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## Nickel(II) complexes of di- and tri-substituted thiourea mono- and di-anions

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## A R T I C L E I N F O

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## ABSTRACT

Reaction of nickel(II) acetate, 1,2-bis(diphenylphosphino)ethane (dppe), and a di- or tri-substituted thiourea R<sup>1</sup>NHC(S)R<sup>2</sup>R<sup>3</sup> (R<sup>3</sup> = H or alkyl) with trimethylamine in hot methanol gave cationic nickel(II) complexes containing *N*,S-chelated thiourea monoanion ligands [Ni{SC(NR<sup>2</sup>R<sup>3</sup>)NR<sup>1</sup>}(dppe)]<sup>+</sup>, which can be readily isolated as their BPh<sub>4</sub><sup>-</sup> salts. The X-ray crystal structure of [Ni{SC(NMe<sub>2</sub>)NPh}(dppe)]<sup>+</sup>BPh<sub>4</sub><sup>-</sup> is reported.

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## 1. Introduction

Thioureas are versatile ligands capable of binding to a wide range of metal ions in various coordination modes [1]. Depending on the actual thiourea ligand, they are capable of binding in either a monodentate or bidentate chelating fashion, in a range of protonation states as neutral ligands, or mono- or di-anions. Thiourea monoanion complexes of a range of transition metals including chromium [2], rhodium [3–5], ruthenium [3,6,7], technetium [8], rhenium [9,10], gold [11], nickel [12,13], palladium [14] and platinum [15,16] have been reported in the literature. The ligands bind predominantly in an *N*,*S*-chelating mode giving four-membered rings. There have also been many studies on ligands of the general type  $R_2NC(S)NHC(O)Ph$ , which often bind as monoanions, giving six-membered rings through sulfur and oxygen [17].

In this contribution we report on some new nickel(II) complexes containing thiourea monoanion ligands in conjunction with the bidentate phosphine dppe [1,2-bis(diphenylphosphino)ethane]. Examination of the literature reveals that such complexes have not been described previously though some phosphine nickel(II) complexes of 2,4,6-trimercaptotriazine, which contain fourmembered Ni–S–C(NR)–NR rings have been described [18]. In contrast, bis(thiourea monoanion) complexes of the type [NiL<sub>2</sub>] [12,13] and nickel complexes of heterocyclic thiones [19–21] are well documented in the literature.

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## 2. Results and discussion

Reaction of nickel(II) acetate with one equivalent of 1,2bis(diphenylphosphino)ethane (dppe) in warm methanol, followed by addition of a tri-substituted thiourea R<sup>1</sup>NHC(S)R<sup>2</sup>R<sup>3</sup> and Me<sub>3</sub>N base resulted in the formation of orange solutions which were shown by positive ion electrospray ionisation mass spectrometry (ESI MS) to contain solelv the thiourea cations [Ni{SC(NR<sup>2</sup>R<sup>3</sup>)NR<sup>1</sup>}(dppe)]<sup>+</sup>. Excellent agreement was observed between the observed and calculated isotope patterns, including masses of the base peak (<sup>58</sup>Ni isotopomer). The cations can easily be isolated by addition of an excess of NaBPh<sub>4</sub> to the hot reaction mixtures, giving orange tetraphenylborate salts 1. Although the yields of the products are moderate (typically around 60% isolated yield based on nickel(II) acetate) they are obtained in a high state of purity, as shown by excellent elemental microanalytical data on the as-isolated products. Attempts at preparing analogous complexes using triphenylphosphine in place of dppe were unsuccessful. The range of complexes synthesised is summarised in Scheme 1.

In a related fashion the one-pot reaction of nickel(II) acetate, dppe, a *sym*-disubstituted thiourea RNHC(S)NHR (R = Ph or *n*-Bu) and trimethylamine likewise gave orange solutions from which the monocations can be isolated as orange solids **2** by precipitation with excess NaBPh<sub>4</sub>. In this case, the addition of the large BPh<sub>4</sub><sup>-</sup> anion promotes the precipitation of the *cationic* complex containing a mono-deprotonated thiourea ligand, as opposed to the neutral complex containing a thiourea dianion.

