ELSEVIER

Journal of Organometallic Chemistry 656 (2002) 262–269

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Bimetallic nickel complexes with bridging dithiolato Schiff base ligands: synthesis, mass spectral characterisation and electrochemistry

Richard M. Moutloali [a], Funzani A. Nevondo [a], James Darkwa [a,*], Emmanuel I. Iwuoha [a], William Henderson [b]

[a] *Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville 7535; South Africa*
[b] *Department of Chemistry, University of Waikaito, Private Bag 3105, Hamilton, New Zealand*

Received 11 February 2002; accepted 18 May 2002

Abstract

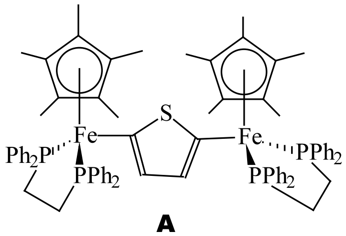
Schiff base dithiols with thiophene or phenyl linkers were prepared from condensation of the dialdehydes 2,5-$(OHC)_2C_4H_2S$, 1,3-$(OHC)_2C_6H_4$, 1,4-$(OHC)_2C_6H_4$ and 1,4′-$(OHC)_2(C_6H_4)_2$ with 4-$H_2NC_6H_4(SH)$. The Schiff base dithiols readily reacted with $Ni(\eta^5\text{-}C_5H_5)(PR_3)Br$ (R = Bu or Ph) in the presence of Et_3N to form bimetallic complexes $(\eta^5\text{-}C_5H_5)(PR_3)Ni{-}SC_6H_4N{=}C(H)ArC(H){=}NC_6H_4S{-}Ni(PR_3)(\eta^5\text{-}C_5H_5)$ (Ar = C_4H_2S (**6**), 1,3-C_6H_4 (**7**), 1,4-C_6H_4 (**8**), 1,4′-$(C_6H_4)_2$ (**9**). The bimetallic nature was established from elemental analysis and mass spectrometry. Cyclic voltammetry of complexes **6**, **8** and **9** are indicative of electronic communication between the nickel centres via the bridging dithiolato Schiff base ligands. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dithiolato Schiff base; Bimetallic nickel complexes; Mass spectrometry; Cyclic voltammetry

1. Introduction

Compounds that have units with π-conjugation ability have been investigated for their potential use as nonlinear optical materials [1], light emitting diodes [2], and as molecular wires [3]. Homo- and hetero-bimetallic complexes with π-conjugated bridging ligands are particularly interesting for their potential application as molecular wires [3]. Most of these bridged bimetallic complexes feature polyene bridging units, as polyenes are known to allow long range electronic coupling through π-delocalisation [4]. In these polyene-bridged metal complexes, the metal–ligand interaction is usually a metal–carbon σ-bond, but the bond assumes some double bond character through electron delocalisation as one of the metal centres is oxidised. This mechanism allows electron communication in both homometallic polymers with Ni, Pd and Pt [5,6] and heterobimetallic (Ru/Pd, Fe/Pd and Fe/Ni) [7] oligomers with the 1,4-diethynylbenzene unit ($-C{\equiv}C{-}C_6H_4{-}C{\equiv}C-$).

A recent report by Guerchais et al. [7] has demonstrated that communication between two iron centres can be effected through bridging thiophene (A) and biphenyl (B) units when one of the iron centres is oxidised. Such intramolecular electron transfer should also be possible if the bridging ligand has a metal–sulphur bond. For example a number of phenylethynyl thiolate molecules inserted into alkyl thiolate matrix are known to conduct electrons when adsorbed on gold surfaces [8]. This demonstrates that sulphur bound to a metal is capable of acting as electron conduit from a metal if there is a π-conjugated organic molecule attached to it.

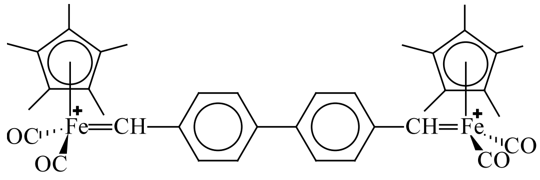


A

---

* Corresponding author
E-mail address: jdarkwa@uwc.ac.za (J. Darkwa).

PII: S0022-328X(02)01626-1



B

Other complexes featuring metal σ-acetylides like Ni(C≡C–C_6H_5)(PPh_3)(η^5-C_5H_5) have oxidisable metal centres and show nonlinear optical properties, because the donor–acceptor composition is enhanced by the π-conjugation in the ligand [9]. We envisage that by using Schiff base ligands with two end sulphur atoms that bridge the two metal centres, we could effect the transfer of electrons via the bridging ligands from one metal to the other. Such dithiolato complexes should be easy to prepare since alkyldithiols are known to form bridged cyclopentadienyl complexes like (η^5-C_5H_5)(PBu_3)Ni–S$(CH_2)_n$S–Ni(PBu_3)(η^5-C_5H_5) ($n = 2$, 4, 6) [10]. This illustrates that the (η^5-C_5H_5)(PBu_3) fragment is capable of binding dithiolato ligands. We report here the synthesis of cyclopentadienylnickel complexes with bridging dithiolato Schiff base ligands. We have also investigated their electrochemistry to demonstrate that the π-conjugated dithiolato Schiff base ligands allow electronic communication between the two nickel atoms.

2. Experimental

2.1. Materials and instrumentation

The starting material 4-aminothiophenol was obtained from Fluka and used as received, whilst NiBr(PR_3)(η^5-C_5H_5) (R = Bu, Ph) [11a,11b] and bis(diphenylphosphino)ferrocenepalladium dichloride $PdCl_2$(dppf) [12] were prepared by the literature methods. Reagent grade hexane was distilled and stored over molecular sieves, while toluene was distilled over sodium and CH_2Cl_2 from P_2O_5. All reactions were performed using standard Schlenk techniques under a dinitrogen atmosphere.

