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π-CYCLOPENTADIENYLS OF NICKEL(II)

XIII. THE PREPARATION AND PROPERTIES OF THE COMPOUNDS π-$C_5H_5NiPBu_3SC(S)X$ (X = OR, R AND NRH) AND π-$C_5H_5NiPBu_3$-SC(O)NRH

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Summary

Compounds of the type π-$C_5H_5NiPBu_3SC(S)X$ (X= R, OR and NRH) are obtained from reactions between $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ and $SC(S)X^-$ in aqueous solution. Compounds such as π-$C_5H_5NiPBu_3SC(S)NRH$ are also obtained by reactions of π-$C_5H_5NiPBu_3SH$ with RNCS.

Reactions of C_6H_5NCS with π-$C_5H_5NiPBu_3SEt$ or $[\pi\text{-}C_5H_5NiPBu_3S(CH_2)_n]_2$ (n = 1, 2 and 3) give π-$C_5H_5NiPBu_3[SC(NC_6H_5)SC_2H_5]$ or $[\pi\text{-}C_5H_5NiPBu_3\{SC(NC_6H_5)S(CH_2)_n\}]_2$ respectively.

Similar reactions of π-$C_5H_5NiPBu_3SH$ and RNCO give π-$C_5H_5NiPBu_3SC(O)NRH$.

Treatment of π-$C_5H_5NiPBu_3SC(S)R$ with HCl gives π-$C_5H_5NiSC(S)R$.

Introduction

Recently we have investigated the preparation and reactivity of compounds of the type π-$C_5H_5NiPBu_3X$ [1] (X = anion). It has been shown that π-$C_5H_5NiPBu_3SR$ compounds readily undergo carbon disulphide insertion to produce the stable compounds π-$C_5H_5NiPBu_3SC(S)SR$ [1d], and that π-$C_5H_5NiPBu_3SC_2H_5$ also undergoes phenyl isothiocyanate insertion to give π-$C_5H_5NiPBu_3[SC(NC_6H_5)SC_2H_5]$ [1e]. The preparation of compounds of the type π-$C_5H_5NiSC(S)R$ 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-$C_5H_5NiPBu_3SC(S)X$ (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-$C_5H_5NiPBu_3SC(S)X$ (X = R, OR and NRH) were obtained from reactions between $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ and $[SC(S)\text{-}X]^-$ in aqueous solution; this is a generally accepted route for preparation of compounds of the type $\pi\text{-}C_5H_5NiPBu_3X$ (X = anion) [1].

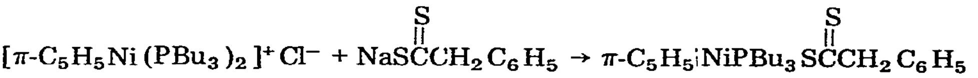
The compounds $\pi\text{-}C_5H_5NiPBu_3SC(S)NRH$ were also obtained from reactions of $\pi\text{-}C_5H_5NiPBu_3SH$ with RNCS.

Results and discussion

Reactions of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ with $SC(S)X^-$ (X = R, OR and NRH)

When excess $NaSC(S)CH_2C_6H_5$ was added to an aqueous solution of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$, 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} [$\gamma(C_5H_5)$]. NMR peaks appeared at τ2.6—3.2 (aromatic 5H), 4.93($\pi\text{-}C_5H_5$, S 5H), 5.82(CH_2—Ph, s, 2H) and 8.3—9.6 ppm (PBu_3, 27H). These results, together with the analytical and reactivity data described later, indicate that the product is $\pi\text{-}C_5H_5NiPBu_3SC(S)CH_2C_6H_5$ with structure (Ia) (eqn. 1).



$$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^- + NaS\overset{S}{\overset{\|}{C}}CH_2C_6H_5 \rightarrow \pi\text{-}C_5H_5NiPBu_3S\overset{S}{\overset{\|}{C}}CH_2C_6H_5 \qquad (1)$$

(Ia)

Similar treatment of other NaSC(S)R compounds (R = C_2H_5 and C_6H_5) with $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ 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 $\pi\text{-}C_5H_5NiPBu_3SC(S)R$.

