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Synthesis, crystal structure and protonation of the asymmetric iron-only hydrogenase model $[Fe_2(CO)_3(\mu\text{-pdt})\{\mu,\eta^2\text{-}Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}]$ (pdt = $SCH_2CH_2CH_2S$)

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Abstract

Heating $[Fe_2(CO)_6(\mu\text{-pdt})]$ (pdt = $SCH_2CH_2CH_2S$) and bis(2-diphenylphosphinoethyl) phenylphosphine (triphos) in toluene gives $[Fe_2(CO)_3(\mu\text{-pdt})\{\mu,\eta^2\text{-}Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}]$, the major form of which has been characterised crystallographically. The complex is highly asymmetric; while one iron centre has the expected square-based pyramidal coordination environment, the second is nearer a trigonal bipyramid. In solution at room temperature, four isomers of the major form interconvert *via* two processes which can be frozen out at low temperature, while protonation affords a bridging hydride complex which appears to be static at all temperatures.

Keywords: Iron-only hydrogenase; Dithiolate; Diiron; Triphos; Fluxionality; Hydride

There has been a recent resurgence in interest in the chemistry of dithiolate-bridged diiron complexes, $[Fe_2(CO)_6(\mu\text{-}SR)_2]$, due to the realisation that they closely resemble the two-iron unit of the H-cluster active site of iron-only hydrogenases [1–5]. In the enzyme a three atom unit bridges the two sulphur atoms and widely studied model complexes have been based on complexes of the type $[Fe_2(CO)_6(\mu\text{-}SCH_2XCH_2S)]$ (X = O, NH, CH_2) [6–10]. Despite significant advances in our understanding of this system gleaned from the study of these model complexes, a number of major limitations still need to be addressed as identified in a recent theoretical study of the system by Tye et al. [11]. Notably, a key role of the two-iron unit of the H-active cluster is to promote the reduction of protons to dihydrogen, which almost certainly involves proton binding to the diiron unit. This probably occurs at a single iron atom although to date no model complex has been able to replicate this. Hexacarbonyl, $[Fe_2(CO)_6(\mu\text{-pdt})]$ (pdt = $SCH_2CH_2CH_2S$), is not basic enough to bind a proton but this shortcoming can be overcome by substituting two carbonyls for more basic phosphine or cyanide ligands [12–20]. In almost all cases, however, substitution occurs in a symmetrical fashion, with each iron atom bearing a single phosphine or cyanide ligand. From their recent theoretical work, Hall and co-workers, came to the conclusion that "asymmetric substitution of strong donor ligands is the most viable method of making better synthetic diiron complexes that will serve as both structural and functional models" of the active site of iron-only hydrogenase [11]. To date the only reported phosphine complex that fulfils this criteria is $[Fe_2(CO)_4(\mu\text{-pdt})(\eta^2\text{-dppm})]$ (dppm = $Ph_2PCH_2PPh_2$), prepared by ourselves as a minor component of the thermal reaction of dppm with $[Fe_2(CO)_6(\mu\text{-pdt})]$ [21]. A second major limitation of all current iron-only hydrogenase models is the *unrotated* nature of the two square-planar iron centres. Thus, in models the two $Fe(CO)_2L$ units roughly eclipse one another (*unrotated*) while in contrast in the enzyme they are staggered with

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one of the carbonyls residing in the area between the two iron centres (*rotated*) [11].

Our efforts in the area of modelling the active site of the iron-only hydrogenenase enzyme have been focused on coordinating bidentate ligands [21,22] in an attempt to perturb both the steric and electronic nature of the diiron core. As an extension to this work we identified tridentate phosphines as potentially useful ligands since they would provide a more basic iron centre, being capable of strongly binding a proton, while also leading to an asymmetric diiron environment. This could possibly lead to significant structural perturbations perhaps leading to the formation of a *rotated* model, while also providing electronic asymmetry whereby one of the iron atoms is significantly more basic, potentially leading to the formation of a terminal hydride. We present here our first efforts in this area utilising the well-known triphosphine ligand, bis(2-diphenylphosphinoethyl) phenylphosphine (triphos).

