# C−H Activation by AlCl Monomers: Characterization of $HAl(Cl)CH_3$ as the Product of the Photoactivated Reaction Between AlCl and $CH_4$ in a Solid Ar Matrix at 12 K

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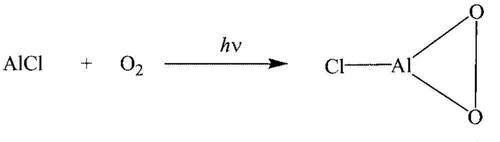
In a solid Ar matrix at 12 K and upon photoactivation AlCl inserts into the C–H bond of $CH_4$ to give the new monomeric aluminium hydride $HAl(Cl)CH_3$, which was identified and characterized with the aid of the IR spectra recorded for several isotopomers [$Cl(H)Al^{12}CH_3$, $Cl(D)Al^{12}CD_3$, and $Cl(H)Al^{13}CH_3$], comparison with the known IR properties of related molecules and detailed quantum chemical calculations. Calculations yield a $C_s$ symmetric global energy minimum structure for this compound, and that the reaction is slightly exothermic (reaction energy of –43.2 kJ·mol$^{-1}$). This work demonstrates impressively how reactive photoactivated AlCl molecules are.

## Introduction

Subvalent compounds of the general formula MX [M = Al, Ga or In, and X = F, Cl, I, or a cyclopentadienyl (Cp) derivative] react readily, when photoactivated, with a number of molecules.[1] Examples include the reaction of AlCl with $H_2$ to give $H_2AlCl$,[2] with O atoms to give OAlCl,[3] with $O_2$ to give $ClAlO_2$ [4] or, when the concentration of $O_2$ is increased, $ClAl(O_2)_2$,[5] and with HX (X = F, Cl or Br) to give HAl(Cl)X.[6,7] With GaCl[8] and InCl,[9] reactions with $H_2$ and with HCl afford the hydrides $H_2MCl$ and $HMCl_2$ (M = Ga or In), respectively. GaF reacts with O atoms to give OGaF.[10] Finally, matrix-isolated AlCp* reacts with $H_2$ upon photoactivation to yield $H_2AlCp^*$.[11] Although these species are generally highly reactive, there are some remarkable differences between AlX, GaX and InX with respect to their reactivities and the structures and composition of the end-products. Whereas AlCl reacts, as already mentioned, upon photoactivation with $O_2$ [Equation (1)], GaCl or InCl show no matrix reaction, photoactivated or not, with $O_2$ [Equation (2)].[12]



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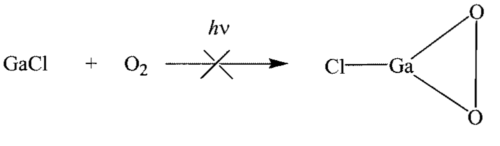

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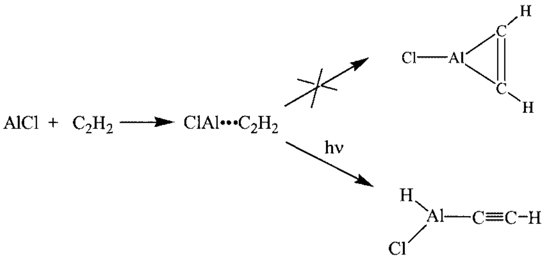
Some of the differences can be explained by an "inert-pair" effect. The strength of the bonds in the lighter homologues is usually higher than in their heavier counterparts and can thus more easily compensate the loss of one binding interaction in the reactant. In other cases it might be of some importance that Al prefers a higher coordination number than Ga. For example, a bis(superoxo) complex, $[XM(O_2)_2]$, can be formed for M = Al, but not for M = Ga.

