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(Trifluoroacetylcamphorato(silver(I) and Derived Olefin Complexes

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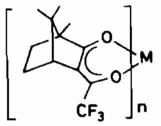
The chiral silver complex (trifluoroacetylcamphorato)silver (2) has been prepared and its interaction with olefins and triphenylphosphine has been examined. Addition of 2 *to solutions of alkenes causes downfield shifts (0.1–0.6 ppm) of their olefinic proton n.m.r. absorptions indicative of π-complexation. Isolable adducts were obtained and characterized for the ligands cyclooctadiene, norbornadiene, norbornylene, cycloheptatriene, 3-methylcyclohexene, and triphenylphosphine. Attempts to utilize* 2 *as an enantioselective gas chromatographic complexing agent for racemic alkenes failed, apparently due to its solution and thermal instability.*

Introduction

As part of a program whose ultimate objective is the development of chromatographic systems capable of resolving unsaturated racemates, we have been interested in the preparation of chiral, low-valent transition metal complexes. Because of the well documented history of silver(I) ion as an unsaturate-complexing agent [1] and the anticipated advantages of creating a rigid asymmetric environment about the metal center, silver complexes with covalently bound chiral ligands appear to be particularly suited for such resolutions. Previous studies which established the stability of Ag(hfacac)(olefin) complexes (hfacac = hexafluoroacetylacetonate) [2] and the widespread usage of lanthanide chelates of trifluoroacetylcamphorate (tfacCam), *e.g. 1,* as chiral nmr shift reagents [3], prompted our attempts to synthesize analogous silver derivatives. We now report the preparation of the title compound, *2,* and its interaction with olefin and phosphine ligands.



1: M = Eu, n = 3
2: M = Ag, n = 1

Results and Discussion

Trifluoroacetylcamphoratosilver(I), Ag(tfacCam), *2,* was obtained in moderate yield as a white, light-sensitive precipitate (mp 101–103 °C) upon mixing an aqueous ethanol solution of Na(tfacCam) [4] with aqueous $AgNO_3$ (eq. 1, 2).

$$\text{TfacCamH} + \text{Na} \longrightarrow \text{Na(TfacCam)} + 1/2\text{H}_2 \quad (1)$$

$$\text{Na(TfacCam)} + \text{AgNO}_3 \longrightarrow \text{Ag(TfacCam} + \text{NaNO}_3 \quad (2)$$

The structure of *2* is of more than passing interest since although the related Ag(acac) had been prepared as early as 1893 [5], little is known about its structure beyond the apparent O,O-chelate type bonding of the diketonate based on IR data [6]. The absence of vibrational absorptions in the 1700–1800 cm^{-1} region and the presence of peaks at 1635 and 1540 cm^{-1} are indicative of a similar bonding mode for *2.* Both the IR and NMR spectra of *2* tend to rule against the presence of ligated water. While this spectral data is consistent with an uncommon non-linear two coordinate complex geometry, a dimeric or polymeric structure resulting in additional silver–oxygen bonding interactions has not been ruled out.*

NMR spectra of solutions of various alkenes containing Ag(tfacCam) exhibited significantly deshielded (0.2–0.5 ppm) olefinic resonances, indicative of π-complexation. The dependence of the coordination shift (Δδ) on relative metal/olefin concentration and the absence of separate resonances for free and complexed olefin species even with excess olefin indicates that ligand exchange is rapid on the NMR time scale.

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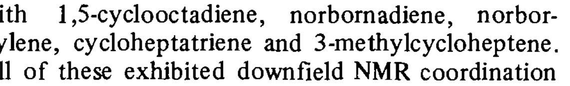
*The limited solubility of Ag(tfacCam) in noncoordinating solvents and its ready decomposition in solution producing silver metal, precluded acquisition of a completely satisfactory elemental analysis or a reliable osmometric molecular weight.

