The manipulation sequence was continued and the decamers were lined up along one fcc domain to separate the racemic mixture into the pure compounds with the (*R*)-decamers in the top right part of the domain and the (*L*)-decamers below (Figure 3c). We note that in terms of the two-dimensional chiral NN molecules this is equivalent to an enantiomeric excess of 60%.

The present experiment adds the important capability of enantiomer separation to the previous studies on atomic-scale manipulation,[16] selective dissociation,[17–19] conformational analysis,[20] and chiral recognition.[2–11] Hence scanning probe based techniques are emerging as an important arsenal for nanochemistry. Both chiral recognition and enantioselective manipulation are key capabilities for future stereoselective chemical reactions on a single molecule basis.

Experimental Section

The NN clusters were obtained by dosing sub-monolayer amounts of NN (purified by vacuum sublimation at 300 K prior to use) onto the clean Au(111) substrate at room temperature in ultra-high vacuum and with subsequent cooling to 50 K within 24 h.

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The Carbonyl Chlorine(I) Cation $[ClCO]^+$**

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The cation $[ClCO]^+$ belongs to a family of linear, three-atom molecules with 30 electrons (such as OCS, ONP, ONS^+, and $ArCN^+$) which are of interest to theoreticians and which exhibit interesting spectroscopic properties. The carbonyl halogen(I) cations $[XCO]^+$ (X = F, Cl, Br) are also of practical importance as reactive intermediates in Friedel–Crafts reactions and in plasma etching processes. Whereas the $[XCO]^+$ ions (X = F,[1, 2] Cl,[3] Br[4]) have been extensively studied in the gas phase (mass spectra, dissociation energies, electron affinities,[2] rotational[5] and photoelectron[6] spectra for $[FCO]^+$), and both $[FCO]^+$[5] and $[ClCO]^+$[7, 8] have also been the subjects of theoretical calculations, there is only a single report in which the cations $[XCO]^+$ (X = Cl, Br, I) have been detected in the condensed phase as transients.[9] In this study[9] of the reaction of CO with Cl_2, Br_2, or I_2 in SO_2ClF/SbF_5 by ^{13}C NMR spectroscopy at −78 °C, three new singlets at $\delta = 133.7$, 127.0, and 100.4 are observed and attributed to the $[XCO]^+$ ions (X = Cl, Br, I) by comparison to the spectra of the corresponding X_2CO molecules. Thus short-lived carbon species are produced in superacidic solutions; however, ^{13}C NMR resonances alone are not sufficient evidence to conclusively and unambiguously establish the existence of the carbonyl halogen cations in the condensed phase.

While this manuscript was in preparation, we became aware, from two presentations at conferences,[10, 11] and of a comprehensive, so far unpublished, study of the $[ClCO]^+$ ion,[12] in which vibrational and ^{13}C NMR spectra as well as thermodynamic and ab initio calculations are discussed. The results appear to confirm and complement our observations, which are reported here.

We generated the $[ClCO]^+$ ion accidentally during attempts to synthesize the homoleptic carbonyl cation $[Fe(CO)_6]^{3+}$. In the reaction of $Fe(CO)_5$ with CO and Cl_2 as oxidizing agent in SbF_5, the salt $[Fe(CO)_6][Sb_2F_{11}]_2$ was obtained in high yield and found to be thermally stable to 100 °C.[13–15] The IR spectrum of this salt contains a new band at $2256\ cm^{-1}$, which was tentatively attributed to the unknown $[Fe(CO)_6]^{3+}$ ion,[13, 14] because the IR-active fundamental $\tilde{\nu}_{CO}$ (F_{1u}) of $[Ir(CO)_6]^{3+}$[16] is observed at $2254\ cm^{-1}$. We have found in the meantime that the band at $2256\ cm^{-1}$ is also observed when CO and Cl_2 are combined in SbF_5 in the absence of $Fe(CO)_5$. Hence the band is re-assigned as the $\tilde{\nu}_{CO}$ band of the $[ClCO]^+$

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ion. Optimization of the reaction conditions allows the $[ClCO]^+$ ion to be generated in such a high yield that its complete vibrational spectrum can be recorded.

If pure SbF_5 is combined with $COCl_2$ or $^{13}COCl_2$ or with a 1:1 mixture of CO or ^{13}CO and Cl_2 at a molar ratio of 4:1 in a sealed glass reactor bulb, the reaction mixture solidifies immediately. After ten minutes the mixture liquefies and the characteristic Raman bands of SbF_5 have disappeared. Instead the bands of the $[ClCO]^+$ or the $[Cl^{13}CO]^+$ ion, respectively, are observed (listed in Table 1), together with bands, attributed to oligomeric fluoroantimonate(v) anions of the type $[Sb_nF_{5n+1}]^-$ with $n > 2$. An unambiguous identification of the counteranion is not possible in the complex reaction mixture. Attempts to record a ^{13}C NMR spectrum of the suspension containing the $[Cl^{13}CO]^+$ ion were unsuccessful. The salt is apparently insoluble in SbF_5 and the width of the ^{13}C NMR resonance line is too large to permit a comparison with the results from the earlier study.[9] Within three days the intensities of the Raman lines of the $[ClCO]^+$ ion decreased noticeably. The suspension changed to a clear liquid, in which among others bands due to the $[SbCl_4]^+$ ion are observed at 444, 392, 140, and 124 cm^{-1}.[17, 18] This implies a Cl/F exchange has taken place, and COFCl and COF_2 as well as small amounts of CF_4 and CO_2 were detected in the gas phase by IR spectroscopy. The IR spectrum of the suspension was recorded on a thin film between silicon discs, prepared inside a drybox.

