

INORGANIC CHEMISTRY | RESEARCH ARTICLE

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Varying the flexibility of the aromatic backbone in half sandwich rhodium(III) dithiolato complexes: A synthetic, spectroscopic and structural investigation

Phillip S. Nejman¹, Alexandra M.Z. Slawin¹, Petr Kilian¹ and J. Derek Woollins^{1*}

Abstract: A series of rhodium(III) half sandwich complexes of the type $[\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{S}-\text{R}-\text{S})]$; $\text{S}-\text{R}-\text{S}$ = naphthalene-1,8-dithiolate, acenaphthene-5,6-dithiolate, [1,1'-biphenyl]-2,2'-dithiolate and [2,2'-binaphthalene]-1,1'-dithiolate are reported. In the case of [2,2'-binaphthalene]-1,1'-dithiolate, this represents an infrequent example of a metal complex containing this ligand. All the complexes have been fully characterised using multinuclear NMR spectroscopy and single-crystal X-ray diffraction. The single-crystal X-ray structure of the starting material $[\text{Cp}^*\text{Rh}(\text{PMe}_3)_2\text{Br}]$ (**1**) is also reported for the first time.

Subjects: Chemistry; Chemical Spectroscopy; Inorganic Chemistry

Keywords: dithiolates; half sandwich; complexation; rhodium

1. Introduction

The coordination of S,S' -bidentate ligands remains an important area of chemistry. Complexes bearing this type of ligand have a number of industrial applications including vulcanisation (Bond & Martin, 1984; Burns & McAuliffe, 1979; Burns, McCullough, & McAuliffe, 1980; Eisenberg, 2007), lubricant additives (Phillips et al., 1995) and catalysis (Bond & Martin, 1984; Burns & McAuliffe, 1979; Burns et al., 1980; Eisenberg, 2007). In addition, S,S' -donors can support unusual magnetic properties (Tuna et al., 2012; Zhou, Wang, Wang, & Gao, 2011) and are important in biological systems (Woollins, 1996). As part of our interest in the properties of sulfur donor systems, we have investigated a series of dithiolate ligands bound to aromatic backbones of varying flexibility (Figure 1).

There has been little study on the coordination chemistry of these types of ligands compared to dithiolates such as benzene-1,2-dithiolate or ethane-1,2-dithiolate. One of the most notable exceptions to this was a series of publications by Teo and co-workers in the late 1970s and early 1980s (Teo, Bakirtzis, & Snyder-Robinson, 1983; Teo & Snyder-Robinson, 1978, 1979a, 1979b, 1981, 1984; Teo, Wudl, Hauser, & Kruger, 1977; Teo, Wudl, Marshall, & Kruger, 1977). They investigated the oxidative addition of the structurally related compounds tetrathionaphthalene (TTN), tetrachlorotetrathionaphthalene (TCTTN) and tetrathiotetracene (TTT) (Figure 2) to a variety of low-valent metal

ABOUT THE AUTHOR

J. Derek Woollins has a long-standing interest in the synthetic and structural chemistry of group 16 elements and their coordination compounds. Recent work has investigated peri substituted naphthalenes and related systems, and the work described here examines the coordination of some peri and related ligand systems.

PUBLIC INTEREST STATEMENT

S,S' -bidentate ligands remain an important area of chemistry. Complexes bearing this type of ligand have a number of industrial applications including vulcanisation, lubricant additives and catalysis. In addition, S,S' -donors can support unusual magnetic properties and are important in biological systems. This work describes the coordination of some simple bidentate S,S ligands to Iridium

Figure 1. Dithiolate ligands studied in this work (charges omitted for clarity).

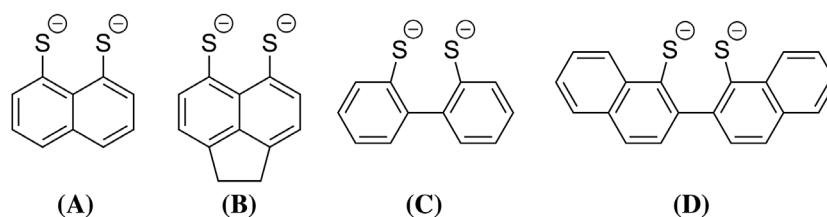
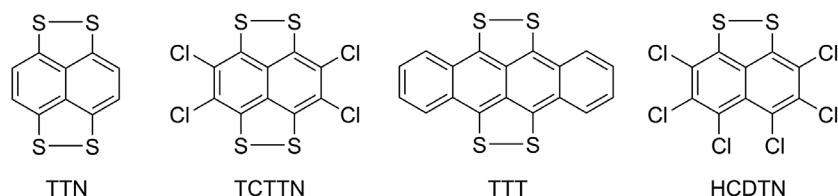


Figure 2. Structurally related aromatic sulfur donating ligands.

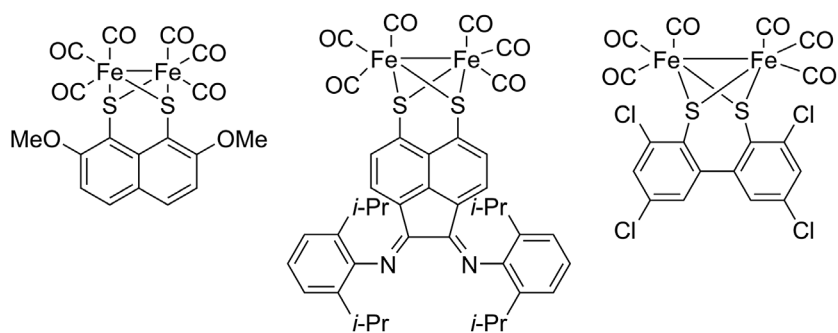


centres. With the work focusing on the extensive redox chemistry associated with these “non-innocent” ligands and their potential use as organic solid-state conductors (Teo & Snyder-Robinson, 1978, 1979a, 1979b, 1981, 1984; Teo, Wudl, Hauser, et al., 1977; Teo, Wudl, Marshall, 1977, Teo et al., 1983). Another interesting system bearing the related hexachlorodithionaphthalene (HCDTN) (Figure 2) resulted in an unusual trinuclear nickel complex $[\text{Ni}_3(\text{PPh}_3)_3(\text{S}_2\text{C}_{10}\text{Cl}_6)_3]$ with the HCDTN acting as a bridging ligand (Bosman & van der Linden, 1977).

Some of the most recent work involving derivatives of naphthalene-1,8-dithiolate (A) has been in designing [FeFe]-hydrogenase mimics for the production of hydrogen, by both electrochemical and photochemical processes (Figure 3) (Figliola, Male, Horswell, & Grainger, 2015; Figliola et al., 2014; Samuel, Co, Stern, & Wasielewski, 2010; Wright, Lim, & Tilley, 2009). Complexes involving [1,1'-biphenyl]-2,2'-dithiolate (C) bound to iron have also been investigated as electron transfer catalysts designed to mimic iron hydrogenases (Figure 3) (Albers et al., 2014; Ballmann, Dechert, Demeshko, & Meyer, 2009; Charreter et al., 2010). The coordination chemistry of the structurally related ligand acenaphthene-5,6-dithiolate (B) has received very little investigation out with our own research. (Topf, Monkowius, and Knör (2012) used the acenaphthene backbone as a linker between a 1,2-diimine unit and a dithiolate binding site. The iron carbonyl complex formed using this ligand showed potential as a multielectron transfer photosensitiser for artificial photosynthesis and as a bio-inspired photoredox catalyst (Figure 3).

Beyond the electron transfer mimics, there are few examples of complexes incorporating ligand C. Two molybdenum complexes have been reported with one containing an Mo oxygen triple bond (Conry & Tipton, 2001; McNaughton, Tipton, Rubie, Conry, & Kirk, 2000). In addition, two methods to synthesise titanocene-2,2'-dithiolatobiphenyl have been published (Aucott et al., 2005; Stafford, Rauchfuss, Verma, & Wilson, 1996). The 2,2'-binaphthalene-based ligand, D, has been largely

Figure 3. Iron-based catalysts based on A (left), B (centre) and C (right).



overlooked with regards to its complexation chemistry compared to the 1,1'-binaphthalene derivative. The only work reported involving this ligand thus far has been its preparation by Armarego (1960), the single-crystal X-ray structure (Kempe, Sieler, Hintzsche, & Schroth, 1993), one titanium complex (Aucott et al., 2005) and a platinum complex (Aucott, Kilian, Robertson, Slawin, & Woollins, 2006).

