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The design and synthesis of a new potentially C_3-symmetric ferrocenylphosphine

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Abstract

A new potentially C_3-symmetric phosphine ligand '*manphos*' has been obtained and fully characterized. The ligand which is a tri-ferrocenyl-tetra-phosphine is obtained in a simple and effective two step synthesis starting from 1,1′-dibromoferrocene via the intermediate compound tris-(1′-bromoferrocenyl)phosphine or alternatively via 1'-bromo-1-diphenylphosphinoferrocene. The *iso*-propylphosphino-analogue of *manphos*, tris-(1'-diisopropylphosphinoferrocenenyl)phosphine, has also been obtained, in addition to several functionalised derivatives of triferrocenylphosphine where the ferrocene rings have been substituted in the 1′-position.

Keywords: Ferrocene; Phosphine; Ligand; Lithiation

1. Introduction

Ferrocenylphosphines are one of the most widely used classes of ligand in use as ligands in catalytic applications today. We have had a longstanding interest in the synthesis of a range of ferrocenylphosphines for specific applications, which range from catalysis to material science [1]. In a recent paper we have described the synthesis of 1-lithio-1'-diphenylphosphinoferrocene (**1**), which was obtained directly from 1,1'-dibromoferrocene in a one-step procedure, Scheme 1a [2]. Compound **1** is obtained in extremely high yield (ca. $>85\%$) This method of synthesis we used complements the pre-existing synthetic procedures which were either using the ring-opening reaction of the ferrocenophane, Scheme 1b, [3] or using the bis tri-*n*-butylstannylferrocene as a key precursor, Scheme 1c [4].

In addition to compound **1**, a range of diferrocenyl compounds may also be obtained, for example the compound **2** which is a very useful precursor in its own right in the preparation of a range of new ligands of general structure **3**. These have a range of interesting coordination properties [5] (Scheme 2).

For example the compounds **1** and **2** are both key precursors in the preparation of a range of ferrocenylphosphines such as the recently described *triphosfer* **4**, Scheme 3 [6]. During the course of the work we decided to investigate the rational extension of the work which to attempt the preparation of substituted tri-ferrocenylphosphines which should be interesting tripodal ligands. The prototype ligand in this area, triferrocenylphosphine [7] is a highly basic, highly hindered ligand, which has been used extensively in the formation of ferrocyne (1,2-didehydroferrocene) complexes [8] in which we have a particular interest. This paper describes the synthesis of the first of these ligands, and includes a general synthetic methodology, which should be applicable to the preparation of a broad range of ferrocenylphosphines.

2. Experimental

All reactions with air or moisture sensitive reagents were carried out under an inert atmosphere of dry

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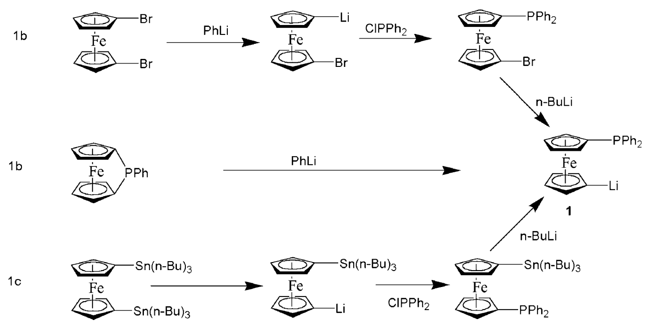


Scheme 1.

