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SYNTHESIS AND CHARACTERIZATION OF GROUP 10 METAL COMPLEXES WITH A NEW TRIFUNCTIONAL ETHER PHOSPHINE. THE X-RAY CRYSTAL STRUCTURES OF BIS[BIS(2-ETHOXYETHYL)BENZYLPHOSPHINE] DICHLORONICKEL(II) AND BIS[BIS(2-ETHOXYETHYL)BENZYLPHOSPHINE]CHLOROPHENYLNICKEL(II)

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Abstract—The syntheses and characterizations of the new trifunctional ligand bis(2-ethoxyethyl)benzylphosphine (OPO; **1**) and some new group 10 metal complexes are described. Reactions of this potentially hemilabile ligand with the nickel, palladium and platinum chlorides have been studied, resulting in isolation of the series, $MCl_2(OPO)_2$, where M = Ni (**2**), Pd (**3**) or Pt (**4**). The X-ray crystal structure of **2** shows the metal to have a square planar *trans* arrangement with η^1-bonding of the ligand through the phosphorus centre. Compounds **3** and **4** are also *trans*. The attempted formation of an oxygen/phosphorus chelate with nickel using $NaBPh_4$ resulted in the new complex *trans*-$NiClPh(OPO)_2$ (**5**), which has been shown to be square planar, with *trans* chloro and phenyl groups, by X-ray crystallography. The dibromo analogue of **2** has also been prepared (**6**), from which bromide abstraction has been attempted.

In recent years there has been considerable interest in the use of so-called hemilabile ligands (i.e. ligands containing two or more possible chelating sites, of differing donor ability). Some studies have been performed using combinations such as phosphorus/nitrogen[1] and phosphorus/sulphur,[2] but the majority of recent work has been concerned with the application of phosphorus/oxygen ligands.[3, 4] These ligands commonly contain either simple acyclic chain ethers[5] or cyclic ethers in saturated or unsaturated ring systems;[6] examples of other types of oxygen donor can be found.[3]

These systems are of interest due to the differing reactivities of the two types of donor atom in the ligand, which lends them to applications in catalysis, since the more labile centre can readily dissociate from the metal, thus facilitating a vacant coordination site which can produce an active intermediate for catalysis.[7] Lindner and co-workers have succeeded in demonstrating catalysis with complexes of hemilabile ligands for a number of processes, such as hydroformylation, hydrogenation and methanol carbonylation.[3] Preparations and applications of these types of compounds have been extensively reviewed.[3]

Bis(2-ethoxyethyl)benzylphosphine (OPO) is a potentially tridentate chelating ligand, and its reactions with halides of the nickel triad have been studied. Its synthesis is straightforward by radical-catalysed coupling of benzylphosphine with ethyl vinyl ether.

RESULTS AND DISCUSSION

Bis(2-ethoxyethyl)benzylphosphine (OPO; **1**) was prepared by the well-established addition of alkene functions to P—H bonds. Thus, the incor-

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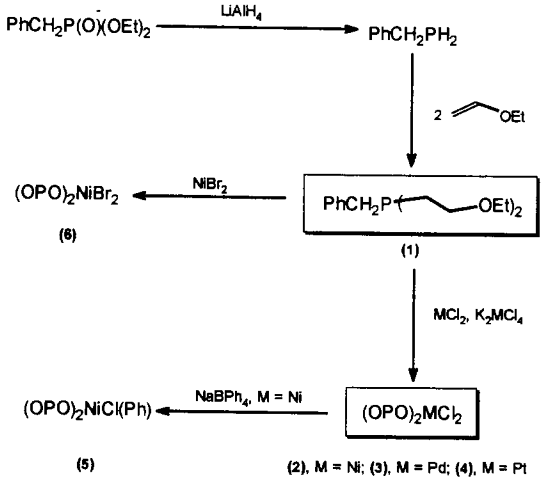
poration of two ether functions is readily effected in one step from a primary phosphine and an alkenyl ether (see Scheme 1); for the purposes of this study ethyl vinyl ether was chosen, since the resulting phosphine would potentially give rise to five-membered chelates. It can also be conveniently used as solvent for the coupling reaction. Benzylphosphine may be prepared by the straightforward hydride reduction of the corresponding benzyl phosphonate, $PhCH_2P(O)(OEt)_2$, itself very readily prepared in large quantities. The yield of primary phosphine from reduction of the phosphonate is significantly improved (80%) from that of a previous report[8] if the reduction is carried out in the presence of ultrasonic activation.



Scheme 1. Synthetic route to the new phosphine and group 10 metal complexes. Note: (OPO) = **1**.

The radical-catalysed coupling reaction was most conveniently carried out by UV photolysis. Addition of a radical initiator (2,2′-azobis(2-methylpropionitrile)) significantly improved the rate of reaction. If the photolysis was stopped before completion, the 'half-coupled' secondary phosphine $PhCH_2P(H)CH_2CH_2OEt$ could be isolated and was identified by its ^{31}P and $^{31}P\{^1H\}$ NMR. The reaction was then followed by ^{31}P NMR to ensure completion of the coupling reaction, although any isolated secondary phosphine (readily separated by distillation) was recycled in further reactions. The conditions could indeed be adjusted to favour the formation of secondary phosphine product, and this may have use in the selective preparation of unsymmetrical ligands.

