Co-ordination Chemistry of Higher Oxidation States. Part 8.[1] Nickel(III) Complexes of Bi- and Multi-dentate Phosphorus and Arsenic Ligands; Crystal and Molecular Structure of [Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Br$_3$]·C$_6$H$_5$Me †

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The five-co-ordinate nickel(III) complexes [Ni(L–L)Cl$_3$] [L–L = Ph$_2$PCH$_2$CH$_2$PPh$_2$, Ph$_2$P(CH$_2$)$_3$PPh$_2$, Ph$_2$PCHCHPPh$_2$, *o*-C$_6$H$_4$(PPh$_2$)$_2$, or Me$_2$PCH$_2$CH$_2$PMe$_2$] have been obtained by Cl$_2$ or NOCl oxidation of [Ni(L–L)Cl$_2$] in CCl$_4$ or CH$_2$Cl$_2$. The bromides [Ni(L–L)Br$_3$] [L–L = as above, *o*-C$_6$H$_4$(AsPh$_2$)$_2$, or *o*-C$_6$H$_4$(PPh$_2$)(SMe)] are obtained similarly using Br$_2$–CCl$_4$. On gentle heating, [Ni(L–L)X$_3$] (X = Cl or Br) lose X$_2$ to reform [Ni(L–L)X$_2$]. Unstable [Ni{*o*-C$_6$H$_4$(AsMe$_2$)$_2$}X$_3$] have been prepared by halogenation of the dicarbonyl [Ni(CO)$_2${*o*-C$_6$H$_4$(AsMe$_2$)$_2$}]. The complexes have been characterised by i.r., electronic, and e.s.r. spectroscopy, and by magnetic measurements, and the structure of [Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Br$_3$]·C$_6$H$_5$Me established by a single-crystal *X*-ray study. It is monoclinic, space group $P2_1/n$, and has a = 15.567(3), b = 14.627(2), c = 15.151(3) Å, β = 113.38(2)°, and Z = 4. The structure was refined to R = 0.0562 from 1 583 reflections. The five-co-ordinate nickel is in an approximately square-pyramidal arrangement [Ni–Br 2.346(3), 2.417(3), and 2.363(3); Ni–P 2.223(5) and 2.236(5) Å], and lies above the P$_2$Br$_2$ plane toward the apical bromine. The synthesis and properties of pseudo-octahedral [Ni(L′–L′)$_2$X$_2$]Y [L′–L′ = *o*-C$_6$H$_4$(PMe$_2$)$_2$, *o*-C$_6$H$_4$(AsMe$_2$)(PMe$_2$), *o*-C$_6$H$_4$(PMe$_2$)(SbMe$_2$), or Me$_2$P(CH$_2$)$_2$PMe$_2$; X = Cl or Br; Y = BF$_4$ or ClO$_4$] are described. The compounds *mer*-[Ni{PhP(CH$_2$CH$_2$PPh$_2$)$_2$}X$_3$] have also been obtained, but attempts to prepare nickel(III) complexes with quadridentate phosphines were unsuccessful.

For many years nickel(III) was regarded as a very rare oxidation state, represented by complex oxides and fluorides, and by a small number of unstable complexes.[2] Recently many nickel(III) complexes of hard N-donor ligands, tetra-aza macrocycles, amides, peptides, and oximes have been characterised,[3] and it has been shown that diprimary amines form either nickel(III) or mixed-valence nickel(II,IV) compounds.[1,4] Nickel(III) sites, identified by their characteristic e.s.r. spectra, have been found in some hydrogenases.[5]

Although [Ni(PEt$_3$)$_2$Br$_3$] was one of the first characterised nickel(III) complexes,[6] studies of phosphine and arsine complexes are much less complete than those with harder donors,[3] and detailed studies are limited to three systems: [Ni(PMe$_2$Ph)$_2$Br$_3$] shown by an *X*-ray study to be trigonal bipyramidal with axial phosphines,[7,8] [Ni{*o*-C$_6$H$_4$(AsMe$_2$)$_2$}$_2$X$_2$][ClO$_4$] and [Ni{*o*-C$_6$H$_4$(PMe$_2$)$_2$}$_2$X$_2$][ClO$_4$] (X = Cl or Br) both of which have *trans* octahedral cations.[9–11] Single-crystal e.s.r. studies of the diphosphine and diarsine complexes have shown extensive delocalisation of the odd electron ($t_{2g}^6e_g^1$) onto the donor atoms.[12–14] Several other tribromo(diphosphine)nickel compounds have been reported,[15–18] sometimes as ' postscripts ' to work on nickel(II) complexes, and most are incompletely characterised.

Here we report a systematic study of the synthesis and properties of bi- and multi-dentate phosphine and arsine complexes of nickel(III), which is also an extension of our previous studies of platinum(IV) [19] and palladium(IV) [20] systems.

Results

[Ni(L–L)X$_3$] (L–L = *phenyl-diphosphine or -diarsine*, X = Cl *or* Br).—Treatment of dry CH$_2$Cl$_2$ solutions of [Ni(L–L)Br$_2$] [L–L = Ph$_2$PCH$_2$CH$_2$PPh$_2$, Ph$_2$P(CH$_2$)$_3$PPh$_2$, *cis*-Ph$_2$PCHCHPPh$_2$, or *o*-C$_6$H$_4$(PPh$_2$)$_2$] with a small excess of bromine gave [16,17] brown-black [Ni(L–L)Br$_3$]. The olive-green chloro-complexes [Ni(L–L)Cl$_3$] (Table 1), none of which has been reported previously, were initially obtained by treatment of [Ni(L–L)Cl$_2$] with nitrosyl chloride (NOCl) in CH$_2$Cl$_2$. Subsequently we found that chlorine oxidation can also be used, provided excess of chlorine which tends to decompose the complexes is avoided. The compounds [Ni(Ph$_2$PCH$_2$PPh$_2$)X$_2$] (X = Cl or Br) were decomposed by halogens, and the chloride gave a green nitrosyl on treatment with NOCl. In contrast the pseudotetrahedral polymers [{Ni(*trans*-Ph$_2$PCHCHPPh$_2$)Br$_2$}$_n$] and [{Ni[Ph$_2$P(CH$_2$)$_4$PPh$_2$]X$_2$}$_n$] were neither oxidised nor decomposed by halogens. Studies of the aryldiarsines were limited to the bromides since nickel(II) chloride complexes of these ligands have not been isolated.[21] Bromine oxidation of [Ni{*o*-C$_6$H$_4$(AsPh$_2$)$_2$}Br$_2$] gave the unstable black [Ni{*o*-C$_6$H$_4$(AsPh$_2$)$_2$}Br$_3$], but [Ni(L–L)Br$_2$] (L–L = Ph$_2$AsCH$_2$CH$_2$AsPh$_2$ or *cis*-Ph$_2$AsCHCHAsPh$_2$) decomposed on reaction even with stoicheiometric amounts of Br$_2$, although e.s.r. spectral evidence for transient nickel(III) intermediates was obtained (Table 3). The stabilising effect of the rigid *o*-phenylene backbone was also evident in the ready isolation of [Ni{*o*-C$_6$H$_4$(AsPh$_2$)(PPh$_2$)}Br$_3$], whereas attempts to isolate [Ni(Ph$_2$PCH$_2$CH$_2$AsPh$_2$)Br$_3$] failed. Particularly interesting was the preparation of black [Ni{*o*-C$_6$H$_4$(PPh$_2$)(SMe)}Br$_3$] containing the first example of a nickel(III)–thioether linkage. [Nickel(II)–dithioether complexes do not oxidise on treatment with halogens.[22]] This unstable solid decomposes in a few hours, and decomposition occurs immediately in solution, although an e.s.r. spectrum in CH$_2$Cl$_2$ can be obtained in the presence of excess of Br$_2$ (Table 3). Planar [Ni{*o*-C$_6$H$_4$(PPh$_2$)(SMe)}Cl$_2$] decomposed on treatment with Cl$_2$, and gave a green nitrosyl complex with NOCl.

These [Ni(L–L)X$_3$] complexes have $\mu_{\text{eff.}}$ *ca.* 1.7—2.1 B.M. consistent with a low-spin d^7 metal centre, and are non-electrolytes in 1,2-C$_2$H$_4$Cl$_2$ solution. The compound [Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Br$_3$] was shown to be five-co-ordinate with a distorted square-pyramidal geometry (below), and from the similar pattern of Ni–X stretching vibrations in their i.r.

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† [1,2-Bis(diphenylphosphino)ethane]tribromonickel(III)–toluene-(1/1).

Supplementary data available (No. SUP 23810, 14 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. units employed: B.M. ≈ 9.27 × 10^{-24} A m^2, G = 10^{-4} T.