nitrogen using standard Schlenk techniques unless otherwise stated. Low boiling petrol was the fraction collected between 40 and 60 °C. All solvents were thoroughly dried and distilled as described by Leonard et al. [9] followed by degassing by passing a stream of argon through the solvent before use, all other chemicals were supplied by either Lancaster or Aldrich chemical companies and were used without further purification. Routine NMR, ^{1}H-NMR (250.133 MHz), ^{13}C{^{1}H}-NMR (62.896 MHz) and ^{31}P{^{1}H}-NMR (101.254 MHz) spectra were recorded at room temperature (r.t.) on a Bruker AC-250 spectrometer as solutions in deuterated chloroform ($CDCl_3$). All chemical shifts are quoted in δ relative to the trace resonance of protonated chloroform (δ 7.25 ppm), $CDCl_3$ (δ 77.0 ppm) and external 85% aqueous H_3PO_4 (δ 0.0 ppm). *Abbreviations used:* bm, broad multiplet; pt, psuedo triplet. Mass spectra (EI) were measured at 70 eV on a Finnigan MAT 8430 spectrometer or they were obtained using the high-resolution instruments at the EPSRC service at the University of Wales, Swansea. Data is presented as *m*/*z* (relative intensity). Prior to all column chromatographic work, standard TLC was used as a method for the identification of the major product fraction. (*Note:* it is usually not possible to determine the correct solvent mix using TLC methods as the products tend to adhere strongly to the silica, when loaded onto a column and thus a more polar mix is usually required). Column chromatography was carried out on silica gel eluting in each case with progressively polar mixtures of petroleum ether, diethyl ether, ethyl acetate, and finally methanol. Elemental analysis was carried out by Mr G. Connolly (U.W.B) using a Carlos Erba EA1108 elemental analyser (using helium as the carrier gas).

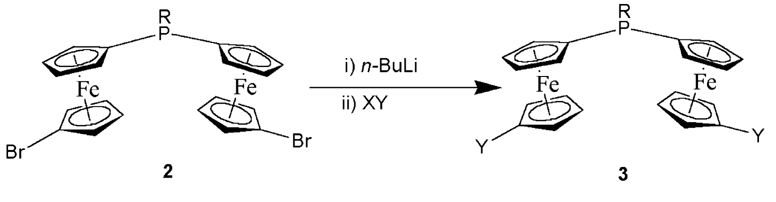
2.1. Preparation of tris-(1′-bromoferrocenyl)phosphine (5)

A sample of 1,1′-dibromoferrocene [10], (10.32 g, 30 mmol) dissolved in THF (ca. 100 ml) was cooled to -70 °C before being treated with a solution of *n*-butyllithium (12 ml of a 2.5 M solution in hexanes). The colour of the solution darkens slightly. The mixture was stirred for 30 min before phosphorus trichloride (1.37 g, 10 mmol) was added dropwise. The mixture was allowed to warm to r.t. and it was stirred for a further 30 min. The mixture was then added to silica gel (ca. 30 g) and the solvent was removed to leave the products adhered to silica gel. The solid silica powder was then added as a top layer to the column. The column was then eluted with the standard eluants as described above, collecting each of the coloured fractions. The major yellow product fraction was eluted with neat diethyl ether, although further product was obtained by addition of ethyl acetate to the eluant due to strong adherence by some of the product to silica. Removal of the solvent and recrystallisation from a mixture of diethyl ether and hexanes gave the product as a bright yellow powder or crystals.

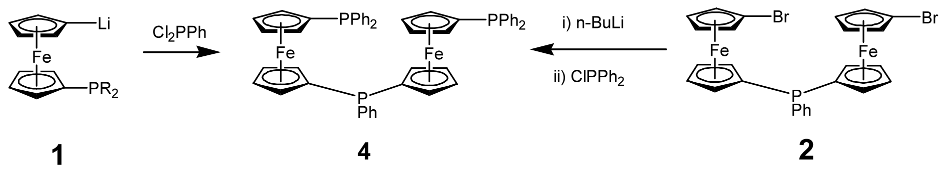
Compound **5**: $C_{30}H_{24}Br_3Fe_3P$: δ_H (250 MHz; $CDCl_3$), 3.96 (pq, 6H), 4.20 (pq, 6H), 4.28 (pt, 6H), 4.34 (pt, 6H); δ_C (62.8 MHz; $CDCl_3$), 68.49, 69.17, 71.03, 71.54, 73.66, 74.85(d *J* (^{31}P–^{13}C) 14.4 Hz))(*ipso* C not observed) δ_P (101.26 MHz; $CDCl_3$), -41.33; Mass spectrum, *m*/*z* (FAB) parent ion cluster at *m*/*z* 820–826 (822, 100%), 824 (95), with other clusters at 744 (47), 664 (5), 559 (30), 479 (15). 399 (54), 313 (60). Elemental Anal. Calc. C, 43.75; H, 2.94. Found C, 44.83; H, 3.50%. M.p. 165–167 °C.

