Trialkoxysilyl-Functionalized Silver(I) Carboxylates: New Building Blocks for the Synthesis of Immobilizable and Immobilized Homogeneous Catalysts

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Partly fluorinated trialkoxysilyl-substituted carboxylic acids $(RO)_3Si(CH_2)_3N(R')C(O)(CF_2)_3COOH$ (**3a**: R = Et, R′ = H; **3b**: R = R′ = Me) have been prepared in a straightforward synthesis from the respective trialkoxysilyl-substituted primary and secondary amines and hexafluoroglutaric anhydride. Treatment with silver(I) oxide yields the corresponding silver carboxylates **4a**,**b** which have been thoroughly characterized in solution and in the solid state, including an X-ray crystallographic analysis of **4a**. The molecular structure of **4a** consists of archetypal carboxylate-bridged disilver(I) pairs with a strong closed-shell Ag–Ag (d^{10}–d^{10}) interaction and a unique intramolecular bond between a silyl ether group and the metal ion. In addition the amide oxygen atoms are involved in H-bonding and in intermolecular silver coordination, giving rise to an unusual two-dimensional network structure. Silyl-free acid $iPr_2NC(O)(CF_2)_3COOH$ (**5**) and its silver salt **6** have been prepared and structurally characterized for comparison. It is shown that the trialkoxysilyl tail in **4a**,**b** allows for convenient attachment of these silver complexes to silica surfaces, as is corroborated by DRIFT measurements. The immobilized silver carboxylates **7a**,**b** exhibit remarkable stability and are expected to open an easy access to a wide variety of SiO_2-grafted transition metal catalysts via transfer of the carboxylate ligand in simple exchange reactions.

Introduction

For several decades, the immobilization of homogeneous catalysts has been a major topic and has been pursued in various academic and industrial laboratories.[1] Stimulus for this comes from the great benefits of combining the advantages of homogeneous (high activity, high selectivity, high reproducibility) and heterogeneous (easy separation and recovery of the catalyst from the reaction mixture) catalysis.[2]

One of the major drawbacks of homogeneous catalysts is the need for separation of the relatively expensive catalysts from the reaction mixture at the end of the process. A solution to this separation problem is the use of immobilized homogeneous catalysts, which can be recovered from the reaction mixture by simple filtration or centrifugation and then, potentially, be reused.[3,4] In addition to this separation advantage, the catalytic performance of the immobilized catalysts, e.g. stability and selectivity, are sometimes improved compared to their homogeneous analogs.[5,6] Therefore, there is a growing need to develop more efficient and practical immobilization methods.

The most widely used method of immobilization of homogeneous transition metal catalysts is the binding of at least one of the catalyst ligands to a solid support via a covalent bond. Immobilization can be done either on inorganic or organic polymer support materials. Inorganic materials such as silica have many advantages compared to the organic materials: high chemical stability, high mechanical stability, no swelling properties, excellent thermal stability and an almost unlimited access to tailor-made particles including tailor-made surfaces.[7] A common and easy method for the immobilization of functionalities on SiO_2 surfaces is the reaction of alkoxysilyl-substituted functionalities with the OH groups of silica.[5,7] However, the number of available alkoxysilyl-substituted catalyst ligands is limited – especially alkoxysilyl-substituted anionic ligands are very rare. Thus there is great interest in new and versatile building blocks, which can easily be covalently combined with the support material on one side and with the metal atom of the homogeneous catalyst on the other.

Many homogeneous catalysts based on e.g. ruthenium, rhodium, tungsten, cobalt, palladium or copper contain halogen atoms, which do not participate in the catalytic cycle.[8–10] Replacement of those halogen atoms by other ligands such as anionic carboxylates has recently been explored for several catalyst systems.[11–13] It has often been observed that the catalytic performance of the carboxylate-

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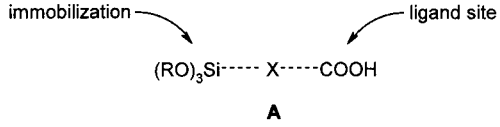
substituted catalysts is in the same range as the parent halogen-substituted catalysts. Therefore, we were searching for new type **A** building blocks bearing two functionalities (Scheme 1): an immobilizable alkoxysilyl-group and an accessible carboxylic acid group that after deprotonation may act as a ligand towards transition metal ions. Silver salts of these functional carboxylates are sought as suitable synthons that will allow subsequent attachment of the metal complex fragment via halide exchange, forming the respective silver halide.



Scheme 1.

With respect to the spacer X, fluorinated moieties are of particular interest, since they may provide favorable solubility and higher stability of the silver salts and of the resulting metal carboxylate complexes. In addition, electron-withdrawing carboxylates have proven superior in various catalytic processes.[12–14]

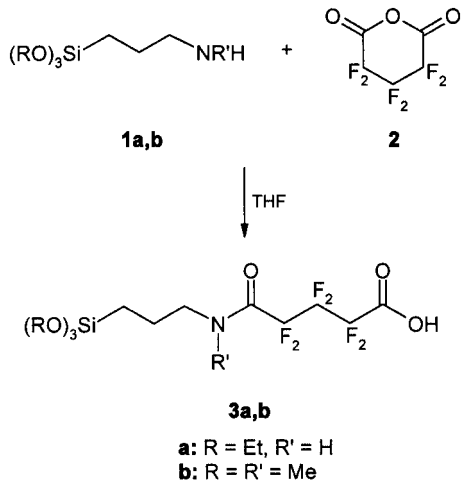
In this contribution, we report on the synthesis and spectroscopic properties of two new partly fluorinated trialkoxysilyl-substituted silver(I) carboxylates with a type **A** backbone. A related fluorinated silver(I) carboxylate lacking the silyl group has been prepared for comparison, and unusual structural features of these complexes in the solid state are described. It should be noted that silver(I) carboxylates have been intensively studied for their rich and diverse structural chemistry in the solid state,[15–17] and silver(I) complexes with fluorinated carboxylates have previously attracted interest as potential precursors for chemical vapor deposition (CVD) yielding metallic silver layers.[18–20]

Results and Discussion

Synthesis and Spectroscopy

Partly fluorinated trialkoxysilyl-substituted carboxylic acids **3** were prepared in almost quantitative yields by the reaction of the trialkoxysilyl-substituted primary amine **1a** and secondary amine **1b** with hexafluoroglutaric anhydride (**2**) in tetrahydrofuran (Scheme 2). The reactions have to be carried out in the absence of water to avoid hydrolysis of the silyl function, which is catalyzed by acidic protons. Products **3a** and **b** can be isolated as colorless oils or used in situ in the next step of the synthetic sequence. Compound **3a** has been mentioned previously but was not isolated.[13]

IR spectra of acids **3a**,**b** (Table 1) show the characteristic bands for $\tilde{\nu}_{as}$(COO) at 1775 cm^{-1} (**3a**) or 1781 cm^{-1} (**3b**) and for $\tilde{\nu}_{s}$(COO) at 1445 cm^{-1} (**3a**) or 1464 cm^{-1} (**3b**) as well as



Scheme 2. Synthesis of the trialkoxysilyl-functionalized carboxylic acids **3**.

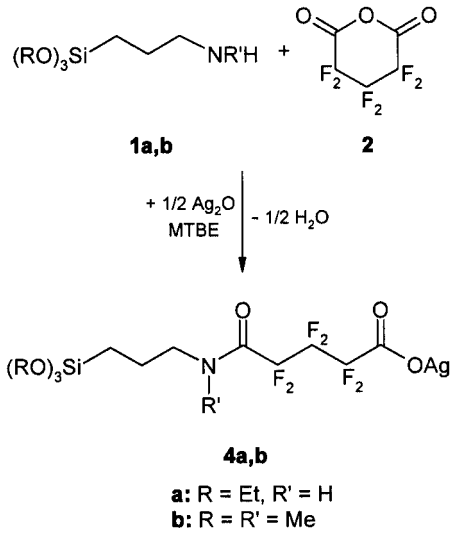
strong absorptions for the C–F stretches around 1165 cm^{-1}. As expected for an *N*-monosubstituted amide,[21] **3a** features two bands at 1703 and 1549 cm^{-1} (amide I and amide II, respectively), while a single band at 1679 cm^{-1} is observed for *N*,*N*-disubstituted amide **3b**. Distinct ^{1}H, ^{13}C, and ^{19}F NMR signals for the *E* and *Z* amide isomers are detected for **3b**, revealing an *E*/*Z* ratio of 0.62:1 at 297 K.