The ^1H NMR of **1** is consistent with the formulation, and all resonances can be assigned on the basis of multiplicities, intensities and chemical shifts. The multiplets due to the PCH_2CH_2 and PCH_2CH_2 protons indicate that $^2J_{PH}$ is small and not observed, since the resonance assigned to the α-proton is an apparent quartet (or overlapping doublet of triplets as the α-protons are magnetically inequivalent), whereas the resonance due to the β-protons is more complex (nine lines), and $^3J_{PH} > {}^2J_{PH}$, as has previously been commented on for related systems.* On reaction of the metal chlorides with **1**, all three of the group 10 metals give empirically analogous products, as determined by elemental analysis. All products analyse as $MCl_2(OPO)_2$ and additional characterizations confirm this assignment. It should be noted that an identical product is prepared from a 1 : 1 or 1 : 2 stoichiometry of metal halide: OPO for **2**. This shows that the bis-ligand product is preferentially formed, even when insufficient ligand is used (i.e. in a 1 : 1 stoichiometric reaction). This indicates that chelation via the oxygen donor does not readily occur. Compounds **2**, **3** and **4** are diamagnetic in the solid state and in solution, implying a square planar geometry. This is confirmed for **2** by the single crystal X-ray structure (Fig. 1), which shows a slightly distorted square planar arrangement [Cl—Ni—P has an angle of 92.47(4)°] with bond lengths similar to those observed in other nickel–phosphine complexes.† Bond lengths and angles are listed in Table 1. Compound **2** is *trans*, as may be expected from steric considerations, and it is likely that **3** and **4** would be the same. Further evidence for this from NMR data is discussed later.

Table 2 lists the major peaks observed in the mass spectra for **2** and **3**, which fragment in a very similar manner, indicating that they are of a similar structure. Some weak peaks of greater mass than the molecular ion were observed and are presumably due to recombination ions; the molecular ion was not observed in either case.

In **4**, platinum (^{195}Pt, 33% abundant) couples with phosphorus ($^1J_{PtP} = 2435$ Hz), and this is in good agreement with values for other *trans*-platinum phosphine complexes found in the literature.‡ Variable temperature $^{31}P\{^1H\}$ NMR spectroscopy for **3** and **4** shows no significant variation in the spectra from -60 to $+60$°C. Spectra of **2** are temperature dependent and are detailed in Fig. 2,

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* In the aminophosphines $HN(CH_2CH_2PR_2)_2$ (R = Me, Pr^i) $^3J_{PH}$ is estimated to be 14 Hz, whereas $^2J_{PH} < 2$ Hz.[9]

† In *trans*-$NiCl_2(Ph_2PCH_2C(O)Ph)_2$, Ni—P = 2.246(1) Å and Ni—Cl = 2.162(1) Å,[10] as compared with bond lengths of 2.2431(11) and 2.1628(10) Å for Ni—P and Ni—Cl, respectively (this work).

‡ In *cis*-$[PtCl_2(Bu_3P)_2]$, $^1J_{PtP} = 3504$ Hz, whilst in the *trans* analogue, $^1J_{PtP} = 2386$ Hz.[11]

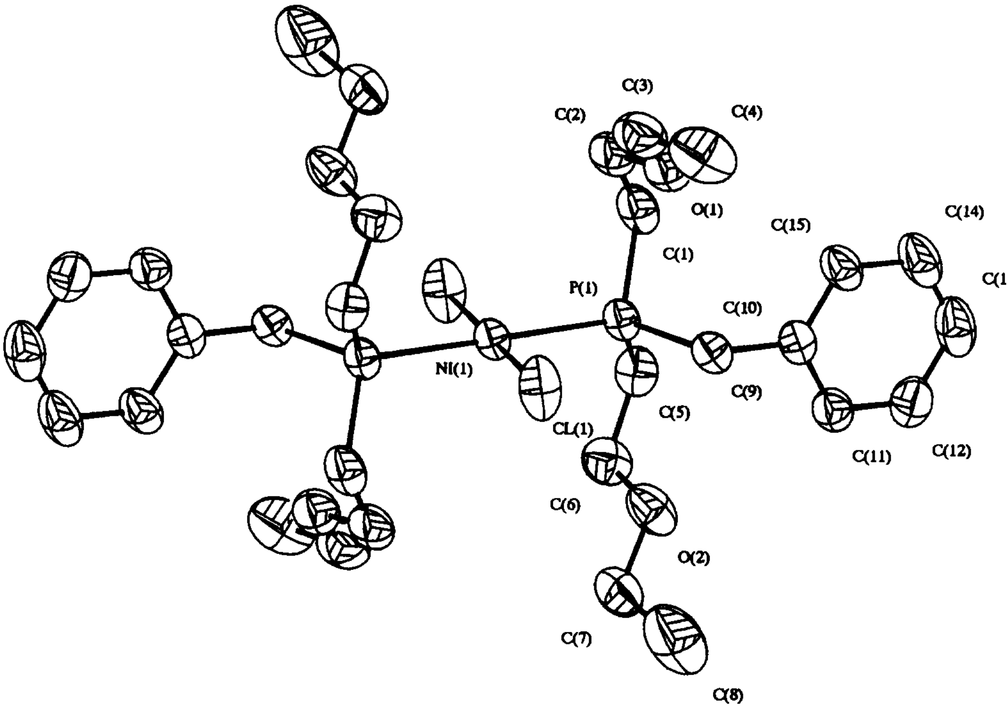

Fig. 1. The structure of centrosymmetric $NiCl_2(OPO)_2$ (**2**).

