

Preparation and NMR Spectra of Difluoromethylated Silver(I) and Silver(III) Compounds. Structure of [PNP][Ag(CF₂H)₄][†]

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The thermally unstable [Ag(CF₂H)₂][−] moiety is obtained in solution by reaction of silver(I) salts with Cd(CF₂H)₂ in DMF/diglyme at −80 °C. Oxidation with I₂ leads to the argentate(III) [Ag(CF₂H)₄][−], which has been isolated as its PNP salt. According to DSC/TG analysis, the exothermic decomposition of this air-stable salt proceeds in two steps at 121 and 150 °C with formal elimination of one and three CFH units, respectively. Difluoromethylation of [Ag(CN)₂][−] in the presence of acetyl chloride leads to the argentate(I) [Ag(CF₂H)(CN)][−], which is oxidized by bromine at low temperatures to the thermally labile [*trans*-Ag(CF₂H)₂(CN)₂][−] anion. Stable argentates(III) containing both difluoromethyl and trifluoromethyl groups are obtained by reaction of [Ag(CF₃)_n(CN)_{4−n}][−] (*n* = 1, 2-*cis*, 2-*trans*, and 3) with Cd(CF₂H)₂—the *cis* and *trans* configurations of the reactants being retained in their products for *n* = 2. The compounds are identified and characterized by multinuclear NMR spectroscopy. Crystals of [PNP][Ag(CF₂H)₄] belong to the tetragonal space group *P*₄ with *a* = 9.475(1) Å, *c* = 42.159(6) Å, and *Z* = 4. The coordination of the silver atom is approximately square-planar with an average Ag–C bond length of 2.083(14) Å. The ligands are so oriented that each C–H bond is geared between the C–F bonds of a neighboring CF₂H group—the overall symmetry being approximately *C*_{4h}.

Introduction

Silver in its oxidation state +3 is well stabilized by perfluorinated methyl groups. The surprisingly stable argentate(III) [Ag(CF₃)₄][−] was described first by Dukat and Naumann.¹ It is readily formed when silver(I) salts are treated with Cd(CF₃)₂. The intermittently observed bis(trifluoromethyl)argentate(I) disproportionates to silver metal and Ag[Ag(CF₃)₄]. This “binary” salt is stable in air and water; its thermal degradation requires a temperature of almost 100 °C,¹ while the decomposition of the PNP or PPh₄ salts begins around 150 °C.² An almost square-planar coordination of the silver atom, which is expected for a diamagnetic d⁸ complex, has been confirmed by X-ray analyses on a tetrathiofulvene-based cation-radical salt³ as well as on its tetraphenylphosphonium salt.² In a preceding publication,⁴ we showed that the CF₃ groups may be replaced in part by functions such as the CN or the CH₃ group and halides or by donor molecules. The stability of these silver(III) compounds decreases as the number of CF₃ groups decreases. The tetraphenylphosphonium salts of [*trans*-Ag(CF₃)₂(CN)₂][−] and [Ag(CF₃)₃(CH₃)][−] have been isolated as air-stable compounds and characterized by NMR and X-ray structure analyses.

Instead of the replacement of complete CF₃ groups, substitutions within the CF₃ groups may be useful to test the relative stability of such silver(III) compounds, the simplest being an exchange of one fluorine atom by a hydrogen atom. A reagent suitable for the transfer of CF₂H groups is bis(difluoromethyl)-cadmium, Cd(CF₂H)₂. While the DMF complex of this compound has been known for some time,⁵ the much more

reactive uncoordinated species has become available only recently.⁶ It has been successfully used to prepare (difluoromethyl)copper(I) compounds which could be oxidized to copper(III) species. Of these, the cuprate [Cu(CF₂H)₄][−] has been isolated as its PNP salt. Structural characterization has shown that the symmetry of the anion, *C*_{4h}, is at variance with the *D*_{2d} arrangement found in [PNP][Cu(CF₃)₄],⁷ and the different nature of the interligand interactions in these complexes has been delineated. Furthermore, the mixed difluoromethyl/trifluoromethyl cuprates(III), [Cu(CF₃)_n(CF₂H)_{4−n}][−], *n* = 1–3, have been identified and characterized by multinuclear NMR spectroscopy.⁶

In this contribution, we extend these studies to the corresponding (difluoromethyl)silver(III) moieties, which, due to the presence of the highly abundant spin 1/2 isotopes ¹⁰⁹Ag and ¹⁰⁷Ag, are especially suited for certain identification by NMR techniques.

Experimental Section

(a) General Procedures and Materials. Volatile material was handled on a vacuum line equipped with greaseless stopcocks. Air-sensitive, nonvolatile material was manipulated under an argon or a nitrogen atmosphere. Raman spectra were obtained on a Cary 82 spectrometer, with Kr⁺ excitation at 647.1 nm. Infrared spectra were recorded with a Bruker IFS 25 spectrometer as KBr pellets for solids and with 10 cm gas cells for gases. Combined calorimetric and thermogravimetric analyses (DSC/TGA) 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. Bis(difluoromethyl)cadmium was prepared by following published procedures.⁶

(b) NMR Spectra. NMR spectra were recorded with a Bruker ARX 400 (¹H, 400.13 MHz; ¹³C, 100.63 MHz; ¹⁹F, 376.50 MHz) or a Bruker AC 250 instrument (¹H, 250.13 MHz; ¹⁹F, 235.36 MHz; ¹³C, 62.90

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(1) Dukat, W.; Naumann, D. *Rev. Chim. Miner.* **1986**, 23, 589.

(2) (a) Naumann, D. Private communication. (b) Roy, T. Dissertation, Universität Köln, 1993.

(3) Geiser, U.; Schlueter, J. A.; Williams, J. M.; Naumann, D.; Roy, T. *Acta Crystallogr.* **1995**, B51, 789.

(4) Eujen, R.; Hoge, B.; Brauer, D. J. *Inorg. Chem.* **1997**, 36, 1464.

(5) Hartgraves, G. A.; Burton, D. J. *J. Fluorine Chem.* **1988**, 39, 425.

(6) Eujen, R.; Hoge, B.; Brauer, D. J. *J. Organomet. Chem.* **1996**, 519, 7.

(7) Naumann, D.; Roy, T.; Tebbe, K. F.; Crump, W. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1482.

MHz; ^{109}Ag , 11.64 MHz). Spectra were 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. The last 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 DEPT⁸ pulse sequence was used to record the 1D spectra of the less sensitive nuclei ^{109}Ag and ^{13}C . For the latter, this was particularly helpful because all resonances without a coupling to the fluorine nuclei were suppressed. Two-dimensional spectra (^{13}C – ^{19}F , ^{109}Ag – ^{19}F) were recorded with the pulse sequence given by Bax⁹ and were used for assignments and for determining relative signs of coupling constants.

Computer simulations of high-order NMR spectra were carried out with the program gNMR.¹⁰

(c) Synthetic Reactions. (i) Solutions of Bis(difluoromethyl)-argentate(I). To a solution of 3.9 g (8.8 mmol) of $(\text{CF}_2\text{H})_2\text{Cd}$ tetraglyme in 5 mL of a 1:1 mixture of DMF and diglyme was added a solution of 1.5 g (8.8 mmol) of AgNO_3 in 5 mL of DMF/diglyme at -80°C with vigorous stirring. The solids contained in the black suspension were separated from the mixture by centrifugation at -80°C . Conversion rates and yields were monitored by integration of ^{19}F NMR signals after addition of a reference quantity of fluorobenzene.

