Supporting Information

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Cationic Tri(ferrocenecarbonitrile)silver(I)

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Dynamic ligand exchange studies

Because of the small chemical shift differences between complexes **3** and **2** in the ^{1}H NMR spectra it is expected that low temperature NMR analysis will not show a significant signal splitting for **2** and **3**. Therefore, the ligand exchange in solution was proven by the reaction of different molar ratios of silver(I) triflate (**1**) and **2** in dichloromethane (molar ratios of 1 : 4 to 3 : 1). After 24 h a sample of the reaction solution was taken off and dried under reduced pressure, followed by ^{1}H NMR analysis. The results are shown in Figure S1.

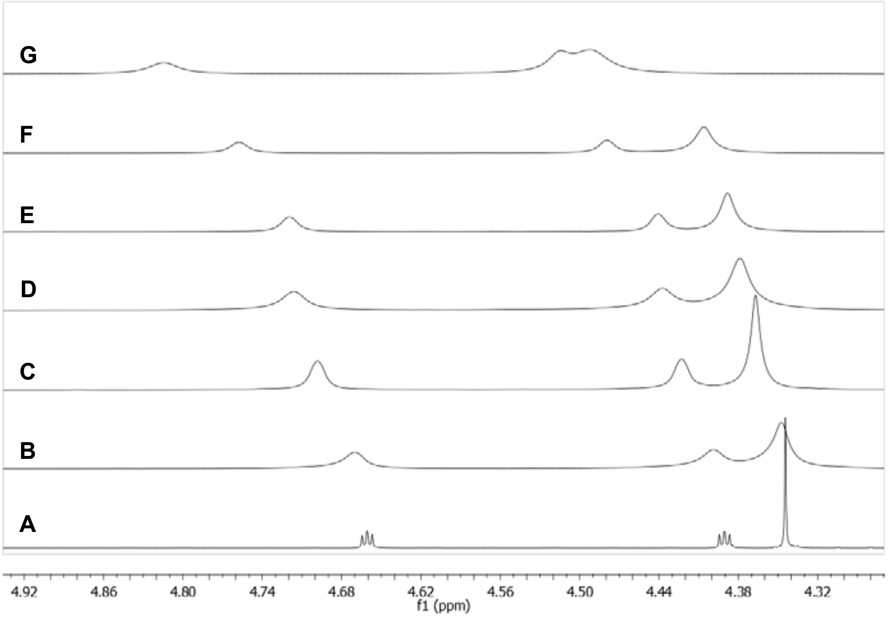

Figure S1 ^{1}H NMR spectra (CDCl$_3$) of the reaction solutions of different molar ratios of **1**:**3**: **A** pure **2**; **B** 0.25:3; **C** 0.5:3; **D** 0.75:3, **E** 1.3, **F** 1:1, **G** isolated complex **3**.

As shown in Figure S1 the increase of the amount of **1** resulted in a progressive shift to lower field without any separation between the signals of **2** and **3**. Also the coupling pattern of the *α*- and *β*-protons, which is observable for pure **2** (**A**) is not resolved. Due to the incompleted turnover (maximum yield is about 60 %) even reaction mixture **F**, which formally contains an excess of **2**, shows signal positions shifted to higher field than the isolated complex **3** (**G**).

X-ray crystallography

As described in the manuscript, intensity data for **3** was collected with an Oxford Gemini S diffractometer with MoK*α* radiation. SHELXS-2013 / SHELXL-2013 were used to solve/refine the structure [1]. Crystal data and numbers pertinent to data collection and structure refinement are summarized in Table S1.

Some comments are required: During the refinement of **3** several problems were recognized, which are closely related to observations made by Xu *et al.* for the described complex 1,3,5-tris{[4-cyano-bis-(2,5,8-trioxanonyl)phenyl]ethynyl}-benzene*4AgOTf (**21**) (CSD Refcode: NANHOZ1[1]) [2]. Here we refer at first to problems reported by Xu *et al.* [2] in assigning the correct space group. Handling the dataset of **3** in rhombohedral symmetry gave systematic extinctions for space groups as observed and reported for **21**. In contrast to **21** [2], however, for **3** all likely rhombohedral space groups lead to a complex disorder. It is then not only due to checks of different possible rhombohedral space groups with PLATON [3] and/or the IUCr checkcif procedure that the space group $R3_2$ has been selected for **3**, we also handled the dataset in monoclinic symmetry. Such final data sets were rejected by PLATON and instead the rhombohedral space group $R3_2$ has been assigned.

