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Copper(I) and Silver(I) Bis(trifluoromethanesulfonyl)imide and Their Interaction with an Arene, Diverse Olefins, and an NTf_2^--Based Ionic Liquid

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Abstract: The chemistry of coinage metal bis(triflyl)imides of technological interest, $CuNTf_2$ and $AgNTf_2$, their synthesis and complexes with excess of comparatively weakly coordinating NTf_2^- as well as with ether, olefins, and the arene mesitylene are described. The existence of the solvent-free pure phase $[CuNTf_2]_\infty$ has not been evidenced so far. Contrary to the literature, in which the preparation of $[CuNTf_2]_\infty$ is supposed to be carried out by reacting mesityl copper, $[Cu(Mes)]_5$, and $HNTf_2$, we found that in fact this reaction leads reproducibly to the interesting copper diarene sandwich complex $[Cu(\eta^3\text{-MesH})_2][Cu(NTf_2)_2]$ (**1**) (MesH = 1,3,5-trimethylbenzene). The unexpectedly stable molecular etherate $[Cu(Et_2O)(NTf_2)]$ (**2**) turned out to be the best precursor for $CuNTf_2$ having only an inert and easily exchangeable solvent ligand. The coordination mode of NTf_2^- in **1** and **2** as well as in the hitherto unknown crystalline phase of $[AgNTf_2]_\infty$ (**3**) is described. The complex formation, which takes place when dissolving **2** or **3** in the room temperature ionic liquid (RTIL) $[emim]NTf_2$ ($[emim]^+$ = 1-ethyl-3-methylimidazolium), has been studied. Furthermore, the reaction of **1**–**3** towards the diolefins 1,5-cyclooctadiene (COD), 2,5-norbornadiene (NBD) and isoprene (2-methylbuta-1,3-diene) and towards ethylene has been investigated. The products **4**–**13** of these conversions have been isolated and fully characterized by NMR- and IR spectroscopies, mass spectrometry, and elemental- and XRD analyses. The potential of $[Cu(\eta^3\text{-MesH})_2][Cu(NTf_2)_2]$ (**1**), $[Cu(Et_2O)(NTf_2)]$ (**2**) and $[AgNTf_2]_\infty$ (**3**) as well as of $[emim][M(NTf_2)_2]$ (M = Cu **4**, Ag **5**) as chemisorbers for ethylene was studied by NMR spectroscopy.

Keywords: chemisorption · copper · ionic liquids · olefins · silver

Introduction

The syntheses of the bis(trifluoromethanesulfonyl)imide (also known as bis(triflyl)imide, NTf_2^-) salts of the coinage metal ions Cu^+ and Ag^+ have been reported in the 1990s.[1,2] However, in the case of the copper(I) salt it has not been proven by common methods (such as elemental- or crystal structure analyses) that the solvent-free compound really exists. Very recently, the groups of Binnemans and Fransaer published the synthesis and solid state structure of the ionic liquids (ILs) $[Cu(CH_3CN)_4]NTf_2$, $[AgL_n]NTf_2$ (L = CH_3CN, n = 1, 2, 4; L = Im^2, n = 2; Im^2 = 1-ethylimidazole) and $[Ag(CH_3CN)_4]_2[Ag(NTf_2)_3]$ and their use in the electrodeposition of copper and silver.[3] The copper(I) complex was synthesized by using $Cu(NTf_2)_2$, which was reduced by copper metal in acetonitrile. Fehr et al. also described the synthesis of $[Cu(CH_3CN)_4]NTf_2$ just recently, but starting from copper(I) oxide and $HNTf_2$.[4] Our interest in copper- and silver-containing ILs such as thermally stable $[Cu(Im^n)_2][CuX_2]$ (n = 2, 6, 12; X = Cl, Br) arises from their catalytic activity in oxidative methanol carbonylation[5] and by their use as supported ionic liquid phase (SILP) catalysts in a continuous gas phase reaction towards dimethyl carbonate.[6]

In contrast to copper(I) bis(triflyl)imide, silver(I) bis(triflyl)imide has been completely characterized with the exception of its crystal structure determination.[2,7–11] Within the last two decades $AgNTf_2$ has attracted a lot of interest due to its versatility: $AgNTf_2$ is used as catalyst for a variety of organic transformations, such as C−C-coupling reactions or hydroamination of siloxy alkynes.[12] In addition, $AgNTf_2$ has been applied as a transfer reagent for the introduction of the NTf_2^- moiety, for example, for metathesis reactions within the preparation of trialkylsilyl and trialkylstannyl bis(triflyl)imides[2] and of catalytically active cationic gold(I) bis(triflyl)imides,[12] in electrochemical studies[7,8] and for alkene/alkane separation processes.[9,13,14] With respect to silver's lighter homologue copper, the existence of $[Cu(CO)_n(NTf_2)]$ (n = 1–3) was reported, of which the dicarbonyl complex was crystallographically characterized.[1b] Moreover, it was patented that adsorbents of the type $[CuL_nX]$ (L = CO or olefin; $n \geq 0$) containing a uniform or complex monovalent anion X^-, for example, NTf_2^-, are applicable for CO and olefin adsorption.[1a] However, no example of a Cu^I–bis(triflyl)imide–olefin complex is given in this patent. Additionally, reportedly solvent-free $CuNTf_2$ was used as a Lewis acidic, reactive compound in a non-volatile liquid for

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safe storage and delivery of hazardous specialty gases, such as PH_3 and AsH_3.[15]

Since the beginning of the 20th century it is known that copper(I) halides are capable of forming π complexes with ethylene.[16] In 1901, Berthelot showed that a complex with a $CuCl:C_2H_4$ ratio of 1:0.17 is formed when applying a hydrochloric acid solution of CuCl.[16a] In contrast, ethylene under pressure yields a 1:1 adduct with solid CuCl.[16e] By the distribution method it was proven that olefins are prone to form π complexes with silver(I) in aqueous solution.[17] In the case of ethylene the 1:1 complex is preferably formed.[18]

Currently, regarding the selective absorption of an olefin from an olefin/paraffin mixture, membrane-separation processes have become more and more important due to their manifold ecological and economical advantages.[19] Moreover, ionic liquids (ILs) are auspicious for the application in facilitated transport membranes (FTMs), that is, immobilized/supported liquid membranes (ILMs/SLMs), which results mostly from their high thermal stability and low vapor pressure, as well as from their differing ability to dissolve various gases.[19a,20] It has been shown that pure RTILs, silver(I)–RTIL mixtures or even liquid compounds exhibiting cationic silver(I) olefin complexes can be applied for the absorption of diverse alkenes.[9,13,14,21–23] Huang et al. reported on the synthesis of new Ag^I-containing ILs of the type $[Ag(olefin)]NTf_2$ containing 1-pentene, 1-hexene or isoprene for the use in advanced liquid membranes.[14] However, these ILs have only been identified by means of ^1H NMR, ^{13}C NMR and IR spectroscopies. Recently, the group of Wasserscheid reacted $AgNTf_2$ with gaseous propylene yielding a liquid complex salt $[Ag(propylene)_x]NTf_2$ with $x \approx 1.7$ at atmospheric propylene pressure. The separation of light alkene/alkane mixtures in ILMs was suggested as a use for this compound.[9] For propene/propane separation, Steigelmann and Hughes (Standard Oil) developed a pilot plant using the FTM technology.[19a] Ortiz et al. studied mixtures of $AgBF_4$ and the room temperature ionic liquids (RTILs) $[bmim]BF_4$ and $[bmpy]BF_4$ ($[bmim]^+ =$ 1-*n*-butyl-3-methylimidazolium, $[bmpy]^+ =$ *N*-butyl-4-methylpyridinium) for the separation of propylene from propane.[22] In addition, the group of Meindersma investigated solutions of $AgNO_3$, AgOTf and $AgNTf_2$ in RTILs having the same anion in each case for the ethylene/ethane separation.[13] The preferential usage of silver(I) salts within studies concerning gas separation processes probably results from their advantages over copper(I) salts: They are stable against oxygen and humidity, do not tend to undergo disproportionation reactions,[9] and reveal weaker π interactions favoring the reversibility of the olefin coordination. However, the synthesis of monomeric, bimetallic salts $MM'X_n$ (M = group 11 metal, preferably Cu; M′ = group 13 metal, preferably Al) and their application for complexation of ethylene, propene, and CO was patented.[24] To the best of our knowledge, despite their potential use in technology, the interaction of $CuNTf_2$ and $AgNTf_2$ with olefins has not yet been studied on a molecular basis, for example, by XRD studies.

In summary, the application of (ligand-deficient) Cu^I or Ag^I compounds in combination with the NTf_2^- moiety seems to be promising for the accomplishment of one of today's industrial challenges, namely olefin/paraffin separations. This is due to the fact that coinage metal compounds readily form π complexes with unsaturated hydrocarbons, a trend which is enhanced by the NTf_2^- moiety increasing the Lewis acidity of the respective metal ion compared with the respective triflates[12] or chlorides.[2] Consequently, there is a demand for fundamental knowledge of the chemical and structural characteristics of copper(I) and silver(I) bis(triflyl)imide. In this context we were particularly interested in the determination of their solid-state structures that are presented in the first part of this paper. The second part deals with our results regarding the reactivity of **1**–**3** towards the ionic liquid $[emim]NTf_2$ and towards several olefins. Within these investigations we succeeded in determining the solid state structures of nine new compounds incorporating the NTf_2^- anion. Finally, we studied the stability of several in situ generated Cu^I and Ag^I bis(triflyl)imide ethylene adducts by means of NMR spectroscopy.

Results and Discussion

Cu^I and Ag^I Bis(trifluoromethanesulfonyl)imide: *Synthesis and characterization*: To prepare solvent-free $CuNTf_2$ we applied the synthetic protocol described by Strauss[1] and coworkers. By reacting mesityl copper[25] with $HNTf_2$[26] they obtained a pink-brown powder postulated to be solvent-free $CuNTf_2$, which was not further characterized, but used as a CO scavenger.[1a] According to Strauss et al. the following reaction takes place:

$$2\,[Cu(Mes)]_5 + 10\,HNTf_2 \xrightarrow[-\,10\,MesH]{CH_2Cl_2} 10\,CuNTf_2$$

However, by means of NMR spectroscopy we realized that mesitylene remains in the coordination sphere of the copper(I) ion, even though the product was washed with *n*-pentane and dried at 30 °C/10^{-5} mbar. Not only the signal of the aromatic protons but also that of the methyl groups is slightly shifted downfield with respect to uncoordinated mesitylene. Conversely, in the ^{13}C NMR spectrum an upfield shift is observed for all resonances. In the ^{19}F NMR spectrum the signal of **1** is shifted upfield by about $\Delta\delta = 1$ ppm compared with that of the starting material $HNTf_2$. The elemental analysis of the obtained colorless solid suggests a ratio of 1:1 for $CuNTf_2$ and mesitylene, which was also proven by the result of the crystal structure analysis (see below). The reaction, which actually takes place when converting [Cu(Mes)] with $HNTf_2$ (1:1), is the following:

$$2\,[Cu(Mes)]_5 + 10\,HNTf_2 \xrightarrow{CH_2Cl_2} 5\,\underset{\mathbf{1}}{[Cu(\eta^3\text{-}MesH)_2][Cu(NTf_2)_2]}$$

The crystal structure of the ionic compound **1**, comprising the bis(arene) Cu^I cation $[Cu(\eta^3\text{-}MesH)_2]^+$ and the cuprate(I) anion $[Cu(NTf_2)_2]^-$, is shown in Figure 1. All relevant parameters concerning the crystal structure determinations of **1**–**3** are listed in Table S1 of the Supporting Information. In addition, selected bond lengths and angles of all structurally characterized compounds are given in the Supporting Information.

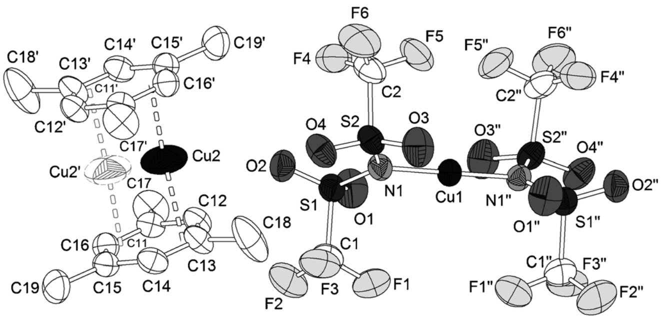
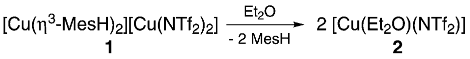


Figure 1. Molecular structure of $[Cu(\eta^3\text{-}MesH)_2][Cu(NTf_2)_2]$ (**1**). Atoms created by inversion symmetry or due to a C_2 rotation axis are marked by (′) and (″), respectively.

