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# Synthesis and spectroscopic characterisation of CpCoFe$_2$(CO)$_5$($\mu_3$-Se)$_2$($\mathrm{P}^\frown\mathrm{P}$) [$\mathrm{P}^\frown\mathrm{P}$ = dppm or dppe]: crystal structure of CpCoFe$_2$(CO)$_5$($\mu_3$-Se)$_2$(dppm)

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## Abstract

The room temperature reactions of CpCoFe$_2$(CO)$_6$($\mu_3$-Se)$_2$ (1) with bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane gave the phosphine derivatives of mixed-metal chalcogen clusters, CpCoFe$_2$(CO)$_5$($\mu_3$-Se)$_2$($\mathrm{P}^\frown\mathrm{P}$) [$\mathrm{P}^\frown\mathrm{P}$ = dppm (2), dppe (3)], respectively. Compounds 2 and 3 have been characterised by IR, and $^1$H, $^{13}$C, $^{31}$P and $^{77}$Se NMR spectroscopy and their compositions have been confirmed by elemental analysis. The structure of 2 has been elucidated by X-ray crystallography. Compound 2 crystallised in the monoclinic, space group $P2_1/n$, with $a = 20.705(5)$, $b = 11.603(4)$, $c = 32.528(9)$ Å, $\beta = 107.38(2)°$, $V = 7108(4)$ Å$^3$, $Z = 8$, $D_c = 1.716$ Mg m$^{-3}$ and $R = 0.053$ ($Rw = 0.057$). The structure consists of an Fe$_2$CoSe$_2$ metal core in which the dppm ligand bridges Co and one of the Fe atoms.

*Keywords:* Iron; Cobalt; Selenium; Phosphorous; Carbonyl; Cluster

## 1. Introduction

Bridging chalcogens play an important role in the synthesis and stabilisation of transition metal cluster compounds, including mixed-metal clusters [1–5]. Work on the use of S, Se and Te has shown that cluster syntheses and structures of products formed depend on which chalcogen is used [6]. The availability of mixed-chalcogenide transition metal carbonyl complexes, as starting materials for cluster growth reactions, has given additional variety to the types of cluster which can be obtained by using chalcogens as bridging ligands [7–9]. One class of compounds which are convenient as starting materials for the preparation of metal–chalcogenide clusters is Fe$_2$(CO)$_6$($\mu$-EE′), where E, E′ = S, Se or Te [7–12]. The simplest type of cluster growth products obtained from these are compounds of the form Fe$_2$M(CO)$_9$($\mu_3$-E)($\mu_3$-E′), where M = Fe, Ru, which are formed by a formal addition of M across the reactive E–E′ bond of Fe$_2$(CO)$_6$($\mu$-EE′), followed by one Fe–M bond formation to give a square-pyramidal core of Fe$_2$MEE′, where M occupies a basal site [7,8,13–16]. There are instances, however, where the heterometal atom occupies the apical site of the square pyramid [11,17–19]. The cluster CpRhFe$_2$(CO)$_6$($\mu_3$-Te)$_2$ exists in solution as an equilibrating mixture of the two forms, one in which the rhodium is in a basal site and the other in which it occupies the apical site of the RhFe$_2$Te$_2$ square pyramid [20]. Reactions of CpRhFe$_2$(CO)$_6$($\mu_3$-Te)$_2$ with PPh$_3$ yield two isomers: in the major isomer, the phosphine is bonded to an Rh atom while the minor isomer is proposed to contain the Fe(CO)$_3$(PPh$_3$) moiety (Fig. 1). In an earlier report, we described the synthesis and structures of CpCoFe$_2$(CO)$_6$($\mu_3$-Se)$_2$ (1) and CpCoFe$_2$(CO)$_6$($\mu_3$-S)($\mu_3$-Se), both of which have the Co atom occupying the apical site of the square-pyramidal core (type A) [9]. The second form, in which the Co occupies a basal site (type B), is not observed (Fig. 2). Here we describe the reactions of 1 with the bidentate phosphines bis(diphenylphosphino)methane