Heating a toluene solution of $[Fe_2(CO)_6(\mu\text{-pdt})]$ [23] and triphos in toluene for 16 h results in the clean formation of a single product identified as $[Fe_2(CO)_3(\mu\text{-pdt})\{\mu,\eta^2\text{-}Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}]$ (**1**) [24]. The molecular structure [25] of the major component **1a** (Fig. 1) shows that the triphos ligand binds in a μ,η^2-fashion to the diiron unit, bridging the diiron centre [Fe(1)–Fe(2) 2.5279(5) Å] and chelating to one of the iron atoms, Fe(1). Here the two phosphorus atoms bind to one apical and one basal site, while the across the iron–iron vector a *transoid* basal–basal conformation is adopted. The latter is analogous to that found in $[Fe_2(CO)_4(\mu\text{-pdt})(\mu\text{-dppm})]$, but the chelate unit differs from the basal–basal conformation in $[Fe_2(CO)_4(\mu\text{-pdt})(\eta^2\text{-dppm})]$ [21]. The three iron–phosphorus vectors vary only slightly [Fe(1)–P(2) 2.1953(7), Fe(1)–P(1) 2.2016(7), Fe(2)–P(3) 2.2109(7) Å], suggesting that there is not a great deal of strain in the binding mode adopted. Coordination of the triphos ligand renders the two sulfur atoms of the dithiolate-bridge inequivalent, thus completely breaking the symmetry of the system and generating a highly asymmetric diiron centre. Unfortunately, this does not perturb the relative geometry of the two iron atoms significantly which are still essentially in an *unrotated* form [11] (Fig. 2). However, while the coordination geometry around Fe(1) is in line with that of previously characterised complexes of this type, being best described as square-based pyramidal, the basal plane being defined by *trans* angles of 162.54(3)° and 157.61(3)° between S(1)–C(1) and S(2)–P(2) respectively, that around Fe(2) is significantly perturbed. Here the geometry is best described as trigonal bipyramidal with S(2) and P(3) occupying axial sites [S(2)–Fe(2)–P(3) 164.92(3)°] and S(1), C(2) and C(3) lying in the equatorial plane. Indeed, the sum of the angles at Fe(2) subtended by these three atoms totals 359.98°.

