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Reversible sulfur dioxide reactions with cyclopentadienylnickel(II) organochalcogenide complexes

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Abstract

A series of cyclopentadienylnickel(II) organochalcogenides containing different phosphines have been prepared by either reacting [CpNi(μ-SC$_6$H$_4$X-4)]$_2$ (Cp$^{\#}$ = η^5-C$_5$H$_5$,(Cp), η^5-C$_5$H$_5$Me, (Cp′); X = Cl, Br) with phosphines or Cp$^{\#}$Ni(PR$_3$)Br with HSC$_6$H$_4$X-4 and Et$_3$N or NaSeC$_6$H$_4$Cl-4. The complexes that were isolated have the general formula CpNi(PR$_3$)(EC$_6$H$_4$X-4) {E = S, X = Cl, R = Ph (**1a**), Bu (**2a**), OPh (**3a**), OEt (**4a**), OMe (**5a**); X = Br, R = Bu (**6a**), Ph (**7a**)}. In addition to spectroscopic characterisation, the complexes CpNi(PBu$_3$)(SC$_6$H$_4$Cl-4) (**2a**) and Cp’Ni(PPh$_3$)(SeC$_6$H$_4$Cl-4) (**9a**) were subjected to single-crystal X-ray diffraction studies. While the solution and solid state structures of CpNi(PBu$_3$)(SC$_6$H$_4$Cl-4) were found to be the same, that of Cp’Ni(PPh$_3$)(SeC$_6$H$_4$Cl-4) were different. The orientation of the methyl group of **9a** in the solid state is almost *trans* to the phosphine, but solution NMR data indicate that the methyl substituent on the cyclopentadienyl ligand is *cis* to the phosphorus. All the complexes, **1a**–**9a**, were found to react reversibly with SO$_2$ to form SO$_2$ adducts and the reversibility could be monitored by visible and ^{1}H-NMR spectroscopy. Electrochemical studies show that **2a** and **6a** have reversible couples whereas **1a** and **7a** are only quasi-reversible. The PBu$_3$ complexes are easier to oxidise as compared with the PPh$_3$ analogues. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopentadienylnickel(II); Organochalcogenide; Reversible; Sulfur dioxide

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1. Introduction

Interest in the chemistry of sulfur dioxide is primarily driven by environmental concerns about this gas. A potential solution for this problem lies in the ability to trap the gas before it gets to the atmosphere. Efforts directed towards solving this problem have led to the reactions of metal complexes with sulfur dioxide. Two main reaction types have been identified in this regard. First, reactions in which the sulfur dioxide binds to the metal centre [1]; and secondly, those where the gas is bound to a ligand in a metal complex [2–5]. The former seldom leads to reversible absorption, whereas the latter almost invariably gives products that easily release sulfur dioxide; presumably because the ligand–SO$_2$ interaction is generally weak. Most of these ligand based adducts are thiolato complexes [2](a), [3–5], with the sulfur of the thiolato ligand behaving as a Lewis base—though this behaviour is not restricted to sulfur containing ligands. One of the earliest known ligand bound SO$_2$ complexes is Pt(PPh$_3$)$_2$(CH$_3$)I·SO$_2$ [6], where the SO$_2$ is bound to the iodo ligand. Other examples are oxygen and selenium organochalcogenide compounds which form adducts that are less stable than their sulfur analogues [2](a), due to their poorer Lewis base character.

In this paper we describe the synthesis of cyclopentadienylnickel(II) organochalcogenide compounds, some

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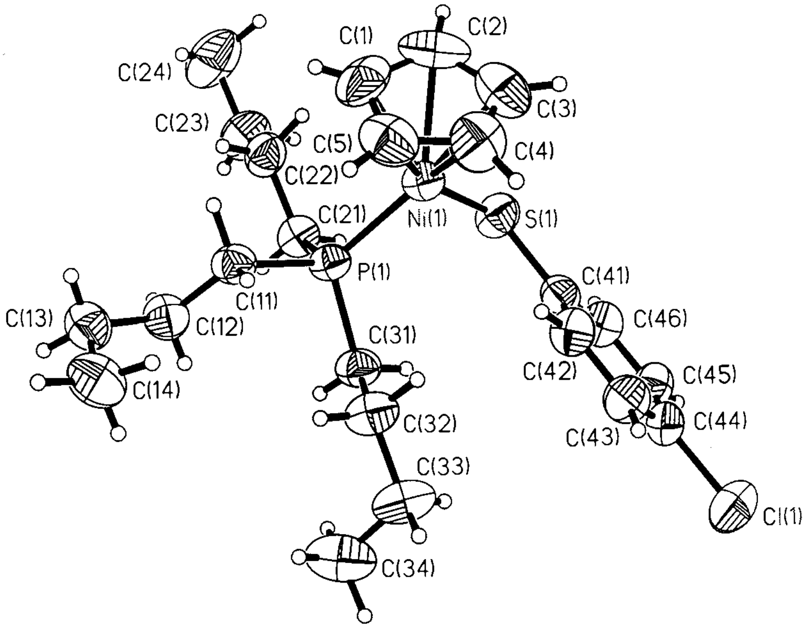

Fig. 1. ORTEP plot for $CpNi(PBu_3)(SC_6H_4Cl\text{-}4)$.

of which are known, and their reversible reactions with SO_2. The SO_2 adducts have the SO_2 bound to the chalcogen of the ligands.

2. Experimental section

2.1. Materials and instrumentation

All reactions were performed under a nitrogen atmosphere but products were air-stable and could be worked-up in air. Solvents were of analytical grade but THF was dried and distilled over sodium benzophenone ketyl. The phosphines, 4-chlorothiophenol and bis(4-chlorophenyl)diselenide (Aldrich) were used as received. Nickelocene (Cp_2Ni) [7], $CpNi(PR_3)Br$ [7], Cp'-$Ni(PR_3)Br$ [8] and $[CpNi(\mu\text{-}SC_6H_4X\text{-}4)]_2$ (X = Cl, Br) [9] were prepared by the literature procedure. Infrared spectra were recorded on a Nicolet 205 FT-IR as KBr pellets. The ^1H, ^{13}C, ^{31}P-NMR spectra were on a Varian Gemini 2000 and referenced to residual $CHCl_3$ for ^1H (δ 7.26), ^{13}C (δ 77.0) and to 85% H_3PO_4 for ^{31}P. Elemental analyses were performed by the microanalytical laboratory at the University of Cape Town, South Africa, as a service.

