The synthesis and characterisation of bis(phenylpyridylphosphino)ethane

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Abstract

A novel synthesis has been devised for the preparation of unsymmetrical phosphine substituted derivatives of bis(diphenylphosphino)ethane [*dppe*]. The title ligand has been prepared in a two step procedure from *dppe*. A palladium(II) complex of this new ligand has been prepared and characterised by single crystal X-ray diffraction. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The ligand bis(diphenylphosphino)ethane [*dppe*] is the archetypal bidentate phosphine ligand which has probably been the most extensively used of all bidentate phosphine ligands in organometallic chemistry [1,2]. There are several derivatives of this ligand which may be prepared conveniently from bis(dichlorophosphino)-ethane [*dcpe*] [3]. An example of such a ligand is bis(diisopropylphosphino)ethane [*dippe*] [4–6] which is symmetrical with respect to phosphine substitution. The ease of synthesis of symmetrical ligands as opposed to non-symmetrical ligands is apparent. The electron donor ability of *dppe* derivative ligands is, however, altered by simple changes in the substituent groups on the phosphorus. This is manifested in the chemistry and structure of their transition metal complexes [2]. We are interested in the preparation of derivatives of *dppe*, in particular unsymmetrically substituted derivatives. There are several possible synthetic strategies towards the synthesis of unsymmetrical (with respect to phosphorus) bidentate phosphines, the most obvious of which would be to use the precursor *dcpe*. However, control of the stepwise substitution would obviously cause problems leading to the formation of a mixture of undesired products. An alternative method of synthesis builds on the chemistry of Kimpton and co-workers [7] who reported an improved synthesis of bis(phenylphosphino)ethane [*mppe*]. The use of this compound allows the facile preparation of ligands of the general type [PhRP–(CH$_2$)$_2$–PRPh] on appropriate substitution. Of particular interest to us in the synthesis of such ligands is the incorporation of pyridyl groups. The chemistry of simple monophosphine ligands which contain *P*-2-pyridyl groups is well developed and many interesting results have been obtained using this class of ligands [8–13], hence targeting the preparation of the title compound was a natural step. Recently a paper from the Berners-Price research group [14], caught our attention in that it described the preparation of a range of pyridylphosphines, which were obtained from the reaction of either pyridyllithium salts with chlorophosphines or the reaction of lithium metal with triphenylphosphine followed by the reaction with halopyridines. This prompted the publication of this work, which was carried out originally as an undergraduate project [15].

2. Results and discussion

The synthesis of *mppe* was achieved essentially using the methodology described by Kimpton et al. [7] (Scheme 1). The only variation was the observation that we were able to separate the diastereomers formed in

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i), ii)

i) Li, thf, 0°C, 14 days

ii) H₂O
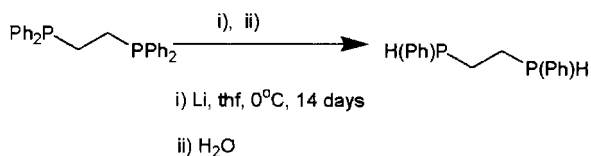
Scheme 1.

the system by carefully controlled vacuum distillation. We observed a substantial difference in the shifts observed in the ³¹P-NMR spectra of the diastereomers (-41.23, -47.50 ppm, respectively for the *meso*- and *rac*-forms). Similarly in the ¹H-NMR spectra large differences were observed: the literature data for the P*H* resonance is quoted at δ 4.29 ppm [7], in contrast to the observed broad singlet resonances at 4.95 and 5.83 ppm for the *meso*-diastereomer and at 3.51 and 4.62 ppm for the *rac*-diastereomer. We can only assume this to be an aggregation effect. The ¹³C-NMR were generally in accord with the literature assignments.

