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Synthesis of a polymer-supported *o*-phenylene(diphosphine) and characterization of some metal complexes

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Abstract

The synthesis is described of the polymer-supported diphosphine, PolPP, in which an *o*-$C_6H_3(PPh_2)_2$ unit is linked *via* a $-CH_2O$ group in the 4-position of the benzene ring to a Merrifield resin. The preparations of the complexes (PolPP)$NiCl_2$, (PolPP)$PtCl_2$, (PolPP)$Rh(PPh_3)Cl$ and (PolPP)$Ru(PPh_3)Cl_2$ and related model compounds are reported, and their characterization by UV-visible spectroscopy and metal edge EXAFS is described.

Key words: Nickel; Platinum; Rhodium; Ruthenium; Diphosphine; Polymer; Supported catalyst

1. Introduction

The development of polymer-supported catalysts in the last 25 years arose from attempts to combine the specificity of homogeneous catalysts with the ease of separation of catalyst and products achieved with heterogeneous catalysts. A variety of phosphine-based systems have been described, mostly with the metal centre coordinated to single pendant $-PR_2$ groups [1–3], although there are a few supported diphosphine systems [4–6]. Among the problems experienced were the often ill-defined coordination sphere of the metal and/or the presence of several metal environments, and the loss of the metal from the support. Here we report an attempt to address both problems by using a polymer supported *o*-phenylene diphosphine.

The ligands *o*-$C_6H_4(PR_2)_2$ normally function as chelates, with very few established examples of monodentate or bridging bidentate behaviour [7]. Recent studies of transition metals in high oxidation states bound to diphosphine ligands [8–10] have shown that complexes of ligands with *o*-phenylene backbones are unusually stable. This "*o*-phenylene backbone effect" has been traced to the rigidity of the backbone which resists dissociation from the metal centre, such dissociation allowing oxidation of the phosphorus centres and reduction of the metal. Thus a supported *o*-phenylene diphosphine should have a single and well-defined metal geometry, with the metal bound to the chelate arms, whilst the "*o*-phenylene backbone effect" should inhibit loss of the metal from the support.

2. Results and discussion

2.1. Polymer diphosphine synthesis

The route chosen involved anchoring of the diphosphine to the polymer through a suitable functional group incorporated into the backbone of the *o*-phenylene ring. The polymer support selected was a Merrifield resin (a chloromethylated styrene–1% divinylbenzene copolymer with *ca.* 1.7 mmol Cl/g), and hence the diphosphine would be attached by substitution of the chlorine in the $-CH_2Cl$ group. The most convenient synthesis of the "parent" diphosphine *o*-$C_6H_4(PPh_2)_2$ involves reaction of *o*-$C_6H_4F_2$ with $NaPPh_2$ in liquid ammonia [11] or $LiPPh_2$ in tetrahy-