Table 1. Characteristic IR spectral frequencies in cm^{-1}.

Compound	$\tilde{\nu}_{as}$(COO)	$\tilde{\nu}_{s}$(COO)	$\Delta\tilde{\nu}$[a]	$\tilde{\nu}$(CON)	$\tilde{\nu}$(CF)
3a (film)	1775	1445	330	1703/ 1549	1168
3b (film)	1781	1464	317	1679	1160
5 (film)	1785	1452	333	1654	1172/1158
5 (KBr)	1769	1451	318	1642	1176/1151
4a (THF)	1691	1391	300	1716/1550	1153
4a (MTBE)	1658	1407	251	1722/1541	1169
4a (KBr)	1687	1393	294	1706/1549	1163
4b (THF)	1685[b]	1401	[b]	1658[b]	1164
4b (MTBE)	1685[b]	1407	[b]	1659[b]	1166
4b (film)	1651(br)	1401	250	1651(br)	1160
6 (THF)	1679	1384	295	1679	1151
6 (MTBE)	1681	1386/1369	≈300	1658	1159
6 (KBr)	1687(sh)/1675	1393	≈290	1687(sh)/1675	1150
7a (DRIFT)	1664	n.a.	n.a.	1713/1539	n.a.
7b (DRIFT)	1669(br)	n.a.	n.a.	1669(br)	n.a.

[a] $\Delta\tilde{\nu} = \tilde{\nu}_{as}$(COO) – $\tilde{\nu}_{s}$(COO) for the silver(I) carboxylate. [b] assignment of $\tilde{\nu}_{as}$(COO) and $\tilde{\nu}$(CON) is tentative, hence no value for $\Delta\tilde{\nu}$ is included. n.a. = not assignable because of SiO_2 absorptions.

Conversion of carboxylic acids **3** into the appropriate silver(I) carboxylates **4** can be achieved by reacting the respective acid **3a**,**b** with silver(I) oxide in MTBE. Alternatively, acids **3** generated in situ from the respective amine **1a**,**b** and hexafluoroglutaric anhydride (**2**) can be directly converted into **4a**,**b** by the addition of silver(I) oxide in MTBE (Scheme 3). Following the latter method the reaction mixture was stirred overnight at room temperature in the dark. After filtration and removal of the solvent, complex **4a** was obtained as a colorless solid while **4b** was isolated as a colorless oil.

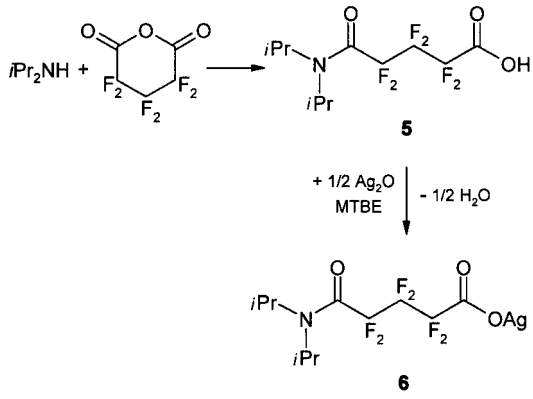


Scheme 3. Synthesis of the trialkoxysilyl-functionalized silver carboxylates **4**.

Formation of the silver carboxylate complexes **4a**,**b** is confirmed by the absence of $\tilde{\nu}_{as}$(COO), $\tilde{\nu}_{s}$(COO) vibrations for the free acids and the appearance of distinct $\tilde{\nu}_{as}$(COO) and $\tilde{\nu}_{s}$(COO) stretches around 1680 and 1395 cm^{-1} (Table 1).[22] In contrast, the characteristic bands for the amide functions in **4a**,**b** are barely shifted from their position in **3a**,**b**.[23] The separation of the $\tilde{\nu}_{as}$(COO) and $\tilde{\nu}_{s}$(COO) stretches of around $\Delta\tilde{\nu}$ = 290 cm^{-1} for **4a** may indicate a bridging carboxylate coordination (compare the crystallographic results, vide infra).[23,24] As noted previously, however, the precise type of carboxylate coordination cannot be proposed on the basis of the $\Delta\tilde{\nu}$ parameter.[19,24] Formation of silver carboxylate complexes is further corroborated by a significant low-field shift of the carboxylic ^{13}C NMR resonance from around 160.8 ppm in the acids **3a**,**b** to around 163.8 ppm in **4a**,**b**. At the same time the ^{13}C NMR resonance for the amide group is almost unchanged at around 158.7 ppm.

Proper solvent selection is critical for the formation of pure products **4**. While the reaction mixture is colorless in MTBE and a colorless product is isolated from this solvent, the reaction mixture turns yellow in THF and a deeply yellow product is obtained in the latter case. The color of the product remains yellow even after complete removal of THF. All attempts to further purify these yellow products or to identify the colored species failed. However, the highly colored impurity can only be present in trace amounts, since X-ray crystallographic analyses of the materials **4a** obtained from both solvents gave identical results (vide infra) and the IR spectra of KBr pellets of both materials are basically identical ($\Delta\tilde{\nu} \approx 294\ cm^{-1}$). In contrast to MTBE, THF appears to coordinate to the silver ions in **4a** in solution, since ^{1}H NMR spectroscopic experiments in CD_2Cl_2 reveal a slight shift of the THF solvent signal to lower field. Furthermore, IR absorptions for the $\tilde{\nu}_{as}$(COO) and $\tilde{\nu}_{s}$(COO) stretches of **4a** measured in either THF or MTBE solution show significant differences (Table 1), with $\Delta\tilde{\nu}$ being 300 cm^{-1} in THF while being 251 cm^{-1} in MTBE (amide I and amide II bands for **4a** are quite similar in the two solvents). If isolated as pure compounds **4a** and **4b** are stable at room temperature and show no significant light sensitivity. Upon heating the color of solid **4a** and **4b** changes from colorless via red to brown, and at 160 °C formation of a silver film occurs. In solution, compounds **4** start to decompose under light at room temperature within several days. No decomposition is observed when keeping the solution at –20 °C under exclusion of light.

In order to investigate the influence of the alkoxysilyl group on the stability and structural features of type **4** compounds, an analog of **4** devoid of the alkoxysilyl group has been synthesized from the route shown in Scheme 4. The alkoxysilyl-free acid **5** can be readily prepared from diisopropylamine and hexafluoroglutaric anhydride in dichloromethane. Crystallization from dichloromethane/hexane at room temperature gave colorless X-ray quality crystals of **5**. Attempts to carry out the synthesis of **5** in MTBE or THF leads to the formation of the diamide $iPr_2NC(O)(CF_2)_3C(O)NiPr_2$.



Scheme 4. Synthesis of the silyl-free carboxylic acid **5** and the silver carboxylate **6**.

