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Preparation and NMR Spectra of the (Trifluoromethyl)argentates(III) $[Ag(CF_3)_nX_{4-n}]^-$, with X = CN (n = 1−3), CH_3, $C{\equiv}CC_6H_{11}$, Cl, Br (n = 2, 3), and I (n = 3), and of Related Silver(III) Compounds. Structures of $[PPh_4][trans\text{-}Ag(CF_3)_2(CN)_2]$ and $[PPh_4][Ag(CF_3)_3(CH_3)]$†

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Trifluoromethylation of $[Ag(CN)_2]^-$ with $(CF_3)_2Cd{\cdot}$diglyme yields $[Ag(CF_3)(CN)]^-$. The anion is readily oxidized by bromine to the argentates(III), $[Ag(CF_3)_n(CN)_{4-n}]^-$, n = 1−4. The stability of these species decreases with an increasing number of CN groups. Halogenation of these complexes with acetyl chloride or with bromine affords the moderately stable (n = 3) or unstable (n = 2) haloargentates of the type $[Ag(CF_3)_nX_{4-n}]^-$, X = Cl or Br. Their dehalogenation with $AgNO_3$ in a donor solvent D gives the adducts $[Ag(CF_3)_3D]$ and $[Ag(CF_3)_2D_2]^+$, respectively. Decomposition of most argentates(III) proceeds by reductive elimination of CF_3X (X = Cl, Br, or CN), but ligand exchange with participation of the CF_3 groups is also observed. The latter is used to prepare $Ag(CF_3)_3$ derivatives from the readily accessible $[trans\text{-}Ag(CF_3)_2(CN)_2]^-$ anion. The syntheses of methyl(trifluoromethyl)argentates(III) and of (cyclohexylethynyl)(trifluoromethyl)argentates(III) are accomplished by reaction of the cyanoargentates (n = 2, 3) with CH_3MgCl or $LiC{\equiv}CC_6H_{11}$, respectively. Often multinuclear (^{109}Ag, ^{19}F, ^{13}C, ^1H) NMR data of transient and stable Ag(III) species establish unambiguously not only their constitution but also the square-planar coordination of the metal. Couplings to the spin-$^1/_2$ silver nuclei are interpreted on the basis of 5s(Ag) orbital participation in competition with 4d orbital contributions to Ag−CF_3 bonding. Crystals of $[PPh_4][Ag(CF_3)_2(CN)_2]$ belong to the monoclinic space group $C2/c$, with a = 18.174(2) Å, b = 7.8881(8) Å, c = 18.881(2) Å, β = 93.036(8)°, and Z = 4, whereas $[PPh_4][Ag(CF_3)_3(CH_3)]$ crystallizes in the orthorhombic space group $Pca2_1$, with a = 24.941(3) Å, b = 7.2629(6) Å, c = 14.9985(14) Å, and Z = 4. The coordination environments of these two argentates are approximately square planar. The Ag-CF_3 bonds in the dicyano complex (2.105(4) Å) are distinctly longer than the Ag−CN linkages (2.013(3) Å). In the $[Ag(CF_3)_3(CH_3)]^-$ anion, the Ag−CH_3 distance (2.097(5) Å) is slightly shorter than the average Ag−CF_3 bond lengths (2.119(10) Å).

Introduction

Molecular silver(III) coordination compounds are rare[1] and are mainly limited to complexes containing multidentate nitrogen ligands such as ethylenebis(guanidine), tetraazacycloalkanes, or porphyrines. An outstanding organometallic Ag(III) complex, the argentate $[Ag(CF_3)_4]^-$, has been described 10 years ago by Dukat and Naumann.[2] This surprisingly stable ion forms by the facile disproportionation of bis(trifluoromethyl)argentate(I) according to

$$(CF_3)_2Cd + Ag^+ \xrightarrow[30\ °C]{glyme/DMF} [Ag(CF_3)_2]^- + Cd^{2+}$$

$$2[Ag^I(CF_3)_2]^- + Ag^+ \rightarrow [Ag^{III}(CF_3)_4]^- + 2Ag^0 \qquad (1)$$

Alternatively, the oxidation of the argentate(I) to silver(III) may be achieved with bromine or iodine. Similar reactions have been used to produce the cuprates(III) $[Cu(CF_3)_4]^-$ [3] and $[Cu(CF_2H)_4]^-$.[4] Their unexpectedly low oxidative power as well as their stability in air and water has led to attempts to describe these compounds as metal(I) complexes with an oxidized CF_3 group.[5] Such a description, however, contradicts the usual chemical formalism and has been criticized.[6] From a more chemical point of view, these systems with a strong and simultaneously highly electronegative ligand are more closely related to isoelectronic platinum(II) systems than to "typical" Ag(III) compounds such as the AgF_4^- ion.[7] But in general, all properties are in agreement with a formulation as M(III) d^8-systems; e.g. the ^{109}Ag NMR signal of $[Ag(CF_3)_4]^-$ at ca. 2200 ppm is clearly offset from the usual values near 500 ppm for Ag(I) compounds.[2] The square-planar coordination of the silver atom has been confirmed recently by X-ray structure analysis.[8] Furthermore, treatment of $[Ag(CF_3)_4]^-$ with HCl has given planar $[Ag(CF_3)_3Cl]^-$ as shown by the 2:1 ratio of the CF_3

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† Dedicated to Professor Alois Haas on the occasion of his 65th birthday.

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groups in its ^{19}F NMR spectrum.[2] Though detailed structural data is not available for CF_3 substituted Ag(I) species, donor-stabilized $CF_3Ag{\cdot}D$ (D = solvent, PR_3) and the $[Ag(CF_3)_2]^-$ ion have been identified in solution with chemical properties which clearly contrast those of $[Ag(CF_3)_4]^-$.[2,9]

Recently, the $[M^{III}(CF_3)_4]^-$ ions have attracted additional interest as counterions in tetrathiofulvene-based organic superconductors with T_c values up to 11 K.[8,10] An extended knowledge of the coinage metals in high oxidation states may also be helpful for understanding high-temperature superconductors.

The aim of this contribution is to explore the general stability limits of Ag(III) compounds by substituting CF_3 with other ligands such as halides or alkyl groups. A promising ligand for the stabilization of both low and high oxidation states is the CN group. Its σ-bonding properties resemble those of a CF_3 group whereas its π-acceptor capability helps to stabilize low oxidation states.

Experimental Section

(a) General Procedures. Volatile material was handled on a vacuum line equipped with greaseless stopcocks. Air-sensitive non-volatile material was handled under argon or nitrogen atmosphere. NMR spectra were recorded with a BRUKER ARX 400 instrument (^1H, 400.13 MHz; ^{13}C, 100.63 MHz; ^{19}F, 376.50 MHz) and a BRUKER AC 250 (^1H, 250.13 MHz; ^{19}F, 235.36 MHz; ^{13}C, 62.90 MHz; ^{109}Ag, 11.64 MHz). The latter spectrometer was equipped with a ^{19}F decoupler which used the pulse trains generated by the ^1H decoupler and allowed ^{19}F broad-band decoupling over a range of more than 20 kHz after tuning the decoupler coil to the fluorine frequency. If possible, polarization transfer from ^{19}F by means of the DEPT pulse sequence was used to record the 1D spectra of less sensitive nuclei such as ^{13}C and ^{109}Ag. Two-dimensional spectra ($^{13}C-^{19}F$, $^{109}Ag-^{19}F$) taken with the pulse sequence given by Bax[11] were used to determine relative signs of coupling constants. Spectra have been referenced to external TMS (^1H, ^{13}C), $CFCl_3$ (^{19}F) and 1 *m* $AgNO_3$ in D_2O (^{109}Ag), corrections being made for different lock substances. Computer simulations of high-order NMR spectra was carried out with the BRUKER WINNMR/WINDAISY program package. Raman spectra were obtained with a Cary 82 model, excitation Kr^+ at 647.1 nm. Infrared spectra were taken with a BRUKER IFS 25 spectrometer as KBr pellets for solids and with 10 cm gas cells for gases. Calorimetric analyses were made with a simultaneous DSC/TG instrument NETZSCH STA 409. Elemental analyses were performed with a Perkin-Elmer 240B microanalysis device.

Chemicals were obtained from commercial sources and used without further purification. The diglyme adduct of bis(trifluoromethyl)cadmium was prepared following published procedures.[12]

(b) Synthetic Reactions. (i) Solutions of Cyano(trifluoromethyl)argentate(I). (a) To a solution of 309 mg (1.82 mmol) of $AgNO_3$ in 2 mL of DMF was added at −30 °C 350 mg (0.91 mmol) of $(CF_3)_2Cd{\cdot}$diglyme. After 10 min of stirring in the dark was added 850 mg (5.45 mmol) of solid $Et_4N^+CN^-$, and the mixture was stirred for another 10 min and warmed to room temperature. (b) To a solution of 600 mg (3.00 mmol) of $K[Ag(CN)_2]$ in 5 mL of DMF was added 578 mg (1.5 mmol) of $(CF_3)_2Cd{\cdot}$diglyme at ambient temperature in the dark, and the mixture was stirred for 20 min. The solution was cooled to −30 °C, and 234 mg (3.0 mmol) of acetyl chloride was added slowly. Volatile material (CH_3COCN) was removed *in vacuo*, and precipitated $CdCl_2$ was separated by centrifugation. The constituents of the solution were examined by means of ^{19}F and ^1H NMR spectroscopy after addition of fluorobenzene as integration standard.

(ii) Synthesis of the Tricyano(trifluoromethyl)argentate(III) Anion. A solution containing a 1:1 mixture of the $[Ag(CN)_2]^-$ and $[Ag(CF_3)(CN)]^-$ ions was obtained according to (i) using 7.4 g (37.2 mmol) of $K[Ag(CN)_2]^-$ and 3.6 g (9.3 mmol) of $(CF_3)_2Cd{\cdot}$digylme in 50 mL of DMF with 1.46 g (18.6 mmol) of acetyl chloride being added. After 20 min of stirring, CH_3COCN was pumped off, the solution was cooled to −50 °C, and a solution of Br_2 (3.2 g, 20 mmol) in 3 mL of diglyme was added. With continuous pumping, the reaction mixture was slowly warmed to 0 °C until the volume was reduced to ca. 20 mL. Precipitated AgBr and $CdCl_2$ were separated at −10 °C by centrifugation. The resulting colorless solution was examined by NMR spectroscopy utilizing fluorobenzene as the internal standard.

(iii) Synthesis of $[P(C_6H_5)_4][Ag(CF_3)_2(CN)_2]$. A solution containing 37 mmol of the $[Ag(CF_3)(CN)]^-$ ion in 50 mL of DMF was oxidized at −50 °C with 3.2 g (20 mmol) of Br_2 dissolved in 3 mL of diglyme. After warming to ambient temperature, 3.5 g (9.4 mmol) of tetraphenylphosphonium chloride was added. After 20 min of stirring and addition of 100 mL of $CHCl_3$, the reaction mixture was repeatedly extracted with water. The organic phase was dried over $MgSO_4$ and the solvent removed *in vacuo*. The solid residue was re-dissolved in 50 mL of $CHCl_3$ and precipitated again by slow addition of diethyl ether. This procedure was repeated until ^{19}F NMR spectroscopy proved that the resulting white powder was free of $[PPh_4]$[*cis*-$Ag(CF_3)_2(CN)_2$] and $[PPh_4][Ag(CF_3)_3(CN)]$. Recrystallization from chloroform in an atmosphere of diethyl ether afforded 6 g (25% yield) of colorless crystals. Anal. Calcd for $C_{28}H_{20}AgF_6N_2P$: H, 3.16; C, 52.77; N, 4.40. Found: H, 3.00; C, 52.87; N, 4.25. Infrared (cm^{-1}), KBr pellet: 3060 w, 1588 w, 1486 w, 1438 m, 1193 m, 1110/1094 vs (ν_s CF_3), 1048/1032 vs (ν_{as} CF_3), 995 w, 752 m, 726 s, 687 s, 528 s, 450 m. Raman (cm^{-1}): 3067 w, 2181 m (ν CN), 1593 m, 1167 w, 1114 w, 1102 w, 1087 w (ν_s CF_3), 1030 m, 1003 s, 709 m (δ_s CF_3), 682 w, 618 w, 525 w (δ_{as} CF_3), 402 m (ν_s AgC_N), 293 w, 260 w, 250 m (δ AgCN), 227 m, 211 s (ν_s AgC_F), 136 m (δ AgC_n), 83 s, 67 s, 57 vs, 34 s, 25 vs.