To study in more depth the reactions with small model hydrocarbons we have looked at the reaction with $C_2H_2$ leading to the acetylide species HAl(Cl)CCH. Interestingly, the cyclic alumina-cyclopropene derivative [see Equation (3)] is not formed.[13] That comparatively small modifications of the reactants can lead to different products is shown by comparing the reaction between AlCl and HCCH with that between AlCl and $H_3CCCCH_3$. Photoactivated AlCl reacts with 2-butyne to give two products, one of them being the alumina-cyclopropene derivative.[13] Thus, the replacement of the hydrogen atoms in $C_2H_2$ by methyl groups alters the structures (cyclic vs. acetylide form) of the reaction products.



(3)

We are also currently studying the reaction of AlCl with CpH ($C_5H_6$).[14] The reaction of AlCp* with $H_2$ gives $H_2AlCp^*$, in which the $C_5$ ring is coordinated in $\eta^5$-fashion

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to the Al center.[11] Theoretical studies and a series of experimental results obtained with suitable derivatives suggest that the energy differences between $\eta^5$-, $\eta^3$-, $\eta^2$- and $\eta^1$-coordination for $CpAlH_2$ are very small (< 13 kJ·mol$^{-1}$).[15] The coordination mode of the Cp ring in HAl(Cl)Cp, the likely product of the reaction between AlCl and CpH, is therefore difficult to predict. It should, though, be easy to distinguish between these forms on the basis of the matrix IR spectra.

Here it will be shown that matrix-isolated AlCl inserts on photoactivation into the C−H bond of $CH_4$ to give the new species $Cl(H)AlCH_3$. This reaction shows impressively how reactive photoactivated AlCl molecules are. Such C−H activation mechanisms are important in catalytic processes.

## Results

The IR spectrum taken upon deposition of AlCl together with 2% $CH_4$ in an Ar matrix showed strong absorptions due to $CH_4$ and AlCl. However, there are no bands due to a reaction product. The matrix was therefore exposed for a period of 10 min to broad-band UV/Visible radiation (200 < λ < 800 nm). Several new bands in the spectrum recorded after the photolysis period indicate that the photoactivated AlCl molecules readily react with $CH_4$. The difference between a spectrum taken after and before photolysis is shown in Figure 1, a. A family of bands appears at 3015.2, 2998.1, 2984.4, 1905.2, 1199.7, 743.7, 672.8, 657.7, 604.4, 488.1/482.8, and 421.4 cm$^{-1}$. With different concentrations of $CH_4$ and AlCl in the matrix the relative intensities of these bands remain unchanged, indicating that they all belong to the same absorber. The strongest band is at 1905.2 cm$^{-1}$, a region characteristic of the ν(Al−H) stretching fundamentals of $Al^{III}$ compounds [cf. $AlH_3$ 1882.9,[16] $H_2AlNH_2$ 1899.3,[17,18] $H_2AlPH$ 1874.7/1866.1,[19] $HAlCl_2$ 1967.6,[6] $H_2AlCl$ 1928.1/1915.9,[2] HAl(Cl)CCH 1952.2 cm$^{-1}$ [13]]. Strong, but somewhat broader, features are at 743.7, 672.8 and 657.7 cm$^{-1}$ (the second one being a shoulder of the more intense band at 657.7 cm$^{-1}$). The band at 743.7 cm$^{-1}$ occurs in the region of the $\rho(CH_3)$ rocking mode of a methyl group (cf. $HGaCH_3$ 752.9,[20] $HBeCH_3$ 704.1 cm$^{-1}$ [21]). The bands at 3015.2, 2998.1 and 2984.4 cm$^{-1}$ qualify for ν(C−H) stretching vibrations.

A weak additional feature at 1965.7 cm$^{-1}$, which grew in on photolysis, can be assigned to the ν(Al−H) stretching fundamental of HAl(Cl)OH.[13] This species is formed from reaction of AlCl with $H_2O$ that is present as a trace impurity. Additionally, a sharp relatively intense band appeared at 769.9 cm$^{-1}$ and very weak ones at 1928.1, 1915.9, 604.9, 549.9, and 518.6 cm$^{-1}$. These were previously assigned to $H_2AlCl$,[2] representing the product of the photoactivated reaction between AlCl and $H_2$. Traces of $H_2$ in the matrix are a consequence of the generation of AlCl in the oven, from reaction between liquid Al and HCl at ca. 1000 °C to give AlCl and $H_2$. Finally, some experiments revealed very small amounts of $HAlCl_2$ in the matrix, arising from traces of HCl in the matrix (HCl that has not reacted with the liquid Al in the oven).[6] These bands were, however, extremely weak.

