(2) Both diastereoisomers are obtained in a *meso/dl* ratio of 60:40. However, recrystallization of the mixture results in the pure meso form.

(3) The diastereoisomerization barrier of *meso* → *d*(or *l*) (98 kJ mol^{-1}) is similar to that of a related monoradical as could have been inferred from the analogy of their steric hindrances and interconversion two-ring flip mechanisms expected for both compounds.

(4) The obtained ESR spectra (zfs parameters) are consistent with the C_s and C_2 symmetries expected for *meso*-**3** and *dl*-**3**, respectively.

(5) The diastereoisomers have both in solution and in solid state triplet ground states irrespective of the lack of planarity and distinct symmetry. Consequently, the current theories for the prediction of ground-state multiplicities in nondisjoint AH are validated, regardless of these geometrical features.

Finally, the results obtained with the biradical **3** open the possibility of obtaining molecules such as polymer **1** with a very large spin multiplicity and for which a high stability is expected.

Acknowledgment. This research was supported by the Programa Nacional de Nuevos Materiales, CIC y T (Grant MAT88-0268). We thank Mrs. A. Diez for operating the ESR spectrometer and the Faraday magnetometer and Mrs. N. Jullian for some computer programs used in the simulation of ESR spectra.

Registry No. 3, 127316-84-1; **4**, 131380-97-7; **5**, 2136-96-1; **6**, 131380-98-8; $CHCl_3$, 67-66-3; C_6HCl_5, 608-93-5; 1,2,3,5-tetrachlorobenzene, 634-90-2.

Activation of α-Bromo Ketones by Complexation with Hard and Soft Lewis Acids. A Combined X-ray and NMR Study[1]

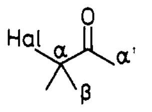
Thomas Laube,* André Weidenhaupt,† and Richard Hunziker

Contribution from the Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule Zürich, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland.

Received August 20, 1990

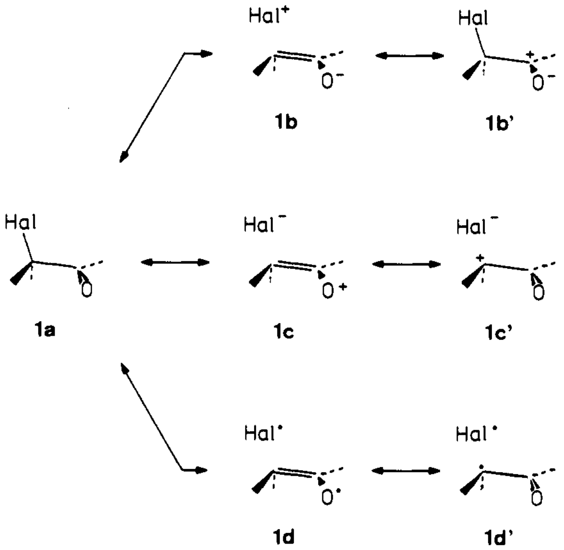
Abstract: α-Halo ketones have two heteroatoms with lone pairs where a Lewis acid can be bound, depending on the softness or hardness of the Lewis acid (HSAB principle). The crystal structures of the complexes **2**·$SbCl_5$, **3**·$SbCl_5$, **8**·$AgSbF_6$, and $(\mathbf{2})_2\cdot AgSbF_6$ have been determined in order to analyze the structural and electronic changes in the bromo ketone molecules upon complexation and the different binding properties of a hard ($SbCl_5$) and a soft Lewis acid (Ag^+). The monodentate Lewis acid $SbCl_5$ binds to the oxygen atom, whereas the silver ion is coordinated to the O and the Br atom of a bromo ketone in a chelate-like manner and to the π-systems of phenyl rings. ^1H and ^{13}C NMR measurements of the complexes and of the pure bromo ketones in solution support and complete the results of the X-ray structure determinations: $SbCl_5$ activates the C=O bond by raising the contribution of the $C^+—O^-$ resonance formula, whereas Ag^+ activates preferentially the C—Br bond by raising the contribution of the C^+Br^- resonance formula. The observations are in agreement with reactivity data from the literature.

α-Halo ketones **1** react with a wide variety of reagents[2,3] and are thus an important class of organic compounds. Nucleophiles can not only attack **1** at the carbonyl-C atom (nucleophilic addition), at the halogen (Hal)-substituted α-C atom (nucleophilic substitution), or even at the halogen atom but also deprotonate the α-, α′-, or the β-C atom and initialize different subsequent reactions.[3] The neighborhood of two C atoms prone to nucleophilic attack (**1** can be considered as an ambident electrophile) complicates the prediction of the chemical behavior as well as the conformation of **1**,[4] and therefore some of the earliest works about stereochemical effects by Corey et al.[5] deal with the interaction between the C=O and the C—Hal bonds. In terms of the valence bond (VB) theory, resonance structures **1a** and **1b** are often used in order to explain the variation of the properties of the C—Hal bond with the torsion angle Hal—C—C=O[4,5] (see Scheme I).



1

Scheme I



The credibility of the resonance formula **1b**, however, suffers from the positive charge on the halogen atom (although there is no question about the existence of halonium ions[6,7]), but alternative formulas like **1c** and **1c′** are not better because of the neighborhood of a carbocationic center and a carbonyl group (although the

---

† Present address: Eidgenössische Anstalt für Wasserversorgung, Abwasserreinigung and Gewässerschutz (EAWAG), CH-8600 Dübendorf, Switzerland.

(1) Contains parts of the diploma theses of A.W. (ETH Zürich, June 1989) and R.H. (ETH Zürich, June 1990).

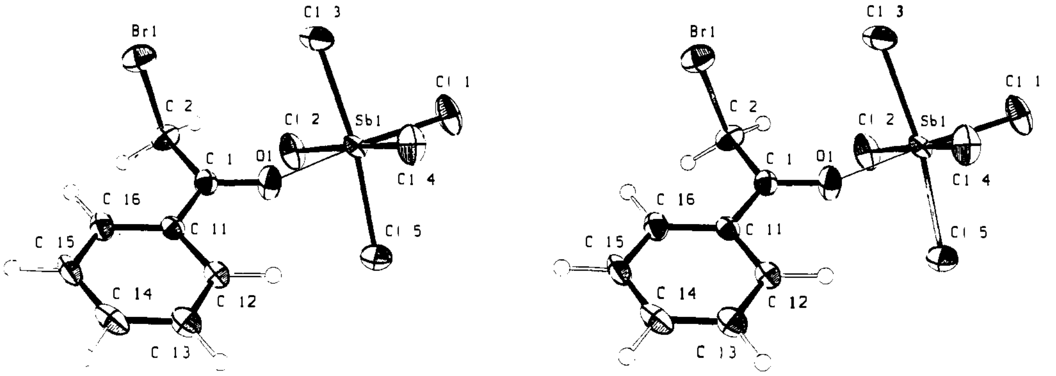


Figure 1. Stereodrawing (ORTEP) of the crystal structure of **2**·$SbCl_5$. The ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are represented by spheres with a radius of 0.1 Å.