TABLE. Equilibrium Constants for Ag(tfacCam) + Olefin $\rightleftharpoons$ Ag(tfacCam)(Olefin).

Olefin	[Olefin]$_{tot}$	[Ag]$_{tot}$	$\Delta\delta_{ob}$(ppm)	$\Delta\delta_{max}$(ppm)	K(l/mol)	$\bar{K}$(L/mol)
Cyclopentene	0.024 *M*	0.122 *M*	0.28	0.77	5.1	4.6
	0.071	0.119	0.24		4.7	
	0.116	0.116	0.18		4.1	
Cyclohexene	0.045	0.176	0.26	0.51	7.6	7.3
	0.088	0.172	0.24		7.2	
	0.109	0.169	0.23		7.2	
Cyclooctene	0.045	0.074	0.16	0.50	7.7	7.5
	0.056	0.073	0.15		7.4	
	0.078	0.072	0.14		7.4	
1,5-Cyclooctadiene	0.023	0.075	0.50	0.63	69	
	0.069	0.073	0.36		40	
	0.112	0.071	0.24		22	
	0.133	0.070	0.20		16	

Olefin complex formation constants were determined by measuring the dependence of the coordination shift on olefin and Ag(tfacCam) concentration according to the method of Solodar [7] (see Experimental). Results of the determinations are presented in the Table. The K values for cyclopentene, cyclohexene, and cyclooctene are reasonably constant with changing concentrations supporting the assumption of 1:1 complex stoichiometry. The order of stability suggested is $C_8 \sim C_6 > C_5$. The K values for the diolefin 1,5-cyclooctadiene exhibit a substantial decreasing trend with increasing olefin concentration. This implicates the intrusion of secondary equilibria such as coordination of the second π bond via chelation and/or olefin bridging, *i.e.* 3 or 4.



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In some cases it proved possible to isolate the olefin complexes, Ag(tfacCam)(olefin). This was best achieved by metathesis of the corresponding silver nitrate complex, generated *in situ*, with Na(tfacCam) in aqueous ethanol. Solid complexes were obtained with 1,5-cyclooctadiene, norbornadiene, norbornylene, cycloheptatriene and 3-methylcycloheptene. All of these exhibited downfield NMR coordination shifts ($\Delta\delta$) of the olefinic protons in the range 0.2–0.5 ppm. NMR integration revealed that the complexes contain one olefin molecule per silver atom except for the norbornadiene complex for which a 1:2 stoichiometry is indicated. Other silver norbornadiene complexes of this composition have been reported previously [7–9]. The propensity of the Ag(tfacCam)(olefin) complexes to decompose in solution with deposition of metallic silver prevented further characterization and analysis.

Ag(tfacCam) formed an adduct of somewhat greater stability with triphenylphosphine. Thus mixing dmf solution of *2* and triphenylphosphine (a slight deficiency) produced Ag(tfacCam)(PPh$_3$), *5*, as an off-white solid upon addition of the reaction mixture to water. The nmr spectrum of *5* supports its formulation as a 1:1 adduct and its IR spectrum exhibited bands at 1646 cm^{-1} and 1554 cm^{-1} characteristic of chelate bonding to the camphorate ligand. This phosphine complex is assumed to be trigonal in solution by analogy to the known Ag(tfacCam)(PPh$_3$) [10].

Unfortunately, the thermal and solution instability of Ag(tfacCam) prevented its practical use as a complexing agent in gas chromatography. Although diethylene glycol solutions of *2* were reasonably stable at room temperature in the absence of light and oxygen, operating at 50–70 °C g.c. columns which had been packed with chromosorb P coated with solutions of *2* in diethylene glycol failed to consistently retard olefins to a greater extent than silver-free reference columns. Studies in progress are focusing on the design and preparation of more robust chiral complexes.

Experimental

All solvents were dried by standard procedures and stored over molecular sieves. Manipulations of silver-containing compounds and solutions were carried out under nitrogen and in the dark.

