Metal Dithiocarbamates and Related Complexes. Part I. Reactions of Tris(dithiocarbamato)nickel(IV) Cations with Lewis Bases

By **Jon A. McCleverty** * and **Norman J. Morrison**, Department of Chemistry, The University, Sheffield S3 7HF

Treatment of $[Ni(S_2CNR_2)_3][PF_6]$ (R = Et or Bu^n) with Lewis bases [L = CNR′ (R′ = Pr^i, Bu^t, or C_6H_4Cl-*p*), $PMePh_2$, or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$(dppe)] gives $[NiL_2(S_2CNR_2)][PF_6]$; when L = CNR′, the thiuram disulphide $(R_2NCS_2)_2$ has been also isolated. Reaction of $[Ni(S_2CNR_2)_3][PF_6]$ with PPh_3 affords PPh_3S, $[PPh_3\{C(NR_2)S\}][PF_6]$, and $[Ni(S_2CNR_2)_2]$; only very low yields of $[Ni(PPh_3)_2(S_2CNR_2)][PF_6]$ have been isolated. Similar products have been obtained in the reaction between $[Ni(PPh_3)_2(S_2CNEt_2)][PF_6]$ and $(Et_2NCS_2)_2$. The species $[NiL_2(S_2CNR_2)][PF_6]$ (L = $PMePh_2$ or PPh_3) have been obtained from $[NiL(S_2CNR_2)X]$ (X = halide), L, and $M[PF_6]$ (M = K, Tl, or Ag), and modified procedures for making $[NiL(S_2CNR_2)X]$ are described. Reaction of $[Ni(PPh_3)(S_2CNR_2)][PF_6]$ with $PMePh_2$ gives $[Ni(PMePh_2)(S_2CNR_2)X]$ (X = I), and with $Tl(C_5H_5)$ and Na[SR″] the complexes $[Ni(\eta\text{-}C_5H_5)I(PPh_3)]$ and $[\{Ni(SR'')(S_2CNR_2)\}_2]$ (R″ = Me, Pr^i, Bu^t, $PhCH_2$, or Ph) are formed, respectively. The n.m.r., electronic, and i.r. spectral properties of these complexes are discussed. The complex $[NiCl(PPh_3)(S_2CNEt_2)]$ readily undergoes phosphine exchange with free PPh_3, and while $[NiI(dppe)(S_2CNBu^n_2)]$ is four-co-ordinate (iodide salt) in chlorinated hydrocarbon and polar solvents it is apparently five-co-ordinate in benzene.

OXIDATION of $[Ni(S_2CNR_2)_2]$ (R = Et, Bu^n, or $PhCH_2$) with Br_2 (or, when R = Bu^n, with I_2), or reaction of nickel halides with $(R_2NCS_2)_2$, has given [1] the unusual cations $[Ni(S_2CNR_2)_3]X$ (X = halide). That these complexes should be regarded as containing Ni^{IV} seems to be confirmed [2] by the following observations: (*i*) a magnetic moment of 0.71 B.M. (R = Bu^n, X = Br),† consistent with a $3d^6$ low-spin octahedral configuration for the cation; (*ii*) the correspondence of the electronic spectra of $[Ni(S_2CNR_2)_3]^+$ with the isoelectronic $[Co(S_2CNR_2)_3]$; and (*iii*) the molecular structure of $[Ni(S_2CNBu^n_2)_3]Br$. The last observation shows that the metal is surrounded by three normal dithiocarbamate groups in trigonally distorted octahedral co-ordination. There is no evidence of interligand S–S bonding, in contrast to the situation in the highly oxidised trigonal-prismatic dithiolene complexes $[M(S_2C_2R_2)_3]$.[3] Fackler *et al.*[4] have shown that treatment of deep red-brown solutions of the $[Ni(S_2CNBu^n_2)_3]^+$ cation in certain solvents (*e.g.* MeCN, $MeNO_2$, MeOH, or EtOH but not $CHCl_3$, $CHBr_3$, or CH_2Cl_2) with strong visible light results in the disappearance of the red-brown colour, leaving a pale yellow solution. With these solvents a gradual return of the dark red-brown colour occurs when the solution is allowed to stand in the dark, but with co-ordinating solvents (*e.g.* pyridine, 4-methylpyridine, or triethylamine–chloroform mixtures) the bleaching is irreversible. A spectrophotometric study showed that the reversible bleaching could be interpreted as in equation (1). Thermal bleaching in MeCN and nitrobenzene was also observed, and reactions with some Lewis bases were found to yield uncharacterised nickel(II) species and $(Bu^n_2NCS_2)_2$, although no products were actually isolated. Reaction of $[Ni(S_2CNBu^n_2)_3]Br$ with PPh_3 gave a purple solution with a visible spectrum similar to that of $[NiBr(PPh_3)(S_2CNEt_2)]$, which has been prepared alternatively by Maxfield.[5]

$$[Ni(S_2CNBu^n_2)_3]^+ + Br^- \longrightarrow \tfrac{1}{2}[Ni(S_2CNBu^n_2)_2] + \tfrac{1}{2}NiBr_2 + (Bu^n_2NCS_2)_2 \quad (1)$$

These reactions suggest that $[Ni(S_2CNR_2)_3]^+$ may undergo a facile internal redox reaction, producing the transient nickel(II) thiuram disulphide species $[Ni\{(S_2CNR_2)_2\}(S_2CNR_2)]^+$. This species would be expected to readily undergo displacement of the thiuram disulphide in the presence of basic solvent or added ligand, giving $[NiL_2(S_2CNR_2)]^+$. When L = solvent, attack by halide anion X^- would give $[Ni(S_2CNR_2)X]$ (solvated), and it is pertinent to note that the species $[\{Pd(S_2CNR_2)X\}_2]$ have been isolated.[6] When L = Lewis base, the species $[NiL_2(S_2CNR_2)]^+$ and $[NiL(S_2CNR_2)X]$ should be sufficiently stable to isolate.

In this paper we describe the reactions of $[Ni(S_2CNR_2)_3]^+$ with Lewis bases, and report on the properties of the products, $[NiL_2(S_2CNR_2)]^+$ and $[NiL(S_2CNR_2)X]$. A preliminary account of some of this work has been given.[7]

RESULTS AND DISCUSSION

Syntheses.—The complexes $[Ni(S_2CNR_2)_3]Br$ (R = Bu^n, or Et) were prepared by oxidation of $[Ni(S_2CNR_2)_2]$ with

---

† 1 B.M. ≈ 9.27×10^{-24} A m^2.

[1] H. C. Brinkhoff, J. A. Cras, J. J. Steggarda, and J. Willemse, *Rec. Trav. chim.*, 1969, **88**, 633.

[2] A. Avdeef, J. P. Fackler, and R. G. Fischer, *J. Amer. Chem. Soc.*, 1970, **92**, 6972.

