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Metal Complexes of Sulphur Ligands.
Part 19 [1]. Reaction of Nickel(II) Monothioacetate and -benzoate Complexes with some Nitrogen, Phosphorus and Arsenid Donor Lewis Bases

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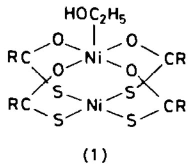
Reaction of $[\{Ni(SOCR)_2 0.5EtOH\}_2]$ *(1) (R = Me, Ph) with various heterocyclic nitrogen donor ligands (L) gives the green, paramagnetic, octahedral complexes* $[Ni(SOCR)_2L_2]$ *(2) (L =* C_5H_5N, $4\text{-}MeC_5H_4N$, *½bipy). In contrast reaction of (1) with various monotertiary phosphines and* $Ph_2P(CH_2)_xPPh_2$ *(x = 1 or 2) give the red, diamagnetic, square planar, complexes* $[Ni(SOCR)_2(PR'_3)_2]$ *(3b)* (PR'_3 = PPh_3, $PMePh_2$, PMe_2Ph) *and* $[Ni(SOCR)_2(Ph_2P(CH_2)_xPPh_2)]$ *(3a) respectively, shown by ir spectroscopy to contain unidentate S-bonded* ^-SOCR *groups. Molecular weight, electronic spectra and variable temperature* ^1H *and* $^{31}P\text{–}\{^1H\}$ *nmr studies indicate that the monophosphine complexes (3b), although stable in solution below 220 K, are substantially dissociated at ambient temperature and also in dynamic equilibria with small amounts of paramagnetic isomer. Finally, reaction of (1) with triphenylarsine gives red, paramagnetic complexes* $[\{Ni(SOCR)_2AsPh_3\}_n]$ $(H_2O)_n$ *(5) believed to be of similar structure to compounds (1) (*i.e. *n = 2).*

Introduction

Recently we reported the syntheses of the sulphur bridged polymers $[\{M(SOCPh)_2\}_n]$ ($n \geqslant 3$, M = Pd, Pt) and their reactions with a variety of Lewis bases L or L–L [L = PPh_3, $PMePh_2$, PMe_2Ph, $AsPh_3$, $SbPh_3$, C_5H_5N; L–L = 2,2'-bipyridyl, $Ph_2P[CH_2]_xPPh_2$ (x = 1 or 2)] which gave the neutral, square-planar, monomeric complexes $[M(SOCPh)_2L_2]$ or $[M(SOCPh)_2(L\text{–}L)]$ containing unidentate, S-bonded $SOCPh^-$ groups [2].

In contrast, earlier workers [3–5] have reported that reaction of various nickel(II) salts with either $Na[SOCPh]$ or HSOCR (R = Me, Et) gave the dimeric $[\{Ni(SOCR)_2 0.5EtOH\}_2]$ complexes, shown by X-ray analysis [4] (for R = Ph) to have structure (1). Furthermore, reaction of (1) with various unidentate, heterocyclic nitrogen donor ligands (L) resulted in the formation of green, monomeric, octahedral complexes $[Ni(SOCR)_2L_2]$ (2) [L = C_5H_5N, $2\text{-}MeC_5H_4N$, $3\text{-}MeC_5H_4N$, $4\text{-}MeC_5H_4N$ *etc.*] [3–5] in which the monothiocarboxylate groups are coordinated in bidentate fashion. Similar octahedral nickel(II) complexes $[Ni(S\text{–}O)_2L_2]$ containing nitrogen bases and other monothioacid ligands ($S\text{–}O^-$ = ^-SOCOEt [6], $^-SOCNR_2$ [7]) have also been synthesised.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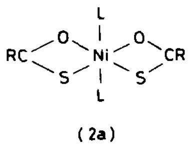
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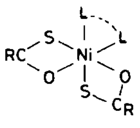
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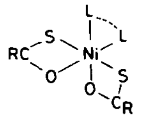
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In this paper, we now wish to describe, for the first time, reactions of $[\{Ni(SOCR)_2 0.5EtOH\}_2]$ (R = Me, Ph) with various phosphorus donor ligands and to compare the results with those found using nitrogen donor ligands.

