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Nine- and ten-membered diauracycles with the $C_3S_5^{2-}$ ligand. Crystal structure of NBu₄[Au₂(μ -C₃S₅)(μ -CH₂PPh₂CH₂)]

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Abstract

The synthesis of hetero-bridged dinuclear gold(1) complexes with the $C_3S_5^{-2}$ (1,3-dithiole-2-thione-4,5-dithiolate) ligand has been tested by different methods: (i) reaction of $[Au(\mu-L-L)X_2]^{n-1}$ with Na₂C₃S₅ ethanolic solutions; (ii) reaction of $[Au_2(C_3S_5)(AsPh_3)]_n$ with different bidentate ligands. The resulting complexes $Q[Au_2(\mu-C_3S_5)(\mu-CH_2PPh_2CH_2)]$ (1), $[Au_2(\mu-C_3S_5)(\mu-dppe)]$ (2) and $Q[Au_2(C_3S_5)(S_2CNR_2)]$ (R = Me (3), Et (4) or CH₂Ph (5)) have been characterized by analysis, conductivity, IR, ³¹P and ¹H NMR. Complex (PPN)₂[Au(C_3S_2)_2] (6) (PPN=N(PPh_3)_2) has been achieved by reaction of [AuCl(tht)] (tht=tetrahydrothiophene) or $[AuCl(AsPh_3)]$ with Na₂C₃S₅ and addition of (TFN)Ci. Reaction of 1 with (TTF)₃(BF₄)₂ (TTF=tetrahiafulvalene) affords (TTF)[Au₂(C₃S₅)(CH₂PPh₂CH₂)] (7) and reaction of 6 with AgClO₄ gives a polynuclear complex $[Au_2Ag_2(C_3S_5)_2]$ (8). Compacted pellets of 7 and 8 show conductivities of 2×10^{-7} and 3×10^{-5} S cm⁻¹ at room temperature. The structure of NBu₄- $[Au_2(C_3S_5)(CH_2PPh_2CH_2)]$ (1a) has been established by an X-ray diffraction study and shows a nine-membered diauracycle with an Au...Au distance of 3.026(1) Å.

Keywords: Crystal structures; Gold complexes; Diauracycle complexes; Sulfur ligand complexes

1. Introduction

The synthesis of dmit $(C_3S_5^{2-} (1,3-dithiole-2-thione-4,5-dithiolate))$ complexes of various metals has received a great deal of attention [1,2], largely because of their interesting electrical properties. The preparation of compounds $(\operatorname{cation})_x[M(C_3S_5)_2]$ [3–9] $(\operatorname{cation} = TTF \text{ or } NMe_4)$ (TTF = tetrathiafulvalene), which show superconducting properties, from the first $(TTF)[Ni(C_3S_5)_2]$ [8] to the recently reported (α -EDT-TTF)[Ni(C_3S_5)_2] [9] (EDT-TTF= ethylenedithio-tetrathiafulvalene), which becomes superconducting at ambient pressure, have prompted research activity in this area.

Because of the preparation procedures, namely reaction of methanolic $C_3S_5^{2-}$ solutions with metals salts, most known complexes are homoleptic $[M(C_3S_5)_m]^{n-}$ [1,2,10]. A few heteroleptic complexes with chelating dmit $[M(C_3S_5)(L-L)]^{n-}$ (L-L = other bidentate ligand) are known [1,2]. Only recently have complexes with the dmit ligand acting as a bridge between two or three gold atoms been reported [11,12].

Continuing our interest in the synthesis and reactivity of diauracycles [13–15], we used dmit as a bidentate bridging ligand to prepare such systems. It is noteworthy that eight-membered rings are the usual size [16] for diauracycles, the higher-membered rings being less abundant [17–19]. The backbone of the dmit ligand in a diauracycle leads necessarily to a nine-membered (for hetero-bridged derivatives) or a ten-membered ring.