An alternative route to one of the complexes (1e) utilised the reaction of the known, green nickel(II) bis(thiourea monoanion) complex  $[Ni{SC(N(CH_2CH_2)_2O)NPh}_2]$  [12] with dppe in methanol







Complex	<b>R</b> <sub>1</sub>	R <sub>2</sub> ,R <sub>3</sub>	
1a	Ph	Me, Me	
1b	Ph	Су, Су	
1c	Ph	(CH <sub>2</sub> ) <sub>4</sub>	
1d	Ph	(CH <sub>2</sub> ) <sub>5</sub>	
1e	Ph	$(CH_2CH_2)_2O$	
1f	Ph	$(CH_2CH_2)_2S$	
1g	Ph	CH <sub>2</sub> Ph, (R)-CHMePh	
1h	$p-C_6H_4NO_2$	Me, Me	
1i	$p-C_6H_4NO_2$	$(CH_2CH_2)_2O$	
2a	Ph	Ph, H	
2b	<i>n</i> -Bu	<i>n</i> -Bu, H	

**Scheme 1.** The range of new nickel(II)-phosphine-thiourea complexes reported in this work.

which gave an orange solution from which [Ni{SC(N(CH<sub>2</sub>-CH<sub>2</sub>)<sub>2</sub>O)NPh}(dppe)]BPh<sub>4</sub> **1e** was isolated by addition of excess NaBPh<sub>4</sub>.



The complexes **1** and **2** are soluble in chlorinated hydrocarbon solvents, but generally only sparingly soluble in methanol and ethanol, and insoluble in water; the exception is the cyclohexyl (Cy) complex **1b**, which is moderately soluble in methanol, accounting for the lower isolated yield of this complex, even when some water was added to aid precipitation.

The complexes have <sup>31</sup>P{<sup>1</sup>H} NMR spectra consistent with their structures; for all complexes two doublets (due to <sup>2</sup>*J*(PP) coupling between the two inequivalent phosphines) were observed, with chemical shifts indicative of a five-membered dppe-Ni ring [22]. By comparison with analogous triphenylphosphine platinum(II) thiourea monoanion complexes, where the <sup>195</sup>Pt isotope provides additional information on ligand arrangements, the more downfield resonance is assigned as the PPh<sub>2</sub> group *trans* to the sulfur do-nor [16]. The <sup>1</sup>H NMR spectra show the expected features; it is noteworthy that there is an upfield shift for the ligand protons on coordination, as exemplified by complex **1e**. Here, the morpholine protons shift (with the greatest shift for the CH<sub>2</sub>N protons) from the ligand PhNHC(S)N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O [CH<sub>2</sub>O  $\delta$  3.80 (m) and CH<sub>2</sub>N  $\delta$  3.72 (m)] to the complex **1e** [CH<sub>2</sub>O  $\delta$  3.40 and CH<sub>2</sub>N  $\delta$ 



**Fig. 1.** Structure of the cation of [Ni{SC(NMe<sub>2</sub>)NPh}(dppe)]BPh<sub>4</sub> **1a** showing the atom numbering scheme. Thermal displacement ellipsoids are depicted at 50% probability and hydrogen atoms are omitted for clarity.

3.09]. The thiourea ligand binds strongly as a bidentate ligand in these complexes and addition of an additional donor ligand does not effect conversion to a monodentate thiourea ligand. Thus, an NMR experiment investigating the reaction between complex **1e** and 1 molar equivalent of PPh<sub>3</sub> in CDCl<sub>3</sub> showed peaks attributable only to the starting materials.

The IR spectra of the complexes (where recorded) show a strong absorption in the range 1503–1562 cm<sup>-1</sup> due to the C=N group. Additionally, the nitrophenyl derivative **1i** shows a strong absorption for the NO<sub>2</sub> group in the expected region at 1329(s) cm<sup>-1</sup>.