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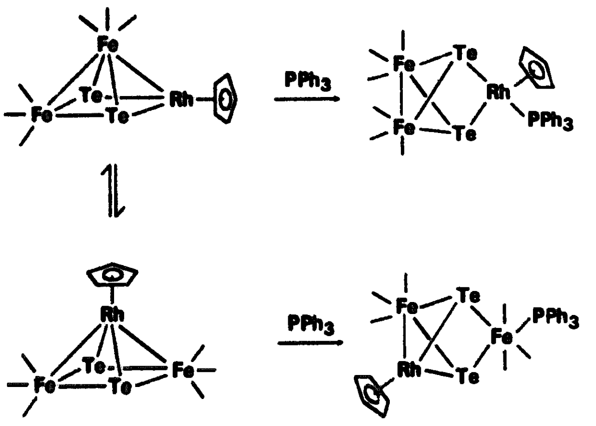


Fig. 1. Reactions of the two isomers of $CpRhFe_2(CO)_6(\mu_3\text{-}Te)_2$ with $PPh_3$.

and 1,2-bis(diphenylphosphino)ethane, along with the single crystal X-ray diffraction analysis of $CpCoFe_2(CO)_5(\mu_3\text{-}Se)_2(dppm)$ (**2**).

## 2. Results and discussion

When a $CH_2Cl_2$ solution containing **1** and bis(diphenylphosphino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe) was stirred at room temperature for 36h, dark red $CpCoFe_2(CO)_5(\mu_3\text{-}Se)_2(dppm)$ (**2**) or dark green $CpCoFe_2(CO)_5(\mu_3\text{-}Se)_2(dppe)$ (**3**) was obtained as the major product after chromatographic work-up (Scheme 1). Compounds **2** and **3** have been characterised by IR and $^1H$, $^{13}C$, $^{31}P$ and $^{77}Se$ NMR spectroscopy. Their elemental compositions have been confirmed by elemental analysis.

An ORTEP diagram of the molecular structure of **2** is shown in Fig. 3. The structure of **2** can be described as consisting of an $Fe_2CoSe_2$ metal core and a dppm group bridging Co and one of the Fe atoms. The Fe atom associated with the dppm group has two terminal carbonyl groups, while the other Fe atom has three terminal carbonyl groups. The average Se–Co bond distance in **2** (2.378 Å) is longer than the average Se–Co bond distances in **1** (2.288 Å) [9], $CpCoFe_2(CO)_6(\mu_3\text{-}S)(\mu_3\text{-}Se)$ (2.291 Å) [9] and $FeCo_2(CO)_9(\mu_3\text{-}Se)$ (2.283 Å) [21]. The average Se–Fe bond distance in **2** (2.411 Å) is longer than the average Se–Fe bond distances in **1** (2.363 Å), $CpCoFe_2(CO)_6(\mu_3\text{-}S)(\mu_3\text{-}Se)$ (2.323 Å), $Fe_3(CO)_9(\mu_3\text{-}Se)_2$ (2.35 Å) [22] and $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}Se)$ (2.351 Å) [23].

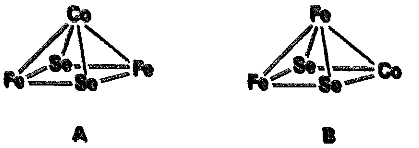
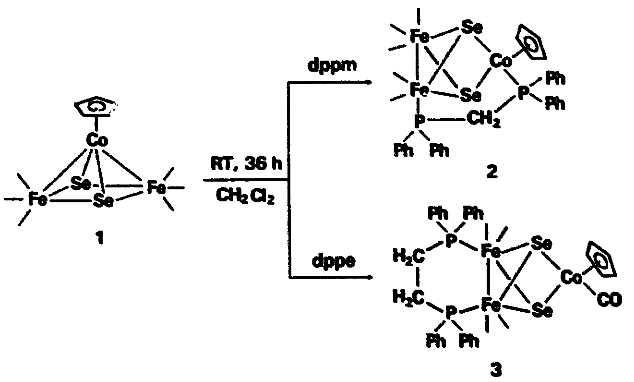


Fig. 2. Possible isomers of **1**.



Scheme 1. Formation of **2** and **3**.