where, as the solution is warmed, a broadening of the signal can be observed. In order to establish whether the broadening was due to a conformational equilibrium (e.g. between square planar and tetrahedral), the magnetic susceptibility by ^1H NMR (Evans' method[12]) was measured as a function of temperature. The sample was diamagnetic (over the range −60 to +60°C), indicating that fluxionality is responsible for the broadening in the $^{31}P\{^1H\}$ NMR. One possible fluxional process is the formation of a five-coordinate nickel species in equilibrium with the square planar structure at higher temperatures. This five-coordinate species would chelate through an oxygen centre and may explain the absence of similar line-broadening in the palladium and platinum analogues, where metal–oxygen bond formation would likely be more unfavourable, and formation of five-coordinate species is less likely.

Attempts to abstract chloride from **2** have proved unsuccessful. Reactions of **2** with silver triflate ($AgCF_3SO_3$) and potassium perrhenate ($KReO_4$)

Table 1. Bond lengths (Å) and angles (°) for $NiCl_2(OPO)_2$ (**2**)

Ni—Cl	2.1628(10)	Ni—P	2.2431(11)
P—C(5)	1.832(3)	P—C(1)	1.828(3)
P—C(9)	1.838(3)	C(1)—C(2)	1.513(5)
C(2)—O(1)	1.405(4)	O(1)—C(3)	1.411(5)
C(3)—C(4)	1.484(6)	C(5)—C(6)	1.506(5)
C(6)—O(2)	1.403(4)	C(7)—O(2)	1.410(5)
C(7)—C(8)	1.479(6)	C(9)—C(10)	1.507(4)
Cl—Ni—P	92.47(4)	C(1)—P—Ni	109.89(11)
C(5)—P—Ni	112.43(11)	C(9)—P—Ni	118.37(11)
C(5)—P—C(1)	103.9(2)	C(1)—P—C(9)	105.63(14)
C(5)—P—C(9)	105.4(2)	C(2)—C(1)—P	111.9(3)
O(1)—C(2)—C(1)	109.3(3)	C(2)—O(1)—C(3)	114.1(3)
O(1)—C(3)—C(4)	109.3(4)	C(6)—C(5)—P	113.3(3)
O(2)—C(6)—C(5)	110.1(3)	C(6)—O(2)—C(7)	114.6(3)
O(2)—C(7)—C(8)	110.1(4)	C(10)—C(9)—P	116.6(2)

Table 2. Summary of mass spectral data for $NiCl_2(OPO)_2$ (**2**) and $PdCl_2(OPO)_2$ (**3**)

Proposed fragment	*m/z* for **2** (M = Ni)	*m/z* for **3** (M = Pd)
CH_2CH_2OEt	73	73
Bz	91	91
Bz–P	122	122
$Bz{-}P(CH_2CH_2)$	152	152
$Bz{-}P(CH_2CH_2OEt)$	195	195
OPO	269	269
OPO + 16(O?)	285 (base peak)	285
(OPO)Cl	—	303 (base peak)
M(OPO)	326	373
M(OPO) + Et	356	—
$M^{35}Cl(OPO)$	363	409
$M^{37}Cl(OPO)$	—	411
—	—	465
$M(OPO)_2{-}OEt$	550	—
$M^{35}Cl^{37}Cl(OPO)(OPO{-}OEt)$	624	—
—	—	661
$M^{35}Cl(OPO)_2$	629	677
$M^{37}Cl(OPO)_2$	631	679

have only resulted in isolation of starting materials, or yellow oils which readily decompose to intractable materials on work-up, and from which no discrete complex could be identified. Attempted chelate formation by abstraction of halide prior to addition of ligand **1** [e.g. reactions of $Ni(OH_2)_6^{2+}(CF_3SO_3)_2]$ has also proved unsuccessful, yielding similarly intractable products. Sodium tetraphenylboron ($NaBPh_4$) has also been used and results vary according to the order of addition. When $NaBPh_4$ was added to **2**, again no discrete product could be isolated. However, when $NaBPh_4$ was added initially to $NiCl_2 \cdot 6H_2O$, and **1** was then added to this resulting solution, the nickel–phenyl complex **5** could then be isolated. Microanalysis and NMR studies on this compound indicate that the product is $NiClPh(OPO)_2$. This has been confirmed by a single crystal X-ray structure (Fig. 3), which shows a *trans* square planar arrangement with a phenyl ring coordinated to the metal centre. The bond lengths are within the values expected, and the Ni—C bond of 1.916(1) Å on the phenyl ring is similar to that found in other literature examples.* It can also be observed that in **5** the Ni—P bond lengths are slightly shorter and the Ni—Cl bond is slightly longer (0.07 Å) than those found in **2**. Thus, phenyl has a higher *trans* influence than chloride in these compounds. Bond lengths and angles are listed in Table 3. $^{31}P\{^1H\}$ NMR exhibits a sharp singlet at δ 1.94 ppm, which indicates that **5** is not fluxional at room temperature, unlike **2**. This is probably due to the increased steric bulk of the phenyl group. It is assumed that the phenyl ligand derives from $^-BPh_4$; this indicates that the metal will go to extraordinary lengths to avoid chelating through the oxygen centre of the OPO ligand. Examples of phenyl migration have been observed previously,[13] but it is not a general reaction.

