using CH_2Cl_2–petroleum ether (1:5). The first fraction gave 36 mg (6.6%) of **6a**. The second fraction was concentrated to afford 288 mg (39%) of 9-mesityl-9-(*p*-methoxyphenyl)thioxanthene (**32**) which was recrystallized from CH_2Cl_2–petroleum ether to form colorless prisms: mp 211–213 °C; ^1H NMR ($CDCl_3$) δ 1.51 (s, 2- and 6-Me of mesityl group), 2.32 (s, 4-Me of mesityl group), 3.73 (s, OMe), 6.87 (br s, H-3 and H-5 of mesityl group), 6.68–7.50 (m, Ar H); mass spectrum, *m/e* (relative intensity) 422 (M^+, 65), 407 (M^+ – Me, 9), 315 (100), 303 (100), 259 (11). Anal. Calcd for $C_{29}H_{26}OS$: C, 82.43; H, 6.20. Found: C, 82.14; H, 6.27. The third fraction gave 101 mg (13%) of unidentified product (**33**) as colorless needles after recrystallization from CH_2Cl_2–MeOH: mp 142–143 °C; ^1H NMR ($CDCl_3$) δ 2.22 (s, 4-Me of mesityl group), 2.40 (s, 2- and 6-Me of mesityl group), 3.78 (s, OMe), 6.73–7.49 (m, Ar H); mass spectrum, *m/e* (relative intensity) 454 (M^+, 100), 345 (41), 335 (24), 315 (91), 243 (38), 239 (38), 206 (37). Anal. Calcd for $C_{29}H_{26}O_3S$: C, 76.62; H, 5.76. Found: C, 76.72; H, 5.75. Finally, CH_2Cl_2 was used as a developing solvent to give 52 mg (8%) of 9-hydroxy-9-mesitylthioxanthene 10,10-dioxide (**34**) which was recrystallized from CH_2Cl_2–petroleum ether to form colorless prisms: mp 231–233 °C; IR (KBr) 3470 (OH), 1309 and 1146 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 1.97 (br, $W_{1/2}$ = 0.24 ppm, 2- and 6-Me of mesityl group), 2.33 (s, 4-Me of mesityl group), 2.76 (br, OH), 6.88 (br s, H-3 and H-5 of mesityl group), 7.03–7.35 (m, H-1 and H-8), 7.37–7.73 (m Ar H), 8.04–8.35 (m, H-4 and H-5). Anal. Calcd for $C_{22}H_{20}O_3S$: C, 72.50; H, 5.53. Found: C, 72.64; H, 5.54.

9-Mesityl-9-(*p*-methoxyphenyl)thioxanthene (32). To an ethereal solution of *p*-methoxyphenylmagnesium bromide prepared from *p*-methoxyphenyl bromide (1.2 g), Mg (150 mg), ether (10 mL), and catalytic amounts of I_2 was added **36a** (1 g) in limited amounts under a nitrogen atmosphere. After addition of THF (20 mL), the mixture was refluxed for 5 h and hydrolyzed by adding an NH_4Cl solution. The reaction mixture was extracted with ether, washed with water, dried over anhydrous $MgSO_4$, and concentrated to dryness. The resulting oil was purified by preparative thin-layer chromatography on silica gel using CH_2Cl_2–petroleum ether (1:3) to give 445 mg (44%) of **32** which was recrystallized from CH_2Cl_2–petroleum ether to form colorless prisms: mp 211–213 °C.

Registry No. **4**, 36943-39-2; **5a**, 90133-31-6; **5b**, 90133-57-6; **6a**, 53512-25-7; **6b**, 66572-01-8; **7a**, 90133-33-8; **7b**, 90133-62-3; **7c**, 90133-64-5; **7d**, 66571-82-2; **7e**, 66571-84-4; **7f**, 66571-86-6; **9a**, 90133-34-9; **9b**, 90133-65-6; **9c**, 90133-66-7; **9d**, 66571-96-8; **9e**, 66571-97-9; **9f**, 66571-98-0; **10b**, 72751-72-5; **10c**, 72751-73-6; **10f**, 72731-25-0; **12**, 90133-55-4; **13**, 90133-58-7; **14**, 583-68-6; **15**, 42872-73-1; **16**, 90133-35-0; **17**, 90133-36-1; **18**, 84964-63-6; **18**-ol, 90133-39-4; **19**, 90133-38-3; **20**, 90133-56-5; **21**, 90133-59-8; **22**, 73083-79-1; **24**, 90133-40-7; **28**, 90133-60-1; **27**, 90133-42-9; **29**, 90133-43-0; **30**, 90133-47-4; **32**, 90133-54-3; **34**, 72780-38-2; **35a**, 90133-44-1; **35b**, 90133-45-2; **36a**, 90133-53-2; **36b**, 90133-49-6; **37a**, 90133-50-9; **37b**, 90133-51-0; **38**, 73083-77-9; 2-ClC_6H_4CHO, 89-98-5; C_6H_5SH, 108-98-5; C_6H_5OMe, 100-66-3; 4-$MeOC_6H_4Br$, 104-92-7; MeI, 74-88-4; EtI, 75-03-6; PrI, 107-08-4; 3-MeC_6H_4SH, 108-40-7; mesityl bromide, 576-83-0; thioxanthone, 492-22-8; duryl bromide, 1646-53-3; 2,3,4-trimethylphenyl bromide, 40101-33-5; 1,2,3-trimethylbenzene, 526-73-8.

