Unsymmetrical Bisphosphorus Compounds. Routes to the Successful Preparation of $Ph_2P(CH_2)_nPR_2$ (n = 6, 8; R = Me, Et)

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Abstract

An improved route to the preparation of the unsymmetrical bisphosphines $Ph_2P(CH_2)_nPR_2$ (n = 6, 8; R = Me, Et) is reported as well as ^{31}P and ^{13}C NMR spectra. This route was not successful for the preparation of bisphosphines with longer methylene bridges.

Introduction

Ditertiary phosphine ligands are used widely in coordination chemistry and the ubiquitous dppe, $Ph_2PCH_2CH_2PPh_2$, is now being rivalled in use by dppm, $Ph_2PCH_2PPh_2$. These air-stable solid materials are easily prepared, but analogues with other terminal substituents are not so available, although symmetrical diphosphines $R_2P(CH_2)_nPR_2$ (R = Me, Et, Bu^t, cyclo-C_6H_{11}, etc) are known [1–5]. By contrast, unsymmetrical bisphosphines are much less well known, though even here the progress made in synthetic procedures is quickening. Grim's group has produced $RPhP(CH_2)_nPPh_2$ (n = 1–3; R = Me, Et, Pr, Pr^i, Bu^i, Bu^s) and $R_2P(CH_2)_nPPh_2$ (n = 1, R = Me, Pr^i; n = 3, R = Me), but the routes are difficult [6–9]. Briggs and Dyer [10, 11] have developed a much more facile synthesis of the $R_2P(CH_2)_nPPh_2$ (n = 3–6; R = Me, Et, cyclo-C_6H_{11}) molecules. We extended the method developed by Briggs and Dyer [10, 11] to synthesize the four unsymmetrical ligands $R_2P(CH_2)_nPPh_2$ (n = 3 or 4; R = Me or Et) and studied their complexation of manganese(II) salts [12]. Because of our interest in the complexes of long chain diphosphines [13, 14] we have attempted to extend the method of Briggs and Dyer to ligands of type $R_2P(CH_2)_nPPh_2$ (n = 6–12; R = Me, Et), but have found that some significant modifications have to be made in the early stages, and, even then, some ligands cannot be obtained pure. We here report our synthetic methods and the NMR spectra of the new ligands and some of their precursors.

Results and Discussion

The basic method of Briggs and Dyer [11, 12] is as follows:

$$Br(CH_2)_nBr + Ph_3P \xrightarrow{\text{benzene}} [Ph_3P(CH_2)_nBr]Br$$

$$[Ph_3P(CH_2)_nBr]Br + Me_2PPh \xrightarrow{\text{DMF}} [Ph_3P(CH_2)_nPPhMe_2]Br_2$$

$$[Ph_3P(CH_2)_nPPhMe_2]Br_2 \xrightarrow{\text{NaOH}} Ph_2P(O)(CH_2)_nP(O)Me_2$$

$$Ph_2P(O)(CH_2)_nP(O)Me_2 \xrightarrow{SiHCl_3} Ph_2P(CH_2)_nPMe_2$$

In the original method [11, 12], a large excess of the dibromide in benzene was used. The monophosphonium salt (chain length of 2, 3 and 4 methylene groups) precipitated from the solution. However, with a chain length of six or eight methylene groups, the desired monophosphonium salt does not precipitate from the non-polar medium (e.g. benzene or toluene) used for the reaction. When the dibromoalkane is heated with triphenylphosphine (5:1 mole ratio) at 90 °C for 5–6 h without any solvent, the reaction product is the monophosphonium salt, obtained as a sticky solid. Temperature and time of reaction are very critical for this step. Higher temperatures lead to disubstitution and reaction for a period of less than 5 h leaves substantial amounts of unreacted triphenylphosphine (as seen in the ^1H NMR). It is very difficult to wash out the unreacted triphenylphosphine from the sticky monophosphonium salt. The formation of diphosphonium salt