Table 1
Selected bond distances and bond angles for $Cp'Ni(PBu_3)(SC_6H_4Cl\text{-}4)$

Bond distances (Å)			
Ni–S(1)	2.194(9)	Ni–P(1)	2.140(8)
Ni–Cp[a]	1.754	P(1)–C(11)	1.841(3)
P(1)–C(21)	1.824(3)	P(1)–C(31)	1.829(3)
S(1)–C(41)	1.762(3)	Cl(1)–C(44)	1.767(3)
Bond angles (°)			
Cp–Ni–P(1)	134.9	Cp–Ni–S(1)	132.0
P(1)–Ni–S(1)	92.48(4)	C(11)–P(1)–Ni	115.58(9)
C(21)–P(1)–Ni	111.94(11)	C(31)–P(1)–Ni	115.13(11)
C(21)–P(1)–C(11)	104.45(14)	C(31)–P(1)–C(11)	103.76(13)
C(21)–P(1)–C(31)	104.80(13)	—	—

[a] The distance from the centroid of the C_5H_5 ring to the nickel atom.

Cyclic voltammetric studies were carried out on a Bio-Analytical Systems CV-50W electrochemical analyser, at a glassy carbon electrode (area = 0.07 cm^2). The reference electrode was a silver wire coated with silver chloride. A platinum wire was used as a counter electrode. All experiments were carried out under prepurified and dry nitrogen atmosphere. Samples were measured in dichloromethane solution (10^{-3} M) with $[n\text{-}Bu_4N[ClO_4]$ as supporting electrolyte (0.1 M). Potentials were referenced internally to the potential for the oxidation of ferrocene (0.44 V) versus the saturated calomel electrode (SCE), as described in an earlier report [10].

2.2. One pot synthesis of $CpNi(PPh_3)(SC_6H_4Cl\text{-}4)$ (**1a**)

A mixture of Cp_2Ni (1.00 g, 5.29 mmol) and 4-chlorothiophenol (0.79 g, 5.46 mmol) was stirred in CH_2Cl_2 (50 ml) for 2 h. The green solution turned dark brown and PPh_3 (1.09 g, 4.16 mmol) was added and the solution stirred for a further 20 h. The mixture was filtered, concentrated to about 20 ml and an equal volume of hexane was added and stored at −15°C to yield green crystals of $CpNi(PPh_3)(SC_6H_4Cl\text{-}4)$ (1.17 g,

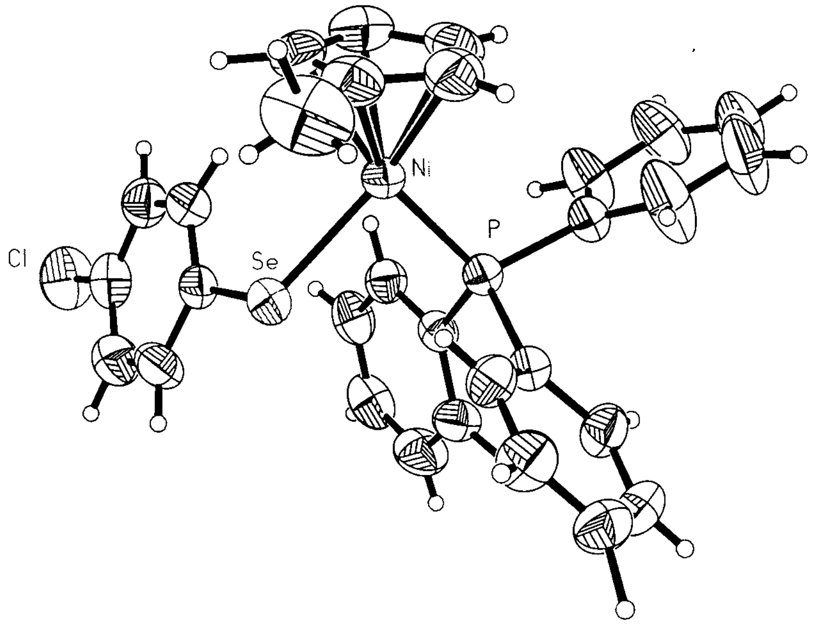

Fig. 2. ORTEP plot for Cp'Ni(PPh$_3$)(SeC$_6$H$_4$Cl-4).

56%). Anal. Calcd. for C$_{29}$H$_{24}$ClPSNi: C, 65.76; H, 4.57%. Found: C, 65.88; H, 4.67%. ^{1}H-NMR (CDCl$_3$): δ 7.68–7.62 (m, 6H, PPh$_3$), 7.38–7.30 (m, 9H, PPh$_3$), 7.25 (d, 2H, $J_{\mathrm{HH}} = 8.50$ Hz, SC$_6$H$_4$Cl-4), 6.82 (d, 2H, $J_{\mathrm{HH}} = 8.50$ Hz, SC$_6$H$_4$Cl-4), 5.11 (s, 5H, C$_5$H$_5$). ^{31}P{^{1}H}-NMR: δ 35.8 (s, PPh$_3$). IR (nujol mull cm^{-1}): 1586(m), 1570(m), 1543(m), 1480(s), 1466(vs), 1433(vs), 1400(m), 1387(m), 1348(m), 1313(m), 1283(m), 1266(w) 1228(w), 1182(m), 1168(w), 1157(w), 1116(w), 1091(vs), 1069(m), 1045(m), 1009(s), 998(m), 971(w), 903(w), 848(w), 834(w), 810(s), 785(vs), 766(w), 750(s), 740(s), 698(vs), 692(vs), 618(w), 533(vs), 509(vs), 492(s), 482(s), 454(m), 441(w), 427(m).

Table 2
Selected bond distances and bond angles for Cp'Ni(PPh$_3$)(SeC$_6$H$_4$Cl-4)

Bond distances (Å)			
Ni–Se(1)	2.317(6)	Ni–P(1)	2.136(10)
Ni–Cp[a]	1.746	P(1)–C(11)	1.822(4)
P(1)–C(21)	1.835(4)	P(1)–C(31)	1.825(4)
Se(1)–C(41)	1.912(4)	Cl(1)–C(44)	1.74 9(5)
Bond angles (°)			
Cp–Ni–P(1)	137.0	Cp–Ni–Se(1)	130.7
P(1)–Ni–Se(1)	91.24(3)	C(11)–P(1)–Ni	114.45(11)
C(21)–P(1)–Ni	115.07(13)	C(31)–P(1)–Ni	112.55(13)
C(21)–P(1)–C(11)	103.1(2)	C(31)–P(1)–C(11)	107.7(2)
C(21)–P(1)–C(31)	102.9(2)	—	—

[a] The distance from the centroid of the C$_5$H$_4$Me ring to the nickel atom.

