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# High-Coordinate Gold(I) Complexes with Dithiocarboxylate Ligands

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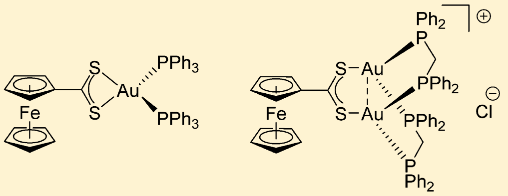
Supporting Information



**ABSTRACT:** Ferrocene dithiocarboxylate has been introduced into the chemistry of gold(I) and copper(I). First, a modified synthesis of piperidinium ferrocene dithiocarboxylate (**1**) is reported. Reaction of this reagent with [Au(tht)Cl] in the presence of different phosphines resulted in monomeric, dimeric, and polymeric structures. Although gold(I) is usually two coordinate, mainly three- and four-fold coordinated compounds were obtained by using ferrocene dithiocarboxylate as ligands. The isolated compounds are $[(FcCSS)Au(PPh_3)_2]$ (**2**) (FcCSS = ferrocene dithiocarboxylate), $[(FcCSS)Au_2(dppm)_2]$ (**3**) (dppm = bis(diphenylphosphino)methane), and $[(FcCSS)Au(dppf)]_n$ (**4**) (dppf = bis(diphenylphosphino)ferrocene) $[\{(FcCSS)Au\}_2(dppp)]$ (**5**) (dppp = bis(diphenylphosphino)propane). The FcCSS ligand shows a remarkable flexible coordination mode. It coordinates either in a monodentate, a chelating, or in a metal bridging mode. In the four gold(I) complexes **2**–**5** four different coordination modes of the FcCSS ligand are seen. Attempts to extend this rich coordination chemistry to other coinage metals were only partly successful. $[(FcCSS)Cu(PPh_3)_2]$ (**6**) was obtained from the reaction of piperidinium ferrocene dithiocarboxylate with $[(Ph_3P)_3CuCl]$. $^{57}$Fe–Mössbauer spectroscopy was performed for compounds **2**–**4**. The spectra show isomer shifts and quadrupole splittings that are typical for diamagnetic ferrocenes.

## INTRODUCTION

The coordination and organometallic chemistry of gold is currently an emerging field in chemistry.[1] The rapid development in this area has been summarized in some recent reviews. It covers the synthesis and applications of gold and gold compounds in synthesis,[2−10] material and surface sciences,[11−15] for biological applications,[16,17] in heterogeneous catalysis,[14,18−22] and especially, in homogeneous catalysis.[23−27] Molecular gold(I) compounds with a closed shell $d^{10}$ electronic configuration are linearly coordinated in most cases. However, gold(I) complexes possessing higher coordination numbers also exist, although they are less common. In particular, high coordinate gold(I) ions with gold–gold contacts are rare.[1] These contacts are commonly a result of strong relativistic contractions and low coordination numbers. The gold(I) ion is, according to Pearson's HSAB concept,[28] usually considered a soft metal ion preferring coordination by soft ligands such as phosphines, organic sulfur ligands, and N-heterocyclic carbenes (NHCs). Sulfur containing ligands derived from dithiocarbamate[29−32] and xanthate[33] usually act as monodentate ligands but in a few cases bidentate coordination to two metal centers has been reported.[29−32] Although it is known that dithiocarboxylates are as flexible in coordination as dithiocarbamates they are less common in gold(I) chemistry.[34−39]

We were interested to introduce ferrocene dithiocarboxylate as redox active ligand into gold(I) chemistry. Originally we intended to influence the reactivity and the solubility of the resulting products. Although ferrocene dithiocarboxylate has been known as a ligand since 1974,[40] it has been rarely used in coordination chemistry. Although some metal salts,[40] as well as cyclopentadienyl,[41] nitrido,[42] and carbonyl complexes[43] of ferrocene dithiocarboxylate have been reported, to the best of our knowledge no structurally characterized derivative and no gold complex is known. Thus, ferrocene dithiocarboxylate has been neglected as ligand. This is surprising since ferrocene based ligands are widely used, for example, 1,1′-bis(diphenylphosphino)ferrocene[44] because of their rigid backbones in catalytic systems.[45] They are also used for the construction of coordination polymers.[46] Ferrocene-containing compounds have also been studied in terms of their magnetic and electronic properties.[47] Herein, we report the synthesis and characterization of the first structurally characterized metal complexes of ferrocene dithiocarboxylate.

## EXPERIMENTAL SECTION

**General Procedures.** Although all products are not very air-sensitive most manipulations were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware or in an argon-filled MBraun glovebox. Dichloromethane was distilled from $LiAlH_4$ under nitrogen prior to use. Hydrocarbon solvents (THF, toluene, and *n*-pentane) were dried using an MBraun solvent purification system (SPS-800). Deuterated solvents were obtained from Carl Roth GmbH (99.5 atom % D). NMR spectra were recorded on a Bruker Avance II 300 MHz or Avance 400 MHz. Chemical shifts are referenced to the residue $^{1}$H and $^{13}$C resonances of the deuterated solvents and are reported relative to tetramethylsilane

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and 85% phosphoric acid ($^{31}$P NMR). IR spectra were obtained on a Bruker Tensor 37. Mass spectra were recorded at 70 eV on a Thermo Scientific DFS and on a IonSpec FT-ICR (7 T) ESI-MS. UV−vis spectra were recorded on a Varian Cary 50 spectrophotometer. X-ray powder diffraction patterns (XRD) for different samples of **4** were measured on a STOE STADI P diffractometer (Cu−K$_\alpha$ radiation, Germanium monochromator, Debye−Scherrer geometry) in sealed glass capillaries. The theoretical powder diffraction pattern was calculated on the basis of the atom coordinates obtained from single crystal X-ray analysis by using the program package *Mercury 3.1* by CCDC.[48] Elemental analyses were carried out with an Elementar Vario EL or Micro Cube. [Au(tht)Cl][49,50] (tht = tetrahydrothiophene) and [(PPh$_3$)$_3$CuCl][51] were prepared according to modified standard procedures.