The formation of starting materials with no chloride present was undertaken by preparing $[Ni(OH_2)_6][BF_4]_2$ and $[Ni(OH_2)_6][PF_6]_2$ from the reactions of nickel metal with HBF_4 and NiO with HPF_6, respectively (both reactions in water). Reactions of **1** with the former complex result in isolation of intractable orange oils, from which no discrete complex could be obtained. $^{31}P\{^1H\}$ NMR shows the formation of a new phosphine complex, and its solubility implies that it is not a salt, and therefore probably not a chelate. Reactions of **1** with $[Ni(OH_2)_6][PF_6]_2$ also proved unsuccessful in the attempt to prepare oxygen/phosphorus chelates. The reaction using dichloromethane as solvent

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*The Ni—C bond in $NiPh[Ph_2AsCH_2CH_2)_3N]$ = 1.874(16) Å,[13] compared with 1.9163(11) Å for $NiClPh(OPO)_2$ (this work).

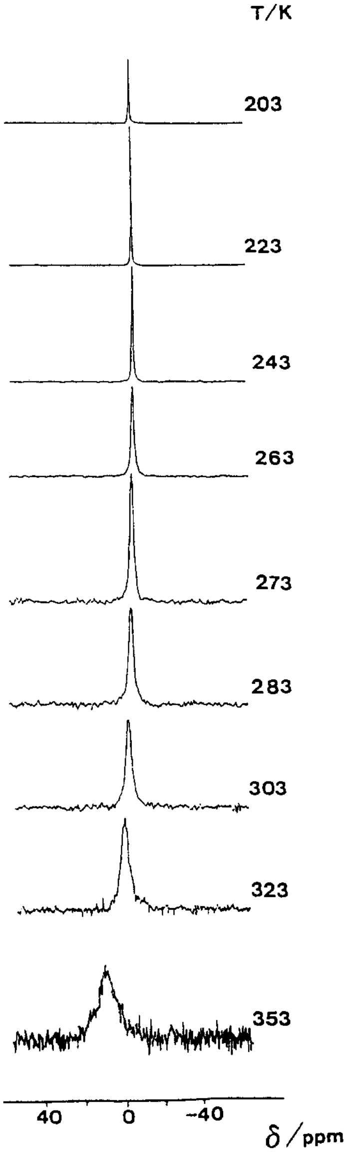

Fig. 2. Variable temperature $^{31}P\{^1H\}$ NMR spectra of (**2**).

results in the isolation of **2** in good yield, as characterized by microanalysis and ^{31}P NMR.* Presumably this has been produced by chloride abstraction from the solvent, again implying that chelate formation is unfavourable. This is supported by the observed lack of reactivity when toluene is used as solvent. Here, hydride abstraction from the solvent would be less favourable than chloride abstraction from dichloromethane, and chelate formation does not occur. This reaction again shows this ligand's unusually high reluctance to chelate through the ether function on the nickel centre, preferring to abstract chloride from the solvent.

Compound **6** was readily prepared by the addition of **1** to a solution of nickel bromide in ethanol, and the red crystals were characterized by microanalysis and NMR. The ^{31}P NMR is similar to the chloro analogue **2** and shows a broad singlet (δ 14 ppm). Bromide abstractions using $AgCF_3SO_3$, $AgBF_4$ and $NaBPh_4$ were attempted, since bromide is commonly more readily substituted than chloride. However, no reaction to form oxygen/phosphorus chelates was observed. Compounds **3** and **4** also appear reluctant to form these chelates by chloride abstraction, but in view of the behaviour of nickel with this ligand this is not surprising. Although it is not surprising that nickel prefers to bond to phosphorus rather than oxygen in these systems, it is surprising that nickel shows such reluctance to chelate through the oxygen donor, and that should this bonding be forced, the resulting chelates be so relatively unstable and difficult to isolate.

In conclusion, the chemistry of these complexes suggests that the formation of a phosphorus/oxygen chelating species proves difficult to attain in this aliphatic linear ether–phosphine ligand, although NMR studies may indicate transient chelation for nickel. The preparation of metal–OPO complexes with exclusively η^1-bonding through the phosphorus centre only is relatively easy, but the formation of these potentially catalytically important chelates requires further study. Further work on these types of compound is currently in progress.

