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Synthesis and characterisation of iron and cobalt complexes with phosphinothiolate ligands

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Abstract

Neutral iron complexes of a series of arenephosphinothiol proligands, $Ph_xP(ArSH)_{3-x}$, $(x = 0-2, Ar = C_6H_4, C_6H_3SiMe_3)$ have been synthesised. Compounds [Fe{2-(Ph_2PO)C_6H_4S}_3] (1), [Fe{2-(Ph_2P)-6(Me_3Si)C_6H_3S}_3] (2), [Fe{2-(Ph_2PO)-6(Me_3Si)C_6H_3S}_3] (3) and [Fe_2{PhP(C_6H_4S-2)_2}_3] (4) were obtained most conveniently by the electrochemical oxidation of an iron anode in a cell containing an acetonitrile solution of the corresponding proligand. [Fe{2-(Ph_2P)C_6H_4S}_2(CO)_2] (5) was obtained by the addition of the appropriate proligand to an acetonitrile solution of FeCl₂ saturated with CO. The reaction of FeCl₂ with PhP(C₆H_4SH-2)_2 in methanol in the presence of CO and bis-diphenylphosphinoethane (dppe) gave [Fe{PhP(C_6H_4S-2)_2}(dppe)(CO)] (6) in good yield. The reaction of FeCl₂ with the potentially tetradentate P(C₆H_4SH-2)_3 proligand in presence of PMe_2Ph or dppe allows the synthesis of [Fe{P(C₆H_4S-2)_3}(PMe_2Ph)_2] (7) and [Fe{P(C₆H_4S-2)_3}(dppe)] (8). Corresponding reactions of the phosphinothiolates with CoCl₂ in the presence of CO and/or phosphine ligands gave [CoCl{PhP(C₆H_4S-2)_2(dppe)] (9), [Co{PhP(C₆H_4S-2)_2}(dppe)(CO)]BPh4 (10), [Co{PhP(C₆H_4S-2)_2(dppe)] (11), [Co(P(C₆H_4S-2)_3L] (L = dppe, 12, L = PMe_2Ph, 13. The X-ray crystal structures of complexes 2, 4, 7 and 8, are discussed.

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1. Introduction

There is considerable current interest in heterodonor polydentate ligands involving tertiary phosphine groups in combinations with nitrogen, oxygen or sulphur donors. Of these, phosphinothiolates derived from thiophenol have been shown to be very versatile ligands that form stable complexes with a wide range of elements including lanthanides, transition and post transition metals [1]. Although there are many examples of thiolate ligands in combination with tertiary phosphines [2], their chemistry with iron and cobalt has received relatively little attention. The reported complexes with iron are restricted to a recent report of the monomeric species [FeX{P(C₆H₃-3-SiMe₃-2-S)₃}], X = Cl, Br, I, and the dinuclear complex [Fe₂{P(C₆H₃-3-SiMe₃-2-S)₃}₂] [3]. There are no reported complexes of iron with the tridentate ligand PhP(C₆H₄S-2)₂ and the only example with tetradentate P(C₆H₄S-2)₃ is [Fe₂{P(C₆H₄S-2)₃}₂S₂] in which two trigonal bipyramidal iron centres are linked by a bridging S₂ ligand [4]. Complexes with cobalt are also rare and limited to complexes of the type [CoL₃] where L = 2-(Ph₂P)-

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 $6(Me_3Si) C_6H_4S$ or 2-(Ph₂PO)- $6(Me_3Si)C_6H_3$ [5]. We here describe the synthesis and structures of new homoleptic iron and cobalt complexes with bi-, triand tetradentate phosphinothiolate ligands, with and without sterically hindering substituents, together with complexes also containing coordinated phosphines or carbon monoxide. The structures of the ligands used are summarised in Fig. 1. The synthesis of the complexes with the bidentate ligands is shown to proceed more cleanly using electrochemical oxidation of the metal than by direct reaction with metal salts.

2. Results and discussion

2.1. Iron complexes with bidentate and tridentate phosphinothiolates

2.1.1. Electrochemical syntheses

Iron (III) phosphinothiolato complexes 1-4 were prepared in good yield by oxidation of an iron anode in a cell containing a solution of the proligand and a small amount of tetramethylammonium perchlorate as support electrolyte. The compounds obtained are air stable crystalline solids soluble in chloroform, dichloromethane and other common organic solvents.

The electrochemical efficiency for the process, $E_{\rm f}$, defined as the number of moles of metal dissolved per faraday of charge, was always close to 0.5 mol F⁻¹. These values suggest that the anodic oxidation of the metal leads initially to an Fe(II) species, which is further oxidised to Fe(III) in solution. This and the evolution of the hydrogen at the cathode is compatible with a mechanism such as:

cathode: $2 PSH + 2e^- \rightarrow 2PS^- + H_2$ anode: $Fe + 2PS^- \rightarrow [Fe(PS)_2] + 2e^ [Fe(PS)_2] + PSH \rightarrow [Fe(PS)_3] + 1/2H_2$

where PSH represents one of the bidentate phosphi-



Fig. 1. Structures and formulae of phosphinothiolate ligands used.

nothiolate proligands. This type of mechanism has previously been observed in the synthesis of other metal complexes in which low oxidation state species are the initial electrochemical products [6,10]. In the case of 1, the analytical data show that all the phosphorous atoms have been oxidised, and the compound has to be formulated as $[Fe\{2-(Ph_2PO)C_6H_4S\}_3]$. The IR data of 1 confirm the presence of the P=O group, vide infra.

The IR spectra of these complexes show no bands attributable to v(S-H), which in the free proligands appear at 2500–2400 cm⁻¹. This is indicative that the ligands are in the anionic thiolate form in the complex. The spectra also show bands in the aromatic region characteristic of the co-ordinated phosphinothiolate ligand. The IR spectrum of compound **2**, containing trimethylsilyl groups, shows a strong band at 854 cm⁻¹ characteristic of the v(Si-C). The IR spectra of **1** and **3** also exhibit a strong band around 1130 cm⁻¹ due to v(P-O).