The experiment was repeated with $CD_4$ in place of $CH_4$. Again, no reaction product was evident from the spectrum recorded immediately after deposition. However, photolysis furnished a family of new bands at 2212.0, 1386.1, 947.1, 630.1, 569.0, 518.4, 471.7, 435.4/430.6, and 308.1 cm$^{-1}$ (Figure 2). All the features were red-shifted with respect to their counterparts with $CH_4$. The strongest band in the spectrum is at 1386.1 cm$^{-1}$, which can confidently be attributed to a ν(Al−D) stretching fundamental, experienced a marked shift, corresponding to a ν(H):ν(D) ratio of 1.3745:1. The absorptions at 743.7, 672.8 and 657.7 cm$^{-1}$ in the experiments with $^{12}CH_4$ now occurred at 630.1, 518.4 and 569.0 cm$^{-1}$, respectively. A band at 2212.0 cm$^{-1}$ appeared in a region characteristic of ν(C−D) stretching fundamentals.

Finally, in experiments conducted with $^{13}CH_4$, as with $CH_4$ and $CD_4$, no absorption due to any product of a thermal reaction between AlCl and $^{13}CH_4$ appeared in the IR spectrum recorded immediately after deposition. Photolysis

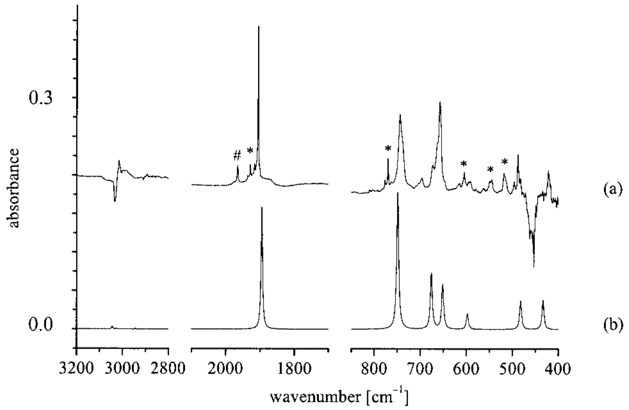


Figure 1. (a) IR difference spectrum, between the spectra after and before 40 min of photolysis of an Ar matrix containing AlCl together with $^{12}CH_4$. (b) Calculated IR spectrum for HAl(Cl)$^{12}CH_3$. #: Band due to HAl(Cl)OH. *: Bands due to $H_2AlCl$

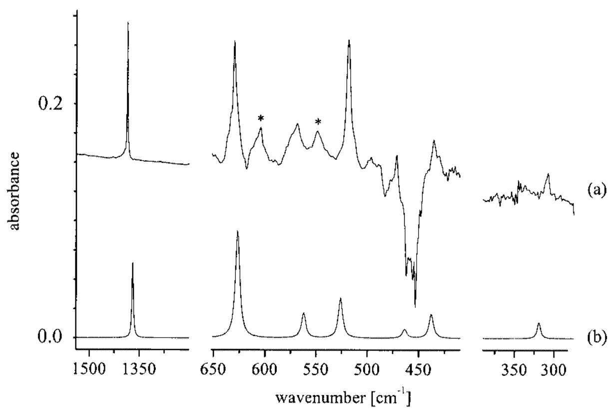


Figure 2. (a) IR difference spectrum, between the spectra after and before 40 min of photolysis of an Ar matrix containing AlCl together with $^{12}CD_4$. (b) Calculated IR spectrum for DAl(Cl)$^{12}CD_3$. *: Bands due to $H_2AlCl$