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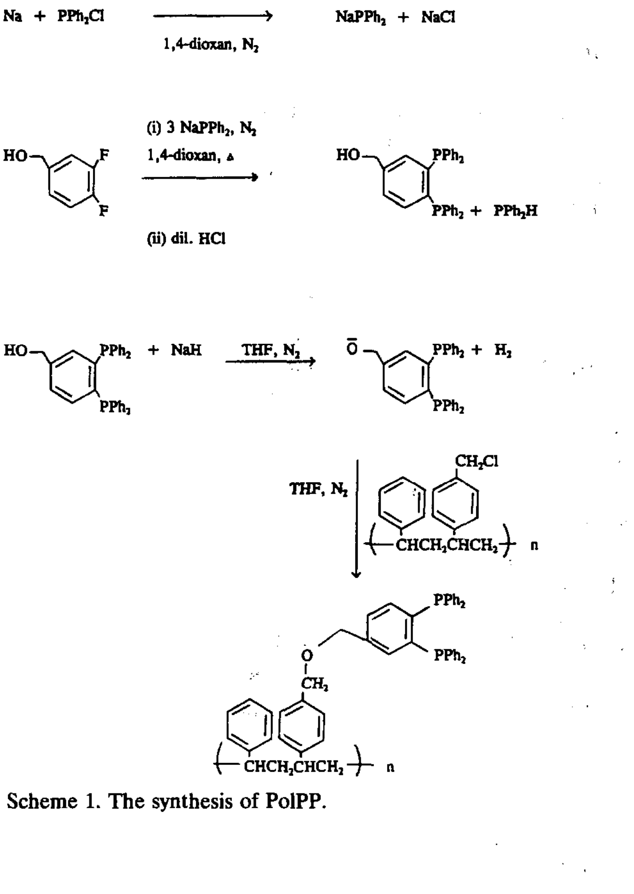
drofuran (THF) [12]. Since F is more easily substituted than Cl or Br by PPh_2^- in polyhalobenzenes [11], we initially investigated the reaction of 1,2-F_2-4-BrC_6H_3 with $LiPPh_2$ in THF, in the hope that 1,2-$(PPh_2)_2$-4-BrC_6H_3 would result. However, the reaction yielded a complex mixture of mono- and diphosphines, the major components of which were identified by a combination of mass spectrometry and ^{31}P NMR spectroscopy as isomers of $C_6H_3F(PPh_2)_2$. Studies were switched to the phenol 1,2-F_2-4-HOC_6H_3, but we found that the phenol group deactivated the C–F bonds towards substitution by PPh_2^-, and even under forcing condition with an excess of phosphide only one fluorine was substituted. The deactivating effect was overcome by changing to 1,2-F_2-4-$HOCH_2C_6H_3$, which reacted with 4 equiv. of $LiPPh_2$ in THF to form a mixture of 1,2-$(PPh_2)_2$-4-$HOCH_2C_6H_3$, PPh_2H and $Ph_2PCH_2CH_2CH_2CH_2OH$. The 4-hydroxybutyl(diphenylphosphine) resulted from ring opening of the THF by PPh_2^-, and was avoided by using $NaPPh_2$ in 1,4-dioxan as the phosphide reagent. The latter reacted with 1,2-F_2-4-$HOCH_2C_6H_3$ in a 4:1 mol ratio to give 1,2-$(PPh_2)_2$-4-$HOCH_2C_6H_3$ and PPh_2H. The PPh_2H was removed by distillation in high vacuum to leave the diphosphine as a pale yellow oil, which was identified by mass spectrometry (showing a parent ion at m/e = 476, and the characteristic fragmentation pattern of *o*-phenylene bidentates [13]). The ^{31}P NMR spectrum was a four-line AB pattern centred at -12.6 ppm which was analysed [14] to give $\nu_0\delta$ 173 Hz and $^3J(PP)$ = 161 Hz, with the correct line intensities. The ^{31}P NMR parameters are similar to those for other polyphosphinobenzenes [15].

The hydroxy function was deprotonated with NaH in THF, and the product stirred with the Merrifield resin overnight. The polymer was washed with copious amounts of water, CH_2Cl_2, THF and diethyl ether, and finally dried in high vacuum. The polymer-supported diphosphine is an air-stable white solid. The synthetic route is summarized in Scheme 1. The Merrifield resin used had *ca.* 1.7 mmol of Cl/g (confirmed by analysis) which corresponds to approximately one chlorine for every five styrene units. After attachment of the diphosphine, analysis showed an approximate 1:1 P/Cl ratio, consistent with the replacement of one third of the chlorines by diphosphine units. This places one diphosphine group on average for about every 15 styrene building blocks in the polymer, and thus coordination of an individual metal centre to more than one diphosphine is unlikely. Whilst some of the chlorine sites may be inaccessible to the large diphosphine group, a higher diphosphine loading might be obtainable under more forcing conditions, or by using a resin with a higher initial Cl concentration.

2.2. Metal complexes

The long term aim of this work is to obtain new polymer-supported catalysts, but this initial study was limited to binding some common metal substrates to the polymer and characterizing the metal environment. As a result of the strong chelating nature of the diphosphine and the large separations between neighbouring diphosphine moieties, we expected that only a single metal environment would be present in most cases, of the type $(PolPP)ML_n$ (PolPP = polymer–$OCH_2C_6H_3(PPh_2)_2$, L = ancillary ligands). Hence identification of the metal site should be greatly aided by comparison of the spectroscopic and structural data on the compounds with those of model compounds of type $(PP)ML_n$ (PP = *o*-$C_6H_4(PPh_2)_2$).