Supplementary Material Available: Characteristics of compounds **5b**, **6b**, **7b–f**, **9b–f**, **10c,f**, **12**, **13**, **20**, **21**, **25**, and **26** not described in the Experimental Section (5 pages). Ordering information is given on any current masthead page.

Silver(I) Interactions with Ketones. Site of Complexation with Acetophenones and Effectiveness as a Lewis Acid Catalyst[1]

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Received February 28, 1984

Aromatic ketones present three possible sites for complexation of Ag^+: the oxygen lone pair, the π electrons of the carbonyl bond, and the π electrons of the aromatic ring. Upfield shifts of ^{13}C chemical shifts of meta and para carbons of acetophenone in the presence of silver nitrate showed that Ag^+ complexes with the aromatic ring moiety in water. This contrasts with previous results in methylene chloride in which the carbonyl group is not hydrogen bonded to solvent and acts as an n donor toward Ag^+. In the solid state, an X-ray structure determination of (*p*-methylacetophenone)$_2AgBF_4$ showed that Ag^+ was tetracoordinated to two carbonyl oxygens (2.36 Å) and to two aromatic rings of different ketone molecules (2.55- and 2.72-Å distances to meta and ortho carbons, respectively). Thus in the solid state, acetophenone acts *both* as an n and π donor. The Ag–O bond was shorter than most Ag–O bonds and appears to contribute more to the stabilization of the complex than Ag^+ interactions with the benzene rings. An sp^2 hybridization at oxygen was indicated by an AgOC angle of 137° and the fact that Ag^+ is only 6.2° above the plane of the carbonyl bond. Although Ag^+ catalyzed an aldol condensation of acetophenone in 1,2-dichloroethane at 70–80 °C, rates of hydrogen exchange for acetone in deuterated water at 44 °C showed no catalytic activity of $AgNO_3$ or $LiNO_3$.

Complexes of Ag^+ with π donors (alkenes and aromatics) and n donors (amines and ethers) are well-known.[2] However, very little has been reported about Ag^+ interactions with ketones, an important class of compounds that could act as n or π donors.

Previous work in our laboratory[3] showed that both aliphatic and aromatic ketones acted as n donors toward $AgBF_4$ in methylene chloride. This result was based on comparison of ^{13}C chemical shift changes with model complexes (Et_2O–Ag^+, cyclohexene–Ag^+, and toluene–Ag^+) and IR data. However, in one isolated report[4] a linear free-energy relationship of formation constants suggested that in water Ag^+ complexed with the benzene moiety of acetophenone.

(1) Supported in part by The Petroleum Research Corp.

(2) (a) Beverwijk, C. D. M.; Van der Kerk, G. J. M.; Leusink, A. J.; Noltes, J. G. *Organomet. Chem. Rev., Sect. A* **1970**, *5*, 215. (b) Gclumbic, C. *J. Am. Chem. Soc.* **1952**, *74*, 5777. (c) Pauley, J. L.; Hau, H. H. *J. Phys. Chem.* **1966**, *70*, 3363. (d) Comyns, A. E.; Lucas, H. J. *J. Am. Chem. Soc.* **1954**, *76*, 1019. (e) Meerwein, H.; Hederich, V.; Wunderlich, K. *Arch. Pharm. (Weinheim, Ger.)* **1958**, *291*, 541. (f) Ahrland, S.; Chatt, J.; Davies, N. R.; Williams, A. A. *J. Chem. Soc.* **1958**, 264, 276; *Q. Rev., Chem. Soc.* **1958**, *12*, 265.

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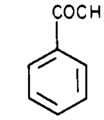
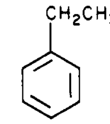
0022-3263/84/1949-2478$01.50/0

Table I. Carbon-13 Chemical Shifts for Acetophenone[a] and Ethylbenzene[b] Complexes with Silver Ion

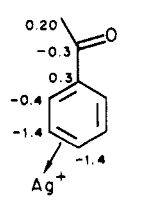
donor	position	δ_{donor}	$\delta_{complex}$	$\Delta\delta^c$
	α-CH_3	29.0	29.2	0.2
	CO	207.2	206.9	−0.3
	C_1	139.5	139.8	0.3
	C_2	131.4	131.0[d]	−0.4
	C_3	131.7	130.3[d]	−1.4
	C_4	137.0	135.6	−1.4
	CH_3	15.62	15.28	−0.34
	α-CH_2	28.96	28.70	−0.26
	C_1	144.22	147.15	2.93
	C_2	128.38	127.43	−0.95
	C_3	127.91	125.36	−2.55
	C_4	125.66	121.74	−3.92

[a] Donor 0.0525 M in 50% D_2O containing 0 or 2.85 M $AgNO_3$ and relative to sodium 3-(trimethylsilyl)propanesulfonate. [b] Donor 3.15 M in $CDCl_3$ containing 0 or 1.57 M $AgBF_4$ and relative to Me_4Si. [c] $\Delta\delta = \delta_{complex} - \delta_{ketone}$ for corresponding carbons. [d] Assignments uncertain.