The formation of the di-lithio salt of *mppe* (the *meso* isomer used) was readily achieved by the standard method of metallation with *n*-butyllitium; subsequently the low temperature reaction of the lithio species with 2-chloropyridine proceeded efficiently with the formation of the ligand bis(phenylpyridylphosphino)-ethane [*bppye*] in 88% yield (Scheme 2). This was a particularly clean reaction in accordance with previous observations that the reactions of chloropyridines with lithiophosphines are superior to the identical reactions of bromopyridines, where more by-products are normally observed due to metathesis reactions.

The confirmation of the identification of the *meso*-derivative of the new ligand [*bppye*] was successfully carried out by the preparation of a palladium(II) complex on reaction of the new ligand with [Pd(1,5-COD)Cl₂]. The product was obtained as a pale yellow crystalline solid, which was structurally characterised by ³¹P-NMR and single crystal X-ray diffraction. The co-ordination shift of the phosphorus resonance was

large ($+107$ ppm) with the bound resonance being observed at $+66.3$ ppm compared to -47.5 ppm in the free ligand. This large shift concurs with shifts observed in the related chromium carbonyl complexes of *meso*- and *rac-mppe* where the shifts are $+94.6$ and $+97.2$ ppm, respectively. The structure of the complex was found to be square-planar (angles about Pd $\pm 5.5°$ those of ideal geometry) about palladium with the ligand binding bidentately (through both phosphorus atoms) in a *cis*-geometry (Fig. 1). Cremer Pople puckering analysis [16] calculates that the chelate ring is in a half chair conformation due to a twist about the C12–C13 bond (P1–C12–C13–P2 = 48.9°), whilst the substituent rings are, as expected, all planar.

The present work complements that of the Berners-Price group [14] in that it adds the possibility of making chiral ligands, which should be water soluble in weakly acidic solutions. Our work is continuing on the preparation of chiral ligands using a modification of the synthetic methodology. In conclusion, the synthesis of the bidentate ligand bis(phenylpyridylphosphino)-ethane [*bppye*] has been achieved and the palladium complex of the *meso*-ligand has been characterised by single crystal X-ray diffraction. The synthetic method used is clearly adaptable to the synthesis of a range of related ligands using the metathesis reaction of the lithium salts with halo-heteroaromatic compounds.

3. Experimental

3.1. General considerations

All reactions with air or moisture sensitive reagents were carried out under an inert atmosphere of dry argon 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. [17] followed by degassing by passing a stream or

i) 2.2 equiv. n-BuLi, Et₂O, 0°C

ii) 2-Chloropyridine, 2.2 equiv. , -78°C-R.T *meso*
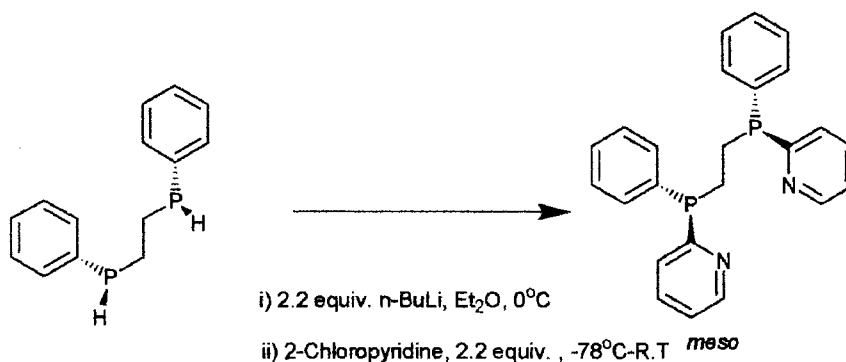
Scheme 2.

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 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$_3$PO$_4$ (δ 0.0 ppm). Mass spectra (EI) were measured at 70 eV on a Finnigan MAT 8430 spectrometer. Elemental analysis was carried out by Mr G. Connolly (University of Wales, Bangor) using a Carlos Erba EA1108 elemental analyser (using helium as the carrier gas).