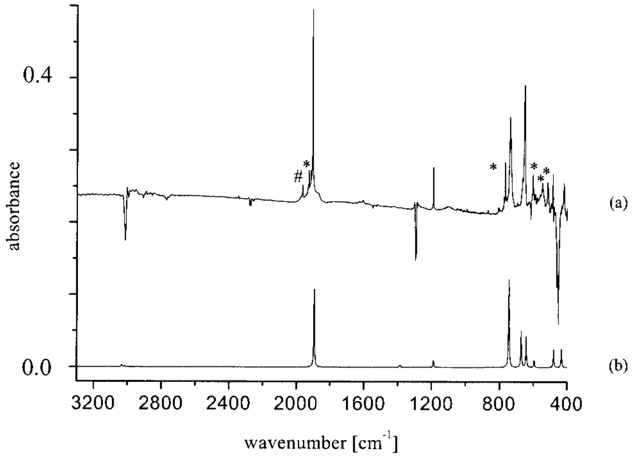


Figure 3. (a) IR difference spectrum, between the spectra after and before 40 min of photolysis of an Ar matrix containing AlCl together with $^{13}CH_4$. (b) Calculated IR spectrum for $HAl(Cl)^{13}CH_3$. #: Band due to HAl(Cl)OH. *: Bands due to $H_2AlCl$

was needed to initiate a reaction. Figure 3 shows the difference between the IR spectrum taken after photolysis and the one taken before photolysis. In its $^{13}$C version, the product of the reaction between AlCl and methane is the author of bands at 3003.9, 2972.6, 2951.9, 1905.2, 1375.5, 1191.0, 739.9, 667.2, 652.7, 604.7, 486.5, and 421.1 cm$^{-1}$.

## Discussion

The experimental results clearly show that AlCl reacts with $CH_4$ upon photoactivation to give a single reaction product.[22] The detection of a ν(Al−H) stretching fundamental and its location indicate that this product contains a terminal Al−H bond; it also shows all the hallmarks of a species featuring a methyl ($CH_3$) group. Finally, the band at 482.0 cm$^{-1}$ indicates a terminal Al−Cl bond. The obvious inference is that photoactivated AlCl inserts into one of the C−H bonds of $CH_4$ to give the new monomeric Al hydride species $HAl(Cl)CH_3$.

Quantum chemical calculations on the possible structure of such a product suggest that $HAl(Cl)CH_3$ exhibits a $C_s$ symmetric global energy minimum structure characterized by the bond lengths (in pm) Al−Cl 212.7, Al−H 160.1, C−H 111.2/111.4, Al−C 195.5. The H−Al−Cl, Cl−Al−C and H−Al−C bond angles are 115.8°, 118.5° and 125.7°, respectively. Thus, in agreement with the predictions of VSEPR theory,[23] the smallest angle at the Al center is for H−Al−Cl.

