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Coordination Chemistry of Higher Oxidation States.
Part 9 [1]. Nickel(III) Complexes of Monodentate Phosphines and Related Ligands

SIMON J. HIGGINS, WILLIAM LEVASON* and DEBORAH J. WILKES

Department of Chemistry, The University, Southampton SO9 5NH, U.K.

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The known nickel(III) complexes [Ni(PR$_3$)$_2$X$_3$] (X = Cl, Br) with monodentate phosphines (PMe$_3$, PEt$_3$, P^{n}Bu$_3$, PMe$_2$Ph X = Br only) have been re-examined, some being obtained in a pure state for the first time. New complexes with PMe$_2$Ph, PEt$_2$Ph and PMePh$_2$ are described. Detailed spectroscopic data (IR, UV/Visible and EPR) are reported and assigned for all complexes, leading to the proposal of trans-*trigonal bipyramidal structures (D$_{3h}$). Evidence for the formation in solution of nickel(III) complexes of P(OMe)$_3$, AsEt$_3$, PCy$_3$ (Cy = cyclohexyl), PPh$_3$ is also given. Factors influencing the stability of these complexes are discussed.*

Introduction

The first nickel(III) phosphine complex prepared was [Ni(PEt$_3$)$_2$Br$_3$] reported by Jensen in 1936 [2]. The corresponding chloride was subsequently obtained, and on the basis of dipole moment measurements in pentane, they were formulated as *trans* trigonal bipyramidal molecules (D$_{3h}$) [3]. Analogues with P^{n}Pr$_3$, P^{n}Bu$_3$ and PMe$_3$ have been described, but not all have been obtained in a pure state [3], and spectroscopic data is fragmentary. The complex [Ni(PMe$_2$Ph)$_2$Br$_3$] has been shown by a single crystal X-ray study [4, 5] (on a material of composition 2Ni(PMe$_2$Ph)$_2$Br$_3$·Ni(PMe$_2$Ph)$_2$Br$_2$·2C$_6$H$_6$) to be a distorted trigonal bipyramid. We have recently investigated [1] some Ni(III) complexes of bidentate phosphines and arsines (L–L) of type [Ni(L–L)X$_3$] (X = Cl, Br) and on the basis of spectroscopic data and an X-ray study of [Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Br$_3$] have shown these to be distorted square pyramids (C$_s$). Here we report a reinvestigation of the monodentate phosphine analogues, the preparation of new Ni(III) complexes, and the oxidation of Ni(II) complexes with other monodentate ligands.

Experimental

Physical measurements were made as described previously [1, 6, 7]. The nickel(III) complexes were made in dried solvents under a dinitrogen atmosphere, and manipulated in an efficient dry box (⩽10 ppm H$_2$O). Most are stable for 3–4 days if stored at −20 °C in dry conditions, but all deteriorate rapidly in moist air. Nickel(II) complexes were prepared by literature methods; [Ni(L)$_2$X$_2$] (X = Cl, Br, L = PMe$_3$ [8], PEt$_3$ [9], P^{n}Bu$_3$ [10], PMe$_2$Ph [11], PEt$_2$Ph [12], PMePh$_2$ [13], PPh$_3$ [14], PCy$_3$ [14], P(OMe)$_3$ [15], P(OEt)$_3$ [15], PMe$_2$(o-C$_6$H$_4$OMe) [16] and PPh$_3$O [17].