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TABLE I. The $^{31}P\{^1H\}$ NMR Chemical Shifts[a] of the Diphosphonium Salts, the Diphosphine Dioxides and some Unsymmetrical Diphosphine Ligands

Compound	Chemical shift		Relative area P_Φ/P_R
	P_Φ[b]	P_R[b]	
$[Ph_3P(CH_2)_nPPhR_2]Br_2$			
R = Me			
$n = 6$	25.3	26.5	1.03
$n = 8$	24.8	25.7	1.21
$n = 10$	25.0	26.2	2.00
$n = 12$	25.4	24.6	1.43
R = Et			
$n = 6$	24.6	34.8	0.93
$n = 8$	24.8	34.6	1.10
$n = 10$	25.1	35.3	1.85
$n = 12$	24.5	34.6	1.80
$Ph_2P(O)(CH_2)_nP(O)Me_2$			
$n = 6$	32.9	43.0	1.07
$n = 8$	33.1	43.1	1.10
$n = 10$	33.3	43.9	1.9
$n = 12$	33.3	43.3	1.5
$Ph_2P(O)(CH_2)_nP(O)Et_2$			
$n = 6$	32.8	51.8	1.05
$n = 8$	33.1	52.1	1.08
$n = 10$	33.0	52.0	1.9
$n = 12$	33.1	51.8	2.7
$Ph_2P(CH_2)_nPMe_2$			
$n = 6$	−16.0	−51.8	1.03
$n = 8$	−16.1	−52.0	1.08
$n = 10$	−16.0	−52.1	1.8
$Ph_2P(CH_2)_nPEt_2$			
$n = 6$	−15.9	−22.8	1.12
$n = 8$	−15.8	−22.4	1.06

[a]Chemical shifts relative to 85% phosphoric acid external reference. [b]P_Φ is the phosphorus attached to the phenyl groups. P_R is the phosphorus attached to the alkyl groups.

is effected by refluxing a 1:1 mixture of the monophosphonium salt and $PPhR_2$ in a polar solvent such as dimethylformamide or nitrobenzene. The diphosphonium salt is precipitated from the polar solvent by the addition of toluene. The unsymmetrical diphosphonium salt is then converted to the diphosphine dioxide by alkaline hydrolysis; direct reduction by sodium or $LiAlH_4$ results in poor yields. The production of the pure ligand results from the reduction of the diphosphine dioxide by $SiHCl_3$. The $^{31}P\{^1H\}$ NMR chemical shifts of products and intermediates are shown in Table I.

Examining the data in Table I shows that for chain lengths of 6 and 8 methylenes, both the diphosphonium salts and the phosphine oxides give 1:1 integration ratios for the two phosphorus atoms attached to the ends of the methylene bridge. However, for the chain lengths of 10 and 12, the integration values are quite different from the expected 1:1 value. The higher ratio of P_Φ/P_R in the diphosphonium salt suggests that substantial disubstitution has occurred in the first step of the reaction sequence. The disubstitution product is then carried through the subsequent steps as shown by the subsequent integration ratios. The possibility that $PPhR_2$ displaces some Ph_3P from the monophosphonium salt in the second step is unlikely since that requires replacement of a Ph_3P group compared to the easily replaceable Br from the other end. Also, the reaction in the second step is carried out in a 1:1 mole ratio. Silane reduction of the phosphine oxide reduces the oxide to free phosphine without any change in the relative intensities of the two phosphorus resonances.

^1H NMR was also used to characterize the ligands. The methyl protons attached to phosphorus appear at 1.0 ppm as a doublet. The protons of the CH_2 groups appear as multiplets at 2.04 ppm and the protons of the remaining CH_2 groups resonate in the 1.2–1.5 ppm range. The phenyl protons appear as two sets of multiplets (split by phosphorus) at 7.1–7.5 ppm. Because of overlapping resonances, the multiplicity of the resonances for individual types of protons cannot be determined accurately.