Compound **1** is only the second example of a homoleptic Cu^I arene sandwich complex characterized by an X-ray crystal structure determination. The first example, namely $[Cu(1,2\text{-}F_2C_6H_4)_2)][Al(OC(CF_3)_3)_4]$, was published by the group of Krossing in 2009.[27] In the inversion symmetric sandwich complex cation of **1** all of the twelve Cu–C distances varying from 1.962(4) to 3.037(4) Å are within the sum of the van der Waals radii of copper and carbon (3.1 Å[28]). In contrast, each of the two independent centrosymmetric cations of $[Cu(1,2\text{-}F_2C_6H_4)_2)][Al(OC(CF_3)_3)_4]$ exhibits only four Cu–C contacts being that short (d(Cu–C) = 2.085(8) Å–3.026(7) Å). The bonding situation of the arene ligands of the $[Cu(1,2\text{-}F_2C_6H_4)_2)]^+$ cation was described as a η^1/η^2 coordination or as a η^3/η^4 coordination considering much weaker Cu–C interactions.[27] The authors of a theoretical study dealing with Cu^+–π interactions[29] report that copper(I) is prone to adopt the η^2 coordination mode with aromatic compounds in the condensed phase if a coordinating counterion is present. Moreover, within their studies concerning cation–π complexes of Cu^I with 1,3,5-trisubstituted benzenes, Zhang et al.[29] found that electron-donating groups, such as methyl substituents, contribute to the enhancement of the binding energy of such complexes. For the $[Cu(MesH)_2]^+$ cation in **1** we suggest a η^3 coordination as the best description, regarding only the six most significant Cu–C interactions varying from 1.962(4) to 2.456(4) Å. In contrast, at room temperature in solution the cation seems to reveal D_{3h} symmetry, as is suggested by the signal patterns of the ^1H and ^{13}C NMR spectra. This is due to either a η^6 coordination or a fluctuating coordination of the mesitylene ligands that cannot be resolved on the NMR timescale. According to a search in the Cambridge Structural Database, the cuprate(I) anion of **1** is the first example of a structurally characterized d^{10} metallate of the type $[M(NTf_2\text{-}\kappa N)_2]^-$ (M = any transition metal). Within the herein presented studies this structural motif was observed in another case (see below). Moreover, compound **1** is also a rare example of a solid-state structure containing the NTf_2^- anion in the κ*N* coordination mode,[30] which is expected for soft metal ions, for example, copper(I),[1b] silver(I),[31,32] gold(I),[33] and iron(II).[10] In **1** the copper atom is linearly coordinated by the two NTf_2 entities with ∢(N1-Cu1-N1″) = 179.50(17)°. The Cu1–N1 distance is found to be 1.890(3) Å and thus in the expected range for copper(I) being linearly coordinated by two NQ_2 (Q = non-metal) moieties.[34] The two SNS planes are twisted with respect to each other at an angle of 49.5°.

Facing the problem that $[Cu(\eta^3\text{-}MesH)_2][Cu(NTf_2)_2]$ (**1**) is an inconvenient starting material for further reactions due to the expected release of mesitylene (b.p. 163–165 °C) we recrystallized **1** from a highly diluted ethereal solution at −20 °C yielding single crystals of the diethyl ether adduct of copper(I) bis(trifluoromethanesulfonyl)imide, that is, $[Cu(Et_2O)(NTf_2)]$ (**2**), instead of solvent-free $CuNTf_2$:



$$\underset{\mathbf{1}}{[Cu(\eta^3\text{-}MesH)_2][Cu(NTf_2)_2]} \xrightarrow[-\,2\,MesH]{Et_2O} \underset{\mathbf{2}}{2\,[Cu(Et_2O)(NTf_2)]}$$

Both the proton and the carbon NMR spectrum only show downfield-shifted signals for the diethyl ether due to complexation. Compounds **1** and **2** show only slightly different values for δ_F.

The crystal structure of **2** is depicted in Figure 2. The copper(I) ion reveals a linear coordination with an O5-Cu1-N1 angle of 178.81(13)°. The NTf_2^- anion serves as monodentate N-donor ligand as in the case of **1**. Complex **2** is a rare example[35] of a crystal structure with a Cu^I ion being linearly coordinated by one N-donor and one O-donor ligand. There exist several solid-state structures revealing tetrahydrofuran in the coordination sphere of copper(I), but only a single one in which diethyl ether is bonded to a Cu^I ion: $[Cu\{=CR^1(OR^2)\}(CH_3CN)(Et_2O)]PF_6$ (R^1 = (*E*)-CH=CH-2-furyl, R^2 = (1*R*,2*S*,5*R*)-menthyl).[36] In the latter compound, the Cu–O distance is found to be 2.345(2) Å and therefore

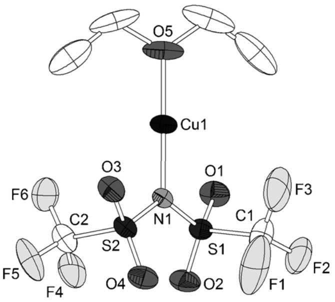


Figure 2. Molecular structure of $[Cu(Et_2O)(NTf_2)]$ (**2**).

significantly longer than the relevant one of complex **2** (d(Cu1−O5) = 1.886(2) Å), which may be attributed to the different coordination geometries at Cu^I. No additional Cu−O contacts below the sum of the van der Waals radii are observed in the case of **2** (d(Cu1…O1) = 2.998(2) Å, d(Cu1…O3) = 2.984(2) Å). The Cu1−N1 bond length of **2** (1.901(2) Å) is significantly shorter than the corresponding one in [Cu(CO)$_2$(NTf$_2$)][1b] (2.029(4) Å), which is due to the different coordination geometries at the copper atom: linear versus trigonal planar. This statement is evidenced by the statistical evaluation of two searches in the Cambridge Structural Database.[37]

In the case of AgNTf$_2$ (**3**) manifold preparation methods are described in the literature.[2,7–11] In addition, compound **3** has been characterized by means of NMR [2,9,11] and IR[2,9] spectroscopies, ESI mass spectrometry,[9] and elemental analysis.[2,8,10]

Within the herein presented studies, two different synthetic strategies were applied for the preparation of AgNTf$_2$ (**3**). At first, compound **3** was prepared according to a slightly modified literature method,[9] namely from Ag$_2$O and HNTf$_2$ in aqueous solution, and recrystallized from dichloromethane:

$$Ag_2O + 2\,HNTf_2 \xrightarrow[-\,H_2O]{} \underset{\mathbf{3}}{2\,AgNTf_2}$$

Furthermore, we applied the same procedure as in the case of **1** and thus started from [Ag(Mes)]$_4$[25] and HNTf$_2$. However, instead of a mesitylene complex analogous to **1**, pure AgNTf$_2$ (**3**) was obtained in good yield:

$$[Ag(Mes)]_4 + 4\,HNTf_2 \xrightarrow[-\,4\,MesH]{CH_2Cl_2} \underset{\mathbf{3}}{4\,AgNTf_2}$$

The fluorine spectrum of **3** in [D$_2$]CH$_2$Cl$_2$ shows only one signal at $\delta = -74.8$ ppm, which is identical to the δ_F value of **1**. Because of the poor solubility of **3** in CH$_2$Cl$_2$ the carbon NMR spectrum was recorded in [D$_2$]CH$_2$Cl$_2$/[D$_8$]THF at a ratio of 11:1. In comparison with the literature known values for δ_C of tetrahydrofuran[38] the ^{13}C NMR resonances of the cyclic ether are shifted upfield due to interaction with the coinage metal. When dissolving compound **3** in [D$_4$]MeOH to compare the spectroscopic data to that reported in the literature,[9] formation of elemental silver was observed.

Single crystals of **3** were obtained when trying to crystallize [emim][Ag(NTf$_2$)$_2$] (**5**; see below) from CH$_2$Cl$_2$. Figure 3 shows both a AgNTf$_2$ unit within the crystal structure of **3** and the layer structure of **3**.

Compound **3** forms a layered structure, the layers are separated by CF$_3$ groups facing towards each other. Every silver atom is coordinated by six oxygen atoms and one nitrogen atom. Up to now there are fifteen examples of organometallic solid state structures listed in the Cambridge Structural Database revealing the coordination number seven for silver(I).[39]

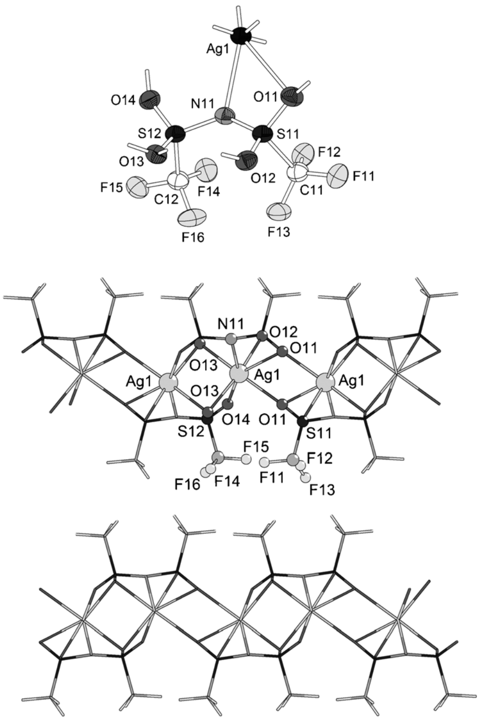
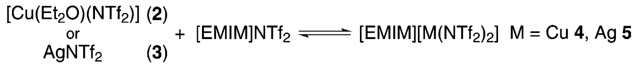


Figure 3. Top: AgNTf$_2$ unit within the crystal structure of [AgNTf$_2$]$_\infty$ (**3**). Bottom: layered structure of [AgNTf$_2$]$_\infty$ (**3**), view along the *a* axis. Atoms generated by symmetry are not distinguished by primes.

The layered structure of **3** exhibits two crystallographically different rhombic Ag$_2$(μ-O)$_2$ cores as a significant structural motif, which is due to the fact that the oxygen atoms O11 and O13 bridge the Ag^I ions along the *b* axis. In addition, every NTf$_2^-$ anion interconnects five silver atoms. Altogether, three coordination modes are adopted by the five donor atoms of each NTf$_2^-$ ligand: κ*N* by N11, κ*O* for O12 and O14 as well as μ-O in the case of O11 and O13. All Ag−O bond lengths (2.458(4)–2.849(4) Å) are within the sum of the van der Waals radii of silver and oxygen (3.2 Å[28]). For the silver(I) complex [Ag(bet)(NTf$_2$)]$_6$[32] (bet = *N*,*N*,*N*-trimethylammonioacetate) only one (CF$_3$SO)O−Ag contact is reported being 2.529(4) Å and therefore within the range found for **3**. The shortest of the Ag−N(Tf$_2$) distances in [Ag(bet)(NTf$_2$)]$_6$,[32] ranging between 2.430(5) and 2.808(6) Å, is similar to that of **3** (d(Ag1−N11) = 2.411(4) Å). However, the Ag−N bond in **3** is significantly longer than those reported for a silver(I) complex of a dimeric paracyclophane containing κ*N*-coordinated NTf$_2^-$: 2.345(5) and 2.369(5) Å.[31]

Reactivity of 1—3: *Reactivity towards [emim]NTf$_2$*: The copper(I) compound [Cu(Et$_2$O)(NTf$_2$)] (**2**) and [emim]NTf$_2$ were blended at a molar ratio of 1:1 yielding analytically pure [emim][Cu(NTf$_2$)$_2$] (**4**). Applying AgNTf$_2$ (**3**) instead of **2** gives the analogous silver(I) compound, namely [emim][Ag(NTf$_2$)$_2$] (**5**).



In this context it should be mentioned that Meindersma and co-workers used mixtures of **3** and [emim]NTf$_2$ for ethylene extraction,[13] but did not clarify the nature of the silver(I) species involved. Metallate complexes containing coordinated NTf$_2^-$ ligands have been thoroughly investigated by Mudring et al. for alkaline earth metals and lanthanides.[40] Very recently, a homoleptic argentate anion with three NTf$_2^-$ ligands has been described in [Ag(CH$_3$CN)$_4$]$_2$[Ag(NTf$_2$)$_3$].[3c]

Compared with the proton and the carbon NMR spectra of [emim]NTf$_2$ both for **4** and for **5** the C2 and H2 signals of the imidazolium ring are most significantly affected upon the formation of **4** and **5**. The upfield shifts of these resonances, which are found to be more significant in the case of **4**, might be due to the loss of cation–anion interactions in solution: Hydrogen bonds between the NTf$_2^-$ anion and the proton in 2-position of the imidazolium cation are blocked by coordination of the anion to copper(I) or silver(I). The δ_F value of **4** and **5** is shifted to lower field by about $\Delta\delta = 3$ and 2 ppm, respectively, in comparison to [emim]NTf$_2$.

The high resolution negative atmospheric-pressure chemical ionization (APCI) mass spectrum of **5** shows the signal assigned to the argentate(I) anion as the main peak, whereas the analogous signal of the cuprate(I) anion of **4** is not observed by means of APCI mass spectrometry.

The crystal structure of **4** is depicted in Figure 4. All relevant parameters concerning the crystal structure determinations of **4** and **6**–**10** are listed in Table S2 of the Supporting Information. The crystallographically important parameters of **12**, **12a**, and **13** are given in Table S3 of the Supporting Information.

