# Inorganic Chemistry

Article

# Unprecedented Formation of Novel Phosphonodithioate Ligands from Diferrocenyldithiadiphosphetane Disulfide

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*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., E-50009 Zaragoza, Spain, and Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany*

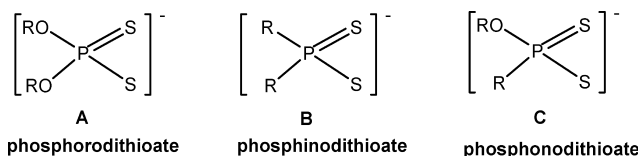The reaction of the phosphetane disulfide, $FcP(S)S_2P(S)Fc$ (**1**) ($Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$), the ferrocenyl analogue of the Lawesson reagent, with gold and palladium complexes leads to the unprecedented formation of phosphonodithioate ligands upon coordination to the metal centers. The reaction of **1** with gold complexes such as $[AuCl(PR_3)]$ affords the species $[Au\{S_2P(OH)Fc\}(PR_3)]$ ($PR_3 = PPh_3$ (**2**), $PPh_2Me$ (**3**)), in which the phosphonodithioate ligand $Fc(OH)PS_2^-$ has been formed. The same ligand is present in the compound $[Au_2\{S_2P(OH)Fc\}_2] \cdot [N(PPh_3)_2]Cl$ (**4**), obtained by reaction of **1** with $[N(PPh_3)_2][AuCl_2]$. It crystallizes with one molecule of $[N(PPh_3)_2]Cl$, whereby complex **4** acts as an anion receptor and forms strong hydrogen bonds between the chloro and the hydroxyl groups. The reaction with palladium derivatives is different; two complexes, $[Pd_2(S_4OP_2Fc_2)_2]$ (**5**) and $[Pd_4Cl_4(S_4OP_2Fc_2)_2]$ (**6**), are obtained in molar ratio 2:1 and 1:1, respectively. In these complexes a new phosphonodithioate ligand is present and probably arises from the condensation of two molecules of $Fc(OH)PS_2^-$. Complex **5** has also been characterized by X-ray methods.

## Introduction

Organodithio derivatives of phosphorus and their metal complexes have been thoroughly studied because of their many commercial applications. These include their use as agents for flotation, in the recovery of the metals from solution,[1] as additives to lubricant oils,[2] as pesticides, and for chemical warfare.[3] More recent applications of phosphodithioate compounds have been largely focused on their use as precursors in materials chemistry for the preparation of thin layers by chemical vapor deposition (CVD) or polymer-inorganic nanocomposites[4] and as reagents in biological and medicinal chemistry.[5] Oligo(nucleoside phosphorothioate)s are among the most promising of the nucleotide analogues which have been tested as antisense modulators of gene expression.[6]

Among these types of ligands the chemistry of phosphorodithioates, $(RO)_2PS_2^-$ (**A**), and phosphinodithioates, $R_2PS_2^-$ (**B**), ligands has been thoroughly investigated.[7] However, complexes with the phosphonodithioate ligands $R(RO)PS_2^-$ (**C**) are poorly represented because of the synthetic difficulties, and few have been structurally characterized.



**A**
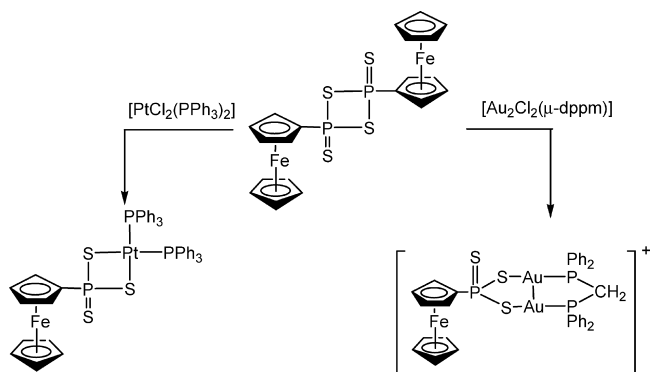phosphorodithioate

**B**
phosphinodithioate

**C**
phosphonodithioate

The traditional methods which consist of the reaction of the 2,4-diaryl-1,3-dithiaphosphetane disulfide dimers $\{RP(S)S\}_2$ with alcohols at elevated temperatures to give the acids $HSP(S)R(OR')$ is unsatisfactory because of the hazardous conditions to obtain the dimer precursors.[8] Phosphetane disulfides are used in organic synthesis as thionation