It is shorter than the average Se–Fe bond distance of 2.437 Å reported for $Fe_3(CO)_9(\mu_3\text{-}Se)(\mu_3\text{-}Te)$ [23]. The average Co–Se–Fe bond angle in **2** (96°) is larger than the corresponding angle in the parent molecule **1** (66.7°), but the average bond angles Se–Co–Se (75.5°), Se–Fe–Se (74.3°) and Fe–Se–Fe (63.2°) in **2** are smaller than the corresponding angles in the parent compound **1** (85.5, 82.2 and 97.3° respectively), consistent with the dppm causing a contraction of the $Fe_2CoSe_2$ core, thereby reducing the bond angles in **2**.

The infrared spectra of **2** and **3** in the carbonyl region show four bands, each between 2052 and 1927 $cm^{-1}$, indicating the presence of terminally bonded carbonyl groups. The $\nu$(CO) stretching bands in **2** and **3** are shifted towards lower frequency values with respect to the parent compound **1**, consistent with the replacement of carbonyl groups by a stronger donor and weaker $\pi$-acceptor ligand. The $^1H$ NMR spectrum of **2** shows a doublet of doublet centred at $\delta$ 3.48 ppm ($J_{H-P}$ = 10.4 Hz) for the protons of the $CH_2$ group coupled to

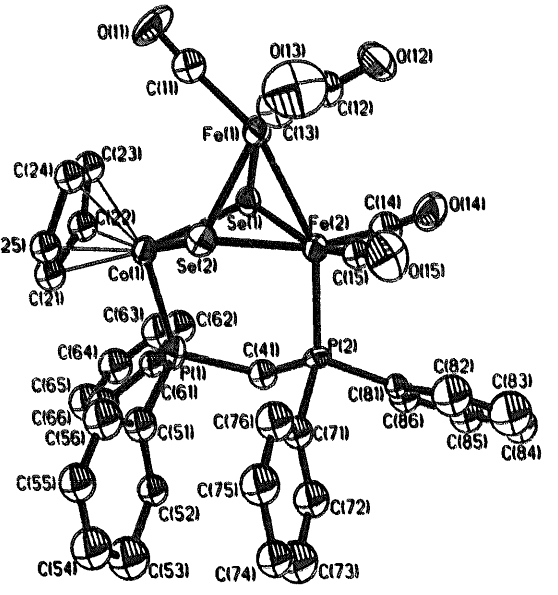


Fig. 3. Molecular structure of **2**.

two non-equivalent phosphorus atoms, and a single peak at $\delta$ 4.51 ppm for the Cp ligand. Multiplets in the range $\delta$ 7.13–7.55 ppm are observed for the phenyl groups.

The $^{13}$C NMR spectrum of **2** shows a signal at $\delta$ 29.8 ppm for the $CH_2$ group, a signal at $\delta$ 89.2 due to the $C_5H_5$ group, and a cluster of peaks at $\delta$ 128.2–132.6 ppm due to the phenyl groups. Two signals, at $\delta$ 210.8 and 211.8 ppm, are seen for the CO groups. The $^{31}$P NMR spectrum shows two signals at $\delta$ 60.1 and 60.5 ppm, indicating non-equivalence of the two phosphorus atoms. The $^{77}$Se NMR spectrum displays a single peak at $\delta$ $-667.6$ ppm, indicating the equivalent nature of the Se ligands.

The $^1$H NMR spectrum of **3** shows a doublet centred at $\delta$ 2.21 ppm ($J_{H-P} = 9$ Hz) for the $CH_2$ groups coupled with two equivalent phosphorus atoms, and a single peak at $\delta$ 5.81 ppm for the Cp ligand. Multiplets in the range $\delta$ 7.38–7.54 ppm are observed for the phenyl groups. The $^{13}$C NMR spectrum of **3** shows a signal at $\delta$ 30.5 ppm for the $CH_2$ groups, a signal at $\delta$ 81.2 ppm due to the $C_5H_5$ group and a cluster of peaks at $\delta$ 128.5–132.1 ppm due to the phenyl groups. A signal at $\delta$ 211.5 ppm is seen for the CO groups. The $^{31}$P NMR spectrum shows a signal at $\delta$ 68.2 ppm, indicating the identical environment of the two phosphorus atoms. The $^{77}$Se NMR spectrum displays a single peak at $\delta$ 637.3 ppm, indicating the equivalent nature of the Se ligands.

