

π -CYCLOPENTADIENYLS OF NICKEL(II)

XIII. THE PREPARATION AND PROPERTIES OF THE COMPOUNDS

π -C₅H₅NiPBu₃SC(S)X (X = OR, R AND NRH) AND π -C₅H₅NiPBu₃-SC(O)NRH

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Summary

Compounds of the type π -C₅H₅NiPBu₃SC(S)X (X = R, OR and NRH) are obtained from reactions between $[\pi$ -C₅H₅Ni(PBu₃)₂]⁺Cl[−] and SC(S)X[−] in aqueous solution. Compounds such as π -C₅H₅NiPBu₃SC(S)NRH are also obtained by reactions of π -C₅H₅NiPBu₃SH with RNCS.

Reactions of C₆H₅NCS with π -C₅H₅NiPBu₃SEt or $[\pi$ -C₅H₅NiPBu₃S-(CH₂)_n]₂ (n = 1, 2 and 3) give π -C₅H₅NiPBu₃[SC(NC₆H₅)SC₂H₅] or $[\pi$ -C₅H₅NiPBu₃{SC(NC₆H₅)S(CH₂)_n}]₂ respectively.

Similar reactions of π -C₅H₅NiPBu₃SH and RNCO give π -C₅H₅NiPBu₃SC(O)NRH.

Treatment of π -C₅H₅NiPBu₃SC(S)R with HCl gives π -C₅H₅NiSC(S)R.

Introduction

Recently we have investigated the preparation and reactivity of compounds of the type π -C₅H₅NiPBu₃X [1] (X = anion). It has been shown that π -C₅H₅NiPBu₃SR compounds readily undergo carbon disulphide insertion to produce the stable compounds π -C₅H₅NiPBu₃SC(S)SR [1d], and that π -C₅H₅-NiPBu₃SC₂H₅ also undergoes phenyl isothiocyanate insertion to give π -C₅H₅-NiPBu₃[SC(NC₆H₅)SC₂H₅] [1e]. The preparation of compounds of the type π -C₅H₅NiSC(S)R has been also reported in a preliminary communication [1f]. As there have been few reports on organonickel compounds [4] containing an M—SC(S)X linkage, in contrast to the other transition metals [2], we describe below the preparation and reactivity of compounds of the type π -C₅H₅-NiPBu₃SC(S)X (X = R, OR and NRH) and give details of the results which have been reported in preliminary communications [1e,f].

Compounds of the type π -C₅H₅NiPBu₃SC(S)X (X = R, OR and NRH)

were obtained from reactions between $[\pi\text{-C}_5\text{H}_5\text{Ni(PBu}_3)_2]^+\text{Cl}^-$ and $[\text{SC(S)-X}]^-$ in aqueous solution; this is a generally accepted route for preparation of compounds of the type $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{X}$ (X = anion) [1].

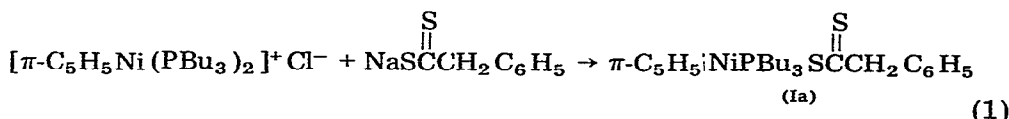
The compounds $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(S)NRH}$ were also obtained from reactions of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SH}$ with RNCS.

Results and discussion

Reactions of $[\pi\text{-C}_5\text{H}_5\text{Ni(PBu}_3)_2]^+\text{Cl}^-$ with SC(S)X^- (X = R, OR and NRH)

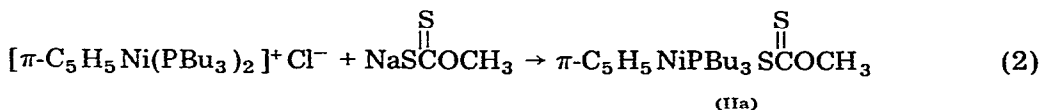
When excess $\text{NaSC(S)CH}_2\text{C}_6\text{H}_5$ was added to an aqueous solution of $[\pi\text{-C}_5\text{H}_5\text{Ni(PBu}_3)_2]^+\text{Cl}^-$, a brown precipitate appeared; recrystallization of the precipitate gave brown crystals in almost quantitative yield, based on nickel.