*Piperidinium Ferrocene Dithiocarboxylate (**1**).* The synthesis was carried out as described in the literature with slight modifications.[40] A few drops of an ethereal solution (15 mL) of bromo ferrocene (4.00 g, 15.0 mmol) and iodomethane (0.5 mL, 7.5 mmol) were added to magnesium turnings (1.10 g, 45.0 mmol) in diethyl ether (10 mL). The Grignard reaction was initiated by adding iodomethane (0.1 mL) and brief heating of the solvent. The rest of the bromoferrocene solution was added dropwise and the reaction was stirred for 3 h. To the resulting orange suspension, carbondisulfide (1.8 mL, 30.0 mmol) dissolved in THF (50 mL) was added dropwise at 0 °C. After warming up to room temperature overnight, the reaction mixture was poured into ice cooled hydrochloric acid (25 mL, 16%) and the product was extracted with diethyl ether (200 mL). The solvent was removed in vacuo and the residue was extracted with sodium hydroxide (150 mL, 16%) and water (100 mL). After filtering and acidifying the solution with hydrochloric acid (100 mL, 32%) at 0 °C, the product was extracted with diethyl ether (3 × 100 mL). The ether layer was dried over magnesium sulfate and treated with piperidine (2 mL). The precipitate was filtered off and washed with diethyl ether. The desired product was obtained as a red microcrystalline solid (2.90 g, 8.35 mmol, 55%). $^1$H NMR (CDCl$_3$, 300 MHz, 25 °C): $\delta$ (ppm) = 7.14 (br. s, 2H, N$H_2$), 5.32 (m, 2H, *o*-Cp), 4.54 (m, 2H, *m*-Cp), 4.19 (s, 5H, C$_5H_5$), 3.27 (m, 4H, pip-NC$H_2$), 1.85 (m, 4H, pip−C$H_2$), 1.62 (m, 2H, pip−C$H_2$). $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz, 25 °C): $\delta$ (ppm) = 253.9 (CSS), 94.8 (*i*-Cp), 72.2 (*o*-Cp), 71.5 (*m*-Cp), 71.4 (C$_5$H$_5$), 45.2 (pip-NC), 23.1 (pip-NCC), 22.4 (pip-CH$_2$). UV−vis (CH$_2$Cl$_2$): $\lambda_{max}$ (nm) [$\varepsilon_{max}$ (l·mol$^{-1}$·cm$^{-1}$)] = 310 (sharp) [11918]; 335 (shoulder) [6297]; 529 (broad) [1462]. The analytical data matches with the literature.[40] C$_{16}$H$_{21}$NFeS$_2$ (347.33): calculated C 55.33, H 6.09, N 4.03, S18.46; found C 54.86, H 6.10, N 3.93, S 18.48.

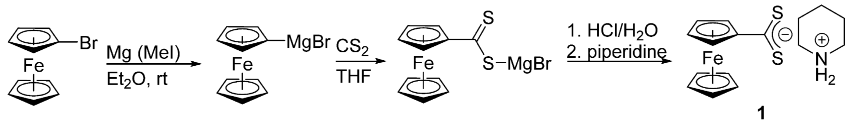
*[(FcCSS)Au(PPh$_3$)$_2$] (**2**).* The synthesis was carried out in air. [Au(tht)Cl] (162 mg, 0.50 mmol) and triphenylphosphine (264 mg, 1.00 mmol) were dissolved in dichloromethane (10 mL). A solution of piperidinium ferrocene dithiocarboxylate (175 mg, 0.50 mmol) in dichloromethane (5 mL) was added dropwise and the mixture was stirred for 30 min at room temperature. After washing the solution with water (3 × 20 mL) and drying over magnesium sulfate, the solvent was removed in vacuo and the residue was washed with ethanol (3x 10 mL) and pentane (2 × 10 mL). To achieve a higher purity the reaction mixture was removed and the residue was dissolved in dry THF (3.5 mL). After the filtration, the product was crystallized by slow diffusion of pentane into the solution. Yield (red crystals): 298 mg, 0.29 mmol, 58%. $^1$H NMR (300 MHz, C$_6$D$_6$, 25 °C): $\delta$ (ppm) = 7.46 (m, 12H, *o*-Ph), 6.96 (m, 18H, *m*-Ph, *p*-Ph), 5.53 (m, 2H, *o*-Cp), 4.25 (m, 2H, *m*-Cp), 4.17 (s, 5H, C$_5H_5$), 3.56 (m, 4H, THF−OCH$H_2$), 1.41 (m, 4H, THF−OCHH$_2$C$H_2$). $^{13}$C{$^1$H} NMR (75 MHz, C$_6$D$_6$, 25 °C): $\delta$ (ppm) = 247.3 (CSS), 134.0 (d, $J_{PC}$ = 16.2 Hz, Ph), 133.7 (Ph), 129.8 (d, $J_{PC}$ = 1.4 Hz, Ph), 128.6 (d, $J_{PC}$ = 9.5 Hz, Ph), 94.1 (*i*-Cp), 72.0 (*o*-Cp), 71.7 (C$_5$H$_5$), 71.2 (m-Cp), 67.5 (THF-OC), 25.5 (THF−OCHC). $^{31}$P{$^1$H} NMR (121 MHz, C$_6$D$_6$, 25 °C): $\delta$ (ppm) = 20.4 (s). EI-MS (70 eV): *m*/*z* (%) = 720 [M − PPh$_3$]$^+$, 656 [M − PPh$_3$ − C$_5$H$_5$]$^+$, 552, 538, 534, 504, 490, 470, 428, 426, 396, 394, 372, 368, 362, 294, 262 [PPh$_3$]$^+$, 215, 183, 139, 107, 77. IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3051 (w), 2966 (w), 2857 (w), 1585 (w), 1478 (m), 1432 (m), 1395 (w), 1378 (w), 1329 (w), 1307 (w), 1256 (m), 1205 (w), 1182 (m), 1157 (w), 1095 (m), 1064 (w), 1045 (w), 1026 (w), 993 (m), 955 (w), 913 (w), 836 (w), 811 (m), 744 (s), 705 (m), 691 (s), 668 (m), 618 (w), 531 (m), 515 (s). C$_{47}$H$_{39}$AuFeS$_2$P$_2$·0.5 C$_4$H$_8$O (1018.76): calculated C 57.77; H 4.25; S 6.29; found C 57.39; H 4.27; S 6.22. UV−vis (CH$_2$Cl$_2$): $\lambda_{max}$ (nm) [$\varepsilon_{max}$ (l·mol$^{-1}$·cm$^{-1}$)] = 384 (broad) [6509], 531 (very broad) [2441] − (THF) $\lambda_{max}$ (nm) = 383 (broad), 512 (very broad).

*[(FcCSS)Au$_2$(dppm)$_2$]Cl (**3**).* The synthesis was carried out in air. [Au(tht)Cl] (640 mg, 2.00 mmol) and bis(diphenylphosphino)-methane (770 mg, 2.00 mmol) were dissolved in dichloromethane (20 mL). A solution of piperidinium ferrocene dithiocarboxylate (350 mg, 1.00 mmol) in dichloromethane (10 mL) was added dropwise and the mixture was stirred for 30 min. After washing the solution with water (3 × 100 mL) and drying over magnesium sulfate, the solvent was removed in vacuo and the residing solid was washed with ethanol (3 × 10 mL) and pentane (2 × 10 mL). Yield (red powder): 950 mg, 0.61 mmol, 61.5%. Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a saturated solution of dry dichloromethane. $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ (ppm) = 7.73 (m, 16H, *o*-Ph), 7.39 (m, 24H, *m*-Ph, *p*-Ph), 5.13 (s, 2H, o-Cp), 4.60 (s, 2H, m-Cp), 4.32 (br. s, 4H, PC$H_2$P), 4.07 (s, 5H, C$_5H_5$). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$, 25 °C): $\delta$ (ppm) = 133.5 (Ph), 131.8 (Ph), 129.0 (Ph), 71.8 (C$_5$H$_5$). Because of poor solubility, not all carbon atoms were detected. $^{31}$P{$^1$H} NMR (121 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ (ppm) = 31.3 (s). ESI-MS (CH$_2$Cl$_2$) 1423.15 ([(FcCSS)-Au$_2$(dppm)$_2$]$^+$), 1289.10. IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 3048 (w), 3011 (w), 2901 (w), 2843 (w), 2819 (w), 1653 (w), 1574 (w), 1559 (w), 1540 (w), 1484 (w), 1434 (m), 1419 (w), 1392 (w), 1366 (w), 1319 (w), 1275 (w), 1241 (w), 1196 (w), 1168 (w), 1099 (m), 1039 (w), 1027 (w), 998 (m), 979 (w), 836 (w), 823 (m), 796 (m), 784 (m), 737 (m), 723 (m), 688 (s), 665 (m), 616 (w), 508 (w). UV−vis (CH$_2$Cl$_2$): $\lambda_{max}$ (nm) [$\varepsilon_{max}$ (l·mol$^{-1}$·cm$^{-1}$)] = 397 (broad); 548 (very broad). Because of lattice solvent $\varepsilon_{max}$ could not be determined. C$_{61}$H$_{53}$Au$_2$ClFeP$_4$S$_2$·CH$_2$Cl$_2$ (1544.26): calculated C 48.22; H 3.59; S 4.15; found C 48.12; H 3.55; S 4.11.