This paper reports the synthesis of heteroleptic derivatives $Q[Au_2(C_3S_5)(L-L)]$ (L-L = CH₂PPh₂CH₂ (dppm), PPh₂-CH₂CH₂PPh₂ (dppe), S₂CNR₂ (R = Mc, Et, CH₂Ph)) and the homoleptic $Q_2[Au_2(C_3S_5)_2]$ (Q = PPN and/or NBu₄). The molecular structure of NBu₄[Au₂(μ -C₃S₅)(μ -CH₂PPh₂CH₂)] has been established by a single crystal X-ray study, revealing a nine-membered diauracycle with an intramolecular Au...Au distance of 3.026(1) Å.

2. Experimental

2.1. Materials

4,5-Bis(benzoylthio)1,3-dithiole-2-thione [20], Q[Au₂-(μ-CH₂PPh₂CH₂)X₂] [21], [Au₂(dppe)Cl₂] [22], [Au₂-

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 $(dppe)(C_6F_5)_2$ [23], $(TTF)_3(BF_4)_2$ [24], [AuCl(tht)][25], $[Au_2(\mu-C_3S_5)(PPh_3)_2]$ [12] and $[Au_2(C_3S_5)-(AsPh_3)]$ [12] were prepared by previously published methods.

2.2. General data

IR spectra were recorded on a Perkin-Elmer 559 or 883 spectrophotometer, over the range 4000–250 cm⁻¹, using Nujol mulls between polyethylene sheets, ¹H and ³¹P NMR spectra on a Varian UNITY 300 in CDCl₃ solutions; chemical shifts are quoted relative to SiMe₄ (¹H) and H₃PO₄ (external ³¹P). The C, H, N and S analyses were performed with a Perkin-Elmer 2400 microanalyzer; Au + Ag was determined by ashing the sample with an aqueous solution of hydrazine. Conductivities were measured in acetone with a Philips PW 9509 apparatus. Mass spectra were recorded on VG Autospec using nitrobenzyl alcohol as matrix. The yields and C, H, N and S analyses are listed in Table 1. Electric conductivity measurements were carried out using the two probe method in compacted pellets.

2.3. Preparations

2.3.1. $Q[Au_2(\mu-C_3S_5)(\mu-CH_2PPh_2CH_2)](Q=NBu_4(Ia), N(PPh_3)_2(PPN)(Ib))$

4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (81 mg, 0.2 mmol) was dissolved under a dinitrogen atmosphere in a methanol (20 ml) solution containing sodium metal (9 mg,

Table I Analytical data for products

0.4 mmol) affording Na₂[C₃S₅]. A dichloromethane (5 ml) solution of NBu₄[Au₂(μ -CH₂PPh₂CH₂)Br₂] (242 mg, 0.2 mmol) or PPN[Au₂(μ -CH₂PPh₂CH₂)Cl₂] (236 mg, 0.2 mmol) was added, to give yellow and orange solutions, respectively. After stirring for 4 h the solutions were evaporated to dryness, and acetone (15 ml) was added affording a white solid NaX, which was filtered off. The remaining solutions were concentrated to 5 ml. Addition of diethyl ether (10 ml) precipitated yellow (1a) and orange (1b) solids. ³¹P NMR 1a: 39.2 (s); 1b: 39.0 (s).

2.3.2. $[Au_2(\mu - C_3S_5)(\mu - PPh_2CH_2CH_2PPh_2)](2)$

(a) A dichloromethane solution (5 ml) of $[Au_2(\mu-dppe)Cl_2]$ (129 mg, 0.15 mmol) was added to a methanolic solution (20 ml) of Na₂[C₃S₅] prepared as above. An orange solid appeared, which after 6 h was filtered off and washed with diethyl ether (2×5 ml) Yield 85%. ³¹P NMR 2: 32.8 (s).

(b) To a dichloromethane solution (25 ml) of $[Au_2(\mu-C_3S_5)(PPh_3)_2]$ (110 mg, 0.1 mmol) was added $[Au_2(\mu-dppe)(C_6F_5)_2]$ (112 mg, 0.1 mmol) and the solution turned yellow. After 3 h stirring the solution was concentrated to 5 ml. Addition of diethyl ether (10 ml) precipitated orange (2) in 70% yield.