The FAB mass spectra of 1–4 show peaks at m/z 674 $[M-L]^+$, 786 $[M-L]^+$, 818 $[M-L]^+$ and 1085 $[M]^+$, respectively. Peaks associated with further loss of ligands are also observed. The peak clusters have appropriate isotope distributions.

Crystals suitable for X-ray studies of **2** were obtained by recrystallisation from dichloromethane + ethanol and those of **4** by slow concentration of an acetonitrile solution. Attempts to obtain crystals of **1** and **3** suitable for X-ray studies were unsuccessful, but analytical and spectroscopic data confirm the presence of Fe(III) compounds with three bidentate monoanionic ligands. Presumably these complexes have octahedral structures similar to that of **2**, vide infra; in these cases with [FeO₃S₃] environments. The presence of the bulky Me₃Si group in the six position of the thiophenolate arene group does not influence the stoichiometry or structures of the [FeL₃] type complexes.

2.1.2. Reactions of $2-(Ph_2P)C_6H_4SH$ with iron dichloride

Anhydrous FeCl₂ reacts with an excess of 2-(Ph₂P)C₆H₄SH in acetonitrile at room temperature for 1 h to give a brick red solid. Elemental analysis was not consistent with the formation of [Fe{2-(Ph₂P)C₆H₄S}₃] and the observation of 1% nitrogen suggested some incorporation of acetonitrile in the product. However the FAB mass spectrum shows a major peak at m/z 642 corresponding to [Fe{2-(Ph₂P)C₆H₄S}₂]⁺. It proved impossible to purify the complex by recrystallisation and it appears probably that [Fe{2-(Ph₂P)C₆H₄S}₃] is produced, albeit in an impure form.

When this reaction was carried out in MeCN saturated with CO an orange solid was produced, which analysed closely as $[Fe\{2-(Ph_2P)C_6H_4S\}_2(CO)_2]$ (5). The IR spectrum showed an intense sharp band at 1979 cm⁻¹ due to ν (C=O). The observation of a single CO

stretching vibration suggests a *trans*-CO, *trans*(P,P), *trans*(S,S) symmetrical structure The complex loses CO on standing in the solid state to give a brown solid. This is very insoluble in all solvents and presumably is polymeric with thiolate–S bridges.

Attempts to prepare mixed Fe complexes with the PSH ligand and mono- or di-tertiary phosphines or isocyanide produced complexes, which although containing the additional ligand, were clearly mixtures, and could not be purified.

2.1.3. Reactions of $PhP(C_6H_4SH-2)_2$ with iron dichloride

Reaction of FeCl₂ with PhP(C₆H₄SH-2)₂ in acetonitrile gave a dark red solid, which was soluble in dichloromethane to give a red solution, which turned blue in air after a few hours. HPLC measurements suggested that this was essentially a single species in CH₂Cl₂ solution. However no satisfactory formulation could be derived from the elemental analysis. The observation of one doublet in the Mössbauer spectrum with isomer shifts and quadruple splitting indicative of single Fe(III) site, suggests that the asymmetric dimer 4 formed by electrolysis as described above is not formed. This is supported by the lack of any peak at m/z 1085 due to the $[Fe_2{PhP(C_6H_4S-2)_2}_3]$ species. No suitable crystals could be obtained for an X-ray structure determination and the exact formulation remains unclear. However it is certainly not the complex 4.

In view of the problems encountered with the FeCl₂/ PhP(C₆H₄SH-2)₂ system, we attempted to simplify the chemistry by introduction of the chelating ditertiary phosphine Ph₂PCH₂CH₂PPh₂ (dppe). Reaction of FeCl₂ with dppe and PhP(C₆H₄SH-2) in methanol in the presence of CO gave orange neutral [Fe{PhP(C₆H₄S-2)₂}(dppe)(CO)] (6) in reasonable yield. This complex was diamagnetic and showed a single strong IR band assigned to v(C=O) at 1930 cm⁻¹. The Mössbauer spectrum is consistent with the presence of Fe(II) with a narrow doublet with isomer shift 0.11 mm s⁻¹ and quadruple splitting of 0.23 mm s⁻¹.

2.1.4. Reactions of $P(C_6H_4SH-2)_3$ with iron dichloride

Anhydrous FeCl₂ was stirred at room temperature with 2 equiv. of PMe₂Ph in acetonitrile and 1 equiv. of P(C₆H₄SH-2)₃ was added to give a dark red solution. On heating under reflux for 1 h and cooling a dark red precipitate was formed. The elemental analysis of the initial product gave values intermediate between [Fe{P(C₆H₄S-2)₃}(PMe₂Ph)] and [Fe{P(C₆H₄S-2)₃}(PMe₂Ph₂)₂] and the FAB MS showed peaks assignable to both species. As has been reported for the [Tc{P(C₆H₄S-2)₃}(PrNC)_n] species (n = 1, 2) there is a facile equilibrium between the five and six co-ordinate species [7]. Recrystallisation gave the bis(phosphine) product 7 essentially pure, and this showed a single doublet in the Mössbauer spectrum, (isomer shift 0.1 mm s⁻¹ and quadruple splitting 2.90 mm s⁻¹) characteristic of low spin Fe(III). Crystals of this compound suitable for X-ray studies were obtained from dichloromethane-hexane. The directly analogous complex [Fe{P(C₆H₄S-2)₃}(dppe)] **8** was prepared similarly and fully characterised by X-ray studies.