2.2. Preparation of manphos (6) and i-Pr manphos (7)

A sample of **5** (3.3 g, 4 mmol) in diethyl ether (100 cm^3) maintained at -70 °C was treated with a slight excess of *n*-butyllithium (5.0 ml of 2.5 M solution in hexanes). The colour of the solution reddens. The mixture was subsequently removed from the cooling bath, for a period of 5 min, to ensure complete reaction, and thereafter it was re-cooled. Chlorodiphenylphosphine (2.75 g, 12.5 mmol) or (chlorodi-isopropylphosphine) (1.80 g, 12.5 mmol) was then added (the colour of the solution reverts to a yellow one with the



Scheme 2.



Scheme 3.

precipitation of lithium chloride). The mixture was allowed to warm to r.t. and it was stirred for a further 30 min. The crude reaction mixture was the added to silica gel (without hydrolysis) and the solvent was removed to leave the products adhered to silica. The column was eluted using the standard eluants as described above, collecting each of the coloured fractions. The major product fraction was eluted with neat diethyl ether. Removal of the solvent and recrystallisation from hot hexanes gave the product as bright orange-brown nodules. In the case of the *i*-Pr analogue the yellow product was co-eluted using petroleum ether as eluant. In the latter case the solvent was removed to leave an orange–yellow oil, which was re-dissolved in the minimum volume of petrol. The mixture was subsequently cooled to −20 °C for 48 h, after which time the product had crystallised as pale yellow needles. (Total yield: *manphos* (**6**), 4.58 g, 78%, *i-Pr manphos* (**7**), 65%.)

Manphos: $C_{66}H_{54}Fe_3P_4$: δ_H (250 MHz; $CDCl_3$), 3.95 (bm, 6H), 4.02 (bm, 6H), 4.10 (bm, 6H), 4.13 (bm, 6H), 7.01–7.28 (bm's, 30H); δ_C (62.8 MHz; $CDCl_3$), 67.87, 71.51, 72.24, 73.25, 73.31, 73.45, 76.40, 80.02 (*ipso*).; δ_P (101.26 MHz; $CDCl_3$), −17.67, −45.67 *m/z* (FAB) parent ion cluster at *m/z* 1135–1141 [1138(95%)], other clusters at *m/z* 1061 (21), [M^+–Ph], 954 (38), [M^+–PPh_2], 905 (17), 889 (23), 768 (100), 705 (25). M.p. = 174–176 °C. Calc. for $C_{66}H_{54}Fe_3P_4$: C, 69.6; H, 4.8, Found: C, 69.3; H, 5.1%.

A sample of *manphos* was recrystallised and several crystals were selected: these were found to be of the monophosphine oxide of the ligand (on standing monophosphine oxide appears)—δ_P (101.26 MHz; $CDCl_3$), −47.78, −17.65, +31.84. Calc. for $C_{66}H_{54}Fe_3OP_4$: C, 68.7; H, 4.7. Found: C, 68.9; H, 5.0%.

2.3. Alternative preparation of manphos

A solution of 1'-bromo-1-diphenylphosphinoferrocene [2] (13.47 g, 30 mmol) in diethyl ether (200 cm^3) cooled to −30 °C was treated with *n*-butyllithium to give the lithium salt (solution darkens with partial precipitation of salt) in situ, which was quenched after 15 min with phosphorus trichloride (1.37 g, 10 mmol). The work up was carried out as described above to yield the product as a fluffy powder of product free from the phosphine oxide.