We have recently published two papers investigating the use of ligands **A–C** in the formation of half sandwich rhodium and iridium complexes (Nejman, Morton-Fernandez, Black, et al., 2015; Nejman, Morton-Fernandez, Moulding, et al., 2015). This paper describes the synthesis of a further four half sandwich rhodium (III) dithiolato complexes bearing a neutral phosphine donor. In this contribution, a different phosphine donor has been used compared to the previous work (trimethylphosphine instead of triethylphosphine) (Nejman, Morton-Fernandez, Black, et al., 2015). Additionally, a new ligand has been investigated [2,2'-binaphthalene]-1,1'-dithiolate (**D**). Two synthetic methods were employed due to the varying difficulty in preparing the ligand precursors. Both of these methods were different to the procedures used within our previous work (Nejman, Morton-Fernandez, Black, et al., 2015; Nejman, Morton-Fernandez, Moulding, et al., 2015). Furthermore, the single-crystal X-ray structure of the complex precursor, [Cp*Rh(PMe₃)Br₂] (**1**), is reported for the first time. All the complexes have been fully characterised, principally by multinuclear NMR spectroscopy, mass spectrometry and single-crystal X-ray diffraction.

2. Results and discussion

2.1. Synthetic methods

The dithiol pro-ligands [Naphth(SH)₂] (**H₂a**), [Acenap(SH)₂] (**H₂b**) and [Biphen(SH)₂] (**H₂c**) were prepared from their respective disulphides, naphtho[1,8-*cd*]-1,2-dithiole (Ashe, Kampf, & Savla, 1994), 5,6-dihydroacenaphtho[5,6-*cd*]-1,2-dithiole (Benson et al., 2013) and dibenzo[*c,e*]-1,2-dithiine (Cossu, Delogu, Fabbri, & Maglioli, 1991). The reduction of the disulphides was performed using NaBH₄ followed by an acidic work up which afforded the three pro-ligands (Figure 6) (Yui, Aso, Otsubo, & Ogura, 1988). The disulphide precursor to **D**, [2,2'-BinapS₂], was prepared according to the literature procedure by Armarego (1960). The reduction to the dithiol was not attempted as the amount of disulphide prepared was not sufficient. For this reason, the reduction to the reactive dithiolate was performed *in situ* using lithium triethylborohydride.

Figure 4. The section of the ¹H NMR spectrum of **2c** showing the four pseudo triplet of doublets with a splitting diagram showing how these signals are formed.

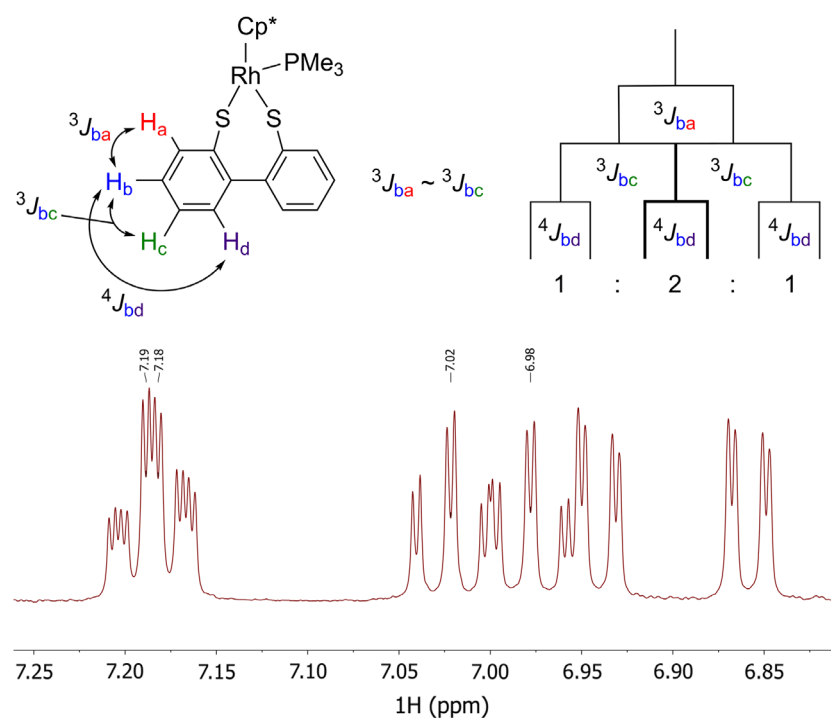


Figure 5. Crystal structures of 1 (Top), 2a (Middle left), 2b (Middle right), 2c (Bottom left) and 2d (Bottom right). Hydrogen atoms are omitted from all structures for clarity. Ellipsoids are plotted at the 50% probability level.

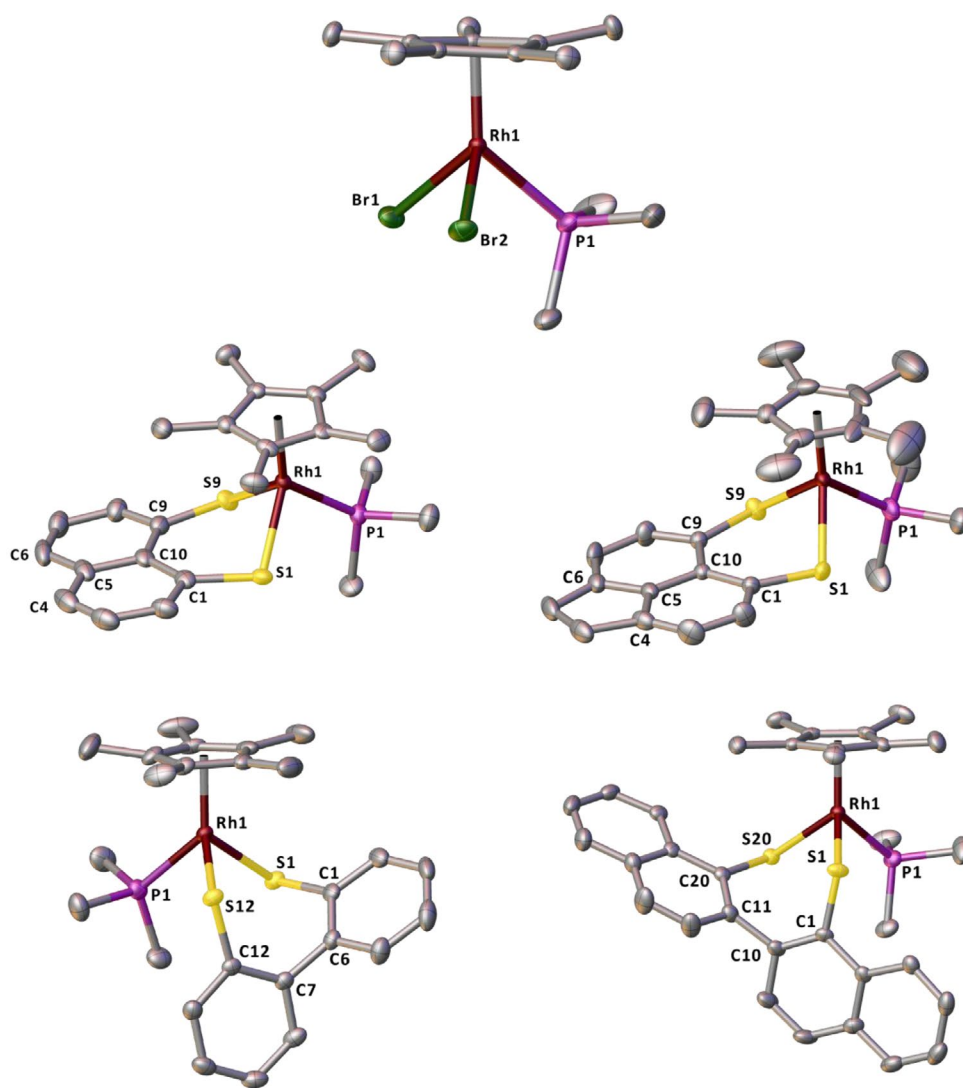


Figure 6. Synthesis of the proligands H²a-c.