EXPERIMENTAL

All syntheses described were carried out under strictly anaerobic conditions using a Halco Engineering 140 FF glove box, or using standard vacuum line techniques. All solvents were refluxed under N_2 over sodium/benzophenone and were distilled immediately prior to use, except for ethanol and dichloromethane, which were dried over CaH_2. The metal chlorides, salts and ethyl vinyl ether were used as received. Benzylphosphine ($BzPH_2$) was prepared using a modified literature route,[8] the only difference being the use of an ultrasonic cleaning bath (Decon FS400b, 400 W at 40 kHz) to increase the yield (*ca* 80%). Photolyses were performed with a Hanovia 50 W medium pressure mercury lamp in quartz glassware. ^{31}P NMR and variable temperature ^1H NMR data were collected on a Jeol FX90Q spectrometer (^{31}P at 36.23 MHz and ^1H at 89.55 MHz) or on a Bruker WM360 spectrometer (^1H, 360.134 MHz). Spectra were referenced exter-

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* $^{31}P\{^1H\}$ NMR (C_6D_6): δ −1.08 ppm (brd). Microanalysis found: C, 54.6; H, 7.6. $C_{30}H_{50}Cl_2P_2O_4Ni$ (**2**) requires: C, 54.1; H, 7.6%.

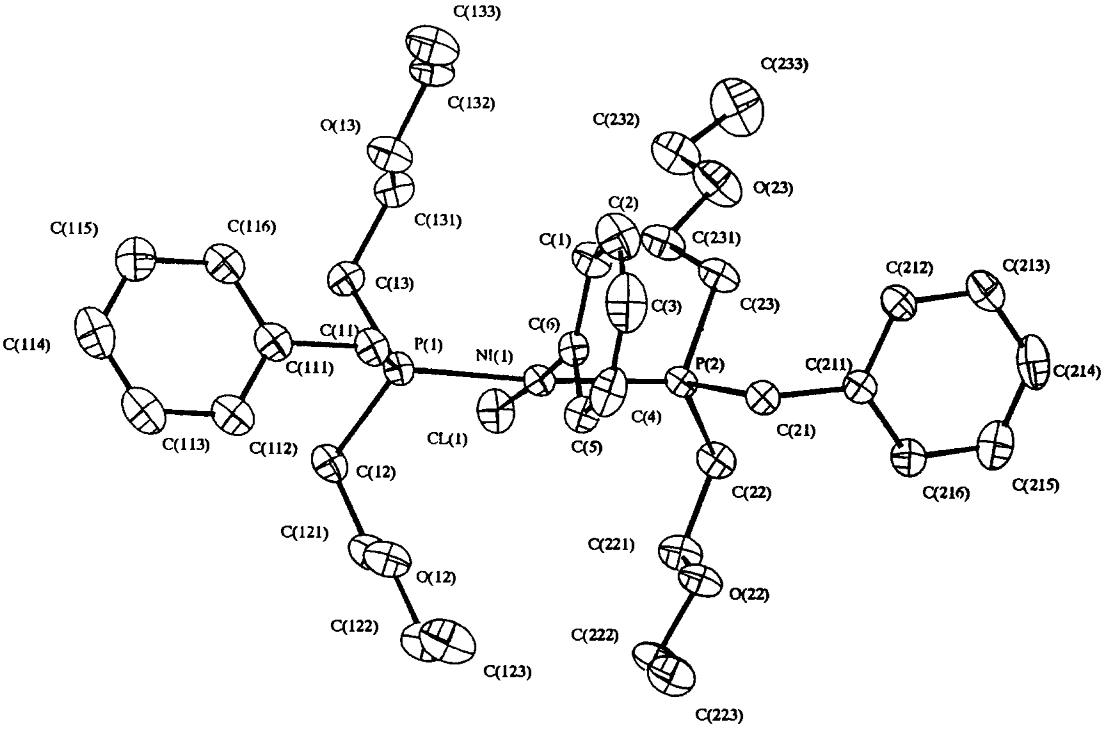

Fig. 3. The structure of $NiClPh(OPO)_2$ (**5**).

nally to 85% H_3PO_4 (^{31}P) or $SiMe_4$ (^1H). IR data were obtained from a Perkin–Elmer 577 Grating IR spectrophotometer, and UV–vis data from a Philips PU 8740. All elemental analyses were performed in this department on a Perkin–Elmer 240B or 240C elemental analyser. Magnetic susceptibilities of solids were obtained from a Sherwood Scientific Magnetic Susceptibility Balance or by Evan's method in solution (see Discussion). Mass spectrometry data were collected at the S. E. R. C. service at University College, Swansea. Melting points were measured in capillaries and are uncorrected.

Preparation of bis(2-*ethoxyethyl*)*benzylphosphine* (OPO; **1**)

$BzPH_2$ (55.53 g, 0.45 mol), ethyl vinyl ether (75.4 g, 1.05 mol) and AIBN [IUPAC 2,2′-azobis(2-methylpropionitrile); 0.1 g, 0.61 mmol] were placed in a photolytic reactor and photolysed for 2 days. Excess volatiles were removed *in vacuo*, and **1** was collected by vacuum distillation [b.p. 126–132°C/0.1 mmHg (0.75 Pa)] in a yield of 80% (96.0 g, 0.36 mol). The remainder of the phosphorus-containing material could be accounted for in a forerun (b.p. 78–120°C/0.1 mmHg) identified by ^{31}P and $^{31}P\{^1H\}$ NMR as the 'half-coupled' OP phosphine, $BzP(H)CH_2CH_2OEt$. This material was collected and recycled in further preparations with appropriate adjustment of the quantity of ethyl vinyl ether.