The Ag atoms of **3A** and **3B** are located at Wyckoff 6*c* sites, thus having a multiplicity of 3, along a threefold screw axis (3_2). Both **3A** and **3B** possess thus C_3 molecular symmetry. For C_3 symmetric **3A**/**3B** the Ag atom would thus have an occupation factor of 1/3 and one crystallographic independent ferrocenecarbonitrile ligand. Such a refinement, as described for **21** [2], did give, however, non-reliable results and/or was not conceivable. A reasonable refinement was possible only by assuming a statistical disorder of the cationic $[Ag(FcC{\equiv}N)_3]^+$ fragments along the 3_2 screw axes. This statistical disorder could be then reasonably modelled, at least for the cationic parts of **3A** and **3B**. Due to this disorder the number of required symmetry codes increases (Figures S2 and S3) of the molecular structure of **3A** and **3B**, respectively.

For the triflate counter ions the situation is even more complicated. For **21**, Xu *et al.* described precisely how the OTf$^-$ ions have been treated, especially those which was closely interacting with one Ag atom, namely Ag1 [2]. As the distance between the

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[1] Unless stated otherwise, here and in the following sequences of six capital letters refer to CSD Refcodes [4].

Ag1 atoms (both atoms are located along 3_2 screw axes at 6*c* sites) is 7.32 Å only, Xu *et al.* did place the OTf^- ions not in between the silver atoms. That is fully reasonable as in such a case “either the oxygen or the fluorine atoms of the triflate ions would approach Ag1 sites at chemically unreasonable distances” [2]. Thus, Xu *et al.* placed the OTf^- ions away from the 3_2 screw axes and managed its refinement as a 6-fold disordered ion excellently.

In our case, however, the situation is different. With the atoms Ag1 and Ag2 at 6*c* sites being statistically disordered along the 3_2 screw axes we observed possible Ag···Ag “contacts” with an OTf^- ion within the “contact path” of 7.44 Å and 8.63 Å. The shorter Ag···Ag “contact” can be ruled out due to the statistical disorder and consequently the OTf^- ion can be placed with its 3-fold axis on the 3_2 screw axes. (Additionally, it should be emphasized that all trials to refine OTf^- in a canted orientation with respect to the 3_2 screw axes gave non-reliable results and/or were not possible.) Provided that this is correct, a curious observation is made. So far, OTf^- ions are observed to interact with explicitly one Ag(I) ion in the κO or $\kappa^2 O,O'$ fashion. Thus, a $\kappa^3 O,O',O''$ interaction of OTf^- ions with Ag(I) ions and, moreover, any other transition metal ions, has never been observed. For the κO coordination an Ag-O bond range of 2.075 Å (ECABAN) to 3.017 Å (PURZUY) is already reported with a median of 2.470 Å and a lower/higher quartile of 2.328/2.640 Å for 1047 observations. For the $\kappa^2 O,O'$ coordination an Ag-O bond range of 2.487 Å (OGEXEE) to 2.905 Å (PEXSEQ) is reported, the median is 2.714 Å and the lower/higher quartile 2.634/2.838 Å for 22 observations. With Ag···O contacts of 3.11(2)/3.00(2) Å for **3A/3B** we observed values, which are already placed at the almost upper end compared to already reported entries. For completeness it should be mentioned that the sum of the van der Waals radii of Ag and O amounts to 3.22 Å. In summary we rule out that there is a dative bond between the OTf^- ions and the Ag atoms of **3A/3B**.

Table S1 Crystal structure data for **3**.

Formula	$C_{68}H_{54}Ag_2F_6Fe_6N_6O_6S_2$
M_r	1780.13
Cryst. size, mm^3	0.32 × 0.22 × 0.1
Crystal system	Trigonal
Space group	$R3_2$
a, Å	16.6846(6)
b, Å	16.6846(6)
c, Å	20.4137(9)
γ, deg	120.0
V, Å^3	4921.3(4)
Z	3
D_{calcd}, g cm^{-3}	1.802
$\mu(MoK_\alpha)$, cm^{-1}	2.009
$F(000)$, e	2664
hkl range	-19 - 19; -19 - 19; -24 – 22
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.595
Refl. measured	12049
Refl. unique	1913
R_{int}	0.0540
Param. refined	142
$R(F)$ / $wR(F^2)$[a] (all reflexions)	0.1095 / 0.2718
x(Flack)	0.48(3)
GoF (F^2)[b]	1.077
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	1.820 / -1.065

[a] $R1 = ||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2)+(\mathrm{A}P)^2+\mathrm{B}P]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0)+2F_c^2)/3$; [b] $\mathrm{GoF} = [\Sigma w(F_o^2-F_c^2)^2/(n_{\mathrm{obs}}-n_{\mathrm{param}})]^{1/2}$