The polymer diphosphine "swollen" in THF was treated with $NiCl_2$, $Pd(MeCN)_2Cl_2$, $Pt(MeCN)_2Cl_2$, $Rh(PPh_3)_3Cl$, $Ru(PPh_3)_3Cl_2$, and *trans*-$Ir(CO)(PPh_3)_2Cl$ as described in the Experimental section. The products were Soxhlet extracted with THF for 8 h to remove unbound metal complex, displaced ligands etc. and then dried in high vacuum. Approximate compositions were established by analysis (Experimental section), and the metal environment examined principally by diffuse reflectance UV/visible spectroscopy and metal edge EXAFS (extended X-ray absorption



Scheme 1. The synthesis of PolPP.

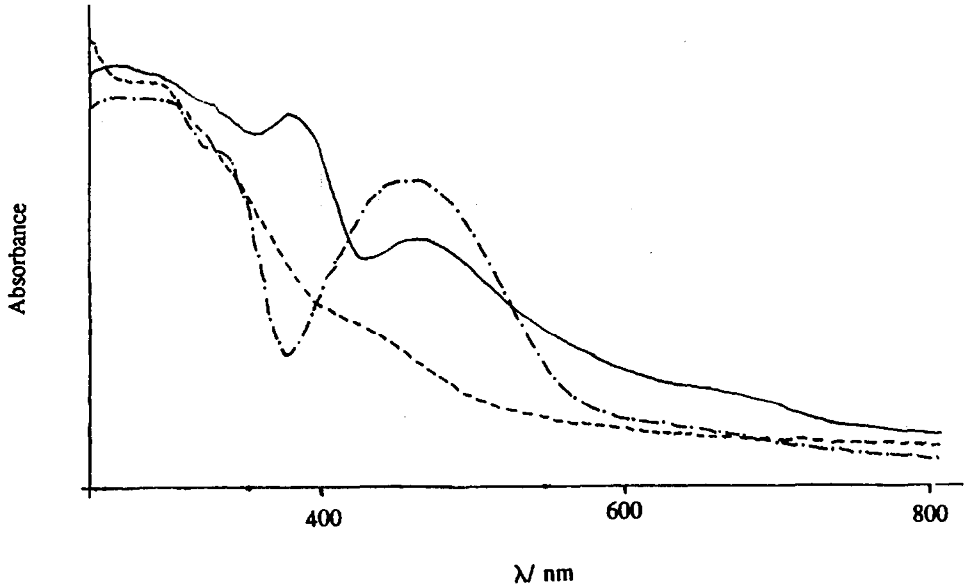


Fig. 1. Diffuse reflectance UV-visible spectra of Ni(PP)Cl_2 (–·–·–); (PolPP)$NiCl_2$ (———); and PolPP (- - - -).

fine structure) studies. Of the substrates tested, only *trans*-Ir(CO) $(PPh_3)_2Cl$ did not react with the polymer diphosphine under the conditions used. * It is convenient to discuss each metal separately.

2.2.1. Nickel

The reaction of PolPP with $NiCl_2$ in THF gave a fawn polymer. The free diphosphine afforded orange-yellow Ni{4-$HOCH_2C_6H_4(PPh_2)_2$}Cl_2, which was diamagnetic and had bands at 21 700 and 30 000 cm^{-1} in its UV-visible spectrum, consistent with a square planar geometry, and very similar to the reported spectroscopic data for Ni(PP)Cl_2 [16]. The $^{31}P\{^1H\}$ NMR spectrum was an AB pattern centred at δ 56.5 ppm ($\delta\nu_0 = 175$ Hz, $^3J(PP) = 78$ Hz), *cf.* Ni(PP)Cl_2 $\delta = 58$ ppm. The fawn polymer was formulated as (PolPP) $NiCl_2$, and assumed to contain square planar coordinated nickel (P_2Cl_2 donor set) on the basis of UV-visible absorptions at 20,600 and *ca.* 26,000 cm^{-1} in its diffuse reflectance spectrum (Fig. 1). The nickel K-edge EXAFS data on the model compound Ni(PP)Cl_2 refined to place Ni–Cl at 2.21 Å and Ni–P at 2.13 Å, which compare well with the X-ray crystallographic data on $Ni(Ph_2PCH_2CH_2PPh_2)Cl_2$ [17] (Table 1). However two sets of fluorescence EXAFS data on (PolPP)$NiCl_2$ did not model particularly well to a P_2Cl_2 set, reflected in high FI and *R*-factors, but placed Ni–P = 2.15 Å and Ni–Cl = 2.24 Å, both reasonable values when compared to the model complex. Examination of the EXAFS data suggested that a low Z backscatterer was present near the nickel, and incorporation of a single oxygen atom as shell 1 produced a dramatic improvement in the fit, with *R* falling by 5% and FI by 25%. This indicates coordination of a fifth ligand by the polymer supported complex, an effect not observed in the "free" model compound, but possibly promoted by the environment within the polymer. The identity of this extra ligand is most likely to be THF from the method of preparation, although water cannot be ruled out. Distinction between square planar and square pyramidal Ni^{II} is sometimes difficult by UV-visible spectroscopy [3,16] and the effect of binding of the weak field O-donor will not greatly change the spectrum.

