# Synthesis and thermal behaviour of cyclopentadienylnickel(II) thiolato Schiff base complexes. Molecular structures of $Ni(\eta^5\text{-}C_5H_5)(PBu_3)(SC_6H_4NC(H)C_6H_4C_6H_5)$ and $Ni(\eta^5\text{-}C_5H_5)(PBu_3)(SC_6H_4NC(H)C_6H_4OC_4H_9)$

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## Abstract

The new complexes $Ni(\eta^5\text{-}C_5H_5)(PR_3)(SC_6H_4NC(H)C_6H_4OC_nH_{2n+1})$, $Ni(\eta^5\text{-}C_5H_5)(PR_3)(SC_6H_4NC(H)C_6H_4C_6H_5)$ and $Ni(\eta^5\text{-}C_5H_5)(PR_3)(SC_6H_4NC(H)C_6H_4OCH_2C_6H_5)$, (R = Ph or Bu; $n$ = 4, 6, 8, 10, 14, 16 and 20), were synthesised from equimolar amounts of $Ni(\eta^5\text{-}C_5H_5)(PR_3)Br$ (R = Ph or Bu) and the appropriate thiol ligand and were characterised by NMR and elemental analysis. In addition **1a** and **3a** were characterised by single crystal X-ray diffraction studies. These new complexes were also examined by thermal analytical methods (DSC and TGA) and polarising hot-stage microscopy, but were not found to exhibit any liquid crystalline behaviour. Thermal analysis showed that the complexes were generally stable up to about 180 °C and decomposed finally to a species with empirical formula $NiSC_6H_5$. Two decomposition pathways were established, depending on the phosphine used. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Cyclopentadienylnickel(II); Thiolato Schiff base complexes; Thermal behaviour

## 1. Introduction

The search for metal Schiff base complexes is driven in part by their potential use in material science. Two specific applications are liquid crystals [1] and non-linear optical materials [2]. In most complexes that behave as liquid crystals or exhibit non-linear optical behaviour, the imine group of the Schiff base only forms part of the ligand backbone and is not coordinated to the metal centre. The imine group is thus used as a linker between aromatic rings in both of these applications.

We have recently reported the preparation of nickel complexes that contain Schiff base ligands bound to the metal through a sulfur atom [3]. This was done in an attempt to prepare nickel Schiff base metallomesogens,

using what could be described as a non-conventional approach. The conventional approach involves complexation of an organic liquid crystalline compound with a metal fragment. However, metal complexes thus formed by this conventional route do not always show liquid crystalline properties [4].

In preparing the complexes reported here we have combined features found in two types of metallomesogens. The first type is a Schiff base metal complexes that have the Schiff base directly bound to the metal, with the imine group as part of the ligand backbone, $HgCl(C_6H_4\text{-}4\text{-}N=CH\text{-}C_6H_4\text{-}4'\text{-}OMe)$, $Hg(C_6H_4\text{-}4\text{-}N=CH\text{-}C_6H_4\text{-}4'\text{-}OMe)_2$ [5a] and $M(CO)_2Cl(NC_5H_5\text{-}4\text{-}N=CH\text{-}C_6H_4\text{-}4'\text{-}C_nH_{2n+1})$ (M = Rh, Ir; $n$ = 5–12) [5a,b]. The second type is metal thiolato complexes that have either monothiolato ligands, $AgSC_nH_{2n+1}$ ($n$ = 4, 6, 8, 10, 12, 16, 18) [6], or dithiolato ligands, $Ni_2(S_2C\text{-}C_nH_{2n+1})_4$ ($n$ = 5–12) [7], $Ni(S_2C\text{-}C_6H_4\text{-}4\text{-}OC_nH_{2n+1})_2$ ($n$ = 4, 8) [8] and $Ni(S_3C\text{-}C_6H_4\text{-}4\text{-}OC_nH_{2n+1})(S_2C\text{-}C_6H_4\text{-}4\text{-}OC_nH_{2n+1})$ ($n$ = 4, 8) [9]. We

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Table 1
$^1$H NMR data and elemental analysis for Schiff bases (calculated values in brackets)

| Compound | $^1$H-NMR | Elemental analysis | | |
|---|---|---|---|---|
| | | C | H | N |
| **1** | 8.48(s), 7.96(d), 7.75(d), 7.64 (m), 7.14(d) | 74.68 (75.20) | 5.56 (5.36) | 4.32 (4.38) |
| **2** | 8.37(s), 7.83(d), 7.40(m), 7.08(dd), 5.14(s), 3.47(s) | 74.92 (74.74) | 5.85 (5.33) | 4.45 (4.36) |
| **3** | 8.36(s), 7.82(d), 7.30(d), 7.10(d), 6.97(d), 3.47(s) | 71.72 (71.55) | 6.43 (6.71) | 5.04 (4.91) |
| **4** | 8.36(s), 7.82(d), 7.52(d), 7.14(d), 6.96(d) | 72.86 (72.81) | 7.51 (7.39) | 4.60 (4.47) |
| **5** | 8.35(s), 7.84(d), 7.52(d), 7.16(d), 6.97(d) | 74.11 (74.08) | 7.49 (7.70) | 4.23 (4.11) |
| **6** | 8.35(s), 7.82(d), 7.52(d), 7.15(d), 6.96(d) | 73.73 (74.29) | 10.08 (9.86) | 3.67 (4.15) |
| **7** | 8.35(s), 7.81(d), 7.51(d), 7.14(d), 6.96(d) | 76.55 (76.18) | 8.95 (9.23) | 3.75 (3.29) |
| **8** | 8.36(s), 7.82(d), 7.30(d), 7.10(d), 6.96(d), 3.47(s) | 76.61 (76.77) | 10.77 (9.99) | 2.78 (3.09) |
| **9** | 8.35(s), 7.82(d), 7.51(d), 7.14(d), 6.96(d), 3.47(s) | 77.52 (77.74) | 9.75 (10.08) | 3.33 (2.75) |

have thus prepared the Schiff base thiols (**I**) and their nickel complexes (**II**) in an effort to obtain metallo-mesogens. Thermal studies of the ligands and the complexes using differential scanning calorimetry (DSC) and polarising hot-stage microscopy showed that neither the ligands nor the complexes have any mesogenic properties. They, however, show the effect of alkoxy chain length on the thermal behaviour of both the ligands and the complexes, which is reported herein.



$(R = Ph, Bu; X = OC_nH_{2n+1}, n = 2, 4, 6, 8, 10, 14, 16, 20; C_6H_5, OCH_2C_6H_5)$

$$(1)$$
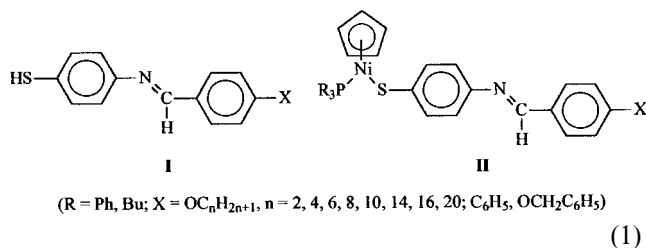
## 2. Experimental

### 2.1. Materials and instrumentation

All commercially available chemicals were used as received. The following specialty chemicals were purchased: 4-aminothiophenol (Fluka), 1-bromooctane (Saarchem, South Africa), 4-hydroxybenzaldehyde, 4-biphenylcarboxyaldehyde, 4-benzyloxybenzaldehyde, 4-butyloxybenzaldehyde, 1-bromodecane, 1-bromohexadecane, $Et_3N$ (Aldrich). The nickel compounds $Ni(\eta^5-C_5H_5)(PPh_3)Br$ and $Ni(\eta^5-C_5H_5)(PBu_3)Br$ were prepared by literature methods [10]. The compounds $OHCC_6H_4OR-4$ ($R = C_nH_{2n+1}$, $n = 2, 6, 8, 10, 14, 16$ and 20) were prepared by a modified literature procedure [11]. The Schiff base compounds were synthesised by the condensation reaction between the aldehydes and 4-aminothiophenol in ethanol as recently reported [3] and characterised by $^1$H-NMR, GC–MS and elemental analysis. Reagent grade hexane was distilled and then stored over molecular sieves, while toluene was distilled from sodium. All reactions were performed using standard Schlenk techniques under dinitrogen atmosphere.

