

# Articles

## Development of a Synthetic Route to Unsymmetrical Triphosphine Ligands and an Investigation of Their Coordination Chemistry with Nickel and Palladium

G. Dyer<sup>†</sup> and J. Roscoe<sup>\*,‡</sup>

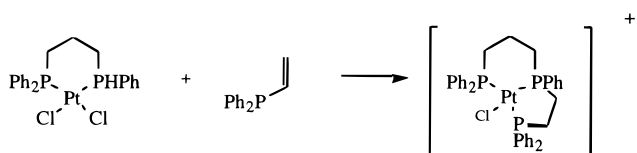
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K., and Department of Chemistry, University of Central Lancashire, Preston PR1 2HE, U.K.

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Chiral tridentate phosphines,  $R_2P(CH_2)_3PPh(CH_2)_2PPh_2$  where  $R = C_6H_5$ ,  $p\text{-ClC}_6H_4$ , and  $p\text{-FC}_6H_4$ , can be prepared from simple starting materials, ( $R_3P$ ,  $I(CH_2)_3I$ , and  $Ph_2P(CH_2)_2PPh_2$ ), in a few stages involving phosphonium salts and phosphine oxides as intermediates. Crystalline diamagnetic complexes of nickel(II) and palladium(II) have been isolated. In solution these show first-order 12 line  $^{31}P$  NMR spectra consistent with three nonequivalent phosphorus nuclei coupled to one another in a square planar geometry. A single X-ray crystallographic study of  $NiI_2\{P(CH_2)_3PPh(CH_2)_2PPh_2\}$  showed that this was square pyramidal in the solid state with a weakly held apical iodo ligand.

### Introduction

The unsymmetrical triphosphine ligand  $R_2P(CH_2)_3PPh(CH_2)_2PPh_2$  ( $R = C_6H_5$ , "eptp",<sup>1</sup> is not well-known. Its synthesis was reported by Meek and co-workers in 1975.<sup>2</sup> It was prepared on a small scale by heating (3-(diphenylphosphino)propyl)phenylphosphine with vinylidiphenylphosphine in the presence of 2,2-azoisobutyronitrile (AIBN). Later it was shown that the ligand could also be synthesized rapidly on platinum by an  $Et_3N$ -catalyzed reaction of vinylidiphenylphosphine with the coordinated secondary phosphine:<sup>3</sup>



These preparations use expensive and difficult-to-prepare starting materials. In contrast, the aim here was to produce the ligand, and some variations with substituted phenyl groups, from readily available starting materials, in a few simple stages involving phosphonium salts and phosphine oxides as intermediates.

This ligand is a simple tridentate analogue of the well-known bidentate ligands  $Ph_2P(CH_2)_nPPh_2$ , ( $n = 2, 3$ , etc.). It is able to chelate to three of the four coordination sites of a square planar complex. Unlike the much studied symmetrical "tpp" ligand,  $PhP[(CH_2)_3PPh_2]_2$ ,<sup>2–4</sup> the ligand eptp contains a chiral phosphorus center and three nonequivalent phosphorus nuclei.

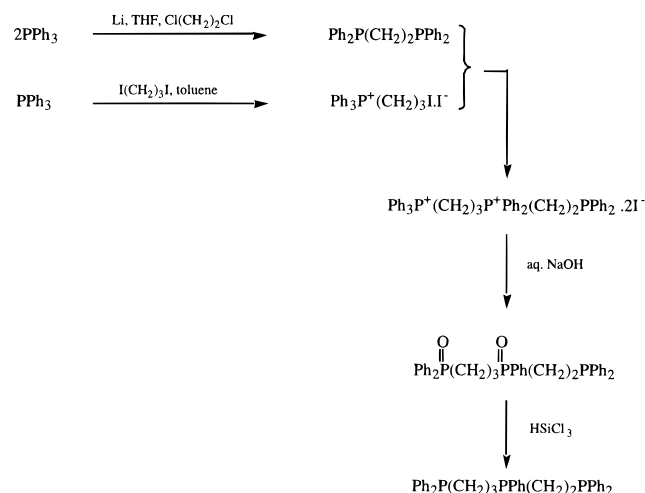
<sup>†</sup> University of Central Lancashire.

<sup>‡</sup> University of East Anglia.