*[(FcCSS)Au(dppf)]$_n$ (**4**).* Piperidinium ferrocene dithiocarboxylate (87 mg, 0.25 mmol) and [Au(tht)Cl] (80 mg, 0.25 mmol) were dissolved in dichloromethane (10 mL) forming a black suspension. A solution of bis(diphenylphosphino)ferrocene (139 mg, 0.25 mmol) in dichloromethane (10 mL) was added, and the resulting red solution was stirred for 1 h. After a few minutes, a red solid started precipitating which was separated by filtration and washed with dichloromethane (2 × 5 mL). Yield (red powder): 100 mg, 40%. Crystals were grown by overlaying a solution of piperidinium ferrocenedithiocarboxylate (87 mg, 0.25 mmol) and bis-diphenylphosphinoferrocene (139 mg, 0.25 mmol) in dichloromethane (5 mL) with a solution of [Au(tht)Cl] (80 mg, 0.25 mmol) dissolved in a mixture of dichloromethane (3.5 mL) and THF (2.5 mL). (C$_{45}$H$_{37}$Fe$_2$AuS$_2$P$_2$)$_n$: calculated C 53.38, H 3.68, S 6.33, found C 53.17, H 3.70, S 6.03. IR (ATR): (cm$^{-1}$) = 3072 (w), 3051 (w), 1653 (w), 1559 (w), 1479 (w), 1434 (w), 1392 (w), 1310 (w), 1259 (w), 1207 (w), 1168 (w), 1100 (w), 1069 (w), 1041 (w), 1027 (w), 1002 (w), 997(w), 958 (w), 821 (w), 811 (w), 751 (w), 739 (w), 696 (w), 667 (m), 637 (m), 619 (w), 540 (m), 513 (m).

*[{(FcCSS)Au}$_2$(dppp)] (**5**).* Bis(diphenylphosphino)propane (124 mg, 0.30 mmol) and [Au(tht)Cl] (192 mg, 0.60 mmol) were dissolved in dichloromethane (15 mL) and stirred for 30 min. Piperidinium ferrocene dithiocarboxylate (208 mg, 0.6 mmol) was added. After stirring for another 30 min, the solvent was removed in vacuo and the residue was dissolved in THF. The insoluble piperidinium hydrochloride was separated by filtration. The solvent was removed in vacuo and the solid was suspended in pentane (2 mL). Dichloromethane was added until a clear solution had formed which was stored for 12 days at −20 °C. Yield (red crystals): 119 mg; 0.091 mmol, 28%. C$_{49}$H$_{44}$Au$_2$Fe$_2$P$_2$S$_4$·CH$_2$Cl$_2$. $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ (ppm) = 7.84 (m, 8H, *o*-Ph), 7.47 (m, 12H, *m*-Ph, *p*-Ph), 5.34 (s, 2H, DCM), 5.21 (m, 2H, *o*-Cp), 4.61 (m, 2H, *m*-Cp), 4.27 (s, 10H, C$_5H_5$), 2.99 (m, 4H, PC$H_2$), 1.98 (m, 2H, C$H_2$). $^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ (ppm) = 246.4 (CSS), 133.7 (d, $^1J_{PC}$ = 13.3 Hz, *i*-Ph), 131.8 (d, $^2J_{PC}$ = 2.5 Hz, *o*-Ph), 130.0 (d, $^3J_{PC}$ = 54.7 Hz, *m*-Ph), 129.4 (d, $^4J_{PC}$ = 11.3 Hz, *p*-Ph), 93.1 (*i*-Cp), 72.7 (*o*-Cp), 71.9 Cp, 71.3 (*m*-Cp), 28.2 (dd, $^1J_{PC}$ = 34.2 Hz, $^3J_{PC}$ = 10.2 Hz, PC), 19.7

**Scheme 1. Synthesis of Piperidinium Ferrocene Dithiocarboxylate**



**1**

yield: 55 %

(t, $^3J_{PC}$ = 2.5 Hz, PCC). $^{13}C\{^1H, ^{31}P\}$ NMR (100 MHz, $CD_2Cl_2$, 25 °C): $\delta$ (ppm) = 133.7 (*i*-Ph), 131.8 (*o*-Ph), 130.0 (*m*-Ph), 129.4 (*p*-Ph), 93.4 (*i*-Cp), 72.8 (o-Cp), 72.0 ($C_5H_5$), 71.3 (*m*-Cp), 28.2 (PCC), 19.7 (PCC). $^{31}P\{^1H\}$ NMR (121 MHz, $C_6D_6$, 25 °C): $\delta$ (ppm) = −27.5. IR (ATR): ($cm^{-1}$) = 1483 (w), 1443 (w), 1436 (w), 1426 (w), 1408 (w), 1397 (w), 1375 (w), 1256 (m), 1205 (w), 1133 (w), 1105 (w) 1059 (w), 1046 (w), 1034 (w), 1026 (w), 995 (m), 939 (w), 837 (w), 820 (w), 797 (m), 774 (w), 750 (w), 738 (m), 714 (w), 699 (w), 688 (m), 665 (w), 651 (w), 616 (w), 590 (w), 529 (w), 513 (m), 496 (s), 476 (m), 457 (w). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ (nm) [$\varepsilon_{max}$ (l·mol$^{-1}$·cm$^{-1}$)] = 386 (broad); 530 (very broad). Because of the lattice solvent, $\varepsilon_{max}$ could not be determined. $C_{49}H_{44}P_2S_4Fe_2Au_2$ (1328.73): calculated C 44.29, H 3.34, S 9.65; found C 42.97, H 3.33, S 9.24. In the elemental analysis we frequently observed low carbon values.