2.2.2. Platinum

The reaction of $Pt(MeCN)_2Cl_2$ with PolPP gave a pale cream solid, analysis of which showed Pt/Cl/P of 0.8 : 4 : 2 consistent with the formation of (PolPP)$PtCl_2$ (recall that the free polymer has a Cl/P ratio of 1 : 1 see above). The appropriate model complex is Pt(PP)Cl_2 [18,19]. The (PolPP)$PtCl_2$ exhibited a shoulder in the diffuse reflectance spectrum at *ca.* 29,000 cm^{-1} consistent with a planar d^8 centre. The parameters obtained from the platinum L_{III}-edge EXAFS data for both Pt(PP)Cl_2 and (PolPP)$PtCl_2$ are listed in Table 1, along with published X-ray crystallographic data for a related complex. As can be seen, the data for (PolPP)$PtCl_2$ are in excellent agreement with the proposed metal environment (P_2Cl_2).

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* *trans*-Ir(CO)$(PPh_3)_2Cl$ reacted with *o*-$C_6H_4(PPh_2)_2$ in refluxing THF to form orange Ir{*o*-$C_6H_4(PPh_2)_2$}$_2$Cl.

TABLE 1. Structural data

Compound	d(M–P) (Å) [a]	$2\sigma^2$ (Å^2) [b]	d(M–Cl) (Å)	$2\sigma^2$ (Å^2)	FI [c]	R [d]	Ref. [e]
Ni(PP)Cl_2	2.132(2)	0.004(1)	2.207(2)	0.005(2)	3.7	24.5	–
(PolPP)$NiCl_2$ [g]	2.149(2)	0.001(1)	2.256(3)	0.005(1)	4.9	29.4	–
Ni($Ph_2PCH_2CH_2PPh_2$)Cl_2 [f]	2.151(8)		2.200(4)				17
Pt(PP)Cl_2	2.260(8)	0.012(3)	2.312(5)	0.004(1)	4.6	26.8	–
(PolPP)$PtCl_2$	2.256(12)	0.011(4)	2.302(7)	0.003(1)	7.6	32.7	–
Pt($Ph_2PCH_2CH_2PPh_2$)Cl_2 [f]	2.227(4)		2.355(2)				20
Pd(PP)Cl_2	2.238(3)	0.005(1)	2.335(3)	0.004(1)	2.9	20.9	–
Pd($Ph_2PCH_2CH_2PPh_2$)Cl_2 [f]	2.230(4)		2.359(4)				21
(PolPP)Rh(PPh_3)Cl	2.193(3)	0.009(1)	2.308(5)	0.002(1)	2.4	16.5	–
Rh(PPh_3)$_3$Cl [f]	2.304(4) 2.225(4) 2.338(4)		2.404(4)				22
(PolPP)Ru(PPh_3)Cl_2	2.219(20) 2.339(45)	0.007(4) 0.028(22)	2.391(30)	0.012(4)	9.9	32.4	–
Ru(PPh_3)$_3$$Cl_2$	2.230(8) 2.374(6) 2.412(6)		2.387(7)				28

[a] Standard deviations in parentheses. Note that the systematic errors in bond distances arising from the data collection and analysis procedures are *ca.* 0.02–0.03 Å for well defined coordination shells. [b] $2\sigma^2$ is the Debye–Waller factor. [c] The fit index is defined as: $FI = \Sigma_i[(\chi^T - \chi^E)k_i^3]^2$. [d] The R-factor is defined as: $R = [\int(\chi^T - \chi^E)k^3dk/\int\chi^E k^3dk] \times 100\%$. [e] This work unless otherwise indicated. [f] X-Ray crystallographic data. [g] Data for "PolPPNiCl_2(THF)", see text. Ni–O = 1.865(11) Å, $2\sigma^2$ = 0.014(3) Å^2.

