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SYNTHESIS AND PHYSICAL PROPERTIES OF CHLORODI(*o*-TOLYL)PHOSPHINE, LITHIUM DI(*o*-TOLYL)PHOSPHIDE AND THE DIPHOSPHINE SERIES (*o*-TOLYL)$_2$P(CH$_2$)$_n$P(*o*-TOLYL) (n = 1—4, 6, 8)

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Summary

The starting material chlorodi(*o*-tolyl)phosphine has been prepared by the reaction of phosphorus trichloride and the Grignard of *o*-chlorotoluene. The intermediate lithium di(*o*-tolyl)phosphide was obtained by the direct reaction of lithium metal and chlorodi(*o*-tolyl)phosphine in tetrahydrofuran. Lithium di(*o*-tolyl)phosphide reacted smoothly with ω,ω'-dihaloalkanes, X(CH$_2$)$_n$X (n = 1—4, 6, 8, X = Cl or Br) to form the tertiary diphosphines (*o*-tolyl)$_2$P(CH$_2$)$_n$P(*o*-tolyl)$_2$. Chlorodi(*o*-tolyl)phosphine and the diphosphines (*o*-tolyl)$_2$P(CH$_2$)$_n$P(*o*-tolyl)$_2$ (n = 1—4, 6, 8) were characterised by elemental analyses and ^{1}H, ^{31}P and ^{13}C NMR spectral analyses.

Introduction

Investigations into the reactions of sterically hindered tertiary phosphine ligands with transition metal complexes has led to the discovery of a wide variety of unusual and interesting complexes. Some ligands which have been used are the t-butyl phosphines e.g. PBu$^t_3$ [1] or Bu$^t_2$P(CH$_2$)$_n$PBu$^t_2$ [2—10], *o*-tolylphosphines e.g. P(*o*-tolyl)$_3$ [11] and the bibenzyl phosphine *o*-(C$_6$H$_5$)$_2$PC$_6$H$_4$CH$_2$CH$_2$C$_6$H$_4$P(C$_6$H$_4$)$_2$-*o* [12]. Because of their bulky nature metallation reactions occur readily. Tri-t-butylphosphine metallates [Ir(C$_8$H$_{14}$)Cl]$_2$ in the presence of γ-picoline forming a four-membered ring [1], while Bu$^t_2$P(CH$_2$)$_n$PBu$^t_2$ (n = 5 or 6) reacts with rhodium trichloride to form RhHCl(PBu$^t_2$PCH$_2$CH$_2$CHCH$_2$CH$_2$PBu$^t_2$) [8] and RhCl(Bu$^t_2$PCH$_2$CH$_2$CH=CHCH$_2$CH$_2$PBu$^t_2$) [5,7], respectively. In refluxing 2-methoxyethanol, tri-*o*-tolylphosphine undergoes the coupling-dehydrogenation reaction with rhodium trichloride to form

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the square-planar complex $\overline{RhCl[(o\text{-tolyl})_2PC_6H_4CH{=}CHC_6H_4P(o\text{-tolyl})_2]}$ [11], while $o\text{-}(C_6H_5)_2PC_6H_4CH_2CH_2C_6H_4P(C_6H_5)\text{-}o$ reacts smoothly with $[RhCl(C_8H_{12})]_2$ to form a similar product, $\overline{RhCl(o\text{-}(C_6H_5)_2PC_6H_4CH{=}CHC_6H_4P\text{-}(C_6H_5)\text{-}o]}$ [12,14]. In this present paper we discuss the preparation of the diphosphines $(o\text{-tolyl})_2P(CH_2)_nP(o\text{-tolyl})_2$ and the intermediary compounds chlorodi-*o*-tolylphosphine and lithium di-*o*-tolylphosphide. In a later paper we will discuss some preliminary results of the reactions of these ligands with transition metal complexes [15].