(c) To an acetone (20 ml) suspension of $[Au_2-(C_3S_5)(AsPh_3)]$ (89 mg, 0.1 mmol) was added dppe (40 mg, 0.1 mmol). After 3 h stirring the solid residue was

Complex	Yield (%)	Analysis: found (calc.) (%)			Л _м ª	M.p.	¹ H NMR ^d [² J(P-H)] ^e	
		с	н	N	S		(0)	
10 NBu4[Au2(µ-C3S5)(µ-CH2PPh2CH2)]	74	37.25 (37.9)	4.55	1.4 (1.35)	15.1 (15.3)	100	126	1.57(d)[12.3]
1b PPN[Au ₂ (μ-C ₃ S ₅)(μ-CH ₂ PPh ₂ CH ₂)]	78	46.95 (47.45)	3.45 (3.3)	1.15 (1.1)	12.2 (11.9)	101	128	1.55(d)[12.1]
$2 [Au_2(\mu - C_3S_5)(\mu - dppe)]$	78	35.85 (35.25)	2.4 (2.45)		16.9 (16.3)	4	214 °	4.81(s)
3 PPN[Au ₂ (μ -C ₃ S ₅)(μ -S ₂ CNMe ₂)]	60	40.8 (40.4)	2.8 (2.9)	2.1 (2.25)	17.6 (18.0)	89	175 °	3.39(s)
$4 \text{ NBu}_{4}[\text{Au}_{2}(\mu - C_{3}S_{5})(\mu - S_{2}CNEt_{2})]$	50	29.65 (29.4)	4.6 (4.7)	2.3 (2.85)	22.1 (22.8)	113	140	3.4(c); 1.35(t) ^f
5a NBu ₄ [Au ₂ (μ -C ₃ S ₅)(μ -S ₂ CN(CH ₂ Fh) ₂)]	76	36.95 (37.0)	3.9 (4.4)	2.7 (2.5)	18.9 (20.3)	112	140	5.12(s)
5b PPN[Au ₂ (μ -C ₂ S ₅)(μ -S ₂ CN(CH ₂ Ph) ₂)]	60	45.85 (46.3)	3.15 (3.15)	1.25 (1.0)	16.45 (16.0)	111	140	5.12(5)
$6 (PPN)_2 [Au_2(\mu - C_3S_5)_2]$	90	50.05 (50.25)	3.4 (3.25)	1.55 (1.5)	17.25 (17.2)	174	210°	
7 (TTF)[Au ₂ (μ -C ₃ S ₅)(μ -CH ₂ PPh ₂ CH ₂)]	95	27.6 (27.4)	1.81 (1.8)		28.9 (28.65)	b	180	b
8 [Au ₂ Ag ₂ (C ₃ S ₅) ₂]	95	7.5 (7.2)			30.8 (3 cfm	Þ	190	

^a In acetone, Ω⁻¹ cm² mol⁻¹.

b Low solubility.

° Decomposed without melting.

d In ppm, only PhCH2 or R group of S2CNR2.

° In Hz.

 $^{f}J(H-H) = 7.1$ Hz.

filtered off and the solution concentrated to 5 ml. Addition of diethyl ether (10 ml) precipitated a yellow solid (2) in a 48% yield.

2.3.3. $Q[Au_2(\mu-C_3S_5)(\mu-S_2CNR_2)]$ (R = Me, Q = PPN (3); $R = Et, Q = NBu_4$ (4); $R = CH_2Ph, Q = NBu_4$ (5a) or Q = PPN (5b))

To an acetone (20 ml) suspension of $[Au_2-(C_3S_5)(AsPh_3)]$ (89 mg, 0.1 mmol) was added NaS₂CNEt₂ (17 mg, 0.1 mmol), NaS₂CN(CH₂Ph)₂ (29 mg, 0.1 mmol) or NaS₂CNMe₂ (19 mg, 0.1 mmol), followed by a solution (5 ml) of NBu₄Br (32 mg, 0.1 mmol) or PPNCl (57 mg, 0.1 mmol). The solutions turned orange. After stirring for 6 h the solutions were concentrated to 5 ml; addition of diethyl ether (15 ml) led to the precipitation of orange (**3**, **5b**) or brown (**4**, **5a**) solids, which were filtered off and washed with diethyl ether.