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- (1) The ligand abbreviations are derived from the lengths of the alkyl chains connecting the phosphorus atoms. The nonsymmetric triphosphine  $Ph_2P(CH_2)_3PPh(CH_2)_2PPh_2$ , (2-(diphenylphosphino)ethyl)(3-(diphenylphosphino)propyl)phenylphosphine then becomes abbreviated to eptp.
- (2) Dubois, D. L.; Myers, W. H.; Meek, D. W. *J. Chem. Soc., Dalton Trans.* **1975**, 1011.
- (3) Waid, R. D.; Meek, D. W. *Inorg. Chem.* **1984**, *23*, 778–782.
- (4) King, R. B.; Cloyd, J. C. *Inorg. Chem.* **1975**, *14*, 114.

### Scheme 1. Preparation of Eptp



These features are of course imparted to its square planar complexes which could therefore have applications as homogeneous catalysts for asymmetric syntheses since molecular models show that the third group on the central phosphorus atom must be directed to one side of the square plane. This causes an incoming fifth ligand to attach to the metal on the other side of the square plane and experience a chiral array of four different ligand groups in a given clockwise order. The complexes are also ideally suited to  $^{31}P$  NMR studies. The only complexes reported by Meek and co-workers<sup>3,5</sup> were  $[Pt(eptp)Cl]AsF_6$  and  $[RhNO(eptp)]$ . In this study we report analogous nickel(II) and palladium(II) complexes.

### Results and Discussion

The new synthetic route to eptp is shown in Scheme 1. Each stage was monitored by  $^{31}P\{^1H\}$  NMR spectroscopy, which confirmed that each reaction proceeded effectively quantitatively. The eptp ligand was collected as an oil.

- (5) Mazanec, T. J.; Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1980**, *19*, 85–91.

**Table 1.** Summary of  $^{31}\text{P}\{^1\text{H}\}$  NMR Spectra ( $\text{CDCl}_3$  at 25 °C)

complex	chemical shift (ppm)			coupling const (Hz)			coord shift (ppm)		
	P(2)	P(3)	P(1)	P(2-3)	P(3-1)	P(2-1)	P(2)	P(3)	P(1)
$\text{P}(2)^+(\text{CH}_2)_3\text{P}(3)^+(\text{CH}_2)_2\text{P}(1)$	23.9	29.0	-11.1	10.2	47.3				
$\text{P}(2)(\text{O})(\text{CH}_2)_3\text{P}(3)(\text{O})(\text{CH}_2)\text{P}(1)$	32.5	41.5	-11.4		45.5				
$\text{P}(2)(\text{CH}_2)_3\text{P}(3)(\text{CH}_2)_2\text{P}(1)$ , eptp	-16.7	-20.9	-12.6		29.8				
eptp- $\text{Cl}_2$	-18.9	-22.0	-13.4		29.4				
eptp- $\text{F}_2$	-18.7	-21.2	-11.6		28.0				
<i>o</i> -anisyl $_2$ -eptp	-34.8	-20.6	-11.9		26.3				
$[\text{Ni}(\text{eptp})\text{I}]$	0.2	53.3	60.6	72.3	20.9	281.8	16.9	74.2	73.2
$[\text{Ni}(\text{eptp})\text{ClO}_4]$	1.7	54.9	60.9	80.9	28.8	276.9	18.4	75.8	73.5
$[\text{NiBr}(\text{eptp})\text{ClO}_4]$	3.1	56.9	60.0	80.0	47.7	276.6	19.8	77.8	72.6
$[\text{PdBr}(\text{eptp})\text{ClO}_4]$	1.1	54.8	58.5	38.6	0	414.0	17.8	75.7	71.1
$[\text{PdBr}(\text{eptp})\text{PF}_6]$	0.9	53.9	58.2	38.5	0	413.4	17.6	74.8	70.8
$[\text{Ni}(\text{eptp}-\text{Cl}_2)\text{I}]$	0.6	52.2	62.4	69.8	18.1	285.2	19.5	74.2	75.8
$[\text{Ni}(\text{eptp}-\text{Cl}_2)\text{ClO}_4]$	1.1	53.9	63.2	71.4	21.3	283.1	20.0	75.9	76.6
$[\text{NiBr}(\text{eptp}-\text{Cl}_2)\text{ClO}_4]$	4.2	57.2	60.9	80.2	45.2	280.4	23.1	79.2	74.3
$[\text{PdBr}(\text{eptp}-\text{Cl}_2)\text{PF}_6]$	1.1	56.4	59.6	36.8	0	415.2	20.0	78.4	73.0
$[\text{Ni}(\text{eptp}-\text{F}_2)\text{I}]$	0.1	52.8	62.5	71.5	20.2	283.8	18.8	74.0	74.1
$[\text{Ni}(\text{eptp}-o\text{-anisyl}_2)\text{I}]$	6.2	59.5	66.1	73.7	24.0	273.1	41.0	80.1	78.0