2.4. Complexation study

A sample of *manphos* (114 mg) was reacted with [Pd(COD)Cl_2] (29 mg) in dichloromethane (25 cm^3) for 2 h. The product was subsequently precipitated by the addition of diethyl ether to give a violet powder. The powder was redissolved in the minimum of dichloromethane and layered with diethyl ether. The mixture was allowed to diffuse overnight. The product microcrystalline material was filtered off. Analysis showed that the product was a mixture of complexes which were characterised as such: (mixed complexes) $C_{66}H_{54}Cl_2Fe_3P_4Pd$: as violet powder, δ_P (101.26 MHz; $CDCl_3$), series of singlets at +40.04, 33.10, 29.05, 29.40, 27.66, 22.49, 15.14, 14.75. Found C, 52.1, H. 4.64. Mass spec: weak cluster at *m/z* 1313, strong cluster at 1295 (129–1302), 1257–1265, 1095, 975, 939 (all clusters).

i-Pr Manphos: $C_{48}H_{66}Fe_3P_4$: δ_H (250 MHz; $CDCl_3$), 1.07 (dd, 36H), 1.65 (2spt's, 6H) 4.02 (pt, 6H), 4.09 (pt, 6H), 4.16 (bm, 6H), 4.26 (bm, 6H); δ_C (62.8 MHz; $CDCl_3$), 19.99, 20.13, 20.24, 23.31, 23.50 (coupling constants), 68.93, 70.97, 73.17,73.40 coupling constants, 79.38, 77.51.; δ_P (101.26 MHz; $CDCl_3$), −0.02, −44.74; *m/z* (FAB) 935 (92), [M^++H], 891 (100), 769 (17), 753 (22), 633 (72), 337 (26), 304 (26). M.p. = 73–75 °C Calc. for $C_{48}H_{66}Fe_3P_4$: C, 61.67; H, 7.12. Found: C, 60.29; H, 7.65%.

2.5. Preparation of tris-[(1′-thiomethyl)ferrocenyl]phosphine (*8*) and of tris-[(1′-carboxylic acid)ferrocenyl]phosphine (*9*)

A sample of tris-(1′-bromoferrocenyl)phosphine (**5**), (1.65 g, 2 mmol) dissolved in diethyl ether (100 ml) was cooled to ca. −70 °C. A solution of *n*-butyllithium (2.5 cm^3 of a 2.5 M solution, 6.25 mmol) was added and the solution was stirred for 30 min before the quenching reagent, carbon dioxide (bubbled, excess) or dimethylsulfide (0.6 g, 6.4 mmol) was added. The solutions were then allowed to warm to r.t.

Compound **8**: After the addition of water the organic phase was separated and the aqueous phase was further extracted with diethyl ether. The combined organic fractions were added to a small portion of silica gel and the solvent was removed to leave the product adhered to the silica gel. The silica gel was then placed on the top of a column and the column was eluted initially with petrol to remove impurities and finally with diethyl ether to elute the product. It was dried under high vacuum and was essentially pure.

8: $C_{33}H_{33}Fe_3PS_3$: ^{1}H-NMR: 2.27 (s, 9H), 4.08 (m, 6H), 4.22 (m, 12H), 4.35 (m, 6H). ^{13}C-NMR: 30.89, 68.92, 70.22, 71.97, 73.80, 79.74, 84.07. ^{31}P-NMR − 44.99 (s). Mass spectrum: cluster at *m/z* 724 (100), 709(11), 678 (31), 493 (29), 399 (22), 304 (24). (N.B. contains trace phosphine oxide at *m/z* 740.) Calc. for $C_{33}H_{33}Fe_3PS_3$ C, 55.7; H, 4.6. Found: C, 55.3; H, 4.5%.

Compound **9**: In the case of the acid product the product was extracted into dilute (2 M) potassium hydroxide solution and the neutral ether layer was discarded. The basic aqueous solution was then treated slowly with a phosphoric acid solution until it became turbid. The product was subsequently extracted into diethyl ether and the solid, which was not extracted, was simply filtered off and ether washed. After drying the combined ether fractions over magnesium sulfate the ether was removed to leave the product acid, which was added to the solid already collected (the acid had the distinctive odour of a ferrocene carboxylic acid).