Dibromobis(triethylarsine)nickel(II) [Ni(AsEt$_3$)$_2$Br$_2$]

A suspension of powdered anhydrous NiBr$_2$ (0.6 g, 2.7 mmol) in dry CH$_2$Cl$_2$ (25 cm^3) was treated with AsEt$_3$ (0.8 g, 5 mmol) under nitrogen. After stirring for 48 hours, the dark green solution was filtered (Schlenk stick) and the solvent slowly removed *in vacuo* yielding dark green-brown crystals. These were filtered off and dried *in vacuo*. 1.09 g, 80%. Fd C = 26.9, H = 5.3. C$_{12}$H$_{30}$As$_2$Br$_2$Ni req C = 26.5, H = 5.5%. ν(Ni–Br) = 324 cm^{-1}. E$_{max}$ (dr) 13.7(sh), 16.1(sh), 17.0, 18.4(sh), 24.5 × 10^3 cm^{-1}. The corresponding chloride was made similarly as a purple-red power. Found C = 30.5, H = 6.7%. C$_{12}$H$_{30}$As$_2$Cl$_2$Ni req C = 31.7, H = 6.6%. ν(NiCl) = 400 cm^{-1}. E$_{max}$ (dr) = 16.2sh, 17.2, 18.6(sh), 25.1 × 10^3 cm^{-1}.

Dibromobis(dimethylamine)nickel(II) [Ni(NMe$_2$H)$_2$-Br$_2$]

The ligand (2 cm^3) was distilled *in vacuo* on to anhydrous NiBr$_2$ (3.3 g, 15 mmol). After shaking at

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*Author to whom all correspondence should be addressed.

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TABLE I. Analytical and Physical Data.

Complex	Colour[a]	C%[b]	H%	μ_{eff}[d]	IR (cm^{-1})[c]
$[Ni(PMe_3)_2Cl_3]$	purple-red	23.2(22.7)	5.6(5.7)	1.84	328
$[Ni(PMe_3)_2Br_3]$	purple-black	15.5(16.0)	3.6(4.0)	2.20	262
$[Ni(PEt_3)_2Cl_3]$	turquoise	36.4(35.9)	7.6(7.5)	1.95	294
$[Ni(PEt_3)_2Br_3]$	dark green	26.5(26.9)	5.6(5.6)	1.72[e]	226
$[Ni(P^nBu_3)_2Cl_3]$	dark blue	44.3(44.5)	8.3(8.7)	2.16	317
$[Ni(P^nBu_3)_2Br_3]$	dark green	41.5(41.0)	8.0(7.7)	1.88	228
$[Ni(PPhMe_2)_2Cl_3]$	blue-purple	44.1(43.9)	5.0(5.1)	2.15	308
$[Ni(PPhMe_2)_2Br_3]$	red-black	33.6(33.4)	4.0(3.8)	2.17[e]	247
$[Ni(PPhEt_2)_2Cl_3]$	blue-green	48.9(48.3)	6.2(6.1)	1.70	310
$[Ni(PPhEt_2)_2Br_3]$	dark green	37.7(38.1)	4.5(4.8)	1.70	224
$[Ni(Ph_2PMe)_2Cl_3]$	blue-green	55.5(55.2)	4.7(4.6)	dec	317
$[Ni(Ph_2PMe)_2Br_3]$	dark green	44.6(44.7)	3.8(3.7)	1.87	245

[a] Ni(III) complexes are dichroic. [b] Found (calc). [c] ν_{Ni-X}. The ir spectra showed no evidence for $\nu_{P=O}$ when freshly prepared samples were used. [d] Measured on Ni(III) species generated by X_2 oxidation *in situ* in $CHCl_3$, by the Evans nmr method. Units BM. [e] Lit. values [3, 4] (Gouy measurements).

room temperature for 1 hour, the excess Me_2NH was removed *in vacuo* and the green powder stored under N_2. Fd C = 15.5, H = 4.4, N = 9.2%. $C_4H_8Br_2N_2Ni$ req C = 15.5, H = 4.5, N = 9.1%. E_{max} (dr) = 17.4(br), 23.7sh, 25.7 X 10^3 cm^{-1}.

Nitrosyl chloride was prepared by reaction of $POCl_3$ and $NaNO_2$ and purified by repeated distillation *in vacuo.*

Nickel(III) Complexes

All physical measurements were made on freshly prepared samples (within *ca.* 6 hours of preparation), which were stored at −20 °C until required.