At 195.5 pm, the Al−C bond length is in pleasing agreement with those measured for several compounds containing Al−C bonds. Thus, on the basis of gas-phase electron diffraction studies, the Al−C distance in monomeric $Al(CH_3)_3$ was determined to be 195.7(3) pm.[24] In $(Me_2AlNC_6H_{12})_2$, an example for Al with a coordination number of 4, Al−C bond lengths of 196.3(4) and 198.0(6) pm are adopted according to an X-ray diffraction analysis.[25] One further example is the compound $[(tmpCO_2)_2AlMe]_2$, which features an Al atom with a coordination number of 5 and an Al−C distance of 195.2(4) pm.[26] In general, the Al−C bond lengths cover a large range (189.7 to 236.6 pm) with an average of 198.3 pm according to the Cambridge Structural Database.[27] However, these statistics include compounds with different coordination numbers. Some structurally characterized monomeric alanes containing terminal Al−H bonds are now known. The Al−H bond length ($r_0$ value) in $(Ar^*)_2AlH$ [Ar* = (*tert*-butyl)$_3C_6H_2$] is 153(4) pm,[28] whereas in $Mes^*Al(H)N(SiMe_3)_2$ an Al−H distance of 151(3) pm was found by X-ray diffraction.[29] However, X-ray measurements give, at best, estimates significantly different from $r_e$. For $AlH_3$, an Al−H bond length ($r_e$ value) of 157.1−159.7 was calculated, depending on the applied theoretical method.[16,30] These values compare satisfactorily with the $r_e$ of 160.1 pm calculated for $HAl(Cl)CH_3$. The Al−H bond lengths in general cover a large range, adopting values as low as ca. 125 pm and up to more than 180 pm.[31] Finally, electron diffraction measurements yielded an Al−Cl distance of 206.2(3) pm in monomeric $AlCl_3$ (which is in equilibrium with its dimer in the gas-phase at 400 °C),[32] which is reasonably close to that calculated for $HAl(Cl)CH_3$ (212.7 pm). Thus the dimensions derived for $HAl(Cl)CH_3$ from quantum chemical calculations are wholly reasonable.

Table 1 compares the experimentally observed wavenumbers with those forecast by the DFT calculations, and also includes an attempt to describe the molecular motions of the modes. Obviously any such attempt is limited by the degree of mode coupling in this rather unsymmetrical molecule ($C_s$ symmetry). The ν(C−H) stretching region showed a sharp band at 3015.2 cm$^{-1}$, red-shifted from the ν(C−H) stretching mode of $CH_4$, which can be assigned to one of the antisymmetric ν(C−H) stretching modes, namely $\nu_1(a')$. The calculations predict a wavenumber of 3044.4 cm$^{-1}$ for this mode. The calculated shifts upon $^{12}$C/$^{13}$C and H/D substitution agree well with the experimental ones (Table 1). Additional weaker bands at 2998.1 and 2984.4 cm$^{-1}$ can be assigned to the second antisymmetric and the symmetric ν(C−H) stretching fundamental, $\nu_{11}(a'')$ and $\nu_2(a')$, respectively. Again, the calculated wavenumbers of 3026.5 and 2944.0 cm$^{-1}$ pleasingly match the experimental ones.

As already mentioned, the wavenumber of the ν(Al−H) stretching mode comes in a region that is characteristic of Al$^{III}$ compounds (ca. 1850−2000 cm$^{-1}$). The only exception is $H_2AlCp^*$, for which the antisymmetric and symmetric ν(Al−H) stretching fundamentals were detected at 1801.5 and 1773.7 cm$^{-1}$, respectively.[11] Such low values can be explained by the back-donation from the Cp* ring

Table 1. Comparison of IR properties observed and calculated for $HAl(Cl)CH_3$ and isotopomers (wavenumbers in $cm^{-1}$, intensities in $km\ mol^{-1}$)