*[(FcCSS)Cu(PPh$_3$)$_2$] (**6**).* [$(PPh_3)_3CuCl$] (443 mg, 0.50 mmol) and piperidinium ferrocenedithiocarboxylate (175 mg, 0.50 mmol) were dissolved in dichloromethane (15 mL) and the mixture was stirred for 2 h. The solvent was removed in vacuo and the residue was dissolved in THF (4 mL). After filtration, the product was crystallized by slow diffusion of pentane into the solution. Yield (red crystals): 381 mg, 0.41 mmol, 83%. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ (ppm) = 7.55 (m, 12H, *o*-Ph), 6.95 (m, 18H, *m*-Ph, *p*-Ph), 5.49 (m, 2H, *o*-Cp), 4.22 (m, 2H, *m*-Cp), 4.13 (s, 5H, $C_5H_5$), 3.56 (m, 4H, THF−OCH$H_2$), 1.40 (m, 4H, THF−OCHC$H_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ (ppm) = 249.0 (CSS), 134.2 (Ph), 133.8 (Ph), 129.5 (Ph), 128.4 (Ph), 92.2 (*i*-Cp), 71.5 (*o*-Cp), 71.3 ($C_5H_5$), 69.7 (*m*-Cp), 68.0 (THF-O*C*), 25.7 (THF−OCH*C*). $^{31}P\{^1H\}$ NMR (121 MHz, $C_6D_6$, 25 °C): $\delta$ (ppm) = −0.8 (s). IR (ATR): $\nu$;~ ($cm^{-1}$) = 3049 (w), 1699 (w), 1653 (w), 1584 (w), 1558 (w), 1540 (w), 1478 (w), 1432 (m), 1376 (w), 1327 (w), 1308 (w), 1260 (w), 1204 (w), 1182 (w), 1156 (w), 1092 (w), 1067 (w), 1042 (w), 1026 (m), 993 (w), 920 (w), 871 (w), 838 (w), 813 (w), 742 (m), 692 (s), 667 (w), 618 (w), 526 (m), 516 (m). $C_{47}H_{39}CuFeP_2S_2$ (849.29): calculated C 66.47; H 4.63; S 7.55; found C 65.60; H 4.77; S 7.00. $C_{47}H_{39}CuFeP_2S_2 \cdot C_4H_8O$

*Electrochemistry.* Cyclic voltammetry measurements were performed with an METROHM potentiostat (PGSTAT 101) and an electrochemical cell for sensitive compounds. We used a freshly polished Pt disk working electrode, a Pt stick as the counter electrode, and a Ag wire as (pseudo) the reference electrode ([$^n$Bu$_4$N][PF$_6$] (0.1 M) as electrolyte). Potentials were calibrated against the Fc/Fc$^+$ couple, which has a potential of $E^0_{1/2}$ = 0.35 V vs Ag/AgCl (Supporting Information Figures S3−S5).

*X-ray Crystallographic Studies of **2**−**6**.* A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE IPDS 2 diffractometer.

All structures were solved by the Patterson method (SHELXS-97[52]). The remaining non-hydrogen atoms were located from difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $(F_0 - F_c)^2$, where the weight is defined as $4F_0^2/2(F_0^2)$ and $F_0$ and $F_c$ are the observed and calculated structure factor amplitudes using the program SHELXL-97.[52] Carbon-bound hydrogen atom positions were calculated. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond lengths and angles have been deposited as Supporting Information.

Crystal data for **2**: $C_{47}H_{39}AuFeP_2S_2 \cdot 0.5(C_4H_8O)$, M = 1018.71, $a$ = 12.348(3) Å, $b$ = 13.089(3) Å, $c$ = 15.366(3) Å, $\alpha$ = 97.82(3)°, $\beta$ = 95.82(3)°, $\gamma$ = 113.23(3)°, $V$ = 2227.9(9) Å$^3$, $T$ = 173(2) K, space group $P\bar{1}$, $Z$ = 2, $\mu$(MoK$\alpha$) = 3.814 mm$^{-1}$, 22187 reflections measured, 7951 independent reflections ($R_{int}$ = 0.0395). The final $R_1$ values were 0.0310 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1051 (all data). The goodness of fit on $F^2$ was 1.092.

Crystal data for **3**: $[C_{61}H_{53}Au_2FeP_4S_2]Cl$, M = 1459.26, $a$ = 11.6660(3) Å, $b$ = 22.0215(4) Å, $c$ = 23.4212(5) Å, $\beta$ = 95.948(2)°, $V$ = 5984.6(2) Å$^3$, $T$ = 150(2) K, space group $P2_1/n$, $Z$ = 4, $\mu$(MoK$\alpha$) = 5.388 mm$^{-1}$, 32828 reflections measured, 11255 independent reflections ($R_{int}$ = 0.0417). The final $R_1$ values were 0.0308 ($I > 2\sigma(I)$). The final wR($F^2$) values were 0.0687 (all data). The goodness of fit on $F^2$ was 0.923.

Crystal data for **4**: $C_{45}H_{37}AuFe_2P_2S_2 \cdot 2(CH_2Cl_2)$, M = 1109.47, $a$ = 11.104(2) Å, $b$ = 26.986(5) Å, $c$ = 17.106(3) Å, $\beta$ = 107.65(3), $V$ = 4884(2) Å$^3$, space group $P2_1/c$, $Z$ = 4.

Crystal data for **4′**: $C_{45}H_{37}AuFe_2P_2S_2$, M = 1012.47, $a$ = 11.040(2) Å, $b$ = 21.488(4) Å, $c$ = 17.106(3) Å, $\beta$ = 107.62(3)°, $V$ = 3874.6(15) Å$^3$, space group $P2_1/n$, $Z$ = 4.

Crystal data for **5**: $C_{49}H_{44}Au_2Fe_2P_2S_4 \cdot 0.25\ CH_2Cl_2$, M = 1349.88, $a$ = 15.180(3) Å, $b$ = 20.750(4) Å, $c$ = 16.740(3) Å, $\beta$ = 105.80(3)°, $V$ = 5074(2) Å$^3$, $T$ = 200(2) K, space group $P2_1/n$, $Z$ = 4, $\mu$(MoK$\alpha$) = 6.612 mm$^{-1}$, 46244 reflections measured, 6235 independent reflections ($R_{int}$ = 0.0876). The final $R_1$ values were 0.0485 ($I > 2\sigma(I)$). The final wR($F^2$) values were 0.1252 (all data). The goodness of fit on $F^2$ was 0.936.

Crystal data for **6**: $C_{47}H_{39}CuFeP_2S_2 \cdot C_4H_8O$, M = 921.33, $a$ = 10.780(2) Å, $b$ = 13.154(3) Å, $c$ = 19.292(4) Å, $\alpha$ = 95.35(3)°, $\beta$ = 100.13(3)°, $\gamma$ = 94.48(3)°, $V$ = 2668.6(10) Å$^3$, $T$ = 200(2) K, space group $P\bar{1}$, $Z$ = 2, $\mu$(MoK$\alpha$) = 0.840 mm$^{-1}$, 17611 reflections measured, 9393 independent reflections ($R_{int}$ = 0.0368). The final $R_1$ values were 0.0377 ($I > 2\sigma(I)$). The final wR($F^2$) values were 0.0945 (all data). The goodness of fit on $F^2$ was 0.862.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. 976102 (**2**), 976103(**3**), 976104 (**5**), and 976105(**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: (+(44)1223−336−033; email: deposit@ccdc.cam.ac.uk).

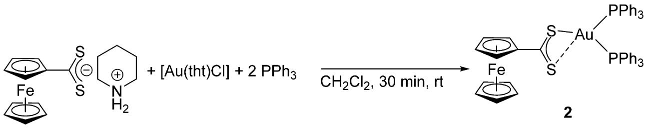
*Mössbauer Spectroscopy.* Mössbauer spectra were recorded using a conventional spectrometer in the constant-acceleration mode using both a continuous flow cryostat (Oxford Instruments) and a closed cycle cryostat equipped with a superconducting magnet as described earlier.[53] Isomer shifts are given relative to $\alpha$-Fe at room temperature. The spectra were analyzed by least-squares fits using Lorentzian line shapes.[54] Mössbauer spectra obtained under high magnetic fields were simulated by means of the spin Hamiltonian formalism which enables full diagonalization of the nuclear Hamiltonian and subsequent powder averaging.[54,55]

## ■ RESULTS AND DISCUSSION

Piperidinium ferrocene dithiocarboxylate (**1**) was synthesized by a modified literature procedure[40] starting from bromoferrocene, which was reacted with magnesium to give the corresponding Grignard reagent. In contrast to the literature procedure,[40] the reaction was run without cooling and the extraction steps were slightly modified. Treatment of this reagent with carbondisulfide resulted in the formation of ferrocene dithiocarboxylate, which was treated with piperidine to give **1** in moderate yield (Scheme 1).

