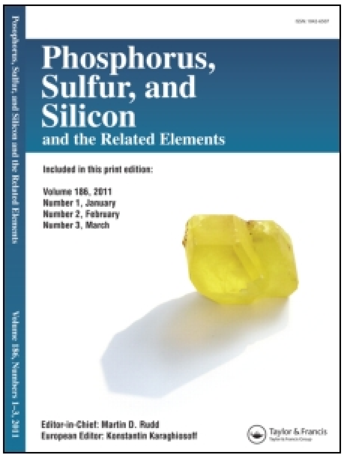

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SYNTHESIS OF 1, n-BIS (2,5-DIPHENYLPHOSPHOL-1-YL) ALKANES

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SYNTHESIS OF 1,n-BIS (2,5-DIPHENYLPHOSPHOL-1-YL)ALKANES

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1,n-bis (2,5-diphenylphospholyl)alkanes (n = 2–6) are easily prepared in a one pot high-yield reaction and fully characterized by multinuclear NMR spectroscopy.

Keywords: Diphosphines; Phospholes; Diphospholes; Synthesis; NMR

INTRODUCTION

Chelating compounds especially diphosphanes have found extensive applications as ligands in organometallic chemistry and in homogeneously transition-metal catalyzed reactions such as hydrogenation, hydroformylation, cross-coupling, etc...[1] Many optically-active diphosphanes have been designed for use as ligands in enantioselective catalysis, most of them containing the diphenylphosphanyl moiety.[2]

Some years ago, we initiated a program aimed at finding applications of phospholes in homogeneous catalysis and reported that 1,2,5-triphenylphosphole is a very efficient ligand for the rhodium-catalyzed hydroformylation of aliphatic, aromatic and functionalized olefins.[3] Since diphosphanes (diphosphines and diphosphites) have been found to be better ligands than monophosphanes for transition metal-catalyzed hydroformylation of olefins,[4] we sought to investigate 1,n-bis(2,5-

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diphenylphosphol-1-yl)alkanes. Many diphosphines, optically active or not, containing two dibenzophosphol-1-yl[5] groups are known and several diphosphines containing two dinaphtophosphol-1-yl[6] groups have been recently reported. However examples of simple 1,n-bis(phosphol-1-yl)alkanes are less common. Literature mentions the synthesis of 1,2-bis(phosphol-1-yl)ethane (unreported yield),[7] of 1,n -bis(2,3,4,5-tetraphenylphosphol-1-yl)alkanes (n = 1, 2; 12–23% yield)[8] and of 1,n-bis(3,4-dimethylphosphol-1-yl)alkanes (n = 1–4; 38–65% yield).[9] In addition we have already described the synthesis of optically active 1,4-diphospholes bearing 2,5-diphenylphosphol-1-yl or 3,4-dimethylphosphol-1-yl groups.[10] We now wish to report the high-yield synthesis and NMR characterization of the still unknown simple 1, n-bis(2,5-diphenylphosphol-1-yl) alkanes.

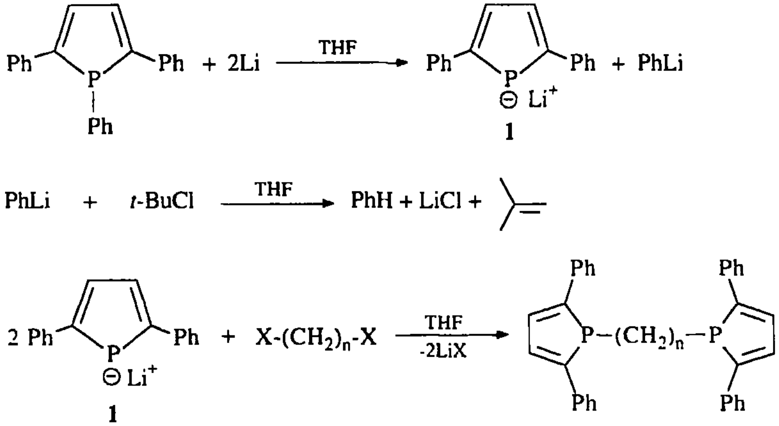
RESULTS AND DISCUSSION

The synthesis of 1,n -bis(2,5-diphenylphosphol-1-yl)alkanes **2–6** was performed from 2,5-diphenylphosphol-1-yllithium **1** using the conventional methodology outlined in scheme 1.

