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SYNTHESIS OF THREE NEW DITERTIARY PHOSPHINES: 1-DIPHENYLPHOSPHINO-2-BIS(*m*-FLUOROPHENYL)PHOSPHINOETHANE, 1-DIPHENYLPHOSPHINO-2-BIS(*p*-FLUOROPHENYL)PHOSPHINOETHANE AND 1-DIPHENYLPHOSPHINO-2-*m*-BIS(TRIFLUOROMETHYL)PHENYLPHOSPHINOETHANE

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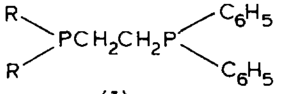
Summary

The syntheses of 1-diphenylphosphino-2-bis(*m*-fluorophenyl)phosphinoethane, 1-diphenylphosphino-2-bis(*p*-fluorophenyl)phosphinoethane and 1-diphenylphosphino-2-*m*-bis(trifluoromethylphenyl)phosphinoethane are reported. They were prepared by base-catalysed addition of $>$P–H bonds of the diarylphosphines to the C=C double bond of the diphenylvinylphosphine using KOBu^t as a catalyst. The new ditertiaryphosphines thus produced are air-stable crystalline solids, and have been characterised by ^{1}H and ^{31}P NMR spectroscopy.

Introduction

1,2-Bis(diphenylphosphino)ethane has been used extensively as a ligand [1,2]. It forms chelate as well as bridging complexes with transition metals [3]. The complexes formed are sparingly soluble in organic solvents, and so their reactions with other species could not be followed by NMR spectroscopy [1]. In order to improve the solubility characteristics of the transition metal complexes, we have replaced the phenyl groups of one of the phosphorus atoms by *m*- or *p*-fluorophenyl or *m*-trifluoromethylphenyl groups, which would be expected to increase the solubility and also to modify the electronic properties of the phosphorus atom. Unsymmetrical ditertiaryphosphine ligands [4–7] which have chemically and magnetically different phosphorus nuclei attached to the same chelate backbone are important because of the availibility of ^{31}P NMR as a probe for investigation and elucidation of the factors which determine the stereochemistry and reactivity of the resulting transition metal complexes. Another advantage of introducing fluorine groups on *m*- or *p*-positions of the phenyl ring is that this would permit the use of ^{19}F NMR



(I)

(Ia, R = m-FC_6H_4 ; Ib, R = p-FC_6H_4 ; Ic, R = m-$CF_3C_6H_4$)

spectroscopy in characterization of the complexes. We report here the synthesis of three new ligands, Ia–Ic.

Results and discussion

The new ligands were prepared by the base catalysed addition [8] of a $>$P–H bond of the appropriate diarylphosphine to the C=C double bonds of the diphenylvinylphosphine in tetrahydrofuran using $KOBu^t$ as a catalyst:

$$Ph_2PCH=CH_2 + R_2PH \xrightarrow{KOBu^t} R_2PCH_2CH_2PPh_2$$

$$(R = m\text{-}FC_6H_4, p\text{-}FC_6H_4 \text{ or } m\text{-}CF_3C_6H_4)$$

The ligands Ia–Ic are white, air-stable crystalline solids, soluble in benzene, toluene, chloroform and methylene chloride, Ia and Ib are insoluble in methanol, but Ic is soluble in this alcohol. Incorporation of fluorine or trifluoromethyl groups in the *m*- or *p*-position of the phenyl ring lowers the m.p. of the ligands (Ia, 92–93°C; Ib, 93–94°C; Ic, 88–89°C, compared with 1,2-bis(diphenylphosphino)ethane, 142–44°C) and increases the solubility of ligands and of their metal complexes [9,10].

The ^1H NMR spectra of the ligands Ia–Ic are not very informative; they show the expected complex multiplet at ~7.30–6.80 due to the phenyl protons and a multiplet at 2.0–1.90 due to the methylene protons. The ^{31}P NMR spectra obtained at 24.3 MHz on Bruker WP60 spectrometer shows that chemical shift difference of both the phosphorus nuclei in Ia and Ic are small, and only one line appears in the spectra in each case (see Table 1), whereas in the case of Ib two doublets are observed (AB pattern) at −12.40 and −14.60 ppm, J(P–P) 34.5 Hz, indicating the

TABLE 1

$^{31}P(^1H)$NMR DATA FOR NEW DITERTIARY PHOSPHINES

(Chemical shifts are reported in ppm to high frequency of external 85% H_3PO_4)

Ligand	(δ, ppm)^a	(δ, ppm)^b	
		Ph_2P	PR_2
Ia	−12.50	−12.13	−11.10, J(P–P) 34.8 Hz
Ib	−12.40, −14.6 J(P–P) 34.5 Hz	−12.20	−14.48 J(P–P) 35.0 Hz
Ic	−12.48	−12.20	−11.20 J(P–P) 35.1 Hz

[a] Spectra obtained with a Bruker WP-60 Spectrometer at 24.3 MHz in deuterobenzene. [b] Spectra obtained with a Bruker WH-400 Spectrometer at 161.98 MHz in benzene.

non-equivalence of phosphorus nucleii. This can be attributed to the fact that the transmission of electronic effects from the *m*-position (Ia, Ic) in the phenyl ring to the phosphorus nuclei is different from that from the *p*-position in Ib [11]. However, when the spectra were obtained at 161.98 MHz on the Bruker WH400 Spectrometer, all the three ligands gave the expected AB patterns (see Table 1), confirming the non-equivalence of both the phosphorus nuclei. The ^{31}P NMR chemical shifts also indicate that the phosphorus nucleus attached to the *p*-FC_6H_4 group is more shielded than that attached to the C_6H_5 group, whereas the phosphorus attached to the *m*-FC_6H_4 or *m*-$CF_3C_6H_4$ group is less shielded than that attached to the C_6H_5 group.