Tribromobis(triethylphosphine)nickel(III) [Ni(PEt$_3$)$_2$Br$_3$]

A solution of $[Ni(PEt_3)_2Br_2]$ (0.4 g, 0.88 mmol) in CH_2Cl_2 (25 cm^3) was treated with bromine in CCl_4 (1.3 cm^3 of 2% v/v) with rapid stirring. The solvent was removed as rapidly as possible *in vacuo* and the dichroic green solid dried briefly *in vacuo.* $[Ni(P^nBu_3)_2Br_3]$, $[Ni(PPhMe_2)_2Br_3]$, $[Ni(PEt_2Ph)_2Br_3]$ and $[Ni(PMePh_2)_2Br_3]$ were prepared similarly. Yields *ca.* quantitative.

Tribromobis(trimethylphosphine)nickel(III) [Ni(PMe$_3$)$_2$Br$_3$]

A solution of $[Ni(PMe_3)_2Br_2]$ (0.31 g, 0.84 mmol) in CH_2Cl_2 (20 cm^3) was treated with bromine in CCl_4 (1.2 cm^3 of 2% v/v) with rapid stirring. The solution was filtered (Schlenk stick) and petroleum ether (40–60 °C) (25 cm^3) was added slowly. The resulting red-black precipitate was filtered off, rinsed with petroleum ether and dried *in vacuo,* 0.32 g (83%).

Trichlorobis(phenyldiethylphosphine)nickel(III) [Ni(PPhEt$_2$)$_2$Cl$_3$]

A solution of $[Ni(PPhEt_2)_2Cl_2]$ (0.2 g, 0.43 mmol) in CH_2Cl_2 (20 cm^3) was cooled to −78 °C, and excess NOCl condensed in, with vigorous stirring. The colour changed from red to dark blue. The solvent and excess NOCl were removed *in vacuo* the mixture being allowed to warm to room temperature. After brief drying *in vacuo* at ambient temperature, the product was stored at −20 °C under dinitrogen. The other Ni(III) chlorocomplexes were prepared similarly. Yields *ca.* quantitative.

Attempted preparation of [Ni(PPh$_3$)$_2$Cl$_3$]

Green $[Ni(PPh_3)_2Cl_2]$ was recrystallised from CH_2Cl_2 to produce the red planar isomer [14]. This was cooled to −78 °C, and pure NOCl condensed onto it, the colour changing to dark green. After a few minutes, the excess NOCl was pumped away. The product is a green solid which decomposes very rapidly at room temperature. Found C = 61.3, H = 4.4, N = 0.5%. Required for $C_{36}H_{30}Cl_3NiP_2$ C = 62.7, H = 4.4 (N = 0%).

Results and Discussion

[Ni(PR$_3$)$_2$X$_3$] (X = Cl, Br)

Addition of a small excess of bromine to dichloromethane solutions of $[Ni(PR_3)_2Br_2]$ (PR_3 = PMe_3, PEt_3, P^nBu_3, PMe_2Ph, PEt_2Ph, $PMePh_2$), followed by rapid removal of the solvent gave the blue/green-purple dichroic $[Ni(PR_3)_2Br_3]$ (Table I). Although chlorine oxidation of $[Ni(diphosphine)Cl_2]$ gave

TABLE II. Electronic Spectra.