2.2. X-ray crystal structures of complexes 2, 4, 7 and 8

2.2.1. Molecular structure of $[Fe\{2-(Ph_2P)-6(Me_3Si)C_6H_3S\}_3]$ (2)

The molecular structure of $[Fe{2-(Ph_2P)-6(Me_3 SiC_6H_3S_3$ (2), together with the atom labelling scheme, is showed in Fig. 2. Selected bond distances and angles are given in Table 2. A summary of the X-ray data for complexes 2, 4, 7 and 8 appears in Table 1. The compound 2 consists of discrete molecules with the metal co-ordinated to three monoanionic (P, S) bidentate ligands. The geometry around the metal can be described as [FeP₃S₃] slightly distorted octahedral; all the dihedral angles between the coordination planes defined by four donor atoms being close to 90°. Angles defined by two trans donor atoms and the metal, are in the range $168.05(3)-175.16(3)^{\circ}$, and those involving the iron and two mutually cis donor atoms, lie in the range of $82.55(3)-101.76(3)^\circ$, and are also close to the expected values. Even those corresponding to five membered chelate rings are close to optimal with values of 83.09(3), 86.58(2) and 85.20(2)°.

The three sulfur and phosphorous atoms are meridional. This is the arrangement found in other complexes containing similar ligands, such as [Tc{2- $(Ph_2P)C_6H_4S_3$] and $[Re\{2-(Ph_2P)C_6H_4S\}_3]$ [8], $[Ir\{2-(Ph_2P)C_6H_4S\}_3]$ $(Ph_2P)C_6H_4S_3$ [9], $[In\{2-(Ph_2P)C_6H_4S\}_3$ [10] and $[Co{2-(Ph_2P)-6-(Me_3Si)C_6H_3S_3]$ [5]. The Fe-S and Fe-P distances are unremarkable and close to the values found in complexes such as $[FeCl{P(C_6H_4S)_3}]^2$. It appears that the bulky trimethylsilyl substituents have little impact on the overall structure adopted.

2.2.2. Molecular structure of $[Fe_2{PhP(C_6H_4S-2)_2}_3]$ (4)

The molecular structure of $[Fe_2{PhP(C_6H_4S-2)_3]}(4)$ is shown in Fig. 3, together with the atomic numbering scheme adopted. Selected bond distances and angles are in Table 3. The compound is a dimer with each iron having distorted octahedral geometry and sharing a common face comprising three bridging thiolate sulphur atoms. The environment around each metal atom is different due to the variation in the bonding mode of the phosphinothiolate ligands. One of them uses both sulfurs as terminal donors and on the other, one of the sulfurs is terminal and the other acts as a bridge between the metals. Both sulfurs of the third ligand bridge the



Fig. 2. Representation of the structure of $[Fe{2-(Ph_2P)-6(Me_3Si)C_6H_3S]_3]$, complex 2, showing the atom labelling scheme.

Table 1								
Summary of	crystallographic	data	for	$[Fe{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}_3]$ (2),	$[Fe_2{PhP(C_6H_4S-2)_2}_3]$ (4),	$[Fe{PC_6H_4S-2}]_3(PMe_2Ph)]$	(7)	and
$[Fe{P(C_6H_4S-2)]$	2) ₃ }(dppe)] (8)							

	2	4	7	8
Chemical formula	C ₆₃ H ₆₆ FeNP ₃ S ₃ Si ₃	$C_{54}H_{39}Fe_2P_3S_6$	C34H34FeP3S3	$C_{22}H_{18}Fe_{0.5}P_{1.5}S_{1.5}$
Formula weight	1152.37	1083.83	687.55	404.83
T (K)	293(2)	293(2)	293(2)	293(2)
Crystal size (mm ³)	$0.12 \times 0.12 \times 0.15$	$0.20 \times 0.20 \times 0.30$	0.2 imes 0.1 imes 0.1	$0.5 \times 0.7 \times 1.1$
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_{1/n}$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions				
a (Å)	12.6337(4)	10.8055(2)	9.9489(19)	11.2538(13)
b (Å)	14.0774(4)	39.7963(3)	9.9539(19)	20.424(2)
c (Å)	19.2919(6)	13.0715(2)	16.757(4)	16.628(2)
α (°)	73.2977(9)	90	89.642(17)	90
β(°)	82.9835(6)	103.4240(10)	88.230(17)	98.110(9)
γ (°)	76.5493(9)	90	73.828(17)	90
$V(Å^3)$	3190.53(17)	5467.42(14)	1593.0(6)	3783.6(7)
Ζ	2	4	2	8
$\mu ({\rm mm}^{-1})$	0.502	0.881	0.845	0.724
Reflections collected	23283	33828	6768	6563
Independent reflections	15070	12956	4417	3337
R ^a	0.0494	0.0928	0.0399	0.0268
$R_{\rm w}^{\rm b}$	0.1122	0.1707	0.1017	0.06560

^a $R = \Sigma(|F_{\rm o}| - |F_{\rm c}|)/\Sigma|F_{\rm o}|.$

^b
$$wR_2 = [(\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}.$$

metal atoms. Fe(1), therefore, has a $[FePS_5]$ array of donors produced by two terminal sulfurs, the phosphorus atoms of one ligand and three bridging sulfurs belonging to two other ligands. The donor set around Fe(2) is $[FeS_4P_2]$, with the metal coordinated to one phosphorus and two bridging sulfur atoms of one ligand, and to one phosphorus, a terminal sulfur and a

bridging sulfur of the other ligand. The metal-metal distance, 2.8212(11) Å, is similar to the 2.715(Å) found in the $[Fe_2{P(C_6H_3-3-SiMe_3-2-S)_3}_2]$ complex with two iron(III) atoms in a pentacoordinate environment and a bond distance that is in the range of 2.5–3.0 Å suggested for metal-metal interaction in polynuclear iron complexes [2].