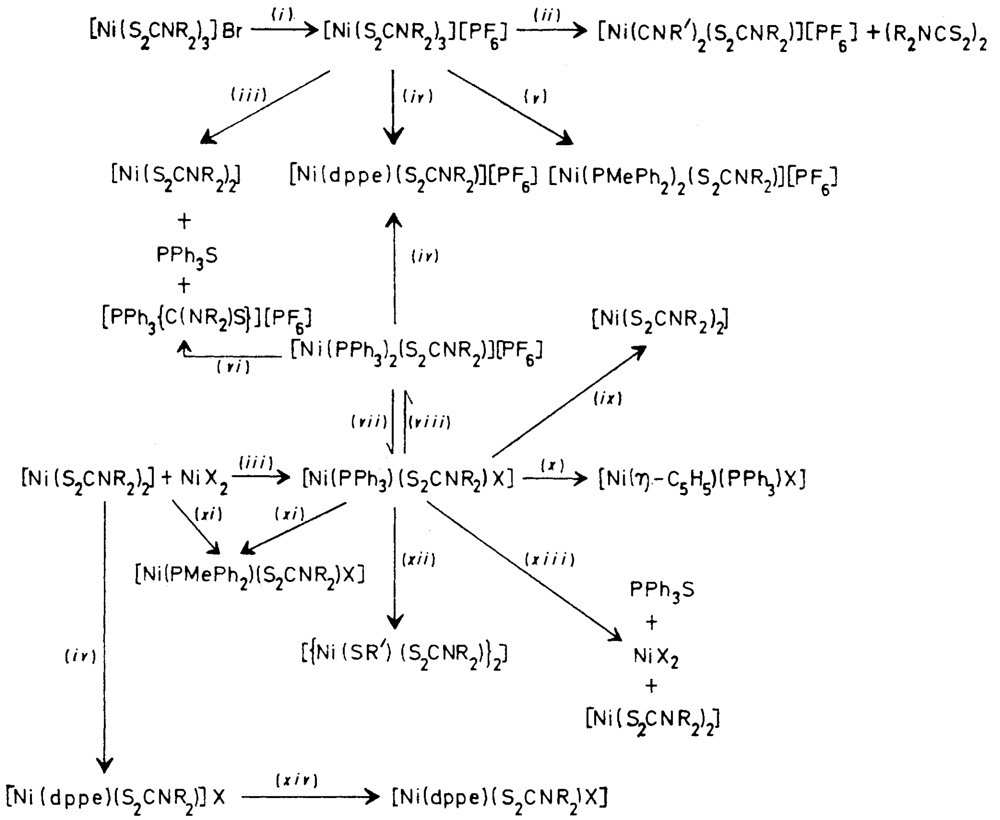
[3] J. A. McCleverty, *Progr. Inorg. Chem.*, 1968, **10**, 49; R. Eisenberg, *ibid.*, 1970, **12**, 295.

[4] A. Avdeef, J. P. Fackler, and R. G. Fischer, *J. Amer. Chem. Soc.*, 1973, **95**, 774.

[5] P. L. Maxfield, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 693.

[6] T. A. Stephenson, personal communication.

[7] A. K. M. Groves, N. J. Morrison, and J. A. McCleverty, *J. Organometallic Chem.*, 1975, **84**, C5.



SCHEME (*i*), Ag[PF$_6$]; (*ii*) R′NC; (*iii*), PPh$_3$; (*iv*), dppe; (*v*), PMePh$_2$; (*vi*), (R$_2$NCS$_2$)$_2$; (*vii*) [NBu$_4$]X; (*viii*), PPh$_3$ and K[PF$_6$]; (*ix*), Na[S$_2$CNR$_2$]·*x*H$_2$O; (*x*), Tl(C$_5$H$_5$); (*xi*), PMe$_2$Ph; (*xii*), Na[SR′]; (*xiii*), S$_8$; (*xiv*), benzene solution

Infrared spectrum (cm^{-1}) of the compounds

Compound	ν(CN) [a]		
[Ni(S$_2$CNEt$_2$)$_3$][PF$_6$]	1 528	(1 533)	
[Ni(S$_2$CNBu$^n{}_2$)$_3$][PF$_6$]	1 527	(1 539)	
[Ni(CNPr^i)$_2$(S$_2$CNEt$_2$)][PF$_6$]	1 544	(1 549)	
	2 212(sh) [b]	(2 210)(sh)	
	2 224 [b]	(2 223)	
[Ni(CNPr^i)$_2$(S$_2$CNBu$^n{}_2$)][PF$_6$]	1 542	(1 558)	
	2 212(sh) [b]	(2 220)	
	2 224 [b]	(2 232)(sh)	
[Ni(CNBu^t)$_2$(S$_2$CNEt$_2$)][PF$_6$]	1 544	(1 547)	
	2 208(sh) [b]	(2 215)(sh)	
	2 204 [b]	(2 223)	
[Ni(CNBu^t)$_2$(S$_2$CNBu$^n{}_2$)][PF$_6$]	1 542	(1 556)	
	2 267(sh) [b]	(2 217)(sh)	
	2 220 [b]	(2 228)	
[Ni(CNC$_6$H$_4$Cl-*p*)$_2$(S$_2$CNEt$_2$)][PF$_6$]	1 546	(1 536)	
	2 192 [b]	(2 185)	
	2 204(sh) [b]	(2 201)(sh)	
[Ni(CNC$_6$H$_4$Cl-*p*)$_2$(S$_2$CNBu$^n{}_2$)][PF$_6$]	1 544	(1 540)	
	2 192 [b]	(2 192(sh)	
	2 204(sh) [b]	(2 203)	
[Ni(PMePh$_2$)$_2$(S$_2$CNEt$_2$)][PF$_6$]	1 534	(1 530)	
[Ni(PMePh$_2$)$_2$(S$_2$CNBu$^n{}_2$)][PF$_6$]	1 532	(1 536)	
[Ni(dppe)(S$_2$CNMe$_2$)][PF$_6$]	1 559		
[Ni(dppe)(S$_2$CNEt$_2$)][PF$_6$]	1 532	(1 528)	
[Ni(dppe)(S$_2$CNBu$^n{}_2$)][PF$_6$]	1 528	(1 532)	
[Ni(dppe)(S$_2$CNBu$^n{}_2$)]I	1 528		
[Ni(PPh$_3$)$_2$(S$_2$CNMe$_2$)][PF$_6$]	1 561		
[Ni(PPh$_3$)$_2$(S$_2$CNEt$_2$)][PF$_6$]	1 536	(1 539)	
[Ni(PPh$_3$)$_2$(S$_2$CNBu$^n{}_2$)][PF$_6$]	1 532	(1 536)	
[PPh$_3${C(NEt$_2$)S}][PF$_6$]		(1 483),	(1492)(sh)
[PPh$_3${C(NBu$^n{}_2$)S}][PF$_6$]	1 481	(1 483),	(1 487)(sh)
[NiCl(PPh$_3$)(S$_2$CNMe$_2$)]	1 552		
[NiI(PPh$_3$)(S$_2$CNMe$_2$)]	1 553		
[NiI(PPh$_3$)(S$_2$CNEt$_2$)]			
[NiCl(PPh$_3$)(S$_2$CNBu$^n{}_2$)]	1 524		
[NiBr(PPh$_3$)(S$_2$CNBu$^n{}_2$)]	1 522		
[NiI(PPh$_3$)(S$_2$CNBu$^n{}_2$)]			
[NiI(dppe)(S$_2$CNBu$^n{}_2$)]			
[NiCl(PMePh$_2$)(S$_2$CNMe$_2$)]	1 552		
[NiI(PMePh$_2$)(S$_2$CNMe$_2$)]	1 553		
[NiCl(PMePh$_2$)(S$_2$CNEt$_2$)]	1 520		
[{Ni(SPh)(S$_2$CNBu$^n{}_2$)}$_2$]	1 509		
[{Ni(SMe)(S$_2$CNMe$_2$)}$_2$]	1 549		
[{Ni(SPr^i)(S$_2$CNMe$_2$)}$_2$]	1 552		
[{Ni(SBu^t)(S$_2$CNMe$_2$)}$_2$]	1 548,	1 560(sh)	
[{Ni(SCH$_2$Ph)(S$_2$CNMe$_2$)}$_2$]	1 556		
[{Ni(SPh)(S$_2$CNMe$_2$)}$_2$]	1 554		

