Note

Catalytic air oxidation of tertiary arylphosphines in the presence of tin(IV) iodide

William Levason *, Rina Patel, Gillian Reid

Department of Chemistry, University of Southampton, Southampton SO17 1BJ, UK

Abstract

Arylphosphines including Ph_3P, o-$C_6H_4(PPh_2)_2$ and $Ph_2PCH_2CH_2PPh_2$ are cleanly and quantitatively converted into the corresponding phosphine oxides on reaction with dry air or dioxygen in CH_2Cl_2 solution in the presence of catalytic amounts of SnI_4.
© 2003 Elsevier B.V. All rights reserved.

Keywords: phosphine; phosphine oxide; tin

1. Introduction

Tertiary arylphosphines are essentially air-stable both in the solid state and in solution in common organic solvents. Oxidation has been observed on reaction of triarylphosphines with high oxidation state, early transition metal halides, where halogenation of the phosphine followed by hydrolysis yields the phosphine oxide, often as a metal complex [1,2]. Later transition metals, including cobalt(II), rhodium(I), iridium(I), palladium(II) and platinum(II) in appropriate systems, can promote air-oxidation of phosphines to phosphine oxides. In these cases it is likely that metal–dioxygen complexes are intermediates [1,3,4]. During recent studies of tin(IV) phosphine complexes [5], we observed that the complexes were often contaminated with the corresponding phosphine oxides unless rigorous Schlenk line and dry-box techniques were used. The oxidation reactions appeared particularly easy with tin(IV) iodide, and from SnI_4 and o-$C_6H_4(PPh_2)_2$ in dry CH_2Cl_2 solution we obtained $[SnI_4(o\text{-}C_6H_4(P(O)Ph_2)_2)]$ which was thoroughly characterised both by single-crystal X-ray diffraction and by comparison of its spectroscopic properties with a sample made from o-$C_6H_4(P(O)Ph_2)_2$

[5]. The promotion of the oxidation by p-block metal halides was unexpected and here we report further investigations of these oxidations occurring in SnI_4–arylphosphine systems.

2. Results and discussion

Our initial studies were carried out in 10 mm NMR tubes containing CH_2Cl_2 with o-$C_6H_4(PPh_2)_2$ and SnI_4 in (a) a 1:1 molar ratio and (b) a ca 50:1 molar ratio, and (c) as a control, a solution of o-$C_6H_4(PPh_2)_2$ alone. The tubes were filled initially with dry dinitrogen and monitored by $^{31}P\{^1H\}$-NMR spectroscopy over a period of a few days. No reaction was apparent in any of the tubes. The tubes were then filled with dry dioxygen and again monitored. There was no change in the spectrum obtained from sample (c) containing only the diphosphine (δ -13) over the period of the experiment. In sample (a) no ^{31}P-NMR resonance was observed initially since the $[SnI_4(o\text{-}C_6H_4(PPh_2)_2)]$ complex undergoes rapid, reversible ligand dissociation in solution at ambient temperatures, although the resonance of the complex (δ -52.5) can be observed from solutions cooled to 190 K [5]. However, after 1 day, a resonance at δ $+39.8$, attributable to $[SnI_4(o\text{-}C_6H_4(P(O)Ph_2)_2)]$ was evident, and after 5 days $[SnI_4(o\text{-}C_6H_4(P(O)Ph_2)_2)]$ had precipitated from the solution as an orange solid. In

---

* Corresponding author. Tel.: +44-2380-593-792; fax: +44-2380-593-781.
E-mail address: wxl@soton.ac.uk (W. Levason).

sample (b) the initial free diphosphine resonance decreased over time and a resonance at δ +31 grew in. This is assigned to o-$C_6H_4(P(O)Ph_2)_2$ [5] which, after 1 day, was the only phosphorus species present. The reaction of o-$C_6H_4(PPh_2)_2$ with dry air in CH_2Cl_2 in the presence of a small crystal of SnI_4 also gave complete conversion to o-$C_6H_4(P(O)Ph_2)_2$ in 2d.

Dichloromethane solutions of Ph_3P [$\delta(^{31}P)$ −6], and $Ph_2PCH_2CH_2PPh_2$ [$\delta(^{31}P)$ −13] containing a small crystal of SnI_4 were similarly cleanly converted into Ph_3PO [$\delta(^{31}P)$ +26, $\nu(PO) = 1195$ cm^{-1}] and $Ph_2P(O)CH_2CH_2P(O)Ph_2$ [$\delta(^{31}P)$+36, $\nu(PO) = 1177$ cm^{-1}], over a few days, the products being identified by comparison of their $^{31}P\{^1H\}$-NMR and IR spectra with those of genuine samples. The $^{31}P\{^1H\}$-NMR spectra showed no other phosphorus-containing products were formed. The reaction can be converted into a synthesis for the phosphine oxides using either dry air or dry dioxygen. However, in marked contrast, a CH_2Cl_2 solution of Ph_3As containing a small crystal of SnI_4 showed no reaction after 1 week, the IR spectrum of the recovered solid showing only Ph_3As and no evidence for Ph_3AsO.