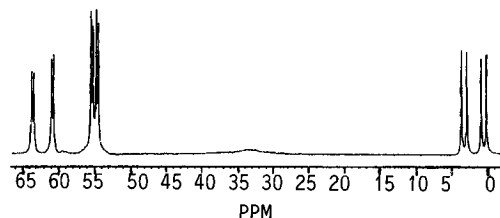
The  $^{31}\text{P}$  NMR spectrum comprised two doublets, (-20.9 and -12.6 ppm with a coupling constant of 29.8 Hz), and a singlet, (-16.7 ppm), in the phosphine region, the chemical shifts and coupling constants being identical to those reported by Meek and Tau.<sup>2,6</sup> Surprisingly no trace of phosphine oxide was detectable in the  $^{31}\text{P}$  NMR spectrum even after many months of exposure to air.

Using this synthetic route, eptp is easily prepared from very simple starting materials, in a few stages which do not require the use of organometallic reagents, dried solvents, or even a nitrogen atmosphere. All intermediates are air stable and readily characterized by  $^{31}\text{P}$  NMR spectroscopy and elemental analysis as pure materials. Since dppe can be quickly made from  $\text{PPh}_3$  by a slight modification of the usual literature method,<sup>7</sup> all three phosphorus atoms originate simply from  $\text{PPh}_3$ , while the  $-(\text{CH}_2)_2-$  and  $-(\text{CH}_2)_3-$  backbones originate from dichloroethane and diiodopropane respectively.

Tridentate ligands  $\text{R}_2\text{P}(\text{CH}_2)_3\text{PPh}(\text{CH}_2)_2\text{PPh}_2$ , where  $\text{R} = p\text{-ClC}_6\text{H}_4$  and  $p\text{-FC}_6\text{H}_4$  were made with the same ease by substituting  $\text{PR}_3$  into the first step of the reaction sequence in place of triphenylphosphine. All observations and intermediates were similar and  $^{31}\text{P}$  NMR spectra almost identical, with the exception of the final tridentate phosphine products. Here the peak for the phosphorus atom at the end of the trimethylene backbone was shifted upfield by about 2 ppm due to the substitution of a halogen onto the phenyl ring. It is expected that other unsymmetrical tridentate phosphine ligands with different substituents will be made with similar ease. The ligands were isolated as oils and used for complexation after recrystallization from methanol by cooling to -20 °C.

The triphosphine eptp has interesting steric features resulting from its lack of symmetry, including three nonequivalent phosphorus nuclei, one of which is chiral. This chirality will inevitably be induced onto the metal center of a complex, so that the metal and any substrate molecule which attaches to it will exist in a rigidly defined, highly asymmetric environment. Suitable substituents introduced into the phenyl rings could enhance chiral recognition.

Orange-brown nickel(II) complexes containing the  $[\text{NiX}(\text{eptp})]^+$  cation ( $\text{X} = \text{Br}$  or  $\text{I}$ ) were easily prepared in 50–90% yield by reaction of the appropriate nickel(II) salts in ethanol solution with the stoichiometry quantity of eptp. The complexes are stable to air and water, and may be crystallized from dichloromethane/ethanol. They behave as 1:1 electrolytes in


**Figure 1.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{NiI}_2(\text{eptp})$  (25 °C,  $\text{CDCl}_3$ ) (60.6 ppm (d of d), 53.3 ppm (d of d), 0.2 ppm (d of d),  $J = 72.3, 20.9, 281.8$  Hz).

ethanol solution. Melting points and elemental analysis data are given in Table 3. The orange-brown colors and diamagnetism strongly indicate a square planar structure in solution. Consistent with this, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra (Table 1 and Figure 1) showed 12 sharp lines, i.e. a doublet of doublets for each phosphorus atom.

Nickel(II) phosphine complexes have been widely used as the basis for studying steric effects in terms of “cone angle”,<sup>8</sup> and for investigating the “ring contribution” to coordination shifts. However problems can arise when polydentate ligands are examined which have the potential to form different size chelate rings as in eptp. The very large coordination shifts observed when phosphorus is incorporated in a five-membered chelate ring are well-known and usually attributed to some form of “ring strain”.<sup>9</sup> The series of nickel(II) complexes prepared here are ideal for investigating such phenomena since of the three phosphorus atoms, one is in a five-membered chelate ring, one is in a six-membered ring, and one is in both.

