# Notes

## Unsymmetrical Bis(phosphorus) Compounds: Synthesis of Unsymmetrical Ditertiary Phosphines, Phosphine Oxides, and Diquaternary Phosphonium Salts

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A convenient preparative route to the unsymmetrical bidentate phosphines $R_2P(CH_2)_nPPh_2$ (R = Me or Et; $n$ = 3 or 4) is described. This involves the synthesis of unsymmetrical diphosphonium salts, $[R_2PhP(CH_2)_nPPh_3]Br_2$, and diphosphine oxides, $R_2P(O)(CH_2)_nPPh_2$, as intermediates. The symmetrical ligand $Et_2P(CH_2)_3PEt_2$ was also prepared by the same route. New co-ordination complexes of manganese(II) with these ligands have been isolated.

There continues to be much interest in the use of diphosphine ligands in such areas as catalysis [1-4] and structural studies [5-8] of transition-metal complexes, particularly in the steric effects of the terminal substituent groups and the backbone chain linking the two phosphorus atoms. There is, therefore, a need for readily accessible synthetic routes to diphosphines with various terminal groups and backbone chains.

Although the symmetrical diphosphines, $Ph_2P(CH_2)_nPPh_2$, are easily prepared as air-stable solids,[9,10] analogous ligands with other terminal substituents are not so readily available. Symmetrical diphosphines with terminal alkyl groups, $R_2P(CH_2)_nPR_2$ (R = Me, Et, Bu$^t$, cyclo-$C_6H_{11}$, *etc.*), have been reported.[7,9,11-13] However, the synthetic routes are rather inconvenient and frequently involve highly air-sensitive intermediates.

Unsymmetrical diphosphines, in which the two phosphorus atoms have different terminal substituents, are less well known. Grim *et al.*[14-17] have synthesised diphosphines of types $RPhP(CH_2)_nPPh_2$ ($n$ = 1—3; R = Me, Et, Pr, Pr$^i$, Bu$^t$, or Bu$^s$) and $R_2P(CH_2)_nPPh_2$ ($n$ = 1, R = Me or Pr$^i$; $n$ = 3, R = Me), but again the preparative routes are rather difficult. Briggs and Dyer [18,19] have recently reported a more facile synthesis of the diphosphines $RPhP(CH_2)_nPPh_2$ with $n$ = 3—6 and R = Me, Et, or cyclo-$C_6H_{11}$.

### Discussion

The method developed by Briggs and Dyer [19] has been extended to synthesise the four unsymmetrical ligands $R_2P(CH_2)_nPPh_2$ ($n$ = 3 or 4; R = Me or Et), Scheme 1, and also the symmetrical $Et_2P(CH_2)_3PEt_2$. The synthesis depends on the stepwise formation of the mono- and di-phosphonium salts, by using a non-polar solvent for the first stage and a polar solvent for the second, and on the loss of phenyl in preference to alkyl at the hydrolysis stage.

A mixture of $Br(CH_2)_nBr$ ($n$ = 1—4) and triphenylphosphine, on warming in a non-polar solvent such as toluene, produces the monophosphonium bromide, $[Br(CH_2)_nPPh_3]Br$, but in a polar, higher-boiling point solvent such as *NN*-dimethylformamide, the diphosphonium salt, $[Ph_3P(CH_2)_nPPh_3]Br_2$, is obtained.[20,21] By treating a dibromoalkane first with triphenylphosphine in toluene, then with a dialkylphenylphosphine in *NN*-dimethylformamide, the synthesis of the unsymmetrical salts [Table, compounds (1)—(4)] is possible.

The symmetrical salt $[Et_2PhP(CH_2)_3PPhEt_2]Br_2$ [compound (3)] was made simply by heating a 2 : 1 mixture of diethylphenylphosphine with 1,3-dibromopropane in *NN*-dimethylformamide or chloroform.

The diphosphonium bromides were characterised by their $^1H$ and $^{31}P$ n.m.r. spectra. A $P^+-CH_3$ group displays a doublet with $^2J(PCH)$ *ca.* 14 Hz, while a $P^+-CH_2CH_3$ group displays a multiplet, with $^3J(PCCH)$ *ca.* 20 Hz. The unsymmetrical salts with a $-(CH_2)_3-$ backbone have $^4J(PP)$ in the range 8.4—9.0 Hz.

