Ab Initio and Cryospectroscopic Investigation of the Van der Waals Complexes of Methylcyclopropane with Hydrogen Chloride and Boron Trifluoride

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The mid infrared spectra of methylcyclopropane−HCl and methylcyclopropane−BF_3 mixtures, dissolved in liquid argon (LAr) or liquid nitrogen (LN_2), have been examined. In LAr solutions, evidence was found for the formation of two different isomers of the 1:1 van der Waals complexes—an asymmetric complex, in which the electron acceptor interacts with the C−C bond adjacent to the methyl group, and a symmetric complex in which the interaction occurs with the opposite C−C bond. At higher concentrations, indications were found for the formation of a chain-type 1:2 complex. In LN_2 solutions, only the two 1:1 isomers of the HCl complex have been observed. Using spectra recorded at different temperatures, the complexation enthalpy $\Delta H°$ in LAr was determined to be −9.5(4) and −8.3(3) kJ mol^{-1} for the symmetric and asymmetric MCP·HCl complexes, and −9.1(2) and −6.7(5) kJ mol^{-1} for the symmetric and asymmetric MCP·BF_3 complexes, respectively. In addition, for all investigated species, full MP2/6-31+G(d,p) geometry optimizations and B3LYP/6-311++G(d,p) frequency calculations were performed, and the complexation energies were calculated at the MP2/6-311++G(3df,2pd) level. These calculations indicate that the isomers of the MCP·HCl complex are of comparable strength, while the asymmetric MCP·BF_3 complex is significantly less stable than its symmetric counterpart. Using Free Energy Perturbation Monte Carlo simulations to calculate the solvent influences, and using statistical thermodynamics to account for zero-point vibrational and thermal contributions, from the experimental complexation enthalpies, the complexation energies are estimated to be −15.7(8) and −16.0(9) kJ mol^{-1} for the symmetric and asymmetric MCP·HCl complexes, which is in agreement with the ab initio results, and −14.0(8) and −15.3(5) kJ mol^{-1} for the corresponding MCP·BF_3 species.

Introduction

The special nature of the carbon−carbon bonds in three-membered ring hydrocarbons[1−4] has drawn significant attention. For instance, in the field of weak intermolecular interactions, the van der Waals complexes between cyclopropane and various electron acceptors have been studied using theoretical[5−13] as well as experimental[5,6,14−22] methods. These studies have triggered interest in similar complexes, in which a methyl-substituted cyclopropane is the Lewis base. The interest stems from the inequivalence of the pseudo-π C−C bonds of the ring, which should allow the formation of two isomers. This has been investigated for several methyl derivatives,[23,24] using matrix isolation infrared spectroscopy. With hydrogen halides and molecular halogens as Lewis acids, however, these authors were able to identify a single isomer only, namely that which benefits most from the electron donating effect of the methyl group. For methylcyclopropane this is the complex in which the Lewis acid interacts with the C−C bond adjacent to the methyl-substituted carbon. Following Truscott et al.,[23] we will refer to this isomer as the asymmetric complex. The complex of methylcyclopropane with HCl has also been investigated by Forest et al.,[25] who report on pulsed nozzle Fourier transform microwave spectroscopy, supported by theoretical calculations. Their distributed multipole electrostatic calculations suggest that the symmetric isomer, in which HCl interacts with the C−C bond opposite to the methyl substituent, should be more stable, by approximately 0.6 kJ mol^{-1}, than the asymmetric complex. In the same study, reference is made to unpublished ab initio calculations at the RHF/6-31G level.[26] These calculations also predict the symmetric complex to be more stable. However, in the microwave spectra only the asymmetric isomer was identified.[25] Hence, there is an at-present unresolved discrepancy between the theoretical predictions and the published experimental results. Therefore, we have initiated a study of mixtures of methylcyclopropane (MCP) and hydrogen chloride disolved in liquid argon (LAr) and in liquid nitrogen (LN_2), in which complexes are formed under equilibrium conditions.[27] In the paragraphs below it will be shown that, in agreement with ab initio predictions, in the infrared spectra of the solutions two different 1:1 complexes have been detected, and that the assignment of the observed bands to the symmetric and asymmetric 1:1 complexes can be made on the basis of ab initio calculations.

Complexes with boron trifluoride as the Lewis acid in general are somewhat stronger than the corresponding HCl complexes.[12,28,29] More importantly, BF_3 is much bulkier than HCl, and, in view of the sterical hindrance due to the methyl substituent, it is reasonable to expect that this could influence the relative stability of its symmetric and asymmetric complexes with methylcyclopropane. To complement our results on the HCl complexes, we have also studied the complexes of methylcyclopropane with boron trifluoride. The results obtained will also be discussed below.

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Experimental Section

Methylcyclopropane was prepared from an intramolecular Wurtz-type reaction of 1,3- dibromobutane with zinc dust in molten acetamide[30] and was purified by pumping the reaction mixture through a 180 K slush, followed by purification on a low-temperature, low-pressure fractionation column. NMR and IR spectra of the obtained product showed the presence of significant fraction of olefins. These were eliminated by repeatedly adding small amounts of bromine to the sample at 180 K, until no further reaction occurred, followed by a second low-temperature fractionation. HCl and DCl were synthesized in small amounts by hydrolyzing PCl_3 with H_2O or D_2O, and were purified by low-temperature fractionation. BF_3 (CP grade) was purchased from Union Carbide, and was used without further purification. The argon and nitrogen solvent gases, with a purity of 99.9999%, were supplied by L'Air Liquide.

A detailed description of the liquid noble gas setup has been given before.[31] All spectra were recorded on a Bruker IFS 113v or a Bruker IFS 66v interferometer, using a globar source, a Ge/KBr beam splitter, and a liquid N_2-cooled broad-band MCT detector. All spectra were averaged over 200 scans, Happ-Genzel apodized and Fourier transformed with a zero filling factor of 4, to yield spectra with a resolution of 0.5 cm^{-1}.

DFT geometry optimizations were carried out at the B3LYP/6-311++G(d,p) level, with the Berny procedure,[32] using normal convergence criteria. Vibrational frequencies were derived from analytical second derivatives of the total energy of the optimized structures. Using the optimized DFT structures, energies were calculated at the MP2 level of theory, including all molecular orbitals to calculate the correlation energy. The complexation energies of the complexes were calculated by subtracting the calculated energies of the monomers from those of the complexes, correcting for basis set superposition errors using the counterpoise method.[33] All ab initio and density functional calculations were carried out using the GAUSSIAN 98 program.[34] Solvation Gibbs energies were obtained from Monte Carlo perturbation calculations,[35-37] using a modified version of BOSS 4.1.[38] All simulations were run in the NPT ensemble, using standard procedures including a cubic box and periodic boundary conditions. The systems consisted of one solute molecule surrounded by 256 solvent atoms. For all simulations, the Metropolis sampling was augmented by preferential sampling[39] in which the probability of attempting to move a solvent atom was made proportional to $1/(r^2 + c)$ where r is the solute−solvent distance. The constant c was fixed at 250 $Å^2$ which causes the solvent atoms nearest the solute to be moved twice as often as the most distant solvent atoms. An attempt to move the solute molecule was made on every 50th configuration and a change in volume was tried on every 600th configuration. The ranges for the attempted moves were the same in each calculation, and provided a ∼40% acceptance probability for new configurations.