IR spectra were obtained on a Perkin–Elmer Paragon 1000 PC FT spectrometer as Nujol mulls. The $^1$H- and $^{31}$P-NMR spectra were acquired on a Varian Gemini 2000 spectrometer at 200 and 80.961 MHz and referenced to residual $CHCl_3$ ($\delta$ 7.26) and externally to $PPh_3$ ($\delta - 5.00$), respectively. Thermal analyses were performed on a Universal V2.3H TA instrument. Elemental analysis and GC–MS (in electron impact mode) were performed in the Department of Chemistry at the University of the Western Cape.

X-ray diffraction data were collected at a low temperature on a Nonius Kappa CCD with 1.5 kW graphite monochromated Mo radiation. A selection of crystal and refinement data is given in Table 3. The strategy for the data collection was evaluated using the COLLECT software [12]. The data were scaled and reduced using DENZO-SMN [13]. Unit cell dimensions were refined on all data. The data were treated for absorption using the program SORTAV [14]. The structures were solved and refined using SHELX97 [15]. Hydrogen atoms were placed in calculated positions and refined as riding atoms. Molecular graphics and additional material for publication were obtained using the program PLATON [16].

Table 2
Melting points of selected complexes

| Complex | Melting point (°C) |
|---|---|
| **3a** | 99.97 |
| **3b** | 138.83 |
| **6a** | 62.24 |
| **6b** | 120.11 |
| **7a** | 52.26 |
| **7b** | 90.21 |
| **8b** | 89.70 |
| **9a** | 49.70 |
| **9b** | 101.77 |
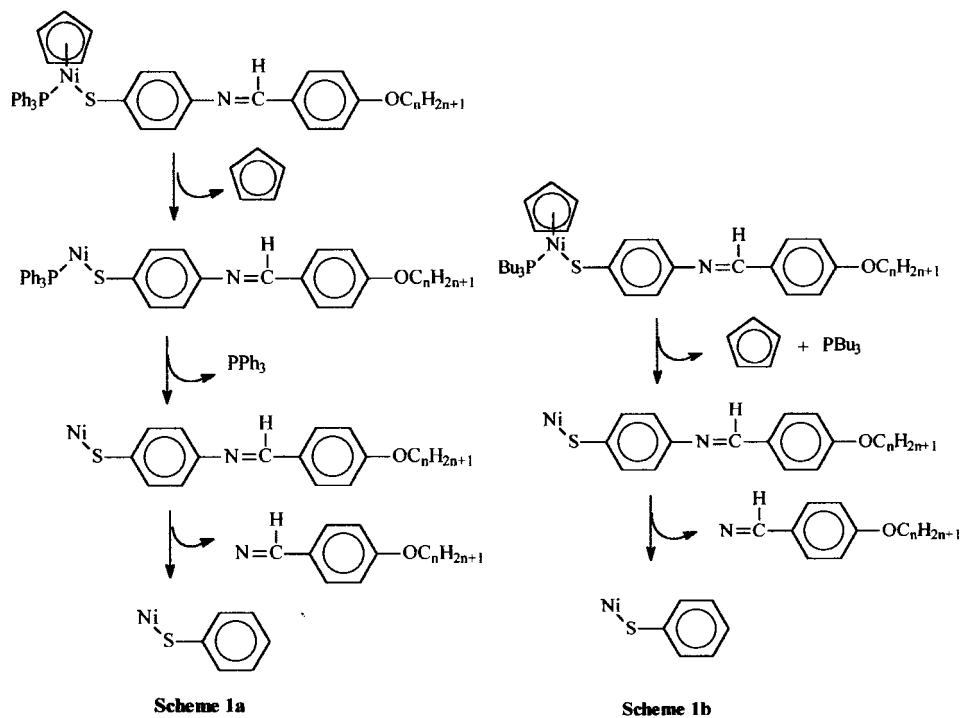
Scheme 1. Thermal decomposition patterns of: (a) PPh$_3$ complexes; and (b) PBu$_3$ complexes.
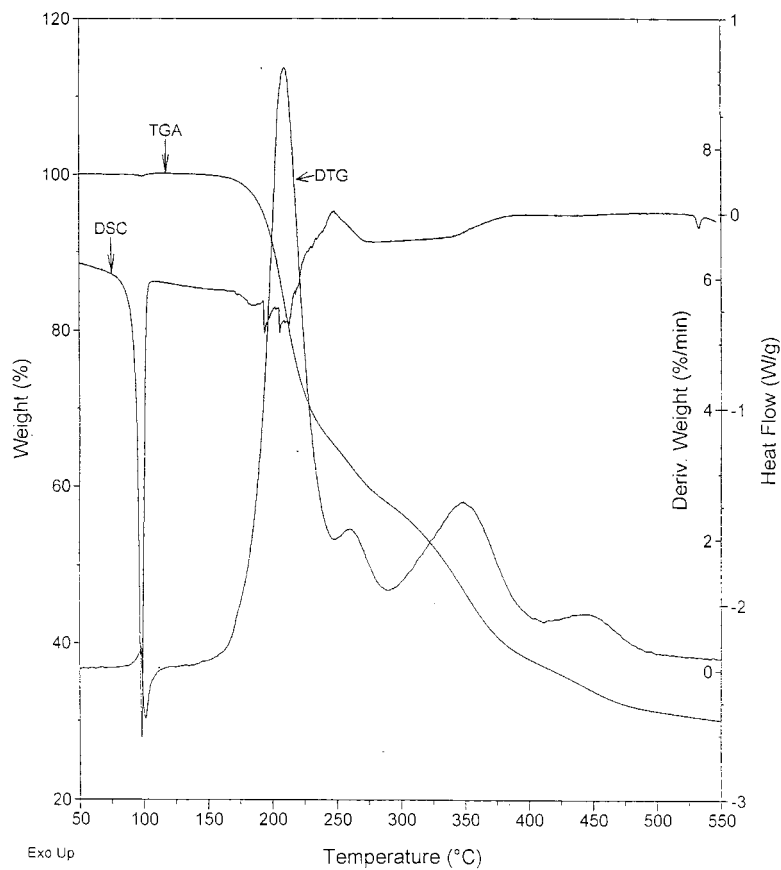


Fig. 1. TGA-DSC curves for **3a**.

