Direct Electrochemical Synthesis and Crystallographic Characterization of Metal Diphenylphosphido and Diphenylthiophosphinato Compounds, and some Derivatives†

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The electrochemical oxidation of a number of metals in acetonitrile solutions of PPh_2H gives rise to $M(PPh_2)_n$ compounds (M = Co, Zn or Cd, n = 2; M = Cu, Ag or Au, n = 1). With anodic nickel the product is $Ni(PPh_2)\cdot PPh_2H$. In the presence of elemental sulphur such oxidation reactions yield $[M(S_2PPh_2)_2]$ (M = Co, Zn or Cd). The electrochemical processes involved have been identified. The crystal structure of the addition compound $[Cu_4(PPh_2)_4(dppm)_2]\cdot 4MeCN$ **1** [dppm = bis(diphenylphosphino)methane] has been determined by X-ray crystallography, which reveals a Cu_4P_4 ring, capped by $Cu_2PCP'_2$ rings. Crystal parameters: triclinic, space group $P\bar{1}$, a = 14.719(4), b = 13.649(5), c = 17.112(5) Å, α = 112.40(3), β = 106.22(2), γ = 115.39(2)° and Z = 1; R = 0.0632 for 3622 observed reflections [$I \geqslant 3\sigma(I)$]. The compound $Ni(PPh_2)\cdot PPh_2H$ is oxidized by elemental oxygen, sulphur or selenium to give $[Ni(E_2PPh_2)_2]$ (E = O, S or Se), and also reacts with PhNCS to yield $[Ni\{PPh_2(SCNPh)\}_2]$ **2**. Crystal parameters: triclinic, space group $P\bar{1}$, a = 8.950(6), b = 9.745(4), c = 10.366(7) Å, α = 112.28(4), β = 99.09(5), γ = 90.88(4)° and Z = 1. Disorder prevented this structure from being refined beyond R = 0.1612, but the essential features of the square-planar NiS_2P_2 core were identified. The crystal parameters of $[Ni(O_2PPh_2)_2(HO_2PPh_2)_2(MeCN)_2]$ **3** are monoclinic, space group $P2_1/c$, a =12.420(5), b = 9.737(7), c = 20.729(16) Å, β = 100.29(5)° and Z = 2. The nickel atom is co-ordinated by two monodentate $Ph_2PO(O)^-$ ligands and two monodentate $Ph_2P(O)OH$ ligands which are hydrogen-bonded to their anionic analogues, and by two MeCN molecules, to give a $NiO_2O'_2N_2$ core.

The recent increase in interest in the preparation and study of the organophosphido derivatives of metals has been prompted in part by the use of such compounds as precursors of binary phosphides for the electronics industry. There is also a longer-standing history involving the incorporation of PR_2 groups into various metal carbonyl complexes. The synthetic methods which have been used for the preparation of $M(PR_2)_n$ molecules include transmetallation *via* the lithio compound,[1,2] alkane elimination between PR_2H and a metal alkyl,[3] the elimination of $SiMe_3Cl$ from $SiMe_3(PR_2)$ and metal halide,[4] and the reaction of a metal alkyl with bis(diphenylphosphino)ethane.[5]

In a number of papers from this laboratory, we have reported the use of direct electrochemical synthesis methods in which the anodic oxidation of a metal by a ligand present (or generated) in a non-aqueous solution gives rise to compounds in a simple one-step high-yield procedure. This technique has been found to be especially useful for the preparation of derivatives of weak acids, and recent examples include the synthesis of metal carboxylates,[6] dipyridylamines,[7] catecholates,[9] thiolates[10] and dithiolates.[11] The present paper reports an extension of the method to diphenylphosphido compounds of a number of metals, and their derivatives; a preliminary account of part of this work has been published.[12]

Experimental

Metals were in the form of sheets (Ni, Au, In or Rh), *ca.* 1 × 2 cm^2, or rods (Co, Cu, Ag, Zn or Cd), diameter 0.5 cm, and were used as supplied (Aldrich), except for being dipped into dilute nitric acid, washed with water, dried and lightly abraded before use. Solvents were distilled from calcium hydride and stored over molecular sieves. All other reagents were used as supplied.

Metal analysis was carried out by atomic absorption spectrophotometry, using an IL-251 instrument. Microanalysis was performed by Guelph Chemical Laboratories Ltd. Infrared spectra were recorded on a Nicolet 5DX instrument, using KBr discs, and ^{31}P NMR spectra on a Bruker AC-300L spectrometer.

Electrochemical Synthesis of $M(PPh_2)_n$ *Compounds.*—The method was essentially that used in previous work, using a cell of the form Pt(−)|MeCN + PPh_2H(+L)|M(+) (L = neutral ligand) with solution compositions summarized in Tables 1 and 3. The current, in the range 10–50 mA (current density *ca.* 15 mA cm^{-2}), was supplied by a Coutant LQ 50/50 power supply. The solution phase was contained in a tall-form beaker (100 cm^3), and the cathode was a coil of platinum wire, suspended *ca* 1–2 cm from the anode. All operations were carried out in an atmosphere of dry nitrogen, which bubbled gently through the solution and also served to mix the contents of the cell.

The following specific experimental details should be noted. For cobalt, the crystalline material which deposited throughout the electrolysis was collected, washed with cold MeCN (20 cm^3) and dried. This compound, which is soluble in tetrahydrofuran (thf) and methylene chloride, is very unstable in air, and decomposes slowly to an unidentified blue solid even when stored under nitrogen. With rhodium, only very small quantities of metal were lost from the anode, even after long electrolysis (Table 1). The white crystalline substance which formed in the cell was collected, and found to be identical with samples of P_2Ph_4 prepared electrochemically (see below). The nickel product, identified as the unusual species $Ni(PPh_2)\cdot PPh_2H$, was collected in the same manner, and found to be soluble in hot benzene, toluene and thf.

Electrolysis at a copper anode caused the solution to turn yellow, and small quantities of an unidentified yellow oil deposited in the cell; orange-red crystals were formed during the

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

oxidation, and continued to deposit for some hours after the end of the experiment. The solution phase was decanted off, and the residue (oil + solid) triturated with toluene (60 cm^3), at which point the oil dissolved leaving a red solid residue which was collected, washed (15 cm^3 MeCN, 15 cm^3 toluene, 50 cm^3 pentane) and dried *in vacuo*. With silver, gold, zinc and cadmium, a solid product formed at the anode as soon as current flowed, and this solid was collected, washed (MeCN) and dried *in vacuo*. These compounds are insoluble in all common organic solvents. In the case of indium, an off-white solid precipitated during the electrolysis and was collected in the usual way, but this substance proved to be quite unstable, decomposing with sparking on some occasions, and was not studied further.