DSC/TG analysis of single crystals showed an exothermic decomposition with melting of the sample at 133 °C connected with a loss of weight of 6.0%. For analysis of decomposition products, 350 mg of $[PPh_4]$[*trans*-$Ag(CF_3)_2(CN)_2$] were sealed in a 4 mm glass ampule and heated to 135 °C for a short time. After the ampule was opened under vacuum, volatile material was examined by gas phase IR spectroscopy and was afterward condensed onto $CDCl_3$ for NMR investigation. The solid residue was dissolved in DMF containing fluorobenzene as the integration standard for quantitative evaluation of the constituents.

The combined $CHCl_3/Et_2O$ solutions collected after precipitation of $[PPh_4]$[*trans*-$Ag(CF_3)_2(CN)_2$] were evaporated to dryness, re-dissolved in 10 mL of $CHCl_3$ and treated with 100 mL of diethyl ether in order to precipitate $[PPh_4]$[*cis*-$Ag(CF_3)_2(CN)_2$]. Successive crystallization yielded a 200 mg sample of $[PPh_4]$[*cis*-$Ag(CF_3)_2(CN)_2$] in 95% purity.

(iv) Synthesis of $[P(C_6H_5)_4][Ag(CF_3)_3(CH_3)]$. To a solution of 450 mg (0.64 mmol) of $[PPh_4][Ag(CF_3)_3(CN)]$ in 3 mL of THF was added a 3-fold excess of a 1 M solution of CH_3MgCl in THF. After 10 min of stirring at ambient temperature, the solution was cooled with ice. Excess Grignard reagent was destroyed with 10 mL of H_2O, and

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thereafter 100 mL of $CHCl_3$ was added. The organic layer was washed repeatedly with water and dried over $MgSO_4$. Evaporation of the solvent gave a reddish powder which was recrystallized from chloroform in an etheral atmosphere, yielding 360 mg (0.53 mmol, 90% yield) of pale reddish $[PPh_4][Ag(CF_3)_3(CH_3)]$. Anal. Calcd for $C_{28}H_{23}AgF_9P$: C, 50.25; H, 3.46. Found: C, 50.24; H, 3.47. Infrared (cm^{-1}), KBr pellet: 3102 vw, 3072 m, 3023 vw, 2926 s, 1652 m, 1587 m, 1486 m, 1438 s, 1261 m, 1191 w, 1113 vs, 1085 vs, 1017 vs, 984 s/sh, 849 w, 755 m, 725 s, 692 s, 528 vs.

Solutions of *cis* and *trans* $[PPh_4][Ag(CF_3)_2(CH_3)_2]$ were obtained from the corresponding cyanoargentates following a similar procedure, however maintaining a temperature of −20 °C. Replacement of the Grignard reagent by a solution of (cyclohexylethynyl)lithium, $LiC{\equiv}CC_6H_{11}$, gave $[PPh_4][Ag(CF_3)_3(C{\equiv}CC_6H_{11})]$, $[PPh_4]$[*trans*-$Ag(CF_3)_2(C{\equiv}CC_6H_{11})_2$], and $[PPh_4]$[*cis*-$Ag(CF_3)_3(C{\equiv}CC_6H_{11})$], starting from the respective cyanoargentates.

(v) Halogenation of Cyanoargentates(III). Chlorination reactions of the cyanoargentates were carried out under a nitrogen atmosphere using a 4−10-fold excess of acetyl chloride, the progress of the reaction being monitored by ^{19}F NMR spectroscopy. After removal of solvents *in vacuo*, samples were obtained with a purity of ca. 90% as determined by ^1H and ^{19}F NMR spectroscopy. Bromination of $[PPh_4][Ag(CF_3)_3(CN)]$ was carried out at 0 °C within 4 h using a 4-fold excess of Br_2, while that of $[PPh_4]$[*trans*-$Ag(CF_3)_2(CN)_2$] was conducted directly under NMR control at temperatures between −10 and 0 °C utilizing a 10 mm NMR tube. $[PPh_4][Ag(CF_3)_3I]$ was obtained by treating a solution of $[PPh_4][Ag(CF_3)_3Cl]$ in DMF with a 2-fold excess of NaI.

Chlorination of $[PPh_4]$[*trans*-$Ag(CF_3)_2(CN)_2$] and Synthesis of $[PPh_4][Ag(CF_3)_3(CN)]$. A solution of 1.50 g (2.3 mmol) of $[PPh_4]$[*trans*-$Ag(CF_3)_2(CN)_2$] in 5 mL of DMF was treated at −30 °C with a 5-fold excess of acetyl chloride. The reaction mixture was warmed within 3 h to ambient temperature and stirred for another 9 h. Glyme (20 mL) was added in order to precipitate $[PPh_4][AgCl_2]$ quantitatively. After filtration 10 mL of DMF and 1.5 g of KCN were added, and the mixture was stirred for 1 h at ambient temperature. Then chloroform (100 mL) was added, and the solution was extracted several times with water. The organic phase was separated and dried over $MgSO_4$. Evaporation of the solvent *in vacuo* afforded 660 mg (0.9 mmol) of a white powder containing 95% $[PPh_4][Ag(CF_3)_3(CN)]$ and 5% $[PPh_4][Ag(CF_3)_4]$ which could not be separated by fractional crystallization.

(vi) Dehalogenation Reactions. A saturated solution of $AgNO_3$ in DMF was added dropwise to a solution of $[PPh_4][Ag(CF_3)_3X]$ (X = Cl, Br, I) in DMF until precipitation of AgX ceased. After filtration, the ^{19}F NMR spectra showed an identical pattern of a $Ag(CF_3)_3$ unit which did not change upon mixing of the three solutions. Addition of NaI, NEt_4Br, or PPh_4Cl to the reaction mixture re-formed the respective halide.

Synthesis of $[PPh_4]$[*cis*-$Ag(CF_3)_2(CN)_2$]. A solution of $[PPh_4]$[*trans*-$Ag(CF_3)_2Br_2$] in DMF, which was obtained by bromination of 610 mg (0.96 mmol) of $[PPh_4]$[*trans*-$Ag(CF_3)_2(CN)_2$] in 3 mL of DMF at −10 °C, was cooled to −30 °C and a saturated $AgNO_3$ solution (3 mL) was added. After stirring for 10 min the precipitated AgBr was removed by centrifugation at ca. −40 °C. A 5-fold excess of KCN was added to the cold reaction mixture which was warmed over a time period of 2 h to ambient temperature. Chloroform (100 mL) was added, and the mixture was extracted several times with small amounts of water. After separation of the organic phase, drying over $MgSO_4$, and evaporation of the solvent, a powder mainly consisting of *cis*- and *trans*-$[PPh_4][Ag(CF_3)_2(CN)_2]$ was obtained. The powder was redissolved in $CHCl_3$, and diethyl ether was added until the *trans* isomer was precipitated quantitatively. Evaporation of the solution afforded 100 mg of a pale yellow powder which contained some $[PPh_4][Ag(CF_3)_3(CN)]$ and $[PPh_4][Ag(CF_3)_4]$ in addition to $[PPh_4]$[*cis*-$Ag(CF_3)_2(CN)_2$].

(c) Crystal Structure Determinations. Crystals were grown by isothermal distillation of diethyl ether into a $CHCl_3$ solution of the corresponding salt and were shaped by cleaving. The chosen fragments were glued to glass fibers and mounted on a Siemens P3 diffractometer which employed graphite-monochromatized Cu Kα radiation. The Laue groups found by diffractometry were consistent with those revealed by preliminary Weissenberg examinations. The lattice constants were derived by least-squares methods from the setting angles of 40 centered reflections. Data were collected using the $\theta-2\theta$ scan mode with $5° \leq 2\theta \leq 138°$. The intensities were corrected by integration for absorption—the distances between the crystal faces being optimized so as to reproduce the intensity variations found in ψ profiles. After locating the atomic positions with direct methods and subsequent difference Fourier techniques, the structures were refined on F^2 using all unique data. Crystal data are presented in Table 1. Structural solution, refinement and graphical display were all made with a SHELXTL[13] program package.

Table 1. Crystallographic Data

compound	[PPh][*trans*-$Ag(CF_3)_2(CN)_2$]	$[PPh_4][Ag(CF_3)_3(CH_3)]$
formula	$C_{28}H_{20}AgF_6N_2P$	$C_{28}H_{23}AgF_9P$
fw	637.3	669.3
cryst syst	monoclinic	orthorhombic
space group	$C2/c$	$Pca2_1$
a (Å)	18.174(2)	24.941(3)
b (Å)	7.8881(8)	7.2629(6)
c (Å)	18.881(2)	14.9985(14)
β (deg)	93.036(8)	
V (Å^3)	2702.9(5)	2716.8(4)
Z	4	4
ρ_{calc} (g cm^{-3})	1.566	1.636
λ (Å)	1.54184	1.54184
T (°C)	23	18
μ(Cu Kα) (mm^{-1})	7.095	7.228
transm	0.261−0.617	0.258−0.477
$R(F)^a$ ($I > 2\sigma(I)$)	0.034	0.032
$R_w(F^2)^b$ (all data)	0.094	0.082

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

$[P(C_6H_5)_4][Ag(CF_3)_2(CN)_2]$. A plate-shaped crystal, 0.08 × 0.18 × 0.41 mm, was oriented with its long dimension roughly parallel to the ϕ axis. The 2794 reflections in the $\pm h,k,l$ quadrant were measured. Of these, 2518 are unique—2204 having $I > 2\sigma(I)$. The CF_3 group exhibits rotational disorder with respect to the Ag−C bond—the occupancies found being 0.46(2) and 0.54(2) for rotamers A and B, respectively. While the hydrogen positions were all evident from a difference Fourier map, they were entered and refined with a riding model (C−H = 0.95 Å). The 205 variables, which included anisotropic temperature factors for the non-hydrogen atoms and an extinction parameter, converged rapidly.

$[P(C_6H_5)_4][Ag(CF_3)_3(CH_3)]$. A block-shaped crystal with the approximate measurements 0.14 × 0.15 × 0.34 mm was mounted with its major dimension parallel to the ϕ axis. Of the 11481 reflections collected in the $\pm h$, k, $\pm l$ hemisphere, 5066 are unique in the presence of anomalous dispersion—4374 having $I > 2\sigma(I)$. The structural solution was complicated by a pseudomirror plane perpendicular to the c axis which arises from the close match of the z coordinates of the Ag and P atoms; furthermore, since this plane nearly coincides with a approximate coordination plane of the anion, only the phenyl carbon positions severely violate the pseudosymmetry. While phenyl hydrogen atoms were treated with a riding model, the methyl hydrogen positions were taken from a difference Fourier map, idealized (C−H = 0.95 Å), and refined with a riding model which also optimized the torsional rotation about the Ag−C(1) bond. Using one restraint, the 356 variables, which included anisotropic temperature factors for the non-hydrogen atoms as well as an extinction and Flack x parameter,[14] converged smoothly. The value of the Flack x parameter, 0.347(9), indicates marked inversion twinning.