$NaSC(S)OCH_3$ reacted readily with $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ in aqueous solution to give the expected $\pi\text{-}C_5H_5NiPBu_3SC(S)OCH_3$ (IIa) as brown crystals in 88% yield (eqn. 2).

$$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^- + NaS\overset{S}{\overset{\|}{C}}OCH_3 \rightarrow \pi\text{-}C_5H_5NiPBu_3S\overset{S}{\overset{\|}{C}}OCH_3 \qquad (2)$$

(IIa)

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 τ4.92($\pi\text{-}C_5H_5$, s, 5H), 6.18(O—CH_3, s, 3H) and 8.40—9.50(PBu_3, 27H) in the NMR spectrum.

Analogous treatment of other compounds of the type NaSC(S)OR (R = C_2H_5, i-C_3H_7 and CH_2=$CHCH_2$) with $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ gave the corresponding $\pi\text{-}C_5H_5NiPBu_3SC(S)OR$ (IIb—d).

$\pi\text{-}C_5H_5NiPBu_3SC(S)NHCH_3$ (IIIa) was obtained from reaction between $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ and $[SC(S)NHCH_3]^-$ in aqueous solution in 87% yield (eqn. 3).

$$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^- + [S{-}\overset{\overset{S}{\|}}{C}NHCH_3]^- \rightarrow \pi\text{-}C_5H_5NiPBu_3S\overset{\overset{S}{\|}}{C}NHCH_3 \qquad (3)$$

(IIIa)

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 ν(NH) at 3330 cm^{-1}; the NMR spectrum shows signals at τ1.89(NH, br, 1H), 5.06 (π-C_5H_5, s, 5H), 7.03 [N—CH_3, d, J-(H—CH_3) 5Hz, 3H] and 8.20—9.30 (PBu_3, 27H). By similar treatment of other $[SC(S)NHR]^-$ (R = C_2H_5, n-C_3H_7, CH_2=$CHCH_2$, cyclo-C_6H_{11} and C_6H_5) with $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$, the corresponding substances π-$C_5H_5NiPBu_3$-SC(S)NHR (III b—f) were obtained in excellent yield.

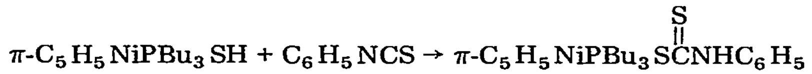
Surprisingly the reactions of $[SC(S)NRR']^-$ (R = C_6H_5 and R' = CH_3 or C_2H_5, and R = R' = CH_3 or C_2H_5) with $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ gave Ni[SC-(S)NRR'$_2$ [2a] as main products and none of the expected products π-C_5H_5-$NiPBu_3SC(S)NRR'$, but it is not clear why such differences exist between the reactivities of $[SC(S)NRH]^-$ and $[SC(S)NRR']^-$.

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

Reactions of π-$C_5H_5NiPBu_3SH$ with RNCS

The well known result that RNCS rects 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 π-$C_5H_5NiPBu_3SH$ with RNCS because we have already found that phenylacetylene inserts into the SH bond of π-$C_5H_5NiPBu_3SH$ [1b].

Adding, at room temperature, excess phenyl isothiocyanate to a hexane solution of π-$C_5H_5NiPBu_3SH$ gave brown crystals in quantitative yield. The melting point, IR spectrum and NMR spectrum of these crystals are coincident with those of (IIIf) (eqn. 4). Similarly, the compounds π-$C_5H_5NiPBu_3SC(S)$-NHR (R = CH_3, C_2H_5, CH_2=$CHCH_2$ and cyclo-C_6H_{11}) (IIIa,b,d,e) were obtained in excellent yields from the reaction between π-$C_5H_5NiPBu_3SH$ and RNCS.