$^{31}P\{^1H\}$ NMR: $\delta -30.22$ ppm. ^1H NMR: δ 1.1 (6H, t, $J = 7$ Hz, CH_3), 1.7 (4H, q, line splitting = 7 Hz, PCH_2CH_2), 2.8 (2H, s, PCH_2Ph), 3.2 (4H, q, $J = 7$ Hz, OCH_2CH_3), 3.4 (4H, m, OCH_2CH_2), 7.0–7.2 (5H, m, Ph) ppm.

$BzP(H)CH_2CH_2OEt$: $^{31}P\{^1H\}$ NMR: δ -67.09 ppm. ^{31}P NMR: $\delta -67.15$ ppm (d, $^1J_{PH} = 199.21$ Hz).

Preparation of bis[*bis*(2-*ethoxyethyl*)*benzylphosphine*]*dichloronickel*(II) (**2**)

To a solution of $NiCl_2 \cdot 6H_2O$ (0.23 g, 0.97 mmol) in ethanol (20 cm^3) was added a standard solution of **1** in diethyl ether (2.0 cm^3, 1.94 mmol), and the red solution thus formed allowed to stir for approximately 10–15 min. After this time, precipitation of **2** as a red crystalline air-stable solid occurred in almost quantitative yield. **2** was recrystallized as red prisms from diethyl ether.

Found: C, 54.3; H, 7.5. $C_{30}H_{50}Cl_2P_2O_4Ni$ requires: C, 54.1; H, 7.6%. M.p. 81–83°C. ^1H NMR ($CDCl_3$): δ 1.3 (12H, t, $J = 7$ Hz, CH_3), 1.55 (4H, s, brd, $PhCH_2$), 1.85 (8H, q, $J = 7$ Hz, PCH_2), 3.65 (8H, q, $J = 7$ Hz, OCH_2CH_3), 4.0–4.2 (8H, m, CH_2CH_2O), 7.2–7.3 (2H, d, $J = 7$ Hz, aryl), 7.35

Table 3. Bond lengths (Å) and angles (°) for NiClPh(OPO)$_2$ (**5**)

Ni(1)—C(6)	1.9163(11)	Ni(1)—P(1)	2.2073(7)
Ni(1)—P(2)	2.2142(7)	Ni(1)—Cl	2.2352(7)
P(1)—C(13)	1.836(2)	P(1)—C(12)	1.839(2)
P(1)—C(11)	1.840(2)	P(2)—C(22)	1.834(2)
P(2)—C(23)	1.844(2)	P(2)—C(21)	1.852(2)
O(12)—C(121)	1.418(3)	O(12)—C(122)	1.418(3)
O(13)—C(131)	1.411(3)	O(13)—C(132)	1.425(3)
O(22)—C(221)	1.416(3)	O(22)—C(222)	1.419(3)
O(23)—C(232)	1.391(3)	O(23)—C(231)	1.439(2)
C(11)—C(111)	1.525(2)	C(12)—C(121)	1.508(3)
C(13)—C(131)	1.523(3)	C(21)—C(211)	1.523(2)
C(22)—C(221)	1.513(3)	C(23)—C(231)	1.511(2)
C(122)—C(123)	1.502(4)	C(132)—C(133)	1.493(4)
C(222)—C(223)	1.493(4)	C(232)—C(233)	1.461(4)
C(6)—Ni(1)—P(1)	89.02(5)	C(6)—Ni(1)—P(2)	88.05(5)
P(1)—Ni(1)—P(2)	175.72(3)	C(6)—Ni(1)—Cl	177.34(5)
P(1)—Ni(1)—Cl	89.46(2)	P(2)—Ni(1)—Cl	93.35(3)
C(13)—P(1)—C(12)	100.32(11)	C(13)—P(1)—C(11)	106.46(11)
C(12)—P(1)—C(11)	105.44(12)	C(13)—P(1)—Ni(1)	109.12(8)
C(12)—P(1)—Ni(1)	114.62(8)	C(11)—P(1)—Ni(1)	119.01(7)
C(22)—P(2)—C(23)	100.55(11)	C(22)—P(2)—C(21)	104.80(11)
C(23)—P(2)—C(21)	101.91(11)	C(22)—P(2)—Ni(1)	116.65(8)
C(23)—P(2)—Ni(1)	112.69(8)	C(21)—P(2)—Ni(1)	117.89(8)
C(121)—O(12)—C(122)	111.9(2)	C(131)—O(13)—C(132)	112.8(2)
C(221)—O(22)—C(222)	112.5(2)	C(232)—O(23)—C(231)	113.1(2)
C(5)—C(6)—Ni(1)	120.15(8)	C(1)—C(6)—Ni(1)	119.83(8)
C(111)—C(11)—P(1)	116.9(2)	C(121)—C(12)—P(1)	114.1(2)
C(131)—C(13)—P(1)	114.6(2)	C(211)—C(21)—P(2)	116.6(2)
C(221)—C(22)—P(2)	113.6(2)	C(231)—C(23)—P(2)	114.64(14)
C(112)—C(111)—C(11)	119.39(14)	C(116)—C(111)—C(11)	120.60(14)
O(12)—C(121)—C(12)	109.0(2)	O(12)—C(122)—C(123)	109.0(2)
O(13)—C(131)—C(13)	109.1(2)	O(13)—C(132)—C(133)	108.1(2)
C(212)—C(211)—C(21)	119.09(13)	C(216)—C(211)—C(21)	120.83(13)
O(22)—C(221)—C(22)	108.6(2)	O(22)—C(222)—C(223)	108.0(2)
O(23)—C(231)—C(23)	107.11(12)	O(23)—C(232)—C(233)	111.8(3)