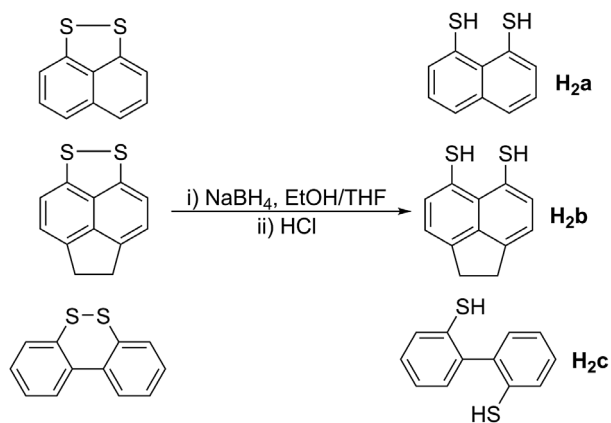
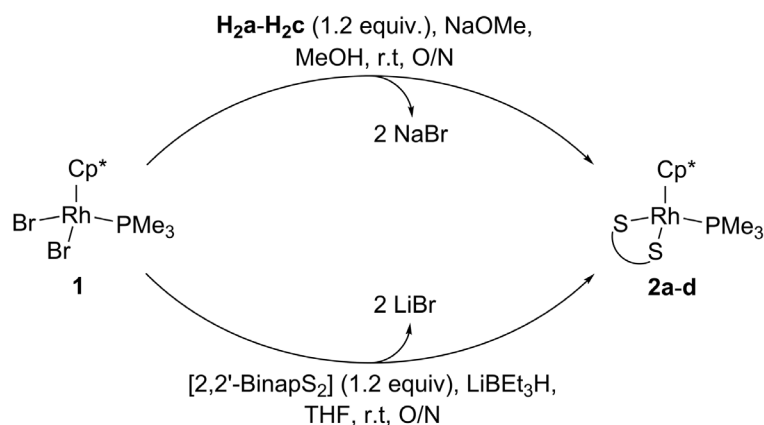


Figure 7. Reaction conditions for the preparation of **2a-d**.



The synthesis of $[\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{NaphthS}_2)]$ (**2a**), $[\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{AcenapS}_2)]$ (**2b**), $[\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{BiphenS}_2)]$ (**2c**) and $[\text{Cp}^*\text{Rh}(\text{PMe}_3)(2,2'\text{-BinapS}_2)]$ (**2d**) is shown in Figure 7. The metathesis of the bromide ligands with dithiolates **A-D** proceeds smoothly at room temperature. The presence of the phosphine group allowed the reaction progress to be monitored by ^{31}P NMR spectroscopy. In the case of **2a-c**, this meant the loss of the signal from **1**, whilst for **2d**, the product and **1** are soluble in THF so the conversion could be observed. Upon completion of the reaction for **2a-c** filtration of the precipitate followed by washing with methanol was sufficient to afford pure compound. For **2d**, purification by column chromatography was required (silica/ CH_2Cl_2). Excellent isolated yields of between 82 and 91% were obtained after purification. Compared to the similar complexes incorporating triethylphosphine, this represents an increase in the isolated yield of approximately 10% (Nejman, Morton-Fernandez, Black, et al., 2015). The synthesis of **2a-d** all proceeded via a reactive dithiolate intermediate, whereas the triethylphosphine derivatives were prepared by reacting $\text{H}_2\text{a-c}$ directly with the dichloro rhodium precursor. The dithiols represent a less reactive sulfur centre which could explain the higher yields obtained for the complexes reported here.

2.2. Data analysis

The ^1H NMR spectra (CDCl_3) for **2a** and **2b** show the expected signals, with splitting, from the aromatic backbones in the range of 7.88–6.91 ppm. In the case of **2c** and **2d**, we observe 8 and 10 signals, respectively, as the two joined aryl ring systems are inequivalent. This is due to the inability of the ligand backbones to rotate around the aryl–aryl bond. Four of the aromatic signals observed for **2c** appear as a *pseudo* triplet of doublets instead of the expected doublet of doublet of doublets. This is due to the $^3J_{\text{HH}}$ coupling constants observed between H_b and H_a as well as H_b and H_c (Figure 4) being almost identical. Two of these signals overlap closely (δ_{H} 7.19 and 7.18 ppm, Figure 4); however, both can be distinctly observed and the coupling constants easily extracted. These observations mirror those made for other similar rhodium complexes we have prepared incorporating ligands **A-C** (Nejman, Morton-Fernandez, Black, et al., 2015). For **2d**, this signal is not observed as the equivalent positions from each of the two naphthalene ring systems overlap resulting in multiplets. The $\eta^5\text{-Cp}^*$ methyl signals range from 1.58 to 1.42 ppm and are split into doublets by long range phosphorus coupling ($^4J_{\text{HP}} = 3.0\text{--}3.2$ Hz). The signals from the methyl groups attached to the phosphorus atom appear as a doublet of doublets for **2a-c**, with $^3J_{\text{HP}}$ coupling ($^3J_{\text{HP}} = 10.3\text{--}10.5$ Hz) and long range $^4J_{\text{HRh}}$ coupling ($^4J_{\text{HRh}} = 0.6\text{--}0.7$ Hz). Only a doublet is observed for this signal in **2d** with a similar $^3J_{\text{HP}}$ coupling to that seen in complexes **2a-c**.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (CDCl_3) for **1** and **2a-d** are shown in Table 1. Complexes **2a-d** all display an upfield shift in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra compared to the starting material **1** ($\Delta\delta = 0.7\text{--}3.3$ ppm). The coordination of the dithiolate ligand is also accompanied by a small increase in the $^1J_{\text{PRh}}$ coupling ($\Delta^1J_{\text{PRh}} = 11\text{--}15$ Hz) in **2a-d** when compared to **1**. Both of these observations match those made in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the triethylphosphine derivatives of **2a-c** (Nejman, Morton-Fernandez, Black, et al., 2015).

Table 1. $^{31}\text{P}\{^1\text{H}\}$ NMR data (CDCl_3) for **1** and **2a-d**. All δ values are in ppm and J values are in hertz

	1[†]	2a	2b	2c	2d
δ_p	3.6	1.7	2.9	0.3	2.2
$^1J_{\text{P-Rh}}$	137	150	148	153	152

[†]Values obtained from a sample run on a Bruker Avance II 400 NMR spectrometer (162 Hz).

Table 2. Selected bond lengths [\AA] and angles [$^\circ$] for **1**

	1
Rh1-P1	2.284(2)
Rh1-Br1	2.529(1)
Rh1-Br2	2.550(1)
P1-Rh1-Br1	87.14(3)
P1-Rh1-Br2	86.91(3)
Br1-Rh1-Br2	94.82(2)

As expected, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **2a-d** mirrors that of the ^1H NMR spectra, with distinct signals for all carbons in the biphenyl and binaphthyl examples. Interestingly, only one of the quaternary carbons bound to the sulfur atoms is split into a doublet ($^3J_{\text{Cp}} = 6.5$ Hz (**2c**) and 6.7 Hz (**2d**)) by the phosphorus atom in **2c** and **2d**. This provides further support of the difference between the two sides of the aryl-aryl bond. The mass spectra of **2a-d** each showed a peak corresponding to $[\text{M}-\text{PMe}_3 + \text{H}]^+$ ions at m/z 429, 455, 455 and 555, respectively. Homogeneity of the complexes **2a-d** was confirmed by means of accurate elemental analysis.

2.3. Single-crystal X-ray diffraction

Despite the previously reported synthesis and spectroscopic characterisation of precursor complex **1** (Jones & Feher, 1984), its single-crystal X-ray data have not been published. Therefore, for completeness we include it here. The crystal structures of **1** and **2a-d** are shown below in Figure 5 with selected structural parameters in Tables 2 and 3.