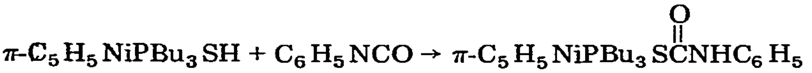


$$\pi\text{-}C_5H_5NiPBu_3SH + C_6H_5NCS \rightarrow \pi\text{-}C_5H_5NiPBu_3S\overset{\overset{S}{\|}}{C}NHC_6H_5 \qquad (4)$$

(IIIf)

Reactions of π-$C_5H_5NiPBu_3SH$ 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 π-C_5-H_5NiPBu_3SH with RNCO. Similarly to the reactions with C_6H_5NCS, π-C_5H_5-$NiPBu_3SH$ reacted readily with C_6H_5NCO at room temperature to give the expected π-$C_5H_5NiPBu_3SC(O)NHC_6H_5$ (IVd) as brown crystals in 87% yield



$$\pi\text{-}C_5H_5NiPBu_3SH + C_6H_5NCO \rightarrow \pi\text{-}C_5H_5NiPBu_3S\overset{\overset{O}{\|}}{C}NHC_6H_5 \qquad (5)$$

(IVd)

(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
				C	H	N	(calcd.)
(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 $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$.

TABLE 2

^{1}H NMR AND IR DATA FOR COMPOUNDS (I), (II) AND (III)

Compound	^{1}H NMR data ^{a} (τ ppm)				IR data ^{b} (cm^{-1})				
	π-C_5H_5	PBu_3	NH	Other	γ(π-C_5H_5)	ν(R—O—C=S)	ν(N—C=S)	ν(NH)	Other
(Ia)	4.93(s) ^{c}	8.3—9.6		5.82(s) (CH_2) 2.6—3.2 (C_6H_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)^{f} (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)^{f} [O—C—(CH_3)$_2$]	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, 928	3330	
(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, 960	3300	
(IIIc)					^{g}		1480, 1335, 945	3280	
(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)					792		1470, 1330, 930	3300	
(IIIf)	4.92(s)	8.2—9.3	—0.25(br)	2.1—2.4 2.6—3.1 (N—C_6H_5)	^{g}		1505, ^{g}, 960 1490	3230	

^{a} Measured in CS_2. ^{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 [ν(C=O) amide I band] and 3350 cm^{-1} [ν(N—H)] in the IR spectrum, and at τ2.30 (NH, s, 1H), 2.60—3.40 (C_6H_5, 5H), 4.80 (π-C_5H_5, s, 5H) and 8.30—9.45 ppm (PBu_3, 27H) in the NMR spectrum.

Similarly the compounds π-$C_5H_5NiPBu_3SC(O)NHR$ (R = CH_3, C_2H_5 and cyclo-C_6H_{11}) (IVa—c) were obtained from reaction between π-$C_5H_5NiPBu_3$-SH and RNCO.

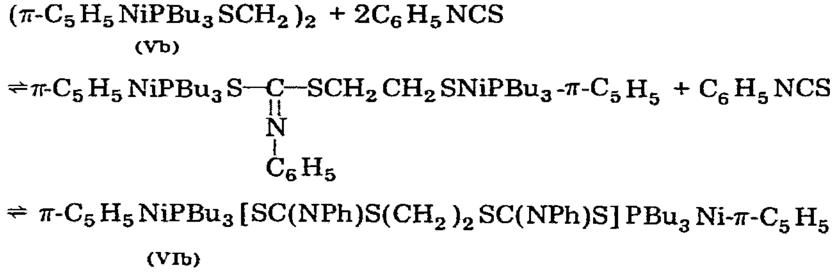
The properties and elemental analysis data of compounds (IV) are given in Table 3, and in Table 4 are listed the IR and NMR data.