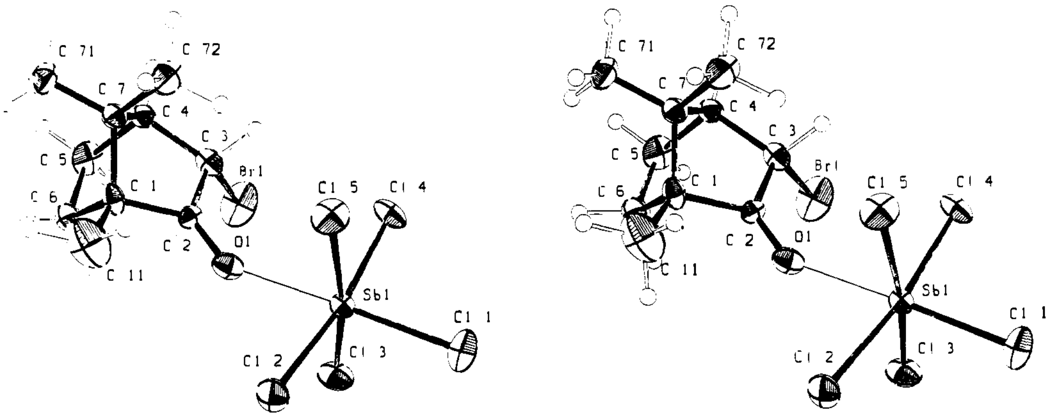


Figure 2. Stereodrawing (ORTEP) of the crystal structure of **3**·$SbCl_5$. The ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are represented by spheres with a radius of 0.1 Å.

normal polarity of the C—Hal bond is here only enhanced and α-keto cations are also proven[8]). Finally, even resonance formulas **1d** and **1d′** deserve some attention because of the photoreactivity of α-halo ketones.[9] Resonance formula **1b** seems to be valid only for torsion angles |Hal—C—C=O| about 90°, whereas **1c** (and perhaps also **1d**) can be operative at any torsion angle (the structure of α-keto cations is controversial[10,11]). The Fourier analysis of the rotation barrier in chloroacetaldehyde[4] (computed by ab initio methods) shows that the coplanar arrangement of the C—Cl bond orbital and the carbonyl-C p orbital raises the energy if compared with a coplanar arrangement of a C—H bond orbital and the carbonyl-C p orbital (i.e, $V_2 > 0$), and this result indicates that none of the resonance formulas **1b–d** is stabilizing the coplanar arrangement of the C—Hal bond and carbonyl-C p orbitals (the V_1 and V_3 terms do not point to any unexpected effects).

In order to clarify the ambiguity concerning the influence or validity of the previously mentioned resonance formulas (and the related charge distributions) in α-halo ketones, we have carried

Table I. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of **2**·$SbCl_5$

Br1–C2	1.950 (8)	C1–C11	1.45 (1)	C1–C2	1.50 (1)
C1–O1	1.247 (9)	C11–C12	1.41 (1)	C11–C16	1.38 (1)
C12–C13	1.39 (1)	C13–C14	1.38 (1)	C14–C15	1.39 (1)
C15–C16	1.37 (1)	O1–Sb1	2.168 (5)	Br1–C13	3.671 (3)
C11–C1–C2	122.0 (7)	C11–C1–O1	117.5 (7)		
C2–C1–O1	120.5 (7)	Br1–C2–C1	107.0 (5)		
C1–O1–Sb1	146.0 (5)				
Sb1–O1–C1–C2	−7 (1)	O1–C1–C2–Br1	−99.3 (7)		
O1–C1–C11–C16	+172.1 (7)	O1–C1–C11–C12	−4 (1)		

Table II. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of **3**·$SbCl_5$

Br1–C3	1.95 (1)	C1–C11	1.58 (2)	C1–C2	1.49 (2)
C1–C6	1.59 (2)	C1–C7	1.53 (2)	C2–C3	1.47 (2)
C2–O1	1.20 (1)	C3–C4	1.53 (2)	C4–C5	1.53 (2)
C4–C7	1.55 (2)	C5–C6	1.52 (2)	C7–C71	1.47 (2)
C7–C72	1.54 (2)	O1–Sb1	2.23 (1)	Br1–C14	3.599 (5)
C2–C1–C6	105 (1)	C2–C1–C7	102 (1)		
C1–C2–C3	105 (1)	C1–C2–O1	127 (2)		
C3–C2–O1	128 (2)	Br1–C3–C2	111 (1)		
C2–O1–Sb1	147 (1)				
Sb1–O1–C2–C3	+35 (3)	C6–C1–C2–O1	−111 (2)		
C7–C1–C2–O1	+142 (2)	C11–C1–C2–O1	+13 (2)		
O1–C2–C3–Br1	+57 (2)	O1–C2–C3–C4	−178 (1)		

---

(2) De Kimpe, N.; Verhé, R. *The Chemistry of α-Haloketones, α-Haloaldehydes and α-Haloimines*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1988.

(3) Reviews about synthesis and reactions of α-halocarbonyl compounds: Tchoubar, B. *Bull. Soc. Chim. Fr.* **1955**, 1363–1383. Bayer, O. *Methoden Org. Chem.* (*Houben-Weyl*), 4th ed.; Thieme: Stuttgart, 1977; Vol. 7, Issue 2c, pp 2145–2170. Bouquet, M. *Janssen Chim. Acta* **1984**, *2*, 12–16.

(4) Laube, T.; Ha, T.-K. *J. Am. Chem. Soc.* **1988**, *110*, 5511–5517 and references cited therein.

(5) Corey, E. J. *Experientia* **1953**, *9*, 329–331. Corey, E. J. *J. Am. Chem. Soc.* **1953**, *75*, 2301–2304. Corey, E. J. *J. Am. Chem. Soc.* **1953**, *75* 3297–3299. Corey, E. J. *J. Am. Chem. Soc.* **1953**, *75*, 4832–4834. Corey, E. J. *J. Am. Chem. Soc.* **1954**, *76*, 175–179. Corey, E. J.; Topie, T. H.; Wozniak, W. A. *J. Am. Chem. Soc.* **1955**, *77*, 5415–5417. Corey, E. J.; Burke, H. J. *J. Am. Chem. Soc.* **1955**, *77*, 5418–5420.

(6) Olah, G. A. *Halonium Ions*; John Wiley & Sons: New York, 1975.

(7) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504–4508.

(8) See, for example: (a) Takeuchi, K.; Kitagawa, T.; Okamoto, K. *J. Chem. Soc., Chem. Commun.* **1983**, 7. Reviews: (b) Bégué, J.-P.; Charpentier-Morize, M. *Acc. Chem. Res.* **1980**, *13*, 207–212. (c) Tidwell, T. T. *Angew. Chem., Int., Ed. Engl.* **1984**, *23*, 20. (d) Creary, X. *Acc. Chem. Res.* **1985**, *18*, 3–8.

(9) Morrison, H. *Rev. Chem. Intermed.* **1987**, *8*, 125–145.

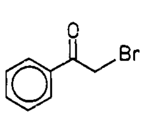
(10) Creary, X.; Hopkinson, A. C.; Lee-Ruff, E. *Adv. Carbocation Chem.* **1989**, *1*, 45–92.

(11) Charpentier-Morize, M.; Bonnet-Delpon, D. *Adv. Carbocation Chem.* **1989**, *1*, 219–253.

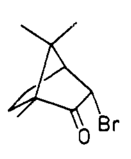
out X-ray structure analyses of complexes between α-bromo ketones and a hard[12] Lewis acid ($SbCl_5$), that is bound to the oxygen atoms (and should therefore raise the influence of the resonance formulas **1b** and **1b′**)[13] or a soft Lewis acid (Ag^+; in the form of $AgSbF_6$) that is mainly bound to the bromine atom (and should therefore raise the influence of the resonance formulas **1c** and **1c′**). In addition to these structural studies, the ^{13}C NMR spectra of the complexes and the corresponding pure α-bromo ketones were compared in order to deduce experimentally the changes of partial charges upon complexation.