All of the complexes, **1** and **2a-d**, adopt the piano stool geometry around the rhodium centre we have seen previously (Nejman, Morton-Fernandez, Black, et al., 2015; Nejman, Morton-Fernandez, Moulding, et al., 2015). The $\eta^5\text{-Cp}^*$ ring in **1** is slightly tilted as the Rh-C bond lengths vary from 2.141(4) to 2.252(4) \AA . The Rh-Br bond lengths (2.550(1) and 2.529(1) \AA) and Rh-P bond length (2.284(2) \AA) are similar to those previously reported within the Cambridge Structural Database for compounds of a similar type (Rh-Br; 2.543 \AA , Rh-P; 2.288 \AA) (Bruno et al., 2002; Macrae et al., 2008; Thomas et al., 2010). The angles around the rhodium centre vary with the two P-Rh-Br angles being below the idealised 90° . This is accompanied by a widening of the Br-Rh-Br angle to $94.82(2)^\circ$ as the two larger atoms try and sit further apart.

The Rh-S bond lengths of **2a** and **2b** were almost identical (**2a**; 2.331(1) and 2.332(1) \AA , **2b**; 2.330(2) \AA), whilst in **2c** and **2d** there was more variation and they were slightly longer (**2c**; 2.3691(8) and 2.3705(8) \AA , **2d**; 2.3677(7) and 2.3994(8) \AA). These are comparable to other half sandwich complexes with Rh-S bonds reported by ourselves and Jin and co-workers ranging from 2.340 to 2.386 \AA (Nejman, Morton-Fernandez, Black, et al., 2015; Wang, Lin, Blacque, Berke, & Jin, 2008; Xiao & Jin, 2008; Yao, Xu, Huo, & Jin, 2013). The Rh-P bond lengths show no appreciable change compared to **1** with little variation across the series of **2a-d**.

All of the non-Cp* angles around the rhodium centre are reduced to less than 90° for **2a** and **2b**. This is a consequence of the rigid ligand backbone preventing the sulfur atoms from adopting a more ideal geometry. The effect is most obvious for the naphthalene system as the *peri* positions are restricted to a slightly shorter distance than those in the acenaphthene system. For both **2a** and **2b**,

Table 3. Selected bond lengths [Å], angles [°] and displacements [Å] for 2a-d

	2a	2b	2c	2d
Rh1-P1	2.284(1)	2.272(2)	2.2773(9)	2.2851(8)
Rh1-S1	2.331(1)	2.330(2)	2.3691(8)	2.3677(7)
Rh1-S9	2.332(1)	2.330(2)		
Rh1-S12			2.3705(8)	
Rh1-S20				2.3994(8)
P1-Rh1-S1	89.85(5)	87.02(3)	88.79(3)	96.29(3)
P1-Rh1-S9	84.87(5)	87.37(4)		
P1-Rh1-S12			91.27(3)	
P1-Rh1-S20				84.11(3)
S1-Rh1-S9	85.41(5)	87.78(3)		
S1-Rh1-S12			93.94(3)	
S1-Rh1-S20				95.00(3)
Splay angle ^a	19.2(5)	21.0(3)		
<i>Torsion angles</i>				
S1-C1...C9-S9	8.9(3)	5.2(2)		
C1-C10-C5-C6	177.5(6)	178.5(3)		
C9-C10-C5-C4	178.1(6)	177.3(3)		
C1-C6-C7-C12			68.0(4)	
C1-C10-C11-C20				79.0(4)
<i>Out of plane displacements</i>				
S1	0.213	0.117	0.184	0.189
S9	0.149	0.121		
S12			0.003	
S20				0.086

^aCalculated as [(S1-C1-C10)+(C1-C10-C9)+(C10-C9-S9)-360].

the splay angles are large and positive (**2a**; 19.2(5)°, **2b**; 21.0(3)°) as the rhodium centre forces the sulfur atoms apart. The S1-C1...C9-S9 torsion angle is larger in **2a** than **2b**, again as a consequence of the more limited movement of the sulfur atoms imposed by the backbone. The central C-C-C torsion angles are similar in both complexes showing limited buckling of the ring system. The out of plane displacement of the sulfur atoms is slightly greater in **2a** than **2b**.

In complexes **2c** and **2d** the non-Cp* angles show a broader range than in **2a** and **2b** ranging from 88.79(3)-93.94(3)° to 84.11(3)-96.29(3)°, respectively. The ability of the backbone to twist around the aryl-aryl bond allows the sulfur atoms to adopt a more idealised geometry. The torsion angle between the two aryl rings is larger in **2d** (79.0(4)°) than **2c** (68.0(4)°) most likely due to the added steric bulk of having a binaphthyl instead of biphenyl-based system. In both **2c** and **2d**, the out of plane displacement of the sulfur atoms are similar.

3. Conclusions

We have prepared and fully characterised a series of new rhodium(III) η^5 -e have prepared and fully characterised a series of new rhodium(III) η^3 Br₂ with a series of dithiolates attached to aromatic backbones. Similar features were seen in both the NMR spectra and single-crystal X-ray structures compared to previous rhodium complexes incorporating ligands **A-C** we have reported (Nejman, Morton-Fernandez, Black, et al., 2015; Nejman, Morton-Fernandez, Moulding, et al., 2015). The work herein clearly demonstrates the utility of these sulfur ligands in organometallic complexes, with complexes of this type having potential uses in the formation of multimetallic systems.

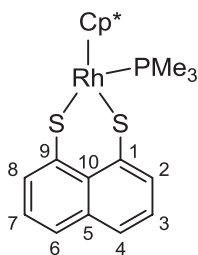
4. Experimental

4.1. General

Unless otherwise stated all manipulations were performed under an oxygen-free nitrogen atmosphere using standard Schlenk techniques and glassware. Solvents were collected from an MBraun Solvent Purification System or dried and stored according to common procedures (Armarego & Chai, 2009). $[\text{Cp}^*\text{Rh}(\text{PMe}_3)\text{Br}_2]$ was prepared following literature procedures (Ojima, Vu, & Bonafoux, 2002). The disulphide ligand precursors were made according to literature methods (Armarego, 1960; Ashe et al., 1994; Benson et al., 2013; Cossu et al., 1991). The pro-ligand H_2a was prepared following the literature procedure (Yui et al., 1988), with H_2c prepared following an identical procedure. H_2b was prepared according to literature (Nejman, Morton-Fernandez, Black, et al., 2015). ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{31}P and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained on either a Bruker Avance II 400 or Bruker Avance III 500 spectrometer. Full assignments of the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were made with the aid of H-H DQF COSY, H-C HSQC and H-C HMBC experiments. For ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra δ_{H} and δ_{C} are reported relative to TMS, residual solvent peaks (CDCl_3 ; δ_{H} 7.26, δ_{C} 77.2 ppm) were used for calibration. For ^{31}P and $^{31}\text{P}\{^1\text{H}\}$ spectra δ_{P} are reported relative to external 85% H_3PO_4 . All measurements were performed at 21°C with shifts reported in ppm. *p*-td has been used to denote a pseudo-triplet of doublet. IR spectra were collected on a Perkin Elmer 2000 NIR/Raman Fourier transform spectrometer with a dipole pumped NdYAG near-IR excitation laser. Mass spectra were acquired by the EPSRC UK National Mass Spectrometry Facility at Swansea University. Elemental analysis was performed by Stephen Boyer at the London Metropolitan University.