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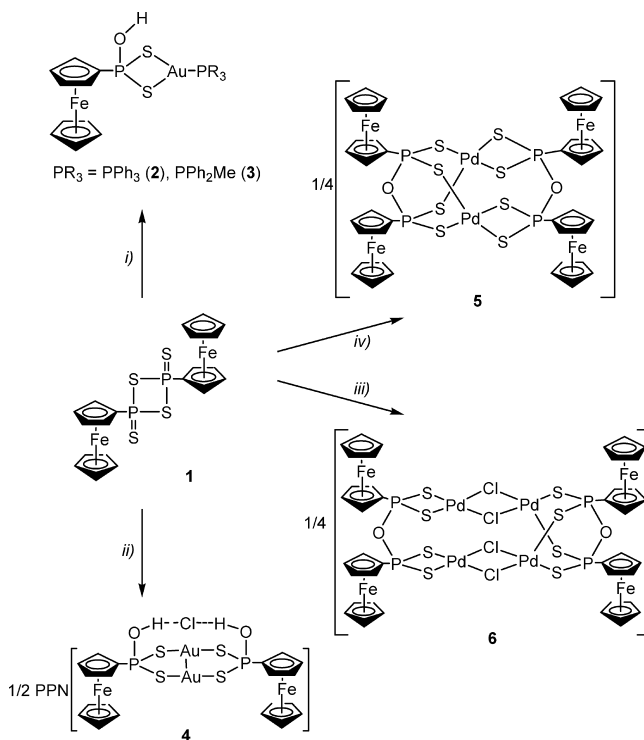† Universidad de Zaragoza-C.S.I.C.
‡ Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig.

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**Scheme 1.** Metal Complexes Obtained by Direct Reaction with FcP(S)S₂P(S)Fc



**Scheme 2.** (i) [AuCl(PR₃)], (ii) PPN[AuCl₂], (iii) 2 [PdCl₂(cod)], (iv) [PdCl₂(cod)]



reagents; the best known is Lawesson's reagent.[9] The discovery that the reaction of the Lawesson reagent, which is easily prepared, with alcohols also gives these phosphonodithioate compounds has opened up research into the coordination properties of these ligands. Several metal complexes have been prepared through this method, including gold compounds of the type [Au₂{S₂PR(OR′)}₂] or square planar complexes such as [M{S₂PR(OR′)}₂] for nickel, palladium, and platinum.[10–13]

The analogous ferrocenyl derivative of the Lawesson reagent FcP(S)S₂P(S)Fc (Fc = ferrocenyl) has been prepared by Woollins et al.[14] and several cycloaddition reactions with C−N have been described whereby C−P−N rings were generated.[15] The reaction of these phosphetane disulfides directly with [PtCl₂(PR₃)₂] leads to chelate complexes with the [FcPS₃]⁻ anion (Scheme 1).[14] The reaction of Fc(O-Et)P(S)SNa, previously obtained with EtONa in EtOH, with several metals gives the phosphonodithioate complexes.[10–13]

Here we describe an unprecedented reactivity of the ferrocenyl Lawesson reagent, FcP(S)S₂P(S)Fc, with gold and palladium complexes (Scheme 2). The direct reaction of this compound with the metal complexes occurs in a different way to that previously reported for platinum and gold, and it is also different from that reported for other metals. With gold, complexes with the phosphonodithioate ligand, Fc(OH)PS₂⁻, are obtained that have a hydroxy group capable of forming strong hydrogen bonds, whereas with palladium complexes a new tetradentate phosphonodithioate species, O(FcPS₂)₂²⁻, is synthesized, which is probably the result of the condensation of two molecules of Fc(OH)PS₂⁻. The gold complex [Au₂{S₂P(OH)Fc}₂] crystallizes with a molecule of [N(PPh₃)₂]Cl and acts as anion receptor toward the chloride

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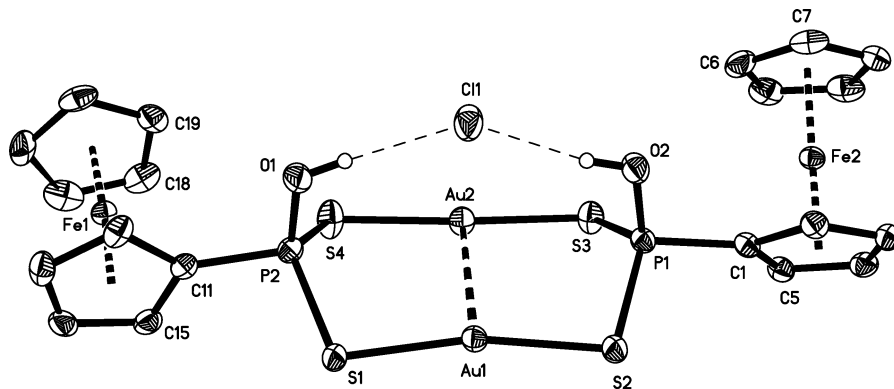
**Figure 1.** Structure of complex **4** showing the atom labeling scheme. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.

atom, forming strong hydrogen bonds between the chloro ligand and the hydroxy groups.