2.3.4. $(PPN)_2[Au_2(\mu-C_3S_5)_2]$ (6)

4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (81 mg, 0.2 mmol) was dissolved under a dinitrogen atmosphere in methanol (20 ml) together with sodium metal (9 mg, 0.4 mmol) affording $Na_2[C_3S_5]$. A dichloromethane (5 ml) solution of [AuCl(tht)] (114 mg, 0.2 mmol) or [AuCl(AsPh₃)] (264 mg, 0.2 mmol) and PPNCl (114 mg, 0.2 mmol) were added to give orange solutions. After stirring for 4 h the solutions were evaporated to dryness, and acetone (15 ml) was added affording a white solid NaX, which was filtered off. The solution was concentrated to 5 ml. Addition of diethyl ether precipitated an orange solid.

2.3.5. $(TTF)[Au_2(\mu - C_3S_5)(\mu - CH_2PPh_2CH_2)](7)$

To an acetonitrile (20 ml) solution of **1a** (104 mg, 0.1 mmol) or **1b** (104 mg, 0.1 mmol) was added $(TTF)_3(BF_4)_2$ (102 mg, 0.15 mmol). A dark red solid precipitated immediately, which was filtered off after 30 min and dried in vacuo.

2.3.6. $[Au_2Ag_2(C_3S_5)_2]$ (8)

To an acetone (20 ml) solution of 6 (186 mg, 0.1 mmol) was added AgClO₄ (41 mg, 0.2 mmol). A black solid appeared immediately. After stirring for 2 h the solid was filtered off and dried in vacuo. Calc. for $C_6S_{10}Au_2Ag_2$: Au + Ag, 60.7. Found: Au + Ag, 59.2%.

2.4. X-ray structure determination of compound la

2.4.1. Crystal data

C₃₃H₅₀Au₂NPS₅, M_r = 1045.94, triclinic, space group $P\bar{1}$, a = 9.297(2), b = 12.814(2), c = 17.393(4) Å, α = 81.02(2), β = 82.00(2), γ = 70.85(2)⁶, U = 1924.8(7) Å³, D_x = 1.805 Mg m⁻³, F(000) = 1016, λ (Mo K α) = 0.71073 Å, μ = 7.949 mm⁻¹.

2.4.2. Data collection and reduction

A yellow prism $\sim 0.22 \times 0.14 \times 0.1$ mm was mounted in inert oil on a glass fiber and transferred to the cold gas stream of the diffractometer (Siemens type R3 with LT2 low temperature attachment). Data were collected using monochromated Mo K α radiation; of 8658 intensities to $2\theta_{max}$ 50°, 6807 were unique (R_{int} 0.079). Cell constants were refined from setting angles of 50 reflections in the range 2 θ 20–23°. Absorption corrections were applied on the basis of Ψ -scans, with transmission factors 0.78–0.97.

2.4.3. Structure solution and refinement

Structures were solved by the heavy atom method and refined anisotropically on F^2 using the program SHELXL-92 [25]. Hydrogen atoms were included using a riding model or with rigid methyl groups. The final $wR(F^2)$ for all reflections was 0.136, with conventional R(F) 0.047, for 373 parameters and 259 restraints (to light atom displacement parameters and local symmetry of phenyl rings). Max. Δ/σ 0.002; max. $\Delta\rho$ 3.1 e Å⁻³; S 1.03. Final atomic coordinates are given in Table 2, with selected bond lengths and angles in Table 3. See also Section 4.