In contrast to the reaction of $CpRhFe_2(CO)_6(\mu_3\text{-}Te)_2$ with $PPh_3$, which yields two separable isomers, the reaction of **1** with $PPh_3$ was found to form a large number of products which could not be separated chromatographically to facilitate their characterisation. With the bidentate phosphines, dppm and dppe, the reaction proceeded cleanly and a reasonable yield of product could be obtained in each case. By analogy with the reaction of the two isomers of $CpRhFe_2(CO)_6(\mu_3\text{-}Te)_2$ with $PPh_3$, the product expected from our reaction of **1** was one in which one Fe–Co bond would be retained. Formation of the product **2** is therefore somewhat unusual.

## 3. Experimental details

### 3.1. General procedures

Reactions and manipulations were carried out under an inert atmosphere of argon by means of standard Schlenk techniques. The solvents were dried over appropriate drying agents, and distilled under a nitrogen or argon atmosphere prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer in NaCl cells of 0.1 mm pathlength as $CH_2Cl_2$ solutions. $^1$H, $^{13}$C, $^{31}$P and $^{77}$Se NMR spectra were obtained on a Varian VXR-300S spectrometer in $CDCl_3$ solution using appropriate references at 25 °C. The $^{77}$Se NMR spectra were referenced to $Me_2Se$ as an external standard ($\delta$ 0 ppm) and the spectra were obtained at the operating frequency of 57.23 MHz; 90° pulses were used with 1.0 s delay and 1.0 s acquisition time. Elemental analyses were performed on a Carlo Erba automatic analyser. $CpCoFe_2(CO)_6(\mu_3\text{-}Se)_2$ (**1**) was prepared as reported earlier [9]. Bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane (Strem) were used as received.

### 3.2. Reaction of 1 with dppm and dppe

To a $CH_2Cl_2$ solution (25 ml) of **1** (0.05 g, 0.089 mmol) was added an equimolar amount of dppm

Table 1
Summary of crystallographic data for compound **2**

| | |
|---|---|
| *Crystal data* | |
| Molecular formula | $C_{35}H_{27}O_5P_2Fe_2CoSe_2$ |
| Molecular weight | 918.1 |
| Crystal colour and habit | Dark red, prismatic |
| Crystal size ($mm^3$) | 0.15×0.20×0.10 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| *Unit cell parameters* | |
| $a$ (Å) | 20.705(5) |
| $b$ (Å) | 11.603(4) |
| $c$ (Å) | 32.528(9) |
| $\beta$ (°) | 107.38(2) |
| $V$ (Å$^3$) | 7108(4) |
| $Z$ | 8 |
| $D_{calc}$ ($Mg\,m^{-3}$) | 1.716 |
| Absorption coefficient ($mm^{-1}$) | 3.445 |
| *Data collection* | |
| Diffractometer used | Siemens R3m/V |
| Radiation used | Mo K$\alpha$ |
| Temperature (K) | 220 |
| $2\theta$ range (°) | 3.5–44.0 |
| Scan type | $\omega$ |
| Scan width (°) | 1.20° + K$\alpha$ separation |
| Standard reflections | three measured every 300 reflections |
| Reflections collected | 6863 |
| Observed reflections $F > 6.0\sigma(F)$ | 2200 |
| Absorption correction | Semi-empirical |
| Max./min. transmission | 0.985/0.734 |
| *Refinement* | |
| System used | Siemens SHELXTL-PLUS (PC version) |
| Solution | Heavy-atom methods |
| Refinement method | Full-matrix least-squares |
| Weighting scheme | $w = [\sigma^2(F_o + 0.001(F_o)^2]^{-1}$ |
| No. of parameters refined | 497 |
| Final $R$ | 0.053 |
| Weighted $R$ | 0.057 |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 0.51 |
| $\Delta\rho_{min}$ (e Å$^{-3}$) | $-0.50$ |
| GOF | 1.10 |