Complex	E_{max} (diffuse reflectance)[a] 10^3 cm^{-1}	E_{max} (ϵ_{mol})[b] 10^3 cm^{-1} (dm^3 cm^{-1} mol^{-1})
$[Ni(PMe_3)_2Cl_3]$	16.6(sh), 18.1, 18.9(sh), 26.0	18.5(6105), 25.9(5940), 37.9(8030)
$[Ni(PMe_3)_2Br_3]$	13.6(sh), 16.8(br), 18.1, 24.2	18.1(6700), 21.7(3885), 25.5(4650), 35.2(13160)
$[Ni(PEt_3)_2Cl_3]$	13.6(sh), 14.6(sh), 16.6, 18.3, 24.5, 27.6(sh), 28.9	16.9(1590), 24.8(1455), 27.3(5315), 37.0(6950)
$[Ni(PEt_3)_2Br_3]$	16.0(br), 18.2, 23.8, 26.3	16.3(6610), 21.6(11520)sh, 22.7(12370), 33.6(40500)
$[Ni(PBu_3{}^n)_2Cl_3]$	16.2(sh), 16.9, 17.7(sh), 24.6, 33.1	16.9(–), 24.5(–), 27.2(–)
$[Ni(PBu_3{}^n)_2Br_3]$	13.1(sh), 14.3, 15.0, 24.2(sh), 26.0, 27.8	16.2(4690), 21.6(2625)(sh), 23.0(3020)(sh), 25.0(3100), 32.9(7150)
$[Ni(PPhMe_2)_2Cl_3]$	14.7(sh), 15.1(sh), 16.2, 17.5(sh), 23.5 33.1	17.4(3387), 24.9(3380), 27.3(8805)
$[Ni(PPhMe_2)_2Br_3]$	13.8(sh), 15.9(sh), 16.7, 18.2(sh), 20.6, 24.8	16.8(2670), 21.3(1140)(sh), 24.8(2100)(sh), 26.2(2225), 30.1(1311)
$[Ni(PPhEt_2)_2Cl_3]$	13.8(sh), 14.5, 15.5(sh), 16.6(sh), 24.2	16.6(–), 24.0(–)
$[Ni(PPhEt_2)_2Br_3]$	13.6(sh), 15.1, 16.6(sh), 17.4(sh), 20.9, 25.8, 35.7(sh)	16.1(6360), 20.8(3150), 26.0(6560), 30.1(6430)
$[Ni(Ph_2PMe)_2Cl_3]$	15.5(br), 16.8(sh), 20.9, 24.2	Decomposes too quickly
$[Ni(Ph_2PMe)_2Br_3]$	13.9(sh), 15.9, 17.0, 20.0, 30.1	16.4(7070), 20.5(3225), 24.5(7940), 29.8(6950)
‘$Ni(Et_3As)_2Br_3$’	–	14.7, 21.4, 23.8, 33.8

[a] Spectra 12–35000 cm^{-1}. [b] ϵ_{mol} values are approximate. Species generated *in situ* byX_2 oxidation of NiL_2X_2 in CH_2Cl_2. Solutions decompose at varying rates.

Ni(III) complexes [1], the reactions with $[Ni(PR_3)_2Cl_2]$ resulted in extensive decomposition. However if the Cl_2–CH_2Cl_2–$[Ni(PR_3)_2Cl_2]$ mixture is frozen to a glass in liquid nitrogen immediately upon combination, the presence of substantial amounts of $[Ni(PR_3)_2Cl_3]$ can be detected by comparison of the EPR spectra of the glasses with those of genuine samples (below). Jensen [2, 3] obtained $[Ni(PEt_3)_2Cl_3]$ by oxidation of the nickel(II) complex with neat NOCl. We examined various systems using NOCl alone or diluted with CCl_4, $CFCl_3$ or CH_2Cl_2, and found that pure samples of $[Ni(PR_3)_2Cl_3]$ (Table I) were best made using NOCl/CH_2Cl_2 at –78 °C. Isolation of analytically pure samples of either chlorides or bromides is critically dependent upon the rigorous exclusion of moisture, and upon isolation of the solids as rapidly as possible. Moisture results in the contamination of the products with nickel(II) phosphine oxide complexes (the $[Ni(PMe_3)_2Cl_3]$ is particularly prone to this), and once contaminated, purification of the nickel(III) complexes by recrystallisation is ineffective due to their poor stability in solution. The tetrahedral $[Ni(PPh_3)_2X_2]$ (X = Cl, Br) are decomposed by halogens and no evidence for Ni(III) complexes was obtained. However treatment of the red planar isomer $[Ni(PPh_3)_2Cl_2]$ [14] with Cl_2/CCl_4 and immediate quenching to –196 °C, gave a green glass with an EPR spectrum characteristic of nickel(III) (Table III). An attempt to isolate this complex using NOCl, gave a green solid with a rather poor analysis for ‘$Ni(PPh_3)_2Cl_3$’, and which contained some nitrosyl impurity, as shown both by the nitrogen analysis, and the presence of an ν(NO) vibration in the IR spectrum at 1855 cm^{-1}. The material decomposes in minutes at room temperature and has defied further characterisation.