3.2. Preparation of bis(phenylphosphino)ethane [mppe] [7]

A dry 2 l three necked flask equipped for reflux and magnetic stirring was charged with bis(diphenylphosphino)ethane [*dppe*] (70.3 g, 0.18 mol), dry THF (700 ml) and finely cut lithium wire (4.9 g, 0.70 mol). The resulting solution was stirred at 0°C (ice bath) for 14 days whilst maintaining an atmosphere of dry argon within the flask. After 14 days, any residual lithium wire was carefully removed from the flask and disposed of accordingly before quenching the reaction with cold degassed water (250 ml). The resulting solution was stirred at room temperature overnight before separa-

tion and extraction with diethyl ether. The combined organic fractions were dried over anhydrous magnesium sulphate, filtered and excess solvent removed by simple distillation. The crude product, a straw coloured highly viscous oil consisting of two diastereomers in ratio 1:1, was purified (separated) by careful fractional distillation. The separated diastereomers were isolated as colourless viscous oils, total combined yield 35.9 g (83%). Diastereomer 1 [(*RS*) *meso*-]; b.p. 121°C at 1 mbar; δ_H (250 MHz; CDCl$_3$), 1.5–2.4 (4H, bm), 4.95 (1H, s), 5.83 (1H, s), 7.35 (6H, m), 7.50–7.70 (4H, m); δ_C (62.8 MHz; CDCl$_3$), 22.63(dd, J(^{31}P-^{13}C) 8.17, 94.34 Hz),129.07, 129.31, 133.04, 135.85; δ_P (101.26 MHz; CDCl$_3$), −41.23; *m/z* (EI) 246(18), 218(11), 201(100), 183(31), 124(32), 108(35), 77(92). Diastereomer 2 [(*RR*)(*SS*), *rac*-] b.p. 141°C at 5.1 mbar, δ_H (250 MHz; CDCl$_3$), 1.84 (4H, m), 3.51 (1H, s), 4.62 (1H, s), 7.23 (6H, m), 7.30–7.60 (4H, m); δ_C (62.8 MHz; CDCl$_3$), 21.92(dd, J(^{31}P-^{13}C) 12.57, 18.87 Hz),128.34, 126.64, 134.04, 134.82; δ_P (101.26 MHz; CDCl$_3$), −47.50; *m/z* (EI) 246(58), 218(62), 213(23), 185(72), 139(21), 109(100), 77(31).

3.3. Preparation of lithio [mppe]

A dry 100 ml Schlenk tube was charged with (*meso*-) *mppe* (1.0 g, 4.1 mmol) and dry diethyl ether (20 ml), the resulting solution was stirred magnetically at 0°C whilst *n*-butyl lithium 2.2 equivalents [9 mmol] (i.e. 3.6 ml of 2.5 M solution) was added to the solution dropwise. The reaction mixture was then allowed to warm
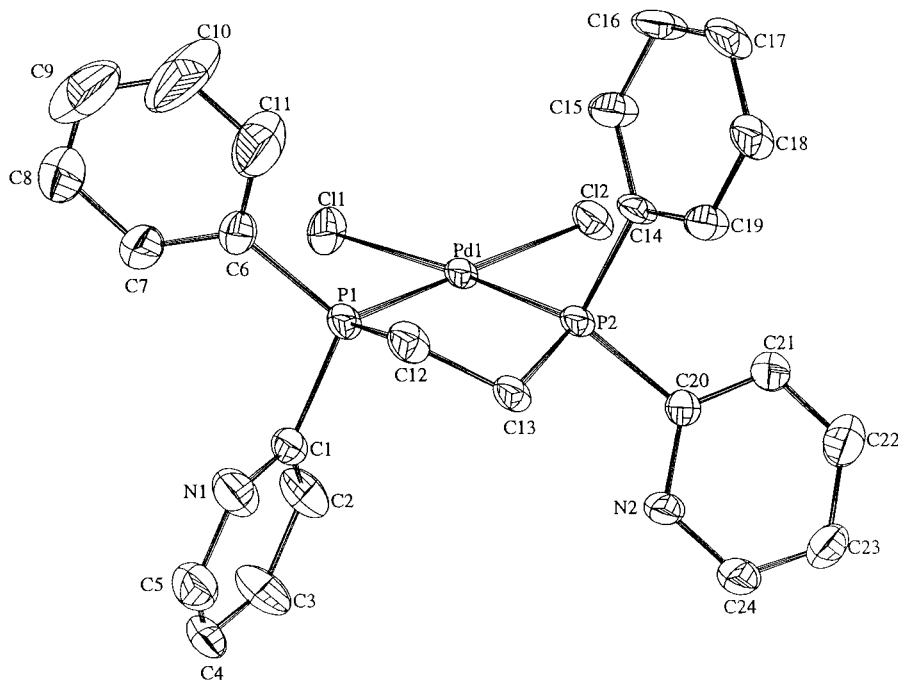