In order to characterise the mode of binding of the thiourea ligand to nickel, an X-ray structure determination on [Ni{SC(N-Me<sub>2</sub>)NPh}(dppe)]BPh<sub>4</sub> **1a** was carried out. The structure of the cation is shown in Fig. 1, together with the atom numbering scheme, whilst Table 1 gives selected bond lengths and angles. The Ni has adopted a four-coordinate, distorted square-planar geometry and is coordinated by two phosphorus atoms of the dppe ligand and the nitrogen and sulfur of the thiourea ligand. The angles about the Ni reflect this distorted environment (see Table 1), and can be quantified by the  $\tau_4$  parameter of Houser and co-workers [23] which gives a  $\tau_4$  value of 0.184 for **1a**; on this scale a regular square-planar geometry has a  $\tau_4$  parameter of 0.00 whilst a tetrahedron has 1.00. The Ni-P(1) bond trans to the sulfur of the thiourea ligand [2.1716(7) Å] is slightly longer than the other Ni-P distance [2.1523(7) Å, trans to nitrogen], reflecting the higher trans-influence [24] of the sulfur donor compared to the nitrogen donor.

Although there appear to be few relevant structures in the literature to provide suitable comparisons with **1a**, the bis(thiourea monoanion) complex [Ni{SC(N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O)NPh}<sub>2</sub>] **3** has been structurally characterised. [12] In this complex the Ni–S bond distance [2.211(2) Å] is slightly longer than in **1a** [2.2079(7) Å], presumably as a result of two mutually *trans*, high *trans*-influence sulfur donors. However the Ni–N bond distance of **1a** [1.936(2) Å] is considerably longer than that in **3** [1.888(7) Å], be-

Table 1
Selected bond lengths (Å) and angles (°) for [Ni{SC(NMe <sub>2</sub> )NPh}(dppe)]BPh <sub>4</sub> <b>1a</b> .

Ni(1)-N(1)	1.936(2)	Ni(1)-P(2)	2.1523(7)	Ni(1)-P(1)	2.1716(7)
Ni(1)-S(1)	2.2079(7)	Ni(1)…C(1)	2.502(2)	S(1)-C(1)	1.755(3)
N(1)-C(1)	1.327(3)	N(1)-C(4)	1.428(3)	N(2)-C(1)	1.332(3)
N(2)-C(3)	1.462(4)	N(2)-C(2)	1.472(4)	C(10)-C(11)	1.531(3)
P(1)-C(18)	1.813(3)	P(1)-C(12)	1.814(2)	P(1)-C(10)	1.835(2)
P(2)-C(24)	1.811(3)	P(2)-C(30)	1.819(2)	P(2)-C(11)	1.834(2)
N(1)-Ni(1)-P(2)	168.69(6)	N(1)-Ni(1)-P(1)	104.47(6)		
P(2)-Ni(1)-P(1)	86.38(3)	N(1)-Ni(1)-S(1)	74.67(6)		
P(2)-Ni(1)-S(1)	95.66(3)	P(1)-Ni(1)-S(1)	165.37(3)		
C(1)-S(1)-Ni(1)	77.38(8)	C(1)-N(1)-C(4)	123.8(2)		
C(1)-N(1)-Ni(1)	98.43(16)	C(4) - N(1) - Ni(1)	131.86(16)		
C(1)-N(2)-C(3)	120.9(2)	C(1)-N(2)-C(2)	123.1(2)		
C(3)-N(2)-C(2)	115.6(2)	N(1)-C(1)-N(2)	128.8(2)		
N(1)-C(1)-S(1)	109.05(18)	N(2)-C(1)-S(1)	122.1(2)		
N(1)-C(1)-Ni(1)	49.92(12)	N(2)-C(1)-Ni(1)	176.15(18)		

cause of lengthening by the high *trans*-influence phosphine ligand, compared to the mutually *trans* N donors in **3**. The sulfur in **1a** is also in a slightly constrained geometry with an Ni–S–C angle of 77.39(8)° [compared to a corresponding angle of 76.49° in **3**], whilst the ligand has a bite angle N(1)–Ni(1)–S(1) of 74.67(6)°, identical to that in **3**. There is a long transannular contact of 2.503(2) Å from Ni to C(1); this is within Van der Waals contact, but is unlikely to be a bonding interaction.