The $[Ni(PR_3)_2X_3]$ are intensely coloured, dichroic, crystalline solids, which can be stored in sealed tubes at –20 °C for a few days, but which decompose in a few hours at room temperature, and in minutes in CH_2Cl_2 solution. An approximate stability order is $PMe_3 \sim PEt_3 > PMe_2Ph \sim P^nBu_3 > PEt_2Ph \geqslant PPh_2Me$. The bromides are more stable than the chlorides, and this is probably due to the weaker binding of the soft PR_3 to the harder $NiCl_3$ acceptor grouping. Unlike $[Ni(L–L)X_3]$ most of which decompose cleanly to $[Ni(L–L)X_2]$ on heating *in vacuo* [1], the $[Ni(PR_3)_2X_3]$ decompose on warming to a mixture of $[Ni(PR_3)_2X_2]$, phosphine oxide complexes, and phosphonium salts.

The X-ray study [4, 5] of $[Ni(PMe_2Ph)_2Br_3]$ showed a distorted trigonal bipyramid with axial

TABLE III. Electron Paramagnetic Resonance Data.

Complex	g-values, linewidths^{a}
$[Ni(PMe_3)_2Cl_3]$	Unresolvable under expt conditions^{b}
	$g = 1.75(2400)^{c}$
$[Ni(PMe_3)_2Br_3]$	$g = 2.55; g = 2.11(350)^{b}$
	$g = 1.86(1425)^{c}$
$[Ni(PEt_3)_2Cl_3]$	$g = 2.39; g = 2.17; g = 1.95^{b}$
	$g = 2.37; g = 1.90(75); g = 1.83^{c}$
$[Ni(PEt_3)_2Br_3]$	$g = 2.26(190)$ – isotropic^{b}
	$g = 2.51; g = 2.08(75); g = 1.97^{c}$
$[Ni(PBu_3{}^{n})_2Cl_3]$	$g = 2.62; g = 2.18(400); g = 1.94^{b}$
	$g = 2.49(br); g = 1.84(350)^{c}$
$[Ni(PBu_3{}^{n})_2Br_3]$	$g = 2.50, g = 2.13(270); g = 1.99^{b}$
	$g = 2.53; g = 2.07$(anisotropic)^{c}
$[Ni(PPhMe_2)_2Cl_3]$	$g = 2.68; g = 2.21(500); g = 1.93^{b}$
	$g = 2.30; g = 1.90(213)^{c}$
$[Ni(PPhMe_2)_2Br_3]$	EPR spectrum unobtainable under conditions available
$[Ni(PPhEt_2)_2Cl_3]$	$g = 2.47; g = 2.10(500); g = 1.94^{b}$
$[Ni(PPhEt_2)_2Br_3]$	$g = 2.18(240)$ – isotropic^{b}
	$g = 2.54; g = 2.08(190)^{c}$
$[Ni(Ph_2PMe)_2Cl_3]$	$g = 1.97(725)$ isotropic^{b}
$[Ni(Ph_2PMe)_2Br_3]$	$g = 2.17(286)$ – isotropic^{b}
$[Ni(o\text{-}C_6H_4(PMe_2)(OMe))_2Br_3]$	$g = 2.18(230)$ – isotropic^{b}
'$Ni(PPh_3)_2Cl_3$'	$g = 2.58; g = 2.14(660); g = 2.03^{b}$
'$Ni(AsEt_3)_2Cl_3$'	$g = 2.52; g = 2.12(500); g = 1.81^{b}$
'$Ni(AsEt_3)_2Br_3$'	$g = 2.19(245); g = 1.98^{b}$
'$Ni(PCy_3)_2Cl_3$'	$g = 2.06(800)^{d}$
'$Ni(P(OMe)_3)_2Cl_3$'	$g = 2.02(1000)^{d}$
'$Ni(P(OMe)_3)_2Br_3$'	$g = 1.98(1750)^{d}$
'$Ni(P(OEt)_3)_2Br_3$'	$g = 2.06(750); g = 1.81^{d}$