The ^{1}H- and $^{31}P\{^1H\}$-NMR spectra were acquired on a Varian Gemini 2000 spectrometer at 200 and 80.96 MHz, respectively, and referenced to residual $CHCl_3$ (δ 7.26) and externally to PPh_3 (δ −5.00), respectively. Elemental analysis was performed on a Carlo Erba NA 1500 in the Department of Chemistry at the University of the Western Cape. Fast Atom Bombardment (FABMS) were run on a Fannigan MAT GCQ GC–MS and Electrospray mass spectra (ESMS) were run on a VG Platform II instrument in a positive ion mode. Electrochemical measurements were performed on a BAS 50W instrument using a standard three electrode electroanalytical cell configuration equipped with a platinum disc working electrode (1.5 mm diameter), a silver/silver chloride (Ag/AgCl) reference electrode and a silver wire counter electrode. Supporting electrolyte was tetrabutylammonium tetrafloroborate (TBA-TFB) [13] as 0.1 M solution in CH_2Cl_2, and the concentration of the analyte was 0.03×10^{-3}M. The potential measurements were referenced internally to the ferrocene/ferrocenium redox peak at 0.441 V.

2.2. Ligand synthesis

2.2.1. $OHCC_6H_4C_6H_4CHO$ (*1*)

Acetone (60 ml) was added to a mixture of 4-formylboronic acid (0.5 g, 3.3 mmol), 4-bromobenzaldehyde (0.61 g, 3.3 mmol), potassium carbonate (1.2 g, 6.6 mmol) and Pd(dppf)Cl_2 (0.5% mol equivalent) and refluxed for 48 h. The resultant mixture was filtered and the solvent removed in vacuo to give an off-white residue, which was chromatographed on silica gel (60 mesh) using 1:1 CH_2Cl_2–hexane eluent. The eluate was evaporated to dryness and the residue recrystallised from CH_2Cl_2–hexane. Yield = 0.5 g (73%). Anal. Calc. for $C_{14}H_{10}O_2$, C, 79.98; H, 4.79. Found: C, 81.14; H, 4.30%. ^{1}H-NMR ($CDCl_3$) δ 10.09 (s, 2H, CHO), 8.01 (d, 4H, $J_{HH} = 8.6$ Hz, $OHCC_6H_4$), 7.80 (d, 4H, $J_{HH} = 8.2$ Hz, $C_6H_4C_6H_4$).

2.2.2. $HSC_6H_4NC(H)$-2-C_4H_2S-5-$C(H)NC_6H_4SH$ (*2*)

To a mixture of 4-aminothiophenol (1.79 g, 14.27 mmol) and 2,5-thiophenedicarboxyaldehyde (0.95 g, 7.13 mmol) was added ethanol (40 ml) and the mixture stirred overnight at room temperature (r.t.). An insoluble yellow precipitate was isolated by suction filtration and washed with ethanol. Yield = 84%. Anal. Calc. for $C_{18}H_{14}N_2S_2$, C, 67.05; H, 4.38; N, 8.68. Found: C, 67.15; H, 4.43; N, 8.71%.

Compounds **3**, **4** and **5** were synthesised in a similar manner to compound **2** using two equivalents of 4-aminothiophenol and one equivalent of the appropriate dicarboxyaldehyde. The products were all insoluble in common organic solvents but gave good elemental analyses.

2.2.3. $HSC_6H_4NC(H)C_6H_4$-3-$C(H)NC_6H_4SH$ (*3*)

A yellow solid was obtained in 87% yield. Anal. Calc. for $C_{20}H_{16}N_2S_2$, C, 68.96; H, 4.59; N, 8.04. Found: C, 68.91; H, 4.66; N, 7.09%.

2.2.4. $HSC_6H_4NC(H)C_6H_4$-4-$C(H)NC_6H_4SH$ (*4*)

A yellow solid was isolated in 84% yield. Anal. Calc. for $C_{20}H_{16}N_2S_2$, C: 68.96; H: 4.59; N: 8.04. Found: C, 68.99; H, 4.73; N, 8.10%.

2.2.5. $HSC_6H_4NC(H)C_6H_4C_6H_4C(H)NC_6H_4SH$ (5)

A yellow precipitate was isolated in a yield of 82%. Anal. Calc. for $C_{26}H_{20}N_2S_2$, C, 73.55; H, 4.75; N, 6.60. Found: C, 73.16; H, 4.74; N, 5.97.

2.3. Complexation of ligands with $NiBr(PR_3)(\eta^5\text{-}C_5H_5)$ (R = Bu or Ph)

All the complexes were synthesised in a similar manner to the procedure described for complex **6**.

2.3.1. $[Ni(\eta^5\text{-}C_5H_5)PBu_3]_2(SC_6H_4NC(H)C_4H_2S\text{-}5\text{-}C(H)NC_6H_4S)$ (6)

A mixture of 2 (0.24 g, 0.69 mmol) and $NiBr(PBu_3)$-(η^5-C_5H_5) (0.53 g, 1.38 mmol) was suspended in toluene to which Et_3N (1.5 ml) was added. The maroon colour changed to dark green after several hours and stirring continued for 72 h. After filtration, the filtrate was evaporated to dryness and the residue recrystallised from CH_2Cl_2–hexane to give a maroon solid in a yield of 69%. Anal. Calc. for $C_{52}H_{76}N_2P_2S_3Ni_2$, C, 64.92; H, 7.81; N, 2.86. Found. C, 65.49; H, 8.32; N, 2.91. ^1H-NMR ($CDCl_3$) δ 8.57 (s, 2H, N=C(H)), 7.62 (d, 4H, J_{HH} = 8.4 Hz, NC_6H_4), 7.40 (s, 2H, C_4H_2S), 6.99 (d, 4H, J_{HH} = 8.4 Hz, SC_6H_4), 5.28 (s, 10H, C_5H_5), 1.54–1.34 (m, 36H, PBu_3), 0.92 (t, 18H, PBu_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ 22.40, (s, PBu_3).