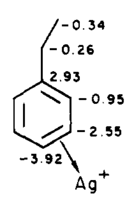
We now report our results on the site of complexation of Ag^+ with acetophenone in water by ^{13}C NMR data and with *p*-methylacetophenone in the solid state by an X-ray structure determination. Also, the effectiveness of Ag^+ as a Lewis acid catalyst was investigated in two typical ketone reactions, the aldol condensation of acetophenone and α-H exchange of acetone.

Results and Discussion

Aqueous Studies. To determine the site of complexation of Ag^+ with a typical aromatic ketone in water, the ^{13}C NMR spectrum of acetophenone was taken in 50% D_2O. From chemical shifts shown in Table I, it can be seen that the α-methyl carbon and the ipso carbon (C_1) underwent small downfield shifts ($+\Delta\delta$ values) in the presence of 2.85 M $AgNO_3$, while meta and para carbon atoms underwent large upfield ($-\Delta\delta$ values) shifts on complexation (see 1). These upfield shifts are characteristic of carbon atoms whose π electrons are complexed to Ag^+, as for example, with donors such as cyclohexene,[5] toluene,[3] and styrene.[6] The upfield $\Delta\delta$ values of ethylbenzene, taken as a model for Ag^+ aromatic bonding, indicate that Ag^+ is localized over the meta–para bond as shown in 2. The similar pattern of sign and magnitude[7] of $\Delta\delta$ values for 1 and 2 shows that in water Ag^+ is complexed to the benzene ring of acetophenone in agreement with LFER data.[4]

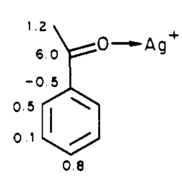


1 (in water)

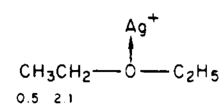


2 (in $CHCl_3$)

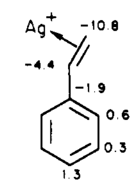
This result is different from that obtained in methylene chloride in which acetophenone acts as an n donor toward Ag^+.[3] The largest $\Delta\delta$ in methylene chloride was for the carbonyl carbon (see 3), and it underwent a downfield shift, behaving like a carbon bearing complexed oxygen (cf. 4, which can be considered a model of neutral oxygen as an n donor). Furthermore, the pattern of sign and magnitude of $\Delta\delta$ values of ring carbons of acetophenone in methylene chloride paralleled those for styrene[6] 5 in which Ag^+ is known to complex at the allylic double bond.[6,8,9] An explanation for this solvent effect is that the carbonyl oxygen may be preferentially hydrogen bonded to water,[4,10] leaving only the aromatic π system available as the donor site in that solvent. Evidence for this explanation is that the carbonyl carbon of acetophenone is 11.2 ppm more downfield in water compared to methylene chloride, presumably due to hydrogen bonding.



3 (in CH_2Cl_2)



4



5

Solid State. An X-ray structure determination on the crystalline (*p*-methylacetophenone)$_2$$AgBF_4$ complex showed that Ag^+ is tetracoordinated to four ligand molecules, with bonds to two carbonyl oxygens and two aromatic rings. This bonding, which combines the results found in methylene chloride and water, is indicated in Figure 1 and in the stereoscopic projection of Figure 2. Selected bond distances and nonbonding distances, bond angles, and dihedral angles are given in Tables II–IV, re-

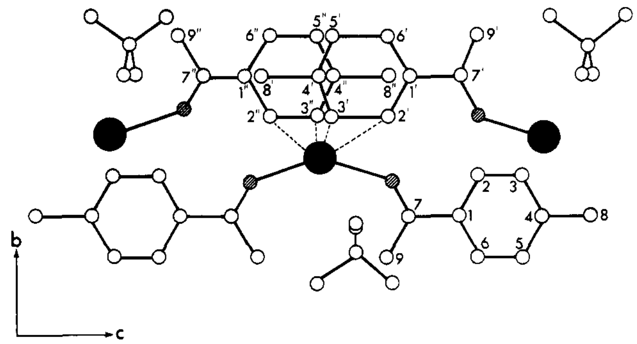


Figure 1. Projection of (*p*-methylacetophenone)$_2$$AgBF_4$ on the *bc* plane: silver (●), oxygen (⊖); carbons numbered as in text.

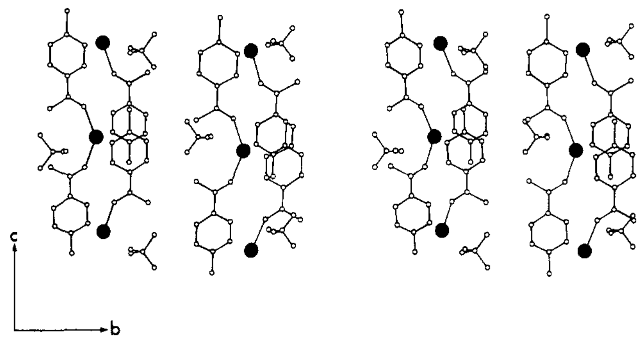


Figure 2. Stereoscopic projection of (*p*-methylacetophenone)$_2$$AgBF_4$ unit cell on bc plane.