3. Results and discussion

We have explored different routes for the preparation of heterocyclic-dinuclear derivatives $[Au_2(\mu-C_3S_5)(\mu-L-L)]^n$ (n=0 or 1; Scheme 1 and Eqs. (1)-(3)). As bridging ligands L-L (apart from dmit), we selected: 1,2-bis-(diphenylphosphino)methane (dppm), 1,3-bis(diphenylphosphino)ethane (dppe), diphenylphosphoniumbis(methylene) (CH₂PPh₂CH₂)⁻ and various dithiocarbamates S₂CNR₂ (R = Me, Et or CH₂Ph). Not all them can be tested in all three processes because the necessary starting materials are not always available.

The addition of dihalo-digold(I) complexes $[Au_2(\mu-L-L)X_2]^{n-}$ to a methanolic solution of $Na_2[C_3S_3]$ (Scheme 1) affords hetero-bridged $C_3S_5^{2-}$ derivatives of gold(I). This reaction was tested with $[Au_2(\mu-dppm)Cl_2]$, $[Au_2(\mu-dppe)Cl_2]$, $PN[Au_2(\mu-CH_2PPh_2CH_2)Cl_2]$ and NBu_4 - $[Au_2(\mu-CH_2PPh_2CH_2)Br_2]$, leading to the previously known $[Au_4(\mu-C_3S_5)_2(\mu-dppm)_2]$ [12] and the novel derivatives **1a**, **1b** and **2**.

Complexes 1 and 2 are yellow (1a) or orange (1b, 2) solids, stable to air and moisture at room temperature. Complexes 1a and 1b behave as 1:1 electrolytes in acetone solution, whereas the acetone solutions of 2 are non-conducting. The IR spectra show two bands at ~1056(s) and 1037(m) cm⁻¹ assignable to ν (C=S), and a band at ~1436(s) cm⁻¹ arising from ν (C=C) of the C₃S₅²⁻¹ ligand [26]. Complexes 1a and 1b show in addition a band at 588(m) cm⁻¹ characteristic of ν (Au-C_{ylide}) [27]. ³¹PNMR spectra show a singlet at ~39 ppm for the ylide phosphorus (1a,b), and a singlet at 32.8 ppm for the dppe complex. ¹H NMR spectra show a doublet at 1.5 ppm for the ylide methylene protons, whereas complex 2 shows the methylene resonances as a broad singlet at 4.81 ppm (Table 1). The mass spectrum (FAB⁺) of complex 2 shows the parent peak at m/z988 (70%), but the mass

Table 3

Table 2 Atomic coordinates ($\times10^4$) and equivalent isotropic displacement parameters (Å²×10³) for compound 1a

	x	у	z	<i>U</i> _{eq} *
Au(1)	2291.9(6)	6556.4(4)	2574.9(3)	29.1(3)
Au(2)	4223.8(6)	4892.9(4)	3758.9(3)	29.1(3)
S(1)	3297(4)	5663(3)	1475(2)	32(2)
S(2)	5734(4)	3742(3)	2868(2)	34(2)
S(3)	2550(4)	3662(3)	1287(2)	35(2)
S(4)	4396(4)	2166(3)	2421(2)	40(2)
S(5)	2595(6)	1295(4)	1519(3)	60(3)
C(1)	3582(13)	4247(10)	1780(7)	28(7)
C(2)	4455(14)	3543(10)	2305(7)	30(8)
C(3)	3156(16)	2313(12)	1735(8)	43(9)
P	2224(4)	7243(3)	4280(2)	30(2)
C(4)	1096(13)	7506(11)	3484(7)	27(6)
C(5)	2919(8)	5812(6)	4633(5)	27(7)
C(11)	1091(8)	8014(6)	5054(5)	34(7)
C(12)	1691(8)	7859(6)	5767(5)	41(8)
C(13)	774(16)	8363(11)	6399(8)	49(7)
C(14)	-718(15)	8994(12)	6317(8)	47(8)
C(15)	- 1310(15)	9178(11)	5618(8)	41(7)
C(16)	-434(14)	8671(10)	4986(7)	35(6)
C(21)	3827(15)	7781(10)	4007(7)	39(7)
C(22)	5003(16)	7451(12)	4487(8)	49(8)
C(23)	6181(16)	7944(14)	4319(10)	59(6)
C(24)	6138(18)	8727(13)	3702(9)	57(7)
C(25)	5003(17)	9046(11)	3207(10)	50(8)
C(26)	3842(16)	8556(10)	3351(8)	40(7)
N	7742(11)	6577(8)	1500(6)	28(5)
C(31)	8345(14)	5679(10)	951(7)	29(6)
C(32)	7535(14)	4826(10)	1015(8)	31(7)
C(33)	8392(16)	3890(11)	559(9)	39(8)
C(34)	7654(17)	2989(11)	625(10)	47(9)
C(35)	8757(14)	7310(10)	1291(8)	29(5)
C(36)	8388(16)	8301(11)	1745(9)	39(8)
C(37)	9492(17)	8970(11)	1451(9)	44(8)
C(38)	9134(17)	9983(11)	1869(10)	52(9)
C(39)	7744(14)	6089(11)	2356(8)	31(7)
C(40)	9253(14)	5219(12)	2590(8)	35(7)
C(41)	9181(16)	4918(12)	3497(8)	41(8)
C(42)	10662(17)	4081(14)	3723(9)	57(9)
C(43)	6059(14)	7234(11)	1397(8)	33(5)
C(44)	5719(15)	7813(11)	604(8)	37(7)
C(45)	4010(16)	8512(12)	647(10)	48(7)
C(46)	3562(18)	9160(13)	- 157(10)	53(10)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