Table 2 Bond lengths (Å) and bond angles (°) for $[Fe\{2\text{-}(Ph_2P)\text{-}6(Me_3\text{-}Si)C_6H_3S\}_3]$ (2)

Bond lengths			
Fe-S(2)	2.2449(7)	Fe-S(1)	2.2821(7)
Fe-P(2)	2.2926(7)	Fe-S(3)	2.3068(7)
Fe-P(3)	2.3264(7)	Fe-P(1)	2.3289(7)
S(1) - C(11)	1.767(3)	S(2)-C(41)	1.771(2)
S(3)-C(76)	1.753(2)	P(1) - C(16)	1.827(3)
P(1)-C(31)	1.831(3)	P(1)-C(21)	1.846(3)
P(2)-C(46)	1.817(3)	P(2)-C(51)	1.848(2)
P(2)-C(61)	1.849(3)	P(3)-C(71)	1.813(3)
P(3)-C(81)	1.848(3)	P(3)-C(91)	1.849(3)
Bond angles			
S(2)-Fe-S(1)	101.76(3)	S(2)-Fe-P(2)	86.58(2)
S(1)-Fe-P(2)	85.59(2)	S(2)-Fe-S(3)	175.16(3)
S(1)-Fe-S(3)	82.55(3)	P(2)-Fe-S(3)	91.58(2)
S(2)-Fe-P(3)	90.52(3)	S(1)-Fe-P(3)	167.70(3)
P(2)-Fe-P(3)	95.80(3)	S(3)-Fe-P(3)	85.20(2)
S(2)-Fe-P(1)	91.98(3)	S(1)-Fe-P(1)	83.09(3)
P(2)-Fe-P(1)	168.05(3)	S(3)-Fe-P(1)	90.74(3)
P(3)-Fe-P(1)	96.08(3)		

The three Fe–S bridge bond distances are slightly different, 2.3984(17) and 2.2999(17) Å for S(2), 2.3932(17) and 2.2621(16) Å for S(3), and 2.3006(15) and 2.2832(15) Å for S(4). The Fe–S terminal bond distances are similar, 2.2299(17), 2.2144(17) and 2.2809(18) Å. The Fe–S terminal and Fe–P bond distances, 2.2083(15) , 2.2111(17) and 2.2195(17) Å are close to those found in other dinuclear iron complexes

with phosphinothiolate ligands such as $[Fe_2(\mu S_2){P(C_6H_4S)_3}_2]^{2-}$, for which the average value for Fe-S(thiolate) and Fe-P bond distances are 2.20 and 2.212(2) Å, respectively [3].

2.2.3. Molecular structures of 7 and 8

Representations of the molecular structures of complexes 7 and 8 are shown in Figs. 4 and 5 and selected bond lengths and angles in Tables 4 and 5. Both complexes are essentially octahedral with comparable distortions arising from the presence of the tetradentate PS_3 ligands. The Fe–P and Fe–S distances are comparable with other Fe(III) complexes with phosphinothiolate ligands [3]. It appears that the relatively small and basic dimethylphenylphosphine and the chelating diphosphine are able to impose an octahedral geometry on these systems whereas co-ligands such as halide give trigonal bipyramidal species.

2.3. Synthesis of cobalt complexes

2.3.1. With potentially tridentate phosphinothiolate ligands

Reaction of CoCl₂ with PhP(C₆H₄SH-2)₂ (PS₂H₂) in acetonitrile in the presence of Et₃N gave a purple solid which was evidently a mixture and could not be purified. However in the presence of dppe a dark green solid analysing as [CoCl(PS₂)(dppe)] **9** was obtained. The FAB mass spectrum showed a peak at m/z 851 corresponding to the $[M+1]^+$ ion, together with a peak due to $[M-Cl]^+$, both having appropriate isotope



Fig. 3. Representation of the structure of $[Fe_2{PhP(C_6H_4S-2)_2}_3]$, complex 4, showing the atom labelling scheme.

Table 3 Selected bond lengths (Å) and bond angles (°) for $[Fe_2\{PhP(C_6H_4S-2)_2\}_3]$ (4)

Bond lengths			
Fe(1) - P(1)	2.2083(15)	Fe(1) - S(12)	2.2144(17)
Fe(1) - S(1)	2.2299(17)	Fe(1) - S(4)	2.3006(15)
Fe(1) - S(3)	2.3932(17)	Fe(1) - S(2)	2.3984(17)
Fe(1)-Fe(2)	2.8212(11)	Fe(2) - P(3)	2.2111(17)
Fe(2)-P(7)	2.2195(17)	Fe(2) - S(3)	2.2621(16)
Fe(2)-S(22)	2.2809(18)	Fe(2) - S(4)	2.2832(15)
Fe(2)-S(2)	2.2999(17)		
Bond angles			
P(1)-Fe(1)-S(12)	88.32(6)	P(1)-Fe(1)-S(1)	87.94(6)
S(12) - Fe(1) - S(1)	98.12(7)	P(1)-Fe(1)-S(4)	173.95(7)
S(12) - Fe(1) - S(4)	96.18(6)	S(1) - Fe(1) - S(4)	87.43(6)
P(1)-Fe(1)-S(3)	88.36(6)	S(12) - Fe(1) - S(3)	92.17(7)
S(1) - Fe(1) - S(3)	168.96(7)	S(4) - Fe(1) - S(3)	95.48(6)
P(1)-Fe(1)-S(2)	95.15(6)	S(12) - Fe(1) - S(2)	167.10(7)
S(1) - Fe(1) - S(2)	94.42(6)	S(4) - Fe(1) - S(2)	81.34(5)
S(3) - Fe(1) - S(2)	75.56(6)	P(3)-Fe(2)-P(7)	109.56(6)
P(3)-Fe(2)-S(3)	87.73(6)	P(7)-Fe(2)-S(3)	161.70(7)
P(3)-Fe(2)-S(22)	88.85(7)	P(7)-Fe(2)-S(22)	85.00(7)
S(3) - Fe(2) - S(22)	89.55(7)	P(3)-Fe(2)-S(4)	85.71(6)
P(7)-Fe(2)-S(4)	87.88(6)	S(3) - Fe(2) - S(4)	99.71(6)
S(22) - Fe(2) - S(4)	169.05(7)	P(3)-Fe(2)-S(2)	162.39(7)
P(7)-Fe(2)-S(2)	84.23(6)	S(3) - Fe(2) - S(2)	80.10(6)
S(22)-Fe(2)-S(2)	103.62(7)	S(4) - Fe(2) - S(2)	83.88(6)

distributions. Despite the formal Co(III) oxidation state and the presence of ligands likely to induce spin-pairing, it proved impossible to obtain satisfactory ¹H or ³¹P NMR spectra. This may be due to the presence of paramagnetic impurities. However, crystals suitable for an X-ray structure determination were grown from dichloromethane-hexane and the structure verifies the formulation above, but is not discussed here.