From Table 1 it can be seen that the coordination shifts are about the same for palladium(II) as for nickel(II), being 18–25 ppm for P(2) and 70–83 ppm for P(3) and P(1) (the lettering system used is  $\text{Ph}_2\text{P}(2)(\text{CH}_2)_3\text{P}(3)\text{Ph}(\text{CH}_2)_2\text{P}(1)\text{Ph}_2$  as shown on Figure 2). The last compound in the table is exceptional because of the *o*-anisyl groups on P(2), which obviously affects the coordination shift of P(2) very markedly.

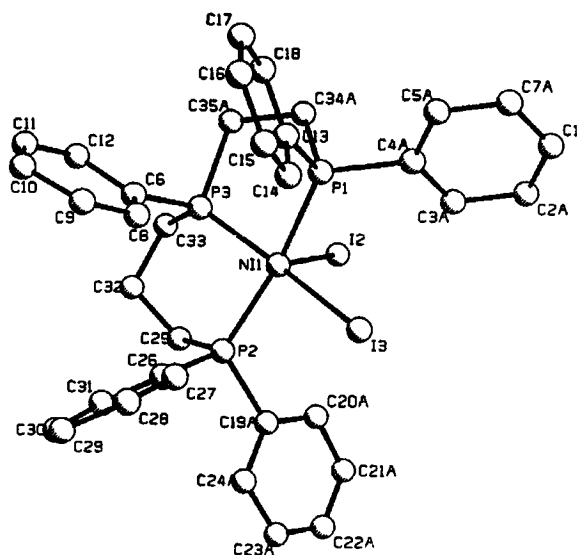
To compliment the solution studies, which firmly indicated that the unsymmetrical chiral tridentate phosphine produced chelate mononuclear square planar species, it was decided to grow crystals for X-ray analysis. X-ray crystallography (see

(6) Tau, K. D. Ph.D. Thesis; The Ohio State University, 1978.

(7) Hewertson, W.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490.

(8) Butler, I. S.; Harrod, J. F. *Inorganic Chemistry-Principles and Applications*; Benjamin/Cummings: Reading, MA, 1989; p 678.

(9) Bell, C. F. *Principles and Applications of Metal Chelation*; Oxford University Press: Oxford, England, 1977.



**Figure 2.** X-ray crystal structure of  $[\text{NiI}_2(\text{eptp})] \cdot 10$  Table 2 shows important bond lengths and bond angles.

**Table 2.** Summary of X-ray Data for  $\text{NiI}_2(\text{eptp})$

(a) Intramolecular Distances (Å)			
Ni–I(1)	2.544(2)	Ni–P(2)	2.233(4)
Ni–I(2)	2.974(2)	Ni–P(3)	2.164(5)
Ni–P(1)	2.217(4)		
(b) Intramolecular Bond Angles (deg)			
I(1)–Ni–I(2)	105.08(8)	I(2)–Ni–P(2)	96.5(1)
I(1)–Ni–P(1)	92.1(1)	I(2)–Ni–P(3)	91.6(1)
I(1)–Ni–P(2)	91.3(1)	P(1)–Ni–P(2)	170.6(2)
I(1)–Ni–P(3)	163.0(1)	P(1)–Ni–P(3)	84.0(2)
I(2)–Ni–P(1)	91.1(1)	P(2)–Ni–P(3)	90.2(2)

Figure 2 and Table 2) of  $[\text{NiI}_2(\text{eptp})]^{10}$  surprisingly revealed five coordination (an only slightly distorted square pyramid), in the solid state. However, the Ni–I bond lengths show that the second iodide ligand in the apical position is only weakly held which explains the square planar structure found in solution. As is usual in square pyramidal stereochemistry, the nickel lies just above the basal plane.

A number of interesting features revealed in the solid-state structure deserve further comment.

(a) Five-coordinate complexes of nickel(II) and other  $d^8$  metal ions are quite well-known, but the majority are trigonal bipyramidal, rather than square pyramidal (e.g.  $\text{Fe}(\text{CO})_5$ ). Where ligands are not all equivalent, distortion of the trigonal bipyramidal structure necessarily occurs, sometimes toward an approximately square pyramidal arrangement, although crystal packing forces may sometimes favor this so that the structure in solution may be markedly different.