spectra (FAB⁻) of complexes **1a**,**b** do not show the parent ion.

The structure of 1a has been determinated by X-ray analysis; the anion is shown in Fig. 1. It displays a nine-membered ring with a pseudo-chair conformation; the a'oms S(1), C(4), C(5), Au(1), Au(2), S(2) are coplanar (mean deviation 0.06 Å), with the $C_3S_5^{2-}$ ligand pointing up from this plane (interplanar angle 61°) and the PPh₂ group down (50°). The intramolecular gold-gold distance is 3.026(1) Å, which is longer than those found in hetero-bridged dinuclear compounds with eight-membered rings, $[Au_2(\mu-CH_2-PPh_2CH_2)(\mu-S_2CNEt_2)]$ (2.868(1) Å) [13], or in ninemembered rings, $[Au_2(i-MNT)(dppe)]$ (2.867(1) Å) [19]

Au(1)-C(4)	2.107(12)	Au(1)-S(1)	2.308(4)
Au(1)-Au(2)	3.0263(11)	Au(2)-C(5)	2.069(7)
Au(2)-S(2)	2.301(4)	S(1)-C(1)	1.752(12)
S(2)-C(2)	1.743(13)	S(3)-C(3)	1.72(2)
S(3)-C(1)	1.766(13)	S(4)-C(3)	1.72(2)
S(4)-C(2)	1.763(13)	S(5)-C(3)	1.664(14)
C(1)-C(2)	1.33(2)	P-C(5)	1.772(8)
PC(4)	1.776(11)	P-C(11)	1.799(8)
P-C(21)	1.815(14)		
C(4)-Au(1)-S(1)	171.5(3)	C(4)-Au(1)-Au(2)	89.1(3)
S(1)-Au(1)-Au(2)	98.(9)	C(5)-Au(2)-S(2)	175.1(2)
C(5)-Au(2)-Au(1)	89.0(2)	S(2)-Au(2)-Au(1)	95.60(9)
C(1)-S(1)-Au(1)	105.8(4)	C(2)-S(2)-Au(2)	104.9(4)
C(3)-S(3)-C(1)	98.7(7)	C(3)-S(4)-C(2)	98.9(7)
C(2)-C(1)-S(1)	131.1(10)	C(2)-C(1)-S(3)	115.3(9)
\$(1)-C(1)-\$(3)	113.6(7)	C(1)-C(2)-S(2)	130.4(10)
C(1)-C(2)-S(4)	115.5(10)	S(2)-C(2)-S(4)	113.9(7)
S(5)-C(3)-S(3)	123.4(10)	S(5)-C(3)-S(4)	125.1(9)
S(3)-C(3)-S(4)	111.6(8)	C(5)-P-C(4)	113.0(5)
C(5)-P-C(11)	109.8(5)	C(4)-P-C(11)	108.6(5)
C(5)-P-C(21)	109.2(5)	C(4)-P-C(21)	110.7(6)
C(11)-P-C(21)	105.4(5)	P-C(4)-Au(1)	111.1(6)
P-C(5)-Au(2)	111.1(4)		