9: $C_{33}H_{27}Fe_3PO_6$: ^{1}H-NMR: 3.96 (m, 6H), 4.22 (6H), 4.31 (6H), 4.39 (6H). ^{13}C-NMR: 70.71, 72.22, 72.37, 73.66, 73.70., 171.98. ^{31}P-NMR: −43.06. Mass spectrum (FAB): 719, (100), [M+H], 718 (97), (M), 675 (55), 674 (73), 333 (30), 304 (30). (additional peaks observed at 759.1 (43), [M+K], 799.1 [M+2K]. as mono hydrate) Calc. C, 55.15; H, 3.76, as 4.5 hydrate: Calc. 49.6, 4.54. Found: C, 49.71; H, 4.65%.

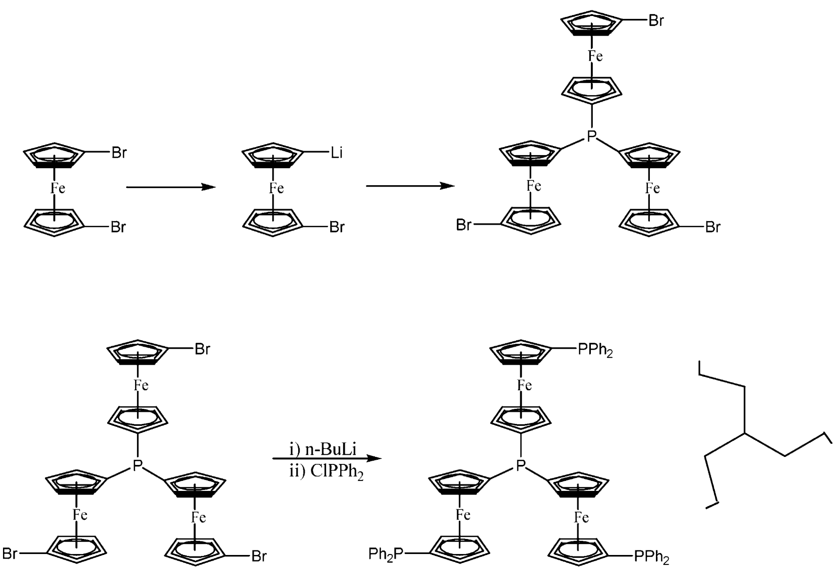
2.6. Crystallographic determination of the structure of manphos oxide

Crystal data, $C_{66}H_{54}$ $Fe_30_{0.96}P_4$, $M = 1189.68$, triclinic, spacegroup $P\bar{1}$, $a = 14.268(16)$, $b = 14.583(16)$, $c = 15.133(17)$ Å, $\alpha = 98.43(1)$, $\beta = 108.19(1)$, $\gamma = 110.35(1)°$, $U = 2687$ Å^3, Z = 2, $\mu = 0.965$ mm^{-1}, dc = 1.470 mg m^{-3} $F(0\,0\,0) = 1227$. 9433 reflections were collected on a MAR Research Image Plate System with Mo–K$_\alpha$ radiation. The structure was solved by direct methods and refined on F^2 using SHELXL [12] with all non-hydrogen atoms given anisotropic thermal parameters and hydrogen atoms included in calculated positions given isotropic thermal parameters equivalent to 1.2 * that of the atom to which they were bonded. Residual electron density was located at bonding distances from each of the three external phosphorus atoms and this was interpreted as an oxygen atom with reduced occupancy. The thermal parameters were set to be equal to those of the phosphorus atom to which they were bonded and their occupancies were allowed to refine and converge to values of 0.15(1), 0.46(1), and 0.35(1), respectively, for O(2), O(3), and O(4), respectively. The final R values were R_1 0.0728, $wR_2 = 0.1781$ for 4726 data with $I > 2s(I)$ and R_1 0.1842, $wR_2 = 0.2347$ for all data.