(b) The chirality of the molecule is clearly accentuated by the coordination of the apical iodo ligand which “sees” either a clockwise or an anticlockwise arrangement of  $\text{C}_2$  backbone,  $\text{C}_3$  backbone, and the other ligand. Chiral recognition between the molecules is presumably very strong, and the X-ray study shows a regular array of alternating *R*- and *S*-enantiomers in the solid crystal, which is therefore not optically active.

(c) The structure clearly shows that three phenyl groups, one on each phosphorus, are directed to the side of the molecule opposite to the apical iodide. The planes of these three phenyl rings are approximately perpendicular to that of the  $\text{NiP}_3\text{I}$  square

plane, and these may be termed “axial” phenyl groups in contrast to the other two which are “equatorial”. Such a conformation leads to considerable steric blocking on one side of the nickel by three bulky, nonpolar, hydrophobic phenyl groups, while the other side is remarkably uncluttered. Coordination of the apical iodine naturally occurs on the sterically unhindered side.

(d) Unlike the solution studies, the X-ray result proved that the  $[\text{NiI}(\text{eptp})]^+$  species is capable of weakly binding a fifth ligand in an apical position, the conventional first stage of many catalytic cycles. It is important that the binding is not too strong, otherwise the process either stops completely or proceeds but with a slow turnover rate. The 298 pm bond distance to the apical iodine indicates significant interaction with the nickel, but the binding is obviously much weaker than the other iodine at 254 pm from the nickel.

(e) The central phosphorus of the tridentate ligand is significantly closer to the nickel (217.0 pm) than the other two phosphorus atoms (222.0, 223.5 pm), presumably because it is required to be simultaneously part of a five-membered and a six-membered ring. The “double chelate effect” could encourage stronger bonding, and the bicyclo structure could restrict vibrational freedom and/or force this phosphorus atom closer to nickel.

(f) There are several possibilities for the conformation of the  $\text{C}_3$  backbone in the six-membered chelate ring. The arrangement observed here is loosely analogous to the “chair” conformation of cyclohexane.

The ligands  $\text{R}_2\text{P}(\text{CH}_2)_3\text{PPh}(\text{CH}_2)_2\text{PPh}_2$ , where  $\text{R} = p\text{-ClC}_6\text{H}_4$  and  $p\text{-FC}_6\text{H}_4$ , were used to prepare the analogous complexes with  $\text{NiI}_2$ , which gave analogous  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra. All the spectra showed the typical 12 lines, and coupling was similar with all three ligands. The fluoro-substituted ligands are probably the most interesting since the nonequivalence of the two *p*-fluoro substituents on the terminal phosphorus can be determined using  $^{19}\text{F}$  NMR spectroscopy. The 75 MHz  $^{19}\text{F}$  NMR spectrum of the  $\text{NiI}_2$  complex of  $\text{eptp-F}_2$  showed two sharply-resolved signals separated by 2.15 ppm corresponding to a rigid structure with two different fluorine environments which may loosely be described as “axial” and “equatorial”, (attached to C(29) and C(22A) in Figure 2).

Palladium(II) complexes based on the same structure as the nickel complexes were prepared with  $\text{eptp}$  by addition of the ligand to a solution of palladium(II) bromide perchlorate or palladium(II) bromide hexafluorophosphate. The  $^{31}\text{P}$  NMR spectra of these complexes were slightly different from the pattern set by the nickel complexes. The spectra showed only eight sharp peaks, ( $\text{PF}_6^-$  being ignored). The phosphorus at the end of the two carbon chain was only coupled to the other terminal phosphorus through the metal and did not show coupling to its phosphorus neighbor along the two-carbon chain. This is presumably due to the fact that the coupling along the carbon chain is equal to the coupling through the palladium but opposite in sign.

Many other complexes can be envisaged with interesting structures based on this unusual asymmetrical tridentate ligand system. The complexes made to date with nickel and palladium are all crystalline solids, stable in air and stereochemically rigid at room temperature on the NMR time scale making investigation and characterization relatively straight forward.

## Experimental Section

All Fourier-mode, proton-decoupled phosphorus-31 NMR spectra were collected on a Bruker 250 MHz spectrometer at 101 Hz in  $\text{CDCl}_3$  at 25 °C. Elemental analyses were performed by The University of Manchester Microanalytical Laboratory.

(10) The X-ray crystallographic study was carried out by R. G. Pritchard and C. A. McAuliffe of the University of Manchester Institute of Science and Technology. The X-ray data will be published at a later date.

