Journal of Organometallic Chemistry, 169 (1979) 283—287

A CONVENIENT SYNTHESIS FOR (*o*-METHOXYPHENYL)DIMETHYLPHOSPHINE

WILLIAM LEVASON * and KENNETH G. SMITH

Department of Chemistry, The University, Southampton SO9 5NH (Great Britain)

(Received October 26th, 1978)

Summary

(*o*-Methoxyphenyl)dimethylphosphine *o*-$C_6H_4(PMe_2)(OMe)$, PO, is readily prepared from *o*-bromoanisole and lithium dimethylphosphide in tetrahydrofuran. The nickel(II) complexes $Ni(PO)_2X_2$ (X = Cl, Br, NCS) are described and compared with those of phenyldimethylphosphine.

Introduction

o-Alkoxyphenylphosphines have attracted considerable interest recently. Under certain conditions their platinum(II) complexes undergo *O*-dealkylation [1], whilst direct interaction between the oxygen and the metal has been postulated to explain the greatly increased rate of oxidative addition reactions of *trans*-$Ir(CO)(PO)_2Cl$ compared with *trans*-$Ir(CO)(PhMe_2P)_2Cl$ [2]. Alkoxyphenylphosphines are also useful intermediates in the synthesis of the interesting, but little studied ligands phosphinophenols $C_6H_4(PR_2)(OH)$ [3].

The ligand PO has previously been obtained [2] by the route

$$\begin{tikzcd}
PCl_2(NEt_2) \arrow[r, "", "\begin{array}{c}(1)\ o\text{-}C_6H_4(OMe)MgBr\\(2)\ HCl\end{array}"'] & o\text{-}C_6H_4(OMe)PCl_2 \arrow[d, "MeLi"] \\
 & o\text{-}C_6H_4(OMe)(PMe_2)
\end{tikzcd}$$

During studies aimed at developing improved syntheses for *o*-phenylenebis(dimethylarsine) analogues [4], we found a synthesis for PO from readily available materials.

Experimental

Proton NMR spectra were obtained on ca. 50% solutions in $CDCl_3$ with TMS as internal reference, on a Perkin—Elmer R12 spectrometer. ^{31}P NMR spectra on benzene solutions on a JEOL FX60 spectrometer referenced to external 85% H_3PO_4. Mass spectra were recorded as described previously [5]. IR spectra were measured on Beckmann IR11 and Perkin—Elmer PE225 spectrometers and electronic spectra on a Unicam SP700.

(o-Methoxyphenyl)dimethylphosphine

Dimethylphenylphosphine (27.6 g, 0.2 mol) was added to a vigorously stirred suspension of lithium (4.5 g, 0.6 mol) in rigorously dry tetrahydrofuran (400 cm^3), under a dinitrogen atmosphere. The mixture rapidly developed a dark green colour and became hot; it was cooled in ice and stirred for 12 h. The deep red solution produced was filtered through glass wool, cooled to 0°C and treated dropwise with t-butyl chloride (11.0 g, 0.12 mol). The deep red solution was transferred under dinitrogen to a 500 cm^3 pressure-equalising dropping funnel and added dropwise to a solution of *o*-bromoanisole (22.4 g, 0.12 mol) in tetrahydrofuran (100 cm^3) at 0°C at such a rate that the red colour was rapidly discharged. When discharge became slower the mixture was heated to reflux and the remaining phosphide solution added. The product was cautiously hydrolysed with saturated aqueous ammonium chloride (200 cm^3), separated and the organic layer dried (Na_2SO_4).

Distillation yielded a low boiling (30—35°C/1 Torr) fraction (ca. 1 g) and the ligand PO, b.p. 70—72°C/2 Torr (10.8 g, 53%). ^{1}H NMR: τ 6.3 (s, 3H, OMe), 8.8 (d, 6H, PMe_2, J(P—H) 3.5 Hz), 2.7—3.2 ppm (m, 4H, C_6H_4). ^{31}P NMR: 53.3 ppm, (J(P—H) 3.5 Hz).

A monomethiodide was prepared by the reaction of PO with iodomethane in diethyl ether and recrystallised from ethanol/diethyl ether. Anal.: Found: C, 38.9; H, 5.5; I, 41.1. $C_{10}H_{13}IOP$ calcd.: C, 38.7; H, 5.2; I, 40.95%. M.p. 265°C (dec.). ^{1}H NMR: τ 6.02 (s, 3H, OMe), 7.84 (d, 9H, PMe_3, J(P—H) 15.3 Hz), 2.6—3.0 ppm (m, 4H, C_6H_4).