Selected bond lengths (Å) and angles (°) for compound 1a



and $[Au_2(i-MNT)(dppAs)]$ (2.90 Å) [19], and shorter than in a hetero-bridged ten-membered ring, $[Au_2(S-(CH_2)_3S)(dppm)]$ (3.128(1)Å) [18]. The Au–S distances (2.308(4) and 2.301(4)Å) are shorter than those observed in other dinuclear compounds where the $C_3S_5^{2-}$ ligand acts



rig. 1. The anion of NBu₄[Au(μ -C₃S₃)(μ -CH₂PPh₂CH₂)] in the crystal, showing the numbering scheme. H atoms are omitted.

as a bridge $[Au_3(\mu-C_3S_5)(PPh_3)_3]CIO_4$ (2.336(2) and 2.2338(2) Å) [12], $[Au_2(\mu-C_3S_5)(PPh_3)_2]$ (2.347(1) and 2.343(1) Å) and $[Au_4(\mu-C_3S_5)_2(\mu-dppm)_2]$ [12] (~2.34 Å). Au-C_{ylide} (2.069(7), 2.107(12) Å) resemble those of related complexes: $[Au_2(\mu-CH_2PPh_2CH_2)(\mu-S_2CNEt_2)]$ (2.083 and 2.052 Å) [13].

We believe that the structure of complex 2 could be similar, but with a ten-membered diauracycle, because (i) this is consistent with the mass spectrum and (ii) a higher degree of nuclearity (as in the dppm derivative) should give a more complicated NMR spectra.

Another way to obtain cyclic derivatives is shown in Eq. (1), starting from the recently reported $[Au_2(\mu-C_3S_5)-(PPh_3)_2]$ and by reaction with $[Au_2(\mu-L-L)(C_6F_5)_2]$. This type of reaction, affording diauracycles after elimination of $[Au(C_6F_5)PPh_3]$, has been reported previously [15].

$$[\operatorname{Au}_{2}(\mu-C_{3}S_{5})(\operatorname{PPh}_{3})_{2}] + [\operatorname{Au}_{2}(\mu-L-L)(C_{6}F_{5})_{2}] \rightarrow 2[\operatorname{Au}(C_{6}F_{5})(\operatorname{PPh}_{3})] + [\operatorname{Au}_{2}(\mu-C_{3}S_{5})(L-L)]$$
(1)

This reaction has been tested with L-L=dppm or dppe; the results are the same as in Scheme 1, because complexes $[Au_4(\mu-C_3S_5)_2(\mu-dppm)_2]$ and $[Au_2(\mu-C_3S_5)(\mu-dppe)]$ (2) are obtained, but in worse yield.

The third method tested has previously been used in the preparation of $[Au_4(\mu-C_3S_5)_2(\mu-dppm)_2]$ [12], and consists of the addition of the bidentate ligand to a suspension of $[Au_2(C_3S_5)(AsPh_3)]_{\odot}$

$$\frac{1/n[Au_{2}(C_{3}S_{5})(A^{\prime}Ph_{3})]_{4} + L - L \rightarrow}{[Au_{2}(\mu - C_{3}S_{5})(\mu - L - L)]}$$
(2)

When dppe is used as the bidentate ligand, complex 2 can be prepared, but if anionic ligands such as dithiocarbamates are used, and after adding ammonium or phosphonium salts, complexes $Q[Au_2(\mu-C_3S_5)(\mu-S_2CNR_2)]$ (3-5) can be obtained (Eq. (3))

$$[Au_{2}(C_{3}S_{5})(AsPh_{3})] + Na_{2}S_{2}CNR_{2} + QX \rightarrow Q[Au_{2}(\mu-C_{3}S_{5})(\mu-S_{2}CNR_{2})]$$
(3)

