

The synthesis and properties of a new linear NPN proligand

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Following upon the synthesis of new proligands $\text{Me}_2\text{NCH}_2\text{XCH}_2\text{NMe}_2$ ($\text{X} = \text{O}$ or NMe), we have now prepared quarternised derivatives of the related phosphorus compounds, $\text{R}_2\text{NCH}_2\text{XCH}_2\text{NR}_2$ ($\text{R} = \text{Me}$ or Et , $\text{X} = \text{PPh}$). The ethyl compound can act as a phosphorus donor even when the nitrogen atoms are protonated, and we have characterised fully $[\text{NiBr}_4\{\text{PhP}(\text{CH}_2\text{NHEt}_2)_2\}_2][\text{NiBr}_4]$ as well as a polymeric adduct of NiBr_2 and thf, $[\{\text{Ni}_3\text{Br}_6(\text{thf})_5\}_n]$.

Introduction

We have recently described a related series of compounds $\text{Me}_2\text{NCH}_2\text{XCH}_2\text{NMe}_2$ ($\text{X} = \text{NMe}$, O or CH_2).¹ Of these compounds, those with $\text{X} = \text{NMe}$ or O are unknown in the free state and have not been characterised except by us and then only in complexes.¹ They apparently require a metal template to form easily. When we attempted to replace $\text{X} = \text{NMe}$ by $\text{X} = \text{NPr}$, we obtained a complex of an η^3 -triazacyclohexane. The reaction we employed was of a salt such as $(\text{Me}_2\text{N}=\text{CH}_2)\text{Br}$ with the amine PrNH_2 . Such proligands can also be obtained directly by reaction of primary amines with aldehydes.² It was of interest to discover whether a related phosphorus compound with labile hydrogen, such as PhPH_2 , would react with $(\text{Me}_2\text{N}=\text{CH}_2)\text{Br}$ to form a six-membered ring, $(\text{CH}_2\text{PPh})_3$, or an open-chain material, $\text{Me}_2\text{NCH}_2\text{PPhCH}_2\text{NMe}_2$.

Results and discussion

The reaction of $(\text{Me}_2\text{N}=\text{CH}_2)\text{Br}$ with one molar equivalent of PhPH_2 in refluxing thf afforded a fine white solid, which was subsequently recrystallised from methanol–dichloromethane as colourless crystals. The quality of the diffraction data collected in the single-crystal X-ray structure analysis was not high, but the presence of the $[\text{PhP}(\text{CH}_2\text{NHMe}_2)_2]\text{Br}_2$ was unequivocally established. This was first time $[\text{PhP}(\text{CH}_2\text{NHMe}_2)_2]\text{Br}_2$ had been observed, though related neutral compounds are such as $\text{PhP}(\text{CH}_2\text{NPh}_2)_2$, obtained from diphenylamine, phenylphosphine and paraformaldehyde in toluene, are known.³ In an attempt to improve the crystal quality of the product, $(\text{Et}_2\text{N}=\text{CH}_2)\text{Br}$ was used in the preparation instead of $(\text{Me}_2\text{N}=\text{CH}_2)\text{Br}$. The reaction between $(\text{Et}_2\text{N}=\text{CH}_2)\text{Br}$ and one molar equivalent of PhPH_2 in refluxing thf also produced a fine white suspension. Isolation of the white powder by filtration, and subsequent recrystallisation from a dichloromethane solution layered with hexane produced colourless crystals, analysed as $[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ (**I**), in 35% yield. The mother liquor, layered with hexane, yield colourless crystals of $[\text{PhP}(\text{O})(\text{CH}_2\text{NHEt}_2)_2][\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ (**II**). Both compounds are soluble in methanol and dichloromethane, and insoluble in thf, hexane, diethyl ether and toluene. The EI mass spectrum of **I** showed the expected parent ion and the FAB mass spectrum contained an ion with $m/z = 361$ corresponding to $(\text{C}_{16}\text{H}_{31}\text{PN}_2\text{Br})^+$ with its expected isotopic pattern. The ^1H NMR spectrum of **I** in d^2 -dichloromethane at room temperature (Table 1) displayed the resonance of the NH protons as a singlet at 10.8 ppm. The ^{31}P NMR spectrum showed a single resonance at -41.5 ppm.