2.2.3. *Palladium*

The reaction of Pd(MeCN)$_2$$Cl_2$ with PolPP in THF proved to be very sensitive to the reaction conditions, materials varying in colour from pale yellow to dark brown being obtained. It was subsequently found that the (phosphine-free) Merrifield polymer turned brown when warmed with Pd(MeCN)$_2$$Cl_2$ in THF, indicating deposition of a palladium species on the polymer. We were unable to model the palladium K-edge EXAFS data collected from a pale yellow sample of "(PolPP)PdCl_2", although the Fourier transform of the raw data showed features at *ca.* 1.8, 2.2 and 2.8 Å that are not unreasonable for Pd–C, Pd–P/Cl, and Pd–Pd distances. It is clear that this route does not yield a

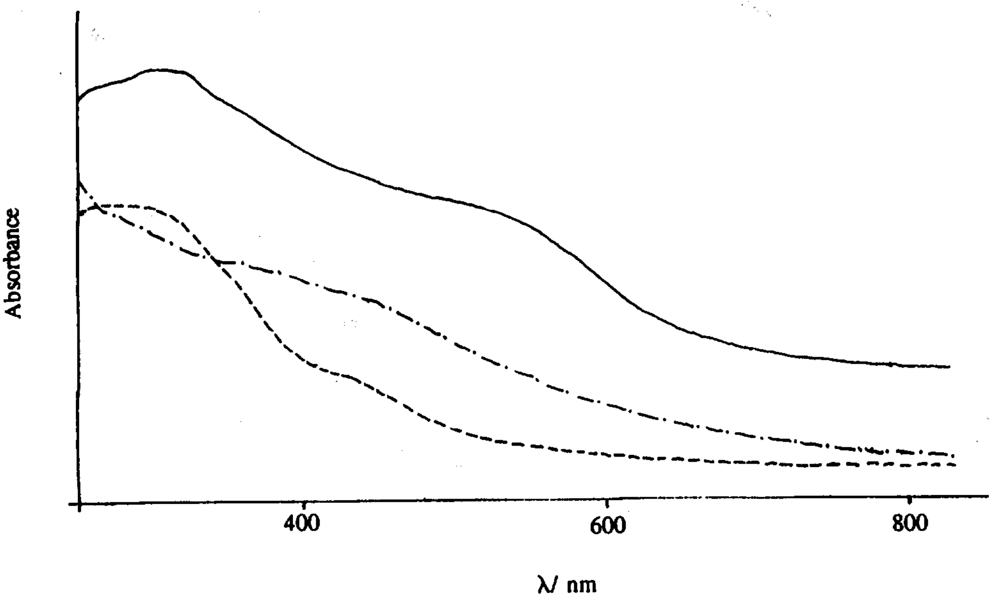

Fig. 2. Diffuse reflectance UV-visible spectra of Rh(PPh_3)$_3$Cl (–·–·–); (PolPP)Rh(PPh_3)Cl (———); and PolPP (------).

single palladium site on the polymer. EXAFS data for the model Pd(PP)Cl_2 were collected and solved (Table 1).

2.2.4. Rhodium

The reaction of Wilkinson's complex $Rh(PPh_3)_3Cl$, with PolPP in THF under oxygen-free conditions, gave an orange solid. The solid appeared to be air-stable when dry, and analysis showed a Rh/Cl/P ratio of *ca.* 0.7 : 3 : 3, which suggested the most likely metal species to be (PolPP)Rh(PPh_3)Cl (for which 1 : 3 : 3 was expected after allowing for the residual chlorine in the polymer). Attempts to make Rh(PP)(PPh_3)Cl serve as a model were unsuccesful. The $^{31}P\{^1H\}$ NMR spectrum of a freshly prepared oxygen-free THF solution of $Rh(PPh_3)_3Cl$ and PP in a 1 : 1 ratio was consistent with the presence of Rh(PP)(PPh_3)Cl and free PPh_3 as the main species, but the spectrum changed with time, and the required complex was not isolated as a solid. * The orange form of $Rh(PPh_3)_3Cl$ [22] was therefore used as a model complex. The diffuse reflectance spectrum of the polymer-bound rhodium species showed a broad absorption at *ca.* 19,000 cm^{-1}, and a shoulder at 26,000 cm^{-1}. The orange form of $Rh(PPh_3)_3Cl$ has absorptions at 23,450 and 27,900 cm^{-1} (Fig. 2).