To obtain gold(I) complexes, **1** was treated with [Au(tht)-Cl]. This resulted in a blue solution. After some time, a black insoluble polymeric species precipitated out of this solution. To avoid polymer formation different phosphines were reacted with [Au(tht)Cl] before **1** was added. For the formation of complexes, it was found that the order, in which the reactants are added to the reaction mixture, does not matter. Thus, the reaction of **1** with [Au(tht)Cl] and triphenylphosphine at room temperature in $CH_2Cl_2$ resulted in a red solution. After work-up, the iron/gold compound [(FcCSS)Au($PPh_3$)$_2$] (**2**) (FcCSS = ferrocene dithiocarboxylate) was obtained as red crystals (Scheme 2). In compound **2**, the gold(I) atom is surrounded by the ferrocene dithiocarboxylate and two triphenylphosphine ligands.

**Scheme 2. Synthesis of 2**



Compound **2** was fully characterized by standard spectroscopic/analytic techniques. In the $^1H$ NMR spectrum characteristic signals for the cyclopentadienyl rings were detected. The unsubstituted ring shows one singlet at $\delta$ = 4.17 ppm, whereas the signals of the other ring were split into two pseudo triplets at $\delta$ = 5.53 and 4.25 ppm. In the $^{31}P\{^1H\}$ NMR spectrum, the expected signal is seen at $\delta$ = 20.4 ppm (30.1 ppm in [$PPh_3AuCl$]).[56] The quaternary carbon atoms of the $CS_2$ group ($\delta$ = 247.3) and the Cp ($\delta$ = 94.1) ring were detected in the $^{13}C\{^1H\}$ NMR spectrum of **2**. The signal of the $CS_2$ group is shifted to high field in comparison to **1** ($\delta$ = 253.9), whereas the signal of the quaternary Cp carbon atom is not influenced ($\delta$ = 94.8 in **1**). Although no molecular peak was detected in the EI-MS spectrum, the fragments $[M - PPh_3]^+$ ($m/z$ = 720) and $[M - PPh_3 - C_5H_5]^+$ ($m/z$ = 656) were observed.

Compound **2** crystallized in the triclinic space group $P\bar{1}$ with two molecules of **2** and one molecule of THF in the unit cell. In contrast to most gold(I) compounds the metal is not linearly coordinated but instead it is three coordinated. Distorted trigonal planar coordination is observed. The sum of the angles P1–Au–P2 132.04(6)°, S1–Au–S2 66.13(6)°, and P1–Au–S2 103.23(6)°, P2–Au–S1 118.74(6)° is 358.57°, which is close to the ideal value of 360° for a trigonal planar arrangement. The P1–Au–P2 angle of 132.04(6)° is in the range of related dithiocarboxylate compounds, e.g. 137.4(8)° in [($PhCS_2$)Au($PPh_3$)$_2$][38] and 132.04(6)° [($MesCS_2$)Au($PPh_3$)$_2$].[57] The Au–P and Au–S bond lengths of **2** are in the range of [($PhCS_2$)Au($PPh_3$)$_2$][38] and [($MesCS_2$)Au($PPh_3$)$_2$].[57] A secondary interaction of the sulfur atom S2 to the gold atom with a significant longer Au–S2 2.808(2) Å distance compared to Au–S1 (2.583(2) Å) is observed. This interaction is indicated as dotted lines in Figure 1 and Scheme 2. Compound **2** turned out to be, to a certain extent, solvatochromic. In tetrahydrofuran or chloroform, the solutions appear either red or violet, originating from a shift of the maximum of one of its absorption bands from 512 to 531 nm (Supporting Information Figure S1).

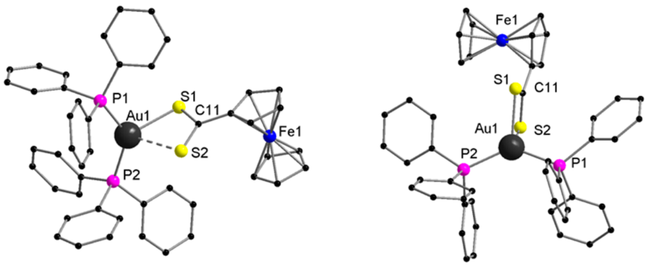


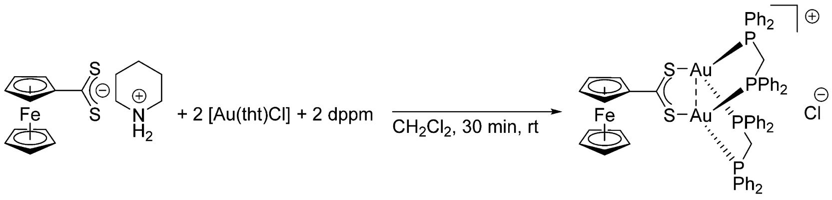
**Figure 1.** Molecular structure of **2** (front and side view). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Au–P1 2.323(2), Au–P2 2.308(2), Au–S1 2.583(2), Au–S2 2.808(2), S1–C11 1.706(7), S2–C11 1.6707(7); P1–Au–P2 132.04(6), S1–Au–S2 66.13(6), P1–Au–S1 107.79(6), P1–Au–S2 103.23(6), P2–Au–S1 118.74(6), P2–Au–S2 105.43(6), S1–C11–S2 121.6(4).

To study the influence of the phosphine ligand on the formation of the gold(I) complexes, **1** was treated with [Au(tht)Cl] in the presence of bis(diphenylphosphino)-methane (dppm) in a 2:2:1 ratio in $CH_2Cl_2$. The digold compound [(FcCSS)$Au_2$(dppm)$_2$] (**3**) was obtained in moderate yield (Scheme 3). Complex **3** is a bimetallic gold(I) complex in which the gold atoms are bridged by two dppm ligands and one ferrocene dithiocarboxylate ligand. Furthermore, an Au–Au interaction is observed which results in highly coordinated gold(I) atoms. Complex **3** resembles a bicyclic structure, in which the gold atoms are located in the bridgehead position. Obviously, the dithiocarboxylate ligand adopts a very flexible coordination mode. The slight change within the geometry of the donating phosphine ligand results in a complete change of the coordination environment of the gold(I) atoms. Thus, a monodentate coordination mode with a secondary interaction (compound **2**) and a metal bridging coordination mode (compound **3**) are observed, although the donating ligand atoms are the same.