$^{13}C\{^1H\}$ NMR of some symmetrical bidentate phosphines and arsines have been reported [15–17], and for some unsymmetrical bisphosphine ligands with a trimethylene backbone, assignment of each carbon resonance has been possible [17]. However, for the longer chain lengths, assignment of the carbon resonances of the methylene bridges become difficult. The ^{13}C NMR spectra of the unsymmetrical diphosphines can be divided into three regions: (a) the aromatic region; (b) the methylene-bridge region; and (c) the region of methyl or ethyl substituents on phosphorus.

Carbon resonances for methyl groups (or ethyl groups) attached to phosphorus appear in the 9–20 ppm range, well upfield from the methylene-backbone region. In the case of the ethyl substituted derivative, $^2J_{(P-C)} > {}^1J_{(P-C)}$.

The aromatic region shows resonances for *ortho*, *meta* and *para* carbons of the phenyl groups attached to phosphorus. The *ipso* carbon does not possess a directly bound hydrogen atom, and hence decoupling does not result in any Nuclear Overhauser Enhancement. This resonance is observed as a small doublet at 139 ppm.

Spectral data for both the symmetrical bisphosphine with six methylene bridges and the unsymmetrical bisphosphine are reported in Table II.

TABLE II. The $^{13}C\{^1H\}$ NMR Data for $Ph_2(CH_2)_6PPh_2$ and $Ph_2P(CH_2)_6PMe_2$

	$Ph_2P-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-PPh_2$						
ppm[a]	30.7	25.5	27.9				
$J_{(P-C)}$[b]	11.8	14.5	11.0				
	$Ph_2P-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_2-PMe_2$						
ppm	30.9	25.8	27.9	28.0	25.6	32.0	14.0
$J_{(P-C)}$	12.0	15.1	11.0	11.6	12.7	9.0	12.5

[a]Chemical shifts measured in ppm relative to TMS standard. [b]Coupling constants in Hz.

Comparison of chemical shifts and coupling constants for the two compounds with the same number of methylene bridges helps in assigning the ^{13}C chemical shift and coupling constant for the methylene bridges of the unsymmetrical bisphosphine ligand. As expected, the chemical shifts and coupling constants for the aromatic region and the three methylene groups nearest to the $-PPh_2$ end remain almost unchanged in both the symmetrical and unsymmetrical bisphosphine ligands.

The $^{13}C\{^1H\}$ NMR spectrum of ligands with 10 and 12 methylene groups were not obtained since $^{31}P\{^1H\}$ NMR ratios of the two phosphorus signals were substantially different from the expected 1:1 integration ratio; therefore these ligands were considered impure.

Experimental

Preparation of 1-Bromo-6-triphenylphosphoniumhexyl Bromide [$Br(CH_2)_6PPh_3$]Br

Triphenylphosphine (17.5 g, 0.067 mol) and 1,6-dibromohexane (84.0 g, 0.34 mol) were mixed in a 250 cm^3 round-bottom flask fitted with a reflux condenser and heated in an oil bath at 90 °C for 5–6 h. The flask was then allowed to cool to room temperature, and after 3 h two layers were obtained. The monophosphonium salt formed a sticky solid on the top, and excess liquid dibromoalkane remained at the bottom; this was decanted off. The monophosphonium salt was washed with dry benzene (3 × 50 cm^3) to remove any unreacted triphenylphosphine. Finally, the paste-like solid was washed with ether and dried *in vacuo*. The monophosphonium salt was obtained as a white solid in almost quantitative yield, 98%.