Generation of **1** was achieved, as usual, by cleavage of the exocyclic phosphorus-carbon bond of the readily available 1,2,5- triphenylphosphole[11] with lithium in THF,[8] followed by selective destruction of the concomitantly generated phenyllithium by *tert*-butyl chloride.[12] Analysis of the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy revealed the clean formation of **1** (THF solution, $\delta = 83.6$ ppm) sometimes contaminated by a small amount of 2,3,5-triphenylphospholyllithium[13] ($\delta = 106$ ppm). The reaction of **1** and 1,n-dichloroalkanes (n = 2–4) either did not proceed at room temperature or gave rise at reflux to a mixture of products ($^{31}P\{^1H\}$ NMR analysis) from which the diphospholes **2–4** could be isolated in low yields (25–30%). However, using 1,n-dibromoalkanes (n = 2–6) allowed a clean reaction at room temperature and resulted in the isolation of diphospholes **2–6** with the yields reported in scheme 1.

The phospholes **2–6** have been characterized by mass spectrometry, elemental analysis (see experimental section) and thoroughly studied by multinuclear NMR spectroscopy.

$^{31}P\{^1H\}$ NMR data (Table I) indicate that the chemical shift for **2–6** is comparable to that of 1,2,5-triphenylphosphole ($\delta\ ^{31}P = +3.0$ ppm)[14] and



overall isolated yield (X = Br)

2	n = 2	89%
3	n = 3	91%
4	n = 4	93%
5	n = 5	70%
6	n = 6	47%

SCHEME 1 Synthesis of 1,n -bis(2,5-diphenylphosphol-1-yl)alkanes **2–6**

significantly different from that of 1-methyl–2,5-diphenylphosphole (δ $^{31}P = -15.5$ ppm).[13] Thus the diphospholes **2–6** are expected to exhibit the same coordination chemistry as 1,2,5-triphenylphosphole.

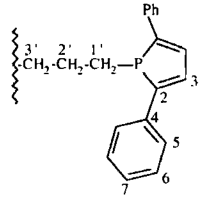
The ^{1}H NMR spectra do not give specific information except a characteristic doublet for the H^3 hydrogen atoms [$\delta = 6.90–7.10$ ppm ; $^{3}J(H\text{-}P)= 10$ Hz] (Table I).

All the resonances of carbon 13 NMR spectra of diphospholes **2–6** (Table II) have been assigned on the basis of the $^{13}C\{^{1}H\}$, $^{13}C\{^{31}P\}$ and $^{13}C\{^{1}H,^{31}P\}$ NMR spectra. The observed chemical shifts are in the expected range except for the carbon atom $C^{3'}$ of diphosphole **5** which appears to be the more deshielded of the aliphatic carbon atoms as ascertained by a 2D (δ,δ) $^{13}C\{^{31}P\}$, $^{1}H\{^{31}P\}$ NMR correlation obtained by a HMQC sequence.

CONCLUSION

1,n-bis(2,5-diphenylphosphol-1-yl)alkanes (n = 2–6) can be prepared in good yield by an efficient one pot experimental procedure. Work is in progress to study their coordination chemistry and their potential applications as ligands in transition metal-catalyzed hydrofunctionalisation of olefins.

TABLE I ^{31}P and ^{1}H NMR data of diphospholes **2–6**



Diphospholes		$2^{(a)}$	$3^{(a)}$	$4^{(a)}$	$5^{(b)}$	$6^{(c)}$
^{31}P{^{1}H} δ (ppm)		+6	+2.1	+2.5	+3.3	+3.5
^{1}H δ (ppm) *J* (Hz)	H^3	7.10 (d) $^3J_{H\text{-}P}$ = 10 Hz	6.90 (d) $^3J_{H\text{-}P}$ = 10 Hz	7.10 (d) $^3J_{H\text{-}P}$ = 10 Hz	6.95 (d) $^3J_{H\text{-}P}$ = 10 Hz	7.11 (d) $^3J_{H\text{-}P}$ = 10 Hz
	$H^{1'}$	1.55 (t) $^3J_{H\text{-}P}$ = 6 Hz	1.57 (m)	1.60 (m)	1.51 (m)	1.65 (m)
	$H^{2'}$	1.55 (t) $^3J_{H\text{-}P}$ = 6 Hz	0.80 (m)	0.80 (m)	0.76 (dqt)$^{(d)}$ $^3J_{H\text{-}H}$ = 8 Hz $^3J_{H\text{-}P}$ = 8 Hz	0.77 (m)
	$H^{3'}$	-	1.57 (m)	-	0.44 (qt)$^{(d)}$ $^3J_{H\text{-}H}$ = 8 Hz	0.67 (m)

(a) Bruker AC 200, in $CDCl_3$ solution at 200.13 and 81.015 MHz for ^{1}H and ^{31}P{^{1}H} NMR, respectively.
(b) Bruker AMX 400, in C_6D_6 solution at 400.14 and 161.99 MHz for ^{1}H and ^{31}P{^{1}H} NMR, respectively. In $CDCl_3$ solution, $H^{2'}$ and $H^{3'}$ are superimposed at 0.82 ppm.
(c) Bruker AMX 400, in $CDCl_3$ solution at 400.14 and 161.99 MHz for ^{1}H and ^{31}P{^{1}H} NMR, respectively.
(d) qt = quintuplet.