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(7) Solubility measurements in water show that for acetophenone as a donor significant amounts of a D–Ag_2^{2+} complex forms in addition to D–Ag^+.[4] From values of their formation constants, it was calculated that the mole fractions of free acetophenone, D–Ag^+, and D–Ag_2^{2+} under our conditions were 0.35, 0.5, and 0.15, respectively. The observed $\Delta\delta$ value thus is a weighted average of values for each species.
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Table II. Selected Bond Lengths (Å) and Nonbonded Distances (<4 Å) for (p-Methylacetophenone)$_2$AgBF$_4$[a]

atoms	bond lengths	atoms	nonbonding distances
Ag–O	2.36 (1)	Ag–C_5'	2.97 (2)
C_1–C_2	1.41 (2)	Ag–C_4'	3.24 (2)
C_2–C_3	1.39 (2)	Ag–C_1'	3.55 (1)
C_3–C_4	1.39 (2)	Ag–C_9	3.72 (2)
C_4–C_5	1.42 (2)	Ag–F_1	3.44 (1)
C_5–C_6	1.37 (2)	Ag–C_9'	3.92 (1)
C_6–C_1	1.39 (2)	Ag–C_8'	3.97 (1)
C_1–C_7	1.49 (2)		
C_4–C_8	1.52 (2)		
C_7–C_9	1.54 (2)		
C_7–O	1.25 (2)		
B–F_1	1.31 (2)		
B–F_2	1.32 (2)		
Ag–C_3'	2.55 (1)		
Ag–C_2'	2.72 (1)		

[a] The primed atoms and unprimed atoms are not in the same 2:1 complex.

Table III. Selected Bond Angles for (p-Methylacetophenone)$_2$AgBF$_4$

atoms	angles, deg	atoms	angles, deg
O(1)–Ag–O(2)[a]	140.0 (5)	Ag–C_2'–C_3'	67.7 (7)
O(1)–Ag–C_3'[b]	88.9 (4)	Ag–C_3'–C_2'	81.9 (8)
O(1)–Ag–C_3''[b]	109.4 (4)	C_3–C_4–C_5	119 (1)
O(2)–Ag–C_3'	109.4 (4)	C_3–C_4–C_8	120 (2)
O(2)–Ag–C_3''	88.9 (4)	C_5–C_4–C_8	121 (2)
C_2'–Ag–C_2''	129.3 (6)	C_4–C_5–C_6	121 (1)
C_3'–Ag–C_3''	125.7 (7)	C_5–C_6–C_1	120 (1)
C_3'–Ag–C_2'	30.4 (4)	C_1–C_7–O	117 (2)
C_3'–Ag–C_2''	118.1 (4)	C_1–C_7–C_9	124 (2)
C_3–Ag–C_5''	89.0 (4)	C_9–C_7–O	119 (2)
C_6–C_1–C_2	120 (1)		
C_6–C_1–C_7	120 (2)	F–B–F	105 (2), 107 (1)
C_2–C_1–C_7	121 (1)		114 (1), 108 (2)
C_1–C_2–C_3	121 (1)		
C_2–C_3–C_4	119 (1)	C_7–O–Ag	136 (1)

[a] Parentheses on the atom indicates atom in the same molecule. [b] The primed, double primed, and unprimed atoms are not in the same molecule.

Table IV. Dihedral Angles Formed by Two Planes

plane 1	plane 2	dihedral angles, deg
O–Ag–O	C_3–Ag–C_3''	102.1 (5)
O–Ag–O	C_2'–Ag–C_2''	68.1 (4)
O–Ag–O	C_2'–Ag–C_3''	85.2 (4)

spectively. Final positional parameters are given in the Experimental Section. Various structural features are shown schematically in Figure 3 and discussed below.

The Ag–O bond distance of 2.36 Å is intermediate between covalent (2.18 Å) and ionic (2.66 Å) sums of radii.[11] Interestingly, it is essentially the same as that for water oxygens in (naphthalene)·4AgClO$_4$·H$_2$O (2.34 and 2.38 Å)[12] and significantly shorter than that for a dioxane oxygen in (dioxane)$_3$AgClO$_4$ (2.46 Å),[13] both of which involve neutral oxygen ligands. In general it is substantially shorter than Ag$^+$ bonds to oxygen atoms in ClO$_4^-$ anions. Thus, compared to other oxygen donors, the carbonyl group forms a relatively short and presumably strong bond to Ag$^+$.

