1,1′-Bis(diphenylthiophosphoryl)ferrocene as a *trans*-Chelating Ligand in Gold(I) and Silver(I) Complexes

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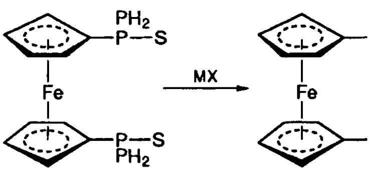
The reaction of 1,1′-bis(diphenylthiophosphoryl)ferrocene (dptpf) with $AgClO_4$ or $[Au(tht)_2]CF_3SO_3$ (tht = tetrahydrothiophene) in a 1:1 molar ratio led to complexes of the stoichiometry $[M(dptpf)]^+$ The crystal structures of both complexes revealed a linear co-ordination geometry with a novel *trans* co-ordination by the ligand.

Although the chelate effect is one of the oldest concepts in co-ordination chemistry, it was not until recently that studies carried out with bidentate tertiary phosphine and arsine ligands[1-9] with suitable long carbon backbones have shown that *trans*-chelated square-planar complexes with rhodium(I), iridium(I), nickel(II), palladium(II) or platinum(II) can be obtained. Since the first report of a *trans*-bonded bidentate chelate complex by Issleib and Hohlfield[10] a wide range of this type of complex has been isolated and specific routes are now available for d^8 transition metals. However, few studies have been performed with other transition-metal systems. In particular, we are interested in silver(I) and gold(I) chemistry. Venanzi and co-workers[11,12] have reported the preparation of complexes with the stoichiometry [MCl(L)] {M = Cu^I, Ag^I or Au^I; L = 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene}, for which crystal structures show three-co-ordination with a change in the P–M–P angle from 132 (Cu) to 141 (Ag) to 176° (Au).

We are currently studying the co-ordination chemistry of phosphinoferrocenes;[13,14] this area has attracted a great deal of interest because the resultant complexes often find synthetic applications in transition-metal-catalysed processes.[15] The oxidation of 1,1′-bis(diphenylphosphino)ferrocene (dppf) with elemental sulfur gives 1,1′-bis(diphenylthiophosphoryl)-ferrocene (dptpf),[16] the co-ordination chemistry of which has scarcely been studied. Here we report the synthesis and crystal structures of the complexes $[M(dptpf)]^+$ (M = Ag or Au) which show a novel structural framework with the dptpf acting as a *trans*-bidentate chelate ligand. As far as we are aware this is the first example for silver and the second for a gold complex.[11]

The reaction of dptpf with $AgClO_4$ or $[Au(tht)_2]CF_3SO_3$ (tht = tetrahydrothiophene) in a 1:1 molar ratio affords yellow or orange solids of [M(dptpf)]X (M = Ag **1** or Au **2**, X = ClO_4 **1** or CF_3SO_3 **2**).† Complexes **1** and **2** behave as 1:1 electrolytes in acetone solution. The ^1H NMR spectra show three multiplets in a 1:1:5 ratio, assignable to the α and β protons of the cyclopentadienyl ring and to the phenyl protons, respectively. In the $^{31}P-\{^1H\}$ NMR spectra only one singlet is observed because of the equivalence of the phosphorus atoms. The positive-ion fast atom bombardment spectra show the cationic peaks $[M(dptpf)]^+$ at *m*/*z* = 726 (100) and 815 (100%).



MX = $AgClO_4$ or $[Au(tht)_2]CF_3SO_3$

Complexes **1** and **2** have been structurally characterized by X-ray diffraction.‡ Fig. 1 shows the cation of **1**. The silver atom