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for 2

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Se(1) | 7825(1) | 121(3) | 664(1) | 36(1) |
| Se(2) | 7533(2) | 245(3) | 1484(1) | 42(1) |
| Se(3) | 7167(2) | 1556(3) | −573(1) | 41(1) |
| Se(4) | 7564(2) | 3004(3) | −1213(1) | 40(1) |
| Co(1) | 6754(2) | −66(4) | 794(1) | 38(2) |
| Co(2) | 8251(2) | 1703(4) | −684(1) | 40(2) |
| Fe(1) | 8244(2) | 1599(4) | 1233(1) | 41(2) |
| Fe(2) | 8513(2) | −623(4) | 1354(1) | 36(2) |
| Fe(3) | 6904(2) | 3669(4) | −752(1) | 46(2) |
| Fe(4) | 6501(2) | 1998(4) | −1303(1) | 36(2) |
| P(1) | 6739(4) | −2060(8) | 775(2) | 36(4) |
| P(2) | 8238(4) | −2542(7) | 1325(2) | 34(4) |
| P(3) | 8132(4) | 72(8) | −1082(2) | 34(3) |
| P(4) | 6627(4) | 398(8) | −1668(2) | 41(4) |
| C(11) | 7734(16) | 2931(33) | 995(10) | 51(11) |
| C(12) | 8965(17) | 1858(30) | 1100(9) | 56(10) |
| C(13) | 8609(17) | 2143(32) | 1759(11) | 67(12) |
| C(14) | 9184(16) | −860(30) | 1131(10) | 52(11) |
| C(15) | 8994(14) | −560(26) | 1897(9) | 36(9) |
| C(16) | 6161(17) | 3653(31) | −583(10) | 60(11) |
| C(17) | 6637(18) | 4965(40) | −1114(12) | 83(13) |
| C(18) | 7447(18) | 4448(33) | −301(11) | 70(12) |
| C(19) | 6031(16) | 2955(29) | −1737(10) | 49(10) |
| C(20) | 5774(15) | 1480(27) | −1162(9) | 34(9) |
| O(11) | 7455(11) | 3720(21) | 815(7) | 87(12) |
| O(12) | 9503(11) | 2003(20) | 1021(7) | 83(12) |
| O(13) | 8887(14) | 2493(23) | 2098(7) | 122(15) |
| O(14) | 9630(11) | −920(20) | 988(7) | 84(12) |
| O(15) | 9320(10) | −482(20) | 2259(6) | 79(11) |
| O(16) | 5698(12) | 3587(23) | −476(9) | 127(16) |
| O(17) | 6528(20) | 5760(25) | −1320(9) | 197(25) |
| O(18) | 7742(14) | 4962(24) | −4(8) | 124(15) |
| O(19) | 5707(10) | 3488(22) | −2011(7) | 92(12) |
| O(20) | 5353(11) | 1078(23) | −1053(7) | 95(13) |
| C(21) | 5684(14) | −100(27) | 531(8) | 51(9) |
| C(22) | 6017(13) | 397(27) | 236(8) | 45(9) |
| C(23) | 6325(13) | 1501(27) | 407(8) | 46(9) |
| C(24) | 6279(13) | 1647(27) | 824(8) | 47(9) |
| C(25) | 5885(13) | 622(26) | 901(9) | 48(9) |
| C(31) | 9294(14) | 1287(28) | −419(8) | 54(10) |
| C(33) | 8842(15) | 3161(33) | −343(9) | 71(11) |
| C(34) | 8687(14) | 2363(26) | −60(9) | 45(9) |
| C(35) | 8969(14) | 1215(28) | −77(9) | 56(10) |
| C(41) | 7533(12) | −2925(25) | 842(8) | 43(9) |
| C(42) | 7276(12) | −649(23) | −1343(8) | 38(8) |
| C(51) | 6352(14) | −2815(30) | 1131(9) | 53(10) |
| C(52) | 6273(13) | −4046(27) | 1112(9) | 44(9) |