Results and Discussion

(a) Synthetic Aspects. (i) Preparation and Oxidation of (Trifluoromethyl)silver(I) Species. The high stability constant of the dicyanoargentate(I) complex anion along with its dynamic behavior—fast exchange of the CN groups and formation of higher coordinated $[Ag(CN)_n]^{(n-1)-}$ species[15]—have prompted

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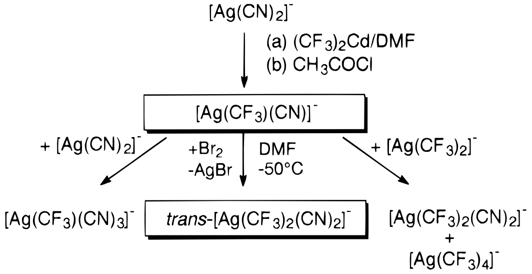
Scheme 1



us to investigate its trifluoromethylation to $[Ag(CF_3)(CN)]^-$. The trifluoromethylation of Ag^+ with $(CF_3)_2Cd$ is known to produce donor-stabilized CF_3Ag and $[Ag(CF_3)_2]^-$.[2,8] When a mixture of $(CF_3)_2Cd$ and excess $AgNO_3$ in DMF is treated with tetraethylammonium cyanide, the formation of a new CF_3Ag(I) compound along with some $[Ag(CF_3)_2]^-$ is evident from the ^{19}F NMR spectra. The same moiety is obtained by reacting either AgCN or $K[Ag(CN)_2]$ with $(CF_3)_2Cd$, e.g.

$$(CF_3)_2Cd + K[Ag(CN)_2] \rightleftharpoons CF_3CdCN + K[Ag(CF_3)(CN)] \quad (2)$$

With the starting materials in a 1:1 ratio, no more than 40% of the $(CF_3)_2Cd$ is consumed. The equilibrium, however, is shifted almost completely to the right by adding at -30 °C acetyl chloride in the exact amount to remove the released cyanide

$$(CF_3)_2Cd + 2[Ag(CN)_2]^- + 2CH_3COCl \xrightarrow[-30\ °C]{DMF} CdCl_2 + 2[Ag(CF_3)(CN)]^- + 2CH_3COCN \quad (3)$$

Attempts to isolate the air- and moisture-sensitive (trifluoromethyl)argentates(I) from DMF solutions have failed. Replacement of DMF by other solvents such as THF or acetonitrile gives much lower conversion rates and considerably more impurities which we have not been able to separate from the products.

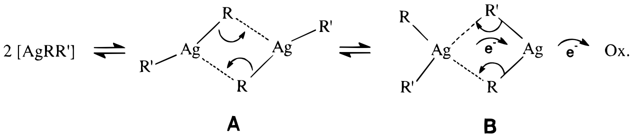
The $[Ag(CF_3)(CN)]^-$ anion is readily oxidized in DMF solution at -50 °C by elemental bromine or iodine to square-planar cyano(trifluoromethyl)argentates(III)

$$2[Ag(CF_3)(CN)]^- + Br_2 \xrightarrow[-50\ to\ -30\ °C]{DMF} [Ag(CF_3)_n(CN)_{4-n}]^- + AgBr + Br^- \ (n = 1-4) \quad (4)$$

The product composition, as monitored by multinuclear NMR spectroscopy (see below), is greatly influenced by the relative amounts of $[Ag(CN)_2]^-$, $[Ag(CF_3)(CN)]^-$, and $[Ag(CF_3)_2]^-$ present among the starting materials. Thus, oxidation of a 1:1 mixture of $[Ag(CN)_2]^-$ and $[Ag(CF_3)(CN)]^-$ gives the thermally labile argentate $[Ag(CF_3)(CN)_3]^-$ as the main product (Scheme 1).

The bromine oxidation of a solution containing $[Ag(CF_3)(CN)]^-$ as the only Ag(I) moiety yields the [*trans*-$Ag(CF_3)_2(CN)_2]^-$ anion quite selectively. Its isolation is accomplished by cation exchange with PPh_4Cl or [PNP]Cl. Cadmium salts are removed from the etheral solution by washing with water, and the PPh_4 and PNP salts are obtained by repeated fractional crystallization as colorless crystals in an overall yield of 25% with respect to $(CF_3)_2Cd$. The ions [*cis*-$Ag(CF_3)_2(CN)_2]^-$, $[Ag(CF_3)_3(CN)]^-$, and $[Ag(CF_3)_4]^-$ have been identified by ^{19}F NMR analysis as byproducts with a total amount of less than 10%. While [*cis*-$Ag(CF_3)_2(CN)_2]^-$ is prepared more efficiently from [*trans*-$Ag(CF_3)_2(CN)_2]^-$ (see below), attempts to obtain the $[Ag(CF_3)_3(CN)]^-$ ion directly by oxidizing a 1:1 mixture of $[Ag(CF_3)(CN)]^-$ and $[Ag(CF_3)_2]^-$ with bromine have failed. Instead, a mixture is formed which contains the ions $[Ag(CF_3)_2(CN)_2]^-$ and $[Ag(CF_3)_4]^-$ along with minor amounts of $[Ag(CF_3)_3(CN)]^-$ (Scheme 1), the latter being readily detected by its characteristic coupling patterns in the ^{19}F NMR spectrum. This anion, however, is best prepared via a dismutation reaction (see below).

The selectivity of the oxidation reaction seems to be related to the dynamic behavior of the Ag(I) species: Though the couplings to the silver nuclei are clearly recognizable, the ^{19}F NMR signals of bis(trifluoromethyl)argentate(I) dissolved in polar solvents such as acetonitrile are significantly broadened, sharp signals being obtained upon cooling to -20 °C. Similarly, when a solution of $K[Ag(CN)_2]$ in DMF is recorded at room temperature a broad ^{13}C signal without any fine structure is detected. However, when cooled to -50 °C the exchange of the cyano groups is so slow that the $^1J(^{109}Ag^{13}C)$ and $^1J(^{107}Ag^{13}C)$ coupling constants can be determined. In case of the cyano complex $[Ag(CF_3)(CN)]^-$, rather sharp ^{19}F and ^{13}C signals with couplings to the silver nuclei characterize the CF_3 group whereas the exchange of the cyano groups remains fast on the NMR time scale even at -80 °C. Since a dissociative exchange mechanism is not likely to account for the scrambling of the CF_3 groups in the bis(trifluoromethyl)argentate(I), we favor a dimeric transition state (**A**) similar to the structure found for the dimeric dichloroargentate unit in $[PPh_4][AgCl_2]$.[16] Since the cyano group is a much better bridging ligand than the CF_3 group, the exchange of the CF_3 groups in $[Ag(CF_3)(CN)]^-$ is unfavorable and hence slow. Concomitantly, the scrambling of the more ionic cyano groups will be faster than in the dicyanoargentate(I). The formation of Ag(III) may well proceed from such a symmetric transition state (**A**) via an asymmetric intermediate (**B**). The second silver will donate its ligands irreversibly to the first upon electron transfer. The silver will either precipitate or, in the presence of a halogen, will be converted to the corresponding halide, eq 4. In a 1:1 mixture of $[Ag(CF_3)(CN)]^-$ and $[Ag(CF_3)_2]^-$, the better bridging ability of the cyano group will make dimers formed by two $[Ag(CF_3)(CN)]^-$ units much more prevalent than those formed with at least one $[Ag(CF_3)_2]^-$ entity. Accordingly, oxidation of such a mixture first forms $[Ag(CF_3)_2(CN)_2]^-$. Only when $[Ag(CF_3)(CN)]^-$ becomes depleted does oxidation of $[Ag(CF_3)_2]^-$ to $[Ag(CF_3)_4]^-$ become competitive. Furthermore, such a transition state explains the preferential formation of the *trans* isomer of $[Ag(CF_3)_2(CN)_2]^-$ as the kinetically favored pathway.



(a) R = R' = CN
(b) R = CN, R' = CF_3
(c) R = R' = CF_3

The thermal stability of the cyano(trifluoromethyl)argentates(III) decreases as the number of cyano groups attached to the silver atom increases. Thus, a solution of $[PPh_4][Ag(CF_3)(CN)_3]$ in DMF degrades within 2 h at room temperature with elimination of CF_3CN and re-formation of the dicyanoargentate(I), but may be stored for weeks at -78 °C. Solutions of $[PPh_4]$[*cis*-$Ag(CF_3)_2(CN)_2]$ in DMF decompose quantitatively within 1 week at ambient temperature whereas the degradation of the [*trans*-$Ag(CF_3)_2(CN)_2]^-$ and $[Ag(CF_3)_3(CN)]^-$ anions requires warming to 50 and 80 °C, respectively—CF_3CN being evolved in both cases. Crystals of $[PPh_4]$[*trans*-$Ag(CF_3)_2(CN)_2]$ decompose exothermically upon melting at 135 °C. Combined DSC/TG studies as well as NMR and IR analyses of the volatile and involatile products show that no elimination of difluorocarbene takes place. Instead, the primary reaction appears to be a dismutation which yields $[Ag(CF_3)_4]^-$ and the much less stable $[Ag(CF_3)(CN)_3]^-$ ion—the latter eliminating either $(CN)_2$ or CF_3CN to form the Ag(I) anions $[Ag(CF_3)(CN)]^-$ or $[Ag(CN)_2]^-$, respectively.

(ii) Alkylation Reactions. The cyanoargentates(III) enter displacement reactions in which the Ag−CF_3 bonds are not attacked. Alkylations with Grignard type reagents such as CH_3MgCl or with cyclohexylethynyllithium result in the formation of the corresponding methyl and cyclohexylethynyl derivatives, respectively, e.g.

$$[PPh_4][Ag(CF_3)_n(CN)_{4-n}] \xrightarrow[\text{THF}]{\text{(i) or (ii)}} [PPh_4][Ag(CF_3)_nR_{4-n}] \qquad (5)$$

$$\text{(i) } CH_3MgCl;\ n = 2 \text{ or } 3$$

$$\text{(ii) } LiC{\equiv}CC_6H_{11};\ n = 2 \text{ or } 3$$

Thus, methylation of $[PPh_4][Ag(CF_3)_3(CN)]$ gives $[PPh_4][Ag(CF_3)_3(CH_3)]$ in almost quantitative yield. The salt is isolated as pale-red crystals which are stable in air at ambient temperature. Similarly, treatment of the dicyanobis(trifluoromethyl)argentates(III) with CH_3MgCl produces the corresponding methyl derivatives with complete (>98%) retention of the *cis* or *trans* geometries. Their lower stability—solutions containing the [*trans*-$Ag(CF_3)_2(CH_3)_2]^-$ ion may be handled shortly at ambient temperature whereas the *cis* isomer decomposes rapidly above 0 °C—have prevented accumulation and isolation. The replacement of the first CN group of [*trans*-$Ag(CF_3)_2(CN)_2]^-$ by the Grignard reagent is much faster than that of the second. Thus, controlled addition of 1 equiv of CH_3MgCl at −30 °C gives [*trans*-$Ag(CF_3)_2(CH_3)(CN)]^-$ selectively which is further transformed to [*trans*-$Ag(CF_3)_2(CH_3)_2]^-$ by a second equivalent of CH_3MgCl. In contrast, there is no evidence for the intermediate species during a controlled methylation of [*cis*-$Ag(CF_3)_2(CN)_2]^-$. Here, the first methylation step appears to labilize the remaining cyano group.

Similarly, replacement of the cyano groups by means of $LiC{\equiv}CC_6H_{11}$ affords the corresponding ethynyl derivatives $[Ag(CF_3)_3(C{\equiv}CC_6H_{11})]^-$ as well as *cis*- and *trans*-$[Ag(CF_3)_2(C{\equiv}CC_6H_{11})_2]^-$ almost quantitatively. Though their stabilities are somewhat higher than those of their methyl analogs, we have not yet succeeded in isolating them in analytically pure form. Their identity, however, is unambiguously established by NMR spectroscopy.

(iii) Halogenation of the Cyanoargentates(III). Dukat and Naumann[2] have already presented clear evidence for the existence of the $[Ag(CF_3)_3Cl]^-$ ion, traces of which were obtained from $[Ag(CF_3)_4]^-$ and HCl in CH_3CN. A better route to this anion is the mild chlorination of the cyano derivative with acetyl chloride

$$[Ag(CF_3)_3(CN)]^- + CH_3COCl \xrightarrow{\text{DMF/RT}} [Ag(CF_3)_3Cl]^- + CH_3COCN \qquad (6)$$

Similarly, reaction of the cyano complex with elemental bromine at 0 °C produces the corresponding bromide while the iodide is obtained from the chloride by halide exchange with NaI. Although these halides are stable at room temperature and formed rather selectively, all attempts to prepare the corresponding fluoride by halide exchange with fluorides have failed so far—decomposition to the $[Ag(CF_3)_2]^-$ ion being detected instead. The stability of the halides with respect to reductive elimination of CF_3X and formation of $[Ag(CF_3)_2]^-$ increases in the order I < Br < Cl.