Results

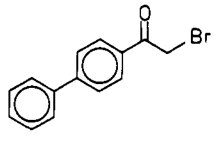
Complexes with the Hard Lewis Acid $SbCl_5$. X-ray Structure Analyses. The activation of carbonyl groups by complexation with Lewis acids (H^+, metal ions, neutral Lewis acids like BF_3, etc.) takes place prior to almost every nucleophilic attack to a carbonyl group,[14] and therefore, many theoretical,[15] IR,[16] NMR,[17] and X-ray[18] investigations of activated ketones or other types of carbonyl compounds have already been carried out but none with α-halo ketones. In order to display any effect most clearly, we have chosen a very strong Lewis acid ($SbCl_5$) that can bind the bromo ketone only as a monodentate ligand via the oxygen atom. Among a wide variety of commercially available α-halo ketones, phenacyl bromide (**2**), and (+)-3-*endo*-bromocamphor (**3**) gave upon reaction with $SbCl_5$ and recrystallization from CH_2Cl_2 suitable crystals for a crystal structure analysis (see Figures 1 and 2 and Tables I and II).



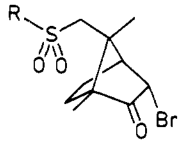
2



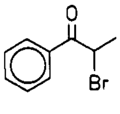
3



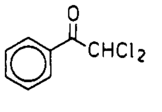
4



5



6



7

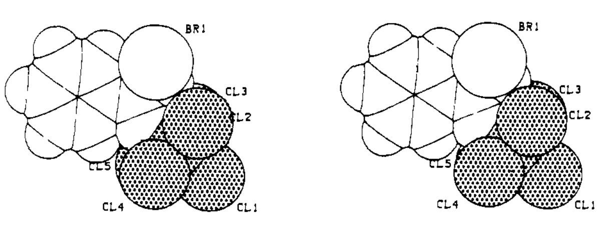
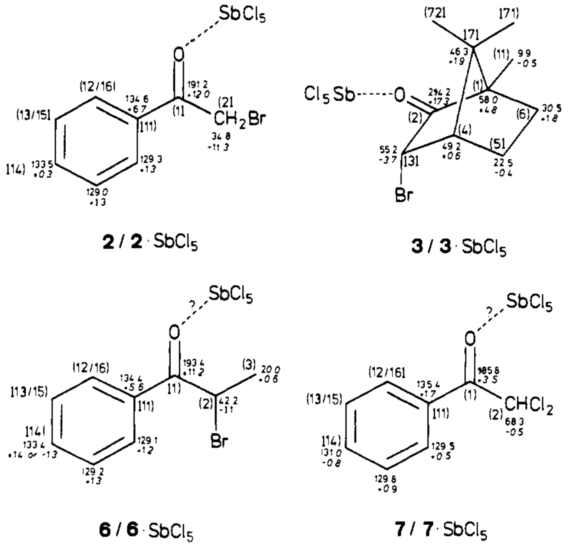


Figure 3. Stereodrawing of a space-filling model of **2**·$SbCl_5$ (atoms of **2**, white; $SbCl_5$, rastered). The atoms are represented by spheres with the corresponding van der Waals radii.



2 / 2·$SbCl_5$ **3 / 3**·$SbCl_5$

6 / 6·$SbCl_5$ **7 / 7**·$SbCl_5$

Figure 4. ^{13}C NMR chemical shifts (upper values) of **2**, **3**, **6**, and **7** and ^{13}C NMR chemical shift *differences* (lower values) between the $SbCl_5$ complexes and the pure halo ketones. The assignments of the *o*- and *m*-C atoms were made by comparison with literature data and are therefore unsafe. All measurements were done in CD_2Cl_2 at −80 °C.

The complex **2**·$SbCl_5$ shows that the Lewis acid is bound to the oxygen atom in the usual way; i.e., the O1—Sb1 vector points approximately into the direction of an sp^2-like oxygen lone pair.[13] As in many other complexes between carbonyl compounds and Lewis acids, the C=O bond is lengthened by ca. 0.05 Å upon complexation (C1=O1, 1.247 (9) Å). The best crystal structure that delivers data for a comparison between **2**·$SbCl_5$ and an uncomplexed α-bromo ketone is that of 2-bromo-4′-phenylacetophenone (**4**) by Sim[19] because all other structures are less precise or less similar to **2**. The most striking feature of **2** in **2**·$SbCl_5$ is the torsion angle O1=C1—C2—Br1 of −99.3 (7)° because **4** has a synperiplanar arrangement of the C—Br and the C=O bond (O1=C1—C2—Br1, +1.5 (7)°). The C2—Br1 bond of **2**·$SbCl_5$ is lengthened to 1.950 (8) Å if compared with **4** (1.915 (6) Å), and the C1—C2—Br1 angle is significantly reduced to 107.0 (5)° (**4**, 114.4 (4)°). Remarkable too is the shortening of the C1—C11 bond (**2**·$SbCl_5$, 1.45 (1) Å; **4**, 1.481 (7) Å). The unusual conformation of **2** in **2**·$SbCl_5$ may be due to a van der Waals interaction between the bromine atom and the $SbCl_5$ moiety (see Figure 3).

The crystal structure of **3**·$SbCl_5$ is less precise than that of **2**·$SbCl_5$ (perhaps due to the effect that **3** is a small spherelike molecule and thus shows even in the complex **3**·$SbCl_5$ a considerable libration,[20] see Experimental Part) and can therefore only serve as a confirmation of the binding of the Lewis acid to the oxygen of **3** (Figure 2). The rigid cage of **3** does not allow any easy change of the conformation upon complexation, and therefore, the observed torsion angle O1=C2—C3—Br1 (+57 (2)°) of **3**·$SbCl_5$ is only slightly larger than in **5**[21] (+52 (1)°). The C2=O1

---

(12) For the HSAB theory, see: Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581–587. Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 643–648. Ho, T.-L. *Hard and Soft Acids and Bases Principle in Organic Chemistry*; Academic Press: New York, 1977.

(13) For the activation of a ketone by complexation with $SbCl_5$ and the induced charge redistribution in the ketone, see: Laube, T.; Stilz, H. U. *J. Am. Chem. Soc.* **1987**, *109*, 5876–5878.

(14) Schinzer, D., Ed. *Selectivities in Lewis Acid Promoted Reactions*; Kluwer Academic Publishers: Dordrecht, 1989.

(15) LePage, T. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 6642–6650.

(16) Susz, B. P. *Bull. Soc. Chim. Fr.* **1965**, 2671–2675. Vančik, H.; Sunko, D. E. *J. Am. Chem. Soc.* **1989**, *111*, 3742–3744.

(17) Olah, G. A.; Calin, M.; O'Brien, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 3586–3590. Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 5801–5810. Olah, G. A.; Grant, J. L. *J. Org. Chem.* **1977**, *42*, 2237–2240. Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1982**, *104*, 2373–2376.

(18) Some examples: (a) Reetz, M. T.; Harms, K.; Reif, W. *Tetrahedron Lett.* **1988**, 5881–5884. (b) Brun, L.; Brändén, C.-I. *Acta Crystallogr.* **1966**, *20*, 749–758. (c) Poll, T.; Metter, J. O.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 112. (d) Denmark, S. E.; Henke, B. R.; Weber, E. *J. Am. Chem. Soc.* **1987**, *109*, 2512–2514. (e) Reetz, M. T.; Hüllmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405–2408. (f) Oppolzer, W.; Rodriguez, I.; Blagg, J.; Bernardinelli, G. *Helv. Chim. Acta* **1989**, *72*, 123–130. Protonated or O-alkylated ketones: (g) Childs, R. F.; Faggiani, R.; Lock, C. J. L.; Mahendran, M.; Zweep, S. D. *J. Am. Chem. Soc.* **1986**, *108*, 1692–1693. (h) Chadda, S. K.; Childs, R. F.; Faggiani, R.; Lock, C. J. L. *J. Am. Chem. Soc.* **1986**, *108*, 1694–1695. (i) Montgomery, L. K.; Grendze, M. P.; Huffmann, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4749–4750.

(19) Sim, G. A. *Acta Crystallogr., Sect. C* **1986**, *C42*, 1411–1413. We do not use the atom numbers of the author but prefer a numbering in analogy to **2**·$SbCl_5$.