Unfortunately, the X-ray structure determination of **I** showed that all the atoms except the N and Br are disordered about a two-fold axis. The $\text{N}-\text{H}\cdots\text{Br}$ moieties are exactly related by symmetry. Although the molecular structure is

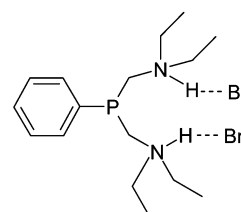
Table 1 ^1H NMR data for $[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ (**I**) in d^2 -dichloromethane (in ppm, δ -scale, room temperature)

	Proton	Chemical shift
	CH_3	1.5 (s, 6H) 1.4 (s, 6H)
	NCH_2	3.4 (s, 4H) 3.5 (s, 4H)
	PCH_2N	3.6 (s, 4H)
	Ph	7.6 (m, 3H) 7.9 (m, 2H)
	NH	10.8 (s, 2H)

Table 2 Selected bond lengths (\AA) and angles ($^\circ$) for $[\text{PhP}(\text{O})(\text{CH}_2\text{NHEt}_2)_2][\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ (**II**), occupancy 0.69/0.31 (e.s.d.s are in parentheses)

P–O	1.426(7)	P–C(7)	1.853(7)
P–C(1)	1.800(7)	N(1)–C(7)	1.504(9)
P–C(12)	1.825(7)	N(2)–C(13)	1.496(10)
O–P–C(1)	115.8(4)	C(12)–N(2)–C(13)	112.5(6)
O–P–C(12)	116.6(4)	C(12)–P–C(7)	103.7(3)
C(1)–P–C(12)	101.3(3)	N(1)–C(7)–P	115.1(5)
O–P–C(7)	116.1(4)	N(2)–C(12)–P	115.7(5)
C(7)–N(1)–C(10)	110.2(6)		

evident, bond lengths and angles are unreliable, even with a final $R1$ for all $I > \sigma(I)$ of 0.078, and cannot be discussed further. However, the basic structure was unequivocally established.



The presence of the oxygen in compound **II** was probably due to inadvertent contamination by moisture/air. The X-ray diffraction analysis (Fig. 1 and Table 2) revealed a $\text{P}=\text{O}$ oxygen occupancy of 0.69. The shortest intermolecular contact between the cation and anion is 3.30(8) \AA , and involves one of the nitrogen atoms of the cation and one of the bromides. The other bromide does not appear to be involved in any intermolecular bonding. **II** has an average $\text{P}-\text{C}$ bond length close to that in the $(\text{PhPCHNMe}_2)_2$ and the $\text{P}-\text{C}-\text{N}$ angles and mean $\text{P}-\text{C}_{\text{Ph}}$ and $\text{C}-\text{N}$ bond distances are also similar to those in $[(\text{PhPCHNMe}_2)_2]$ (116° and 1.837 and 1.453 \AA , respectively).⁴

Since $[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ contains a potential P-donor, we investigated its reaction with a Lewis acid. The reaction of

Table 3 Selected bond lengths (Å) and angles (°) for $[\{\text{Ni}_3\text{Br}_6(\text{thf})_5\}_n]$ (**III**) (e.s.d.s are in parentheses)

Ni(1)–O(1)	2.108(10)	Ni(1)–Br(2)	2.597(2)
Ni(1)–O(2)	2.125(10)	Ni(2)–O(3)	2.009(17)
Ni(1)–Br(3)	2.527(2)	Ni(2)–Br(3)	2.482(2)
Ni(1)–Br(1)	2.529(2)	Ni(2)–Br(2)	2.509(2)
Ni(1)–Br(1) ^{''}	2.557(2)		
O(1)–Ni(1)–O(2)	178.4(4)	Ni(1)–Br(1)–Ni(1) ^{''}	93.04(7)
O(1)–Ni(1)–Br(3)	89.5(3)	Ni(2)–Br(2)–Ni(1)	92.35(8)
O(1)–Ni(1)–Br(1)	90.8(3)	Br(2)–Ni(2)–Br(2)	91.91(11)
Br(3)–Ni(1)–Br(1)	179.78(11)	O(3)–Ni(2)–Br(3)	98.8(3)
O(1)–Ni(1)–Br(1) ^{''}	91.0(3)	Br(3)–Ni(2)–Br(3)'	87.95(11)
Br(3)–Ni(1)–Br(1) ^{''}	93.02(8)	Br(3)–Ni(2)–Br(2)'	164.00(14)
O(1)–Ni(1)–Br(2)	89.4(3)	Br(3)–Ni(2)–Br(2)	87.88(5)
Br(3)–Ni(1)–Br(2)	85.05(7)		