Results and Discussion

As found by other workers, $[\{Ni(SOCR)_2 0.5EtOH\}_2]$ (1) (R = Me, Ph) readily reacted with a 5 to 10 fold excess of pyridine or 4-methylpyridine (L) in ethanol to give green solutions from which green solids of stoichiometry $[Ni(SOCR)_2L_2]$ (2) were readily isolated. As reported earlier, these complexes are monomeric, paramagnetic (Table I) and on the basis of electronic spectral studies contain octahedrally co-ordinated nickel(II) ions. Similarly, reaction of (1) (R = Me, Ph) with 2,2'bipyridyl (1:2 molar ratio) gave green $[Ni(SOCR)_2bipy]$ com-

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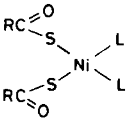
TABLE I. Analytical Data, some Characteristic IR Bands (Nujol mull) and Magnetic Moments for Some Nickel(II) Monothiocarboxylates.

Complex	Colour	(Mp/°C)	Analyses (%)[a]				Infrared Bands (cm^{-1})		μ_{eff}[b]
			C	H	N	M[c]	ν_{CO}	ν_{CS}	
$[Ni(SOCPh)_2 0.5C_2H_5OH]_2$	Maroon	176–177	50.8(50.6)	3.7(3.6)	–	–	1508s	958vs	3.32[d]
$[Ni(SOCPh)_2(C_5H_5N)_2]$	Green	186–187	58.5(58.7)	4.1(4.1)	5.7(5.7)	365(490)	1600s	960vs	2.99 (3.00)
$\{Ni(SOCPh)_2(4\text{-}MeC_5H_4N)_2\}$	Green	202–203	60.3(60.1)	4.7(4.6)	5.4(5.4)	431(519)	1610vs	965vs	(3.40)
$[Ni(SOCPh)_2(bipy)]$	Green	117–118	58.7(58.9)	3.7(3.7)	5.8(5.7)	–	1600s, 1570w	960s	(3.07)
$[Ni(SOCPh)_2(PPh_3)_2]$	Orange	154	68.7(68.4)	4.6(4.6)	–	317(877)	1590s, 1570s	910vs	diam.
$\{Ni(SOCPh)_2(PMePh_2)_2\}$	Dark Red	151	65.3(65.5)	4.8(4.9)	–	–	1580s, 1550vs	915s	diam.
$\{Ni(SOCPh)_2(PMe_2Ph)_2\}$	Red	157–159	59.3(59.1)	5.2(5.3)	–	417,634[e](609)	1590s, 1560s	900vs[f]	diam.
$\{Ni(SOCPh)_2(Ph_2PCH_2PPh_2)\}$	Orange	160	65.2(65.3)	4.5(4.5)	–	–	1590m, 1560w	910w	–
$[Ni(SOCPh)_2(Ph_2P\{CH_2\}_2PPh_2)]$	Orange	180	65.5(65.7)	4.6(4.7)	–	760(731)	1580s, 1555s	910s	–
$\{Ni(SOCPh)_2AsPh_3\}_n(H_2O)_n$	Red-Brown	169–171	57.7(59.0)	3.9(4.1)	–	(too insoluble)	1510vs	950vs	–
$[Ni(SOCMe)_2 0.5C_2H_5OH\}_2$	Black	150(decomp)	25.6(25.8)	3.7(3.9)	–	–	1540s	975s	3.29[d]
$[Ni(SOCMe)_2(4\text{-}MeC_5H_4N)_2]$	Dark Green	95(decomp)	48.8(48.6)	5.1(5.1)	7.0(7.1)	–	1610s	960(s)	(3.01)
$[Ni(SOCMe)_2(bipy)]$	Green	140–150(decomp)	46.7(46.0)	3.9(3.8)	8.0(7.7)	–	1590s, 1560m	965(s)	(2.81)
$\{Ni(SOCMe)_2(PPh_3)_2]$	Red-Orange	144–145(decomp)	65.3(65.5)	4.9(4.9)	–	265(733)	1600(vs)broad	940(s)	diam.
$[Ni(SOCMe)_2(PMePh_2)_2]$	Red-Orange	153(decomp)	59.2(59.1)	5.2(5.3)	–	362(609)	1600vs	940(s)	diam.
$[Ni(SOCMe)_2(PMe_2Ph)_2]$	Red-Orange	122–123	49.6(49.5)	5.8(5.8)	–	–	1600vs	938(s)	diam.
$\{Ni(SOCMe)_2(Ph_2PCH_2PPh_2)\}$	Dark red	130–132(decomp)	58.5(58.7)	4.7(4.7)		580(593)	1610vs(broad)	940(s)	diam.
$[Ni(SOCMe)_2(Ph_2P\{CH_2\}_2PPh_2)\}$	Orange yellow	201–203	59.1(59.3)	4.9(4.9)	–	–	1590(vs)(broad)	945(s)	–
$[Ni(SOCMe)_2AsPh_3]_n(H_2O)_n$	Dark red	135(decomp)	49.6(49.3)	4.1(4.3)	–	too insoluble	1605vs	970(s)	2.52[g]