(4H, t, $J = 7$ Hz, aryl), 7.5 (4H, d, $J = 7$ Hz, aryl) ppm. $^{31}P\{^1H\}$NMR (CDCl$_3$) : δ 7.4 ppm. Variable temperature data are detailed in Fig. 2. IR (KBr disc) : 3090 (w), 3060 (w), 3035 (w), 2980 (s), 2925 (m), 2860 (s, br), 2795 (m), 2695 (w), 2000 (w), 1970 (w), 1960 (w), 1915 (w), 1900 (w), 1825 (w), 1785 (w), 1710 (w), 1600 (s), 1585 (w), 1575 (w), 1495 (s), 1485 (s), 1470 (w), 1455 (m), 1440 (m), 1410 (m), 1400 (m), 1375 (s), 1350 (s), 1290 (m), 1270 (w), 1220 (s), 1170 (m), 1100 (s, br), 1040 (m), 1000 (s), 935 (w), 910 (m), 840 (m), 820 (m), 780 (m), 710 (m), 690 (w), 660 (m), 580 (m), 500 (m), 475 (m), 440 (w), 410 (m) cm^{-1}. UV–vis (CHCl$_3$) λ_{max}, nm : 241.0, 373.9 and 497.6 (ε, dm^3 mol^{-1} cm^{-1} : 12,905, 12,735 and 476). Mass spectral data are detailed in Table 2.

Preparation of bis[bis(2-ethoxyethyl)benzylphosphine]dichloropalladium(II) (**3**)

To a solution of potassium tetrachloropalladate(II) (0.25 g, 0.77 mmol) in ethanol (35 cm^3) was added a standard solution of **1** (1.6 cm^3, 1.53 mmol) in diethyl ether, and the solution stirred (2 days), giving an orange solution, and a light precipitate of unwanted byproduct (mainly KCl). The yellow air-stable crystals of **3** were isolated from this solution in good yield.

Found : C, 49.7 ; H, 7.2. $C_{30}H_{50}Cl_2P_2O_4Pd$ requires : C, 50.5 ; H, 7.1%. M.p. 96–98°C. ^1H NMR (CDCl$_3$) : δ 1.2 (12H, t, $J = 7$ Hz, CH$_3$), 1.6 (4H, s, brd, PhCH_2), 2.1 (8H, m, brd, PCH$_2$), 3.4–3.6 (8H, m, brd, OCH_2CH$_3$), 3.8–4.0 (8H, m, brd,

CH_2CH_2O), 7.2–7.5 (10H, m, aryl). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 6.5 ppm. IR (KBr disc): as detailed for **2**. UV–vis ($CHCl_3$) λ_{max}, nm: 243.6 and 327.9 (ε, $dm^3\ mol^{-1}\ cm^{-1}$: 10,571 and 15,618). Mass spectral data are detailed in Table 2.

Preparation of bis[bis(2-ethoxyethyl)benzylphosphine]dichloroplatinum(II) (**4**)

To a solution of potassium tetrachloroplatinate (II) (0.26 g, 0.63 mmol) in ethanol (20 cm^3) was added a standard solution of **1** (1.29 cm^3, 1.25 mmol) in diethyl ether, and the solution stirred (2 days). After filtering the unwanted byproduct (mainly KCl), the pale green crystals of **4** were isolated from the reaction mixture in reasonable yield.

Found: C, 44.7; H, 6.3. $C_{30}H_{50}Cl_2P_2O_4Pt$ requires: C, 44.9; H, 6.3%. M.p. 96–98°C. IR (KBr disc): as detailed for **2**. ^1H NMR ($CDCl_3$): δ 1.25 (12H, t, $J = 7$ Hz, CH_3), 1.65 (4H, s, brd, $PhCH_2$), 2.0–2.2 (8H, m, brd, PCH_2), 3.55 (8H, q, $J = 7$ Hz, OCH_2CH_3), 3.8–4.0 (8H, m, brd, CH_2CH_2O), 7.25 (2H, d, $J = 7$ Hz, aryl), 7.3 (4H, t, $J = 7$ Hz, aryl), 7.45 (4H, d, $J = 7$ Hz, aryl). $^{31}P\{^1H\}$ NMR: δ 0.8 ppm ($^1J_{PtP} = 2435$ Hz). UV–vis ($CHCl_3$) λ_{max}, nm: 248.9 and 269.0 (ε, $dm^3\ mol^{-1}\ cm^{-1}$: 8595 and 12,343).

Preparation of bis[bis(2-ethoxyethyl)benzylphosphine]chlorophenylnickel(II) (**5**)

To a solution of $NiCl_2 \cdot 6H_2O$ (0.24 g, 1.01 mmol) in ethanol (20 cm^3) was added $NaBPh_4$ (0.69 g, 2.02 mmol) and the solution stirred (12 h). The light green solution was filtered, and a standard solution of **1** (2.0 cm^3, 2.02 mmol) in diethyl ether was added dropwise and the solution stirred (12 h). The reaction mixture was filtered, leaving a light coloured precipitate containing a mixture of products (as shown by ^{31}P NMR). A batch of analytically pure pale orange crystals of **5** were isolated in poor yield from the orange supernatant. No further recrystallization of these crystals was necessary.