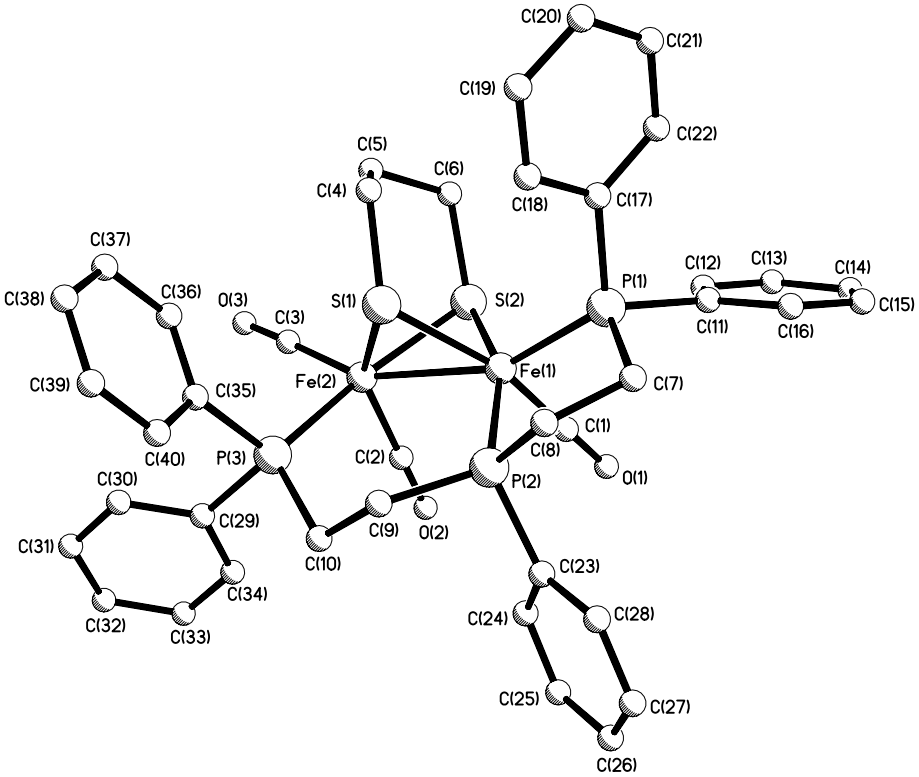


Fig. 1. Molecular structure of $[Fe_2(CO)_3(\mu\text{-pdt})\{\mu,\eta^2\text{-}Ph_2PCH_2\ CH_2P(Ph)CH_2CH_2PPh_2\}]$ (**1a**) with selected bond lengths (Å) and angle (°): Fe(1)–C(1) 1.750(3), Fe(1)–P(2) 2.1953(7), Fe(1)–P(1) 2.2016(7), Fe(1)–S(1) 2.2589(7), Fe(1)–S(2) 2.2644(7), Fe(1)–Fe(2) 2.5279(5), Fe(2)–C(3) 1.760(3), Fe(2)–C(2) 1.761(3), Fe(2)–P(3) 2.2109(7), Fe(2)–S(1) 2.2718(7), Fe(2)–S(2) 2.2918(7), P(1)–Fe(1)–Fe(2) 156.05(2), P(2)–Fe(1)–Fe(2) 101.66(2), P(3)–Fe(2)–S(2) 164.92(3), P(3)–Fe(2)–Fe(1) 109.52(2), C(1)–Fe(1)–Fe(2) 106.46(8), C(2)–Fe(2)–Fe(1) 88.00(8), C(3)–Fe(2)–Fe(1) 154.24(8), Fe(1)–S(1)–Fe(2) 67.83(2), Fe(1)–S(2)–Fe(2) 67.39(2), P(2)–Fe(1)–P(1) 88.37(3), S(1)–Fe(1)–C(1) 162.54(8), S(1)–Fe(2)–C(2) 140.62(8), S(2)–Fe(1)–P(2) 157.61(3).

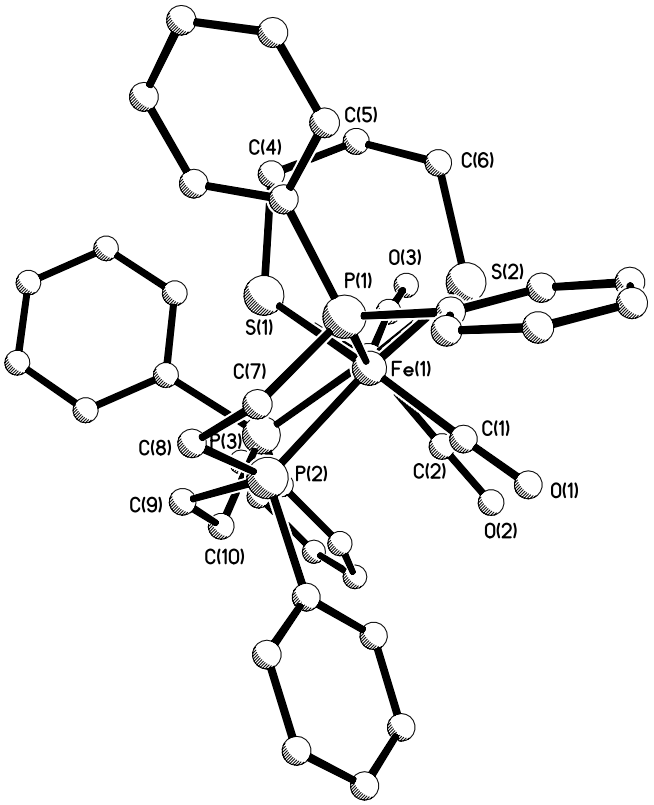


Fig. 2. Molecular structure of $[Fe_2(CO)_3(\mu\text{-pdt})\{\mu,\eta^2\text{-}\ Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}]$ (**1a**) looking along the iron–iron vector with selected atom labeling.