Hydrolysis of quaternary phosphonium salts using aqueous sodium hydroxide yields tertiary phosphine oxides by the mechanism shown in Scheme 2.[22] If the four groups ($R_4$) are different, the one ejected is that which forms the most stable anion, so that phenyl is displaced much more easily than alkyl. For diphosphonium salts with terminal phenyls, hydrolysis is only successful for $n \geq 3$.

The new diphosphonium salts were successfully hydrolysed to the expected diphosphine oxides [Table, compounds (6)—(10)]. Their $^1H$ n.m.r. spectra were as expected; for the terminal methyl protons, $^2J(PCH)$ is *ca.* 15 Hz. The trimethylene-based diphosphine oxides show a $^4J(PP)$ coupling of 2.0 Hz; $\nu(PO)$ occurs at 1 150—1 200 cm$^{-1}$.

The diphosphines [Table, compounds (11)—(15)] were easily prepared from their oxides by reduction with trichlorosilane,[23] as dense, air-sensitive oils. In their $^1H$ n.m.r. spectra, the methyl protons give a signal at $\delta$ 1.3—1.4 p.p.m., with $^2J(PCH)$ of 1 Hz. A detailed study of $^{31}P$ and $^{13}C$ n.m.r.

$$Br(CH_2)_nBr \xrightarrow{(i)} [Br(CH_2)_nPPh_3]Br \xrightarrow{(ii)} [R_2PhP(CH_2)_nPPh_3]Br_2 \xrightarrow{(iii)} R_2P(O)(CH_2)_nP(O)Ph_2 \xrightarrow{(iv)} R_2P(CH_2)_nPPh_2$$

**Scheme 1.** (*i*) $PPh_3$, toluene; (*ii*) $PPhR_2$, *NN*-dimethylformamide; (*iii*) 2NaOH, $H_2O$; (*iv*) $2SiHCl_3$–$NEt_3$, toluene

$$PR_4^+ + OH^- \rightleftharpoons PR_4(OH) \overset{OH^-}{\rightleftharpoons} PR_4O^- \xrightarrow{slow} P(O)R_3 + R^- \xrightarrow{H_2O} RH + OH^-$$

**Scheme 2.**

**Table.** Physical data for the complexes

| Compound | Yield/% | M.p./°C | $\delta(^{31}P)$ [a]/p.p.m. | |
|---|---|---|---|---|
| (1) $[Me_2PhP(CH_2)_3PPh_3]Br_2$ [b] | 94 | 69—74 | 22.22 | 20.12 [c] |
| (2) $[Et_2PhP(CH_2)_3PPh_3]Br_2$ [d] | 100 | 181—183 | 31.16 | 21.17 [e] |
| (3) $[Et_2PhP(CH_2)_3PPhEt_2]Br_2$ [f] | 98 | 185—186 | 29.29 | — |
| (4) $[Me_2PhP(CH_2)_4PPh_3]Br_2$ [g] | 99 | 92—94 | 24.78 | 23.95 |
| (5) $[Et_2PhP(CH_2)_4PPh_3]Br_2$ [h] | 94 | 90—93 | 33.72 | 20.44 |
| (6) $Me_2P(O)(CH_2)_3P(O)Ph_2$ | 92 | 125—129 | 39.39 | 28.97 [i] |
| (7) $Et_2P(O)(CH_2)_3P(O)Ph_2$ | 99 | Oil | 45.90 | 27.46 [i] |
| (8) $Et_2P(O)(CH_2)_3P(O)Et_2$ | 82 | Oil | 49.10 | — |
| (9) $Me_2P(O)(CH_2)_4P(O)Ph_2$ | 98 | 66.71 | 39.30 | 29.14 |
| (10) $Et_2P(O)(CH_2)_4P(O)Ph_2$ | 85 | Oil | 47.16 | 28.17 |
| (11) $Me_2P(CH_2)_3PPh_2$ | 40 | Oil | −52.69 | −16.43 [j] |
| (12) $Et_2P(CH_2)_3PPh_2$ | 47 | Oil | −23.05 | −16.33 |
| (13) $Et_2P(CH_2)_3PEt_2$ | 83 | Oil | −23.61 | |
| (14) $Me_2P(CH_2)_4PPh_2$ | 86 | Oil | −50.09 | −15.47 [k] |
| (15) $Et_2P(CH_2)_4PPh_2$ | 56 | Oil | −21.72 | −15.84 [k] |
| (16) $Me_2P(S)(CH_2)_3P(S)Ph_2$ [l] | — | 128—129 [m] | | |
| (17) $Et_2P(S)(CH_2)_3P(S)Ph_2$ [n] | — | 78—79 | | |
| (18) $Me_2P(S)(CH_2)_4P(S)Ph_2$ [o] | — | 139—140 | | |
| (19) $Et_2P(S)(CH_2)_4P(S)Ph_2$ [p] | — | 106—108 | | |