Preparation of 1-Dimethylphenylphosphonium-6-triphenylphosphoniumhexyl Dibromide [$Me_2PhP(CH_2)_6PPh_3$]Br_2

The monophosphonium salt [$Br(CH_2)_6PPh_3$]Br (12.7 g, 0.025 mol) was dissolved in dimethylformamide (125 cm^3) and the mixture was placed in a 250 cm^3 three-necked round-bottom flask fitted with a water-cooled reflux condenser, a nitrogen inlet, and a dropping funnel. N_2 was passed through the reaction vessel for 15 min and $PPhMe_2$ (3.5 g; 0.025 mol) was added dropwise to the solution of the monophosphonium salt and refluxed for 4 h under N_2. After cooling to room temperature the liquid was transferred to a beaker. Dry toluene (400 cm^3) was added slowly with stirring; an oily semisolid precipitated. The solvent was decanted. The sticky solid in the beaker was washed once with dry toluene (50 cm^3) and anhydrous ether (2 × 30 cm^3). The diphosphonium salt was obtained as a white sticky solid in almost quantitative yield, 99%.

Preparation of 1-Dimethylphosphoryl-6-diphenylphosphorylhexane [$Me_2P(O)(CH_2)_6P(O)Ph_2$]

The unsymmetrical diphosphonium salt [$PhMe_2P(CH_2)_6PPh_3$]Br_2 (16.1 g, 0.025 mol) was placed in a 500 cm^3 beaker with 25% aqueous sodium hydroxide (20 cm^3). The mixture was stirred rapidly and heated to boiling for 1 h. As the reaction proceeded the solid diphosphonium salt gradually disappeared and a viscous oil formed, which floated on the surface of the solution. Benzene produced during the reaction boiled away. The mixture was allowed to cool and the oil was separated using a separatory funnel. (The very hygroscopic oil should not be left in air for long periods of time.) The diphosphine dioxide was purified by dissolving in a mixture of hot toluene (40 cm^3) and ethanol (2:1 by volume). The undissolved solid was filtered off. The solution was boiled at 100 °C and cooled; the diphosphine dioxide was precipitated by adding dry diethyl ether. The solid was dried *in vacuo*. Yield 92%.

Preparation of 1-Dimethylphosphino-6-diphenylphosphinohexane [$Me_2P(CH_2)_6PPh_2$]

Trichlorosilane (10.8 g, 0.08 mol) was pipetted into a 250 cm^3 three-necked flask fitted with a reflux condenser, a dropping funnel, and a N_2 inlet. Triethylamine (8.0 g, 0.08 mol) (dried over NaOH) in sodium-dried toluene (100 cm^3) was added carefully to the silane through the dropping funnel, while cooling the flask with an ice-water bath. The unsymmetrical diphosphine dioxide, $Me_2P(O)(CH_2)_6P(O)PPh_2$ (7.2 g; 0.02 mol) in dry warm toluene (75 cm^3) was added to the mixture in the flask over 5 min and was refluxed for 5 h under a slow stream of N_2. (A rapid flow of N_2 removes silane (b.p. 32 °C) from the flask.) The flask was then cooled in ice, and 50% aqueous sodium hydroxide (75 cm^3) was added

dropwise cautiously. The mixture was then stirred for about 1 h until most of the solid in the toluene layer had dissolved. The top toluene layer was pipetted out under N_2. The aqueous layer was washed with toluene (25 cm^3) which was added to the toluene fraction previously separated. The toluene fraction was filtered under N_2 through a Buchner funnel, and the solvent was removed *in vacuo*. The product, $Me_2P(CH_2)_6PPh_2$, was obtained as a white semisolid and was dried on the vacuum line for several days to remove toluene. Yield 82%. The ^{31}P chemical shifts are −16.00 (PPh_2) and −51.8 ($-PMe_2$) ppm, for the two phosphorus atoms. A product of incomplete reduction due to less trichlorosilane or shorter reflux period or air exposure shows phosphine oxide peaks at 32.9 ($-P(O)PPh_2$) and 43.0 ($-P(O)Me_2$) ppm respectively for the phosphorus atoms in the ^{31}P NMR.

The other ligands were prepared similarly.

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