Experimental

All the reactions were performed under dry dinitrogen. Infrared spectra were run on a PE-180 infrared spectrometer as Nujol mull or clear liquid between the KBr plates. Elemental analysis was performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada. Diphenylvinylphosphine was purchased from Strem Chemicals and was checked for purity by ^{31}P NMR (δ -10.96 ppm).

Preparation of the starting materials

The two new secondary phosphine oxides (*m*-$FC_6H_4)_2P(O)H$ and (*p*-$FC_6H_4)_2P(O)H$ were prepared as described for (*m*-$CF_3C_6H_4)_2P(O)H$ (12). The corresponding secondary phosphines were obtained by reducing the secondary phosphine oxide with $LiAlH_4$ in ether [12]. (The preparations of (*m*-$FC_6H_4)_2PH$ and (*p*-$FC_6H_4)_2PH$ have been previously described [13,14], but involved $LiAlH_4$ reduction of (*m*-$FC_6H_4)_2PCl$ and (*p*-$FC_6H_4)_2PCl$ which are difficult to obtain.) Some physical data are given in Table 2

Synthesis of the Ligands

Ia: A mixture of 3.5 g (1.64 mmol) of diphenylvinylphosphine and 3.6 g (1.64 mmol) of bis(*m*-fluorophenylphosphine) and 0.3 g of $KOBu^t$ in 60 ml of freshly

TABLE 2

IR AND NMR PARAMETERS FOR SECONDARY PHOSPHINES AND THEIR OXIDES

(^{31}P NMR spectra were obtained in $CDCl_3$ solution relative to an external H_3PO_4)

Compound	IR ν(P–H) (cm^{-1})	^1H NMR δ(P–H) (ppm)	^{31}P NMR $\delta(^{31}P)$ (ppm)
(*m*-$FC_6H_4)_2P(O)H$ [a]	2365	8.42(d)	+19.04
		J(P–H) 490.7 Hz	
(*p*-$FC_6H_4)_2P(O)H$ [b]	2360	8.34(d)	
		J(P–H) 488.8 Hz	+19.54
(*m*-$FC_6H_4)_2PH$ [c]	2280	5.4(d)	
		J(P–H) 220.4 Hz	−40.9
(*p*-$FC_6H_4)_2PH$ [d]	2285	5.60(d)	
		J(P–H) 219.7 Hz	−44.01

[a] Analysis. Found, C, 60.18, H, 3.73. $C_{12}H_9F_2PO$ calcd.: C, 60.4; H, 3.80%. [b] Analysis. Found, C, 60.12, H, 3.70. $C_{12}H_9F_2PO$ calcd.: C, 60.4, H, 3.80%. [c] B.p. 115–118 °C/2.5 mmHg (lit. [13] b.p. 144 °C/0.13 mmHg). [d] B.p. 110–113 °C/2.0 mmHg (lit. [14] b.p. 140 °C/0.12 mmHg).

distilled tetrahydrofuran was refluxed for 6 h. The solvent was removed to leave an orange yellow residue, which was washed with MeOH and recrystallised from benzene/MeOH to give a white crystalline solid, 5.6 g (78%); m.p. 92–93°C. Analysis, Found: C, 71.83, H, 5.22, P, 14.42. $C_{26}H_{22}F_2P_2$ calcd.: C, 71.88, H, 5.09, P. 14.27%

Ib: Ligand Ib (9 g, 73%) was similarly obtained from the reaction of diphenylvinylphosphine 6.0 g (2.8 mmol) and bis(*p*-fluorophenylphosphine) 6.2 g (2.8 mmol) in tetrahydrofuran; m.p. 93–94°C. Analysis, Found: C, 71.82; H, 5.26, P, 14.34. $C_{26}H_{22}F_2P_2$ calcd.: C, 71.88; H, 5.09, P, 14.27%.

Ic: Ligand Ic was obtained from the reaction of diphenylvinylphosphine 3.5 g (1.64 mmol) and 5.3 g (1.64 mmol) of bis(*m*-trifluoromethylphenylphosphine). The oily residue obtained after removal of the solvent under vacuum was dissolved in MeOH. The solution was cooled to give a white crystalline solid, 5.26 g (60%), m.p. 88–89°C. Analysis Found: C, 63.09, H, 4.23, P, 11.48. $C_{28}H_{22}F_6P_2$ calcd.: C, 62.92; H, 4.14; P, 11.60%.

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