The IR spectrum of these crystals showed characteristic absorption bands at 1595 [ν (C=C) aromatic], 1205 [ν (C=S)] and 795 cm^{-1} [γ (C_5H_5)]. NMR peaks appeared at $\tau 2.6\text{--}3.2$ (aromatic 5H), 4.93 ($\pi\text{-C}_5\text{H}_5$, S 5H), 5.82 ($\text{CH}_2\text{--Ph}$, s, 2H) and $8.3\text{--}9.6$ ppm (PBu_3 , 27H). These results, together with the analytical and reactivity data described later, indicate that the product is $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(S)CH}_2\text{C}_6\text{H}_5$ with structure (Ia) (eqn. 1).



Similar treatment of other NaSC(S)R compounds (R = C_2H_5 and C_6H_5) with $[\pi\text{-C}_5\text{H}_5\text{Ni(PBu}_3)_2]^+\text{Cl}^-$ gave brown oily products (Ib,c). These could not be isolated because of their instability, but IR spectra and reactivity data, shown later, indicate that they are $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(S)R}$.

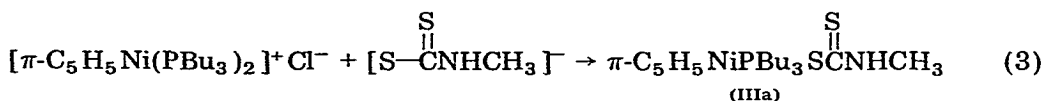
NaSC(S)OCH_3 reacted readily with $[\pi\text{-C}_5\text{H}_5\text{Ni(PBu}_3)_2]^+\text{Cl}^-$ in aqueous solution to give the expected $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(S)OCH}_3$ (IIa) as brown crystals in 88% yield (eqn. 2).



Structure (IIa) could be assigned by elemental analysis and spectral data. The IR spectrum of (IIa) showed a series of bands (1195 , 1145 and 1060 cm^{-1}) which originate from the structure R--O--C=S and a strong out-of-plane deformation band of π -cyclopentadienyl at 795 cm^{-1} in the IR spectrum as well as signals at $\tau 4.92$ ($\pi\text{-C}_5\text{H}_5$, s, 5H), 6.18 (O--CH_3 , s, 3H) and $8.40\text{--}9.50$ (PBu_3 , 27H) in the NMR spectrum.

Analogous treatment of other compounds of the type NaSC(S)OR (R = C_2H_5 , $\text{i-C}_3\text{H}_7$ and $\text{CH}_2=\text{CHCH}_2$) with $[\pi\text{-C}_5\text{H}_5\text{Ni(PBu}_3)_2]^+\text{Cl}^-$ gave the corresponding $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(S)OR}$ (IIb-d).

$\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(S)NHCH}_3$ (IIIa) was obtained from reaction between $[\pi\text{-C}_5\text{H}_5\text{Ni(PBu}_3)_2]^+\text{Cl}^-$ and $[\text{SC(S)NHCH}_3]^-$ in aqueous solution in 87% yield (eqn. 3).



The elemental analysis and spectral data support the structure (IIIa). The IR spectrum of (IIIa) shows characteristic bands for the N=C=S group (1485, 1315 and 928 cm^{-1}) and $\nu(\text{NH})$ at 3330 cm^{-1} ; the NMR spectrum shows signals at τ 1.89(NH, br, 1H), 5.06 ($\pi\text{-C}_5\text{H}_5$, s, 5H), 7.03 [N-CH₃, d, J -(H-CH₃) 5Hz, 3H] and 8.20–9.30 (PBu₃, 27H). By similar treatment of other [SC(S)NHR][−] (R = C₂H₅, n-C₃H₇, CH₂=CHCH₂, cyclo-C₆H₁₁ and C₆H₅) with $[\pi\text{-C}_5\text{H}_5\text{Ni(PBu}_3)_2]^+\text{Cl}^-$, the corresponding substances $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{-SC(S)NHR}$ (III b–f) were obtained in excellent yield.