## Results and Discussion

**Synthesis and Spectroscopic Properties.** The phosphetane disulfide ligand, $FcP(S)S_2P(S)Fc$ (**1**), has been prepared previously by Woollins et al. by reaction of $P_4S_{10}$ with ferrocene in hot xylene.[14] The compound is insoluble in cold organic solvents. We have studied the reactivity of this compound toward gold and palladium derivatives. The reactivity depends on the metal and is different to that previously described for the same compound or for the Lawesson reagent with platinum or gold, from which complexes with the ligand $[FcPS_3]^-$ were obtained (Scheme 1).[14]

The reactions with gold or palladium compounds were carried out in air, leading to oxidation of the ligand. In the first case the oxidation affords the phosphonodithioate ligand (Scheme 2); in the second case, the oxidation is followed by the condensation of two phosphonodithioate species and a new ligand is synthesized as described in eq 1. In the case of gold, the treatment of **1** with $[AuCl(PR_3)]$ leads to the synthesis of the phosphonodithioate derivatives $[Au\{S_2P\text{-}(OH)Fc\}(PR_3)]$ ($PR_3 = PPh_3$ (**2**), $PPh_2Me$ (**3**)). They are yellow air- and moisture-stable solids that behave as nonconductors in acetone solutions. The IR spectra display a weak absorption from the vibration $\nu(Au-S)$ at about 247 $cm^{-1}$. The $^1H$ NMR spectra show the presence of three multiplets for the $\alpha$ and $\beta$ protons of the cyclopentadienyl rings and for the phenyl protons, respectively; compound **3** also shows a multiplet for the methyl protons. The $^{31}P\{^1H\}$ NMR spectra show two different phosphorus environments corresponding to the phosphonodithioate ligand and the tertiary phosphine. The mass spectra (LSIMS+) display the peaks corresponding to the fragments $[M - OH]^+$ at $m/z = 740$ (20%, **2**) and 678 (25%, **3**), respectively.

The reaction of **1** with $[N(PPh_3)_2][AuCl_2]$ gives the 1:1 adduct $[Au_2\{S_2P(OH)Fc\}_2]\cdot[N(PPh_3)_2]Cl$ (**4**), a yellow solid. Complex **4** shows conductivity in acetone solutions corresponding to a 1:1 electrolyte, which is in agreement with the formulation as the chloride ligand is trapped in the gold complex. The $^1H$ NMR spectrum shows the presence of both ferrocene and phenylic protons. The $^{31}P\{^1H\}$ NMR spectrum presents two singlets corresponding to two types of

$$\text{L1} \xrightarrow{-H_2O} 1/2 \text{ L2} \qquad (1)$$
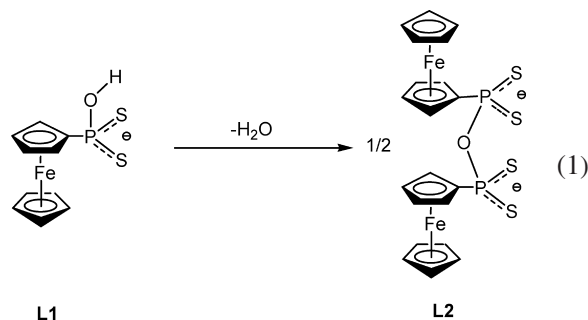
phosphorus environments, one at 21.6 attributed to the $[N(PPh_3)_2]^+$ cation and the other at 94.9, assigned to the phosphorus of the ligand.

The reactivity of **1** with $[PdCl_2(cod)]$ in a 2:1 ratio is different, giving the species $[Pd_2(S_4OP_2Fc_2)_2]$ (**5**). Complex **5** is a red air- and moisture-stable solid that behaves as a nonconductor in acetone solutions. The $^1H$ NMR spectrum shows two inequivalent ferrocenyl units, each showing two multiplets for the $\alpha$ and $\beta$ protons of the substituted cyclopentadienyl ring and a singlet for the unsubstituted cyclopentadienyl moiety. This inequivalence is caused by the different mode of coordination of the palladium atoms to the two ligands (see Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum also presents two singlets assigned to the two inequivalent ligands. The mass spectrum (LSIMS+) shows the molecular peak at $m/z = 1365$ (28%).