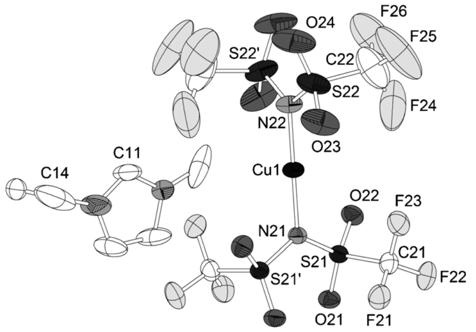
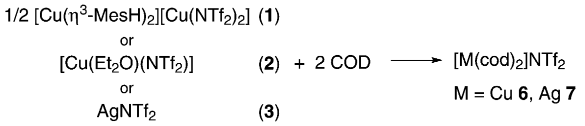


Figure 4. Crystal structure of [emim][Cu(NTf$_2$)$_2$] (**4**). The second position of the disordered imidazolium cation is omitted for clarity. Atoms marked (′) and non-labeled atoms of the NTf$_2^-$ ligands are symmetry-generated.

The cuprate(I) anion of **4** reveals the same coordination mode as the respective anion in complex **1**. However, the crystallographically imposed symmetry of **4** implies a value of 180.0° for the N21-Cu1-N22 angle. The copper-nitrogen distances have values of 1.900(3) Å (d(Cu1−N21)) and 1.896(4) Å (d(Cu1−N22)). Both of these bond lengths are not only in the expected range,[34] but also nearly identical to those found for the anion in **1** (d(Cu1−N1) = 1.890(3) Å). In contrast to the solid state structure of **1**, the C_2 rotation axis is identical to the N21-Cu1-N22 axis and not perpendicular to it. Consequently, the SNS planes of the anion are twisted with respect to each other at an angle of 83.6°. Between the imidazolium cation and two different cuprate(I) anions exist two short intermolecular contacts that are below the sum of the van der Waals radii of the relevant atoms: d(O21…H11) = 2.39 Å (Σ(vdW radii) = 2.9 Å[28]) and d(F25…H14 A) = 2.37 Å (Σ(vdW radii) = 2.9 Å[28]).

Reactivity towards COD: The reaction of **1**–**3** with 2.5 equivalents of 1,5-cyclooctadiene (COD) gave the analytically pure compounds [M(cod)$_2$]NTf$_2$ (M = Cu **6**, Ag **7**), as expected.



With respect to the ^{1}H NMR spectrum of free COD, both **6** and **7** show slightly downfield-shifted signals of the CH groups due to complexation, whereas the resonances of the CH$_2$ groups are essentially not influenced. For the olefinic protons of **6**, a $\Delta\delta_H$ value of approximately $\Delta\delta = 0.3$ ppm is determined, whereas for the CH protons of the silver(I) complex **7**, the $\Delta\delta_H$ value is somewhat larger at approximately $\Delta\delta = 0.5$ ppm. The ^{13}C NMR spectra of **6** and **7** are identical with the following exception: Compared with free COD, the signal of the CH groups is shifted upfield by almost $\Delta\delta = 6$ ppm in the case of **6**, whereas the respective $\Delta\delta_C$ value of **7** is found to be approximately $\Delta\delta = 2$ ppm. In comparison with the relevant starting materials, the δ_F reveals an upfield shift of approximately $\Delta\delta = 3$ ppm for **6** and **7**, respectively. The complex cation [M(cod)$_2$]$^+$ probably also exists in solution, which is in accord with the observations for [Cu(cod)$_2$]ClO$_4$ and [Ag(cod)$_2$]BF$_4$ in [D$_6$]acetone[41] and for [Ag(cod)$_2$]ClO$_4$ in [D$_3$]CH$_3$CN.[42]

The IR spectrum of COD exhibits two frequency regions that are affected significantly upon coordination to a metal ion, namely the C=C stretching mode of uncoordinated COD between 1655 to 1660 cm^{-1}[43,44] and two C=C−H deformation frequencies at 722 and 710 cm^{-1}.[43] For comparison, the relevant data of **6** and of similar complexes described in the literature[43,44] is given in Table 1. The authors of all studies quoted in Table 1 report a C=C vibration roughly between 1590 and 1600 cm^{-1} for the copper(I)-COD complexes.

For **6** and **7** the C=C stretching vibration is shifted to lower frequencies only by 65 and 54 cm^{-1}, respectively, with regard to uncoordinated COD. In contrast, in the case of

Table 1. IR frequencies (in cm^{-1}) of $[Cu(cod)_2](WCA)$ (WCA = weakly coordinating anion).

	free COD	BF_4^-	ClO_4^-	NTf_2^- (**6**)[a]
ν(C=C)	1656[a] 1655[43] 1660[44]	1588[43]	1590[43] 1638, 1595[44]	1591
δ(C=C-H)	720, 706[a] 722, 710[43]	770, 740[43]	770, 740[43]	791, 735[b]

[a] Own measurements. [b] Preliminary assignment of the bands due to strongly interfering spectral region.

the isovalence-electronic $[Ni(cod)_2]$ (ν(C=C) = 1328 cm^{-1}[45]) the $\Delta\nu$(C=C) value is found to be 328 cm^{-1}.

In comparison with zerovalent d^{10} metals like nickel(0), both Cu^I and Ag^I show much weaker π-bonding ability towards σ donor/π acceptor ligands such as olefins.[46] This difference can be correlated to the differing promotion energies,[47] which is evidenced by the above-mentioned values for ν(C=C).

Complex **6** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, whereas compound **7** crystallizes in the monoclinic space group $C2/c$ with $Z = 4$. Thus, compounds **6** and **7** are not isotypic. In the solid state structures of **6** and **7** the COD moieties do not reveal the "boat" conformation as observed in the presence of highly symmetrical weakly coordinating anions, that is, cubic ones like ClO_4^-,[42,48] but the "twisted-boat" conformation.

In contrast to all other solid state structures presented herein, compounds **6** and **7** are the only ones containing NTf_2^- as non-coordinating anion. In both cases the *transoid* configuration is adopted, that is, the CF_3 groups are located at different sides with respect to the SNS plane. Whether the bis(triflyl)imide anion is *cisoid*- or *transoid*-configurated is evidenced by the C−C distance of approximately 4 (*cisoid*) and 5 Å (*transoid*), respectively. A statistical evaluation of a search in the Cambridge Structural Database predicated on this criterion did not result in a trend regarding the preference of one configuration, for example, dependent on the coordination mode. Figure 5 shows the crystal structure of **6**, whereas the crystal structure of **7** is depicted in Figure 6.

Each of the two COD molecules in **6** adopts the typical η^2:η^2 coordination mode. The dihedral angle between the planes $(C1\text{-}C2)_{centroid}$-Cu1-$(C5\text{-}C6)_{centroid}$ and $(C9\text{-}C10)_{centroid}$-Cu1-$(C13\text{-}C14)_{centroid}$ determined at 88.0° implies a slightly distorted tetrahedral coordination. The distances between Cu1 and the olefinic carbon atoms range from 2.227(6) to 2.329(5) Å and are thus similar to those of $[Cu(cod)_2]ClO_4$,[41,48] revealing values between 2.253(3) and 2.273(3) Å.[48] The double bonds in **6** (d(C=C) = 1.337(8)–1.373(7) Å) are in part shorter than those of the neutral d^{10} complexes $[Ni(cod)_2]$[49] (1.384(11)–1.392(13) Å; measured at ca. 295 K) and $[Pt(cod)_2]$[50] (1.329(8)–1.470(9) Å; measured at 200 K), which is in accordance with the different π-back-donation characteristics of copper(I) and the zerovalent group 10 metals nickel(0) and platinum(0), expressed by their promotion energies (see the above IR discussion).[47]

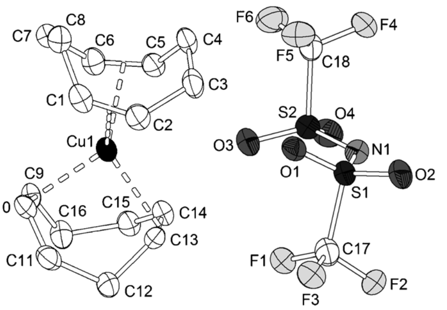


Figure 5. Molecular structure of $[Cu(cod)_2]NTf_2$ (**6**).

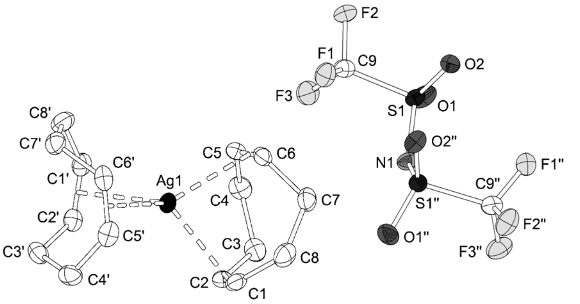


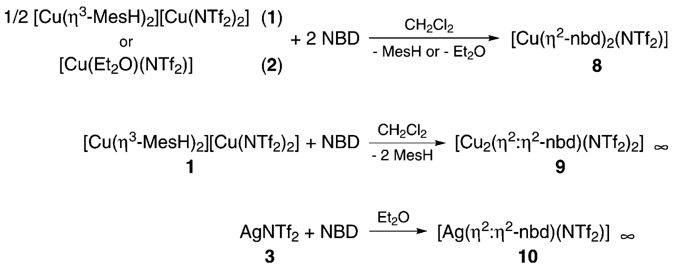
Figure 6. Molecular structure of $[Ag(cod)_2]NTf_2$ (**7**). Atoms labeled with (′) or (″) are generated by symmetry.

In compound **7**, silver(I) also adopts the tetrahedral coordination. In contrast to **6**, a higher distortion is observed as the dihedral angle between the planes $(C1\text{-}C2)_{centroid}$-Ag1-$(C5\text{-}C6)_{centroid}$ and $(C1'\text{-}C2')_{centroid}$-Ag1-$(C5'\text{-}C6')_{centroid}$ is 83.9°. The four different distances between Ag1 and the olefinic carbon atoms, which vary from 2.4307(18) to 2.5405(19) Å, are significantly longer than the corresponding ones in the analogous Cu^I compound **6**. Additionally, the average value of $d(Ag{-}C_{olefin})$ is comparable to those of $[Ag(cod)_2]$WCA (weakly coordinating anion (WCA) = BF_4^-,[51] ClO_4^-,[42] PF_6^-[52]). The C=C distances in **7** being 1.341(3) and 1.345(3) Å are in part shorter than in the case of $[Ni(cod)_2]$[49] and $[Pt(cod)_2]$[50] with differences being marginally larger than for **6** (see above). This is in compliance with the fact that Ag^I reveals a slightly higher promotion energy than Cu^I.[47]

Reactivity towards NBD: The reaction of **1**–**3** with 2,5-norbornadiene (NBD) yielded the monomeric copper(I) complex $[Cu(\eta^2\text{-nbd})_2(NTf_2)]$ (**8**) as well as the polymeric compounds $[Cu_2(\eta^2{:}\eta^2\text{-nbd})(NTf_2)_2]_\infty$ (**9**) and $[Ag(\eta^2{:}\eta^2\text{-nbd})(NTf_2)]_\infty$ (**10**).

The molar olefin/metal ratios applied for the synthesis of **8**–**10** are given in Table 2.

By analyzing the proton and carbon NMR spectra of **8**, C_{2v} symmetry is suggested for NBD, although only one of the double bonds of the diolefin is coordinated to the metal in the solid state (see below). In the ^1H NMR spectrum, only the signal assigned to the bridgehead protons is affect-



$$\tfrac{1}{2}\,[Cu(\eta^3\text{-MesH})_2][Cu(NTf_2)_2]\ (\mathbf{1})\ \text{or}\ [Cu(Et_2O)(NTf_2)]\ (\mathbf{2}) + 2\,\text{NBD} \xrightarrow[\text{- MesH or - }Et_2O]{CH_2Cl_2} [Cu(\eta^2\text{-nbd})_2(NTf_2)]\ (\mathbf{8})$$

$$[Cu(\eta^3\text{-MesH})_2][Cu(NTf_2)_2]\ (\mathbf{1}) + \text{NBD} \xrightarrow[\text{- 2 MesH}]{CH_2Cl_2} [Cu_2(\eta^2{:}\eta^2\text{-nbd})(NTf_2)_2]_\infty\ (\mathbf{9})$$

$$AgNTf_2\ (\mathbf{3}) + \text{NBD} \xrightarrow{Et_2O} [Ag(\eta^2{:}\eta^2\text{-nbd})(NTf_2)]_\infty\ (\mathbf{10})$$

Table 2. Molar olefin/metal ratios within the syntheses of **8**–**10**. $[Cu(\eta^3\text{-}MesH)_2][Cu(NTf_2)_2]$ (**1**), $[Cu(Et_2O)(NTf_2)]$ (**2**) and $AgNTf_2$ (**3**) were used as starting materials.

	1	2	3
$[Cu(\eta^2\text{-nbd})_2(NTf_2)]$ (**8**)	2.5	2.6	–
$[Cu_2(\eta^2{:}\eta^2\text{-nbd})(NTf_2)_2]_\infty$ (**9**)	0.5[a]/2.5[b]	[c]	–
$[Ag(\eta^2{:}\eta^2\text{-nbd})(NTf_2)]_\infty$ (**10**)	–	–	2.5[d]

[a] Concentration with respect to copper: approximately 0.5 mol L^{-1}. [b] Concentration with respect to copper: approximately 0.2 mol L^{-1}. [c] Not carried out. [d] Concentration with respect to silver: approximately 0.5 mol L^{-1}.

ed upon coordination to the Cu^I ion, namely by a slight downfield shift. The carbon NMR spectrum of **8** shows the most significant influence for the olefinic carbon atoms, that is, a shift to higher field by about $\Delta\delta = 6$ ppm. The CH_2 group is also upfield-shifted by approximately $\Delta\delta = 3$ ppm. The δ_F value of **8** is similar to that observed for the starting materials **1** and **2**.