| C(53) | 5979(15) | −4785(35) | 1387(10) | 84(12) |
| C(54) | 5821(16) | −4064(33) | 1696(10) | 77(12) |
| C(55) | 5897(15) | −2857(31) | 1742(9) | 61(10) |
| C(56) | 6166(15) | −2217(32) | 1452(10) | 73(11) |
| C(61) | 6274(14) | −2564(24) | 225(8) | 34(8) |
| C(62) | 6543(15) | −2292(26) | −102(9) | 56(10) |
| C(63) | 6163(17) | −2579(29) | −519(10) | 79(12) |
| C(64) | 5551(17) | −3035(29) | −615(10) | 72(11) |
| C(65) | 5279(17) | −3304(29) | −298(10) | 80(12) |
| C(66) | 5631(14) | −3084(26) | 133(9) | 56(10) |
| C(71) | 7975(14) | −3292(29) | 1756(9) | 45(9) |
| C(72) | 7935(14) | −4496(30) | 1763(9) | 60(10) |
| C(73) | 7748(14) | −5084(33) | 2087(10) | 76(11) |
| C(74) | 7667(14) | −4504(30) | 2417(9) | 52(9) |
| C(75) | 7725(15) | −3245(31) | 2423(10) | 64(10) |
| C(76) | 7905(14) | −2646(30) | 2101(9) | 62(11) |
| C(81) | 8909(13) | −3559(24) | 1291(8) | 27(8) |
| C(82) | 9467(17) | −3706(31) | 1644(10) | 79(12) |
| C(83) | 9973(18) | −4411(33) | 1620(11) | 95(13) |
| C(84) | 10000(15) | −5068(29) | 1259(10) | 66(10) |
| C(85) | 9451(15) | −4925(30) | 911(9) | 61(10) |
| C(86) | 8884(14) | −4178(26) | 912(9) | 49(9) |
| C(91) | 8518(12) | −1177(23) | −740(7) | 21(7) |
| C(92) | 9111(15) | −1793(29) | −756(9) | 64(10) |
| C(93) | 9404(16) | −2672(28) | −474(9) | 63(11) |
| C(94) | 9117(16) | −3080(31) | −171(9) | 71(11) |
| C(95) | 8538(17) | −2480(29) | −131(10) | 78(12) |
| C(96) | 8213(14) | −1639(27) | −438(8) | 49(9) |
| C(101) | 8529(12) | 91(27) | −1509(7) | 33(8) |
| C(102) | 8762(12) | 1196(25) | −1612(8) | 31(8) |
| C(103) | 9059(15) | 1282(30) | −1951(9) | 67(11) |
| C(104) | 9108(14) | 207(30) | −2167(9) | 57(10) |
| C(105) | 8848(16) | −855(32) | −2093(10) | 77(12) |
| C(106) | 8555(14) | −915(28) | −1758(9) | 53(10) |
| C(111) | 5847(14) | −572(29) | −1835(8) | 37(8) |
| C(112) | 5876(16) | −1703(32) | −1745(9) | 61(10) |
| C(113) | 5256(19) | −2483(35) | −1879(10) | 92(13) |
| C(114) | 4693(18) | −1922(35) | −2091(10) | 81(12) |
| C(115) | 4678(20) | −701(37) | −2199(11) | 101(14) |
| C(116) | 5282(18) | −31(35) | −2061(10) | 82(12) |
| C(121) | 6839(13) | 531(27) | −2191(8) | 32(8) |
| C(122) | 7136(13) | 1524(28) | −2285(8) | 47(9) |
| C(123) | 7359(15) | 1552(30) | −2666(9) | 64(10) |
| C(124) | 7219(14) | 574(30) | −2935(9) | 60(10) |
| C(125) | 6913(14) | −399(29) | −2831(9) | 56(10) |
| C(126) | 6706(14) | −491(30) | −2456(9) | 64(10) |