Table 1. Analytical and physical data

Complex	Colour	Analysis (%) [a]			$\mu_{eff.}$ [b]/ B.M.	Λ [c]/ohm^{-1} cm^2 mol^{-1}	ν(NiX) [d]/cm^{-1}
		C	H	X			
$[\mathrm{Ni(Ph_2PCH_2CH_2PPh_2)Cl_3}]$	Olive green	55.1 (55.4)	4.4 (4.5)	18.3 (18.9)	2.10	0	325, 308
$[\mathrm{Ni(Ph_2PCH_2CH_2PPh_2)Br_3}]$	Dark brown	44.4 (44.8)	3.3 (3.5)	—	1.98	—	284, 269, 215w
$[\mathrm{Ni}\{\mathrm{Ph_2P(CH_2)_3PPh_2}\}\mathrm{Cl_3}]$	Olive green	56.5 (56.2)	4.5 (4.5)	18.5 (18.4)	2.01	0	338, 310, 286
$[\mathrm{Ni}\{\mathrm{Ph_2P(CH_2)_3PPh_2}\}\mathrm{Br_3}]$	Brown-black	45.8 (45.6)	3.3 (3.8)	—	1.81	—	276, 265, 220w
$[\mathrm{Ni(Ph_2PCHCHPPh_2)Cl_3}]$	Olive green	55.8 (55.6)	4.0 (4.0)	18.8 (19.0)	1.80	0	334, 315
$[\mathrm{Ni(Ph_2PCHCHPPh_2)Br_3}]$	Dark brown	45.2 (44.9)	3.2 (3.2)	—	2.00	—	276, 265, 210w
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(PPh_2)_2}\}\mathrm{Cl_3}]$	Dark green	59.3 (58.9)	4.2 (4.0)	—	2.02 [e]	—	346, 311, 297w
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(PPh_2)_2}\}\mathrm{Br_3}]$	Dark brown	48.2 (48.4)	3.2 (3.2)	31.9 (32.2)	—	—	293, 267, 211w
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsPh_2)_2}\}\mathrm{Br_3}]$	Black	42.2 (41.8)	3.5 (3.6)	25.2 (26.4)	1.72	decomp.	282, 252, 197w
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(PPh_2)(SMe)}\}\mathrm{Br_3}]$	Black	38.0 (37.6)	2.9 (2.8)	38.5 (39.6)	—	decomp.	307, 232
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsPh_2)(PPh_2)}\}\mathrm{Br_3}]$	Black	45.4 (45.7)	3.2 (3.1)	31.8 (30.4)	1.75	—	261, 248, 212w
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}\mathrm{Cl_3}]$	Dark brown	26.4 (26.6)	3.5 (3.6)	25.2 (26.4)	2.3	insoluble	340, 329
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}\mathrm{Br_3}]$	Brown-black	19.8 (20.55)	2.7 (2.8)	43.0 (41.1)	2.4	insoluble	298, 267
$[\mathrm{Ni(Me_2PCH_2CH_2PMe_2)Cl_3}]$	Red-brown	23.1 (22.9)	5.2 (5.2)	—	—	insoluble	320, 295 (?)
$[\mathrm{Ni(Me_2PCH_2CH_2PMe_2)Br_3}]$	Green-black	15.8 (16.1)	3.8 (3.6)	—	2.1	insoluble	304w, 258
$[\mathrm{Ni}\{\mathrm{PhP(CH_2CH_2PPh_2)_2}\}\mathrm{Cl_3}]$	Dark green	58.7 (58.4)	4.7 (4.75)	—	—	decomp.	323, 303, 250
$[\mathrm{Ni}\{\mathrm{PhP(CH_2CH_2PPh_2)_2}\}\mathrm{Br_3}]$	Light brown	48.6 (49.0)	4.3 (4.0)	—	—	decomp.	250, 224, 198
$[\mathrm{Ni}\{\mathrm{MeAs(CH_2CH_2CH_2AsMe_2)_2}\}\mathrm{Br_3}]$	Red-purple	19.1 (19.4)	4.2 (4.0)	—	—	—	250, 244 (sh), 196
$[\mathrm{Ni(Me_2PCH_2CH_2PMe_2)_2Cl_2}][\mathrm{BF_4}]$	Light green	28.2 (27.9)	6.3 (6.2)	14.1 (13.7)	2.01 [e]	96 [f]	248
$[\mathrm{Ni(Me_2PCH_2CH_2PMe_2)_2Br_2}]\mathrm{Br}$	Dark brown	24.0 (24.1)	5.2 (5.4)	39.4 (40.0)	1.90	70 [f]	176
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(PMe_2)_2}\}_2\mathrm{Cl_2}][\mathrm{ClO_4}]$	Light green	38.3 (38.4)	5.3 (5.2)	—	1.86 [e]	—	263
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(PMe_2)_2}\}_2\mathrm{Br_2}][\mathrm{ClO_4}]$	Orange-brown	33.8 (33.6)	4.4 (4.5)	—	2.10 [e]	—	180
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)(PMe_2)}\}_2\mathrm{Cl_2}][\mathrm{ClO_4}]$	Green	34.2 (33.7)	4.5 (4.5)	—	2.07	91 [f]	248
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)(PMe_2)}\}_2\mathrm{Br_2}][\mathrm{ClO_4}]$	Light brown	29.7 (29.9)	4.1 (4.0)	—	1.90 [e]	80 [f]	189
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(PMe_2)(SbMe_2)}\}_2\mathrm{Br_2}][\mathrm{ClO_4}]$	Red	26.5 (26.8)	3.6 (3.6)	—	1.99 [e]	100 [f]	189

[a] Calculated values in parentheses. [b] ±0.05 B.M.; Gouy method except where indicated otherwise. [c] 10^{-3} mol dm^{-3} in 1,2-dichloroethane. [d] Nujol mulls. [e] Evans method in CH_3CN or CH_2Cl_2. [f] 10^{-3} mol dm^{-3} in nitromethane. 1 : 1 Electrolytes have $\Lambda = 70$—120 ohm^{-1} cm^2 mol^{-1}.

spectra, a similar five-co-ordinate structure is assigned to all the aryl-diphosphine and -diarsine compounds, although it is expected that the extent of the distortion will vary with the ligands.[23] For a $[\mathrm{Ni(L{-}L)X_3}]$ molecule with C_s local symmetry, three ν(NiX) are expected ($2A' + A''$). All the complexes exhibit two strong bands, and usually a weak third Ni–X stretching vibration at lower frequency can be identified (Table 1), the latter corresponding to the axial Ni–X bond, which is long due to the presence of an electron in the d_{z^2} orbital.[10,11,24] The electronic spectra (Table 2) are similar consisting of a main band in the visible region at *ca.* 20 000 cm^{-1}, with weaker bands at *ca.* 15 000 and *ca.* 9 000 cm^{-1}, although the latter is often only observed in the solid reflectance spectra. All the complexes are unstable to some extent in solution, and the absorption coefficients in Table 2 should be treated as approximate values. The compounds $[\mathrm{Ni(L{-}L)Cl_3}]$ gave isotropic e.s.r. spectra both as solids and in CH_2Cl_2 solution with $g \approx 2.2$ (Table 3); $[\mathrm{Ni(L{-}L)Br_3}]$ also gave isotropic spectra as solids, but in CH_2Cl_2 a four-line hyperfine coupling sometimes with further ill defined fine structure was observed (Figure 1). The four-line pattern indicates coupling to a single bromine (^{79}Br, ^{81}Br, $I = \frac{3}{2}$), con-

Table 2. Electronic spectral data

Compound		$E_{max.}/10^3$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})
$[Ni(Ph_2PCH_2CH_2PPh_2)Cl_3]$	d.r.[a]	8.9 (br), 15.5, 22.0, 31.3
	CH_2Cl_2	16.08 (460), 21.60 (1 600), 31.85 (sh) (4 200)
$[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]$	d.r.	7.9, 14.5 (br), 19.5, 25.0
	CH_2Cl_2	14.50 (850), 20.90 (3 400), 27.30 (sh) (5 200), 29.7 (sh) (7 300)
$[Ni\{Ph_2P(CH_2)_3PPh_2\}Cl_3]$	d.r.	9.2 (sh), 14.3, 21.3, 29.1
	CH_2Cl_2	14.90 (930), 23.50 (2 500), 31.5 (4 100)
$[Ni\{Ph_2P(CH_2)_3PPh_2\}Br_3]$	d.r.	13.1, 20.2 (sh)
	CH_2Cl_2	14.00 (1 400), 20.80 (3 000), 25.50 (sh) (5 300), 28.80 (6 700)
$[Ni(Ph_2PCHCHPPh_2)Cl_3]$	d.r.	15.1, 22.0, 25.0 (sh)
	CH_2Cl_2	15.40 (640), 22.20 (1 830), 26.70 (sh) (2 700), 29.20 (sh) (3 800)
$[Ni(Ph_2PCHCHPPh_2)Br_3]$	d.r.	8.3, 13.5, 20.0, 25.5
	CH_2Cl_2	8.1 (20), 14.30 (270), 21.00 (2 800), 26.90 (2 200)
$[Ni\{o\text{-}C_6H_4(PPh_2)_2\}Cl_3]$	d.r.	14.4, 20.0 (sh), 21.8 (sh), 25.25, 29.4
	CH_2Cl_2	15.4 (1 336), 21.75 (sh) (2 485), 22.8 (2 770), 29.6 (7 020)
$[Ni\{o\text{-}C_6H_4(PPh_2)_2\}Br_3]$	d.r.	13.7 (br), 18.3, 23.9, 25.1, 28.6
	CH_2Cl_2 [b]	14.20 (—), 21.88 (—), 25.97 (—), 28.33 (—)
$[Ni\{o\text{-}C_6H_4(AsPh_2)_2\}Br_3]$	d.r.	12.8, 17.6, 25.3
$[Ni\{o\text{-}C_6H_4(PPh_2)(SMe)\}Br_3]$	d.r.	12.1, 18.2, 29.3
$[Ni\{o\text{-}C_6H_4(AsPh_2)(PPh_2)\}Br_3]$	d.r.	13.45, 18.25, 20.5, 24.4
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}Cl_3]$	d.r.	8.0, 11.8, 17.0, 18.2 (sh), 25.4
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}Br_3]$	d.r.	9.7, 12.0, 15.4, 20.0 (sh), 24.1, 28.4
$[Ni(Me_2PCH_2CH_2PMe_2)Cl_3]$	d.r.	—, 14.4, 15.6 (sh), 18.6 (sh), 23.15, 25.5 (sh)
$[Ni(Me_2PCH_2CH_2PMe_2)Br_3]$	d.r.	—, 16.4 (sh), 16.95, 22.4, 24.5
$[Ni\{PhP(CH_2CH_2PPh_2)_2\}Cl_3]$	d.r.	14.8 (sh), 16.4, 22.6, 27.0 (br)
$[Ni\{PhP(CH_2CH_2PPh_2)_2\}Br_3]$	d.r.	15.2, 19.0, 22.8, 30.85
$[Ni\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}Br_3]$	d.r.	14.8 (sh), 16.7, 19.45, 22.2 (sh), 27.0
	CH_2Cl_2	18.55 (1 440), 23.58 (sh), 28.09 (sh) (4 820)
$[Ni(Me_2PCH_2CH_2PMe_2)_2Cl_2][BF_4]$	CH_2Cl_2	15.15 (103), 28.6 (6 300)
$[Ni(Me_2PCH_2CH_2PMe_2)_2Br_2]Br$	d.r.	14.2 (br), 17.1 (w), 21.0, 26.9
	CH_2Cl_2	14.58 (53), 22.4 (750), 28.74 (4 020)
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][ClO_4]$	CH_2Cl_2	14.8 (60), 28.4 (8 000), 30.7 (8 930)
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Br_2][ClO_4]$	CH_3CN	14.30 (42), 21.90 (850), 28.10 (4 920), 31.85 (7 070)
$[Ni\{o\text{-}C_6H_4(AsMe_2)(PMe_2)\}_2Cl_2][ClO_4]$	CH_3CN	13.93 (62), 26.74 (10 500), 31.85 (9 300)
$[Ni\{o\text{-}C_6H_4(AsMe_2)(PMe_2)\}_2Br_2][ClO_4]$	CH_2Cl_2	13.44 (24), 25.38 (5 400), 28.70 (7 100)
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]$	CH_3CN	13.27 (22), 24.00 (2 260), 26.20 (5 540)
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Br_2][ClO_4]$	CH_3CN	12.80 (41), 24.20 (7 750), 29.1 (sh) (8 400)
$[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Br_2][ClO_4]$	CH_2Cl_2	12.92 (93), 19.23 (sh) (400), 23.90 (3 300), 27.80 (3 070)
	d.r.	12.5, 19.2 (sh), 22.7, 26.6