The path from $\lambda = 0$ (pure argon) to $\lambda = 1$ (a solution with one solute molecule) was completed in 32 steps, each step corresponding roughly to $\Delta\lambda = 0.0312$. Advantage was taken of double-wide sampling[40] that permits us to obtain two free energy changes at each step, i.e., that between the reference system at which the simulation is performed ($\lambda = \lambda_\circ$) and two perturbed systems with $\lambda = \lambda_\circ \pm \Delta\lambda$. Each step consisted of an equilibrium for 10.0×10^6 configurations, followed by a production phase of 30.0×10^6 configurations. The Gibbs energy changes between perturbed and reference systems were always small enough ($\approx kT$) to guarantee reliable results by the statistical perturbation theory. A single determination of $\Delta_{sol}G$, involving all necessary steps from $\lambda = 0$ to $\lambda = 1$, approximately 22 h on a dual processor 800 MHz Pentium III computer running Redhat Linux 6.2. To extract the enthalpy of solvation, $\Delta_{sol}H$, and the entropy of solvation, $\Delta_{sol}S$, in LAr, the Gibbs energy of solvation, $\Delta_{sol}G$, was calculated at 11 different temperatures between 88 and 138 K, at a pressure of 28.2 bar, i.e., the vapor pressure of LAr at 138 K.[41]

Theoretical Calculations

Previous ab initio calculations on the stability of the 1:1 complexes of MCP with HCl were made at the RHF/6-31G level.[25] These calculations do not account for the dispersion energy between the monomers, which for van der Waals molecules is known to give a significant contribution to their stability.[42,43] To obtain more reliable energies, we have repeated the calculations at the MP2 level, with the slightly expanded basis set 6-31+G**. Apart from the benificial influence of a larger basis set, the inclusion of p orbitals on the hydrogen atoms in this basis set was judged of significance in view of the interaction between MCP and HCl taking place via the hydrogen atom of HCl. The same level was also used to predict the structures and energies of the BF_3 complexes.

For the present study predicted vibrational frequencies are of great value. For calculational economy we have predicted them using DFT/B3LYP calculations using the 6-311++G(d,p) basis set. There is some debate about the extent to which these calculations account for dispersion energy[44,45] and, hence, their applicability for predicting vibrational frequencies of van der Waals complexes may be questioned. However, we have recently shown[46,47] there is an excellent correlation between complexation shifts, at the same level, calculated in the single-molecule approach, with experimental shifts observed in liquid argon. Therefore, it appears justified to base the present assignments on such calculations. As the force fields are calculated around the equilibrium structure, the DFT calculations also produce energies and structures of the complexes.

It has been observed[48] that single point MP2 calculations with an extended basis set, using the structure converged at the DFT/B3LYP/6-311++G(d,p) level, produces good estimates of the complexation energies of van der Waals molecules. Therefore, we have made such calculations for the present complexes, using the 6-311++G(3df,2pd) basis set.

Both at MP2 and DFT level, the calculated geometry of the 1:1 complexes with MCP is similar to those of the complexes with cyclopropane.[12,13] Thus, the electron acceptor very nearly lies in the plane of the ring, with its electrophilic center directed toward the middle of a C−C bond of the ring. The two possible isomers for each complex are shown in Figure 1. In the *asymmetric* isomers, Figure 1, parts a and c, the Lewis acid interacts with the C−C bond adjacent to the CH_3 group, while in the *symmetric* isomers, Figure 1, part b and d, the interaction occurs with the C−C bond opposite to the CH_3 substituent.

Complexation energies, BSSE corrections and BSSE-corrected energies have been collected in Table 1. It is immediately obvious that the uncorrected DFT energies are substantially smaller than the corrected MP2 values. Because, in the light of what was said above, these energies most likely are seriously underestimated, no attempts were made to correct them for the BSSE. The MP2 calculations predict much more stable complexes. It may be remarked that the single point calculations with the 6-311++G(3df,2pd) basis set lead to complexes that are significantly more stable than those of the fully optimzed MP2/6-31+G(d,p) calculations. This emphasizes the need for extended basis sets when calculating stabilities of weak intermolecular complexes.

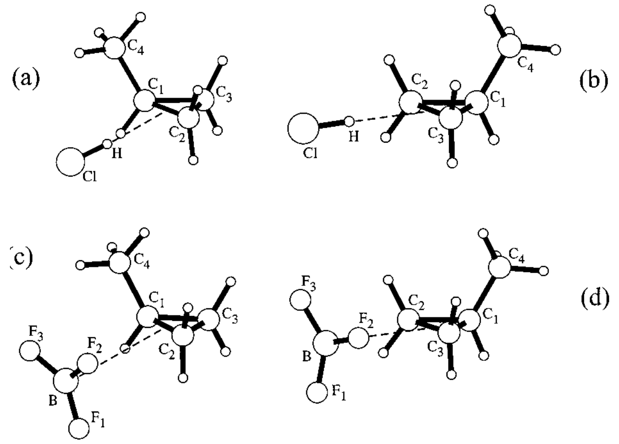

Figure 1. MP2/6-31+G(d,p) equilibrium structures for the *asymmetric* isomers (a,c), and the *symmetric* isomers (b,d) of MCP·HCl and MCP·BF_3.

TABLE 1: Complexation Energies, in kJ mol^{-1}, for the 1:1 Complexes of MCP with HCl and BF_3

	MCP·HCl asymmetric	MCP·HCl symmetric	MCP·BF_3 asymmetric	MCP·BF_3 symmetric
B3LYP/6-311++G(d,p)				
ΔE	−2.62	−3.95	−4.69	−5.93
MP2/6-31+G(d,p)				
ΔE	−16.66	−16.58	−16.22	−16.46
E_{BSSE}	−8.59	−7.58	−9.80	−8.76
ΔE_{corr}	−8.07	−9.00	−6.42	−7.70
MP2/6-311++G(3df,2pd)//B3LYP/6-311++G(d,p)				
ΔE	−19.38	−18.80	−15.34	−16.14
E_{BSSE}	−5.22	−4.73	−5.41	−5.37
ΔE_{corr}	−14.16	−14.07	−9.93	−10.76

TABLE 2: MP2/6-31+G(d,p) and B3LYP/6-311++G(d,p) Bond Lengths, in Å, for the 1:1 Complexes of MCP with HCl and BF_3

	symmetric		asymmetric	
	MP2	B3LYP	MP2	B3LYP
HCl complex				
C_1-C_2	1.501	1.507	1.514	1.522
C_1-C_3	1.501	1.507	1.499	1.504
C_2-C_3	1.517	1.525	1.506	1.512
C_1-C_4	1.506	1.513	1.508	1.514
H−Cl	1.276	1.295	1.276	1.295
R_{vdW}	2.262	2.322	2.265	2.234
BF_3 complex				
C_1-C_2	1.501	1.507	1.511	1.515
C_1-C_3	1.501	1.508	1.501	1.506
C_2-C_3	1.516	1.520	1.505	1.512
C_1-C_4	1.506	1.513	1.508	1.514
$B-F_1$	1.328	1.319	1.328	1.319
$B-F_2$	1.327	1.319	1.326	1.318
$B-F_3$	1.327	1.319	1.327	1.319
R_{vdW}	2.985	3.265	3.057	3.361

monomers	MP2	B3LYP	expt.
C_1-C_2	1.498	1.509	1.509[a]
C_1-C_3	1.498	1.509	1.509[a]
C_2-C_3	1.507	1.513	1.509[a]
C_1-C_4	1.506	1.513	1.517[a]
H−Cl	1.269	1.287	1.2746[b]
B−F	1.326	1.318	1.3070[c]

[a] Gas electron diffraction data taken from ref 49, the C−C bonds in the cyclopropyl group are assumed equal. [b] Taken from ref 50. [c] Taken from ref 51.