(ii) Synthesis of $\{[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}\}[\text{Ag}(\text{CF}_2\text{H})_4]$. A solution of iodine (ca. 5 mmol) in diglyme was added slowly to a vigorously stirred solution of 8.8 mmol of $[\text{Ag}(\text{CF}_2\text{H})_2]^-$ in 10 mL of DMF at -50°C until the iodine color persisted. The solution was allowed to warm to ambient temperature within 1 h. A measured quantity of fluorobenzene was added as an integration standard in order to determine the amount of the $[\text{Ag}(\text{CF}_2\text{H})_4]^-$ ion being formed, and a stoichiometric quantity of $[\text{PNP}]\text{Cl}$ was added. The suspension was treated with 150 mL of CHCl_3 and filtered, and the filtrate was repeatedly washed with water and dried over MgSO_4 . After removal of the solvent, a yellow powder was obtained. Recrystallization from CHCl_3 /diethyl ether afforded 2.6 g (3.1 mmol) (35% yield) of $[\text{PNP}][\text{Ag}(\text{CF}_2\text{H})_4]$ as colorless crystals. Anal. Calcd for $\text{C}_{40}\text{H}_{34}\text{AgF}_8\text{NP}_2$: H, 4.03; C, 56.49; N, 1.65. Found: H, 4.04; C, 55.73; N, 1.7. Infrared (cm^{-1}) (KBr pellet): 3060 w, 2909 m, 1589 w, 1482 w, 1438 m, 1297 s, 1265 vs (broad), 1185 m, 1118 s, 1008 vs, 952 vs, 802 w, 741 m, 721 s, 690 s, 666 m, 618 w, 599 w, 549 s, 535/525 s, 498 s, 457 m. Raman (cm^{-1}): 3068 s, 2917 w, 1592 m, 1250 w, 1187 w, 1166 w, 1113 m, 1031 m, 1003 vs, 667 m, 618 m, 580 sh, 567 s, 532 w, 370 w, 267 w, 252 w, 238/230 s, 107 m, 90 s, 75 s. DSC/TG analysis: exothermic decomposition peaks at 121°C , $\Delta m -3.4\%$ (calcd for elimination of CFH: $\Delta m -3.7\%$), and 150°C , $\Delta m -11.1\%$ (calcd for elimination of 3 CFH: $\Delta m -11.7\%$).

(iii) Solutions of (Difluoromethyl)cynoargentate(I) and Bis(difluoromethyl)dicyanoargentate(III). A solution consisting of 2.0 g (10 mmol) of $\text{K}[\text{Ag}(\text{CN})_2]$ and 2.2 g (5 mmol) of $(\text{CF}_2\text{H})_2\text{Cd}$ tetraglyme in 10 mL of DMF was stirred for 1 h at 0°C . After the solution was cooled to -30°C , 790 mg (10 mmol) of acetyl chloride in 3 mL of diglyme was added slowly. Volatile material was removed in vacuo at -5°C . The amount of the argentate(I) $[\text{Ag}(\text{CF}_2\text{H})(\text{CN})]^-$ being formed was determined by low-temperature ^{19}F NMR spectroscopy with reference to a known amount of added fluorobenzene.

To a cold (-50°C) solution of 10 mmol of $[\text{Ag}(\text{CF}_2\text{H})(\text{CN})]^-$ in 10 mL of DMF and 3 mL of diglyme was added with vigorous stirring 2.7 g of bromine in 5 mL of diglyme. After removal of solids by centrifugation at -50°C , products were identified by NMR spectroscopy. When the solution was allowed to warm above -30°C , decomposition and formation of CF_2HCN , $\delta(^{19}\text{F}) -125.1$ ppm (d, 52.8 Hz), were observed.

(iv) Synthesis of $[\text{P}(\text{C}_6\text{H}_5)_4][\text{trans-Ag}(\text{CF}_3)_2(\text{CF}_2\text{H})_2]$. A solution of 650 mg (1.0 mmol) of $[\text{PPh}_4][\text{trans-Ag}(\text{CF}_3)_2(\text{CN})_2]$ in 10 mL of DMF was treated at -30°C with 900 mg (2.1 mmol) of $(\text{CF}_2\text{H})_2\text{Cd}$ tetraglyme for 10 min. A solution of 310 mg (4 mmol) of acetyl

Table 1. Crystallographic Data for $[\text{PNP}][\text{Ag}(\text{CF}_2\text{H})_4]$

formula	$\text{C}_{40}\text{H}_{34}\text{AgF}_8\text{NP}_2$	ρ_{calc} (g cm^{-3})	1.493
fw	850.5	T ($^\circ\text{C}$)	23
cryst syst	tetragonal	λ ($\text{\AA}$)	1.54184
space group	$P4_3$	$\mu(\text{Cu K}\alpha)$ (mm^{-1})	5.68
a ($\text{\AA}$)	9.475(1)	transm factor	0.247–0.377
c ($\text{\AA}$)	42.159(6)	$R(F)^a$ ($F_o > 4\sigma(F_o)$)	0.045
V ($\text{\AA}^3$)	3784.7(9)	$R_w(F^2)^b$ (all data)	0.117
Z	4		

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

chloride in 3 mL of diglyme was added dropwise. To remove the precipitated CdCl_2 , the suspension was treated with 150 mL of CHCl_3 and filtered, and the filtrate was repeatedly washed with water and dried over MgSO_4 . Recrystallization of the crude yellow powder gave 550 mg (0.8 mmol) of $[\text{PPh}_4][\text{trans-Ag}(\text{CF}_3)_2(\text{CF}_2\text{H})_2]$ as colorless air-stable crystals. Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{AgF}_{10}\text{P}$: H, 3.23; C, 48.93. Found: H, 3.57; C, 48.83. Infrared (cm^{-1}) (KBr pellet): 3083 vw, 3067 w, 3056 vw, 2929 w, 1587 w, 1485 m, 1439 s, 1260 vs, 1191 w, 1112 s, 1089 vs, 1022 vs, 753 m, 726 s, 690 s, 525 vs.

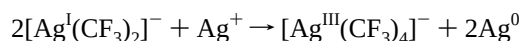
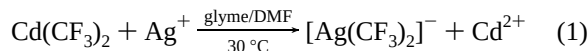
Other mixed difluoromethyl/trifluoromethyl argentates(III) were obtained similarly but were not isolated.

(d) Crystal Structure Determination of $\{[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}\}[\text{Ag}(\text{CF}_2\text{H})_4]$. Crystals were grown by isothermal distillation of diethyl ether into a CHCl_3 solution of $[\text{PNP}][\text{Ag}(\text{CF}_2\text{H})_4]$. A truncated tetragonal-bipyramidal specimen was glued to a glass fiber and mounted on a Siemens P3 diffractometer which employed graphite-monochromatized Cu K α radiation. The Laue group (4/*m*) found by diffractometry was consistent with that revealed by a preliminary Weissenberg examination. The lattice constants were derived from the setting angles of 32 centered reflections by least-squares calculations. An octant of data ($5^\circ \leq 2\theta \leq 138^\circ$) was collected using the θ – 2θ scan mode. Of the 4076 reflections measured, 3595 were unique, and 3444 had $F_o > 4\sigma(F_o)$. 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 of eight strong reflections.