[*] Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

(0.034 g, 0.089 mmol for **2**) or dppe (0.035 g, 0.089 mmol for **3**) and the reaction mixtures were stirred at room temperature for 36 h. After removal of the solvent in vacuo the residue was subjected to chromatographic work-up on a silica gel column using hexane/dichloromethane (60:40, v/v) mixture as eluant to yield dark red **2** (0.035 g, 43%) and dark green **3** (0.03 g, 36%) respectively.

Compound **2**. IR ($\nu$(CO), cm$^{-1}$): 2054 (w), 2019 (vs), 1959 (s), 1927 (w). M.p. 220–221 °C. Anal. Found: C, 46.3; H, 3.25. $C_{35}H_{27}O_5P_2Fe_2CoSe_2$ Calc.: C, 45.8; H, 2.96%.

Compound **3**. IR ($\nu$(CO), cm$^{-1}$): 2054 (w), 2019 (vs), 1959 (s), 1927 (w). M.p. 231–232 °C. Anal. Found: C, 46.7; H, 3.48. $C_{35}H_{27}O_5P_2Fe_2CoSe_2$ Calc.: C, 46.4; H, 3.14%.

### *3.3. X-ray diffraction study of compound 2*

Dark red crystals of **2** were grown from a $CH_2Cl_2$/hexane solution mixture by slow evaporation of solvent at −5 °C. The data were collected on a Siemens R3m/V diffractometer under a low-tempera-

Table 3
List of selected bond lengths (Å) [a] for 2

| | | | |
|---|---|---|---|
| Se(1)–Co(1) | 2.387(5) | Fe(1)–C(13) | 1.759(33) |
| Se(2)–Co(1) | 2.366(4) | Fe(2)–C(14) | 1.766(38) |
| Se(1)–Fe(1) | 2.427(5) | Fe(2)–C(15) | 1.752(25) |
| Se(1)–Fe(2) | 2.414(5) | Co(1)–C(21) | 2.124(26) |
| Se(2)–Fe(1) | 2.408(6) | Co(1)–C(22) | 2.056(23) |
| Se(2)–Fe(2) | 2.396(6) | Co(1)–C(23) | 2.170(28) |
| Fe(1)–Fe(2) | 2.526(6) | Co(1)–C(24) | 2.152(30) |
| Co(1)–P(1) | 2.206(9) | Co(1)–C(25) | 2.077(30) |
| Fe(2)–P(2) | 2.194(9) | P(1)–C(51) | 1.800(35) |
| P(1)–C(41) | 1.858(27) | P(1)–C(61) | 1.847(24) |
| P(2)–C(41) | 1.847(22) | P(2)–C(71) | 1.845(33) |
| Fe(1)–C(11) | 1.843(34) | P(2)–C(81) | 1.816(28) |
| Fe(1)–C(12) | 1.698(38) | | |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

ture nitrogen stream. Final unit cell parameters, given in Table 1, were obtained by a least-squares fit of the angles of 24 accurately centred reflections ($18° \leq 2\theta \leq 29°$). Relevant data collection conditions are listed in Table 1. Three standard reflections monitored every 150 reflections did not show any significant change in intensity during the data collection. The data were corrected for Lorentz and polarization effects. A semi-empirical absorption study was applied with max./min. transmission 0.985/0.734 respectively. The structure was solved by heavy-atom methods and subsequent difference Fourier syntheses using the SHELXTL-PLUS package [24]. Two discrete molecules were found in an independent unit. Scattering factors, as well as anomalous dispersion corrections for P, Fe, Co and Se atoms, were taken from the *International Tables for X-ray Crystallography* [25]. Full-matrix refinements were performed. Atoms of O, P, Fe, Co and Se were refined anisotropically, while C atoms were treated isotropically. Hydrogen atoms were placed at geometrically idealized positions. The weighting had the form $w[\sigma^2(F_o)+0.001(F_o)^2]^{-1}$. Final cycles of refinement converged at $R = \Sigma||F_o|-|F_c||/\Sigma|F_o = 0.053$, $wR = [\Sigma w(|F_o| - |F_c|^2)/\Sigma w(F_o)^2]^{1/2} = 0.057$, GOF = 1.10 for 2200 observed reflections [$F > 6.0\sigma(F)$]. The maximum and minimum residuals found on the final difference Fourier map were 0.51 and $-0.50\,e\,Å^{-3}$ respectively. The atomic coordinates and equivalent isotropic displacement coefficients are listed in Table 2, whilst bond distances and angles are shown in Tables 3 and 4 respectively. General displacement parameters, bond distances and angles and structure factor tables are available from the authors.

