

Silver(I) Complexes with the 1,1'-Bis(diethyldithiocarbamate)ferrocene Ligand. Polymeric Chain Species

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Dedicated to Prof. Hubert Schmidbaur on the occasion of his 70th birthday

The reaction of $\text{Fc}(\text{S}_2\text{CNEt}_2)_2$ ($\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2$) with $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$ ($\text{OTf} = \text{trifluoromethanesulfonate}$) or $[\text{Au}(\text{OCIO}_3)(\text{PPh}_3)]$ in various molar ratios gives complexes of stoichiometry $[\text{Ag}(\text{PPh}_3)\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]\text{OTf}$, $[\text{Ag}(\text{PPh}_3)_2\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]\text{OTf}$, $[\text{Ag}_2(\text{PPh}_3)_2\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}](\text{ClO}_4)_2$ or $[\text{Ag}_3(\text{PPh}_3)_3\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}](\text{ClO}_4)_3$. Treatment of $\text{Fc}(\text{S}_2\text{CNEt}_2)_2$ with $\text{Ag}(\text{OTf})$ gives the complex $[\text{Ag}(\text{OTf})\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]$, which can easily react with bidentate ligands such as 1,10-phenanthroline (phen), bis(diphenylthiophosphoryl)methane ((SPPH_2) $_2\text{CH}_2$) or $\text{NaS}_2\text{CNEt}_2$ to afford the cationic complexes $[\text{Ag}(\text{phen})\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]\text{OTf}$, $[\text{Ag}\{(\text{SPPH}_2)_2\text{CH}_2\}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]\text{OTf}$ or the neutral $[\text{Ag}(\text{S}_2\text{CNEt}_2)\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]$. The crystal structure of $[\text{Ag}(\text{PPh}_3)_2\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]\text{OTf}$ reveals that silver coordinates to the dithiocarbamate sulfur atoms of two ferrocene ligands, thus forming a chain polymer.

Key words: Silver Complexes, Ferrocene, Dithiocarbamates, Polymeric Chain

Introduction

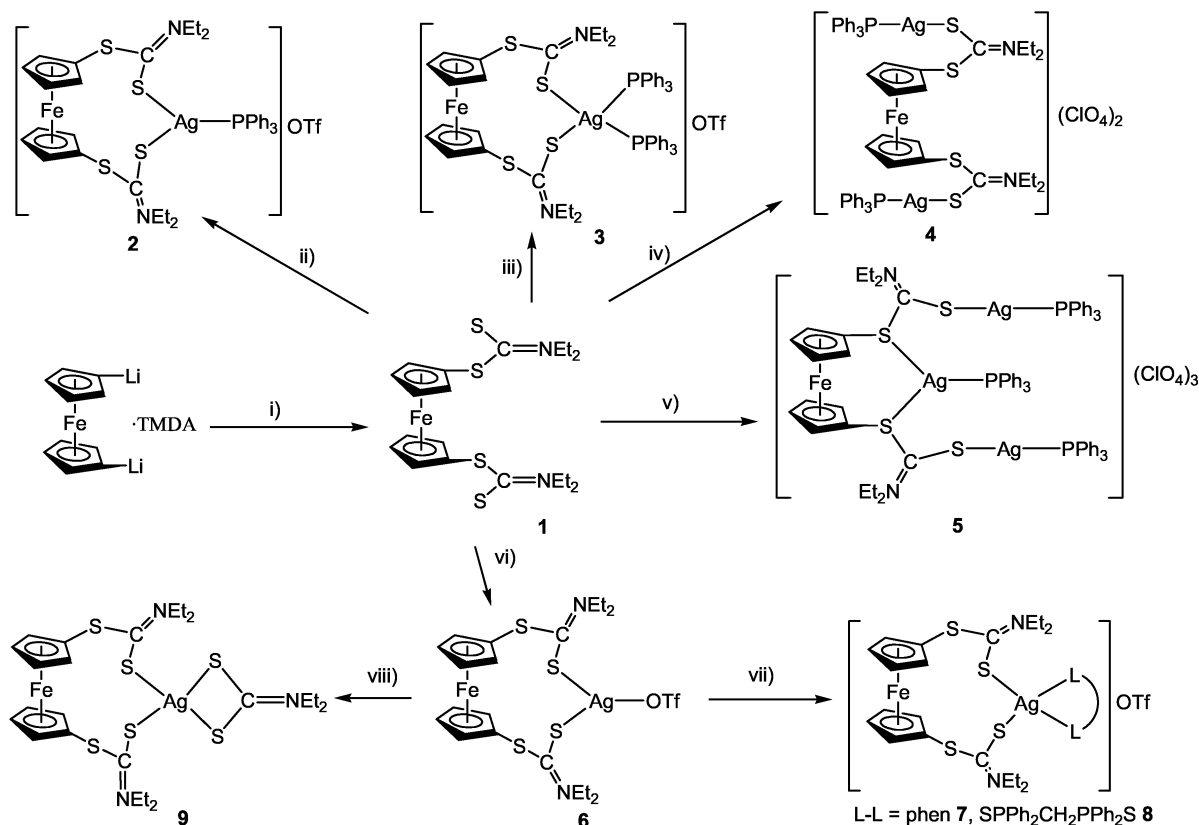
Ferrocene is a very versatile molecule with important properties such as high electron density, aromaticity and redox reversibility. These characteristics, together with the ease of preparation of mono and 1,1'-disubstituted ferrocene derivatives with a great variety of organic fragments that may contain O, N, S, P, *etc.* as donor atoms, make ferrocene a very suitable building block in many fields of research [1–3]. These functional ferrocene derivatives and the study of their coordination to metal centers are an important topic of research in many areas that seek special properties of such species, e.g. non-linear optical properties, charge transport, liquid crystals, electrochemical recognition, catalysis or even nanoparticles [1–12].