Fig. 5. Representation of the structure of $[Fe{P(C_6H_4S-2)_3}(dppe)]$, complex 8, showing the atom labelling scheme.

Reaction of 9 with CO at atmospheric pressure in methanol for few minutes gave a vivid purple solution from which $[Co(PS_2)(CO)(dppe)]^+$ 10 was isolated in high yield as a tetraphenylborate salt. The IR spectrum showed a strong band at 2052 cm⁻¹ due to the CO ligand as well as bands characteristic of the PS₂ and dppe ligands. The complex was not sufficiently stable for complete characterisation as it decomposed rapidly in solution with loss of CO to give poorly-defined polymeric materials. The complex and the high CO stretching frequency reflects the relatively high formal metal oxidation state and the overall positive charge. Attempts



Fig. 4. Representation of the structure of $[Fe{P(C_6H_4S-2)_3}(PMe_2Ph)_2]$, complex 7, showing the atom labelling scheme.

Table 4 Selected bond lengths (Å) and bond angles (°) for $[Fe\{PC_6H_4S-2)\}_3(PMe_2Ph)]$ (7)

Bond lengths			
Fe-P(1)	2.1604(10)	Fe-S(1)	2.2549(10)
Fe-S(3)	2.2924(11)	Fe-S(2)	2.2929(11)
Fe-P(3)	2.3095(11)	Fe-P(2)	2.3694(11)
S(1)-C(12)	1.771(3)	S(2)-C(22)	1.758(3)
S(3)-C(32)	1.772(4)	P(1) - C(31)	1.799(4)
P(1)-C(11)	1.807(3)	P(1) - C(21)	1.817(3)
P(2)-C(61)	1.823(4)	P(2)-C(51)	1.828(3)
P(2) - C(41)	1.838(4)	P(3)-C(91)	1.819(4)
P(3)-C(81)	1.821(4)	P(3)-C(71)	1.826(3)
Bond angles			
P(1)-Fe-S(1)	87.68(4)	P(1)-Fe-S(3)	81.96(4)
S(1) - Fe - S(3)	165.62(4)	P(1) - Fe - S(2)	85.70(4)
S(1)-Fe-S(2)	95.49(4)	S(3)-Fe-S(2)	93.66(4)
P(1) - Fe - P(3)	167.91(4)	S(1)-Fe-P(3)	95.27(4)
S(3) - Fe - P(3)	96.92(4)	S(2) - Fe - P(3)	82.36(4)
P(1) - Fe - P(2)	96.07(4)	S(1)-Fe-P(2)	85.65(4)
S(3) - Fe - P(2)	85.56(4)	S(2) - Fe - P(2)	177.94(4)
P(3)-Fe-P(2)	95.84(4)		
S(1) - Fe - S(2) P(1) - Fe - P(3) S(3) - Fe - P(3) P(1) - Fe - P(2) S(3) - Fe - P(2) P(3) - Fe - P(3) S(3) - Fe - P(2) S(3) - Fe - Fe - P(2) S(3) - Fe - F	95.49(4) 167.91(4) 96.92(4) 96.07(4) 85.56(4) 95.84(4)	$\begin{array}{l} F(1) = Fe^{-1}Fe$	93.66(4) 95.27(4) 82.36(4) 85.65(4) 177.94(4)

Table 5 Bond lengths (Å) and bond angles (°) for $[Fe{P(C_6H_4S-2)_3}(dppe)]$ (8)

Bond lengths			
Fe-P(1)	2.1725(8)	Fe-S(3)	2.2747(14)
Fe-S(1)	2.2875(8)	Fe-P(3)	2.2985(7)
Fe-S(2)	2.3208(8)	Fe-P(2)	2.3275(14)
P(1)-C(31)	1.785(5)	P(1)-C(21)	1.798(4)
P(1)-C(11)	1.820(3)	P(2)-C(51)	1.830(3)
P(2)-C(2)	1.848(3)	P(2)-C(41)	1.849(5)
P(3)-C(1)	1.833(5)	P(3)-C(71)	1.833(4)
P(3)-C(61)	1.845(3)		
Bond angles			
P(1)-Fe-S(3)	86.47(4)	P(1)-Fe-S(1)	85.70(3)
S(3)-Fe-S(1)	95.40(4)	P(1)-Fe-P(3)	174.45(5)
S(3)-Fe-P(3)	88.47(4)	S(1)-Fe-P(3)	97.07(3)
P(1)-Fe-S(2)	79.48(3)	S(3)-Fe-S(2)	94.95(4)
S(1)-Fe-S(2)	161.34(3)	P(3)-Fe-S(2)	98.69(3)
P(1)-Fe-P(2)	103.36(4)	S(3)-Fe-P(2)	169.29(3)
S(1)-Fe-P(2)	81.30(4)	P(3)-Fe-P(2)	81.87(4)
S(2)-Fe-P(2)	91.09(4)		

to introduce hydrazide type ligands by reaction of 9 with Me_2NHNH_2 gave a virtually insoluble amber solid, which based on analysis has the empirical formula $[Co(PS_2)(dppe)]$ (11). No MS or solution spectroscopic data could be obtained, but the lack of solubility suggests the product 11 is a thiolate bridged oligomer.