Rhodium EXAFS data for $Rh(PPh_3)_3X$ (X = Cl or Br) and for rhodium bound to a phosphinated polymer (as Pol{$(PPh_2)_2$-$Rh_2(\mu\text{-}Cl)_2(PPh_3)_2$}) were reported some years ago [23,24]. The best fit for the rhodium K-edge EXAFS data on (PolPP)Rh(PPh_3)Cl was for a two-shell model with P_3 as shell 1 and a single chlorine as shell 2 (Fig. 3). Three different Rh–P distances might have been expected for this material, and indeed three are present in the structure of $Rh(PPh_3)_3Cl$ determined by X-ray diffraction [22]. However, attempts to split shell 1 into two or three shells were unsuccesful, the shells merging on iteration, and the two-shell fit is given in Table 1. The systematic errors arising from data collection and treatment of the EXAFS data are *ca.* ± 0.02–0.03 Å for well defined shells, and may be somewhat greater in these dilute polymer systems, and hence closely spaced shells would not be distinguished. The possibility of other donor sets about the rhodium centre was also investigated by fitting the EXAFS data to single shells of P_4 or Cl_4, and two-shell models of PCl_3, P_2Cl_2 and P_3Cl. The single-shell fits were poor, but, as would be expected given the similar back-scattering of chlorine and phosphorus, the two-shell fits gave reasonable agreement with the experimental data. Comparison of the various models showed that the minimum value of the fit index (defined in Table 1) corresponded to the P_3Cl model, providing support for the presence of this coordination environment, although a P_2Cl_2 model gave only a slightly poorer fit.

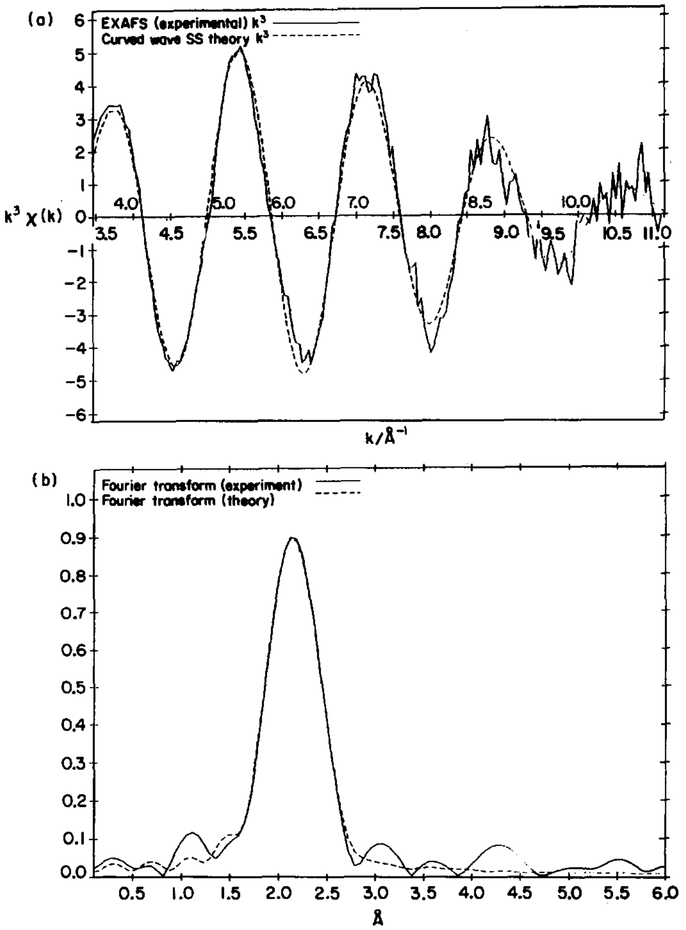

Fig. 3. (a) Background subtracted k^3 weighted EXAFS data and (b) the Fourier transform of (PolPP)Rh(PPh_3)Cl (full line experimental data, broken line calculated).