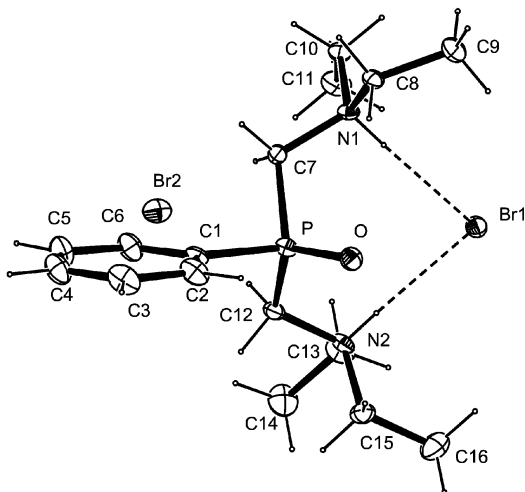


Fig. 1 Molecular structure of $[\text{PhP}(\text{O})(\text{CH}_2\text{NHEt}_2)_2]/[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ (**II**), with the atom numbering scheme.

NiBr_2 for 5 h with four molar equivalents of $[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ in a very dilute solution in refluxing thf produced a purple suspension. A white solid, unreacted $[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$, was filtered from the reaction mixture. The filtrate afforded red crystals with the formulation $[\{\text{Ni}_3\text{Br}_6(\text{thf})_5\}_n]$ (**III**). This was surprising but obviously NiBr_2 had reacted with thf, possibly because the reaction was carried out at high temperature in very dilute solution. We have been unable to determine whether $[\{\text{Ni}_3\text{Br}_6(\text{thf})_5\}_n]$ is accessible by the reaction of NiBr_2 with hot thf. Preliminary experiments failed to yield crystalline material.

$[\{\text{Ni}_3\text{Br}_6(\text{thf})_5\}_n]$ (Fig. 2 and Table 3) contains nickel atoms in two quite different coordination environments. The structure consists of infinite chains along the 'b' crystal axis with mirror planes through the Ni(2) atoms. Ni(2) is five-coordinate and shows a distorted trigonal-bipyramidal geometry formed by four of the bridging bromides in the equatorial plane and one axial thf. Ni(1) has octahedral geometry arising from four

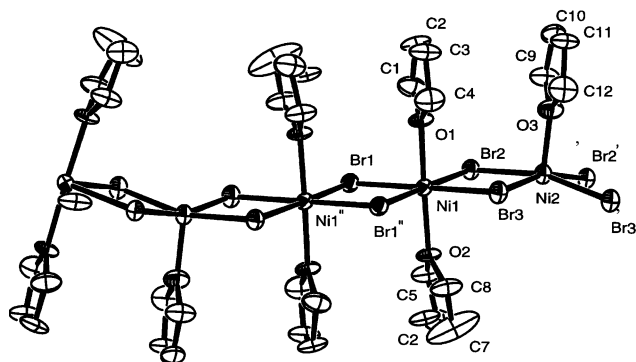


Fig. 2 Molecular structure of $[\{\text{Ni}_3\text{Br}_6(\text{thf})_5\}_n]$ (**III**) showing the atom numbering scheme.

Table 4 Selected interatomic distances (Å) and bond angles (°) for $[\text{NiBr}_4\{\text{PhP}(\text{CH}_2\text{NHEt}_2)_2\}_2][\text{NiBr}_4]$ (**IV**) (e.s.d.s are in parentheses)