The reaction of **1** with $[PdCl_2(cod)]$ in a molar ratio 1:1 gives a complex of stoichiometry $[Pd_4Cl_4(S_4OP_2Fc_2)_2]$ (**6**) for which we propose a similar structure to that found in complex **5** but now with bridging chlorine ligands between the palladium centers. In the $^1H$ NMR spectrum there are six resonances in a ratio 2:2:2:2:5:5, which correspond to two different types of monosubstituted ferrocenyl units. The $^{31}P\{^1H\}$ NMR spectrum presents two close singlets at 120.8 and 120.3 ppm for the two different phosphorus environments. The mass spectrum (LSIMS+) shows the fragment at $m/z = 876$ (8%) which corresponds to the species with a halved molecular weight.

**Crystal Structure Determinations.** The crystal structure of adduct **4** has been established by X-ray diffraction. The skeleton of the structure of **4** is an eight-membered ring constructed with two gold atoms and the $PS_2$ units of two $FcP(OH)S_2^-$ ligands (Figure 1). Such rings normally display

**Table 1.** Selected Bond Lengths (Å) and Angles (°) for Complex **4**

| | |
|---|---|
| Au(1)−S(2) | 2.2894(8) |
| Au(1)−S(1) | 2.2928(9) |
| Au(1)−Au(2) | 3.0509(3) |
| Au(2)−S(3) | 2.3021(9) |
| Au(2)−S(4) | 2.3064(9) |
| P(1)−O(2) | 1.571(2) |
| P(1)−C(1) | 1.771(3) |
| P(1)−S(3) | 2.0269(11) |
| P(1)−S(2) | 2.0308(11) |
| P(2)−O(1) | 1.565(2) |
| P(2)−S(4) | 2.0226(12) |
| P(2)−S(1) | 2.0262(11) |
| S(2)−Au(1)−S(1) | 167.94(3) |
| S(2)−Au(1)−Au(2) | 95.90(2) |
| S(1)−Au(1)−Au(2) | 94.02(2) |
| S(3)−Au(2)−S(4) | 169.79(3) |
| S(3)−P(1)−S(2) | 116.12(5) |
| S(4)−P(2)−S(1) | 115.70(5) |

a chair conformation, but, in this case, a boat conformation is observed. The gold atoms show a distorted linear environment (S−Au−S angles 167.94(3)°, 169.79(3)°, Table 1). This distortion may be associated with an aurophilic interaction (Au−Au 3.0509(3) Å). A search in the Cambridge Structural Database for the "$S_2P(OH)$" fragment leads to only one gold(III) complex: [Au{S$_2$P(OH)Ph}$_2$]Cl.[10b] But it is possible to compare the Au−S distances with those in gold(I) complexes with ligands that contain the unit "$S_2PR(OR)$", which show values similar to those in **4** (2.2894(8)−2.3064(9) Å): [AuS$_2$PPh(OC$_5$H$_9$)] (2.300(2) Å), [AuS$_2$P(4-C$_6$H$_4$OMe)(O-menthyl)]$_2$ (2.295(6)−2.303(6) Å), or [AuS$_2$PFc(O(CH$_2$)$_2$-O(CH$_2$)$_2$OCH$_3$)]$_2$ (2.299(4)−2.318(4) Å).[10e] The Au−S distances are also in the range found in dithiocarbamate[16] or dithiolate (2.299(2)−2.298(2) Å)[17] complexes of similar geometry. Compound **4** crystallizes as a [N(PPh$_3$)$_2$]Cl adduct. Hydrogen bonds are formed by the OH groups and the chloride anion, leading to a system O−H···Cl···H−O. The H···Cl distances are 2.130(19) and 2.13(2) Å, with O···Cl 2.928(2) and 2.930(2) Å. These hydrogen bonds explain the unexpected boat conformation.