Addition of **5** to a suspension of silver(I) oxide in MTBE leads to the formation of the silyl-free silver(I) carboxylate **6** (Scheme 4). After stirring the reaction mixture in the dark for 4 h at room temperature, the colorless product is conveniently isolated by filtration followed by removal of the solvent. Crystals of **6** could be obtained by diffusion of hexane into a saturated solution of the crude product in chloroform. If carried out in THF instead of MTBE the color of the reaction solution turned yellow and a yellow product was isolated, just like the observation made with the earlier described silver(I) carboxylates **4a** and **4b**. IR spectral features of **6** are quite similar if measured either in THF or MTBE solution or as KBr pellets, showing a single broad band for $\tilde{\nu}_{as}$(COO) and $\tilde{\nu}(CO)_{amide}$ at ca. 1680 cm^{-1} and a $\tilde{\nu}_{s}$(COO) band at ca. 1380 cm^{-1}. Compared to the alkoxysilyl-containing silver(I) carboxylates **4** the silyl-free silver(I) carboxylate **6** exhibits much lower thermal stability and much higher light sensitivity. **6** cannot be handled in air due to its strong hygroscopic behavior, and it decomposes within minutes under exposure to light in both solution and

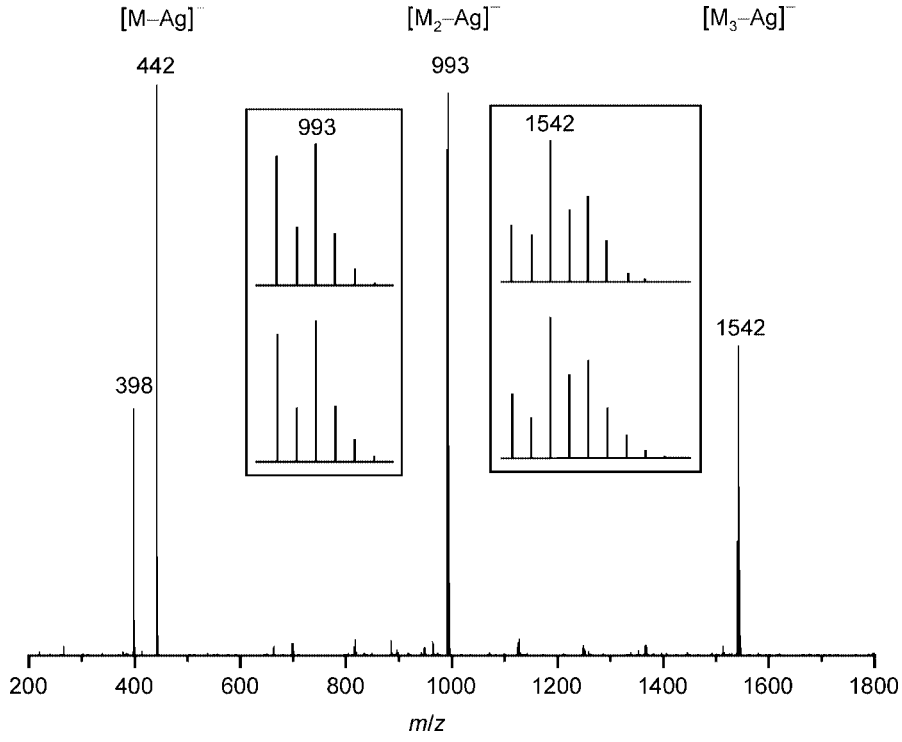


Figure 1. Part of the negative ion ESI mass spectrum of **4a**. The insets show the experimental (upper) and calculated (lower) isotopic distribution pattern for distinct ions $[M_x - Ag]^-$ (x = 2, 3).

as a solid. Upon heating **6** decomposes at around 95 °C turning into a dark colored solid.

Positive ion ESI mass spectra of acetonitrile solutions of all silver carboxylate complexes **4a**, **4b**, and **6** show a prominent peak for simple $[Ag(NCMe)_2]^+$, but minor signals characteristic for various ions $[M_x + Ag]^+$ (x = 1–3) or $[M_x + Na]^+$ (x = 1, 2) are also discernible, thus suggesting the presence of oligomeric aggregates in solution. This is most apparent from the negative ion ESI mass spectrum of **4a** depicted in Figure 1, where all major peaks can be clearly assigned to ions $[M_x - Ag]^-$ (x = 1–3). Aggregation also takes place in the solid state, as is described in the following section.

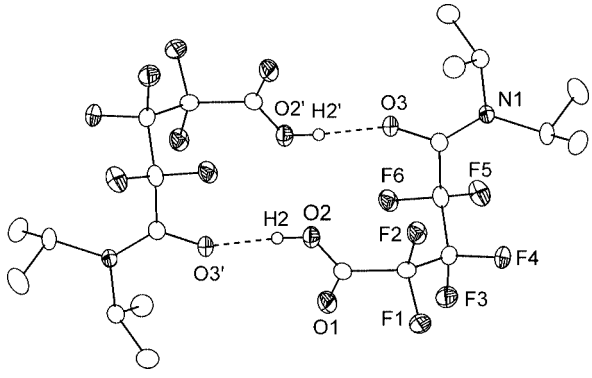


Figure 2. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **5**. For the sake of clarity all hydrogen atoms except H2 have been omitted. Selected atom distances [Å] and angles [°]: O2–H2 0.85(3), H2···O3′ 1.75(3), O2···O3′ 2.595(2); O2–H2···O3′ 175(3). Symmetry transformation used to generate equivalent atoms (′): 1 – x, 1 – y, 1 – z.

Crystal Structures

Silver complexes **4a** and **6** have been investigated by X-ray crystallography in order to fully understand their distinct spectroscopic and mass-spectrometric features and to rationalize the different thermal stability and light sensitivity of the alkoxysilyl-substituted and silyl-free silver(I) carboxylates **4** and **6**, respectively. For comparison, the structure of acid **5** has also been determined crystallographically and is shown in Figure 2. Molecular structures of **4** and **6** are depicted in Figure 3, Figure 4 (complex **6**), Figure 5, and Figure 6 (complex **4a**), along with selected atom distances and bond angles.

In the solid state carboxylic acid **5** exists as a dimer composed of two acid molecules that are linked via intermolecular hydrogen bonding (Figure 2). The hydrogen bond occurs between the carboxylic group as an H-donor and the amide-O atom as an H-acceptor, forming an unusual 16-membered ring structure. Though dimer or catemer formation of carboxylic acids via hydrogen bonds between two acid functionalities (**B**; Scheme 5) is an archetypal structural motif and is a mainstay of organic crystal engineering,[25,26] carboxylic acid association involving other groups

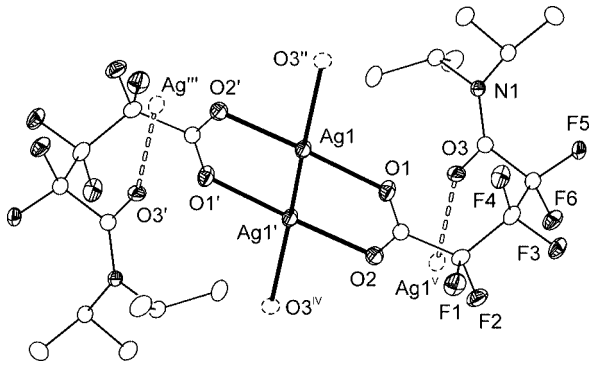


Figure 3. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **6**. For the sake of clarity all hydrogen atoms have been omitted. Selected atom distances [Å] and angles [°]: Ag1–O1 2.192(3), Ag1–O2′ 2.219(3), Ag1–O3′′ 2.444(3), Ag1–Ag1 2.9362(8); O1–Ag1–O2′ 159.1(1), O1–Ag1–O3 105.3(1), O1–Ag1–Ag1′ 76.07(7), O2′–Ag1–O3′′ 87.53(9), O2′–Ag1–Ag1′ 85.25(7), O3′′–Ag1–Ag1′ 154.33(7). Symmetry transformations used to generate equivalent atoms (^{I}): 1 – *x*, 1 – *y*, 1 – *z*, (^{II}): 1 + *x*, *y*, *z*, (^{III}): 2 – *x*, 1 – *y*, 1 – *z*, (^{IV}): –*x*, 1 – *y*, 1 – *z*, (^{V}): *x* – 1, *y*, *z*.