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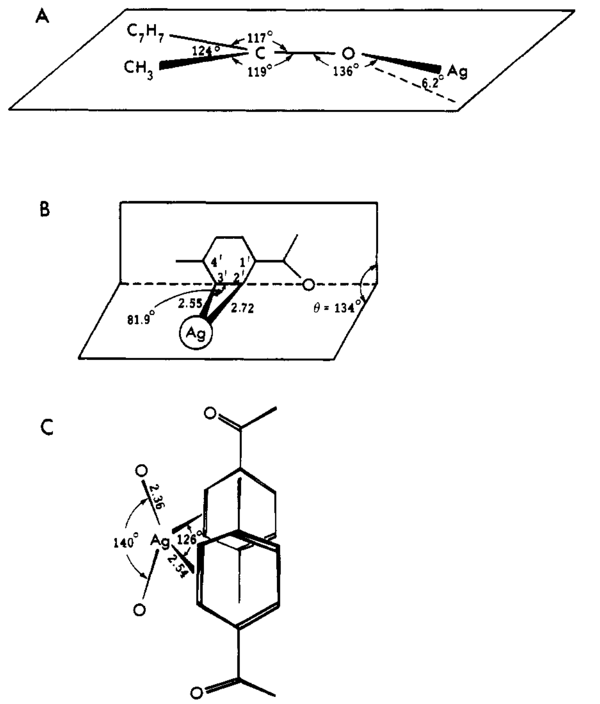

Figure 3. Selected features of Ag$^+$ bonding to p-methylacetophenone from X-ray data: the ketone as an n donor (A); asymmetric bonding to aromatic carbons with 44° of distortion (B); distorted tetrahedral bonding of ligands to Ag$^+$ (C).

That the carbonyl group is acting as an n donor is clear from the Ag–O–C angle of 136° and the fact that Ag is only 6.2° above the plane of the carbonyl group (see Figure 3A). This sp^2 orientation about the carbonyl oxygen is the same as found by Olah[14] where syn and anti isomers of protonated ketones were observed in ^{13}C NMR spectra.

The carbonyl C–O bond distance of 1.25 (2) Å is slightly longer than that reported for acetophenone (1.216 (2) Å).[15] This lengthening of the carbonyl bond implies bond weakening due to electron polarization toward Ag$^+$ consistent with IR results ($\Delta\nu_{CO}$ = 20 cm^{-1}). The above can be taken as experimental evidence for calculations[16] that showed that Lewis acids bonded to n electrons in a sp^2 orbital lower ν_{CO} by decreasing the force constant and not by increasing the effective mass of oxygen.

Bonding to the aromatic rings is evident from Ag–C bond distances that are similar to those of known alkene or aromatic distances (Table V). Characteristically, Ag$^+$ is asymmetrically bonded to adjacent carbon atoms,[17,18] in this case 2.55 Å from C_3 and 2.72 Å from $C_{2'}$ as shown in Figure 3B. The stronger bond to $C_{3'}$ also indicated by a $C_{2'}C_{3'}$Ag angle of 81.9°, may be due to more favored resonance forms assuming a carbocation center at $C_{4'}$ as well as steric factors. The Ag$^+$ is not located directly over the $C_{2'}$–$C_{3'}$ bond but rather is at an angle of 44° off perpendicular (see Figure 3B).

In comparison to other aromatic donors, the Ag$^+$ interaction with p-methylacetophenone is probably weaker for two reasons. The shorter Ag–C distance of 2.55 Å is

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Table V. Bond Lengths and Angles of Silver to Adjacent Oxygen and Carbon Atoms of Model Donors in Solid Complexes

structure	Ag–O, Å	Ag–C, Å	angle[a] Ag–Ar plane, θ, deg	ref
(p-methylacetophenone)$_2$AgBF$_4$	2.36	2.55	134	*b*
		2.72		
(dioxane)$_3$AgClO$_4$	2.46[c]			13
(o-xylene)$_2$AgClO$_4$	2.56	2.44		18f
	2.60	2.49		
		2.53		
		2.57		
(m-xylene)$_2$AgClO$_4$	2.49	2.45		18a
		2.61		
(acenaphthene)AgClO$_4$	2.46	2.44	98.5	18e
	2.42	2.51	94.2	
	2.40	2.51		
	2.34	2.58		
(cyclohexylbenzene)$_2$AgClO$_4$	2.68	2.48		18e
	2.83	2.67		
(benzene)AgAlCl$_4$		2.47	98.0	18c
		2.92		
(benzene)AgClO$_4$	2.66	2.50	101.0	19c
	2.70	2.63		
	2.68			
	3.20			
(naphthalene)·4AgClO$_4$·H$_2$O	2.34[d]	2.60		12
	2.38[d]	2.61		
	2.65	2.62		
	2.90	2.63		
	2.59			
	2.77			
(geijerene)$_2$AgNO$_3$	2.31	2.22[e]		19a
	2.48	2.39[e]		
	2.42	2.53[e]		
	2.49			
(norbornadiene)$_2$AgNO$_3$	2.29	2.31		19d
	2.34	2.41		
(cyclooctatetraene)AgNO$_3$	2.36	2.46		19b
	2.43	2.51		
		2.78		
		2.84		

[a] See Figure 3B and text for definition. [b] Present work. [c] Distance between silver and dioxane oxygen. [d] Distance between silver and water oxygen. [e] Distance between silver and the center of the carbon double bond.

longer than the common value of 2.44–2.48 Å for aromatic compounds as observed by Amma.[18] Furthermore, the dihedral angle of 134° between the plane of the benzene ring and the Ag, $C_{2'}$, and $C_{3'}$ atoms (see Figure 3B) was much larger than the 94–100° values for other alkene and aromatic donors (see Table V). This 44° of distortion of Ag from the axis of p orbitals decreases the overlap of electrons to empty orbitals of Ag^+.