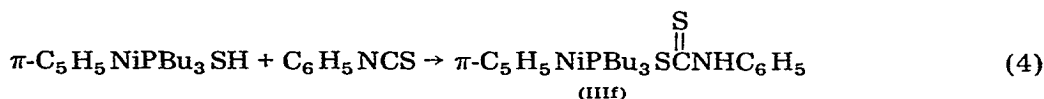
Surprisingly the reactions of [SC(S)NRR'][−] (R = C₆H₅ and R' = CH₃ or C₂H₅, and R = R' = CH₃ or C₂H₅) with $[\pi\text{-C}_5\text{H}_5\text{Ni(PBu}_3)_2]^+\text{Cl}^-$ gave Ni[SC(S)NRR']₂ [2a] as main products and none of the expected products $\pi\text{-C}_5\text{H}_5\text{-NiPBu}_3\text{SC(S)NRR}'$, but it is not clear why such differences exist between the reactivities of [SC(S)NRH][−] and [SC(S)NRR'][−].

The properties and elemental analysis data of the compounds (I), (II) and (III) are given in Table 1, and in Table 2 the IR and NMR data are listed.

Reactions of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SH}$ with RNCS

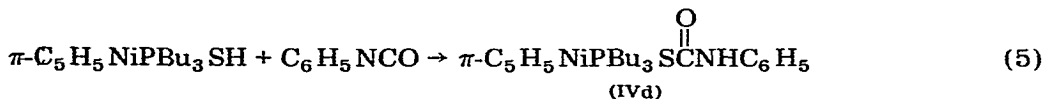
The well known result that RNCS reacts with mercaptan (R'SH) or NaSH to give the dithiocarbamate ester R'SC(S)NRH or NaSC(S)NHR, respectively [3] encouraged us to investigate the reaction of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SH}$ with RNCS because we have already found that phenylacetylene inserts into the SH bond of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SH}$ [1b].

Adding, at room temperature, excess phenyl isothiocyanate to a hexane solution of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SH}$ gave brown crystals in quantitative yield. The melting point, IR spectrum and NMR spectrum of these crystals are coincident with those of (III f) (eqn. 4). Similarly, the compounds $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(S)-NHR}$ (R = CH₃, C₂H₅, CH₂=CHCH₂ and cyclo-C₆H₁₁) (IIIa,b,d,e) were obtained in excellent yields from the reaction between $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SH}$ and RNCS.



Reactions of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SH}$ with RNCO

As it is also known that RNCO react with R'SH or NaSH to give R'SC(O)-NHR or NaSC(O)NHR, respectively [3], we investigated the reaction of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SH}$ with RNCO. Similarly to the reactions with C₆H₅NCS, $\pi\text{-C}_5\text{H}_5\text{-NiPBu}_3\text{SH}$ reacted readily with C₆H₅NCO at room temperature to give the expected $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(O)NHC}_6\text{H}_5$ (IV d) as brown crystals in 87% yield



(Continued on p. 146)

TABLE 1
SOME PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR THE COMPOUNDS (I), (II), (III) AND (VII)

Compound	Colour	M.p. (°C)	Yield (%)	Analyses found (calcd.) (%)			Mol. wt. ^a found (calcd.)
				C	H	N	
(Ia)	Brown	73.5–74.0	96	60.57 (60.89)	8.17 (7.92)		
(IIa)	Brown	87.5–88.0	88	52.70 (52.69)	8.14 (8.09)		
(IIb)	Brown	113.5–114.5	88	53.14 (53.73)	8.29 (8.28)		
(IIc)	Brown	95.0–96.0	85	53.98 (54.70)	8.45 (8.47)		
(IId)	Brown	104.5–105.5	82	54.38 (54.94)	7.99 (8.07)		
(IIIa)	Brown	102–103	87	51.63 (52.81)	8.43 (8.34)	3.09 (3.24)	
(IIIb)	Brown	108–109	91	53.01 (53.85)	8.28 (8.53)	3.02 (3.14)	
(IIIc)	Brown	95.5–96.0	82	53.82 (54.82)	8.79 (8.70)	2.88 (3.05)	
(IIId)	Brown	120–121	68	54.14 (55.06)	8.39 (8.30)	2.89 (3.06)	
(IIIe)	Brown	88.5–89.5	71	56.74 (57.63)	8.96 (8.81)	2.80 (2.80)	
(IIIf)	Brown	105–106	85	57.54 (58.34)	7.78 (7.70)	2.84 (2.84)	
(VIIa)	Brown	92–93	56 ^b	53.65 (53.61)	4.25 (4.21)		268 (291)
(VIIb)	Purple	Oil	28 ^c	42.06 (41.92)	4.18 (4.37)		
(VIIc)	Black	100.5–101.5	61 ^c	50.87 (51.99)	3.57 (3.61)		243 (277)