2.3. *Reactions of [CpNi(μ-SC$_6$H$_4$Cl-4)]$_2$ with PPh$_3$: formation of CpNi(PPh$_3$)(SC$_6$H$_4$Cl-4) (**1a**)*

A mixture of [CpNi(μ-SC$_6$H$_4$Cl-4)]$_2$ (1.00 g, 3.74 mmol) and PPh$_3$ (1.96 g, 7.48 mmol) in CH$_2$Cl$_2$ (50 ml) was stirred for 18 h. The colour of the solution remained brown–black without much change. After filtration the solution was concentrated to about 15 ml and an equal volume of hexane added. Upon cooling at −15°C overnight green crystals of pure CpNi(PPh$_3$)(SC$_6$H$_4$Cl-4) were obtained. Yield = 1.58 g, 80%. The rest of the phosphine reactions were performed with two equivalents of the appropriate phosphine and 0.30 g (0.56 mmol) of [CpNi(μ-SC$_6$H$_4$Cl-4)]$_2$. The yields and analytical data are given below for each reaction.

2.4. *CpNi(PBu$_3$)(SC$_6$H$_4$Cl-4) (**2a**)*

Yield = 0.42 g, 80%. Anal. Calcd. for C$_{23}$H$_{36}$ClPSNi: C, 58.81; H, 7.70; S, 6.83%. Found: C, 58.91; H, 8.00; S, 6.58%. ^{1}H-NMR (CDCl$_3$): δ 7.53 (d, 2H, $J_{\mathrm{HH}} = 8.60$ Hz, SC$_6$H$_4$Cl-4), 6.94 (d, 2H, $J_{\mathrm{HH}} = 8.60$ Hz, SC$_6$H$_4$Cl-4); 5.25 (s, 5H, C$_5$H$_5$); 1.48 (m, 18H, PBu$_3$); 0.91 (t, 9H, $J_{\mathrm{HH}} = 7.00$ Hz, PBu$_3$). ^{31}P{^{1}H}-NMR: δ (s, 22.4, PBu$_3$). IR (KBr pellet cm^{-1}): 3036(m), 2931(vs), 2868(vs), 1567(m), 1546(m), 1475(vs), 1412(s), 1377(s), 1342(s), 1278(m), 1257(m) 1222(m), 1201(s), 1180(m), 1082(vs), 1018(m), 1004(s), 976(m), 962(m), 906(m), 857(w), 835(w), 814(vs), 786(vs), 737(m), 716(s), 688(m), 540(m), 484(s), 463(m), 435(m).

Table 3
^{1}H-NMR chemical shifts (ppm) for Cp$^{\#}$Ni(PR$_3$)(EC$_6$H$_4$X-4) and Cp$^{\#}$Ni(PR$_3$)(E(SO$_2$)C$_6$H$_4$X-4)

Cp$^{\#}$Ni(PR$_3$)(EC$_6$H$_4$X-4)			Cp$^{\#}$Ni(PR$_3$)(E(SO$_2$)C$_6$H$_4$X-4)		
	Cp$^{\#}$	EC$_6$H$_4$X-4		Cp$^{\#}$	(E(SO$_2$)C$_6$H$_4$X-4)
1a	5.13	—, 6.83(d)	**1b**	5.38	—, 6.96(d)
2a	5.25	7.53(d), 6.93(d)	**2b**	5.48	7.44(d), 7.12(d)
3a	4.98	—, 6.85(d)	**3b**	5.16	—, 7.01(d)
4a	5.30	7.52(d), 6.94(d)	**4b**	5.53	7.52(d), 7.20(d)
5a	5.33	7.52(d), 6.96(d)	**5b**	5.51	7.40(d), 7.20(d)
6a	5.24	7.23(d), 6.96(d)	**6b**	5.43	7.43(d), 7.19(d)
7a	5.14	—, 6.98(d)	**7b**	5.39	—, 7.10(d)
8a	5.07	—, 6.87(d)	**8b**	5.30	—, 7.05(d)
9a	5.15, 4.70	—, 6.83(d)	**9b**	5.25, 5.00	—, 6.98(d)

*2.5. CpNi(P(OPh)$_3$)(SC$_6$H$_4$Cl-4) (**3a**)*

Yield = 0.22 g, 68%. Anal. Calcd. for C$_{29}$H$_{24}$ClO$_3$PSNi: C, 60.30; H, 4.19; S, 5.62%. Found: C, 60.15; H, 4,20; S, 5.32%. ^{1}H-NMR (CDCl$_3$): δ 7.37–7.18 (m, P(OPh)$_3$); 6.85 (d, 2H, $J_{HH} = 8.20$ Hz, SC$_6$H$_4$Cl-4); 4.98 (s, 5H, C$_5$H$_5$); 1.48 31P{^{1}H}-NMR: δ (s, 63.6, P(OPh)$_3$). IR (KBr pellet cm^{-1}): 3086(m), 3071(m), 1635(w), 1589(m), 1567(m), 1548(w), 1491(s), 1485(vs, sh), 1466(vs), 1455(s), 1419(m), 1400(m), 1386(m), 1348(w), 1332(w), 1302(w), 1286(m), 1231(m, sh) 1195(vs), 1184(vs), 1171(vs), 1110(w), 1086(vs), 1075(m), 1045(s), 1026(s), 1007(m), 976(w), 914(vs), 897(vs, sh), 864(m, sh), 834(m), 810(s), 796(s), 777(vs), 760(vs), 744(vs), 717(s), 689(s), 618(s), 596(s), 561(w), 536(m), 498(m), 479(s), 465(s), 432(w), 422(w).

*2.6. CpNi(P(OEt)$_3$)(SC$_6$H$_4$Cl-4) (**4a**)*

Yield = 0.35 g, 72%. ^{1}H-NMR (CDCl$_3$): δ 7.52 (d, 2H, $J_{HH} = 8.60$ Hz, SC$_6$H$_4$Cl-4), 6.94 (d, 2H, $J_{HH} = 8.60$ Hz, SC$_6$H$_4$Cl-4); 5.30 (s, 5H, C$_5$H$_5$); 4.09 (q, 6H, P(OEt)$_3$); 1.22 (t, 9H, P(OEt)$_3$). ^{31}P{^{1}H}-NMR: δ (s, 65.4, P(OEt)$_3$). IR (nujol mull cm^{-1}): 3064(m), 2980(s), 2931(s), 2896(m), 2875(m), 1573(s), 1553(w), 1474(s), 1441(m), 1389(s), 1370(m), 1348(w), 1294(m), 1258(s), 1179(m), 1162(s), 1097(s), 1075(s, sh), 1034(s, br), 1012(s), 975(s), 894(w), 815(s), 744(m), 681(w), 569(m), 550(m), 495(m).