Found: C, 61.1; H, 8.0. $C_{36}H_{55}C1P_2O_4Ni$ requires: C, 61.1; H, 7.8%. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 1.94 ppm. $^{31}P\{^1H\}$ NMR on the bulk solid precipitate shows a mixture of products of which this is one part (peaks observed at δ 29.83, 11.63, 9.58, 7.97, 1.62 and 5.92 ppm).

Preparation of bis[bis(2-ethoxyethyl)benzylphosphine]dibromonickel(II) (**6**)

To a solution of $NiBr_2 \cdot 3H_2O$ (0.26 g, 0.95 mmol) in ethanol (50 cm^3) was slowly added a standard solution of **1** (1.8 cm^3, 1.91 mmol) in petroleum ether, and the red solution formed was stirred (15 min). After this time, precipitation of **6** had occurred in high yield (95%).

Found: C, 47.8; H, 7.2. $C_{30}H_{50}Br_2P_2O_4Ni$ requires: C, 47.7; H, 6.7%. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 14.2 ppm. IR (Nujol mull): as detailed for **2**.

X-ray structure determinations for **2** *and* **5**

Crystals of **2** suitable for X-ray work were recrystallized from diethyl ether. Crystals of **5** from the mother liquor (ethanol) were used without further recrystallization.

Crystal data

Complex **2**. $C_{30}H_{50}Cl_2NiO_4P_2$. $M_r = 666.25$, monoclinic, $a = 10.414(5)$, $b = 17.820(6)$, $c = 10.502(2)$ Å, $\beta = 115.73(3)°$, $U = 1755.7(11)$ Å^3, space group $P2_1/c$ (No. 14), $Z = 2$, $D_c = 1.260$ g cm^{-3}, $F(000) = 708$, $\mu = 8.26$ cm^{-1}, $T = 150$ K, red prisms, crystal size $0.20 \times 0.15 \times 0.15$ mm^3 (approx.).

Complex **5**. $C_{36}H_{55}ClNiO_4P_2$. $M_r = 707.90$, monoclinic, $a = 19.786(4)$, $b = 10.172(3)$, $c = 20.424(2)$ Å, $\beta = 115.990(7)°$, $U = 3695(2)$ Å^3, space group $P2_1/a$ (alternative No. 14), $Z = 4$, $D_c = 1.273$ g cm^{-3}, $F(000) = 1512$, $\mu = 7.20$ cm^{-1}, $T = 150$ K, orange prisms, crystal size $0.15 \times 0.10 \times 0.20$ mm^3 (approx.).

Data collection and processing[14]

Delft instruments FAST TV area detector diffractometer at the window of a rotating anode FR591 generator (50 kV, 40 mA), with a molybdenum target [$\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å], controlled by a Micro Vax 3200 and driven by MADNES[15] software. Both data sets were recorded at 150 K using an Oxford cryostream low temperature cooling system.

Complex **2**. 8140 reflections collected ($3.14 < \theta < 29.75°$), index ranges $-14 < h < 12$; $-17 < k < 23$; $-14 < l < 14$, giving 4312 unique data [$R_{int} = 0.0434$ after absorption correction, (DIFABS)[16]].

Complex **5**. 18,444 reflections collected ($2.22 < \theta < 29.98°$), index ranges $-27 < h < 24$; $-14 < k < 8$; $-25 < l < 28$, giving 9570 unique

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* $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$.

† $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$.

data [R_{int} = 0.0504 after absorption correction, (DIFABS)[16]].

Structure analysis and refinement

Both structures were solved by heavy atom methods (SHELX-S[17]) and then subjected to full-matrix least squares refinement based on F_0^2 (SHELX-93[18]). Non-hydrogen atoms were refined anisotropically with all hydrogens included in idealized positions (C—H distance = 0.97 Å, C/H—C—H angles = 109.5°) with isotropic thermal parameters free to refine. Phenyl rings were idealized as regular hexagons (C—C distance = 1.395 Å, C—C—C angles = 120°). The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$.

Complex **2.** Final wR_2* and R_1† values are 0.1312 and 0.0828 respectively, for all 4312 data and 205 parameters (ρ_{max}, ρ_{min} 0.503, −0.223 eÅ^{-3}). The corresponding wR_2 and R_1 values for 1965 data with $F_o > 4\sigma(F_o)$ are 0.0820 and 0.0364, respectively.

Complex **5.** Final wR_2* and R_1† values are 0.1190 and 0.0615 respectively, for all 9570 data and 408 parameters (ρ_{max}, ρ_{min} 1.078, −0.0357 eÅ^{-3}). The corresponding wR_2 and R_1 values for 5417 data with $F_o > 4\sigma(F_o)$ are 0.0910 and 0.0372, respectively.

Diagrams were drawn with SNOOPI.[19] All calculations were performed on a 486DX2/66 personal computer. Sources of scattering factor data are given in Ref. 18. Anisotropic displacement parameters of non-hydrogen atoms, hydrogen atom parameters and tables of structure factors and atomic coordinates have been deposited as supplementary materials.

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