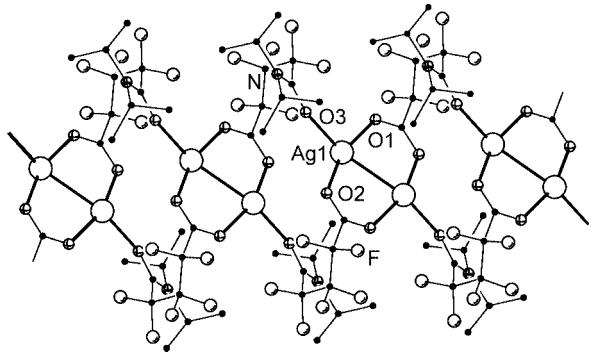


Figure 4. Plot of the chain structure of **6**. For the sake of clarity all hydrogen atoms have been omitted.

such as, e.g., a carbonyl or amide is rather rare if both groups are present in the same molecule.[27]

Reaction of **5** with Ag_2O gives yellow crystals of **6**. The structure consists of carboxylate-bridged metal-pairs **C**, featuring a strong closed-shell interaction that leads to a short Ag–Ag distance of 2.94 Å (Figure 3). Such interactions are quite common for the heavier coinage metals, and metal-metal distances of comparable magnitude have been reported for numerous compounds.[28] Since the coordination sphere of the Ag^+ ions in type **C** dimeric units is generally not satisfied by the two oxygen atoms, coordination of additional donors typically leads to polymeric or oligomeric arrays, and silver carboxylate dimers **C** have thus been exploited as building blocks for the assembly of extended coordination networks.[29] In the present case the Ag–Ag pairs are coated by their two acid molecules, and these pairs constitute subunits of a chain structure that is created through intermolecular coordination of the amide oxygen atoms to next neighbor metal pairs (Figure 4). Taking into account the closed-shell interaction and the coordination of three oxygen atoms, each silver is found in a strongly distorted

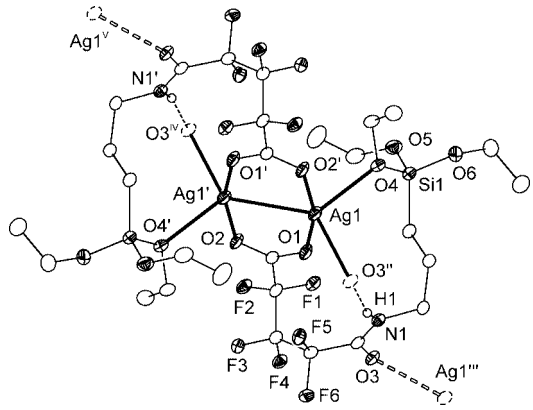


Figure 5. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **4a**. For the sake of clarity all hydrogen atoms except H1 have been omitted. Selected atom distances [Å] and angles [°]: Ag1–O1 2.185(3), Ag1–O2′ 2.196(3), Ag1–O3′′ 2.606(2), Ag1–O4 2.606(2), Ag1–Ag1′ 2.9682(6), N1–H1 0.81(4), H1···O3′′ 2.22(4), N1···O3′′ 3.017(4); O1–Ag1–O2′ 161.12(9), O1–Ag1–O3′′ 86.55(8), O1–Ag1–O4 100.13(9), O1–Ag1–Ag1′ 78.42(6), O2′–Ag1–O3′′ 106.47(8), O2′–Ag1–O4 89.67(9), O2′–Ag1–Ag1′ 82.74(6), O3′′–Ag1–O4 105.51(7), O3′′–Ag1–Ag1′ 129.15(6), O4–Ag1–Ag1′ 124.78(5), N1–H1···O3′′ 165(4). Symmetry transformations used to generate equivalent atoms (′): 1 – *x*, 1 – *y*, 1 – *z*, (′′): *x*, ½ – *y*, –½ + *z*, (′′′): *x*, ½ – *y*, ½ + *z*, (^{IV}): 1 –*x*, ½ + *y*, ½ – *z*, (^{V}): 1 – *x*, ½ + *y*, ½ – *z*.

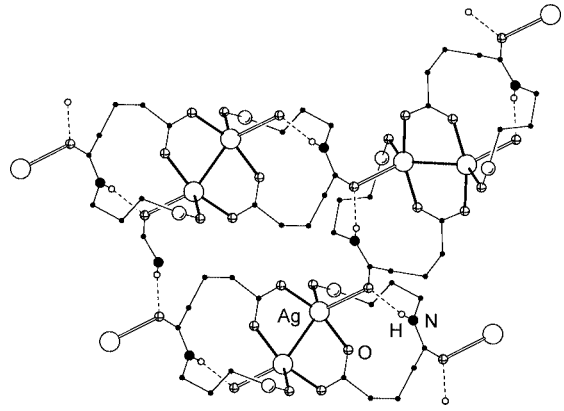
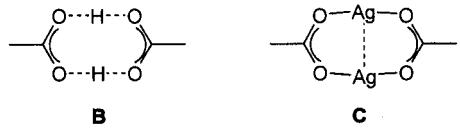


Figure 6. Plot of the network structure of **4a**. For the sake of clarity all hydrogen atoms except H1, all fluorine atoms, two ethoxy groups and the carbon atoms of the coordinating ethoxy group have been omitted.



Scheme 5.

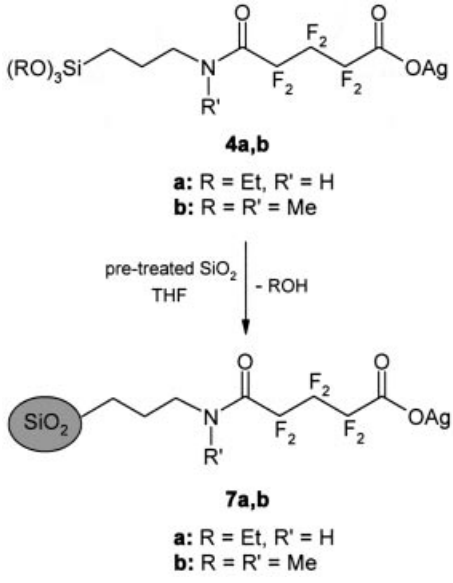
square-planar environment [distance to the least-squares planes of the four surrounding atoms is 0.415(1) Å].

A similar type **C** motif with d^{10}–d^{10} interaction and a short Ag–Ag distance of 2.97 Å is also observed for **4a**. In contrast to **6**, however, the silver ions in **4a** show a distorted trigonal-bipyramidal coordination environment, because a silyl ether group is involved in metal ion binding [*d*(Ag1–O4) = 2.606(2) Å, Figure 5]. Oxygen atoms from the car-

boxylic acid functionalities occupy the axial positions, whereas the adjacent silver ion, an amide oxygen atom and an oxygen atom from the silyl ether group make up the equatorial positions. Direct coordination of silyl ethers to transition metal atoms is quite rare and **4a** is one of the very few structurally characterized examples for the heavier group 11 elements. To the best of our knowledge, **4a** is the only silver compound with a distance between the metal center and the oxygen atom of a Si–O–C fragment which is distinctly below 3 Å.[30] Like in **4a** the Ag–Ag pairs are coated by acid molecules, and additional coordination of oxygen atoms from two adjacent dimeric building blocks results in the formation of a two-dimensional network structure (Figure 6). Each of these amide oxygen atoms at the same time acts as a hydrogen-bond acceptor for the N–H protons of an adjacent amide.

Immobilization

Immobilization of the silver(I) carboxylates **4** onto silica was performed by a pre-treatment step of the silica material followed by the actual immobilization step (Scheme 6). First the silica was successively washed with methanol, dichloromethane and hexane in order to remove any impurities from the SiO_2, and the treated material was dried at 200 °C under high vacuum for 4 h to achieve thermal desorption of physically adsorbed water molecules from the silica gel surface.



Scheme 6. Immobilization of **4** onto silica gel.

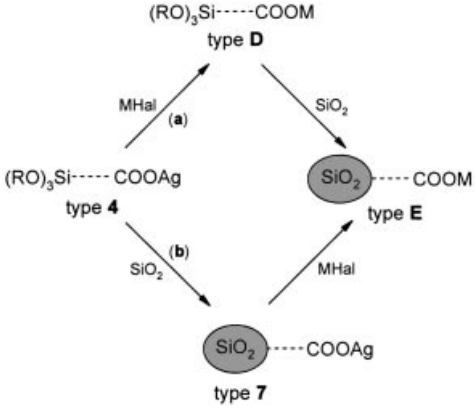
Silver(I) carboxylates **4** were subsequently attached to the silica surface by adding a solution of **4** in THF to a silica/THF suspension and stirring the reaction mixture at room temperature for 21 h in the dark. Immobilized silver(I) carboxylates **7a** and **b** were isolated as white solids by filtration and thoroughly washed with THF and hexane. The combined filtrates were evaporated under vacuum and checked for any remaining starting material. No residual **4** was detected, thus confirming that complete immobilization had occurred. This corresponds to an immobilization ratio of 0.1 mmol of **4** per g of SiO_2 and accordingly 5 wt.-% of **4**, which is a good ligand loading rate for a potential subsequent transformation of the silver(I) carboxylates into powerful immobilized catalysts.[31–33] Immobilized silver(I) salts **7** show remarkable stability when taking into account that stabilization of their homogeneous silver(I) precursors **4** occurred by aggregation, which is necessarily reduced upon covalent immobilization of **4** on the silica surface. The immobilized silver(I) salts **7** start to decompose under light at room temperature within several days; when kept under the exclusion of light they can be stored over a period of a few weeks without decomposition. Upon heating, the color of **7** changes from white to yellow (90 °C) to brown (180 °C).