Crystallographic data has been deposited at the Cambridge Crystallographic Data Centre with reference CCDC No. 205257.

3. Results and discussion

In recent work it has been shown that the generation of 1-lithio-1′-bromoferrocene is a particularly clean process. This compound which was generated in situ in THF was reacted directly with phosphorus trichloride. High yields of the triferrocenyl-compound **5** were obtained following column chromatography. The compound was found to be relatively air stable and could be stored in normal sample tubes without apparent decomposition, over extended periods. The phosphorus chemical shift of for this compound was observed at −41.3 ppm which is broadly indicative of a highly basic ligand [11]. The proton NMR spectrum consisted of the expected four ferrocenyl multiplets between 3.9 and 4.4 ppm. This compound was obtained as a bright yellow solid. The subsequent reaction of this compound with three equivalents of *n*-butyllithium generated the trilithium salt cleanly. This reaction may be carried out in THF or diethyl ether at low temperature however diethyl ether was adopted as the solvent of choice because product isolation is facilitated. Quenching with three equivalents of chlorodiphenylphosphine again relatively cleanly resulted in the formation of the triferrocenyltetraphosphine (**6**), which was named *manphos*, because of its structural similarity with the 'legs of Man', see Scheme 4. The spectral properties of *manphos* (**6**) were entirely as expected—the chemical shifts of the central phosphorus was *P* observed at −45.67 ppm while the terminal phosphorus nuclei were observed at +16.67 ppm, which falls within the characteristic range of related mono-substituted phosphines. The new compound was, however, observed to contain some phosphine oxide which was confirmed by phosphorus NMR spectroscopy, even after carefully chromatography. The impure sample when crystallised resulted in the isolation of crystals of the patially-oxidised product. The problem was thought to be due to the direct use of commercial chlorodiphenylphosphine samples, which were invariably contaminated with the oxide of diphenylphosphinic chloride, however it is more likely that oxidation occurred during the workup. Clearly it is still advisable to distill the commercial phosphine before use (the use of commercial samples of chlorodiphenylphosphine is not a problem generally in ferrocenylphosphine ligand synthesis but in the present case where three lithium atoms are quenched there is a much higher probability in the incorporation of at least one phosphine oxide.) A second preparation was made using 1-bromo-1′-diphenylphosphinoferrocene as the starting material, Scheme 4b. In this manner it proved relatively easy to obtain



Manphos

Scheme 4.

pure samples of the ligand without the phosphine oxide contaminant. It proved difficult to crystallise the ligand though after isolation. The isopropyl analogue of *manphos* was similarly characterised and the spectral data is summarised as follows: the terminal phosphorus nuclei was observed at ca. 0.0 ppm and the central phosphorus observed at −44.7 ppm. The terminal phosphorus nuclei are observed at their expected chemical shift in line with previous data [12]. The central phosphorus atom is also in accord with previous data for triferrocenylphosphines. A crystal of the phosphine oxide derivative of *manphos* was selected for study in the absence of a suitable crystal of the ligand itself.

3.1. Crystallographic discussion

The structure of **6a** is shown in Fig. 1 and it can be seen that the structure has an approximate local C_3-symmetry axis through the central phosphorus atom P(1). The three C–P(1)–C angles are 98.9(3), 102.3(3) and 100.7(3)°. A good indicator of the threefold symmetry is that the three equivalent C–P–C–C torsion angles describing the orientation of the cyclopentadienes bonded to P(1) are very similar at 68.8, 63.5 and 79.6, respectively. However the symmetry is broken significantly by the positions of the three external phosphorus atoms as in the three ferrocene moieties the P–C···C–P torsion angles are 68.1, −122.3 and 156.5°. P(1)–P(n) distances are 4.99 ($n = 2$), 6.35 ($n = 3$) and 6.96 Å $n = 4$. However more symmetric are the position of the oxygen atoms relative to the ferrocene rings and the Fe···C–P–O torsion angles are all similar at −15.0, −38.8 and −43.1°, no doubt became in each case the bulky phenyl rings are positioned well away from the centre of the molecule.