*2.7. CpNi(P(OMe)$_3$)(SC$_6$H$_4$Cl-4) (**5a**)*

Yield = 0.30 g, 63%. ^{1}H-NMR (CDCl$_3$): δ 7.52 (d, 2H, $J_{HH} = 8.60$ Hz, SC$_6$H$_4$Cl-4), 6.95 (d, 2H, $J_{HH} = 8.60$ Hz, SC$_6$H$_4$Cl-4); 5.33 (s, 5H, C$_5$H$_5$); 3.67 (s, 9H, P(OMe)$_3$). ^{31}P{^{1}H}-NMR: δ (s, 67.2, P(OMe)3). IR (nujol mull cm^{-1}): 3064(m), 2945(s), 2839(m), 1570(m), 1548(w), 1469(s), 1441(m, sh), 1400(m), 1387(s), 1351(m), 1283(s), 1266(s), 1175(s), 1143(m), 1091(s), 1024(s, br), 935(w), 900(w), 853(m, sh), 834(s, sh), 799(s, br), 755(s), 698(w), 667(w), 629(w), 569(w), 539(s), 487m), 465(w), 449(w).

2.8. Reaction of [CpNi(μ-SC$_6$H$_4$Br-4)]$_2$ with PPh$_3$ and PBu$_3$: formation of CpNi(PR$_3$)(SC$_6$H$_4$Br-4)

In a typical reaction [CpNi(μ-SC$_6$H$_4$Br-4)]$_2$ (0.30 g, 0.48 mmol) in CH$_2$Cl$_2$ (50 ml) was reacted with PBu$_3$ (0.19 ml, 0.96 mmol). The mixture was stirred at room temperature for 18 h. A green solution was obtained, which was filtered and the solvent removed on a rotary evaporator to give an oil residue. This was dissolved in a minimum amount of hexane and cooled at −15°C for several days, forming green crystals of CpNi(PBu$_3$)(SC$_6$H$_4$Br-4) (**6a**). Yield = 0.31 g, 63%. Anal. Calcd. for C$_{23}$H$_{36}$BrPSNi: C, 53.73; H, 7.06; S, 6.24%. Found: C, 53.57; H, 7.25; S, 6.46%. ^{1}H-NMR (CDCl$_3$): δ 7.48 (d, 2H, $J_{HH} = 8.60$ Hz, SC$_6$H$_4$Br-4), 7.06 (d, 2H, $J_{HH} = 8.60$ Hz, SC$_6$H$_4$Br-4); 5.24 (s, 5H, C$_5$H$_5$); 1.47 (m, 18H, PBu$_3$); 0.90 (t, 9H, $J_{HH} = 7.00$ Hz, PBu$_3$). ^{31}P{^{1}H}-NMR: δ (s, 22.5 PBu$_3$). IR: (KBr pellet cm^{-1}): 2951(vs), 2921(vs), 2865(s), 1571(m), 1556(s), 1462(vs), 1415(s), 1403(s), 1375(s), 1346(s), 1303(m), 1278(m), 1265(m) 1255(w), 1206(m), 1168(m), 1087(s), 1078(vs), 1050(s), 1000(s), 934(w), 903(s), 887(s), 836(m), 823(s), 810(s), 781(vs), 761(s, sh), 740(m), 719(s), 625(w), 590(w), 493(s), 482(s), 459(m), 432(w), 402(m).

*2.9. CpNi(PPh$_3$)(SC$_6$H$_4$Br-4) (**7a**)*

This compound was prepared using the same procedure for **6a**, using [CpNi(μ-SC$_6$H$_4$Br-4)]$_2$ (0.20 g, 0.32 mmol) and PPh$_3$ (0.16 g, 0.64 mmol). Yield = 0.14 g, 77.3%. Anal. Calcd. for C$_{29}$H$_{24}$BrPSNi: C, 60.67; H, 4.21; S, 5.58%. Found: C, 60.82; H, 4.30; S, 5.37%. ^{1}H-NMR (CDCl$_3$): δ 7.66 (m, 6H, PPh$_3$), 7.37 (m, 9H, PPh$_3$); 7.23 (d, 2H, $J_{HH} = 8.60$ Hz, SC$_6$H$_4$Br-4), 6.96 (d, 2H, $J_{HH} = 8.60$ Hz, SC$_6$H$_4$Br-4); 5.30 (s, 5H, C$_5$H$_5$). ^{31}P{^{1}H}-NMR: δ (s, 35.2 PPh$_3$). IR: (nujol mull cm^{-1}): 1569(m), 1559(m), 1498(m), 1477(s), 1461(s), 1431(m),