D-3-trifluoroacetylcamphor [4] and sodium trifluoroacetylcamphorate [4] were obtained by minor adaptations of the literature procedures.

Preparation of (Trifluoroacetylcamphorato)silver

A solution containing 1.54 g (5.72 mmol) of sodium trifluoroacetylcamphorate in 22 ml of 1:10 ethanol/water was added dropwise to 2 ml of a vigorously stirred solution of aqueous silver nitrate (0.48 g, 2.9 mmol). After one hour the white precipitate was collected by filtration in a Schlenk tube and washed with several small portions of distilled water. The product was dried at 1 mm in a vacuum desiccator over concentrated sulfuric acid for 12 hr. Typical yields were 50–60% (mp 101–103 °C). IR-(KBr): 1635 cm^{-1}, 1540 cm^{-1}, 1509 cm^{-1}, 921 cm^{-1}, 814 cm^{-1}. NMR($CDCl_3$) δ 0.79(s, 3H), 0.90(s, 3H), 0.95(s, 3H), 1.1–2.5(m, 4H), 2.77(s, 1H). $[\alpha]^{23}_{D}$ = +71° (c 0.020 pyridine). *Anal.* Calcd for $C_{12}H_{14}AgF_3O_2$: C, 40.5; H, 3.9; Ag, 30.4; F, 16.0. Found: C, 39.6; H, 4.2; Ag, 29.9; F, 15.5.

Formation Constants for Ag(tfacCam)(olefin)

Aliquots of standard solutions of olefins in CCl_4 were added to CCl_4 solutions of Ag(tfacCam) of known concentration in an nmr tube and the nmr spectra recorded after each addition. All $\Delta\delta_{max}$ values were obtained by adding solid Ag(tfacCam) to a solution of olefin until no further shift downfield of the olefinic proton resonance was observed. Equilibrium constants were calculated using equation 3 [7]. The data and results are presented in Table I.

$$K = \frac{\dfrac{\Delta\delta_{ob}}{\Delta\delta_{max}}[\text{olefin}]}{\left([\text{Ag}] - \dfrac{\Delta\delta_{ob}}{\Delta\delta_{max}}[\text{olefin}]\right)\left([\text{olefin}] - \dfrac{\Delta\delta_{ob}}{\Delta\delta_{max}}[\text{olefin}]\right)} \quad (3)$$

Preparation of Ag(tfacCam)(olefin)

The general procedure employed is illustrated by the preparation of Ag(tfacCam)(1,5-cyclooctadiene). Silver nitrate (0.30 g, 1.78 mmol), 1,5-cyclooctadiene (0.19 g, 1.76 mmol), and 10 ml of water were stirred vigorously in an ice bath for 30 min. A solution of 0.59 g (2.18 mmol) of NaTfacCam in 30 ml of water and 2 ml of ethanol was filtered into a pressure equalizing dropping funnel and degassed with nitrogen. This solution was added dropwise under nitrogen to the $AgNO_3$–olefin mixture and the reaction mixture allowed to stir for one hour. The product was filtered at 0 °C and washed several times with cold, degassed water. The product was dried for 12 hours in a vacuum desiccator over concentrated sulfuric acid under static aspirator vacuum (*ca.* 20 mm). A yield of 0.508 g (62%) of white solid complex was obtained. IR(KBr) 1654 cm^{-1} (broad), 1509 cm^{-1}, 1258 cm^{-1}, 1173 cm^{-1}, 1004 cm^{-1}, 924 cm^{-1}, 814 cm^{-1}, 799 cm^{-1}. NMR(CCl_4) δ 0.81(s, 3H), 0.86(s, 3H), 0.89(s, 3H), 2.53(s, 6.4), 2.73(s, 1H), 5.95(t, 3.1H). *Anal.* Calcd for $C_{20}H_{26}AgF_3O_2$: C, 51.8; H, 5.82; Ag, 23.3; F, 12.3. Found: C, 50.5; H, 5.5; Ag, 23.7; F, 11.6.