## 2.2. Ni(η⁵-C₅H₅)(PBu₃)(SC₆H₄NC(H)C₆H₄C₆H₅) (1a)

Preparation of cyclopentadienylnickel thiolato Schiff base is representative and will only be described in detail for compound **1a**. To a degassed solution of $HSC_6H_4NC(H)C_6H_4C_6H_5$ (0.2 g, 0.63 mmol) and $Ni(\eta^5\text{-}C_5H_5)(PBu_3)Br$ (0.28 g, 0.68 mmol) in toluene (50 ml) was added excess $Et_3N$ (1.5 ml). The maroon solution immediately turned to dark green immediately and was stirred at room temperature (r.t.) for 15 h. The mixture was filtered to remove the white $Et_3NHBr$ by-product and the filtrate evaporated. The residue was recrystallised from hexane at $-15°C$ to give green crystalline product in a yield of 0.12 g (38%). $^1H$-NMR (CDCl₃, $\delta$ ppm): 8.52 (s, 1H, N=C(H)), 7.94 (d, 2H, $J_{HH} = 8.4$ Hz, C(H)C₆H₄), 7.67 (m, 5H, NC₆H₄, C₆H₅), 7.43 (m, 4H, C(H)C₆H₄, C₆H₅), 6.99 (d, 2H, $J_{HH} = 8.6$ Hz, SC₆H₄), 5.28 (s, 5H, $\eta^5$-C₅H₅), 1.52–1.35 (m, 18H, butyl), 0.92 (t, 9H, CH₃). $^{31}P\{^1H\}$-NMR (CDCl₃, $\delta$ ppm): 25.36. Anal. Found: C, 68.78; H, 7.89; N, 2.14. Calc. for $C_{36}H_{46}NPSNi$: C, 69.17; H, 7.53; N, 2.18%
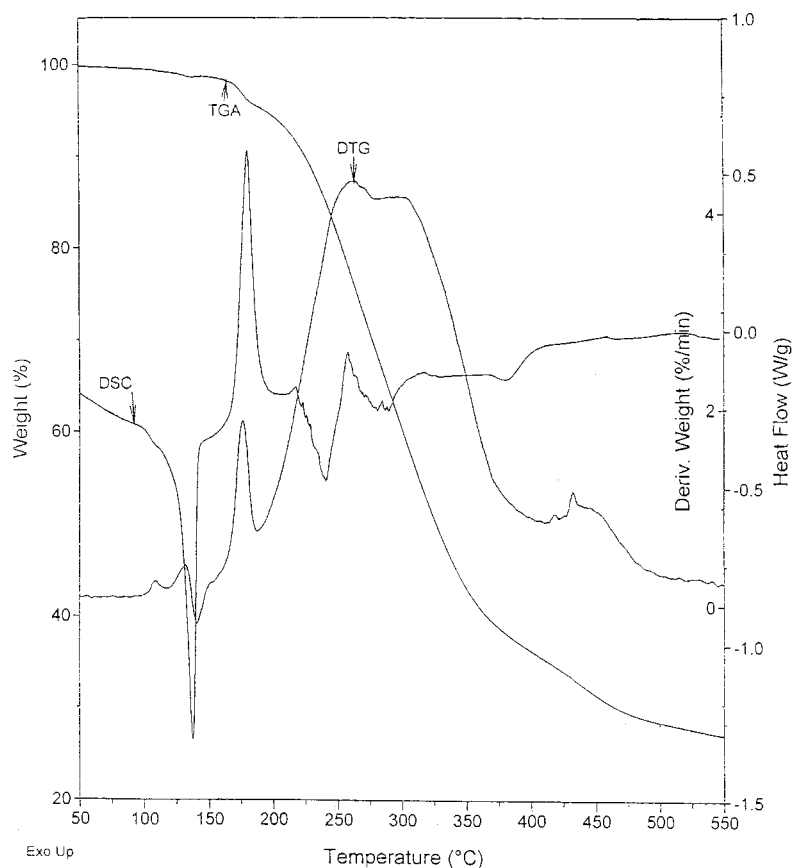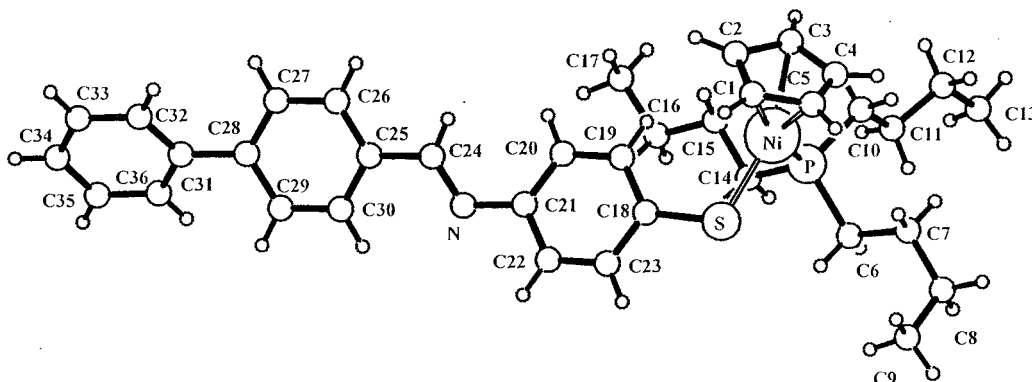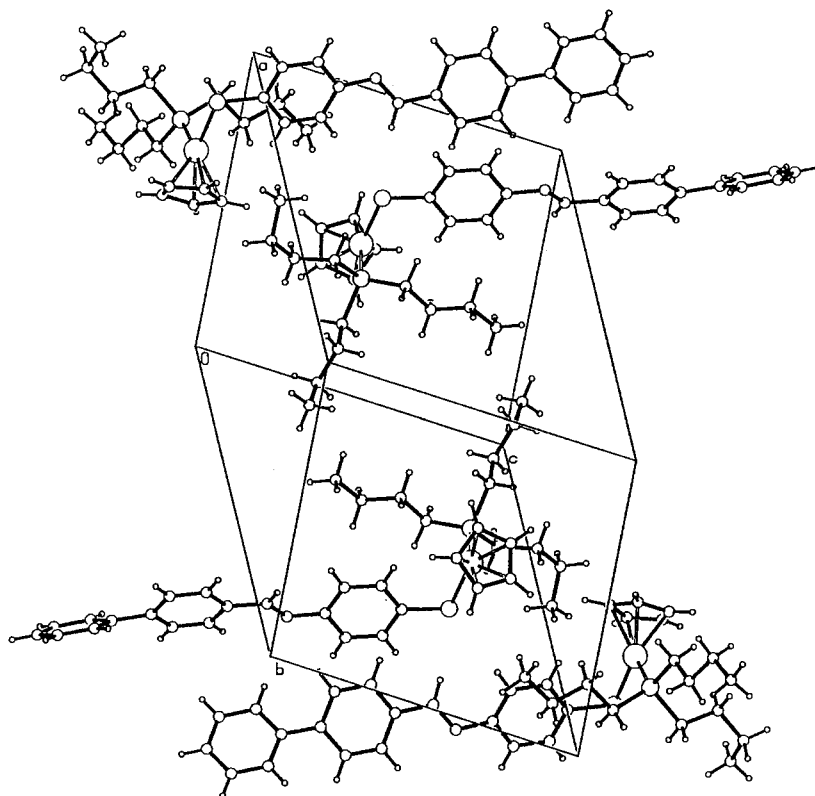


Fig. 2. TGA-DSC curves for **3b**.



Fig. 3. Molecular structure of **1a**.

Fig. 4. Packing diagram for **1a**.

The synthetic route for the remaining complexes is similar to **1a**.

### 2.3. Ni($\eta^5$-$C_5H_5$)(PBu$_3$)(SC$_6$H$_4$NC(H)C$_6$H$_4$OCH$_2$C$_6$H$_5$) (2a)

A green solid was obtained with a yield of 0.34 g (33%). $^1$H-NMR (CDCl$_3$, $\delta$ ppm): 8.40 (s, 1H, N=C(H)), 7.82 (d, 2H, $J_{HH}$ = 8.4 Hz, C(H)C$_6$H$_4$), 7.62 (d, 2H, $J_{HH}$ = 8.0 Hz, NC$_6$H$_4$), 7.40 (m, 5H, OCH$_2$C$_6$H$_5$), 7.04 (d, 2H, $J_{HH}$ = 8.4 Hz, OC$_6$H$_4$), 6.93 (d, 2H, $J_{HH}$ = 8.4 Hz, SC$_6$H$_4$), 5.27 (s, 5H, $\eta^5$-C$_5$H$_5$), 5.13 (s, 2H, OCH$_2$), 1.43–1.27 (m, 18H, butyl), 0.92 (t, 9H, CH$_3$). $^{31}$P{$^1$H}-NMR ($\delta$ ppm): 27.33. Anal. Found: C, 69.22; H, 7.62; N, 2.08. Calc. for C$_{37}$H$_{48}$NOPSNi: C, 68.95; H, 7.22, N, 2.18%.