R=Me, Q=PPN (3); $R=Et, Q=NBu_4$ (4); $R=CH_2Ph, Q=NBu_4$ (5a) or PPN (5b)

Complexes 3-5 are isolated as brown $(Q=NBu_4)$ or orange (Q=PPN) solids, air- and moisture-stable at room

temperature. They behave as 1:1 electrolytes (90–113 Ω^{-1} cm² mol⁻¹) in acetone solution. Their IR spectra show the bands characteristic of the C₃S₅²⁻ ligand and bands at 1267 (4), 1211 (5), 1249 (6) cm⁻¹ due to $v(C-S_{dithiccarbanate})$. The ¹H NMR spectra show only one resonance for each group of the dithiccarbamate protons (Table 1), in accordance with the equivalence of the two R groups of the dithiccarbamate.

To synthesize the homo-bridged complex with two dmit ligands, we have used gold compounds with labile ligands such as tetrahydrothiophene (tht) or triphenylarsine (AsPh₃) giving the 'AuCl' unit in solution, which is able to react with $Na_2[C_3S_5]$ according to Eq. (4). Addition of PPNCl affords the expected complex.

AuCl(tht)
Na₂[C₃S₅] + or + 2PPNCl
$$\rightarrow$$

AuCl(AsPh₃)
(PPN)₂[Au₂(μ -C₃S₅)₂] (6) (4)

Complex 6 is an air- and moisture-stable orange solid at room temperature. It behaves as a 2:1 electrolyte in acetone solution and the IR spectra show the bands assignable to the $C_3S_5^{2-}$ ligand and the counter-cation PPN.

Complexes 1-6 are good starting materials for oxidative processes leading to conducting materials. We have tested the reactions with $(TTF)_3(BF_4)_2$ but only in the case of 1 is it possible to isolate a pure product (Eq. (5))

$$Q[Au_{2}(\mu-C_{3}S_{5})(\mu-CH_{2}PPh_{2}CH_{2})] + (TTF)_{3}(BF_{4})_{2} \rightarrow$$

$$(TTF)[Au_{2}(C_{3}S_{5})(CH_{2}PPh_{2}CH_{2})] \quad (7) \qquad (5)$$

 $(Q = NBu_4, PPN)$

The reaction of complex 1 with an excess of $(TTF)_3(BF_4)_2$ leads to the precipitation of a dark solid in a high yield (Eq. (5)). The IR spectrum of 7 shows the v(C=C) band at 1437 cm⁻¹, characteristic of the existence of $C_3S_5^{2-}$ units. The presence of an absorption at 1414 cm⁻¹ in Raman is in accordance with the presence of TTF⁺ moieties [28]. These data indicate that no oxidation has taken place in complex 7. The electrical conductivity of this complex at room temperature using the two probe method in compared pellets is 2×10^{-7} S cm⁻¹; this value is relatively low compared with other C_3S_5 complexes with TTF as cation [1].

Complex 6 reacts with AgClO₄ in a 1:2 ratio affording a heteronuclear derivative $[Au_2Ag_2(C_3S_5)_2]$ (8) as a black solid. PPNClO₄ can be isolated from the mother liquor. Because of the insolubility of 8, no crystals could be grown to determine the exact polymeric structure, and we only know the stoichiometry deduced by elemental analysis: C, H, S, Au + Ag (see Section 2). Complex 8 does not show an EPR signal.

$$(PPN)_{2}[Au_{2}(C_{3}S_{5})_{2}] + 2AgClO_{4} \rightarrow$$

$$[Au_{2}Ag_{2}(C_{3}S_{5})_{2}] + 2PPNClO_{4} \qquad (6)$$

Probably a polymeric structure is responsible for the electrical conductivity that complex 8 shows at room temperature in compacted pellets: 3×10^{-5} S cm⁻¹.

4. Supplementary material

Further details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD 404176.

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