Table 4
List of selected bond angles (°) [a] for 2

| | | | |
|---|---|---|---|
| Co(1)–Se(1)–Fe(1) | 93.6(2) | Se(2)–Fe(2)–C(15) | 93.5(11) |
| Co(1)–Se(1)–Fe(2) | 97.3(2) | Fe(1)–Fe(2)–C(14) | 104.2(11) |
| Co(1)–Se(2)–Fe(1) | 94.6(2) | Fe(1)–Fe(2)–C(15) | 98.7(10) |
| Co(1)–Se(2)–Fe(2) | 98.4(2) | Se(1)–Co(1)–C(21) | 147.5(8) |
| Fe(1)–Se(1)–Fe(2) | 62.9(2) | Se(1)–Co(1)–C(22) | 107.8(8) |
| Fe(1)–Se(2)–Fe(2) | 63.4(2) | Se(1)–Co(1)–C(23) | 94.0(8) |
| Se(1)–Fe(1)–Se(2) | 74.0(2) | Se(1)–Co(1)–C(24) | 113.2(8) |
| Se(1)–Fe(2)–Se(2) | 74.5(2) | Se(1)–Co(1)–C(25) | 153.5(8) |
| Se(1)–Fe(1)–Fe(2) | 58.3(1) | Se(2)–Co(1)–C(21) | 135.8(8) |
| Se(2)–Fe(1)–Fe(2) | 58.0(2) | Se(2)–Co(1)–C(22) | 156.5(8) |
| Se(1)–Fe(2)–Fe(1) | 58.8(1) | Se(2)–Co(1)–C(23) | 118.6(7) |
| Se(2)–Fe(2)–Fe(1) | 58.5(2) | Se(2)–Co(1)–C(24) | 91.1(6) |
| Se(1)–Co(1)–Se(2) | 75.5(1) | Se(2)–Co(1)–C(25) | 99.5(7) |
| Se(1)–Co(1)–P(1) | 95.0(3) | P(1)–Co(1)–C(21) | 88.1(9) |
| Se(2)–Co(1)–P(1) | 99.9(2) | P(1)–Co(1)–C(22) | 102.9(8) |
| Se(1)–Fe(2)–P(2) | 102.6(2) | P(1)–Co(1)–C(23) | 141.5(7) |
| Se(2)–Fe(2)–P(2) | 99.9(3) | P(1)–Co(1)–C(24) | 151.5(8) |
| Fe(1)–Fe(2)–P(2) | 153.3(3) | P(1)–Co(1)–C(25) | 111.4(9) |
| Co(1)–P(1)–C(41) | 120.5(9) | P(2)–Fe(2)–C(14) | 93.8(11) |
| Fe(2)–P(2)–C(41) | 112.8(9) | P(2)–Fe(2)–C(15) | 98.2(10) |
| P(1)–C(41)–P(2) | 115.3(15) | Co(1)–P(1)–C(51) | 116.9(12) |
| Se(1)–Fe(1)–C(11) | 100.9(10) | Co(1)–P(1)–C(61) | 109.2(9) |
| Se(1)–Fe(1)–C(12) | 93.5(10) | Fe(2)–P(2)–C(71) | 122.4(11) |
| Se(1)–Fe(1)–C(13) | 157.6(12) | Fe(2)–P(2)–C(81) | 114.0(9) |
| Se(2)–Fe(1)–C(11) | 107.9(12) | C(41)–P(1)–C(51) | 103.5(13) |
| Se(2)–Fe(1)–C(12) | 149.8(11) | C(41)–P(1)–C(61) | 98.3(12) |
| Se(2)–Fe(1)–C(13) | 90.6(13) | C(41)–P(2)–C(71) | 101.9(12) |
| Se(1)–Fe(2)–C(14) | 89.3(9) | C(41)–P(2)–C(81) | 103.3(12) |
| Se(1)–Fe(2)–C(15) | 157.5(10) | C(51)–P(1)–C(61) | 106.2(13) |
| Se(2)–Fe(2)–C(14) | 160.7(10) | C(71)–P(2)–C(81) | 100.0(13) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

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