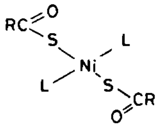
[a] Calculated values given in parentheses. [b] Magnetic moment measured by Faraday method (solid) at 295 K; in parentheses, as measured by Evans' method in CH_2Cl_2 at 301 K. [c] Osmometrically at 37 °C in acetone; calculated values for monomer are given in parentheses. [d] Value taken from ref. 4; calculated per dimer. [e] Higher value measured on more concentrated solution. [f] Partially masked by strong PMe_2Ph vibration at 900 cm^{-1}. [g] Calculated assuming $n = 2$.

plexes with similar spectroscopic and magnetic properties (Table I).

In contrast, reaction of (1), (R = Me, Ph) with an excess of various tertiary phosphines (PR'_3) gave orange-red compounds of stoichiometry $[Ni(SOCR)_2(PR'_3)_2]$ (3) (PR'_3 = PPh_3, $PMePh_2$, PMe_2Ph) which were diamagnetic in the solid state. Similarly, orange, diamagnetic compounds $[Ni(SOCR)_2(Ph_2P[CH_2]_xPPh_2)]$ (x = 1 or 2) were isolated on reaction of (1) (R = Me, Ph) with $Ph_2P[CH_2]_xPPh_2$ (1:2 molar ratio).



(3a)



(3b)

As discussed elsewhere [2, 3], the positions of the ν_{CO} and ν_{CS} vibrations in the ir spectra of the compounds are diagnostic of the mode of bonding of the monothiocarboxylate group. Thus for $[\{Ni(SOCPh)_2 \cdot 0.5EtOH\}_2]$, ($\nu_{CO}$ 1508; ν_{CS} 958 cm^{-1}), the values are very similar to those found in Na[SOCPh], (ν_{CO} 1500; ν_{CS} 960 cm^{-1}), indicative of more or less symmetrical bonding of the oxygen and sulphur atoms to nickel, as expected for the bridged structure (1). However, the ir spectra of compounds (3) (R = Ph) all show ν_{CS} vibrations at *ca.* 910 cm^{-1} and ν_{CO} vibrations between 1550–1590 cm^{-1} (Table I) indicative of strong Ni–S and weak Ni–O interactions respectively [*cf.* $[Pd(SOCPh)_2(PMe_2Ph)_2]$, (ν_{CO} 1595, 1560; ν_{CS} 910 cm^{-1}) [2], shown by X-ray analysis [8] to have a square planar structure with *trans* S-bonded ^-SOCPh groups]. Similarly, comparing $[\{Ni(SOCMe)_2 0.5EtOH\}_2]$ (ν_{CO} 1540; ν_{CS} 975 cm^{-1}) with compounds (3) (R = Me) (ν_{CO} *ca.* 1600 cm^{-1}, ν_{CS} *ca.* 940 cm^{-1}) (Table I) suggests strong Ni–S and weak Ni–O interactions respectively in the latter.

For the green $[Ni(SOCR)_2(4\text{-}MeC_5H_4N)_2]$ (2) ν_{CS} occurs at 965 cm^{-1} (R = Ph), 960 cm^{-1} (R = Me). Note, however, that the ν_{CO} vibrations in compounds (2) are at *ca.* 1600 cm^{-1}, suggesting that some weakening of the Ni–O interaction compared to that in compound (1) has occurred. This is probably due to a substantial *trans* bond weakening effect produced by either the sulphur and/or the nitrogen donor atoms, depending on whether structure (2a, b or c) is present. In fact, a recent X-ray analysis on $[Ni(SOCMe)_2(C_5H_5N)_2]$ [9] shows the structure to be (2c) although the structure adopted may vary with slight changes of ligand (*cf.* the related $[Ni(S_2PPh_2)_2(C_5H_5N)_2]$ which has a *trans* configuration [10]). For $[Ni(SOCR)_2bipy]$, only structures (2b or c) are of course possible.