As part of our investigations of ferrocene derivatives as ligands in coordination chemistry [13], here we describe the synthesis of silver complexes with 1,1'-bis(diethyldithiocarbamate)ferrocene. We have reported previously the synthesis of a polymeric chain complex of this ligand with silver [14], in which the silver atoms are bound to the dithiocarbamate unit

and also, in an η^2 fashion, to the cyclopentadienyl ring, and several gold(I) and gold(III) derivatives [15]. As far as we are aware no other metal complexes have been reported with this ligand. Several silver derivatives have been prepared by merely reacting the ligand and silver compounds in different molar ratios. The structural characterization of the complex $[\text{Ag}(\text{PPh}_3)_2\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]\text{OTf}$ reveals that the complex is also a chain polymer, although the silver center is coordinated to two triphenylphosphine ligands.

Discussion

The 1,1'-bis(diethyldithiocarbamate)ferrocene ligand is obtained by reaction of dilithioferrocene (as TMDA complex) with tetraethylthiuram disulfide as described previously [16]. The reactivity of this ligand towards several silver compounds has been studied (see Scheme 1). The reaction of **1** with $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$ gives the complex $[\text{Ag}(\text{PPh}_3)_2\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]\text{OTf}$ (**2**), which is a yellow air- and moisture-stable solid. It behaves as a 1:1 electrolyte in acetone solutions. In the IR spectrum of **2**



Scheme 1. i) $\text{Et}_2\text{NCS}_2\text{-S}_2\text{CNEt}_2$, ii) $[\text{Au}(\text{OTf})(\text{PPh}_3)]$, iii) $[\text{Au}(\text{OTf})(\text{PPh}_3)_2]$, iv) $2 [\text{Au}(\text{OCIO}_3)(\text{PPh}_3)]$, v) $3 [\text{Au}(\text{OCIO}_3)(\text{PPh}_3)]$, vi) $\text{Ag}(\text{OTf})$, vii) phen or $(\text{SPPH}_2)_2\text{CH}_2$, viii) $\text{NaS}_2\text{CNEt}_2$.

the absorptions arising from the triflate anion appear at 1263 (br, vs), 1225 (vs) and 1157 (s) cm^{-1} , and the vibration $\nu(\text{C}=\text{N})$ of the dithiocarbamate moiety at 1504(m) cm^{-1} is also present. The ^1H NMR spectrum shows two multiplets at 4.39 and 4.44 ppm for the α and β protons of the cyclopentadienyl rings, respectively, and also two quartets and two triplets corresponding to the inequivalent ethyl protons of the dithiocarbamate moieties. The $^{31}\text{P}(^1\text{H})$ NMR spectrum at room temperature consists of a broad signal that splits into two doublets because of the coupling of the phosphorus atom with the two silver nuclei, ^{109}Ag and ^{107}Ag . The mass spectrum (FAB+) shows as the most intense peak the fragment $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$ at $m/z = 589$ and the cation molecular peak appears at $m/z = 851$ (3%). When the reaction is carried out with the silver compound $[\text{Ag}(\text{OTf})(\text{PPh}_3)_2]$, the complex $[\text{Ag}(\text{PPh}_3)_2\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]\text{OTf}$ (**3**) is isolated. Complex **3** is an air- and moisture-stable yellow solid that behaves as a uni-univalent electrolyte in acetone so-

lutions. The ^1H NMR spectrum presents similar resonances to complex **2**, namely two multiplets for the ferrocene moiety, two triplets and two quartets for the inequivalent ethyl groups of the dithiocarbamate and the multiplets arising from the phenyl protons. The $^{31}\text{P}(^1\text{H})$ NMR at low temperature shows two doublets because of the coupling of the equivalent phosphorus atoms with the silver nuclei. In the mass spectrum only the fragment $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$ at $m/z = 589$ (100%) is observed.