[a] In CH$_2$Cl$_2$ solution; values for KBr discs are given in parentheses. [b] For CNR.

bromine, and could also be obtained by mixing cold ethanolic solutions of $NiBr_2$ and $(R_2NCS_2)_2$ ($R = Et$ or $R_2 = C_5H_{10}$). Only trace amounts of $[Ni(S_2CNMe_2)_3]Br$ could be obtained by these methods, and the brown solutions were characterised by a singlet (τ 6.58) in their ^1H n.m.r. spectra. Mixing hot ethanolic solutions of nickel halides and $(R_2NCS_2)_2$ ($R = Me$, Et, or $R_2 = C_5H_{10}$) resulted in the formation of brown solutions from which green crystals of $[Ni(S_2CNR_2)_2]$ separated. High yields of $[Ni(S_2CNMe_2)_2]$ could be obtained by heating (briefly) under reflux an ethanolic solution of $NiCl_2 \cdot 6H_2O$ with $(Me_2NCS_2)_2$ or $Me_2NC(S) \cdot S \cdot C(S)NMe_2$, but the other products of these two reactions were not investigated.

The complex $[NiBr(PPh_3)(S_2CNEt_2)]$ could be isolated from the reaction of $[Ni(S_2CNEt_2)_3]Br$ with PPh_3 and so, because of the possibility of bromide involvement in reactions of $[Ni(S_2CNR_2)_3]^+$, the bromide salts were converted into the $[PF_6]^-$ salts by metathesis with $Ag[PF_6]$. Analytical, ^1H n.m.r., and conductivity data * for all complexes are consistent with their formulations (infrared spectral information is given in the Table). Identification of products for which analytical data are not quoted was achieved by comparison of i.r. spectra and melting points with those of authentic samples. The reactions are represented in the Scheme, and were in CH_2Cl_2, a solvent in which photobleaching was not observed.

Reaction of $[Ni(S_2CNR_2)_3]^+$ with $R'NC$ ($R' = Pr^i$, Bu^t, or C_6H_4Cl-*p*) afforded, in very high yield, $[Ni(CNR')_2(S_2CNR_2)]^+$ and $(R_2NCS_2)_2$. The thiuram disulphides were obtained as white crystals ($R = Et$) or orange-yellow oils ($R = Bu^n$). With $PMePh_2$ and $Ph_2PCH_2CH_2PPh_2$ (dppe), $[Ni(PMePh_2)_2(S_2CNR_2)]^+$ and $[Ni(dppe)(S_2CNR_2)]^+$, respectively, were produced in lower yield, but with PPh_3 the yields of $[Ni(PPh_3)_2(S_2CNR_2)]^+$ were very low unless a large excess of PPh_3 was used. The salts $[Ni(S_2CNR_2)_3][PF_6]$ could be recovered unchanged after treatment for 4 h at room temperature in CH_2Cl_2 solution with $AsPh_3$, CO, or cyclo-octa-1,5-diene, but with 2,2′-bipyridyl the salt $[Ni(bipy)_3][PF_6]_2$ was formed.

A careful study of the major products of the reaction of $[Ni(S_2CNR_2)_3][PF_6]$ with PPh_3 revealed that PPh_3S and $[Ni(S_2CNR_2)_2]$ were formed together with a new phosphonium salt, $[PPh_3\{C(NR_2)S\}][PF_6]$. The same products (for $R = Et$) were obtained from the reaction of $[Ni(PPh_3)_2(S_2CNEt_2)][PF_6]$ with $(Et_2NCS_2)_2$, so it is possible that the last two complexes are intermediates and that the first step for reactions of phosphines as well as of isocyanides with $[Ni(S_2CNR_2)_3]^+$ is displacement of thiuram disulphide in a two-electron internal redox process (2).

$$[Ni(S_2CNR_2)_3]^+ + 2L \longrightarrow [NiL_2(S_2CNR_2)]^+ + (R_2NCS_2)_2 \quad (2)$$

The cation $[PPh_3\{C(NMe_2)S\}]^+$ has been prepared independently and will be described elsewhere. The red species $[Ni(PR''_3)_2(S_2CNR_2)]^+$ ($PR''_3 = PPh_3$, $PMePh_2$, or $2PR''_3$ = dppe; $R = Me$, Et, or Bu^n) could be obtained more readily by reacting $M[PF_6]$ ($M = K$, Tl, or Ag) with the purple complexes $[Ni(PR''_3)(S_2CNR_2)X]$. The solvates $[Ni(PPh_3)_2(S_2CNEt_2)][PF_6] \cdot CH_2Cl_2$ and $[Ni(PPh_3)_2(S_2CNBu^n_2)][PF_6] \cdot 0.5CH_2Cl_2$ were isolated first and the CH_2Cl_2 was then removed by heating the complexes. The isolation of low yields of $[Ni(PPh_3)_2(S_2CNBu^n_2)]^+$ from the reaction between $Ag[PF_6]$, PPh_3, and $[NiCl(PPh_3)(S_2CNBu^n_2)]$ was due to preferential co-ordination of PPh_3 to Ag^+, and $[Ag(PPh_3)_4][PF_6]$ was isolated from the reaction mixture; all reactions attempted with $K[PF_6]$ afforded high yields of the desired product. The precursors $[Ni(PR''_3)(S_2CNR_2)X]$ ($PR''_3 = PPh_3$, $R = Me$, $X = Cl$ or I, $R = Et$, $X = I$, $R = Bu^n$, $X = Cl$ or Br; $PR''_3 = PMePh_2$, $R = Me$, $X = Cl$ or I, $R = Et$, $X = Cl$; $2PR''_3$ = dppe, $R = Bu^n$, $X = I$) were prepared by stirring mixtures of PR''_3, $NiX_2 \cdot nH_2O$, and $[Ni(S_2CNR_2)_2]$ in refluxing ethanol. This represents a slight modification of the method originally used by Maxfield.[5]