### 2.4. Ni($\eta^5$-$C_5H_5$)(PBu$_3$)(SC$_6$H$_4$NC(H)C$_6$H$_4$OC$_4$H$_9$) (3a)

Green crystals with a yield of 0.94 g (88%) were obtained. $^1$H-NMR (CDCl$_3$, $\delta$ ppm): 8.39 (s, 1H, N=C(H)), 7.80 (d, 2H, $J_{HH}$ = 8.8 Hz, C(H)C$_6$H$_4$), 7.61 (d, 2H, $J_{HH}$ = 8.4 Hz, NC$_6$H$_4$), 6.94 (d, 2H, $J_{HH}$ = 8.8 Hz, OC$_6$H$_4$), 6.93 (d, 2H, $J_{HH}$ = 8.6 Hz, SC$_6$H$_4$), 5.26 (s, 5H, $\eta^5$-C$_5$H$_5$), 4.02 (t, 2H, OCH$_2$), 1.80 (q, 2H, OCH$_2$CH$_2$), 1.41 (m, 20H, alkoxy, butyl), 0.98 (t, 12H, alkoxy, butyl). $^{31}$P{$^1$H}-NMR (CDCl$_3$, $\delta$ ppm): 25.29. Anal. Found: C, 66.82; H, 8.33; N, 2.77. Calc. for C$_{34}$H$_{50}$NOPSNi: C, 66.89; H, 8.25; N, 2.29%.

### 2.5. Ni($\eta^5$-$C_5H_5$)(PBu$_3$)(SC$_6$H$_4$NC(H)C$_6$H$_4$OC$_6$H$_{13}$) (4a)

A green solid with a yield of 76% (0.58 g) was obtained. $^1$H-NMR (CDCl$_3$, $\delta$ ppm): 8.39 (s, 1H, C(H)N), 7.80 (d, 2H, $J_{HH}$ = 8.2 Hz, C(H)C$_6$H$_4$), 7.60 (d, 2H, $J_{HH}$ = 8.2 Hz, NC$_6$H$_4$), 6.94 (d, 2H, $J_{HH}$ = 8.4 Hz, OC$_6$H$_4$), 6.93 (d, 2H, $J_{HH}$ = 8.6 Hz, SC$_6$H$_4$), 5.26 (s, 5H, $\eta^5$-C$_5$H$_5$), 4.02 (t, 2H, OCH$_2$), 1.80–1.25 (m, 26H, alkyl), 0.92 (t, 12H, alkoxy, butyl). $^{31}$P{$^1$H}-NMR (CDCl$_3$, $\delta$ ppm): 25.26. Anal. Found: C, 68.04; H, 8.62; N, 2.40. Calc. for C$_{36}$H$_{54}$NOPSNi: C, 67.93; H, 8.55; N, 2.20%.

### 2.6. Ni($\eta^5$-$C_5H_5$)(PBu$_3$)(SC$_6$H$_4$NC(H)C$_6$H$_4$OC$_8$H$_{17}$) (5a)

A green solid with a yield of 0.43 g (75%) was obtained. $^1$H-NMR (CDCl$_3$, $\delta$ ppm): 8.39 (s, 1H, N=C(H)), 7.80 (d, 2H, $J_{HH}$ = 8.4 Hz, C(H)C$_6$H$_4$), 7.60 (d, 2H, $J_{HH}$ = 8.4 Hz, NC$_6$H$_4$), 6.94 (d, 2H, $J_{HH}$ = 8.8 Hz, OC$_6$H$_4$), 6.93 (d, 2H, $J_{HH}$ = 8.6 Hz, SC$_6$H$_4$), 5.26 (s, 5H, $\eta^5$-C$_5$H$_5$), 4.01 (t, 2H, OCH$_2$), 1.80–1.23 (m, 30H, alkoxy, butyl), 0.92 (t, 12H, alkoxy, butyl). $^{31}$P{$^1$H}-NMR (CDCl$_3$, $\delta$ ppm): 25.26. Anal. Found: C, 69.65; H, 8.52; N, 1.69. Calc. for C$_{38}$H$_{58}$NOPSNi: C, 69.71; H, 8.93; N, 2.14%.

## 2.7. Ni($\eta^5$-C₅H₅)(PBu₃)(SC₆H₄NC(H)C₆H₄OC₁₀H₂₁) (6a)

A green solid with a yield of 0.26 g (46%) was obtained. ¹H NMR (CDCl₃, $\delta$ ppm): 8.39 (s, 1H, N=C(H)), 7.80 (d, 2H, $J_{HH}$ = 8.8 Hz, C(H)C₆H₄), 7.61 (d, 2H, $J_{HH}$ = 8.4 Hz, NC₆H₄), 6.95 (d, 2H, $J_{HH}$ = 8.8

Table 3
Crystal data and structure refinement parameters for compounds **1a** and **3a**

|  | **1a** | **3a** |
|---|---|---|
| Empirical formula | C₃₄H₅₀NOPSNi | C₃₆H₄₆NPSNi |
| Formula weight | 610.49 | 614.48 |
| Temperature (K) | 150(2) | 173(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ |
| Unit cell dimensions |  |  |
| $a$ (Å) | 10.455(1) | 13.164(2) |
| $b$ (Å) | 12.375(1) | 20.277(2) |
| $c$ (Å) | 13.567(1) | 12.740(2) |
| $\alpha$ (°) | 104.25(1) | 90.0 |
| $\beta$ (°) | 99.31(1) | 106.46(1) |
| $\gamma$ (°) | 92.47(1) | 90.0 |
| $V$ (Å³) | 1672.6(2) | 3261.2(11) |
| $Z$ | 2 | 4 |
| $D_{calc}$ (Mg m⁻³) | 1.212 | 1.252 |
| Absorption coefficient (mm⁻¹) | 0.716 | 0.733 |
| $F$(000) | 656 | 1312 |
| Crystal size (mm) | 0.35 × 0.35 × 0.25 | 0.41 × 0.37 × 0.25 |
| Reflections collected | 13 454 | 12 387 |
| Unique reflections | 7614 | 6623 |
| Completeness to $\theta$ = 25° (%) | 99.8 | 97.9 |
| $R_{int}$ | 0.0191 | 0.0326 |
| Data/restraints/parameters | 7614/0/357 | 6623/0/463 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0338, $wR_2$ = 0.0717 | $R_1$ = 0.0409, $wR_2$ = 0.0845 |
| $R$ indices (all data) | $R_1$ = 0.0495, $wR_2$ = 0.0774 | $R_1$ = 0.0693, $wR_2$ = 0.0950 |
| Largest difference peak and hole (e Å⁻³) | 0.332 and −0.353 | 0.445 and −0.418 |

Table 4
Selected bond lengths (Å) and bond angles (°) for **1a**

| Bond lengths |  |  |  |
|---|---|---|---|
| Ni–S | 2.193(1) | Ni–P | 2.145(1) |
| Ni–Cp ᵃ | 1.750(3) | C(18)–S | 1.764(2) |
| C(24)–N | 1.277(3) | C(6)–P | 1.828(2) |
| C(10)–P | 1.834(2) | C(14)–P | 1.824(2) |

| Bond angles |  |  |  |
|---|---|---|---|
| S–Ni–Cp | 132.43(1) | P–Ni–Cp | 136.28(1) |
| C(18)–S–Ni | 107.5(1) | C(14)–P–Ni | 115.1(1) |
| P–Ni–S | 91.7(1) | C(6)–P–Ni | 113.6(1) |
| C(10)–P–Ni | 114.6(1) |  |  |

ᵃ Cp is the cyclopentadienyl ring centroid.