The Ag–BF$_4$ interaction in the present case is rather weak, since the Ag–F nonbonding distance of 3.44 Å is much greater than the sum of their ionic radii (2.62 Å).[11] In comparison to previous cases,[12,18,19] therefore, Ag–O bonds contribute more than Ag–F interactions to the stabilization of the complex which can be described as a distorted tetrahedron (Figure 3C). The $C_{3'}$–Ag–$C_{3''}$ angle of 125.7° and O–Ag–$C_{3'}$ angle of 88.9° may indicate that Ag^+ behaves predominantly as an electron acceptor, using p or sp^2 orbitals.

Table VI. First-Order Rate Constants for Acid-Catalyzed Hydrogen Exchange of Acetone[a]

[HNO$_3$], M	10^6k_{obsd}, s^{-1}	[HNO$_3$], M	10^6k_{obsd}, s^{-1}
0.0	0.302 ± 0.20	0.100	8.14 ± 0.06
0.050	4.14 ± 0.16	0.125	10.1 ± 0.3
0.050	4.18 ± 0.07	0.150	11.8 ± 0.4
0.050[b]	4.19 ± 0.14	0.200	15.6 ± 0.3
0.075	5.68 ± 0.30	0.250	19.3 ± 0.6

[a] 0.50 M acetone in D$_2$O at 43.6 ± 0.1 °C; enough KNO$_3$ was added to provide 0.5 M ionic strength. [b] No added KNO$_3$.

Table VII. First-Order Rate Constants for Hydrogen Exchange of Acetone in the Presence of Metal Ions[a]

[AgNO$_3$], M	[LiNO$_3$], M	10^6k_{obsd}, s^{-1}
b	*b*	5.59 ± 0.14
4.95[c]		5.78 ± 0.14
0.150		4.33 ± 0.11
0.300		3.81 ± 0.09
0.450		4.19 ± 0.10
	0.100	4.28 ± 0.05
	0.300	4.25 ± 0.14
	0.450	4.31 ± 0.14
	2.45[c]	5.43 ± 0.16

[a] 0.50 M acetone and 0.05 M nitric acid in D$_2$O at 43.6 ± 0.1 °C; enough KNO$_3$ was added to provide 0.5 M ionic strength. [b] 4.95 M in KNO$_3$. [c] No added KNO$_3$.

The packing of silver complexes in the unit cell as shown in Figure 2 is of particular interest. Silver ions are held together as one-dimensional chains parallel to the c axis by alternate σ and π bonding to p-methylacetophenone ligands. This linear character of the crystal structure is unusual and suggests the possibility of highly anisotropic electrical or physical properties. Also possibly significant in this regard is the near planarity of aromatic rings of the complex, with a dihedral angle of 24°.

Ag^+-Catalyzed Reactions of Ketones. In 1,2-dichloroethane at 70–80 °C, acetophenone was converted in 23% yield to 1,3,5-triphenylbenzene in the presence of 0.12 equiv of AgBF$_4$. Water was evolved in a reaction analogous to the formation of mesitylene from acetone. The initial steps probably involve Ag^+ bonding to the oxygen n electrons as in methylene chloride[3] followed by proton abstraction to give an enol.

In order to obtain quantitative data on the effectiveness of Ag^+ as a Lewis acid catalyst for typical ketone reactions, rates of deuterium exchange of acetone in D$_2$O were measured with KNO$_3$ to maintain constant ionic strength. Acetone was chosen because of a single proton signal in its NMR spectrum simplifying quantitation, only one type of exchangeable hydrogen, and only one site of complexation with Ag^+. For comparison purposes, the catalytic effect of H^+ was measured, and 0.05 M HNO$_3$ was added to all subsequent runs to maintain a low, constant pH without the use of buffers which would complicate the role of Ag^+. In addition to AgNO$_3$, the effect of LiNO$_3$ was also studied.

The disappearance of methyl hydrogens of a 0.5 M acetone solution at 43.6 °C followed good first-order kinetics over 2.5 half-lives with rate constants given in Table VI for HNO$_3$ and Table VII for AgNO$_3$ and LiNO$_3$. A plot of k_{obsd} vs. [H$^+$] was linear with a near-zero intercept of $3.7 \pm 0.8 \times 10^{-7}$ s^{-1} and slope of $7.6 \pm 0.1 \times 10^{-5}$ M^{-1} s^{-1}, showing the expected first-order dependence on [H$^+$].[20-22]

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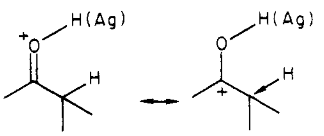
The value of k_{H^+} was in reasonable agreement with that of 5.1×10^{-5} M^{-1} s^{-1} obtained for acetone in the presence of HCl at 42 °C by mass spectrometry methods.[23]

In contrast, no catalytic effect was observed for Ag^+ and Li^+ as seen by rate constants in Table VII. Increasing $[Ag^+]$ by a factor of 33 from 0.45 to 4.95 M caused only a 33% rate increase. Since this was essentially the same as that found for KNO_3 (first two entries in Table VII), the increase is due to a salt effect. Similar results were found for $LiNO_3$.