The C-S bond distance of **1a**, 1.755(3) Å, is shorter than that expected for a C–S single bond (e.g. of a thioether, around 1.82 Å [25]) but longer than a C=S double bond (around 1.71 Å in Me<sub>2</sub>NC(S)NH<sub>2</sub> [26]). Comparison of the C–S and C–N bond distances in the cores of the thiourea ligands of **1a** and **3** reveals that in **1a** the C–S bond is longer than in **3** [1.7357(3) Å] and the exocyclic C–N bond is considerably shorter than in **3** [1.332(3) vs. 1.3397(2) Å]. These indicate that in **1a** the ligand has more C–S single bond character. Of the five N–C bonds in **1a**, C(1)–N(1) [1.327(3) Å] and C(1)–N(2) [1.332(3) Å] are the shortest, and their similarity reflects delocalisation within the ligand, whose bonding is best represented by the structure in Scheme 1. C(4)–N(1), to the *sp*<sup>2</sup> hybridised carbon of the phenyl ring is the next longest at 1.428(3) Å, with C(3)–N(2) [1.462(4)] and C(2)–N(2) [1.472(4)] being the longest (single) bonds to the two methyl groups, as expected.

The four-membered Ni(1)–S(1)–C(1)–N(1) is planar, but the NMe<sub>2</sub> group [defined by C(3), N(2) and C(2)] of the thiourea ligand is twisted by 14.91° from the plane of the four-membered ring [producing a C(2)–N(2)–C(1)–N(1) torsion angle of 17.07°]. The same distortion is observed in **3**, with an angle of 14.84° between the corresponding planes. As a result of slight pyramidalisation of the ring nitrogen N(1) in **1a** [the sum of the bond angles around N(1) is 354.09°, compared to 360° for a planar nitrogen] the attached carbon C(4) of the phenyl ring is bent out of the plane of the four-membered ring. The phenyl ring is also inclined at an angle of 72.19° to the least squares plane of the four-membered ring. These distortions presumably minimise steric interactions between the phenyl ring and the NMe<sub>2</sub> group.

## 3. Experimental

Nickel(II) acetate tetrahydrate (BDH), sodium tetraphenylborate (BDH) and aqueous trimethylamine (BDH, 25–30% w/v), 1,3-di-*n*-butylthiourea, 1,3-diphenylthiourea (thiocarbanilide, BDH) and 1,2-bis(diphenylphosphino)ethane (dppe, Aldrich) were used as supplied. The thioureas PhNHC(S)NMe<sub>2</sub>, PhNHC(S)N(CH<sub>2</sub>)<sub>4</sub>, PhNHC(S)N(CH<sub>2</sub>)<sub>5</sub>, PhNHC(S)N(CH<sub>2</sub>Ph)((R)-CHMePh), PhNHC(S)N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O, PhNHC(S)N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S, *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NHC(S)NMe<sub>2</sub> and *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NHC(S)N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O were prepared by the standard method, by addition of the appropriate amine to PhNCS or *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NCS (Aldrich) in diethyl ether, as de-

scribed previously [16]. The thioureas precipitated in high yields, and were isolated by filtration, washed with diethyl ether and used without further purification.

ESI mass spectra were recorded on a Bruker MicrOTOF instrument, which was calibrated using a solution of sodium formate. Samples of isolated products were prepared for analysis by dissolution in a few drops of dichloromethane followed by dilution with methanol and centrifugation. Assignment of ions was assisted by comparison of experimental and theoretical isotope patterns, the latter calculated using an internet-based programme [27]. NMR spectra were recorded in CDCl<sub>3</sub> solution (unless otherwise stated) on a Bruker AC300P instrument. Elemental analyses were carried out by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. IR spectra were recorded as KBr disks on a Perkin–Elmer Spectrum 100 FT-IR spectrometer.