(20) The phenomenon of plastic crystallinity, resulting from rotation of small spherelike molecules in the crystal is well-known; see, for example: Sherwood, J. N. *The Plastically Crystalline State (Orientationally-Disordered Crystals)*; John Wiley & Sons: Chichester, 1979.

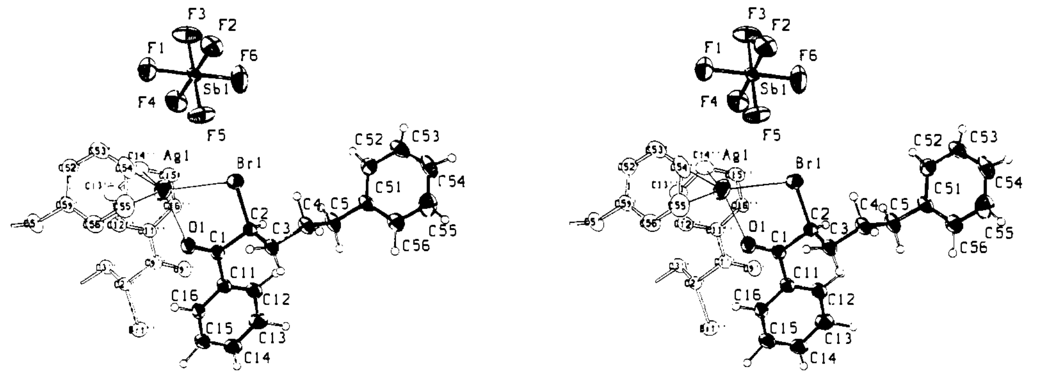


Figure 5. Stereodrawing (ORTEP) of the crystal structure of 8·$AgSbF_6$. The ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are represented by spheres with a radius of 0.1 Å. The partially shown symmetry-related molecules 8 were generated with the symmetry operations x, y, $z - 1$ (primed atoms) and $1 - x$, $1 - y$, $-z$ (doubly primed atoms).

bond, the C3—Br1 bond, and the C2—C3—Br1 angle of 3·$SbCl_5$ (1.20 (1), 1.95 (1) Å, 111 (1)°) do not differ from the corresponding values of 5[21] (1.198 (8), 1.950 (6) Å, 110.2 (3)°).[23]

NMR Spectroscopy. In order to obtain information about the change or generation of the partial charges in α-bromo ketones upon complexation, we have carried out ^{13}C NMR measurements of the ketones and their complexes in solution (CD_2Cl_2, -80 °C). In all cases, the samples of the complexes were generated by dissolving the recrystallized complexes in CD_2Cl_2. The chemical shifts of the α-bromo ketones **2**, **3**, **6**, and **7** and their *changes upon complexation with $SbCl_5$* are given in Figure 4 (the crystals of 6·$SbCl_5$ and 7·$SbCl_5$ were not suitable for an X-ray structure analysis).

In all cases, the carbonyl-C atom is shifted downfield and the bromine-substituted α-C atom is shifted upfield upon complexation. We thus assume that **6** and **7** are, like **2** and **3**, coordinated with their oxygen atoms to the Lewis acid (although the solid-state structure needs not necessarily be identical with the solution structure). Interestingly, the other α-C atoms (i.e., the ipso atoms C11 in **2**, **6**, and **7** and C1 in **3**) are shifted downfield upon complexation.

Complexes with the Soft Lewis Acid Ag^+. X-ray Structure Analyses. The literature contains already several examples of crystal structure analyses of compounds with a carbon-halogen bond whose halogen atoms is coordinated to a metal ion.[24] In order to study C—Br···Ag^+ interactions,[25] the use of silver(I) salts with very poorly coordinating counterions (in poorly coordinating solvents) is necessary to obtain stable complexes where the halogenated compound must not compete with the counterion or solvent molecules for the silver(I) ion. Therefore, only $AgSbF_6$ (i.e., the silver salt of a super acid) has up to now been used for the complexation of α-bromo ketones. The groups of Charpentier-Morize[26] and Anselme[27] reported already in the seventies the preparation and isolation of several complexes between α-bromo ketones and $AgSbF_6$, but no crystal structure analysis was performed. We report here the results of our crystallographic studies about the complexes 8·$AgSbF_6$[8b,26a] and $(2)_2$·$AgSbF_6$.[27]

Scheme II

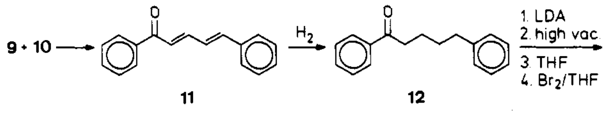


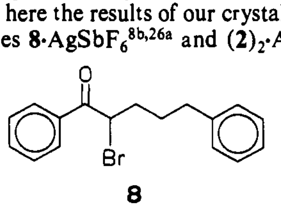
Table III. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of 8·$AgSbF_6$[a]

Ag1–Br1	2.738 (1)	Ag1–C54′	2.479 (7)	Ag1–C55′	2.504 (9)
Ag1–C14″	2.551 (8)	Ag1–O1	2.378 (4)	Br1–C2	1.963 (6)
C1–C11	1.491 (8)	C1–C2	1.534 (8)	C1–O1	1.202 (7)
C11–C12	1.381 (8)	C11–C16	1.392 (8)	C12–C13	1.402 (8)
C13–C14	1.39 (1)	C14–C15	1.38 (1)	C15–C16	1.388 (9)
C2–C3	1.505 (9)	C3–C4	1.547 (9)	C4–C5	1.482 (9)
C5–C51	1.510 (8)	C51–C52	1.385 (9)	C51–C56	1.367 (9)
C52–C53	1.37 (1)	C53–C54	1.32 (1)	C54–C55	1.42 (1)
C55–C56	1.40 (1)	Ag1–F5	3.390 (6)		

Ag1–Br1–C2	100.8 (2)	C11–C1–C2	116.9 (5)
C11–C1–O1	120.0 (5)	C2–C1–O1	123.1 (5)
Br1–C2–C1	110.7 (4)	Br1–C2–C3	110.7 (4)
C1–C2–C3	108.6 (5)	Ag1–C1–O1	130.1 (4)

Ag1–O1–C1–C2	+22 (1)	O1–C1–C2–Br1	−18.8 (8)
O1–C1–C2–C3	+102.9 (8)	C11–C1–C2–C3	−74.1 (7)
O1–C1–C11–C12	+163.8 (7)	O1–C1–C11–C16	−16.4 (9)
C2–C1–C11–C12	−19.0 (9)	C2–C1–C11–C16	+160.7 (6)
C1–C2–C3–C4	−178.1 (6)	C2–C3–C4–C5	−64.6 (8)
C3–C4–C5–C51	−176.0 (6)	C4–C5–C51–C52	−86.3 (9)
C4–C5–C51–C56	+92.5 (8)		

[a] For the symmetry operations, see Figure 5.



8

The bromo ketone **8** was synthesized according to literature procedures (see Scheme II), starting from cinnamaldehyde (**9**) and acetophenone (**10**) and yielding **11**,[28] which was hydrogenated

---

[21] For comparison with the structure of uncomplexed 3, we choose the averaged values of three precise crystal structures of the sulfo derivative 5 from the literature, which should have an unperturbed O=C—C—Br fragment. The references for these three structures and their Cambridge File[22] reference codes (in parentheses) are as follows: (a) Sato, M.; Sato, Y.; Yano, S.; Yoshikawa, S.; Toriumi, K.; Itoh, H.; Itoh, T. *Inorg. Chem.* **1982**, *21*, 2360–2364 (BIFNUZ). (b) Davis, F. A.; Jenkins, R. H., Jr.; Awad, S. B.; Stringer, O. D.; Watson, W. H.; Galloy, J. *J. Am. Chem. Soc.* **1982**, *104*, 5412–5418 (BOFTOF). (c) Hammershøi, A.; Sargeson, A. M.; Steffen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 2819–2837 (CIDLEG).