Experimental section

The ^{13}C NMR and ^{31}P NMR spectra were recorded on a JEOL FX-100 spectrometer. The ^{13}C NMR spectra were recorded using the internal lock and referenced to internal TMS while the ^{31}P NMR spectra were recorded using the external lock and referenced to 85% H_3PO_4. The ^1H NMR spectra were obtained on a JEOL JNM PS-100 spectrometer referenced to internal TMS. All NMR spectra were recorded on samples dissolved in $CDCl_3$. The mass spectra were recorded on an AEI MS 902S instrument and the analyses were obtained from the University of Queensland Microanalytical Service and the Australian Microanalytical Service, CSIRO, Melbourne. The preparative conditions and yields of the diphosphines are given in Table 1 while the analytical data are given in Table 2. The reagents were standard reagent grade chemicals and were dried before use. The *o*-chlorotoluene was distilled and stored over molecular sieves and the THF was stored over sodium wire. The method for the preparation of chlorodi-*o*-tolylphosphine, lithium di-*o*-tolylphosphide and one of the diphosphines 1,6-bis(di-*o*-tolylphosphino)hexane are given below. The other diphosphines were prepared via the same method.

Preparation of chlorodi-o-tolylphosphine

The *o*-tolyl Grignard reagent was prepared by the dropwise addition of 177 g (1.4 mol) of *o*-chlorotoluene in 300 ml of anhydrous THF to 36 g (1.5 mol) of magnesium turnings in 250 ml of THF under reflux conditions (in a one-litre 3-neck flask fitted with a pressure-equalising dropping funnel, mechanical stirrer and condenser). After the addition was complete (ca. 2 h) the solution was refluxed for a further 5 h, at which stage little magnesium metal still remained. At this time the Grignard was cooled in an ice bath.

To a 3-neck 3-litre flask was added 82 g (0.60 mol) of phosphorus trichloride in 1500 ml of anhydrous THF. This solution was cooled in a dry-ice/acetone bath. The Grignard solution was then transferred under nitrogen through a tube connected by two stopcocks into a one-litre pressure-equalising dropping funnel. Then the Grignard solution was added slowly in a dropwise manner over a $2\frac{1}{2}$ h period to the solution of phosphorus trichloride with the aid of a mechanical stirrer. After the addition was complete, the solution was stirred overnight at room temperature. Some white precipitate (magnesium chloride) had formed at this stage. The solution was then heated to reflux whereupon large amounts of the white precipitate formed, making stirring difficult. The solution was refluxed for 1 h and then as much as possible of the THF was distilled off. One litre of benzene was then added and the benzene solution filtered to remove

TABLE 1

PREPARATIVE CONDITIONS FOR THE DIPHOSPHINES $(o\text{-tolyl})_2P(CH_2)_nP(o\text{-tolyl})_2$

Diphosphine	Starting materials	Yield
$(o\text{-tolyl})_2PCH_2P(o\text{-tolyl})_2$	$P(o\text{-tolyl})_2Cl$, 20.0 g (80.6 mmol); CH_2Cl_2, 3.44 g (40.4 mmol)	11.5 g (64.8%)
$(o\text{-tolyl})_2P(CH_2)_2P(o\text{-tolyl})_2$	$P(o\text{-tolyl})_2Cl$, 10.0 g (40.3 mmol); $Cl(CH_2)_2Cl$, 2.00 g (20.2 mmol)	5.4 g (59.0%)
$(o\text{-tolyl})_2P(CH_2)_3P(o\text{-tolyl})_2$	$P(o\text{-tolyl})_2Cl$, 10.0 g (40.3 mmol); $Br(CH_2)_3Br$, 4.10 g (20.3 mmol)	4.5 g (47.7%)
$(o\text{-tolyl})_2P(CH_2)_4P(o\text{-tolyl})_2$	$P(o\text{-tolyl})_2Cl$, 10.0 g (40.3 mmol); $Br(CH_2)_4Br$, 4.30 g (19.9 mmol)	5.2 g (54.2%)
$(o\text{-tolyl})_2P(CH_2)_6P(o\text{-tolyl})_2$	$P(o\text{-tolyl})_2Cl$, 10.0 g (40.3 mmol); $Br(CH_2)_6Br$, 4.42 g (18.1 mmol)	6.5 g (70.3%)
$(o\text{-tolyl})_2P(CH_2)_8P(o\text{-tolyl})_2$	$P(o\text{-tolyl})_2Cl$, 10.0 g (40.3 mmol); $Br(CH_2)_8Br$, 5.48 g (20.1 mmol)	8.0 g (74.1%)