The products were characterized by elemental analysis (Table 2) and by IR and NMR spectroscopy. All decompose on exposure to air, with the cobalt and indium compounds being the most unstable; the decomposition products include obnoxious evil-smelling gas(es), which were not identified.

The yields of these syntheses varied from *ca.* 60% in the case of Cu, through 80% for Ag, to almost quantitative for Au, Zn and Cd, based on the quantity of metal dissolved from the anode.

Copper–PPh_2H*–Bis(diphenylphosphino)methane (dppm).*—A solution containing PPh_2H (2 cm^3) and dppm (2 g) in MeCN–toluene (45 + 25 cm^3) formed the electrolyte phase. Electrolysis over 8 h at 15 V and 20 mA resulted in the loss of 370 mg Cu from the anode. A yellow coloration developed near the cathode when current flowed, and at the same time hydrogen gas was evolved. The intensity of the colour of the solution increased as the experiment proceeded. Some yellow-orange material deposited during the electrolysis, and the formation of crystalline material continued for *ca.* 12 h after the end of the electrolysis. This product was collected, washed with cold MeCN (15 cm^3) and dried *in vacuo*. Infrared spectroscopy showed the absence of MeCN in this solid, and analysis corresponded to the formula $2Cu(PPh_2)$·dppm·C_6H_5Me (Found: C, 68.2; H, 5.45. Calc.: C, 69.1; H, 5.15%). Recrystallization from acetonitrile gave the solvate $2Cu(PPh_2)$·dppm·2MeCN **1** whose IR spectrum had vibrations associated with PPh_2^- and dppm, and a band at 2248 cm^{-1} assigned as ν(C≡N) of MeCN. This compound, obtained in 95% yield, is soluble in hot benzene or toluene. Its crystal structure is discussed below.

Electrochemical Synthesis of $M(S_2PPh_2)_2$ *Compounds.*—The electrolyte phase was prepared by mixing MeCN, toluene, PPh_2H and powdered sulphur in the quantities shown in Table 3, and stirring this slurry for *ca.* 15 min to dissolve most of the sulphur. In a typical experiment, some small amounts of sulphur remained at the bottom of the cell at the beginning of the electrolysis, but dissolved as the experiment proceeded. Electrolysis was then carried out in the usual way, and the solid products which formed throughout the experiment were collected, washed (MeCN, then pentane) and dried *in vacuo*. The only significant variation from this description occurred in the case of cobalt; in this case a green solid precipitated during the electrolysis and when the filtrate obtained after removing this solid was cooled and reduced in volume (by *ca.* 30%), further product was obtained.

The yields were 80–90%, based on metal dissolved. The products were characterized by elemental analysis, and IR and ^{31}P NMR spectroscopy. These compounds are more air-stable than their PPh_2 analogues.

Synthesis of $[Ni(O_2PPh_2)_2(HO_2PPh_2)_2(MeCN)_2]$.—The aerial oxidation of $Ni(PPh_2)$·PPh_2H, which gives rise to an interesting nickel(II) derivative of diphenylphosphinic acid, was carried out in two different ways.

(*i*) When the yellow solution of $Ni(PPh_2)$·PPh_2H obtained by electrolysis (see above) was slowly evaporated under reduced pressure and over *ca.* 16 h green-yellow crystals deposited. These were collected, washed with cold MeCN (2 × 10 cm^3) and dried *in vacuo*.

(*ii*) A similar electrolytically prepared solution was reduced in volume by 50%, and the yellow powder so obtained was washed and dried *in vacuo*. This substance had a strong IR absorption at 2246 cm^{-1} [ν(P–H)] and a medium-intensity band at 2320 cm^{-1} [ν(C≡N) of co-ordinated MeCN]. A small quantity (100 mg) was dissolved in hot toluene (10 cm^3), and this solution was allowed to stand open to the atmosphere. After 2 d the green-yellow crystals which formed were collected, washed and dried *in vacuo*; yield 70 mg.

Both products had identical IR spectra; the important features were the absence of ν(P–H), and the presence of broad bands at 1350m cm^{-1} [ν(P=O)] and 800–1000s (vbr) cm^{-1} [ν(P–OH)]. Analysis identified this compound as $[Ni(O_2PPh_2)_2(HO_2PPh_2)_2(MeCN)_2]$ (Found: C, 61.4; H, 4.60; N, 3.00; Ni, 5.75. Calc. for $C_{52}H_{48}N_2NiO_8P_4$: C, 61.7; H, 4.80; N, 2.75; Ni, 5.80%). The molecular structure was established by X-ray crystallography.

Chemical Synthesis of $[Ni(E_2PPh_2)_2]$ (E = S *or* Se).—(*i*) When elemental sulphur (0.28 g, 1.09 mmol S_8) was added to $Ni(PPh_2)$·PPh_2H (0.47 g, 1.10 mmol) in benzene (60 cm^3) under a stream of nitrogen the solution immediately became deep red. After being stirred overnight, the mixture was filtered to remove traces of unreacted sulphur; the filtrate subsequently deposited red-violet crystals, which were collected, washed with toluene (10 cm^3) and dried *in vacuo*. This product was identified as $[Ni(S_2PPh_2)_2]$, identical to the compound prepared electrochemically (see Tables 3 and 4); yield 90%.

The nitrogen gas which flushed through the vessel was passed through aqueous $CuSO_4$, solution to absorb H_2S given off in this reaction. The resultant black precipitate of CuS was collected, dried (120 °C) and weighed (0.051 g, 0.53 mmol).

(*ii*) In an analogous experiment, black selenium (0.52 g, 6.59 mmol Se) was stirred with a solution of $Ni(PPh_2)$·PPh_2H (0.47 g) in benzene (70 cm^3) for 2 d at room temperature. The resultant deep red solution was filtered to remove unreacted Se, and left for 2 d under a gentle nitrogen flow. The deep red crystals which deposited were collected, washed (pentane), dried and identified as $[Ni(Se_2PPh_2)_2]$ (Found: C, 39.1; H, 2.80; Ni, 7.15. Calc.: C, 38.7; H, 2.70; Ni, 7.90%). Yield 20%, based on Ni originally dissolved.

Synthesis of $[Ni\{PPh_2(SNCPh)\}_2]$.—(*i*) *Electrochemical.* The solution phase consisted of PPh_2H (2 cm^3), PhNCS (1.5 cm^3) and NEt_4ClO_4 (50 mg) in MeCN (50 cm^3). Electrolysis at 10 V and 20 mA for 2 h resulted in the dissolution of 67 mg of nickel (E_F = 0.51 mol F^{-1}). The yellow-orange oil which was thrown down as the reaction proceeded was collected, dissolved in CH_2Cl_2 (10 cm^3) and precipitated as an orange solid by the addition of MeCN (20 cm^3). This material was washed with cold MeCN (5 cm^3) and dried *in vacuo*. Analysis and spectroscopy identified this solid as being identical with that obtained by the chemical route (see below). Yield 73%, based on Ni originally dissolved.