The crystal structure of compound **3** (as its dichloromethane solvate) has been established by X-ray diffraction and confirms that the silver center coordinates to two triphenylphosphine ligands and to the sulfur atoms of the dithiocarbamate moiety (Fig. 1), but, instead of bonding to the sulfur atoms of the same ferrocene unit and thus forming a discrete four-coordinate silver compound, the metal is bonded to two sulfurs from different ferrocene units, forming a chain polymer parallel to the y axis (Fig. 2). A

Table 1. Selected bond lengths [Å] and angles [°] for complex **3**.

Ag-P(1)	2.4674(6)	P(2)-C(71)	1.821(2)
Ag-P(2)	2.4705(6)	P(2)-C(51)	1.825(2)
Ag-S(4) ^{#1}	2.6047(6)	S(1)-C(1)	1.751(2)
Ag-S(2)	2.7025(6)	S(1)-C(11)	1.782(2)
P(1)-C(21)	1.824(2)	S(2)-C(11)	1.685(2)
P(1)-C(31)	1.828(2)	S(3)-C(6)	1.753(2)
P(1)-C(41)	1.830(2)	S(3)-C(16)	1.786(2)
P(2)-C(61)	1.821(2)	S(4)-C(16)	1.686(2)
P(1)-Ag-P(2)	121.828(19)	C(41)-P(1)-Ag	110.69(7)
P(1)-Ag-S(4) ^{#1}	116.796(19)	C(61)-P(2)-C(71)	102.52(9)
P(2)-Ag-S(4) ^{#1}	100.212(19)	C(61)-P(2)-C(51)	104.67(9)
P(1)-Ag-S(2)	103.601(18)	C(71)-P(2)-C(51)	105.45(9)
P(2)-Ag-S(2)	116.503(19)	C(61)-P(2)-Ag	115.19(7)
S(4) ^{#1} -Ag-S(2)	95.239(19)	C(71)-P(2)-Ag	117.46(7)
C(21)-P(1)-C(31)	102.15(9)	C(51)-P(2)-Ag	110.32(7)
C(21)-P(1)-C(41)	103.57(9)	C(1)-S(1)-C(11)	102.32(10)
C(31)-P(1)-C(41)	105.60(9)	C(11)-S(2)-Ag	117.50(7)
C(21)-P(1)-Ag	115.18(7)	C(6)-S(3)-C(16)	102.14(10)
C(31)-P(1)-Ag	118.18(7)	C(16)-S(4)-Ag ^{#2}	111.48(7)

Symmetry transformations used to generate equivalent atoms: ^{#1} $x, -y + 1/2, z - 1/2$; ^{#2} $x, -y + 1/2, z + 1/2$.

selection of bond lengths and angles are collected in Table 1. The silver center has a tetrahedral geometry with some angle distortions, namely the narrow S4^{#1}-Ag-S2 angle of 95.239(19)° and the wide P(1)-Ag-P(2) angle of 121.828(19)°. The Ag-S bond distances are 2.6047(6) and 2.7025(6) Å and are slightly longer than those found in other tetrahedral complexes such as [AgBr(18S₆)] [17] (18S₆ = 1, 4, 7, 10, 13, 16-hexathiacyclooctadecane) (2.514(1)–2.636(1) Å) or [Ag{(SPPh₂)₂CH₂}{(PPh₂)₂C₂B₁₀H₁₀}]ClO₄ [18] (2.540(2), 2.588(2) Å). These Ag-S distances are much longer than those in the polymeric complex [Ag{Fc(S₂CNEt₂)₂}]_n(ClO₄)_n (2.386(3) Å) [14] where the silver atom is linearly bonded to the sulfur atoms and also in an η^2 fashion to the cyclopentadienyl rings. In complex **3** there are no interactions between the silver and the carbon atoms, probably because of the presence of the two triphenylphosphine ligands. The Ag-P bond lengths of 2.4674(6) and 2.4705(6) Å are similar to those found in the complex [Ag(dppe)₂]NO₃ [19] (range 2.488(3)–2.527(3) Å), also with a tetracoordinate silver center. The triflate anion and the dichloromethane molecule are well-ordered and are linked by the contacts H99A...O3 and H99B...O2, both 2.45 Å and both within the asymmetric unit.