EXPERIMENTAL SECTION

General Procedure

All sample manipulations were carried out under argon using standard Schlenk tube and vacuum techniques. Solvents and reagents were purified according to literature procedures[15] and stored under argon. Argon U (L'Air Liquide) was used after passage through 3-Å molecular sieves. Lithium (wires, Aldrich), *tert*-butyl chloride (Fluka), 1,2-dibromoethane (Prolabo), 1,3-dibromopropane (Fluka), 1,4-dibromobutane, 1,5-dibromopentane and 1,6-dibromohexane (Aldrich), were used as received. 1,2,5-triphenylphosphole was prepared by a reported procedure.[11]

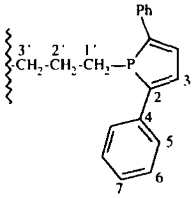
^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ or C_6D_6 solutions on Bruker AC 80 (^{31}P : 32.43 MHz) (analysis of reaction mixtures), AC 200 (^{1}H : 200.13 MHz, ^{31}P : 81.015 MHz, ^{13}C : 50.32 MHz) or AMX 400 (^{1}H : 400.14 MHz, ^{31}P : 161.99 MHz, ^{13}C : 100.62 MHz) spectrometers. ^{1}H and ^{13}C NMR chemical shifts are referenced to tetramethylsilane assigning the $CDCl_3$ resonances at 7.27 and 77.0 ppm, respectively and the C_6D_6 resonances at 7.16 and 128.0 ppm, respectively. ^{31}P NMR chemical shifts are referenced to external 85% H_3PO_4 in D_2O.

Mass spectra were obtained on a Nermag R10/10 (EI, 70 eV; CI, NH_3) spectrometer and Elemental analyses were performed on a Perkin Elmer 2400 serie II apparatus. Melting point (uncorrected) were measured on a Buchi SMP 20 apparatus. All the compounds synthesized except **2** show a change in color between 90 and 100°C but melt at the reported temperature.

1,2-bis(2,5-diphenylphosphol-1-yl)ethane (2)

A 250-mL Schlenk flask containing a teflon-coated magnetic stirring bar was charged with 1,2,5-triphenylphosphole (2.7 g, 8.6 mmol) and submitted to three vacuum-argon cycles. Freshly distilled THF (50 mL) was syringed into the Schlenk flask and the mixture cooled to 0°C. Small cuts of lithium (0.15 g, 21.6 mmol) were added and the reaction medium stirred at 10–15 °C for 5 h. After filtration through celite into another Schlenk flask to remove unreacted lithium, *tert*-butyl chloride (1.2 mL, 11.2 mmol) was added and the filtrate stirred for 16 h. 1,2-dibromoethane (0.37 mL, 4.3 mmol) was then added and the reaction medium stirred for 5 h. Addition of distilled water (60 mL) gave a two-phase system which was vigorously stirred. Water was decanted with a syringe and THF (20 mL) and water (60 mL) were added. This procedure was repeated twice. The THF solution was evaporated to dryness to leave an orange solid. Recrystallization from methanol afforded a yellow solid which was dried under reduced pressure up to constant weight (1.9 g, 89%). m.p. >245°C. – MS (EI, 70 eV): *m/z* (%) = 499 (23), 498 (69) [M^+]. 470 (22) [M^+-C_2H_4], 235 (53). – $C_{34}H_{28}P_2$ (498.5): calc. C 81.91, H 5.66; found C 81.13, H 5.82.