(*ii*) *Chemical.* The compound $Ni(PPh_2)$·PPh_2H (0.47 g, 1.10 mmol) was added to a solution of PhNCS (3 cm^3, 3.39 g, 25 mmol) in CH_2Cl_2 (50 cm^3) at room temperature. The clear red-brown solution was left for 24 h, after which the volume was reduced to *ca.* 5 cm^3; the addition of MeCN (10 cm^3) precipitated an orange solid, which was collected, washed (MeCN) and dried (Found: C, 64.5; H, 4.55; N, 4.75; Ni, 8.30. Calc. for $[Ni\{PPh_2(SNCPh)\}_2]$: C, 65.3; H, 4.30; N, 4.00; Ni, 8.40%). Yield 67%, based on $Ni(PPh_2)$·PPh_2H.

Electrochemical Synthesis of P_2Ph_4.—The electrolysis of a solution of PPh_2H (5 cm^3) in MeCN (50 cm^3) containing NEt_4ClO_4 (40 mg) was carried out between two platinum electrodes at 20 V, 20 mA, for 24 h under nitrogen. The colourless crystals which formed were collected, washed (cold

MeCN, 20 cm^3) and dried. This product was spectroscopically identical to an authentic sample of P_2Ph_4.

Crystallographic Studies.—(*i*) A suitable crystal of $[Cu_4(\mu\text{-}PPh_2)_4(dppm)_2]\cdot 4MeCN$ **1** was obtained by slow evaporation of a solution of the parent compound in acetonitrile (see Table 5 for crystal size and other relevant information). Diffraction experiments on this, and on the other crystals discussed below, were carried out on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) at 21 °C. Other constant factors were the scan type [θ (crystal)–2θ (counter)], the scan width ($K\alpha_1$ − 1° to $K\alpha_1$ + 1°), and the variable scan speed (2.02–4.88° min^{-1}). The initial orientation matrix was determined from 15 machine-centred reflections, selected from rotation photographs, and these results were also used to determine the crystal system. Partial rotation photographs around each axis were consistent with a triclinic system, and ultimately 40 intense reflections in the range $15 < 2\theta < 25°$ were used to obtain the final lattice parameters and the orientation matrices. There were no systematic absences; the space group $P\bar{1}$ was used, and taken to be correct in view of the successful refinement. Three standard reflections were recorded at regular intervals throughout the data collection; some decay was observed and an appropriate decay correction was applied. The data were processed by using the SHELX 76 program package[13] in the computing facilities at the University of Windsor. In view of the low values of the absorption coefficients (< 10 cm^{-1}) no absorption correction was applied. All the structures have crystallographically imposed symmetry.

The positions of the copper atoms were obtained by direct methods (SHELX 76),[13] and the remaining non-hydrogen atoms were located from successive Fourier difference map calculations. Refinements were carried out by using block-matrix methods, with block 1 containing Cu(1), Cu(2), P(1)–P(4) and C(01), and the remaining atoms being included in block 2. All the atoms were refined anisotropically to a final convergence of R = 0.0632 and R' = 0.0645. Hydrogen atoms were subsequently included in ideal positions [r(C–H) = 0.95 Å, H–C–H 109.5°], and were assigned U values 1.10 times larger than those of the carbons attached. The convergence minimized the function $\Sigma w(|F_o| - |F_c|)^2$, and in the final cycles the weighting scheme $w = [\sigma^2(F) + \rho F^2]^{-1}$ was employed, with ρ = 0.000 01. The electron density in the final difference map was associated with the disordered acetonitrile molecules.

The final atomic coordinates for compound **1** are presented in Table 6, and the important interatomic distances and angles in Table 7. Fig. 1 shows the molecular structure; a diagram of the central Cu_4P_4 ring and its capping $Cu_2PCP'_2$ rings has been published elsewhere.[12]

(*ii*) Orange crystals of $[Ni\{PPh_2(SCNPh)\}_2]$ **2** were grown from acetonitrile solution, and subjected to crystallographic examination by methods essentially identical to those described for **1**, and employing the same conditions in the structure refinement. Isotropic unit-weighted refinement of the 23 non-hydrogen atoms of the nickel–ligand system, and a scale factor, gave R = 0.201 and R' = 0.232 for the 1348 reflections having $I > 3\sigma(I)$. Anisotropic refinement of Ni, S, P, C and N atoms then gave R = 0.161 and R' = 0.177.

At this point, a Fourier difference synthesis, phased on the refined parameters, showed peaks of electron density near the phenyl rings, and these results, coupled with the high thermal parameters for some of the carbon atoms of the phenyl rings, led to the conclusion that these rings were positionally disordered. Attempts to model the rings did not improve the R factor, and the refinement was therefore discontinued. The main features of the core of the molecule are shown in Fig. 2; the fractional co-ordinates of the Ni, S, P, N, C and H atoms have been deposited.

(*iii*) A suitable crystal of $[Ni(O_2PPh_2)(HO_2PPh_2)_2\text{-}(MeCN)_2]$ **3** was selected, sealed in a capillary tube and mounted along its longest dimension. The intensities of three

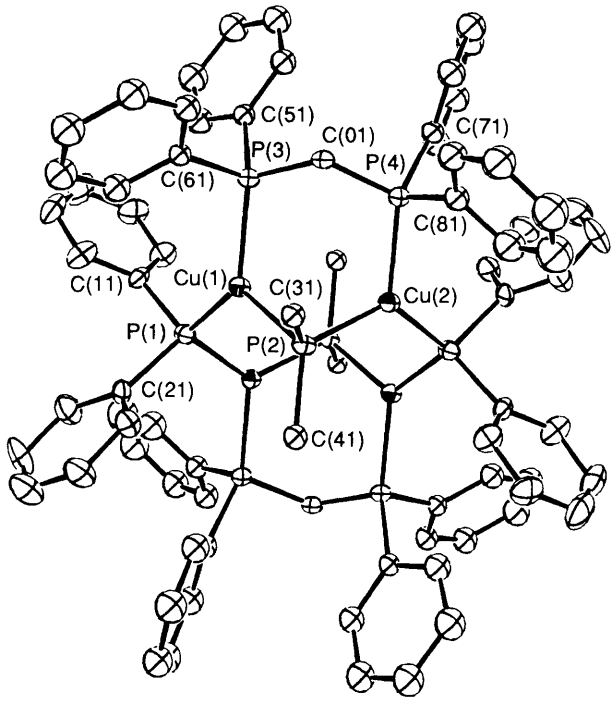


Fig. 1 ORTEP diagram of $[Cu_4(PPh_2)_4(dppm)_2]$ **1** with atoms shown as 30% probability ellipsoids. Hydrogen atoms, and the phenyl rings at C(31) and C(41), have been omitted for clarity.