2.3.2. $[Ni(\eta^5\text{-}C_5H_5)PBu_3]_2(SC_6H_4NC(H)C_6H_4\text{-}3\text{-}C(H)NC_6H_4S)$ (7)

A dark green solid was isolated in a yield of 58%. Anal. Calc. for $C_{54}H_{78}N_2P_2S_2Ni_2$, C, 64.92; H, 7.81; N, 2.80. Found: C, 64.90; H, 7.83; N, 2.80. ^1H-NMR ($CDCl_3$) δ 8.55 (s, 2H, N=C(H)), 8.35 (s, 1H, *iso*-C_6H_4), 7.98 (d, 2H, J_{HH} = 8.0 Hz, *iso*-C_6H_4); 7.64 (d, 4H, J_{HH} = 8.4 Hz, NC_6H_4); 7.53 (t, 1H, *iso*-C_6H_4); 6.98 (d, 4H, J_{HH} 8.0 Hz, SC_6H_4); 5.28 (s, 10H, C_5H_5); 1.52–1.34 (m, 36H, PBu_3); 0.92 (t, 18H, PBu_3).

2.3.3. $[Ni(\eta^5\text{-}C_5H_5)PBu_3]_2(SC_6H_4NC(H)C_6H_4\text{-}4\text{-}C(H)NC_6H_4S)$ (8)

A brown solid with a yield of 64% was isolated. Anal. Calc. for $C_{54}H_{78}N_2P_2S_2Ni_2$, C, 64.92; H, 7.81; N, 2.80. Found: C, 65.01; H, 7.83; N, 2.91. ^1H-NMR ($CDCl_3$) δ 8.52 (s, 2H, N=C(H)), 7.95 (s, 4H, $C(H)C_6H_4C(H)$), 7.65 (d, 4H, J_{HH} = 8.4 Hz, NC_6H_4), 7.00 (d, 4H, J_{HH} = 8.4 Hz, SC_6H_4), 5.28 (s, 10H, C_5H_5), 1.54–1.27 (m, 36H, PBu_3), 0.92 (t, 18H, PBu_3).$^{31}P\{^1H\}$-NMR ($CDCl_3$) δ 22.39, (s, PBu_3).

2.3.4. $[Ni(\eta^5\text{-}C_5H_5)PBu_3]_2(SC_6H_4NC(H)\text{-}C_6H_4C_6H_4C(H)NC_6H_4S)$ (9)

A green solid was isolated in a yield of 68%. Anal. Calc. for $C_{60}H_{82}N_2P_2S_2Ni_2$, C, 67.06; H, 7.69; N, 2.61. Found: C, 67.14; H, 7.81; N, 2.78. ^1H-NMR ($CDCl_3$) δ 8.53 (s, 2H, N=C(H)); 7.95 (d, 4H, J_{HH} = 8.4 Hz, $C_6H_4C_6H_4$); 7.74 (d, 4H, J_{HH} = 8.4 Hz, $C_6H_4C_6H_4$); 7.64 (d, 4H, J_{HH} = 8.6 Hz, NC_6H_4); 6.90 (d, 4H, J_{HH} = 8.4 Hz, SC_6H_4); 5.28 (s, 10H, C_5H_5); 1.58–1.34 (m, 36H, PBu_3); 0.93 (t, 18H, PBu_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ 22.41 (PBu_3).

2.3.5. $[Ni(\eta^5\text{-}C_5H_5)PPh_3]_2(SC_6H_4NC(H)C_4H_2S\text{-}5\text{-}C(H)NC_6H_4S)$ (10)

A brown solid was isolated in a yield of 70%. Anal. Calc. for $C_{64}H_{52}N_2S_3P_2Ni_2$, C, 68.32; H, 4.62; N, 2.49. Found: C, 67.78; H, 4.59; N, 2.47. ^1H-NMR ($CDCl_3$) δ 8.55 (s, 2H, N=C(H)), 7.69 (m, 12H, PPh_3), 7.35 (m, 24H, PPh_3, SC_6H_4, C_4H_2S), 6.89 (d, 4H, J_{HH} = 8.2 Hz, SC_6H_4), 5.15 (s, 10H, C_5H_5). $^{31}P\{^1H\}$-NMR ($CDCl_3$) δ 35.33 (s, PPh_3).

2.3.6. $[Ni(\eta^5\text{-}C_5H_5)PPh_3]_2(SC_6H_4NC(H)C_6H_4\text{-}3\text{-}C(H)NC_6H_4S)$ (11)

A black crystalline solid was isolated in 51% yield. Anal. Calc. for $C_{66}H_{54}N_2P_2S_2Ni_2$, C, 70.87; H, 4.83; N, 2.50. Found: C, 70.56; H, 4.81; N, 2.21. ^1H-NMR ($CDCl_3$) δ 8.54 (s, 2H, N=C(H)), 8.28 (s, 1H, C_6H_4), 8.15 (d, 2H, J_{HH} = 8.6 Hz, C_6H_4), 7.98 (d, 1H, J_{HH} = 8.4 Hz, C_6H_4), 7.71 (m, 12H, PPh_3), 7.35 (m, 22H, PPh_3, SC_6H_4,), 6.89 (d, 4H, J_{HH} = 8.6 Hz, SC_6H_4), 5.16 (s, 10H, C_5H_5).

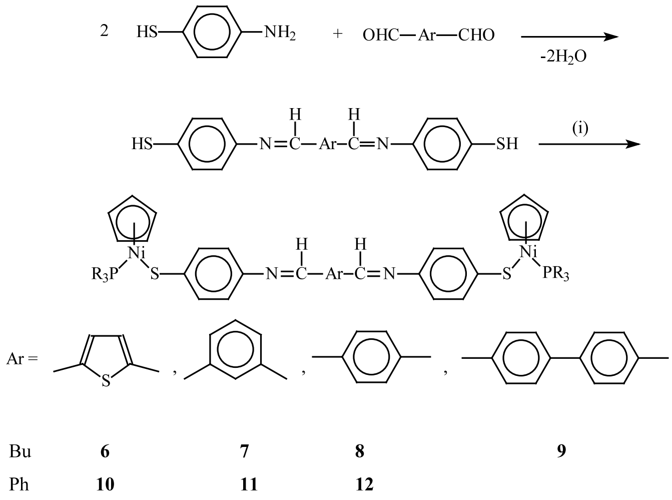
2.3.7. $[Ni(\eta^5\text{-}C_5H_5)PPh_3]_2(SC_6H_4NC(H)C_6H_4\text{-}4\text{-}C(H)NC_6H_4S)$ (12)