Reactions of π-$C_5H_5NiPBu_3SR$ with C_6H_5NCS [1e]

It has been shown that π-$C_5H_5NiPBu_3SC_2H_5$ (Va) reacts with C_6H_5NCS to give π-$C_5H_5NiPBu_3[SC(NPh)SC_2H_5]$ (VIa) and that the product reversibly dissociates to the reactants in solution, as in eqn. (6) [1e].

$$\underset{\text{(Va)}}{\pi\text{-}C_5H_5NiPBu_3SC_2H_5} + C_6H_5NCS \overset{\text{solvent}}{\rightleftharpoons} \underset{\text{(VIa)}}{\pi\text{-}C_5H_5NiPBu_3[SC(NPh)SC_2H_5]} \quad (6)$$

The dithiol dianion bridged nickel compound π-$C_5H_5NiPBu_3S(CH_2)_2$-$SPBu_3Ni$-π-C_5H_5, (Vb) [1c], similarly undergoes C_6H_5NCS insertion readily at room temperature, producing the compound π-$C_5H_5NiPBu_3[SC(NPh)S$-$(CH_2)_2SC(NPh)S]PBu_3Ni$-π-C_5H_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 π-C_5H_5 protons at τ4.71, 4.73, 4.79 and 4.81 ppm, and four peaks which are assigned to methylene protons of S—CH_2—CH_2—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).



$$\underset{\text{(Vb)}}{(\pi\text{-}C_5H_5NiPBu_3SCH_2)_2} + 2C_6H_5NCS$$
$$\rightleftharpoons \pi\text{-}C_5H_5NiPBu_3S\text{—}\underset{\underset{C_6H_5}{|}}{\underset{N}{\overset{}{\underset{\|}{C}}}}\text{—}SCH_2CH_2SNiPBu_3\text{-}\pi\text{-}C_5H_5 + C_6H_5NCS \quad (7)$$
$$\rightleftharpoons \underset{\text{(VIb)}}{\pi\text{-}C_5H_5NiPBu_3[SC(NPh)S(CH_2)_2SC(NPh)S]PBu_3Ni\text{-}\pi\text{-}C_5H_5}$$

Similarly, $(\pi$-$C_5H_5NiPBu_3SCH_2CH_2)_2$ and $(\pi$-$C_5H_5NiPBu_3SCH_2CH_2$-$CH_2)_2$ undergo C_6H_5NCS insertion reactions and give the products $(\pi$-C_5H_5-$NiPBu_3SC(NC_6H_5)SCH_2CH_2]_2$, (VIc) and $(\pi$-$C_5H_5NiPBu_3SC(NC_6H_5)SCH_2$-$CH_2CH_2]_2$, (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 π-$C_5H_5NiPBu_3SC(S)R$ (I) with HCl [1f]

We could obtain the stable compounds π-$C_5H_5NiSC(S)CH_2C_6H_5$ (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)

[a] All compounds are brown in colour.

from reaction between π-$C_5H_5NiPBu_3SC(S)CH_2C_6H_5$ (Ia) and HCl, and the compounds π-$C_5H_5NiSC(S)R$ (VIIb,c) (R = C_2H_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 π-$C_5H_5NiSC(S)SR$ [4] are known to be unstable, and that in contrast to these results the compounds π-$C_5H_5NiPBu_3SC(S)SR$ [1d] (R = C_2H_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 ν(C=N) [6] (Table 6), and no other bands characteristic of the N—C=S group.

Dialkyl xanthates, dixanthogens 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 R—O—C=S [7]. Compounds (II) show three bands near to these ranges (Table 2).

There is reasonably good agreement that the ν(C=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 ν(C=S), though (VIIa) shows another strong absorption at 995 cm^{-1}. Thiocarbamates of the type RSCONHR′ (R′ = alkyl or aryl) are known to show ν(C=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 π-$C_5H_5NiPBu_3$ moiety.

TABLE 4

^{1}H NMR AND IR DATA FOR COMPOUNDS (IV)

Compound	^{1}H NMR data[a] [τ(ppm)]				IR data[b] (cm^{-1})		
	π-C_5H_5	PBu_3	NH	Other	γ(π-C_5H_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_2) [c] (N–C–CH_3)	?	3380	1615
(IVc)					792	3400	1615
(IVd)	4.80(s)	8.3–9.5	2.30(br)	2.6–3.4(N–C_6H_5)	?	3350	1630

[a] Measured in CS_2. [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	7.98	2.71
			(59.84)	(8.05)	(2.68)
(VIb)	98—99	97	59.56	7.83	2.81
			(59.17)	(7.69)	(2.76)
(VIc)	98.5—99.5	98	60.66	7.99	2.64
			(59.88)	(7.87)	(2.69)
(VId)	98.5—99.0	98	59.65	8.13	2.47
			(60.56)	(8.04)	(2.62)

[a] All compounds are brown in colour.