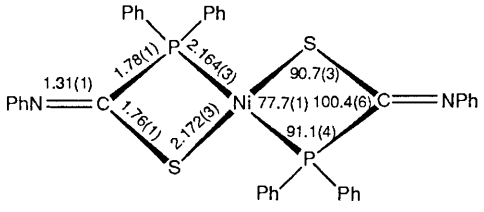


Fig. 2 The core of the structure of $[Ni\{PPh_2(SCNPh)\}_2]$ **2** showing important bond distances (Å) and angles (°)

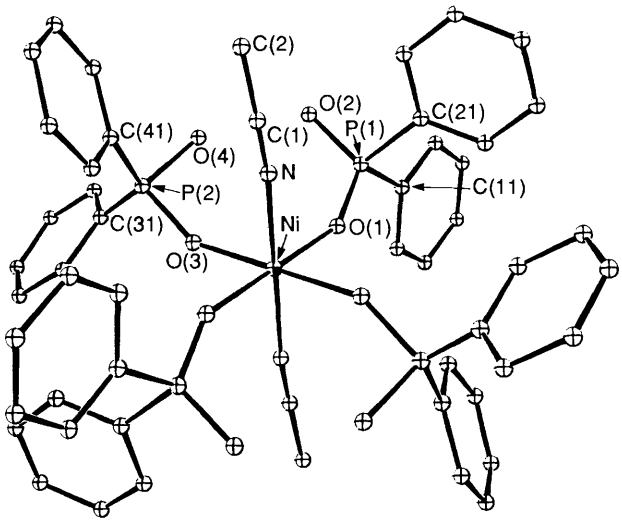


Fig. 3 ORTEP diagram of $[Ni(O_2PPh_2)_2(HO_2PPh_2)_2(MeCN)_2]$ **3** with atoms shown as 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

check reflections were monitored at regular intervals and no significant change was observed during the data collection. The cell parameters were measured and refined from results of 50 reflections in the range $10 < 2\theta < 20°$. The data used in the structure determination were corrected for Lorentz and

Table 1 Experimental conditions for the electrochemical synthesis of $M(PPh_2)_n$ compounds

Metal	Solution composition/cm^3 MeCN[a]	PPh_2H	Initial voltage/V	Current/mA	Time of electrolysis/h	Metal dissolved/mg	Product[b]	E_F/mol F^{-1}
Co	50[c]	3	10	20	7	131	ML_2	0.43
Rh	60	4	10	20	44	0.9	*d*	—
Ni	80	2.5	20	50	1.25	64	ML·HL	0.48
Cu	60	1	35	20	4.4	229	ML	1.08
Ag	50	2	30	20	1	88	ML	1.09
Au	50	3	35	20	2	139	ML	0.47
Zn	50	2	35	20	8	215	ML_2	0.55
Cd	50	5	30	20	8	359	ML_2	0.54
In	50	2	20	50	1	224	*d*	1.05

[a] Plus *ca.* 50 mg tetraethylammonium perchlorate. [b] L = PPh_2. [c] Plus 25 cm^3 tetrahydrofuran. [d] See text.

Table 2 Analytical results for $M(PPh_2)_n$ compounds with calculated values in parentheses

Compound	Colour	Analysis (%) M	C	H
$[Co(PPh_2)_2]$	Red-brown	13.2 (13.7)	68.3 (67.1)	4.70 (5.45)
$Ni(PPh_2)\cdot PPh_2H$	Yellow	14.0 (13.7)	67.9 (67.2)	5.50 (4.70)
$Cu(PPh_2)$	Red	24.9 (25.6)	—	—
$Ag(PPh_2)$	Pale yellow	36.0 (36.8)	—	—
$Au(PPh_2)$	Pale yellow	—	38.3 (37.7)	2.80 (2.65)
$[Zn(PPh_2)_2]$	Colourless	14.5 (15.0)	—	—
$[Cd(PPh_2)_2]$	Colourless	23.8 (23.3)	—	—

polarization effects. The density was measured by the flotation method in carbon tetrachloride–benzene mixtures. The pertinent crystal and experimental data are given in Table 5.

The nickel atom position was obtained by using the results of *SHELXS* 86 direct-method analysis.[14] The structure was refined in the space group $P2_1/c$. The successive electron-density syntheses, phased with the contribution of the nickel atom, showed clearly all the non-hydrogen atoms. Three cycles of isotropic refinement on all of the atoms and three cycles with anisotropic thermal parameters for Ni, P and O atoms, followed by the inclusion of the hydrogen atoms of the diphenylphosphinate ligands in calculated positions (C–H 0.95 Å) and by a final refinement cycle, gave R and R' values of 0.0533 and 0.0616 respectively. The average shift per error in the last cycle was 0.01. The convergence and weighting schemes were those used in (*i*) above.

The final structure is shown in Fig. 3, and the final atomic coordinates are listed in Table 8, with the important interatomic distances and angles in Table 9.

Additional material for all three structures available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis of Diphenylphosphido Compounds.—Although there have been reports in the literature over many years of the preparation of PR_2^- derivatives of transition-metal carbonyls,[15] there has been relatively little work on the simple $M(PR_2)_n$ compounds themselves. The present work establishes that the diphenylphosphides of a number of metals can be readily prepared by a simple one-step electrochemical synthesis, from which the products are obtained in high yield and good purity. The electrochemical efficiencies of these systems, defined as moles of metal dissolved per Faraday of charge passed through the cell, correspond to the sequence (1) and (2) with $n = 1$ for

$$\text{cathode: } n\text{PPh}_2\text{H} + ne \longrightarrow n\text{PPh}_2^- + \frac{n}{2}\text{H}_2(\text{g}) \quad (1)$$

$$\text{anode: } n\text{PPh}_2^- + \text{M} \longrightarrow \text{M(PPh}_2)_n + ne \quad (2)$$

M = Cu, Ag, Au and In, and $n = 2$ for Co, Ni, Zn and Cd. The systems involving Cu, Co, Zn and Cd call for no comment, since the products correspond to the sequence in equations (1) and (2) (see Table 1). We discuss the case of nickel in detail below. For indium, the product collected may well be $In(PPh_2)$, but this proved to be too unstable and dangerous to permit characterization. Rhodium is obviously too noble a metal to be oxidized under these experimental conditions, since the weight loss of the anode over a long electrolysis was negligible, and in this system, as in that with a platinum anode, the only identifiable product was P_2Ph_4, formed by the sequence (3) and

$$\text{PPh}_2^- \longrightarrow \text{PPh}_2^{\bullet} + \text{e} \quad (3)$$

$$2\text{PPh}_2^{\bullet} \longrightarrow \text{P}_2\text{Ph}_4 \quad (4)$$

(4). These reactions have been the subject of detailed study by Dessy *et al.*[16] and can obviously form the basis of an electrochemical synthesis of P_2Ph_4.