DRIFT (Diffuse Reflectance Infra-red Fourier Transform) measurements of **7a**,**b** confirm the adsorption of the silver carboxylate compounds onto the silica. The pre-treated silica shows, inter alia, the expected sharp peak at 3747 cm^{-1} for isolated noninteracting silanol groups and broad bands at 1993, 1862, 1625, 1195, 980, and 845 cm^{-1} for the H–O–H (adsorbed water) and Si–O–Si modes of silica itself.[34–36] While these features remain unchanged in **7a**,**b**, additional peaks appear at 1713, 1664 and 1539 cm^{-1} (**7a**) or 1669 cm^{-1} (**7b**). This is close to the position of the $\tilde{\nu}_{as}$(COO) and $\tilde{\nu}$(CON) modes of the respective precursor compounds **4a**,**b** (Table 1), in agreement with nondestructive adsorption of complexes **4a**,**b** onto the silica.

Conclusions and Outlook

A straightforward synthetic approach is reported for some new silver(I) carboxylates that incorporate a partly fluorinated tail with an appended trialkoxysilyl substituent. The silver carboxylate complexes have been thoroughly characterized both in solution and in the solid state and have been found to form oligonuclear or polymeric assemblies that are based on archetypal carboxylate-bridged disilver(I) units with short d^{10}–d^{10} interactions. Inter alia, an unusual coordination of an alkoxysilyl oxygen atom towards silver has been discovered.

The trialkoxysilyl anchor enables a convenient attachment of complexes **4a**,**b** to silica surfaces. The future potential of the newly prepared immobilizable type **4** compounds and immobilized type **7** compounds is summarized in Scheme 7. The development of the flexible fluorinated silver carboxylates reported in this work is expected to open an easy access to a wide variety of SiO_2-grafted transition metal species **E** (M = transition metal complex fragment) via simple exchange reactions. Metal exchange may be carried out either before [route (**a**)] or after [route (**b**)] the immobilization step, depending on the specific requirements of the particular system. Since separation of the insoluble silver halides from the silica-bound catalyst may pose a problem, the former route (**a**) should in most cases be advantageous.



Scheme 7.

A detailed evaluation of various type **E** immobilized transition metal complexes in catalytic reactions will be reported in due course.

Experimental Section

General Remarks: All operations were carried out under argon using standard vacuum and Schlenk techniques or in a glovebox under argon (Labmaster 130, MBraun, Germany). All solvents were dried and purified by passing them through suitable drying columns or by employing standard drying agents.[37,38] 3-(Triethoxysilyl)propylamine (Fluka), 3-(methylamino)propyltrimethoxysilane (ABCR), hexafluoroglutaric anhydride (ABCR), diisopropylamine (Merck) and silver(I) oxide (Merck) were used as received. All stoichiometric calculations involving silica gel (KG 60, Merck) are based on an average surface area of 510 $m^2 g^{-1}$. ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX 250 Advance, Bruker AMX 300 or Bruker DRX 500 Advance at ambient temperature. Data are given in ppm relative to solvent signals for ^1H and ^{13}C NMR spectra or relative to an external standard for ^{19}F NMR experiments ($CFCl_3$ at 0 ppm). IR spectra were recorded with a Bruker Equinox 55 FT-IR instrument as KBr pellets, as films between KBr plates or in solution using a CaF_2 cell. DRIFT measurements (Diffuse Reflectance Infra-red Fourier Transform) were recorded with a Bruker IFS-66 FT-IR instrument; the samples were scanned 256 times. Elemental analyses were measured with a Vario EL. Melting points were obtained with a BÜCHI capillary apparatus B-540. Mass spectra were collected with a Finnigan MAT 8200 (EI, 70 eV) or a Finnigan MAT LCQ (ESI).

$(EtO)_3Si(CH_2)_3N(H)C(O)(CF_2)_3COOH$ (3a):[13] Hexafluoroglutaric anhydride (**2**) (192 μL, 1.40 mmol) dissolved in THF (7.5 mL) was added dropwise to a solution of 3-(triethoxysilyl)propylamine (**1a**) (331 μL, 1.40 mmol) in THF (7.5 mL). The mixture was stirred for 30 min at room temperature, and all volatiles were then removed under reduced pressure at 25 °C. **3a** was isolated as a colorless oil. Yield: 615 mg (99%). $C_{14}H_{23}F_6NO_6Si$ (443.41). ^1H NMR (250 MHz, [D$_8$]THF): δ = 0.58 (t, ^3J = 8.3 Hz, 2 H, SiCH_2), 1.17 (t, ^3J = 7.0 Hz, 9 H, CH_3), 1.63 (pseudo-quint, ^3J = 8.0 Hz, 2 H, SiCH$_2$CH_2), 3.25 (pseudo-q, ^3J = 6.8 Hz, 2 H, CH_2N), 3.78 (q, ^3J = 7.0 Hz, 6 H, OCH_2), 8.32 (br, 1 H, N*H*), 13.53 (s, 1 H, COO*H*) ppm. ^{19}F NMR (235 MHz, [D$_8$]THF): δ = –125.5 (s, 2 F, CF_2), –120.5 (t, $^4J_{F,F}$ = 9.5 Hz, 2 F, CF_2CONH), –119.5 (t, $^4J_{F,F}$ = 9.5 Hz, 2 F, CF_2COOH) ppm. $^{13}C\{^{19}F\}$ NMR (75 MHz, [D$_8$]-THF): δ = 8.4 (SiCH_2), 18.7 (CH_3), 23.5 (SiCH$_2$CH_2), 43.1 (CH_2NH), 58.9 (OCH_2), 109.5 (CF_2COOH), 110.3 (CF_2CON), 111.5 (CF_2), 158.6 (CON), 160.7 (COOH) ppm. MS (EI): *m*/*z* (%) = 425 (47) [M$^+$ – H$_2$O], 352 (100) [M$^+$ – EtOH, – EtO], 220 (33) [(EtO)$_3$SiC$_3$H$_6$NH$^+$], 163 (68) [(EtO)$_3$Si$^+$], 45 (50) [EtO$^+$]. MS (ESI+): *m*/*z* (%) = 1662 (15) [M$_4^+$ – 2 EtOH – H$_2$O], 1634 (13) [M$_4^+$ – 3 EtOH], 1606 (14) [M$_4^+$ – 4 EtOH + H$_2$O], 1578 (7) [M$_4^+$ – 5 EtOH + 2 H$_2$O], 1550 (4) [M$_4^+$ – 6 EtOH + 3 H$_2$O], 1339 (100) [M$_3^+$ + EtOH – 2 H$_2$O], 1311 (72) [M$_3^+$ – H$_2$O], 1283 (26) [M$_3^+$ – EtOH], 1255 (8) [M$_3^+$ – 2 EtOH + H$_2$O], 942 (20) [M$_2^+$ + 2 EtOH – 2 H$_2$O]. IR (film): $\tilde{\nu}$ = 3326 (br), 3088 (w), 2980 (m), 2937 (m), 2896 (m), 1916 (w), 1775 (vs), 1703 (vs), 1549 (m), 1484 (w), 1445 (m), 1412 (w), 1393 (m), 1370 (w), 1350 (w), 1297 (w), 1271 (m), 1246 (m), 1169 (vs), 1081 (s), 1050 (s), 944 (m), 915 (w), 877 (w), 783 (m), 720 (w), 646 (m), 593 (w), 562 (w), 491 (m), 456 (m) cm^{-1}.