2.2.5. Ruthenium

A green-brown polymer product resulted from reaction of $Ru(PPh_3)_3Cl_2$ with PolPP in THF, the colour suggesting five-coordinate Ru^{II}, since six-coordinate complexes are usually pale yellow or fawn [7,25]. Analysis indicated a P/Cl ratio of 4 : 4 compared with the 3 : 4 expected for (PolPP)Ru(PPh_3)Cl_2. As with the rhodium system, we were unable to prepare an exact model for the supposed environment since reaction of $Ru(PPh_3)_3Cl_2$ and PP in a 1 : 1 ratio in CH_2Cl_2 resulted in precipitation of the insoluble complex *trans*-$Ru(PP)_2Cl_2$. Other diphosphines have given a variety of complexes from similar reactions [25,26]. The diffuse reflectance spectrum of the green material had broad absorptions at *ca.* 15,500, 20,000 sh, 28,500 cm^{-1}, which may be compared with that of $Ru(PPh_3)_3Cl_2$

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* A 2 : 1 PP/$Rh(PPh_3)_3Cl$ ratio gave $Rh(PP)_2Cl$.

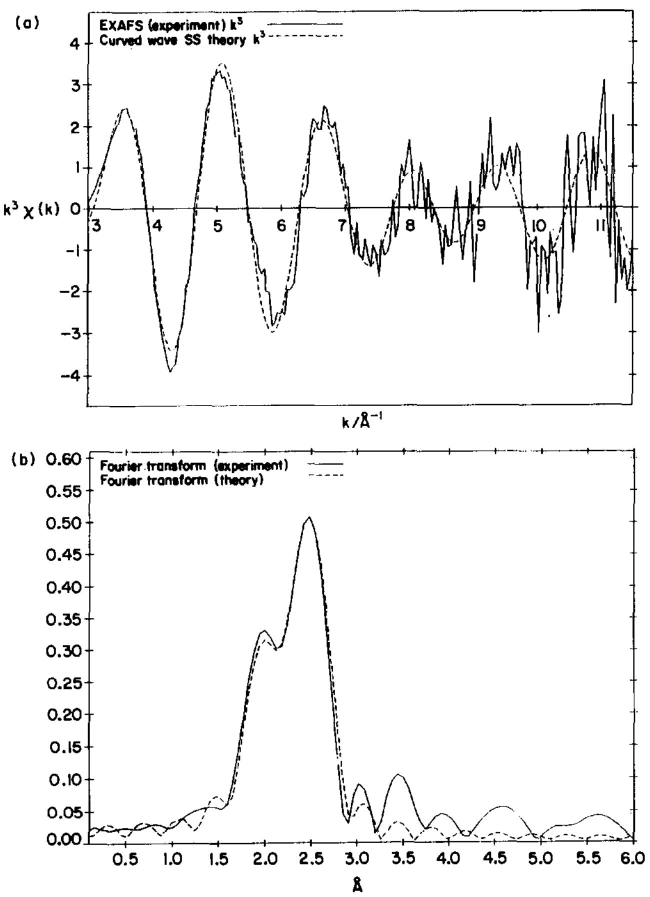

Fig. 4. (a) Background subtracted k^3 weighted EXAFS data and (b) the Fourier transform of (PolPP)Ru(PPh$_3$)Cl$_2$ (full line experimental data, broken line calculated).

(13,600, 20,600, 29,500 cm^{-1}) and with that of a typical six-coordinate diphosphine complex *trans*-Ru(PP)$_2$Cl$_2$ (22,470, 31,150 cm^{-1}) [27]. The spectrum thus provides strong support for the five-coordinate model.

The ruthenium K-edge EXAFS data was modelled to various coordination shells, the best fit (Table 1) being for a P$_3$Cl$_2$ donor set. However, in contrast to the rhodium case, here two different phosphorus shells were resolved (Fig. 4), and the bond lengths may be compared with those determined for Ru(PPh$_3$)$_3$Cl$_2$ [28]. The latter is square pyramidal with an apical phosphine and with *trans* phosphines in the basal plane. Although the detailed geometry of (PolPP)Ru-(PPh$_3$)Cl$_2$ is unknown, the constraints imposed by the chelating diphosphine will produce significant differences, and hence in this system the model data are not expected to be such a good match as with the other metal compounds studied.

3. Experimental details

Physical measurements were made as described previously [29], except that UV-visible spectra were obtained with a Perkin Elmer Lambda 19 spectrometer by using the diffuse reflectance attachment from samples diluted with BaSO$_4$. Microanalytical data were provided by the microanalytical service of University College, London (C, H, P, Cl) and B.P. Chemicals, Sunbury (metals). These are not easy systems to analyse, and the precision of the P and metal analyses is *ca.* ± 0.5%. Hence the analytical data reported should be viewed as indicating approximate average compositions of the polymer-supported complexes.