The salts $[Ni(dppe)(S_2CNR_2)][PF_6]$ ($R = Me$, Et, or Bu^n) were prepared by rapid displacement of PPh_3 from $[Ni(PPh_3)_2(S_2CNR_2)][PF_6]$ by dppe. The species $[Ni(dppe)(S_2CNBu^n_2)]I$ dissolved in $CHCl_3$, CH_2Cl_2, $MeNO_2$, or EtOH and in cold or refluxing tetrahydrofuran or acetone to form orange-red solutions. Comparison of the ^1H n.m.r. spectrum in $CDCl_3$, the i.r. and electronic spectra in CH_2Cl_2, and the conductivity in $MeNO_2$ solution with those of the $[PF_6]^-$ salt confirms the presence of identical cations in these solvents. The iodide was slightly soluble in benzene, forming a purple solution. The sharp signals in the ^1H n.m.r. spectrum indicated that the complex was diamagnetic in this solvent. The dppe is probably bidentate since there was no reaction with sulphur under conditions (in benzene solution at 50 °C for 5 min) in which dppe normally forms its disulphide, and the complex could also be recovered unchanged after treatment with methyl iodide. A five-co-ordinate structure is postulated on the basis of the electronic spectrum (see below). Crystallisation from benzene, however, afforded the yellow planar ionic form, as indicated by the i.r. spectrum. Trace amounts of the solid purple form could be obtained by adding diethyl ether to a concentrated ethanolic solution of the complex and allowing the mixture to stand overnight. There was no change in the electronic spectrum in the 400—700 nm region on adding PPh_3 to a solution of $[NiI(PPh_3)(S_2CNBu^n_2)]$ in benzene, thus ruling out the possibility of a five-co-ordinate analogue of the dppe complex under similar conditions. Reaction of $[Ni(PPh_3)_2(S_2CNBu^n_2)]^+$ with $[NBu^n_4]I$ in acetone solution resulted in displacement of PPh_3 by I^-, and the complex $[NiI(PPh_3)(S_2CNBu^n_2)]$ was isolated. The complexes $[Ni(PPh_3)_2(S_2CNBu^n_2)]^+$ ($R = Me$, Et, or Bu^n) reacted qualitatively with tetra-alkylammonium halides to form the purple complexes $[Ni(PPh_3)(S_2CNR_2)X]$,

---

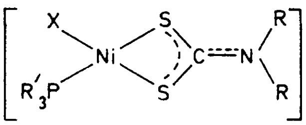
* These data have been deposited as Supplementary Publication No. SUP 21679 (10 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

but $[\mathrm{Ni(dppe)(S_2CNBu^n{}_2)}]^+$ showed no reaction with halide ions in acetone solution.

The complexes $[\mathrm{Ni(PPh_3)(S_2CNR_2)X}]$ could be useful intermediates in synthesis since they are crystalline, air-stable, easily prepared, and soluble in organic solvents such as benzene or acetone. The $\mathrm{PPh_3}$ in $[\mathrm{NiI(PPh_3)(S_2CNMe_2)}]$ was replaced rapidly by $\mathrm{PMePh_2}$ to form $[\mathrm{NiI(PMePh_2)(S_2CNMe_2)}]$. The labile nature of $\mathrm{PPh_3}$ in $[\mathrm{NiCl(PPh_3)(S_2CNMe_2)}]$ was demonstrated by reaction with sulphur in refluxing benzene, which afforded $\mathrm{PPh_3S}$, $[\mathrm{Ni(S_2CNMe_2)_2}]$, and $\mathrm{NiCl_2}$. Both $\mathrm{PPh_3}$ and $\mathrm{Cl^-}$ were replaced by $[\mathrm{SR'}]^-$ in the reaction of $[\mathrm{NiCl(PPh_3)(S_2CNR_2)}]$ with $\mathrm{Na[SR']}$ which afforded the green high-melting solids $[\{\mathrm{Ni(SR')(S_2CNR_2)}\}_2]$ ($\mathrm{R = Me}$, $\mathrm{R' = Me}$, $\mathrm{Pr^i}$, $\mathrm{Bu^t}$, $\mathrm{CH_2Ph}$, or Ph; $\mathrm{R = Bu^n}$, $\mathrm{R' = Ph}$). The complex $[\{\mathrm{Ni(SPh)(S_2CNBu^n{}_2)}\}_2]$ was sufficiently soluble in $\mathrm{CHCl_3}$ for a molecular-weight determination, which confirmed its dimeric nature (M 697. calc.: 743). Electrochemical studies revealed that these complexes underwent (in $\mathrm{CH_2Cl_2}$ using a rotating Pt electrode) two irreversible oxidation waves, but no reduction processes were detected at -1.8 V *versus* the standard calomel electrode (s.c.e.). The electrochemical behaviour is in contrast with that in $[\{\mathrm{Ni(\eta\text{-}C_5H_5)(SR)}\}_2]$ and $[\{\mathrm{M(SR)(S_2CSR)_2}\}_2]$ (M = Fe or Co) where, in some cases, reversible electrode properties were established.[8]

The dimer $[\{\mathrm{Ni(SCH_2Ph)(S_2CNEt_2)}\}_2]$ has been prepared[9] by treatment of $[\{\mathrm{Ni(SCH_2Ph)(S_2CSCH_2Ph)}\}_2]$ with $\mathrm{NEt_2H}$ and, more simply, by mixing $\mathrm{Na[SCH_2Ph]}$ with $\mathrm{Na[S_2CNEt_2]\cdot 3H_2O}$ in water and then adding aqueous $\mathrm{NiCl_2}$. Treatment of $[\mathrm{NiI(PPh_3)(S_2CNMe_2)}]$ with $\mathrm{Tl(C_5H_5)}$ resulted in the isolation of a low yield of maroon $[\mathrm{Ni(\eta\text{-}C_5H_5)I(PPh_3)}]$, which has also been prepared by displacement of CO from $[\mathrm{Ni(\eta\text{-}C_5H_5)(CO)I}]$ by $\mathrm{PPh_3}$.[10]

Spectral Studies.—N.m.r. spectra. The ^{1}H n.m.r. spectra of the complexes described herein were consistent with the formulations and were generally unremarkable. Inequivalence of the alkyl groups R in the spectra of complexes of structure (I) was expected but could not be detected even at -70 °C, at which temperature viscosity effects began to broaden all of the proton signals. A ^{13}C n.m.r. spectrum of $[\mathrm{NiI(PPh_3)(S_2CNEt_2)}]$ likewise failed to reveal resolved methylene or methyl C resonances. It therefore appears unlikely that accidental degeneracy is responsible for the occurrence of a single set of proton resonances for these groups. A ^{31}P n.m.r. spectrum of $[\mathrm{NiCl(PPh_3)(S_2CNEt_2)}]$ in $\mathrm{CDCl_3}$ revealed one signal at δ 20.43 p.p.m. A mixture of the complex and $\mathrm{PPh_3}$ (1 : 1 molar ratio) also exhibited a broad line at δ 9.04 p.p.m. ($W_{\frac{1}{2}}$ 50 Hz), while the ^{31}P signal due to $\mathrm{PPh_3}$ alone occurred at δ 5.31 p.p.m. (relative to $\mathrm{H_3PO_4}$). On cooling a $\mathrm{CD_2Cl_2}$ solution of $[\mathrm{NiCl(PPh_3)(S_2CNEt_2)}]$, the ^{31}P signal ($W_{\frac{1}{2}}$ 11 Hz at probe temperature) broadened slightly at -52 °C ($W_{\frac{1}{2}}$ 14 Hz), and then narrowed at -90 °C ($W_{\frac{1}{2}}$ 8.3 Hz). The chemical shift also changed with temperature, being initially 21.08, then 22.45 (-52), and finally 23.59 p.p.m. (-90 °C). The overall spectral behaviour is generally consistent with an exchange of bound and unbound $\mathrm{PPh_3}$, which is rapid at -90 °C. A possible mechanism whereby this could occur is represented by equilibrium (3), but the occurrence of linewidth variations with temperature suggests[11] the presence of a very low concentration of a paramagnetic species. The exchange process, however, is consistent with the chemistry of the complexes containing $\mathrm{PPh_3}$ since that ligand is readily displaced by $\mathrm{PMePh_2}$. Also reaction with $\mathrm{S_8}$ easily affords $\mathrm{PPh_3S}$ and $[\mathrm{Ni(S_2CNR_2)_2}]$ as described earlier.