| $HAl(Cl)^{12}CH_3$ | | $HAl(Cl)^{13}CH_3$ | | $DAl(Cl)^{12}CD_3$ | | | |
|---|---|---|---|---|---|---|---|
| obsd. | calcd. | obsd. | calcd. | obsd. | calcd. | assign. | approx. descrip. |
| 3015.2 | 3044.4 (4) | 3003.9 | 3033.6 (5) | 2212.0 | 2260.8 (1) | $\nu_1(a')$ | $\nu_{asym}(C-H)$ |
| 2984.4 | 2944.0 (1) | 2951.9 | 2940.8 (1) | [a] | 2121.9 (0.03) | $\nu_2(a')$ | $\nu_{sym}(C-H)$ |
| 1905.2 | 1894.6 (172) | 1905.2 | 1894.7 (172) | 1386.1 | 1369.4 (104) | $\nu_3(a')$ | $\nu(Al-H)$ |
| [a] | 1390.3 (3) | [a] | 1388.1 (3) | [a] | 1006.8 (3) | $\nu_4(a')$ | $\delta_{asym}(CH_3)$ |
| 1199.7 | 1196.9 (18) | 1191.0 | 1187.9 (16) | 947.1 | 941.9 (27) | $\nu_5(a')$ | $\delta_{sym}(CH_3)$ |
| 743.7 | 748.7 (191) | 739.9 | 744.8 (192) | 630.1 | 626.7 (146) | $\nu_6(a')$ | $\rho(CH_3)$ |
| 657.7 | 651.0 (62) | 652.7 | 642.3 (67) | 569.0 | 562.2 (34) | $\nu_7(a')$ | $\delta(Cl-Al-H)$ |
| 604.4 | 597.6 (22) | 604.7 | 594.8 (16) | 471.7 | 463.7 (12) | $\nu_8(a')$ | $\nu(Al-C)$ |
| 488.1/ 482.8 | 482.0 (39) | 486.5 | 479.9 (38) | 435.4/430.6 | 437.8 (33) | $\nu_9(a')$ | $\nu(Al\text{-}Cl)$ |
| [b] | 176.8 (5) | [b] | 174.7 (5) | [b] | 160.0 (4) | $\nu_{10}(a')$ | $\delta(ClAlC)$ |
| 2998.1 | 3026.5 (1) | 2972.6 | 3016.1 (2) | [a] | 2244.6 (0.03) | $\nu_{11}(a'')$ | $\nu_{asym}(C-H)$ |
| [a] | 1386.0 (4) | 1375.5 | 1383.4 (4) | [a] | 1006.1 (4) | $\nu_{12}(a'')$ | $\delta(CH_3)$ |
| 672.8 | 675.6 (79) | 667.2 | 671.9 (78) | 518.4 | 526.0 (54) | $\nu_{13}(a'')$ | $\gamma$ |
| 421.4 | 433.1 (40) | 421.1 | 433.1 (40) | 308.1 | 319.1 (22) | $\nu_{14}(a'')$ | $\rho(Al-H)$ |
| [a] | 230.5 (0.1) | [a] | 230.4 (0.2) | [b] | 162.8 (0.1) | $\nu_{15}(a'')$ | |

[a] Too weak to be observed. [b] Outside the experimental detection range.

to the Al center which leads to a significant weakening of the Al−H bonds. At 1894.6 $cm^{-1}$, the calculated wavenumber for the $\nu(Al-H)$ mode is in excellent agreement with the experimental one. Calculation and experiment also agree that this mode shows virtually no shift upon $^{12}C/^{13}C$ isotopic substitution. Conversely, H/D substitution strongly affects this mode [calculated and experimental $\nu(H):\nu(D)$ ratios of 1.3835:1 and 1.3745:1 respectively].

The weak feature at 1199.7 $cm^{-1}$ can be assigned to a mode with a high $CH_3$ "umbrella" [$\delta_{sym}(CH_3)$] character. Wavenumbers of 1158, 1179, 1147.9 and 1115.3 $cm^{-1}$ have been reported for the $\delta_{sym}(CH_3)$ mode in $LiCH_3$,[33] $BeCH_3$,[21] $GaCH_3$ [20,34] and $InCH_3$,[20,34] respectively. For $Al(CH_3)_3$ and $HGa(CH_3)_2$, isolated in Ar matrices, the "umbrella" mode shows up at 1196[35] and 1202.5 $cm^{-1}$,[36] respectively. The calculations yielded 1196.9 $cm^{-1}$ for this mode in $HAl(Cl)CH_3$. The experimental and calculated $\nu(H):\nu(D)$ ratios are 1.2667:1 and 1.2707:1, respectively. Unfortunately, with only one exception, the other two $\delta(CH_3)$ deformation fundamentals [$\nu_4(a')$ and $\nu_{12}(a'')$] escaped experimental detection. The only sign of the $\nu_{12}(a'')$ mode was a very weak feature at 1375.5 $cm^{-1}$ in the experiments with $^{13}CH_4$. The calculations predict wavenumbers of 1390.3 and 1386.0 $cm^{-1}$ and very low intensities for these modes.

