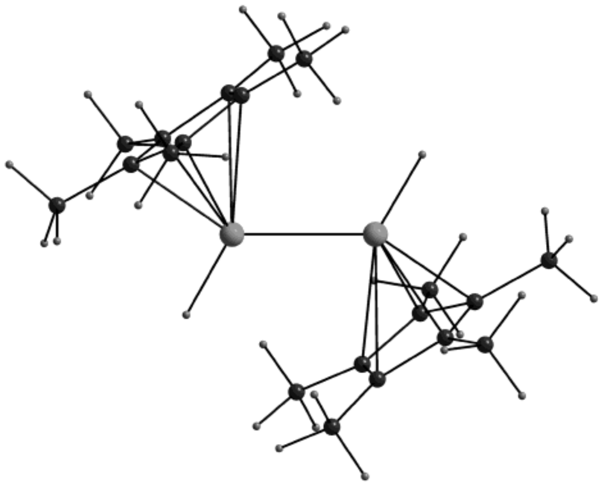
is clearly different from the subhalides AlX (X = F, Cl, or Br), which readily form dimers $[AlX]_2$ with halogen atoms in bridging positions (D_{2h} symmetry).[33] To draw a final conclusion about the amount of interaction between two AlCp* units, much more sophisticated quantum chemical methods have to be employed. However, in the absence of any experimental evidence of such a dimer, this is beyond the scope of the present work.

As will be shown in the following, the experiments failed also to show any bands attributable to a possible reaction product between the “dimer” or two AlCp* molecules and H_2. A very interesting potential product is $[HAlCp^*]_2$, with the two hydrogen atoms forming one Al−H bond to each of the Al atoms. According to our calculations, the lowest energy form of this species has a *trans-bent* configuration, the angle H−Al−Al being 119.2°. The Al−Al distance is 2.575 Å, i.e., in between the distances calculated for the neutral HAlAlH molecule (2.649 Å) and $[HAlAlH]^{2-}$ (2.4386 Å),[34,35] which both exhibit C_{2h} symmetry in their global energy minimum forms. The Al−H distance is 1.638 Å. Other dimensions include (bond distances in Å) Al−C 2.192−2.580, C−C 2.670−2.750 (C atoms within the C_5 ring), $C-CH_3$ 2.842−2.853, and C−H 1.110−1.116.



$[HAlCp^*]_2$

The calculated IR spectrum of $[HAlCp^*]_2$ is shown in Figure 5. The antisymmetric ν(Al−H) stretching mode is predicted to occur at 1710.9 cm^{-1}. The almost IR-inactive symmetric stretching mode is predicted to show at 1728.3 cm^{-1}. Thus the ν(Al−H) stretching modes appear at wavenumbers much lower than the ones of known Al(III) species (see above). The experimental spectra gave no sign of any absorption in this region, and it is therefore unlikely that this compound is formed in significant amounts.

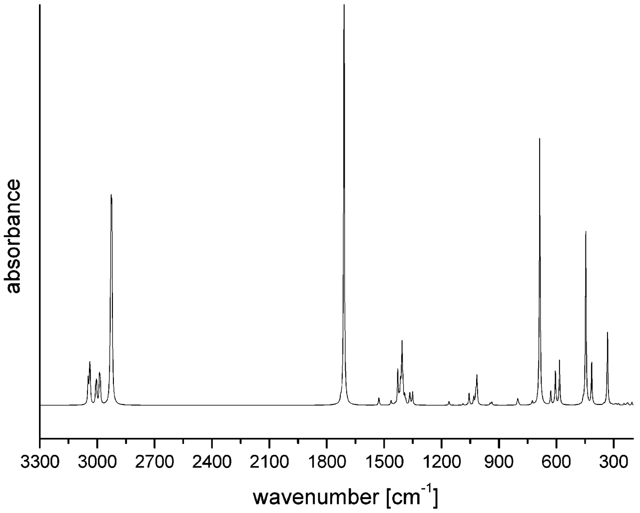


Figure 5. Calculated IR spectrum of $[HAlCp^*]_2$.

Table 4. Reaction Energies ΔE and Enthalpies ΔH at 0 K (in kJ mol^{-1}) for the Reactions Discussed in This Work

reaction	ΔE	ΔH (0 K)
$Cp^*Al + H_2 \rightarrow Cp^*AlH_2$	−18.5	−9.5
$2\,[Cp^*Al] \rightarrow [Cp^*Al]_2$	−4.5	−1.1
$[Cp^*Al]_2 + H_2 \rightarrow [Cp^*AlH]_2$	+436.9	+444.1

According to our calculations, the reaction energy and enthalpy at 0 K for the reaction between $[Cp^*Al]_2$ and H_2 to give $[HAlCp^*]_2$ is largely endothermic (by as much as ca. 440 kJ mol^{-1}), a value close to the energy needed to cleave the H−H bond in H_2. Therefore $[HAlCp^*]_2$ represents a highly energetic species, and it is unlikely that such a molecule can be formed, even at the conditions of matrix isolation. Table 4 lists all the reaction energies and enthalpies at 0 K calculated in this work.

5. Conclusions

The monomeric aluminum(I) species AlCp* and its reactivity have been studied for the first time in matrix isolation experiments. The molecule was shown to react with dihydrogen under photoactivation to give the new aluminum hydride species H_2AlCp^*, which was characterized experimentally by its IR spectrum and theoretically by quantum chemical calculations. The dimensions and properties are compared with those of related species, namely, H_2AlX (X = Cl, NH_2, CH_3, H) and $H_3Al\cdot NH_3$. H_2AlCp^* exhibits the lowest wavenumber for the ν(Al−H) stretching modes and, together with $H_3Al\cdot NH_3$, the longest Al−H bonds. The reason for these differences can be found in the influence of the Cp* group on the bonding properties. Calculations were also carried out to study a possible $[AlCp^*]_2$ dimer and its potential reaction product with H_2, although the experiments found no evidence of such species.

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