The products were characterized by elemental analysis and by IR spectroscopy. The most important feature in the IR spectra is the absence of ν(P–H), and in addition, one observes characteristic bands in the region 1700–1900 cm^{-1} (monosubstituted phenyl) and strong aromatic-phosphorus bands at 995–1070 and 1435 cm^{-1}. There is little change in these values between PPh_2H and the metal complexes, or from one complex to another. With the exception of $Co(PPh_2)_2$ and $Cu(PPh_2)$, the compounds listed in Table 2 are insoluble in common organic solvents, and it was not possible to record NMR spectra. The case of $Cu(PPh_2)$ is discussed below. In view of the structural similarities between $[Cu_4(\mu\text{-PPh}_2)_4(\text{dppm})_2]$ and $[Cu_4(\mu\text{-SC}_5\text{H}_{11})_4(\text{dppm})_2]$, it seems reasonable to assume that the insolubilities of PPh_2^- and RS^- derivatives lie in the same cause, namely strong cross-linking to give homopolymeric solids.

The Structure of $[Cu_4(\mu\text{-PPh}_2)_4(\text{dppm})_2]$.—The crystal structure of this substance **1** consists of a Cu_4P_4 ring, capped by $Cu_2PCP'_2$ rings, with four molecules of MeCN in the unit cell, but independent of the tetrameric cage. The close analogy between this structure and the thiolato species $[Cu_4(\mu$-

Table 3 Experimental conditions for the electrochemical synthesis of $M(S_2PPh_2)_2$ compounds

Metal	Solution composition[a]/cm^{-1}			Initial voltage/ V	Initial current/ mA	Time of electrolysis/ h	Metal dissolved/ mg	E_F/mol F^{-1}
	MeCN	PPh_2H	S[b]					
Co	40	1.1	0.40	10	30	2.5	68	0.42
Ni	30	1.5	0.47	10	30	2	67	0.51
Zn	30	1	0.30	15	30	3	110	0.51
Cd	40	1.4	0.50	20	30	2	125	0.50

[a] Plus *ca.* 50 mg tetraethylammonium perchlorate and 20 cm^3 toluene. [b] In g.

Table 4 Analytical and ^{31}P NMR results for $M(S_2PPh_2)_2$ with calculated values in parentheses

M	Colour	Analysis (%)			$\delta(^{31}P)$[a]
		M	C	H	
Co	Green	9.95 (10.6)	—	—	*b*
Ni	Violet	10.0 (10.5)	5.08 (51.6)	3.65	75.4[c]
Zn	Colourless	12.6 (13.1)	—	—	61.2
Cd	Colourless	17.9 (18.4)	—	—	65.0
$[Ni(Se_2PPh_2)_2]$	Dark red	7.15 (7.90)	39.1 (38.7)	2.80 (2.70)	12.1

[a] In ppm, relative to external 85% H_3PO_4 (δ 0); solutions in Me_2SO. [b] Paramagnetic. [c] In benzene solution.

Table 5 Summary of crystal data, intensity collection and structure refinement

	1	2	3
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
M	1845.8	698.8	1011.6
a/Å	14.719(4)	8.950(6)	12.420(5)
b/Å	13.649(5)	9.745(4)	9.737(7)
c/Å	17.112(5)	10.366(7)	20.729(16)
α/°	112.40(3)	112.28(4)	—
β/°	106.22(2)	99.09(5)	100.29(5)
γ/°	115.39(2)	90.88(4)	—
U/Å^3	2434.8	823.2	2466.5
Z	1	1	2
D_c/g cm^{-3}	1.26	1.41	1.36
D_m/g cm^{-3}	1.28	1.39	1.35
Crystal dimensions/mm	0.2 × 0.25 × 0.37	0.14 × 0.18 × 0.24	0.18 × 0.25 × 0.22
μ/cm^{-1}	9.82	7.83	5.25
2 θ/°	4–45 ($+h$, $\pm k$, $\pm l$)	4–40 ($+h$, $\pm k$, $\pm l$)	4–40 ($+h$, $\pm k$, $\pm l$)
Background time/scan time	0.5	0.5	0.5
Total reflections measured	6697	2466	2307
Unique data used [$I \geqslant 3\sigma(I)$]	3622	1348	1893
No. of parameters	351 (two blocks)	127	172
R	0.0632	0.1612	0.0533
R'	0.0645	0.177	0.0616
Maximum (e Å^{-3}) in the final difference map	0.73	2.2	0.51

$SC_5H_{11})_4(dppm)_2]$ has been discussed elsewhere.[12] We should also note that $Cu(PPh_2)$ is insoluble in MeCN, benzene or toluene, but soluble in piperidine and in acetonitrile solutions of PPh_3 or $Ph_2PC_2H_4PPh_2$, suggesting that adducts of these ligands should also be accessible. In view of the wide variety of structures reported for $Cu(SR)L_n$ compounds, it may well be that a similar range will emerge for copper(I) phosphido systems.

The bond lengths and angles listed in Table 7 do not require detailed comments, since they are within generally accepted ranges for the atoms in question. There appear to be no examples of Cu^I–PR_2 structures against which to compare the copper–phosphorus bond parameters.

Synthesis of $M(S_2PPh_2)_n$ *Complexes.*—The results in Tables 3 and 4 establish a simple electrochemical synthesis of diphenylthiophosphinato derivatives of Co, Ni, Zn and Cd. Other routes to such compounds have been described by McCleverty *et al.*,[17] and for other $R_2PS_2^-$ compounds by Kuchen and Hertel.[18] The characterization of these products depended upon elemental analysis and spectroscopy. The ^{31}P NMR resonance (Table 4) for $[Zn(S_2PPh_2)_2]$ is almost identical to that reported[15] for this compound in $CDCl_3$ (62.8 ppm), and there are only small changes in frequency for the analogues of Cd and Ni. The ^{31}P NMR spectrum of the electrolyte solution (PPh_2H + S, see Table 3) used in the preparation of these compounds showed resonances at −40.28 (s), +21.75 (s) and 55.5 + 55.1 (d) ppm (from 85% H_3PO_4) in the intensity ratio 12:23:1. The first of these is readily identified as unreacted PPh_2H, and the major component is $PPh_2(S)H$ (lit.,[19] 22.0 ppm), with the remaining resonance assigned to $PPh_2(S)SH$ (lit.,[20] 52.3 ppm), suggesting the solution phase reactions (5).