Compound **3** is air-stable but it decomposes in polar solvents such as DMSO and DMF. $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded in $CH_2Cl_2$. In the $^1H$ NMR spectrum, several multiplets for the phenyl groups were observed in the region of $\delta$ = 7.74–7.71 ppm and 7.47–7.30 ppm. The signal of the nonsubstituted cyclopentadienyl ring ($\delta$ = 4.07) is characteristic. Interestingly, the signal of the P–C$H_2$–P group is not split into a triplet. Instead, a broad singlet at $\delta$ = 4.32 ppm was observed. A similar behavior was observed in [dppm(AuCl)$_2$] and the authors suggested a small scalar contribution of the $^2J_{PH}$ coupling.[58] The observed chemical shift of the P–C$H_2$–P group is in the range of other dppm gold(I) compounds, for example, $\delta$ = 3.80 ppm in [dppm-(AuI)$_2$].[58] In the $^{31}P\{^1H\}$ NMR spectrum, a characteristic singlet was observed at $\delta$ = 31.3 ppm, which is in the expected range. A molecular peak corresponding to the cation of **3** was detected in the ESI-MS spectrum at $m/z$ = 1423.15 amu (Supporting Information Figure S2).

Compound **3** crystallized in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. Some $CH_2Cl_2$ molecules were heavily disordered and removed by using *SQUEEZE*.[59] The gold(I) atoms are each coordinated by two phosphorus atoms of two dppm ligands and one sulfur atom of the ferrocene dithiocarboxylate. This results in a distorted trigonal planar coordination polyhedron. The angles within this polyhedron range from 91.82(4)° to 156.46(5)° and thus significantly deviate from the ideal angle of 120°. As a result of the complex geometry, the Au atoms are forced into a close proximity and an Au–Au distance of 2.9461(2) Å is observed. This distance is in the typical range of aurophilic interactions, which ranges from about 2.70–3.50 Å.[1,60−66] However, because

Scheme 3. Synthesis of 3



3

of the rigid complex geometry, we cannot clearly prove if there is an attractive force between the gold atoms. The Au−S bond lengths (Au1−S1 2.6773(4) Å and Au2−S2 2.6511(13) Å) are, in contrast to compound **2**, almost equivalent showing a heteroallylic arrangement of the ferrocene dithiocarboxylate ligand. The other bond parameters are within the expected range. The gold(I) atoms are within the bridgehead of a bimetallabicyclo[3.3.3]undecane structure. This kind of structural motif is rare in gold chemistry. It has not been previously observed for dithiocarboxylate ligands but it has been reported for dithiophosphonates, for example, in bis($\mu_2$-(4-methoxyphenyl)-*O*-(cyclopentyldithiophosphonato)-digold(I).[67] It is worth noticing that in the closely related compound [(PhCSS)$Au_2$($dppm_2$)]Cl, in contrast to **3**, the dithiocarboxylato moiety coordinates as a monodentate ligand to only one of the gold atoms.[68]

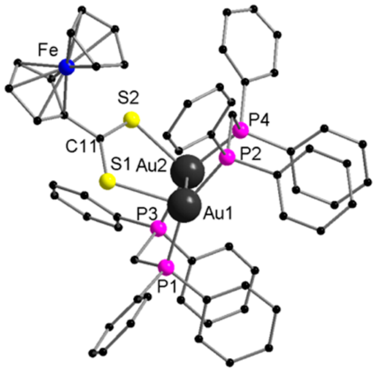


**Figure 2.** Molecular structure of the cation of **3**. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Au1−Au2 2.9461(2), Au1−S1 2.6773(4), Au1−P1 2.3309(11), Au1−P2 2.3007(12), Au2−S2 2.6511(13), Au2−P3 2.3104(12), Au2−P4 2.3408(12) C11−S1 1.693(5), C11−S2 1.708(5); P2−Au1−Au2 93.28(3), P2−Au1−S1 111.67(4), P2−Au1−P1 156.46(5), P1−Au1−Au2 88.93(3), P1−Au1−S1 91.82(4) P3−Au2−Au1 93.05(3), P3−Au2−S2 110.38(4), P3−Au2−P4 156.01(4), P4−Au2−Au1 88.69(3), P4−Au2−S2 93.60(4), S1−Au1−Au2 87.84(3), S2−Au2−Au1 87.46(3), S1−C11−S2 125.5(3).

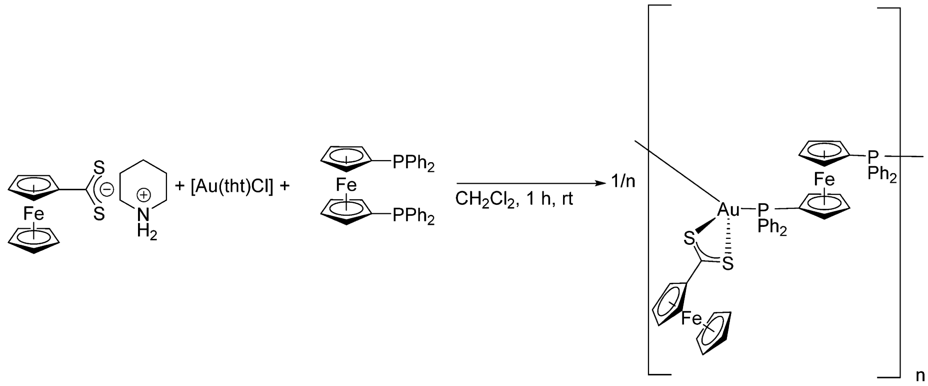
Compounds **1**−**3** were investigated by cyclic voltammetry measurements (Supporting Information Figures S3−S5). All measurements were performed in THF at room temperature. Potentials are quoted relative to the ferrocene/ferrocenium couple (Fc/$Fc^+$) as the internal standard. For each compound we observed an irreversible oxidation process at about $E_{pa}$ = ∼0.1−0.2 V. We suggest that this process is caused by an irreversible oxidation of the dithiocarboxylate function. To further address this behavior, we applied a different conducting salt [N(*n*Bu)$_4$][PF][69] ($PF^-$ = {Al(OC($CF_3$)$_3$)$_4$}) to exclude reactions with the [N(*n*Bu)$_4$][$PF_6$] salt. As there appeared to be no change in the cyclovoltammograms upon exchanging the conducting salt, we assume that the irreversible oxidation steps are located on the dithiocarboxylate moiety. Note: compounds **2** and **3** exhibit further quasi-reversible oxidation waves centered at $E^0_{1/2}$ = 0.22 V and $E^0_{1/2}$ = 0.52 V for **2** and $E^0_{1/2}$ = 0.21 V for **3** respectively (see Supporting Information Figures S4 and S5). However, the origin of these redox processes remains unassigned, as this is under currently investigation.

By treating the mixture of **1** and [Au(tht)Cl] with bis(diphenylphosphino)ferrocene (dppf), the polymeric product [(FcCSS)Au(dppf)]$_n$ (**4**) was obtained (Scheme 4). Complex **4** could not be dissolved in common organic solvents without decomposition. Thus, a characterization by NMR was not possible. Single crystals of **4** were obtained by overlaying a solution of **1** and dppf in dichloromethane with a solution of [Au(tht)Cl] in a mixture of dichloromethane and THF. Red crystals were grown at the phase border.