The determination of the crystal structure of complex **3** reveals that in the solid state the structure is a chain polymer, although this is unlikely to be maintained in solution. We propose that in view of the sol-

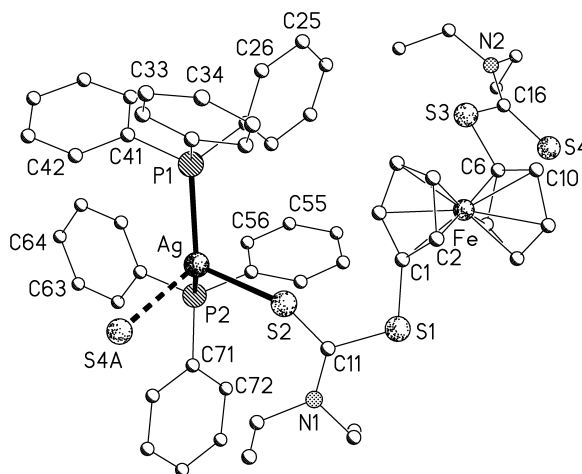


Fig. 1. Structure of the cation of complex **3** in the crystal (asymmetric unit extended by one sulfur to complete the ligand sphere at silver) showing the atom labelling scheme. Radii are arbitrary; hydrogen atoms are omitted for clarity.

ubility of these complexes and the fact that the mass spectra do not show any peak with a higher molecular weight, that the behaviour of these type of derivatives may be as monomers in solution.

Treatment of **1** with two equivalents of [Au(OCIO₃)-(PPh₃)] leads to the complex [Ag₂(PPh₃)₂{Fc(S₂-CNEt₂)₂}] (ClO₄)₂ (**4**), which is a yellow air- and moisture-stable solid that behaves as a 1:2 electrolyte in acetone solutions. In this complex the coordination of the silver centers probably takes place through the sulfur atoms of the dithiocarbamate, leading to a discrete dinuclear complex. In the IR spectrum the absorptions of the anionic perchlorate at 1092 (vs) and 623 (m) cm⁻¹ appear; the vibration ν (C=N) appears at 1511 (m) cm⁻¹. The ¹H NMR spectrum shows similar resonances to the complexes mentioned above, whereby two multiplets for the α and β protons of the cyclopentadienyl groups and two triplets and two quartets for the ethyl protons are present. The ³¹P(¹H) NMR carried out at -85 °C in (CD₃)₂CO shows two doublets because of the coupling of the equivalent phosphorus atoms to the silver nuclei. The mass spectrum shows again as the most intense peak the fragment [Ag{Fc(S₂CNEt₂)₂}]⁺ at m/z = 589 and also the peak at m/z = 959 (1%) corresponding to the fragment [Ag₂(PPh₃)₂{Fc(S₂CNEt₂)₂}]²⁺ appears.

The reaction of **1** with three equivalents of [Au(OCIO₃)(PPh₃)] gives the trinuclear silver derivative [Ag₃(PPh₃)₃{Fc(S₂CNEt₂)₂}] (ClO₄)₃ (**5**). We

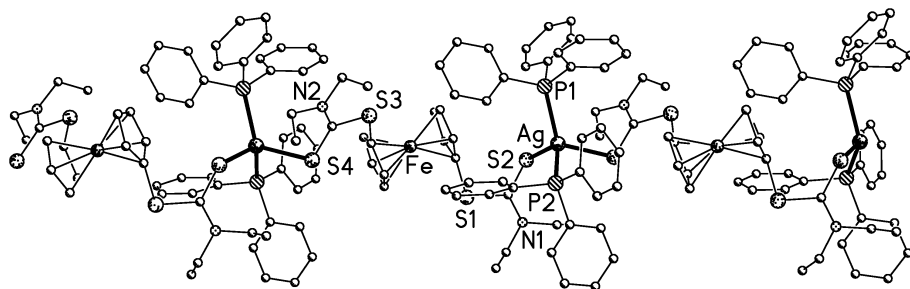


Fig. 2. Polymeric chain formed by the cations of complex **3**. Radii are arbitrary; hydrogen atoms are omitted for clarity.

propose a structure where two AgPPh_3 units are coordinated to the free sulfur atom of the dithiocarbamate units and the third AgPPh_3 would coordinate to the two sulfur atoms bonded to the cyclopentadienyl unit, leading to a tricoordinated silver center. Compound **5** is an air- and moisture-stable yellow solid with a conductivity in acetone solutions of $290 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$, which corresponds to a 3:1 electrolyte. In the IR spectrum the absorptions arising from ionic perchlorate at 1096 (vs) and 624 (s) cm^{-1} and the vibration $\nu(\text{C}=\text{N})$ at 1587 (m) cm^{-1} appear. Here we observed a significant change in the vibration $\nu(\text{C}=\text{N})$ that maybe a consequence of the different coordination of the ligand **1** to the silver centers, in this compound we propose that both sulfur atoms of each dithiocarbamate unit are involved in the bonding. The ^1H NMR spectrum shows the resonances for the α and β protons of the cyclopentadienyl groups, those corresponding to two different ethyl units and the phenylic protons. The $^{31}\text{P}(^1\text{H})$ NMR presents two different phosphorus environments, approximately in a ratio 2:1; this would correspond to the two different types of phosphorus atoms.