$$PPh_2H \xrightarrow{S} PPh_2(S)H \xrightarrow{S} Ph_2P(S)SH \qquad (5)$$

The electrochemical synthesis probably involves the sequence (6) and (7) in agreement with E_F = 0.5 mol F^{-1} for each of the metals studied. There may be alternative paths involving PPh_2^- to give $M(PPh_2)_2$, with a subsequent reaction between this

Table 6 Final fractional coordinates for the non-hydrogen atoms of $[Cu_4(PPh_2)_4(dppm)_2]\cdot 4MeCN$, with standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	0.0549(1)	0.3558(1)	0.4235(1)	C(51)	0.1771(8)	0.6900(9)	0.8999(7)
Cu(2)	0.1120(1)	0.5877(1)	0.6723(1)	C(52)	0.1912(10)	0.7754(10)	0.9870(7)
P(1)	−0.1449(2)	0.5549(2)	0.4110(2)	C(53)	0.2971(11)	0.8593(12)	1.0775(9)
P(2)	0.1450(2)	0.7695(2)	0.6792(2)	C(54)	0.3883(13)	0.8576(13)	1.0814(10)
P(3)	−0.1316(2)	0.6280(2)	0.6752(2)	C(55)	0.3777(13)	0.7749(13)	0.9970(10)
P(4)	0.0436(2)	0.5826(2)	0.7757(2)	C(56)	0.2729(11)	0.6901(11)	0.9074(9)
C(01)	−0.0277(7)	0.6659(8)	0.7908(6)	C(61)	−0.0510(8)	0.4344(9)	0.7684(7)
C(11)	−0.0982(9)	0.6904(10)	0.3933(7)	C(62)	−0.1096(9)	0.3136(10)	0.6842(8)
C(12)	−0.1643(11)	0.6744(12)	0.3085(8)	C(63)	−0.1915(11)	0.1955(12)	0.6703(9)
C(13)	−0.1258(15)	0.7772(16)	0.2961(11)	C(64)	−0.2097(10)	0.2061(11)	0.7465(8)
C(14)	−0.0168(15)	0.8952(15)	0.3689(13)	C(65)	−0.1484(10)	0.3254(11)	0.8343(9)
C(15)	0.0504(12)	0.9137(12)	0.4537(11)	C(66)	−0.0685(10)	0.4412(11)	0.8455(8)
C(16)	0.0110(10)	0.8134(10)	0.4669(8)	C(71)	−0.2762(8)	0.4844(8)	0.6293(6)
C(21)	−0.3063(8)	0.4667(10)	0.3506(6)	C(72)	−0.3699(9)	0.4264(10)	0.5379(7)
C(22)	−0.3569(9)	0.5311(11)	0.3618(7)	C(73)	−0.4828(11)	0.3201(11)	0.4991(9)
C(23)	−0.4790(12)	0.4615(14)	0.3232(9)	C(74)	−0.5023(11)	0.2658(12)	0.5528(9)
C(24)	−0.5489(12)	0.3289(16)	0.2720(10)	C(75)	−0.4128(10)	0.3210(11)	0.6425(8)
C(25)	−0.5023(10)	0.2612(11)	0.2582(8)	C(76)	−0.2996(9)	0.4314(9)	0.6825(7)
C(26)	−0.3836(9)	0.3265(10)	0.2949(7)	C(81)	−0.1458(8)	0.7629(8)	0.7251(6)
C(31)	0.1970(9)	0.9133(8)	0.7990(6)	C(82)	−0.1721(9)	0.8067(10)	0.6661(8)
C(32)	0.2902(10)	0.9580(11)	0.8871(8)	C(83)	−0.1757(10)	0.9132(11)	0.7047(9)
C(33)	0.3212(12)	1.0639(12)	0.9799(10)	C(84)	−0.1508(10)	0.9782(12)	0.7979(9)
C(34)	0.2611(12)	1.1115(13)	0.9767(10)	C(85)	−0.1238(9)	0.9387(10)	0.8586(8)
C(35)	0.1744(12)	1.0762(13)	0.8938(10)	C(86)	−0.1241(8)	0.8304(9)	0.8205(7)
C(36)	0.1427(10)	0.9733(11)	0.8025(9)	N(1)	0.1074(14)	0.3116(12)	0.0261(10)
C(41)	0.2476(8)	0.8502(9)	0.6475(7)	N(2)	0.4720(11)	0.4144(12)	0.0226(5)
C(42)	0.3132(10)	0.9845(11)	0.6900(8)	C(02)	0.1969(17)	0.4420(18)	−0.0359(14)
C(43)	0.3929(11)	1.0428(13)	0.6640(9)	C(03)	0.1455(12)	0.3650(13)	−0.0001(10)
C(44)	0.4075(11)	0.9682(12)	0.5964(9)	C(04)	0.4655(29)	0.4047(19)	−0.0443(11)
C(45)	0.3404(10)	0.8357(11)	0.5493(9)	C(05)	0.4607(18)	0.4022(19)	−0.1316(9)
C(46)	0.2611(9)	0.7763(11)	0.5762(7)				

Table 7 Selected bond lengths (Å) and angles (°) for $[Cu_4(PPh_2)_4(dppm)_2]\cdot 4MeCN$, with standard deviations in parentheses

Cu(1)–Cu(2)	3.106(2)	Cu(2)–P(2)	2.262(4)
Cu(1)–P(1)	2.271(3)	Cu(2)–P(1)*	2.266(4)
Cu(1)–P(2)	2.274(3)	Cu(2)–P(3)	2.275(4)
Cu(1)–P(31)	2.304(4)		
P(1)–C(11)	1.853(15)	P(3)–C(61)	1.828(12)
P(1)–C(21)	1.841(11)	P(3)–C(01)	1.846(14)
P(2)–C(31)	1.846(10)	P(4)–C(71)	1.818(9)
P(2)–C(41)	1.810(13)	P(4)–C(81)	1.841(13)
P(3)–C(51)	1.831(9)	P(4)–C(01)	1.837(11)
P(1)–Cu(1)–Cu(2)	122.9(1)	Cu(2)*–P(1)–C(11)	111.7(5)
P(1)–Cu(1)–P(2)	131.3(1)	Cu(2)*–P(1)–C(21)	108.1(4)
P(1)*–Cu(2)–P(2)	129.5(1)	C(11)–P(1)–C(21)	102.2(6)
P(1)*–Cu(2)–P(4)	126.5(1)	Cu(1)–P(2)–C(31)	110.4(4)
P(2)–Cu(1)–P(3)	105.7(1)	Cu(1)–P(2)–C(41)	122.3(3)
P(2)–Cu(2)–P(4)	104.0(1)	Cu(2)–P(2)–C(31)	117.5(4)
Cu(1)–P(2)–Cu(2)	86.5(1)	Cu(2)–P(2)–C(41)	120.1(5)
Cu(1)–P(3)–C(5)	123.5(4)	Cu(31)–P(2)–C(41)	100.9(5)
Cu(1)–P(3)–C(6)	109.3(4)	Cu(1)–P(3)–C(01)	112.6(4)
C(01)–P(4)–C(71)	106.0(5)	Cu(2)–P(4)–C(01)	114.3(4)
C(01)–P(4)–C(81)	101.0(5)	Cu(2)–P(4)–C(7)	104.8(4)
C(71)–P(4)–C(81)	101.7(5)	Cu(2)–P(4)–C(8)	125.6(4)
Cu(1)–P(1)–C(11)	109.3(3)	C(01)–P(3)–C(51)	102.4(5)
Cu(1)–P(1)–C(21)	112.1(4)	C(01)–P(3)–C(61)	103.5(6)
Cu(2)*–P(1)–Cu(1)	112.9(2)	C(51)–P(3)–C(61)	103.5(5)