(I)

$$2[\mathrm{NiCl(PPh_3)(S_2CNEt_2)}] \rightleftharpoons [\{\mathrm{NiCl(S_2CNEt_2)}\}_2] + 2\mathrm{PPh_3} \qquad (3)$$

It may be noted that splitting of the resonances due to the ethyl protons in the bidentate dithiocarbamate group of square-planar $[\mathrm{Pt(PMePh_2)(S_2CNEt_2)_2}]$ was not observed at -60 °C, but it was concluded that the asymmetric part of the molecule was too far from the two ethyl groups to cause a detectably large splitting.[12] However, the protons of the inequivalent R groups in $[\mathrm{Pt(PR'_3)(S_2CNR_2)X}]$ (X = halide) have been distinguished by ^{1}H n.m.r. spectroscopy at room temperature.[6]

Electronic Spectra.—The spectra of the complexes $[\mathrm{NiL_2(S_2CNR_2)}]^+$ and $[\mathrm{Ni(PR''_3)(S_2CNR_2)X}]$ contained intense bands at *ca.* 280 and *ca.* 320 nm, which have been assigned to $\pi \rightarrow \pi^*$ transitions within the dithiocarbamate ligands,[13] and these often masked weaker transitions. In general, the electronic spectra were insensitive to changes in the alkyl substituent on the dithiocarbamate group. The cations $[\mathrm{Ni(CNR')_2(S_2CNR_2)}]^+$ exhibited well defined shoulders at 350, 425, and 475 nm, whereas only one shoulder could be observed for $[\mathrm{Ni(PR''_3)_2(S_2CNR_2)}]^+$. This occurred at 470, 460, and 425 nm for the phosphine ligands $\mathrm{PPh_3}$, $\mathrm{PMePh_2}$, and dppe, respectively. The one broad lower-energy band observed for neutral $[\mathrm{Ni(PPh_3)(S_2CNR_2)X}]$ had a molar absorption coefficient (ε) of *ca.* 500 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$. The wavelength of maximum absorption shifted from 537 to 522 to 513 nm as the halide was changed from I to Br to Cl, in accord with the known relative positions of halides in the spectrochemical series.

The visible spectrum of $[\mathrm{NiI(dppe)(S_2CNBu^n{}_2)}]$ in

---

[8] P. D. Frisch, M. K. Lloyd, J. A. McCleverty, and D. Seddon, *J.C.S. Dalton*, 1973, 2268.

[9] J. P. Fackler and W. C. Seidel, *Inorg. Chem.*, 1969, **8**, 1631.

[10] W. K. Schropp, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1670.

[11] 'N.M.R. of Paramagnetic Molecules,' eds. G. N. La Mar, W. de W. Horrocks, and R. H. Holm, Academic Press, London, 1973.

[12] J. M. C. Alison and T. A. Stephenson, *J.C.S. Dalton*, 1973, 254.

[13] M. J. Janssen, *Rec. Trav. chim.*, 1960, **79**, 454.

benzene solution, however, showed a maximum at 400 nm, a broad band with maximum at 543 nm (ε 740 dm^3 mol^{-1} cm^{-1}), and a broad shoulder centred at *ca.* 665 nm (ε 350 dm^3 mol^{-1} cm^{-1}). A comparison of the spectrum with those of known five-co-ordinate nickel species [14] suggests that in this solvent the complex has a distorted square-pyramidal geometry.

Vibrational Spectra.—Infrared spectra of the dithiocarbamate complexes described were obtained from KBr discs and CH_2Cl_2 solutions. The large differences in ν(CN) which were obtained by these two methods can be seen in the Table. Values obtained from CH_2Cl_2 solutions, which eliminate irregularities due to solid-state effects, are used in the following discussion. The usual observation that ν(CN) of the S_2CNR_2 group depends on the alkyl substituent R in the order Me > Et > Bu^n was made. In all cases ν(CN) for the neutral species $[Ni(PR''_3)(S_2CNR_2)X]$ was higher than for $[Ni(S_2CNR_2)_2]$. Replacement of one S_2CNR_2 group (which donates charge to an orbital consisting mainly of nickel $4p_z$ character) by Cl and PPh_3 (which is likely to accept charge from this orbital) could result in a greater mesomeric drift of electrons from the remaining dithiocarbamate group to the metal, with a resultant increase in ν(CN). As expected, ν(CN) for the cations $[NiL_2(S_2CNR_2)]^+$ (R = Et or Bu^n), where L is a π-accepting phosphine or isocyanide, was higher still. For the phosphine complexes (L = PPh_3, $PMePh_2$, or L_2 = dppe), ν(CN) decreased in the range 1 529—1 536 cm^{-1}, whereas ν(CN) for the isocyanide complexes (L = CNPr^i, CNBu^t, or CNC_6H_4Cl-*p*) was in the higher range 1 542—1 546 cm^{-1}. This observation could be explained by assuming that isocyanides are better able to withdraw charge from the $4p_z$ orbital than are the phosphines used. {In the low-oxidation-state system $[CoL_2(CO)(NO)]$ measurements of ν(CO) and ν(NO) led to the deduction that, by a combination of σ and π effects, isocyanides were better able to withdraw charge from the metal than were triarylphosphines.[15]}

EXPERIMENTAL

Conductivity measurements were made at room temperature using a Phillips conductivity bridge, and molecular weights were determined with a Mechrolab 301 A vapour-pressure osmometer. Melting points are uncorrected. The ^{1}H n.m.r. spectra were measured at either 60 or 100 MHz using Perkin-Elmer R 12A or Varian HA 100 spectrometers, respectively, both of which were fitted with a variable-temperature probe. ^{13}C N.m.r. spectra (quoted in p.p.m. on the δ scale using $SiMe_4$ as internal reference) and ^{31}P n.m.r. spectra (in p.p.m. on the δ scale using H_3PO_4 as internal reference) were recorded on Jeol PFT-100 and Bruker HFX-90 instruments. In each case the sign convention, 'positive to higher frequency', was adopted. Infrared spectra were recorded using Perkin-Elmer 457 and 180 spectrometers. Ultraviolet and visible spectra were obtained on a Cary-14 spectrometer, mass spectra on an A.E.I. MS 12 instrument. Electrochemical data were obtained using a Beckman Electroscan 30 polarograph. Elemental analyses were made by the Microanalytical Laboratory of this Department.