[22] Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153.

[23] Two C—C bonds of 3·$SbCl_5$ (C1–C11, 1.58 (2) Å; C7–C71, 1.47 (2) Å) deviate by three standard deviations from the corresponding values of 5 and are considered as manifestation of the low precision of the crystal structure of 3·$SbCl_5$.

[24] Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361–1366. Winter, C. H.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7560–7561. Crabtree, R. H.; Burk, M. J.; Segmuller, B. *Organometallics* **1987**, *6*, 2241–2246. Crabtree, R. H.; Kulawiec, R. J. *Organometallics* **1988**, *7*, 1891–1893. Waters, J. M.; Bown, M. *J. Am. Chem. Soc.* **1990**, *112*, 2442–2443. Colsman, M. R.; Noirot, M. D.; Miller, M. M.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1988**, *110*, 6886–6888. Newbound, T. D.; Colsman, M. R.; Miller, M. M.; Wulfsberg, G. P.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1989**, *111*, 3762–3764. Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfsberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 2349–2362.

[25] Only one other crystal structure analysis with a C—Br···Ag^+ interaction is known (silver bromomethanesulfonate), see: Charbonnier, F.; Faure, R.; Loiseleur, H. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3598–3601. The authors report C—Br = 1.938 (8) Å and Br···Ag^+ = 2.970 (5) Å.

[26] (a) Bégué, J. P.; Charpentier-Morize, M.; Pardo, C. *Tetrahedron* **1975**, *31*, 1919–1924. (b) Baudry, D.; Charpentier-Morize, M. *Tetrahedron Lett.* **1972**, 2561–2564. (c) Cambillau, C.; Charpentier-Morize, M. *J. Chem. Soc., Chem. Commun.* **1982**, 211–212.

[27] Nishiyama, K.; Anselme, J.-P. *J. Org. Chem.* **1978**, *43*, 2045–2048.

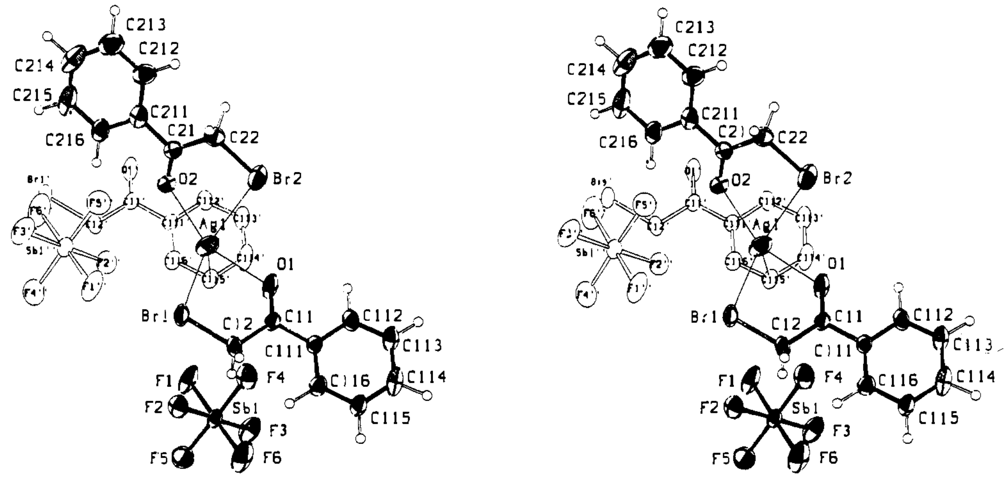


Figure 6. Stereodrawing (ORTEP) of the crystal structure of $(\mathbf{2})_2\cdot AgSbF_6$. The ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are represented by spheres with a radius of 0.1 Å. The symmetry-related molecules were generated with the symmetry operations $x + 1, y, z$ (primed atoms) and $1 - x, 1 - y, 1 - z$ (doubly primed atoms).

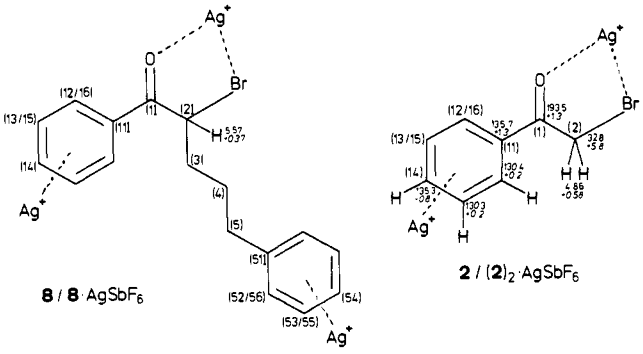
to the saturated ketone **12**.[29] In order to obtain **8** without any purification, we quenched the amine-free solution of the lithium enolate of **12** in THF (generated by evaporation of solvent and amine from the enolate solution to dryness and addition of pure THF) with Br_2/THF at low temperature.[30] The reaction of **8** with $AgSbF_6$ in CH_2Cl_2 (diffusion method) yielded crystals suitable for an X-ray structure analysis. The ORTEP diagram of **8**$\cdot AgSbF_6$ (see Figure 5) shows that the silver(I) ion is simultaneously coordinated to three different molecules of **8**: one molecule is bound as a chelating ligand with its oxygen and its bromine atoms (α-alkoxy ketones are bound in a similar way to Lewis acids[18a]), one is coordinated with its C1-phenyl ring, and one is coordinated with its C5-phenyl rings.

Vice versa, every bromo ketone molecule is bound to three silver(I) ions, and this polymer-like network may be responsible for the very low solubility of **8**$\cdot AgSbF_6$ in noncoordinating solvents.[31] The silver ion is pentacoordinated (to the atoms O1, Br1, C14″, C54′ and C55′, see Figure 5 and Table III), but the counterion SbF_6^- is *not* involved in the coordination[32] (the shortest Ag···F distance is Ag1···F5, 3.390 (6) Å). Although the silver ion is bound to the O *and* to the Br atom of one of the bromo ketone molecules and although both the Ag1···O1 and the Ag1···Br1 distances (2.378 (4) and 2.738 (1) Å) are normal,[33,34] the silver ion seems to influence practically only the C2—Br1 bond, which is significantly lengthened to 1.963 (6) Å if compared with **4**[19] (1.915 (6) Å). In contrast to **2**$\cdot SbCl_5$, the O1=C1—C2—Br1 torsion angle has a value −18.8 (8)° and is therefore similar to that in **4**. The C1=O1 bond has a length of 1.202 (7) Å and does not differ from the corresponding bond in **4** (1.196 (7) Å), whereas simple ketones[33] undergo a C=O lengthening upon complexation with Ag^+. The aliphatic chain in **8**$\cdot AgSbF_6$ shows a gauche arrangement (C2—C3—C4—C5, −64.6 (8)°) and is thus not in its ground-state conformation.[35] The bonds between the π systems

Table IV. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of $(\mathbf{2})_2\cdot AgSbF_6$[a]