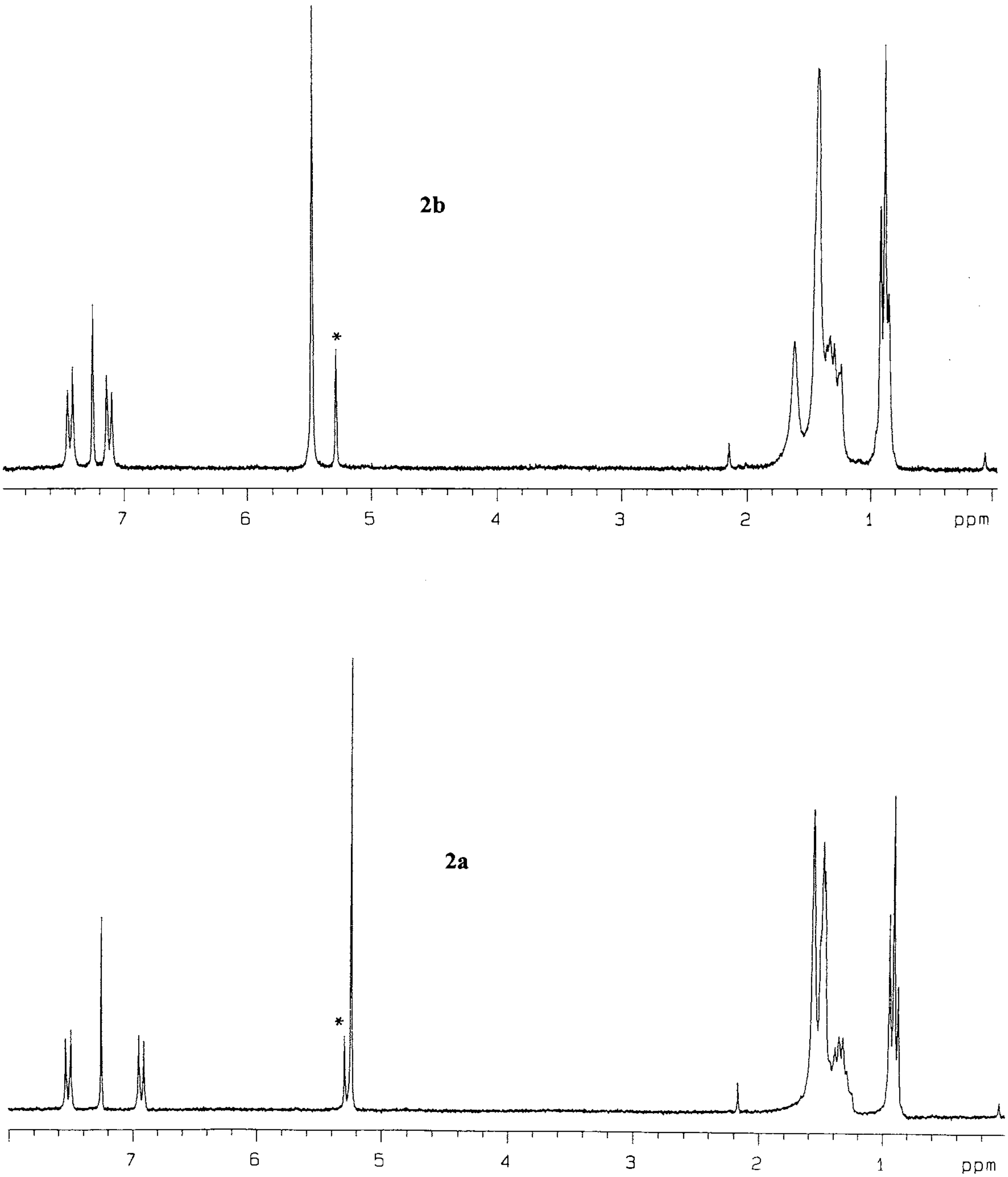

Fig. 3. ^{1}H-NMR spectra of CpNi(PBu$_3$)(SC$_6$H$_4$Cl-4) (**2a**) and its SO$_2$ adduct (**2b**). * Represents residual CH$_2$Cl$_2$ in each of the complexes.

1397(s), 1380(m), 1306(m), 1180(m), 1093(s), 1080(s), 1019(m), 1005(s), 995(s), 971(m), 902(m), 834(m), 806(s), 784(s), 748(s), 740(s), 691(s), 617(w), 533(s), 509(s), 492(s), 479(s), 454(m), 426(m).

*2.10. Synthesis of CpNi(PPh$_3$)(SeC$_6$H$_4$Cl-4) (**8a**)*

To a mixture of bis(4-chlorophenyl)diselenide (0.95 g, 3.04 mmol) and sodium borohydride (0.19 g, 5.02 mmol) was added methanol (30 ml). After vigorous evolution of gas the resultant yellow solution was stirred for 2 h to allow the complete dissolution of the diselenide. A solution of CpNi(PPh$_3$)Br (1.04 g, 2.23 mmol) in CH$_2$Cl$_2$ (40 ml) was added via a pressure equalising dropping funnel to give a dark brown mixture. The mixture was stirred at room temperature for 24 h, filtered and the filtrate evaporated on a rotary evaporator. The resultant green residue was recrystallised from CH$_2$Cl$_2$/hexane to give crystalline CpNi(PPh$_3$)(SeC$_6$H$_4$Cl-4). Yield = 0.37 g, 43%. Anal. Calcd. for C$_{29}$H$_{24}$ClPSeNi: C, 60.31; H, 4.36%. Found: C, 61.96; H, 4.36%. ^{1}H-NMR (CDCl$_3$): δ 7.69 (t, 6H, PPh$_3$), 7.61–7.35 (m, 9H, PPh$_3$), 6.86 (d, 2H, $J_{\mathrm{HH}} =$ 8.40 Hz, SC$_6$H$_4$Cl-4), 5.06 (s, 5H, C$_5$H$_5$). ^{31}P{^{1}H}-