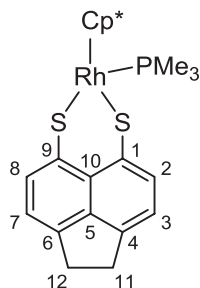
4.2. Dithiolato complexes

4.2.1. $[\text{Cp}^*\text{Rh}(\text{PMe}_3)(\text{NaphthS}_2)]$ (2a)



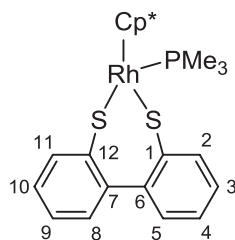
A methanol (20 mL) solution of $[\text{Cp}^*\text{Rh}(\text{PMe}_3)\text{Br}_2]$ (120 mg, 0.25 mmol), $[\text{Naphth}(\text{SH})_2]$ (60 mg, 0.31 mmol) and NaOMe (17 mg, 0.31 mmol) was stirred at room temperature overnight. The red precipitate was filtered, washed with MeOH then dried under vacuum for 3 h. The product was obtained as a red solid (110 mg, 0.21 mmol, 83%). Crystals suitable for X-ray work were obtained by slow evaporation from CH_2Cl_2 . **Anal. calcd.** for $\text{C}_{23}\text{H}_{30}\text{PRhS}_2$ (504.06 g mol⁻¹): C, 54.76; H, 5.99. Found: C, 54.69; H, 5.96. **^1H NMR (400 MHz, CDCl_3):** δ 7.88 (dd, $^3J_{\text{HH}} = 7.3$, $^4J_{\text{HH}} = 1.3$ Hz, 2 H, H2,8), 7.47 (dd, $^3J_{\text{HH}} = 8.1$, $^4J_{\text{HH}} = 1.1$ Hz, 2 H, H4,6), 7.05 (dd, $^3J_{\text{HH}} = 8.1$ & 7.3 Hz, 2 H, H3,7), 1.54 (dd, $^2J_{\text{Hp}} = 10.3$, $^3J_{\text{HRh}} = 0.7$ Hz, 9 H, PMe_3), 1.49 (d, $^4J_{\text{Hp}} = 3.0$ Hz, 15 H, $\text{Cp}^*\text{-Me}$). **$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3):** δ 139.5 (d, $^3J_{\text{Cp}} = 5.4$ Hz, C_q , C1,9), 136.3 (C_q , C5), 133.9 (C_q , C10), 128.1 (CH, C2,8), 124.9 (CH, C4,6), 123.8 (CH, C3,7), 99.7 (dd, $^1J_{\text{CRh}} = 4.5$, $^2J_{\text{Cp}} = 2.9$ Hz, C_q , Cp^*), 14.9 (d, $^1J_{\text{Cp}} = 32.7$ Hz, CH_3 , PMe_3), 8.9 (CH_3 , Cp^*). **^{31}P NMR (162 MHz, CDCl_3):** δ 1.7 (br d, $^1J_{\text{PRh}} = 149$ Hz). **$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3):** δ 1.7 (d, $^1J_{\text{PRh}} = 150$ Hz). **HRMS (APCI+):** *m/z* (%) Calcd. for $\text{C}_{20}\text{H}_{22}\text{RhS}_2$: 429.0212, found 429.0209 (100) [$\text{M-PMe}_3 + \text{H}$]. **IR (KBr):** $\nu_{\text{max}}/\text{cm}^{-1}$ 3040w ($\nu_{\text{Ar-H}}$), 2907 m ($\nu_{\text{C-H}}$), 1536s, 1195 m, 952s, 810 m, 761 m.

4.2.2. [Cp*Rh(PMe₃)(AcenapS₂)] (2b)



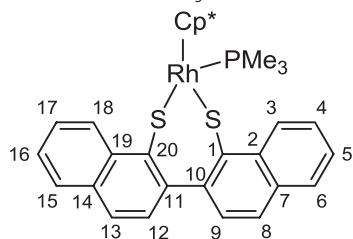
A methanol (20 mL) solution of [Cp*Rh(PMe₃)Br₂] (120 mg, 0.25 mmol), [Acenap(SH)₂] (68 mg, 0.31 mmol) and NaOMe (17 mg, 0.31 mmol) was stirred at room temperature overnight. The red precipitate was filtered, washed with MeOH then dried under vacuum for 3 h. The product was obtained as a red solid (121 mg, 0.22 mmol, 91%). Crystals suitable for X-ray work were obtained by slow evaporation from CH₂Cl₂. **Anal. calcd.** for C₂₅H₃₂PRhS₂ (530.07 g mol⁻¹): C, 56.60; H, 6.08. Found: C, 56.49; H, 6.11. **¹H NMR (400 MHz, CDCl₃):** δ 7.77 (d, ³J_{HH} = 7.2 Hz, 2 H, H2,8), 6.91 (d, ³J_{HH} = 7.2 Hz, 2 H, H3,7), 3.17 (s, 4 H, H11,12), 1.54 (dd, ²J_{H_P} = 10.3, ³J_{H_{Rh}} = 0.7 Hz, 9 H, PMe₃), 1.50 (d, ⁴J_{H_P} = 3.0 Hz, 15 H, Cp*-Me). **¹³C{¹H} NMR (100 MHz, CDCl₃):** δ 141.7 (C_q, C4,6), 141.1 (C_q, C5), 134.8 (d, ²J_{CRh} = 5.5 Hz, C_q, C1,9), 132.3 (C_q, C10), 128.6 (CH, C2,8), 117.9 (CH, C3,7), 99.5 (dd, ¹J_{CRh} = 4.9, ²J_{C_P} = 2.9 Hz, C_q, Cp*), 30.1 (CH₂, C11,12), 15.0 (d, ¹J_{C_P} = 33.0 Hz, CH₃, PMe₃), 8.9 (CH₃, Cp*). **³¹P NMR (162 MHz, CDCl₃):** δ 2.9 (br d, ¹J_{PRh} = 148 Hz). **³¹P{¹H} NMR (162 MHz, CDCl₃):** δ 2.9 (d, ¹J_{PRh} = 148 Hz). **HRMS (APCI+):** *m/z* (%) Calcd. for C₂₂H₂₄RhS₂: 455.0369, found 455.0362 (80) [M-PMe₃ + H], 216.0060 (95) [C₁₂H₈S₂], 184.0339 (55) [C₁₂H₈S], 152.0618 (100) [C₁₂H₈]. **IR (KBr):** ν_{max}/cm⁻¹ 3037w (ν_{Ar-H}), 2907 m (ν_{C-H}), 1552 m, 1404 m, 1027 m, 952s, 837 m, 734 m.

4.2.3. [Cp*Rh(PMe₃)(BiphenS₂)] (2c)



A methanol (20 mL) solution of [Cp*Rh(PMe₃)Br₂] (120 mg, 0.25 mmol), [Biphen(SH)₂] (71 mg, 0.33 mmol) and NaOMe (19 mg, 0.33 mmol) was stirred at room temperature overnight. The red precipitate was filtered, washed with MeOH then dried under vacuum for 3 h. The product was obtained as a red solid (110 mg, 0.21 mmol, 83%). Crystals suitable for X-ray work were obtained by slow evaporation from CH₂Cl₂. **Anal. calcd.** for C₂₅H₃₂PRhS₂ (530.07 g mol⁻¹): C, 56.60; H, 6.08. Found: C, 56.49; H, 6.15. **¹H NMR (400 MHz, CDCl₃):** δ 7.66 (dd, ³J_{HH} = 7.6, ⁴J_{HH} = 1.3 Hz, 1 H, H2), 7.64 (dd, ³J_{HH} = 7.7, ⁴J_{HH} = 1.3, 1 H, H11), 7.19 (p-td, ³J_{HH} = 7.5, ⁴J_{HH} = 1.4 Hz, 1 H, H4), 7.18 (p-td, ³J_{HH} = 7.6, ⁴J_{HH} = 1.4 Hz, 1 H, H9), 7.03 (p-td, ³J_{HH} = 7.6, ⁴J_{HH} = 1.6 Hz, 1 H, H3), 6.98 (p-td, ³J_{HH} = 7.6, ⁴J_{HH} = 1.6 Hz, 1 H, H10), 6.94 (dd, ³J_{HH} = 7.5, ⁴J_{HH} = 1.5 Hz, 1 H, H5), 6.86 (dd, ³J_{HH} = 7.5, ⁴J_{HH} = 1.5 Hz, 1 H, H8), 1.58 (d, ⁴J_{H_P} = 3.2 Hz, 15 H, Cp*-Me), 1.39 (dd, ²J_{H_P} = 10.5, ³J_{H_{Rh}} = 0.6 Hz, 9 H, PMe₃). **¹³C{¹H} NMR (100 MHz, CDCl₃):** δ 151.0 (C_q, C6), 150.0 (C_q, C7), 143.0 (d, ³J_{C_P} = 6.5 Hz, C_q, C1), 140.2 (C_q, C12), 137.2 (CH, C2), 135.2 (CH, C11), 130.9 (CH, C8), 130.6 (CH, C5), 126.2 (CH, C3,9), 125.7 (CH, C4), 125.5 (CH, C10), 99.3 (dd, ¹J_{CRh} = 5.3, ²J_{C_P} = 3.2 Hz, C_q, Cp*), 15.9 (d, ¹J_{C_P} = 31.6 Hz, CH₃, PMe₃), 8.8 (CH₃, Cp*). **³¹P NMR (162 MHz, CDCl₃):** δ 0.3 (br d, ¹J_{PRh} = 153 Hz). **³¹P{¹H} NMR (162 MHz, CDCl₃):** δ 0.3 (d, ¹J_{PRh} = 152 Hz). **MS (APCI+):** *m/z* (%) Calcd. for C₂₂H₂₄RhS₂: 455.0369, found 455.0365 (100) [M-PMe₃ + H]. **IR (KBr):** ν_{max}/cm⁻¹ 3037w (ν_{Ar-H}), 2905 m (ν_{C-H}), 1451 m, 1404 m, 1280w, 959s, 750s.