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† To a solution of dptpf (0.062 g, 0.1 mmol) in dichloromethane (25 cm^3) was added $AgClO_4$ (0.021 g, 0.1 mmol) or $[Au(tht)_2]CF_3SO_3$ (0.052 g, 0.1 mmol) and the mixture was stirred for 1 h. Concentration of solvent to *ca.* 5 cm^3 and addition of diethyl ether (15 cm^3) gave a yellow (**1**, 77% yield) or an orange solid (**2**, 82% yield). **1** (Found: C, 49.55; H, 3.25; S, 7.45. Calc. for $C_{34}H_{28}AgClFeO_4P_2S_2$: C, 49.45; H, 3.4; S, 7.75%), Λ_M 129.3 Ω^{-1} cm^2 mol^{-1}; NMR ($CDCl_3$): ^1H (300 MHz), δ 4.33 (m, 4 H, C_5H_4), 4.64 (m, 4 H, C_5H_4) and 7.5–7.68 (m, 20 H, Ph); $^{31}P-\{^1H\}$ (121 MHz), δ 46.1(s); **2** (Found: C, 43.7; H, 2.55; S, 9.65. Calc. for $C_{35}H_{28}AuF_3FeO_3P_2S_3$: C, 43.6; H, 2.9; S, 9.95%), Λ_m 123.5 Ω^{-1} cm^2 mol^{-1}; NMR ($CDCl_3$): ^1H (300 MHz), δ 4.47 (m, 4 H, C_5H_4), 4.64 (m, 4 H, C_5H_4) and 7.5–7.7 (m, 20 H, Ph); $^{31}P-\{^1H\}$ (121 MHz), δ 45.6 (s).

‡ Crystal data: **1**·CH_2Cl_2, $C_{34}H_{28}AgClFeO_4P_2S_2·CH_2Cl_2$, M_r = 910.72, orthorhombic, space group $Pna2_1$, *a* = 25.942(3), *b* = 12.1213(14), *c* = 11.292(2) Å, *U* = 3550.8(9) Å^3, *Z* = 4, D_c = 1.704 Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ = 1.43 mm^{-1}, *F*(000) = 1832, *T* = −100 °C. A yellow tablet 0.80 × 0.30 × 0.20 mm was used to record 6059 intensities to $2\theta_{max}$ 50° (Siemens R3 diffractometer) of which 5567 were unique (R_{int} 0.032); absorption corrections applied on the basis of ψ scans, with transmission factors 0.695–0.892; cell constants refined from setting angles of *ca.* 60 reflections in the range 2θ 10–25°. The structure was solved by direct methods and subjected to full-matrix least-squares refinement on F^2 (SHELXL 93);[17] all non-H atoms refined anisotropically and H atoms were included using a riding model. Refinement proceeded to $wR(F^2)$ 0.054 for 5564 reflections, 433 parameters and 1 restraint, conventional *R*(*F*) 0.029, $S(F^2)$ = 0.93, maximum Δρ 0.36 e Å^{-3}. **2**·$CHCl_3$, $C_{35}H_{28}AuF_3FeO_3P_2S_3·CHCl_3$, M_r = 1083.88, triclinic, space group $P\bar{1}$, *a* = 12.924(2), *b* = 17.485(3), *c* = 20.458(3) Å, α = 64.985(8), β = 74.296(8), γ = 70.576(12)°, *U* = 3904.8(9) Å^3, *Z* = 4, D_c = 1.844 Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ = 4.62 mm^{-1}, *F*(000) = 2120, *T* = −100 °C. An orange prism 0.45 × 0.20 × 0.20 mm was used to collect 16 409 intensities to $2\theta_{max}$ 48°, 11 508 independent (R_{int} 0.081), transmission factors 0.759–0.988. The structure was solved by the heavy-atom method with other data as for complex **1**. Refinement proceeded to $wR(F^2)$ 0.111 for 11 502 reflections, 578 parameters and 228 restraints, conventional *R*(*F*) 0.050, $S(F^2)$ = 0.84, maximum Δρ 1.7 e Å^{-3}. Full details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference numbers CSD 401891 (**1**), 401892 (**2**).

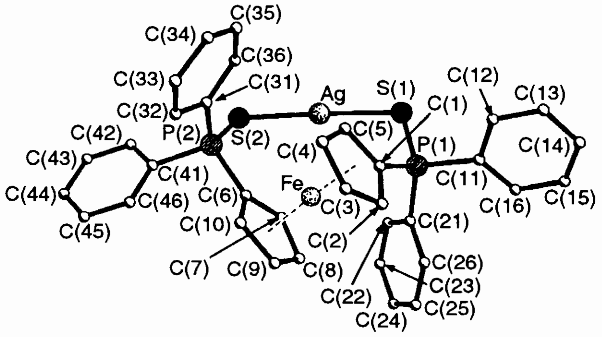

Fig. 1 Structure of the cation $[Ag(dptpf)]^+$ in the crystal showing the atom numbering scheme. Radii are arbitrary; H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag–S(1) 2.3812(13), Ag–S(2) 2.3815(12), P(1)–C(1) 1.795(4), P(2)–C(6) 1.782(4), P(1)–S(1) 1.9937(14), P(2)–S(2) 1.994(2); S(2)–Ag–S(1) 176.83(5)