Surprisingly, two cyano groups can be replaced by halogens as long as the reaction conditions are carefully controlled. Thus bromination of [*trans*-$Ag(CF_3)_2(CN)_2]^-$ proceeds via intermediate formation of [*trans*-$Ag(CF_3)_2(CN)Br]^-$ to the thermally unstable [*trans*-$Ag(CF_3)_2Br_2]^-$. Unfortunately, a temperature of 0 °C is required to achieve a measurable reaction rate, and at this temperature about 20% of the product is decomposed before completion of the reaction—CF_3Br being evolved.

The chlorination of bis(trifluoromethyl)dicyanoargentates(III) with acetyl chloride requires room temperature as well as a highly polar and strong donor solvent such as DMF. In the first step the *trans* isomer is converted cleanly to [*trans*-$Ag(CF_3)_2(CN)Cl]^-$. Prolonged reaction times and excess CH_3COCl finally produces [*trans*-$Ag(CF_3)_2Cl_2]^-$ which, however, is not stable under the reaction conditions—dismutating to $[Ag(CF_3)_3Cl]^-$ and presumably $[Ag(CF_3)Cl_3]^-$. We have not been able to trap the latter due to its apparent instability. Instead, CF_3Cl is evolved and crystals of $[PPh_4][AgCl_2]$ have been collected and identified by X-ray analysis.[16]

The chlorination of $[PPh_4]$[*trans*-$Ag(CF_3)_2(CN)_2]$ as well as the following dismutation are very selective and open a new preparative route to the otherwise hardly accessible tris(trifluoromethyl)argentates(III), Scheme 2. On the basis of [*trans*-$Ag(CF_3)_2(CN)_2]^-$, 75% of the expected $[Ag(CF_3)_3Cl]^-$ is formed along with some (ca. 5%) $[Ag(CF_3)_4]^-$ as the only CF_3-containing contaminant. The chloro complex is readily transformed to $[Ag(CF_3)_3(CN)]^-$ by addition of KCN. In contrast to $[PPh_4][Ag(CF_3)_3Cl]$, the stability of $[PPh_4][Ag(CF_3)_3(CN)]$ to moisture allows it to be washed free of water soluble impurities.

The *cis* isomer of the $[Ag(CF_3)_2(CN)_2]^-$ ion is converted by acetyl chloride first to [*cis*-$Ag(CF_3)_2(CN)Cl]^-$ and then to a new *cis*-$(CF_3)_2Ag^{III}$ species which is markedly stable—decomposing in DMF solution to form CF_3Cl and $CF_3Ag{\cdot}DMF$ only when warmed to 50 °C. Since the *cis* isomers of all other $(CF_3)_2Ag^{III}$ species are more reactive and thermally less stable than their *trans* counterparts, the stability of this complex is higher than we would expect for [*cis*-$Ag(CF_3)_2Cl_2]^-$. Unfortunately, the lack of analytically pure material prevented a detailed structural study. Essentially the same situation has been noticed in case of the isoelectronic (trifluoromethyl)platinum compounds where a [*cis*-$(CF_3)_2PtCl_2]^{2-}$ could not be prepared as well. Instead, evidence for a bridged dimer, $[(CF_3)_2Pt(\mu\text{-}Cl)_2Pt(CF_3)_2]^{2-}$, had been presented.[17] Though no $^{109}Ag^{107}Ag$ coupling is discernible in the ^{109}Ag NMR spectrum (see below), we favor a corresponding dimer for the silver(III) complex

$$2[\textit{cis}\text{-}Ag(CF_3)_2(CN)_2]^- \xrightarrow[\text{DMF/RT}]{CH_3COCl} 2[\textit{cis}\text{-}Ag(CF_3)_2(CN)Cl]^- \xrightarrow[\text{DMF/RT}]{CH_3COCl} [(CF_3)_2Ag(\mu\text{-}Cl)_2Ag(CF_3)_2] \qquad (7)$$

In contrast to all replacement reactions described above, exchange of the chlorine atoms of this dimer by other ligands does not occur with strict stereoselectivity. Thus, reaction with KCN affords the *cis* and *trans* isomers of $[Ag(CF_3)_2(CN)_2]^-$ in

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(16) Helgesson, G.; Jagner, S. *J. Chem. Soc., Dalton Trans.* **1988**, 2117.

(17) Appleton, T. G.; Berry, R. D.; Hall, J. R.; Neale, D. W. *J. Organomet. Chem.* **1989**, *364*, 249.

Scheme 2

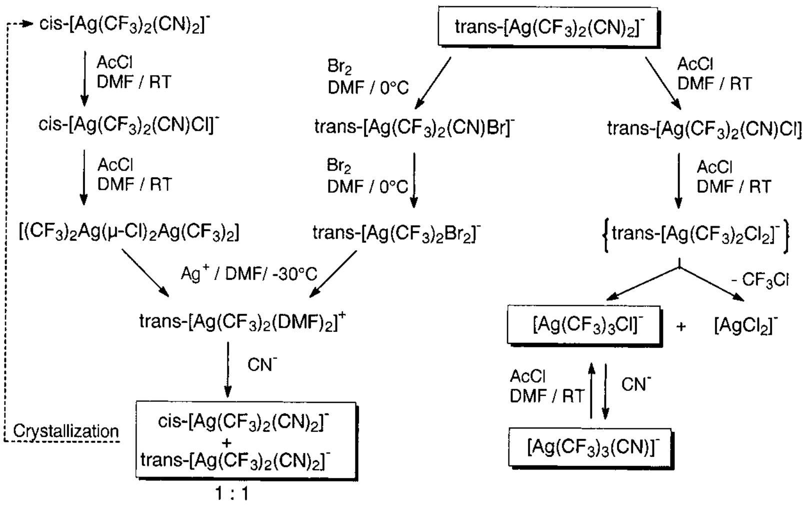
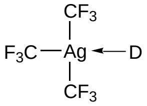


Table 2. ^{19}F NMR Shifts of Solvent adducts, $(CF_3)_3Ag{-}D^a$

D	 $F_3C{-}Ag(CF_3)_2{\leftarrow}D$	
dimethoxyethane	−25.7	−29.7
pyridine	−23.6	−33.9
dimethyl sulfoxide	−22.2	−35.5
dimethylformamide	−23.0	−36.9
acetonitrile	−21.5	−36.4

[a] Chemical shifts in ppm vs external $CFCl_3$, internal lock C_6D_6; spectra recorded at 298 K.

a ratio of 1.5:1 while methylation with CH_3MgCl proceeds with ca. 80% retention of the *cis* configuration.

(iv) Dehalogenation of Bis- and Tris(trifluoromethyl)haloargentates(III). When solutions of the tris(trifluoromethyl)haloargentates $[PPh_4][Ag(CF_3)_3X]$ (X = Cl, Br, I) in DMF are treated with a slight excess of $AgNO_3$, silver halide precipitates, and the signal pattern of a new $(CF_3)_3Ag^{III}$ species appears in the ^{19}F NMR spectrum. This signal pattern is independent of the nature of X. Upon addition of halide ions in form of PPh_4Cl, NMe_4Br, or NaI, the new species is reconverted to the corresponding haloargentate(III). The dehalogenated $(CF_3)_3Ag$ moiety slowly decomposes at room temperature with loss of C_2F_6—$CF_3Ag{\cdot}DMF$ being formed. While in general the ^{19}F NMR resonances hardly depend on the nature of the solvent, this is not true for the ^{19}F chemical shifts of this new $(CF_3)_3Ag$ species, Table 2. The formation of a nitrato complex is excluded by the fact that $AgBF_4$ may be used in place of $AgNO_3$. Based on these observations, we postulate the formation of neutral solvent complexes, $(CF_3)_3Ag{\cdot}D$ (D = donor, solvent).

$$[Ag(CF_3)_3X]^- + Ag^+ + D \xrightarrow{D} [Ag(CF_3)_3D] + AgX$$
$$D = DMF, DMSO, CH_3CN, glyme, pyridine \qquad (8)$$

An alternative, albeit less selective route to the same species is the bromination of $Ag[Ag(CF_3)_4]$ in CH_3CN at room temperature. Requiring 2−4 days, the reaction is so slow that extensive decomposition of the products occurs before completion. So the yield is optimized by removal of bromine after 70−80% of the $[Ag(CF_3)_4]^-$ is consumed. Consequently, such samples are adulterated by appreciable amounts of the starting material and decomposition products.

$$Ag[Ag(CF_3)_4] + Br_2 \xrightarrow{CH_3CN} [Ag(CF_3)_3NCCH_3] + AgBr + CF_3Br \qquad (9)$$

When $AgNO_3$ is added to $[PPh_4][Ag(CF_3)_3Cl]$ in small portions, an intermediate compound with reasonable thermal stability is formed in the first step. The same intermediate is observed upon treatment of the donor adducts $(CF_3)_3Ag{\cdot}D$ with small portions of PPh_4Cl. The NMR parameters of this species are hardly dependent on the solvent, making a formulation as halide-bridged dimer $[(CF_3)_3Ag(\mu\text{-}Cl)Ag(CF_3)_3]^-$ plausible

$$2[Ag(CF_3)_3Cl]^- \underset{+Cl^-}{\overset{+Ag^+/-AgCl}{\rightleftharpoons}}$$
$$[(CF_3)_3Ag(\mu\text{-}Cl)Ag(CF_3)_3]^- \underset{+Cl^-}{\overset{+Ag^+/-AgCl}{\rightleftharpoons}} 2[Ag(CF_3)_3D] \qquad (10)$$

The same species is formed exclusively when triisopropyl phosphite is used as the dehalogenation reagent. A corresponding bromine-bridged intermediate with almost degenerate ^{19}F resonances at −26.5 ppm is detected when $[Ag(CF_3)_3Br]^-$ is debrominated with triisopropyl phosphite or when KBr is added to $[Ag(CF_3)_3D]$, D = DMF. Upon addition of $AgNO_3$ to the bromo or iodo complex, the ^{19}F signals broaden and gradually shift to the positions of the neutral donor complex.

In principal, the dehalogenation of the bis(trifluoromethyl)dihaloargentates(III) proceeds in a similar manner (Scheme 2). Treatment of the presumably bridged complex $[(CF_3)_2Ag(\mu\text{-}Cl)_2Ag(CF_3)_2]$ with $AgNO_3$ affords a new Ag(III) compound. On the basis of the large values of the $^4J(FF)$ and $^3J(CF)$ coupling constants, a *trans* arrangement of the two CF_3 groups is most likely. The same species is also obtained from [*trans*-$Ag(CF_3)_2Br_2]^-$ and $AgNO_3$, $[Ag(CF_3)_3D]$ being formed as a major byproduct. Its formulation as Ag(III) complex is validified by treatment with KCN which gives a 1:1 mixture of the *cis*- and *trans*-$[Ag(CF_3)_2(CN)_2]^-$ ions. This latter reaction is well suited as a preparative route to the otherwise hardly accessible [*cis*-$Ag(CF_3)_2(CN)_2]^-$. The different solubility of the PPh_4^+ salts of the *cis* and *trans* isomers in ether enables separation via precipitation of the *trans* isomer. Thus, samples of $[PPh_4]$[*cis*-$Ag(CF_3)_2(CN)_2]$ are obtained which are contaminated with 5−10% of $[PPh_4][Ag(CF_3)_3(CN)]$ and $[PPh_4][Ag(CF_3)_4]$.