**Preparation of the Tridentate Phosphine Ligand, eptp.** **Preparation of  $[\text{Ph}_3\text{P}^+(\text{CH}_2)_3\text{I}]\text{I}^-$  (I).** A solution of triphenylphosphine (5.25 g, 0.02 mol) in toluene (30 mL) was added dropwise over 15 min, by way of a dropping funnel, to a refluxing, stirred solution of diiodopropane (5.92 g, 0.02 mol) in toluene (10 mL). Reflux was maintained for 1.5 h, and then the resulting white precipitate was filtered on a sinter from the hot toluene (yield 7.60 g, 68%).  $^{31}\text{P}\{^1\text{H}\}$  NMR: 25.2 ppm (s).

**Preparation of  $[\text{Ph}_3\text{P}^+(\text{CH}_2)_3\text{P}^+\text{Ph}_2(\text{CH}_2)_2\text{PPh}_2](\text{I}^-)_2$  (II).** Bis(1,2-diphenylphosphino)ethane, "dppe",  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$  (11.95 g, 0.03 mol), was dissolved in hot dimethylformamide, DMF (60 mL, 120 °C). Product I (5.58 g, 0.01 mol) was added as a powder to the hot DMF solution and the resulting clear colorless solution was heated at 120 °C for 30 min and then cooled to room temperature with continuous stirring, during which time the excess bidentate phosphine crystallized out and could be filtered from the cooled DMF solution (5.58 g, i.e. 73% recovery of the 0.02 mol excess of bidentate phosphine used). Dry diethyl ether (180 mL) was added to the filtrate to precipitate the product. The solvent mixture was decanted off and the product washed with warm toluene (100 mL, 60 °C) to remove any remaining dppe starting material. The pure product was collected by filtration from warm toluene as a white powder and washed with diethyl ether ( $2 \times 10$  mL) (yield 9.16 g, 96%).  $^{31}\text{P}\{^1\text{H}\}$  NMR: 29.0 ppm (d of d), 23.9 ppm (d),  $-11.1$  ppm (d)  $J = 10.2, 47.3$  Hz.

**Preparation of  $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_3\text{P}(\text{O})\text{Ph}(\text{CH}_2)_2\text{PPh}_2$  (III).** Product II (9 g, 0.009 mol) was added to sodium hydroxide solution (5 g of NaOH in 50 mL of  $\text{H}_2\text{O}$ ), in a 250 mL conical flask equipped with a magnetic stirrer bar and a reflux condenser. The sodium hydroxide solution was brought to reflux. On heating the solid phosphonium salt became a brown oil and was stirred vigorously for 2 h at reflux. After this time the sodium hydroxide solution was cooled to below room temperature and decanted off to leave the product as a viscous light brown oil which was washed with cold water ( $2 \times 15$  mL), and dried in an oven (120 °C) for 2 h. The water-free product became solid on cooling to room temperature (yield 4.02 g, 77%).  $^{31}\text{P}\{^1\text{H}\}$  NMR: 32.5 ppm (s), 41.5 ppm (d),  $-11.4$  ppm (d),  $J = 45.5$  Hz.

**Preparation of  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}(\text{CH}_2)_2\text{PPh}_2$ , eptp (IV).** The dry product III (4.21 g, 0.0073 mol) was dissolved in acetonitrile (65 mL) in a conical flask equipped with a magnetic stirrer bar and a long air condenser. Triethylamine (5.87 g, 0.0584 mol) was added to the solution with stirring. Trichlorosilane (7.86 g, 0.0584 mol) was added dropwise with care to the stirring solution producing white fumes. The white mixture in the flask was heated at 76 °C for 30 min. After this time the now yellow mixture was heated to gentle reflux (82 °C), for 24 h and then cooled to room temperature. The mixture was poured slowly, in portions, into sodium hydroxide solution (12.50 g of NaOH in 50 mL of  $\text{H}_2\text{O}$ ) and stirred for 30 min, resulting in two clear phases with the product dissolved in the organic layer. The organic layer was evaporated to dryness, yielding the product as a clear brown oil. No phosphine oxide or other impurities were detected by  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectroscopy (yield 3.37 g, 84%).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $-12.6$  ppm (d),  $-16.7$  ppm (s),  $-20.9$  ppm (d),  $J = 29.8$  Hz. The oil was recrystallized by dissolving in hot methanol, and on cooling to  $-20$  °C the product was precipitated as a white solid. This was separated and dried in a vacuum; on warming to room temperature, the white solid became a clear brown oil.