$[Ni(S_2CNC_5H_{10})_3]Br$.—A solution of $(C_5H_{10}NCS_2)_2$ (4.8 g, 0.015 mol) in benzene (120 cm^3) was added to a solution of $NiBr_2{\cdot}3H_2O$ (2.7 g, 0.01 mol) in ethanol (100 cm^3). Partial evaporation of the resulting red-brown solution afforded green crystals of $[Ni(S_2CNC_5H_{10})_2]$ which were removed by filtration, and further evaporation afforded a black *solid* which was collected, washed with diethyl ether, and recrystallised from chloroform–light petroleum (3.2 g, 55%) (analyses were unsatisfactory).

Reaction of $(Me_2NCS_2)_2$ *with* $NiCl_2{\cdot}6H_2O$.—A mixture of $NiCl_2{\cdot}6H_2O$ (2.4 g, 0.01 mol) and $(Me_2NCS_2)_2$ (2.4 g, 0.01 mol) was heated under reflux in ethanol (40 cm^3) for 30 min. The mixture was cooled and the green crystals of $[Ni(S_2CNMe_2)_2]$ were collected and washed with ethanol and diethyl ether (2.8 g, 90%). Similarly, a 90% yield of $[Ni(S_2CNMe_2)_2]$ (based on Ni) was obtained from $Me_2NC(S){\cdot}S{\cdot}C(S)NMe_2$ (4.2 g, 0.02 mol).

Tris(diethyldithiocarbamato)nickel(IV) *Hexafluorophosphate*, $[Ni(S_2CNEt_2)_3][PF_6]$.—A solution of $[Ni(S_2CNEt_2)_2]$ (53.3 g) in CH_2Cl_2 (2.5 l) was mixed with a solution of Br_2 (16.0 g) in CH_2Cl_2 (100 cm^3) and stirred for 4 h. The resulting solution was reduced to about half its original volume, the precipitated $NiBr_2$ filtered off, and to the filtrate was added a solution of $Ag[PF_6]$ (25.3 g) in CH_2Cl_2 (150 cm^3). The precipitate of AgBr was removed by filtration, and addition of n-hexane to the filtrate followed by partial evaporation afforded black *needles* which were collected, washed with diethyl ether, and recrystallised from dichloromethane–n-hexane (42.0 g, 65%).

Tris(di-n-butyldithiocarbamato)nickel(IV) *Hexafluorophosphate*, $[Ni(S_2CNBu^n_2)_3][PF_6]$.—A solution of $[Ni(S_2CNBu^n_2)_3]Br$ (75.1 g) in CH_2Cl_2 (500 cm^3) was shaken with a solution of $Ag[PF_6]$ (25.3 g) in CH_2Cl_2 (150 cm^3). The precipitate of AgBr was filtered off, and addition of n-hexane to the filtrate followed by partial evaporation afforded black *needles*. These were collected, washed with diethyl ether, and recrystallised from dichloromethane–n-hexane (58.0 g, 78%).

(Di-n-butyldithiocarbamato)bis(isopropyl isocyanide)-nickel(II) *Hexafluorophosphate*, $[Ni(CNPr^i)_2(S_2CNBu^n_2)][PF_6]$.—The deep red-brown solution of $[Ni(S_2CNBu^n_2)_3][PF_6]$ (4.1 g, 5 mmol) in CH_2Cl_2 (25 cm^3) was mixed with a solution of Pr^{i}NC (0.01 mol) in CH_2Cl_2 (10 cm^3) and was stirred for 30 min. Upon slow addition of diethyl ether (*ca.* 20 cm^3) to the resulting solution, yellow *needles* of the complex formed. These were filtered off [the filtrate (A) being retained], washed with diethyl ether, and recrystallised from dichloromethane–n-hexane (2.5 g, 93%). The following complexes were prepared similarly: $[Ni(CNR')_2(S_2CNR_2)][PF_6]$[R = Bu^n, R' = Bu^t (87) or C_6H_4Cl-*p* (92); R = Et, R' = Pr^i (89), Bu^t (92), or C_6H_4Cl-*p* (88%)]. All are yellow or orange solids.

Recovery of $(R_2NCS_2)_2$ *from the Reaction of* $[Ni(S_2CNR_2)_3][PF_6]$ *with* R'NC.—Evaporation of the filtrates (A) afforded pale yellow crystals (R = Et) or orange-yellow oils (R = Bu^n). The *crystals* were washed with n-pentane and recrystallised from diethyl ether. The *oils* were extracted with n-pentane and the extracts were filtered and evaporated, this procedure being repeated and the second evaporated extract being pumped on *in vacuo*.

---

[14] J. R. Preer and H. B. Gray, *J. Amer. Chem. Soc.*, 1974, **96**, 4428.

[15] W. de W. Horrocks and R. C. Taylor, *Inorg. Chem.*, 1963, **2**, 723.

(Di-n-butyldithiocarbamato)bis(methyldiphenylphosphine)-nickel(II) *Hexafluorophosphate*, $[Ni(PMePh_2)_2(S_2CNBu^n_2)][PF_6]$.—A solution of $[Ni(S_2CNBu^n_2)_3][PF_6]$ (4.1 g, 0.01 mol) in CH_2Cl_2 (10 cm^3) was mixed with a solution of $PMePh_2$ (2.0 g) in CH_2Cl_2 (15 cm^3) under N_2, and the mixture was stirred for 30 min. Slow addition of n-hexane caused precipitation of $[Ni(S_2CNBu^n_2)_2]$ which was removed by filtration. Diethyl ether was added to the filtrate and the resulting red *crystals* were collected, washed with diethyl ether, and recrystallised from dichloromethane–diethyl ether (1.7 g, 42%). The following complexes were obtained similarly: $[Ni(PMePh_2)_2(S_2CNEt_2)][PF_6]$, red (40%); $[Ni(dppe)(S_2CNR_2)][PF_6]$, R = Et (orange-yellow, 31%), R = Bu^n (yellow, 17%). Crystallisation of the last complex was achieved by cooling in a bath of acetone and solid CO_2.

Reaction of $[Ni(S_2CNEt_2)_3]Br$ *with* PPh_3.—Treatment of a stirred solution of $[Ni(S_2CNEt_2)_3]Br$ (5.8 g, 0.01 mol) in CH_2Cl_2 (50 cm^3) with a solution of PPh_3 (2.62 g, 0.01 mol) in CH_2Cl_2 (20 cm^3) afforded a green precipitate of $[Ni(S_2CNEt_2)_2]$, which was removed by filtration. Addition of diethyl ether to the filtrate caused precipitation of purple $[NiBr(PPh_3)(S_2CNEt_2)]$, which was filtered off, washed with diethyl ether, and recrystallised from dichloromethane–n-hexane.