Experimental

$[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ and $\pi\text{-}C_5H_5NiPBu_3SH$ were prepared as previously described [1a]. The anions of SC(S)NRR′, SC(S)OR and SC(S)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 $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ with $SC(S)CH_2Ph^-$

When an aqueous solution of $NaSC(S)CH_2Ph$ (10mmoles) was added to an aqueous solution of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ (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 $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ with $SC(S)OCH_3$

When an aqueous solution of $NaSC(S)OCH_3$ (10 mmoles) was added to an aqueous solution of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ (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 $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ with $SC(S)NHC_6H_5$

An aqueous solution of $NH_4[SC(S)NHC_6H_5]$ (10 mmoles) was added to an aqueous solution of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ (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 (IIIf).

TABLE 6

^{1}H NMR AND IR DATA FOR COMPOUNDS (VI)

Compound	^{1}H NMR data^a					IR data (cm^{-1})^b	
	π-C_5H_5	C_6H_5	PBu_3	S—CH_2	Other	ν(C=N)	γ(π-C_5H_5)
(VIa)	4.82(s)	2.6—3.5	8.2—9.4^c	6.86(q) 7.88(q)^d	^{d}(S—C—CH_3)	1530	800
(VIb)	4.71(s) 4.73(s)^d 4.79(s) 4.81(s)	2.5—3.5	8.0—9.4	5.28(s) 6.35(m) 7.35(m) 7.51(s)^d		1520	800
(VIc)	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}[S—C—$(CH_2)_2$]	1525	793

^{a}Measured in C_6D_6. ^{b}KBr. ^{c}Overlapped. ^{d}Assigned to complex (V).

Reaction of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ *with* $NaSC(S)N(CH_3)_2$

An aqueous solution of $Na[SC(S)N(CH_3)_2]$ (10 mmoles) was added to an aqueous solution of $[\pi\text{-}C_5H_5\text{-}Ni(PBu_3)_2)]^+Cl^-$ (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 $Ni[SC(S)N(CH_3)_2]$ [2a] in 86% yield. (Found: C,23.51; H,3.81; N,8.92. $C_6H_{12}N_2NiS_4$ calcd.: C,24.08; H,4.01; N,9.36%.)

Reaction of $\pi\text{-}C_5H_5NiPBu_3SH$ *with* C_6H_5NCS

After standing a few hours at room temperature, a mixture of n-hexane solution of $\pi\text{-}C_5H_5NiPBu_3SH$ (2 mmoles) and excess C_6H_5NCS (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 (IIIf).

Reaction of $\pi\text{-}C_5H_5NiPBu_3SH$ *with* C_6H_5NCO

A benzene solution of $\pi\text{-}C_5H_5NiPBu_3SH$ (2 mmoles) and C_6H_5NCO (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 (IVd).

Reaction of $\pi\text{-}C_5H_5PBu_3NiS(CH_2)_2SNiPBu_3\pi\text{-}C_5H_5$ *with* C_6H_5NCS

After standing a few hours at room temperature, a mixture of n-pentane solution of $\pi\text{-}C_5H_5PBu_3NiS(CH_2)_2SNiPBu_3\pi\text{-}C_5H_5$ (1 mmole) and excess C_6H_5NCS (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 (VIb).

Preparation of $\pi\text{-}C_5H_5NiSC(S)C_6H_5$

When an aqueous solution of $NaSC(S)C_6H_5$ (10 mmoles) was added to an aqueous solution of $[\pi\text{-}C_5H_5Ni(PBu_3)_2]^+Cl^-$ (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 VIIc).

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