The relevant C=C stretching vibrations for the free diene were determined at 1641, 1543, 724, and 655 cm^{-1}. The IR spectrum of **8** exhibits the C=C vibrations at 1561 and 1457 cm^{-1}. Additionally, a single band corresponding to δ(C=C-H) occurs at 689 cm^{-1}. These findings for **8** are in compliance with those reported for copper(I)–NBD complexes containing η^2-coordinated NBD ligands.[43,53,54]

In contrast to complex **8**, the infrared spectrum of **9** reveals only one very weak band for the C=C stretching vibration at 1456 cm^{-1}, whereas the bands related to the C=C−H deformation modes are not observed. These findings are typical of a $\eta^2{:}\eta^2$-bound NBD ligand.[43] Additionally, the band assigned to the rocking of the methylene group does not occur.

The proton, carbon, and fluorine NMR spectra in $[D_2]CH_2Cl_2$ of the polymeric silver(I) compound **10** with $\eta^2{:}\eta^2$-bound NBD moieties exhibit major differences with respect to the monomeric copper(I) complex **8** containing NBD as an η^2-coordinated ligand. Generally, in both the ^{1}H- and ^{13}C NMR spectrum of **10**, all the NBD resonances are shifted to lower field upon complexation, whereas δ_F is (within the limits of error) identical to the relevant chemical shift of the starting material **3**. The signals of the protons are more strongly affected than in the case of **8**, in which the largest deshielding is found for the olefinic protons with $\Delta\delta_H$ values of approximately 0.5 ppm.

In the IR spectrum of **10** the C=C stretching frequency occurs at 1485 cm^{-1}, which is in accordance with the spectra of $[Ag_2(\eta^2{:}\eta^2\text{-nbd})(NO_3)_2]_\infty$[55] and $[Ag(\eta^2{:}\eta^2\text{-nbd})(ClO_4)]_\infty$,[56] exhibiting a medium band at 1470 and at 1485 cm^{-1}, respectively. Remembering the frequency of the relevant absorption band of $[Cu_2(\eta^2{:}\eta^2\text{-nbd})(NTf_2)_2]_\infty$ (**9**) ($\nu(C{=}C) = 1456$ cm^{-1}) the differences concerning the π-back-bonding characteristics of Cu^I and Ag^I become evident again.

The molecular structure of $[Cu(\eta^2\text{-nbd})_2(NTf_2)]$ (**8**) is depicted in Figure 7.

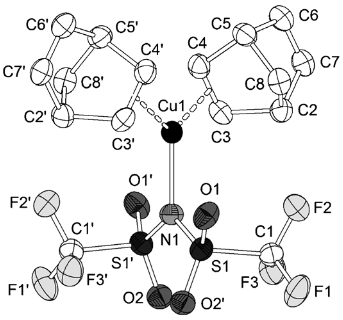


Figure 7. Molecular structure of $[Cu(\eta^2\text{-nbd})_2(NTf_2)]$ (**8**). Atoms labeled (′) are symmetry-generated.

Compound **8** is the first example of a structurally characterized copper(I)–NBD 1:2 complex. The Cu1−N1 bond length (2.055(3) Å) is comparable to the corresponding value of $[Cu(CO)_2(NTf_2)]$[1b] (d(Cu−N) = 2.030(4) Å). With angles of 122.9° ($(C3\text{-}C4)_{centroid}\text{-}Cu1\text{-}(C3'\text{-}C4')_{centroid}$) and 118.6° ($(C3\text{-}C4)_{centroid}\text{-}Cu1\text{-}N1$) the geometry at Cu1 is trigonal planar. In the case of $[Cu_2(\eta^2{:}\eta^2\text{-nbd})(NTf_2)_2]_\infty$ (**9**) (Figure 8), the coordination mode of the two crystallographically different Cu^I ions can be described as distorted trigonal planar. A section of the solid-state structure of the polymeric compound $[Cu_2(\eta^2{:}\eta^2\text{-nbd})(NTf_2)_2]_\infty$ (**9**) is shown in Figure 8.

The solid-state structure of compound **9** exhibits two independent copper(I) bis(trifluoromethanesulfonyl)imide units. On the one hand, there are centrosymmetric eight-membered rings consisting of two $CuNTf_2$ entities that are connected in a 1κ*N*:2κ*O* coordination mode. The Cu1−N1 bond length is found to be 2.012(6) Å and the Cu1−O2′ bond

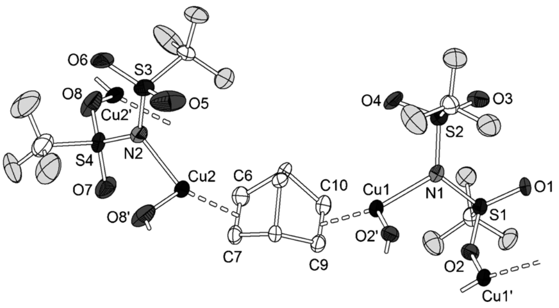


Figure 8. Section of the layered structure of $[Cu_2(\eta^2{:}\eta^2\text{-nbd})(NTf_2)_2]_\infty$ (**9**). The second position of the disordered SO_2CF_3 group located at S3 is omitted for clarity.

length is 2.086(5) Å. A search in the Cambridge Structural Database regarding the common ranges for *d*(Cu−N) and *d*(Cu−O) in the structural motif CuL_3 ($L^1 = N$, $L^2 = O$, $L^3 =$ non-metal) resulted in a broad distribution in each case. The maximum for *d*(Cu−N) was found to be approximately 1.9 Å, whereas the most frequent value for *d*(Cu−O) was determined at approximately 2.3 Å. Interestingly, the triflate, which is also commonly regarded as a weakly coordinating anion, forms an analogous structural motif in the solid-state structure of $[Cu_2(PPh_3)_2\{\eta^2{:}\eta^2\text{-isoprene}\}(OTf)_2]_\infty$, namely eight-membered $[CuSO_2]_2$-rings.[57] On the other hand, the copper atom Cu2 in **9** also has two crystallographically identical NTf_2^- ligands in its coordination sphere, of which one is κ^2N,O-coordinated and the second one is κO-bound. The crystal structure of **9** comprises $CuNTf_2$ strings along the *a* axis as a second structural motif. The Cu2−N2 distance is 2.015(7) Å, which is nearly identical to the value determined for Cu1−N1. One of the two Cu2−O bond lengths, namely *d*(Cu2−O8′) = 2.053(6) Å, is in the same range as *d*(Cu1−O2′). There exists a weak secondary interaction between Cu2 and O7 (*d*(Cu2−O7) = 2.871(6) Å). The two basic structural motifs of the solid state structure of **9**, that is, the $[Cu_2\{(NTf_2)_2\text{-}1\kappa N{:}2\kappa O;1\kappa O{:}2\kappa N\}]$ rings and the $(NTf_2\text{-}1\kappa^2N,O{:}2\kappa O)$-copper(I) strands along the *a* axis, are bridged by $\eta^2{:}\eta^2$-coordinating NBD ligands, resulting in an strongly undulating sheet structure.

Selected bond lengths of NBD,[58] **8**, **9** and comparative complexes are listed in Table 3. The $Cu{-}C_{olefin}$ distances in **8** are found to be significantly longer than those determined for **9**. The values of $d(Cu{-}C_{olefin})$ in **9** differ less from each other than those of $[Cu_4Cl_4(\eta^2{:}\eta^2\text{-nbd})_2]_\infty$.[59] Interestingly, the literature-known Cu^I–NBD complexes incorporating η^2-coordinated NBD show $Cu{-}C_{olefin}$ distances similar to those of **9** instead of **8**, for example in $[CuCl(\eta^2\text{-nbd})]_4$.[54,59] In the case of isostructural $[CuBr(\eta^2\text{-nbd})]_4$, at least one value is within the range of **9**.[60] The copper atom in **8** is coordinated by one σ donor and two π acceptors, whereas up to three donor atoms and only one π acceptor are present in all other cases. Consequently, the copper atom in **8** is less electron rich and thus a weaker π-donor, which explains the deviation in $d(Cu{-}C_{olefin})$ of **8**, **9** and the literature-known complexes. Both the coordinated double bond of the η^2-bound NBD ligand in **8** and those in **9** are longer than the C=C bond of free NBD in the solid state.

A section of the crystal structure of $[Ag(\eta^2{:}\eta^2\text{-nbd})(NTf_2)]_\infty$ (**10**) is shown in Figure 9.

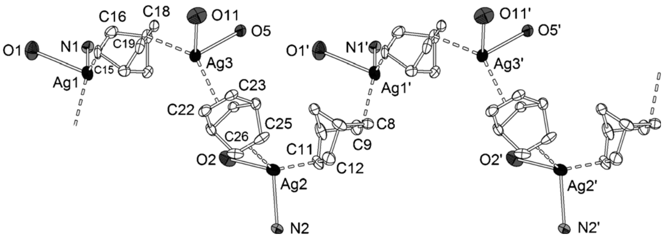


Figure 9. Helix-like $[Ag(\eta^2{:}\eta^2\text{-nbd})(NTf_2)]_\infty$-strand in the crystal of **10**, view along the *c*-axis. Uncoordinated atoms of the NTf_2^- ligands are omitted for clarity. Atoms labeled (′) are generated by symmetry.

Compound **10** is the third example of a structurally characterized silver(I)–NBD compound revealing the starting materials in a 1:1 stoichiometry. The crystal structure of **10** comprises polymeric helices of $[Ag_3(nbd)_3]^{3+}$ units (Figure 9), at which the three independent silver atoms are interconnected by $\eta^2{:}\eta^2$-bound NBD ligands with $Ag{-}C_{olefin}$ distances between 2.377(8) and 2.494(9) Å. In comparison, the corresponding values of $[Ag(\eta^2{:}\eta^2\text{-nbd})(ClO_4)]_\infty$ varying from 2.416(7) to 2.472(8) Å[56] are within the range determined for **10**, whereas most of the relevant distances of $[Ag(\eta^2{:}\eta^2\text{-nbd})(NO_3)]_\infty$ (2.496(6)–2.561(6) Å[42]) are above those of **10**. The mentioned valuations for the $Ag{-}C_{olefin}$ distances suggest a similar coordination sphere for the silver atoms in **10** and $[Ag(\eta^2{:}\eta^2\text{-nbd})(ClO_4)]_\infty$,[56] which is in compliance with the bonding situations in their solid-state structures. However, taking into account that one of the two crystallographically independent silver atoms in $[Ag(\eta^2{:}\eta^2\text{-nbd})(NO_3)]_\infty$[42] has three σ-donors in its coordination sphere (instead of two as in **10** and $[Ag(\eta^2{:}\eta^2\text{-nbd})(ClO_4)]_\infty$)[56] the $Ag{-}C_{olefin}$ distances should be at least in part shorter due to the comparatively larger π-donor ability of one of the crystallographically different silver atoms in this compound. This finding may be attributed to steric reasons.

In Table 4 the C=C bond lengths of NBD,[58] **10** and of two literature-known complexes are given.

Besides two NBD ligands, every Ag^I ion in **10** has two σ-donors in its coordination sphere, namely two oxygen atoms (Ag3) or one nitrogen atom and one oxygen atom (Ag1, Ag2), belonging to one or two NTf_2^- units. The Ag−N bond lengths are found to be 2.298(7) and 2.544(6) Å and are therefore far below the sum of the van der Waals radii of silver and nitrogen (3.3 Å[28]). The values for *d*(Ag−O) varying from 2.405(7) Å to 3.081(7) Å are all within the sum of the relevant van der Waals radii (3.2 Å[28]),

Table 3. Selected bond lengths *d* (in Å) of NBD,[58] **8**, **9**, and of the comparative complexes $[CuX(\eta^2\text{-nbd})]_4$ (X = Cl,[59] Br[60]) and $[Cu_4Cl_4(\eta^2{:}\eta^2\text{-nbd})_2]_\infty$.[59]

	NBD[a]	**8**[b]	**9**[b]	$[CuCl(nbd)]_4$[c]	$[CuBr(nbd)]_4$[d]	$[Cu_4Cl_4(nbd)_2]_\infty$[c]
$Cu{-}C_{olefin}$	–	2.176(2)	2.030(7)	2.052(8)	2.052(10)	2.021(6)
	–	2.166(2)	2.034(7)	2.072(9)	2.110(11)	2.045(7)
	–	–	2.069(8)	–	–	2.115(7)
	–	–	2.076(7)	–	–	2.135(8)
C=C coord.	–	1.354(3)	1.365(10)	1.335(12)	1.345(17)	1.332(11)
	–	–	1.383(11)	–	–	1.381(10)
C=C uncoord.	1.337(1)	1.322(3)	–	1.280(12)	1.333(17)	–

[a] Determined at approximately 110 K. [b] Determined at 100(2) K. [c] Determined at approximately 298 K. [d] Determined at approximately 138 K.

Table 4. Lengths d (in Å) of the coordinated C=C bonds in **10** and in the comparative compounds $[Ag(\eta^2:\eta^2\text{-nbd})(NO_3)]_\infty$[42] and $[Ag(\eta^2:\eta^2\text{-nbd})(ClO_4)]_\infty$.[56] For the purpose of comparison: d(C=C) in uncoordinated NBD is 1.337(1) Å.