[a] Solvent $CDCl_3$; p.p.m. is downfield relative to 85% $H_3PO_4$ external standard. [b] Analysis(%): C, 57.1 (57.8); H, 5.3 (5.4); P, 9.7 (10.3) (calculated values in parentheses). [c] $^4J$(PP) 8.4 Hz. [d] C, 58.9 (59.1); H, 5.6 (5.8); P, 9.6 (9.8)%. [e] $^4J$(PP) 9.0 Hz. [f] C, 51.4 (51.7); H, 6.7 (6.8); P, 11.5 (11.6)%. [g] C, 58.3 (58.5); H, 5.7 (5.6); P, 9.6 (10.0)%. [h] C, 59.4 (59.6); H, 5.7 (5.9); P, 9.3 (9.6)%. [i] $^4J$(PP) 2.0 Hz. [j] Lit.[17] values 52.9 and 16.9 p.p.m. [k] $^5J$(PP) 1.3 Hz. [l] C, 57.9 (57.9); H, 6.4 (6.3); P, 17.3 (17.6)%. [m] Lit.[17] 126—127 °C. [n] C, 59.9 (60.0); H, 6.7 (6.9); P, 16.3 (16.3)%. [o] C, 59.1 (59.0); H, 6.6 (6.6); P, 16.4 (16.9)%. [p] C, 61.2 (60.9); H, 7.0 (7.2); P, 15.5 (15.7)%.

and mass spectral measurements for these ligands has been published.[24]

The co-ordination chemistry of the diphosphines is currently being investigated. Continuing the work of McAuliffe *et al.*[25] with complexes of general empirical formula $[MnX_2(PR_3)]$, (X = Cl, Br, I, or SCN; R = alkyl or aryl), analogous complexes of diphosphines have now been isolated. The structure obtained appears to depend more on the nature of the terminal groups than on the length of the backbone chain. For instance, stirring a suspension of anhydrous $MnBr_2$ in tetrahydrofuran (thf) with an excess of diphosphine gives a solid of formula $[MnBr_2$(diphosphine)] with $Me_2P(CH_2)_nPPh_2$ ($n$ = 3 or 4), but gives $[Mn_2Br_4$(diphosphine)-(thf)] with $Et_2P(CH_2)_nPPh_2$ ($n$ = 3 or 4) and $Et_2P(CH_2)_3PEt_2$. The actual modes of co-ordination of the diphosphines in these complexes are not yet clear, but all complexes reversibly co-ordinate dioxygen.

## Experimental

The phosphines, except triphenylphosphine, were made and handled under nitrogen. Diethyl ether and AnalaR toluene were dried over sodium wire. $^1H$ N.m.r. and $^{31}P$ n.m.r. spectra were obtained as previously described.[24] Elemental analyses were carried out at U.M.I.S.T. microanalytical laboratory.

*Preparations.—Dimethylphenylphosphine.* This was prepared by standard Grignard technique from methylmagnesium iodide and dichlorophenylphosphine, in 75% yield after distillation at 41—45 °C/0.1 mmHg (lit.[26] 83—84 °C/13 mmHg) (1 mmHg ≈ 133 Pa).

*Diethylphenylphosphine.* This was prepared from ethylmagnesium bromide and dichlorophenylphosphine, in 63% yield after distillation at 55—60 °C/0.5 mmHg (lit.[26] 96—98 °C/10 mmHg).

*(3-Bromopropyl)triphenylphosphonium bromide.*[20] 1,3-Dibromopropane (202 g, 1.0 mol), triphenylphosphine (262 g, 1.0 mol) and dry toluene (500 cm³) were refluxed for 5 h, during which time the solid product crystallised out. The product was filtered off, washed with toluene and then light petroleum (b.p. 40—60 °C) to give colourless crystals (305 g, 66%), m.p. 214—216 °C (lit.[20] 210—215 °C).