Ag(tfacCam)(norbornadiene) was obtained similarly in 30% yield. IR(KBr) 1640 cm^{-1}, 1508 cm^{-1}, 1370 cm^{-1}, 923 cm^{-1}, 799 cm^{-1}. NMR(CCl_4) δ 0.83(s, 7.2H), 0.91(s, 7.2H), 0.94(s, 7.2H), 2.07(m, 2H), 2.80(s, 2.4H), 3.92(m, 2H), 6.97(4H); Δδ 0.38. *Anal.* Calcd for $C_{31}H_{36}Ag_2F_6O_4$: C, 46.40; H, 4.45; Ag, 26.88; F, 14.21. Found: C, 45.17; H, 4.50; Ag, 25.69; F, 13.59.

Ag(tfacCam)(norbornylene) was produced in 27% yield. NMR(CCl_4) δ 0.84(s, 3H), 0.88(s, 3H), 0.95(s, 3H), 1.00–2.70(m), 2.28(s), 2.78(s, 1H), 3.22(m, 3H), 6.17(s, 2H); Δδ 0.21.

Ag(tfacCam)(1,3,5-cycloheptatriene) was isolated in 10% yield. NMR(CCl_4) δ 0.83(s), 0.91(s), 0.98(s), 1.2–2.5(m), 2.74(s), 5.64(m), 6.3(m), 6.65(m); Δδ 0.35, 0.28, 0.15.

Ag(tfacCam)(3-methylcyclohexene) was isolated in 27% yield. NMR(CCl_4) δ 0.83(s), 0.95(s), 0.99(s), 1.09(d), 1.23–2.73(m), 2.80(s, 6H), 5.84(m, 2H); Δδ 0.19.

Preparation of (Triphenylphosphine)(trifluoroacetylcamphorato)silver(I)

A freshly prepared batch of Ag(TfacCam) (1.07 mmol) was dissolved with shaking in 6 ml of dmf in a glove bag. The mixture was filtered into a 50 ml round bottomed flask. Triphenylphosphine (0.84 mmol) was dissolved in two ml of dmf, degassed, and added dropwise under nitrogen to the AgTfacCam solution with stirring. After 15 minutes, the reaction mixture was added dropwise to 200 ml of degassed water. The product was filtered on a glass frit, under nitrogen, and washed with distilled water. The white solid obtained was dried *in vacuo* (1 torr) and recrystallized from pentane (yield 42%). IR(KBr) 1646 cm^{-1}, 1626 cm^{-1}, 1554 cm^{-1}, 1435 cm^{-1}, 1266 cm^{-1}, 1181 cm^{-1}, 746 cm^{-1}, 695 cm^{-1}. NMR(CCl_4) δ 0.85(s, 3H), 0.88(s, 3H), 0.95(s, 3H), 2.83(s, 1H), 7.39(m, 15H). *Anal.* Calcd for $C_{30}H_{29}AgF_3O_2P$: 58.4; H, 4.74; Ag, 17.5; F, 9.24; P, 5.02. Found: C, 60.33; H, 5.00; Ag, 16.08; F, 8.21; P, 5.19.

Gas Chromatographic Studies Employing 2

Reference columns (6′ × ¼″ ss) of 10% and 20% diethylene glycol (DEG) on chromosorb P were prepared by standard methods and conditioned at 100 °C overnight. The following silver-impregnated columns were prepared in a glove bag under nitrogen and conditioned overnight at 70 °C: 0.1 *M* 2/10% DEG, 0.114 *M* 2/10% DEG and 0.946 *M* 2/20% DEG. Operating at column temperatures of 70 °C and 75 °C and with cyclopentene, *cis*- and *trans*-2-octene, α-pinene and 3-methylcyclohexene as reference compounds, retention times on the silver-containing columns were not consistently longer than on the reference columns.

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