Table 5
Selected bond lengths (Å) and bond angles (°) for **3a**

| Bond lengths |  |  |  |
|---|---|---|---|
| Ni–S | 2.184(1) | Ni–P | 2.145(1) |
| Ni–Cp ᵃ | 1.752(3) | C(18)–S | 1.761(3) |
| C(24)–N | 1.271(3) | C(14)–P | 1.820(2) |
| C(6)–P | 1.822(2) | C(10)–P | 1.834(2) |

| Bond angles |  |  |  |
|---|---|---|---|
| S–Ni–Cp | 131.6(1) | Cp–Ni–P | 136.3 (1) |
| C(18)–S–Ni | 109.7(1) | C(10)–P–Ni | 113.7(1) |
| C(6)–P–Ni | 113.4(1) | C(14)–P–Ni | 115.2(1) |
| P–Ni–S | 91.2(1) |  |  |

ᵃ Cp is the cyclopentadienyl ring centroid.

Hz, OC₆H₄), 6.92 (d, 2H, $J_{HH}$ = 8.6 Hz, SC₆H₄), 5.26 (s, 5H, $\eta^5$-C₅H₅), 4.01 (t, 2H, OCH₂), 1.78 (q, 2H, OCH₂CH₂), 1.57–1.27 (m, 28H, alkoxy, butyl), 0.92 (m, 12H, butyl, alkoxy). ³¹P{¹H}-NMR (CDCl₃, $\delta$ ppm): 25.29. Anal. Found: C, 70.15; H, 9.04; N, 2.11. Calc. for C₄₀H₆₂NOPSNi: C, 69.16; H, 9.95; N, 2.02%.

## 2.8. Ni($\eta^5$-C₅H₅)(PBu₃)(SC₆H₄NC(H)C₆H₄OC₁₄H₂₉) (7a)

A green solid with a yield of 0.48 g (49%) was obtained. ¹H-NMR (CDCl₃, $\delta$ ppm): 8.40 (s, 1H, N=C(H)), 7.81 (d, 2H, $J_{HH}$ = 8.8 Hz, C(H)C₆H₄), 7.62 (d, 2H, $J_{HH}$ = 8.4 Hz, NC₆H₅), 6.95 (d, 2H, $J_{HH}$ = 8.4 Hz, OC₆H₄,), 6.94 (d, 2H, $J_{HH}$ = 8.4 Hz, SC₆H₄) 5.27 (s, 5H, $\eta^5$-C₅H₅), 4.02 (t, 2H, OCH₂), 1.81 (q, 2H, OCH₂CH₂), 1.59–1.27 (m, 22H, alkoxy, butyl), 0.93 (t, 12H, alkoxy, butyl). Anal. Found: C, 70.87; H, 9.33; N, 1.62. Calc. for C₄₄H₇₀NOPSNi: C, 70.40; H, 9.40; N, 1.85%.

## 2.9. Ni($\eta^5$-C₅H₅)(PBu₃)(SC₆H₄NC(H)C₆H₄OC₁₆H₃₃) (8a)

Green crystals with a yield of 0.14 g (87%)b were isolated. ¹H-NMR (CDCl₃, $\delta$ ppm): 8.39 (s, 1H, N=C(H)), 7.80 (d, 2H, $J_{HH}$ = 8.6 Hz, C(H)C₆H₄), 7.60 (d, 2H, $J_{HH}$ = 8.4 Hz, NC₆H₄), 6.94 (d, 2H, $J_{HH}$ = 8.6 Hz, OC₆H₄), 6.93 (d, 2H, $J_{HH}$ = 8.4 Hz, SC₆H₄), 5.26 (s, 5H, $\eta^5$-C₅H₅), 4.01 (t, 2H, OCH₂), 1.80–1.30 (m, 46H, alkoxy, butyl), 0.92 (t, 12H, alkoxy, butyl). ³¹P{¹H}-NMR (CDCl₃, $\delta$ ppm): 22.31 (s). Anal. Found: C, 70.22; H, 10.52; N, 1.67. Calc. for C₄₆H₇₄NOPSNi: C, 69.96; H, 9.74; N, 1.73%.

## 2.10. Ni($\eta^5$-C₅H₅)(PBu₃)(SC₆H₄NC(H)C₆H₄OC₂₀H₄₁) (9a)

A green solid with a yield of 0.21 g (19.5%) was isolated. ¹H-NMR (CDCl₃, $\delta$ ppm): 8.40 (s, 1H, N=C(H)), 7.81 (d, 2H, $J_{HH}$ = 8.8 Hz, C(H)C₆H₄), 7.62 (d, 2H, $J_{HH}$ = 8.4 Hz, NC₆H₄), 6.95 (d, 2H, $J_{HH}$ = 8.8

Hz, $OC_6H_4$), 6.94 (d, 2H, $J_{HH} = 8.4$ Hz, $SC_6H_4$), 5.27 (s, 5H, $\eta^5$-$C_5H_5$), 4.01 (t, 2H, $OCH_2$), 1.81 (q, 2H, $OCH_2CH_2$), 1.52–1.27 (m, 34H, alkoxy, butyl), 0.93 (t, 3H, alkoxy, butyl). $^{31}P\{^1H\}$-NMR ($\delta$ ppm): 22.45. Anal. Found: C, 71.21; H, 10.26; N, 1.92. Calc. for $C_{50}H_{82}NOPSNi$: C, 71.93; H, 9.90; N, 1.68%.

### 2.11. $Ni(\eta^5$-$C_5H_5)(PPh_3)(SC_6H_4NC(H)C_6H_4C_6H_5)$ (1b)

A brown solid with a yield of 0.55 g (64%) was obtained. $^1H$-NMR (CDCl$_3$, $\delta$ ppm): 8.36 (s, 1H, N=C(H)), 7.83 (d, 2H, $J_{HH} = 8.8$ Hz, $C(H)C_6H_4$), 7.68 (t, 6H, PPh$_3$), 7.49 (m, 15H, PPh$_3$, $NC_6H_4$, C6H5), 7.13 (d, 2H, $J_{HH} = 8.4$ Hz, $C(H)C_6H_4C_6H_5$), 7.05 (d, 2H, $J_{HH} = 8.8$ Hz, $SC_6H_4$), 5.14 (s, 5H, $\eta^5$-$C_5H_5$). Anal.

Found: C, 74.14; H, 5.42; N, 3.27. Calc. for $C_{42}H_{34}NPSNi$: C, 74.80; H, 5.08; N, 2.08%.