$Ni(PO)_2Cl_2 \cdot H_2O$

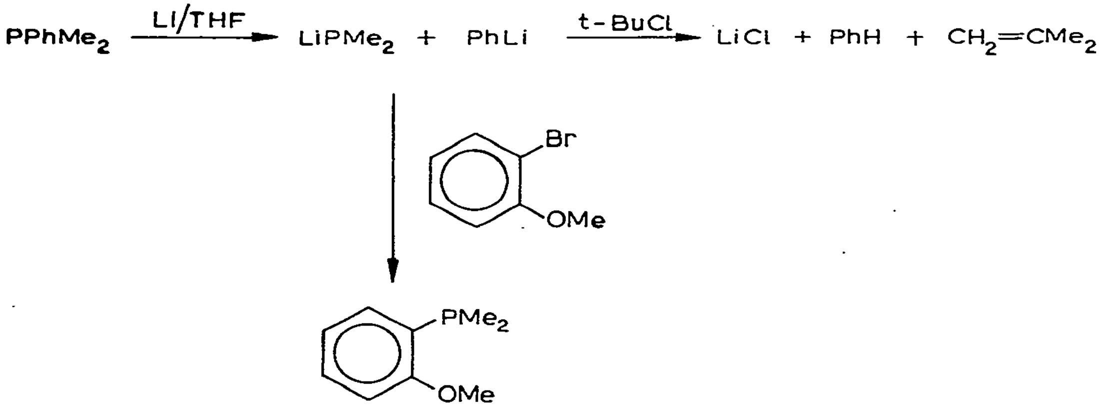
Nickel(II) chloride hexahydrate (0.5 g, 2.1 mmol) was dissolved in ethanol (15 cm^3) and treated with PO (0.66 g, 4 mmol). The mixture was rotary evaporated to dryness and the residue recrystallised from dichloromethane/hexane. $Ni(PO)_2Br_2$ was prepared similarly.

$Ni(PO)_2(NCS)_2$

Nickel(II) nitrate hexahydrate (0.8 g, 2.75 mmol) was dissolved in ethanol (10 cm^3) and treated with a solution of potassium thiocyanate (0.6 g, 6 mmol) in ethanol (15 cm^3). The mixture was heated to reflux, cooled, filtered and the filtrate treated with PO (0.93 g, 5.5 mmol). The solution was evaporated and the residue recrystallised from dichloromethane/hexane.

Results and discussion

Dimethylphenylphosphine is readily cleaved by lithium in rigorously dry tetrahydrofuran to lithium dimethylphosphide and phenyllithium. After destruction of the latter with t-butyl chloride, dropwise addition of the phosphide solution to *o*-bromoanisole in tetrahydrofuran at 0°C produced (*o*-methoxyphenyl)dimethylphosphine, PO, in ca. 53% yield.



The result was rather unexpected since Mallion and Mann [6] found that anisole (PhOMe) is rapidly demethylated by the less strongly nucleophilic PPh_2^- ion. In the present study the good yield of PO and the lack of any appreciable amount of trimethylphosphine indicates that under the conditions used, attack of PMe_2^- on the C—Br bond is much more rapid than on the O—Me bond.

The preparation was conducted so as to avoid the presence of an excess of the nucleophile in the reaction mixture.

The ligand PO was characterised as its monomethiodide $[o\text{-}C_6H_4\overset{+}{P}Me_3(OMe)]$ I^- and by its ^1H, ^{31}P NMR and mass spectrum. The latter has the base peak at *M/e* 168, corresponding to the molecular ion $C_9H_{13}PO$ and prominent peaks at *M/e* 167, $C_9H_{12}PO$ and 153, $C_8H_{10}PO$ (P—Me).

Nickel(II) complexes

The nickel(II) complexes of PO were briefly examined. They resemble closely those of phenyldimethylphosphine [7]. The complexes $Ni(PO)_2X_2$ (X = Cl, Br, NCS) were formed on reaction with the appropriate nickel(II) salt in ethanol, the chloro complex being isolated as a monohydrate (Table 1). The electronic spectra, both in the solid state and in solution, (Table 2) are consistent with square planar nickel(II) [7] and the presence of a single strong absorption at 404 (Cl) and 310 (Br) cm^{-1} in the far IR spectra suggests a *trans* planar structure [8]. The vibrations of the thiocyanato groups also suggests the presence of *trans*-NCS coordinated groups [9].

TABLE 1

Compound	Colour	C (Found (calcd.)) (%)	H (Found (calcd.))(%)	ν(M—X) (cm^{-1})	^1H NMR [a]	
					$\tau(PMe_2)$	$\tau(OMe)$
$Ni(PO)_2Cl_2 \cdot H_2O$	violet	44.87(44.67)	5.75(5.83)	404	6.25	5.85
$Ni(PO)_2Br_2$	violet	39.01(38.96)	4.87(4.72)	310	4.0	5.85
$Ni(PO)_2(NCS)_2$ [b]	orange	47.51(47.08)	5.46(5.13)	— [c]	8.4	6.0

[a] Cf. free ligand: PMe_2 τ 8.8, OMe τ 6.3. [b] N = 5.25 (5.48)%. [c] ν(CN) = 2085, ν(CS) 810, δ(NCS) = 460 cm^{-1}.