(b) NMR Spectra. The variety and abundance of spin-$^1/_2$ nuclei (^{19}F, ^{13}C, ^1H, ^{109}Ag, ^{107}Ag) with distinct couplings across and to the central atom and hence characteristic multiplet patterns makes the NMR spectroscopy the preferred tool for the investigation and characterization of (trifluoromethyl)-

Table 3. NMR Data for (Trifluoromethyl)silver(I) Compounds[a]

				CF$_3$				CN	
	$\delta(^{119}Ag)$	$\delta(^{19}F)$	$^2J(^{109}AgF)$	$\delta(^{13}C)$	$^1J(^{109}AgC)$	$^1J(CF)$	$^3J(CF)$	$\delta(^{13}C)$	$^1J(^{109}AgC)$
$Ag(CF_3)\cdot DMF$	*b*	−22.4	121.7	*b*	*b*	*b*			
$[Ag(CF_3)_2]^-$ [c,d]	565.5	−25.3	100.1	154.9	277.2	370.0	8.0		
$[Ag(CF_3)(CN)]^-$ [d]	566.0	−25.0	106.7	153.9	325.5	369.2		143.9	
$[Ag(CN)_2]^-$ [d]	584.3							143.0	203.9

[a] In DMF/diglyme at 298 K, internal lock C_6D_6. Chemical shifts are in ppm; coupling constants are in Hz. References are external TMS, $CFCl_3$, and 1 *m* $AgNO_3$ in D_2O; $^nJ(^{107}AgX) = {}^nJ(^{109}AgX)/1.15$ within experimental error. [b] Not observed or not resolved. [c] $^4J(FF) < 1$ Hz. [d] Recorded at 223 K.

Table 4. NMR Data of the $(CF_3)_nAg$ Part of (Trifluoromethyl)silver(III) Derivatives[a]

	$\delta(^{119}Ag)$	$\delta(^{19}F)$	$^2J(^{109}AgF)$	$^4J(FF)$	$\delta(^{13}C)$	$^1J(^{109}AgC)$	$^1J(CF)$	$^3J(CF)$
$[Ag(CF_3)_4]^-$ [d]	2233.1	−32.7	40.7	12.9 (tr)	139.0	119.9	393.0	45.2 (tr)
				6.2 (cis)				8.1 (cis)
$[Ag(CF_3)_3(CN)]^-$	2250.4	−25.9[c]	35.8	15.4 (tr)	136.8	96.7	399.0	50.8 (tr)/12.4 (cis)
		−30.1	55.7	7.3 (cis)	133.5	163.2	384.7	10.8 (cis)
$[Ag(CF_3)_3Cl]^-$	2187.8	−29.0[c]	30.8	17.5 (tr)	137.2	93.2	406.0	55.0 (tr)/15.5 (cis)
		−26.0	70.8	8.8 (cis)	129.3	199.4	394.7	13.0 (cis)
$[Ag(CF_3)_3Br]^-$	2135.2	−26.7[c]	31.0		136.6	93.1	*b*	*b*
		−25.5	72.6	9.1 (cis)	126.3	204.0	401.6	12.7 (cis)
$[Ag(CF_3)_3I]^-$ [e]	2003.0	−20.3[c]	31.6		134.8	95.2	*b*	*b*
		−28.6	67.1	8.4 (cis)	117.5	195.0	*b*	*b*
$[(CF_3)_3Ag(\mu\text{-}Cl)Ag(CF_3)_3]^-$	2264.4	−25.8[c]	35.7		137.1	95.6	*b*	*b*
		−29.5	57.7	7.4 (cis)	133.1	165.9	*b*	*b*
$[Ag(CF_3)_3(NCCH_3)]$[f]	2323.7	−36.4[c]	25.5	19 (tr)	137.5	91.1	409.3	58 (tr)/18 (cis)
		−21.5	85.3	9.0 (cis)	124.1	228.5	391.2	15 (cis)
$[Ag(CF_3)_3(DMF)]$	2403.5	−36.9[c]	25.0	19 (tr)	137.5	90.4	408.2	56 (tr)/19 (cis)
		−23.0	83.6	8.6 (cis)	124.4	230.6	392.4	15.4 (cis)
$[Ag(CF_3)_3(CH_3)]^-$ [g]	2046.1	−31.5[c]	49.0	9.4 (tr)	142.9	136.0	387.8	36 (tr)
		−33.9	33.1	3.6 (cis)	151.1	104.8	395.1	
$[Ag(CF_3)_3(C{\equiv}CC_6H_{11})]^-$ [m]	2232.4	−26.8[c]	41.2		137.4	106.7	*b*	*b*
		−32.9	50.7	6.1 (cis)	139.2	144.2	*b*	*b*
trans-$[Ag(CF_3)_2(CN)_2]^-$	2292.5	−18.9	30.9	19.2	133.7	71.1	407.0	61.2
trans-$[Ag(CF_3)_2(CN)Cl]^-$ [e]	2263.5	−21.6	24.6	23.1	134.4	63.5	419.0	70.0
trans-$[Ag(CF_3)_2(CN)Br]^-$ [e]	*b*	−18.6	23.4	*b*	*b*	*b*	*b*	*b*
trans-$[Ag(CF_3)_2Cl_2]^-$	*b*	−24.0	14.9	*b*	*b*	*b*	*b*	*b*
trans-$[Ag(CF_3)_2Br_2]^-$ [e]	*b*	−17.1	15.8	29.9	129.9	55.3	433.3	81.3
trans-$[Ag(CF_3)_2(NCCH_3)_2]^+$ [e]	*b*	−23.8	50.8	22	*b*	*b*	411	*b*
trans-$[Ag(CF_3)_2(DMF)_2]^+$ [e]	2519.4	−26.3	49.4	20.7	121.5	161.2	417.8	50
trans-$[Ag(CF_3)_2(CN)(CH_3)]^-$	2034.0	−27.4	45.8	10.1	141.9	121.3	390.4	39.2
trans-$[Ag(CF_3)_2(CH_3)_2]^-$ [h]	2038.5	−30.3	54.8	6.9	145.3	148.2	382.3	30.7
trans-$[Ag(CF_3)_2(C{\equiv}CC_6H_{11})_2]^-$ [m]	2255.9	−20.9	42.3	13.0	136.8	95.4	393.5	48.3
cis-$[Ag(CF_3)_2(CN)_2]^-$	2301.6	−22.2	48.3	9.9	130.7	131.3	390.3	22.2
cis-$[Ag(CF_3)_2(CN)Cl]^-$ [i]	*b*	−16.7	62.5	12.2	*b*	*b*	*b*	*b*
		−27.8	39.5					
$[Ag(CF_3)_2(\mu\text{-}Cl)_2Ag(CF_3)_2]$[i]	2227.8	−20.9	51.6	16.1	128.3	149.8	409.7	*b*
cis-$[Ag(CF_3)_2(CH_3)_2]^-$ [h,k]	*b*	−34.2	36.8	*b*	152.6	110	*b*	*b*
cis-$[Ag(CF_3)_2(C{\equiv}CC_6H_{11})_2]^-$	*b*	−26.2	48.7	*b*	*b*	*b*	*b*	*b*
$[Ag(CF_3)(CN)_3]^-$	2343.7	−10.2	39.8		126.4	89.9	394.9	

[a] See Table 3, cations are PPh_4^+ or PNP^+. [b] Not observed or not resolved. [c] CF_3 groups in *cis* position to the fourth ligand. [d] As $Ag[Ag(CF_3)_4]$ in CH_3CN. [e] Spectra recorded at 253 K. [f] In CH_3CN at 253 K. [g] $^3J(C_FH)^{cis} = 0.5$ Hz, $^3J(C_FH)^{trans} = 5.9$ Hz, and $^4J(HF)^{trans} = 1.2$ Hz. [h] In THF at 243 K. [i] In THF at 298 K. [k] $^3J(C_FH)^{cis} = 2.6$ Hz; $^3J(C_FH)^{trans} = 5.2$ Hz. [m] $^4J(AgH) = 1.0$ Hz.

argentates. Even minor and thermally labile components of complex mixtures are quite often safely identified. The high quality of the spectra strongly indicates that paramagnetic Ag(II) species are not formed. The connectivity of a CF_3 group to the central silver atom is apparent from the couplings to the ^{109}Ag (48.2%) and ^{107}Ag (51.8%) nuclei, which give raise to a characteristic pair of doublets with coupling constants in a ratio of 1.15:1. Despite their high abundance, the NMR resonances of the two silver nuclei are usually not readily detected directly due to their low and negative magnetogyric ratios as well as their extremely long relaxation times. The more sensitive ^{109}Ag nucleus resonates at the utmost low-frequency edge of commercial broad-band probes where the quality factor of the receiver coil is low. The coupling to the sensitive ^{19}F nuclei, however, allows a polarization transfer by the DEPT or INEPT technique which widely overcomes these deficits and makes the ^{109}Ag resonance readily detectable as long as exchange of the CF_3 groups is slow on the NMR time scale. Similarly, the DEPT technique with polarization transfer from ^{19}F can be used to increase the sensitivity of the ^{13}C resonance and to suppress all signals not coupled to fluorine. The results are presented in

Table 5. ^{13}C NMR Data of the Cyano Groups in Cyanoargentates(III)[a]

	$\delta(^{13}C)$	$^1J(^{109}AgC)$	$^3J(CF)$
$[Ag(CF_3)_3(CN)]^-$	130.8	101.7	29 (tr)/8.3 (cis)
trans-$[Ag(CF_3)_2(CN)_2]^-$	124.0	143.2	10.4 (cis)
trans-$[Ag(CF_3)_2(CN)Cl]^-$	119.5	176.6	12.3 (cis)
trans-$[Ag(CF_3)_2(CN)(CH_3)]^-$ [d]	142.8	81.1	*b*
cis-$[Ag(CF_3)_2(CN)_2]^-$	126.9	87.9	*b*
$[Ag(CF_3)(CN)_3]^-$	118.2	125.4	18.5 (cis)
	120.3[c]	74.7	40.9 (tr)

[a] See Table 3. [b] Not observed or not resolved. [c] CN group in *trans* position to CF_3. [d] $^3J(CH) = 3.5$ Hz.

Table 6. NMR Data of the Methyl and Cyclohexylethynyl Groups in Argentates(III)[a]

	$CH_3/C^\alpha{\equiv}C^\beta$			CH_3		
	$\delta(^{13}C)$	$^1J(^{109}AgC)$	$^3J(CF)$	$^1J(CH)$	$\delta(^1H)$	$^2J(^{109}AgH)$
$[Ag(CF_3)_3(CH_3)]^-$	16.5	38.7	34.7 (tr)	139.6	1.0	5.1
			8.1 (cis)			
trans-$[Ag(CF_3)_2(CH_3)_2]^-$	11.0	38.2	6.7	132.5	0.3	4.3
trans-$[Ag(CF_3)_2(CH_3)(CN)]^-$	20.3	49.2	7.6	142.9	1.3	6.7
cis-$[Ag(CF_3)_2(CH_3)_2]^-$	9.2	46	*b*	135	0.5	5.7
$[Ag(CF_3)_3(C^\alpha{\equiv}C^\beta C_6H_{11})]^-$	91.2(α)	107.2	*b*			
	101.1(β)	20[c]	5.2 (tr)[d]			
trans-$[Ag(CF_3)_2(C^\alpha{\equiv}C^\beta C_6H_{11})_2]^-$	93.1(α)	117.3	11.2 (cis)			
	99.6(β)	25.3[c]	1.2 (cis)[d]			

[a] See Table 3. [b] Not observed or not resolved. [c] $^2J(^{109}AgC)$. [d] $^4J(CF)$.