The structure of complex **5** has been confirmed by X-ray diffraction studies. In compound **5** (Figure 2) each ligand is coordinated in a different mode to the palladium atoms. One is coordinated to the palladium center through the sulfur atoms of different "$PS_2$" units, thus forming a six-membered metallacycle (PdSPOPS), whereas the other is attached to the palladium center through the sulfur atoms of the same "$PS_2$" unit, affording a four-membered metallacycle (PdSPS). The S−Pd−S angles for the four-membered metallacycles are near 84°, whereas those for the six-membered metallacycles are about 96° (see Table 2); the other angles at palladium are 90°, and thus the coordination remains planar to a good approximation. Few systems "$S_4Pd···PdS_4$" can be found in the CDS. The ligands involved in these systems are dithiocarbamate or dithionate derivatives. Most of them consist of $PdS_4$ square planar units, connected via Pd···Pd
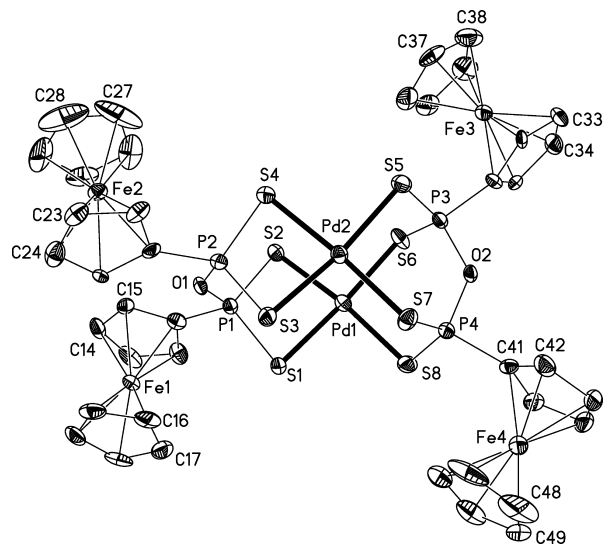


**Figure 2.** Molecular structure of complex **5**, with the atom labeling scheme. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.

contacts, in which all the ligands are chelating[18] but in a few cases the ligands act as a bridge between the palladium centers.[18d,19] The Pd···Pd distance in **5** corresponds to a long metallophilic interaction (3.348 Å). In [Pd$_2$(dpt)$_4$][20] the Pd···Pd distance is 2.7247(5) Å and these dinuclear units are connected through Pd···Pd interactions of 3.428(2) Å. The Pd−S bond distances in **5** range from 2.3392(18)−2.3577(18) Å, longer than those found in [Pd$_2$(dpt)$_4$] (2.3252(7), 2.357(9) Å). Two points reflect the different steric strain in both metallacycles. One is the distance of the palladium center to the phosphorus atom in the metallacycle. In the four-membered rings the palladium centers are 2.9 Å from the phosphorus atom, whereas the corresponding distance in the six-membered rings is 3.4 Å. The second point is the P−O−P angle, which is narrower for the six-membered ring [130.8(2)°] than for the four-membered ring [135.5(3)°]. The P−S distances (1.998(2)−2.005(2) Å) lie in between those of the free ligand S$_4$P$_2$Fc$_2$ for the exocyclic P−S bonds (P=S 1.930 Å) and those in the ring (P−S 2.101(3)−2.134(3) Å).[14] The P−O distances (1.623(4)−1.631(4) Å) are similar to those in the species Fc(o-C$_6$H$_4$O$_2$)PS (1.627(3)−1.634(4) Å).[14]

**Electrochemistry.** The electrochemical behavior of the gold adduct **4** and the palladium complex **5** has been studied by cyclic voltammetry at a platinum electrode in CH$_2$Cl$_2$. The low solubility of the FcP(S)S$_2$P(S)Fc compound precludes the study of its electrochemical properties. The cyclic voltammogram, at scan rate of 100 mV s$^{-1}$, of the gold

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**Table 2.** Selected Bond Lengths (Å) and Angles (°) for Complex **5**