[a] Diffuse reflectance diluted with $BaSO_4$. [b] Compound decomposes rapidly in solution.

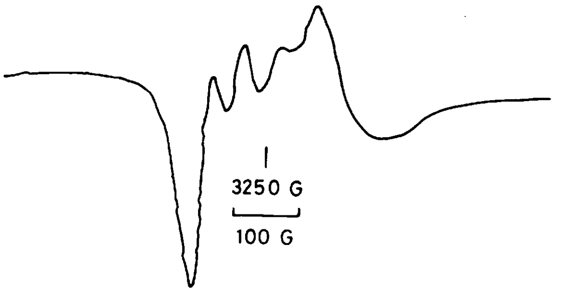

Figure 1. E.s.r. spectrum of $[Ni\{Ph_2P(CH_2)_3PPh_2\}Br_3]$ in CH_2Cl_2 solution at room temperature

sistent with a $(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{z^2})^1(d_{x^2-y^2})^0$ ground state for the square-pyramidal molecules, with coupling of the axial bromine to the odd electron in the d_{z^2} orbital.

All the $[Ni(L\text{-}L)X_3]$ decomposed slowly at room temperature, and were easily decomposed on heating *in vacuo*, or in a dynamic argon atmosphere. T.g.a. data (Experimental section) for representative samples showed weight changes corresponding to loss of $\frac{1}{2}X_2$ per mol of compound, and analysis and i.r. spectra of the products showed them to be the corresponding $[Ni(L\text{-}L)X_2]$. The neutral ligand is not oxidised under these conditions.

Although high oxidation states are often more stable in anions, attempts to prepare $[Ni(L\text{-}L)X_4]^-$ were unsuccessful. Oxidation of $[Ni(L\text{-}L)Br_2]$ ($L\text{-}L = Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCHCHPPh_2$) in the presence of NBu^n_4Br gave only $[Ni(L\text{-}L)Br_3]$, and addition of NBu^n_4Br to $[Ni(L\text{-}L)Br_3]$ in CH_2Cl_2 did not result in any change in the e.s.r. spectrum.

Structure of $[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]\cdot C_6H_5Me$.—Numerous attempts failed to obtain single crystals of various $[Ni(L\text{-}L)X_3]$ suitable for *X*-ray study, either by crystallisation of $[Ni(L\text{-}L)X_3]$ from chlorocarbon solvents or by *in situ* oxidation of $[Ni(L\text{-}L)X_2]$. Black crystals of the title complex were obtained by slow cooling of a CH_2Cl_2–toluene (1 : 2 v/v) solution of $[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]$ to −20 °C. The discrete molecule which has approximate C_s symmetry is shown in Figure 2, and the packing in Figure 3 shows the toluene filling holes in the lattice. Toluene solvates are common but frequently the molecule is not well defined. Selected bond lengths and angles are given in Table 4. Only two nickel(III) complexes with heavy group 5B donors have been structurally characterised previously, $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]$[10] and $[Ni(PMe_2Ph)_2Br_3]$,[8] but useful comparisons can be drawn with the latter and with isoelectronic (d^7) cobalt(II) complexes.

The $[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]$ molecule is a distorted square pyramid with an apical bromine. The basal plane is distorted by the chelating diphosphine; the P–M–P angle is

Table 3. E.s.r. spectral data [a]

Compound	g Values, linewidths, and comments
$[Ni(Ph_2PCH_2CH_2PPh_2)Cl_3]$	(*a*): $g = 2.21$ (200) (isotropic) (*b*): $g = 2.20$ (200) (isotropic)
$[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]$	(*a*): $g = 1.93$ (700) (isotropic) (*b*): $g_{av.} = 2.10$ (quartet, $A_{iso} = 65$ G)
$[Ni\{Ph_2P(CH_2)_3PPh_2\}Cl_3]$	(*a*): $g = 2.13$ (400) (isotropic) (*b*): $g = 2.09$ (110) (isotropic)
$[Ni\{Ph_2P(CH_2)_3PPh_2\}Br_3]$	(*a*): $g = 2.15$ (260) (isotropic) (*b*): $g_{av.} = 2.105$ (quartet, $A_{iso} = 60$ G); $g = 2.015$ (90)
$[Ni(Ph_2PCHCHPPh_2)Cl_3]$	(*a*): $g = 2.21$ (200) (isotropic) (*b*): $g = 2.16$ (85) (isotropic)
$[Ni(Ph_2PCHCHPPh_2)Br_3]$	(*c*): $g = 2.09$ (280) (isotropic) (*b*): $g_{av.} = 2.15$ (quartet, $A_{iso} = 65$ G)
$[Ni\{o\text{-}C_6H_4(PPh_2)(SMe)\}Br_3]$	(*a*): $g = 2.11$ (300) (isotropic) (*b*): $g_{av.} = 2.12$ (some ill defined fine structure)
$[Ni\{o\text{-}C_6H_4(AsPh_2)_2\}Br_3]$	(*a*): $g = 2.14$ (100) (isotropic)
$[Ni\{o\text{-}C_6H_4(AsPh_2)(PPh_2)\}Br_3]$	(*a*): $g = 2.00$ (250) (isotropic) (*b*): $g_{av.} = 2.21$ (quartet, $A_{iso} = 53$ G; split further into partly resolved triplets, A_{iso} *ca.* 6 G); $g_{av.} = 2.00$ (partly resolved into 2 lines)
$[Ni\{o\text{-}C_6H_4(PPh_2)_2\}Cl_3]$	(*a*): $g = 2.25$ (95); $g = 2.073$ (br) (*b*): $g = 2.197$ (43) (isotropic)
$[Ni\{o\text{-}C_6H_4(PPh_2)_2\}Br_3]$	(*a*): $g_{av.} = 2.167$ (120) (anisotropic, 2 lines partly resolved) (*b*): $g_{av.} = 2.175$ (quartet; $A_{iso} = 60$ G)
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}Cl_3]$	(*a*): $g = 2.10$ (110) (isotropic). In $CHCl_3$ gives spectrum highly characteristic of $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]^+$ [13]
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}Br_3]$	(*a*): $g = 2.12$ (250) (isotropic). In CH_2Cl_2 or CH_3CN gives spectrum characteristic of $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Br_2]^+$ [13]
$[Ni(Me_2PCH_2CH_2PMe_2)Cl_3]$	(*a*): $g = 2.179$ (100) (isotropic)
$[Ni(Me_2PCH_2CH_2PMe_2)Br_3]$	(*a*): $g = 2.155$ (150) (isotropic)
$[Ni\{PhP(CH_2CH_2PPh_2)_2\}Cl_3]$	(*a*): $g = 2.193$ (180) (isotropic)
$[Ni\{PhP(CH_2CH_2PPh_2)_2\}Br_3]$	(*a*): $g = 2.181$ (135) (isotropic)
$[Ni\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}Br_3]$	(*a*): $g = 2.101$ (110) (isotropic) (*b*): $g_{av.} = 2.077$ (10 lines, $A_{iso} = 68$ G)
$[Ni(Me_2PCH_2CH_2PMe_2)_2Cl_2][BF_4]$	(*a*): $g = 2.157, 2.116$ (35) (*b*): $g_{av.} = 2.117$ (9 lines, $A_{iso} = 15$ G)
$[Ni(Me_2PCH_2CH_2PMe_2)_2Br_2]Br$	(*a*): $g_{av.} = 2.08$ (2 or 3 superimposed signals). In CH_3CN: $g_{av.} = 2.095$ (7 lines, $A_{iso} = 57$ G)
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][ClO_4]$	(*a*): $g = 2.12$ (complex pattern); $g = 2.03$. In CH_3CN: $g_{av} = 2.130$ (9 lines, $A_{iso} = 28$ G)
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Br_2][ClO_4]$	(*a*): $g = 2.107$ (90) (isotropic). In CH_3CN: extremely complex pattern, *cf.* ref. 14
$[Ni\{o\text{-}C_6H_4(AsMe_2)(PMe_2)\}_2Cl_2][ClO_4]$	(*a*): $g = 2.24, 2.16, 2.01$ (*b*): complex pattern
$[Ni\{o\text{-}C_6H_4(AsMe_2)(PMe_2)\}_2Br_2][ClO_4]$	(*a*): $g = 2.08$ (95) (isotropic)
$[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Br_2][ClO_4]$	(*a*): $g = 2.09$ (65), 2.00
$[Ni(Ph_2PCH_2CH_2AsPh_2)Br_3]$ [b]	(*a*): $g = 2.12$ (200) (isotropic) $t_{\frac{1}{2}}$ *ca.* 15 s
$[Ni(Ph_2AsCHCHAsPh_2)Br_3]$ [b]	(*a*): $g = 2.02$ (190) (isotropic) $t_{\frac{1}{2}}$ *ca.* 30 s

[a] Figures in parentheses are linewidths (derivative peak-to-peak) in G. Conditions used: (*a*) powdered solid, room temperature; (*b*) CH_2Cl_2 solution, room temperature; (*c*) powdered solid, −196 °C. [b] Generated *in situ* by addition of Br_2–CCl_4 to the solid nickel(II) complex.