The equilibrium constant for formation of a Ag^+–acetone complex[10a] is probably considerably larger than that for protonation[24] (0.14 vs. 10^{-6}, though the former is only an estimate[10a]). A tentative conclusion is that the Ag^+ complex must be much less reactive in forming the enol than protonated acetone. Similarly, the formation constant for the $LiClO_4$–menthone complex in ether is 7,[25] which is at least 70 times greater than that for the HCl–menthone complex, yet $LiClO_4$ showed no catalytic activity toward racemization in that solvent even when Cl^- was added.

In contrast to protonated ketones, these observations show that complexed Ag^+ and Li^+ do not weaken the C–H bond nearly as effectively as H^+. The extraordinary high charge density of H^+ can polarize the oxygen lone pair to the extent of full covalent bond formation, resulting in **6** ↔ **7**[26] wherein the C–H bond is weakened. The much



6 7

lower charge density of Ag^+ (as well as back-bonding capability) lowers the degree of covalent bond formation in **6**. Indeed, from an Ag–O bond distance of 2.36 Å found in the present work for *p*-methylacetophenone it can be estimated that this bond is 36% covalent.[27] The overall effect is to lessen the importance of **7**, thus accounting for the decreased reactivity of Ag^+ complexes of acetone.

Conclusions

The site of complexation of Ag^+ with acetophenone depends on the medium. In methylene chloride, the ketone oxygen acts as an n donor, while in water this site is preferentially hydrogen bonded and Ag^+ bonds to the aromatic π system. In the solid state, *p*-methylacetophenone acts as both an n and aromatic π donor, although the Ag–O bond appears to be the dominant stabilizing factor in its $AgBF_4$ complex. Silver ion is ineffective as a catalyst for hydrogen exchange of acetone compared to H^+, presumably due to the low charge density of Ag^+.

Experimental Section

NMR Studies. ^{13}C spectra of acetophenone in water were taken in 1:1 H_2O/D_2O on a Bruker WH/HFX-90 (MHz) FT spectrometer at 22.63 MHz, using D_2O as the lock signal and sodium 3-(trimethylsilyl)propanesulfonate (0.2%) as internal standard. A pulse width of 4.0 μs corresponding to a pulse angle of ca. 40° and a repeat time of 6 s were used. Materials were described previously.[3]

Table VIII. Crystal Data for (*p*-Methylacetophenone)$_2$AgBF$_4$

extinction	$hkl, h + k = 2n + 1; h0l, l = 2n + 1$
space group	$C2/c$ or Cc
a	7.763 (1) Å
b	19.771 (4) Å
c	12.77 (2) Å
β	103.32 (2)°
T	22 °C
Z	4
V	1907.39 Å^3
ρ_{calcd}	1.61 g/cm^3
λ	0.7107 Å
μ	11 cm^{-1}

X-ray Determination. Crystalline (*p*-methylacetophenone)$_2$AgBF$_4$ was prepared and analyzed as described earlier.[3] The colorless crystals with dimensions about $0.1 \times 0.1 \times 0.2$ mm were sealed in 0.1-mm capillaries due to their sensitivity toward atmospheric moisture. Preliminary Weissenberg and precession photographs exhibited monoclinic symmetry from the systematic absences in Table VIII leading to a space group assignment of either $C2/c$ or Cc. Cell dimensions were subsequently determined by least-squares refinement to fit the $\pm 2\theta$ values for 20 high-angle reflections centered on a Picker FACS-I diffractometer. Crystallographic data are presented in Table VIII. The density calculated on the basis of four molecules per unit cell is 1.61 g/cm^3. Although the density of this complex was not measured because it decomposed in most solvents, the calculated value is consistent with densities of silver perchlorate complexes of comparable molecular weights.[18c]

Diffractometer data were obtained by using Zr-filtered Mo Kα radiation by the θ–2θ scan technique at a take-off angle of 3°. Peaks were scanned at a rate of 1.0°/min from 1.0° on the low angle side of the Kα_1 peak to 1.0° on the high-angle side of the Kα_2 peak. Diffracted beams were counted by using a scintillation counter and were attenuated with Zr foil. Stationary-crystal, stationary-counter background counts of 10 s were taken at each end of the scan. A unique data set was collected to $2\theta = 40°$. The intensities of three reflections ($4,0,\bar{2}$; 0,6,2; $\bar{2}$,0,6) were monitored as standards every 50 reflections, and only very slight loss in intensity was observed throughout data collection.

Data were corrected for background, and standard deviations were assigned according to the equations $I = C - 0.5(t_c/t_b)(B_1 + B_2)$ and $\sigma(I) = [C + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$, where C is the integrated peak count obtained in time t_c and B_1 and B_2 are the background counts obtained in time t_b, all corrected for scalar truncation. A value of 0.04 was used for p to avoid overweighting strong reflections. The data were corrected for Lorentz and polarization effects. A total of 735 reflections with $I \geq 2\sigma(I)$ were used in the solution and refinement of the structure. No absorption correction was made.

The silver atom, as revealed by Patterson synthesis, could be located in three possible positions: (1) on the twofold axis at the special position 4e (0, y, $^1/_4$) in space group $C2/c$, (2) at special position 4a (0, 0, 0) in space group $C2/c$, (3) at the general position in space group Cc.