The 657.7 $cm^{-1}$ band can be assigned to the $\delta(HAlCl)$ deformation fundamental. This is close to that measured for the corresponding mode in $HAl(Cl)CCH$ (671.4 $cm^{-1}$).[13] The calculated value of 651.0 $cm^{-1}$ pleasingly matches the experimental value. As anticipated, the effect of $^{12}C/^{13}C$ substitution is again relatively small. In $Cl(H)Al^{13}CH_3$, the mode appears at 652.7 $cm^{-1}$, shifted by not more than 5.0 $cm^{-1}$ to lower wavenumbers. Conversely, the large $\nu(H):\nu(D)$ ratio (observed 1.1559:1 and calculated 1.1580) again indicates substantial H atom motion in this vibration.

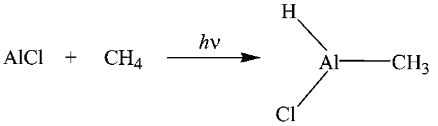
The strong band at 672.8 $cm^{-1}$ in the spectra recorded for $^{12}CH_4$ belongs to a mode which can be approximately described as the *out-of-plane* Al−H bending mode, $\gamma$. The corresponding mode in $H_2AlCl$[2] and $HAlCl_2$ [6] occurs at 604.9 and 654 $cm^{-1}$, respectively. The calculations yielded 675.6 $cm^{-1}$. This approximate description of this mode is supported by the substantial $\nu(H):\nu(D)$ ratio (observed 1.2978:1 and calculated 1.2844:1).

The spectra also gave evidence for a band at 604.4 $cm^{-1}$ in the experiments with $^{12}CH_4$ and the corresponding mode should have a high contribution from the $\nu(Al-C)$ stretching mode. The value compares with 615.9 $cm^{-1}$ for a mode of $HAl(Cl)CCH$ also with a high contribution from the $\nu(Al-C)$ stretching vibration.[13] In the radical $HAlCH_3$, which can be generated by the matrix reaction between Al atoms and $CH_4$, the $\nu(Al-C)$ stretching mode appears at 610 $cm^{-1}$.[37] In $Al(CH_3)_3$, the $\nu(Al-C)$ stretching fundamentals were observed at 691 (e′ mode) and 530 $cm^{-1}$ ($a_1'$ mode) for the molecule in the gas phase.[38] Obviously, this mode couples significantly with other modes of the same symmetry and therefore these wavenumbers cannot be compared directly. The calculations yielded 597.6 $cm^{-1}$, in close conformity with the experimental value.

The bands at 488.1/482.8, 486.5 and 435.4/430.6 $cm^{-1}$ in the experiments with $^{12}CH_4$, $^{13}CH_4$ and $^{12}CD_4$ are obvious candidates for modes with a significant degree of $\nu(Al\text{-}Cl)$ stretching. Modes in related molecules which also exhibit high $\nu(Al\text{-}Cl)$ stretching mode character have the wavenumbers (in $cm^{-1}$) $H_2AlCl$ 549.9,[2] $HAlCl_2$ 579,[6] $HAl(Cl)CCH$ 505.8.[13] The small $\nu(H):\nu(D)$ ratios observed and calculated (1.1210:1 and 1.1010:1, respectively) agree with this assignment. The doublet pattern seen in experiments with $^{12}CH_4$ and $^{12}CD_4$ probably arises from $^{35}Cl/^{37}Cl$ isotopic splitting. The relative intensities of the two components at 488.1 and 482.8 $cm^{-1}$ for $^{12}CH_4$ and at 435.4 and 430.6 $cm^{-1}$ for $^{12}CD_4$ are in good agreement with the relative abundances of $^{35}Cl$ and $^{37}Cl$.

Overall, the comparison of the data measured for the three isotopomers with the properties measured previously for related molecules and the results of quantum chemical calculations affirm that $HAl(Cl)CH_3$ is the product of the photolytically induced matrix reaction between AlCl and $CH_4$.