**Preparation of (2-(Diphenylphosphino)ethyl)(3-(dichlorophosphino)propyl)phenylphosphine.** Tri(*p*-chlorophenyl)phosphine was substituted into the preparation used for I in place of triphenylphosphine. The product after the silane reduction (IV) was stored under nitrogen, as a clear brown oil (yield 2.11 g, 47%).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $-13.4$  ppm (d),  $-18.9$  ppm (s),  $-22.0$  ppm (d),  $J = 29.4$  Hz.

**Preparation of (2-(Diphenylphosphino)ethyl)(3-(difluorophosphino)propyl)phenylphosphine.** Tri(*p*-fluorophenyl)phosphine was substituted into the preparation used for I in place of triphenylphosphine. The product was isolated as a clear brown oil (yield 3.50 g, 82%).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $-11.6$  ppm (d),  $-18.7$  ppm (s),  $-21.2$  ppm (d),  $J = 28.0$  Hz.

**Preparation of Tridentate Phosphine Complexes.** **Preparation of  $[\text{Ni}(\text{eptp})]\text{I}$ .** The tridentate ligand eptp (IV) (1.84 g, 0.0034 mol) was recrystallized from ethanol and dissolved in dichloromethane (5 mL) and added dropwise to a solution of  $\text{NiI}_2$  (1.04 g, 0.0034 mol) in

**Table 3.** Elemental Analyses of Nickel and Palladium Tridentate Phosphine Complexes

complex	mp (°C)	found (calculated)		
		% C	% H	% P
$[\text{Ni}(\text{eptp})]\text{I}$	276	48.8 (48.8)	4.0 (4.1)	10.3 (10.7)
$[\text{Ni}(\text{eptp})]\text{ClO}_4$	242	50.0 (50.4)	4.3 (4.2)	10.7 (11.1)
$[\text{NiBr}(\text{eptp})]\text{ClO}_4$	242	53.5 (53.4)	4.4 (4.4)	11.6 (11.8)
$[\text{PdBr}(\text{eptp})]\text{PF}_6$	191	47.6 (47.8)	4.2 (4.0)	12.8 (14.1)
$[\text{PdBr}(\text{eptp})]\text{ClO}_4$	218	47.4 (50.4)	4.0 (4.2)	10.1 (11.1)
$[\text{Ni}(\text{eptp}-\text{Cl}_2)]\text{I}$	212	46.5 (45.2)	4.1 (3.6)	10.1 (10.0)
$[\text{Ni}(\text{eptp}-\text{F}_2)]\text{I}$	267	44.9 (46.8)	3.7 (3.7)	10.2 (10.4)
$[\text{NiBr}(\text{eptp}-\text{Cl}_2)]\text{ClO}_4$	168	50.1 (49.1)	4.6 (3.9)	10.8
$[\text{Ni}(\text{eptp}-\text{Cl}_2)]\text{ClO}_4$	215	46.2 (46.6)	4.2 (3.7)	9.7 (10.3)

ethanol (30 mL). On addition of each drop of ligand solution, a dark brown powder precipitated. The dichloromethane was removed and the product collected on a sinter. The product was recrystallized from dichloromethane and ethanol giving a black crystalline solid (mp 276 °C; yield 2.72 g, 93%).  $^{31}\text{P}\{^1\text{H}\}$  NMR: 60.6 ppm (d of d), 53.3 ppm (d of d), 0.2 ppm (d of d),  $J = 72.5, 20.9, 281.8$  Hz.

**Preparation of  $[\text{Ni}(\text{eptp})]\text{ClO}_4$ .**<sup>11</sup>  $\text{NiI}_2$  (500 mg, 1.6 mmol) dissolved in ethanol (16 mL) was mixed with  $\text{Ni}(\text{ClO}_4)_2$  (590 mg, 1.6 mmol) dissolved in ethanol (10 mL), resulting in a pale green solution. Recrystallized eptp (IV) (194 mg, 3.5 mmol) dissolved in dichloromethane (5 mL) was added dropwise to the nickel(II) iodide perchlorate solution, resulting in the precipitation of a deep brown colored powder in a brown/red solution. The dichloromethane was removed and the product collected on a sinter. The product was recrystallized from dichloromethane and ethanol (mp 242 °C; yield 1.25 g, 52%).  $^{31}\text{P}\{^1\text{H}\}$  NMR: 1.7 ppm (d of d), 54.9 ppm (d of d), 60.9 ppm (d of d),  $J = 80.9, 28.8, 276.9$  Hz.