Fig. 1. Crystal structure of Pd(II) complex of *meso*-(*bppye*), compound **1**.

to room temperature and stirred for 45 min. During this period, the colourless solution reacted to yield a yellow–green finely divided suspension. Removal of all solvent in-vacuo yielded the lithio salt as an off white fine crystalline powder, the product could not be characterised due to very rapid decomposition.

3.4. Preparation of bis(phenylpyridylphosphino)ethane (bppye)

To a stirring solution of unisolated lithio-salt (as prepared above) at $-78°C$ 2-chloropyridine (1.02 g, 9.0 mmol) was added dropwise. The resulting solution was then allowed to warm to room temperature and was stirred for 30 min before removing the solvent was removed in-vacuo. The product was isolated as a white powder, which was recrystallised from hot propan-2-ol (3 ml) yielding a white crystalline solid, 1.45 g (88%). δ_H (250 MHz; CDCl$_3$), 2.2–2.6 (4H, bm), 7.01 (2H, m), 7.10 (2H, m), 7.30 (8H, m), 7.43 (4H, m), 7.57 (2H, m), 8.34 (2H, bs), 8.60 (2H, bs); δ_C (62.8 MHz; CDCl$_3$), 23.34(d J(^{31}P-^{13}C) 8.17 Hz), 124.30(d J(^{31}P-^{13}C) 10.06 Hz), 127.46, 133.7 (d J(^{31}P-^{13}C) 12.3 Hz), 134.02, 134.27, 149.63, 149.90, 151.46, 164.73; δ_P (101.26 MHz; CDCl$_3$), -41.33; m/z (EI) 400(42), 338(21), 322(33), 263(18), 211(62), 187(62), 186(64), 185(100), 108(35), 77(92).

3.5. Reaction of bis(phenylpyridylphosphino)ethane with Pd(COD)Cl$_2$

A solution of *meso*-bis(phenylpyridylphosphino)-ethane (0.07 g, 0.17 mmol) in dry degassed dichloromethane (5 ml) was prepared in a 25 ml Schlenk tube. To the stirring solution, a solution of Pd(1,5-COD)Cl$_2$ (0.05 g, 0.17 mmol), in dry degassed dichloromethane (5 ml) was carefully added. The resulting solution was stirred for 2 h before layering with low boiling petrol was carried out to facilitate precipitation. Once complete, the mother liquor was removed using a syringe and the remaining solid washed with low boiling petrol and recrystallised from dichloromethane and diethyl ether by the layering method yielding the product as a pale yellow crystalline solid. (Found: C, 45.26; H, 3.49; N, 4.16; C$_{24}$H$_{22}$Cl$_2$N$_2$P$_2$Pd.CH$_2$Cl$_2$ (compound **1**) requires C, 45.31; H, 3.65; N; 4.23%); δ_H (250 MHz; CDCl$_3$), 2.54 (2H, bd, $J = 22.01$ Hz), 6.30 (2H, bs), 7.36–7.50 (6H,m), 7.75 (2H, m),8.01 (4H, m), 8.46 (2H, m), 8.71 (2H, m); δ_P (101.256 MHz; CDCl$_3$), $+66.54$.