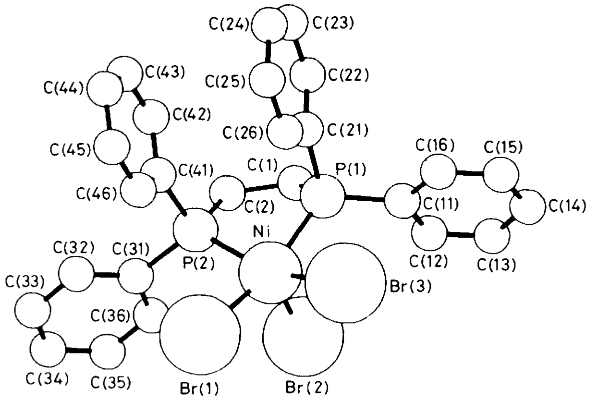

Figure 2. A discrete molecule of $[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]$ showing the atom-numbering scheme and excluding H atoms for clarity

82.6(2)°, which is similar to that found in the square-pyramidal isomer of $[Co(Ph_2PCH_2CH_2PPh_2)_2Cl][SnCl_3]$ [25] (82.7, 81.7°), but smaller than those in $[Ni^{II}(Ph_2PCH_2CH_2PPh_2)Br(\eta\text{-}C_3H_4Me)]$ (88.8°) [26] or $[Pd(Ph_2PCH_2CH_2PPh_2)Cl_2]$ (85.8°).[27] The Br–Ni–Br angle in the basal plane is 95.3°, whilst those involving the basal and apical bromines are 101 and 105°. The nickel atom lies *ca.* 0.34 Å above the P_2Br_2 plane, and the two methylene carbon atoms of the diphosphine backbone are above the plane in a similar conformation to that found in $[Co(Ph_2PCH_2CH_2PPh_2)_2Cl]^+$.[25] The internal dimensions of the diphosphine are unexceptional.[25,26] The basal Ni–Br distances differ by *ca.* 6σ [2.346(3) and 2.363(3) Å], and the bond to the apical bromine is much longer, *ca.* 20σ [2.417(3) Å], than the average of the basal Ni–Br bonds. Square-pyramidal d^7 and d^8 complexes with apical halides (X) usually have long apical M–X bonds,[23,25,26,28] which is ascribed to the presence of one or two electrons in the antibonding d_{z^2} orbital. The Ni–Br bond lengths in the title complex can be compared with those [8] in trigonal bipyramidal $[Ni(PMe_2Ph)_2Br_3]$ [2.349(2), 2.339(2), and 2.375(2) Å]. In this case one bond is also longer (*ca.* 15σ) than the average of the other two, and the distortion is attributed [8] to the unsymmetrical arrangement of *d* electrons in the orbitals in the trigonal plane $[(d_{xz})^2(d_{yz})^2(d_{x^2-y^2})^2(d_{xy})^1(d_{z^2})^0]$ (Jahn–Teller distortion).

$[Ni(L\text{–}L)X_3]$ (L–L = *alkyl-diphosphine or -diarsine*).—The compounds $[Ni(Me_2PCH_2CH_2PMe_2)X_3]$ (X = Cl or Br) were easily prepared from planar $[Ni(Me_2PCH_2CH_2PMe_2)X_2]$ [15] and X_2 in CCl_4, but this route cannot be used for complexes of $o\text{-}C_6H_4(AsMe_2)_2$ [9] or $o\text{-}C_6H_4(PMe_2)_2$,[11] neither of which forms 1 : 1 complexes on reaction with nickel(II) halides. Nyholm [29] obtained $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}Br_3]$ by bromination of the dicarbonyl $[Ni(CO)_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$, and the

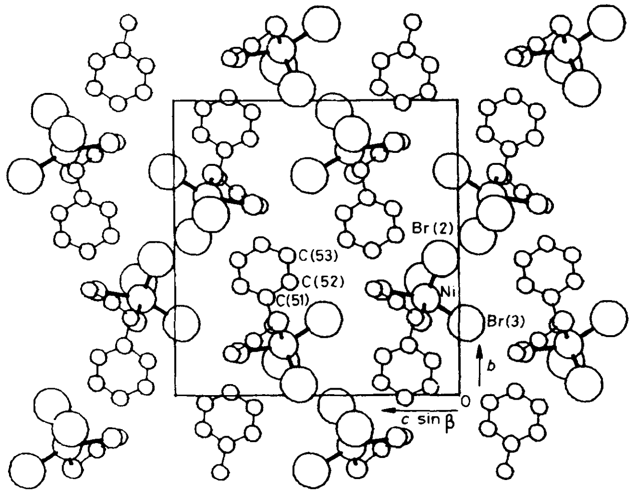

Figure 3. A packing diagram for $[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]\cdot C_6H_5Me$ viewed from the *a* direction. The phenyl groups on P atoms and H atoms have been omitted

corresponding chloride can be made from the latter and Cl_2–CCl_4 under anhydrous conditions. Both complexes are very moisture sensitive, and decompose immediately in solution, and neither has been obtained completely pure, as shown by the analytical data and the rather high magnetic moments ($\mu_{eff.}$ *ca.* 2.3—2.4 B.M.). The reaction of $[Ni(CO)_2\{o\text{-}C_6H_4(PMe_2)_2\}]$ [30] with Cl_2–CCl_4 produced an extremely moisture-sensitive pale blue paramagnetic powder, which appeared to be mainly a nickel(II) phosphine oxide complex. The corresponding reaction with Br_2 gave a dark green oil, also containing much phosphine oxide. Interestingly, bromination of $[Ni(CO)_2(Me_2PCH_2CH_2PMe_2)]$ [15] gave a mixture of $[Ni(Me_2PCH_2CH_2PMe_2)Br_3]$ and phosphine oxide, but with an excess of chlorine the product was a pale blue phosphine oxide complex. The compound $[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}Cl_2]$ decomposed on treatment with Cl_2–CCl_4.

The structures of $[Ni(L\text{–}L)X_3]$ [L–L = $Me_2PCH_2CH_2PMe_2$ or $o\text{-}C_6H_4(AsMe_2)_2$] are not known but from their similar i.r. and electronic spectra to those of the phenyldiphosphine complexes it is likely that these are five-co-ordinate, rather than halide-bridged octahedral dimers as originally proposed.[18,29] The solids give isotropic e.s.r. spectra, but the spectra of CH_3CN solutions of $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}X_3]$ are very different, and show that the main nickel(III) species present is $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2X_2]^+$. This suggests that the instability of the 1 : 1 complexes is due to the tendency of this ligand [11] to produce $[Ni(L\text{–}L)_2X_2]^{n+}$ complexes. The rearrangement involves dissociation of the diarsine, and since the free ligand is strongly reducing at least partial reduction of the Ni^{III} will occur. The preference for 2 : 1 complexes is even greater with $o\text{-}C_6H_4(PMe_2)_2$,[11,19,20] in keeping with our failure to prepare $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}X_3]$.

$[Ni(L\text{–}L)_2X_2]Y$ (X = Cl *or* Br; Y = X, ClO_4, *or* BF_4).—These are exemplified by the well known complexes with L–L = $o\text{-}C_6H_4(PMe_2)_2$ or $o\text{-}C_6H_4(AsMe_2)_2$,[9–14] which are obtained by oxidation of $Ni(L\text{–}L)_2X_2$ with O_2–HX, FeX_3, X_2,* Ce^{IV}, *etc.* The salts $[Ni(Me_2PCH_2CH_2PMe_2)_2X_2]Y$ and $[Ni\{o\text{-}C_6H_4(AsMe_2)(PMe_2)\}_2X_2][ClO_4]$ were easily obtained using X_2 as oxidant and from their spectroscopic properties (Tables 1—3) are close analogues with *trans* octahedral (D_{2h}) cations. In particular the presence of a single Ni–X (B_{1u}) stretch at unusually low frequency is characteristic of the d^7 ion with axial X groups.[11,24] The electronic spectra contain a single weak *d-d* absorption at 12 000—15 000 cm^{-1} which in D_{2h} symmetry can be assigned [14] to the nearly degenerate $^2A_g \rightarrow {}^2B_{2g},{}^2B_{3g}$ transitions, and charge-transfer bands at $>$20 000 cm^{-1}.