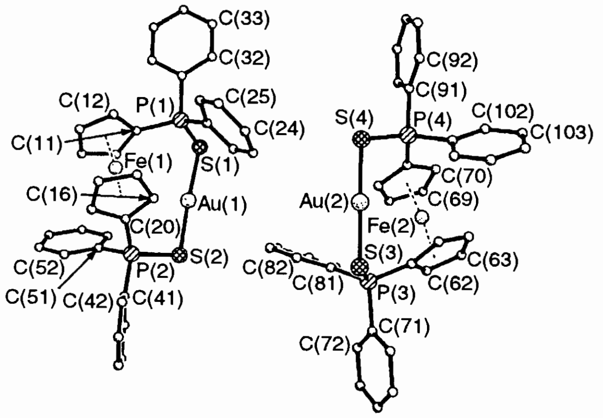

Fig. 2 Structure of the two independent formula units of complex **2** in the crystal showing the atom labelling scheme. Radii are arbitrary; H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)–S(1) 2.302(3), Au(1)–S(2) 2.300(3), P(1)–S(1) 2.028(4), P(2)–S(2) 2.013(4), Au(2)–S(3) 2.288(3), Au(2)–S(4) 2.280(3), P(3)–S(3) 2.002(5), P(4)–S(4) 2.011(4), Au(1)–Au(1^I) (I = $-x+1, -y, -z+1$) 3.3700(10), Au(2)–Au(2^{II}) (II = $-x+1, -y+1, -z$) 3.3050(11); S(2)–Au(1)–S(1) 176.43(12), S(4)–Au(2)–S(3) 178.26(11)

displays an almost ideal linear geometry with an S(2)–Ag–S(1) angle of 176.83(5)°, and is also involved in contacts of 3.28 Å to a perchlorate oxygen and 3.766 Å to the iron atom. The Ag–S bond distances are 2.3812(13) and 2.3815(12) Å, similar to those in other linear silver derivatives, *e.g.* $[\{Ag(CH_2PPh_2S)\}_2]$ [Ag–S 2.382(3) Å].[18] In the ferrocene moiety the cyclopentadienyl (cp) rings are staggered by 24° [torsion angle C(1)–cp–cp–C(7)].

The crystal structure of complex **2** (Fig. 2) shows two independent formula units per asymmetric unit. In both, the coordination around the gold atom is linear, with S(2)–Au(1)–S(1) 176.43(12) and S(4)–Au(2)–S(3) 178.26(11)°. The intramolecular gold–iron contacts are 3.874 and 3.963 Å and there are also short intermolecular gold–gold interactions of 3.370 and 3.305 Å across inversion centres (Fig. 3). The latter type of interaction has been associated with relativistic effects in the molecular orbitals of gold;[19] these effects are more important for gold than for silver.

The Au–S bond lengths are 2.300(3) and 2.302(3) Å for one molecule and 2.280(3) and 2.288(3) Å for the other; there is no obvious reason for this difference. The cyclopentadienyl rings are staggered by 14 and 10° about the cp•••cp axis [torsion angles C(11)–cp–cp–C(16) and C(65)–cp–cp–C(66)].

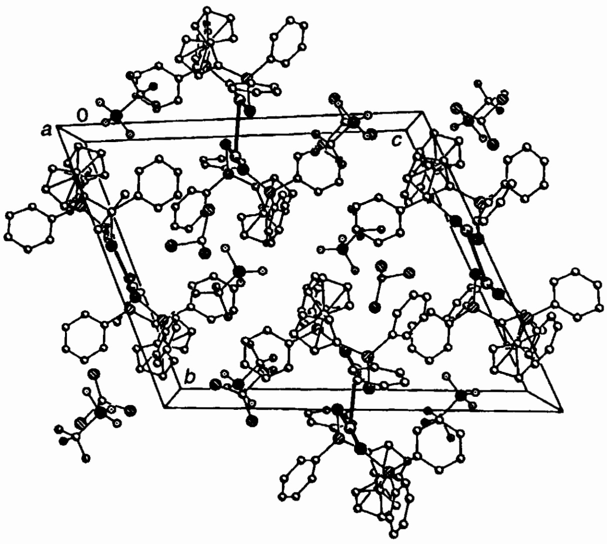

Fig. 3 Packing diagram of complex **2** showing the intermolecular gold–gold interactions

Acknowledgements

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