3.6. Determination of X-ray structure

A tablet ($0.36 \times 0.18 \times 0.14$ mm) was mounted on a glass fibre under inert oil and transferred to a Nonius FAST TV area detector diffractometer, equipped with an Oxford Cryosystems liquid nitrogen cooling device [18] and a FR591 rotating anode X-ray generator

Table 1
Selected bond lengths (Å)

Pd(1)–P(1)	2.228(2)	Pd(1)–P(2)	2.2364(13)
Pd(1)–Cl(2)	2.356(2)	Pd(1)–Cl(1)	2.3609(13)
P(1)–C(6)	1.816(6)	P(1)–C(1)	2.3609(5)
P(1)–C(12)	1.842(5)	P(2)–C(14)	1.815(5)
P(2)–C(13)	1.835(5)	P(2)–C(20)	1.838(6)
N(1)–C(5)	1.352(8)	N(1)–C(1)	1.355(7)
N(2)–C(20)	1.335(7)	N(2)–C(24)	1.363(8)
C(12)–C(13)	1.522(8)		

Table 2
Selected bond angles (°)

P(1)–Pd(1)–P(2)	85.75(5)	P(1)–Pd(1)–Cl(2)	175.74(5)
P(2)–Pd(1)–Cl(2)	90.37(5)	P(1)–Pd(1)–Cl(1)	89.00(5)
P(2)–Pd(1)–Cl(1)	174.58(5)	Cl(2)–Pd(1)–Cl(1)	94.92(5)
C(6)–P(1)–C(1)	107.0(3)	C(6)–P(1)–C(12)	105.5(3)
C(1)–P(1)–C(12)	104.9(2)	C(6)–P(1)–Pd(1)	117.9(2)
C(1)–P(1)–Pd(1)	111.8(2)	C(12)–P(1)–Pd(1)	108.9(2)
C(14)–P(2)–C(13)	107.6(2)	C(14)–P(2)–C(20)	106.2(2)
C(13)–P(2)–C(20)	104.2(2)	C(14)–P(2)–Pd(1)	111.8(2)
C(13)–P(2)–Pd(1)	108.3(2)	C(20)–P(2)–Pd(1)	118.0(2)

($\lambda_{Mo-K_\alpha} = 0.71069$ Å). Data collection followed previously described procedures [19].

3.7. Crystal data

C$_{24}$H$_{22}$Cl$_2$N$_2$P$_2$Pd.CH$_2$Cl$_2$. $M = 662.60$. monoclinic, space group $P2(1)/c$ (no. 14), $a = 11.851(4)$, $b = 15.722(3)$, $c = 15.202(2)$ Å, $\beta = 106.22(2)°$, $V = 2719.6(11)$ Å^3, $T = 150$ K, $Z = 4$, μ(Mo–K$_\alpha$) = 1.211 mm^{-1}, $F(000) = 1328$, $D_{calc} = 1.618$ Mg m^{-3}. 10980 reflections were collected with θ range 1.79–25.07° (index ranges; $h = -11$ to 12, $k = -18$ to 18, $l = -17$ to 17), which merged to give 4099 unique reflections ($R_{int} = 0.0781$) to refine against 313 parameters. Final R indices were $wR_2 = 0.1370$ and $R_1 = 0.0568$ [$I > 2\sigma I$] and 0.1409 and 0.0659, respectively for all data.

The structure was solved by direct methods (SHELXS [20]) and then subjected to full-matrix least-squares refinement based on F_o^2 (SHELXL-93 [21]). Non hydrogen atoms were refined anisotropically with hydrogen atoms included in idealised positions (C–H = 0.97 Å) with isotropic parameters free to refine. The weighting scheme used was $w = 1/[\sigma^2(F_o^2)]$. An absorption correction (DI-FABS [22]) was applied once the structure had been fully elucidated, giving absorption correction factors of 0.854 and 1.053 (Tables 1 and 2).

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Data Centre, CCDC

no. 134620 for compound **1**, $C_{24}H_{22}Cl_2$-N_2P_2Pd·CH_2Cl_2. Copies of this information may be obtained free of charge from — The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www/ccdc.cam.ac.uk).

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