Ni(1)–P(1)	2.503(3)	P(1)–C(12)	1.861(12)
Ni(1)–Br(1)	2.5440(19)	N(4)–C(28)	1.498(15)
Ni(1)–Br(2)	2.6068(19)	P(2)–C(17)	1.855(11)
Ni(2)–Br(7)	2.3945(19)	N(1)–C(7)	1.520(14)
Ni(2)–Br(6)	2.406(2)	N(2)–C(12)	1.491(14)
P(1)–C(1)	1.832(12)	N(3)–C(23)	1.498(14)
P(1)–C(7)	1.857(10)		
P(2)–Ni(1)–P(1)	174.15(12)	C(23)–P(2)–C(28)	93.3(5)
P(2)–Ni(1)–Br(1)	87.82(9)	C(1)–P(1)–C(7)	102.6(5)
P(1)–Ni(1)–Br(1)	86.52(8)	C(17)–P(2)–C(28)	105.1(5)
P(2)–Ni(1)–Br(4)	95.01(9)	C(1)–P(1)–Ni(1)	123.3(4)
Br(1)–Ni(1)–Br(3)	97.87(6)	C(17)–P(2)–Ni(1)	121.2(4)
Br(6)–Ni(2)–Br(6)	106.86(8)	N(2)–C(12)–P(1)	115.0(7)
C(7)–P(1)–Ni(1)	114.9(4)	N(1)–C(7)–P(1)	114.6(7)
C(7)–P(1)–C(12)	92.5(5)	N(4)–C(28)–P(2)	116.4(8)
C(23)–P(2)–Ni(1)	115.5(4)		

bridging bromides and two axial oxygens of thf. The Ni–Ni separations are 3.685(2) and 3.690(2) Å, implying no metal–metal bonding.

We could find no report of the structure of a simple adduct of a nickel(II) halide and thf. In this context, it is noteworthy that there are no data on cobalt(II) halide adducts, and the simple adduct of FeCl_2 and thf is tetranuclear. The only other structural report of a nickel halide with thf is of $[\text{Ni}_2(\mu\text{-Cl})_3(\text{thf})_6][\text{SnCl}_4(\text{thf})_5]$,⁵ obtained by reaction of NiCl_2 with SnCl_4 in hot thf. The cation, composed of two octahedral nickel(II) ions bonded through three bridging Cl atoms, has an Ni...Ni distance of 2.993(3) Å.

Because the preparation of **III** involved reflux temperatures and very dilute solutions, we repeated the experiment, but using higher concentrations and lower temperatures. The reaction of NiBr_2 with one molar equivalent of $[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ at room temperature afforded a moderate yield of a green paramagnetic solid $[\text{NiBr}_4\{\text{PhP}(\text{CH}_2\text{NHEt}_2)_2\}_2][\text{NiBr}_4]$ (**IV**). This was characterised by elemental analysis, IR and mass (FAB), ¹H, ¹³C and ³¹P NMR spectroscopies and X-ray crystallographic analysis. Complex **IV**, recrystallised from $\text{CH}_3\text{CN}-\text{Et}_2\text{O}$, is soluble in acetonitrile, poorly soluble in dichloromethane, and insoluble in thf, hexane, diethyl ether and toluene.

The magnetic moment of **IV** in d^3 -acetonitrile solution is 2.4 μ_B per nickel ion, not unexpected for a compound containing a tetrahedral nickel and a distorted octahedral nickel (Fig. 3 and Table 4). The quaternised nitrogen atoms are hydrogen-bonded to Br. The shortest intermolecular distance (3.195 Å) involves Br(2) of the NiBr_4 and the N(2) atom of the $\text{PhP}(\text{CH}_2\text{NHEt}_2)_2$.

The average Ni–P bond length is 2.502(3) Å, but Ni–P bonds vary considerably in length. For instance, the average Ni–P

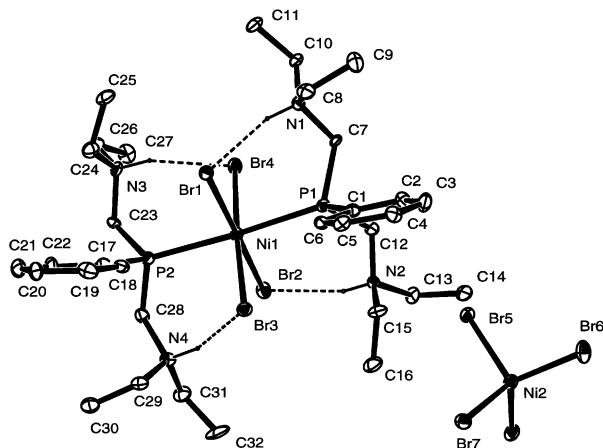


Fig. 3 Molecular structure of $[\text{NiBr}_4\{\text{PhP}(\text{CH}_2\text{NHEt}_2)_2\}_2][\text{NiBr}_4]$ (**IV**) showing the atom numbering scheme.