Full Cartesian coordinates, from which the other structural characteristics can be derived, are given in Table S1 of the Supporting Information. The more important bond lengths of monomers and complexes are given in Table 2. The DFT results show that the C−C bond involved in the interaction with the Lewis acid becomes longer, by 0.013 Å for the asymmetric HCl complex, and by 0.012 Å for the symmetric one, and by 0.006 and 0.007 Å for the asymmetric and symmetric BF_3 complexes, respectively. The other C−C bonds of the ring become shorter, typically by some 0.001−0.005 Å. The complexation also influences the Lewis acids: the H−Cl bond lengths increase by 0.007−0.008 Å, while the B−F bond lengths increase by some 0.001 Å. Similar trends are observed for the MP2 results. All these changes are similar to those calculated for the corresponding complexes of cyclopropane.[12,13]

The complexation induces a small deviation from planarity of the BF_3 submolecule: the B−F bonds are at an angle of 1.5° with the plane perpendicular to the symmetry axis of the BF_3 moiety.

For the HCl complexes, the van der Waals bond length R_{vdW}, defined as the distance between the HCl hydrogen atom and the perpendicular projection of the HCl hydrogen atom on the complexed C−C bond, has different values in the asymmetric and symmetric complex, the trend in the B3LYP results being opposite to that in the MP2 results. Thus, no correlation is found with the stability data in Table 1. In contrast, both methods predict the shorter van der Waals bond length, similarly defined, in the symmetric BF_3 complex, which is in line with the stabilities in Table 1.

The calculated frequencies and infrared intensities of the 1:1 complexes and of the monomers, together with their assignments, have been collected in Tables S2 and S3 of the Supporting Information. The calculated complexation shifts will be discussed in relation to the experimental infrared spectra in the following paragraph.

Vibrational Spectra

a. Monomers. The infrared spectra of HCl[31] and BF_3[52] in cryosolutions have been studied in detail before, and the assignments need not be discussed here. For MCP, the infrared and Raman spectra have been reported by several groups.[53−56] The relatively low symmetry and the interference of the methyl modes with the methylene and ring modes, however, appear to have prevented reliable assignments for several modes.[57] The infrared frequencies of this compound observed in LAr at 105 K and in LN_2 at 100 K are compared with the vapor-phase frequencies in Table S4 of the Supporting Information, along with tentative assignments that are based on group theoretical arguments and on a comparison with the DFT frequencies. In the discussion below, we will use the Herzberg numbering of the modes for BF_3 and for MCP, as given in Table S4. For vibrational modes of the complexes that are located in either of the monomers we will use the Herzberg numbering of the parent monomer, with the monomer indicated as a superscript, where necessary.

b. Methylcyclopropane/HCl Mixtures. Mid infrared spectra were investigated at different temperatures between 80 and 110 K for a series of MCP/HCl mixtures in LAr, in which the mole fractions were varied between 8.0×10^{-6} and 5.8×10^{-5} for MCP and 2.4×10^{-4} and 5.2×10^{-4} for HCl. In the spectra of the mixtures, new bands are observed for several fundamentals and overtones. These bands are assigned to complexes formed between MCP and HCl.

HCl Stretches. In Figure 2 the HCl stretching region of spectra of a mixture with a mole fraction of 5.8×10^{-5} for MCP and 3.2×10^{-4} for HCl, recorded at 99.0, 106.4, and 123.0 K, are compared with the spectra of the monomers in LAr. In the region

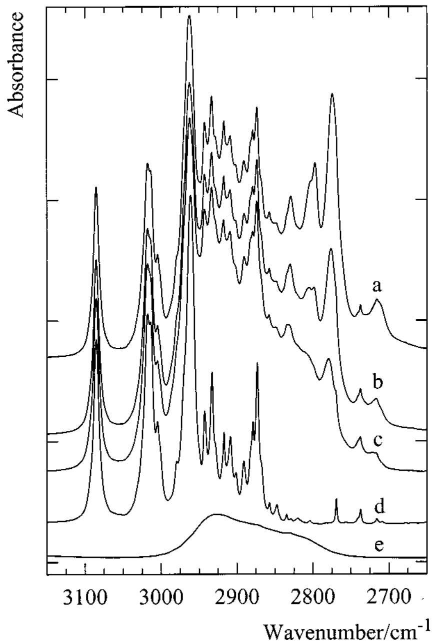

Figure 2. The ν_{HCl} region of a MCP/HCl mixture in LAr, recorded at (a) 99 K; (b) 106 K; (c) 123 K; compared with a LAr solution containing (d) only MCP, recorded at 96 K; and (e) only HCl, recorded at 110 K. The ordinate tick interval equals 0.5 absorbance units. For clarity, the different spectra have been shifted vertically.

between 2850 and 2700 cm^{-1}, several new bands can be seen to grow in with decreasing temperature: a band at 2828 cm^{-1}, a somewhat stronger doublet with main maximum at 2797 cm^{-1}, and a shoulder at 2801 cm^{-1}, the strongest of the new bands at 2771 cm^{-1} and a weaker band at 2710 cm^{-1}. Comparison with the HCl oligomer spectra[31] shows that the 2828 cm^{-1} band must be due to the HCl dimer, and the 2799 cm^{-1} band must be assigned to the HCl trimer. The bands at 2801, 2772, and 2710 cm^{-1}, however, must be due to complexes of MCP with HCl. In analogy with other HCl complexes, the more prominent feature at 2772 cm^{-1} is assigned to a 1:1 species. For HCl complexes where only a single isomer can be formed, the HCl stretching band is usually asymmetric, tailing toward high frequencies. This has been explained by the presence of hot bands as a consequence of the thermal excitation of the low-frequency van der Waals modes of the complex:[58] because of the pronounced anharmonictiy of the van der Waals bond, excited states tend to shift the HCl stretching toward its monomer value, i.e., toward higher frequency. Close inspection of the 2772 cm^{-1} band reveals, however, that at the lowest temperatures an intense shoulder becomes visible on the low-frequency side of the main maximum, at 2768 cm^{-1}. In view of their origin,[58] it is unlikely for hot bands to appear on the low-frequency side of the fundamental mode. Therefore, the shoulder is taken to be evidence that a second isomer of the 1:1 complex MCP·HCl is present. It will be shown below that this is confirmed by the complex bands observed in the fingerprint region of MCP.

The appearance of two weaker complex bands, one on each side of the 1:1 bands, is similar to what has been observed for other HCl complexes,[13,46,58−61] where it was shown that they arise in 1:2 species in which the second HCl molecule is hydrogen-bonded to the chlorine atom of the first. Therefore, we assign these bands to a chain-type complex with stoichiometry MCP·(HCl)$_2$.