In solution the structure of **1** is more complex. At room temperature the ^{31}P NMR spectrum in CD_2Cl_2 shows two sets of three resonances in an approximate 3:1 ratio assigned to isomers **1a** and **1b**. The minor set, **1b**, are all sharp and consist of two doublets at 89.7 (*J* 17.2 Hz) and 61.6 ppm (*J* 9.2 Hz) and a doublet of doublets at 86.3 ppm. The major set, **1a**, which are observed at 83.3, 81.8 and 63.9 ppm are all broad at this temperature and individual coupling constants cannot be extracted. In each isomer, we assign the low-field resonances to the phosphorus bound to the iron dicarbonyl unit, the intermediate resonance to the central phosphorus atom of the triphos ligand and the high-field resonance to the chelate end of the triphosphine. Upon cooling resonances associated with **1b** do not vary significantly, however, those associated with **1a** broaden and collapse until at 183 K they are replaced by twelve new sharp resonances associated with four separate isomeric forms [24]. In recent work we have shown that $[Fe_2(CO)_4(\mu\text{-pdt})(\mu\text{-dppm})]$ undergoes two separate fluxional processes; a flipping of the central methylene group of the pdt ligand which renders the two iron atoms equivalent and a concerted trigonal twist of each $Fe(CO)_2L$ unit which equivalences the thiolate bridges [21]. We propose that similar processes occur in the major isomer of **1a**, which would lead to the formation of four interconverting isomers as shown (Fig. 3).

The nature of the minor component **1b**, which shows an essentially temperature independent ^{31}P NMR spectrum, is more contentious. We suggest a structure in which the two phosphorus atoms at Fe(1) bind in a basal–basal fashion. The temperature independent nature of the ^{31}P NMR spectrum of **1b** suggests that the fluxional processes proposed to occur in **1a** are either significantly faster or slower in this isomer. The reduced steric interactions between the phosphine and pdt ligand in this form could account for a lower activation barrier to the methylene flip process, while the trigonal twist at the $Fe(CO)_2L$ centre would be expected to have a higher activation barrier as this would lead to two PPh_2 end groups becoming co-planar. We have been unable to separate **1a** and **1b** and note that upon dissolution of crystals prepared for X-ray crystallography both isomers were present in approximately the same ratio as seen for the uncrystallised material.

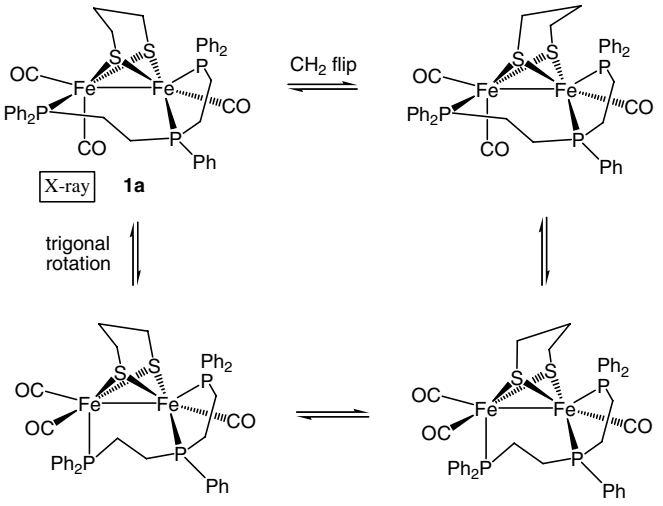
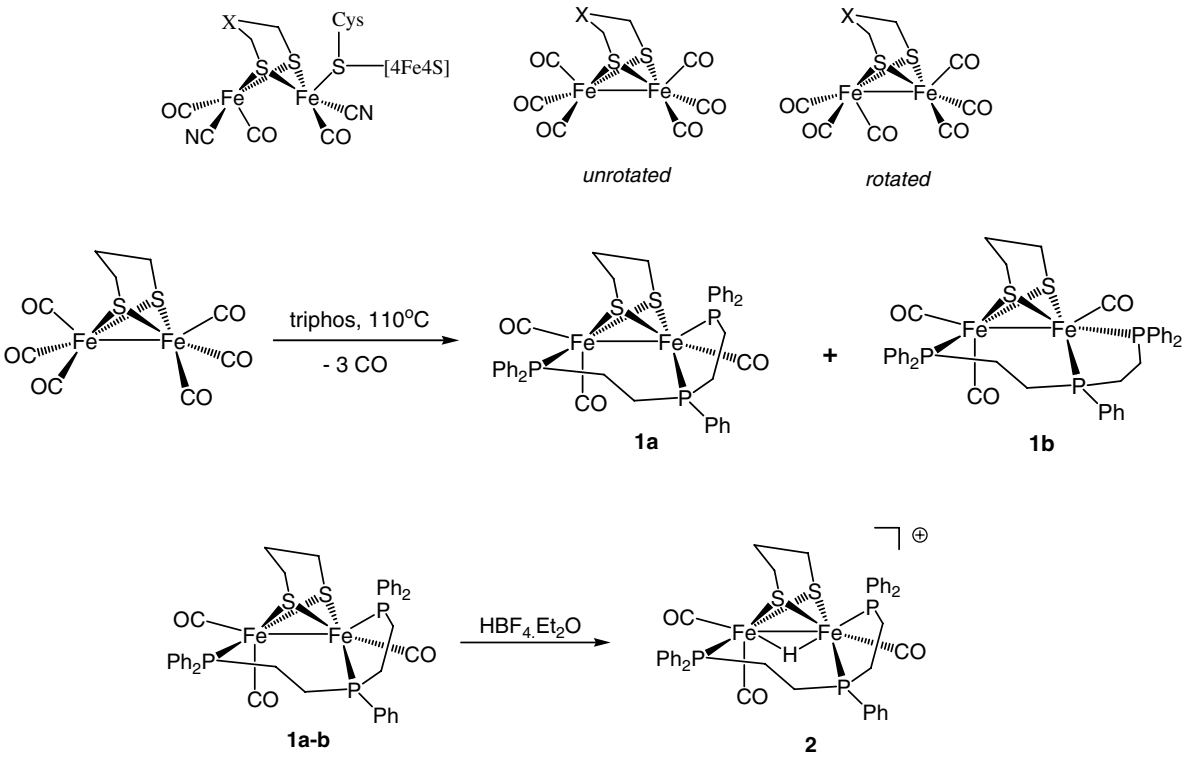