4.2.4. [Cp*Rh(PMe₃)(2,2'-BinapS₂)] (2d)



To a THF (15 mL) solution of [2,2'-BinapS₂] (117 mg, 0.37 mmol) was added lithium triethylborohydride (0.80 mL, 0.80 mmol, 1 M solⁿ in THF) at room temperature. The reaction was left to stir for 0.5 h during which time the solution turned from yellow to almost colourless. To this was added [Cp*Rh(PMe₃)Br₂] (148 mg, 0.31 mmol) and the solution turned instantly to a very dark red/purple colour. The reaction was left to stir at room temperature overnight. The solvent was removed under vacuum and the crude product purified by column chromatography (silica/CH₂Cl₂). The solvent was removed to afford the product as a dark purple solid (147 mg, 0.23 mmol, 82%). Crystals suitable for X-ray work were obtained by slow evaporation from CH₂Cl₂. **Anal. calcd.** for C₃₃H₃₆PRhS₂ (630.11 g mol⁻¹): C, 62.84; H, 5.75. Found: C, 62.73; H, 5.66. **¹H NMR (500 MHz, CDCl₃):** δ 9.20 (d, ³J_{HH} = 8.6 Hz, 1 H, H3), 9.17 (d, ³J_{HH} = 8.5 Hz, 1 H, H18), 7.80 (d, ³J_{HH} = 8.3 Hz, 1 H, H6), 7.77 (d, ³J_{HH} = 8.2 Hz, 1 H, H15), 7.65 (d, ³J_{HH} = 8.3 Hz, 1 H, H13), 7.64 (d, ³J_{HH} = 8.2 Hz, 1 H, H8), 7.54–7.48 (m, 2 H, H4,17), 7.45–7.39 (m, 2 H, H5,16), 7.01 (d, ³J_{HH} = 8.3 Hz, 1 H, H9), 6.86 (d, ³J_{HH} = 8.3 Hz, 1 H, H12), 1.42 (d, ⁴J_{Hp} = 3.2 Hz, 15 H, Cp*-Me₃), 1.31 (d, ²J_{Hp} = 10.6 Hz, 9 H, PMe₃). **¹³C{¹H} NMR (125 MHz, CDCl₃):** δ 150.1 (C_q, C11), 148.1 (C_q, C10), 140.8 (d, ³J_{Cp} = 6.7 Hz, C_q, C1), 138.3 (C_q, C2), 138.0 (C_q, C19), 137.5 (C_q, C20), 132.9 (C_q, C14), 132.1 (C_q, C7), 129.5 (CH, C12), 129.2 (CH, C3,9), 128.0 (CH, C15), 127.9 (CH, C18), 127.7 (CH, C6), 125.4 (CH, C17), 125.0 (CH, C13), 124.8 (CH, C8,16), 124.7 (CH, C5), 124.3 (CH, C4), 99.7 (dd, ¹J_{CRh} = 5.5, ²J_{Cp} = 3.5 Hz, C_q, Cp*), 15.7 (d, ¹J_{Cp} = 31.5 Hz, CH₃, PMe₃), 9.2 (CH₃, Cp*). **³¹P NMR (202 MHz, CDCl₃):** δ 2.2 (br d, ¹J_{PRh} = 152 Hz). **³¹P{¹H} NMR (202 MHz, CDCl₃):** δ 2.2 (d, ¹J_{PRh} = 152 Hz). **HRMS (APCI+):** *m/z* (%) Calcd. for C₃₀H₂₈RhS₂: 555.0687, found 555.0729 (90) [M-PMe₃ + H], 284.0738 (100) [C₂₀H₁₂S]. **IR (KBr):** ν_{max}/cm⁻¹ 3044w (ν_{Ar-H}), 2906 m (ν_{C-H}), 1493 m, 1281 m, 949s, 815s, 747s, 672 m, 546w.

Table 4. Crystallographic data for complexes 1, 2a and 2b

	1	2a	2b
Empirical formula	C ₁₃ H ₂₆ Br ₂ PRh	C ₂₃ H ₃₀ PRhS ₂	C ₂₅ H ₃₂ PRhS ₂
M	474	504	530
Crystal system	Tetragonal	Orthorhombic	Monoclinic
Space group	P4 ₃ 2 ₁ 2	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /n
a [Å]	11.994(9)	8.2099(19)	8.265(7)
b [Å]	11.994(9)	13.649(3)	8.706(7)
c [Å]	23.274(19)	19.602(4)	32.87(3)
α [°]	90.0	90.0	90.0
β [°]	90.0	90.0	95.663(7)
γ [°]	90.0	90.0	90.0
V [Å ³]	3348(4)	2196.5(8)	2354(3)
Z	8	4	4
ρ _{calcd} (g. cm ⁻³)	1.881	1.525	1.497
μ [cm ⁻¹]	58.817	10.448	9.791
Measured refln.	30194	29827	22775
Unique refln.	3088	4016	5378
R [I > 2σ(I)]	0.0186	0.0291	0.0378
wR	0.0344	0.0689	0.0981

Table 5. Crystallographic data for complexes 2c and 2d

	2c	2d
Empirical formula	C ₂₅ H ₃₂ PRhS ₂	C ₃₃ H ₃₆ PRhS ₂
<i>M</i>	530	630
Crystal system	Orthorhombic	Monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c
<i>a</i> [Å]	9.5411(15)	10.4996(7)
<i>b</i> [Å]	15.202(3)	22.0450(15)
<i>c</i> [Å]	16.6474(19)	13.3815(9)
α [°]	90.0	90.0
β [°]	90.0	107.216(4)
γ [°]	90.0	90.0
<i>V</i> [Å ³]	2414.6(7)	2958.6(4)
<i>Z</i>	4	4
ρ_{calcd} (g. cm ⁻³)	1.459	1.416
μ [cm ⁻¹]	9.545	7.918
Measured refln.	25505	25373
Unique refln.	5526	5437
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0189	0.0277
<i>wR</i>	0.0454	0.0725

4.3. Crystal structure analysis

Tables 4 and 5 list the details of data collections and refinements. Data for **1**, **2b**, **2c** and **2d** were collected using a Rigaku SCX-Mini (Mo-K α , graphite monochromator) at -100°C; for **2b** using a Rigaku Saturn724 at -148°C. Intensities were corrected for Lorentz polarisation, and adsorption. Structures were solved by direct methods and refined by full-matrix least-squares against *F*² (SHELXL) (Sheldrick, 2008). Hydrogen atoms were assigned riding isotropic displacements parameters and constrained to idealised geometries. Non-hydrogen atoms were refined anisotropically.