A large starting fragment was generated by direct methods, and the remaining non-hydrogen atoms were found by subsequent difference Fourier syntheses. Hydrogen atoms were placed in idealized positions (C–H 0.95 $\text{\AA}$). The structure was refined on F^2 using all data. Refinement of the Flack¹¹ absolute structure parameter ($x = 0.00(1)$) indicated that the crystal belongs to the space group $P4_3$ rather than to $P4_1$, the choice found for the copper crystal.⁶ Crystal data and refinement details are included in Table 1. Structure solution and refinement and graphical display were all made with a SHELXTL¹² program package.

Results and Discussion

(a) Synthetic Aspects. Silver(I) salts are readily trifluoromethylated at low temperatures to $[\text{Ag}(\text{CF}_3)_2]^-$ by means of $\text{Cd}(\text{CF}_3)_2$ in solvents like CH_3CN . At ambient temperature the silver(I) species disproportionates to silver(III) and metallic silver:¹



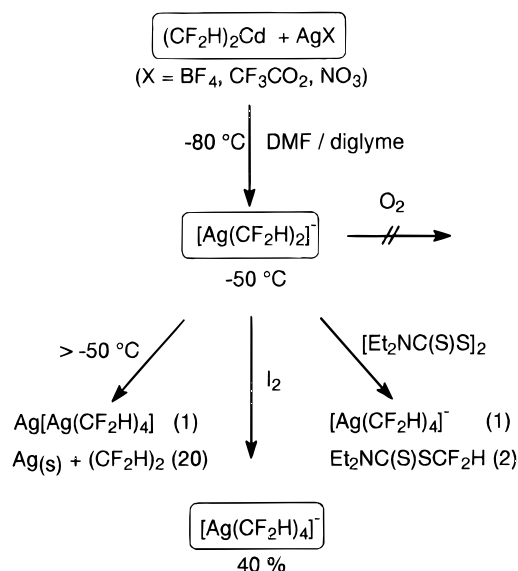
In DMF, the disproportionation is suppressed almost completely.

When the corresponding (difluoromethyl)cadmium compound, $\text{Cd}(\text{CF}_2\text{H})_2$, is reacted with AgX ($\text{X} = \text{NO}_3^-$, CF_3COO^- , or BF_4^-) in CH_3CN at -45°C , there is no evidence for the

- (8) Van de Ven, F. J. M. *Multidimensional NMR in Liquids*; VCH Publishers, Inc.: New York, 1995; p 127 ff.
 (9) (a) Bax, A.; Morris, G. A. *J. Magn. Reson.* **1981**, 42, 501. (b) Bax, A. *J. Magn. Reson.* **1983**, 53, 517. (c) Wilde, J. A.; Bolten, P. H. *J. Magn. Reson.* **1984**, 59, 343.
 (10) Budzelaar, P. H. M. *gNMR Version 3.65*; Cherwell Scientific Publishing Ltd.: Oxford, U.K., 1996.

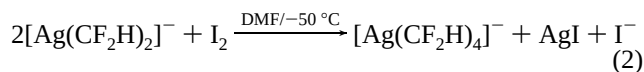
- (11) Flack, H. D. *Acta Crystallogr.* **1983**, A39, 876.
 (12) Sheldrick, G. M. *SHELXTL PC Version 5.0: An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

Scheme 1



formation of the expected $[\text{Ag}(\text{CF}_2\text{H})_2]^-$ ion. Instead, decomposition to $\text{HF}_2\text{CCF}_2\text{H}$ and metallic silver dominates, traces of the silver(III) anion $[\text{Ag}(\text{CF}_2\text{H})_4]^-$ being formed. Usage of DMF down to its melting point ($-60 ^\circ\text{C}$) does not alter the course of the reaction. Only when diglyme is added in order to allow the even lower reaction temperature of $-80 ^\circ\text{C}$ is the formation of $[\text{Ag}(\text{CF}_2\text{H})_2]^-$ clearly indicated by NMR spectroscopy (Scheme 1). Warming the reaction mixture to $-50 ^\circ\text{C}$ results in decomposition to tetrafluoroethane and silver metal, while disproportionation to silver(III) moieties analogous to eq 1 plays a minor role. In contrast to the case of the corresponding trifluoromethylation reaction, an adduct such as $\text{Ag}(\text{CF}_2\text{H})\cdot\text{D}$ is not detected.

Bis(difluoromethyl)argentate(I) is less prone to oxidation than its trifluoromethyl counterpart. No oxidation to silver(III) is observed upon exposure to air. Application of tetraethylthiuram disulfide, $[\text{Et}_2\text{NC}(\text{S})\text{S}]_2$, as the oxidizing agent gives low yields (5–10%) of the argentate(III) $[\text{Ag}(\text{CF}_2\text{H})_4]^-$. Improved conversion is achieved by low-temperature oxidation with bromine or iodine, the best yield, ca. 40%, being obtained with iodine although some CF_2HI is formed as well.

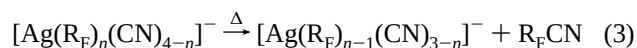


Addition of chloroform and cation exchange with $[\text{PNP}]\text{Cl}$ facilitate the removal of cadmium halides. After washing with water, colorless crystals of $[\text{PNP}][\text{Ag}(\text{CF}_2\text{H})_4]$ are isolated in a 35% yield based on the amount of $\text{Cd}(\text{CF}_2\text{H})_2$ consumed.

Like their CF_3 or their copper analogs, crystals of $[\text{PNP}][\text{Ag}(\text{CF}_2\text{H})_4]$ are not sensitive to air, water, or light. Their thermal stability is quite comparable; that is, the degradation requires a temperature of more than $100 ^\circ\text{C}$. As shown by combined DSC/TG analysis, the decomposition of $[\text{PNP}][\text{Ag}(\text{CF}_2\text{H})_4]$ takes place in two exothermic steps at 121 and $150 ^\circ\text{C}$, respectively. While the first is connected with a loss of mass corresponding approximately to one CFH unit ($\Delta m -3.4\%$), the second ($\Delta m -11.1\%$) is in accord with the loss of the remaining three CFH groups. Examination of the gaseous products, however, indicates that the process is somewhat more complex. In addition to the expected *cis*- and *trans*-difluoroethylenes, $1,1,2,2$ -tetrafluoroethane as well as some CF_2H_2 is detected, which points to a competing homolytic cleavage of the $\text{Ag}-\text{C}$ bonds. Attempts to identify any fluoroargentate(III) or other silver compounds among the solid decomposition residues have failed.

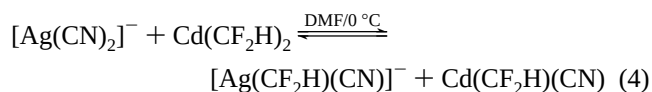
At first glance, the high stability of the difluoromethylated cuprate(III) or argentate(III) is surprising because the electronic stabilization by a CF_2H group should be less than that of a CF_3 group. Furthermore, steric shielding should be more favorable in the perfluorinated species. However, relative destabilization of the perfluorinated compound is also noted for the fluorinated dimethylcadmium compounds $\text{Cd}(\text{CF}_n\text{H}_{3-n})_2$. While pure $\text{Cd}(\text{CF}_3)_2$ decomposes below $0 ^\circ\text{C}$ via CF_2 elimination,¹³ $\text{Cd}(\text{CF}_2\text{H})_2$ is stable below $90 ^\circ\text{C}$ —evolving difluoroethylenes between 90 and $100 ^\circ\text{C}$ and tetrafluoroethane in a vigorous reaction above $100 ^\circ\text{C}$.⁶ The decomposition of $\text{Cd}(\text{CF}_3)_2$ is favored by both the formation of CdF_2 and the relatively high thermodynamic stability of difluorocarbene, CF_2 . An elimination of the thermodynamically less stable CFH entity from $\text{Cd}(\text{CF}_2\text{H})_2$ is not that favorable, and homolytic cleavage of the metal–carbon bonds with formation of the metal becomes competitive. As a consequence, the thermal stability of $\text{Cd}(\text{CF}_2\text{H})_2$ is more like that of $\text{Cd}(\text{CH}_3)_2$.¹⁴ Transfer of these observations to the $\text{Ag}(\text{III})$ and $\text{Cu}(\text{III})$ species helps to understand the high thermal stability of the anions $[\text{Ag}(\text{CF}_2\text{H})_4]^-$ and $[\text{Cu}(\text{CF}_2\text{H})_4]^-$ despite their lower electronic stabilization. The barrier to CFH elimination seems to almost cancel the loss in electronic and steric stability.