| | |
|---|---|
| Pd(1)−S(6) | 2.3392(18) |
| Pd(1)−S(8) | 2.3465(18) |
| Pd(1)−S(1) | 2.3472(18) |
| Pd(1)−S(2) | 2.3547(18) |
| Pd(1)−P(1) | 2.9327(18) |
| Pd(2)−S(3) | 2.3471(18) |
| Pd(2)−S(5) | 2.3522(18) |
| Pd(2)−S(7) | 2.3564(18) |
| Pd(2)−S(4) | 2.3577(18) |
| Pd(2)−P(2) | 2.9419(18) |
| S(1)−P(1) | 2.005(2) |
| S(2)−P(1) | 1.998(2) |
| O(1)−P(1) | 1.623(4) |
| O(1)−P(2) | 1.629(4) |
| S(3)−P(2) | 2.000(2) |
| S(4)−P(2) | 1.998(2) |
| S(5)−P(3) | 2.003(2) |
| S(6)−P(3) | 2.001(2) |
| O(2)−P(4) | 1.623(4) |
| O(2)−P(3) | 1.631(4) |
| S(7)−P(4) | 1.995(2) |
| S(8)−P(4) | 2.004(2) |
| S(6)−Pd(1)−S(8) | 95.67(7) |
| S(6)−Pd(1)−S(1) | 171.45(7) |
| S(8)−Pd(1)−S(1) | 90.29(6) |
| S(6)−Pd(1)−S(2) | 89.77(6) |
| S(8)−Pd(1)−S(2) | 172.38(6) |
| S(1)−Pd(1)−S(2) | 83.76(6) |
| S(6)−Pd(1)−P(1) | 131.85(6) |
| S(8)−Pd(1)−P(1) | 132.42(6) |
| S(1)−Pd(1)−P(1) | 42.86(5) |
| S(2)−Pd(1)−P(1) | 42.69(5) |
| S(3)−Pd(2)−S(5) | 171.96(7) |
| S(3)−Pd(2)−S(7) | 89.96(6) |
| S(5)−Pd(2)−S(7) | 96.18(7) |
| S(3)−Pd(2)−S(4) | 83.87(6) |
| S(5)−Pd(2)−S(4) | 89.52(6) |
| S(7)−Pd(2)−S(4) | 171.97(6) |
| S(3)−Pd(2)−P(2) | 42.61(5) |
| S(5)−Pd(2)−P(2) | 131.62(6) |
| S(7)−Pd(2)−P(2) | 132.18(6) |
| S(4)−Pd(2)−P(2) | 42.55(5) |
| P(1)−O(1)−P(2) | 135.5(3) |
| P(4)−O(2)−P(3) | 130.8(2) |
| S(2)−P(1)−S(1) | 103.28(10) |
| S(4)−P(2)−S(3) | 103.70(10) |
| S(6)−P(3)−S(5) | 119.34(11) |
| S(7)−P(4)−S(8) | 119.27(11) |

derivative **4** shows a quasi reversible wave arising from the oxidation−reduction of the ferrocene moieties at slightly higher potential than in the ferrocene, 0.80 eV, showing no difference between both ferrocene moieties. The cyclic voltammogram of the palladium compound **5** shows only one oxidation process at 0.89 eV for the four ferrocenyl groups.

## Conclusions

The reactions of the phosphetane disulfide compound FcP(S)S$_2$P(S)Fc in dichloromethane with gold and palladium compounds have been carried out, showing unprecedented results. It reacts with gold complexes with formation of the phosphonodithioate ligand Fc(OH)PS$_2^-$, which coordinates as chelate or bridging ligand to the gold atoms. The dinuclear complex with two bridging ligands, [Au$_2${S$_2$P(OH)Fc}$_2$], crystallizes as an adduct with [N(PPh$_3$)$_2$]Cl. The structure involves a central eight-membered ring with a boat conformation, in such a manner that the molecule acts as anion

receptor toward the chloride anion via strong hydrogen bonds in a system O−H···Cl···H−O. The reactions with palladium species lead to complexes that possess an unprecedented phosphonodithioate ligand, O(FcPS$_2$)$_2^{2-}$, which probably arises from the condensation of two molecules of Fc(OH)PS$_2^-$. The structure of one of these complexes shows the ligand O(FcPS$_2$)$_2^{2-}$ acting as a tetradentate bridging ligand.

## Experimental Section

**Instrumentation.** Infrared spectra were recorded in the range 4000−200 cm$^{-1}$ on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in about $5 \times 10^{-4}$ mol dm$^{-3}$ solutions with a Philips 9509 conductimeter. C, H, N, and S analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec, with the liquid secondary-ion mass spectra (LSIMS) technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in CDCl$_3$. Chemical shifts are cited relative to SiMe$_4$ ($^1$H, external) and 85% H$_3$PO$_4$ ($^{31}$P, external). Cyclic voltammetric experiments were performed by employing an EG&G PARC Model 273 potentiostat. A three-electrode system was used, which consists of a platinum disk working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode. The measurements were carried out in CH$_2$Cl$_2$ solutions with 0.1 M Bu$_4$NPF$_6$ as a supporting electrolyte. Under the present experimental conditions, the ferrocenium/ferrocene couple was located at 0.47 V vs SCE.

**Starting Materials.** The starting materials FcP(S)S$_2$P(S)Fc,[14] [AuCl(PR$_3$)],[21] [N(PPh$_3$)$_2$][AuCl$_2$],[22] [PdCl$_2$(cod)][23] were prepared according to published procedures. All other reagents were commercially available.