	10[a]	$[AgNO_3(nbd)]_\infty$[b]	$[AgClO_4(nbd)]_\infty$[c]
C=C, min[d]	1.295(13)	1.307(10)	1.322(9)
C=C, max[d]	1.355(12)	1.346(13)	1.333(11)

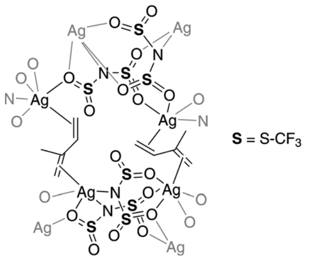
[a] Determined at 193(2) K. [b] Determined at approximately 300 K. [c] Determined at approximately 296 K. [d] Min indicates the shortest C=C bond length, whereas max indicates the longest.

but cover a wider range than found for the starting material **3** (2.458(4)–2.849(4) Å). The helix-like strands of **10** are cross-linked by two of the three crystallographically different NTf_2^- ligands resulting in a three-dimensional network.

Reactivity towards isoprene: Copper(I) and silver(I) complexes with non-cyclic, low-boiling diolefins such as 1,3-butadiene have been of scientific and industrial interest for a long time.[14,61] Nevertheless, only three crystal structures are known for this type of compound; one incorporates 1,3-butadiene[62] and two exhibit isoprene.[57,63] Preliminary data show that it is possible to obtain a defined Ag^I bis(triflyl)imide isoprene complex. By reacting **3** with 2.5 equivalents of isoprene in diethyl ether and subsequent evaporation to dryness, a colorless solid was obtained. In the proton NMR spectrum all resonances occur at slightly lower field compared with the uncoordinated isoprene, in which the signal of the CH proton is the most influenced one. Whereas free isoprene reveals four signals with an integral ratio of 2:1:1:1, only three resonances are observed in the case of the Ag^I complex, namely with an integral ratio of 3:1:1. The largest values for $\Delta\delta_C$ are found for the signals of CH_2C_q and C_qCH, being shifted to higher field by $\Delta\delta = 7.4$ and 2.2 ppm, respectively. The result of the elemental analysis suggests that the isoprene has partly been removed upon drying of the solid in vacuum, so that the starting material **3** might have been recovered in part. Single crystals were grown by recrystallization of the isolated amorphous compound from a dichloromethane solution. Although the crystal quality was not sufficient to give reliable metric parameters, the connectivity of $[Ag_2(\eta^2:\eta^2\text{-isoprene})(NTf_2)_2]_\infty$ (**11**) could be determined.

$$\underset{\mathbf{3}}{2\,AgNTf_2} + \text{isoprene} \xrightarrow{Et_2O} \underset{\mathbf{11}}{[Ag_2(\eta^2:\eta^2\text{-isoprene})(NTf_2)_2]_\infty}$$

Analogous to the crystal structure of $AgNTf_2$ (**3**) the two-dimensional polymeric solid state structure of **11**, which crystallizes in the space group $P\bar{1}$, exhibits rhombic $Ag_2(\mu\text{-}O)_2$-cores as a structural motif. The two $[AgNTf_2]_\infty$ strings are interconnected by the isoprene molecules. The atom connectivity of **11** is shown in the following schematic diagram:



Reactivity towards ethylene: In most of the structurally characterized copper(I) ethylene complexes, the metal exhibits up to three N-donor ligands and one olefin molecule in its coordination sphere.[64] One example is found in which two ethylene molecules and $AlCl_4^-$ are bound to the Cu^I ion.[65] In 2007 Krossing and co-workers[66a] succeeded in isolating the first homoleptic Cu^I ethylene complex cation, namely $[Cu(C_2H_4)_3]^+$, by using $[Al(OC(CF_3)_3)_4]^-$ as a WCA. Only a few months later Dias et al.[67] reported preliminary results regarding the synthesis of an analogous copper(I) ethylene complex, yet revealing the sterically less demanding SbF_6^- anion.

Up to now eleven silver(I) ethylene complexes have been structurally characterized. All compounds having the respective anion bound to the Ag^I cation are monoolefinic complexes,[68] with the exception of the molecular compound $[Ag(C_2H_4)_2\{Al(OCH(CF_3)_2)_4\}]$[69b] bearing two ethylene ligands per silver(I) ion. The ionic compounds published by Krossing et al. incorporate one to three equivalents ethylene per silver(I) ion.[69]

The ethylene complexes $[Cu(C_2H_4)(NTf_2)]_\infty$ (**12**) and $[Ag(C_2H_4)_2(NTf_2)]$ (**13**) were prepared by passing a stream of ethylene through a 0.5 M solution of **1** (CH_2Cl_2) and **3** (Et_2O), respectively.

$$\underset{\mathbf{1}}{[Cu(\eta^3\text{-MesH})_2][Cu(NTf_2)_2]} + 2\,C_2H_4 \xrightarrow[-\,2\,MesH]{CH_2Cl_2} \underset{\mathbf{12}}{2\,[Cu(C_2H_4)(NTf_2)]_\infty}$$

$$\underset{\mathbf{3}}{AgNTf_2} + 2\,C_2H_4 \xrightarrow{Et_2O} \underset{\mathbf{13}}{[Ag(C_2H_4)_2(NTf_2)]}$$

Complex **12** was obtained from the reaction mixture at −20 °C in a single-crystalline form. In the case of the Ag^I compound **13**, the solvent was nearly completely evaporated during which time the gaseous olefin was introduced into the ethereal solution. Upon the addition of dichloromethane, dissolution of the colorless solid was observed suggesting that the polymeric structure of **3** had been cracked due to the formation of a Ag^I ethylene species. As in the case of **12**, single crystals of $[Ag(C_2H_4)_2(NTf_2)]$ (**13**) were obtained from a concentrated dichloromethane solution at −20 °C.

Compared with the proton and carbon NMR spectra of free ethylene ($\delta_H = 5.40$, $\delta_C = 123.20$ ppm[38]) the ^1H NMR spectrum of **12** shows a shift to higher field of $\Delta\delta = 0.34$ ppm for the signal of the olefinic protons and the

^{13}C NMR signal is shifted upfield by $\Delta\delta = 25$ ppm. In contrast, in the case of $[Cu(C_2H_4)_3][Al(OC(CF_3)_3)_4]$,[66a] only a marginal downfield shift is observed for the ethylene protons, but a significant upfield-shift occurs for the corresponding carbon signal. The ^{19}F NMR spectrum of **12** shows (within the limits of error) the same chemical shift as observed for the starting material **1**. In the IR spectrum of **12** a very weak C=C stretching vibration is observed at 1544 cm^{-1}, which means a shift to lower frequencies by 79 cm^{-1} compared to free ethylene (ν(C=C) = 1623 cm^{-1}[46,69a]). The C=C stretching vibrations of miscellaneous transition-metal ethylene complexes are between 1493 cm^{-1} for $[RhCp(C_2H_4)_2]$ and 1584 cm^{-1} for $[Ag(C_2H_4)_2]BF_4$.[46] The pronounced weakening of the double bond in $[RhCp(C_2H_4)_2]$ is attributed to the synergistic effect of the low promotion energy and the medium electron-affinity of Rh^{I}.[46] Compound **12** shows a value for ν(C=C) that is in the middle of the range given in literature.

A section of the solid state structure of the copper(I) compound **12** is depicted in Figure 10.

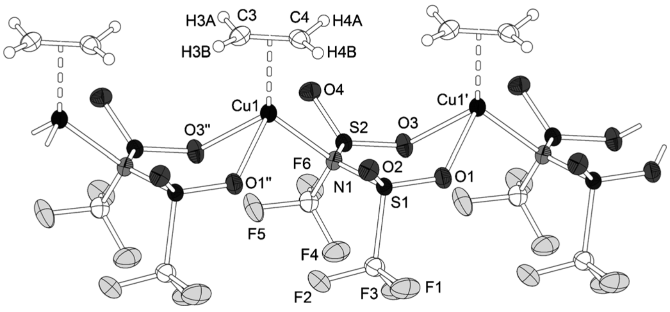


Figure 10. Section of the crystal structure of $[Cu(C_2H_4)(NTf_2)]_\infty$ (**12**). Atoms labeled (′) and (″) are symmetry-generated.

Compound **12** is one of the few structurally characterized copper(I) ethylene complexes exhibiting a polymeric array without bridging chloro ligands.[64,70] The fact that the NTf_2^- anion remains bound to the copper(I) ion in **12** implies that the bis(triflyl)imide anion behaves like the "typical" coordinating counterions of copper(I), for example, Cl$^-$, Br$^-$, I$^-$, and NO_3^-, in the presence of weak Lewis bases such as ethylene.[66b] Expectedly, the NTf_2^- anion is coordinated to Cu1 through its nitrogen atom with a Cu1−N1 bond length of 2.0572(19) Å, which is comparable to those determined for the copper(I)–NBD complex **8** (2.055(3) Å) and for $[Cu(CO)_2(NTf_2)]$[1b] (2.030(4) Å), but significantly longer than that of **2** (1.901(2) Å). Moreover, there exist two strong Cu−O interactions between Cu1 and two oxygen atoms, namely O1″ and O3″, of another NTf_2^- entity resulting in the formation of linear $[Cu(NTf_2\text{-}1\kappa N{:}2\kappa^2 O,O')]$ strings along the *a* axis. The relevant copper–oxygen distances measure 2.4063(17) Å and 2.0812(18) Å, both being far below the sum of the van der Waals radii of copper and oxygen (2.9 Å[28]). Upon coordination to the copper(I) ion the C=C bond of the η^2-bound ethylene molecule is with 1.362(4) Å (determined at 100(2) K) significantly elongated in comparison to solid ethylene (1.3137 Å; determined at 85 K[71]). The Cu−C distances in **12** (2.043(2) Å) are in the same range as the relevant values of the one-dimensional polymer $[Cu(N{-}N)(C_2H_4)]PF_6$[70b] (N−N = 4-(2-pyridyl)pyrimidine) being 2.032(5) and 2.036(6) Å. The shortest contact between two strands is found to be 2.56(4) Å assigned to the H4A-F1 interaction (Σ(vdW-radii) = 2.9 Å[28]).

The result of a crystal structure analysis of single crystals obtained from **12** in non-absolute NMR solvent $[D_2]CH_2Cl_2$ showed that the one-dimensional polymeric structure of **12** can be cracked in the presence of the σ-donor water yielding $[Cu(C_2H_4)(H_2O)(NTf_2)]$ (**12a**) (Figure 11).

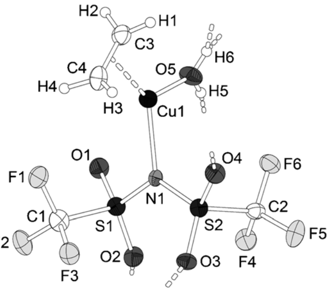


Figure 11. Molecular structure of $[Cu(C_2H_4)(H_2O)(NTf_2)]$ (**12a**).

In the molecular compound **12a**, the copper atom has one η^2-bound ethylene molecule, one κ*N*-coordinated NTf_2^- ligand and one water molecule in its coordination sphere. With bond angles varying from 99.6 to 132.3° the geometry at Cu1 can be described as distorted trigonal planar. The Cu1−N1 distance measures 2.050(4) Å and is therefore similar to the corresponding bond lengths in $[Cu(C_2H_4)(NTf_2)]_\infty$ (**12**) (2.0572(19) Å), $[Cu(\eta^2\text{-nbd})_2(NTf_2)]$ (**8**) (2.055(3) Å) and $[Cu(CO)_2(NTf_2)]$[1b] (2.030(4) Å). Due to the extra ethylene ligand, the bond length of Cu1−O5 (1.966(4) Å) is significantly larger than in the etherate **2** (d(Cu−O) = 1.886(2) Å). However, the Cu−C$_{olefin}$ contacts are with 2.021(5) Å (d(Cu1−C3)) and 2.028(5) Å (d(Cu1−C4)) almost the same as for **12** (2.043(2) Å). Due to intermolecular contacts between the oxygen atoms O2, O3, and O4 of the bis(triflyl)imide anions and the protons H5 and H6 of the water molecules, which are far below the sum of the relevant van der Waals radii (2.9 Å[28]), a hydrogen-bond network is formed. In this context the following interactions are important: d(O2⋯H6) = 2.35(5) Å, d(O3⋯H6) = 2.34(5) Å and d(O4⋯H5) = 2.16(5) Å. This result shows that traces of water in olefin-paraffin gas mixtures will strongly influence the intermolecular interaction of reversible absorbers such as $CuNTf_2$ and $AgNTf_2$.