AlCl in its ground electronic state is expected to interact only very weakly with $CH_4$. Quantum chemical calculations suggest, as anticipated, that a complex of the form $ClAl{\cdot}CH_4$ is, if at all, only very weakly bound. The binding energy seems to be even smaller than that calculated for an $Al{\cdot}CH_4$ complex ($2.6\ kJ{\cdot}mol^{-1}$ according to MP2 calculations and a TZVPP basis set, ZPVE corrections included).[39] The effect of photolysis has been discussed previously.[1] The electronic transition in the AlCl molecule is mainly metal atom-centered and leads to the population of a vacant π-orbital that is expected to be ideally suited to interact with a σ* orbital of an E−H bond. As a consequence, the E−H bond is weakened and the Al atom inserts into the bond yielding the $HAl(Cl)CH_3$ end-product.



(4)

The overall reaction [Equation (4)] is slightly exothermic. According to the calculations, the reaction energy amounts to $-43.2\ kJ{\cdot}mol^{-1}$. The analogous reaction of GaCl with $CH_4$ to give $HGa(Cl)CH_3$ is, by contrast, *endothermic* and requires, according to DFT calculations, an energy of $+32.6\ kJ{\cdot}mol^{-1}$. This again shows the differences in reactivity between AlCl and GaCl. The reaction energy calculated for $AlCl/CH_4$ is nevertheless smaller than that calculated for $AlCl/H_2$ ($-75.6\ kJ{\cdot}mol^{-1}$).[1,2]

## Conclusions

Experiments have shown that matrix-isolated and photoactivated AlCl molecules insert readily into a C−H bond of methane to give the new monomeric Al hydride $HAl(Cl)CH_3$. IR spectra of this $C_s$-symmetric molecule in its $HAl(Cl)^{12}CH_3$, $DAl(Cl)^{12}CD_3$ and $HAl(Cl)^{13}CH_3$ isomeric forms were recorded. The experiments were accompanied by detailed quantum chemical calculations, according to which the reaction of AlCl with $CH_4$ to give $HAl(Cl)CH_3$ is slightly exothermic ($-43.2\ kJ{\cdot}mol^{-1}$).

The reaction with $CH_4$ demonstrates the potential for detailed exploration of the photochemistry of subvalent compounds like AlCl. The experience gained from the matrix-isolated molecules could be vital in developing the photochemistry on a preparative scale.

## Experimental Section

Details of the matrix isolation method can be found elsewhere.[40] Very briefly, in a high vacuum apparatus, HCl was passed over liquid Al (at 1000 °C) inside a Knudsen-type graphite container. Hence AlCl was formed and the vapor emitted from the cell. The AlCl vapor was co-deposited with methane in an excess of Ar onto a freshly polished Cu block kept at 12 K (with a Leybold LB510 refrigerator).

IR spectra were recorded with a Bruker 113v spectrometer equipped with a DTGS and a MCT detector, allowing measurements in the region $5000-200\ cm^{-1}$. The spectra were recorded with a resolution of $0.5\ cm^{-1}$. A Ge/KBr beam splitter was used for the $5000-400\ cm^{-1}$ range, and a Mylar 3.5 beam splitter for measurements down to $200\ cm^{-1}$. Photolysis was achieved with the aid of a medium-pressure mercury lamp (Philips LP 125) operating at 100 W.

$^{12}CH_4$ (99.995 Vol-%) was used as purchased from Messer. $^{12}CD_4$ (98 atom% D) and $^{13}CH_4$ (99 atom% $^{13}C$) were used as delivered from Aldrich.

Quantum chemical calculations were carried out with the aid of the TURBOMOLE program package.[41] The BP method in combination with a TZVPP basis set for Al (and Ga) and a SV(P) basis set for the other elements was used in all calculations. The reaction energies are given with ZPVE corrections.

## Acknowledgments

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