**Synthesis of [Au{S$_2$P(OH)Fc}(PR$_3$)] (PR$_3$ = PPh$_3$ (2), PPh$_2$-Me (3)).** To a suspension of FcP(S)S$_2$P(S)Fc (0.056 g, 0.1 mmol) in dichloromethane (20 mL) was added [AuCl(PPh$_3$)] (0.049 g, 0.1 mmol) or [AuCl(PPh$_2$Me)] (0.043 g, 0.1 mmol), and the mixture was stirred for 1 h during which the solution became clear yellow. The solvent was evaporated to about 5 mL, and addition of hexane gave complexes **2** or **3** as yellow solids. Complex **2**: Yield 90%. $\Lambda_M$ 10.6 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Elemental analysis (%), Found: C, 44.12; H, 3.61; S, 8.54. Calcd for C$_{28}$H$_{25}$AuFeOP$_2$S$_2$: C, 44.46; H, 3.33; S, 8.48. NMR, $^1$H, $\delta$: 4.28 (m, 2H, C$_5$H$_4$), 4.30 (m, 2H, C$_5$H$_4$), 4.32 (s, 5H, C$_5$H$_5$), 7.4−7.6 (m, 15H, Ph). $^{31}$P{$^1$H} NMR, $\delta$: 30.4 (s, PPh$_3$), 71.4 (s, Fc(OH)P). Complex **3**: Yield 92%. $\Lambda_M$ 10 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Elemental analysis (%), Found: C, 39.42; H, 3.10; S, 8.92. Calcd for C$_{23}$H$_{23}$AuFeOP$_2$S$_2$: C, 39.79; H, 3.34; S, 9.24. NMR, $^1$H, $\delta$: 2.14 (m, 3H, PMe), 4.26 (m, 2H, C$_5$H$_4$), 4.33 (m, 2H, C$_5$H$_4$), 4.34 (s, 5H, C$_5$H$_5$), 7.2−7.6 (m, 10H, Ph). $^{31}$P{$^1$H} NMR, $\delta$: 21.0 (s, PPh$_2$Me), 62.9 (s, Fc(OH)P).

**Synthesis of [Au$_2${S$_2$P(OH)Fc}$_2$]·[N(PPh$_3$)$_2$]Cl (4).** To a suspension of FcP(S)S$_2$P(S)Fc (0.056 g, 0.1 mmol) in dichloromethane (20 mL) was added [N(PPh$_3$)$_2$][AuCl$_2$] (0.081 g, 0.1 mmol), and the mixture was stirred for 1 h. The solution became clear yellow; the solvent was evaporated to about 5 mL and addition of diethyl ether gave complex **4** as a yellow solid. Yield 75%. $\Lambda_M$ 117 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Elemental analysis (%), Found: C, 43.20; H, 3.32; N, 1.10; S, 8.17. Calcd for C$_{56}$H$_{50}$Au$_2$ClFe$_2$O$_2$P$_4$S$_4$: C, 43.05; H, 3.22;

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**Table 3.** X-ray Data for Complexes **4** and **5**

| compound | **4·CH$_2$Cl$_2$** | **5·2CH$_2$Cl$_2$** |
|---|---|---|
| formula | C$_{57}$H$_{52}$Au$_2$Cl$_3$Fe$_2$NO$_2$P$_4$S$_4$ | C$_{42}$H$_{40}$Fe$_4$O$_2$P$_4$Pd$_2$S$_8$ |
| $M_r$ | 1647.10 | 1535.10 |
| habit | orange tablet | red tablet |
| crystal size (mm) | 0.48 × 0.32 × 0.19 | 0.20 × 0.10 × 0.05 |
| crystal system | monoclinic | triclinic |
| space group | $P2_1/c$ | $P(-1)$ |
| cell constants: | | |
| $a$ (Å) | 18.0053(16) | 13.134(2) |
| $b$ (Å) | 20.2110(18) | 14.750(2) |
| $c$ (Å) | 18.2127(16) | 16.594(3) |
| $\alpha$ (°) | 90 | 90.524(10) |
| $\beta$ (°) | 118.366(3) | 112.805(10) |
| $\gamma$ (°) | 90 | 114.811(10) |
| $V$ (Å$^3$) | 5831.9(9) | 2632.7(8) |
| $Z$ | 4 | 2 |
| $D_x$ (Mg m$^{-3}$) | 1.876 | 1.937 |
| $\mu$ (mm$^{-1}$) | 5.9 | 2.4 |
| $F(000)$ | 3208 | 1520 |
| $T$ (°C) | −130 | −100 |
| $2\theta_{max}$ | 60 | 50 |
| no. of refl.: | | |
| measured | 78642 | 9130 |
| independent | 17044 | 9077 |
| transmissions | 0.42−0.69 | 0.82−0.99 |
| $R_{int}$ | 0.054 | 0.018 |
| parameters | 699 | 595 |
| restraints | 217 | 344 |
| $wR(F^2$, all refl.) | 0.057 | 0.059 |
| $R(F, >4\sigma(F))$ | 0.029 | 0.039 |
| $S$ | 0.94 | 0.7 |
| max. $\Delta\rho$ (e Å$^{-3}$) | 1.4 | 0.6 |