The reaction of $\text{Ag}(\text{OTf})$ with the ligand **1** affords a complex of stoichiometry $[\text{Ag}(\text{OTf})\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]$ (**6**), which is related to the complex $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}](\text{ClO}_4)$ previously reported by us. The structure of the latter in the solid state consist of a chain polymer in which the silver is bonded to two sulfur atoms of different ferrocene moieties and also is bonded to two carbon atoms of the cyclopentadienyl ring in a η^2 fashion. We assume that this complex with triflate as counteranion may have a similar structure in the solid state but in solution could also be mononuclear as proposed in Scheme 1. The IR spectrum shows the typical absorptions for the triflate anion at 1223 (vs, br), 1199 (s) and 1151 (s) cm^{-1} ; the $\nu(\text{C}=\text{N})$ absorption appears at 1511 (m) cm^{-1} . The ^1H NMR spectrum shows resonances at 4.50 and 4.63 ppm

for the α and β protons of the cyclopentadienyl groups and two triplets and two quartets for the ethyl protons of the dithiocarbamate moieties. In the mass spectrum (FAB+) the fragment $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$ at $m/z = 589$ (100%) can be observed.

The reaction with bidentate ligands such as 1,10-phenanthroline or $(\text{SPhPh}_2)_2\text{CH}_2$ gives the complexes $[\text{Ag}(\text{phen})\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]\text{OTf}$ (**7**) or $[\text{Ag}\{(\text{SPhPh}_2)_2\text{CH}_2\}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]\text{OTf}$ (**8**) as yellow air- and moisture-stable solids. Compounds **7** and **8** behave as uni-univalent electrolytes in acetone solutions. In the IR spectra the absorptions arising from the triflate anion, those from the vibrations $\nu(\text{C}=\text{N})$ at 1514 (m) for **7** and 1541 (m) for **8** and also the vibration $\nu(\text{P}=\text{S})$ at 582 (m) cm^{-1} can be observed. The ^1H NMR spectra present common resonances, namely the two multiplets for the α and β protons of the cyclopentadienyl groups and the two triplets and two quartets coming from the ethyl groups; complex **7** shows the protons of the phenanthroline unit at 7.94 (dd), 7.95 (s), 8.48 (dd) and 8.98 (dd) ppm and compound **8** shows a triplet for the methylene protons of the diphosphine disulfide. The $^{31}\text{P}(^1\text{H})$ NMR spectrum of **8** presents a singlet at 37.1 ppm arising from the two equivalent phosphorus atoms. The mass spectra (FAB+) show the cationic molecular peak at $m/z = 1005$ (30%) for complex **8** and the fragment $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$ at $m/z = 589$ (56%) for compound **7**.

The reaction of compound **6** with sodium diethyldithiocarbamate gives the neutral complex $[\text{Ag}(\text{S}_2\text{CNEt}_2)\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]$ (**9**), which is a yellow air- and moisture-stable solid. The IR spectra presents the absorptions corresponding to the vibrations $\nu(\text{C}=\text{N})$ of both types of dithiocarbamate units at 1490 (m) cm^{-1} . The ^1H NMR spectrum shows the resonances of the cyclopentadienyl protons as two multiplets, and also those from three different ethyl groups of the dithiocarbamate moieties.

Conclusion

In this work, the hitherto poorly explored coordination chemistry of 1,1'-bis(diethyldithiocarbamate)ferrocene ligand has been investigated towards silver(I) compounds. Coordination of the silver centers to both sulfur atoms of the dithiocarbamate moieties is inferred because in all the cases equivalence of the α and β protons of the cyclopentadienyl protons have been observed. The crystal structure determinations of $[\text{Ag}(\text{PPh}_3)_2\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]\text{OTf}$ (**3**) and $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]\text{ClO}_4$, previous communication, have revealed that these complexes are, in fact, chain polymers in the solid state in which the silver centers are tetracoordinated in **3** and with no other ligands around the silver center, this metal bonds in a η^2 fashion to the C-C bond of the cyclopentadienyl units.

Experimental Section

General procedure

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin Elmer 883 spectrophotometer with Nujol mulls between polyethylene sheets. Conductivities were measured in about 5×10^{-4} M solutions with a Philips 9509 conductimeter. C and H analyses were carried out with a Perkin Elmer 2400 microanalyser. Mass spectra were recorded on a VG Autospec by the LSIMS technique with nitrobenzil alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 and a Bruker ARX300 spectrometers in CDCl_3 , otherwise stated. Chemical shifts are cited relative to SiMe_4 (^1H , external) and 85% H_3PO_4 (^{31}P , external). The starting materials $\text{Fc}(\text{S}_2\text{CNEt}_2)_2$ [16], $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$ [20], $[\text{Ag}(\text{OTf})(\text{PPh}_3)_2]$ [20], and $[\text{Au}(\text{OCIO}_3)(\text{PPh}_3)]$ [21] were prepared by published procedures.