## 3.1. Synthesis of $[Ni{SC(NR^2R^3)NR^1}(dppe)]BPh_4$ from tri-substituted thioureas – general method

A mixture of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (100 mg, 0.402 mmol) and dppe (160 mg, 0.402 mmol) in methanol (30 mL) was stirred and gently warmed for 5 min, to give a yellow solution. The thiourea (1 mol equivalent) was added, producing an orange solution. Aqueous trimethylamine (1 mL) was then added, and the mixture briefly warmed to around 60 °C. The resulting orange to red-orange solution was then gravity filtered to remove a small quantity of insoluble material. Solid NaBPh<sub>4</sub> (250 mg, 0.731 mmol) was added to the rewarmed filtrate, producing a precipitate of the product, which was allowed to cool to room temperature. In some cases, some water was added at this point to assist precipitation. The product was filtered, washed, and dried under vacuum.

Using the general method, the following complexes were prepared:

#### 3.1.1. [Ni{SC(NMe<sub>2</sub>)NPh}(dppe)]BPh<sub>4</sub> 1a

PhNHC(S)NMe<sub>2</sub> (73 mg) gave an orange solid that was washed with cold methanol (5 mL) to give 248 mg (65%) of product. *Anal.* Calc. for C<sub>59</sub>H<sub>55</sub>BN<sub>2</sub>NiP<sub>2</sub>S: C, 74.13; H, 5.80; N, 2.93. Found: C, 73.98; H, 5.92; N, 2.86%. ESI MS *m/z* 635.130 (calcd. 635.134), [**1a**-BPh<sub>4</sub>]<sup>+</sup>. <sup>1</sup>H NMR, δ 7.59–6.30 (m, Ph), 2.60 (s, CH<sub>3</sub>), 1.88–1.51 (m, CH<sub>2</sub>, dppe). <sup>31</sup>P{<sup>1</sup>H} NMR, δ 62.0 [d, <sup>2</sup>*J*(PP) 48, P *trans* S], 57.3 [d, <sup>2</sup>*J*(PP) 48, P *trans* N]. IR  $v_{max}$  1562(s) cm<sup>-1</sup>.

## 3.1.2. [Ni{SC(NCy<sub>2</sub>)NPh}(dppe)]BPh<sub>4</sub> 1b

PhNHC(S)NCy<sub>2</sub> (129 mg), with addition of water (5 mL) to the cooled reaction mixture, gave a red-orange solid that was washed with methanol–water (1:1, 10 mL) to give 198 mg (45%) of product. *Anal.* Calc. for  $C_{61}H_{71}BN_2NiP_2S$ : C, 75.88; H, 6.56; N, 2.57. Found: C, 75.83; H, 6.61; N, 2.52%. ESI MS *m/z* 771.309 (calcd.

771.260),  $[1b-BPh_4]^+$ . <sup>31</sup>P{<sup>1</sup>H} NMR,  $\delta$  60.7 [d, <sup>2</sup>J(PP) 44, P trans S] and 55.0 [d, <sup>2</sup>J(PP) 44, P trans N]. IR  $v_{max}$  1503(s) cm<sup>-1</sup>.

### 3.1.3. [Ni{SC(N(CH<sub>2</sub>)<sub>4</sub>)NPh}(dppe)]BPh<sub>4</sub> 1c

PhNHC(S)N(CH<sub>2</sub>)<sub>4</sub> (84 mg) gave an orange solid that was washed with cold methanol (5 mL) to give 246 mg (62%) of product. *Anal.* Calc. for C<sub>61</sub>H<sub>57</sub>BN<sub>2</sub>NiP<sub>2</sub>S: C, 74.61; H, 5.86; N, 2.85. Found: C, 74.65; H, 6.03; N, 2.82%. ESI MS *m*/*z* 661.162 (calcd. 661.150), [**1c**-BPh<sub>4</sub>]<sup>+</sup>. <sup>1</sup>H NMR, δ 7.70–6.33 (m, Ph), 3.50 (s, br, CH<sub>2</sub>), 2.45 (s, br, CH<sub>2</sub>), 1.87–1.53 (m, CH<sub>2</sub>, dppe). <sup>31</sup>P{<sup>1</sup>H} NMR, δ 61.9 [d, <sup>2</sup>*J*(PP) 48, P *trans* S] and 58.1 [d, <sup>2</sup>*J*(PP) 48, P *trans* N]. IR  $v_{max}$  1538(s) cm<sup>-1</sup>.