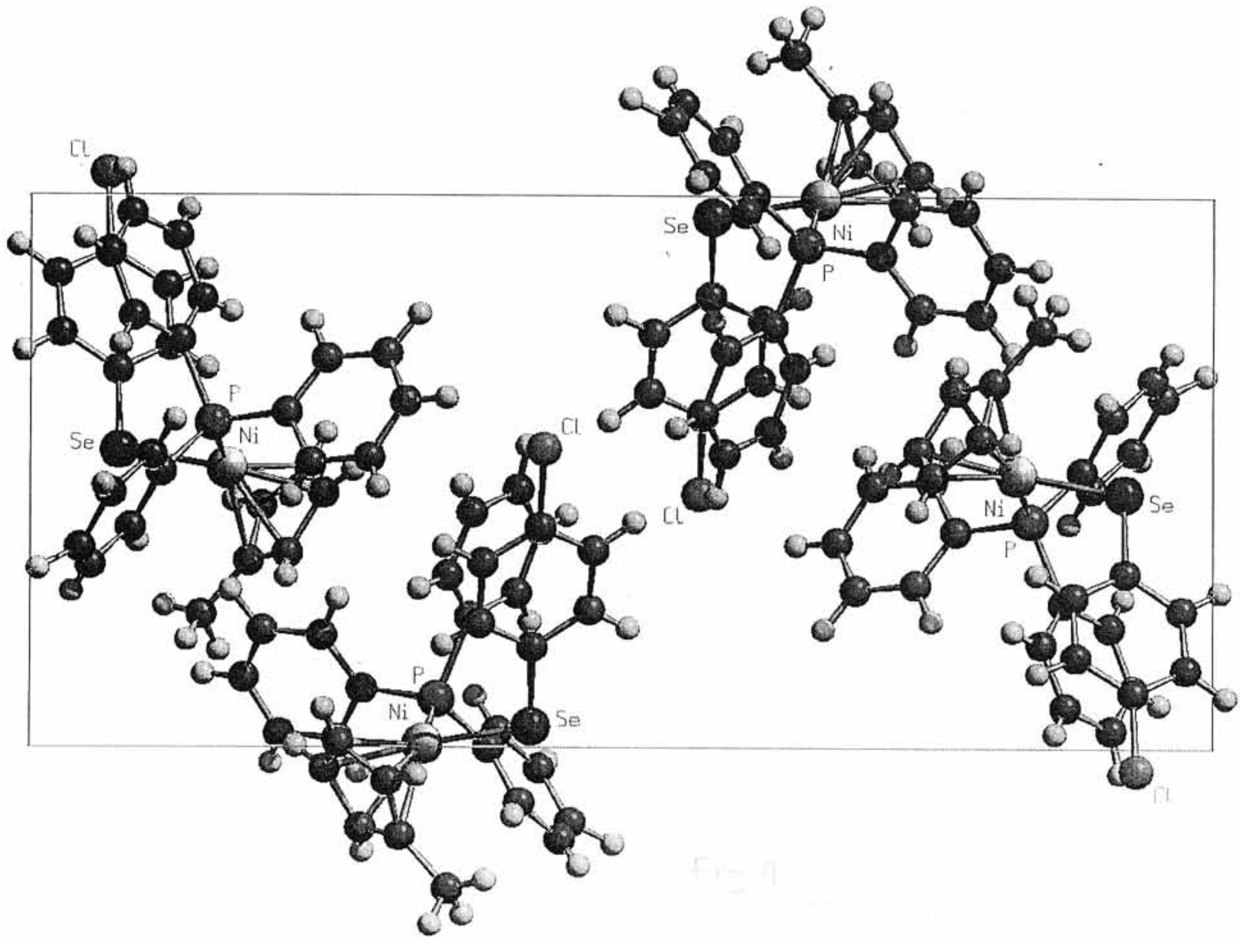

Fig. 4. Packing diagram for Cp'Ni(PPh$_3$)(SeC$_6$H$_4$Cl-4) viewed down the *a* axis.

NMR: δ (s, 39.0 PPh$_3$). IR (nujol mull cm^{-1}): 1589(m), 1570(m), 1477(s), 1464(vs), 1433(vs), 1400(m), 1381(s), 1346(m), 1310(m), 1285(m), 1264(m), 1184(m), 1157(m), 1119(s), 1097(vs), 1086 (vs), 1069(s), 1059(m), 1048(m), 1026(m), 1009s), 996(s), 971(m), 927(m), 900(m), 862(w), 848(m), 834(m), 810(s), 788(s), 750(s), 736(s), 722(s), 695(vs), 618(w), 533(vs), 509(s), 492(s), 479(s), 454(s), 441(m), 424(m), 408(m).

2.11. Synthesis of Cp'Ni(PPh$_3$)(SeC$_6$H$_4$Cl-4) (**9a**)

To a mixture of bis(4-chlorophenyl)diselenide (0.30 g, 1.02 mmol) and NaBH$_4$ (0.08 g, 2.04 mmol) was added methanol (50 ml) to generate NaSeC$_6$H$_4$Cl-4. After the evolution of gas had ceased, a toluene (50 ml) solution of Cp'Ni(PPh$_3$)Br (0.25 g, 0.51 mmol) was added via a pressure equalising dropping funnel to the solution, NaSeC$_6$H$_4$Cl-4. The solution changed from yellow to green and was stirred for 2 h. After filtration, the solvent was removed in vacuo and the residue recrystallised from CH$_2$Cl$_2$/hexane at −15°C to give pure Cp'Ni(PPh$_3$)(SeC$_6$H$_4$Cl-4). Yield = 0.14 g, 58%. Anal. Calcd. for C$_{30}$H$_{26}$ClPSeNi: C, 60.91; H, 4.60%. Found: C, 61.13; H, 4.37%. ^{1}H-NMR (CDCl$_3$): δ 7.63 (t, 6H, PPh$_3$), 7.59–7.35 (m, 11H, PPh$_3$ and SeC$_6$H$_4$Cl-4), 6.84 (d, 2H, $J_{\mathrm{HH}} = 8.40$ Hz, SeC$_6$H$_4$Cl-4), 5.13 (s, 2H, C$_5$H$_4$Me), 4.69 (s, 2H, C$_5$H$_4$Me). 31P{^{1}H}-NMR: δ (s, 39.5, PPh$_3$). IR (nujol mull cm^{-1}): 3142(w), 3071(m), 3001(w), 2959(s), 2924(m), 2868(m), 1584(w), 1573(w), 1559(w), 1471(s), 1433(vs), 1384(m), 1351(w), 1326(w), 1307(w), 1264(m), 1198(m), 1182(m), 1160(m), 1116(s), 1089(s), 1069(m), 1056(m), 1026(m), 1009(s), 914(w), 862(m), 810(s), 744(s), 722(s), 695(s), 618(w), 457(w), 424(m).

2.12. Reactions of CpNi(PR$_3$)(EC$_6$H$_4$Cl-4) with sulfur dioxide NMR tube generation of CpNi(PBu$_3$)(S(SO$_2$)C$_6$H$_4$Cl-4)

In a typical reaction CpNi(PBu$_3$)(SC$_6$H$_4$Cl-4) was dissolved in an NMR tube in CDCl$_3$ and the ^{1}H-NMR of the solution was run. Sulfur dioxide was slowly bubbled through the solution for about 5 min and the ^{1}H-NMR of the solution re-run. The two spectra are shown in Fig. 3. All other reactions with SO$_2$ were performed using the same procedure. The NMR data is summarised in Table 3.

2.13. Crystal Structure determination of **2a** and **9a**

Single crystals of **2a** and **9a** suitable for structural determination were obtained from a CH_2Cl_2/hexane mixture at -15°C. A dark green crystal of **2a** ($0.58 \times 0.52 \times 0.36$ mm) and **9a** ($0.58 \times 0.52 \times 0.36$ mm) were mounted in sealed capillary tube for data collection. All geometric and intensity data were collected on a Siemens SMART diffractometer with a CCD detector. The structures were solved by the Patterson method for primary atom sites and by difference map for atoms in secondary sites [11]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined without restraints. The structures were refined by full-matrix least-squares on F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (0.100P)^2 + 0.00P$, where $P = (F_o^2 + 2F_c^2)/3$ using SHELX-93 [12]. An absorption correction based on multiple redundant data analysis was applied [13]. Crystal data and structure refinement details are listed in Table 4.