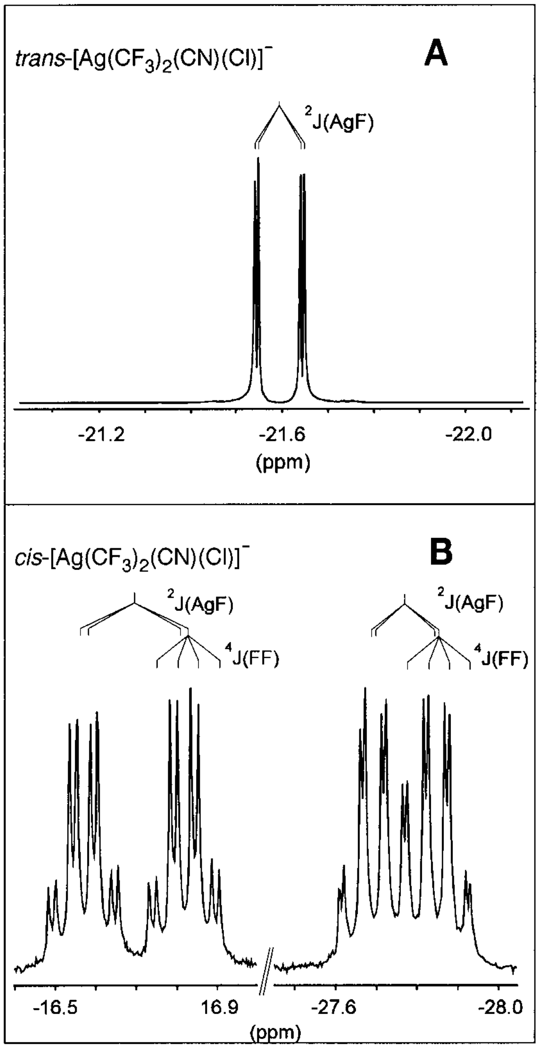


Figure 1. ^{19}F NMR spectra of the (**A**) *trans*- and (**B**) *cis*-$[Ag(CF_3)_2(CN)Cl]^-$ anion with the typical $^{109}Ag/^{107}Ag$ coupling pattern for two equivalent (**A**) and nonequivalent (**B**) CF_3 groups attached to silver.

Table 3 for Ag(I) and in Tables 4–6 for Ag(III) species, respectively.

The ^{19}F NMR spectra often reveal the stereochemistry of the argentates(III). Figure 1 displays the spectra of the *trans* (**A**) and *cis* (**B**) $[Ag(CF_3)_2(CN)Cl]^-$ ions. The former (**A**) shows the simple signal structure of a CF_3Ag moiety whereas spectrum (**B**) exhibits the quartet patterns of two nonequivalent CF_3 groups bonded to silver. Similarly, the presence of a square-planar $Ag(CF_3)_3X$ unit is evident from two ^{19}F NMR signals. These signals with an intensity ratio of 1:2 show characteristic septet and quartet multiplicities, respectively, that are overlaid by the ^{109}Ag and ^{107}Ag couplings, and are easily assigned to the nonequivalent CF_3 groups *trans* and *cis* to the ligand X. Much more information is gained by a combined analysis of the fluorine-coupled ^{13}C spectra and the ^{13}C satellites in the ^{19}F spectra. As long as the multiplicities due to the long-range couplings $^3J(CF)$ and $^4J(FF)$ across the central atom are discernible, the number of CF_3 groups attached to silver is readily evaluated. When *trans* and *cis* couplings occur simultaneously, the resulting spin systems become very complex, and high quality spectra are essential for their interpretation and for the optimization of computer simulations. For example, in their original work on the $[Ag(CF_3)_4]^-$ ion, Dukat and Naumann had concluded from the septet-like appearance of the ^{13}C satellites of the ^{19}F signal that the ion was square-planar with the *trans* $^4J(FF)$ coupling being nonresolvable. The latter statement, however, is incompatible with the general observation—in compliance with our results presented here—that the values of *trans* coupling constants are larger than those of the corresponding *cis* constants. Reexamination of the ^{13}C satellites indeed points to a higher multiplicity of the system. Furthermore, such a system cannot be treated by first-order analysis but has to be analyzed as two overlapping $XA_3B_6C_3M$ systems where X is ^{13}C, A to C are ^{19}F, and M is ^{109}Ag or ^{107}Ag. By combined computer analyses of the fluorine-coupled ^{13}C spectrum and of the ^{13}C satellites in the ^{19}F spectrum, an excellent simulation of the extremely dense experimental spectra has been achieved with the parameters listed in Table 4—*trans*-$^4J(FF)$ being twice as large as *cis*-$^4J(FF)$.

The ^{19}F chemical shifts for all observed CF_3Ag species lie between −10 and −35 ppm, and they do not differentiate between Ag(I) and Ag(III) species. More informative are the couplings to the silver nuclei which exceed 100 Hz for $^2J(^{109}AgF)$ in Ag(I) compounds (Table 3) but are distinctly lower in Ag(III) compounds. Similarly, the $^1J(AgC)$ constants of the Ag(I) species are larger than those of the Ag(III) compounds. The $^4J(FF)$ coupling in the ^{13}C satellites of $[Ag(CF_3)_2]^-$ is not resolved (<1 Hz) and is thus much smaller than the *trans*-$^4J(FF)$ coupling in the Ag(III) ions. The presence of two CF_3 groups in this argentate(I), however, is evident from the quartet of quartet pattern found in the ^{13}C spectrum of $[Ag(CF_3)_2]^-$.

The mobility of the cyano groups in the $[Ag(CN)_2]^-$ ion prevents the observation of the $^1J(AgC)$ coupling at room temperature. However, upon cooling to −50 °C the typical silver pattern becomes clearly visible in the ^{13}C spectrum. The $^1J(AgC)$ coupling constant (Table 3) is larger than those involving the cyano groups of the Ag(III) moieties (Table 5). The outstanding difference between Ag(I) and Ag(III) complexes, however, is the range of ^{109}Ag chemical shifts with values of ca. 550 ppm for trifluoromethylated Ag(I) (Table 3) and ca. 2000–2500 ppm for Ag(III) species (Table 4).

The influence of the ligands or the solvent on the $^{109}Ag(III)$ shifts is not very pronounced. An increasing number of CN groups causes a low-field shift of ca. 30 ppm per CN group. Replacement of one CF_3 group of $[Ag(CF_3)_4]^-$ by a halide

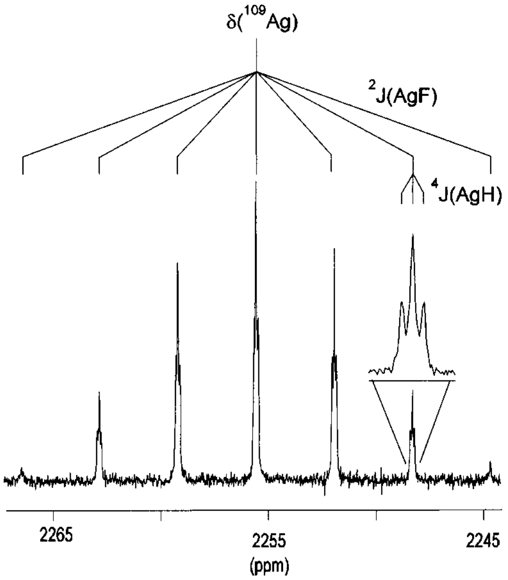


Figure 2. ^{109}Ag NMR spectrum of [PPh_4][*trans*-$Ag(CF_3)_2(C{\equiv}CC_6H_{11})_2$] with large ^2J(AgF) septet multiplicity along with fine triplet (^4J(AgH), insert) splitting. The spectrum was recorded by means of DEPT polarization transfer from ^{19}F (1146 scans, relaxation delay 2 s, evolution time 11.7 ms, variable pulse length 33°, no decoupling).

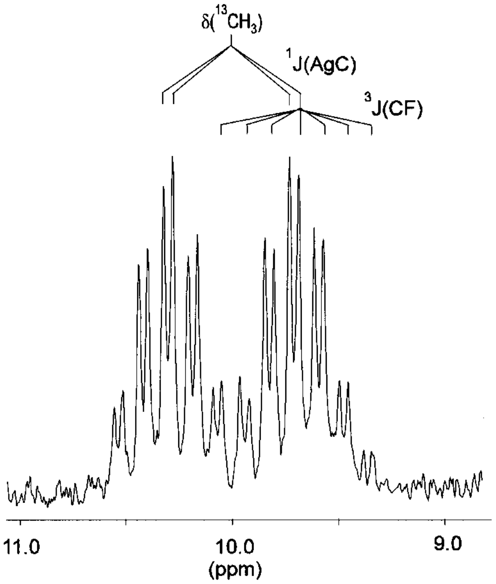


Figure 3. Proton-decoupled ^{13}C NMR spectrum of the CH_3 groups of [PPh_4][*trans*-$Ag(CF_3)_2(CH_3)_2$] in $CDCl_3$ recorded at −10 °C (^{1}H-DEPT, 828 scans, relaxation delay 2 s, evolution time 3.7 ms, variable pulse length 45°).

results in a high-field shift which is largest for the iodide. The neutral donor ligands seem to produce a low-field shift; for example, the highest shift value (+2520 ppm) observed so far was recorded for the DMF adduct of the *trans*-bis(trifluoromethyl)silver(III) cation. The assignment of the ^{109}Ag signals is usually straightforward due to the multiplicity patterns. For example, Figure 2 displays the ^{109}Ag spectrum of the *trans*-[$Ag(CF_3)_2(C{\equiv}CC_6H_{11})_2$]$^-$ ion where a triplet splitting due to the long-range ^4J(AgH) coupling is quite well discernible in addition to the AgF septet structure.

For the methyl and cyclohexylethynyl derivatives, the ^{13}C spectra of the methyl and ethynyl carbons exhibit characteristic couplings to the silver and fluorine nuclei with ^{109}Ag^{13}C couplings of 40 to 50 Hz for the sp^3 carbons whereas those to the sp carbons are significantly larger, Table 6. The $^{13}CH_3$ resonance of [*trans*-$Ag(CF_3)_2(CH_3)_2$] is displayed in Figure 3.

While CH_3 substitution hardly changes the ^{19}F resonance, replacement of a CF_3 group by halide, cyanide or ethynyl group causes a low field shift, the highest ^{19}F frequency being found for [$Ag(CF_3)(CN)_3$]$^-$. The resonance of the *cis*-[$Ag(CF_3)_2L_2$]$^-$ ion is always found upfield from that of the corresponding *trans* isomer. The chloride is no exception since, as mentioned above, the *cis*-conformer is not observed but rather dimerizes to form the chlorine-bridged structure, [$(CF_3)_2Ag(\mu\text{-}Cl)_2Ag(CF_3)_2$]. In principal, for such a dimer a ^{109}Ag−^{107}Ag coupling should be observable in the ^{109}Ag spectrum. The size of this coupling may be estimated from the couplings found in similar platinum dimers. The relation of corresponding coupling constants is mainly determined by the ratio of the magnetogyric ratios, $|\gamma(^{195}\mathrm{Pt})/\gamma(^{109}\mathrm{Ag})| = 4.6$, as well as the ratio of the $|\psi_s(0)|^2$ values;[18] these combine to give a total factor between 15 and 20. This is indeed the ratio found for ^2J(PtF) and ^2J(AgF) couplings, typical values being 800[17] and 50 Hz, respectively. Consequently, a factor of almost 400 is expected for the respective metal−metal couplings. Since the ^{195}Pt^{195}Pt coupling in $R_2Pt(\mu\text{-}Cl)_2PtR_2$ units amounts to ca. 200 Hz,[19] the ^{109}Ag^{107}Ag coupling will be on the order of 1 Hz or less and is not expected to be resolved even in high-resolution spectra, especially if the overlap with the central signal due to the ^{109}Ag^{109}Ag isotopomer is taken into account.

In square planar $(CF_3)_3AgL$ units with their characteristic two ^{19}F signals, the weighted average of the ^{19}F shifts varies by ca. 10 ppm—the low- and high-frequency edges being marked by L = CF_3 and I, respectively. More pronounced are the differences in the relative shifts for the CF_3 groups *cis* and *trans* to the fourth ligand. The resonance for the CF_3 group *trans* to L is much more sensitive than that of the *cis* unit. For example, on going from the chloride to the iodide, the *trans* CF_3 resonance experiences a pronounced low-field shift while the *cis* resonance shifts slightly in the opposite direction and thus cause a crossover of the signals.