MCP Fingerprint Region. In the argon matrix infrared spectra of MCP/HCl mixtures 5 new bands were detected near MCP fundamentals, at 1091, 1031, 844, 826, and 766 cm^{-1}, which were assigned to a 1:1 species.[23] Despite their sharpness, no splitting of the complex bands into doublets could be observed, so that no indication was found for the formation of a second 1:1 species. From the perturbation of the 855 cm^{-1} A′ ring mode it was derived that the asymmetric complex between MCP and HCl was formed in the matrixes.[23]

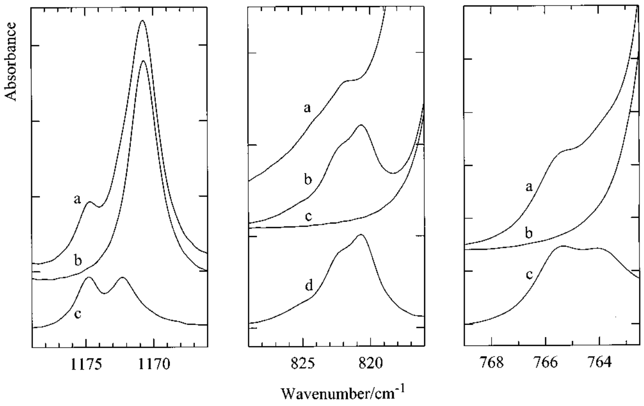

Figure 3. The spectrum of (a) a mixture of MCP and HCl in LAr; (b) a LAr solution containing only MCP; and (c) the result of their subtraction. Left panel: ν_{23}; middle panel: ν_{28}; right panel: ν_{16}. Trace (d) in the middle panel represents the spectrum of a MCP/HCl mixture in LN$_2$. The ordinate tick interval equals 0.02 (left), 0.1 (middle), and 0.05 (right) absorbance units. For clarity, in each panel the different spectra have been shifted vertically.

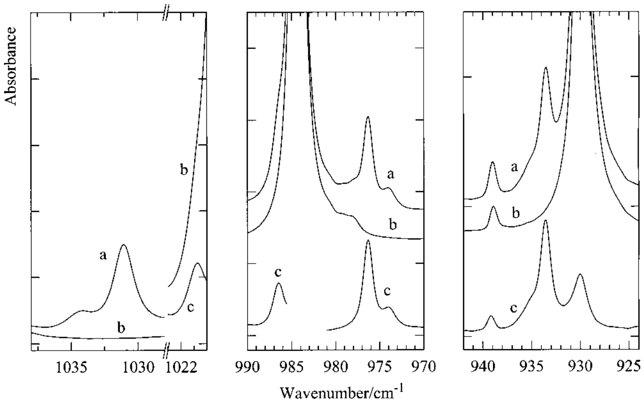

Figure 4. The spectrum of (a) a mixture of MCP and HCl in LAr; (b) a LAr solution containing only MCP; and (c) the result of their subtraction. Left panel: ν_{12}; middle panel: ν_{13}; right panel: ν_{14}. The ordinate tick interval equals 0.2 (left), 0.1 (middle), and 0.1 (right) absorbance units. For clarity, in each panel the different spectra have been shifted vertically.

Rather different behavior is observed for the solutions in LAr, as is illustrated in Figures 3 and 4. In each of the panels of these figures, spectra of a mixed solution and of a solution containing only monomer MCP are compared; also given is the difference spectrum resulting from subtracting out the monomer MCP contribution to the spectrum of the mixed solution. For the subtraction, the spectrum of a solution of MCP in LAr with similar concentration as in the mixed solution, recorded at the same temperature, was used. Because of the dilution used, the presence of HCl in the mixed solution has negligible influence on the band contours of the MCP transitions, so that successful subtractions can in principle be expected. Two factors, however, contribute to the less than ideal difference spectrum near the maxima of some monomer bands. In the first place, it will be appreciated from Figures 3 and 4 that, due to the weakness of the complexes, the complex bands are weak compared with their corresponding monomer band. As a consequence, the more intense monomer transitions show high absorbances near the band maxima, causing some deformation of the contour because of nonlinearity of the detector. In such cases the subtraction does not produce a horizontal baseline in the vicinity of the band maximum. Second, the frequency of some transitions is very temperature sensitive, due mainly to the significant thermal expansion of the solvent.[62,63] With the present cells it is very difficult to reproduce temperatures better than to a few tenths of a Kelvin, and this suffices for the more sensitive bands to give rise to a first-derivative pattern in the difference spectrum. In those cases the region of the monomer band maximum is not shown.

In the matrix spectra[23] no complex band due to ν_{23} of MCP was detected. The region of this mode in the solution spectra is shown in the left-hand panel of Figure 3. It can be seen that for the mixed solution a new band emerges at 1174.8 cm^{-1}. Although no other complex band can be seen on the slope of the monomer band at 1170.7 cm^{-1}, a second complex band, with intensity similar to that of the first one, becomes visible at 1171.9 cm^{-1} in the difference spectrum. It may be remarked that in this case the subtraction is very successful, as virtually no anomalies can be seen in the difference spectrum in the vicinity of the monomer band maximum.

The ν_{28} complex band was observed in the matrixes[23] as a singlet on the high-frequency side of the monomer absorption, at 826 cm^{-1}. This region is shown in the central panel of Figure 3. It is obvious that in our solutions a doublet is present. It can further be seen that near 825 cm^{-1} a third, much weaker band is present in the difference spectrum. In agreement with the low relative intensities of the 1:2 bands in the HCl stretching region, we assign this band to a 1:2 complex. The right-hand panel shows the region in which a single ν_{16} complex band was observed in the matrixes.[23] The difference spectrum, trace c, of the LAr solutions again shows the presence of a doublet with components of similar intensity.

In each of the above three regions of the solution spectra we have observed a doublet, the components of which have similar relative intensities, while in the matrixes only singlet complex bands were identified. It is unlikely that for each of the three MCP modes involved we observe a doubling as a consequence of Fermi resonance in the complex, with the same resonance absent in the monomer, and also absent in the complex bands observed in the matrixes. The doubling also cannot be due to the lowering of the symmetry in the 1:1 complex, or to site effects in the solution. Also, in view of the weakness of the 1:2 complex bands in the HCl stretching region, it is unlikely that the doublet structure can be rationalized in terms of the presence of a 1:2 complex. Therefore, we have to conclude that in our solutions two isomers of the 1:1 complex were present with similar concentrations. This is confirmed by the observations in the spectral regions shown in Figure 4.

The 1031 cm^{-1} complex band observed in the argon matrixes[23] belongs to the ν_{12} fundamental of MCP. This region of the solution spectra is shown in the left-hand panel of Figure 4. The complex mode at 1031 cm^{-1} clearly corresponds to the complex band observed in the matrixes. On the slope of the monomer ν_{12} a faint shoulder can be distinguished, which becomes much better visible in the difference spectrum, trace c, at 1020.5 cm^{-1}. It has an intensity similar to that of the 1031 cm^{-1} band, and we assign it to the second 1:1 complex. Near 1034.5 cm^{-1} a third, much weaker band is seen, which we attribute to a 1:2 complex.