For further insight into the relative electronic stabilization of silver(III) by CF_3 and CF_2H groups, it is essential to open another decomposition channel which involves products with better comparable thermodynamic stabilities. The cyano group is an attractive coligand, since the anions in the trifluoromethyl series $[\text{Ag}(\text{CF}_3)_n(\text{CN})_{4-n}]^-$ have already been characterized. Their stability is known to decrease as the number of CN groups increases, CF_3CN and argentates(I) being the decomposition products.⁴



The conditions for the elimination of the fluorinated acetonitriles from the $[\text{trans-}\text{Ag}(\text{R}_F)_2(\text{CN})_2]^-$ anions ($\text{R}_F = \text{CF}_2\text{H}, \text{CF}_3$) should basically reflect the electronic influence of the R_F group.

The preparation of bis(difluoromethyl)dicyanoargentate(III) follows the principles developed in the synthesis of the corresponding trifluoromethylated argentates(III).⁴ Silver cyanide, suspended in DMF, requires room temperature to react with $\text{Cd}(\text{CF}_2\text{H})_2$, but only decomposition products such as CF_2HCN and silver metal are observed. Usage of the more soluble $\text{K}[\text{Ag}(\text{CN})_2]$ at $0 ^\circ\text{C}$ results in an equilibrium containing ca. 20% $[\text{Ag}(\text{CF}_2\text{H})(\text{CN})]^-$.



An almost quantitative ($>95\%$) conversion to the $[\text{Ag}(\text{CF}_2\text{H})(\text{CN})]^-$ ion is achieved by *in situ* treatment of the reaction mixture at $-30 ^\circ\text{C}$ with an equimolar quantity of acetyl chloride. Acyl cyanides can be prepared from acyl halides with copper or silver cyanides,¹⁵ and this reaction is used here both to eliminate ionic cyanide and to produce a highly reactive chloro complex as an intermediate, eq 5.

(13) Eujen, R.; Hoge, B. J. *Organomet. Chem.* **1995**, C51, 503.

(14) Price, S. J. W.; Trotman-Dickenson, A. F. *Trans. Faraday Soc.* **1957**, 53, 939.

(15) (a) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; p 495. (b) Hünig, S.; Schaller, R. *Angew. Chem., Int. Ed. Engl.* **1982**, 21, 36.

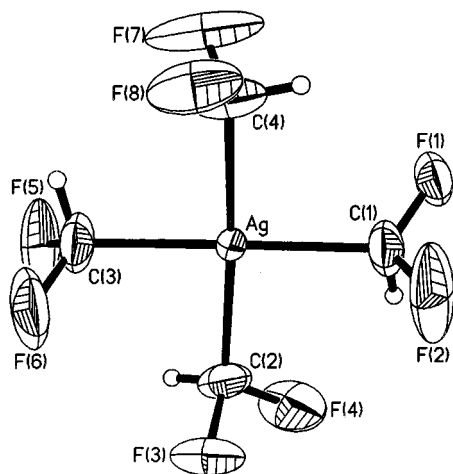
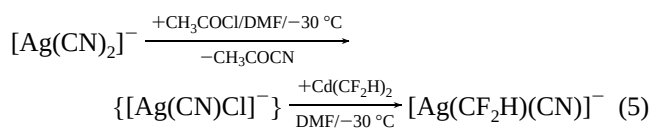
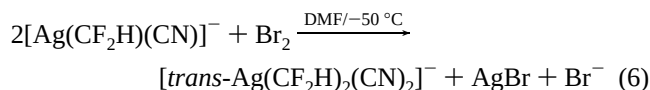


Figure 1. Perspective drawing of the $[\text{Ag}(\text{CF}_2\text{H})_4]^-$ anion in $[\text{PNP}][\text{Ag}(\text{CF}_2\text{H})_4]$ with 20% probability thermal ellipsoids for the non-hydrogen atoms.

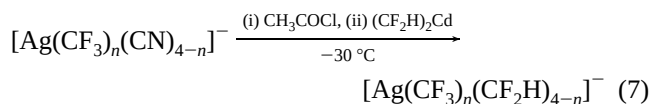


As for the analogous (trifluoromethyl)cynoargentate(I),⁴ the oxidation of the (difluoromethyl)cynoargentate(I) by bromine at -50°C leads to the formation of $[\text{trans-Ag}(\text{CF}_2\text{H})_2(\text{CN})_2]^-$ in 20–30% yield, the course of the reaction being monitored by low-temperature NMR spectroscopy (see below).



Minor amounts of the argentate(III) $[\text{Ag}(\text{CF}_2\text{H})_3(\text{CN})]^-$ are also clearly detected by its characteristic NMR patterns, while no evidence is found for the presumably less stable anions $[\text{cis-Ag}(\text{CF}_2\text{H})_2(\text{CN})_2]^-$ and $[\text{Ag}(\text{CF}_2\text{H})(\text{CN})_3]^-$. The isolation of $[\text{trans-Ag}(\text{CF}_2\text{H})_2(\text{CN})_2]^-$ as its PNP salt is thwarted by its low thermal stability—quantitative decomposition with evolution of CF_2HCN being observed above -30°C . Furthermore, all attempts till now to replace the CN groups have resulted in extensive decomposition. The pronounced difference in thermal stabilities of the CF_3 and CF_2H dicyanoargentates(III) with respect to the elimination of the respective fluoromethyl cyanide— $+90^\circ\text{C}$ vs -30°C —underscores the greater suitability of the CF_3 groups for stabilizing these highly oxidized species.

While mixed difluoromethyl/trifluoromethyl cuprates are accessible by difluoromethylation of the (*N,N*-diethyldithiocarbamato)copper(III) complex $(\text{CF}_3)_2\text{CuS}_2\text{CNEt}_2$, the corresponding reaction of $(\text{CF}_3)_2\text{AgS}_2\text{CNEt}_2$ with $\text{Cd}(\text{CF}_2\text{H})_2$ is unspecific and leads to a large variety of unidentified products. The members of the series $[\text{Ag}(\text{CF}_3)_n(\text{CF}_2\text{H})_{4-n}]^-$ are, however, accessed by difluoromethylation of the (trifluoromethyl)cynoargentates $[\text{Ag}(\text{CF}_3)_n(\text{CN})_{4-n}]^-$, $n = 1-3$. While the attempt to replace the cyano groups directly results in quantitative decomposition, the intermediate low-temperature chlorination with acetyl chloride affords the new argentates specifically and almost quantitatively for $n = 2$ and 3.