Reaction of $[Ni(S_2CNEt_2)_3][PF_6]$ *with* PPh_3.—A solution of $[Ni(S_2CNEt_2)_3][PF_6]$ (0.6 g, 0.025 mol) in CH_2Cl_2 (10 cm^3) was mixed with a solution of PPh_3 (1.3 g, 0.05 mol) in the same solvent (10 cm^3) and was stirred for 30 min. The solvent was evaporated and the residue was collected and washed with diethyl ether [200 cm^3, (A)], then with acetone [10 cm^3, (B)], leaving $[Ni(S_2CNEt_2)_2]$, which was recrystallised from dichloromethane–n-hexane. Evaporation of the ether solution (A) yielded PPh_3S (0.5 g, 65%) which was separated from trace amounts of $[Ni(S_2CNEt_2)_2]$ by recrystallisation three times from boiling ethanol. Addition of ethanol to the red solution (B) followed by partial evaporation afforded yellow crystals of $[PPh_3\{C(NEt_2)S\}][PF_6]$ (0.8 g) which were recrystallised from ethanol. Complete evaporation of the red solution afforded a few red *crystals* of $[Ni(PPh_3)_2(S_2CNEt_2)][PF_6]$. The yield of this complex could be improved to 25% by using, instead, an excess of PPh_3 (5.2 g, 0.02 mol) in CH_2Cl_2 (40 cm^3). Addition of light petroleum (b.p. 40—60 °C) caused precipitation of $[Ni(S_2CNEt_2)_2]$, which was removed by filtration. Red *crystals* were obtained by adding diethyl ether to the filtrate and they were collected, washed with diethyl ether, recrystallised from dichloromethane–n-hexane, and dried at 80 °C for 2 h.

Reaction of $[Ni(PPh_3)_2(S_2CNEt_2)][PF_6]$ *with* $(Et_2NCS_2)_2$.—A solution of $[Ni(PPh_3)_2(S_2CNEt_2)][PF_6]$ (2.18 g, 0.025 mol) in CH_2Cl_2 (15 cm^3) was mixed with a solution of $(Et_2NCS_2)_2$ (0.74 g) in CH_2Cl_2 (5 cm^3), stirred for 30 min, and the solvent was then evaporated. The products $[Ni(S_2CNEt_2)_2]$, $[PPh_3\{C(NMe_2)S\}][PF_6]$, and PPh_3S were isolated in exactly the same manner as the products of the reaction of $[Ni(S_2CNEt_2)_3][PF_6]$ with PPh_3 (1 : 2 molar ratio).

Reaction of $[Ni(S_2CNBu^n_2)_3][PF_6]$ *with* PPh_3.—A solution of $[Ni(S_2CNBu^n_2)_3][PF_6]$ (2.1 g, 0.025 mol) in CH_2Cl_2 (10 cm^3) was mixed with a solution of PPh_3 (1.3 g, 0.05 mol) in the same solvent (10 cm^3) and stirred for 30 min. The solvent was evaporated, and extraction of the residue with diethyl ether [200 cm^3, (A)] left a mixture of red and yellow solids (1.4 g). This mixture was dissolved in acetone. This red solution was filtered and, on addition of ethanol followed by partial evaporation, yellow crystals of $[PPh_3\{C(NBu^n_2)S\}][PF_6]$ were formed. These were filtered off (B) and recrystallised from boiling ethanol. Yields averaged 65%, based on $[PF_6]^-$. Complete evaporation of the filtrate (B) afforded a few red *crystals* of $[Ni(PPh_3)_2(S_2CNBu^n_2)][PF_6]$. The ether extract (A) was evaporated to a mixture of green and white solids which was dissolved in boiling ethanol. On cooling, $[Ni(S_2CNBu^n_2)_2]$ separated as green leaf-like crystals, which were filtered off (C) and recrystallised twice from boiling ethanol (0.9 g, 75% based on Ni). To the filtrate (C) was added n-pentane, which caused precipitation of white PPh_3S. This was collected and recrystallised twice from boiling ethanol (0.5 g, 65%). Complete separation of the products was not achieved and the yields quoted are approximate. Yields of $[Ni(PPh_3)_2(S_2CNBu^n_2)][PF_6]$ were improved by using, instead, an excess of PPh_3 (5.2 g) in CH_2Cl_2 (40 cm^3). On addition of diethyl ether to the reaction mixture, a red oil formed. The supernatant liquor was removed and the red *crystals* which formed overnight were washed with diethyl ether, recrystallised from dichloromethane–n-hexane, and dried at 80 °C for 2 h (0.6 g, 26%).

Chloro(di-n-butyldithiocarbamato)triphenylphosphine-nickel(II), $[NiCl(PPh_3)(S_2CNBu^n_2)]$.—A mixture of $[Ni(S_2CNBu^n_2)_2]$ (11.7 g, 0.025 mol), $NiCl_2{\cdot}6H_2O$ (5.9 g, 0.025 mol), and PPh_3 (13.1 g, 0.05 mol) was stirred in refluxing ethanol (250 cm^3) for 30 min, and then allowed to cool. The purple *crystals* which formed were collected, washed with ethanol and diethyl ether, and recrystallised from dichloromethane–n-hexane (26.0 g, 93%). The following purple complexes were prepared similarly, with the reaction times stated: $[NiBr(PPh_3)(S_2CNBu^n_2)]$ (30 min, 95%); $[Ni(PPh_3)(S_2CNR_2)X]$, R = Et, X = I (1 h, 80%), R = Me, X = Cl (4 h, 70%) or I (4 h, 75%); $[Ni(PMePh_2)(S_2CNR_2)X]$, R = Et, X = Cl or Br (1 h, 85%), R = Me, X = I (4 h, 75%). The reactions of $PMePh_2$ were performed under N_2.

[1,2-Bis(diphenylphosphino)ethane](di-n-butyldithiocarbamato)nickel(II) *Iodide*, $[Ni(dppe)(S_2CNBu^n_2)]I$.—A mixture of NiI_2 (1.6 g), $[Ni(S_2CNBu^n_2)_2]$ (2.3 g), and dppe (4.0 g) was stirred in refluxing ethanol (100 cm^3) for 1 h. The hot solution was filtered and the solvent was then evaporated affording an oil. The oil was washed with diethyl ether, which caused it to solidify. The solid was dissolved in CH_2Cl_2, the red solution filtered, and addition of diethyl ether to the filtrate produced first an oil, then orange crystals of the *complex*. The crystals were collected, washed with diethyl ether, and recrystallised from benzene by slow evaporation.

Treatment of $[Ni(dppe)(S_2CNBu^n_2)]I$ *with Sulphur*.—The purple solution formed by dissolving $[Ni(dppe)(S_2CNBu^n_2)]I$ (0.79 g) in benzene (600 cm^3) at 50 °C was mixed with a solution of sulphur (0.064 g) in benzene (20 cm^3) and was maintained at 50 °C for 5 min. Orange crystals of $[Ni(dppe)(S_2CNBu^n_2)]I$ formed on partial evaporation of the benzene. Under identical conditions, dppe (0.4 g) reacted to form its disulphide which was recrystallised from acetone.

(Di-n-butyldithiocarbamato)bis(triphenylphosphine)-nickel(II) *Hexafluorophosphate*, $[Ni(PPh_3)_2(S_2CNBu^n_2)][PF_6]$.—A solution of $K[PF_6]$ (2.85 g) in acetone (100 cm^3) was added to a solution containing PPh_3 (2.62 g) and $[NiCl(PPh_3)(S_2CNBu^n_2)]$ (5.60 g) in acetone (200 cm^3). The solvent was evaporated and the red solid was extracted with CH_2Cl_2. Addition of light petroleum to the red solution caused the formation of red crystals of the *complex*. These were collected, washed with diethyl ether, recrystallised

from dichloromethane–n-hexane, and dried at 80 °C for 2 h (6.2 g, 67%). The *complexes* [Ni(PPh$_3$)$_2$(S$_2$CNR$_2$)][PF$_6$] (R = Et or Me) were also prepared by this method.