First, the two possible positions with space group $C2/c$ were tried and the Fourier syntheses generated. Only the Fourier map generated with silver located at special position 4e (0, y, $^1/_4$) gave reasonable geometry and bond distances, and R_1 and R_2 values were 0.543 and 0.605. Difference Fourier maps and least-squares refinements were performed and led to the positions of the carbon and oxygen atoms. Three cycles of refinement assuming individual isotropic thermal parameters for all atoms led to values of 0.194 and 0.257 for R_1 and R_2. The difference Fourier map was again computed, and the BF_4 group was identified and located. Two more cycles of least-squares refinement yielded R_1 and R_2 of 0.121 and 0.142. Isotropic refinement in space group Cc at this stage gave no significant improvement in R values. The space group $C2/c$ was thus chosen for subsequent refinement and accepted

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Table IX. Final Positional Parameters[a] for $(p\text{-Methylacetophenone})_2AgBF_4$

atom	x	y	z
Ag	0	−0.012 (1)	0.250
C_1	0.172 (1)	−0.107 (1)	0.593 (1)
C_2	0.234 (2)	−0.047 (1)	0.649 (1)
C_3	0.295 (2)	−0.047 (1)	0.760 (1)
C_4	0.292 (2)	−0.107 (1)	0.817 (1)
C_5	0.227 (2)	−0.167 (1)	0.761 (2)
C_6	0.170 (2)	−0.167 (1)	0.651 (1)
C_7	0.109 (2)	−0.108 (1)	0.474 (1)
C_8	0.353 (2)	−0.106 (1)	0.939 (1)
C_9	0.039 (2)	−0.171 (1)	0.408 (1)
O	0.111 (1)	−0.053 (1)	0.426 (1)
B	0.500	−0.148 (2)	0.250
F_1	0.359 (2)	−0.108 (1)	0.227 (1)
F_2	0.492 (2)	−0.188 (1)	0.168 (1)

[a] Fractional coordinates with standard deviations.

on the basis of successful completion with reasonable geometric parameters.

Four cycles of least-squares refinement, assigning anisotropic thermal parameters to all non-hydrogen atoms, resulted in final values of $R_1 = 0.068$ and $R_2 = 0.075$. A final difference Fourier map revealed all the hydrogen atoms at their expected positions, and the electron densities at these positions varied from 0.7 e/Å^3 to 1.3 e/Å^3. No attempt, however, was made to include hydrogen atoms in the refinements. The map revealed that no significant feature was present (greater than 0.5 e/Å) except at the heavy atom position (1.1 e/Å) and at expected hydrogen positions. Table IX presents the final positional parameters, along with the corresponding standard deviations estimated from the least-squares variance-covariance matrix.

Aldol Condensation. A solution of 10.6 g (88 mmol) of acetophenone and 2.10 g (10.5 mmol) of $AgBF_4$ in 1,2-dichloroethane was stirred for 3 days at 70–80 °C under dry nitrogen. Indicator Drierite showed that water was evolved. A 2-g portion of the cooled reaction mixture was dissolved in ether, washed with water (4 × 25 mL), and dried with $MgSO_4$. Removal of solvent gave 1.7 g of a brown oily liquid.

Column chromatography of 500 mg on 15 g of silica gel (60–200 mesh, Baker) with 10:1 hexane:benzene and recrystallization of the product with benzene gave 36 mg (7.2%) of white crystals of 1,3,5-triphenylbenzene: mp 176–177 °C (lit.[28] mp 172 °C); NMR[29] and IR[30] spectra were in agreement with the literature; MS (70 eV), m/e (relative intensity) 308 (12), 307 (37), 306 (100), 291 (10), 290 (15), 289 (15), 229 (9), 228 (10), 227 (10), 226 (9), 153 (10), 102 (10), 101 (10), 78 (24), 77 (19). Preparative TLC of 25 mg with 30 g of silica gel G7 (Baker) (250-μm thickness) using 10:1 hexane:benzene gave 5.7 mg (calculated 23% overall) of 1,3,5-triphenylbenzene.

Kinetics of Hydrogen Exchange. Solutions were made from stock solutions of 1.00 M acetone in 99.8% (Merck, Sharp and Dohme) D_2O and concentrated HNO_3 (70.5%, $d^{20} = 1.42$). Varying amounts of $AgNO_3$, $LiNO_3$, and KNO_3 were added to give concentrations indicated in Tables VI and VII. Dioxane was used as an internal standard for NMR integration and the reaction followed by measuring areas 1.53 ppm upfield from dioxane with time. Temperatures were maintained at 43.6 ± 0.1 °C. Rate constants were calculated from unweighted least-squares plots of ln (f) vs. time.

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Registry No. $AgBF_4$, 14104-20-2; $(p\text{-methylacetophenone})_2AgBF_4$, 53506-19-7; acetophenone, 98-86-2; triphenylbenzene, 612-71-5; acetone, 67-64-1.

Supplementary Material Available: Listing of anisotropic temperature factors for non-hydrogen atoms (1 page). Ordering information is given on any current masthead page.

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