Table 4. Selected bond lengths (Å) and angles (°) for $[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]\cdot C_6H_5Me$

Ni–Br(1)	2.346(3)	Ni–P(1)	2.223(5)
Ni–Br(2)	2.417(3)	Ni–P(2)	2.236(5)
Ni–Br(3)	2.363(3)		
P(1)–C(1)	1.82(2)	P(2)–C(2)	1.83(2)
P(1)–C(11)	1.78(1)	P(2)–C(31)	1.81(1)
P(1)–C(21)	1.80(1)	P(2)–C(41)	1.82(1)
C(1)–C(2)	1.53(2)	C(5)–C(51)	1.41(3)
C–C(aromatic)	1.395(fixed)		
P(1) · · · P(2)	2.94		
Br(1)–Ni–Br(2)	101.0(1)	Br(1)–Ni–P(1)	165.7(2)
Br(1)–Ni–Br(3)	95.3(1)	Br(1)–Ni–P(2)	89.5(1)
Br(2)–Ni–Br(3)	104.9(1)	Br(2)–Ni–P(1)	91.6(1)
P(1)–Ni–P(2)	82.6(2)	Br(2)–Ni–P(2)	95.2(1)
		Br(3)–Ni–P(1)	87.9(1)
		Br(3)–Ni–P(2)	158.0(2)
Ni–P(1)–C(1)	106.7(5)	Ni–P(2)–C(2)	108.7(5)
Ni–P(1)–C(11)	119.6(4)	Ni–P(2)–C(31)	119.8(4)
Ni–P(1)–C(21)	110.5(4)	Ni–P(2)–C(41)	109.6(4)
C(1)–P(1)–C(11)	106.1(6)	C(2)–P(2)–C(31)	103.4(6)
C(1)–P(1)–C(21)	105.6(6)	C(2)–P(2)–C(41)	108.7(7)
C(11)–P(1)–C(21)	107.4(5)	C(31)–P(2)–C(41)	106.1(6)
P(1)–C(1)–C(2)	112(1)	C(5)–C(51)–C(52)	113(2)
P(2)–C(2)–C(1)	112(1)	C(5)–C(51)–C(56)	127(2)
P(1)–C(1)–C(2)–P(2)	−13.0		

The salt $[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Cl][ClO_4]$ decomposed on treatment with Cl_2–CCl_4, but the bromo-analogue reacted with Br_2 to give red $[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Br_2][ClO_4]$, which contains the first nickel(III)–stibine bond. In spite of this neither $[Ni\{Me_2Sb(CH_2)_3SbMe_2\}_2X]X$ [32] nor $[Ni\{o\text{-}C_6H_4(SbMe_2)_2\}_2X]X$ could be oxidised to Ni^{III}, immediate cleavage of the stibine occurring with the formation of organoantimony(V) halides (*cf.* ref. 20). Attempts to prepare $[Ni(L\text{–}L)_2X_2]^+$ with phenyl-substituted bidentates [L–L = $Ph_2PCH_2CH_2PPh_2$, $Ph_2PCHCHPPh_2$, or $o\text{-}C_6H_4(PPh_2)_2$] were unsuccessful, the products of reaction of $[Ni(L\text{–}L)_2X]Y$ or $Ni(L\text{–}L)_2X_2$ with X_2 being impure $[Ni(L\text{–}L)X_3]$ and the diphosphine dioxide, behaviour reminiscent of the Pd^{II}–Pd^{IV} systems,[20] and rationalised similarly in terms of preferential binding of the number of X groups required to achieve neutrality.

Complexes of Multidentate Ligands.—One complex of a tritertiary arsine, *mer*-$[Ni\{MeAs(o\text{-}C_6H_4AsMe_2)_2\}Br_3]$ has been characterised previously,[33] and an impure sample of $[Ni\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}Br_3]$ obtained.[34] We have prepared pure samples of the latter complex and have isolated $[Ni\{PhP(CH_2CH_2PPh_2)_2\}X_3]$ (X = Cl or Br) by cautious halogen oxidation of the corresponding five-co-ordinate nickel(II) complexes [34,35] suspended in dry CCl_4. All three are reasonably stable solids, but the triphosphine complexes decompose immediately in solution. Identification of the Ni–X stretching vibrations is difficult due to the strong ligand absorptions in the far-i.r. region, but on the basis of the tentative assignments in Table 1 *mer* octahedral structures are proposed.

Benner and Meek [36] showed that the reported [37] nickel(III) complexes of the tetratertiary arsine $As(CH_2CH_2CH_2AsMe_2)_3$

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* Excess of Cl_2 produces nickel(IV) complexes.[11,31]

(L) were trigonal-bipyramidal nickel(II) compounds [NiLX]X, and that attempts to oxidise these to Ni^{III} produced diamagnetic materials with strong As=O vibrations in the i.r. spectra, indicating oxidation of the ligand rather than the metal. Our results with this ligand are completely consistent with the published data,[36] and our attempts to oxidise nickel(II) complexes of the tetraphosphines $P(CH_2CH_2PPh_2)_3$ [38] and $Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$ [39] similarly failed to yield nickel(III) complexes, but appeared to involve partial oxidation of the ligand.

Discussion

The structures and stability of the nickel(III) complexes of phosphorus and arsenic donor ligands depend markedly upon the donor and substituents, much more so than with 4*d* or 5*d* metals, *e.g.* Pd^{IV}.[20] Thus in $[Ni(L^-L)X_3]$ (L^-L = phenyldiphosphine or -diarsine) the stability order is P > As and the order with backbone is o-C_6H_4 > CHCH ⩾ CH_2CH_2. The former is generally true for normal oxidation states of the 3*d* metals including Co^{II} and Ni^{II}.[21,40] We believe the backbone dependence is mainly due to the greater ability of the rigid o-C_6H_4 linkage to resist ligand dissociation (since the *free* ligands are strong reductants, this would lead to reduction of the metal). Warren and Bennett [11] have proposed that the o-C_6H_4 linkage is a major factor in the strong co-ordinating ability of o-$C_6H_4(EMe_2)_2$ (E = P or As). The involvement of the o-C_6H_4 or CH=CH backbone in delocalisation of the odd electron is not thought to be significant (*cf.* ref. 11).* The thermal stabilities of $[Ni(L^-L)X_3]$ (X = Cl or Br) are similar, but in solution there appears to be a halogen dependence of the stability, Br > Cl, which is unexpected for a higher oxidation state. However the neutral ligands are only moderate σ donors towards 3*d* metal ions, and the apparently greater stability of $[Ni(L^-L)Br_3]$ could be rationalised in terms of symbiosis, and more effective bonding of the neutral ligand to the softer $NiBr_3$ acceptor group. The instability of the 1 : 1 complexes of o-$C_6H_4(AsMe_2)_2$ appears to be due to a tendency to rearrange to the 2 : 1 complex rather than to reduce to Ni^{II}, and hence is not readily comparable to that of the phenyldiarsines.

The tetragonal compounds $[Ni(L^-L)_2X_2]^+$ are only obtained with alkyl-substituted ligands, which combine strong σ-donor power, moderate steric requirements, and contribute significantly to ligand-field stabilisation energy as a result of their high positions in both the spectrochemical and nephelauxetic series.[11] The failure of the phenyldiphosphines to give this type of complex is probably due both to their larger steric requirements {in $[Co(Ph_2PCH_2CH_2PPh_2)_2Cl]^+$ the 'sixth' co-ordination site is blocked by the o-H of the phenyl rings} [25] and by the preference of higher oxidation state metals to co-ordinate sufficient (σ + π donor) halide ions to achieve neutrality.[19,20,22] Only with very strong σ-donor neutral ligands is the latter requirement relaxed.

Experimental

Physical measurements were made as described previously.[1,22] Moisture-sensitive materials were made in Schlenk tubes, and manipulated in a dry-box (⩽10 p.p.m. water). Solvents and nickel(II) salts were dried by conventional methods before use. The following nickel(II) complexes were made by literature methods or minor modifications thereof: $[Ni(L^-L)X_2]$ [X = Cl or Br; L^-L = $Me_2PCH_2CH_2PMe_2$,[15] $Ph_2PCH_2PPh_2$,[41] $Ph_2PCH_2CH_2PPh_2$,[16] $Ph_2P(CH_2)_3PPh_2$,[16] *cis*-$Ph_2PCHCHPPh_2$,[42] or o-$C_6H_4(PPh_2)_2$[21]]; $[Ni(L^-L)Br_2]$ [L^-L = $Ph_2AsCH_2CH_2AsPh_2$,[21] *cis*-$Ph_2AsCHCHAsPh_2$,[21] o-$C_6H_4(AsPh_2)_2$,[21] $Ph_2P(CH_2)_4PPh_2$,[43] *trans*-$Ph_2PCHCHPPh_2$,[44] $Ph_2PCH_2CH_2AsPh_2$,[45] or o-$C_6H_4(AsPh_2)(PPh_2)$[46]; $[Ni\{o\text{-}C_6H_4(PPh_2)(SMe)\}Cl_2]$; [47] $Ni(L^-L)_2X_2$, $[Ni(L^-L)_2X]Y$ [X = Cl or Br; Y = ClO_4, BF_4, or BPh_4; L^-L = o-$C_6H_4(AsMe_2)_2$,[9,48] o-$C_6H_4(PMe_2)_2$,[11] o-$C_6H_4(AsMe_2)(PMe_2)$,[49] $Me_2PCH_2CH_2PMe_2$,[15] $Ph_2PCH_2CH_2PPh_2$,[15] *cis*-$Ph_2PCHCHPPh_2$,[42] or $Me_2Sb(CH_2)_3SbMe_2$[32]]. The complexes of the polydentate ligands $PhP(CH_2CH_2PPh_2)_2$,[35] $MeAs(CH_2CH_2CH_2AsMe_2)_2$,[34] $As(CH_2CH_2CH_2AsMe_2)_3$,[36] $P(CH_2CH_2PPh_2)_3$,[38] and $[Ph_2PCH_2CH_2P(Ph)CH_2^-]_2$ [39] were made as described. The compounds $[Ni(CO)_2(L^-L)]$ [L^-L = o-$C_6H_4(AsMe_2)_2$, o-$C_6H_4(PMe_2)_2$, or $Me_2PCH_2CH_2PMe_2$] were obtained from $[Ni(CO)_4]$ and L^-L in benzene [15,30,31] and were recrystallised from cyclohexane immediately before use.

Dibromo(o-*methylthiophenyldiphenylphosphine*)*nickel*(II), $[Ni\{o\text{-}C_6H_4(PPh_2)(SMe)\}Br_2]$.—Anhydrous $NiBr_2$ (0.65 g, 3 mmol) was stirred for 2 d with the ligand (0.62 g, 2 mmol) in CH_2Cl_2 (50 cm^3), during which time a deep purple solution formed. Unreacted nickel(II) bromide was filtered off, the solution concentrated to *ca.* 15 cm^3, cyclohexane (15 cm^3) added, and the mixture cooled to −20 °C overnight. The red-purple crystals were recrystallised from CH_2Cl_2–C_6H_{12}. Yield 0.84 g, 80% (Found: C, 43.4; H, 3.0. $C_{19}H_{17}Br_2NiPS$ requires C, 43.4; H, 3.3%); ν(NiBr) at 300 and 282 cm^{-1}. $10^{-3}E_{max.}$ (CH_2Cl_2 solution) = 18.8 (930), 24.4 (760), and 31.7 (sh) cm^{-1} (ε 5 920 dm^3 mol^{-1} cm^{-1}).