(Diethyldithiocarbamato)bis(triphenylphosphine)nickel(II) *Hexafluorophosphate*, [Ni(PPh$_3$)$_2$(S$_2$CNEt$_2$)][PF$_6$].—A solution of Ag[PF$_6$] (2.53 g) in CH$_2$Cl$_2$ (25 cm^3) was added to a solution containing PPh$_3$ (2.62 g) and [NiCl(PPh$_3$)(S$_2$CNEt$_2$)] (5.0 g) in CH$_2$Cl$_2$ (100 cm^3). The precipitate of AgCl was removed by filtration, and red *crystals* were formed on addition of n-hexane to the filtrate. The crystals were collected, recrystallised from dichloromethane–n-hexane, and dried at 80 °C for 2 h (6.1 g, 70%). The complex [Ni(PPh$_3$)$_2$(S$_2$CNMe$_2$)][PF$_6$] was prepared similarly (70%).

[1,2-*Bis(diphenylphosphino)ethane*](*di-n-butyldithiocarbamato*)*nickel*(II) *Hexafluorophosphate*, [Ni(dppe)(S$_2$CNBu$^n_2$)]-[PF$_6$].—A solution of dppe (0.40 g) in acetone (25 cm^3) was mixed with a solution of [Ni(PPh$_3$)$_2$(S$_2$CNBu$^n_2$)][PF$_6$] (0.93 g) in acetone (25 cm^3). The solvent was evaporated yielding an orange oil. On standing under diethyl ether (50 cm^3) overnight, an orange powder formed. This was collected and recrystallised from acetone–light petroleum by cooling in a bath of acetone–solid carbon dioxide (0.72 g, 90%). The complexes [Ni(dppe)(S$_2$CNR$_2$)][PF$_6$] (R = Me or Et) were prepared similarly in 95% yield.

Reaction of [Ni(PPh$_3$)$_2$(S$_2$CNBu$^n_2$)][PF$_6$] *with* [NBu$^n_4$]I.—A solution of [Ni(PPh$_3$)$_2$(S$_2$CNBu$^n_2$)][PF$_6$] (0.93 g) in acetone (20 cm^3) was mixed with a solution of [NBu$^n_4$]I in the same solvent (10 cm^3). The purple solution was heated under reflux for 10 min and the solvent was then evaporated. The resulting purple oil was extracted with diethyl ether (120 cm^3), which was then evaporated to a small volume (*ca.* 10 cm^3), causing purple *crystals* of [NiI(PPh$_3$)(S$_2$CNBu$^n_2$)] to form. These were collected, washed with diethyl ether (5 cm^3), and recrystallised from dichloromethane–n-hexane (0.51 g, 80%).

Reaction of [NiI(PPh$_3$)(S$_2$CNMe$_2$)] *with* PMePh$_2$.—A solution of PMePh$_2$ (2.0 g, 0.01 mol) in CH$_2$Cl$_2$ (10 cm^3) was mixed with a solution of [NiI(PPh$_3$)(S$_2$CNMe$_2$)] (5.7 g, 0.01 mol) in CH$_2$Cl$_2$ (100 cm^3) under N$_2$ and was stirred for 30 min. Addition of a large volume of diethyl ether caused precipitation of [NiI(PMePh$_2$)(S$_2$CNMe$_2$)] which was collected, washed with diethyl ether, and recrystallised from dichloromethane–n-hexane (4.5 g, 90%).

Reaction of [NiI(PPh$_3$)(S$_2$CNMe$_2$)] *with* Tl(C$_5$H$_5$).—A solution of [NiI(PPh$_3$)(S$_2$CNMe$_2$)] (5.7 g) in tetrahydrofuran (120 cm^3) was shaken for 1 h with Tl(C$_5$H$_5$) (2.7 g). The resulting green solid was removed by filtration and the dark red filtrate was evaporated. Extraction of the residual tar with diethyl ether, and addition of n-pentane to the extract, afforded a low yield of maroon [Ni(η-C$_5$H$_5$)I(PPh$_3$)], which was recrystallised from diethyl ether–n-pentane.

Reaction of [NiCl(PPh$_3$)(S$_2$CNMe$_2$)] *with Sulphur.*—A suspension of [NiCl(PPh$_3$)(S$_2$CNMe$_2$)] (0.95 g, 2 mmol) in benzene (100 cm^3) was heated under reflux with sulphur (0.064 g, 0.25 mmol) for 30 min, by which time the purple solution had turned green. The mixture was allowed to cool and was then filtered (A). The filtrate was evaporated to dryness and PPh$_3$S was obtained as needles by recrystallisation from hot ethanol. The residue (A) was washed with water (green washings) and then with ethanol and diethyl ether, leaving pure [Ni(S$_2$CNMe$_2$)$_2$].

Reaction of [NiCl(PPh$_3$)(S$_2$CNMe$_2$)] *with* Na[S$_2$CNMe$_2$]·2H$_2$O.—A solution of Na[S$_2$CNMe$_2$]·2H$_2$O (0.18 g) in acetone (50 cm^3) was stirred with a suspension of [NiCl(PPh$_3$)-(S$_2$CNMe$_2$)] (0.48 g) in acetone (50 cm^3) for 1 h. The resulting green precipitate of [Ni(S$_2$CNMe$_2$)$_2$] was washed with water, ethanol, and diethyl ether (0.30 g, quantitative). Similarly, [Ni(S$_2$CNEt$_2$)$_2$] was recovered from the reaction of [NiCl(PMePh$_2$)(S$_2$CNEt$_2$)] (0.44 g) with Na[S$_2$CNEt$_2$]·3H$_2$O (0.23 g) in acetone (20 cm^3).

Bis[(*dimethyldithiocarbamato*)(*methylthio*)*nickel*(II)], [{Ni(SMe)(S$_2$CNMe$_2$)}$_2$].—To a 50% dispersion of NaH in mineral oil (0.48 g) in tetrahydrofuran (5 cm^3) at 0 °C was added MeSH (0.48 g) in tetrahydrofuran (5 cm^3). To the white suspension was added, after 30 min, a solution of [NiCl(PPh$_3$)(S$_2$CNMe$_2$)] (4.75 g) in CHCl$_3$ (100 cm^3). The mixture was heated under reflux for 1 h, and the solvent was then evaporated. The residue was extracted with CH$_2$Cl$_2$, and addition of n-hexane to the extract afforded green *crystals*. These were collected, washed with diethyl ether, and recrystallised from dichloromethane–n-hexane (2.0 g, 90%). The complexes [{Ni(SR)(S$_2$CNMe$_2$)}$_2$] (R = Pr^i, Bu^t, PhCH$_2$, or Ph) and [{Ni(SPh)(S$_2$CNBu$^n_2$)}$_2$] were prepared similarly.

We thank Monsanto for support, Drs. B. Taylor and B. E. Mann for discussion of, and help with, the n.m.r. spectral measurements, and Dr. T. A. Stephenson and Professor J. P. Fackler for their timely and appropriate comments.

[5/1500 *Received*, 29*th July*, 1975]