N, 0.90; S, 8.21. NMR, $^1$H, $\delta$: 4.36 (m, 2H, C$_5$H$_4$), 4.62 (m, 2H, C$_5$H$_4$), 4.32 (s, 5H, C$_5$H$_5$), 7.2−7.6 (m, 15H, Ph). $^{31}$P{$^1$H} NMR, $\delta$: 21.6 (s, 2P, N(PPh$_3$)$_2$), 94.9 (s, Fc(OH)P).

**Synthesis of [Pd$_2$(S$_4$OP$_2$Fc$_2$)$_2$] (5).** To a suspension of FcP(S)S$_2$P(S)Fc (0.056 g, 0.1 mmol) in dichloromethane (20 mL) was added [PdCl$_2$(cod)] (0.0142 g, 0.05 mmol), and the mixture was stirred for 1 h. The solution became clear red; the solvent was evaporated to about 5 mL and addition of diethyl ether gave complex **5** as a red solid.Yield 28%. $\Lambda_M$ 4.6 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Elemental analysis (%), Found: C, 35.20; H, 2.43; S, 18.32. Calcd for C$_{40}$H$_{36}$Fe$_4$O$_2$P$_4$Pd$_4$S$_8$: C, 35.18; H, 2.66; S, 18.79. NMR, $^1$H, $\delta$: 4.48 (m, 2H, C$_5$H$_4$), 4.64 (m, 2H, C$_5$H$_4$), 4.74 (m, 2H, C$_5$H$_4$), 4.80 (m, 2H, C$_5$H$_4$), 4.30 (s, 5H, C$_5$H$_5$), 4.48 (s, 5H, C$_5$H$_5$). $^{31}$P{$^1$H} NMR, $\delta$: 98.8 (s), 113.9 (s).

**Synthesis of [Pd$_4$Cl$_4$(S$_4$OP$_2$Fc$_2$)$_2$] (6).** To a suspension of FcP(S)S$_2$P(S)Fc (0.056 g, 0.1 mmol) in dichloromethane (20 mL) was added [PdCl$_2$(cod)] (0.028 g, 0.1 mmol), and the mixture was stirred for 1 h. The solution became clear red; the solvent was evaporated to about 5 mL and addition of diethyl ether gave complex **6** as a red solid.Yield 21%. $\Lambda_M$ 8.7 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Elemental analysis (%), Found: C, 27.54; H, 1.92; S, 14.62. Calcd for C$_{40}$H$_{36}$Cl$_4$Fe$_4$O$_2$P$_4$Pd$_4$S$_8$: C, 27.93; H, 2.11; S, 14.91. NMR, $^1$H, $\delta$: 4.32 (m, 2H, C$_5$H$_4$), 4.34 (m, 2H, C$_5$H$_4$), 4.36 (m, 2H, C$_5$H$_4$), 4.37 (m, 2H, C$_5$H$_4$), 4.41 (s, 5H, C$_5$H$_5$), 4.42 (s, 5H, C$_5$H$_5$). $^{31}$P{$^1$H} NMR, $\delta$: 120.3 (s), 120.8 (s).

**Crystal Structure Determinations.** Data for complexes **4** and **5** were registered on a Bruker SMART 1000 CCD or R3 diffractometer, respectively. Complex **4** crystallizes with one disordered molecule of dichloromethane and complex **5** with two ordered molecules. The structures were refined on $F^2$ using the program SHELXL-97.[24] All non-hydrogen atoms were refined anisotropically. Light atom displacement parameters were subjected to similarity restraints. Hydrogen atoms were included using a riding model, except for the OH hydrogens of adduct **4**, which were refined freely, but with an O−H distance restraint. Further crystallographic data are collected in Table 3.

**Supporting Information Available:** X-ray crystallographic files in CIF format for compounds **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC800470E

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