Table 4
Crystal data and structural refinement for **2a** and **9a**

	2a	**9a**
Formula	$C_{23}H_{36}ClPSNi$	$C_{30}H_{26}ClPSeNi$
FW	469.71	580.60
T (K)	293(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.950(3)	9.579(4)
b (Å)	9.839(2)	11.239(5)
c (Å)	20.274(4)	24.395(11)
β (°)	108.60(3)	95.601(10)
Volume (Å^3), Z	2448.3(9), 4	2613.9(2), 4
Density (calcd.) (Mg m^{-3})	1.274	1.501
Absorption coefficient (mm^{-1})	1.058	2.315
F(000)	1000	1200
Crystal size (mm)	$0.58 \times 0.52 \times 0.360$	$58 \times 0.38 \times 0.25$
θ-range for data collected (°)	1.66–23.28	1.68–28.30
Limiting indices	$-14 \leq h \geq 13$ $-10 \leq k \geq 8$ $-22 \leq l \geq 22$	$-12 \leq h \geq 12$ $-12 \leq k \geq 14$ $-30 \leq l \geq 25$
No. of reflections collected	9033	15595
No. of independent reflections	3497	5873
R(int.)	0.0239	0.0318
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3497/0/388	5873/0/411
Goodness of fit on F^2	1.078	1.113
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0329$ $wR_2 = 0.1195$	0.0483 0.1436
R indices (all data)	$R_1 = 0.0364$ $wR_2 = 0.1248$	0.0647 0.1559
Largest difference peak and hole (e Å^{-3})	0.322 and -0.305	0.588 and -0.403

3. Results and discussion

3.1. Synthesis of complexes

The general synthetic route to the $Cp^{\#}Ni(PR_3)(SC_6H_4X\text{-}4)$ complexes is via the method of Taube et al. [14]. When the dimer, $[CpNi(\mu\text{-}SC_6H_4X\text{-}4)]_2$, ($Cp = \eta^5\text{-}C_5H_5$, X = Cl, Br) is treated with phosphines, PR_3 (R = Bu, Ph, OPh, OEt, OMe), it is cleaved to form complexes of the type $CpNi(PR_3)(SC_6H_4X\text{-}4)$ in moderate to high yields (Eq. (1)). The 4-bromo complexes were isolated for only PPh_3 and PBu_3 to determine if the change of halogen would have any electronic effects. Based on the ^{1}H-NMR data (Table 3); there was no significant electronic effect between the Cl and Br compounds. The products from PPh_3, $P(OPh)_3$ and PBu_3 were brown in solution but green to dark green in the solid state; whereas the products from $P(OEt)_3$ and $P(OMe)_3$ were both green oils. The brown–green colour changes in solution and in the solid state is similar to that observed for PPh_3 complexes of SC_6H_5 and $SC_6H_4Me\text{-}4$ [15].

$$[CpNi(\mu\text{-}SC_6H_4X\text{-}4)]_2 + 2PR_3 \rightarrow 2CpNi(PR_3)(SC_6H_4X\text{-}4) \qquad (1)$$

The PBu_3 complex, $CpNi(PBu_3)(SC_6H_4Cl\text{-}4)$, has previously been prepared by Sato and Yoshida when they reacted $[CpNi(PBu_3)_2]^+Cl^-$ with $NaSC_6H_4Cl\text{-}4$ [16]; but the route described in equation (1) is much simpler and represents a one-pot reaction if $[CpNi(\mu\text{-}SC_6H_4X\text{-}4)]_2$ is generated in situ from Cp_2Ni and $HSC_6H_4X\text{-}4$, followed by the addition of phosphine. All products from reaction (1) were characterised by IR and NMR spectroscopy and by elemental analyses. In addition, the structure of **2a** was determined by X-ray crystallography as shown in Fig. 1 and some selected parameters are shown in Table 1.

In order to compare the behaviour of the Se analogues to the S ones, we prepared $CpNi(PPh_3)(SeC_6H_4Cl\text{-}4)$ via a route similar to that employed for $CpNi(PBu_3)(SeC_6H_4Cl\text{-}4)$ (Eq. (2)) [16].

$$Cp^{\#}Ni(PPh_3)Br + NaSeC_6H_4Cl\text{-}4 \rightarrow Cp^{\#}Ni(PPh_3)(SeC_6H_4Cl\text{-}4) + NaBr \ (Cp^{\#} = \eta^5\text{-}C_5H_5,\ \eta^5\text{-}C_5H_4Me) \qquad (2)$$

The colours of these compounds in solution and in the solid state were also brown and green respectively like those of the sulfur analogues. Spectroscopic characterisation by IR, NMR and elemental analyses confirmed the formulation as in equation (2); and the structure of **9a** established by X-ray crystallography is shown in Fig. 2 and selected parameters are shown in Table 2. Our attempts so far to prepare $Cp'Ni(PPh_3)(SC_6H_4Cl\text{-}4)$ ($Cp' = \eta^5\text{-}C_5H_4Me$) have been unsuccessful.

3.2. Spectroscopic characterisation of complexes and their SO_2 adducts

Infrared spectra of all complexes displayed strong bands in the 800 cm^{-1} region, characteristic of Cp and at 690–780 cm^{-1} for the phenyl containing phosphines. However, attempts to determine the mode of SO_2 binding by the ν(SO) of the infrared spectra of the SO_2 adducts were unsuccessful. This was due to the overwhelming excess of free SO_2 in solution, after bubbling the gas, compared with the presence of bound SO_2. In the NMR spectra of **1a**–**8a**, the peaks due to the Cp were in the range 4.98–5.25 ppm and that of Cp' (**9a**) at 4.70 and 5.15 ppm. Treatment of CH_2Cl_2 solutions of complexes **1a**–**9a** with SO_2 resulted in shifts of the peaks observed for the compounds prior to the addition of SO_2. The SO_2 reactions could be monitored by UV-visible, ^1H and ^{31}P-NMR spectroscopy. The visible spectra generally shifted from a distinct λ_{max} for the starting material to featureless spectra for the SO_2 adducts. When solutions of the SO_2 adducts were subjected to reduced pressure, even on a rotary evaporator, they reverted back to the spectra of the original solution before SO_2 was added. These observation are similar to that made for (dppe)Ni($S_2C_6H_3R$) (R = H, Me) [17]. When the reactions with SO_2 were monitored by ^1H-NMR, a general shift of the Cp peaks downfield was observed (Table 3), which is consistent with the observation made by Shaver and Plouffe for the reaction of $CpRu(PPh_3)_2(SC_6H_4Me\text{-}4)$ with SO_2 [4]. Similar downfield shifts of the *m*-protons to the sulfur in SC_6H_4Cl-4 and SC_6H_4Br-4 were also observed. But the general trend of doublets from the protons next to the sulfur in the ligands is difficult to establish since some of the peaks are obscured by the phenyl peaks of PPh_3 and $P(OPh)_3$ of **1b** and **3b**. However, a clearer picture can be seen when the spectrum of **2a** is compared with that of **2b** (Fig. 3) and that of **7a** with **7b** (Table 3), respectively. In these complexes, the downfield doublets could be assigned to the protons close to the more electronegative halogen atoms and the upfield doublets to the protons next to the sulfur. The protons near the sulfur atom have upfield shifts in the SO_2 adducts. This implies that the SO_2 is bound to the sulfur of the ligand and draws electron density from this sulfur and hence from the nearest protons. On the other hand the protons nearest to the halogens experience very little electron density changes, resulting in only slight changes in chemical shifts (Fig. 3). The general trends in the ^1H-NMR chemical shifts are strongly related to the donor ability of the phosphines. Thus alkyl phosphines that are better σ-donors increase the electron density of the nickel centre. This improved electron density on the nickel results in better π-backbonding between the Ni and S or Se and leads to the Ni reducing electron density on the cyclopentadienyl ligand; hence larger downfield shifts are observed for complexes containing more basic phosphines. The ^{31}P-NMR spectra of all the SO_2 adducts shifted downfield by 1.0 ppm or less from the non-SO_2 adducts.