2.3.2. With potentially tetradentate phosphinothiolate ligands

The reaction of $CoCl_2$ with $P(C_6H_4SH-2)_3$ (PS₃H₃) in the presence of phosphine ligands was analogous to that with FeCl₂. With dppe, red crystalline [Co(PS₃)(dppe)] (12) was obtained and this was shown by X-ray crystallography to be essentially isostructural with the iron complex 8 discussed above. In view of the similarity of the structures the data for the cobalt complex is not included here. As was observed for iron, with PMe₂Ph the product appeared to be a mixture of the mono- and bis(phosphine) adducts with mass ions corresponding to both species being exhibited in the FAB mass spectrum. The facile loss of phosphine in solution precluded meaningful NMR measurements being made.

3. Experimental

All manipulations were carried under an inert atmosphere of dry nitrogen. Iron (Aldrich Chemie) was used as plates (ca. 2×2 cm). Synthesis of ligands were carried out using slight modifications of the standard literature procedure involving lithiation of benzenethiol [11], using Schlenk techniques and dry solvents. Elemental analyses were performed with a Carlo-Erba EA 1108 microanalyser. IR spectra were recorded in KBr discs using a Bruker IFS 66v spectrophotometer. The FAB mass spectra were recorded on a Kratos MS-50TC instrument, using 3-nitrobenzyl alcohol (3-NOBA) as a matrix material.

3.1. Preparation of the complexes

Complexes 1–4 were obtained using an electrochemical procedure. An acetonitrile solution of the ligand containing about 15 mg of tetramethylammonium perchlorate as a support electrolyte was electrolysed using a platinum wire as the cathode and an iron plate as the sacrificial anode. Applied voltages of 10–15 V allowed sufficient current flow for smooth dissolution of the metal. During electrolysis, nitrogen gas was bubbled through the solution to provide an inert atmosphere and also to stir the reaction mixture. The cells can be summarised as: $Fe_{(+)}/CH_3CN + P(SH)_x/Pt_{(-)}$.

3.1.1. $[Fe\{2-(Ph_2PO)C_6H_4S\}_3]$ (1)

Electrolysis of an acetonitrile solution (50 cm³) containing 2-(diphenylphosphino)benzenethiol (0.220 g, 0.75 mmol) at 14 V and 10 mA for 2 h, dissolved 22 mg of metal ($E_{\rm f} = 0.52$ mol F⁻¹). As the reaction proceeded a solid was formed immediately at the anode and hydrogen evolved at the cathode. At the end of the experiment the solid obtained was filtered, washed with cool acetonitrile and ethyl ether and dried under vacuum (0.20 g, 0.214 mmol, 84%). *Anal.* Calc. for C₅₄H₄₂FeO₃P₃S₃: C, 65.9; H, 4.3; S, 9.8. Found: C, 66.0; H, 4.50; S, 9.3%. IR (KBr, cm⁻¹): 1575(m), 1438 (s), 1417 (m), 1122 (s), 1093 (m), 1037 (m), 997 (w), 744 (s), 729 (w), 694 (s), 543 (s).

3.1.2. $[Fe\{2-(Ph_2P)-6(Me_3Si)C_6H_3S\}_3]$ (2)

A solution of acetonitrile (50 cm³) containing 2diphenylphosphino-6-trimethylsilylbenzenethiol (0.273 g, 0.75 mmol) was electrolysed at 17 V and 10 mA during 2 h and 20 mg of iron metal were dissolved from the anode, $E_f = 0.48 \text{ mol F}^{-1}$. The resulting microcrystalline product was washed with acetonitrile and ethyl ether and dried, (0.193 g, 0.168 mmol, 67%). Suitable crystals for X-ray studies were obtained by crystallisation from dichloromethane+methanol. *Anal.* Calc. for C₆₃H₆₆FeP₃S₃Si₃: C, 65.7; H, 5.8; S, 8.3. Found: C, 65.1; H, 5.6; S, 8.1%. IR(KBr, cm⁻¹): 3055(m), 2949(m), 2893(m), 1556(m), 1437(m), 1246(m), 1074(w), 1039(w), 997(w), 854(s), 752(s), 692(m), 557(s).

3.1.3. $[Fe\{2-(Ph_2PO)-6(Me_3Si)C_6H_3S\}_3]$ (3)

Electrochemical oxidation of an iron anode in a solution of 2-(diphenylphosphinyl)-6-(trimethylsilyl) benzenethiol (0.214 g, 0.56 mmol) in acetonitrile (50 cm³), at 10 V and 10 mA for 2 h caused 16 mg of iron to be dissolved ($E_f = 0.51 \text{ mol.F}^{-1}$). During the electrolysis hydrogen was evolved at the cathode and after 1.5 h, black crystalline needles appeared on the electrodes and at the bottom of the vessel. The solid was filtered, washed with acetonitrile and ether and dried under vacuum, (0.14 g, 0.117 mmol, 62%). *Anal.* Calc. for C₆₃H₆₆FeP₃O₃S₃Si₃: C, 63.1; H, 5.5; S, 8.0. Found: C, 62.1; H, 5.6; S, 7.5%. IR (KBr, cm⁻¹): 3057(m), 2951(m), 2891(m), 1554(m), 1439(m), 1354(s), 1244(m), 1130(s), 1074(m), 997(w), 854(s), 750(m), 694(m), 559(s).

3.1.4. $[Fe_2{PhP(C_6H_4S-2)_2}_3]$ (4)

A similar experiment (10 V, 10 mA, 2.5 h) with 0.152 g (0.466 mmol) of the ligand PhP(C₆H₄SH-2)₂ in 50 cm³ of acetonitrile, dissolved 25 mg of iron, $E_f = 0.48$ mol F⁻¹. A black crystalline solid formed at the anode during the electrolysis. Hydrogen was evolved at the cathode. The solid was collected, washed with cool acetonitrile, diethyl ether and dried under vacuum (0.131 g, 0.120 mmol, 78%). Crystals suitable for X-ray studies were obtained by concentration of the acetonitrile solution. *Anal.* Calc. for C₅₄H₃₉Fe₂P₃S₆: C, 59.8; H, 3.6; S, 17.7. Found: C, 58.3; H, 3.5; S, 17.3%. IR (KBr, cm⁻¹): 1572(m), 1442 (s), 1423(m), 1246(m) 1124(s), 1097(m), 999(w), 742(s), 729(w), 692(s), 538(s).