* Symmetry equivalent position.

species and S, but since Ph_2PS_2H is much the strongest acid amongst the three solutes it seems reasonable to identify equations (6) and (7) as the important electrochemical pathway,

$$\text{cathode: } 2Ph_2PS_2H + 2e \longrightarrow 2Ph_2PS_2^- + H_2(g) \quad (6)$$

$$\text{anode: } 2Ph_2PS_2^- + M \longrightarrow M(S_2PPh_2) + 2e \quad (7)$$

despite the low concentration of Ph_2PS_2H in the electrolyte phase.

The infrared spectra of these $M(S_2PPh_2)_2$ compounds also confirm the proposed formulation. In each case we observed the modes identified[18] as ν_1 and ν_2 of the ligand as doublets of mean wavenumbers 580 + 470 (Co), 575 + 470 (Ni), 561 + 473 (Zn) and 579 + 470 cm^{-1} (Cd).

Studies of $Ni(PPh_2)\cdot PPh_2H$.—While the electrochemical procedures discussed earlier give rise to $M(PPh_2)_n$ products in which the metal is in a conventional oxidation state, the product of the electrochemical oxidation of nickel under the conditions noted in Table 1 is an unusual nickel(I) compound, incorporating a molecule of neutral ligand. The most important spectroscopic evidence is the presence of a strong ν(P–H) mode at 2245 cm^{-1} in the infrared spectrum, together with the usual features of the PPh_2^- ligand. No ^{31}P NMR resonance was detected, in keeping with the fact that nickel(I) compounds are paramagnetic. The chemical evidence confirms the oxidation state of the metal. Reaction with sulphur gives $[Ni(S_2PPh_2)_2]$ and H_2S (and thence CuS), according to the stoichiometry (8), and a

$$2Ni(PPh_2)\cdot PPh_2H + \text{excess S} \longrightarrow 2[Ni(S_2PPh_2)_2] + H_2S \quad (8)$$

qualitatively similar reaction with selenium was also observed. In the case of $[Ni(S_2PPh_2)_2]$ the product was identical to that prepared electrochemically. Similarly the aerial oxidation of solutions of $Ni(PPh_2)\cdot PPh_2H$ gives rise to a nickel(II) derivative of diphenylphosphinic acid, whose structure is discussed below.

The electrochemical synthesis of $Ni(PPh_2)\cdot PPh_2H$ apparently involves the initial formation of $[Ni(PPh_2)_2]$ at the anode, since E_F = 0.48 mol F^{-1} (Table 1). The subsequent reaction is probably (9). We were unable to obtain crystals of appropriate

Table 8 Final fractional coordinates for the non-hydrogen atoms of $[Ni(O_2PPh_2)_2(HO_2PPh_2)_2(MeCN)_2]$, with standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	0.0	0.0	0.0	C(22)	0.2850(5)	−0.1803(7)	0.0873(3)
P(1)	0.2362(1)	0.0950(2)	0.0961(1)	C(23)	0.3255(6)	−0.3079(8)	0.1115(4)
P(2)	−0.0835(1)	0.1855(2)	0.1186(1)	C(24)	0.3713(6)	−0.3199(8)	0.1762(4)
O(1)	0.1547(3)	0.0733(4)	0.0350(2)	C(25)	0.3782(6)	−0.2120(8)	0.2156(4)
O(2)	0.2010(3)	0.1718(5)	0.1525(2)	C(26)	0.3389(6)	−0.0828(8)	0.1932(4)
O(3)	−0.0682(3)	0.1425(4)	0.0523(2)	C(31)	−0.1397(5)	0.3563(7)	0.1116(3)
O(4)	0.0180(3)	0.1854(5)	0.1726(2)	C(32)	−0.1780(6)	0.4190(8)	0.1628(4)
N(1)	−0.0132(4)	0.1404(5)	−0.0762(3)	C(33)	−0.2185(7)	0.5527(9)	0.1564(4)
C(1)	−0.0302(5)	0.2186(7)	−0.1167(3)	C(34)	−0.2203(6)	0.6219(9)	0.1005(4)
C(2)	−0.0559(7)	0.3185(8)	−0.1691(4)	C(35)	−0.1817(6)	0.5644(8)	0.0494(4)
C(11)	0.3496(5)	0.1906(6)	0.0753(3)	C(36)	−0.1420(6)	0.4291(8)	0.0542(4)
C(12)	0.3982(6)	0.2948(7)	0.1133(4)	C(41)	−0.1806(5)	0.0801(6)	0.1497(3)
C(13)	0.4852(6)	0.3692(8)	0.0939(4)	C(42)	−0.2910(5)	0.0883(7)	0.1234(3)
C(14)	0.5185(6)	0.4431(8)	0.1201(4)	C(43)	−0.3673(6)	0.0048(8)	0.1462(4)
C(15)	0.4745(6)	0.2321(8)	0.0007(4)	C(44)	−0.3326(6)	−0.0866(8)	0.1954(4)
C(16)	0.3884(5)	0.1570(8)	0.0193(3)	C(45)	−0.2261(6)	−0.0954(8)	0.2224(4)
C(21)	0.2918(5)	−0.0674(7)	0.1270(3)	C(46)	−0.1483(5)	−0.0141(7)	0.2000(3)

Table 9 Selected bond lengths (Å) and angles (°) for $[Ni(O_2PPh_2)_2(HO_2PPh_2)_2(MeCN)_2]$, with standard deviations in parentheses