TABLE 2

ANALYTICAL DATA FOR THE COMPOUNDS P(*o*-tolyl)$_2$Cl AND (*o*-tolyl)$_2$P(CH$_2$)$_n$P(*o*-tolyl)$_2$ (n = 1—4, 6, 8)

Compound	Found (calcd.) (%)				M.p. (°C)
	C	H	P	MW [a]	
P(*o*-tolyl)$_2$Cl [b]	67.53 (67.61)	5.84 (5.67)	12.2 (12.5)	248, 250 (248, 250)	57
(*o*-tolyl)$_2$PCH$_2$P(*o*-tolyl)$_2$	78.87 (79.07)	6.95 (6.87)	13.9 (14.1)	440 (440)	178
(*o*-tolyl)$_2$P(CH$_2$)$_2$P(*o*-tolyl)$_2$	79.20 (79.27)	7.12 (7.10)	13.5 (13.6)	454 (454)	148
(*o*-tolyl)$_2$P(CH$_2$)$_3$P(*o*-tolyl)$_2$	79.27 (79.47)	7.48 (7.31)	12.9 (13.2)	468 (468)	140
(*o*-tolyl)$_2$P(CH$_2$)$_4$P(*o*-tolyl)$_2$	79.14 (79.64)	7.49 (7.52)	12.6 (12.8)	4.82 (482)	196
(*o*-tolyl)$_2$P(CH$_2$)$_6$P(*o*-tolyl)$_2$	79.53 (79.97)	7.90 (7.90)	11.8 (12.1)	510 (510)	162
(*o*-tolyl)$_2$P(CH$_2$)$_8$P(*o*-tolyl)$_2$	79.31 (80.27)	8.60 (8.23)	11.5 (11.5)	538 (538)	124

[a] M^+ is the parent ion in the mass spectrum. [b] Analysis, Found: Cl, 14.1; Mol. wt. 260 (vpo in benzene). $C_{14}H_{14}ClP$ calcd.: C, 14.3; Mol. wt. 249.

the magnesium chloride. Due to the relatively large volumes involved this filtration was carried out in the air, but no phosphine oxide products were detected. The benzene was distilled off at atmospheric pressure and the residue distilled at reduced pressure. A small quantity of liquid, presumably dichloro-*o*-tolylphosphine, distilled at 82—84° C and 2.5 mmHg, but was not characterized. The main fraction of chlorodi-*o*-tolylphosphine distilled at 160° C and 2 mmHg. Upon cooling it set into a hard mass. The yield of chlorodi(*o*-tolyl)phosphine was 96 g (65%).

Preparation of lithium di-o-tolylphosphide

In a typical preparation 1 g (144 mmol) of freshly cut sheets of lithium metal was added to 10 g (40.3 mmol) of chlorodi-*o*-tolylphosphine in 100 ml of anhydrous THF in a 250 ml three-neck flask with a stirring bar and reflux condenser. After ca. 1.5 h (see note) the solution turned an orange colour. After the solution had turned orange, it was refluxed for a further 7.5 h. (Note. The time for the solution to turn orange was quite variable. The shortest time that we experienced was 40 min and the longest was 4 h, but most reactions turned orange in the 1—2 h period. The time seemed to be dependent on the initial condition of the lithium metal.) The solution was now ready for the next step in the preparation of the diphosphines.

Typical preparation of the diphosphines, (o-tolyl)$_2$P(CH$_2$)$_n$P(o-tolyl)$_2$. Preparation of 1,6-bis(di-o-tolylphosphino)hexane

The lithium di-*o*-tolylphosphide solution, as prepared above, was cooled in a salt/ice bath and then transferred under nitrogen through a tube connected by two stopcocks into another 250 ml three-neck flask containing a magnetic

stirring bar. (Note. As the excess lithium is less dense than the THF, it is readily separated. Alternatively, it was passed under nitrogen through a coarse sintered glass filter connecting the two flasks.) To this solution cooled in a salt/ice bath was added dropwise 4.4 g (18.0 mmol) of 1,6-dibromohexane in 20 ml of anhydrous THF. At the end of the addition (ca. 0.5 h) the solution was a pale orange colour. The solution was then stirred overnight at room temperature, and then refluxed for 0.5 h. Any excess lithium di-*o*-tolylphosphide was destroyed by cooling the solution to 0°C and adding 2 ml of water. The solution was heated and the crude product was precipitated by the addition of ethanol. The solution was cooled and then filtered. The crude product was washed with water, then ethanol and then dried. It was the recrystallised using a methylene chloride/ethanol solution. Yield of the recrystallised 1,6-bis(di-*o*-tolylphosphino)hexane was 6.5 g (70.3%).