For the matrix spectra, no complex band due to ν_{13} was reported.[23] This region of the spectra is given in the central panel of Figure 3. The difference spectrum, trace c, clearly reveals the presence of three complex bands, at 986.5, 976.5, and 974 cm^{-1}. The former two are more prominent and are assigned to the 1:1 complexes, while the latter one is much weaker, and we assign this band to a 1:2 species.

For ν_{14} no complex band was observed in the argon matrixes, but this mode was detected in the N$_2$-matrixes, at 937 cm^{-1}.[23] The difference spectrum, trace c, in the right-hand panel of Figure 4 shows the presence of several complex bands in this region of the solution spectra. From a comparison with the MCP monomer spectrum, trace b, it follows that the weak complex band at 939.5 cm^{-1} belongs to the weak, unidentified, MCP monomer combination band at very nearly the same frequency. The complex band at 933.5 cm^{-1} undoubtedly corresponds to the single 937 cm^{-1} complex band of the N$_2$-matrixes. In the solution spectra this band has a weak high-frequency shoulder at approximately 935 cm^{-1}, which, because of its weakness, must be assigned to a 1:2 complex. In the difference spectrum a fourth band shows up at 930.0 cm^{-1}, about 0.1 cm^{-1} above the monomer band maximum. The problems with spectrum subtraction discussed above, suggest that this feature must be treated with some caution. However, in the experimental spectra used in the subtraction, the 930 cm^{-1} monomer MCP fundamental has a peak absorbance of very nearly 0.4, well within the linear regime of the detector, and it is clear from Figure 4 that near 930 cm^{-1} the contour of the difference spectrum shows no sign of first-derivative signatures. It is, therefore, believed that the 930.0 cm^{-1} feature in the difference spectrum is a genuine complex band. In view of its intensity relative to that of the 933.5 cm^{-1} band, we have to assign it to the second 1:1 complex.

Apart from those shown in Figures 2−4, complex bands have been observed in the LAr solutions for several other modes. All the observed frequencies of complex bands have been collected in Table 3: it can be seen that for three more fundamentals of MCP (ν_{15}, ν_{26}, and ν_{27}) 1:1 complex doublets have been observed. This evidently lends support to our conclusion that 2 isomers were formed in the solutions.

Spectra in Liquid Nitrogen. The formation of complexes was also investigated in liquid nitrogen. The frequencies of the observed complex bands are also given in Table 3. In liquid nitrogen the vibrational bands usually have slightly higher widths than in LAr, making observation of complex bands near the maximum of the corresponding monomer band more difficult. It can be seen in Table 2 that, as a consequence of this, fewer complex bands have been observed. However, isomeric doublets have been clearly identified at 822.1/824.0 cm^{-1} and at 1173.5/1175.9 cm^{-1}, so that we conclude that also in LN$_2$ the two isomers were simultaneously present.

Assignment of Complex Bands. In view of the very good correlation of single molecule B3LYP/6-311++G(d,p) complexation shifts with shifts observed in LAr we have observed for other complexes,[46,47] it is of interest to see if the present calculations can be used to assign the components of the isomeric doublets to the predicted isomers. To this end, in Table 3 we have compared the observed complexation shifts, in LAr and in LN$_2$, with the calculated values. It can be seen that for ν_{13}, ν_{15}, and ν_{26} one of the isomers gives rise to a red-shifted complex band, the other to a blue-shifted band. In agreement with these predictions, for each of the fundamentals we have observed one 1:1 complex band on either side of the corresponding monomer band. This is seen as further evidence for the presence of the two isomers in our solutions. In all cases the predicted shifts are somewhat larger than the observed

TABLE 3: Observed Frequencies and Shifts, in cm^{-1}, for the Complexes of MCP with HCl and BF_3 in Cryosolution, Compared with the B3LYP/6-311++G(d,p) Calculated Shifts

liquid argon			liquid nitrogen			B3LYP		
monomer	complex	shift	monomer	complex	shift	shift	assignment	
761.2	764.4	3.2	762.2			1.1	ν_{16}	symm[a]
	765.6	4.4		765.5	3.3	3.0	ν_{16}	asymm[b]
789.0	788.9	−0.1	789.5			−2.9	ν_{15}	symm
	794.5	5.5		795.4	5.9	9.8	ν_{15}	asymm
813.5	820.6	7.1	814.8	822.1	7.3	8.1	ν_{28}	asymm
	822.2	8.7		824.0	9.2	13.1	ν_{28}	symm
	825.0	11.5					ν_{28}	symm 1:2
853.7	847.2	−6.5	853.8	847.1	−6.7	−9.1	ν_{27}	asymm
	853.5	−0.2				−2.1	ν_{27}	symm
929.9	930.1	0.2	930.6			−1.3	ν_{14}	asymm
	933.6	3.7				3.0	ν_{14}	symm
	935.0	5.1		934.3	3.7		ν_{14}	symm 1:2
984.3	976.3	−8.0	984.7			−10.7	ν_{13}	symm
	973.9	−10.4		976.6	−8.1		ν_{13}	symm 1:2
	986.5	2.2				3.6	ν_{13}	asymm
1019.0	1020.9	1.9	1020.7	1022.6	1.9	0.5	ν_{12}	asymm
	1031.0	12.0		1032.7	12.0	14.4	ν_{12}	symm
	1034.2	15.2					ν_{12}	symm 1:2
1042.4	1051.6	9.2	1043.8	1052.9	9.1	12.8	ν_{26}	asymm
	1040.2	−2.2				−2.9	ν_{26}	symm
1085.2	1089.7	4.5	1086.2	1090.3	4.1	5.4	ν_{25}	asymm
						5.0	ν_{25}	symm
1170.7	1171.9	1.2	1171.6	1073.5	1.6	1.0	ν_{23}	symm
	1174.8	4.1		1175.9	4.3	5.6	ν_{23}	asymm
1361.1	1362.0	0.9				0.7	ν_9	symm
1392.9	1395.0	2.1				2.6[c]	ν_8	?
2872.0	2801.9	−70.1	2862.2				ν_{HCl}	(a)symm 1:2
	2778.0	−94.0		2770.0	92.2	−106.8[c]	ν_{HCl}	(a)symm
	2709.9	−162.1					ν_{HCl}	(a)symm 1:2

[a] symm:symmetric complex. [b] asymm:asymmetric complex. [c] Mean value of the calculated shift for the asymmetric and the symmetric complex.

values. This is as before,[47] and presumably explains the results for ν_{14}: for the asymmetric complex, a small shift of −1.3 cm^{-1} is predicted, while both complex bands are observed on the high-frequency side of the monomer. One of them, however, is shifted by a mere +0.2 cm^{-1}, and in view of the differences between observed and calculated complexation shifts, this band must be attributed to the asymmetric complex. For the other isomeric doublets both components are shifted in the same direction, which is consistent with the predictions. In all cases, we have assigned the components in the order predicted.