TABLE 2

Compound	E_{max} (ϵ mol × 10^{-3} cm^{-1}) [a]	E_{max} (× 10^{-3} cm^{-1}) [b]
$Ni(PO)_2Cl_2 \cdot H_2O$	27.00(6383), 20.45(456)	27.00sh, 20.40
$Ni(PO)_2Br_2$	25.66(12362), 18.36(502)	29.00sh, 24.40, 19.20
$Ni(PO)_2(NCS)_2$	26.85(10952), ~20.00sh	27.00, 22.00sh
$Ni(PPhMe_2)_2Cl_2$ [c]	20.60(610)	—
$Ni(PPhMe_2)_2Br_2$ [c]	26.30(8850), 19.20(500)	—
$Ni(PPhMe_2)_2(NCS)_2$ [c]	26.90(11600), 20.80sh	—

[a] CH_2Cl_2 solution. [b] Diffuse reflectance. [c] Data taken from ref. 7.

The ^1H NMR spectra confirm that PO is P-coordinated in these complexes (Table 1). The small downfield shift of the OMe resonance is attributable to inductive effects. In the complex $Ni(PO)_2(NCS)_2$ the PMe_2 resonance is a broad singlet at τ 8.4, while in $Ni(PO)_2Cl_2$ it is broad and shifted to τ 6.25. In $Ni(PO)_2Br_2$ it is very broad and shifted even further to τ 4.0. The complexes are effectively diamagnetic in the solid state and in solution. This effect is most likely attributable to a small contribution from temperature independent paramagnetism in the bromide and chloride, the magnitude of which is sufficiently great to shift and broaden the ^1H NMR signal.

A comparison of the electronic spectra of corresponding complexes of PO and $PPhMe_2$ [7] (Table 2) shows the spectrochemical effects of the two ligands to be very similar with PO producing a very slightly weaker ligand field. However whereas addition of $PPhMe_2$ to the planar complexes in solution generates $Ni(PPhMe_2)_3X_2$ species [7], the electronic spectra of the $Ni(PO)_2X_2$ complexes are hardly affected by the presence of excess ligand. This could be due to steric factors, the presence of *ortho*-OMe groups on the phosphines could hinder the approach of a fifth ligand to the metal. The alternative π-bonding explanation [7] for the reluctance of $C_6F_5PMe_2$ compared with $PhMe_2$ to form five-coordinate complexes is also applicable to PO, where the *ortho*-OMe group increases the tendancy to π-bond Ph → P and hence decreases the Ni → P π-bonding.

Attempts to isolate complexes containing bidentate (P,O-coordinated) (*o*-methoxyphenyl)dimethylphosphine were unsuccessful. The reaction of $[Ni(H_2O)_6]Y_2$ ($Y = ClO_4$, BF_4) with PO in the presence of a dehydrating agent produced only pale green oils and no solid product could be isolated. One notable effect of the OMe group is to increase considerably the tendency of the complexes (compared with the $PPhMe_2$ analogues) to dissolve in organic solvents. Indeed the reaction of PO with cobalt(II) or iron(III) salts produced intensely coloured sticky oils which could not be induced to crystallise and were very soluble in all solvents examined.

The nickel(II) complexes of PO showed no tendency to undergo *O*-demethylation [1] either on heating in the solid state or in high-boiling alcohols.

Acknowledgement

The award of an SRC postdoctoral fellowship (K.G.S.) is gratefully acknowledged.

References

1 C.E. Jones, B.L. Shaw and B.L. Turtle, J. Chem. Soc. (Dalton), (1974) 992.
2 E.M. Miller and B.L. Shaw, J. Chem. Soc. (Dalton), (1974) 480.
3 T.B. Rauchfuss, Inorg. Chem., 16 (1977) 2966.
4 W. Levason, C.A. McAuliffe, S.G. Murray, F.P. McCullough and K.G. Smith, unpublished work.
5 W. Levason, C.A. McAuliffe and R.D. Sedgwick, J. Organometal. Chem., 84 (1975) 239.
6 K.B. Mallion and F.G. Mann, J. Chem. Soc., (1964) 6121.
7 E.C. Alyea and D.W. Meek, J. Amer. Chem. Soc., 91 (1969) 5761.
8 P.M. Boorman and A.J. Carty, Inorg. Nucl. Chem. Lett., 4 (1968) 101.
9 A.H. Norbury, Adv. Inorg. Chem. Radiochem., 17 (1975) 231.