EXAFS data were recorded at the Daresbury Synchrotron Radiation Source, operating at an energy of 2 GeV and a current of *ca.* 200 mA. Data on the nickel and platinum compounds were obtained on station 7.1 using an order sorting silicon 111 monochromator, and on the rhodium, ruthenium, and palladium compounds on station 9.2 using a double crystal silicon 220 monochromator. Data on model compounds were collected in transmission mode on samples diluted with boron nitride and held between "sellotape" in 1 mm thick aluminium holders. Data on the polymer-supported samples were obtained using fluorescence detection (Tl/NaI scintillation counters). Data treatment was carried out as described elsewhere [30] using the programs PAXAS [31] and EXCURVE92 [32].

3.1. Synthesis

3.1.1. Polymer supported o-phenylene diphosphine

To a mixture of Na chips (9.5 g, 0.4 mol) and 1,4-dioxan (250 ml) under reflux, PPh$_2$Cl (38 g, 0.175 mol) was added dropwise during 1 h. The mixture was refluxed for a further 2 h to give an orange mixture, which was then cooled to room temperature. 3,4-Difluorobenzylalcohol (5.0 g, 0.035 mol) was added dropwise, the mixture refluxed for 3 h and then cooled. Ethanol was added dropwise to remove any residual Na metal and the mixture stirred for 30 min. The mixture was hydrolysed with 1 M hydrochloric acid (100 ml) and extracted with CH$_2$Cl$_2$ (50 ml × 2). The combined extracts were dried over MgSO$_4$ overnight then filtered, and the solvent was removed *in vacuo*. The side product, PPh$_2$H, was distilled off under vacuum (0.8 mmHg, 105–110°C) leaving the desired diphosphine product 1,2-(PPh$_2$)$_2$-4-HOCH$_2$C$_6$H$_3$ as a pale yellow oil. This oil (2.4 g, 5 mmol) was added to a suspension of NaH (0.23 g, 5 mmol) in THF (50 ml) under N$_2$ to give an orange suspension, which was then added to a suspension of the "Merrifield" polymer (chloromethylated polystyrene, *ca.* 1.7 mmol Cl/g) (3 g, *ca.* 5 mmol Cl) in THF (50 ml). The mixture was stirred under N_2 overnight and then treated with water (50 ml). The polymer was washed with diethyl ether (20 ml × 4), CH_2Cl_2 (20 ml) and diethyl ether (20 ml) to leave a white solid which was dried *in vacuo*. The phosphinated product was washed with hot THF in a Soxhlet apparatus for 8 h under N_2, and then dried *in vacuo* (3.5 g). Anal. Found: C, 83.9; H, 7.2; Cl, 2.9; P, 2.6%.

3.1.2. Reaction of phosphinated polymer with $RhCl(PPh_3)_3$

A mixture of $RhCl(PPh_3)_3$ [33] (1.0 g, 1.1 mmol) and phosphinated polymer (0.67 g) in THF (30 ml) was refluxed under N_2 for 3 h then cooled and filtered through a Schlenk stick to yield an orange solid. This was dried *in vacuo*, washed repeatedly with hot THF for 8 h, then dried again *in vacuo* (0.81 g). Anal. Found: Rh, 2.3; C, 79.9; H, 6.6; Cl, 3.3; P, 3.0%.

Supported metal complexes were prepared analogously by reaction of the following metal species with the phosphinated polymer.

$NiCl_2$, fawn solid. Anal. Found: C, 83.5; H, 7.0; Cl, 3.4; P, 2.1%. $PtCl_2(MeCN)_2$, pale yellow solid. Anal. Found: Pt, 4.3; C, 77.8; H, 6.9; Cl, 4.5; P, 2.04%. $RuCl_2(PPh_3)_3$, green-brown solid. Anal. Found: C, 83.0; H, 7.1; Cl, 3.1; P, 2.6%.

Model complexes were prepared by published methods, $NiCl_2\{o\text{-}C_6H_4(PPh_2)_2\}$ [16], $PdCl_2\{o\text{-}C_6H_4(PPh_2)_2\}$ [19], $PtCl_2\{o\text{-}C_6H_4(PPh_2)_2\}$ [19], $RuCl_2(PPh_3)_3$ [34]. $NiCl_2\{1,2\text{-}F_2\text{-}4\text{-}HOCH_2C_6H_3\}$ was prepared analogously to $NiCl_2\{o\text{-}C_6H_4(PPh_2)_2\}$.

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