### 2.12. $Ni(\eta^5$-$C_5H_5)(PPh_3)(SC_6H_4NC(H)$- $C_6H_4OCH_2C_6H_5)$ (2b)

A green solid with a yield of 0.34 g (54%) was obtained. $^1H$-NMR (CDCl$_3$, $\delta$ ppm): 8.51 (s, 1H, N=C(H)), 7.97 (d, 2H, $J_{HH} = 8.4$ Hz, $C(H)C_6H_4$), 7.71 (m, 6H, PPh$_3$), 7.44 (m, 15H, PPh$_3$, $OCH_2C_6H_5$, $NC_6H_4$), 7.19 (d, 2H, $J_{HH} = 8.4$ Hz, $OC_6H_4$), 6.90 (d, 2H, $J_{HH} = 8.4$ Hz, $SC_6H_4$), 5.30 (s, 2H, $OCH_2$), 5.15 (s, 5H, $\eta^5$-$C_5H_5$). $^{31}P\{^1H\}$-NMR ($\delta$ ppm): 35.77. Anal. Found: C, 72.19; H, 5.20; N, 1.83. Calc. for $C_{43}H_{36}NOPSNi$: C, 72.79; H, 5.82; N, 1.97%.
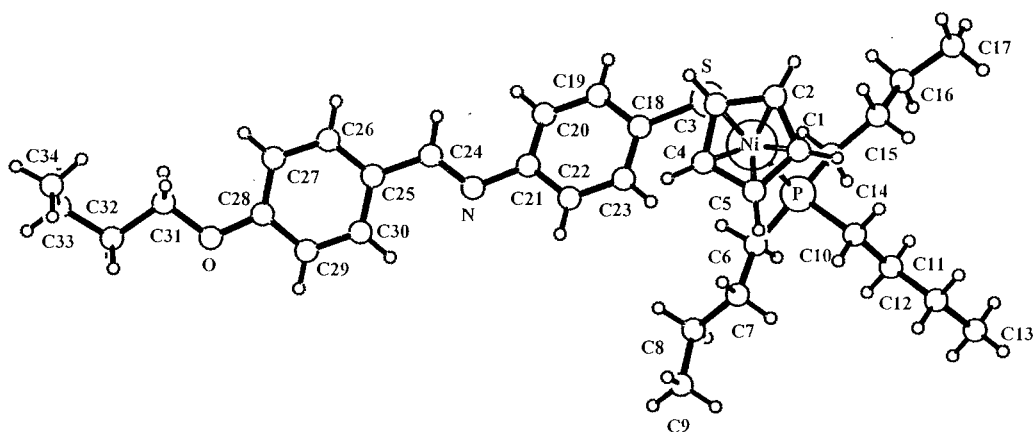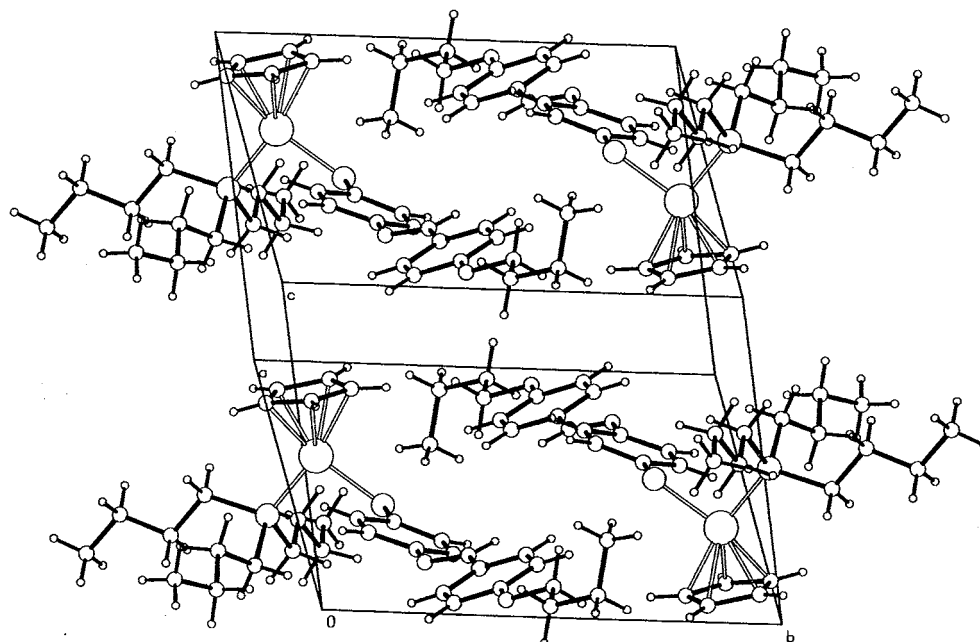


Fig. 5. Molecular structure of **3a**.



Fig. 6. Packing diagram for **3a**.

### 2.13. Ni($\eta^5$-C$_5$H$_5$)(PPh$_3$)(SC$_6$H$_4$NC(H)C$_6$H$_4$OC$_4$H$_9$) (3b)

A brown solid with a yield of 0.38 g (74%) was obtained $^1$H-NMR (CDCl$_3$, $\delta$ ppm): 8.38 (s, 1H, N=C(H)), 7.80 (d, 2H, $J_{HH} = 8.8$ Hz, C(H)C$_6$H$_4$), 7.70 (t, 6H, PPh$_3$), 7.38 (s, 11H, PPh$_3$, NC$_6$H$_4$), 6.95 (d, 2H, $J_{HH} = 8.4$ Hz, OC$_6$H$_4$), 6.85 (d, 2H, $J_{HH} = 6.4$ Hz, SC$_6$H$_4$), 5.13 (s, 5H, $\eta^5$-C$_5$H$_5$), 4.02 (t, 2H, OCH$_2$), 1.78 (q, 2H, OCH$_2$H$_2$), 1.49 (q, 2H, OCH$_2$CH$_2$CH$_2$), 0.99 (t, 3H, CH$_3$). $^{31}$P{$^1$H}-NMR ($\delta$ ppm): 35.40. Anal. Found: C, 71.89; H, 6.39; N, 2.11. Calc. for C$_{40}$H$_{38}$NOPSNi: C, 71.66; H, 5.71; N, 2.09%.

### 2.14. Ni($\eta^5$-C$_5$H$_5$)(PPh$_3$)(SC$_6$H$_4$NC(H)C$_6$H$_4$OC$_8$H$_{17}$) (5b)

A brown solid with a yield of 0.33 g (87%) was obtained. $^1$H-NMR (CDCl$_3$, $\delta$ ppm): 8.38 (s, 1H, N=C(H)), 7.80 (d, $J_{HH} = 8.8$ Hz, C(H)C$_6$H$_4$), 7.71 (t, 8H, PPh$_3$, NC$_6$H$_4$), 7.39 (m, 9H, PPh$_3$), 6.95 (d, 2H, $J_{HH} = 8.80$ Hz, OC$_6$H$_4$), 6.85 (d, 2H, $J_{HH} = 8.6$ Hz, SC$_6$H$_4$), 5.13 (s, 5H, $\eta^5$-C$_5$H$_5$), 4.02 (t, 2H, OCH$_2$), 1.78 (q, 2H, OCH$_2$CH$_2$), 1.6–1.16 (m, 10H, alkoxy), 0.88 (t, 3H, CH$_3$) $^{31}$P-NMR (CDCl$_3$, $\delta$ ppm): 35.40. Anal. Found: C, 72.54; H, 6.44; N, 2.17. Calc. for C$_{44}$H$_{46}$NOPSNi: C, 72.41; H, 6.38; N, 1.93%.

### 2.15. Ni($\eta^5$-C$_5$H$_5$)(PPh$_3$)(SC$_6$H$_4$NC(H)C$_6$H$_4$OC$_{10}$H$_{21}$) (6b)

A brown solid with a yield of 0.36 g (82%) was obtained. $^1$H-NMR (CDCl$_3$, $\delta$ ppm): 8.38 (s, 1H, N=C(H)), 7.80 (d, 2H, $J_{HH} = 8.8$ Hz, C(H)C$_6$H$_4$), 7.72 (t, 8H, PPh$_3$, NC$_6$H$_4$), 7.39 (m, 9H, PPh$_3$), 6.95 (d, 2H, $J_{HH} = 8.8$ Hz, OC$_6$H$_4$), 6.85 (d, 2H, $J_{HH} = 8.8$ Hz, SC$_6$H$_4$), 5.13 (s, 5H, $\eta^5$-C$_5$H$_5$), 4.01 (t, 2H, OCH$_2$), 1.78 (q, 2H, OCH$_2$CH$_2$), 1.58–1.28 (m, 14H, alkoxy), 0.89 (t, 3H, CH$_3$). $^{31}$P-NMR (CDCl$_3$, $\delta$ ppm): 35.38. Anal. Found: C, 73.19; H, 6.79; N, 1.45. Calc. for C$_{46}$H$_{50}$NOPSNi: C, 73.22; H, 6.68; N, 1.86%.