For $n = 1$, the yield of $[\text{Ag}(\text{CF}_3)(\text{CF}_2\text{H})_3]^-$ amounts to less than

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[\text{PNP}][\text{Ag}(\text{CF}_2\text{H})_4]$

Ag—C(1)	2.08(1)	Ag—C(3)	2.07(1)
Ag—C(2)	2.10(2)	Ag—C(4)	2.08(2)
C(1)—Ag—C(2)	91.7(8)	C(2)—Ag—C(3)	88.4(8)
C(1)—Ag—C(3)	177.5(8)	C(2)—Ag—C(4)	176.8(9)
C(1)—Ag—C(4)	91.4(10)	C(3)—Ag—C(4)	88.4(10)

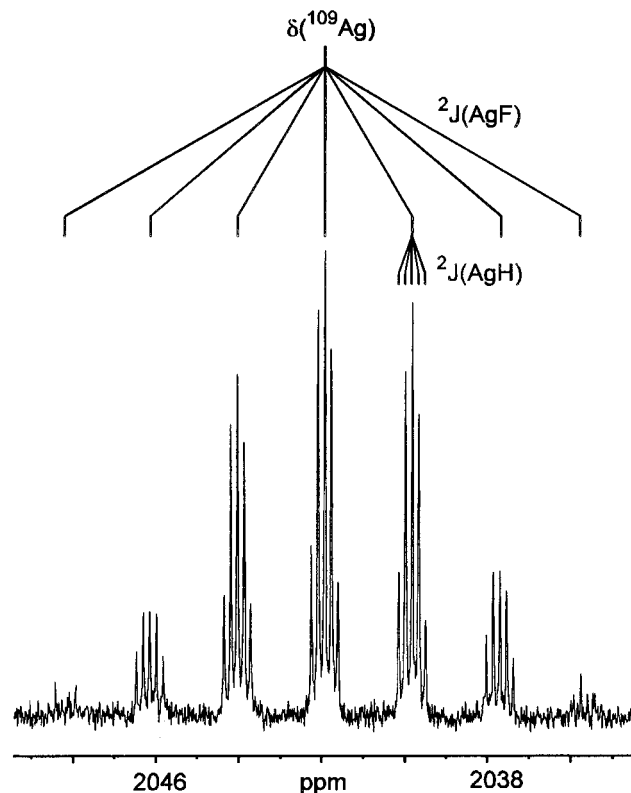


Figure 2. ^{109}Ag NMR spectrum of $[\text{PNP}][\text{Ag}(\text{CF}_2\text{H})_4]$. The spectrum was recorded by means of DEPT polarization transfer from ^{19}F (14 400 scans, relaxation delay 2 s, evolution time 20 ms, variable pulse length 25° , no decoupling).

50%, all other members of the series being formed simultaneously in substantial quantities. Their formation may be ascribed to a metathesis reaction of the dichlorinated intermediates similar to that found for (trifluoromethyl)chloroargentates(III).⁴

(b) Description of the Crystal Structure. The crystal structure of $[\text{PNP}][\text{Ag}(\text{CF}_2\text{H})_4]$ has been determined by X-ray diffraction, and a drawing of the $[\text{Ag}(\text{CF}_2\text{H})_4]^-$ anion is depicted in Figure 1. Selected bond distances and angles are listed in Table 2. The symmetry of the anion is approximately C_{4h} . Deviations of the atoms of the Ag, C(1), C(2), C(3), C(4) fragment from coplanarity are less than $\pm 0.03(1)$ Å, and the Ag—C bond lengths are equal to within experimental error. Their average value, 2.083(14) Å, agrees well with that reported for $[\text{PNP}][\text{Ag}(\text{CF}_3)_4]$ (2.082(13) Å)² and is not significantly shorter than the Ag— CF_3 distances in $[\text{PPh}_4][\text{Ag}(\text{CF}_3)_2(\text{CN})_2]$ and $[\text{PPh}_4][\text{Ag}(\text{CF}_3)_3(\text{CH}_3)]$, 2.105(4) and 2.119(10) Å, respectively.⁴

Each C—H bond of the anion lies near the coordination plane of the metal and is geared between the C—F bonds of a neighboring CF_2H group. Such a rotamer is obviously favored both by dipolar forces and by the minimization of $\text{F}\cdots\text{F}$ nonbonded repulsions, and the same conformation has been found for the anion of $[\text{PNP}][\text{Cu}(\text{CF}_2\text{H})_4]$. The latter compound is isomorphous with the argentate—the 0.15(2) Å longer silver—carbon bonds provoking a 1.5% increase in the unit cell. The large atomic displacement parameters of the fluorine atoms show

Table 3. NMR Data for (Difluoromethyl)cynoargentates(I) and -argentates(III)^a

	$\delta(^{109}\text{Ag})$	$\delta(^{19}\text{F})$	$\delta(^{13}\text{C})$	$^2J(\text{AgF})$	$^2J(\text{AgH})$	$^1J(\text{AgC})$	$^2J(\text{HF})^c$	$^1J(\text{CF})$	$^1J(\text{CH})$
Ag ^I Compounds									
$[\text{Ag}(\text{CF}_2\text{H})_2]^-$ ^d	634.3	-113.0	155.2	53.7	11.3	194.4	43.7	279.9	146.0
$[\text{Ag}(\text{CF}_2\text{H})(\text{CN})]^-$ ^e	579.1	-112.4	151.7	63.5	13.8	264.5	43.3	278.5	150.5
Ag ^{III} Compounds									
<i>trans</i> - $[\text{Ag}(\text{CF}_2\text{H})_2(\text{CN})_2]^-$ ^f	2110.8	-89.7	132.7	15	3	42	49	334	182
$[\text{Ag}(\text{CF}_2\text{H})_3(\text{CN})]^-$ ^g	<i>b</i>	-102.9	<i>b</i>	18	<i>b</i>	<i>b</i>	49	<i>b</i>	<i>b</i>
		-102.2 ^h	<i>b</i>	35	<i>b</i>	<i>b</i>	48	<i>b</i>	<i>b</i>

^a In DMF/diglyme; internal lock C₆D₆. Chemical shifts are in ppm; coupling constants in Hz. References are internal ¹³C₆D₆ at 128.0 ppm, external C¹⁹FC₁₃, and 1 *m* ¹⁰⁹AgNO₃ in D₂O. Couplings involving Ag nuclei are listed for the isotope ¹⁰⁹Ag; ⁿJ(¹⁰⁷AgE) = ⁿJ(¹⁰⁹AgE)/1.150(5). ^b Not observed or resolved. ^c For a *trans*-Ag(CF₂H)₂ unit, the listed value corresponds to ²J(HF) + ⁴J(HF). ^d At 213 K; ³J(CF) 6.3 Hz; ³J(CH) 1.7 Hz. ^e At 273 K; $\delta(^{13}\text{CN})$ 144.0 ppm (broad). ^f At 238 K; ⁴J(FF)_{av} ca. 18 Hz; ³J(CH)_{tr} 16 Hz; ³J(CF)_{tr} 42 Hz; $\delta(^{13}\text{CN})$ 100.5 ppm; ¹J(¹⁰⁹AgCN) 149 Hz. ^g At 273 K. ^h *Trans* to CN.