Similar differences in behaviour towards nickel(II) by nitrogen and phosphorus donor atom ligands have been found with nickel dithioacid compounds. Thus, it is well established that reaction of $[Ni(S\text{–}S)_2]$ $[S\text{–}S^- = {}^-S_2CNR_2, {}^-S_2COR, {}^-S_2P(OR)_2, {}^-S_2PR_2]$ with most nitrogen donor ligands (L) give either paramagnetic, five coordinate $[Ni(S\text{–}S)_2L]$ and/or six coordinate $[Ni(S\text{–}S)_2L_2]$ complexes depending on the nature of the ligand used [11]. However, very recently, reaction of $[Ni(S_2COR)_2]$ with an excess of tri-n-butylphosphine in ethanol was reported to give the red, diamagnetic complexes $[Ni(S_2COR)_2(P^nBu_3)_2]$, formulated as four coordinate, square planar compounds containing unidentate, xanthato groups [12].

Presumably the main reason for this difference in behaviour between N and P donor ligands towards Ni(II) monothio- and dithio- acid compounds is that the P donor ligands are high enough in the spectrochemical series to encourage the Ni(II) ion to adopt a low spin, square planar configuration (*cf.* $Ni(CN)_4^{2-}$ and $Ni(H_2O)_6^{2+}$ [13]). For palladium(II) and platinum(II) however, the larger ligand field splitting values associated with these heavier elements lead to square planar configurations even for weak field ligands [13] and, hence, no structural differences between N and P donor ligand complexes of Pd(II) and Pt(II) monothioacid compounds have been observed [2].

Although there is strong evidence that the $[Ni(SOCR)_2(PR'_3)_2]$ compounds have a square planar configuration in the solid state, molecular weight and electronic spectral studies in acetone and dichloromethane respectively at ambient temperature reveal that substantial changes occur on dissolution. Thus, osmometric molecular weight measurements in acetone are much lower than expected for monomers (Table I) indicating some dissociation of ligands has occurred. Although conductivity measurements in acetone show that no ionic species are formed in solution, electronic spectral studies demonstrate that addition of free tertiary phosphine produces changes in the position of the absorption bands in the visible region, suggesting the following equilibrium is set up at ambient temperature:

$$[Ni(SOCR)_2(PR'_3)_2] \rightleftharpoons [Ni(SOCR)_2(PR'_3)] + PR'_3 \qquad (1)$$

On removal of solvent, however, only $[Ni(SOCR)_2(PR'_3)_2]$ complexes were obtained. The degree of dissociation depended on the PR'_3 groups present, the order observed being $PPh_3 > PMePh_2 > PMe_2Ph$. For $[Ni(SOCR)_2(Ph_2P(CH_2)_xPPh_2)]$, however, normal molecular weights were found and no change in the electronic spectra occurred on addition of $PPh_2(CH_2)_xPPh_2$, indicating that the square planar configuration (3a) was retained in solution. Several possible structures can be written for the inter-

TABLE II. Hydrogen-1 and ^{31}P–{^{1}H} Nmr Data in $CDCl_3$ for Various Nickel Monothiocarboxylate Compounds.

Complex	T/K	^{1}H nmr (δ)[a]			T/K	^{31}P–{^{1}H} nmr (δ)[b]
		Me (monothioacetate)	Me (phosphine)	Ph		
$[Ni(SOCPh)_2(PPh_3)_2]$	221	–	–	7.0–7.5(m)	221	24.1(s)
$[Ni(SOCPh)_2(PMe_2Ph)_2]$	271	–	1.61(s)	7.0–8.0(m)	271	–5.7(s)
	218[c]	–	1.55(t)[d]		218[c]	–4.7(s)
$[Ni(SOCPh)_2(PMePh_2)_2]$	271	–	2.05(s)	7.0–7.8(m)	263	9.0(v. broad)
	243	–	1.98(s)(broad)		243	9.7(s)
	210[c]	–	1.97(s)v. broad		210[c]	10.7(s)
$[Ni(SOCPh)_2(Ph_2P(CH_2)_2PPh_2)]$	301	–	2.20(m)broad[e]	7.0–8.0(m)	301	56.7(s)
	243	–	2.15(m)broad[e]		243	58.3(s)
$[Ni(SOCPh)_2(Ph_2P(CH_2)PPh_2)]$	301	–	3.41(m)(broad)[f]	7.1–7.8(m)	–	–
$[Ni(SOCMe)_2(PMe_2Ph)_2]$	301	2.04(s)	1.63(s)	7.2–7.8(m)	233	–5.3(s)
$[Ni(SOCMe)_2(Ph_2P(CH_2)PPh_2)]$	301	2.06(s)	3.66(m)broad[f]	7.2–8.0(m)	223	26.1(s)

s = singlet; t = triplet, m = multiplet.