Table 1. Assignment of the observed vibrational wavenumbers $\tilde{\nu}$ [cm^{-1}] of $[ClCO]^+$ by comparison with calculated wavenumbers.[a]

Assignment	Repr.		$[Cl^{12}CO]^+$		$[Cl^{13}CO]^+$	
		IR_{calcd}[b]	IR	Raman	IR	Raman
$2\nu_1$	Σ	4479 (0.07)	4486 (0.6)		4376 (0.4)	
$\nu_1 + 2\nu_3$	Σ		3188 (0.6)		3106 (0.5)	
$\nu_1 + \nu_2$ (^{35}Cl)	Σ	3052 (1.4)	3056 (2.4)		2995 (1.2)	
$\nu_1 + \nu_2$ (^{37}Cl)	Σ	3042 (0.5)	3047 (1.4)		2986 (1.1)	
$\nu_1 + \nu_3$	Π		2718 (0.06)		2649 (0.03)	
$5\nu_3$	Π		2344 (4.5)		2279 (1.5)	
ν_1,ν_{CO} (^{16}O)	Σ	2254 (100)	2256 (100)	2256 (100)	2200 (100)	2200 (100)
ν_1,ν_{CO} (^{18}O)	Σ		2212 (0.3)		2155 (1.2)	
$2\nu_3$	Σ		945 (3.0)	945 (14)	918 (1.8)	
ν_2,ν_{CCl} (^{35}Cl)	Σ	800 (5.9)	803 (7.5)	803 (76)	797 (7.1)	797 (65)
ν_2,ν_{CCl} (^{37}Cl)	Σ	790 (2.0)	794 (4.0)	794 (50)	788 (3.7)	789 (54)
ν_3,ν_{ClCO}	Π	475[c]	468 (27)		454 (27)	

[a] The expected band for the overtone $3\nu_3$ is hidden by a group of unassigned bands in the region 1200 – 1700 cm^{-1}. Values in parentheses are relative intensities. The relative intensities for the Raman bands ν_1, ν_2, and ν_3 are calculated by using the basis set RHF/6 – 311G(3df,3pd)[19] to be 100:41:0.4 respectively. [b] Ref. [7]. [c] Ref. [8].

The observed vibrational band positions of the $[ClCO]^+$ ion are listed in Table 1 and compared to calculated values of the gas-phase cation.[7, 8] The calculated band positions were obtained by ab initio calculations with large basis sets,[7, 8] in which all anharmonicity corrections, with the exception of the Fermi resonances by the ν_3 progression, are taken into account. The agreement between calculated band positions for $[ClCO]^+$(g) and the experimentally observed positions for $[ClCO]^+$ is excellent. Hence the existence of the $[ClCO]^+$ ion in the condensed phase is clearly and unambiguously established.

The vibrational spectrum of the $[ClCO]^+$ ion bears some resemblance to those of the isoelectronic species ClCN[20] and SCO:[21] for the Σ representation there are a multitude of anharmonic resonances between various overtones or combinations with ν_1 and ν_2. These resonances impede a normal coordinate analysis, which requires the use of unperturbed fundamentals. Accordingly the band positions of ν_2 in Table 2 are corrected for Fermi resonance with $2\nu_3$ as described previously.[21] By using calculated[8] structural parameters $r_{CO} = 122.2$ pm, $r_{Cl} = 156.6$ pm and the vibrational data from Table 2, the following force constants, normalized to 100 pm, are obtained with the program MOLVIB:[22] $F_{CO} = 19.2(2)$, $F_{CCl} = 6.51(5)$, $F_{CO/CCl} = 0.8(1)$ and $F_{OCCl} = 0.5034(7)$ 10^2 N m^{-1}. Vibrational data calculated with these force constants are compared in Table 2 to the corresponding input data.

Table 2. Assignment of observed and calculated vibrational wavenumbers $\tilde{\nu}$ [cm^{-1}] of the fundamentals of $[ClCO]^+$.

Assignment	$[Cl^{12}CO]^+$		$[Cl^{13}CO]^+$	
	obs.	calcd.[a]	obs.	calcd.[a]
ν_1 (^{16}O)	2255.6	2256.3	2199.6	2199.4
ν_1 (^{18}O)	2212.2	2212.5	2154.8	2154.0
ν_2[b] (^{35}Cl)	810.7	811.5	806.1	806.1
ν_2[b] (^{37}Cl)	801.7	801.8	797.0	796.1
ν_3	467.8	468.0	454.3	454.1

[a] The calculated wavenumbers of the vibrations ν_1 and ν_3 for $[^{37}ClCO]^+$ are 0.3 and 0.5 cm^{-1} smaller respectively, than for $[^{35}ClCO]^+$. [b] Corrected for Fermi resonance with $2\nu_3$ ($X_{33} - X_{ll} = 0.25$, $W_{233} = 32.8$ cm^{-1}), see text.