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References

- Albers, A., Demeshko, S., Dechert, S., Saouma, C. T., Mayer, J. M., & Meyer, F. (2014). Fast proton-coupled electron transfer observed for a high-fidelity structural and functional [2Fe-2S] Rieske model. *Journal of the American Chemical Society*, 136, 3946–3954. <http://dx.doi.org/10.1021/ja412449v>
- Armarego, W. L. F. (1960). 83. The synthesis of two dinaphthothiophenes. *Journal of the Chemical Society (Resumed)*, 1960 433–436. <http://dx.doi.org/10.1039/jr9600000433>
- Armarego, W. L. F., & Chai, C. L. L. (2009). *Purification of Laboratory Chemicals* (6th ed.). Oxford: Butterworth-Heinemann.
- Ashe, A. J., Kampf, J. W., & Savla, P. M. (1994). The reaction of sulfur with dilithio compounds. The syntheses and structures of phenanthro [1, 10-cd]-1,2-dithiole and phenanthro[4,5-cde] [1,2]dithiin. *Heteroatom Chemistry*, 5, 113–119. [http://dx.doi.org/10.1002/\(ISSN\)1098-1071](http://dx.doi.org/10.1002/(ISSN)1098-1071)
- Aucott, S. M., Kilian, P., Milton, H. L., Robertson, S. D., Slawin, A. M. Z., & Woollins, J. D. (2005). Bis(Cyclopentadienyl) Titanium Complexes of Naphthalene-1,8-Dithiolates, Biphenyl 2,2'-Dithiolates, and Related Ligands. *Inorganic Chemistry*, 44, 2710–2718. <http://dx.doi.org/10.1021/ic048483l>
- Aucott, S. M., Kilian, P., Robertson, S. D., Slawin, A. M. Z., & Woollins, J. D. (2006). Platinum complexes of dibenzo[1,2] dithiin, dibenzo[1,2]dithiin oxides and related

- polyaromatic hydrocarbon ligands. *Chemistry - A European Journal*, 12, 895–902.
[http://dx.doi.org/10.1002/\(ISSN\)1521-3765](http://dx.doi.org/10.1002/(ISSN)1521-3765)
- Ballmann, J., Dechert, S., Demeshko, S., & Meyer, F. (2009). Tuning electronic properties of biomimetic [2Fe-2S] clusters by ligand variations. *European Journal of Inorganic Chemistry*, 3219–3225.
<http://dx.doi.org/10.1002/ejic.v2009:22>
- Benson, C. G. M., Schofield, C. M., Randall, R. A. M., Wakefield, L., Knight, F. R., Slawin, A. M. Z., & Woollins, J. D. (2013). Platinum Complexes of 5,6-Dihydroacenaphtho[5,6-cd]-1,2-dichalcogenoles. *European Journal of Inorganic Chemistry*, 427–437.
<http://dx.doi.org/10.1002/ejic.201200967>
- Bond, A. M., & Martin, R. L. (1984). Electrochemistry and redox behaviour of transition metal dithiocarbamates. *Coordination chemistry reviews*, 54, 23–98.
[http://dx.doi.org/10.1016/0010-8545\(84\)85017-1](http://dx.doi.org/10.1016/0010-8545(84)85017-1)
- Bosman, W. P., & van der Linden, H. G. M. (1977). Tris(triphenylphosphine)hexachloronaphthalene-1,8-dithiolatonicel(II), [Ni₃(PPh₃)₃(S₂C₁₀Cl₆)], a Ni₃S₆ metal-sulphur cluster compound; preparation and crystal and molecular structure. *Journal of the Chemical Society, Chemical Communications*, 714–715.
<http://dx.doi.org/10.1039/C39770000714>
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J., & Taylor, R. (2002). New software for searching the Cambridge Structural Database and visualizing crystal structures. *Acta Crystallographica Section B Structural Science*, 58, 389–397.
<http://dx.doi.org/10.1107/S0108768102003324>
- Burns, R. P., & McAuliffe, C. A. (1979). 1,2-Dithiolene complexes of transition metals. *Advances in Inorganic Chemistry and Radiochemistry*, 22, 303–348.
- Burns, R. P., McCullough, F. P., & McAuliffe, C. A. (1980). 1,1-Dithiolato complexes of the transition elements. *Advances in Inorganic Chemistry and Radiochemistry*, 23, 211–280.
- Charreter, K., Kdider, M., Capon, J.-F., Gloaguen, F., Pétillon, F. Y., Schollhammer, P., & Talarmin, J. (2010). Effect of electron-withdrawing dithiolate bridge on the electron-transfer steps in diiron molecules related to [2Fe](H) subsite of the [FeFe]-hydrogenases. *Inorganic Chemistry*, 49, 2496–2501.
<http://dx.doi.org/10.1021/ic902401k>
- Conry, R., & Tipton, A. A. (2001). A mononuclear molybdenum(V) mono-oxo biphenyl-2,2'-dithiolate complex in which the metal resides within a cleft formed by the ligands and that exhibits N-H ... S hydrogen bonding in the solid state. *JBIC Journal of Biological Inorganic Chemistry*, 6, 359–366.
<http://dx.doi.org/10.1007/s007750100207>
- Cossu, S., Delogu, G., Fabbri, D., & Maglioli, P. (1991). A rapid preparation of 2,2'-dimercaptobiphenyl. *Organic Preparations and Procedures International*, 23, 455–457.
<http://dx.doi.org/10.1080/00304949109458237>
- Eisenberg, R. (2007). Structural systematics of 1,1- and 1,2-dithiolato chelates. In *Progress in inorganic chemistry* (pp. 295–369). John Wiley & Sons.
- Figliola, C., Male, L., Horton, P. N., Pitak, M. B., Coles, S. J., Horswell, S. L., & Grainger, R. S. (2014). [FeFe]-Hydrogenase synthetic mimics based on peri-substituted dichalcogenides. *Organometallics*, 33, 4449–4460.
<http://dx.doi.org/10.1021/om500683p>
- Figliola, C., Male, L., Horswell, S. L., & Grainger, R. S. (2015). N-Derivatives of peri-Substituted Dichalcogenide [FeFe]-Hydrogenase Mimics: Towards Photocatalytic Dyads for Hydrogen Production. *European Journal of Inorganic Chemistry*, 2015, 3146–3156.
<http://dx.doi.org/10.1002/ejic.v2015:19>
- Jones, W. D., & Feher, F. J. (1984). Preparation and conformational dynamics of (CMe₅)Rh(PR13)RX. Hindered rotation about rhodium-phosphorus and rhodium-carbon bonds. *Inorganic Chemistry*, 23, 2376–2388.
<http://dx.doi.org/10.1021/ic00184a005>
- Kempe, R., Sieler, J., Hintzsche, E., & Schroth, W. (1993). Crystal structure of dinaphtho[1,2-c][2',1'-e]-1,2-dithiine, C₂₀H₁₂S₂. *Zeitschrift für Kristallographie*, 207, 314–315.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., ... Wood, P. A. (2008). Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures. *Journal of Applied Crystallography*, 41, 466–470.
<http://dx.doi.org/10.1107/S0021889807067908>
- McNaughton, R. L., Tipton, A. A., Rubie, N. D., Conry, R. R., & Kirk, M. L. (2000). Electronic structure studies of oxomolybdenum tetrathiolate complexes: Origin of reduction potential differences and relationship to cysteine-molybdenum bonding in sulfite oxidase. *Inorganic Chemistry*, 39, 5697–5706.
<http://dx.doi.org/10.1021/ic0003729>
- Nejman, P. S., Morton-Fernandez, B., Black, N., Cordes, D. B., Slawin, A. M. Z., Kilian, P., & Woollins, J. D. (2015). The preparation and characterisation of rhodium(III) and Iridium(III) half sandwich complexes with naphthalene-1,8-dithiolate, acenaphthene-5,6-dithiolate and biphenyl-2,2'-dithiolate. *Journal of Organometallic Chemistry*, 776, 7–16.
<http://dx.doi.org/10.1016/j.jorganchem.2014.10.023>
- Nejman, P. S., Morton-Fernandez, B., Moulding, D. J., Athukorala Arachchige, K. S., Cordes, D. B., Slawin, A. M. Z., ... Woollins, J. D. (2015). Structural diversity of bimetallic rhodium and iridium half sandwich dithiolate complexes. *Dalton Transactions*, 44, 16758–16766.
<http://dx.doi.org/10.1039/C5DT02542G>
- Ojima, I., Vu, A. T., & Bonafoux, D. (2002). Product Class 5: Organometallic complexes of rhodium. *Science of Synthesis*, 1, 531–616.
- Phillips, J. R., Poat, J. C., Slawin, A. M. Z., Williams, D. J., Wood, P. T., & Woollins, J. D. (1995). Polymeric and bimetallic complexes of diisopropyl monothiophosphate. *Journal of the Chemical Society, Dalton Transactions*, 2369–2375.
<http://dx.doi.org/10.1039/dt9950002369>
- Samuel, A. P. S., Co, D. T., Stern, C. L., & Wasielewski, M. R. (2010). Ultrafast photodriven intramolecular electron transfer from a zinc porphyrin to a readily reduced diiron hydrogenase model complex. *Journal of the American Chemical Society*, 132, 8813–8815.
<http://dx.doi.org/10.1021/ja100016v>
- Sheldrick, G. (2008). Acta Crystallographica Section A Foundations of Crystallography. *International Union of Crystallography, International Union of Crystallography*, 64, 112–122.
<http://dx.doi.org/10.1107/S0108767307043930>
- Stafford, P. R., Rauchfuss, T. B., Verma, A. K., & Wilson, S. R. (1996). Titanocene complexes of ring-opened dibenzothioephene and related dimercaptobiphenyl ligands. *Journal of Organometallic Chemistry*, 526, 203–214.
[http://dx.doi.org/10.1016/S0022-328X\(96\)06581-3](http://dx.doi.org/10.1016/S0022-328X(96)06581-3)
- Teo, B. K., & Snyder-Robinson, P. A. (1978). Metal tetrathiolenes. 3. Structural study of the first bimetallic tetrathiolene complex, tetrakis(triphenylphosphine)diplatinum tetrathionaphthalene, (Ph₃P)₄Pt₂(C₁₀H₄S₄) revealing an unexpected molecular distortion. *Inorganic Chemistry*, 17, 3489–3497.
<http://dx.doi.org/10.1021/ic50190a034>
- Teo, B. K., & Snyder-Robinson, P. A. (1979a). Metal-tetrathiolene chemistry: the first disulphur bridge in the novel di-iridium cluster (Ph₃P)₂(CO)₂Br₂Ir₂(C₁₀H₄S₄). X-Ray crystal structure. *Journal of the Chemical Society, Chemical Communications*, 255–256.
<http://dx.doi.org/10.1039/C39790000255>