Compound **4** crystallized as two different polymorphs. One polymorph crystallized in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. An X-ray powder diffraction experiment performed with microcrystalline powder of this sample showed good agreement with the calculated powder pattern (*Mercury* 3.1[48] was used for the calculation; Supporting Information Figure S6). The other polymorph crystallized in the monoclinic space group $P2_1/n$ with additional solvent molecules ($CH_2Cl_2$) in the unit cell. Although the ferrocenyl units are orientated slightly differently in both polymorphs, the structural scaffold is the same. Because of disorder problems the X-ray data collected from both polymorphs of **4** were poor but the connectivity of **4** and its composition were deduced. However, further bonding parameters cannot be discussed. The gold atoms are coordinated by two phosphorus and two sulfur atoms, resulting in a coordination number of four. In contrast to **2** the Au−S bond lengths in **4** are almost equivalent. A distorted tetrahedron is formed around the gold atoms. Four-coordinate gold(I) compounds are rare. They are mostly observed in the presence of aromatic sulfur containing ligands, such as dithiocarboxylates,[34,38,57] some phosphines,[38,57,70] and phosphines with tethered thio groups.[71] As a result of the coordination of the flexible and bidentate dppf ligand, an infinite zigzag chain is formed. To the best of our knowledge no other similar gold(I) compound have been structurally characterized before, but a few examples of polymeric gold(I) complexes are known, for example, [(dppf)AuCl]$_n$[72,73] and [(MandyPhos)AuCl]$_n$[74] (MandyPhos =2,2′-bis(*N*,*N*-dimethylamino phenyl methyl)-1,1′-bis(diphenylphosphino)-ferrocene) with trigonal coordination of the gold(I) atom. In **4**, we observed a third coordination mode of the ferrocene dithiocarboxylate ligand, demonstrating the high variability coordination modes exhibited by this ligand.

By using bis(diphenylphospino)propane as the phosphine ligand, the compound [{(FcCSS)Au}$_2$(dppp)] (**5**) was formed (Scheme 5). It was isolated by crystallization from pentane/

**Scheme 4. Synthesis of 4**



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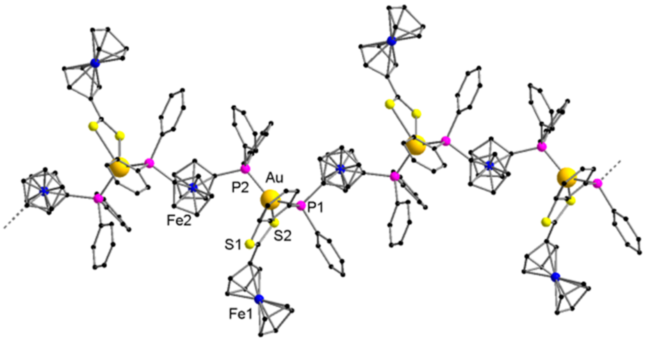


**Figure 3.** Shown is a section of the coordination polymer **4**. Hydrogen atoms and solvent molecules have been omitted for clarity.

$CH_2Cl_2$ in low yield. In contrast to **2**–**4**, the gold atoms of **5** show the common coordination number of two. Folding of the *n*-propyl chain could prevent the formation complexes with higher coordination numbers. However, the ferrocene dithiocarboxylate ligand coordinates again in a new fashion. In the $^1$H NMR spectrum, the expected set of signals was detected. Compared with the free ligand the signals of phosphorus adjacent protons in the bridging dppp ligand are shifted by about 0.8 ppm to lower field, those in the middle position are shifted about 0.2 ppm. The $^{31}P\{^1H\}$ signal was detected at $\delta = 27.5$ ppm. In the $^{13}C\{^1H\}$ NMR spectrum the signal for carbon atoms adjacent to the phosphorus are split into a doublet of doublets at $\delta = 28.2$ ppm through coupling with both phosphorus atoms. The coupling constants are $^1J_{PC} = 34.2$ Hz and $^3J_{PC} = 10.2$ Hz. The carbon atom in the center of the dppp bridge shows a poorly shaped triplet at $\delta = 19.7$ ppm, due to a small $^2J_{PC} = 2.5$ Hz coupling. This interpretation was confirmed by a $^{13}C\{^1H, ^{31}P\}$ NMR experiment in which each signal is observed as a singlet (Supporting Information Figures S7–S10).

Compound **5** crystallized in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit and an additional equivalent of the solvent molecule (Figure 4). The gold atoms are now coordinated in the common linear manner, with the P–Au–S angles (176°) being nearly identical for both atoms. The gold–sulfur distances of the coordinating sulfur atoms are Au1–S1 2.3260(5) Å and Au2–S3 2.3126(6) Å, whereas the distances to the noncoordinating sulfur atoms (S2 and S4) are longer than 3.3 Å. In general, **5** shows some similarities with the related complex $[(dppp)(AuCl)_2]$.[75] The Au–Au separation in **5** is 3.1063(5) Å, which is significantly

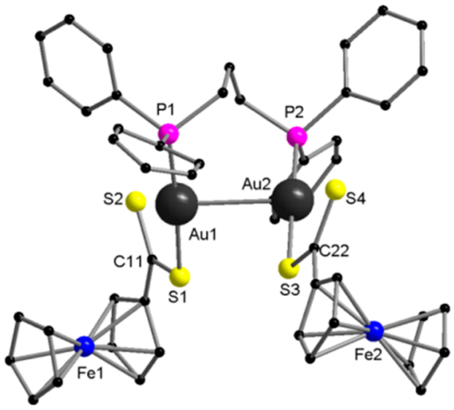
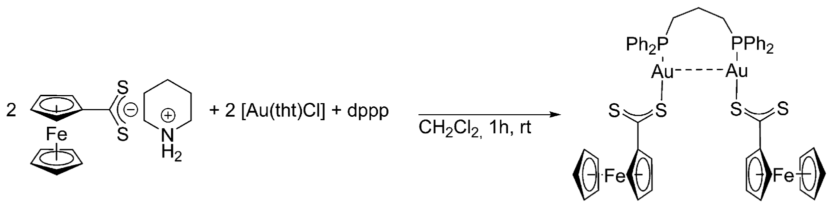


**Figure 4.** Molecular structure of **5**. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Au1–Au2 3.1063(5), Au1–P1 2.2676(4), Au2–P2 2.2608(6), Au1–S1 2.3260(5), Au2–S3 2.3126(6), C11–S1 1.7255(6), C11–S2 1.6604(4), C22–S3 1.7238(3), P1–Au1–S1 176.283(13), P2–Au2–S3 175.945(13), P1–Au1–Au2 92.411(8) P2–Au2–Au1 92.533(8), S1–Au1–Au2 91.281(9), S3–Au2–Au1 87.539(9), S1–C11–S2 124.59(2), S3–C22–S4 122.45(2).

**Scheme 5. Synthesis of 5**



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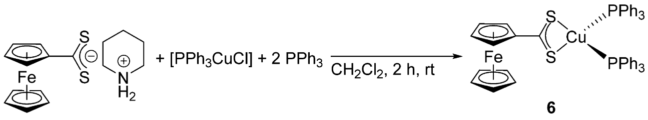
shorter than in its chloro analogue (3.2368(9) Å). The P−Au bond lenghts in **5** (Au1−P1 2.2676(4) Å and Au2−P2 2.2608(6) Å) are only slightly different to the chloro complex (Au1−P1 2.237(3) Å and Au2−P2 2.244(3) Å). For [(dppp)$(AuCl)_2$], an additional isomer has been reported in the literature, in which there are intermolecular Au−Au contacts but no intramolecular ones. As a result of these contacts a linear polymeric structure is formed.[76] In our experiments no related isomer was observed.