c. Methylcyclopropane/BF_3 Mixtures. The formation of complexes between MCP and BF_3 was investigated in LAr. The solubility of BF_3 in LAr is much smaller than that of HCl,[52] so that high concentrations of MCP had to be used in order to form measurable quantities of complex. For all but the weakest MCP fundamentals the high concentrations led to high absorbances, well into the nonlinear regime of the detector. Therefore, it proved impossible to use MCP fundamentals to prove the formation of two isomers of the 1:1 complex. Their presence, nevertheless, can be shown using the complex bands due to the $\nu_3^{BF_3}$ mode of the ^{11}B isotope, which are shown in Figure 5. The dominant complex band at 656.6 cm^{-1} is accompanied by a weaker high-frequency shoulder, near 661 cm^{-1}. The intensity of the 661 cm^{-1} shoulder, relative to the 656.6 cm^{-1} band, is much higher than what has been observed for 1:2 complexes between other Lewis bases and BF_3.[29] As there is no reason why for the present base the stability of the 1:2 complex should be much closer to that of the 1:1 complex than for the other bases, we assign the 661 cm^{-1} band to the second isomer of the 1:1 complex. This assignment is supported by the frequency difference between the two complex bands, 4−5 cm^{-1}, which is in good agreement with the frequency difference predicted by the DFT calculations for the two isomers. This agreement also suggests that the observed bands must be assigned in the calculated order, i.e., the 656.6 cm^{-1} band must be attributed to the symmetric complex, and the 661 cm^{-1} shoulder to the asymmetric complex. The DFT calculations predict similar infrared intensities for the $\nu_3^{BF_3}$ mode in both isomers. This, combined with the statistical advantage of the asymmetric

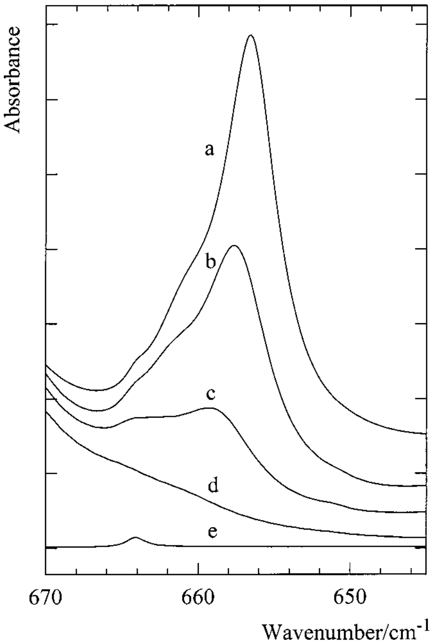

Figure 5. The $\nu_2^{11BF_3}$ region of a mixed MCP/BF_3 solution in LAr, recorded at (a) 90.7 K; (b) 95.6 K; (c) 102.9 K; and (d) 124.3 K; compared with (e) a mixture containing only BF_3, recorded at 101.6 K. The ordinate tick interval equals 0.2 absorbance units. For clarity, the different spectra have been shifted vertically.

complex and the smaller intensity of the 661 cm^{-1} shoulder, suggests that the asymmetric complex is less stable than the symmetric complex, which is in line with the data in Table 1.

Stoichiometry of the Complexes

The stoichiometry of the complexes was determined as before,[31] by using spectra of an isothermal concentration series to plot the intensity of a complex band versus products $(I_{\mathrm{MCP}})^n \times (I_{\mathrm{HCl}})^m$ of the intensity of a band of monomer MCP, I_{MCP}, and of monomer HCl, I_{HCl}, for different values of m and n, the values of m and n producing a linear plot determining the stoichiometry $\mathrm{MCP}_n{\cdot}\mathrm{HCl}_m$ of the complex. It will be appreciated from Figure 1 that the determination of the HCl monomer band intensity in the mixed solutions is problematic due to the presence in the same region of a large number of intense MCP bands. Therefore, the concentration study was performed using DCl: in the DCl stretching region only very weak MCP overtone and combination bands are present, so that the DCl stretch band area can easily be determined. The experience is, however, that neither the equipment used to prepare the DCl, nor the filling manifold of the cell, can be completely deuterated, so that any DCl solution contains a significant, but unknown, fraction of HCl. Because the ab initio calculations do not suggest that the infrared intensities of MCP modes in the DCl complex differ from the corresponding values in the normal complex, this does not affect the complex bands due to vibrational modes localized in the MCP moitey, as they invariably appear accidentally degenerate for both hydrogen chloride isotopes. The use of the DCl band area, however, has to be carefully considered. To investigate this, solutions with different concentrations of DCl, with HCl as isotopic impurity, were studied. The series was generated as follows. After a solution was investigated, a fraction of it was pumped off, whereby not only solvent, but also hydrogen chloride, and to a lesser extent also MCP, were partly removed from the cell. The next solution was then prepared by adding pure solvent to the remainder in the cell. Analysis of the DCl and HCl band areas showed that their ratio was constant throughout the dilution series, which shows that the isotopic ratio was not disturbed by the dilution. It follows that in such a series the DCl band area can be used as a measure for the total hydrogen chloride concentration. As the mixed solutions used to derive the stoichiometries were prepared similarly, we have used this procedure to measure the hydrogen chloride concentrations.

A series of spectra of MCP/DCl solutions in LAr, with mole fractions varying between 5.8×10^{-5} and 1.2×10^{-5} for MCP, and between 5.2×10^{-4} and 1.1×10^{-4} for DCl, were recorded at 110.0 K. The DCl band areas were obtained by using subtraction techniques previously applied for HCl complexes.[13] Band areas for MCP and for the complexes were obtained from least squares band fitting of the spectra with Gauss/Lorentz sum functions.

For the band areas of the 1019 and 1031 cm^{-1} ν_{12} bands a linear relation is obtained for the first-order product of the monomer band areas, proving that both bands arise in 1:1 complexes. The band area of the weaker 1034.4 cm^{-1} band was found to be linearly related to the product of the MCP with the square of the DCl band areas, so that this band must be due to a 1:2 complex $\mathrm{MCP}{\cdot}(\mathrm{HCl})_2$. Similar analysis ofthe 822.2/820.6 cm^{-1} ν_{28} doublet shows that both components are due to 1:1 complexes, which was also found for the 929.9 cm^{-1} band, while its high-frequency shoulder had to be attributed to a 1:2 complex. These results, evidently, confirm the assignments put forward in a previous paragraph.

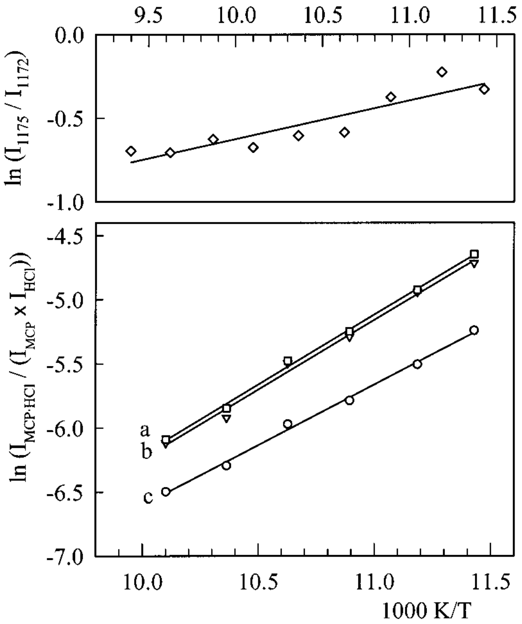

Figure 6. Van't Hoff plots for the MCP·HCl complexes in LAr. Bottom panel: (a) the ν_{14} band of the symmetric complex; (b) the ν_{28} band of the symmetric complex; (c) the ν_{28} band of the asymmetric complex. Top panel: the band area ratio of the ν_{23} complex bands.