Table 4. ¹⁹F NMR Data for Mixed (Difluoromethyl)(trifluoromethyl)argentates(III)^a

	CF ₃		CF ₂ H			CF ₃ -CF ₃ ⁴ J(FF)	CF ₃ -CF ₂ H ⁴ J(FF)	CF ₂ H-CF ₂ H ⁴ J(FF)
	$\delta(^{19}\text{F})$	$^2J(\text{AgF})$	$\delta(^{19}\text{F})$	$^2J(\text{AgF})$	$^2J(\text{HF})^c$			
$[\text{Ag}(\text{CF}_2\text{H})_4]^-$			-111.2	24.4	48.4			7.3 (tr) ~1.5 (cis)
$[\text{Ag}(\text{CF}_3)(\text{CF}_2\text{H})_3]^-$ ^e	-37.3	38.2	-108.8	22.5	47.9		8.6 (tr)	10 / 8 (tr)
			-106.3 ^d	29.3	47.9		1.7 (cis)	1.7 (cis)
<i>cis</i> - $[\text{Ag}(\text{CF}_3)_2(\text{CF}_2\text{H})_2]^-$	-35.8	36.8	-103.6	26.4	47.6	3.3 (cis)	9.9 (tr)	1.6 (cis)
							2.7 (cis)	
<i>trans</i> - $[\text{Ag}(\text{CF}_3)_2(\text{CF}_2\text{H})_2]^-$	-36.7	47.8	-104.4	20.0	48.6	<i>b</i>	3.4 (cis)	13.3/11.3 (tr)
$[\text{Ag}(\text{CF}_3)_3(\text{CF}_2\text{H})]^-$ ^f	-35.1 ^d	44.5	-98.3	22.7	47.1	4.5 (cis)	4.5 (cis)	
	-33.0	34.7					12.2 (tr)	
$[\text{Ag}(\text{CF}_3)_4]^-$ ^g	-32.7	40.7				12.8 (tr) 6.2 (cis)		

^a As Ph₄P⁺ salts in CDCl₃ (internal reference for ¹³C, 77.0 ppm) at 298 K. Otherwise, see Table 3. ^b Not observed. ^c For a *trans*-Ag(CF₂H)₂ unit, the value corresponds to ²J(HF) + ⁴J(HF). ^d *Trans* to CF₃. ^e ⁴J(CF₃CF₂H)_{tr} 2 Hz. ^f ⁴J(CF₃CF₂H)_{tr} 3.7 Hz. ^g As Ag[Ag(CF₃)₄] in CH₃CN.

Table 5. ¹⁰⁹Ag and ¹³C NMR Data for Mixed (Difluoromethyl)(trifluoromethyl)argentates(III)^a

	$\delta(^{109}\text{Ag})$	$^2J(\text{AgH})$	CF ₃			CF ₂ H			
			$\delta(^{13}\text{C})$	$^1J(\text{AgC})$	$^3J(\text{CH})$	$\delta(^{13}\text{C})$	$^1J(\text{AgC})$	$^1J(\text{CH})$	$^3J(\text{CH})$
$[\text{Ag}(\text{CF}_2\text{H})_4]^-$ ^c	2041.9	1.8				140.1	88.5	171.5	8.6 (tr) 2.9 (cis)
<i>cis</i> - $[\text{Ag}(\text{CF}_3)_2(\text{CF}_2\text{H})_2]^-$	2089.7	1.4	144.6	112.6	12.7 (tr) 5.2 (cis)	133.7	91.5	183.1	4.3 (cis)
<i>trans</i> - $[\text{Ag}(\text{CF}_3)_2(\text{CF}_2\text{H})_2]^-$	2098.0	<0.5	140.5 ^d	144.7	4.2 (cis)	137.1	70.8	175.5	11.2 (tr)
$[\text{Ag}(\text{CF}_3)_3(\text{CF}_2\text{H})]^-$	2136.5	<0.5	139.6 ^e	133.9	6.0 (cis)	131.8	76.6	186.2	
			143.9	104.2	14.9 (tr)				
$[\text{Ag}(\text{CF}_3)_4]^-$ ^f	2233.1		139.0	120.0					

^a As Ph₄P⁺ salts in CDCl₃ (internal reference for ¹³C, 77.0 ppm) at 298 K. Otherwise, see Table 3. ^b Not observed. ^c ⁴J(HF)_{trans} 1.8 Hz; $\Delta\delta(^{13}\text{C}-^{13}\text{C}) = 0.101$ ppm; ¹J(CF) 304.5 Hz; ³J(CF)_{cis} 9.8 Hz; ³J(CF)_{trans} 23.0 Hz. ^d ¹J(CF) 388 Hz; ³J(CF)_{trans} 39.1 Hz. ^e *Trans* to CF₃. ^f As Ag[Ag(CF₃)₄] in CH₃CN; ¹J(CF) 393.1 Hz; ³J(CF)_{cis} 8.2 Hz; ³J(CF)_{trans} 45.8 Hz.

that the above-mentioned interactions between the CF₂H groups fail to provide conformational rigidity. As a result the structural parameters determined for the CF₂ fragments (C-F 1.26(5) Å, F-C-F 109(4)°) are of low accuracy. Similar observations have been made for [PNP][Cu(CF₂H)₄], for which the C-F distances and F-C-F angles average 1.30(3) Å and 106(2)°, respectively.

The conformation exhibited by these anions contrasts with that found for the [M(CF₃)₄]⁻ species in the otherwise isomorphous (same space group and similar cell constants) crystals of [PNP][Cu(CF₃)₄]⁶ and [PNP][Ag(CF₃)₄].² The [M(CF₃)₄]⁻ anions show *D*_{2d} symmetry. Such a conformation for an [M(CF₂H)₄]⁻ entity would have, in stark contrast to observation, each M-C-H fragment perpendicular to the coordination plane of the metal with the hydrogen atoms alternately above and below the plane. Such conformational differences in otherwise isomorphous crystals seem surprising and attest to the low specificity of the interactions of these anions with the diphosphazene counterion.

(c) NMR Spectra. The variety and abundance of spin 1/2 nuclei (¹⁹F, ¹³C, ¹H, ¹⁰⁹Ag, ¹⁰⁷Ag) with distinct couplings across

and to the central atom facilitate the unambiguous identification and characterization of fluorinated methylsilver compounds. The connectivity of a CF₂H group to the central silver atom is apparent from the couplings of the ¹⁹F, ¹H, and ¹³C nuclei to the ¹⁰⁹Ag (48.2 %) and ¹⁰⁷Ag (51.8 %) nuclei, which give rise to a characteristic pair of doublets with coupling constants in a ratio of 1.15:1. Despite their high abundance, the two silver nuclei are usually not readily detected directly due to their low and negative magnetogyric ratios as well as to their extremely long relaxation times. The coupling to the sensitive ¹⁹F nuclei, however, allows a polarization transfer to the silver nuclei by DEPT or INEPT pulse sequences or by recourse to inverse spectroscopy. These techniques widely compensate the deficits of the insensitive nuclei and make the ¹⁰⁹Ag resonance readily detectable as long as an exchange of the CF₃ groups is slow on the NMR time scale. The ¹⁰⁹Ag (¹⁹F-DEPT) spectrum of [PNP]-[Ag(CF₂H)₄] is shown in Figure 2. Chemical shifts and coupling constants are listed in Tables 3–5.