Ag1–Br1	2.740 (3)	Ag1–Br2	2.794 (4)	Ag1–C115′	2.53 (2)
Ag1–O1	2.46 (1)	Ag1–O2	2.39 (1)	Ag1–F2″	3.27 (1)
Br1–C12	1.92 (2)	Br2–C22	1.90 (2)	C11–C111	1.50 (2)
C11–C12	1.51 (2)	C11–O1	1.21 (2)	C111–C112	1.41 (2)
C111–C116	1.38 (2)	C112–C113	1.38 (2)	C113–C114	1.45 (3)
C114–C115	1.40 (3)	C115–C116	1.41 (2)	C21–C211	1.51 (2)
C21–C22	1.52 (3)	C21–O2	1.19 (2)	C211–C212	1.37 (3)
C211–C216	1.38 (3)	C212–C213	1.41 (3)	C213–C214	1.38 (4)
C214–C215	1.35 (4)	C215–C216	1.40 (3)		
Ag1–Br1–C12	101.0 (6)	Ag1–Br2–C22	99.0 (7)		
C111–C11–C12	115 (2)	C211–C21–C22	117 (2)		
C111–C11–O1	121 (2)	C211–C21–O2	119 (2)		
C12–C11–O1	124 (2)	C22–C21–O2	124 (2)		
Br1–C12–C11	114 (1)	Br2–C22–C21	112 (2)		
Ag1–O1–C11	128 (1)	Ag1–O2–C21	130 (1)		
Ag1–O1–C11–C12	−6 (3)	Ag1–O2–C21–C22	+10 (3)		
O1–C11–C12–Br1	−5 (3)	O2–C21–C22–Br2	+10 (3)		
O1–C11–C111–C112	+7 (3)	O2–C21–C211–C216	+5 (3)		
O1–C11–C111–C116	−179 (2)	O2–C21–C211–C212	−177 (2)		
C12–C11–C111–C112	−176 (2)	C22–C21–C211–C216	−175 (2)		
C12–C11–C111–C116	−1 (3)	C22–C21–C211–C212	+3 (3)		

[a] For the symmetry operations, see figure 6.



8 / **8**$\cdot AgSbF_6$

2 / $(\mathbf{2})_2\cdot AgSbF_6$

Figure 7. ^1H and ^{13}C NMR chemical shifts (upper values) of **8** and **2** and the corresponding chemical shift *differences* (lower values) between the $AgSbF_6$ complexes and the pure bromo ketones. The assignments of the *o*- and *m*-C atoms were made by comparison with literature data and are therefore unsafe. All measurements were done in SO_2 at room temperature.

---

(28) Overberger, C. G.; Monagle, J. J. *J. Am. Chem. Soc.* **1956**, *78*, 4470–4473.

(29) General procedure taken from: *Organikum*, 9th ed.; Deutscher Verlag der Wissenschaften: Berlin, 1969; p 318.

(30) See also: Bond, F. T.; Ho, C.-Y.; McConnell, O. *J. Org. Chem.* **1976**, *41*, 1416–1420. Stotter, L. P.; Hill, K. A. *J. Org. Chem.* **1973**, *38*, 2576–2578.

(31) **8**$\cdot AgSbF_6$ may be dissolved in acetonitrile, but upon recrystallization, only acetonitrile-solvated $AgSbF_6$ is obtained. For the crystal structure analysis of a compound containing the cation $[Ag(NCCH_3)_4]^+$, see: Nilsson, K.; Oskarsson, A. *Acta Chem. Scand., Ser. A* **1984**, *38*, 79–85.

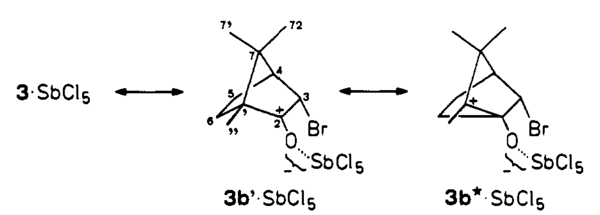
(32) The crystal structures of $AgSbF_6$ (Bode, H. *Z. Anorg. Allg. Chem.* **1951**, *267*, 62–64), $[Ag(NCCl)_2][SbF_6]$ (Roesky, H. W.; Schimkowiak, J.; Jones, P. G.; Noltemeyer, M.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1988**, 2507–2508), and $[Ag(NCH)_2][SbF_6]$ (Jones, P. G.; Roesky, H. W.; Schimkowiak, J. *J. Chem. Soc., Chem. Comm.* **1988**, 730) have shortest Ag···F distances between 2.61 and 2.80 Å!

(33) Only the structure of one comparable ketone–silver(I) complex is known ((*p*-methylacetophenone)$_2\cdot AgBF_4$), see: Crist, D. R.; Hsieh, Z.-H.; Quicksall, C. O.; Sun, M. K. *J. Org. Chem.* **1984**, *49*, 2478–2483. The authors report Ag···O, 2.36 (1) Å; C=O, 1.25 (2) Å; shortest Ag···C, 2.55 (1) Å.

(34) A search in the Cambridge File yields 114 Ag···Br bonds (average distance, 2.76 (1) Å). For AgBr, one finds Ag···Br distances between 2.87 and 2.89 Å, depending on the temperature: Takahashi, H.; Tamaki, S.; Sato, S. *J. Phys. Soc. Jpn.* **1987**, *56*, 3593–3597.

(35) A simple force field calculation for **8** (in the gas phase) with MM2 (in MACROMODEL, Version 1.5, 1987) shows that the observed conformation is ~1 kcal/mol higher in energy than the all-trans conformation. For MM2, see: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127–8134. MACROMODEL: Still, C. Columbia University, New York, NY 10027.

Scheme III



3b′·SbCl5 3b*·SbCl5

of the phenyl rings and the silver atom (shortest Ag···C distances: Ag1···C14″, 2.551 (8) Å; Ag1···C54′, 2.479 (7) Å; Ag1···C55′, 2.504 (9) Å) lie in the expected range.[36]

Similar features were observed in the crystal structure of $(\mathbf{2})_2\cdot AgSbF_6$: the silver ion is coordinated by the two O=C—C—Br units of the crystallographically independent bromo ketone molecules (C11=O1, 1.21 (2) Å; C12—Br1, 1.92 (2) Å; C21=O2, 1.19 (2) Å; C22—Br2, 1.90 (2) Å), and a fifth coordinative bond to a *m*-C atom of a third phenacyl bromide molecule (Ag1···C115′, 2.53 (2) Å) leads also here to a polymeric structure[37] (see Figure 6 and Table IV).

The shortest Ag···F distance (Ag1···F2″, 3.27 (1) Å) excludes also here any coordination between Ag^+ and the counterion. In contrast to $\mathbf{2}\cdot SbCl_5$, the conformation of **2** in $(\mathbf{2})_2\cdot AgSbF_6$ is hardly influenced by the coordination to the silver ion (probably a chelate effect keeps the C=O and the C—Br bonds in a synperiplanar arrangement). The large standard deviations of the positional parameters of the structure limit its value for the comparison of bond lengths: neither the C=O nor the C—Br bonds are significantly lengthened upon complexation (see Table IV).

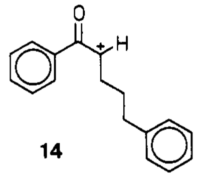
NMR Spectroscopy. The poor solubility of $\mathbf{8}\cdot AgSbF_6$ in CD_2Cl_2 forced us to use sulfur dioxide as solvent for the NMR measurements of the $AgSbF_6$ complexes, which had to be carried out at room temperature (in sealed, medium-walled tubes). Nevertheless, the solubility of $\mathbf{8}\cdot AgSbF_6$ was only sufficient for a ^1H NMR spectrum (see Figure 7). The downfield shift of H (C2) by 0.37 ppm upon complexation indicates an increase of positive charge (the other chemical shifts are far less changed upon complexation). A similar observation was made for the C2-protons of **2** in $(\mathbf{2})_2\cdot AgSbF_6$, where a downfield shift of 0.58 ppm was observed. The ^{13}C NMR shift change in **2** is most pronounced for C2 (+5.8 ppm) but weaker for the carbonyl-C atom and the ipso-C atom C11 (+1.3 ppm for both).