Ni–O(1)	2.056(4)	P(1)–C(11)	1.802(7)
Ni–O(3)	2.036(4)	P(1)–C(21)	1.796(6)
Ni–N	2.073(5)	P(2)–C(31)	1.796(6)
P(1)–O(1)	1.489(4)	P(2)–C(41)	1.787(6)
P(1)–O(2)	1.514(4)	C(1)–N	1.126(7)
P(2)–O(3)	1.483(4)	C(1)–C(2)	1.450(10)
P(2)–O(4)	1.524(4)	O(2)···O(4)	2.399(4)
O(1)–Ni–O(3)	91.6(2)	N–Ni–O(1)	89.0(2)
O(1)–P(1)–O(2)	118.8(2)	N–Ni–O(3)	88.9(2)
O(1)–P(1)–C(11)	108.1(3)	O(4)–P(2)–O(3)	117.2(2)
O(2)–P(1)–C(11)	105.9(3)	O(3)–P(2)–C(31)	107.3(3)
O(1)–P(1)–C(21)	109.7(3)	O(4)–P(2)–C(31)	104.6(3)
O(2)–P(1)–C(21)	107.8(3)	O(4)–P(2)–C(41)	106.4(3)
O(11)–P(1)–C(21)	105.8(3)	O(3)–P(2)–C(41)	112.3(3)
P(1)–O(2)–Ni	145.1(3)	C(31)–P(2)–C(41)	108.5(3)
Ni–N–C(1)	173.5(5)	C(2)–C(1)–N	178.2(7)

$$[Ni(PPh_2)_2] + PPh_2H \longrightarrow Ni(PPh_2)\cdot PPh_2H + \tfrac{1}{2}P_2Ph_4 \quad (9)$$

quality for an X-ray study of this interesting and unusual compound.

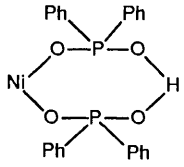
The Reaction between $Ni(PPh_2)\cdot PPh_2H$ *and* PhNCS.—The compound $[Ni\{PPh_2(SCNPh)\}_2]$ can be obtained by two different methods. The electrochemical route involves the oxidation of nickel into a solution phase prepared by mixing PPh_2H and PhNCS in acetonitrile. The ^{31}P NMR spectrum of such a solution lacks any resonance at −40.3 ppm, indicating the complete conversion of PPh_2H into a new species, which gives rise to a singlet at +20.1 ppm, assigned to $Ph_2PC(S)N(H)Ph$, formed by the attack of the C atom of PhNCS at the phosphorus of PPh_2H, and subsequent proton transfer. The electrochemical efficiency for the anodic oxidation was 0.51 mol F^{-1}, so that the electrochemical reactions presumably parallel those in equations (6) and (7).

The reaction between PhNCS and $Ni(PPh_2)\cdot PPh_2H$ gives rise to an identical product, with ^{31}P NMR resonance at 65.6 ppm (in dimethylformamide), and characteristic infrared absorptions at 1555 [ν(C=N)] and 926 cm^{-1} [ν(P–C–S)]. These IR features have been reported for a number of transition-metal compounds containing $M\{Ph_2PC(S)NR\}$ (R = Me or Ph).[21,22] The mechanism of the reaction in question is unclear, since it involves the oxidation $Ni^{I} \longrightarrow Ni^{II}$, together with a reaction which can be regarded formally as the addition of Ni–P across the C=S bond of the phenyl isothiocyanate. The structure of the product was confirmed by an X-ray crystallographic analysis which could not be completed satisfactorily because of disorder problems, but which showed beyond question that the nickel co-ordination is square planar, and that the ligand is the form shown in Fig. 2, which also gives the bond distances and angles. Since most of the X-ray scattering arises from the core structure shown, these values are reliable to the deviations quoted. The Ni–P and Ni–S bond distances are close to those found[23] in $[Ni\{Ph_2PC(S)S\}_2]$ [Ni–P 2.185(2), Ni–S 2.167(3) Å], and the bite angle in that compound [S–Ni–P 77.2(2)°] is also equal to that in Fig. 2. The other features are similar to those reported for organomolybdenum complexes involving ligands of this type.[21,22]

Formation and Structure of $[Ni(O_2PPh_2)_2(HO_2PPh_2)(MeCN)_2]$.—The oxidation of $Ni(PPh_2)\cdot PPh_2H$ by atmospheric oxygen gives rise to a product which is formally analogous to those obtained on treating this compound with either sulphur or selenium, namely $[Ni(E_2PPh_2)_2]$ (E = O, S or Se). Information on the mechanism of these interesting reactions is lacking.

The structure of the product shown in Fig. 3 confirms the oxidation state of nickel, but also reveals the interesting ligand–ligand interactions in this molecule. We first note that the co-ordination kernel is NiO_4N_2, in D_{2h} symmetry. The co-ordinated MeCN molecules show no unusual features and need not be discussed further. The remainder of the molecule can be described as a nickel(II) ion, co-ordinated by four $Ph_2PO_2^-$ ligands, with two protons which stabilize the ligands by O–H···O hydrogen bonding. There are small differences between Ni–O(1) and Ni–O(3), but otherwise the $Ph_2PO_2^-$ ligands centred on P(1) and P(2) are essentially identical in interatomic distances and angles. The sums of the bond angles at P(1) and P(2) are 656.1 and 656.3° respectively, so that each phosphorus is essentially tetrahedrally co-ordinated. The P–C distances are within the accepted range, similar to those in other $Ph_2PO_2^-$ complexes.[24–26]

The co-ordination system can be described as either $H_2[Ni(Ph_2PO_2)_4(MeCN)_2]$, or as $[Ni(MeCN)_2]^{2+}$ co-ordinated by two bidentate $[Ph_2P(O)OHO(O)PPh_2]^-$ ligands. This latter formalism emphasizes that the stability of this complex depends in part on the hydrogen bonding between O(2) and O(4). The interatomic distance of 2.399(4) Å is very close to that reported[26] for the essentially isostructural compound $[Mn(O_2PPh_2)_2(HO_2PPh_2)_2(dmf)_2]$ (dmf = dimethylformamide). An interesting feature is that although the diphenylphosphinato ligands are all monodentate with respect to the nickel atom, the P–O bond lengths do not imply the presence of $Ph_2P(=O)O$. In fact the P–O(1,3) bonds which lead to co-ordination to nickel are slightly shorter than P–O(2,4), which involve the oxygen atoms which are hydrogen-bonded together.



The ring system shown below then apparently involves strong M–O interactions (M = Ni^{2+} or H^+) at each terminus.

One final point is the marked colour change between this complex and the $[Ni(S_2PPh_2)_2]$ and $[Ni(Se_2PPh_2)_2]$ compounds which are red-violet and deep red respectively. These colours, and the absence of solvate molecules, suggest that the large ligating atoms result in square-planar co-ordination at nickel in these compounds.

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