Difluoromethyl groups are easily recognized by their doublet (¹⁹F) and triplet structures (¹H) with ²J(FH) being ca. 43 Hz for Ag(I) and ca. 48 Hz for Ag(III) derivatives. Couplings

across the metal atom are not or barely resolvable for $^4J(\text{HH})$, <0.5 Hz, and $^4J(\text{FH})$, ca. 2 Hz, respectively, whereas the $^4J(\text{FF})$ couplings are considerably larger in *trans* $\text{Ag}(\text{CF}_2\text{H})_2$ units. These units constitute a $[\text{A}(\text{X})_2]_2$ spin system similar to that observed in other compounds with two CF_2H groups.^{6,16,17} The basic doublet splitting in such a system is given by the sum of $^2J(\text{FH})$ and $^4J(\text{FH})$, both being positive. Because of the additional couplings to the two silver nuclei, the resulting two overlapping $[\text{A}(\text{X})_2]_2\text{M}$ systems are usually not resolved in all details.

The complex spin systems of the mixed $\text{CF}_3/\text{CF}_2\text{H}$ argentates(III) are greatly simplified by selective homodecoupling experiments which also demonstrate that the relative signs of the $^2J(\text{AgF})$ coupling constants of the AgCF_3 and AgCF_2H units are equal. Inspection of the ^{19}F NMR data, Table 4, shows that both CF_3 and CF_2H resonances experience a high-field shift as the number of CF_2H groups increases. Whether *cis* or *trans* relations are involved is revealed by the magnitude of the $^4J(\text{FF})$ coupling constant, which is less than 4 Hz for *cis* but exceeds 7 Hz for *trans* arrangements. The size of the latter increases markedly with increasing ionicity of the other ligands. Thus the smallest value is found for the $[\text{Ag}(\text{CF}_2\text{H})_4]^-$ ion, and replacement of a CF_2H group by the more ionic CF_3 entity increases the $^4J(\text{FF})$ coupling. The largest value, ca. 18 Hz, is observed for the $[\text{trans-Ag}(\text{CF}_2\text{H})_2(\text{CN})_2]^-$ ion. The same trend has also been noted for the CF_3 -substituted argentates(III), the largest value, 30 Hz, being found for the $[\text{trans-Ag}(\text{CF}_3)_2\text{Br}_2]^-$ ion.⁴

Essentially the same tendencies as in the ^{19}F spectra are observed for the ^{13}C spectra, Table 5. Broad-band ^{19}F decoupling greatly simplifies the spectra and enables the determination of $^3J(\text{CH})$ couplings, which differ significantly for *cis* and *trans* arrangements. In addition to the $^4J(\text{FF})$ and the much less readily available $^3J(\text{CF})$ couplings, these constants are useful in the determination of the stereochemistry of the respective anion. A proton-decoupled ^{13}C spectrum has been recorded for $[\text{Ag}(\text{CF}_2\text{H})_4]^-$ and analyzed as the sum of two $\text{XA}_2\text{B}_4\text{C}_2\text{M}$ spin systems ($\text{X} = ^{13}\text{C}$; A , B , and $\text{C} = ^{19}\text{F}$; $\text{M} = ^{109}\text{Ag}$ and ^{107}Ag , respectively) by computer simulation.

As shown in Figure 3, the good correlation of $^1J(\text{AgC})$ and $^2J(\text{AgF})$ couplings for the silver(III) compounds (closed squares and circles for CF_2H and CF_3 groups, respectively) is not followed by the silver(I) species (open squares). Also included in this figure is the fit line for the various $\text{CF}_3\text{Ag}^{\text{III}}$ moieties.⁴ In general, the $^2J(\text{AgF})$ coupling constants of the CF_2H groups are significantly smaller than those found in CF_3 derivatives; e.g., the value of 24.4 Hz for $[\text{Ag}(\text{CF}_2\text{H})_4]^-$ is to be compared with the 40.7 Hz coupling of the $[\text{Ag}(\text{CF}_3)_4]^-$ ion (Table 4). The trend in $^2J(\text{AgF})$ couplings in the mixed $\text{CF}_3/\text{CF}_2\text{H}$ derivatives nicely follows the pattern outlined previously.⁴ Since a CF_2H group is less electronegative and therefore more covalently bound than a CF_3 group, the former will demand a silver hybrid orbital which contains more 4d and less 5s character than that demanded by a CF_3 group. In accord with this model, the $^2J(\text{AgF})$ coupling involving the CF_2H groups is smaller in $[\text{trans-Ag}(\text{CF}_3)_2(\text{CF}_2\text{H})_2]^-$ than in $[\text{Ag}(\text{CF}_2\text{H})_4]^-$ whereas that of the AgCF_3 unit is larger in $[\text{trans-Ag}(\text{CF}_3)_2(\text{CF}_2\text{H})_2]^-$ than in $[\text{Ag}(\text{CF}_3)_4]^-$.

Silver(I) and silver(III) species are readily distinguished by their ^{109}Ag chemical shifts, but polarization transfer techniques are necessary to enable registration of these spectra in justifiable

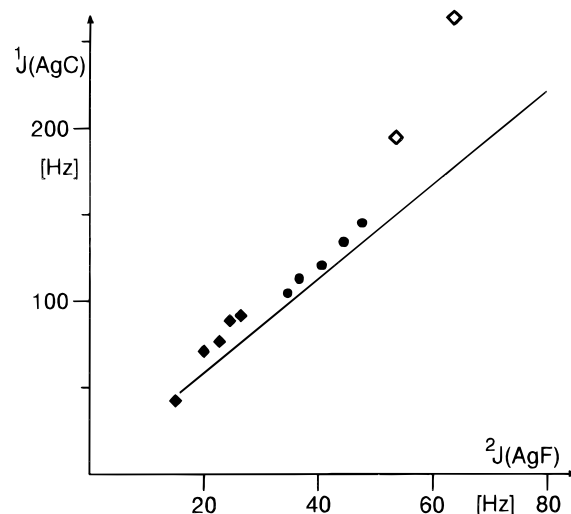


Figure 3. Correlation of $^1J(\text{AgC})$ vs $^2J(\text{AgF})$ in the mixed $\text{CF}_3/\text{CF}_2\text{H}$ -containing argentates $[\text{Ag}(\text{CF}_2\text{H})_n(\text{CF}_3)_{4-n}]^-$ ($n = 0-4$) and *trans*- $[\text{Ag}(\text{CF}_2\text{H})_2(\text{CN})_2]^-$. Closed diamonds correspond to $\text{Ag}(\text{III})-\text{CF}_2\text{H}$, closed circles to $\text{Ag}(\text{III})-\text{CF}_3$ units, and open diamonds to the silver(I) species $[\text{Ag}(\text{CF}_2\text{H})_2]^-$ and $[\text{Ag}(\text{CF}_2\text{H})(\text{CN})]^-$. The solid line is the fit line for $\text{Ag}(\text{III})-\text{CF}_3$ derivatives, taken from ref 4.

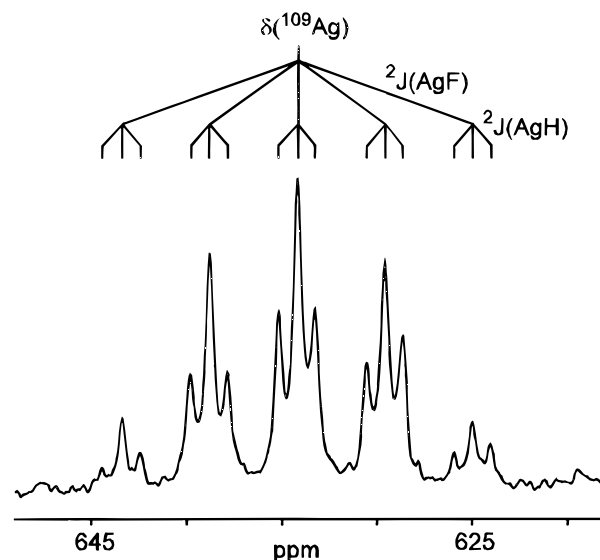


Figure 4. ^{109}Ag NMR spectrum of the silver(I) species $[\text{Ag}(\text{CF}_2\text{H})_2]^-$, recorded at -60°C .

times. Figure 4 displays the low-temperature ^{109}Ag spectrum of the $[\text{Ag}(\text{CF}_2\text{H})_2]^-$ ion, showing a quintet of triplet fine structure due to couplings to the fluorines and hydrogens, respectively. In Figure 5, the ^{109}Ag spectrum of a 1:1 mixture of the *cis*- and *trans*- $[\text{Ag}(\text{CF}_3)_2(\text{CF}_2\text{H})_2]^-$ anions is shown along with a simulation. With respect to their CF_3 analogs, the resonances of the (difluoromethyl)argentates(I) near +600 ppm are shifted to low fields whereas the opposite effect is noticed for the silver(III) compounds with chemical shifts around +2100 ppm.