Discussion

The reaction of a Grignard reagent RMgX with phosphorus trichloride leads predominantly to the trisubstituted phosphorus compounds PR_3 [16—18] and therefore is generally considered unsuitable for the preparation of the less substituted $RPCl_2$ and R_2PCl compounds. However, Voskuil and Arens [19], following on some earlier observations of Issleib and Seidel [20], have shown quite successfully that as long as R is a sterically hindered alkyl, viz. branched primary, secondary or tertiary alkyl, then the intermediate R_2PCl_2 and R_2PCl compounds can be isolated under controlled conditions. We have adapted this procedure for the preparation of chlorodi-*o*-tolylphosphine which can be prepared in 100 g quantities in a good yield (65%). We note that chlorodi-*o*-tolylphosphine has been claimed to have been prepared previously [21] by another reaction sequence but we seriously doubt the validity of the product, which has a reported melting point of 4°C compared to our product which has a melting point of 57°C.

The reaction of chlorodi-*o*-tolylphosphine with lithium is relatively slow compared to the analogous reaction of chlorodiphenylphosphine [22], and this is probably related to an expected slower attack of the lithium on the sterically crowded intermediate bis(di-*o*-tolyl)diphosphine compound, $(o\text{-tolyl})_2PP(o\text{-tolyl})_2$. On the other hand, the reaction of lithium di-*o*-tolylphosphide with the ω,ω'-dihaloalkanes proceeded smoothly and rapidly to give the tertiary diphosphines $(o\text{-tolyl})_2P(CH_2)_nP(o\text{-tolyl})_2$ in good yields (see Table 1).

Results

^{31}P and ^{1}H NMR spectra

The ^{31}P NMR spectra of all the compounds (Table 3) consisted of a single resonance occurring downfield at —74.19 ppm for $P(o\text{-tolyl})_2Cl$ and upfield (+33 to +44 ppm) for the diphosphines $(o\text{-tolyl})_2P(CH_2)_nP(o\text{-tolyl})_2$. The ^{1}H NMR spectrum of $P(o\text{-tolyl})_2Cl$ (Table 3) consisted of phenyl resonances and a methyl resonance at 2.50 ppm, which was a doublet with a ^{31}P coupling of 2.6 Hz. For the diphosphines $(o\text{-tolyl})_2P(CH_2)_nP(o\text{-tolyl})_2$, phenyl, methylene and methyl resonances were observed at 7.6—7.0, 2.6—1.9 and 2.5—2.3 ppm,

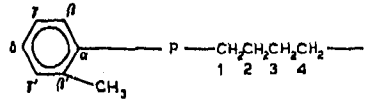
(continued on p. 58)

TABLE 3

^1H AND ^{31}P NMR DATA FOR THE COMPOUNDS P(*o*-tolyl)$_2$Cl AND (*o*-tolyl)$_2$P(CH$_2$)$_n$P(*o*-tolyl)$_2$ [a] (n = 1—4, 6, 8)