[1,4-*Bis*(*diphenylphosphino*)*butane*]*dichloronickel*(II), $[Ni\{Ph_2P(CH_2)_4PPh_2\}Cl_2]$.—To a solution of the ligand (0.85 g, 2 mmol) in n-butanol (30 cm^3) was added $NiCl_2 \cdot 6H_2O$ (0.48 g, 2 mmol) in the same solvent (15 cm^3). The mixture was refluxed briefly whereupon a light purple powder was deposited. This became light fawn on drying *in vacuo* (yield 1.1 g, 84%) (Found: C, 58.9; H, 5.1. $C_{28}H_{28}Cl_2NiP_2$ requires C, 60.5; H, 5.1%); ν(NiCl) at 328 and 289 cm^{-1}. $10^{-3}E_{max.}$ (diffuse reflectance) = 12.2, 18.4, 19.4, 25.5 (sh), and 26.6 cm^{-1}.

Dibromobis(o-*dimethylphosphinophenyldimethylstibine*)-*nickel*(II), $[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Br_2]$.—Under dinitrogen, the ligand (0.26 g, 0.8 mmol) was added to a solution of $NiBr_2$ (0.11 g, 0.5 mmol) in ethanol (10 cm^3). The mixture was warmed to 50 °C, stirred for 5 min, and evaporated to 5 cm^3. Diethyl ether was added to produce a brown solid. After cooling to −20 °C, the brown solid was filtered off and dried *in vacuo*. Yield 0.14 g, 40% (Found: C, 30.3; H, 3.6. $C_{20}H_{32}Br_2NiP_2Sb_2$ requires C, 31.15; H, 4.05%). $10^{-3}E_{max.}$ (CH_2Cl_2) = 19.8 (400), 20.7 (360), and 32.9 cm^{-1} (3 200 dm^3 mol^{-1} cm^{-1}). Λ (CH_3NO_2) = 65 ohm^{-1} cm^2 mol^{-1}.

Dichlorobis(o-*dimethylphosphinophenyldimethylstibine*)-*nickel*(II), $[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Cl_2]$.—Under dinitrogen a warm n-butanol solution (20 cm^3) of $NiCl_2 \cdot 6H_2O$ (0.17 g, 0.7 mmol) was treated with the ligand (0.4 g, 1.4 mmol). After stirring for 20 min, the solution was concentrated to *ca.* 10 cm^3 and cooled to −20 °C overnight. The brown product was filtered off, rinsed with diethyl ether, and dried. Yield 0.27 g, 54%. The complex is insoluble in or decomposed by common solvents (Found: C, 33.8; H, 4.6. $C_{20}H_{32}Cl_2NiP_2Sb_2$ requires C, 33.95; H, 4.6%). $10^{-3}E_{max.}$ (diffuse reflectance) = 18.25 (sh), 19.6, and 37.9 cm^{-1}.

Bis(o-*dimethylphosphinophenyldimethylstibine*)*nickel*(II) *Perchlorate*, $[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2][ClO_4]_2$.—A solu-

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* Interpretation of the single-crystal e.s.r. data on $[Ni(L^-L)X_3]$ would be difficult due to the low symmetry, and there is no obvious diamagnetic host for dilution studies.

tion of $Ni(ClO_4)_2\cdot 6H_2O$ (0.37 g, 1 mmol) in Pr^iOH (25 cm^3) was treated with the ligand (0.44 g, 1.5 mmol). A yellow-green precipitate formed rapidly, which was filtered off, rinsed with Pr^iOH, and dried *in vacuo*. Yield 0.6 g, 81% (Found: C, 28.9; H, 4.4. $C_{20}H_{32}Cl_2NiO_8P_2Sb_2$ requires C, 28.6; H, 3.9%). $E_{max.}$ (diffuse reflectance) $= 27.0 \times 10^3$ cm^{-1}. I.r.: 1 050 and 620 cm^{-1} (ClO_4^-).

Bromobis(o-*dimethylphosphinophenyldimethylstibine*)*nickel*(II) *Perchlorate*, $[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Br][ClO_4]$.—The ligand (0.145 g, 0.5 mmol) was added under dinitrogen to a mixture of $NiBr_2\cdot 6H_2O$ (0.05 g, 0.25 mmol) and $Ni(ClO_4)_2\cdot 6H_2O$ (0.09 g, 0.25 mmol) in ethanol (25 cm^3) and the mixture refluxed. On cooling, purple crystals separated. Yield 0.16 g, 76% (Found: C, 29.4; H, 4.0. $C_{20}H_{32}BrClNiO_4P_2Sb_2$ requires C, 29.4; H, 4.0%). $10^{-3}E_{max.}$ (diffuse reflectance) = 19.4 and 29.1 cm^{-1}. Λ (CH_3NO_2) = 110 ohm^{-1} cm^2 mol^{-1}.

Brown-purple crystals of $[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Cl][ClO_4]$ were prepared similarly (Found: C, 30.8; H, 4.0. $C_{20}H_{32}Cl_2NiO_4P_2Sb_2$ requires C, 31.15; H, 4.2%). $10^{-3}E_{max.}$ (diffuse reflectance) = 18.7 (br) and 30.9 cm^{-1}.

Dichloro(o-*dimethylphosphinophenyldimethylstibine*)*nickel*(II), $[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}Cl_2]$.—The salt $NiCl_2\cdot 6H_2O$ (0.12 g, 0.5 mmol) in ethanol (30 cm^3) was treated with the ligand (0.145 g, 0.5 mmol). The red solution was reduced in volume to *ca.* 10 cm^3, and cyclohexane added slowly. Red crystals separated which were rinsed with diethyl ether and dried. Yield 0.14 g, 65% (Found: C, 28.6; H, 3.7. $C_{10}H_{16}Cl_2NiPSb$ requires C 28.7; H, 3.85%); $\nu(NiCl)$ at 247 and 236 cm^{-1}. $10^{-3}E_{max.}$ (diffuse reflectance) = 19.8 (br), 25.0, and 27.2 cm^{-1}. Λ ($C_2H_4Cl_2$) = 0.3 ohm^{-1} cm^2 mol^{-1}.

Dibromobis[o-*phenylenebis*(*dimethylstibine*)]*nickel*(II), $[Ni\{o\text{-}C_6H_4(SbMe_2)_2\}_2Br_2]$.—Under dinitrogen the ligand (0.35 g, 0.9 mmol) was added to $NiBr_2\cdot 3H_2O$ (0.13 g, 0.5 mmol) in n-butanol (15 cm^3) at *ca.* 45 °C. After 10 min the solution was cooled, concentrated, and diethyl ether added dropwise until crystallisation commenced. The solution was cooled to −20 °C overnight, the purple powder collected and dried. Yield 0.34 g, 75% (Found: C, 24.4; H, 3.3. $C_{20}H_{32}Br_2NiSb_4$ requires C, 24.6; H, 3.3%). $10^{-3}E_{max.}$ = 19.5 (930), 27.5 (sh) (2 940), and 33.3 cm^{-1} (8 900 dm^3 mol^{-1} cm^{-1}). Λ (CH_3NO_2) = 81 ohm^{-1} cm^2 mol^{-1}.

Nickel(III) *Complexes*, $[Ni(L\text{-}L)Br_3]$ [$L\text{-}L = Ph_2PCH_2CH_2PPh_2$, $Ph_2P(CH_2)_3PPh_2$, *or* *cis*-$Ph_2PCHCHPPh_2$].—*General method.* A finely ground suspension of $[Ni(L\text{-}L)Br_2]$ (*ca.* 1 mmol) in dry CCl_4 was treated with Br_2 *ca.* 0.5 mmol) in CCl_4. After stirring for 30 min the nickel(III) complex was filtered off, rinsed with dry CCl_4, and dried *in vacuo*. The products decompose to some extent in damp air and should be stored in sealed containers. Yields were approximately quantitative.

Tribromo[o-*phenylenebis*(*diphenylarsine*)]*nickel*(III), $[Ni\{o\text{-}C_6H_4(AsPh_2)_2\}Br_3]$. To finely powdered $[Ni\{o\text{-}C_6H_4(AsPh_2)_2\}Br_2]$ (0.75 g, 1 mmol) under N_2 in a Schlenk apparatus was added Br_2 in CCl_4 (1.4 cm^3 of a 2% v/v solution, *ca.* 0.5 mmol Br_2). After 10 min, CCl_4 (20 cm^3) was added, the black precipitate filtered off, rinsed with dry CCl_4 (2 × 5 cm^3), and dried. Yield approximately quantitative.

Tribromo(o-*diphenylphosphinophenyldiphenylarsine*)*nickel* (III), $[Ni\{o\text{-}C_6H_4(AsPh_2)(PPh_2)\}Br_3]$. To $[Ni\{o\text{-}C_6H_4(AsPh_2)(PPh_2)\}Br_2]$ (0.71 g, 1 mmol) in CH_2Cl_2 (20 cm^3) was added a two-fold excess of Br_2 in CCl_4 (2% v/v). The dark brown solution was rotatory evaporated to dryness, and the residue stirred with light petroleum (b.p. 40—60 °C)-diethyl ether (15 cm^3, 2 : 1 v/v) for 30 min, filtered off, and dried. Yield 0.55 g, 70%.