### 2.16. Ni($\eta^5$-C$_5$H$_5$)(PPh$_3$)(SC$_6$H$_4$NC(H)C$_6$H$_4$OC$_{14}$H$_{29}$) (7b)

A brick-red solid with a yield of 0.72 g (68.0%) was obtained. $^1$H-NMR (CDCl$_3$, $\delta$ ppm): 8.38 (s, 1H, N=C(H)), 7.80 (d, 2H, $J_{HH} = 8.4$ Hz, C(H)C$_6$H$_4$), 7.70 (t, 6H, PPh$_3$), 7.38 (br s, 11H, PPh$_3$, NC$_6$H$_4$), 6.95 (d, 2H, $J_{HH} = 8.8$ Hz, OC$_6$H$_4$), 6.85 (d, 2H, $J_{HH} = 8.4$ Hz

SC$_6$H$_4$), 5.13 (s, 5H, $\eta^5$-C$_5$H$_5$), 4.01 (t, 2H, OCH$_2$), 1.80 (q, 2H, OCH$_2$CH$_2$), 1.26 (br s, 22H, alkoxy), 0.88 (t, 3H, CH$_3$). $^{31}$P{$^1$H}-NMR ($\delta$ ppm): 35.41. Anal. Found: C, 73.82; H, 7.22; N, 1.32. Calc. for C$_{50}$H$_{58}$NOPSNi: C, 74.08; H, 7.21; N, 1.73%.

### 2.17. Ni($\eta^5$-C$_5$H$_5$)(PPh$_3$)(SC$_6$H$_4$NC(H)C$_6$H$_4$OC$_{16}$H$_{33}$) (8b)

A brick-red solid with a yield of 0.49 g (77%) was obtained. $^1$H-NMR (CDCl$_3$, $\delta$ ppm): 8.38 (s, 1H, N=C(H)), 7.80 (d, 2H, $J_{HH} = 8.4$ Hz, C(H)C$_6$H$_4$), 7.70 (m, 6H, PPh$_3$), 7.38 (m, 11H, PPh$_3$, NC$_6$H$_4$), 6.95 (d, 2H, $J_{HH} = 8.40$ Hz, OC$_6$H$_4$), 6.85 (d, 2H, $J_{HH} = 8.6$ Hz, SC$_6$H$_4$), 5.13 (s, 5H, $\eta^5$-C$_5$H$_5$), 4.01 (t, 2H, OCH$_2$), 1.80–1.25 (m, 28H, alkoxy), 0.88 (t, 3H, CH$_3$). Anal. Found: C, 74.22; H, 7.79; N, 1.53. Calc. for C$_{52}$H$_{62}$NOPSNi: C, 74.46; H, 7.45; N, 1.67%.

### 2.18. Ni($\eta^5$-C$_5$H$_5$)(PPh$_3$)(SC$_6$H$_4$NC(H)C$_6$H$_4$OC$_{20}$H$_{41}$) (9b)

A brick-red solid with a yield of 0.75 g (65.0%) was isolated. $^1$H-NMR (CDCl$_3$, $\delta$ ppm): 8.31 (s, 1H, N=C(H)), 7.80 (d, 2H, $J_{HH} = 8.8$ Hz, C(H)C$_6$H$_4$), 7.70 (t, 6H, PPh$_3$), 7.38 (s, 11H, PPh$_3$, NC$_6$H$_4$), 6.95 (d, 2H, $J_{HH} = 8.8$ Hz, OC$_6$H$_4$), 6.85 (d, 2H, $J_{HH} = $ Hz, SC$_6$H$_4$), 5.13 (s, 5H, $\eta^5$-C$_5$H$_5$), 4.01 (t, 2H, OCH$_2$), 1.78 (q, 2H, OCH$_2$CH$_2$), 1.27 (s, 34H, alkoxy), 0.88 (t, 3H, CH$_3$). $^{31}$P{$^1$H}-NMR ($\delta$ ppm): 35.40. Anal. Found: C, 74.74; H, 7.15; N, 1.45. Calc. for C$_{56}$H$_{70}$NOPSNi: C, 75.08; H, 7.87; N, 1.56%.

## 3. Results and discussion

### 3.1. Synthesis of ligands

The Schiff base ligands, HSC$_6$H$_4$NC(H)C$_6$H$_4$O-C$_n$H$_{2n+1}$ ($n = 4$ (**3**), 6 (**4**), 8 (**5**), 10 (**6**), 14 (**7**), 16 (**8**), 20 (**9**)) and HSC$_6$H$_4$NC(H)C$_6$H$_4$R″ (R″ = C$_6$H$_5$ (**1**), OCH$_2$-C$_6$H$_5$ (**2**)), were prepared by condensation of equimolar amounts of 4-aminothiophenol and the appropriate aldehydes in ethanol Eq. (1). The products precipitated as yellow solids or thick oils within 30 min and were recrystallised from CH$_2$Cl$_2$–hexane solution at −15 °C. The yields ranged from 60 to 100%. The analytical data of these ligands are presented in Table 1.
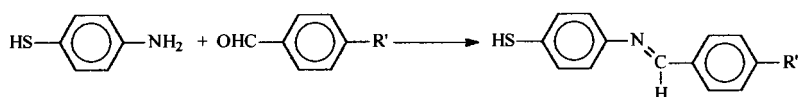


(R′ = C$_6$H$_4$, OCH$_2$C$_6$H$_5$, OC$_n$H$_{2n+1}$; n = 2, 4, 6, 8, 10, 14, 16, 20)

### 3.2. Synthesis and characterisation of complexes

The above ligands were treated with either Ni($\eta^5$-C$_5$H$_5$)(PBu$_3$)Br or Ni($\eta^5$-C$_5$H$_5$)(PPh$_3$)Br to form the new complexes according to previously reported procedures [3]. The complexes were recrystallised from CH$_2$Cl$_2$–hexane at $-15$ °C to give analytically pure products in yields ranging from 30 to 88%. $^1$H-NMR spectral data showed that thiolato resonance of the complexes and that of free ligands were very similar. Changes in the substituents of the thiolato ligands also had no significant influence on the electronic environment of either the cyclopentadienyl or the phosphine ligands. The $^1$H-NMR spectra gave cyclopentadienyl resonance at 5.26–5.28 ppm (**1a**–**9a**) and 5.13–5.15 ppm (**1b**–**9b**) and $^{31}$P-NMR spectra at ca. 22.4 ppm (**1a**–**9a**) and 35.5 ppm (**1b**–**9b**). These differences in peak values between the PBu$_3$ and PPh$_3$ complexes appear to be independent of the nature of the thiolato ligands. Similar chemical shifts have been reported for Ni($\eta^5$-C$_5$H$_5$)(PR$_3$)(SC$_6$H$_4$X-4) (X = Cl, Br, NH$_2$) {R = Bu (5.25, 22.4 ppm), R = Ph (5.13, 35.4 ppm)} [17] and Ni($\eta^5$-C$_5$H$_5$)(PR$_3$)(SC$_6$H$_4$N=CHC$_6$H$_4$X-4$'$) {X = F, Cl, Br, H, OH, Me; R = Bu (5.27, 22.4 ppm), R = Ph (5.14, 35.4 ppm)} [3]. The basicity of the phosphine thus determines the cyclopentadienyl resonance, with the more basic PBu$_3$ deshielding the cyclopentadienyl ligand.