A brown solid with a yield of 70% was obtained. Anal. Calc. for $C_{66}H_{54}P_2S_2N_2Ni_2$, C, 68.48; H, 4.53; N, 2.32. Found: C, 68.34; H, 4.68; N, 2.28. ^1H-NMR ($CDCl_3$) δ 8.54 (s, 2H, N=C(H)), 7.97 (s, 4H, C_6H_4), 7.65 (m, 14H, SC_6H_4, PPh_3), 7.42 (m, 18H, PPh_3), 6.92 (d, 4H, J_{HH} = 8.6 Hz, SC_6H_4), 5.16 (s, 10H, C_5H_5).

3. Results and discussions

3.1. Synthesis of complexes

Dithiol Schiff base compounds (**2**–**5**) were prepared by the condensation of two equivalents of 4-aminothiophenol and one equivalent of the appropriate dialdehyde (Scheme 1). The dialdehyde, $OHCC_6H_4C_6H_4CHO$ (**1**), was prepared by the Suzuki coupling reaction of 4-formylboronic acid with 4-bromobenzaldehyde. Compounds **2**–**5** were isolated as yellow insoluble solids, which appeared to be stable to air and moisture. However, they gradually turned reddish maroon on exposure to light over 2 weeks, though their elemental analysis remained the same. We suggest that the colour change from yellow to reddish maroon could be due to isomerisation between *cis* and *trans* forms of the compounds about the imine bonds. A lack of solubility of these compounds in common organic solvents such as



(i) $NiBr(PR_3)(\eta^5\text{-}C_5H_5)$, Et_3N

Scheme 1.

CH_2Cl_2, toluene and THF made it impossible to prove this isomerisation; though a closer examination of the ^{1}H-NMR spectrum of complex **6** (Fig. 1) suggest that a similar isomerisation about the imine might exist when the ligands form a complex with nickel. Although a plausible explanation for the change in colour when compounds **2**–**5** were exposed to sunlight could be oxidation to disulfides, which will also give the same elemental analysis, the possibility of these compounds oxidising to disulfides was not investigated.

The dithiol compounds reacted with two equivalents of $NiBr(PR_3)(\eta^5\text{-}C_5H_5)$ to form toluene soluble products when excess Et_3N was added to this mixture (Scheme 1). The ^{1}H-NMR spectra of the bimetallic nickel products are typical of cyclopentadienylnickel phosphino thiolato complexes [14]. Cyclopentadienyl chemical shifts of 5.28 and 5.16 ppm for the PBu_3 and PPh_3 complexes, respectively, were slightly more downfield compared with 5.27 and 5.13 ppm observed for the mononuclear complexes $Ni(PBu_3)(SC_6H_4X\text{-}4)(\eta^5\text{-}C_5H_5)$ and $Ni(PPh_3)(SC_6H_4X\text{-}4)(\eta^5\text{-}C_5H_5)$ ($X = F$, Cl, Br), respectively, [14a]. The similarities in the cyclopentadienyl chemical shifts in complexes **6**–**12** and those reported by us recently [14], points to the similar electronic environment around the nickel centres in the bimetallic and the monometallic complexes. We expect this similarity in electronic environment in the bimetallic and the monometallic nickel complexes to result in similar electrochemical behaviour as will be discussed later. There is no obvious effect of the aryl or thiophene linkers on the electronic environment of the nickel centres.

In spite of the considerable solubility of the nickel complexes prepared, particularly the PBu_3 analogues, our attempts to grow crystals of complexes **6**–**12** were unsuccessful. We have thus used mass spectrometry to establish the bimetallic nature of these complexes.

3.2. Mass spectral analysis of complexes

Two mass spectra ionisation techniques were used in characterising the bimetallic complexes isolated in this study, namely FAB and ES ionisation. Both of these ionisation sources are perceived to be soft, however, only complex **8** gave a molecular ion with $m/z = 998$ when the ionisation source was FAB (Fig. 2). This shows that FAB ionisation is harsher for these complexes as they readily fragment. Even the softer ESMS gave generally weak peaks and the spectra had a lot of fragmentation. For example while complex **9** gave no molecular ion in its FABMS, ESMS of this complex at a cone voltage of 5 V yielded both $[M+H]^+$ and $[M+$

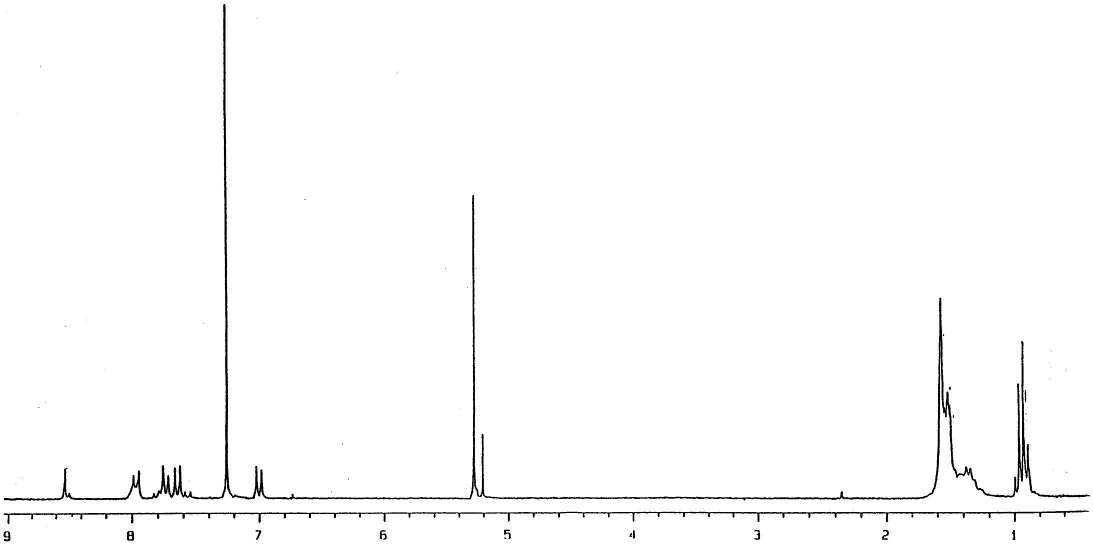


Fig. 1. ^{1}H-NMR spectrum of complex **9**.