An important information for the determination of the configuration is contained in the couplings across the silver atom. In CF_3 derivatives of main group elements such as tin,[20] both ^4J(FF) and ^3J(CF) couplings have the magnitude of a few hertz and are readily estimated by first-order analysis of the ^{13}C satellites of the ^{19}F signals and of the fluorine-coupled ^{13}C spectra, respectively. Inspection of the values given in Table 4 shows that these couplings are substantially larger in the square-planar silver complexes. Therefore, first-order analysis is no longer applicable. The determination of the *trans* couplings in the $(CF_3)_3AgL$ entity requires ^{13}C and ^{19}F spectra of very high quality because of the very complicated $XA_3B_3C_3M$ (X = ^{13}C *cis* to L; A, B, C = ^{19}F; M = ^{109}Ag or ^{107}Ag) subsystems whereas the evaluation of *cis*-^3J(CF) from the corresponding XA_3B_6M subsystem (X = ^{13}C *trans* to L) is much more straightforward. Where determined, the *trans* couplings exceed the values of the *cis* couplings by a factor of 2−3. Transfer of this relation between *cis* and *trans* couplings to the bis(trifluoromethyl)silver(III) compounds gives a reliable indication of whether a *trans* or *cis* configuration is involved, especially if both isomers are observed. Following the computer simulations the signs of both ^4J(FF) and ^3J(CF) couplings are positive with respect to the negative sign of ^1J(CF), in

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(19) Kidd, R. G.; Goodfellow, R. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, U.K., 1978; p 256, and references cited therein.

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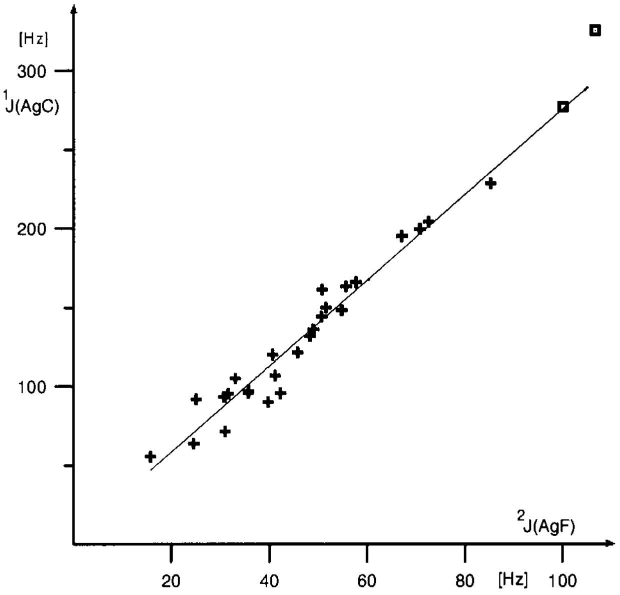

Figure 4. Correlation of $|^1J(AgC)|$ vs $|^2J(AgF)|$. Crosses are for CF_3-Ag^{III}; squares are for CF_3Ag^I derivatives.

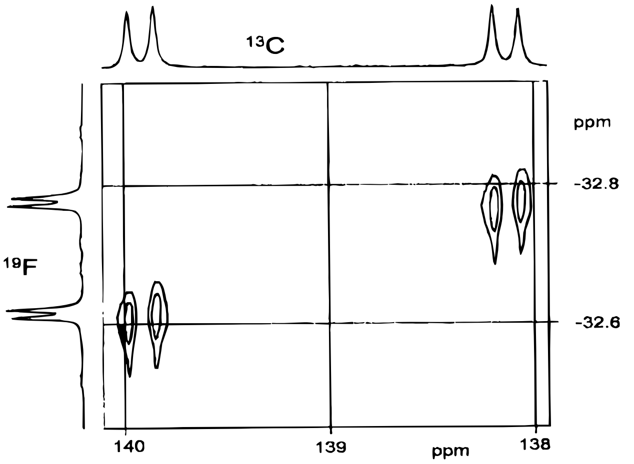

Figure 5. Two-dimensional $^{19}F-^{13}C$ spectrum of $Ag[Ag(CF_3)_4]$ in CH_3CN with FF decoupling in the F_1 (^{19}F) domain (spectral resolutions 4.7 Hz/pt (F_1) and 0.5 Hz/pt (F_2), 96 scans, relaxation delay 3 s, evolution delays 1.26 and 0.63 ms). The positive tilt of the cross-peaks indicates equal signs for $^1J(AgC)$ and $^2J(AgF)$.

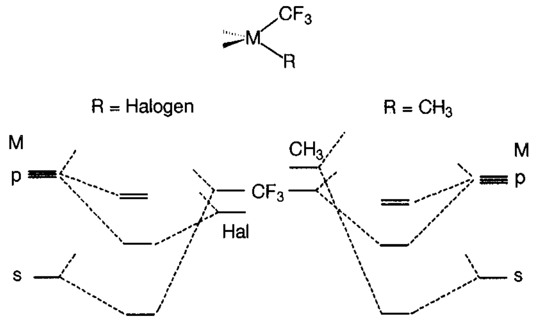

Figure 6. Schematic MO description of s orbital participation in CF_3 derivatives of main group elements where the CF_3 group competes with a halide (left side) or a covalently bonded organic group (right side).

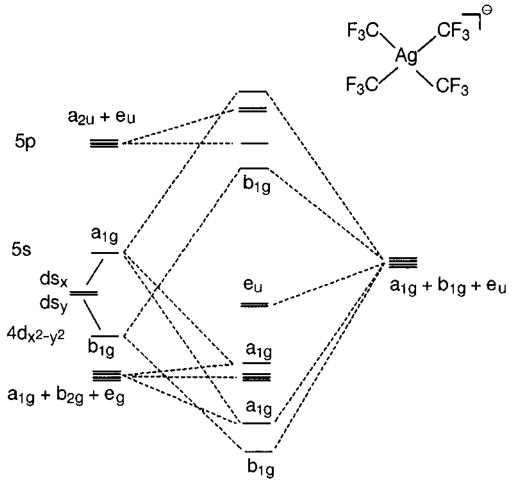

Figure 7. Qualitative MO description of the bonding in square-planar $[Ag(CF_3)_4]^-$.

accordance with results found by the analysis of high-order effects in the spectra of CF_3 derivatives of main group elements.[21] For the argentates containing one or more CN groups, essentially the same trends as for CF_3 groups are observed for the ^{13}C nucleus of the CN groups, e.g. *trans*-$^3J(CF) \gg$ *cis*-$^3J(CF)$, Table 5.

As displayed in Figure 4, $^2J(AgF)$ and $^1J(AgC)$ couplings are well correlated and consequently should be interpreted on a common basis. Variations in these values are presumably dominated by changes in the contribution of the 5s orbital to the AgC bonding orbital. It is interesting to notice that this correlation also includes the Ag(I) species quite satisfactorily. Two-dimensional $^{19}F/^{13}C$ COSY spectra which have been recorded for $[Ag(CF_3)_4]^-$ (Figure 5) and [*trans*-$Ag(CF_3)_2(CH_3)_2]^-$ show that the relative signs of $^2J(AgF)$ and $^1J(AgC)$ are equal. For the $(CF_3)_3AgL$ unit the weighted average of the $^2J(AgF)$ constants hardly changes though there is a pronounced but opposite influence of the ligand L on the coupling to the *trans* and *cis* CF_3 groups. In main groups CF_3 compounds such as the tin derivatives $(CF_3)_nSnR_{4-n}$, $^2J(SnF)$ varies from 200 Hz for R = alkyl to 850 Hz for R = Cl with R = CF_3 adopting a intermediate position, 540 Hz. This variation may well reflect a preference of tin to reserve its 5s orbital for forming the less polar bonds (R = alkyl) with a concomitant release of its higher lying p orbitals for formation of the more polar bonds (R = Cl).[19] The competition for s character is shown in a qualitative MO description (Figure 6) for a tetrahedral $(CF_3)(R)M$ fragment. Thus, the 5s contribution to the $Sn-CF_3$ bond and concomitantly the coupling constants $^1J(SnC)$ and $^2J(SnF)$ will increase as the polarity of the Sn−R bond increases. The bonding situation is quite different for an open d shell system like the d^8 configuration of Ag(III) in the $[Ag(CF_3)_4]^-$ anion. On the metal side, the σ-bonding is dominated by the 4d and 5s orbitals with less contributions from the 5p orbitals, Figure 7. But now the 4d orbitals are lower in energy than the 5s orbital, which is opposite to the s/p relation in main group chemistry. When the symmetry is lowered by substituting one or two CF_3 groups as illustrated in the left and right part of Figure 8 respectively, the 4d orbitals will be involved to a higher degree in the bonding to a less electronegative, but strongly covalently bonded ligand such as the CH_3 group. Consequently, more s character is released into the bond to the CF_3 group. In a simplified picture it is helpful to consider the square-planar skeleton being mainly formed by orthogonal ds-hybrids, $ds_{x,y} = 1/\sqrt{2}\,(s \pm d_{x^2-y^2})$. These hybrids extend along the x and y axis, respectively. Now we turn the discussion to the case of *trans*-bis(trifluoromethyl)-dihaloargentates(III) as shown in right half of the MO diagram in Figure 8. Here, the CF_3 bonding ds_x hybrid will constitute mainly the lower orbital $1a_{1g}$ orbital which has lower 5s character. Consequently, for [*trans*-$Ag(CF_3)_2X_2]^-$ the couplings between ^{109}Ag and ^{19}F or ^{13}C are small when X = halogen,

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(21) Eujen, R. To be published.

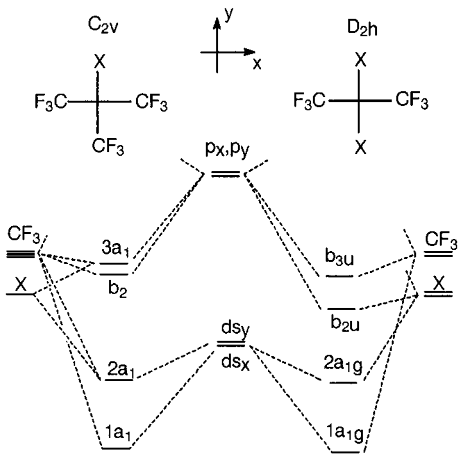

Figure 8. Qualitative MO description (only bonding orbitals are shown) of square-planar $[Ag(CF_3)_3X]^-$ (left side) and [*trans*-$Ag(CF_3)_2X_2]^-$ (right side) where X represents a less s electron demanding group or atom, typically a halide.

intermediate for X = CF_3, and high for X = CH_3 where the $2a_{1g}$ orbital takes part to a larger extent in bonding to the CF_3 group. For tris(trifluoromethyl)haloargentates (left side of Figure 8) the corresponding argumentation implies a decrease of the coupling constants of the CF_3 group *cis* to the halogen atom. The *y* component will have the greater s character contained in the $2a_1$ orbital. In the competition of X and the *trans*-CF_3 group for s character, the more covalent CF_3 bond will dominate and cause the measured large coupling constants. Again, the opposite relation is true for X = CH_3.

In principal, the same changes in s bonding characteristics have been made responsible for the basic differences in the structures of related organometallic main group and transition metal derivatives with an "inversion" of Bent's rules in transition metal compounds.[22−24]

These different trends for main group and transition metal elements are also noticed when changing oxidation states. For CF_3Sn^{II} derivatives the s electron density condenses in the lone pair and is hardly available for bonding. As a consequence, $^2J(SnF)$ values are close to zero and $^1J(SnC)$ ($\gamma_{Sn} < 0$) couplings are positive while the respective couplings in $CF_3Sn(IV)$ compounds are large and negative. Furthermore, the $^1J(CF)$ coupling constants of CF_3Sn derivatives are significantly larger in the lower oxidation states.[20,25] The opposite pattern is found for the Ag(III)/Ag(I) pair. Here AgF and AgC couplings adopt the larger values for Ag(I) complexes for which also the smaller $^1J(CF)$ values are found.

(c) Description of the Crystal Structures. While the lipophilic tetraphenylphosphonium cation has proven invaluable for the isolation and crystallization of the argentate anions, the ions are widely separated in the crystals. The cation symmetry in both structures is approximately S_4. The S_4 axis is coincident with the crystallographic 2-fold axis which passes through the P atom in $[P(C_6H_5)_4][Ag(CF_3)_2(CN)_2]$ and lies close to the bisectors of the C(11)−P−C(41) and C(21)−P−C(31) angles in $[P(C_6H_5)_4][Ag(CF_3)_3(CH_3)]$.