^a Cryoscopy in benzene. ^b Based on (Ia). ^c Based on $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PBu}_3)_2]^+\text{Cl}^-$.

TABLE 2
¹H NMR AND IR DATA FOR COMPOUNDS (I), (II) AND (III)

Com- pound	¹ H NMR data ^a (τ ppm)				IR data ^b (cm ⁻¹)			
	π -C ₅ H ₅	PBu ₃	NH	Other	γ (π -C ₅ H ₅)	ν (R-O-C=S)	ν (N-C=S)	ν (NH)
(Ia)	4.93(s) ^c	8.3-9.6		5.82(s) (CH ₂) 2.6-3.2 (C ₆ H ₅)	795			1595 ^d 1205 ^e
(IIa)	4.92(s)	8.4-9.5		6.18(s) (O-CH ₃)	795	1195, 1145, 1060		
(IIb)	4.92(s)	8.4-9.4 ^f		{ 5.71(q), (O-CH ₂) 8.68(t) (O-C-CH ₃)	795	1180, 1118, 1040		
(IIc)	4.98(s)	8.4-9.3 ^f		{ 4.57(h) (O-CH) 8.75(d) [O-C-(CH ₃) ₂] ¹	795	1195, 1100, 1030		
(IId)	4.92(s)	8.4-9.3		{ 5.25(br, d) (O-CH ₂) 4.53-4.90 (O-C-C=CH ₂) 4.05(m) (O-C-CH=)	790	1160, 1150, 1050		
(IIIa)	5.06(s)	8.2-9.3	1.89(br)	7.03(d) [N-CH ₃ , J(NH-CH ₃), 5 Hz]	790		1485, 1315, 3330 928	
(IIIb)	5.13(s)	8.3-9.4 ^f	2.01(br)	{ 4.57(p) (N-CH ₂) 8.80(t) ^f (N-C-CH ₃)	790		1470, 1305, 3300 960	
(IIIc)					^g		1480, 1335, 3280 945	
(IIId)	5.08(s)	8.3-9.4	2.00(br)	{ 5.96(m) (N-CH ₂) 4.65-4.95 (N-C-C=CH ₂) 4.15(m) (N-C-CH=)	785		1450, ^g , ^g 3280	
(IIIe)								
(IIIf)	4.92(s)	8.2-9.3	-0.25(br)	{ 2.1-2.4 (N-C ₆ H ₅) 2.6-3.1	792		1470, 1330, 3300 930	
					^g		1505, ^g , 960 3230 1490	

^a Measured in CS₂. ^b KBr. ^c s, Singlet; d, doublet; t, triplet; q, quartet; p, pentuplet; h, heptuplet; m, multiplet; br, broad. ^d ν (C=C) aromatic. ^e ν (C=S). ^f Overlapped. ^g Uncertain.

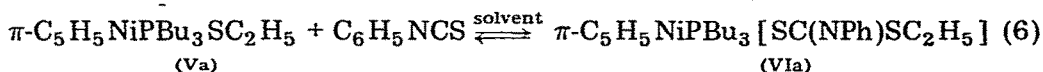
(eqn. 5). Structure (IVd) could be assigned by elemental analysis and spectral data; (IVd) showed intense absorption bands at 1630 [$\nu(\text{C}=\text{O})$ amide I band] and 3350 cm^{-1} [$\nu(\text{N}-\text{H})$] in the IR spectrum, and at τ 2.30 (NH, s, 1H), 2.60–3.40 (C_6H_5 , 5H), 4.80 ($\pi\text{-C}_5\text{H}_5$, s, 5H) and 8.30–9.45 ppm (PBu_3 , 27H) in the NMR spectrum.