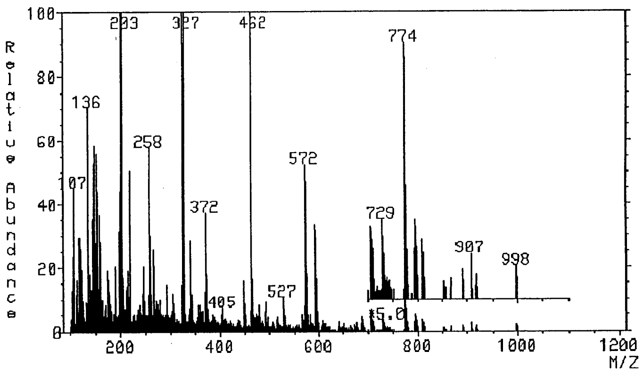


Fig. 2. FABMS of complex **6**.

$NH_4]^+$ molecular ions. On increasing the cone voltage to 20 and 40 V, the former gave only $[M+NH_4]^+$ molecular ion (Fig. 3) while the latter had no molecular ion peak, but only fragmentation peaks. These observations illustrate how harsher conditions easily decompose these bimetallic complexes. We observed no $[2M+H]^+$ or $[2M+NH_4]^+$ ions even at a low cone voltage of 5 V, which is a further indication of how readily molecular ions formed fragment.

In general mass spectroscopy gave structural information about the bimetallic nature of the PBu_3 complexes suggested by ^{1}H-NMR and elemental analysis. However, we were unable to have structural confirmation of the PPh_3 complexes (except complex **8**) from mass spectroscopy. It is quite clear from the fragmentation pattern (Scheme 2) that the observation of molecular ions in the PBu_3 complexes can be attributed to the better σ-donor ability of PBu_3 compared with PPh_3 which contribute to stabilising complexes of the former.

3.3. Electrochemical studies

In order to establish whether the dithiolato Schiff base bridging ligands can act as electron conduit between the nickel centres, cyclic voltammetry experiments were performed on complexes (**6**, **8** and **9**). A major consideration for choosing complexes **6**, **8** and **9** for electrochemical studies was to see how a variation of spacer (Scheme 1) could affect electron conduction. Fig. 4 represents the voltammograms of complexes **6**, **8** and **9** as well as one of the ligands (compound **2**). For example the nature of the redox couples in complex **6** is reminiscent of the coupling of strong adsorption of