Fig. 3. Suggested structures for the interconverting forms of **1a.**

As eluded to in the introduction, a key feature of iron-only hydrogenase models is their ability to bind a proton, preferably in a terminal fashion at a single iron atom and we hoped that the asymmetry in **1** may allow the latter. Protonation of **1** by $HBF_4 \cdot Et_2O$ in dichloromethane is clean and rapid, being easily followed by IR spectroscopy. A red solution of **1** turned cloudy and pink upon addition of acid initial carbonyl absorptions at 1947s and 1889vs cm^{-1} being replaced by new peaks at 2039vs, 1986s and 1964s cm^{-1} assigned to **2** [26]; the average shift to higher wavenumbers of 88 cm^{-1} being consistent with protonation at the diiron centre. The salt produced was stable in air, no further change being noted even after sitting for 3 d. In the ^{31}P NMR spectrum of **2**, a single set of three resonances was observed at 88.9, 85.2 and 46.4 ppm suggesting that both **1a** and **1b** protonate to afford the same product, while upon cooling no significant changes were observed. In the ^{1}H NMR spectrum a doublet of triplets at δ-13.49 (*J* 29.2, 22.4 Hz) is assigned to the new hydride. Both the position of the resonance and the observation that it couples to all three phosphorus nuclei suggest that it bridges the diiron centre. The significant high-field shift (ca.



17.5 ppm) of the resonance associated with the chelate end of the triphosphine suggests that at least one end of the triphos ligand has been significantly perturbed, while in contrast the other two phosphorus atoms change only slightly. Unfortunately as yet we have been unable to grow crystals suitable for X-ray diffraction and thus the precise structural arrangement of the ligands in this species remains unclear.

In conclusion, the facile preparation of $[Fe_2(CO)_3(\mu\text{-pdt})\{\mu,\eta^2\text{-}Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\}]$ suggests that asymmetric diiron μ-pdt complexes are readily accessible and potentially serve as more realistic structural and functional models of the active site of iron-only hydrogenase. We are currently working towards the preparation of variants using asymmetric bi- and tridentate phosphine ligands with the aim of perturbing both the steric and electronic asymmetry of the diiron centre to an even greater extent with the aim of preparing a terminal hydride complex. These results will be reported in due course.