Discussion

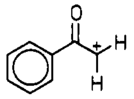
Complexes with a Hard Lewis Acid. The complexes with the hard Lewis acid ($\mathbf{2}\cdot SbCl_5$, $\mathbf{3}\cdot SbCl_5$) provide examples for the activation of α-bromo ketones according to the resonance structures **1b** and **1b′** because of the strong downfield shifts of the carbonyl-C atoms and the upfield shifts of the bromine-substituted α-C atoms.[13] The downfield shifts of the α′-C atoms (C11 in $\mathbf{2}\cdot SbCl_5$, C1 in $\mathbf{3}\cdot SbCl_5$) do not seem to fit into this explanation, but in both cases, an increase of the partial positive charges on these atoms seems to be possible and reasonable via a release of π-electron density from the aromatic ring of **2** (C1—C11 is slightly shortened, see previous text) or a release of σ-electron density from the C1—C6 bond of **3** according to a contribution of the Wagner–Meerwein resonance formula[38] **3b*** (see Scheme III).

The very strong upfield shift of C2 in $\mathbf{2}\cdot SbCl_5$ may be a result of two effects: the change of the conformation[39] and the increase of the positive charge at C1 upon complexation (both of them favor resonance according to **1b**). If we focus our attention for the discussion of the structural changes on the more precise structure ($\mathbf{2}\cdot SbCl_5$), then one can say that the C=O activation enhances the C—Br hyperconjugation,[4] which was already suggested by Corey et al.:[5] the lengthening of the C=O and the C—Br bonds are in agreement with an increased contribution of **1b** for the description of **2** in the complex. The unusual conformation of **2** in $\mathbf{2}\cdot SbCl_5$ (expressed by the torsion angle O1=C1—C2—Br1) may be enforced by a steric interaction between the Br atom of **2** and the $SbCl_5$ molecule, which is bound as in other examples[13,18] to a sp^2-like lone pair of the carbonyl oxygen atom, and the C2—Br1 bond is thus rotated into a position suitable for C—Br hyperconjugation. We do not know whether there is a force that would rotate the C2—Br1 bond back toward a synperiplanar arrangement with the C1=O1 bond if the Lewis acid molecule would be smaller or whether the Br1···C13 contact (Figure 3) is accidental.

Complexes with a Soft Lewis Acid. The soft Lewis acid Ag^+ seems to initialize a C—Br bond cleavage according to resonance formula **1c** because the C2—Br1 bond in $\mathbf{8}\cdot AgSbF_6$ is lengthened and the Ag^+ ion can form only with a Br^- ion (but not with a Br^+ ion) a stable leaving group (this process would lead finally to the secondary α-keto cation **14**;[40] the group of Charpentier-Morize has isolated a formal cyclization product of **14** upon heating of $\mathbf{8}\cdot AgSbF_6$[26a]).



14



15

We do not see a similar lengthening of the C—Br bonds in $(\mathbf{2})_2\cdot AgSbF_6$, but this may be a result of the low precision of the structure (the NMR data indicate an increase of the positive charge at C2 in the complex!). Nevertheless, such a cleavage would lead to the formation of the unfavorable primary α-keto cation **15**,[40,41] and Anselme et al.[27] assume only the intermediacy of a complex between **2** and $AgSbF_6$ but not the intermediacy of **15** in order to explain their results (i.e., a S_N2-like reaction of $(\mathbf{2})_2\cdot AgSbF_6$ may be more probable than a S_N1 reaction).[42] If we focus here too our attention for the discussion of the structural changes on the more precise structure ($\mathbf{8}\cdot AgSbF_6$), then one can

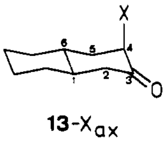
---

(36) According to a Cambridge File search, the shortest Ag···C distances in bonds between Ag^+ and the π-system of phenyl rings are ~2.49 (1) Å.

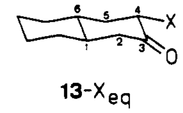
(37) The fact that only one of five bonds emanating from the silver ion is responsible for the polymeric character of $(\mathbf{2})_2\cdot AgSbF_6$ may be the reason for the enhanced solubility if compared with $\mathbf{8}\cdot AgSbF_6$, where three of five bonds contribute to the networking.

(38) In carbocations like the 2-norbornyl cation, this σ-delocalization leads to bridging due to a three-center, two-electron bond. For reviews, see: Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; John Wiley & Sons: New York, 1985; pp 132–142. Brown, H. C. *The Nonclassical Ion Problem*; Plenum Press: New York, 1977; pp 83–122 (with comments by Schleyer, P. v. R.). For crystal structure analyses, see: Laube, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 560–562. Laube, T. *J. Am. Chem. Soc.* **1989**, *111*, 9224–9232.

(39) In order to estimate the influence of the torsion angle Hal—C—C=O in α-halo ketones on the ^{13}C NMR chemical shifts, one can compare the spectra of diastereomers of rigid molecules like 4-X-3-*trans*-decalones **13**-X: Metzger, P.; Casadevall, E.; Casadevall, A.; Pouet, M.-J. *Can. J. Chem.* **1980**, *58*, 1503–1511. See also the data collections in: Whitesell, J. K.; Minton, M. A. *Stereochemical Analysis of Alicyclic Compounds by C-13 NMR Spectroscopy*; Chapman and Hall: London, 1987; pp 211–220. The C4 atom of **13**-Br_{ax} is shifted upfield by 4.1 ppm if compared with **13**-Br_{eq}. It must be emphasized that also the chemical shifts of C2, C3, C5, and C6 show differences (varying with X) between the X_{ax} and X_{eq} diastereomers. Therefore, these data can only indicate the trend.



13-X_{ax}



13-X_{eq}

(40) This formula says nothing about the structure of the α-keto cation. For this controversy, see refs 10 and 11.

(41) For the silver ion assisted solvolysis of primary and secondary α-bromo ketones, see also: Giordano, C.; Castaldi, G.; Casagrande, F.; Abis, L. *Tetrahedron Lett.* **1982**, 1385–1396.

(42) For the silver ion assisted solvolysis of other organohalogen compounds, see, for example: Kornblum, N.; Hardies, D. E. *J. Am. Chem. Soc.* **1966**, *88*, 1707–1711. Pocker, Y.; Wong, W.-H. *J. Am. Chem. Soc.* **1975**, *97*, 7105–7109. For the examination of the intermediate complexes, see, for example: Thiebault, A.; Colin, J. P.; Oliva, P. *Anal. Lett.* **1977**, *10*, 429–435. Smith, J. W. In *The Chemistry of the Carbon–Halogen Bond*; Patai, S., Ed.; John Wiley & Sons: London, 1973; Part I, pp 265–300.

Table V. Data for the Synthesis and the Recrystallization of the $SbCl_5$ Complexes

a (mg), educt	*b* (mL), solvent	*c* (mg)	*d* (mL)	*e* (°C)	appearance
440, **2**	40, $CFCl_3$ + 10, CH_2Cl_2	660	25	−40	yellow crystals
510, **3**	40, $CFCl_3$ + 10, CH_2Cl_2	660	8	−40	yellow crystals
510, **6**	20, $CFCl_3$	670	11	−40	slightly yellow powder (crystals disintegrate upon drying)
510, **7**	40, $CFCl_3$ + 7, CH_2Cl_2	800	15	−20	yellow powder