**Preparation of  $[\text{NiBr}(\text{eptp})]\text{ClO}_4$ .**<sup>11</sup>  $\text{NiBr}_2$  (452 mg, 1.7 mmol) was dissolved in warm ethanol (10 mL) to give a deep green solution.  $\text{Ni}(\text{ClO}_4)_2$  (610 mg, 1.7 mmol) dissolved in warm ethanol (10 mL) was added to the  $\text{NiBr}_2$  solution resulting in a pale green solution when cool. Ligand eptp (1.82 g, 3.3 mmol), dissolved in dichloromethane (5 mL), was added to the  $\text{NiBrClO}_4$  solution. A brown/orange precipitate was formed immediately. The dichloromethane was removed and the product collected on a sinter. The product was recrystallized from dichloromethane and ethanol (mp 242 °C; yield 1.65 g, 60%).  $^{31}\text{P}\{^1\text{H}\}$  NMR: 3.1 ppm (d of d), 56.9 ppm (d of d), 60.0 ppm (d of d),  $J = 80.0, 47.7, 276.6$  Hz.

**Preparation of  $[\text{PdBr}(\text{eptp})]\text{PF}_6$ .**  $\text{PdCl}_2$  (301 mg, 1.7 mmol) was made into a suspension in warm ethanol (40 mL, 30 °C).  $\text{LiBr}$  (590 mg, 6.8 mmol), dissolved in ethanol (10 mL), was added dropwise to the palladium chloride suspension which became more orange/red in color on addition of each drop. The solution was shaken for 10 min until no further color change took place. Ammonium hexafluorophosphate (277 mg, 1.7 mmol), dissolved in ethanol (5 mL), was added to the red palladium solution with no visible change. The solution was now decanted off any excess palladium chloride. Ligand eptp (940 mg, 1.7 mmol), dissolved in dichloromethane (5 mL), was added dropwise to the red solution precipitating a pale brown precipitate in a clear yellow solution. The dichloromethane was removed and the pale brown oily precipitate recrystallized from dichloromethane and ethanol. The product was precipitated as a yellow powder (mp 191 °C; yield 0.81 g, 54%).  $^{31}\text{P}\{^1\text{H}\}$  NMR: 0.9 ppm (d of d), 53.9 ppm (d), 58.2 ppm (d),  $-145$  ppm (sep),  $J = 38.5, 413.4$  Hz.

**Preparation of  $[\text{PdBr}(\text{eptp})]\text{ClO}_4$ .**<sup>11</sup> Lithium perchlorate (180 mg, 1.7 mmol), in ethanol (5 mL), was used in the above reaction in place of ammonium hexafluorophosphate. The product was precipitated as a yellow powder in ethanol and was recrystallized from dichloromethane and ethanol (mp 218 °C; yield 0.92 g, 65%).  $^{31}\text{P}\{^1\text{H}\}$  NMR: 1.1 ppm (d of d), 54.8 ppm (d), 58.5 ppm (d),  $J = 38.6, 414.0$  Hz. The complexes with the fluoro- and chloro-substituted ligands were prepared in the same way, and data are tabulated in Tables 1 and 3.

**X-ray Structure of  $[\text{Ni}(\text{eptp})]\text{I}$ .**<sup>10</sup> Crystals of  $[\text{Ni}(\text{eptp})]\text{I}$  were grown, and a black plate crystal of  $\text{C}_{35}\text{H}_{35}\text{NiI}_2\text{P}_3$  having approximate

(11) Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great caution. *J. Chem. Educ.* **1973**, *50*, A335.]

dimensions of 0.400 by 0.400 by 0.050 mm was mounted on a glass fiber. All measurements were recorded on a Rigaku AFC6S diffractometer with graphite-monochromated Mo K $\alpha$  radiation and a 12 kW rotating anode generator.

The data were collected at a temperature of  $23 \pm 1$  °C using the  $\omega$  scan technique to a maximum value  $2\theta$  value of 50.0°. A total of 6745 reflections were collected. The intensities of six representative reflections which were measured after every 150 reflections declined by 2.02%. A linear correction factor was applied to the data to account for this phenomenon. The linear absorption coefficient for Mo K $\alpha$  is 24.9 cm<sup>-1</sup>. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission

factors ranging from 0.42 to 1.00. The data were corrected for Lorentz and polarization effects.

**Supporting Information Available:** Crystallographic data for (2-(diphenylphosphino)ethyl)(3-(diphenylphosphino)propyl)phenylphosphine, including text giving data collection and experimental details, tables of crystallographic and refinement data, positional parameters, intramolecular bond angles for non-hydrogen atoms, and conformation angles (21 pages). Ordering information is given on any current masthead page.

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