TABLE II $^{13}C\{^{1}H\}$ NMR data of diphospholes **2–6**



	$C^{1'}$	$C^{2'}$	$C^{3'}$	C^{2}	C^{3}	C^{4}	C^{5}	C^{6}	C^{7}
2$^{(a)}$	18.9 (dd) $|^{1}J_{C\text{-}P}|$= 22 Hz $|^{2}J_{C\text{-}P}|$ =4 Hz			149.7 (d) $|^{1}J_{C\text{-}P}|$ = 3 Hz	132.1 (d) $|^{2}J_{C\text{-}P}|$ =9 Hz	136.2 (d) $|^{2}J_{C\text{-}P}|$ = 17 Hz	125.6 (d) $|^{3}J_{C\text{-}P}|$ =9 Hz	128.8 (s)	127.0 (s)
3$^{(a)}$	24.5 (dd) $|^{1}J_{C\text{-}P}|$ = 17 Hz $|^{3}J_{C\text{-}P}|$ = 6 Hz	21.5 (s)		150.5 (s)	132.0 (d) $|^{2}J_{C\text{-}P}|$ = 8 Hz	136.2 (d) $|^{2}J_{C\text{-}P}|$ = 17 Hz|	125.6 (d) $^{3}J_{C\text{-}P}|$ = 10 Hz	128.8 (s)	127.0 (s)
4$^{(a)}$	23.9 (d) $|^{1}J_{C\text{-}P}|$ = 16 Hz	26.3 (d) $|^{3}J_{C\text{-}P}|$ = 6 Hz		151.0 (s)	131.7 (d) $|^{2}J_{C\text{-}P}|$ = 8 Hz	136.9 (d) $|^{2}J_{C\text{-}P}|$ = 17 Hz	126.2 (d) $|^{3}J_{C\text{-}P}|$ = 9 Hz	128.7 (s)	127.0 (s)
5$^{(b)}$	23.9 (d) $|^{1}J_{C\text{-}P}|$ = 15 Hz	24.6 (s)	31.7 (t) $|^{3}J_{C\text{-}P}|$ = 7 Hz	152.0 (s)	132.6 (d) $|^{2}J_{C\text{-}P}|$ = 8 Hz	138.2 (d) $|^{2}J_{C\text{-}P}|$ = 17 Hz	127.2 (d) $|^{3}J_{C\text{-}P}|$ = 10 Hz	129.6 (s)	127.8 (s)
6$^{(b)}$	24.0 (d) $|^{1}J_{C\text{-}P}|$ = 15 Hz	24.9 (s)	29.6 (d) $|^{3}J_{C\text{-}P}|$ = 6 Hz	151.1 (s)	131.8 (d) $|^{2}J_{C\text{-}P}|$ = 9 Hz	137.1 (d) $|^{2}J_{C\text{-}P}|$ = 17 Hz|	126.3 (d) $|^{3}J_{C\text{-}P}|$ = 10 Hz	128.8 (s)	127.1 (s)

(a) : Bruker AC 200, in $CDCl_3$ solution at 50.32 MHz. (b) : Bruker AMX 400, in $CDCl_3$ solution at 100.62 MHz.

1,3-bis(2,5-diphenylphosphol-1-yl)propane (3)

The same procedure was followed by using 1,3-dibromopropane (0.43 mL, 4.3 mmol). **3**: yield 1.95 g (91%) yellow solid, m.p. 133°C – MS (EI, 70 eV): *m/z* (%) = 512 (51) [M^+], 277 (100), 133 (36). – $C_{35}H_{30}P_2$ (512.5): calc. C 82.02, H 5.90; found C 81.44, H 5.89.

1,4-bis(2,5-diphenylphosphol-1-yl)butane (4)

The same procedure was followed by using 1,4-dibromobutane (0.51 mL, 4.3 mmol). **4:** yield 2.15 g (93%) yellow solid, m.p. 142°C – MS (EI, 70 eV): *m/z (%)* = 526 (51) [M^+], 292 (23), 291 (100), 133 (35). – $C_{36}H_{32}P_2$ (526.6): calc. C 82.11, H 6.13; found C 81.44, H 6.57.

1,5-bis(2,5-diphenylphosphol-1-yl)pentane (5)

The same procedure was followed by using 1,5-dibromopentane (0.919 g, 4.00 mmol). **5** was recrystallized twice from CH_2Cl_2-MeOH. **5:** yield 1.5 g (70%) yellow solid, m.p. 135°C – MS (CI, NH_3): *m/z* (%) = 542 (42), 541 (100) [MH^+]. – $C_{37}H_{34}P_2$(540.6): calc. C 82.20, H 6.34; found C 80.52, H 6.49.

1,6-bis (2,5-diphenylphosphol-1-yl)hexane (6)

The same procedure was followed by using 1,6-dibromohexane (0.977 g, 4.00 mmol). **6** yield 1.04 g (47%) yellow solid, m.p. 133°C – MS (CI, NH_3): *m/z* (%) = 556 (45), 555 (100) [MH^+]. – $C_{38}H_{36}P_2$ (554.7): calc. C 82.29, H 6.54; found C 82.01, H 6.82.

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