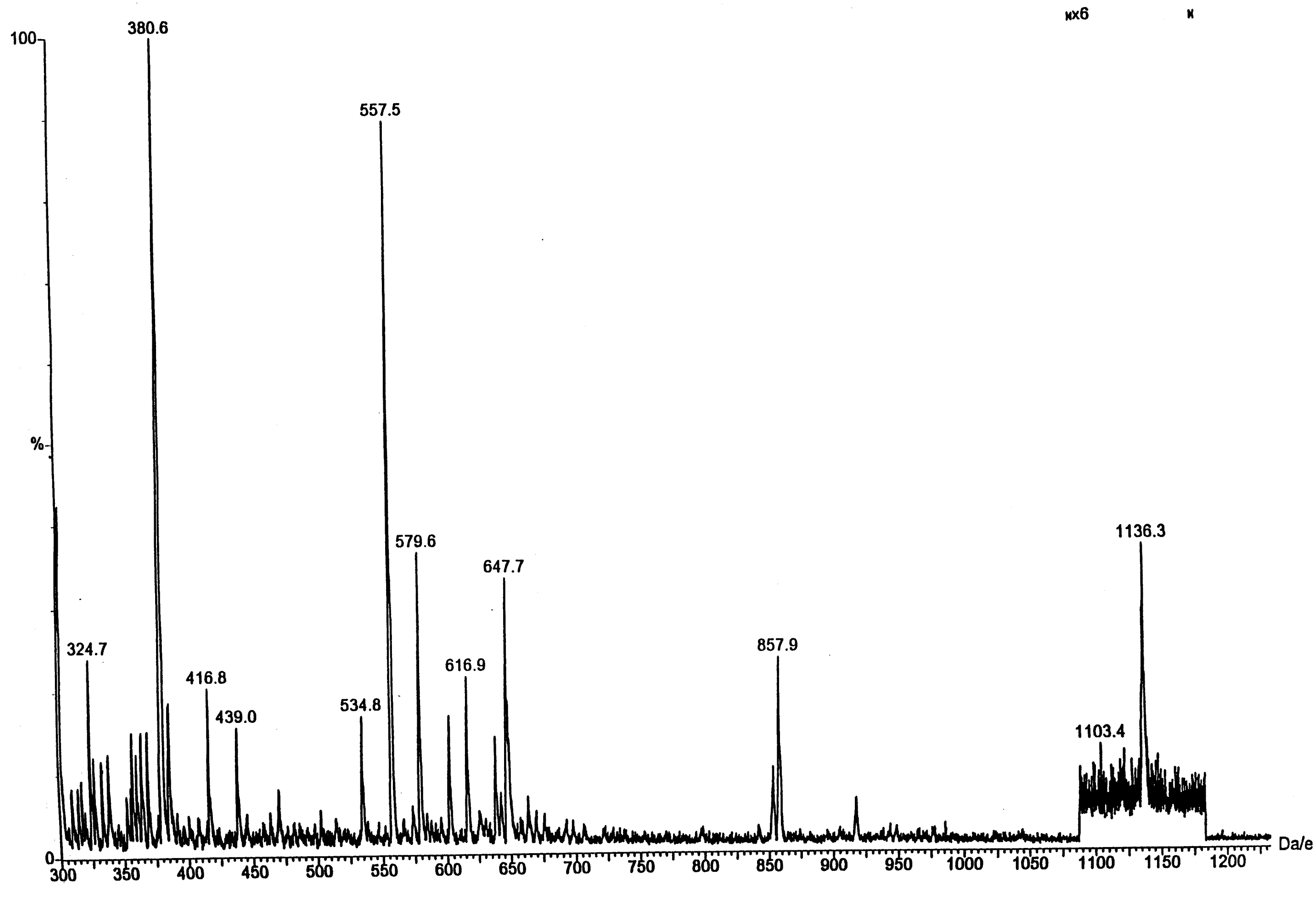
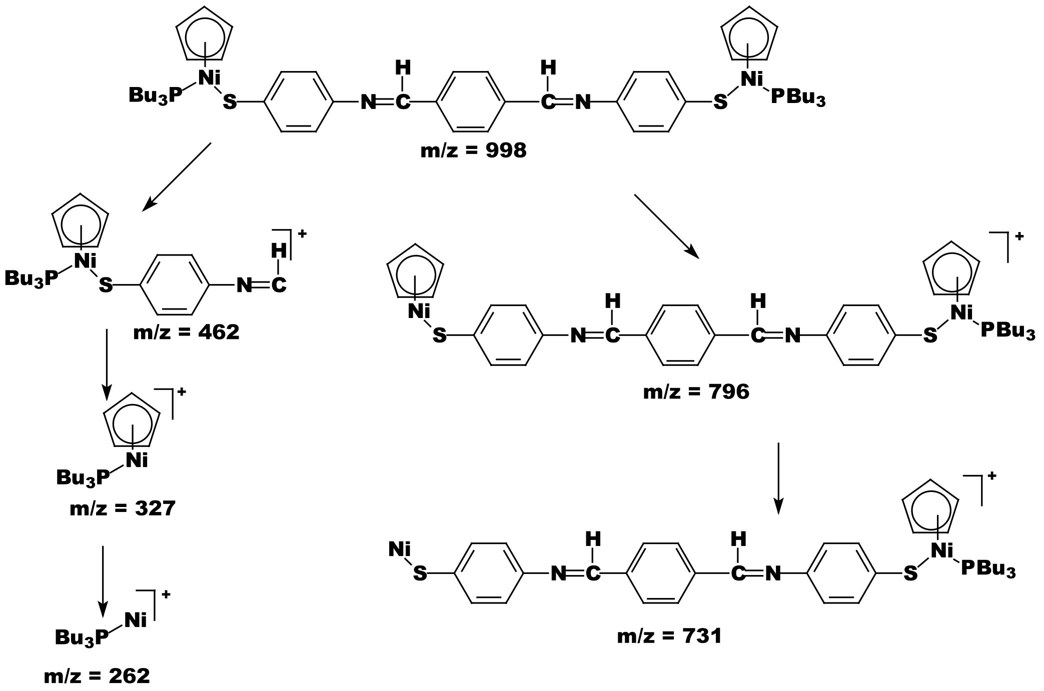


Fig. 3. ESMS of complex **9**.



Scheme 2.

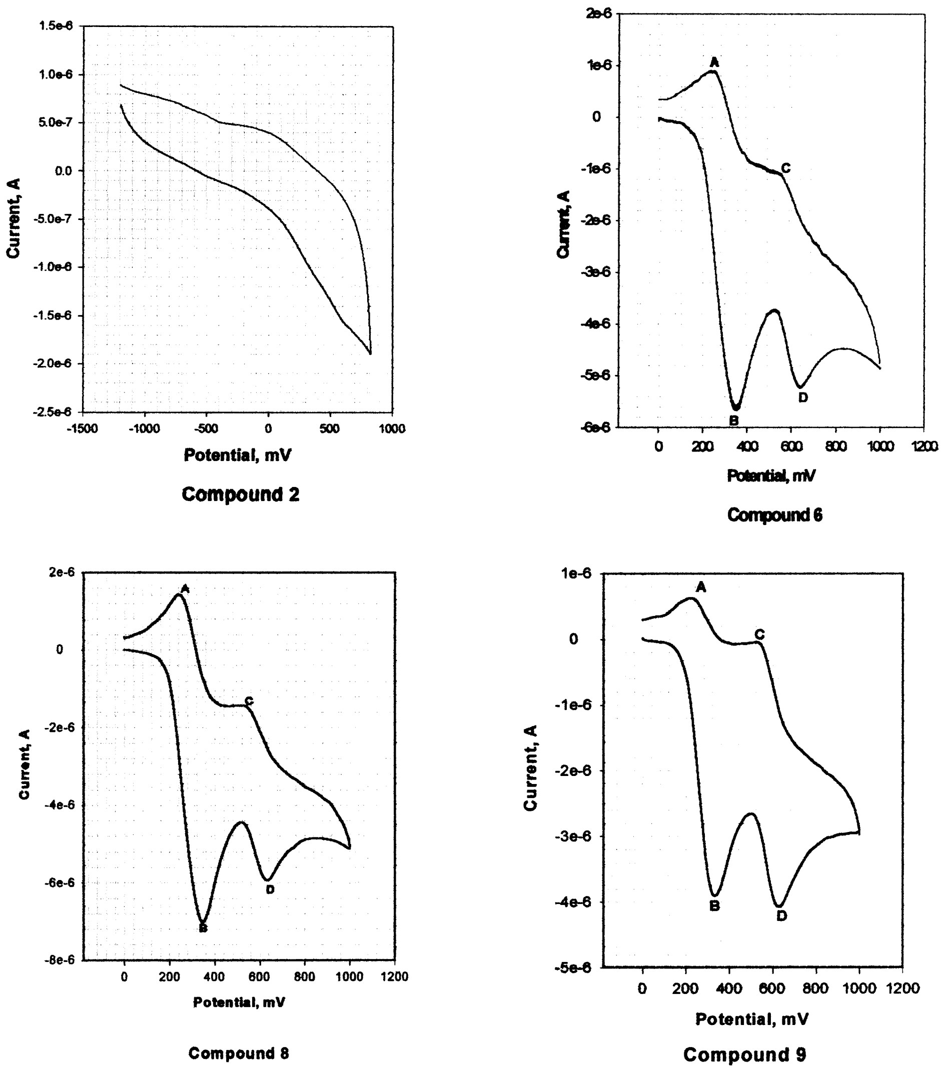
products (C/D: $E_{1/2} = 0.590$ V) on electrode surface to a diffusion controlled electrochemical process (A/B: $E_{1/2} = 0.294$ V) [15]. However, the peak separation ($\Delta E_{pC/D}$) for the second redox process is 0.094 V, a value greater than the upper limit peak separation of 0.065 V for surface-bound species undergoing rapid one electron transfer [16]. In addition the voltammetric peaks in complexes **6**, **8** and **9** are not as symmetrical as expected for adsorbed species. Hence the source of the redox couple C/D cannot be adsorbed species. The peak separation for the first redox couple (($\Delta E_{pA/B}$) is 0.104 V. Since peak separation for both redox couples for **6**, and also for **8** and **9** (Table 1) are greater than 0.060 V, the value for the peak separation of non-equilibrium one electron transfer process, the redox couples in **6**, **8** and **9** are quasi-reversible.