Similarly the compounds $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(O)NHR}$ ($\text{R} = \text{CH}_3$, C_2H_5 and cyclo- C_6H_{11}) (IVa–c) were obtained from reaction between $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{-SH}$ and RNCO .

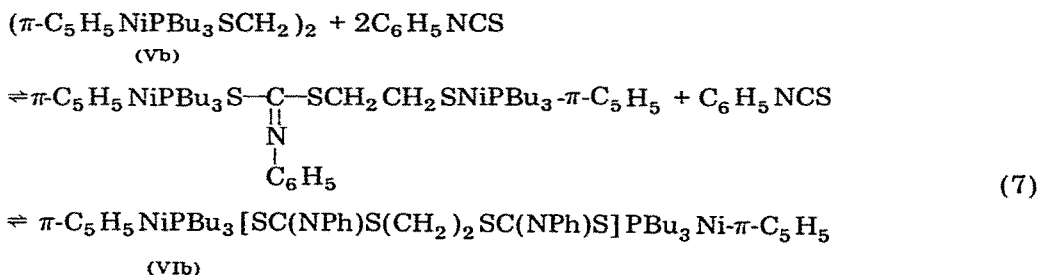
The properties and elemental analysis data of compounds (IV) are given in Table 3, and in Table 4 are listed the IR and NMR data.

Reactions of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SR}$ with $\text{C}_6\text{H}_5\text{NCS}$ [1e]

It has been shown that $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC}_2\text{H}_5$ (Va) reacts with $\text{C}_6\text{H}_5\text{NCS}$ to give $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3[\text{SC(NPh)SC}_2\text{H}_5]$ (VIa) and that the product reversibly dissociates to the reactants in solution, as in eqn. (6) [1e].



The dithiol dianion bridged nickel compound $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{S}(\text{CH}_2)_2\text{-SPBu}_3\text{Ni-}\pi\text{-C}_5\text{H}_5$, (Vb) [1c], similarly undergoes $\text{C}_6\text{H}_5\text{NCS}$ insertion readily at room temperature, producing the compound $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3[\text{SC(NPh)S}(\text{CH}_2)_2\text{SC(NPh)S}] \text{PBu}_3\text{Ni-}\pi\text{-C}_5\text{H}_5$ (VIb). The elemental analysis and IR spectrum support the structure (VIb) and the IR spectrum of the solid (VIb) resembles closely that of the solid (VIa). The NMR spectrum of (VIb) in C_6D_6 shows four peaks, which are assigned to $\pi\text{-C}_5\text{H}_5$ protons at τ 4.71, 4.73, 4.79 and 4.81 ppm, and four peaks which are assigned to methylene protons of $\text{S-CH}_2\text{-CH}_2\text{-S}$ at τ 5.28 [s, due to (VIb)], 6.35(m), 7.35(m) and 7.51 ppm [s, (Vb)]. These NMR results indicate that (VIb) is dissociated in C_6D_6 according to the eqn. (7).



Similarly, $(\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SCH}_2\text{CH}_2)_2$ and $(\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SCH}_2\text{CH}_2\text{-CH}_2)_2$ undergo $\text{C}_6\text{H}_5\text{NCS}$ insertion reactions and give the products $(\pi\text{-C}_5\text{H}_5\text{-NiPBu}_3\text{SC(NC}_6\text{H}_5\text{)SCH}_2\text{CH}_2)_2$, (VIc) and $(\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(NC}_6\text{H}_5\text{)SCH}_2\text{-CH}_2\text{CH}_2)_2$, (VId) respectively. The properties and elemental analytical data of compounds (VI) are given in Table 5, and Table 6 are listed the IR and NMR data.