## 3.1.4. [Ni{SC(N(CH<sub>2</sub>)<sub>5</sub>)NPh}(dppe)]BPh<sub>4</sub> 1d

PhNHC(S)N(CH<sub>2</sub>)<sub>5</sub> (90 mg), with addition of water (2 mL) to the cooled reaction mixture, gave an orange solid that was washed with cold methanol (5 mL) to give 256 mg (64%) of product. *Anal.* Calc. for C<sub>62</sub>H<sub>59</sub>BN<sub>2</sub>NiP<sub>2</sub>S: C, 74.77; H, 5.98; N, 2.81. Found: C, 74.92; H, 6.08; N, 2.75%. ESI MS *m/z* 675.161 (calcd. 675.166), [**1d**-BPh<sub>4</sub>]<sup>+</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR, δ 61.8 [d, <sup>2</sup>*J*(PP) 47, P *trans* S] and 56.8 [d, <sup>2</sup>*J*(PP) 47, P *trans* N]. IR  $v_{max}$  1548(s) cm<sup>-1</sup>.

#### 3.1.5. [Ni{SC(N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O)NPh}(dppe)]BPh<sub>4</sub> 1e

PhNHC(S)N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O (89 mg) gave a light orange solid that was washed with cold methanol (5 mL) to give 234 mg (58%) of product. *Anal.* Calc. for C<sub>61</sub>H<sub>57</sub>BN<sub>2</sub>NiOP<sub>2</sub>S: C, 73.42; H, 5.76; N, 2.81. Found: C, 73.20; H, 5.72; N, 2.74%. ESI MS *m/z* 677.149 (calcd. 677.145), [**1e**-BPh<sub>4</sub>]<sup>+</sup>. <sup>1</sup>H NMR, δ 7.65–6.32 (m, Ph), 3.40 (s, CH<sub>2</sub>O), 3.09 (s, CH<sub>2</sub>N) 1.83–1.56 (m, CH<sub>2</sub>, dppe). <sup>31</sup>P{<sup>1</sup>H} NMR, δ 62.3 [d, <sup>2</sup>*J*(PP) 48, P *trans* S], 57.6 [d, <sup>2</sup>*J*(PP) 49, P *trans* N]. IR  $\nu_{max}$  1550(s) cm<sup>-1</sup>.

#### 3.1.6. [Ni{SC(N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S)NPh}(dppe)]BPh<sub>4</sub> 1f

PhNHC(S)N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S (98 mg) gave a yellow-orange solid that was washed with cold methanol (5 mL) to give 295 mg (72%) of product. *Anal.* Calc. for C<sub>61</sub>H<sub>57</sub>BN<sub>2</sub>NiP<sub>2</sub>S<sub>2</sub>: C, 72.26; H, 5.67; N, 2.76. Found: C, 72.08; H, 5.75; N, 2.71%. ESI MS *m/z* 693.136 (calcd. 693.122), [**1f**-BPh<sub>4</sub>]<sup>+</sup>. <sup>1</sup>H NMR, δ 7.60–6.32 (m, Ph), 3.37 (s, CH<sub>2</sub>S), 3.50 (s, CH<sub>2</sub>N), 1.79–1.53 (m, CH<sub>2</sub>, dppe). <sup>31</sup>P{<sup>1</sup>H} NMR, δ 62.1 [d, <sup>2</sup>*J*(PP) 48, P *trans* S] and 54.3 [d, <sup>2</sup>*J*(PP) 48, P *trans* N]. IR  $v_{max}$  1547(s) cm<sup>-1</sup>.