Figure 9 depicts the structure of the [*trans*-$Ag(CF_3)_2(CN)_2]^-$ anion, and selected bond distances and angles are listed in Table 7. While the Ag−CF_3 bond (2.105(4) Å) is markedly longer than the Ag−CN linkage (2.013(3) Å), the length of the former compares well with the corresponding average value reported for a disordered $[Ag(CF_3)_4]^-$ species.[8] The present study is the first on a cyano complex of silver(III), and a comparison of the Ag−CN distance with those reported for $[Ag(CN)_2]^-$ salts is complicated by the secondary interactions which they often enter. However, for structures[26,27] in which the anion is essentially isolated and σ(Ag−C) is less than 0.01 Å, the average Ag−C bond length (2.053(7) Å) appears to be significantly longer than that of the present structure.

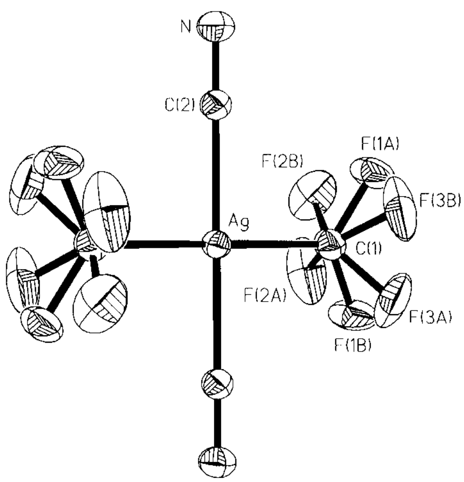

Figure 9. Perspective drawing of the [*trans*-$Ag(CF_3)_2(CN)_2]^-$ anion in $[PPh_4]$[*trans*-$Ag(CF_3)_2(CN)_2]$ with 20% probability thermal ellipsoids.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for $[PPh_4]$[*trans*-$Ag(CF_3)_2(CN)_2]$

Ag−C(1)	2.105(4)	F(1A)−C(1)	1.281(8)
Ag−C(2)	2.013(3)	F(2A)−C(1)	1.302(8)
C(2)−N	1.128(4)	F(3A)−C(1)	1.301(8)
		F(1B)−C(1)	1.262(7)
		F(2B)−C(1)	1.338(8)
		F(3B)−C(1)	1.271(9)
C(1)−Ag−C(2)	90.20(14)	F(1B)−C(1)−F(2B)	103.2(7)
C(1)−Ag−C(2)′ [a]	89.80(14)	F(3B)−C(1)−F(2B)	104.4(8)
C(1)−Ag−C(1)′ [a]	180.0	F(1B)−C(1)−Ag	118.9(4)
C(2)−Ag−C(2)′ [a]	180.0	F(3B)−C(1)−Ag	111.3(6)
N−C(2)−Ag	178.9(4)	F(1A)−C(1)−Ag	118.6(4)
F(1B)−C(1)−F(3B)	107.4(8)	F(3A)−C(1)−Ag	113.2(6)
F(1A)−C(1)−F(3A)	102.7(8)	F(2A)−C(1)−Ag	110.9(5)
F(1A)−C(1)−F(2A)	106.4(9)	F(2B)−C(1)−Ag	110.3(4)
F(3A)−C(1)−F(2A)	103.6(9)		

[a] Symmetry code: $x', y', z' = -x + {}^1/_2, -y + {}^1/_2, -z + 1$.

The C−N distance found in this study, 1.128(4) Å, is inconspicuous. More indicative are the vibrational spectra. Unfortunately, the infrared intensity of the asymmetric CN stretch mode is too low to be identified among the CF overtones and combination bands of the phenyl groups. The symmetric mode, however, sticks out in the Raman spectrum at 2181 cm^{-1}. This value is to be compared with an average of 2140 ± 10 cm^{-1} reported for $[Ag(CN)_2]^-$ salts.[26,28] A similar increase of the CN bond strength is observed when going from Au(I) to Au(III) cyano complexes.[28,29]

Since the Ag atom lies on an inversion center, the four bonds radiating from this atoms are required to be coplanar. While the N atom does not deviate significantly from this plane

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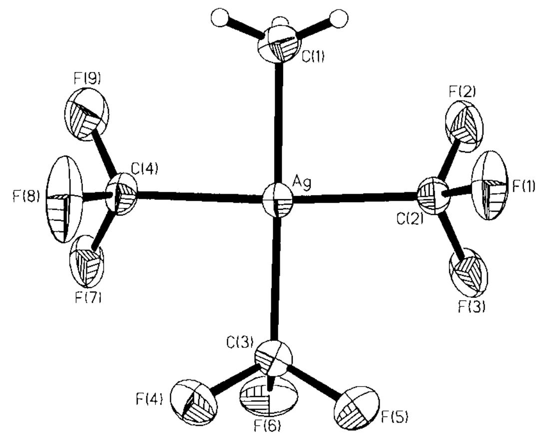

Figure 10. Perspective drawing of the $[Ag(CF_3)_3(CH_3)]^-$ anion in $[PPh_4][Ag(CF_3)_3(CH_3)]$ with 20% probability thermal ellipsoids for the non-hydrogen atoms.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for $[PPh_4][Ag(CF_3)_3(CH_3)]$

Ag−C(1)	2.097(5)	F(4)−C(3)	1.355(6)
Ag−C(2)	2.112(5)	F(5)−C(3)	1.381(6)
Ag−C(3)	2.127(5)	F(6)−C(3)	1.336(6)
Ag−C(4)	2.118(5)	F(7)−C(4)	1.320(7)
F(1)−C(2)	1.314(7)	F(8)−C(4)	1.309(7)
F(2)−C(2)	1.329(6)	F(9)−C(4)	1.344(6)
F(3)−C(2)	1.323(6)		
C(1)−Ag−C(2)	88.0(2)	F(7)−C(4)−Ag	114.8(4)
C(1)−Ag−C(3)	173.8(2)	F(8)−C(4)−Ag	114.8(3)
C(1)−Ag−C(4)	88.3(2)	F(9)−C(4)−Ag	116.7(4)
C(2)−Ag−C(3)	93.2(2)	F(1)−C(2)−F(2)	104.4(5)
C(2)−Ag−C(4)	174.3(2)	F(1)−C(2)−F(3)	105.5(5)
C(3)−Ag−C(4)	90.9(2)	F(2)−C(2)−F(3)	101.9(4)
F(1)−C(2)−Ag	114.6(4)	F(4)−C(3)−F(5)	101.4(4)
F(2)−C(2)−Ag	115.0(4)	F(4)−C(3)−F(6)	103.8(4)
F(3)−C(2)−Ag	114.1(3)	F(5)−C(3)−F(6)	103.1(4)
F(4)−C(3)−Ag	114.3(3)	F(7)−C(4)−F(8)	104.7(5)
F(5)−C(3)−Ag	114.9(3)	F(7)−C(4)−F(9)	101.8(5)
F(6)−C(3)−Ag	117.4(3)	F(8)−C(4)−F(9)	102.2(5)

(0.020(7) Å), the CF_3 groups are rotated by roughly 10° about their Ag−C(1) bond away from the conformation which would have the F(1A) and F(1B) atoms in the coordination plane of the metal. In view of the disorder of the CF_3 groups, the variations in the C−F distances should not be taken seriously.

Figure 10 gives a view of the $[Ag(CF_3)_3(CH_3)]^-$ anion, and selected bond distances and angles are given in Table 8. The coordination plane of the metal atom exhibits a slight tetrahedral distortion from square-planar geometry—the overall symmetry approaching D_{2d} if differences in CF and CH are ignored. Thus the best plane through the Ag,C(1),C(2),C(3),C(4) fragment passes within 0.014(2) Å of the Ag atom while the carbon atoms in the given order are alternately 0.095(5) Å above and below the plane. Furthermore, the CF_2 and CH_3 groups are so oriented that one of their Ag,C,F or Ag,C,H planes lies nearly perpendicular to the coordination plane with the corresponding F or H atom on the same side of the plane as is the C atom to which it is bonded. This geometry is closely related to that reported for the $[Cu(CF_3)_4]^-$ and $[Ag(CF_3)_4]-$ [8] anions. The Ag−CH_3 bond in the $[Ag(CF_3)_3(CH_3)]^-$ anion is to our knowledge the first structurally characterized Ag−R linkage where R is a simple alkyl. Interestingly, the Ag−CH_3 bond length is slightly but significantly (0.030(7) Å) shorter than the Ag−CF_3 bond to which it is *trans* and probably shorter (0.018(7) Å) than the average of the two Ag−CF_3 bond distances to which it is *cis*. The average Ag−CF_3 bond length (2.119(10) Å) does not differ significantly from those reported in the disordered $[Ag(CF_3)_4]^-$ (2.10(1) Å)[8] and $[trans\text{-}Ag(CF_3)_2(CN)_2]^-$ (2.105(4) Å).

To see to what extent the wide range of the C−F bond lengths (0.072(9) Å) in the $[Ag(CF_3)_3(CH_3)]^-$ anion are due to thermal artifacts, the anisotropic displacement parameters of the anion have been fitted with the program THMA11[30] to a rigid-body-motion model which has been augmented by correlated torsional motion[31] of the F atoms about the respective Ag−C bonds. The 84 U_{ij} values are well fit by the 38 parameters of the model (R = 0.052). After applying corrections for librational and torsional motion, the C−F distances average 1.381(17) Å with a notably smaller spread (0.048 Å). Furthermore, the average F··F contact in the CF_3 groups lengthens from 2.091(25) Å to a much more reasonable separation[32] of 2.177(12) Å. Other corrections are small and isotropic, and unless specified, only uncorrected distances are referenced in this manuscript.

Conclusions

The synthesis, NMR and structural characterization of new silver(III)-based organometallics show that Ag(III) is not so uncommon as assumed originally. These d^8 species are more closely related to the isoelectronic palladium or platinum compounds than to the strongly oxidizing Ag(III) complexes with weak ligands such as AgF_4^-. The difference can be rationalized in terms of simple ligand field theory. For AgF_4^-, the high charge density of the small Ag^{3+} ion overcompensates the low ligand field strength of fluoride thus giving raise to a square-planar diamagnetic complex. The LUMO ($d_{x^2-y^2}$), however, is low in energy and therefore quite susceptible for electrons, which means that Ag(III) is readily reduced. On the other hand this orbital is raised in energy by strong ligands such as alkyl groups. In the MO description given in Figure 7, the gap between the filled orbitals and the LUMO (b_{1g}), which arises from the covalence of the respective bonds, is responsible for the observed stability. Additionally, the fluorination of the alkyl groups obviously contributes to the stabilization of Ag(III). Such a perfluoromethyl effect has been noted for $(CF_3)_2Pt^{II}$ derivatives where UV photoelectron studies showed that all bonding orbitals are lowered in energy by ∼1 eV when compared with the corresponding methylplatinum complexes.[33]

In addition to the arguments based on the diamagnetism, the square-planar coordination of silver, or the high-frequency offset of the ^{109}Ag chemical shifts, the high CN stretch frequency in $[PPh_4][trans\text{-}Ag(CF_3)_2(CN)_2]^-$ supports the formulation as a Ag(III) derivative. With respect to Ag(I) compounds the d_π electrons are more tightly bound and thus less available for back-bonding from the Ag(III) center to the anti-bonding CN orbitals. The hardness of the Ag(III) is also expressed by the configurational stability of the donor adducts $(CF_3)_3Ag\cdot D$ where D is a hard donor such as DMSO, CH_3CN, DMF, or other nitrogen-based ligands. Attempts to prepare complexes by replacement of these ligands with soft donors such as PR_3 (R = Me, Ph, or OMe) or AsF_3 have failed so far.

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Supporting Information Available: X-ray crystallographic files in CIF format for $[PPh_4][trans\text{-}Ag(CF_3)_2(CN)_2]$ and $[PPh_4][Ag(CF_3)_3(CH_3)]$ are available on the Internet only. Access information is given on any current masthead page.

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