### 3.3. Thermal studies

Thermal behaviour of the Schiff base ligands and their cyclopentadienylnickelphosphino complexes were investigated by TGA and DSC as well as polarising hot-stage microscope. They were generally stable up to 180 °C before decomposing, however none of the ligands or the complexes showed any birefringence on heating and therefore are not liquid crystalline. The absence of liquid crystalline behaviour by the Schiff base compounds may be due to the terminal SH group. Most of organic compounds that are mesogenic feature nitro, cyano, halo, alkoxy or alkyl groups [18]. It is also known that when there is a potential for hydrogen bonding between molecules of a compound, mesogenic behaviour may be precluded [4a]. In the Schiff base ligands reported here the possibility of hydrogen bonding exists; which would involve the interaction of the thiol hydrogens with the alkoxy oxygens. Hydrogen bonding in the ligands is supported by the presence of S···H and N···H distances in the packing of **3a** (vide infra) that are in the range for hydrogen bonding [19]. Hence this could account for the lack of mesogenic properties when compounds **1**–**9** were heated.

The absence of mesogenic behaviour for the nickel complexes is also not surprising since there are no known bulky metal phosphine complexes that are liquid crystals. In the known mesogenic metal phosphine complex Pt(PMe$_3$)$_2$(C≡CC$_6$H$_4$-4-OC$_n$H$_{2n+1}$)$_2$ [20], the phosphine is less bulky. The lack of mesogenic behaviour for the PBu$_3$ and PPh$_3$ complexes might be due to their steric bulk, which prevents regular ordering on melting. This steric prevention to regular packing is also compounded by the presence of the cyclopentadienyl ring, which is out-of-plane of the phenyl rings of the thiolato ligand, as well as the geometry around the nickel centre. These are some of the issues that need to be addressed for these complexes to be mesogenic. One of the ways of concealing these features is to increase the number of rings in the ligand backbone [21].

Generally, the melting point of both the ligands and the complexes is dependent on the substituent in the 4$'$ position of the ligand (Table 2). The PBu$_3$ complexes also melted at considerably lower temperatures than their PPh$_3$ analogues, some even 60 °C lower. When the substituent was an alkoxy group, the longer the alkoxy chain length the lower the melting point; though some leveling off effect seem to set in when the alkoxy carbons exceeded 10. Similar levelling off of the melting points has previously been observed [22]. For phenyl and benzyloxy substituted ligands the melting points were higher than their alkoxy analogues.

From the TGA data two thermal decomposition pathways could be established which were dependent on the phosphine substituent. Complexes that have PPh$_3$ initially lost the cyclopentadienyl ligand followed by the loss of the phosphine and rapture of the Schiff base ligand (Scheme 1a). Fig. 1 shows representative TGA-DSC curves for the PPh$_3$ complex series, revealing three steps of the decomposition in the TGA and four peaks in the DTA. The first step in the decomposition sequence occurred at 180 °C and corresponds to the loss of the cyclopentadienyl ligand accompanied by a large exothermic effect in the DSC curve. The second step is the gradual endothermic process in the temperature range 190–320 °C centred at 248.5 °C, corresponding to the loss of PPh$_3$ ligand. In comparison to the PBu$_3$ complexes, the PPh$_3$ ligand is lost at a relatively higher temperature suggesting a stronger Ni–P bond. The third step centred at about 400 °C was the exothermic rapture and subsequent loss of the Schiff base moiety, leaving a residual mass that corresponded to the Ni(SC$_6$H$_5$) moiety. The PBu$_3$ analogue, on the other hand, decomposed first by simultaneous loss of cyclopentadienyl and phosphine ligand followed by the rupturing the Schiff base ligand (Scheme 1b). Fig. 2 shows representative TGA-DSC curves for PBu$_3$ complex series. The residual mass in all the cases correspond to a Ni(SC$_6$H$_5$) moiety. The above thermal decomposition pathways demonstrate the relative strengths of the three Ni–ligand interactions. The strongest of these bonds appear to be the Ni–S bond in both types of complexes, which stays intact even at

temperatures above 800 °C. It is interesting to note that the Ni–P bonds of the more basic phosphine ($PBu_3$) only breaks around 200 °C, whilst those of the less basic phosphine ($PPh_3$) are only stable up to about 300 °C.

### 3.4. Molecular structures of 1a and 3a

The molecular structures of **1a** and **3a** determined by X-ray crystallography are shown in Figs. 3 and 5 and confirm that the proposed structures derived from the analytical data are correct. A selection of crystal data and structure refinement parameters for **1a** and **3a** is given in Table 3. Selected bond angles and distances for **1a** and **3a** are shown in Tables 4 and 5, respectively. The structures are typical of monocyclopentadienylnickel complexes that have a monophosphine ligand. The cyclopentadienyl centroid–nickel bond distances in **1a** and **3a** are 1.750(3) and 1.752(3) Å, respectively and lie within the range 1.743–1.764 Å found for complexes $Ni(\eta^5\text{-}C_5H_5)(PR_3)(SC_6H_4X)$ (R = Ph, Bu or Et; E = S, Se or Te; X = H, Cl or Me) and $Ni(\eta^5\text{-}C_5H_5)(PR_3)\text{-}(SC_6H_4NC(H)C_6H_4X\text{-}4)$ (R = Ph or Bu; X = Br or Me) [3,17,23]. The Ni–S distances in **1a** (2.184(1) Å) and **3a** (2.192(1) Å) and the Ni–P distances in **1a** (2.145(1) Å and **3a** (2.145(1) Å) are all similar to distances of Ni–S bonds and Ni–P bonds in cyclopentadienylnickel(II) complexes. The N=C double bond is slightly longer at 1.271(3) Å, compared to 1.261(5) and 1.258(5) Å [24]. However, molecular packing in the unit cell of **1a** (Fig. 4) is different from the packing in $Ni(\eta^5\text{-}C_5H_5)$ $(PPh_3)(SC_6H_4NC(H)C_6H_4Br\text{-}4)$ and $Ni(\eta^5\text{-}C_5H_5)\text{-}(PBu_3)(SC_6H_4NC(H)C_6H_4Me\text{-}4)$ [3] the latter two having the same molecular packing as **3a** (Fig. 6). Even though packing in **1a** is also pairwise as in the two Schiff base nickel complexes above [3], the pairwise association in **1a** has a pair with cyclopentadienylnickel phosphine at one end. For the complexes $Ni(\eta^5\text{-}C_5H_5)(PPh_3)(SC_6H_4NC(H)C_6H_4Br\text{-}4)$ and $Ni(\eta^5\text{-}C_5H_5)\text{-}(PBu_3)(SC_6H_4NC(H)C_6H_4Me\text{-}4)$ each pair consists of head-to-tail, tail-to-head packing, if the cyclopentadienyl end is considered to be the head. Thus the packing in **1a** is two head-to-tail molecular arrangements next to each other. The head-to-tail orientation in **1a** is partly due to the hydrogen bonds S1···H24 (3.101(2) Å) and N1···H36 (2.976(2) Å) that link two tails to each other. The distances are in the range found for hydrogen bonding [19]. Another feature in the structure of **1a** is that all three benzene rings of the thiolato ligand are not co-planar, with the ring next to the sulfur atom at right angles to the terminal ring.

### 4. Conclusions

Nickel complexes containing thiolato Schiff base ligands with long alkoxy chains are readily prepared.

Their thermal stability is independent of the nature of the phosphine but their decomposition pathways differ. Complexes containing $PPh_3$ have stronger Ni–P bonds compared to their $PBu_3$ analogues. Melting points of complexes were lower for all $PBu_3$ complexes compared to their $PPh_3$ analogues and were also progressively lower as the alkoxy chain length increased up to $C_{10}$ after which the melting point levelled off.

### Acknowledgements

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