Reactions of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(S)R}$ (I) with HCl [1f]

We could obtain the stable compounds $\pi\text{-C}_5\text{H}_5\text{NiSC(S)CH}_2\text{C}_6\text{H}_5$ (VIIa)

TABLE 3
SOME PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR COMPOUNDS (IV)^a

Compound	M.p. (°C)	Yield (%)	Analyses found (calcd.) (%)			
			C	H	N	S
(IVa)	72.5–73	86	54.85 (54.85)	9.17 (8.66)	3.33 (3.37)	
(IVb)	61–62	88	55.63 (55.83)	8.65 (8.84)	2.96 (3.26)	
(IVc)	62.5–63	91	58.65 (59.54)	9.22 (9.10)	2.78 (2.89)	
(IVd)	102–104	87	60.03 (60.29)	8.15 (7.95)	2.96 (2.93)	6.59 (6.69)

^aAll compounds are brown in colour.

from reaction between $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(S)CH}_2\text{C}_6\text{H}_5$ (Ia) and HCl, and the compounds $\pi\text{-C}_5\text{H}_5\text{NiSC(S)R}$ (VIIb,c) ($\text{R} = \text{C}_2\text{H}_5$ and C_6H_5) were also obtained by similar treatment of (Ib,c), (which, as mentioned before, could not be isolated) with HCl. These results obviously indicate the existence of compounds (Ib,c).

It is interesting that the compounds (VII) are stable while the isostructural compounds $\pi\text{-C}_5\text{H}_5\text{NiSC(S)SR}$ [4] are known to be unstable, and that in contrast to these results the compounds $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SC(S)SR}$ [1d] ($\text{R} = \text{C}_2\text{H}_5$) are unstable.

The properties and elemental analysis data of the compounds (VII) are collected in Table 1. NMR data of (VII) have been given previously [1f].

Spectral data

It is well known that the C=S vibration is susceptible to coupling effects. Rao et al. [5] described the three characteristic bands in the ranges 1573–1395, 1420–1260 and 1140–940 cm^{-1} as NCS bands I, II and III for the compounds containing an N=C=S group. The dithiocarbamate nickel compounds (III) show three characteristic bands (Table 2) which fit well the assignment by Rao et al. but compounds (VI) show a strong band at about 1530 cm^{-1} , assigned to $\nu(\text{C}=\text{N})$ [6] (Table 6), and no other bands characteristic of the N=C=S group.

Dialkyl xanthates, dioxanthogens and heavy metal xanthates show a series of bands in the ranges 1250–1200, 1140–1110 and 1070–1020 cm^{-1} which originate in the structure $\text{R}-\text{O}-\text{C}=\text{S}$ [7]. Compounds (II) show three bands near to these ranges (Table 2).

There is reasonably good agreement that the $\nu(\text{C}=\text{S})$ band lies between 1225 and 1190 cm^{-1} in dithioesters [8] and therefore the absorption at 1205 cm^{-1} of (Ia) and 1150 cm^{-1} of (VIIa) is identified with $\nu(\text{C}=\text{S})$, though (VIIa) shows another strong absorption at 995 cm^{-1} . Thiocarbamates of the type RSCONHR' ($\text{R}' = \text{alkyl or aryl}$) are known to show $\nu(\text{C}=\text{O})$ in the ranges 1690–1695 and 1699–1662 cm^{-1} , respectively. Surprisingly, compounds (IV) absorb at lower frequencies (1610–1630 cm^{-1} , Table 4). These lower frequency shifts are probably caused either by the heavy atom effect or by the superior electron-donating properties of the $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3$ moiety.

TABLE 4
¹H NMR AND IR DATA FOR COMPOUNDS (IV)

Compound	¹ H NMR data ^a [τ (ppm)]			IR data ^b (cm ⁻¹)			
	π-C ₆ H ₅	PBu ₃	NH	Other	γ(π-C ₆ H ₅)	ν(NH)	ν(C=O)
(IVa)	4.88(s)	8.3-9.6	4.67(br)	7.48(d) N-CH ₃ , J(NH-CH ₃) 6Hz	?	3420	1610
(IVb)	4.86(s)	8.2-9.6 ^c	4.31(br)	7.05(p) (N-CH ₃) c (N-C-CH ₃)	?	3380	1615
(IVc)							
(IVd)	4.80(s)	8.3-9.6	2.39(br)	2.6-3.4(N-C ₆ H ₅)	792	3400	1615
					?	3350	1630

^a Measured in CS₂. ^b KBr. ^c Overlapped.