A Tafel analyses ($\ln|i| = \ln i_o - \alpha FE/RT$) of the oxidation wave A/B and the reduction wave of C/D gave a Tafel slope of 0.120 V per decade in each case, as expected for one-electron transfer process. Thus the A/B and C/D redox couples in **6**, **8** and **9** represent two quasi-reversible process which involve the coupling of diffusion controlled electron transfer at the electrode via electron-hopping along the bridging ligands in the bimetallic complexes [15,16].

The cyclic voltammetry of the two starting materials that were used to prepare the complexes were run to establish the centre of the electrochemical activity. The nickel complex, $NiBr(PBu_3)(\eta^5\text{-}C_5H_5)$, had two irreversible peaks at 0.338 and 0.996 V. Because the ligand is insoluble, its cyclic voltammogram was run by depositing a paste of the compound on the working electrode. It showed an irreversible oxidation peak at 0.699 V (Fig. 4). Table 1 shows that the redox behaviour of complexes **6**, **8** and **9** differ from that of the nickel starting materials and ligand **2**. Thus based on the electrochemistry of the ligand **2**, the nickel starting material and of **6**, **8** and **9** the redox activities of **6**, **8** and **9** are two one-electron redox processes.

From Table 1, it is apparent that the introduction of the electron rich sulphur ligands lowers the oxidation potentials of the nickel starting material and that of the ligands. Compared with $Ni(PBu_3)(SC_6H_4X\text{-}4)(\eta^5\text{-}C_5H_5)$ (X = Cl (0.36 V), Br (0.32 V)) [14a] and $Ni(PBu_3)(SC_6H_4N{=}C(H)C_6H_4X\text{-}4)(\eta^5\text{-}C_5H_5)$ (X = F (0.35 V), Cl (0.37 V), Br (0.36 V), Me (0.35 V)) [14b] oxidation potentials for **6**, **8** and **9** are also lower. The quasi-reversible redox couples found for **6**, **8** and **9** are indicative of stabilisation of the oxidised species by the presence of the electron rich thiolato ligands. This observation is in line with those of the mononickel complexes reported by us recently [14]. Literature reports on the electrochemical oxidation of μ-thiolato nickel complexes, $[(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}SR)]_2$, show they form unstable radical cations if the thiolato ligand has an alkyl group [17], however, the radical cations are stabilised by aryl thiolato ligands [18]. Hence the quasi-reversibility associated with the thiolato Schiff base complexes (**6**, **8** and **9**) must be the result of π-conjugated units that link the sulphur ends of the bridging ligands.

Cyclic voltammetry can be used to establish electronic communication between two metal centres with a bridging ligand [19]. Usually this involves observing



Compound 2

Compound 6

Compound 8

Compound 9

Fig. 4. Cyclic voltammogram of **2**, **6**, **8** and **9** at a scan rate of 300 mV s^{-1}.

two reversible redox couples that are separated. For example redox couple separation, ΔE, for $[(\eta^5\text{-}C_5H_5)FeL]_2(\mu\text{-}CH{=}CH{=}CH)$ ($L = CO$, PMe_3, PPh_3) varies from 0.41 to 0.45 V [20] whereas for $[(\eta^5\text{-}C_5H_5)FeCO]_2(\mu\text{-}1,4\text{-}C_6F_4)$ has a redox couple separation, ΔE of 0.28 V [21]. We observe ΔE values of 0.296, 0.296 and 0.300 V, respectively, for the quasi-reversible redox peaks in **6**, **8** and **9** and suggest that ΔE values of **6**, **8** and **9** are indicative of electronic communication between the two nickel centres in these complexes. As in the $[(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}SR)]_2$ systems [18], electrochemical activities in **6**, **8** and **9** are two sequential one electron processes. Thus the mechanism of electronic communication after the first oxidation could be π-electron delocalisation as observed for the diiron polyene systems [4,19–21].

Table 1
Cyclic voltammetry data of complexes $NiBr(PBu_3)(\eta^5\text{-}C_5H_5)$, **6**, **8** and **9**

Complex	$E_{1/2}$ (V)		$I_{p,a}/I_{p,c}$		ΔE_p (V)		ΔE (V)
	A/B	C/D	A/B	C/D	A/B	C/D	
$NiBr(PBu_3)(\eta^5\text{-}C_5H_5)$	0.338	0.996					
6	0.294	0.590	1.10	0.85	0.104	0.094	0.296
8	0.298	0.594	1.00	0.85	0.104	0.094	0.296
9	0.285	0.583	1.13	0.77	0.103	0.087	0.300

$\Delta E_p = |E_{p,ox} - E_{p,red}|$, $\Delta E = |E_{1/2,C/D} - E_{1/2,A/B}|$.