$(MeO)_3Si(CH_2)_3N(Me)C(O)(CF_2)_3COOH$ (3b): Analogous to the preparation of **3a**, 3-(methylamino)propyltrimethoxysilane (**1b**) (277 μL, 1.40 mmol) and hexafluoroglutaric anhydride (**2**) (192 μL, 1.40 mmol) were used. **3b** was isolated as a colorless oil. Yield: 575 mg (99%). $C_{12}H_{19}F_6NO_6Si$ (415.36). ^1H NMR (250 MHz, [D$_8$]THF): δ = 0.55 (t, ^3J = 8.3 Hz, 2 H, *Z*-SiCH_2), 0.56 (t, ^3J = 8.4 Hz, 2 H, *E*-SiCH_2), 1.66 (pseudo-quint, ^3J = 8.0 Hz, 2 H, *E*-SiCH$_2$CH_2), 1.80 (pseudo-quint, ^3J = 8.0 Hz, 2 H, *Z*-SiCH$_2$CH_2), 2.95 (s, 3 H, *E*-NCH_3), 3.14 (t, $^5J_{H,F}$ = 2.4 Hz, 3 H, *Z*-NCH_3), 3.37 (t, ^3J = 7.6 Hz, 2 H, *Z*-CH_2N), 3.43 (t, ^3J = 7.7 Hz, 2 H, *E*-CH_2N), 3.52 (s, 9 H, *Z*-OCH_3), 3.53 (s, 9 H, *E*-OCH_3), 13.74 (s, 1 H, COO*H*) ppm. ^{19}F NMR (235 MHz, [D$_8$]THF): δ = –122.5 (s, 2 F, *E*-CF_2), –122.3 (s, 2 F, *Z*-CF_2), –116.4 (t, $^4J_{F,F}$ = 10.0 Hz, 2 F, *Z*-CF_2CON), –116.2 (t, $^4J_{F,F}$ = 10.1 Hz, 2 F, *E*-CF_2CON), –110.5 (t, $^4J_{F,F}$ = 10.0 Hz, 2 F, *Z*-CF_2COOH), –109.9 (t, $^4J_{F,F}$ = 10.0 Hz, 2 F, *E*-CF_2COOH) ppm. $^{13}C\{^{19}F\}$ NMR (75 MHz, [D$_8$]THF: δ = 6.7 (*E*-SiCH_2), 6.9 (*Z*-SiCH_2), 20.6 (*E*-SiCH$_2$CH_2), 22.7 (*Z*-SiCH$_2$CH_2), 34.8 (*E*-NCH_3), 35.0 (*Z*-NCH_3), 50.5 (OCH_3), 52.4 (*E*-CH_2N), 52.9 (*Z*-CH_2N), 109.7 (CF_2COOH), 112.0 (CF_2CON), 112.2 (CF_2), 158.7 (CON), 160.9 (COOH) ppm. MS (ESI+): *m*/*z* = 1680 (25), 1297 (75), 1213 (47) [M$_3^+$ – MeOH], 1299 (14) [M$_3^+$ – 2 MeOH + H$_2$O], 960 (33), 830 (100) [M$_2^+$], 816 (10) [M$_2^+$ – MeOH + H$_2$O]. MS (ESI–): *m*/*z* = 1890 (28) [M$_5^-$ – 4 MeOH – Me$_2$O], 1563 (13) [M$_4^-$ – 3 MeOH], 1517 (100) [M$_4^-$ – 3 MeOH – Me$_2$O], 1180 (93) [M$_3^-$ – 2 MeOH], 1134 (8) [M$_3^-$ – 2 MeOH – Me$_2$O], 797 (18) [M$_2^-$ – MeOH]. IR (film): $\tilde{\nu}$ = 3350 (br), 2950 (m), 2846 (m), 2650 (m), 2514 (m), 1918 (w), 1781 (s), 1679 (s), 1489 (w), 1464 (m), 1414 (m), 1374 (w), 1316 (m), 1271 (m), 1243 (m), 1160 (vs), 1094 (s), 1044 (s), 950 (m), 899 (w), 868 (m), 823 (s), 783 (m), 757 (m), 714 (w), 700 (w), 648 (w), 566 (w), 464 (m) cm^{-1}.

$iPr_2NC(O)(CF_2)_3COOH$ (5): Diisopropylamine (590 μL, 4.2 mmol) was added dropwise to a solution of hexafluoroglutaric anhydride (**2**) (577 μL, 4.2 mmol) in dichloromethane (30 mL) and the reaction mixture was stirred for 1 h at room temperature. Aqueous HCl (6 M, 20 mL) was added and the reaction mixture was stirred for an additional 10 min. The organic layer was separated and dried over $MgSO_4$. This solution was allowed to concentrate slowly under vacuum and small amounts of hexane were added. Large, colorless X-ray quality crystals of **5** were obtained after 2 days. Yield: 767 mg (57%), m.p. 125–126 °C. $C_{11}H_{15}F_6NO_3$ (323.23): calcd. C 40.87, H 4.68, N 4.33; found C 41.0, H 4.6, N 4.2. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.28 (d, ^3J = 6.6 Hz, 12 H, *E*-CH_3), 1.43 (d, ^3J = 6.8 Hz, 12 H, *Z*-CH_3), 3.62 (sept, ^3J = 6.8 Hz, 2 H, *Z*-C*H*), 4.38 (sept, ^3J = 6.6 Hz, 2 H, *E*-C*H*), 10.04 (s, 1 H, COO*H*) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –121.4 (m, 2 F, CF_2), –114.3 (m, 2 F, CF_2COOH), –109.3 (m, 2 F, CF_2CON) ppm. $^{13}C\{^{19}F\}$ NMR (62.9 MHz, $CDCl_3$): δ = 19.5 (*E*-CH_3), 20.4 (*Z*-CH_3), 48.7 (*Z*-C*H*), 49.7 (*E*-C*H*), 108.6 (CF_2CON), 110.8 (CF_2COOH), 111.3 (CF_2), 158.2 (CONH), 159.5 (COOH). MS (EI): *m*/*z* = 323 (6) [M$^+$], 308 (24) [M$^+$ – CH$_3$], 280 (17) [M$^+$ – *i*Pr],

266 (100) [M^+ – N*i*Pr], 43 (43) [*i*Pr^+]. IR (KBr): $\tilde{\nu}$ = 3408 (br), 3018 (m), 2986 (s), 2946 (s), 2888 (m), 2831 (m), 2658 (m), 2525 (m), 1769 (vs), 1642 (vs), 1546 (w), 1479 (m), 1451 (m), 1380 (s), 1372 (m), 1359 (m), 1277 (s), 1246 (s), 1176 (vs), 1151 (vs), 1104 (s), 1050 (s), 1020 (s), 941 (s), 927 (m), 904 (m), 896 (m), 877 (m), 820 (m), 774 (m), 740 (m), 718 (s), 637 (m), 626 (m), 589 (m), 560 (m), 516 (w), 488 (w), 414 (w) cm^{-1}. IR (film): $\tilde{\nu}$ = 2981 (s), 2945 (s), 2885 (m), 2831 (m), 2647 (w), 2513 (w), 1785 (s), 1654 (vs), 1477 (m), 1452 (m), 1383 (s), 1353 (m), 1270 (w), 1243 (m), 1172 (vs), 1158 (vs), 1120 (w), 1051 (m), 1026 (m), 942 (m), 927 (w), 895 (m), 874 (m), 815 (m), 801 (m), 780 (w), 755 (w), 719 (m), 653 (w), 619 (m), 572 (w), 495 (w) cm^{-1}.