distance in square-planar $[\text{Ni}(\text{CH}_2\text{SiMe}_3)_2(\text{PMe}_3)_2]^6$ is 2.158(4) Å and in the square pyramidal $[\text{Ni}(\text{CN})_2\{\text{P}(\text{CH}_2\text{OH})\text{Ph}_2\}_3]^7$ they are 2.229(4), 2.246(4) and 2.400(3) Å.

The ^1H NMR resonances of **IV** were slightly broadened, due to the paramagnetism of the sample, but did not shift to higher frequencies as compared with $[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$. The ^1H NMR spectrum (Fig. 4) shows that the CH_2NHCH_2 units in the complex are magnetically non-equivalent, as each distinct proton nucleus produces two resonances. The assignments were confirmed by saturation-transfer and selective-decoupling experiments. The non-equivalence is due to the rigidity of the $\text{NH}\cdots\text{Br}$ bonds, which keep the methylenes in constrained positions. Saturation-transfer experiments at 45 °C showed exchange between two CH_3 groups but no exchange between the two PCH_2N methylene groups. The ^1H NMR spectrum showed no significant changes in the temperature range -30 to $+100$ °C.

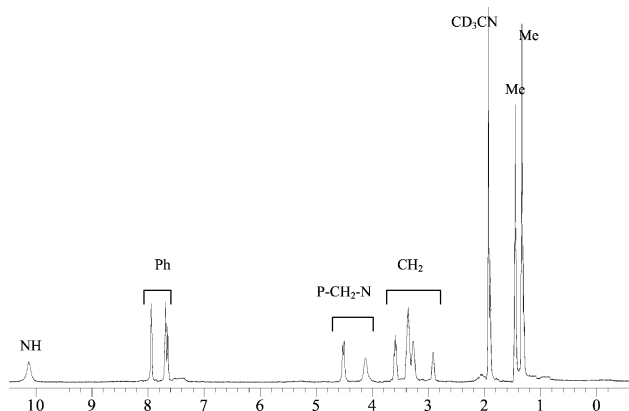


Fig. 4 The ^1H NMR spectrum of $[\text{NiBr}_4\{\text{PhP}(\text{CH}_2\text{NHEt}_2)_2\}_2][\text{NiBr}_4]$ (**IV**), in d^3 -acetonitrile at room temperature.

The ^{31}P NMR spectrum of **IV** in d^3 -acetonitrile showed no detectable resonances at room temperature, probably because of relaxation caused by proximity to the paramagnetic Ni centres. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, with assignments confirmed by ^{13}C and ^{13}C -DEPT NMR experiments, showed no signals for C(1) and C(17) of the Ph rings presumably because they too are close to the paramagnetic Ni centres.

Conclusions

This work was originally carried out to clarify some aspects of the chemistry of triamine complexes. Although the reactions described did not yield the desired triamine Ni^{II} species, we have now isolated an NPN analogue from a reaction that might have been expected to generate a triphosphacyclohexane ring. Although $[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ is a phosphorus donor to nickel(II), the nitrogen might also be a donor were the quaternising protons to be removed. This mixed-donor proligand, which may bind either by phosphorus or by nitrogen, will probably not allow all three donors to coordinate to the same metal ion owing to the single methylene spacers between the donor centres. This offers potential to use ligands such as this to explore metal ion hard/soft character, and to generate dimetal species.

This work extends the known $\text{NCH}_2(\text{NR})\text{CH}_2\text{N}$ and $\text{NCH}_2\text{OCH}_2\text{N}$ compounds to a novel variant of the $\text{NCH}_2(\text{PR})\text{CH}_2\text{N}$ series. Although such compounds are potentially obtainable by other routes, the chemistry displayed here demonstrates just how much we have yet to learn about these systems.

Experimental

All operations were carried out under an inert atmosphere in an argon-filled box or with use of standard Schlenk techniques.