- Teo, B. K., & Snyder-Robinson, P. A. (1979b). Metal tetrathiolenes. 4. Synthesis, characterization, and electrochemistry of new discrete diplatinum-tetrathiolene complexes. *Inorganic Chemistry*, 18, 1490–1495. <http://dx.doi.org/10.1021/ic50196a017>
- Teo, B. K., & Snyder-Robinson, P. A. (1981). Molecular systematics in metal tetrathiolenes. A novel 2-, 4-, 6-, 8-, and 12-electron-donating ligand system upon coordination to one, two, two, three and four metals, respectively. *Inorganic Chemistry*, 20, 4235–4239. <http://dx.doi.org/10.1021/ic50226a041>
- Teo, B. K., & Snyder-Robinson, P. A. (1984). Metal tetrathiolenes. 8. Molecular structures of two isostructural two-electron systems: $(\text{Ph}_3\text{P})_2(\text{CO})\text{XIr}(\text{C}_1\text{OCl}_4\text{S}_4)$ (X=Cl,H). The first member of a novel series of metal tetrathiolene complexes. *Inorganic Chemistry*, 23, 32–39. <http://dx.doi.org/10.1021/ic00169a009>
- Teo, B. K., Wudl, F., Hauser, J. J., & Kruger, A. (1977). Reactions of tetrathionaphthalene with transition metal carbonyls. Synthesis and characterization of two new organometallic semiconductors $(\text{C}_{10}\text{H}_4\text{S}_4\text{Ni})_x$ and $[\text{C}_{10}\text{H}_4\text{S}_4\text{Co}_2(\text{CO})_2]_x$ and a tetrairon cluster $\text{C}_{10}\text{H}_4\text{S}_4\text{Fe}_4(\text{CO})_{12}$. *Journal of the American Chemical Society*, 99, 4862–4863. <http://dx.doi.org/10.1021/ja00456a073>
- Teo, B. K., Wudl, F., Marshall, J. H., & Kruger, A. (1977). Synthesis, characterization, and electrochemistry of a new platinum "tetrathiolene" cluster, tetrakis(triphenylphosphine)tetrathionaphthalenediplatinum(II,II): A novel system with five reversible oxidation states. *Journal of the American Chemical Society*, 99, 2349–2350. <http://dx.doi.org/10.1021/ja00449a060>
- Teo, B. K., Bakirtzis, V., & Snyder-Robinson, P. A. (1983). Syntheses and structures of a novel series of tetrathiolene clusters: $(\eta\text{-}5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{C}_{10}\text{Cl}_4\text{S}_4)(\text{C}_{10}\text{Cl}_4\text{S}_3)$, $(\eta\text{-}5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{C}_{10}\text{Cl}_4\text{S}_4)$, and $(\eta\text{-}5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{C}_{10}\text{Cl}_4\text{S}_4)$. *Journal of the American Chemical Society*, 105, 6330–6332. <http://dx.doi.org/10.1021/ja00358a034>
- Thomas, I. R., Bruno, I. J., Cole, J. C., Macrae, C. F., Pidcock, E., & Wood, P. A. (2010). WebCSD: the online portal to the Cambridge Structural Database. *Journal of Applied Crystallography*, 43, 362–366. <http://dx.doi.org/10.1107/S0021889810000452>
- Topf, C., Monkowius, U., & Knör, G. (2012). Design, synthesis and characterization of a modular bridging ligand platform for bio-inspired hydrogen production. *Inorganic Chemistry Communications*, 21, 147–150. <http://dx.doi.org/10.1016/j.inoche.2012.04.034>
- Tuna, F., Smith, C. A., Bodensteiner, M., Ungur, L., Chibotaru, L. F., McInnes, E. J. L., Winpenny, R. E. P., Collison, D., & Layfield, R. A. (2012). A high anisotropy barrier in a sulfur-bridged organodyprosium single-molecule magnet. *Angewandte Chemie International Edition*, 51, 6976–6980. <http://dx.doi.org/10.1002/anie.201202497>
- Wang, G.-L., Lin, Y.-J., Blacque, O., Berke, H., & Jin, G.-X. (2008). Helical Supramolecular Assemblies of $\{2,4,6\text{-}[\text{Cp}^*\text{Rh}(\text{E}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})(\text{NC}_3\text{H}_4\text{CH}_2\text{S})_3(\text{triazine})\}$ (E = S, Se) Shaped by $\text{Cp}^*\text{-Toluene-Cp}^*\pi$ -Stacking Forces and BH-Pyridine Hydrogen Bonding. *Inorganic Chemistry*, 47, 2940–2942. <http://dx.doi.org/10.1021/ic800105h>
- Woolins, J. D. (1996). Metallacycles with group 15/16 ligands. In S. C. Mitchell (Ed.), *Biological interactions of sulfur compounds* (pp. 1–19). London: Taylor & Francis.
- Wright, R. J., Lim, C., & Tilley, T. D. (2009). Diiron proton reduction catalysts possessing electron-rich and electron-poor naphthalene-1,8-dithiolate ligands. *Chemistry - A European Journal*, 15, 8518–8525. <http://dx.doi.org/10.1002/chem.v15:34>
- Xiao, X.-Q., & Jin, G.-X. (2008). Half-sandwich rhodium complexes containing both N-heterocyclic carbene and ortho-carborane-1,2-dithiolate ligands. *Journal of Organometallic Chemistry*, 693, 316–320. <http://dx.doi.org/10.1016/j.jorganchem.2007.11.005>
- Yao, Z.-J., Xu, B., Huo, X.-K., & Jin, G.-X. (2013). Homonuclear half-sandwich iridium and rhodium complexes containing dichalcogenolato-functionalized σ -carboranyl ligands. *Journal of Organometallic Chemistry*, 747, 85–89. <http://dx.doi.org/10.1016/j.jorganchem.2013.03.002>
- Yui, K., Aso, Y., Otsubo, T., & Ogura, F. (1988). Syntheses and Properties of 2,2'-Binaphtho[1,8-de]-1,3-dithiylidene and Its Selenium Analog, 2-(1,3-Dithiol-2-ylidene)naphtho[1,8-de]-1,3-dithiin, and 2-(4H-Thiopyran-4-ylidene)naphtho[1,8-de]-1,3-dithiin. *Bulletin of the Chemical Society of Japan*, 61, 953–959. <http://dx.doi.org/10.1246/bcsj.61.953>
- Zhou, C.-L., Wang, Z.-M., Wang, B.-W., & Gao, S. (2011). Two Mn6 single-molecule magnets with sulfur-contained capping ligand. *Polyhedron*, 30, 3279–3283. <http://dx.doi.org/10.1016/j.poly.2011.05.046>



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