Relative Stability

Complexation enthalpies of the complexes were determined in the usual way from a Van't Hoff-type analysis.[62,63] Spectra of a solution in LAr containing mole fractions of 5.8×10^{-5} of MCP and 3.2×10^{-4} for HCl were recorded at several temperatures between 87.5 and 123 K. In all cases, band areas were used to represent the infrared intensities. Because the solution contained less MCP than that used to record the spectra in Figure 2, the HCl band area could be obtained, using subtraction techniques,[31] from the HCl stretching region. Band areas for MCP and the complexes were obtained as above, using band fitting. The band areas were used to construct Van't Hoff plots, and ΔH° was determined from the solvent-density corrected slope of the linear regression line through the experimental points.[62] The Van't Hoff plots obtained for the components of the ν_{28} doublet are shown in the lower panel of Figure 6. The 820.6 cm^{-1} band yields a ΔH° of $-8.3(3)$ kJ mol^{-1}, while for the 822.2 cm^{-1} component a value of $-9.5(4)$ kJ mol^{-1} is found. With the assignments in Table 2, these data show that the symmetric complex is more stable by 1.2(5) kJ mol^{-1}. The analysis of the 933.6 cm^{-1} band, assigned to the symmetric complex results in a ΔH° of $-9.5(3)$ kJ mol^{-1}, in neat agreement with the value of the 822.2 cm^{-1} band. The relative stability of the two 1:1 isomers was independently obtained by plotting the band area ratio of the ν_{23} complex bands versus the inverse temperature. The band areas were obtained from fitting the complete triplet in the 1180−1165 cm^{-1} region. The Van't Hoff plot resulting from this analysis is shown in the top panel of Figure 6. The difference in complexation enthalpy between the two isomers derived from this plot is 1.8(3) kJ mol^{-1}, with the symmetric complex more stable. Taking into account the uncertainties as a consequence of fitting a weak complex doublet in the presence of a strong monomer band, this result is in acceptable agreement with that from the ν_{28} doublet.

For the 1:1 complexes between MCP and BF_3, spectra of a mixture with mole fractions of 3.6×10^{-4} for MCP and 4.1×10^{-5} for BF_3 were recorded at several temperatures between

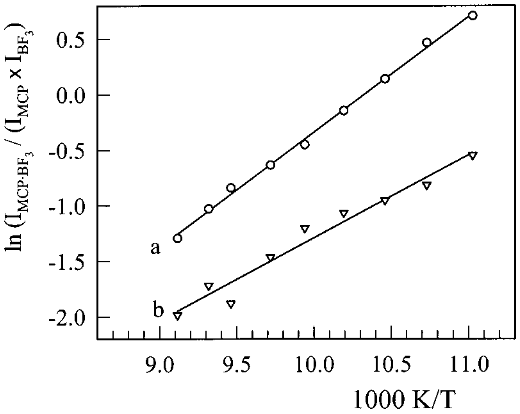

Figure 7. Van't Hoff plots for the MCP·BF_3 complexes in LAr. (a) symmetric complex; (b) asymmetric complex.

TABLE 4: Experimental and Calculated Structural Parameters of Asymmetric MCP·HCl

	experimental[a]	MP2	B3LYP
R_{Cl-X}/Å	3.554(5)	3.5405	3.6439
θ_{H-Cl-X}/deg	5.0[b]	4.9	3.6
$\theta_{Cl-X-CCH_3}$/deg	91(1)	91.7	93.9
$\phi_{H-Cl-X-CH_2}$/deg	0.0[b]	14.7	0.6
$\psi_{Cl-X-CH_2-CH_2}$/deg	8(2)	9.6	10.3

[a] Taken from ref 25. [b] The values of these parameters were fixed at the specified value.

88 and 124 K. The band areas of the $\nu_2^{^{11}BF_3}$ complex bands at 662 and 659 cm^{-1}, derived from least squares band fitting, were used to construct the Van't Hoff plots shown in Figure 7. The complexation enthalpies derived from them are −6.7(5) kJ mol^{-1} for the 662 cm^{-1} component assigned to the asymmetric complex, and −9.1(2) kJ mol^{-1} for the 659 cm^{-1} band assigned to the symmetric complex.

Discussion

Structure of the Complexes. The microwave data on the MCP/HCl complex have been analyzed under the assumption that the complexation does not affect the structures of the monomers.[25] The calculations reported in this study suggest that this is not completely the case; however, the structural changes are small, and the approximation, therefore, can be expected to lead to a satisfactory structure of the complex. The microwave values of the five parameters necessary to specify the orientation of HCl with respect to MCP in the asymmetric complex are compared with the values calculated in this study in Table 4. The symbol X used in the description of the parameters refers to a dummy atom situated at the center of the C−C bond involved in the interaction. It will be seen that in the microwave study, only three parameters could be refined, while two of them had to be fixed. Of the latter, the value of the torsion angle $\varphi_{H-Cl-X-CH_2}$ is well reproduced by the DFT calculation, while a rather different value results from the MP2 calculation. For the other fixed parameter, θ_{H-Cl-X}, both calculations result in a value close to that fixed in the microwave study. Of the three parameters that were refined, the distance R_{Cl-X} is the more interesting, as it is related to the van der Waals distance. The DFT calculation overestimates this parameter by 2.5%, while MP2 results in a value underestimated by 0.4%. It may be expected that the converged van der Waals bond length depends critically on the peripheral properties of the basis set used. Therefore, it is difficult to interpret the difference between the DFT and MP2 results. Nevertheless, we think that the higher value resulting from the DFT calculation is related to the fact that this approximation underestimates the strength of the complex. The calculated values for the other two parameters reflect the sterical hindrance between the HCl molecule and the methyl substituent in the ring; their values are in good agreement with the microwave results.

TABLE 5: Free Energy Perturbation Theory Enthalpies, in kJ mol^{-1}, and Entropies, in J K^{-1} mol^{-1}, of Solvation, and Their Effect on the Complexation Enthalpy of the Different Species

species	$\Delta_{sol}H$	$\Delta_{sol}S$	$\Delta(\Delta_{sol}H)$[a]	$\Delta(\Delta_{sol}S)$[b]
HCl	−9.6 (2)	−35(1)		
BF_3	−7.9(2)	−27(1)		
MCP	−28.6(3)	−106(2)		
MCP·HCl asymmetric	−34.0(6)	−124(5)	4.2(7)	18(6)
MCP·HCl symmetric	−35.5(2)	−129(2)	2.8(4)	12(3)
MCP·BF_3 asymmetric	−31.4(3)	−113(3)	5.1(4)	20(4)
MCP·BF_3 symmetric	−32.4(4)	−118(3)	4.0(5)	15(4)

[a] $\Delta(\Delta_{sol}H) = \Delta_{sol}H$ (complex) − $\Delta_{sol}H$ (monomers). [b] $\Delta(\Delta_{sol}S) = \Delta_{sol}S$ (complex) − $\Delta_{sol}S$ (monomers).