Based on the spectroscopic data, the SO_2 adducts could be formulated as $CpNi(PR_3)(S(SO_2)C_6H_4X\text{-}4)$ (X = Cl, Br) which would be similar to the structurally characterised ruthenium compound, $CpRu(PPh_3)_2(S(SO_2)C_6H_4Me\text{-}4)$ [4]. It must be noted that the ruthenium complex can absorb a further one mole of SO_2 to form $CpRu(PPh)(SO_2)(S(SO_2)C_6H_4Me\text{-}4)$ [4] by substituting one of the PPh_3 ligands. This would offer a second binding site option for the nickel complexes; namely PPh_3 substitution. From the ^{31}P-NMR data of the SO_2 adducts, phosphine substitution do not occur for nickel as this would leave free phosphine in solution. In the case of PPh_3 complexes a peak at -5.0 ppm for free PPh_3 would have been observed, but this was not the case. Unfortunately our products are too labile for us to obtain solid materials for either elemental analyses or crystal structure determination; but the characteristic shifts in the NMR are consistent with a ligand based SO_2 adduct. The highly labile nature of the SO_2 compound could be attributed to the low basicity of nickel compounds as compared with those of its congeners [18].

3.3. Electrochemical properties

Preliminary cyclic voltammetric studies of complexes **1a** (0.48 V), **2a** (0.36 V), **6a** (0.32 V) and **7a** (0.42 V), with their oxidation potentials, show that the PBu_3 complexes are easier to oxidise than their PPh_3 analogues. This suggests that **2a** and **6a**, which contain the more electron donating PBu_3, probably have their highest occupied molecular orbitals lower in energy compared with the corresponding PPh_3 complexes **1a** and **7a**. Also when the halide in the para position of the thiolato ligand was changed from Cl (**1a**, **2a**) to Br (**6a**, **7a**), the less electron withdrawing Br had complexes that were easier to oxidise, since the Ni centre in bromo complexes would be more electron rich than the chloro analogue. In addition oxidation couples of the PBu_3 showed more reversible behaviour than the PPh_3 complexes. A similar observation has been made by Gladysz et al. on $(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)$ [19], where reversibility improves as the σ-donor property of the phosphine increases. This observation corroborates the ^1H-NMR downfield shifts observed for complexes **1a**, **2a**, **6a** and **7a** as the phosphine becomes more basic.

3.4. Molecular structures of **2a** and **9a**

Both complexes show a trigonal geometry around the nickel if the centriod of the cyclopentadienyl ligand is considered to occupy a co-ordination site. This is similar to other cyclopentadienylnickel(II) complexes containing phosphines and organochalcogenide ligands [8,15,20]. A comparison of the Ni–P distances in **2a** (2.140(8) Å) and **9a** (2.136(10) Å) with similar compounds show that the Ni–P bonds lie within the acceptable range. The longest for such bonds is found in CpNi(PPh$_3$)(SC$_6$H$_4$Cl-4) (2.144(1) Å) [20] and the shortest is 2.136(1) Å for CpNi(PPh$_3$)(SeC$_6$H$_5$) [8]. No significant changes in the nickel–chalcogen distances were also observed when compared with the same types of bonds in other compounds, CpNi(PPh$_3$)(SC$_6$H$_4$Cl-4) (2.190(1) Å) [20], CpNi(PPh$_3$)(SeC$_6$H$_5$) (2.303(1) Å) [8]] and [Cp*Ni(μ-SeC$_6$H$_5$)]$_2$ (Cp* = η^5-C$_5$Me$_5$) (2.301(1) Å) [21]. One significant observation is the difference in the structure of **9a** in solution and that in the solid state. This is mainly in the orientation of the methyl group on the cyclopentadienyl ligand with respect to that of the phosphine. From the ^{1}H-NMR spectrum of **9a**, it is clear that there is long range coupling between the phosphorus and the methyl protons, but in the solid state the nearest carbon to the phosphorus is C(2). A good illustration of this is provided by the packing diagram of **9a** (Fig. 4). Similar through space coupling have been observed for Cp'Ni(PPh$_3$)(SC$_6$H$_5$) and Cp'-Ni(PPh$_3$)(SeC$_6$H$_5$) [8], as well as Cp'Ni(PPh$_3$)X (X = Cl, Br, CN) [22] in solution. It is noteworthy that the maximum deviation of the methyl group from the plane of the C$_5$H$_4$ ring is 0.005 and therefore shows no close proximity to the phosphorus. Thus the solid state structure is different from that in solution, unlike Cp'-Ni(PPh$_3$)I where the lack of coupling of the methyl protons to the phosphorus of PPh$_3$ in solution is supported by a solid state structure with the methyl group almost *trans* to the phosphorus [22]. The orientation of the methyl group, nearly *trans* to the phosphorus in **9a**, appears to minimise steric repulsion with the triphenylphosphine ligand in the solid state compared to its structure in solution. Crystal data and structure refinement details are listed in Table 4.

4. Conclusion

A number of cyclopentadienylnickel(II) organochalcogenide phosphine complexes can be prepared by the very simple procedure of reacting the dimer, [CpNi(μ-SC$_6$H$_4$X-4)]$_2$, with a phosphine. The more basic phosphines increases the electron density on the nickel, but it appears the halogen on the chalcogen containing ligand has very little effect on the electrons at the metal centre. A very facile reversible reaction of these complexes with SO$_2$ makes them potential scrubbers of SO$_2$. The electron count for the compounds, Cp'Ni(PPh$_3$)(EC$_6$H$_4$X-4), imply that the SO$_2$ is bound to the chalcogen, instead of the nickel, and this could be a factor in making the SO$_2$ so labile.

5. Supplementary material

Further crystallographic details can be obtained on request from the Director of the Cambridge Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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