[a] ±0.01 ppm. [b] ±0.05 ppm. [c] In CD_2Cl_2. [d] $|{}^2J(PH) + {}^4J(PH)|$ 7.50Hz. [e] C_2H_4 resonance. [f] CH_2 resonance.

mediate complex $[Ni(SOCR)_2PR'_3]$, but in view of the close similarity of the electronic spectra of $[Ni(SOCR)_2(PR'_3)_2]$ in the absence and presence of PR'_3, a square planar configuration (4) with chelating and S-bonded unidentate $^-$SOCPh groups is most likely for the *major* species in solution at ambient temperature.

For some of these tertiary phosphine compounds, solution magnetic measurements at ambient temperature by Evans' method [14] reveal the presence of a very small amount of paramagnetic material (≤5%). By analogy with earlier work on $[NiX_2(PR'_3)_2]$ compounds (X = Cl, Br, I) [15], the most probable explanation for this is the formation, in solution, of small amounts of paramagnetic, tetrahedral isomers although, of course, the formation of paramagnetic five or six coordinate isomers cannot be discounted.

A study of the variable temperature ^{1}H and ^{31}P–{^{1}H} nmr spectra of some of these phosphine complexes provide further information about their behaviour in solution. Thus, the ^{1}H nmr spectra (methyl region) of $[Ni(SOCPh)_2(PMe_2Ph)_2]$ below 220 K in CD_2Cl_2 consist of a 'virtually-coupled' triplet pattern [16] whereas at higher temperatures (up to 303 K) only a sharp singlet (at almost the same chemical shift as the triplet) is observed (Table II). This suggests that at low temperatures, equilibrium (1) lies completely to the left hand side with the square planar, *trans* isomer (3b) exclusively formed (*cf.* the ^{1}H nmr spectrum of *trans*-$[Pd(SOCPh)_2(PMe_2Ph)_2]$ [2]). Similar observations have been made for the related $[Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2$ which are stable at 213 K in $CDCl_3$ but extensively dissociated into $[Pt(S_2CNR_2)_2(PMePh_2)]$ and $PMePh_2$ at ambient temperature (equlibrium [2]) [17]:

$$[Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2 \rightleftharpoons [Pt(S_2CNR_2)_2(PMePh_2)] + PMePh_2 \qquad (2)$$

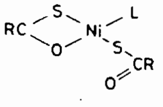
The ^{31}P–{^{1}H} nmr spectra of all the $[Ni(SOCR)_2(PR'_3)_2]$ compounds at temperatures below 220 K showed a singlet and for PR'_3 = PMe_2Ph, selective decoupling of the phenyl protons showed J_{PCH_3} to be present. On raising the temperature, the phosphorus–hydrogen coupling disappeared although the position of the singlet remained virtually invariant up to *ca.* 273 K. Above this temperature, however, the singlet broadened and then disappeared. Addition of an excess of free phosphine at temperatures below 273 K produced two ^{31}P–{^{1}H} nmr signals, one corresponding to free phosphine and the other to the species present in the absence of free phosphine. Thus, this clearly shows that loss of phosphorus–hydrogen coupling, at least below 273 K, is not due to fast intermolecular PR'_3 exchange (see ref. 18 for examples of this process) and also that the $[Ni(SOCR)_2(PR'_3)_2]$ complexes do *not* dissociate significantly in solution below this temperature. Therefore the only explanation we can offer for the loss of phosphorus-hydrogen couplings between 220 and 273 K in compounds (3b) is the generation of increasing amounts of paramagnetic isomers on raising the temperature, accompanied by facile exchange between these and the diamagnetic isomers (3b) (*cf.* nmr studies on the related $[NiX_2(PR'_3)_2]$ complexes [15]).

Above 273 K, broadening and subsequent loss of the ^{31}P nmr signals can be attributed to a combination of facile intermolecular scrambling between $[Ni(SOCR)_2(PR'_3)_2]$, $[Ni(SOCR)_2PR'_3]$ and PR'_3

and the formation of increasing amounts of paramagnetic isomer. Since the effect of the latter will be much less marked on the more distant protons, singlets are still observed at room temperature for the methyl resonances in their ^1H nmr spectra.