Complexation Enthalpy. The complexation enthalpies obtained in this study measure the stability of the complexes in liquid argon. Values characteristic for the gas phase have been obtained by correcting our experimental values for solvent effects. The Gibbs energies of solvation $\Delta G°$ for the different species were obtained from Monte Carlo simulations of the solutions, using Free Energy Perturbation Theory.[35−37] The intermolecular interactions used in these calculations were described by Lennard-Jones functions, one for each pair of atoms. The parameters of these functions for the interactions of the C, H, and Cl atoms with Ar were taken from the OPLS all-atom potential functions[64] included in BOSS 4.1,[38] whereas those for the interaction of the B and F atoms with Ar were used as before.[65] The solvation entropy differences, $\Delta_{sol}S°$, were extracted using a finite difference method similar to the one described by Levy et al.,[66,67] and the solvation enthalpies $\Delta_{sol}H°$ were calculated from the values of $\Delta_{sol}G°$ and $\Delta_{sol}S°$. The resulting values of $\Delta_{sol}H°$ and $\Delta_{sol}S°$ have been collected in Table 5. Also given in Table 5 are the influences of solvation on the complexation enthalpy, $\Delta(\Delta_{sol}H°)$, and on the solvation entropy, $\Delta(\Delta_{sol}S°)$. It will be seen that in the calculation of $\Delta(\Delta_{sol}H°)$ and $\Delta(\Delta_{sol}S°)$ the contribution due to the complex is nearly canceled by those for the monomers. Hence, while the relative uncertainties on $\Delta_{sol}H°$ and $\Delta_{sol}S°$ are small, they propagate into significant uncertainties on $\Delta(\Delta_{sol}H°)$ and $\Delta(\Delta_{sol}S°)$.

Subtraction of the solvent influences from the experimental values for $\Delta H°$ of the HCl complexes results in gas-phase values ΔH_{gas} −12.3(6) kJ mol^{-1} for the symmetric complex, and −12.5(8) kJ mol^{-1} for the asymmetric complex: within the uncertainties, the gas-phase complexation enthalpies are seen to be equal. For the BF_3 complexes the gas-phase values are found to be −13.1(5) kJ mol^{-1} for the symmetric, and −11.8(7) kJ mol^{-1} for the asymmetric complex. In contrast with the HCl complexes, for the BF_3 complexes the higher stability of the symmetric complex persists in the gas phase.

Complexation Energy. In a final step, the ΔH_{gas} were converted into energy differences by correcting for zero point and thermal contributions.[68] The translational and rotational contributions were calculated in the classical limit, while the vibrational zero point and thermal contributions were calculated using the DFT frequencies of the species. The corrections amount to 3.4 and 3.5 kJ mol^{-1} for the symmetric and asymmetric HCl complexes, and 2.2 kJ mol^{-1} for both BF_3 complexes. Assuming an uncertainty of 10% on these corrections, the "experimental" complexation energies for the symmetric and asymmetric HCl complexes are calculated to be $-15.7(8)$ and $-16.0(9)$ kJ mol^{-1}, and $-15.3(5)$ and $-14.0(8)$ kJ mol^{-1} for the BF_3 complexes.

The calculations performed here suggest that in the vapor phase the asymmetric HCl complex could be marginally more stable than the symmetric one, although the difference in complexation energy difference is well within the limits of uncertainty. Comparison with the data in Table 1 shows that for both Lewis acids the "experimental" complexation energy is much higher than the MP2/6-31+G(d,p) value; even taking into account the approximate way in which the subsequent corrections have been applied to our liquid phase complexation enthalpies, this shows that at that level of theory, the ab initio complexation energies are seriously underestimated. In agreement with previous observations,[69] however, it can be seen that the BSSE-corrected single point MP2/6-311++G(3df,2pd) calculations produce complexation energies that are in better agreement with the experimental values; for the HCl complexes the agreement is very good, while for the BF_3 complexes they still are somewhat underestimated. It is worth noting that for the HCl complexes the asymmetric complex is now predicted to be slightly more stable than the symmetric complex, which agrees with the observations. For the BF_3 complexes, the calculations predict that the symmetric isomer is more stable than the asymmetric one, and this is confirmed by the experimental values. Using their structural information, and using a pseudodiatomic force constant for the van der Waals stretching mode, obtained from a distributed multipole analysis, and assuming a Lennard-Jones potential for the stretching mode, Forest et al.[25] have derived an approximate complexation energy for the asymmetric complex. Their result, -9.9 kJ mol^{-1}, clearly is substantially smaller than the value derived in this study. The authors compare their result with the value, derived in the same way, for the cyclopropane/HCl complex. The latter, -9.3 kJ mol^{-1}, is somewhat smaller than for the MCP complex, and the authors conclude that these data presumably reveal the inductive effect of the methyl group in MCP. Our results fully confirm this conclusion, as both the complexation enthalpy, $-7.8(2)$ kJ mol^{-1}, and complexation energy, derived in a similar way, $-14.5(6)$ kJ mol^{-1}, of the cyclopropane complex are smaller than the corresponding values for the MCP complex

1:2 Complexes. Finally, a slightly more detailed assignment of the bands due to the 1:2 complex may be attempted. In a previous paragraph we have assigned the observed 1:2 bands to a chain-type complex, on the basis of the observed HCl stretches. In principle, also 1:2 complexes of a different type can be formed, in which each HCl interacts with one of the ring C−C bonds. The stability of this type of complex is influenced by an anti-cooperative effect,[70,71] i.e., the first hydrogen bond is weakened by the second one. It must, therefore, be expected that in an equilibrium environment the concentration of these complexes will be significantly lower than that of the chain-type complexes, for which a cooperative effect is active.[70,71] Consequently, from the absence of bands attributable to nonchain 1:2 complexes in the HCl stretching region is concluded that their concentration was below the detection level of the experiments.

The cooperative effect in the HCl chain complexes[70,71] tends to strengthen the interaction between the first HCl and the Lewis base. A consequence of this is that in the 1:2 complex the vibrational modes of the Lewis base are shifted slightly further away from their monomer values than in the 1:1 complex. Thus, the 1:2 band at 973.9 cm^{-1}, shifted by -10.4 cm^{-1} from the monomer band, must be associated with the 1:1 band at 976.3 cm^{-1}, which is shifted by -8.0 cm^{-1}. The latter has been assigned to the symmetric complex and, therefore, we assign the 973.9 cm^{-1} band to the 1:2 chain complex derived from the symmetric 1:1 complex. As it is unlikely that the shift for an MCP mode in the 1:2 complex is more than twice the value of the shift in the corresponding 1:1 complex, we have to assign the other 1:2 bands that are visible in Figures 3 and 4 to the same 1:2 complex. Despite its presence in quantities similar to that of the symmetric 1:1 complex, no bands due to the asymmetric 1:2 complex have been detected. Inspection of Figures 3 and 4 shows that this may well be the consequence of unfavorable circumstances in the spectrum, such as overlap by more intense monomer or 1:1 bands, rather than due to its absence in the solutions.

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Supporting Information Available: Table S1 reports MP2/6-31+G(d,p) equilibrium Cartesian coordinates of the 1:1 complexes between MCP and HCl and BF_3. Table S2 gives the B3LYP/6-311++G(d,p) frequencies of the 1:1 complexes between MCP and HCl. Table S3 gives the B3LYP/6-311++G(d,p) frequencies of the 1:1 complexes between MCP and BF_3. Table S4 gives a tentative assignment for methylcyclopropane. This material is available free of charge via the Internet at http://pubs.acs.org.

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