Table VI. Data about the Crystal Structure Analyses

compd	**2**·$SbCl_5$	**3**·$SbCl_5$	**8**·$AgSbF_6$	(**2**)$_2$·$AgSbF_6$
space gp (no.)	$P2_1/n$ (14)	$P2_12_12_1$ (19)	$P\bar{1}$ (2)	$P2_1/c$ (14)
a (Å)	7.507 (2)	7.937 (6)	9.548 (5)	7.441 (2)
b (Å)	17.05 (1)	11.00 (2)	10.926 (3)	26.660 (9)
c (Å)	11.25 (1)	19.44 (3)	11.065 (3)	10.789 (5)
α (deg)	90	90	65.47 (2)	90
β (deg)	93.78 (5)	90	68.83 (4)	108.59 (3)
γ (deg)	90	90	79.48 (3)	90
V (Å^3)	1436 (2)	1697 (4)	978.5 (7)	2028 (1)
measuring temp (°C)	−80	−80	−95	−95
d_X (g·cm^{-3})	2.303	2.074	2.243	2.429
θ_{max} (deg)	32	30	32	32
no. measured reflections	4963	2812	7099	7005
no. reflections with $I > 3\sigma_I$	3942	2460	5440	3507
no. parameters	150	168	298	253
w (final weighting scheme)	$1/\sigma_F^2$	$1/\sigma_F^2$	$1/\sigma_F^2$	1
R	0.057	0.070	0.058	0.095
R_w	0.056	0.071	0.053	0.095
μ (mm^{-1})	5.61	4.75	4.46	6.26

conclude that the beginning silver-mediated Br^- elimination from **8** leads to an increased contribution of **1c** for the description of **8** in the complex. The question for the structure of the corresponding cation **14**, however, remains open because the synperiplanar arrangement of the C=O and the C—Br bonds may be enforced by the chelation of the silver ion, and with the passage of the C—Br bond cleavage, the conformation of **8** with respect to **14** may or may not change.

Conclusion

Our results provide structural information about the known regioselective activation of α-bromo ketones (ambident electrophiles) with Lewis acids in agreement with the HSAB principle: a hard Lewis acid ($SbCl_5$) activates the C=O bond, a soft Lewis acid (Ag^+) activates preferentially the C—Br bond for a nucleophilic attack.

Experimental Part

Synthesis and Crystallization of the $SbCl_5$ Complexes (General Procedure). To a solution of *a* mg of educt in *b* mL of solvent was added *c* mg of $SbCl_5$ in 10 mL of $CF_2ClCFCl_2$ at −80 °C under argon. After the solution was stirred for 30 min, the solvents were evaporated between −40 and −30 °C. The dry complex was dissolved in *d* mL of CH_2Cl_2 at −40 °C, the solution was rapidly filtered, and the filtrate was slowly cooled (starting at *e* °C). After removal of the mother liquor and washing with 1 mL of CH_2Cl_2, the crystals were dried at −30 °C (high vacuum) to give a product with the *appearance* listed in Table V.

Crystallization of 8·$AgSbF_6$. A solution of **8** in CH_2Cl_2 (37 mmol/L) and a solution of $AgSbF_6$ in CH_2Cl_2 (39 mmol/L) were allowed to diffuse into pure CH_2Cl_2 at 4 °C within 3 days under argon in the darkness. After removal of the mother liquor and the solutions, the crystals were dried for 30 min in the high vacuum.

Synthesis and Crystallization of (2)$_2$·$AgSbF_6$. To a solution of 495 mg of **2** in 35 mL of $CFCl_3$ was slowly added a solution of 770 mg of $AgSbF_6$ in 10 mL of CH_2Cl_2 at −78 °C. After the solution was stirred for 1 h, the solvents were removed in the high vacuum and the complex was dissolved in 15 mL of CH_2Cl_2 at −20 °C. After filtration, the solution was slowly cooled (starting at 0 °C). The resulting pink crystals were dried for 30 min in the high vacuum after removal of the mother liquor.

NMR Measurements of the $SbCl_5$ Complexes. About 50 mg of the recrystallized complex was filled into an NMR tube (5-mm diameter) under inert gas and dissolved in CD_2Cl_2 (*internal* standard, tetramethylsilane (TMS)). The 75-MHz spectra were recorded at −80 °C. A slight decomposition of the TMS was observed. The assignment of the signals was in some cases secured by DEPT (distortionless enhancement by polarization transfer) spectra. The spectra of the pure bromo ketones were measured under identical conditions.

NMR Measurements of the $AgSbF_6$ Complexes. The crystalline complex and a capillary with the *external* standard (ca. 90% CD_3COCD_3 + 10% TMS) were filled under inert gas into a medium-walled NMR tube (5-mm diameter, with constriction), which was then connected to a high-vacuum line fitted with an Ace tip-off manifold and evacuated. Dry sulfur dioxide was distilled into the NMR tube, and after several freeze–pump–thaw cycles, the tube was sealed off. The spectra (^1H, 300 MHz; ^{13}C, 75 MHz) were recorded at room temperature in the darkness. The spectra of the pure bromo ketones were measured under identical conditions.

X-ray Crystal Structure Analyses. All structures were measured on a CAD4 diffractometer (Mo Kα radiation, graphite monochromator; for the crystal data, see Table VI). The positions of the heavy atoms (Ag, Br, Sb) were determined with the Patterson or the direct-methods options of SHELXS-86,[43] and the other non-hydrogen atoms were located by a difference Fourier synthesis with SHELX-76.[44] After several cycles of isotropic and anisotropic refinement and subsequent location of hydrogen positions, the following hydrogen atoms were refined with constraints: **2**·$SbCl_5$, all H's riding, H22 and H16 with *U* fixed at 0.08 Å^2; **3**·$SbCl_5$, all H's riding, all H's except those at C6 and at C71 with *U* fixed at 0.08 Å^2; **8**·$AgSbF_6$, H's at C5 riding with *U* fixed at 0.08 Å^2, H's at C16 and at C56 riding; (**2**)$_2$·$AgSbF_6$, all H's riding with *U* fixed at 0.08 Å^2. The crystallographic pictures were drawn with PLUTO[45] and ORTEP.[46] The somewhat diffuse probability density functions of some atoms of **3** in **3**·$SbCl_5$ can be explained by separate thermal motion analyses for **3** and the $SbCl_5$ unit (both treated as rigid bodies) using THMA11[47] (roots of the eigenvalues of the **T** and **L** tensors: **3**, 0.17, 0.15, 0.11 Å, 5.8°, 4.0°, 1.8°; $SbCl_5$, 0.16, 0.14, 0.14 Å, 4.3°, 3.8°, 2.9°).[48]

Acknowledgment. We thank Paul Seiler and Dr. W. Bernd Schweizer for their help during the measurements and evaluation of the X-ray data, and Brigitte Brandenberg, Verena Eggli, and Dr. Bernhard Jaun for the NMR measurements and much helpful advice concerning the preparation of the samples. Dr. Engelbert Zass made several CAS online searches for us. Financial support of the Schweizerischer Nationalfonds is acknowledged. The Fonds der Chemischen Industrie (Federal Republic of Germany) sponsored the work by the allocation of a Dozentenstipendium to T.L.

Supplementary Material Available: Crystal packing diagrams, tables of the positional and thermal parameters, and tables of bond lengths, angles, and torsion angles for the four crystal structures (16 pages); listing of observed and calculated structure factors for the four crystal structures (88 pages). Ordering information is given on any current masthead page.

---

(43) Sheldrick, G. M. SHELXS-86, program for the solution of crystal structures from diffraction data; University of Göttingen: Federal Republic of Germany, 1986.

(44) Sheldrick, G. M. SHELX-76, program for crystal structure determination; University of Cambridge: England, 1976.

(45) PLUTO88, plot package for the display of crystal and molecular structures; Cambridge Crystallographic Data Centre, University Chemical Laboratory: Cambridge, England.

(46) Johnson, C. K. ORTEP-II, thermal ellipsoid plot program for crystal structure illustrations; Oak Ridge National Laboratory: Oak Ridge, TN, March 1976.

(47) Trueblood, K. N. THMA11, version of 18 May 1987; University of California: Los Angeles, 90024.

(48) Separate thermal motion analyses of **2**·$SbCl_5$ yield the following values: **2**, 0.17, 0.15, 0.13 Å, 5.0°, 2.8°, 1.9°; $SbCl_5$, 0.19, 0.14, 0.12 Å, 5.7°, 3.7°, 2.3°.