In support of this explanation, the $^{31}P-\{^1H\}$ nmr spectrum of $[Ni(SOCPh)_2(PPh_2(CH_2)_2PPh_2)]$ (where molecular weight and electronic spectral studies indicate no dissociation even at ambient temperature) shows a sharp singlet from 301 to 243 K.

Finally, on prolonged reaction of $[\{Ni(SOCR)_2 \cdot 0.5EtOH\}_2]$ with an excess of $AsPh_3$ in ethanol at 253 K, dark red solids of empirical formulae $[Ni(SOCR)_2(AsPh_3)]H_2O$ (R = Me, Ph) were isolated. Evidence that these are genuine products and not mixtures of starting material and $[Ni(SOCR)_2(AsPh_3)_2]$ is based on melting points, magnetic moments and the positions of ν_{CO} and ν_{CS} vibrations in their infrared spectra (Table I). Thus, for $[\{Ni(SOCPh)_2(AsPh_3)\}_n](H_2O)_n$, the observation that ν_{CO} 1510, g_{CS} 950 cm^{-1}, together with the occurrence of typical infrared absorption bands of $AsPh_3$, is consistent with these 1:1 adducts having structure (5). Furthermore, although the compounds were too insoluble for molecular weight measurements, the magnetic moment of R = Ph is fairly similar to that of the parent dimer (1). Presumably, the high 'class b' character of $AsPh_3$ inhibits further reaction with the 'class a' nickel ion.



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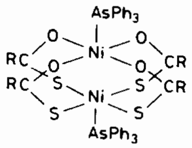

(5)

Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Molecular weights were determined on a Hitachi Perkin Elmer vapour pressure osmometer (model 115) calibrated with benzil. Infrared spectra were recorded in the 250–4000 cm^{-1} region on a Perkin Elmer 557 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Electronic spectra were obtained on a Unicam SP800 spectrophotometer using unmatched silica cells. Hydrogen-1 nmr spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a variable temperature probe; proton-noise-decoupled ^{31}P nmr spectra on a Jeol FX60 spectrometer operating in the pulse and Fourier transform modes at 24.21 MHz (^{31}P chemical shifts quoted in ppm to high frequency of 85% H_3PO_4). Conductivity measurements were obtained on a Portland Electronics 310 conductivity bridge at 298 K. Solution magnetic moments (Evans' method [14]) were obtained on a Varian Associates HA100 spectrometer and magnetic susceptibilities (solid) were measured on a Faraday balance at Dundee University. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Monothiobenzoic and monothioacetic acids (Aldrich), triphenylphosphine, (BDH) dimethylphenylphosphine and methyldiphenylphosphine (Maybridge Chemical Co.) were obtained as indicated. The compounds Na[SOCPh] [19], $Ph_2PCH_2PPh_2$ [20], $Ph_2P[CH_2]_2PPh_2$ [21], $[\{Ni(SOCPh)_2 \cdot 0.5EtOH\}_2]$ [4] $[\{Ni(SOCMe)_2 0.5EtOH\}_2]$ [4] were prepared as described earlier.

Analytical data, characteristic ir bands and magnetic moments for various complexes are given in Table I, and ^1H and $^{31}P-\{^1H\}$ nmr data in Table II. Reactions involving tertiary phosphines were carried out under a nitrogen atmosphere.

General Method of Preparation of $[Ni(SOCR)_2L_2]$ *and* $[Ni(SOCR)_2(L\text{–}L)]$ *Complexes*

The appropriate nickel(II) monothiocarboxylate compound was suspended in ethanol and treated with a 5 to 10 fold excess of an ethanolic solution of the monodentate ligand L. The resulting mixture was then gently warmed with stirring for 1 hour. On removal of some solvent, the product precipitated out in some instances. If not, precipitation was initiated by addition of light petroleum (b.p. 60–80 °C). These products were filtered off, washed with light petroleum (b.p. 60–80 °C) and dried *in vacuo* at 40 °C. For the bidentate ligands (L–L) the molar ratio of ligand to complex used was 2:1 to help prevent complete displacement of the monothiocarboxylate groups.

For the preparation of $[\{Ni(SOCR)_2(AsPh_3)\}_n](H_2O)_n$, after reaction as above, the solution was reduced in volume and then stored at 253 K for 5 days. At the end of this period, the reddish-brown products had precipitated out and these were dried as above.

Acknowledgments

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