3.1.5. $[Fe\{2-(Ph_2P)C_6H_4S-2\}_2(CO)_2]$ (5)

A solution of FeCl₂ (0.02g, 0.15 mmol) in MeCN (30ml) was saturated with CO gas for 15 min at room temperature (r.t.). 2-(Ph₂P)C₆H₄SH (0.1 g, 0.34 mmol) was added and bubbling of CO through the solution was continued for 30 min. An orange precipitate of **5** was produced (0.09 g, 85%). *Anal.* Calc. for C₃₈H₂₈Fe-P₂O₂S₂: C, 65.3; H, 4.0; S, 9.2. Found C, 65.3; H, 4.6%; S, 9.8%. IR 1979[ν (CO)], 1573, 736, 695 cm⁻¹. The complex **5** can be stored under CO but otherwise

rapidly decomposes to leave a CO-free, pale brown polymeric solid.

3.1.6. $[Fe{PhP(C_6H_4S-2)_2} (dppe)(CO)]$ (6)

An MeCN (20ml) solution of FeC1₂ (0.06g, 048 mmol) and dppe (0.18g, 0.45 mmol) was saturated with CO and PhP(C₆H₄SH-2)₂ (0.15g, 0.46 mmol) was added and the slow stream of CO through the solution was maintained for 30 min during which time the complex precipitated as an orange solid (0.27 g, 72%). *Anal.* Calc. for C₄₃H₃₇FeOP₃S₂ C, 67.0; H, 4.0. Found: C, 66.4; H, 4.7% IR 1930[ν (CO)], 1572, 1096, 737, 694 cm⁻¹. Mössbauer: narrow doublet, isomer shift 0.11 mm s⁻¹, quadrupole splitting 0.23 mm s⁻¹. The instability of the complex with respect to CO loss precluded MS measurements.

3.1.7. $[Fe \{ P(C_6H_4S-2)_3 \} (PMe_2Ph)_2]$ (7)

To a pink solution of FeCl₂ (0.06 g, 0.48 mmol) and PMe₂Ph (0.13 ml, 0.95 mmol) was added P(C₆H₄SH-2)₃ (0.16 g, 0.47 mmol). The resulting dark red solution was heated under reflux for 1 h. On cooling the complex precipitated as a dark red solid (0.26 g, 80%).The elemented analysis obtained was intermediate between [Fe{P(C₆H₄S-2)₃}(PMe₂Ph)] and [Fe{P(C₆H₄S-2)₃}(PMe₂Ph)] and [Fe{P(C₆H₄S-2)₃}(PMe₂Ph)]. The FAB MS showed an intense peak at m/z 566 due to the monophosphine adduct, and a much weaker peak due to the bis(phosphine) complex.

3.1.8. $[Fe\{P(C_6H_4S-2)_3\}(dppe)]$ (8)

FeCl₂ (0.068 g, 0.54 mmol), dppe (0.4 g, 0.1 mmol) and P(C₆H₄SH-2)₃ (0.19 g, 0.53 mmol) in MeCN (30ml) were heated under reflux for 1 h. On cooling the complex precipitated as a dark red solid (yield 0.32 g, 74%). Even after attempted recrystallisation no satisfactory analyses could be obtained, but the MS showed an intense peak due to [M+1] at m/z 807.

3.1.9. $[CoCl{PhP(C_6H_4S-2)_2}(dppe)]$ (9)

CoCl₂ (0.30 g, 2.33 mmol) and dppe (0.6 g, 1.5 mmol) were stirred in MeCN (30 ml) for 15 min to give a green solution. PhP(C₆H₄SH-2)₂ (0.5 g, 1.53 mmol) was then added to give a deep red solution which was then heated under reflux for 1 h. Cooling to r.t. gave complex **9** as a dark brown solid (yield 0.76 g, 60%). *Anal.* Calc. for C₄₂H₃₇C1CoP₃S₂: C, 64.7, H, 4.6. Found: C, 64.0, H, 4.6%. IR: 1571, 741, 727, 692 cm⁻¹ FAB MS: m/z 815 (weak) $[M]^+$ m/z 780 (strong), $[M - C1]^+$ m/z 383 strong, $[M - C1 - dppe]^+$. All peaks have appropriate isotope distribution.

3.1.10. $[Co{PhP(C_6H_4S-2)_2}(CO)(dppe)]BF_4$ (10)

Complex 9 (0.06 g) was suspended in MeOH (30 ml) and CO bubbled through the solution at r.t. for 10 min. Na[BPh₄] (0.5 g) was added to the purple solution to precipitate 10 as a purple solid (yield 0.07 g, 84%). The

instability of the complex with respect to loss of CO prevented satisfactory elemental analyses, or solution NMR spectra or mass spectra being obtained. IR: v(CO) 2052 cm⁻¹.

3.1.11. $[Co{PhP(C_6H_4S-2)_2}(dppe)]$ (11)

Prepared in a directly analogous manner to **8** using CoC1₂ as a dark red solid in 70% yield. Analysis of sample recrystallised from CH₂Cl₂-hexane: Calc. for C₄₄.H₃₇ Cl P₃ S₃ Co: C, 62.5; H, 4.7. Found C, 63.5; H, 4.4% IR: bands characteristic of phenyl groups 1568, 740, 639 cm⁻¹ FAB MS: m/z 812 [M^+]. An X-ray crystal structure revealed the complex was essentially isostructural with complex **8**.