Solvents were dried by standard procedures⁸ and distilled under N_2 prior to use. The commercial products NiBr_2 (99.99%, $\text{H}_2\text{O} < 100$ ppm), CH_3COBr (99%), PhPH_2 (98%), CH_2Br_2 (99%), formaldehyde (37 wt% solution in water) were used as received except that the solids were dried in vacuum. N,N,N',N' -tetraethyl- and tetramethyl-methanediamine were refluxed over sodium and distilled under dinitrogen prior to use. $(\text{Me}_2\text{N}=\text{CH}_2)\text{Br}^9$ and $(\text{Et}_2\text{N}=\text{CH}_2)\text{Br}^{10}$ were prepared by literature methods in 60% and 95% yields, respectively.

Microanalyses were carried out at the University of Surrey using a Leenan CE 440 CHN elemental analyzer or by MEDAC, Brunel Science Centre, Surrey. IR spectra were recorded on a Perkin-Elmer Spectrum One model FT-IR spectrometer, from Nujol mulls prepared under argon. NMR spectra were obtained in the appropriate deuterated solvents using a Brüker 300 or 500 MHz instrument. (^{13}C , ^1H)-HETCOR NMR and variable temperature ^1H NMR experiments were carried out by Dr Tony Avent, University of Sussex. Mass spectra were recorded by Dr Ali Abdul-Sada, at the University of Sussex, using a Kratos M580RF instrument for FAB spectra (and 3-nitrobenzyl alcohol as a matrix material) and a Fisons VG Autospec for EI spectra.

X-Ray crystal structure data were collected by the $2\theta-\omega$ scan method at 173(2) K using an Enraf-Nonius Kappa CCD diffractometer and Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). During processing, the data were corrected for absorption by semi-empirical methods. The structures were solved by direct methods in SHELXS and refined by full-matrix least-square methods in SHELXL.¹¹ All non-hydrogen atoms were refined anisotropically. Diagrams of the molecular structures of the complexes were drawn with the ORTEP package.¹² Details of the crystal structure determinations are shown in Table 5.

CCDC reference numbers 201299–201301.

See <http://www.rsc.org/suppdata/dt/b3/b300596h/> for crystallographic data in CIF or other electronic format.

$[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ (**I**) and $[\text{PhP}(\text{O})(\text{CH}_2\text{NHEt}_2)_2]/[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ (**II**)

PhPH_2 (0.50 cm³, 4.6 mmol) was added to a white suspension of $(\text{Et}_2\text{N}=\text{CH}_2)\text{Br}$ (0.82 g, 4.9 mmol) in thf (25 cm³). The reaction mixture was heated for ca. 5 h under reflux, and then left stirring overnight. The mixture was then filtered, giving a white powder (compound **I**, 0.70 g, 35% yield) and a colourless filtrate. The solid was recrystallised from a dichloromethane solution layered with hexane to yield colourless crystals of $[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ (**I**). Found: C, 42.9; H, 7.2; N, 6.3. $\text{C}_{16}\text{H}_{31}\text{Br}_2\text{N}_2\text{P}$ requires: C, 43.4; H, 7.0; N, 6.3%.

The filtrate was layered with hexane to yield colourless crystals of $[\text{PhP}(\text{O})(\text{CH}_2\text{NHEt}_2)_2]/[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ (**II**).

IR for **I** (cm^{-1}): 697(s), 726(s), 749(w), 768(w), 810(s), 861(w), 873(w), 916(w), 930(w), 968(w), 1030(s), 1071(w), 1097(w), 1166(w), 1261(s), 1299(w), 2485(s), 2620(s).

Reaction of NiBr_2 with $[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$

(1) Anhydrous NiBr_2 (0.020 g, 0.10 mmol) and $[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ (0.16 g, 0.36 mmol) were suspended in thf (30 cm³) and heated under reflux for 5 h. During this period, a slow change to light green and then to purple was observed. The mixture was cooled slowly to room temperature and left stirring overnight. A white solid (0.11 g) was then filtered off. The filtrate was layered with hexane to yield light red crystals, analysed as $[\{\text{Ni}_3\text{Br}_6(\text{thf})_5\}_n]$ (**III**). Found: C, 22.5; H, 4.0; N, 0.3. $\text{C}_{20}\text{H}_{40}\text{Br}_6\text{Ni}_3\text{O}_5$ requires: C, 23.6; H, 4.0; N, 0.0%.