In the case of the silver(I) complex **13**, NMR spectroscopy and X-ray structure analysis were applied for identification and characterization. The sample preparation for the elemental analysis failed due to loss of ethylene, which was proven by IR spectroscopy because no C=C stretching vibration was observed. The equilibrium of Equation (1) (see below) is shifted to the side of the starting materials, if complex **13** is handled in the solid state under argon and in the absence of ethene at room temperature.

$$\underset{\mathbf{3}}{AgNTf_2} + 2\,C_2H_4 \rightleftharpoons \underset{\mathbf{13}}{[Ag(C_2H_4)_2(NTf_2)]} \qquad (1)$$

With respect to the ^{1}H NMR resonance of free ethylene, the proton NMR spectrum of **13** reveals a downfield shift of $\Delta\delta = 0.37$ ppm, whereas an upfield shift of about $\Delta\delta = 8.1$ ppm is observed for δ_C indicating that an interaction between the silver(I) ion and ethylene is existing in solution. Interestingly, the corresponding chemical shifts reported for $[D_2]CH_2Cl_2$ solutions of $[Ag(C_2H_4)_3][Al(OC(CF_3)_3)_4]$[69a] and $[Ag(C_2H_4)_2\{Al(OCH(CF_3)_2)_4\}]$[69b] are in the same ranges as those observed for **13**, suggesting that similar species are present in solution in each case. However, more recent NMR data of $[Ag(C_2H_4)_3][Al(OC(CF_3)_3)_4]$ acquired in the same solvent reveal a significant deviation from the formerly reported ones, especially concerning δ_C.[69b] The ^{19}F NMR spectrum of **13** shows (within the limits of error) the same chemical shift for the signal of the CF_3 group as observed in the case of **3**.

The solid-state structure of the monomeric silver(I) compound **13** is depicted in Figure 12.

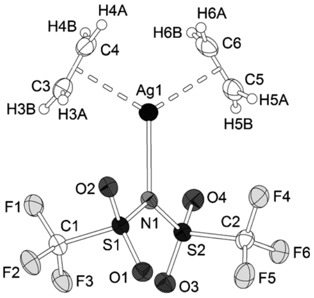


Figure 12. Molecular structure of $[Ag(C_2H_4)_2(NTf_2)]$ (**13**).

The silver atom in complex **13** is essentially trigonally planar coordinated through the nitrogen atom of the NTf_2^- ligand and two η^2-bound ethylene molecules. The Ag1−N1 bond length (2.343(2) Å) is in the expected range.[72] Moreover, there exist two intermolecular Ag···O contacts below the sum of the relevant van der Waals radii (3.2 Å[28]), one above and one below the $(C3\text{-}C4)_{centroid}$-Ag1-N1 plane, with a minimum distance of 2.8509(18) Å. Upon coordination of ethylene to silver(I) an elongation of the C=C bond (1.332(5) Å; determined at 100(2) K) is observed compared to crystalline ethylene (1.3137 Å; 85 K[71]), which is expectedly smaller than in the case of the copper(I) ethylene complex **12**. In comparison with **13**, slightly larger C=C bond lengths of 1.344(3) and 1.345(3) Å (determined at 100 K) are found in $[Ag(C_2H_4)_2\{Al(OCH(CF_3)_2)_4\}]$.[69b] Accordingly, the Ag−C distances determined for the latter compound ranging from 2.355(2) to 2.413(2) Å are shorter than those of **13** (2.413(3)–2.431(3) Å).

NMR studies concerning the stability of in situ generated Cu^I and Ag^I ethylene species: The potential of compounds **1**–**5** as reversible absorbers for ethylene was investigated by NMR experiments using NMR tubes with J. Young valves (for experimental details please refer to the Supporting Information). The chemical shifts for the isolated products (**12**, **13**) and the in situ-generated ethylene complexes as well as the signals observed after evaporation of the samples are listed in Table 5.

Table 5. Chemical shifts (in ppm) for $[D_2]CH_2Cl_2$ solutions of free ethylene,[38] **12**, **13**, and the in situ-generated complexes $\{\mathbf{X}+C_2H_4\}$ ($\mathbf{X}=\mathbf{1}$–$\mathbf{5}$). Additionally, for $\{\mathbf{X}+C_2H_4\}$ the δ_H and δ_C values after evaporation are listed. For δ_H, only the mean value is given in each case regardless of the signal form.

	Metal	δ_H	δ_C
C_2H_4, free		5.40	123.2
$[Cu(C_2H_4)(NTf_2)]_\infty$ (**12**)	Cu	5.06	98.2
1+C_2H_4	Cu	5.26	107.1
1+C_2H_4, after evaporation[a]	Cu	5.04	97.9
2+C_2H_4	Cu	5.05	101.0
2+C_2H_4, after evaporation	Cu	5.02	96.6
4+C_2H_4	Cu	5.19	108.6
4+C_2H_4, after evaporation	Cu	4.91	95.8
$[Ag(C_2H_4)_2(NTf_2)]$ (**13**)	Ag	5.77	115.1
3+C_2H_4	Ag	5.67	116.7
3+C_2H_4, after evaporation[b]	Ag	5.58[c]	–
5+C_2H_4	Ag	5.62	117.4
5+C_2H_4, after evaporation	Ag	5.74[c]	–

[a] Evacuation was carried out both at room temperature and at 50°C, for 1 h in each case. [b] NMR spectra were acquired in $[D_2]CH_2Cl_2$/$[D_8]$THF due to low solubility in $[D_2]CH_2Cl_2$. [c] Very weak signal intensity observed.

In general, it can be stated that an upfield shift is observed in the proton NMR spectra of the copper(I) ethylene complexes with respect to free ethylene. In contrast, in the case of the silver(I) ethylene compounds the corresponding signal is deshielded. For both the Cu^I and Ag^I ethylene species, only one somewhat broadened or slightly textured resonance occurs for the ethylene protons, suggesting coalescence of the signals for coordinated and free ethylene. Therefore, we tried to record a proton NMR spectrum of $\{\mathbf{3}+C_2H_4\}$ (see Table 5) at 193 K. Yet, we failed, presumably due to the lowered solubility of the complex as no signal corresponding to ethylene was present in the received NMR spectrum. Similar results were reported by the group of Krossing on their silver aluminates.[69b]

With respect to free ethylene, both the Cu^I ethylene species and the Ag^I ethylene complexes show an upfield shift by several ppm for the ^{13}C NMR resonance frequency of the olefinic carbon atoms; the shifts are more significant in the case of copper(I).

Upon evacuation of the samples δ_H of the ethylene moieties is, in most cases, only marginally influenced, regardless of the metal. In the case of the silver(I) ethylene complexes the olefin seems to be entirely removed in vacuo as can be seen from the very weak ethylene signals in the ^{1}H NMR spectra and the absence of the corresponding signals in the ^{13}C NMR spectra. After evacuation of the Cu^I-containing samples, a further shift to higher field is observed for the

^{13}C NMR resonances assigned to the ethylene moieties. Moreover, the carbon NMR spectra of these samples show chemical shifts that are rather in the range of that found for isolated **12**. There exist two possible interpretations for these findings: On the one hand, it might be assumed that δ_C observed for the in situ-prepared copper(I) ethylene complexes are averaged values. In other words, the ^{13}C NMR resonances of free ethylene and of the in situ-generated complexes, probably similar to **12**, coalesce (see above). As a consequence, only excess ethylene would have been removed upon evaporation of the Cu^I-containing samples. One the other hand, the shift to higher field should increase with a decreasing number of olefinic ligands coordinated to the copper(I) ion, namely due to the enhancement of the metal–olefin interaction. Thus, it is suggested that in ethylene-saturated solutions of {**X**+C_2H_4} (**X**=**1**, **2**, **4**; Table 5) more than one ethylene molecule interacts with the Cu^I ion, so that even cationic species such as $[Cu(C_2H_4)_n]^+$ (n=2, 3) might be present. In this context it is worth mentioning that Krossing and co-workers also reported that the upfield shift of the ^{13}C NMR signal of $[Ag(C_2H_4)_n]^+$ (n=1–3) is not only dependent on the number of ligands, but also found to be larger in the case of molecular species.[69b]

In summary, the silver(I)-containing compounds **3** and **5**, as well as the chemically more sensitive copper(I) bis(triflyl)imides **1**, **2**, and **4**, can serve as ethylene absorbers. However, in the case of the copper(I) compounds, higher temperatures may be required for ethylene desorption. An application of the well-characterized IL **5** in membrane-based processes might be the most promising perspective.

Conclusion

Herein, we have presented the first comprehensive and comparative reactivity and structural study of silver(I) versus copper(I) bistriflylimides regarding their reactions with the ionic liquid [emim]NTf$_2$, the arene 1,3,5-trimethylbenzene, and diverse olefins. Whereas pure and crystalline $[CuNTf_2]_\infty$ is unknown, we managed to fully characterize two solvent adducts with rather weakly bonded and inert ligands, namely the sandwich complex $[Cu(\eta^3\text{-MesH})_2][Cu(NTf_2)_2]$ (**1**) and the etherate $[Cu(Et_2O)(NTf_2)]$ (**2**). Furthermore, we determined the layer structure of crystalline $[AgNTf_2]_\infty$ (**3**), a technologically interesting compound that is nearly insoluble in non- or weakly-coordinating solvents such as dichloromethane but soluble in coordinating solvents like diethyl ether or in olefins.

Purging solutions of **1** and **3** with excess ethylene yielded $[Cu(C_2H_4)(NTf_2)]_\infty$ (**12**) and $[Ag(C_2H_4)_2(NTf_2)]$ (**13**) in the form of single crystals. Additionally, the two new complexes $[emim][M(NTf_2)_2]$ (M=Cu **4**, Ag **5**) were tested as potential chemisorbers for ethylene. The silver(I) containing compounds **3** and **5** proved to be reversible ethylene absorbers at room temperature.

A large structural diversity was found within the herein presented crystal structures incorporating the bis(triflyl)imide anion. In nearly all of the herein presented compounds (except those containing the olefin 1,5-COD), the NTf$_2^-$ anion is not weakly coordinating, but serves as ligand. As expected, in all cases strong bonds through the nitrogen atom of the NTf$_2^-$ anion are observed. In addition, in most cases the oxygen atoms of the bis(triflyl)imide take part in secondary interactions with the relevant coinage metal ions.

Experimental Section

Specifications of the equipment and methods used for characterization and the preparation of staring materials are given in the Supporting Information. CCDC-876577 (**1**), CCDC-876578 (**2**), CCDC-876579 (**3**), CCDC-876580 (**4**), CCDC-876581 (**6**), CCDC-876582 (**7**), CCDC-876583 (**8**), CCDC-876584 (**9**), CCDC-876585 (**10**), CCDC-876586 (**12**), CCDC-876587 (**12a**), and CCDC-876588 (**13**) 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.

[Cu(MesH)$_2$][Cu(NTf$_2$)$_2$] (1): A solution of HNTf$_2$ (2.81 g, 10.00 mmol) in CH_2Cl_2 (20 mL) was added to a Schlenk flask charged with $[Cu(Mes)]_5$ (1.83 g, 2.00 mmol). Instantly, boiling of the solvent was observed, accompanied by a color change of the reaction mixture from red/yellow to colorless. The reaction mixture was filtered by using a syringe filter and the solvent was removed in vacuo yielding **1** (4.42 g, 95 %) as fine crystalline colorless solid. ^{1}H NMR (250.1 MHz, $[D_2]CH_2Cl_2$): δ=2.32–2.52 (m, 18H; CH_3), 6.97–7.15 ppm (m, 6H; CH); ^{13}C NMR (62.9 MHz, $[D_2]CH_2Cl_2$): δ=21.2 (CH_3), 119.6 (q, ^1J(C,F)=323 Hz; CF_3), 121.3 (CH), 136.2 ppm (CCH$_3$); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): δ=−74.8 (CF_3) ppm; IR (neat): $\tilde{\nu}$=3054 (vw), 2965 (vw), 2931 (vw), 2864 (vw), 1816 (vw), 1590 (w), 1573 (w), 1500 (vw), 1464 (w), 1388 (s), 1376 (s), 1323 (w), 1299 (w), 1217 (s), 1194 (vs), 1130 (vs), 1039 (m), 1022 (m), 967 (vs), 861 (m), 839 (m), 765 (w), 690 (w), 660 (m), 606 (vs), 566 (vs), 534 (w), 507 cm^{-1} (vs); APCI-MS (negative mode): m/z (%) calcd for $C_2F_6NO_4S_2$: 279.9178; found: 279.9171 $[NTf_2]^-$ (35); calcd for $C_2ClF_6NNaO_4S_2$: 337.8765; found: 337.8755 $[NTf_2+NaCl]^-$ (100), 416 (16); elemental analysis calcd (%) for $C_{22}H_{24}Cu_2F_{12}N_2O_8S_4$ (927.78 g mol^{-1}): C 28.48, H 2.61, N 3.02; found: C 28.08, H 2.42, N 3.34. Single crystals of **1** were obtained from CH_2Cl_2 at −20 °C.