Compound	Chemical shifts (ppm) [b]							Coupling constants (Hz)	
	δP [c]	Phenyl	CH_3	H(1)	H(2)	H(3)	H(4)	J(P—CH_3)	J(P—H)
P(*o*-tolyl)$_2$Cl	—74.19	7.6—7.0	2.50(d)	—	—	—	—	2.6	—
(*o*-tolyl)$_2$PCH$_2$P(*o*-tolyl)$_2$	+44.05	7.4—7.0	2.26(s)	2.63(t)	—	—	—	0	3.0
(*o*-tolyl)$_2$P(CH$_2$)$_2$P(*o*-tolyl)$_2$	+33.50	7.2—7.0	2.40(s)	2.10(t)	—	—	—	0	4.0
(*o*-tolyl)$_2$P(CH$_2$)$_3$P(*o*-tolyl)$_2$	+38.98	7.2—7.0	2.38(d)	2.14(t)	~1.6(m)	—	—	~0.5	nr
(*o*-tolyl)$_2$P(CH$_2$)$_4$P(*o*-tolyl)$_2$	+38.39	7.3—7.0	2.42(s)	1.96(m)	~1.5	—	—	0	nr
(*o*-tolyl)$_2$P(CH$_2$)$_6$P(*o*-tolyl)$_2$	+37.44	7.3—7.0	2.42(d)	1.96(m)	1.6 ———	1.3	—	~0.5	nr
(*o*-tolyl)$_2$P(CH$_2$)$_8$P(*o*-tolyl)$_2$	+38.03	7.3—7.0	2.41(s)	1.92(m)	1.6 ———		1.1	0	nr

[a] Numbering system for P(*o*-tolyl)$_2$Cl and (*o*-tolyl)$_2$P(CH$_2$)$_n$P(*o*-tolyl)$_2$, n = 1—4, 6, 8.



[b] s = singlet, d = doublet, t = triplet, m = multiplet, nr = not resolved. [c] + is upfield.

TABLE 4

^{13}C NMR DATA FOR THE COMPOUNDS P(*o*-tolyl)$_2$Cl AND (*o*-tolyl)$_2$P(CH$_2$)$_n$P(*o*-tolyl)$_2$ [a] (n = 1–4, 6, 8)

Compound	Chemical shifts (ppm) [b]										
	C_α	C_β	$C_{\beta'}$	C_γ	$C_{\gamma'}$	C_δ	CH_3	C(1)	C(2)	C(3)	C(4)
P(*o*-tolyl)$_2$Cl	141.4(d)	131.5(d)	135.5(d)	130.3(d)	130.3(s)	126.4(s)	20.5(d)	—	—	—	—
(*o*-tolyl)$_2$PCH$_2$P(*o*-tolyl)$_2$	142.3(t)	129.9(t)	137.4(t)	131.2(s)	128.4(s)	125.9(s)	21.2(t)	26.5(t)	—	—	—
(*o*-tolyl)$_2$P(CH$_2$)$_2$P(*o*-tolyl)$_2$	142.3(t)	130.0(t)	136.3(t)	131.1(s)	128.4(s)	126.0(s)	21.2(t)	22.6(s)	—	—	—
(*o*-tolyl)$_2$P(CH$_2$)$_3$P(*o*-tolyl)$_2$	142.3(d)	129.9(d)	136.9(d)	131.0(s)	128.3(s)	126.0(s)	21.2(d)	22.4(t)	28.9(t)	—	—
(*o*-tolyl)$_2$P(CH$_2$)$_4$P(*o*-tolyl)$_2$	142.3(d)	130.0(d)	137.1(d)	131.1(s)	128.3(s)	126.0(s)	21.2(d)	28.0(d)	26.8(d)	—	—
(*o*-tolyl)$_2$P(CH$_2$)$_6$P(*o*-tolyl)$_2$	142.3(d)	129.9(d)	137.2(d)	131.0(s)	128.2(s)	125.9(s)	21.2(d)	25.9(d)	27.0(d)	31.0(d)	—
(*o*-tolyl)$_2$P(CH$_2$)$_8$P(*o*-tolyl)$_2$	142.3(d)	129.9(d)	137.3(d)	131.0(s)	128.2(s)	125.9(s)	21.2(d)	25.9(d)	27.0(d)	31.2(d)	29.1(s)