(2) Tetrahydrofuran (40 cm³) was added to the mixture of NiBr_2 (0.52 g, 2.3 mmol) and $[\text{PhP}(\text{CH}_2\text{NHEt}_2)_2]\text{Br}_2$ (1.08 g, 2.4 mmol). The reaction mixture was left stirring for 72 h at room temperature in the glove-box. A large amount of a pale green powder (compound **IV**) was filtered off from a dark green solution. The solid was recrystallised from a CH_3CN solution

Table 5 Details of crystal structure determinations

	[PhP(O)(CH ₂ NHEt ₂) ₂]/[PhP(CH ₂ NHEt ₂) ₂]-Br ₂ (II) 0.69/0.31	[{Ni ₃ Br ₆ (thf) ₅ }] _n (III)	[NiBr ₄ {PhP(CH ₂ NHEt ₂) ₂ }] ₂ -[NiBr ₄] (IV)
Empirical formula	C ₁₆ H ₃₁ Br ₂ N ₂ OP	C ₂₀ H ₄₀ Br ₆ Ni ₃ O ₅	C ₃₂ H ₆₂ Br ₈ N ₄ Ni ₂ P ₂
Formula weight	458.22	1016.11	1321.50
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>Cc</i> (no. 9)	<i>P2₁/m</i> (no. 11)	<i>P</i> $\bar{1}$ (no.2)
Unit cell dimensions			
<i>a</i> /Å	17.9448(16)	7.5876(11)	12.1242(14)
<i>b</i> /Å	12.8400(11)	21.728(3)	13.7869(17)
<i>c</i> /Å	10.8881(9)	9.1261(12)	15.5447(17)
<i>a</i> ^o			69.712(6)
<i>β</i> ^o	125.675(4)	92.690(5)	82.206(6)
<i>γ</i> ^o			86.362(6)
<i>V</i> /Å ³	2037.9(3)	1502.9(3)	2414.3(5)
<i>Z</i>	4	2	2
<i>D_c</i> /Mg m ⁻³	1.49	2.245	1.82
<i>μ</i> /mm ⁻¹	4.06	9.865	7.49
Crystal size/mm	0.2 × 0.2 × 0.1	0.20 × 0.10 × 0.01	0.3 × 0.3 × 0.2
<i>θ</i> Range for data collection ^o	3.74–24.97	3.75–21.93	3.72–25.10
Index ranges (<i>h,k,l</i>)	–21→19, –14→15, –12→12	–7→7, –22→22, –9→9	–14→13, –16→16, –17→18
Reflns. collected	5211	4980	16131
Independent reflns. (<i>R</i> _{int})	2991 (0.050)	1809 (0.081)	8425 (0.095)
Reflns., <i>I</i> > 2σ(<i>I</i>)	2638	1357	5473
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.043, <i>wR</i> 2 = 0.090	<i>R</i> 1 = 0.070, <i>wR</i> 2 = 0.177	<i>R</i> 1 = 0.083, <i>wR</i> 2 = 0.188
<i>R</i> indices (all data)	<i>R</i> 1 = 0.054, <i>wR</i> 2 = 0.095	<i>R</i> 1 = 0.093, <i>wR</i> 2 = 0.189	<i>R</i> 1 = 0.135, <i>wR</i> 2 = 0.219

layered with diethyl ether to yield green crystals of [NiBr₄{PhP(CH₂NHEt₂)₂}]₂[NiBr₄] (**IV**). Yield: 1.32 g, 43% based on Ni. Found: C, 30.1; H, 4.9; N, 4.0. C₃₂H₆₂Br₈N₄Ni₂P₂ requires: C, 29.1; H, 4.7; N, 4.2%. IR (cm⁻¹): 695(m), 744(m), 767(w), 802(s), 846(w), 864(m), 903(w), 968(w), 1024(m), 1061(m), 1098(m), 1193(w), 1261(s), 1288(w), 1416(w).

¹³C{¹H} NMR (d³-acetonitrile, room temperature): δ 130.7, 132.1 (Ph); 67.8 (PCH₂N); 48.2, 51.0 (NCH₂); 9.0, 10.1 (CH₃).

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