[Cu(Et$_2$O)(NTf$_2$)] (2): Complex **2** was prepared by dissolving **1** (2.25 g, 2.43 mmol) in Et_2O (25 mL) and storing the solution at −30 °C overnight. The solvent was removed through a syringe at −35 °C and the crystalline colorless solid was washed with cold ether. After removal of the solvent the solid was dried under vacuum to give **2** (1.12 g, 55 %) as colorless needles. ^{1}H NMR (300.1 MHz, $[D_2]CH_2Cl_2$): δ=1.46 (t, ^3J(H,H)=7.1 Hz, 6H; CH_3), 3.87 ppm (q, ^3J(H,H)=7.0 Hz, 4H; CH_2); ^{13}C NMR (62.9 MHz, $[D_2]CH_2Cl_2$): δ=16.2 (CH_3), 72.5 (CH_2), 119.7 ppm (q, ^1J(C,F)=322 Hz; CF_3); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): δ=−75.1 ppm (CF_3); IR (neat): $\tilde{\nu}$=2981 (w), 2955 (vw), 2937 (vw), 2909 (w), 2876 (vw), 1813 (vw), 1490 (vw), 1458 (w), 1448 (w), 1378 (s), 1365 (s), 1301 (w), 1235 (m), 1195 (vs), 1150 (m), 1124 (s), 1085 (m), 1049 (m), 1038 (m), 970 (vs), 926 (m), 850 (m), 834 (m), 763 (w), 656 (m), 601 (vs), 567 (vs), 534 (m), 508 cm^{-1} (vs); APCI-MS (negative mode): m/z (%) calcd for $C_2F_6NO_4S_2$: 279.9178; found: 279.9172 $[NTf_2]^-$ (35); calcd for $C_2ClF_6NNaO_4S_2$: 337.8765; found: 337.8756 $[NTf_2+NaCl]^-$ (100); elemental analysis calcd (%) for $C_6H_{10}CuF_6NO_5S_2$ (417.82 g mol^{-1}): C 17.25, H 2.41, N 3.45; found: C 17.12, H 2.32, N 3.62. Single crystals of **2** were grown from Et_2O at −20 °C. Complex **2** shows disproportionation in MeOH, that is, formation of elemental copper is observed.

AgNTf$_2$ (3): Silver(I) bis(trifluoromethanesulfonyl)imide was prepared by two different methods.

Method A:[9] A solution of NaOH (5.49 g, 137.25 mmol) in water (230 mL) was added dropwise to a solution of $AgNO_3$ (15.55 g, 91.54 mmol) in water (275 mL). The precipitate was collected by filtration and washed with water until the washings were pH neutral. A solution of $HNTf_2$ (18.00 g, 64.02 mmol) in water (260 mL) was added. The reaction mixture was stirred overnight at ambient temperature. The unreacted silver salt was filtered off and the water was removed at the rotary evaporator. The colorless solid was recrystallized from CH_2Cl_2 and dried in vacuo to yield $AgNTf_2$ (12.83 g, 52 %).

Method B: A solution of $HNTf_2$ (141 mg, 0.50 mmol) in CH_2Cl_2 (4 mL) was added to $[Ag(Mes)]_4$ (114 mg, 0.13 mmol). During the addition the color of the reaction mixture changed from yellow to colorless. After stirring overnight at ambient temperature the solution was filtered via a syringe filter and the solvent was removed under vacuum to give **3** in good yield (145 mg, 75 %). ^{13}C NMR (62.9 MHz, $[D_2]CH_2Cl_2/[D_8]THF$ (11:1)): $\delta = 24.9$ ($[D_8]THF$), 67.8 ($[D_8]THF$), 120.2 ppm (q, $^1J(C,F) = 322$ Hz; CF_3); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2/[D_8]THF$ (11:1)): $\delta = -75.7$ ppm (CF_3); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): $\delta = -74.8$ (CF_3) ppm; IR (neat): $\tilde{\nu} = 1758$ (vw), 1329 (m), 1306 (m), 1196 (vs), 1098 (vs), 1020 (vs), 822 (w), 791 (s), 771 (w), 732 (s), 636 (m), 582 (vs), 567 (vs), 533 (m), 502 (vs), 425 (m), 403 cm^{-1} (w); APCI-MS (positive mode): m/z (%): calcd for Ag: 106.9045; found: 106.9044 $[Ag]^+$ (100), 123 (26), 132 (19), 139 (91), 148 (70), 155 (14), 164 (12), 171 (78), 180 (73), 189 (45), 416 (43), 425 (32), 434 (13); APCI-MS (negative mode): m/z (%): calcd for $C_2F_6NO_4S_2$: 279.9178; found: 279.9172 $[NTf_2]^-$ (100); calcd for $C_2ClF_6NNaO_4S_2$: 337.8765; found: 337.8758 $[NTf_2+NaCl]^-$ (47), 422 (65), 424 (85); elemental analysis calcd (%) for $C_2AgF_6NO_4S_2$ (388.02 $g\,mol^{-1}$): C 6.19, H 0.00, N 3.61, S 16.53; found: C 6.54, H 0.00, N 3.97, S 16.74. Single crystals of **3** were obtained from CH_2Cl_2 at −20 °C when attempting to crystallize $[emim][Ag(NTf_2)_2]$ (**5**). Compound **3** shows disproportionation in MeOH, that is, formation of elemental silver is observed.

[emim][Cu(NTf₂)₂] (4): CH_2Cl_2 (5 mL) was added to a mixture of **2** (106 mg, 0.25 mmol) and $[emim]NTf_2$ (99 mg, 0.25 mmol). After the reaction mixture had been stirred at room temperature for 1 h, the solvent was removed in vacuo and the colorless solid was dried under vacuum to give **4** (184 mg, 100 %). M.p. 66 °C (decomp 365 °C); ^1H NMR (250.1 MHz, $[D_2]CH_2Cl_2$): $\delta = 1.56$ (t, $^3J(H,H) = 7.4$ Hz, 3H; CH_2CH_3), 3.91 (s, 3H; CH_3), 4.21 (q, $^3J(H,H) = 7.4$ Hz, 2H; CH_2CH_3), 7.18–7.40 (m, 2H; CH(4,5)), 8.26 ppm (brs, 1H; CH(2)); ^{13}C NMR (62.9 MHz, $[D_2]CH_2Cl_2$): $\delta = 15.3$ (CH_2CH_3), 37.0 (CH_2CH_3), 46.1 (CH_3), 119.7 (q, $^1J(C,F) = 323$ Hz; CF_3), 122.7 (CH(4,5)), 124.4 (CH(4,5)), 134.8 ppm (CH(2)); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): $\delta = -75.2$ ppm (CF_3); IR (neat): $\tilde{\nu} = 3164$ (w), 3110 (w), 3000 (vw), 2962 (w), 1814 (vw), 1608 (w), 1568 (m), 1472 (vw), 1454 (vw), 1427 (vw), 1389 (s), 1372 (m), 1339 (m), 1323 (w), 1300 (vw), 1260 (m), 1192 (vs), 1167 (s), 1123 (vs), 1031 (m), 1022 (m), 965 (vs), 840 (s), 802 (m), 765 (m), 745 (m), 703 (m), 658 (m), 601 (vs), 567 (vs), 536 (m), 508 (vs), 433 (m), 422 cm^{-1} (m); ESI-MS (positive mode): m/z calcd (%) for $C_6H_{11}N_2$: 111.0917; found: 111.0915 $[emim]^+$ (100); APCI-MS (negative mode): m/z calcd (%) for $C_2F_6NO_4S_2$: 279.9178; found: 279.9174 $[NTf_2]^-$ (44); calcd for $C_2ClF_6NNaO_4S_2$: 337.8765; found: 337.8759 $[NTf_2+NaCl]^-$ (100); elemental analysis calcd (%) for $C_{10}H_{11}CuF_{12}N_4O_8S_4$ (735.01 $g\,mol^{-1}$): C 16.34, H 1.51, N 7.62; found: C 16.65, H 1.73, N 7.89. Single crystals of **4** were grown from CH_2Cl_2 at −20 °C.

[emim][Ag(NTf₂)₂] (5): CH_2Cl_2 (10 mL) was added to a Schlenk flask charged with **3** (204 mg, 0.53 mmol) and $[emim]NTf_2$ (206 mg, 0.53 mmol). After the reaction mixture had been stirred at ambient temperature for 1 h, the solvent was removed in vacuo and the colorless, viscous residue was dried by freeze-drying to give **5** (410 mg, 99 %). Glass transition −50 °C; m.p. 21 °C (decomp 392 °C); ^1H NMR (250.1 MHz, $[D_2]CH_2Cl_2$): $\delta = 1.55$ (t, $^3J(H,H) = 7.4$ Hz, 3H; CH_2CH_3), 3.91 (s, 3H; CH_3), 4.21 (q, $^3J(H,H) = 7.4$ Hz, 2H; CH_2CH_3), 7.27 (pt, $^{3,4}J(H,H) = 1.8$ Hz, 2H; CH(4,5)), 8.40 ppm (brs, 1H; CH(2)); ^{13}C NMR (62.9 MHz, $[D_2]CH_2Cl_2$): $\delta = 15.3$ (CH_2CH_3), 36.9 (CH_2CH_3), 46.0 (CH_3), 120.0 (q, $^1J(C,F) = 322$ Hz; CF_3), 122.5 (CH(4,5)), 124.2 (CH(4,5)), 135.2 ppm (CH(2)); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): $\delta = -76.1$ ppm (CF_3); IR (neat): $\tilde{\nu} = 3162$ (w), 3123 (vw), 2990 (vw), 1572 (w), 1471 (vw), 1457 (vw), 1431 (vw), 1370 (m), 1350 (m), 1181 (vs), 1124 (vs), 1058 (m), 998 (vs), 840 (w), 791 (m), 743 (m), 702 (w), 649 (m), 609 (vs), 595 (s), 568 (s), 533 (w), 508 (s), 403 cm^{-1} (vw); ESI-MS (positive mode): m/z (%): 83 (40), calcd for Ag: 106.9045; found: 106.9046 $[Ag]^+$ (39); calcd for Ag: 111.0917; found: 111.0917 (100) $[emim]^+$; (m/z calcd for $C_6H_{11}N_2$: 111.0917), 148 (26), 188 (89); APCI-MS (negative mode): m/z (%) calcd for $C_2F_6NO_4S_2$: 279.9178; found: 279.9180 $[NTf_2]^-$ (89); calcd for $C_4F_{12}N_2NaO_8S_4$: 582.8249; found: 582.8255 $[2\times NTf_2+Na]^-$ (56); calcd for $C_4F_{12}KN_2O_8S_4$: 598.7988; found: 598.7995 $[2\times NTf_2+K]^-$ (53); calcd for $C_4AgF_{12}N_2O_8S_4$: 668.7383; found: 668.7395 $[Ag(NTf_2)_2]^-$ (100); elemental analysis calcd (%) for $C_{10}H_{11}AgF_{12}N_4O_8S_4$ (779.33 $g\,mol^{-1}$): C 15.41, H 1.42, N 7.19, S 16.46; found: C 15.84, H 1.55, N 7.46, S 16.54.

[Cu(cod)₂]NTf₂ (6): COD (0.3 mL, 270 mg, 2.50 mmol) was added to a solution of **2** (417 mg, 1.00 mmol) in CH_2Cl_2 (2 mL). Meanwhile, boiling of the solvent was observed. Stirring was continued for 1 h at room temperature. When covering the colorless solution with a layer of *n*-hexane (1 mL) a colorless crystalline solid precipitated instantly. The supernatant solution was removed by using a syringe and the solid was dried under vacuum yielding **6** (476 mg, 85 %). ^1H NMR (300.1 MHz, $[D_2]CH_2Cl_2$): $\delta = 2.53$ (brs, 16H; CH_2), 5.75–6.10 ppm (m, 8H; CH); ^{13}C NMR (62.9 MHz, $[D_2]CH_2Cl_2$): $\delta = 28.3$ (CH_2), 120.3 (q, $^1J(C,F) = 322$ Hz; CF_3), 123.3 ppm (CH); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): $\delta = -77.8$ ppm (CF_3); IR (neat): $\tilde{\nu} = 3038$ (vw), 3010 (w), 2958 (w), 2901 (m), 2846 (w), 1841 (w), 1791 (w), 1591 (w), 1486 (m), 1452 (w), 1432 (m), 1394 (vw), 1355 (s), 1335 (s), 1238 (m), 1180 (vs), 1164 (vs), 1134 (vs), 1083 (m), 1045 (s), 1032 (s), 1001 (m), 988 (m), 907 (m), 872 (m), 852 (m), 825 (m), 791 (m), 761 (s), 735 (m), 683 (vw), 664 (m), 610 (vs), 566 (s), 510 (s), 406 cm^{-1} (m); ESI-MS (negative mode): m/z (%) calcd for $C_2F_6NO_4S_2$ 279.9178; found: 279.9174 $[NTf_2]^-$ (100); calcd for $C_4F_{12}N_2NaO_8S_4$: 582.8249; found: 582.8233 $[2\times NTf_2+Na]^-$ (18); calcd for $C_6F_{18}N_3Na_2O_{12}S_6$: 885.7320; found: 885.7296 $[3\times NTf_2+2\times Na]^-$ (3); elemental analysis calcd (%) for $C_{18}H_{24}CuF_6NO_4S_2$ (560.06 $g\,mol^{-1}$): C 38.60, H 4.32, N 2.50, S 11.45; found: C 38.62, H 4.30, N 2.52, S 11.58. Single crystals of **6** were grown from CH_2Cl_2/*n*-hexane at room temperature. Complex **6** was also yielded by applying the same procedure, but using **1** as Cu^I starting material.