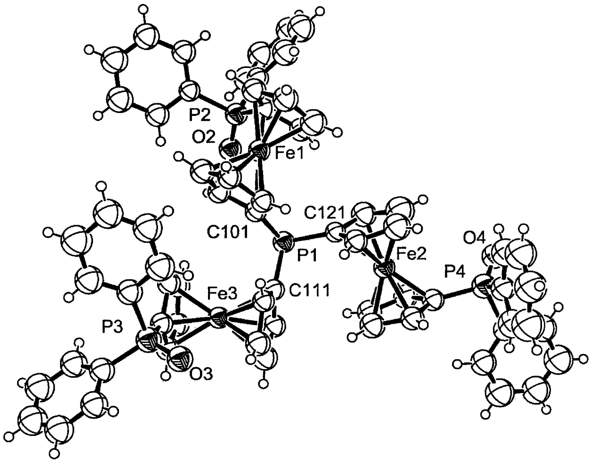
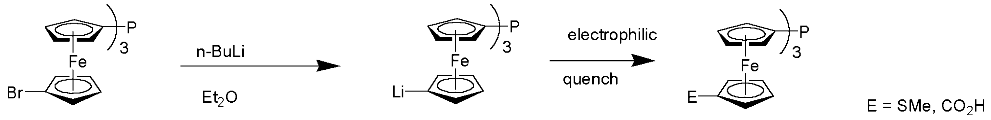


Fig. 1. The structure of (**6a**) with ellipsoids shown at 30% probability. The three oxygen atoms O(2), O(3) and O(4) have occupancy factors of 0.15, 0.46 and 0.35, respectively.

These oxygen atoms with occupancy factors of 0.15, 0.46, and 0.35 bonded to the three external phosphorus atoms are of particular interest. It will be noted that the sum is close to 1.0 and it could be argued that each molecule contains one oxygen which is disordered over three sites. However, given the lack of symmetry in the conformation surrounding the outer phosphorus atoms, it might well be that this sum has a fortuitous value of 1.0 and that individual molecules can have 0, 1, 2 or even 3 oxygen atoms present.

The reaction of *manphos* with one equivalent of palladium(II) dichloride was carried out under aerobic



Scheme 5.

conditions simply by stirring the ligand with (1,5-cyclooctadienyl)palladium dichloride in dichloromethane with the formation of the deep violet product complex. On examination of the phosphorus NMR spectra it was clear that a mixture of products had formed. The chemical shifts ranged between +14 and +50 ppm. Interestingly there was little evidence for uncomplexed phosphine. Again there was no evidence for phosphorus–phosphorus coupling in the spectrum, which may have been expected from unsymmetrical chelate complexes, although it is relatively common for the coupling constants to be small in similar complexes. It can be concluded that the coordination is rapid resulting in a mixture of complexes which are relatively stable once formed. The solubility of the different complexes is variable presumably reflecting the molecular weight and polarity of the complexes. Clearly there is scope for future investigation in this area. It is not expected that the ligands will be useful in nickel or palladium complexes for metal-coupling reactions but they should provide a rich chemistry when reacted, for example, with metal carbonyls.

In addition to the preparation of these new trisphosphines several new derivatives of triferrocenylphosphine were obtained during the course of the work. These were simply prepared by conventional quenching of the trilithium complex tris-(1'-lithioferrocenyl)phosphine with carbon dioxide or dimethyldisulfide using the synthetic methodology described by us [2]. These results are summarised in Scheme 5.

These products were obtained without any synthetic problems. In summary a range of triferrocenylphosphine ligands have been prepared using a relatively simple synthetic methodology which will be useful to the coordination chemist. Work will continue in the preparation of a pure crystalline sample for further crystallographic studies.

Acknowledgements

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