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Appendix A. Supplementary material

CCDC 614638 contains the supplementary crystallographic data for **1a**. These data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche. 2006.09.005.

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[24] IR ν(CO) (CH_2Cl_2): 1947s, 1889vs cm^{-1}; ^1H NMR (CD_2Cl_2, 298 K): δ 8.03–7.16 (m, 25H, Ph), 3.04–2.41 (m, 8H, PCH_2), 2.36 (br, 2H, SCH_2), 2.29 (br, 2H, SCH_2), 2.14 (br, 2H, CH_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 89.7 (*d*, *J* 17.2, **1b**), 86.3 (dd, *J* 17.2, 9.2, **1b**), 83.3 (br, **1a**), 81.8 (brd, *J* 23.4, **1a**), 63.9 (br, **1a**), 61.6 (*d*, *J* 9.2, **1b**); (183 K) δ 91.74 (*d*, *J* 29.1, $\mathbf{1a}^{I}$), 88.34 (*d*, *J* 28.1, $\mathbf{1a}^{II}$), 87.78 (*d*, *J* 16.3, **1b**), 86.11 (dd, *J* 16.3, 9.2, **1b**), 83.52 (dd, 27.7, 9.4, $\mathbf{1a}^{I}$), 80.70 (dd, m, $\mathbf{1a}^{II+III}$), 77.48 (*d*, *J* 25.0, $\mathbf{1a}^{III}$), 76.90 (dd, *J* 25.3, 6.5, $\mathbf{1a}^{IV}$), 74.42 (*d*, *J* 6.6, $\mathbf{1a}^{IV}$), 71.99 (*d*, *J* 6.0, $\mathbf{1a}^{III}$), 70.64 (*d*, *J* 25.0, $\mathbf{1a}^{IV}$), 64.88 (*d*, *J* 9.2, **1b**), 61.44 (*d*, *J* 9.8, $\mathbf{1a}^{II}$), 57.66 (*d*, *J* 9.8, $\mathbf{1a}^{I}$), ratio **1b**:$\mathbf{1a}^{I}$:$\mathbf{1a}^{II}$:$\mathbf{1a}^{III}$:$\mathbf{1a}^{IV}$ ca 1:1:0.7:0.3:0.5; Anal. calc. for $Fe_2P_3S_2O_3C_{40}H_{39}$: C, 57.42, H, 4.67; Found C, 57.54, H, 3.86.
[25] Crystallographic data for $\mathbf{1a} \cdot CH_2Cl_2$ – Single crystals were mounted on a glass fibre and all geometric and intensity data were taken from these samples using a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 150 ± 2 K. Data reduction was carried out with SAINT PLUS and absorption correction applied using the programme SADABS. Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were generally placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package. Orange block, dimensions $0.16 \times 0.15 \times 0.04$ mm, triclinic, space group $P\bar{1}$, $a = 9.4439(8)$ Å, $b = 9.6258(9)$ Å, $c = 22.437(2)$ Å, $\alpha = 99.783(1)°$, $\beta = 95.331(2)°$, $\gamma = 94.278(2)°$, $V = 1992.8(3)$ $Å^3$, $Z = 2$, $F(000)$ 948, $d_{calc} = 1.536$ g cm^{-3}, $\mu = 1.127$ mm^{-1}. 17384 reflections were collected, 9087 unique [R(int) = 0.0228] of which 7520 were observed [$I > 2.0\sigma(I)$]. At convergence, $R_1 = 0.0405$, $wR_2 = 0.0950$ [$I > 2.0\sigma(I)$] and $R_1 = 0.\ 0510$, $wR_2 = 0.0998$ (all data), for 478 parameters.
[26] IR ν(CO) (CH_2Cl_2): 2039vs, 1986s, 1964s cm^{-1}; ^1H NMR (CD_2Cl_2, 298 K): δ 8.01–7.22 (m, 25H, Ph), 3.07–2.53 (m, 8H, PCH_2), 2.31 (br, 4H, SCH_2), 2.01 (br, 2H, SCH_2), −13.49 (dt, J 29.2, 22.4, 1H, μ-H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 88.9 (s), 85.3 (s), 46.4 (s).