TABLE 5
SOME PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR COMPOUNDS (VI)^a

Compound	M.p. (°C)	Yield (%)	Analyses found (calcd.) (%)		
			C	H	N
(VIa)	70.5–71.5	98	59.25 (59.84)	7.98 (8.05)	2.71 (2.68)
(VIb)	98–99	97	59.56 (59.17)	7.83 (7.69)	2.81 (2.76)
(VIc)	98.5–99.5	98	60.66 (59.88)	7.99 (7.87)	2.64 (2.69)
(VI d)	98.5–99.0	98	59.65 (60.56)	8.13 (8.04)	2.47 (2.62)

^aAll compounds are brown in colour.

Experimental

$[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PBU}_3)_2]^+\text{Cl}^-$ and $\pi\text{-C}_5\text{H}_5\text{NiPBU}_3\text{SH}$ were prepared as previously described [1a]. The anions of $\text{SC}(\text{S})\text{NRR}'$, $\text{SC}(\text{S})\text{OR}$ and $\text{SC}(\text{S})\text{R}$ were prepared by the method described in the literature [3].

IR spectra were recorded on a JASCO-IR-G spectrometer. Proton NMR spectra were recorded on a JEOL-JNM-4H 100 NMR spectrometer with TMS as the internal standard. Some typical procedures are shown below, while the data are summarized in Tables 1–6.

Reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PBU}_3)_2]^+\text{Cl}^-$ with $\text{SC}(\text{S})\text{CH}_2\text{Ph}^-$

When an aqueous solution of $\text{NaSC}(\text{S})\text{CH}_2\text{Ph}$ (10mmoles) was added to an aqueous solution of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PBU}_3)_2]^+\text{Cl}^-$ (3 mmoles), at room temperature, a brown precipitate immediately appeared. This was extracted with ether, and the ether solution was dried over anhydrous calcium chloride. The ether was removed under vacuum to leave a brown residue. Recrystallization from n-hexane gave 1.42 g (96% yield) of (Ia).

Reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PBU}_3)_2]^+\text{Cl}^-$ with $\text{SC}(\text{S})\text{OCH}_3$

When an aqueous solution of $\text{NaSC}(\text{S})\text{OCH}_3$ (10 mmoles) was added to an aqueous solution of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PBU}_3)_2]^+\text{Cl}^-$ (3 mmoles), at room temperature, a brown precipitate appeared immediately. This was extracted with benzene, and the benzene solution was dried over anhydrous calcium chloride. The solution was evaporated in vacuo and the residue was recrystallized from a benzene/n-hexane mixture to give 1.14 g (88% yield) of (IIa).

Reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PBU}_3)_2]^+\text{Cl}^-$ with $\text{SC}(\text{S})\text{NHC}_6\text{H}_5$

An aqueous solution of $\text{NH}_4[\text{SC}(\text{S})\text{NHC}_6\text{H}_5]$ (10 mmoles) was added to an aqueous solution of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PBU}_3)_2]^+\text{Cl}^-$ (3 mmoles), at room temperature, and a brown precipitate appeared immediately. This was extracted with benzene, and the benzene solution was dried over anhydrous calcium chloride. The solution was evaporated in vacuo and the residue was recrystallized from a benzene/n-hexane mixture to give 1.26 g (85% yield) of (III f).

TABLE 6
¹H NMR AND IR DATA FOR COMPOUNDS (VI)

Compound	¹ H NMR data ^a			PBu ₃	S-CH ₂	Other	IR data (cm ⁻¹) ^b	
	π-C ₅ H ₅	C ₆ H ₅					ν(C=N)	γ(π-C ₅ H ₅)
(VIa)	4.82(s)	2.6-3.5		8.2-9.4 ^c	6.86(q) 7.88(q) ^d 5.28(s)	d ₁ (S-O-CH ₃)	1530	800
(VIb)	4.71(s) 4.73(s) ^d 4.79(s)	2.5-3.5		8.0-9.4	6.35(m) 7.35(m) 7.51(s) ^d		1520	800
(VIc)	4.81(s) 4.74(s) 4.77(s) ^d	2.6-3.5		8.3-9.5	6.70(m) 7.80(m) ^d	8.00(m)(S-C-CH ₂)	1525	795
(VId)	4.77(s) ^d 4.78(s)	2.6-3.5		8.0-9.4 ^c	6.80(br) 7.85(br) ^d	c ₁ [S-C-(CH ₂) ₂]	1525	793

^a Measured in C₆D₆. ^b KBr. ^c Overlapped. ^d Assigned to complex (V).