Tribromo(o-*methylthiophenyldiphenylphosphine*)*nickel*(III), $[Ni\{o\text{-}C_6H_4(PPh_2)(SMe)\}Br_3]$. To $[Ni\{o\text{-}C_6H_4(PPh_2)(SMe)\}Br_2]$ (0.285 g, 0.54 mmol) in CH_2Cl_2 (25 cm^3) under N_2 and cooled to −20 °C was added a stoicheiometric quantity of Br_2 in CCl_4 (2% v/v) with vigorous stirring. The solvent was evaporated to *ca.* 5 cm^3 *in vacuo*, the black solid filtered off, rinsed with diethyl ether, and dried briefly. Yield 0.24 g, 72%.

Tribromo[o-*phenylenebis*(*diphenylphosphine*)]*nickel*(III), $[Ni\{o\text{-}C_6H_4(PPh_2)_2\}Br_3]$. To $[Ni\{o\text{-}C_6H_4(PPh_2)_2\}Br_2]$ (0.29 g, 0.44 mmol) in CH_2Cl_2 (80 cm^3) was added a five-fold excess of Br_2. The black solution was evaporated to *ca.* 15 cm^3 and pentane (10 cm^3) added dropwise. The black crystals were filtered off and dried *in vacuo*. Yield 0.25 g, 76%.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*trichloronickel*(III),* $[Ni(Ph_2PCH_2CH_2PPh_2)Cl_3]$. Nitrosyl chloride was prepared from KNO_2 and $POCl_3$ and purified by redistillation *in vacuo*. Excess of NOCl was slowly carried in a stream of dry nitrogen through a 0 °C trap containing a stirred solution of $[Ni(Ph_2PCH_2CH_2PPh_2)Cl_2]$ (0.5 g, 0.95 mmol) in CH_2Cl_2 (25 cm^3). The yellow-orange solution turned dark green, the majority of the solvent was pumped off, and the green solid filtered off and dried. Yield 0.32 g, 60%. The complexes $[Ni\{Ph_2P(CH_2)_3PPh_2\}Cl_3]$ and $[Ni(Ph_2PCHCHPPh_2)Cl_3]$ were made similarly.

Trichloro[o-*phenylenebis*(*diphenylphosphine*)]*nickel*(III), $[Ni\{o\text{-}C_6H_4(PPh_2)_2\}Cl_3]$. The compound $[Ni\{o\text{-}C_6H_4(PPh_2)_2\}Cl_2]$ (0.325 g, 0.56 mmol) in CH_2Cl_2 (200 cm^3) was treated with an excess of NOCl as above. The solvent volume was reduced to *ca.* 20 cm^3 and cyclohexane (15 cm^3) added with stirring. The mixture was cooled overnight at −20 °C, the green product filtered off, rinsed with CCl_4, and dried. Yield 0.27 g, 80%.

Trihalogeno[o-*phenylenebis*(*dimethylarsine*)]*nickel*(III), $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}X_3]$. The compound $[Ni(CO)_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$ (*ca.* 2 mmol, 0.8 g) was dissolved in cyclohexane (30 cm^3) under N_2, the solution filtered and the cyclohexane removed *in vacuo*. The waxy crystals were redissolved in CH_2Cl_2 (25 cm^3) and a small excess of the appropriate halogen in CH_2Cl_2 added. Gas was immediately evolved and a dark solid precipitated. This was filtered off, rinsed with CH_2Cl_2, and dried *in vacuo*. The products are very moisture sensitive and were transferred to sealed containers and stored at −20 °C. Yield *ca.* 80%.

[1,2-*Bis*(*dimethylphosphino*)*ethane*]*trihalogenonickel*(III), $[Ni(Me_2PCH_2CH_2PMe_2)X_3]$. These complexes were made by reaction of the nickel(II) complexes with halogen in CH_2Cl_2; $[Ni\{PhP(CH_2CH_2PPh_2)_2\}X_3]$ were made in an analogous manner to the phenyldiphosphine analogues. Dichlorobis-[*o*-phenylenebis(dimethylphosphine)]nickel(III) perchlorate was made by the literature method.[11]

Dibromobis[o-*phenylenebis*(*dimethylphosphine*)]*nickel*(III) *perchlorate*, $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Br_2][ClO_4]$. A suspension of $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Br][ClO_4]$ (0.24 g, 0.42 mmol) in CCl_4 was treated with the stoicheiometric amount of Br_2, and the mixture shaken for 2 h. The brown product was filtered off and dried *in vacuo*. Yield approximately quantitative.

Dichlorobis(o-*dimethylphosphinophenyldimethylarsine*)*nickel*(III) *perchlorate*, $[Ni\{o\text{-}C_6H_4(AsMe_2)(PMe_2)\}_2Cl_2][ClO_4]$. To a solution of $[Ni\{o\text{-}C_6H_4(AsMe_2)(PMe_2)\}_2][ClO_4]_2$ (0.16 g, 0.2 mmol) LiCl (0.04 g) and $LiClO_4$ (*ca.* 0.1 g) in CH_3CN-MeOH (30 cm^3, 1 : 1) was added slowly Cl_2 (0.1 mmol) in CCl_4. The solution was concentrated to 20 cm^3 and cooled to −20 °C for 1 week. Lime-green crystals were produced, which were rinsed with diethyl ether and dried. Yield 0.12 g, 78%.

Dibromobis(o-*dimethylphosphinophenyldimethylstibine*)*nickel*(III) *perchlorate*, $[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Br_2][ClO_4]$. The salt $[Ni\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}_2Br][ClO_4]$ (0.36 g, 0.44

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* These complexes can also be made using a small excess of Cl_2–CCl_4 as for the bromides.

Table 5. Final atomic co-ordinates (× 10^4) for $[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]\cdot C_6H_5Me$ with estimated standard deviations in parentheses

Atom *	*X/a*	*Y/b*	*Z/c*
Ni	3 514(1)	3 284(1)	1 183(1)
Br(1)	2 149(1)	3 855(1)	1 287(1)
Br(2)	4 079(1)	4 628(1)	653(1)
Br(3)	2 725(1)	2 427(1)	−232(1)
P(1)	4 804(3)	2 510(3)	1 371(3)
P(2)	4 298(3)	3 557(3)	2 752(3)
C(1)	5 785(11)	3 158(11)	2 215(11)
C(2)	5 551(10)	3 591(11)	3 016(11)
C(11)	5 080(7)	2 295(7)	354(6)
C(12)	5 462(7)	2 986(7)	−12(6)
C(13)	5 697(7)	2 809(7)	−794(6)
C(14)	5 549(7)	1 941(7)	−1 209(6)
C(15)	5 166(7)	1 250(7)	−843(6)
C(16)	4 932(7)	1 427(7)	−62(6)
C(21)	4 824(8)	1 426(6)	1 946(7)
C(22)	5 684(8)	1 052(6)	2 540(7)
C(23)	5 715(8)	256(6)	3 058(7)
C(24)	4 886(8)	−168(6)	2 982(7)
C(25)	4 025(8)	205(6)	2 388(7)
C(26)	3 994(8)	1 002(6)	1 870(7)
C(31)	4 100(7)	4 612(7)	3 269(8)
C(32)	3 672(7)	4 634(7)	3 921(8)
C(33)	3 529(7)	5 468(7)	4 288(8)
C(34)	3 814(7)	6 280(7)	4 004(8)
C(35)	4 243(7)	6 258(7)	3 351(8)
C(36)	4 386(7)	5 424(7)	2 984(8)
C(41)	4 080(9)	2 636(6)	3 449(8)
C(42)	4 831(9)	2 178(6)	4 141(8)
C(43)	4 668(9)	1 453(6)	4 654(8)
C(44)	3 753(9)	1 187(6)	4 473(8)
C(45)	3 001(9)	1 646(6)	3 781(8)
C(46)	3 165(9)	2 370(6)	3 268(8)
C(5)	3 228(22)	2 412(21)	6 592(32)
C(51)	3 057(11)	3 321(8)	6 791(14)
C(52)	2 595(11)	3 838(8)	5 963(14)
C(53)	2 316(11)	4 731(8)	6 038(14)
C(54)	2 500(11)	5 107(8)	6 941(14)
C(55)	2 961(11)	4 591(8)	7 769(14)
C(56)	3 240(11)	3 698(8)	7 694(14)

* Carbon atoms of the phenyl groups are labelled C(*ij*) where *i* (1—5) indicates the ring and *j* (1—6) the carbon atoms within each ring.

Table 6. T.g.a. data

Complex	Weight loss (%)		Temperature (°C) [b]
	Found	Calc.[a]	
$[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]$	10.6	11.5	170
$[Ni\{Ph_2P(CH_2)_3PPh_2\}Br_3]$	10.3	11.2	170
$[Ni(Ph_2PCHCHPPh_2)Br_3]$	10.7	11.5	*ca.* 100
$[Ni\{o\text{-}C_6H_4(PPh_2)_2\}Cl_3]$	6.2	6.5	280
$[Ni(Ph_2PCH_2CH_2PPh_2)Cl_3]$	6.0	6.3	150

[a] Calc. for $[Ni(L\text{-}L)X_3] \longrightarrow [Ni(L\text{-}L)X_2] + \frac{1}{2}X_2$. [b] Temperature at which decomposition is complete ±*ca.* 10 °C. At ⩾360 °C large weight losses due to loss of the diphosphine occur.

mmol) in CH_3CN (25 cm^3) was treated with Br_2 (0.04 g, 0.25 mmol) in CCl_4 (10 cm^3). The solution was concentrated to *ca.* 10 cm^3, diethyl ether added until crystallisation began, and the solution cooled to −20 °C for 48 h. The red-brown solid was collected, rinsed with diethyl ether, and dried. Yield 0.31 g, 78%. The salt $[Ni\{o\text{-}C_6H_4(AsMe_2)(PMe_2)\}_2Br_2][ClO_4]$ was prepared similarly.

[*Bis*(3-*dimethylarsinopropyl*)*methylarsine*]*tribromonickel*(III), $[Ni\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}Br_3]$. Bromine (0.022 g, 0.15 mmol) in CH_2Cl_2 was added to $[Ni\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}Br_2]$ (0.19 g, 0.3 mmol) in CH_2Cl_2 (20 cm^3). The solvent was rapidly pumped off until a red-brown solid precipitated. This was separated and dried. Yield 0.12 g, 60%.