Caution!

Perchlorate salts of metal complexes with organic ligands may be explosive; only small amounts of material should be prepared, and these should be handled with great caution.

Preparations

1,1'-Bis(diethyldithiocarbamate)ferrocene-triphenylphosphine-silver(I)-trifluoromethanesulfonate (2)

To a solution of $\text{Fc}(\text{S}_2\text{CNEt}_2)_2$ (0.048 g, 0.1 mmol) in dichloromethane (20 ml) was added $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$ (0.0519 g, 0.1 mmol) and the mixture was stirred for 30 minutes. Evaporation of the solvent to *ca.* 5 ml and addition of hexane gave complex **2** as a yellow solid. Yield: 0.057 g (57%). Λ_{M} 108 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Analytical data: $\text{C}_{39}\text{H}_{43}\text{AgF}_3\text{FeN}_2\text{O}_3\text{PS}_5$ (999.43): calcd. C 46.87, H 4.30,

N 2.80, S 16.03; found C 46.42, H 4.10, N 2.75, S 15.49. NMR data, ^1H : δ = 1.29 (3H, t; CH_2CH_3), 1.40 (3H, t; CH_2CH_3), 3.88 (2H, q; CH_2CH_3), 4.03 (2H, q; CH_2CH_3), 4.39 (4H, m; $\alpha\text{-C}_5\text{H}_4$), 4.44 (4H, m; $\beta\text{-C}_5\text{H}_4$). ^{31}P (^1H), -55°C : δ = 13.0 (1P, 2d, $\text{J}(\text{AgP})$ 610, 695 Hz). MS (FAB+): m/z = 589 (100%, $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$), 851 (3%, $[\text{Ag}(\text{PPh}_3)\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$).

1,1'-Bis(diethyldithiocarbamate)ferrocene-bis(triphenylphosphine)-silver(I)-trifluoromethanesulfonate (3)

To a solution of $\text{Fc}(\text{S}_2\text{CNEt}_2)_2$ (0.048 g, 0.1 mmol) in dichloromethane (20 ml) was added $[\text{Ag}(\text{OTf})(\text{PPh}_3)_2]$ (0.0781 g, 0.1 mmol) and the mixture was stirred for 30 minutes. Evaporation of the solvent to *ca.* 5 ml and addition of hexane gave complex **3** as a yellow solid. Yield: 0.089 g (71%). Λ_{M} 101 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Analytical data: $\text{C}_{57}\text{H}_{58}\text{AgF}_3\text{FeN}_2\text{O}_3\text{P}_2\text{S}_5$ (1261.604): calcd. C 54.26, H 4.59, N 2.22, S 12.70; found C 54.01, H 4.42, N 2.32, S 12.32. NMR data, ^1H : δ = 1.27 (3H, t; CH_2CH_3), 1.41 (3H, t; CH_2CH_3), 3.82 (2H, q; CH_2CH_3), 4.22 (2H, q; CH_2CH_3), 4.31 (4H, m; $\alpha\text{-C}_5\text{H}_4$), 4.52 (4H, m; $\beta\text{-C}_5\text{H}_4$). ^{31}P (^1H), -55°C : δ = 15.2 (2P, 2d, $\text{J}(\text{AgP})$ 597, 679 Hz). MS (FAB+): m/z = 589 (100%, $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$).

1,1'-Bis(diethyldithiocarbamate)ferrocene-bis(triphenylphosphine)-silver(I)-bis(perchlorate) (4)

To a solution of $\text{Fc}(\text{S}_2\text{CNEt}_2)_2$ (0.048 g, 0.1 mmol) in dichloromethane (20 ml) was added $[\text{Ag}(\text{OCIO}_3)(\text{PPh}_3)]$ (0.0938 g, 0.2 mmol) and the mixture was stirred for 30 min. Evaporation of the solvent to *ca.* 5 ml and addition of hexane gave complex **4** as a yellow solid. Yield: 0.110 g (78%). Λ_{M} 239 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Analytical data: $\text{C}_{56}\text{H}_{58}\text{Ag}_2\text{Cl}_2\text{FeN}_2\text{O}_8\text{P}_2\text{S}_4$ (1419.307): calcd. C 47.39, H 4.08, N 1.97, S 9.03; found C 47.58, H 4.08, N 1.70, S 8.56. NMR data, ^1H : δ = 1.34 (3H, t; CH_2CH_3), 1.46 (3H, t; CH_2CH_3), 3.99 (2H, q; CH_2CH_3), 4.10 (2H, q; CH_2CH_3), 4.28 (4H, m; $\alpha\text{-C}_5\text{H}_4$), 4.55 (4H, m; $\beta\text{-C}_5\text{H}_4$), 7.2–7.9 (30H, m, Ph). ^{31}P (^1H) -85°C , $(\text{CD}_3)_2\text{CO}$: δ = 15.0 (2P, 2d, $\text{J}(\text{AgP})$ 598.1, 690.0 Hz). MS (FAB+): m/z = 589 (100%, $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$), 959 (1%, $[\text{Ag}_2(\text{PPh}_3)\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^{2+}$).