^{a}Linewidths (in G, derivative peak-to-peak) are in parentheses. ^{b}Generated by X_2 oxidation in CCl_4 solution frozen rapidly and run at −196 °C. ^{c}Powdered solid sample, −196 °C. $^{d}CH_2Cl_2$ glass −196 °C, generated *in situ* as (b).

phosphines, and from the generally similar IR and electronic spectra (Tables I, II), similar structures are proposed for all the complexes. For a D_{3h} molecule one ν(NiX) vibration (E) is expected in the IR spectrum, and these have been identified at 300–330 cm^{-1} (X = Cl), and 220–260 cm^{-1} (Br). The IR spectra also showed the absence of phosphine oxides, and '$Ni(PPh_3)_2Cl_3$' apart, of nitrosyl groups.

For a D_{3h} molecule, with the d^7 configuration, the ground state is $(d_{xz}, d_{yz})^4(d_{xy}, d_{x^2-y^2})^3(d_{z^2})^0$ $[(e'')^4(e')^3(a_1)^0]$. If the expected Jahn–Teller splitting of the e′ level* is taken into account (C_{2v}), $(e'')^4(e_a')^2(e_b')^1(a_1)^0$ results. Using the angular overlap model and a one electron scheme, as devised for trigonal bipyramidal cobalt(II) complexes [18], the electronic spectral transitions predicted are $(e'')^4(e_a')^2(e_b')^1 \rightarrow (e'')^4(e_a')^1(e_b')^2, (e'')^4(e_a')^2(a_1')^1, (e'')^3(e_a')^2(e_b')^2$. The spectra (Table II) consist of two main bands in the visible region *ca.* 16–18000 cm^{-1} and *ca.* 20–25000 cm^{-1}, which may be the transitions to the $(e'')^4(e_a')^2(a_1')^1$, and $(e'')^3(e_a')^2(e_b')^2$ states respectively. The lowest energy transition ($\rightarrow(e'')^4(e_a')^1(e_b')^2$) was not identified and it may lie in the near IR region. The broader bands >*ca.* 26000 cm^{-1} are probably L → Ni charge transfer. It is notable that the bands assigned to essentially d–d transitions have large extinction coefficients (ϵ_{mol} values in Table II are approximate due to the instability of some complexes in solution) as observed for other five-coordinate phosphine complexes.

It is unfortunate that the $[Ni(PMe_2Ph)_2Br_3]$ complex for which X-ray structural data is available is the only complex which fails to give an EPR

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*The X-ray of $Ni(PMe_2Ph)_2Br_3$ shows a very distorted $NiBr_3$ grouping in the equatorial plane, explained [5] as due to the Jahn–Teller effect, although inter-ligand repulsions may also contribute.

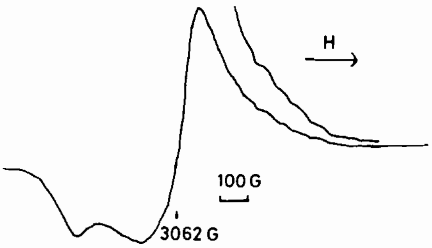

Fig. 1. EPR spectrum of [Ni(PhPEt$_2$)$_2$Cl$_3$] in CCl$_4$ glass at −196 °C.

spectrum (presumably due to fast relaxation). However [Ni(PMe$_2$Ph)$_2$Cl$_3$], which on the basis of X-ray powder data is isostructural with the bromide, gives an EPR spectrum, and the similarity of the other spectra (Table III) supports the assignment of similar structures to all complexes. For a regular TBP molecule, two g-values are expected ($g_{xx} = g_{yy} \neq g_{zz}$), but with distortion three g-values will result, and three g-values were generally found for the glasses. A typical EPR spectrum is shown in Fig. 1.