$(EtO)_3Si(CH_2)_3N(H)C(O)(CF_2)_3COOAg$ (4a): Hexafluoroglutaric anhydride (**2**) (192 μL, 1.40 mmol) dissolved in MTBE (7.5 mL) was added dropwise to a solution of 3-(triethoxysilyl)propylamine (**1a**) (331 μL, 1.40 mmol) in MTBE (7.5 mL). After 10 min the reaction mixture was added to a suspension of silver(I) oxide (324 mg, 1,40 mmol) in MTBE (15 mL). The resulting mixture was stirred for 18 h at room temperature in the dark. After filtration all volatiles were removed under full vacuum and **4a** was obtained as pure colorless crystals. Yield: 674 mg (88%). $C_{14}H_{22}AgF_6NO_6Si$ (550.02): calcd. C 30.39, H 4.01, N 2.53; found C 30.5, H 4.2, N 2.7. ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 0.57 (t, ^3J = 8.3 Hz, 2 H, SiCH_2), 1.16 (t, ^3J = 7.0 Hz, 9 H, CH_3), 1.62 (quint, ^3J = 7.7 Hz, 2 H, $SiCH_2CH_2$), 3.24 (q, ^3J = 6.7 Hz, 2 H, CH_2NH), 3.77 (q, ^3J = 7.0 Hz, 6 H, OCH_2), 8.18 (t, ^3J = 5.5 Hz, 1 H, N*H*) ppm. ^{19}F NMR (235 MHz, [D$_8$]THF): δ = –124.6 (s, 2 F, CF_2), –120.3 (t, $^4J_{F,F}$ = 9.9 Hz, 2 F, CF_2CONH), –115.3 (t, $^4J_{F,F}$ = 9.9 Hz, 2 F, CF_2COOAg). ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 8.2 (SiCH_2), 18.5 (CH_3), 23.3 ($SiCH_2CH_2$), 42.9 (CH_2N), 58.8 (OCH_2), 110.5 (tt, $^1J_{C,F}$ = 264.9, $^2J_{C,F}$ = 31.7 Hz, CF_2CONH), 111.7 (tquint, $^1J_{C,F}$ = 264.9, $^2J_{C,F}$ = 32.2 Hz, CF_2), 112.1 (tt, $^1J_{C,F}$ = 264.4, $^2J_{C,F}$ = 32.8 Hz, CF_2COOAg), 158.9 (t, $^2J_{C,F}$ = 25.8 Hz, CON), 163.8 (t, $^2J_{C,F}$ = 25.5 Hz, COOAg) ppm. MS (ESI+): *m*/*z* = 1757 (6) [M_3^+ + Ag], 1207 (12) [M_2^+ + Ag], 939 (22) [M_2^+ – Si(OEt)$_3$], 699 (41) [M^+ + Ag + MeCN], 388 (15) [M^+ – Si(OEt)$_3$], 189 (100) [Ag(MeCN)$_2^+$]. MS (ESI–): *m*/*z* = 1542 (52) [M_3^+ – Ag], 993 (99) [M_2^+ – Ag], 442 (100) [M^+ – Ag], 398 (40) [M^+ – Ag – CO_2]. IR (KBr): $\tilde{\nu}$ = 3445 (br), 3083 (w), 2977 (m), 2930 (m), 2895 (m), 1706 (vs), 1687 (vs), 1549 (m), 1445 (w), 1393 (m), 1271 (m), 1249 (m), 1163 (vs), 1104 (s), 1079 (s), 958 (m), 944 (m), 811 (m), 790 (m), 761 (m), 488 (br) cm^{-1}. IR (MTBE): $\tilde{\nu}$ = 3303 (br), 3084 (w), 2957 (w), 2929 (w), 2870 (w), 1780 (w), 1722 (s), 1658 (vs), 1541 (m), 1443 (w), 1407 (m), 1392 (m), 1371 (w), 1272 (w), 1247 (m), 1226 (w), 1169 (vs), 1224 (s), 1108 (s), 1077 (vs), 959 (m) cm^{-1}. IR (THF): $\tilde{\nu}$ = 3274 (br), 3068 (w), 2987 (m), 2930 (w), 2884 (m), 1716 (vs), 1691 (vs), 1550 (m), 1445 (w), 1391 (m), 1269 (m), 1245 (m), 1186 (m), 1153 (vs), 1104 (s), 1084 (s), 1059 (m), 959 (m), 941 (m), 898 (w), 807 (m), 791 (m), 759 (m), 679 (w),657 (w), 500 (br) cm^{-1}.

$(MeO)_3Si(CH_2)_3N(Me)C(O)(CF_2)_3COOAg$ (4b): Analogous to the preparation of **4a**, 3-(methylamino)propyltrimethoxysilane (**1b**) (277 μL, 1.40 mmol), hexafluoroglutaric anhydride (**2**) (192 μL, 1.40 mmol), silver(I) oxide (324 mg, 1,40 mmol) and MTBE were used. **4b** was isolated as a pure colorless oil. Yield: 683 mg (93%). $C_{12}H_{18}AgF_6NO_6Si$ (521.99): calcd. C 27.44, H 3.45, N 2.67; found C 27.3, H 3.5, N 2.6. ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 0.56 (t, ^3J = 8.3 Hz, 2 H, SiCH_2), 1.65 (m, 2 H, $SiCH_2CH_2$), 2.96 (s, 3 H, *E*-NCH_3), 3.12 (t, $^5J_{H,F}$ = 2.1 Hz, 3 H, *Z*-NCH_3), 3.38 (t, ^3J = 7.6 Hz, 2 H, *Z*-CH_2N), 3.40 (t, ^3J = 7.5 Hz, 2 H, *E*-CH_2N), 3.51 (s, 9 H, *E*-OCH_3), 3.52 (s, 9 H, *Z*-OCH_3) ppm. ^{19}F NMR (235 MHz, [D$_8$]THF): δ = –121.1 (s, 2 F, *E*-CF_2), –120.9 (s, 2 F, *Z*-CF_2), –112.9 (t, $^4J_{F,F}$ = 10.3 Hz, 2 F, *Z*-CF_2CON), –112.8 (t, $^4J_{F,F}$ = 10.7 Hz, 2 F, *E*-CF_2CON), –109.9 (m, 2 F, *Z*-CF_2COOAg), –109.5 (t, $^4J_{F,F}$ = 10.4 Hz, 2 F, E-CF_2COOAg) ppm. ^{13}C{^{19}F} NMR (75 MHz, [D$_8$]THF: δ = 6.4 (*E*-SiCH_2), 6.6 (*Z*-SiCH_2), 20.3 (*E*-$SiCH_2CH_2$), 22.6 (*Z*-$SiCH_2CH_2$), 34.9 (*E*-NCH_3), 35.0 (*Z*-NCH_3), 50.3 (OCH_3), 52.3 (*E*-CH_2N), 52.9 (*Z*-CH_2N), 111.8 (CF_2), 112.0 (CF_2COOAg and CF_2CON), 158.5 (CON), 163.7 (COOAg) ppm. MS (ESI+): *m*/*z* = 671 (14) [M^+ + Ag + MeCN], 189 (100) [Ag(MeCN)$_2^+$], 148 (21) [Ag(MeCN)$^+$]. IR (film): $\tilde{\nu}$ = 3416 cm^{-1} (br), 3160 (w), 2948 (m), 2892 (w), 2845 (m), 1783 (s), 1651 (vs), 1559 (w), 1490 (w), 1401 (m), 1271 (m), 1242 (m), 1160 (vs), 1091 (s), 1044 (s), 950 (m), 809 (m), 755 (m), 704 (w), 657 (w), 585 (w), 567 (w), 463 (m) cm^{-1}. IR (MTBE): $\tilde{\nu}$ = 3490 (w), 2935 (w), 2902 (w), 2846 (m), 1787 (w), 1685 (s), 1659 (s), 1407 (m), 1371 (w), 1320 (s), 1273 (w), 1244 (w), 1166 (s), 1113 (m), 1069 (m), 1042 (w) cm^{-1}. IR (THF): $\tilde{\nu}$ = 2947 (w), 2865 (w), 1685 (vs), 1658 (vs), 1484 (w), 1401 (m), 1316 (w), 1271 (w), 1164 (vs), 1092 (vs), 1056 (s), 985 (w), 949 (m) cm^{-1}.