*(4-Bromobutyl)triphenylphosphonium bromide.*[21] This was prepared as for $[Br(CH_2)_3PPh_3]Br$, from 1,4-dibromobutane (216 g, 1.0 mol) and triphenylphosphine (262 g, 1.0 mol) in toluene (500 cm³), as colourless crystals (377.5 g, 79%), m.p. 206—207 °C (lit.[21] 205 °C).

*[3-(Dimethylphenylphosphonio)propyl]triphenylphosphonium dibromide.* A mixture of (3-bromopropyl)triphenylphosphonium bromide (93.0 g, 0.2 mol), dimethylphenylphosphine (28.0 g, 0.2 mol) and *NN*-dimethylformamide (200 cm³) was refluxed for 4 h. When cool, the clear solution was transferred to a large beaker and dry toluene (600 cm³) added slowly with stirring to precipitate the product as a viscous oil. The solvents were decanted off, and the product titrated once with toluene then twice with dry diethyl ether, which caused it to become very viscous. It was hydrolysed to the diphosphine oxide without further purification. When a sample was heated to 100 °C/0.01 mmHg for several hours to remove absorbed solvents, it solidified to give an analytically pure powder.

The other unsymmetrical diphosphines were prepared similarly. Yields, melting points, and analytical data are given in the Table.

*[3-(Diethylphenylphosphonio)propyl]diethylphenylphosphonium dibromide.* 1,3-Dibromopropane (12.1 g, 0.06 mol), diethylphenylphosphine (20.5 g, 0.13 mol), and *NN*-dimethylformamide (50 cm³) were refluxed for 5 h. When cool, the clear solution was transferred to a beaker and the product precipitated as a solid with an equal volume of dry toluene. After filtering and washing with toluene, and then light petroleum (b.p. 60—80 °C), the colourless product (31.3 g, 98%) was dried overnight in a vacuum desiccator.

*1-Dimethylphosphinoyl-3-diphenylphosphinoylpropane.* A suspension of $[Me_2PhP(CH_2)_3PPh_3]Br_2$ (114.0 g, 0.19 mol) in excess 20% aqueous sodium hydroxide (400 cm³) was boiled, with rapid stirring, for 1 h, allowing the evolved benzene to boil off. The diphosphonium salt quickly became oily in the hot alkali. When cool, the product settled as a viscous oil on

top of the liquid. Attempts to crystallise the product failed, so it was purified by dissolving it in a mixture of boiling toluene (60 $cm^3$) and ethanol (30 $cm^3$), filtering, boiling off the ethanol (until b.p. ≈ 110 °C) and precipitating with diethyl ether. The oil was left in a vacuum desiccator for 24 h, during which time it set to a ' glass '.

The other diphosphine oxides were hydrolysed in the same way. Because the diphosphine oxides were generally hygroscopic and tended to retain solvents, even after several hours under vacuum, satisfactory analytical results could not be obtained (see Table).

1-*Dimethylphosphino*-3-*diphenylphosphinopropane*. A solution of $Me_2P(O)(CH_2)_3P(O)Ph_2$ (34.3 g, 0.11 mol) in warm dry toluene (100 $cm^3$) was added over *ca.* 5 min to a mixture of trichlorosilane (33 g, 0.24 mol) and triethylamine (24 g, 0.24 mol) in dry toluene (200 $cm^3$). The mixture was then refluxed for 2 h.

The flask was cooled in ice during the cautious addition, with stirring, of 50% aqueous sodium hydroxide (150 $cm^3$). The mixture was stirred for *ca.* 1 h until most of the solid in the toluene layer had dissolved. The toluene layer was syphoned off into a nitrogen-filled separating funnel. The aqueous layer was extracted twice with toluene which was added to the separating funnel. The diphosphine solution was then washed twice with water and filtered through glass wool into a flask. Removal of the toluene by rotary evaporation left the diphosphine as a dense, air-sensitive oil. The $^1H$ n.m.r. spectrum showed retained toluene.

The other diphosphines in the Table were prepared similarly. The unsymmetrical ligands were characterised as their disulphides, made by stirring a toluene solution with a slight excess of sulphur for 2 h. The solution became warm and most of the sulphur dissolved. The toluene was removed and the residue recrystallised from ethanol. In each case, large, air-stable platelets were obtained. Analytical data and melting points are given in the Table.

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