3.1.12. $[Co\{P(C_6H_4S-2)_3\}(PMe_2Ph)_2]$ (13)

This was prepared directly analogously to complex 7 using CoCl₂ as a dark red solid in 72% yield. *Anal.* Calc. for C₃₄H₃₆P₃S₃Co: C, 59.1; H, 5.0. Found: C, 59.0; H, 4.9%. IR 1567, 943, 907, 726, 701 cm⁻¹ FAB MS. Strong peak at m/z 551 $[M - PMe_2Ph]^+$; weak peak at m/z 691 due to $[M]^+$.

3.2. X-ray crystal structure determinations

Compounds 2 and 4 were studied on a Siemens (Bruker) Smart system with a CCD detector. Data collection was carried out under ambient conditions, using graphite monochromated Mo K α ($\lambda = 0.71073$ Å). The crystal parameters and other experimental details of the data collection are summarised in Table 1. A complete description of the details of the crystallographic methods is given in Section 5.

Intensity data of **8** were collected on an Enraf– Nonius CAD4 diffractometer with monochromated Mo K α radiation. Cell constants were obtained from least squares refinement of the setting angles of 25 centred reflections in the range $15 < \theta < 17^{\circ}$. The data were collected in the $\omega/2\theta$ scan mode and three standard reflection were measured every 2 h of exposure. No loss of intensity was observed which was linearly corrected during processing. Three standard reflections were measured every 200 reflections to check the crystal orientation. The data were corrected Lorentz and polarisation factors and an absorption correction was applied using psi-scans of nine reflections.

Intensity data for compound 7 were collected on an Delft-Instruments FAST-TV area detector diffractometer with graphite-monochromated Mo K α radiation. Cell constants were obtained from least-squares refinement of the setting angles of 250 reflections having $\theta = 2.34-25.09$.

The structures were solved by direct methods and refined by a full-matrix least-squares procedure [12]. Neutral atom scattering factors were taken from Cromer and Waber [13] and anomalous dispersion from Cromer [14]. For the compound **4** the squeeze program was used to correct the reflection data for the diffuse scattering due to disorder solvent [15]. All non-hydrogen atoms were anisotropic. The hydrogen atoms were included in idealised positions with Uiso free to refine. The crystal parameters and other experimental details of the data collection are summarised in Table 1. A complete description of the details of the crystallographic methods is given in Section 5 [12,16].

4. Conclusions

A number of new phosphinothiolate complexes of Fe(II), Fe(III), Co(II) and Co(III) have been prepared and fully characterised. The preferred synthetic route to complexes with PSH and PS₂H₂ ligands involves electrochemical oxidation of the metal in the presence of the ligand and direct reaction with metal halides gives impure products unless an additional phosphine ligand is present. Alternatively CO can act as the additional ligand to give Fe(II) carbonyl complexes, and for Co a Co(III) carbonyl was obtained. The dominant structural motif found is pseudo-octahedral geometry with various combinations of P and thiolate S donors making up the coordination sphere. Those ligands with bulky trimethylsilyl groups in the six-position form complexes directly analogous to those which are sterically unencumbered. In the case of tetradentate PS₃ ligands on Fe and Co in combination with dimethylphenylphosphine a facile equilibrium between five and six coordinate forms is observed although the bis(phosphine) adduct appears to be favoured in the solid state.

5. Supplementary material

Supporting information available: tables in CIF format providing atomic positional parameters, bond distances and angles, anisotropic thermal parameters and calculated hydrogen atoms positions for **2** and **4**.

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References

- [1] J.R. Dilworth, N. Wheatley, Coord. Chem. Rev. 199 (2000) 88.
- [2] (a) P.J. Blower, J.R. Dilworth, Coord. Chem. Rev. 76 (1987) 121;
 (b) J.R. Dilworth, J. Hu, Adv. Inorg. Chem. 40 (1994) 411.

- [3] J.D. Niemoth-Anderson, K.E. Clark, T.A. George, C.R. Ross, J. Am. Chem. Soc. 122 (2000) 3977.
- [4] J. Francoli, M. Miller, S.A. Koch, Inorg. Chem. 34 (1995) 1981.
- [5] P. Pérez-Lourido, J. Romero, J.A. García-Vázquez, A. Sousa, J. Zubieta, K. Maresca, Polyhedron 17 (1998) 4457.
- [6] J.H. Green, R. Kumar, N. Seudeal, D.G. Tuck, Inorg. Chem. 28 (1989) 123.
- [7] N. De Vries, A. Davison, A.G. Jones, Inorg. Chim. Acta 165 (1989) 9.
- [8] J.R. Dilworth, A.J. Huston, S. Morton, M. Harman, M.B. Hursthouse, J. Zubieta, C.M. Archer, J.D. Kelly, Polyhedron 11 (1992) 2151.
- [9] J.R. Dilworth, C. Lu, J.R. Miller and Y. Zheng, J. Chem. Soc., Dalton Trans. (1995) 1957.
- [10] P. Pérez-Lourido, J. Romero, J.A. García-Vázquez, A. Sousa, K. Maresca, J. Zubieta, Inorg. Chem. 38 (1999) 1293.

- [11] E. Block, G. Ofori-Okai, J. Zubieta, J. Am. Chem. Soc. 111 (1989) 2327.
- [12] G.M. Sheldrick, Programs for Crystal Structure Analysis (Release 97-2), Institüt für Anorganische Chemie der Universität, Göttingen, Germany, 1998.
- [13] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, Table 2.2A, vol. IV, The Kynoch Press, Birmingham, UK, 1974.
- [14] D.T. Cromer, International Tables for X-ray Crystallography, Table 2.3.1, vol. IV, The Kynoch Press, Birmingham, UK, 1974.
- [15] P. v.d. Sluis, A.L. Spek, Acta Crystallogr., Sect A 46 (1990) 194– 201.
- [16] G.M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1993.