Attempts to extend the rich coordination chemistry of the ferrocene dithiocarboxylate ligand to other coinage metals were only partly successful. One copper complex was obtained but attempts to make a silver complex were unsuccessful. In a comparable procedure to the synthesis of **2**, [$(Ph_3P)_3CuCl$] was reacted with **1** in $CH_2Cl_2$ to give [(FcCSS)Cu$(PPh_3)_2$] (**6**) in good yield. The product was fully characterized by standard analytical/spectroscopic techniques and the solid state-structure was established by single-crystal X-ray diffraction. Compound **6** is comparable to the analogous gold compound **2**. The NMR spectra show the expected set of signals. The signals of the ferrocenyl unit show characteristic signals in the $^1H$ NMR spectrum. For the unsubstituted ring, a singlet is seen at *δ* = 4.13 ppm, whereas the signals of the other ring are observed as mulitplets at *δ* = 5.49 and 4.22 ppm. In the $^{31}P\{^1H\}$ NMR, the expected signal is seen at *δ* = −0.8 ppm, which is close to [$(PPh_3)_2CuCl$] (*δ* = −3.68 ppm in $CDCl_3$).

**Scheme 6. Synthesis of 6**



Complex **6** crystallized in the triclinic space group $P\bar{1}$. In contrast to the gold(I) compound **2**, the tetrahedral coordination observed in **6** is very common in copper chemistry. Although the structure of **2** and **6** appear similar at a first glance, there are some significant differences. In contrast to **2**, the ferrocene dithiocarboxylate ligand in **6** coordinates almost symmetrically to the copper atom (Cu−S1 2.418(2) Å and Cu−S2 2.416(2) Å) in a chelating mode. This results in a significantly larger bite angle of 74.41(5)° (66.13(6)° in **2**) and a smaller P1−Cu−P2 angle (125.22(6)°). The Cu−P bond lengths are in the expected range. As a result of the similar S−C11 bond lengths (S1−C11 1.689(5) Å, S2−C11 1.697(5) Å) the ferrocene dithiocarboxylate ligand coordinates in a hetero allylic-mode.

To check the valence state of the iron centers in compounds **2**, **3**, and **4**, $^{57}Fe$−Mössbauer spectroscopy was performed. Figure 6 shows that all three compounds exhibit one doublet in their Mössbauer spectra obtained at T = 77 K. All three compounds exhibit isomer shifts (*δ* = 0.51 ± 0.03 $mms^{-1}$) and quadrupole splittings ($\Delta E_Q$ = 2.21 ± 0.03 $mms^{-1}$ for **2** and **3** and $\Delta E_Q$ = 2.26 $mms^{-1}$ ± 0.03 $mms^{-1}$ for **4**), which are the same within the experimental error. These values are typical for diamagnetic ferrocenes.[77] The Mössbauer spectrum of **2** obtained at *T* = 5 K and an external field of *B* = 5 T (Supporting Information Figure S11) shows a magnetic splitting which is only due to the external field, which confirms the diamagnetic ground state of the ferrocene centers in **2**, **3**, and **4**.

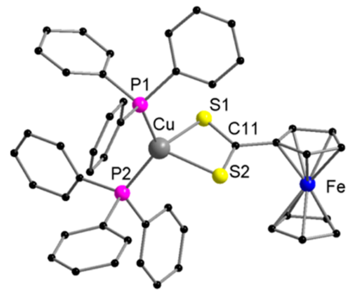


**Figure 5.** Molecular structure of **6**. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu−S1 2.418(2), Cu−S2 2.416(2), Cu−P1 2.250(2), Cu−P2 2.250(2), S1−C11 1.689(5), S2−C11 1.697(5); P1−Cu−P2 125.22(6), S1−Cu−S2 74.41(5), P1−Cu−S1 108.35(6), P1−Cu−S2 113.42(6), P2−Cu−S1 115.43(6), P2−Cu−S2 108.87(6), S1−C11−S2 119.3(3).

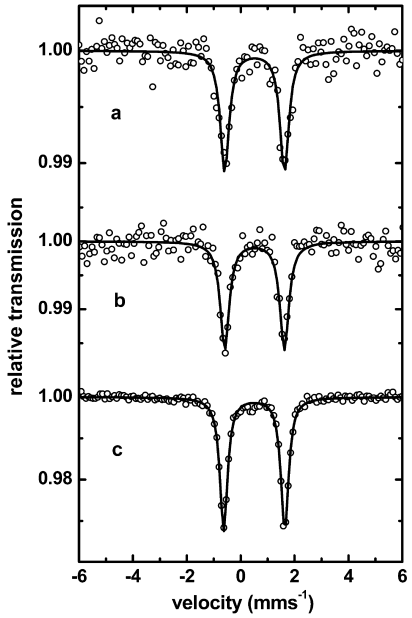


**Figure 6.** $^{57}Fe$−Mössbauer spectra obtained at *T* = 77 K of **2** (a), **3** (b), and **4** (c). The solid lines represent the result of a best fit analysis using Lorentzian line shape. The so obtained Mössbauer values are for **2** and **3** are Isomer shift *δ* = 0.51 ± 0.03 $mms^{-1}$; quadrupole splitting $\Delta E_Q$ = 2.21 ± 0.03 $mms^{-1}$ and line width Γ = 0.40 ± 0.03 $mms^{-1}$ (a and b). Complex **4** exhibits *δ* = 0.50 ± 0.03 $mms^{-1}$, $\Delta E_Q$ = 2.26 ± 0.03 $mms^{-1}$, and Γ = 0.34 ± 0.03 $mms^{-1}$ (c).[78]

## ■ CONCLUSION

We have introduced the ferrocene dithiocarboxylate ligand into the chemistry of gold(I) and copper(I) and the first structurally characterized complexes are reported. Surprisingly, the ferrocene dithiocarboxylate ligand shows very flexible coordination behavior, which allowed for the formation of different coordination polyhedra, although the coordinating ligand atoms were the same in each case. None of the compounds reported herein exhibit coordination by solvent molecules. In the four different gold(I) complexes four different coordination modes of the ligand are seen. In only one example (compound **5**), the expected linear coordination environment of the gold(I) atoms was observed. In all other compounds, coordination polyhedra with high-coordinate gold(I) atoms were formed. Although high-coordinate gold(I) compounds with other dithiocarboxylate ligands are known, the high variability in the coordination chemistry of the ferrocene dithiocarboxylate ligand and the resulting rich structural chemistry is exceptional. We believe that dithiocarboxylates with other organometallic backbones may also be suitable as interesting ligands in gold(I) chemistry. Now that we have a convenient synthesis of **1**, we are currently exploring the coordination chemistry of ferrocene dithiocarboxylate with other metals.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Additional figures and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org

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### Author Contributions

The manuscript was written with contributions from all authors. All authors have given their approval to the final version of the manuscript.

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### Notes

The authors declare no competing financial interest.

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(78) Note: Au atoms strongly scatter and absorb 14.4 keV Mössbauer radiation. Therefore, the statistical quality of the Mössbauer spectra of **2** and **3** presented in Figure 6 is not as high as usually observed for iron containing coordination compounds due to low count rates. The Fe concentration in **4** or, more specifically, the concentration of the resonantly absorbing $^{57}$Fe nuclei, which cause the Mössbauer effect and occurs in 2.1% natural abundance, is about twice as high as in **2** and **3**. Therefore, the Mössbauer spectrum obtained for **4** has a better statistical quality than those of **2** and **3**.