Conclusion

In a preceding paper⁴, we showed that it is possible to replace the CF_3 groups in the argentate(III) $[\text{Ag}(\text{CF}_3)_4]^-$ by other ligands such as the cyano group although the stability of these complexes decreases with decreasing number of CF_3 groups. The amazingly high stability of the "binary" argentate(III) may be traced to several factors. In terms of ligand field theory, the strong field of the CF_3 groups renders the $d_{x^2-y^2}$ orbital

(16) Bürger, H.; Eujen, R.; Moritz, P. *J. Organomet. Chem.* **1991**, 401, 249.

(17) Eujen, R.; Jahn, N.; Thurmman, U. *J. Organomet. Chem.* **1994**, 465, 153.

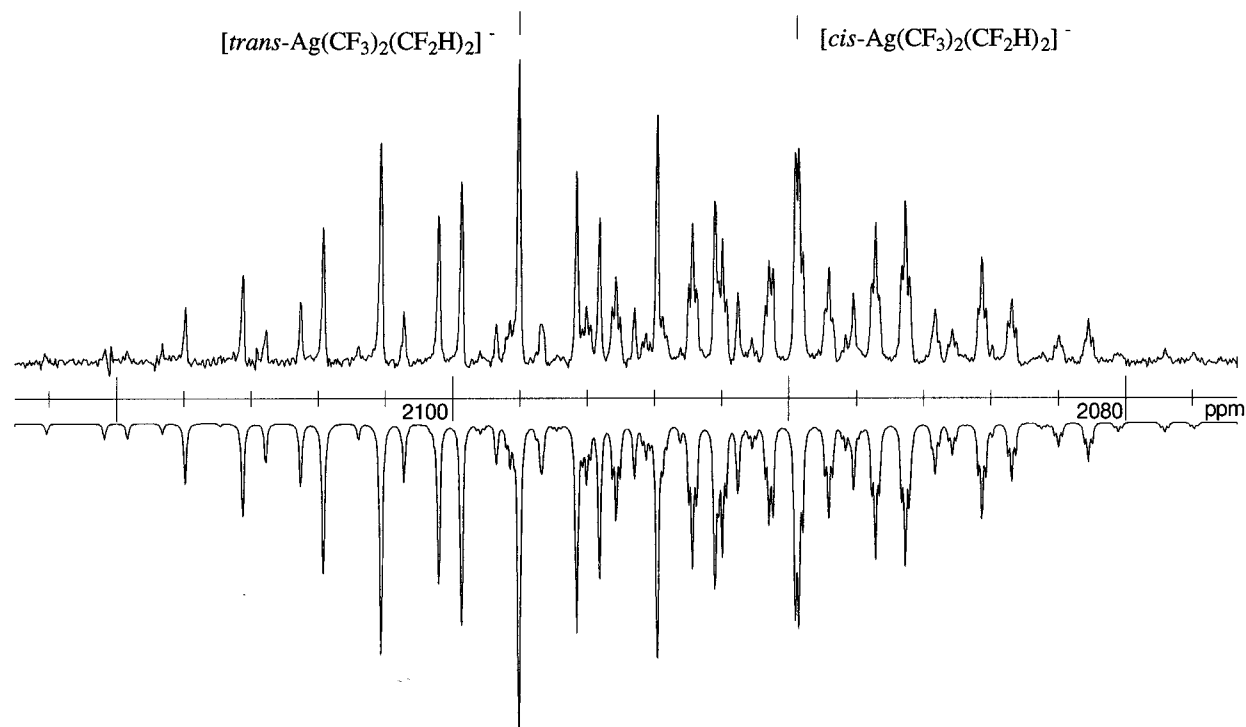


Figure 5. ^{109}Ag NMR spectrum of a 1:1 mixture of *trans*- and *cis*- $[\text{Ag}(\text{CF}_2\text{H})_2(\text{CF}_3)_2]^-$. The simulated spectrum is shown in the lower trace.

hardly accessible for donors. Steric shielding by the fluorines which are positioned above and below the AgC_4 plane might contribute additionally. A general stabilization of orbitals with respect to analogous methyl derivatives, denoted as the “per-fluoromethyl effect”, is evident from the photoelectron spectra of $\text{CF}_3\text{Pt}^{18}$ or $\text{CF}_3\text{Ge}^{19}$ compounds. In contrast to main group chemistry, where $\text{M}-\text{CF}_3$ bonds are rather easily cleaved because either strong covalent $\text{M}-\text{F}$ bonds or ionic fluorides with high lattice energies are formed, the degradation of $\text{Ag}(\text{III})-\text{CF}_3$ units to $\text{Ag}(\text{III})-\text{F}$ bonds is less favorable. Reductive elimination of C_2F_6 does not appear to be a thermodynamically or kinetically favored pathway. Replacement of fluorines by hydrogen atoms, e.g. substitution of one or two CF_3 groups by CH_3 groups, clearly destabilizes the

oxidation state +3 though the anion $[\text{Ag}(\text{CF}_3)_3(\text{CH}_3)]^-$ is still stable at ambient temperature.⁴

The comparable stabilities of the $[\text{Ag}(\text{CF}_3)_4]^-$ and $[\text{Ag}(\text{CF}_2\text{H})_4]^-$ anions may be an artifact arising from the lower tendency of the latter to eliminate a carbene. When kinetically and thermodynamically comparable decomposition pathways are present as in case of the $[\text{trans-Ag}(\text{R}_\text{F})(\text{CN})_2]^-$ anions, the difference in electronic stabilization becomes evident by the respective decomposition temperatures, +90 °C for $\text{R}_\text{F} = \text{CF}_3$ and -30 °C for $\text{R}_\text{F} = \text{CF}_2\text{H}$.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for $[\text{PNP}][\text{Ag}(\text{CF}_2\text{H})_4]$ is available on the Internet only. Access information is given on any current masthead page.

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- (18) Yang, D.-S.; Bancroft, G. M.; Puddephatt, R. J.; Tse, J. S. *Inorg. Chem.* **1990**, 29, 2496.
 (19) (a) Drake, J. E.; Gorzelska, K.; White, G. S.; Eujen, R. *J. Electron Spectrosc. Relat. Phenom.* **1982**, 26, 1. (b) Drake, J. E.; Gorzelska, K.; Helbing, K.; Eujen, R. *J. Electron Spectrosc. Relat. Phenom.* **1982**, 26, 19. (c) Drake, J. E.; Eujen, R.; Gorzelska, K. *Inorg. Chem.* **1982**, 21, 1784.