[Ag(cod)₂]NTf₂ (7): COD (0.3 mL, 287 mg, 2.65 mmol) was added to an ethereal solution (2.5 mL Et_2O) of **3** (412 mg, 1.06 mmol). Instantly, boiling of the solvent was observed and a crystalline precipitate was obtained. The supernatant liquid was removed by decantation and the solid was dried in vacuo to yield **7** as colorless solid. ^1H NMR (250.1 MHz, $[D_2]CH_2Cl_2$): $\delta = 2.37$–2.65 (m, 16H; CH_2), 5.95–6.22 ppm (m, 8H; CH); ^{13}C NMR (62.9 MHz, $[D_2]CH_2Cl_2$): $\delta = 28.3$ (CH_2), 120.3 (q, $^1J(C,F) = 322$ Hz; CF_3), 126.8 ppm (CH); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): $\delta = -77.4$ ppm (CF_3); IR (neat): $\tilde{\nu} = 3032$ (vw), 3003 (vw), 2959 (w), 2935 (w), 2900 (w), 2845 (w), 1839 (vw), 1790 (vw), 1602 (w), 1488 (m), 1452 (w), 1430 (m), 1395 (vw), 1354 (s), 1337 (s), 1296 (w), 1262 (m), 1239 (m), 1165 (vs), 1135 (vs), 1084 (m), 1045 (vs), 1031 (vs), 986 (m), 909 (m), 883 (w), 845 (m), 821 (s), 792 (m), 749 (s), 739 (m), 725 (m), 674 (w), 660 (m), 610 (vs), 566 (vs), 510 (s), 436 cm^{-1} (w); APCI-MS (negative mode): m/z (%): 227 (28), calcd for $C_2F_6NO_4S_2$: 279.9178; found: 279.9180 (31) $[NTf_2]^-$; 338 $[NTf_2+NaCl]^-$ (92), 416 (67); elemental analysis calcd (%) for $C_{18}H_{24}AgF_6NO_4S_2$ (604.39 $g\,mol^{-1}$): C 35.77, H 4.00, N 2.32; found: C 35.43, H 3.98, N 2.65. Single crystals of **7** were obtained from CH_2Cl_2/*n*-hexane at ambient temperature.

[Cu(η²-nbd)₂(NTf₂)] (8): NBD (0.2 mL, 182 mg, 1.98 mmol) was added to a solution of **2** (320 mg, 0.77 mmol) in CH_2Cl_2 (1.5 mL). A colorless crystalline solid precipitated from the reaction mixture at room temperature overnight. The supernatant solution was removed via a syringe and the obtained solid was dried under vacuum yielding **8** in the form of a colorless solid. ^1H NMR (300.1 MHz, $[D_2]CH_2Cl_2$): $\delta = 2.00$ (t, $^3J(H,H) = 1.5$ Hz, 4H; CH_2), 3.86 (sept, $^{3,4}J(H,H) = 1.6$ Hz, 4H; CH), 6.77 ppm (t, $^3J(H,H) = 1.7$ Hz, 8H; CH_{olef}); ^{13}C NMR (62.9 MHz, $[D_2]CH_2Cl_2$): $\delta = 51.7$ (CH), 72.7 (CH_2), 119.9 (q, $^1J(C,F) = 323$ Hz; CF_3), 137.5 ppm (CH_{olef}); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): $\delta = -74.6$ ppm (CF_3); IR (neat): $\tilde{\nu} = 3493$ (vw), 3083 (vw), 3063 (vw), 3027 (w), 2990 (w), 2927 (m), 2864 (m), 1781 (vw), 1597 (vw), 1561 (w), 1481 (vw), 1457 (m), 1384 (s), 1364 (m), 1312 (m), 1272 (w), 1234 (m), 1192 (vs), 1128 (vs), 1010 (m), 964 (vs), 941 (m), 882 (m), 850 (m), 813 (m), 801 (s), 793 (s), 772 (m), 756 (m), 710 (m), 689 (vs), 649 (m), 612 (vs), 566 (vs), 540 (m), 507 (vs), 471 (m), 433 (m), 421 cm^{-1} (m); APCI-MS (negative mode): m/z (%)

calcd for $C_2F_6NO_4S_2$: 279.9181; found 279.9178 $[NTf_2]^-$ (34); calcd for $C_2ClF_6NNaO_4S_2$: 337.8765; found: 337.8765 $[NTf_2+NaCl]^-$ (100); 416 (16); elemental analysis calcd (%) for $C_{16}H_{16}CuF_6NO_4S_2$ (527.98 g mol^{-1}): C 36.40, H 3.05, N 2.65; found: C 36.04, H 2.94, N 2.57. Single crystals of **8** were grown from CH_2Cl_2 at room temperature. Complex **8** was also prepared by applying a 0.5 M solution (with respect to copper) of **1** in CH_2Cl_2, at which **1** and NBD were employed in a molar ratio of 1:5. After covering the reaction mixture with a layer of *n*-hexane, **8** was isolated by decanting the supernatant solution and dried in vacuo.

$[Cu_2(\eta^2{:}\eta^2\text{-nbd})(NTf_2)_2]_\infty$ (9): NBD (0.03 mL, 23 mg, 0.25 mmol) was added to a solution of **1** (232 mg, 0.25 mmol) in CH_2Cl_2 (1 mL). Instantly, a colorless solid precipitated and the supernatant solution was decanted. The solid was washed with CH_2Cl_2 three times and dried under vacuum to give **9** (164 mg, 84%). ^{1}H NMR (250.1 MHz, $[D_2]CH_2Cl_2$): $\delta = 2.03$ (br s, 2H; CH_2), 3.86–3.92 (m, 2H; CH), 6.36 ppm (br s, 4H; CH_{olef}); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): $\delta = -74.6$ ppm (CF_3); IR (neat): $\tilde{\nu} =$ 3504 (w), 3493 (w), 2943 (vw), 1600 (vw), 1471 (vw), 1456 (vw), 1387 (s), 1353 (m), 1344 (m), 1327 (m), 1303 (m), 1285 (w), 1208 (s), 1193 (vs), 1129 (m), 1120 (m), 1104 (s), 1061 (m), 989 (vs), 921 (m), 895 (w), 859 (w), 811 (m), 789 (m), 759 (m), 664 (m), 646 (m), 607 (vs), 594 (s), 569 (s), 540 (m), 507 (vs), 415 cm^{-1} (m); ESI-MS (negative mode): *m/z* (%) calcd for $C_2F_6NO_4S_2$: 279.9178; found: 279.9181 $[NTf_2]^-$ (49); calcd for $C_2ClF_6NNaO_4S_2$: 337.8765; found: 337.8766 $[NTf_2+NaCl]^-$ (100); 416 (17); elemental analysis calcd (%) for $C_{11}H_8Cu_2F_{12}N_2O_8S_4$ (779.53 g mol^{-1}): C 16.95, H 1.03, N 3.59, S 16.45; found: C 16.88, H 1.42, N 3.88, S 16.75.

$[Ag(\eta^2{:}\eta^2\text{-nbd})(NTf_2)]_\infty$ (10): NBD (0.3 mL, 230 mg, 2.50 mmol) was added to an ethereal solution (2 mL Et_2O) of **3** (388 mg, 1.00 mmol). Almost instantly, a colorless crystalline solid precipitated. All volatile components were removed in vacuo yielding **10**. ^{1}H NMR (250.1 MHz, $[D_2]CH_2Cl_2$): $\delta = 2.14$ (t, ^3J(H,H) = 1.5 Hz, 2H; CH_2), 3.96 (sept, $^{3,4}J$(H,H) = 1.8 Hz, 2H; CH), 7.30 ppm (t, ^3J(H,H) = 1.9 Hz, 4H; CH_{olef}); ^{13}C NMR (62.9 MHz, $[D_2]CH_2Cl_2$): $\delta = 51.9$ (CH), 77.9 (CH_2), 120.0 (q, ^1J(C,F) = 323 Hz; CF_3), 144.5 ppm (CH_{olef}); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): $\delta = -74.9$ ppm (CF_3); IR (neat): $\tilde{\nu} = 3093$ (vw), 3068 (vw), 3023 (vw), 2961 (vw), 2926 (vw), 2856 (vw), 1658 (vw), 1521 (vw), 1485 (w), 1460 (w), 1366 (m), 1355 (m), 1343 (m), 1329 (m), 1311 (m), 1261 (w), 1238 (m), 1182 (vs), 1127 (s), 1056 (m), 1009 (s), 980 (m), 953 (m), 926 (m), 887 (m), 791 (m), 771 (m), 731 (m), 670 (m), 634 (m), 608 (vs), 568 (s), 511 (s), 432 (m), 406 cm^{-1} (m); APCI-MS (negative mode): *m/z* (%) calcd for $C_2F_6NO_4S_2$: 279.9178; found: 279.9180 $[NTf_2]^-$ (36); calcd for $C_2ClF_6NNaO_4S_2$: 337.8765; found: 337.8766 $[NTf_2+NaCl]^-$; 416 (14); elemental analysis calcd (%) for $C_{27}H_{24}Ag_3F_{18}N_3O_{12}S_6$ (1440.48 g mol^{-1}): C 22.51, H 1.68, N 2.92, S 13.36; found: C 22.76, H 1.83, N 3.10, S 13.22. Single crystals of **10** were obtained from Et_2O at ambient temperature.

$[Ag_2(\eta^2{:}\eta^2\text{-isoprene})(NTf_2)_2]_\infty$ (11): Isoprene (0.3 mL, 170 mg, 2.50 mmol) was added to a solution of **3** (196 mg, 0.51 mmol) in Et_2O (2 mL). After stirring overnight the reaction mixture was filtered through a syringe filter and the filtrate was evaporated to dryness. The colorless solid was dried by freeze-drying. ^{1}H NMR (250.1 MHz, $[D_2]CH_2Cl_2$): $\delta =$ 2.02 (br s, 3H; CH_3), 5.34–5.43 (m, 3H; C_qCH_2, $CHCH_2$), 5.46 (br s, 1H; $CHCH_2$), 6.92 ppm (dd, ^3J(H,H) = 10.0, 17.1 Hz, 1H; CH); ^{13}C NMR (62.9 MHz, $[D_2]CH_2Cl_2$): $\delta = 18.3$ (CH_3), 106.5 (C_qCH_2), 117.1 ($CHCH_2$), 120.0 (q, ^1J(C,F) = 322 Hz; CF_3), 137.8 ($CHCH_2$), 143.4 ppm (C_q); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): $\delta = -74.9$ ppm (CF_3); elemental analysis calcd (%) for $C_9H_8Ag_2F_{12}N_2O_8S_4$ (844.16 g mol^{-1}): C 12.81, H 0.96, N 3.32, S 15.19; found: C 8.29, H 0.51, N 3.79, S 16.24. Single crystals of **11** were obtained from CH_2Cl_2 at −20 °C.

$[Cu(C_2H_4)(NTf_2)]_\infty$ (12): Ethylene was passed through a solution of **1** (232 mg, 0.25 mmol) in CH_2Cl_2 (1 mL) at room temperature for 1 min. Complex **12** precipitated at −20 °C in the form of colorless single crystals suitable for an X-ray structure analysis. The supernatant solution was removed through a syringe and the colorless crystalline solid was dried in a stream of ethylene yielding **12**. ^{1}H NMR (250.1 MHz, $[D_2]CH_2Cl_2$): $\delta =$ 5.06 ppm (br s, 4H; CH); ^{13}C NMR (62.9 MHz, $[D_2]CH_2Cl_2$): $\delta = 98.2$ (CH), 119.6 ppm (q, ^1J(C,F) = 322 Hz; CF_3); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): $\delta = -74.9$ ppm (CF_3); IR (neat): $\tilde{\nu} = 3097$ (vw), 2988 (vw), 1785 (vw), 1738 (vw), 1544 (vw), 1421 (w), 1390 (m), 1357 (m), 1340 (m), 1306 (w), 1285 (w), 1191 (vs), 1112 (vs), 1060 (m), 980 (s), 963 (vs), 836 (w), 819 (m), 794 (m), 770 (w), 750 (m), 701 (vw), 660 (m), 588 (vs), 568 (vs), 533 (m), 501 (vs), 420 cm^{-1} (m); APCI-MS (negative mode): *m/z* calcd (%) for $C_2F_6NO_4S_2$: 279.9178; found: 279.9178 $[NTf_2]^-$ (21); elemental analysis calcd (%) for $C_4H_4CuF_6NO_4S_2$ (371.75 g mol^{-1}): C 12.92, H 1.08, N 3.77; found: C 12.59, H 1.06, N 4.04. Applying a 0.5 M solution (with respect to copper) of **2** in CH_2Cl_2 yielded a pale purple solution from which **12** could not be isolated. Single crystals of **12** deliquesce when exposed to a stream of ethylene. However, after a short time, excess ethylene is released and **12** recrystallizes.

$[Ag(C_2H_4)_2(NTf_2)]$ (13): A stream of ethylene was introduced into a solution of **3** (194 mg, 0.50 mmol) in Et_2O (1 mL) at ambient temperature for about 30 s. The diethyl ether was almost quantitatively evaporated by passing the gaseous olefin through. Upon addition of CH_2Cl_2 (1 mL) a colorless solution was obtained, from which **13** precipitated at −20 °C as colorless single crystals. ^{1}H NMR (250.1 MHz, $[D_2]CH_2Cl_2$): $\delta = 5.77$ ppm (br s, 8H; CH); ^{13}C NMR (62.9 MHz, $[D_2]CH_2Cl_2$): $\delta = 115.1$ (CH), 120.0 ppm (q, ^1J(C,F) = 322 Hz; CF_3); ^{19}F NMR (282.4 MHz, $[D_2]CH_2Cl_2$): $\delta = -74.8$ ppm (CF_3).

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