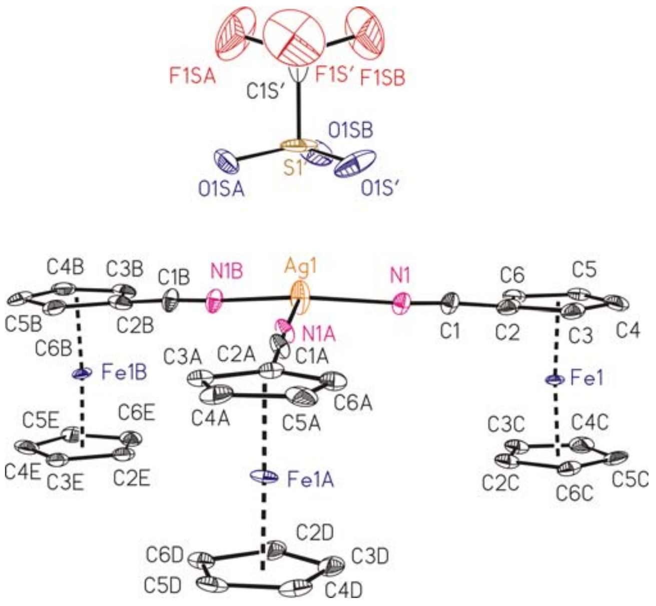

Figure S2 ORTEP diagram (30 % ellipsoid probability) of the molecular structure of **3A**. All hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed. Symmetry code for A–E labelled atoms: A: –y + 1, x – y, z. B: –x + y + 1, 1 – x, z. C: $^4/_3$ – x, –x + y + $^2/_3$, –z + $^5/_3$. D: x – y + $^1/_3$, –y + $^2/_3$, –z + $^5/_3$. E: y + $^1/_3$, x – $^1/_3$, –z + $^5/_3$.

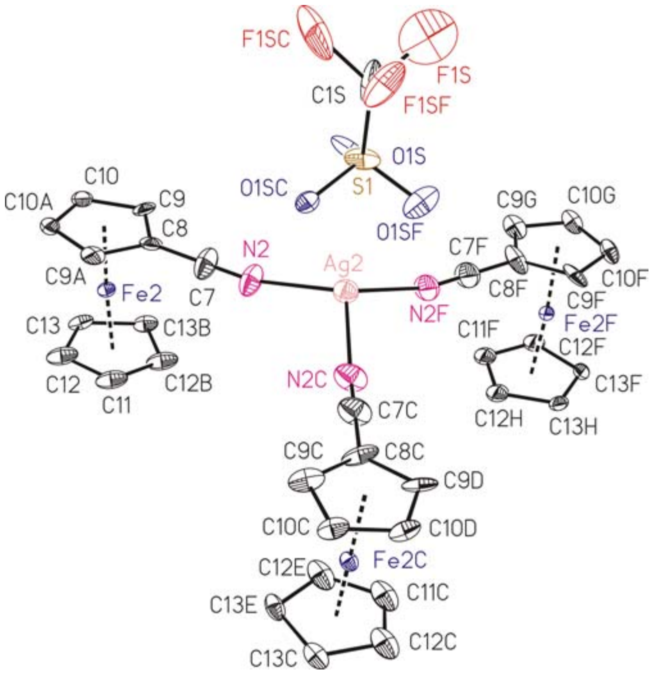

Figure S3 ORTEP diagram (30 % ellipsoid probability) of the molecular structure of **3B**. All hydrogen atoms are omitted for clarity. Of disordered atoms only one atomic position is displayed.

Symmetry code for A–H labelled atoms: A: $^4/_3$ – x, -x + y + $^2/_3$, -z + $^2/_3$. B: y + $^2/_3$, x – $^2/_3$, -z + $^1/_3$. C: 1 – y, x – y, z. D: x – y + $^1/_3$, -y + $^2/_3$, z + $^2/_3$. E: -x + $^5/_3$, -x + y + $^4/_3$, -z + $^1/_3$. F: -x + y +1, 1 – x, z. G: y + $^1/_3$, x – $^1/_3$, -z + $^2/_3$. H: x – y - $^1/_3$, -y + $^1/_3$, -z + $^1/_3$.

Finally, we aim to refer to a report of Murphy *et al.*, where the solid state structure of a polymeric tricoordinated nitrile Ag(I) complex is described. Here, the obviously disordered OTf^- anions have been "squeezed out" [5].

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