***i*Pr_2NC(O)$(CF_2)_3$COOAg (6):** *i*Pr_2NC(O)$(CF_2)_3$COOH **(5)** (71 mg, 0.22 mmol) dissolved in MTBE (1.5 mL) was added at room temperature to a suspension of silver(I) oxide (51 mg, 0.22 mmol) in 3 mL MTBE. The resulting mixture was stirred for 4 h at room temperature in the dark. After filtration all volatiles were removed under full vacuum and the residue was washed three times with hexane and then dried under vacuum yielding **6** as a colorless solid. Crystals of **6** could be obtained by diffusion of hexane into a saturated solution of **6** in chloroform. Yield: 87 mg (92%). $C_{11}H_{14}AgF_6NO_3$ (429.99): calcd. C 30.72, H 3.28, N 3.26; found C 30.7, H 3.3, N 3.3. ^{1}H NMR (250 MHz, [D$_8$]THF): δ = 1.22 (d, ^3J = 6.5 Hz, 12 H, *E*-CH_3), 1.40 (d, ^3J = 6.7 Hz, 12 H, *Z*-CH_3), 3.59 (sept, ^3J = 6.7 Hz, 2 H, *Z*-C*H*), 4.33 (sept, ^3J = 6.5 Hz, 2 H, *E*-C*H*) ppm. ^{19}F NMR (235 MHz, [D$_8$]THF): δ = –118.4 (s, 2 F, CF_2), –110.5 (t, $^4J_{F,F}$ = 10.4 Hz, 2 F, CF_2COOAg), –107.1 (t, $^4J_{F,F}$ = 10.4 Hz, 2 F, CF_2CON) ppm. ^{13}C{^{19}F} NMR (75 MHz, [D$_8$]-THF): δ = 19.9 (*E*-CH_3), 20.5 (*Z*-CH_3), 48.0 (*Z*-CH), 49.2 (*E*-CH), 112.0 (CF_2CON), 112.3 (CF_2), 112.5 (CF_2COOAg), 157.5 (CON), 164.1 (COOAg) ppm. MS (ESI+): *m*/*z* = 948 (24) [M_2^+ + 2 Na + MeCN], 517 (43) [M^+ + 2 Na + MeCN], 493 (23) [M^+ + Na + MeCN], 189 (100) [Ag(MeCN)$_2^+$], 148 (18) [Ag(MeCN)$^+$]. MS (ESI–): *m*/*z* = 322 (100) [M^- – Ag]. IR (KBr): $\tilde{\nu}$ = 3448 (br), 2975 (m), 2941 (m), 2882 (w), 1687 (s), 1675 (vs), 1477 (m), 1449 (m), 1393 (br, m), 1348 (m), 1266 (m), 1241 (m), 1150 (vs), 1120 (m), 1099 (m), 1047 (m), 1032 (m), 1018 (m), 941 (m), 904 (w), 892 (w), 873 (w), 822 (m), 810 (m), 778 (m), 760 (m), 751 (m), 738 (w), 716 (w), 655 (w), 619 (m), 593 (w), 561 (w), 490 (w) cm^{-1}. IR (THF): $\tilde{\nu}$ = 1679 (vs), 1384 (m), 1347 (m), 1269 (m), 1240 (w), 1151 (s), 1086 (m), 1055 (m), 1017 (w), 987 (w), 941 (w), 908 (m), 819 (m), 809 (m), 775 (m), 757 (m), 749 (m), 736 (w), 613 (w), 557 (w) cm^{-1}. IR (MTBE): $\tilde{\nu}$ = 1681 (s), 1658 (s), 1452 (w), 1386 (s), 1369 (s), 1270 (w), 1211 (m), 1193 (m), 1159 (s), 1094 (vs), 1078 (vs), 1023 (m), 942 (w), 857 (w), 822 (m), 805 (m), 756 (w), 746 (w) cm^{-1}.

[KG 60]–$(CH_2)_3$N(H)C(O)$(CF_2)_3$COOAg (7a): Silica gel (KG 60) was washed successively with methanol, dichloromethane and hexane and was dried at 200 °C under full vacuum for 4 h. A solution of $(EtO)_3Si(CH_2)_3N(H)C(O)(CF_2)_3COOAg$ **(4a)** (113.2 mg, 0.2 mmol) in THF (10 mL) was added to a suspension of the pretreated KG 60 (2000 mg) in THF (20 mL). After stirring for 21 h at room temperature in the dark the functionalized silica gel was isolated by filtration with subsequent washing using THF and *n*-hexane. Drying overnight under full vacuum afforded 2089.9 mg of [KG 60]–$(CH_2)_3$N(H)C(O)$(CF_2)_3$COOAg (**7a**). Remaining $(EtO)_3Si(CH_2)_3N(H)C(O)(CF_2)_3COOAg$ **(4a)** was not found in the filtrates. Carbon analysis: found 0.8%, which corresponds to 0.1 mmol **4a** per g KG 60 (5 wt.-%). IR (DRIFT): $\tilde{\nu}$ = 1713 (w), 1664 (w), 1539 (w) cm^{-1}.

Table 2. Crystal data and refinement details for **4a**, **5**, and **6**.

	4a	**5**	**6**
Empirical formula	$C_{14}H_{22}AgF_6NO_6Si$	$C_{11}H_{15}F_6NO_3$	$C_{11}H_{14}AgF_6NO_3$
Formula mass	550.29	323.24	430.10
Crystal size [mm]	0.32×0.22×0.12	0.37×0.32×0.21	0.18×0.14×0.12
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a [Å]	11.9243(14)	10.0312(12)	6.0029(8)
b [Å]	17.5007(15)	10.4731(9)	9.3849(12)
c [Å]	9.9726(10)	13.8976(15)	13.4770(18)
α [°]	90	90	89.299(10)
β [°]	92.595(9)	104.649(9)	79.890(10)
γ [°]	90	90	77.089(10)
V [Å^3]	2079.0(4)	1412.6(3)	728.27(17)
$\rho_{calcd.}$ [g cm^{-3}]	1.758	1.520	1.961
Z	4	4	2
F(000)	1104	664	424
μ [mm^{-1}]	1.110	0.159	1.461
T_{max}/T_{min}	0.8905/0.7195	0.9736/0.9248	0.8830/0.6586
hkl range	±13, ±20, ±11	±11, ±12, ±16	–7 to 6, ±10, –15 to 14
θ range [°]	1.71–24.65	2.47–24.82	2.23–24.54
Measured reflections	11169	8627	6776
Unique refl. [R_{int}]	3340 [0.0451]	2404 [0.0352]	2408 [0.0411]
Observed refl. $I > 2\sigma(I)$	2472	1711	2023
Refined parameters	269	198	203
Goodness-of-fit	0.926	1.006	1.016
R_1, wR_2 [$I > 2\sigma(I)$]	0.0295, 0.0615	0.0313, 0.0685	0.0311, 0.0641
R_1, wR_2 (all data)	0.0481, 0.0658	0.0512, 0.0727	0.0427, 0.0667
Resid. electron density [e Å^{-3}]	0.294/–0.779	0.219/–0.177	0.767/–0.417

[KG 60]–$(CH_2)_3N(Me)C(O)(CF_2)_3COOAg$ (7b): Analogous to the preparation of **7a**, KG 60 (2030 mg) in THF (20 mL) and $(MeO)_3Si(CH_2)_3N(Me)C(O)(CF_2)_3COOAg$ **(4b)** (106.1 mg, 0.2 mmol) in THF (10 mL) were used. Drying overnight under full vacuum afforded 2127.1 mg of [KG 60]–$(CH_2)_3N(Me)C(O)(CF_2)_3COOAg$ (**7b**). Remaining $(MeO)_3Si(CH_2)_3N(Me)C(O)(CF_2)_3COOAg$ **(4b)** was not found in the filtrates. Carbon analysis: found 1.0%, which corresponds to 0.1 mmol **4b** per g KG 60 (5 wt.-%). IR (DRIFT): $\tilde{\nu}$ = 1669 (m) cm^{-1}.

X-ray Crystallographic Study: X-ray data were collected with a STOE IPDS II diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å) by use of ω scans at –140 °C (Table 2). The structures were solved by direct methods and refined on F^2 using all reflections with SHELX-97.[39,40] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms not involved in hydrogen bonding were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. The positional and isotropic thermal parameters of the nitrogen-bonded hydrogen atom H1 in **4a** and the oxygen-bonded H2 in **5** were refined without constraints. Face-indexed absorption corrections were performed numerically with the program X-RED.[41]

CCDC-259720 (for **4a**), -259721 (for **5**) and -259722 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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