In summary, we have successfully prepared binuclear nickel complexes that have bridging dithiolato ligands from Schiff base dithiols. The bimetallic nature of the complexes synthesised was established by mass spectrometry, mainly ESMS. Electronic communication between the nickel centres was established by cyclic voltammetry. Thus electronic coupling of the two nickel centres was possible even though the nickel–sulphur bonds in these complexes is predominantly a σ-bond.

Acknowledgements

Financial support from the National Research Foundation (South Africa) (RMM, FAN, JD) and ESKOM (South Africa) is gratefully acknowledged. We also wish to thank Mr. R.M. Mampa (University of the North, South Africa) for $^{31}P\{^{1}H)$-NMR data.

References

[1] (a) J. Mata, S. Uriel, E. Peris, R. Llusar, S. Hiubrechts, A. Persoons, J. Organomet. Chem. 562 (1998) 197;
(b) I.R. Whitall, A.M. McDonagh, M.G. Humphrey, Adv. Organomet. Chem. 42 (1998) 291.

[2] (a) F. Geiger, M. Stoldt, P. Bauerle, H. Schweizer, E. Umbach, Adv. Mater. 5 (1993) 922;
(b) G. Horowitz, P. Delannoy, H. Bouchriha, F. Deloffe, J.-L. Fave, F. Garnier, R. Hajlaoui, M. Heyman, F. Kouki, P. Valat, V. Wittgens, A. Yassar, Adv. Mater. 6 (1994) 752;
(c) K. Uchiyama, H. Akimichi, S. Hotta, H. Noge, H. Sakaki, Synth. Met. 63 (1994) 57.

[3] (a) D. Touchard, P.H. Dixneuf, Coord. Chem. Rev. 178 (1998) 409 (and references therein);
(b) F. Paul, C. Lapinte, Coord. Chem. Rev. 178 (1998) 431 (and references therein).

[4] (a) S. Woitellier, J.P. Launay, C.W. Spangler, Inorg. Chem. 28 (1989) 758;
(b) J.A. Thomas, C.J. Jones, J.A. McCleverty, D. Collison, F.E. Mables, C.J. Harding, M.G. Hutchings, J. Chem. Soc. Chem. Commun. (1992) 1796.;
(c) S.R. Marder, C.B. Gorman, B.G. Tieman, L.-T. Cheng, J. Am. Chem. Soc. 115 (1993) 3006;
(d) O. Lavastre, J. Plass, P. Bachmann, S. Guesmi, C. Moinet, P.H. Dixneuf, Organometallics 16 (1997) 184.

[5] K. Sonogashira, K. Ohga, S. Takahashi, N. Hagihara, J. Organomet. Chem. 188 (1980) 237.

[6] S. Takahashi, K. Sonogashira, H. Morimoto, E. Murata, S. Kataoka, N. Hagihara, J. Polym. Sci. Polym. Chem. Ed. 20 (1982) 565.

[7] J. Kiessewetter, G. Poignant, V. Guerchais, J. Organomet. Chem. 595 (2000) 81.

[8] (a) L.A. Bumm, J.J. Arnold, M.T. Cygan, T.D. Dunbar, T.P. Burgin, L. Jones, II, D.L. Allara, J.M. Tour, P.S. Weiss, Science 271 (1996) 1705;
(b) M.T. Cygan, T.D. Dunbar, J.J. Arnold, L.A. Bumm, N.F. Shedlock, T.P. Burgin, L. Jones, II, D.L. Allara, J.M. Tour, P.S. Weiss, J. Am. Chem. Soc. 120 (1998) 2721.

[9] O. Lavastre, M. Even, P.H. Dixneuf, A. Pacreau, J.P. Vairon, Organometallics 15 (1996) 1530.

[10] F. Sato, T. Yoshida, M. Sato, J. Organomet. Chem. 37 (1972) 381.

[11a] K.W. Barnett, J. Chem. Educ. 51 (1974) 422.

[11b] J. Darkwa, Organometallics 13 (1994) 4734.

[12] O.L. Caagrande, Jr., A.E. Gerbase, F.C. Atedile, F.O.V. da Cunha, Polyhedron 16 (1997) 171.

[13] A.J. Fry, in: P.T. Kissinger, W.R. Heineman, (Eds.), Laboratory Techniques in Electrochanalytical Chemistry, second ed., Revised and Expanded, Marcel Dekker, New York, pp. 469–485, (Chapter 15).

[14] (a) J. Darkwa, R.M. Moutloali, T. Nyokong, J. Organomet. Chem. 564 (1998) 37;
(b) F.A. Nevondo, A.M. Crouch, J. Darkwa, J. Chem. Soc. Dalton Trans. (2000) 43.

[15] R.H. Wopschall, I. Shain, Anal. Chem. 39 (1967) 1515; Ref: R.H. Wopschall, I. Shain, Anal. Chem. 39 (1967) 1527.

[16] R.W. Murray, in: A.J. Bard (Ed.), Electroanalytical Chemistry, Marcel Dekker, New York, 1984, pp. 191–368.

[17] R.E. Dessy, R. Kornmann, C. Smith, R. Haytor, J. Am. Chem. Soc. 90 (1968) 2001.

[18] (a) P.D. Frisch, M.K. Lloyd, J.A. McCleverty, D. Seddon, J. Chem. Soc. Dalton Trans. (1973) 2268.;
(b) N.-F. Ho, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (1990) 359.

[19] S. Guesmi, D. Touchard, P.H. Dixneuf, J. Chem. Soc. Chem. Commun. (1996) 2773.

[20] B.A. Etzenhouser, M.D. Cavanaugh, H.N. Spurgeon, M.B. Sponsler, J. Am. Chem. Soc. 116 (1994) 2221.

[21] R. Chukwu, A.D. Hunter, B.D. Santarisiero, S.G. Bott, J.L. Atwood, J. Chassaignac, Organometallics 11 (1992) 589.