1,1'-Bis(diethyldithiocarbamate)ferrocene-tris(triphenylphosphine)-silver(I)-tris(perchlorate) (5)

To a solution of $\text{Fc}(\text{S}_2\text{CNEt}_2)_2$ (0.048 g, 0.1 mmol) in dichloromethane (20 ml) was added $[\text{Ag}(\text{OCIO}_3)(\text{PPh}_3)]$ (0.141 g, 0.3 mmol) and the mixture was stirred for 30 minutes. Evaporation of the solvent to *ca.* 5 ml and addition of hexane gave complex **5** as a yellow solid. Yield: 0.132 g (65%). Λ_{M} 290 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Analytical data: $\text{C}_{74}\text{H}_{73}\text{Ag}_3\text{Cl}_3\text{FeN}_2\text{O}_{12}\text{P}_3\text{S}_4$ (1889.485): calcd. C 47.04,

H 3.89, N 1.48, S 6.78; found C 47.39, H 3.75, N 1.60, S 7.21. NMR data, ^1H : $\delta = 1.34$ (3H, t; CH_2CH_3), 1.46 (3H, t; CH_2CH_3), 3.98 (2H, q; CH_2CH_3), 4.11 (2H, q; CH_2CH_3), 4.12 (4H, m; $\alpha\text{-C}_5\text{H}_4$), 4.57 (4H, m; $\beta\text{-C}_5\text{H}_4$), 7.1–7.9 (45H, m, Ph). ^{31}P (^1H): δ ($(\text{CD}_3)_2\text{CO}$, -85°C) = 4.6 (2P, 2d, J(AgP) 611, 706 Hz), 14.2 (1P, 2d, J(AgP) 496, 571 Hz). MS (FAB+): $m/z = 589$ (100%, $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$).

1,1'-Bis(diethyldithiocarbamate)ferrocene-silver(I)-trifluoromethanesulfonate (6)

To a solution of $\text{Ag}(\text{OTf})$ (0.0257 g, 0.1 mmol) in diethyl ether (20 ml) was added $\text{Fc}(\text{S}_2\text{CNEt}_2)_2$ (0.048 g, 0.1 mmol); after a few minutes a yellow solid precipitated and the mixture was stirred for 1 h to complete the reaction. The yellow solid of **6** was filtered off and dried under vacuum. Yield: 0.132 g (59%). Λ_{M} 42.2 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Analytical data: $\text{C}_{21}\text{H}_{28}\text{AgF}_3\text{FeN}_2\text{O}_3\text{S}_5$ (737.26): calcd. C 34.21, H 3.80, N 3.80, S 21.74; found C 33.79, H 3.70, N 4.21, S 22.38. NMR data, ^1H : $\delta = 1.20$ (3H, t; CH_2CH_3), 1.31 (3H, t; CH_2CH_3), 3.95 (2H, q; CH_2CH_3), 4.03 (2H, q; CH_2CH_3), 4.50 (4H, m; $\alpha\text{-C}_5\text{H}_4$), 4.63 (4H, m; $\beta\text{-C}_5\text{H}_4$). MS (FAB+): $m/z = 589$ (100%, $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$).

1,1'-Bis(diethyldithiocarbamate)ferrocene-1,10-phenanthroline-silver(I)-trifluoromethanesulfonate (7) and 1,1'-bis(diethyldithiocarbamate)ferrocene-bis(diphenylthiophosphoryl)methane-silver(I)-trifluoromethanesulfonate (8)