Crystal Structure Determination.—Crystals, unstable in air, were obtained by cooling (−20 °C) CH_2Cl_2–toluene (1 : 2 v/v) solutions of the compound and sealed in Lindemann capillaries in the presence of a small amount of Br_2 (Found: C, 50.7; H, 4.2. Calc. for $C_{33}H_{32}Br_3NiP_2$: C, 50.2; H, 4.1%). Preliminary photographic studies established the crystal system and approximate cell dimensions.

Crystal data. $[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]\cdot C_6H_5Me$, $C_{33}H_{32}Br_3NiP_2$, $M = 789.01$, monoclinic, space group $P2_1/n$, $a = 15.567(3)$, $b = 14.627(2)$, $c = 15.151(3)$ Å, $\beta = 113.38(2)°$, $U = 3\,166.60$ Å^3, D_m (flotation) = 1.61(2), $Z = 4$, $D_c = 1.654$ g cm^{-3}, $F(000) = 1\,572$, $\mu(\text{Mo-}K_\alpha) = 44.22$ cm^{-1}, $\lambda = 0.7107$ Å.

Intensity data were recorded on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. From a crystal (0.25 × 0.1 × 0.15 mm) at room temperature 3 883 reflections were recorded ($2 < \theta < 21°$) including three check reflections which showed no deterioration during the experiment. After averaging multiple measurements (R_{int} 0.008) there remained 3 386 reflections and eliminating those with $F < 3\sigma(F)$ (1 803) left 1 583 unique reflections to be used in the refinement. No absorption correction was applied to the initial data (see later). The normalised structure factors (E) strongly supported a centrosymmetric space group in accord with the systematic absences.

Solution and refinement of the structure. The structure was solved by a combination of direct methods and Patterson techniques. The SHELX[50] centrosymmetric direct-methods strategy yielded two solutions with large figures of merit (2.62 and 2.50) and in both cases gave E maps with pseudosymmetry and showing two overlapping images of the heavy-atom skeleton. Only the second solution was found to be consistent with the Patterson synthesis and a sequence of structure-factor calculations and electron-density syntheses readily located Ni, Br, and the phosphine ligand. A difference electron-density synthesis revealed the toluene solvate molecule, expected from the chemical analysis and measured density, and evidence for some of the H atoms. Hydrogen atoms were added to the model in geometrically calculated positions [d(C–H) = 1.08 Å] with a common thermal parameter (0.1 Å^2) and least-squares refinement with isotropic atoms gave $R = 0.096$. The large thermal parameter for the toluene methyl group [C(5)] was investigated. There was no evidence for disorder or partial occupancy of the toluene molecule and removal of C(5) resulted in its reappearance in a difference electron-density synthesis. Neither well defined crystal faces nor empirical psi-scan measurements were available in order to apply an absorption correction and the empirical method of Walker and Stuart[51] was applied following isotropic refinement. The heavy atoms and C(5) were allowed anisotropic thermal motion and least-squares refinement converged to $R = 0.0562$ ($R' = 0.0505$) {136 parameters, anisotropic [Ni, Br, P, and C(5)] and isotropic (C, H) atoms, rigid phenyl groups (C–C 1.395 Å), empirical weights, $w = 1/[\sigma^2(F) + 0.0003F^2]$}. The ratio of reflections to parameters was 11.6 and a final difference electron-density synthesis showed all features in the range 0.65 to −0.57 e Å^{-3}. The final atomic co-ordinates are given in Table 5. Atomic scattering factors for neutral atoms and anomalous-dispersion corrections were taken from SHELX [50] (Br, P, C, and H) and ref. 52 (Ni), and all calculations were performed on an ICL2970 computer using the programs SHELX,[50] DIFABS,[51] PLUTO,[53] and XANADU.[54]

Acknowledgements

We thank the S.E.R.C. for support of this work and for a postgraduate studentship (to S. J. H.), and Southampton University for a postdoctoral fellowship (to L.R.G.). We also thank Dr. K. G. Smith for preliminary experiments, Dr. M. B. Hursthouse for the *X*-ray data collection using the S.E.R.C./Q.M.C. CAD-4 diffractometer service, Dr. S. G. Murray for the t.g.a. data, Professor G. R. Luckhurst for use of the e.s.r. facilities, and Professor R. Baker for a gift of nickel carbonyl.

References

1 Part 7, D. A. Cooper, S. J. Higgins, and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1983, 2131.
2 W. Levason and C. A. McAuliffe, *Coord. Chem. Rev.*, 1974, **12**, 105.
3 K. Nag and A. Chakravorty, *Coord. Chem. Rev.*, 1980, **33**, 87.
4 M. Yamashita, N. S. Kida, Y. Hamaue, and R. Aoki, *Inorg. Chim. Acta*, 1981, **52**, 43.
5 A. J. Thomson, *Nature* (*London*), 1982, **298**, 602 and refs. therein.
6 K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1936, **229**, 265.
7 E. C. Alyea, D. W. Meek, J. K. Stalick, and J. A. Ibers, *J. Am. Chem. Soc.*, 1969, **91**, 4920.
8 J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 453.
9 R. S. Nyholm, *J. Chem. Soc.*, 1950, 2061.
10 P. Kreisman, G. A. Rodley, R. Marsh, and H. B. Gray, *Inorg. Chem.*, 1972, **11**, 3040.
11 L. F. Warren and M. A. Bennett, *Inorg. Chem.*, 1976, **15**, 3126.
12 P. K. Bernstein and H. B. Gray, *Inorg. Chem.*, 1972, **11**, 3035.
13 P. T. Manoharan and M. T. Rogers, *J. Chem. Phys.*, 1970, **53**, 1682.
14 C. N. Sethulakshmi, S. Subramainan, M. A. Bennett, and P. T. Manoharan, *Inorg. Chem.*, 1979, **18**, 2520; E. Balasivasubramanian, C. N. Sethulakshmi, and P. T. Manoharan, *ibid.*, 1982, **21**, 1684.
15 G. Booth and J. Chatt, *J. Chem. Soc.*, 1965, 3238.
16 G. R. Van Hecke and W. DeW. Horrocks, *Inorg. Chem.*, 1966, **11**, 1968.
17 M. J. Crook, W. Levason, and C. A. McAuliffe, *Inorg. Chem.*, 1978, **17**, 766.
18 C. E. Wymore and J. C. Bailar, *J. Inorg. Nucl. Chem.*, 1960, **4**, 42.
19 D. J. Gulliver, W. Levason, and K. G. Smith, *J. Chem. Soc., Dalton Trans.*, 1981, 2153.
20 D. J. Gulliver and W. Levason, *J. Chem. Soc., Dalton Trans.*, 1982, 1895; L. R. Gray, D. J. Gulliver, W. Levason, and M. Webster, *ibid.*, 1983, 133.
21 W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, 1974, **11**, 33.
22 D. J. Gulliver, W. Levason, K. G. Smith, M. J. Selwood, and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, 1980, 1872.
23 J. S. Wood, *Prog. Inorg. Chem.*, 1972, **16**, 227.
24 K. Konya and K. Nakamoto, *Spectrochim. Acta, Part A*, 1973, **29**, 1965.
25 J. K. Stalick, P. W. R. Corfield, and D. W. Meek, *Inorg. Chem.*, 1973, **12**, 1668.
26 M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 1970, 206.
27 W. L. Steffan and G. J. Palenik, *Inorg. Chem.*, 1976, **15**, 2432.
28 D. W. Meek and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1915.
29 R. S. Nyholm, *J. Chem. Soc.*, 1952, 2906.
30 J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378.
31 R. S. Nyholm, *J. Chem. Soc.*, 1951, 2602.
32 R. J. Dickinson, W. Levason, C. A. McAuliffe, and R. V. Parish, *J. Chem. Soc., Dalton Trans.*, 1978, 177.
33 R. G. Cunninghame, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1972, 229.
34 G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 1961, 4433.
35 J. C. Cloyd and D. W. Meek, *Inorg. Chim. Acta*, 1972, **6**, 607.
36 G. S. Benner and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1398.
37 G. A. Barclay and A. K. Barnard, *J. Chem. Soc.*, 1961, 4269.
38 R. B. King, R. N. Kapoor, and P. N. Kapoor, *Inorg. Chem.*, 1971, **10**, 1851.
39 M. Bacci, S. Midollini, P. Stoppioni, and L. Sacconi, *Inorg. Chem.*, 1973, **12**, 1801.
40 W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, 1975, **14**, 127.
41 C. Ercolani, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chim. Acta*, 1974, **10**, 195.
42 C. A. McAuliffe and D. W. Meek, *Inorg. Chem.*, 1969, **8**, 904.
43 L. Sacconi and J. Gelsomini, *Inorg. Chem.*, 1968, **7**, 291.
44 K. K. Chow, W. Levason, and C. A. McAuliffe, *Inorg. Chim. Acta*, 1973, **7**, 589.
45 K. K. Chow and C. A. McAuliffe, *Inorg. Chim. Acta*, 1975, **14**, 5.
46 T. D. Dubois and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1395.
47 M. O. Workman, G. Dyer, and D. W. Meek, *Inorg. Chem.*, 1967, **4**, 1543.
48 C. M. Harris, R. S. Nyholm, and D. J. Philips, *J. Chem. Soc.*, 1960, 4379.
49 W. Levason and K. G. Smith, *Inorg. Chim. Acta*, 1980, **41**, 133.
50 G. M. Sheldrick, SHELX program for crystal structure determination, University of Cambridge, 1976.
51 N. Walker and D. Stuart, DIFABS empirical absorption correction program, University of London, 1982; *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
52 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1976, vol. 4, pp. 99—101.
53 W. D. S. Motherwell and W. Clegg, PLUTO program for plotting molecular and crystal structures, Universities of Cambridge and Göttingen, 1978.
54 P. Roberts and G. M. Sheldrick, XANADU program for crystallographic calculations, University of Cambridge, 1979.

Received 10*th June* 1983; *Paper* 3/974