## 3.1.7. [Ni{SC(N(CH<sub>2</sub>Ph)((R)-CHMePh)NPh}(dppe)]BPh<sub>4</sub> 1g

PhNHC(S)N(CH<sub>2</sub>Ph)((R)–CHMePh) (141 mg) gave an orange solid that was washed with cold methanol (5 mL) and then methanol–water (1:1, 5 mL) to give 269 mg (60%) of product. *Anal.* Calc. for C<sub>72</sub>H<sub>65</sub>BN<sub>2</sub>NiP<sub>2</sub>S: C, 77.07; H, 5.84; N, 2.50. Found: C, 77.22; H, 5.88; N, 2.47%. ESI MS *m/z* 801.212 (calcd. 801.213). <sup>31</sup>P{<sup>1</sup>H} NMR, δ 62.3 [d, <sup>2</sup>*J*(PP) 47, P *trans* S] and 57.4 [d, <sup>2</sup>*J*(PP) 47, P *trans* N].

#### 3.1.8. [Ni{SC(NMe<sub>2</sub>)NC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>}(dppe)]BPh<sub>4</sub> **1h**

*p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NHC(S)NMe<sub>2</sub> (92 mg) gave a light orange solid that was washed with cold methanol (5 mL) to give 215 mg (53%) of product. *Anal.* Calc. for C<sub>59</sub>H<sub>54</sub>BN<sub>3</sub>NiO<sub>2</sub>P<sub>2</sub>S: C, 70.80; H, 5.44; N, 4.20. Found: C, 70.93; H, 5.48; N, 4.18%. ESI MS *m/z* 680.117 (calcd. 680.119). <sup>31</sup>P{<sup>1</sup>H} NMR, δ 63.1 [d, <sup>2</sup>*J*(PP) 48, P *trans* S] and 57.1 [d, <sup>2</sup>*J*(PP) 48, P *trans* N].

### 3.1.9. [Ni{SC(N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O)NC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>}(dppe)]BPh<sub>4</sub> 1i

*p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NHC(S)N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O (108 mg) gave an orange solid that was washed with cold methanol (5 mL) to give 249 mg (59%) of product. *Anal.* Calc. for C<sub>61</sub>H<sub>56</sub>BN<sub>3</sub>NiO<sub>3</sub>P<sub>2</sub>S: C, 70.25; H, 5.42; N, 4.03. Found: C, 70.06; H, 5.44; N, 4.02%. ESI MS *m*/*z* 722.150 (calcd. 722.130), [**1**i–BPh<sub>4</sub>]<sup>+</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (d<sup>6</sup>-DMSO),  $\delta$  68.4 [d, <sup>2</sup>*J*(PP) 40, P *trans* S], 62.2 [d, <sup>2</sup>*J*(PP) 40, P *trans* N]. IR *v*<sub>max</sub> 1533(s) and 1329(s) cm<sup>-1</sup>.

#### 3.2. Alternative synthesis of complex 1e

The dark green complex  $[Ni{SC(N(CH_2CH_2)_2O)NPh}_2]$  **3** (prepared by a minor modification of the literature procedure [12]) (400 mg, 0.799 mmol) and dppe (319 mg, 0.801 mmol) were stirred in methanol (25 mL) resulting in the rapid formation of a red-orange solution, with a small quantity of insoluble white material. After stirring for 1 h the solution was filtered, and NaBPh<sub>4</sub> (250 mg, 0.731 mmol) added to the filtrate, giving an orange precipitate. The product was filtered, washed with cold methanol (5 mL) and dried to give 409 mg (51%) of **1e**, which had an identical <sup>31</sup>P{<sup>1</sup>H} NMR spectrum to the material prepared in a one-pot reaction from Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O.

# 3.3. Synthesis of $[Ni{SC(NHR^2)NR^1}(dppe)]BPh_4$ from disubstituted thioureas $R^1NHC(S)NHR^2$

The following complexes were synthesised using an analogous procedure for the synthesis of the tri-substituted thiourea complexes:

#### 3.3.1. [Ni{SC(NHPh)NPh}(dppe)]BPh4 2a

PhNHC(S)NHPh (93 mg) gave an orange microcrystalline solid that was washed with cold methanol (5 mL) to give 181 mg (45%) of product. *Anal.* Calc. for C<sub>63</sub>H<sub>55</sub>BN<sub>2</sub>NiP<sub>2</sub>S: C, 75.37; H, 5.53; N, 2.79. Found: C, 75.33; H, 5.51; N, 2.69%. ESI MS *m/z* 683.143 (calcd. 683.134), [**2a**–BPh<sub>4</sub>]<sup>+</sup>. <sup>1</sup>H NMR, δ 7.67–6.42 (m, Ph), 1.87–1.50 (m, CH<sub>2</sub>, dppe). <sup>31</sup>P{<sup>1</sup>H} NMR, δ 62.2 [d, <sup>2</sup>*J*(PP) 50, P *trans* S], 59.7 [d, <sup>2</sup>*J*(PP) 50, P *trans* N]. IR  $\nu_{max}$  1552(s) cm<sup>-1</sup>.

### 3.3.2. [Ni{SC(NHBu)NBu}(dppe)]BPh4 2b

BuNHC(S)NHBu (78 mg) gave an orange microcrystalline precipitate that was washed with cold methanol (5 mL) and dried to give 245 mg (63%) of product. *Anal.* Calc. for  $C_{59}H_{63}BN_2NiP_2S$ : C, 73.51; H, 6.59; N, 2.91. Found: C, 73.55; H, 6.66; N, 2.83%. ESI MS *m*/*z* 643.190 (calcd. 643.197). <sup>31</sup>P{<sup>1</sup>H} NMR,  $\delta$  61.2 [d, <sup>2</sup>*J*(PP) 49, P *trans* S], 58.2 [d, <sup>2</sup>*J*(PP) 49, P *trans* N].

## 3.4. X-ray structure determination of [Ni{SC(NMe<sub>2</sub>)NPh}(dppe)]BPh<sub>4</sub> 1a

The complex crystallises as red block-like crystals by vapour diffusion of diethyl ether into a dichloromethane solution at room temperature.

An arbitrary sphere of data was collected on a crystal having approximate dimensions of  $0.36 \times 0.25 \times 0.11$  mm, on a Bruker APEX-II diffractometer using a combination of  $\omega$ - and  $\varphi$ -scans of  $0.3^{\circ}$  [28]. Data were corrected for absorption and polarisation effects and analysed for space group determination. The structure was solved by direct methods and expanded routinely [29]. The model was refined by full-matrix least-squares analysis of  $F^2$  against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded ( $1.5 \times$  for methyl,  $1.2 \times$  for all others).

There are two molecules of the Ni cation and associated BPh<sub>4</sub> anion and one molecule of diethyl ether of crystallisation in the unit cell of the primitive triclinic space group  $P\bar{1}$ . The diethyl ether of crystallisation is located on the inversion centre at [0.5, 1, 0]. It is disordered over two sites with the methylene carbon split between two positions.

#### 3.5. Crystal data for C<sub>61</sub>H<sub>60</sub>BN<sub>2</sub>NiO<sub>0.50</sub>P<sub>2</sub>S

 $M_r$  = 992.63; triclinic; space group  $P\bar{1}$ ; *a* = 13.4272(3) Å; *b* = 14.3573(4) Å; *c* = 15.1669(4) Å; *α* = 65.0730(10)°; *β* = 83.9350(10)°; *γ* = 72.0430(10)°; *V* = 2521.32(11) Å<sup>3</sup>; *Z* = 2; *T* = 100(2) K;  $\lambda$ (Mo K*α*) = 0.71073 Å;  $\mu$ (Mo K*α*) = 0.533 mm<sup>-1</sup>;  $D_{calc}$  = 1.307 g cm<sup>-3</sup>; 37922 reflections collected; 10321 unique ( $R_{int}$  = 0.0342); giving  $R_1$  = 0.0447,  $wR_2$  = 0.1081 for 8592 data with [*I* > 2*σ*(*I*)] and  $R_1$  = 0.0571,  $wR_2$  = 0.1151 for all 10321 data. Residual electron density (e Å<sup>-3</sup>) max/min: 0.987/-1.061.

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#### **Appendix A. Supplementary material**

CCDC 783826 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2010.12.011.

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