To a solution of $[\text{Ag}(\text{OTf})\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]$ (0.0737 g, 0.1 mmol) in dichloromethane (20 ml) was added the corresponding bidentate ligand phen (0.018 g, 0.1 mmol) or $(\text{SPPH}_2)_2\text{CH}_2$ (0.0448 g, 0.1 mmol) and the mixture was stirred for 2 h. Evaporation of the solvent to *ca.* 5 ml and addition of hexane gave complex **7** or **8** as yellow solids. Complex **7**: Yield: 0.062 g (68%). Λ_{M} 110.8 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Analytical data: $\text{C}_{33}\text{H}_{36}\text{AgF}_3\text{FeN}_4\text{O}_3\text{S}_5$ (917.406): calcd. C 43.20, H 3.92, N 6.10, S 17.47; found C 43.64, H 3.72, N 6.52, S 17.02. NMR data, ^1H : $\delta = 1.29$ (3H, t; CH_2CH_3), 1.41 (3H, t; CH_2CH_3), 3.91 (2H, q; CH_2CH_3), 4.03 (2H, q; CH_2CH_3), 4.43 (4H, m; $\alpha\text{-C}_5\text{H}_4$), 4.45 (4H, m; $\beta\text{-C}_5\text{H}_4$), 7.94 (2H, dd, phen), 7.95 (2H, s, phen), 8.48 (2H, dd, phen), 8.98 (2H, dd, phen). MS (FAB+): $m/z = 589$ (100%, $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$). Complex **8**: Yield: 0.073 g (62%). Λ_{M} 115.3 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Analytical data: $\text{C}_{46}\text{H}_{50}\text{AgF}_3\text{FeN}_2\text{O}_3\text{P}_2\text{S}_7$ (1185.603): calcd. C 46.68, H 4.22, N 2.36, S 17.47; found C 46.44, H 3.97, N 2.17, S 17.13. NMR data, ^1H : $\delta = 1.26$ (3H, t; CH_2CH_3), 1.37 (3H, t; CH_2CH_3), 3.82 (2H, q; CH_2CH_3), 3.97 (2H, q; CH_2CH_3), 4.07 (2H, t, CH_2), 4.38 (4H, m; $\alpha\text{-C}_5\text{H}_4$), 4.47 (4H, m; $\beta\text{-C}_5\text{H}_4$), 7.3–7.8 (20H, m, Ph).

^{31}P (^1H): $\delta = 37.1$ (2P, s, PPh_2). MS (FAB+): $m/z = 1005$ (30%, $[\text{Ag}\{(\text{SPPH}_2)_2\text{CH}_2\}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$), 589 (100%, $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$).

Diethyldithiocarbamate-1,1'-bis(diethyldithiocarbamate)-ferrocene-silver(I) (9)

To a solution of $[\text{Ag}(\text{OTf})\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]$ (0.0737 g, 0.1 mmol) in dichloromethane (20 ml) was added $\text{Na}_2\text{S}_2\text{CNEt}_2 \cdot 3\text{H}_2\text{O}$ (0.022 g, 0.1 mmol) and the mixture was stirred for 2 h. The suspension was filtered off over MgSO_4 in order to eliminate NaOTf and then concentration of the solution to *ca.* 5 ml and addition of hexane gave complex **9** as a yellow solid. Yield: 0.037 g (51%). Λ_{M} 10.2 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$. Analytical data: $\text{C}_{25}\text{H}_{38}\text{AgFeN}_3\text{S}_6$ (736.371): calcd. C 40.77, H 5.16, N 5.70, S 26.12; found C 40.24, H 4.95, N 5.58, S 25.57. NMR data, ^1H : $\delta = 1.25$ (3H, t; CH_2CH_3), 1.39 (3H, t; $\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2$), 1.40 (3H, t; CH_2CH_3), 3.78 (2H, q; CH_2CH_3), 3.94 (2H, q; $\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2$), 3.98 (2H, q; CH_2CH_3), 4.38 (4H, m; $\alpha\text{-C}_5\text{H}_4$), 4.50 (4H, m; $\beta\text{-C}_5\text{H}_4$). MS (FAB+): $m/z = 589$ (100%, $[\text{Ag}\{\text{Fc}(\text{S}_2\text{CNEt}_2)_2\}]^+$).

X-ray structure determination

The crystal ($0.25 \times 0.17 \times 0.06 \text{ mm}^3$) was mounted in inert oil on a glass fibre. Data were measured using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$) on a Bruker SMART 1000 CCD diffractometer. Crystal data: $\text{C}_{58}\text{H}_{60}\text{AgCl}_2\text{F}_3\text{FeN}_2\text{O}_3\text{P}_2\text{S}_5$, $M = 1346.94$, monoclinic, space group $P2_1/c$, $a = 12.7888(10)$, $b = 18.6685(14)$, $c = 25.127(2) \text{ \AA}$, $\beta = 93.755(3)^\circ$, $U = 5986.2(8) \text{ \AA}^3$, $T = 143 \text{ K}$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.941 \text{ mm}^{-1}$, $F(000) = 2760$, 63056 reflections measured ($2\theta_{\text{max}} 56.6^\circ$, ω scans), 14839 unique ($R_{\text{int}} = 0.0563$), absorption correction based on multiple scans (program SADABS) [22]. The structure was refined anisotropically on F^2 using the program SHELXL-97 [23]. All non-hydrogen atoms were refined anisotropically. Final $R1 = 0.0315$, $wR2 = 0.0576$, for 698 parameters and 60 restraints; max. $\Delta\rho = 0.65 \text{ e \AA}^{-3}$.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Center under the number CCDC-247408. Copies may be requested free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England (E-mail: deposit@ccdc.cam.ac.uk).

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