Reaction of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PBu}_3)_2]^+\text{Cl}^-$ with $\text{NaSC}(\text{S})\text{N}(\text{CH}_3)_2$

An aqueous solution of $\text{Na}[\text{SC}(\text{S})\text{N}(\text{CH}_3)_2]$ (10 mmoles) was added to an aqueous solution of $[\pi\text{-C}_5\text{H}_5\text{-Ni}(\text{PBu}_3)_2]^+\text{Cl}^-$ (3 mmoles) at room temperature and a green precipitate appeared immediately. While drying this precipitate, which was filtered in vacuo at room temperature, the colour of the precipitate changed from green to purple. The purple product was very unstable and it changes easily to green product $\text{Ni}[\text{SC}(\text{S})\text{N}(\text{CH}_3)_2]$ [2a] in 86% yield. (Found: C, 23.51; H, 3.81; N, 8.92. $\text{C}_6\text{H}_{12}\text{N}_2\text{NiS}_4$ calcd.: C, 24.08; H, 4.01; N, 9.36%.)

Reaction of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SH}$ with $\text{C}_6\text{H}_5\text{NCS}$

After standing a few hours at room temperature, a mixture of n-hexane solution of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SH}$ (2 mmoles) and excess $\text{C}_6\text{H}_5\text{NCS}$ (20 mmoles) gave reddish brown crystals. These were filtered off and recrystallized from a benzene/n-hexane mixture to give 0.91 g (92% yield) of (III_f).

Reaction of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SH}$ with $\text{C}_6\text{H}_5\text{NCO}$

A benzene solution of $\pi\text{-C}_5\text{H}_5\text{NiPBu}_3\text{SH}$ (2 mmoles) and $\text{C}_6\text{H}_5\text{NCO}$ (20 mmoles) was set aside for about 8h at room temperature and the solution was evaporated in vacuo. Chromatography, on silica gel, of the resulting residue with 50% ether/n-hexane as eluant gave material which was recrystallized from ether/n-hexane to give 0.82 g (87% yield) of (IV_d).

Reaction of $\pi\text{-C}_5\text{H}_5\text{PBu}_3\text{NiS}(\text{CH}_2)_2\text{SNiPBu}_3\pi\text{-C}_5\text{H}_5$ with $\text{C}_6\text{H}_5\text{NCS}$

After standing a few hours at room temperature, a mixture of n-pentane solution of $\pi\text{-C}_5\text{H}_5\text{PBu}_3\text{NiS}(\text{CH}_2)_2\text{SNiPBu}_3\pi\text{-C}_5\text{H}_5$ (1 mmole) and excess $\text{C}_6\text{H}_5\text{NCS}$ (10 mmoles) gave reddish brown crystals. These were filtered off and recrystallized from a benzene/n-hexane mixture to give 0.98 g (98% yield) of (VI_b).

Preparation of $\pi\text{-C}_5\text{H}_5\text{NiSC}(\text{S})\text{C}_6\text{H}_5$

When an aqueous solution of $\text{NaSC}(\text{S})\text{C}_6\text{H}_5$ (10 mmoles) was added to an aqueous solution of $[\pi\text{-C}_5\text{H}_5\text{Ni}(\text{PBu}_3)_2]^+\text{Cl}^-$ (3 mmoles), at room temperature, a brown oily product appeared immediately. This was extracted with 50 ml ether and to this ether solution an 18% HCl aqueous solution (50 ml) was added.

The colour of the ether solution changed from brown to green after vigorous stirring of the two layers. After 15 minutes of stirring the green ether layer was separated and washed twice with 50 ml water, then the solution was evaporated in vacuo. Chromatography, on silica gel, of the resulting residue with ether/n-hexane as the eluant gave material which was recrystallized from n-hexane to give 0.5 g (61% yield) of VII_c.

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