The CO stretching force constant F_{CO} of $19.2(2) \times 10^2$ N m^{-1} is significantly larger than in the free CO molecule (18.6×10^2 N m^{-1}[23]) but clearly smaller than in the $[HCO]^+$ ion (21.3×10^2 N m^{-1}[24]). It follows that in the $[ClCO]^+$ ion, CO is bonded in a very similar manner to that in the homoleptic metal carbonyl cations,[25] $[M(CO)_n]^{m+}$, where π bonding is strongly reduced and σ bonding to M causes a polarization of the CO bond.[25] Hence the agreement in band positions between ν_1 of $[ClCO]^+$ (Tables 1 and 2) and ν_6 (F_{1u}) of $[Ir(CO)_6]^{3+}$,[16] which motivated this work, is not surprising. The force constant F_{CCl} of 6.51×10^2 N m^{-1} is unusually large but characteristic for Cl – C bonds involving sp-hybridized carbon as in C_2Cl_2 (5.2×10^2 N m^{-1};[26] calculated according to ref. [22]) or in ClCN (5.3×10^2 N m^{-1}[8]).

We have shown in this study that the superelectrophilic cation $[ClCO]^+$, generated in the Lewis superacid SbF_5 as reaction medium, can form salts with oligomeric fluoroantimonate(v) anions that are sufficiently stable at ambient temperature to allow a detailed vibrational study. However, the salts cannot be isolated because removal of excess SbF_5 at 25 °C results in slow decomposition, as evidenced by the evolution of COFCl. Interestingly, our earlier attempts[13–15] at the synthesis of $[Fe(CO)_6]^{3+}$ ion led to a solid product mixture, in which the $[ClCO]^+$ ion is one component, that is thermally stable at room temperature for several months.

The reaction of SbF_5 with COF_2 under similar conditions produced the O-bonded adduct $F_2CO \cdot SbF_5$[27] and not the

$[FCO]^+$ ion. From a CO/Br_2 mixture and SbF_5 no evidence for $[BrCO]^+$ was obtainable. It is concluded that the $[FCO]^+$ ion is a stronger electrophile than the $[ClCO]^+$ ion, while the $[BrCO]^+$ ion is less thermally stable than the $[ClCO]^+$ ion.

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The Critical Importance of Water in the Asymmetric Allylboration of *N*-Trimethylsilylbenzaldimines with *B*-Allyldiisopinocampheylborane

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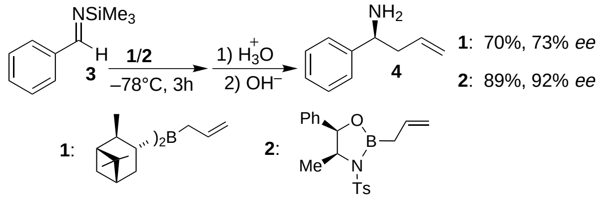
Dedicated to Professor Heinrich Nöth
on the occasion of his 70th birthday

Among the several α-pinene-based asymmetric synthetic methods[1] that we have developed over the last ten years, the allylboration of aldehydes with *B*-allyldiisopinocampheylborane (**1**, D-Ipc_2BAll)[2] has been adopted in numerous syntheses.[3] Recently, we reported an efficient synthesis of C_2-symmetric diols with very high diastereoselectivity (*de*) and enantioselectivity (*ee*) by the allylboration of various dicarboxaldehydes with **1**.[4]

On the contrary, there are only a few reports on the allylboration of aldimines, probably owing to the inherent instability of such imines and the lack of reactivity of the more stable N-substituted imines.[5] Recently, Itsuno and co-workers reported the asymmetric allylboration of various N-masked benzaldimines with a variety of allylborating agents, including **1** (Scheme 1).[6] They concluded that *N*-trimethylsilylaldimine is the most reactive species for such allylborations. The reaction can be carried out at −78 °C to give the corresponding homoallylamines with up to 92 % *ee* upon use of the norephedrine derivative **2** as the chiral auxiliary. Villieras and co-workers adopted Itsuno's methodology for the allylboration of *N*-trimethylsilylaldimines with a 2-ethoxycarbonyl-substituted allylboronate.[7]



Scheme 1. Asymmetric allylboration of **3** with **1** or **2**.

We previously established that the rate of allylboration of aldehydes with **1** is exceptionally fast at −78 °C, and fast even at −100 °C.[8] It appeared desirable to obtain comparable information about the allylboration of imines, especially trimethylsilylaldimines, which Itsuno had reported to be very facile. Accordingly, we mixed *N*-trimethylsilylbenzaldimine (**3**) and **1** in THF at −78 °C and followed the rate of reaction by ^{11}B NMR spectroscopy. To our great surprise, we observed no reaction after several hours, not even after a week at room temperature! Clearly there is a discrepancy with the literature

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