	Coupling constants (Hz)							
	P–C_α	P–C_β	P–$C_{\beta'}$	P–CH_3	P–C(1)	P–C(2)	P–C(3)	P–C(4)
P(*o*-tolyl)$_2$Cl	30.5	3.7	35.4	23.8	—	—	—	—
(*o*-tolyl)$_2$PCH$_2$P(*o*-tolyl)$_2$	13.7	2.4	4.3	11.9	22.9	—	—	—
(*o*-tolyl)$_2$P(CH$_2$)$_2$P(*o*-tolyl)$_2$	12.5	2.1	7.0	10.7	<1.0	—	—	—
(*o*-tolyl)$_2$P(CH$_2$)$_3$P(*o*-tolyl)$_2$	25.6	5.5	13.4	21.4	17.7	12.2	—	—
(*o*-tolyl)$_2$P(CH$_2$)$_4$P(*o*-tolyl)$_2$	25.6	4.9	13.4	21.4	15.3	12.8	—	—
(*o*-tolyl)$_2$P(CH$_2$)$_6$P(*o*-tolyl)$_2$	25.0	4.9	14.0	20.8	16.5	11.6	12.8	—
(*o*-tolyl)$_2$P(CH$_2$)$_8$P(*o*-tolyl)$_2$	25.0	4.3	14.0	21.4	16.5	11.0	12.2	0

[a] See footnote *a* of Table 3. [b] See footnote *b* of Table 3.

respectively. Only for $n = 3$ and $n = 6$ did the methyl resonance show any splitting due to ^{31}P coupling. For the other diphosphines, $n = 1, 2, 4, 8$, the coupling was too small to be observed. Only in the two diphosphines $(o\text{-tolyl})_2P(CH_2)_nP(o\text{-tolyl})_2$, $n = 1$ or 2, was the ^{31}P coupling to the methylene protons readily observable. For the other diphosphines this coupling was not readily distinguishable due to extra $^1H—^1H$ coupling. In the spectrum for $(o\text{-tolyl})_2P(CH_2)_3P(o\text{-tolyl})_2$, the H(1) resonance occurs as a triplet ($J \approx 7$ Hz) but this is probably due to $^1H—^1H$ coupling.

^{13}C NMR spectra

The ^{13}C NMR spectrum of $P(o\text{-tolyl})_2Cl$ (Table 4) consisted of a phenyl region and a methyl resonance while the ^{13}C NMR spectra of the diphosphines consisted of a phenyl region, methyl and methylene resonances. The phenyl and methylene carbon resonances were assigned on the basis of observed chemical shifts and coupling constants with regard to those of similar tertiary phosphines [23—26]. Although C_α, C_β, $C_{\beta'}$ and C_δ resonances were readily assignable on the basis of chemical shifts and ^{31}P coupling constants, C_γ and $C_{\gamma'}$ were not. C_γ and $C_{\gamma'}$ were assigned on the basis of an NOE-enhanced proton coupled spectrum of $(o\text{-tolyl})_2PCH_2P(o\text{-tolyl})_2$. C_γ was assigned to the more complex resonance downfield at 131.2 ppm in $(o\text{-tolyl})_2PCH_2P(o\text{-tolyl})_2$. The phenyl assignments for the other diphosphines were made in accord with the assignments for $(o\text{-tolyl})_2PCH_2P(o\text{-tolyl})_2$. For the diphosphine $(o\text{-tolyl})_2PCH_2P(o\text{-tolyl})_2$, C_α, C_β, $C_{\beta'}$, CH_3 and C(1) are triplets arising from the virtual coupling of the two phosphorus atoms; and for $(o\text{-tolyl})_2PCH_2CH_2P(o\text{-tolyl})_2$, C_α, C_β, $C_{\beta'}$ and CH_3 resonances are triplets but the C(1) resonance is only a singlet which is slightly broadened. It is interesting to note that for $(o\text{-tolyl})_2PCH_2CH_2CH_2P(o\text{-tolyl})_2$, the virtual coupling is strong enough for the methylene resonances to appear as triplets but not strong enough to affect the phenyl and CH_3 resonances, which now appear only as doublets. For the longer chain disphosphines $(o\text{-tolyl})_2P(CH_2)_nP(o\text{-tolyl})_2$, $n = 4$, 6 or 8, doublets are only observed for C_α, C_β, $C_{\beta'}$, CH_3 and methylene carbons, except for the C(4) resonance for $n = 8$ which appears as a singlet. In the compound chlorodi(*o*-tolyl)phosphine, the C_γ resonance appears as a doublet with a ^{31}P coupling of 3.1 Hz. In all other cases C_γ, $C_{\gamma'}$ and C_δ appear as singlets.

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