Other Complexes

Attempts to isolate nickel(III) complexes containing other neutral monodentates were made. Various amine complexes (*e.g.* [Ni(NH$_3$)$_6$]Br$_2$ or [Ni(NMe$_2$-H)$_2$Br$_2$]) were decomposed by bromine. The failure to obtain Ni(III) species* is surprising both in view of the ready preparation of Co(III) amines and of [Ni(H$_2$NCH$_2$CH$_2$NH$_2$)$_2$Cl$_2$]Cl [6, 20]. Phosphine oxide [17] complexes [Ni(OPR$_3$)$_2$X$_2$] (R = Ph, Pr^n) did not oxidise, and neither Me$_2$S nor Me$_2$Se form Ni(II) complexes [21], whilst the stibine complex [22] [Ni(SbMe$_3$)$_3$Br$_2$], is stable in solution only in the presence of a large excess of SbMe$_3$, which precludes halogen oxidation. The preparations of monoarsine complexes were more successful, the reaction of NiX$_2$ (X = Cl, Br) with Et$_3$As in CH$_2$Cl$_2$ under rigorously anhydrous conditions gave [Ni-(AsEt$_3$)$_2$X$_2$], although the chloride has not been obtained analytically pure. When treated with the appropriate halogen in CCl$_4$ at low temperature, these exhibit EPR spectra characteristic of Ni(III) but solid complexes have not been isolated. Similar results were obtained with nickel(II) phosphite complexes (Table III). High oxidation states are often more stable in anions than in neutral complexes, but attempts to product [Ni(PR$_3$)X$_4$]$^-$ or [Ni(PR$_3$)$_2$-X$_4$]$^-$ were unsuccessful. The [Ni(PPh$_3$)Br$_3$]$^-$ decomposed on treatment with Br$_2$/CCl$_4$ and with stronger σ donor trialkylphosphines, the required Ni(II) anions have not been obtained [23]. The [Ni(PR$_3$)$_2$X$_3$] do not react with [Bu$^n_4$N]X in CH$_2$Cl$_2$.

The results show that [Ni(PR$_3$)$_2$X$_3$] have a ‘stability’ which depends markedly upon the phosphine, PMe$_3$ ~ PEt$_3$ > PMe$_2$Ph ~ P^{n}Bu$_3$ > PEt$_2$Ph ⩾ PMePh$_2$ > PPh$_3$. This order approximately parallels the σ donor power, with the exception of PCy$_3$ which is a strong σ donor, but fails to give isolable Ni(III) complexes. The above series is also approximately in order of increasing size, the cone angles [24] varying from 118° (PMe$_3$) to 145° (PPh$_3$). The instability of the PCy$_3$ complexes (Ni(PCy$_3$)$_2$-Cl$_3$ has been detected in solution) is probably attributable to steric effects (cone angle ~170°). There are suggestions [14, 25] that even in [Ni-(PCy$_3$)$_2$X$_2$], the ligand field is smaller than expected, due to steric hindrance lengthening the Ni–P bond, and the weakening of the binding will be more important as the coordination number increases. The adoption of *trans* axial positions by the phosphines will minimise steric effects in [Ni(PR$_3$)$_2$X$_3$], although electronic factors may also be important in deciding the stereochemistry [25]. Since P(OR)$_3$ and AsR$_3$ have smaller cone angles than the corresponding phosphines, the instability of the Ni(III) complexes, must be attributed to their weaker binding to hard metal centres.

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