The mechanism of the oxidation reaction is not clear. Very basic phosphines such as $^tBu_3P$ react [6] with $SnCl_4$ or $GeCl_4$ to form chlorophosphonium salts, $[^tBu_3PCl]^+[Sn(Ge)Cl_3]^-$, which could hydrolyse to phosphine oxides, but similar chemistry has not been observed with arylphosphines. Moreover, the reactions described here occur under anhydrous conditions. In order to provide further insight, the reaction with Ph_3P was conducted using $^{18}O_2$, and the product was shown to be exclusively $Ph_3P^{18}O$ by IR spectroscopy [$\nu(PO) = 1157$ cm^{-1}]. The simple diatomic oscillator model predicts $\nu(P^{18}O)$ as 1148 cm^{-1} and coupling with the appropriate $\nu(P–C)$ at lower frequency accounts for the slightly higher observed value. The EI mass spectrum shows a base peak at m/z 279 which corresponds to $[Ph_3P^{18}O −H]$; the base peak in $Ph_3P^{16}O$ is at m/z 277 corresponding to $[Ph_3P^{16}O −H]$ [7]. This establishes air/dioxygen rather than water as the source of the oxygen in the phosphine oxides, but does not clarify the mechanism any further. It seems likely that the weak Lewis acidity of the SnI_4 promotes the oxidation, whilst the extensive dissociation of the tin iodide adducts formed allows the reaction to cycle, making the use of catalytic amounts of SnI_4 possible. For other tin(IV) halides, the oxidation occurs, but as stronger Lewis acids these tend to precipitate the complexed oxidised ligand, hence removing the tin from the reaction. The reaction offers a convenient alternative route to the synthesis of arylphosphine oxides from the corresponding phosphines. It avoids the potential hazards of using H_2O_2 [8] and is cleaner than the halogen oxidation followed by hydrolysis route [5].

3. Experimental

Dichloromethane was dried by distillation from CaH_2 under nitrogen, and the phosphine ligands dried in vacuo. The SnI_4 (BDH), Ph_3P, Ph_3PO, Ph_3As and Ph_3AsO (Aldrich) were used as received. The diphosphines $Ph_2PCH_2CH_2PPh_2$, o-$C_6H_4(PPh_2)_2$ and their dioxides were made by literature methods [5,9,10]. $^{18}O_2$ was obtained from BOC. All reactions were conducted in flame-dried apparatus under nitrogen or in a glove box unless indicated otherwise.

3.1. NMR experiments

(General procedure) A 10 mm OD NMR tube was charged with the phosphine (0.1 g), dry CH_2Cl_2 (4 ml) and an appropriate amount of SnI_4 (see text). The tube was purged with dry nitrogen, sealed, and the $^{31}P\{^1H\}$-NMR spectrum recorded immediately, and at set intervals over several days. In other experiments the nitrogen was replaced by dry air or dioxygen.

3.2. Preparations

(General procedure) A three necked 250 cm^3 quickfit flask fitted with two Young's taps (gas inlet and outlet), a Suba-seal and a teflon coated stirrer bar, was purged with dry nitrogen. It was then charged with dry CH_2Cl_2 (50 ml) containing the phosphine ligand (2 mmol) and a crystal of SnI_4 and stirred. The gas atmosphere was replaced by dry dioxygen by flushing. Experiments in which dry air was used as oxidant were performed by replacing the suba-seal with a drying tube packed with anhydrous $CaCl_2$. After the reaction was judged complete, the solvent was removed on a vacuum line. The residue was treated with aqueous brine to destroy the tin iodide, and extracted with CH_2Cl_2 (3 × 50 ml), the organic extracts dried over $MgSO_4$, the solvent was then removed, and the residue recrystallised from EtOH. The yield was essentially quantitative.

Acknowledgements

References

[1] T.S. Lobana, F.R. Hartley (Eds.), The Chemistry of Organophosphorus Compounds, vol. 2 (Chapter 8), Wiley, NY, 1992.
[2] A.K. Bhattacharya, N.K. Roy, F.R. Hartley (Eds.), The Chemistry of Organophosphorus Compounds, vol. 2 (Chapter 6), Wiley, NY, 1992.
[3] J. Halpern, B.L. Goodall, G.P. Khare, H.S. Lim, J.J. Plath, J. Am. Chem. Soc., vol. 97.

[4] J. Halpern, A.L. Pickard, Inorg. Chem., vol. 9.

[5] A.R.J. Genge, W. Levason, G. Reid, Inorg. Chim. Acta, vol. 288.

[6] (a) W. Du Mont, B. Neudert, H. Schumann, Angew. Chem. Int. Ed. Engl., vol. 15;
(b) W. Du Mont, H.-J. Kroth, H. Schumann, Chem. Ber., vol. 109.

[7] C. Glidewell, J. Organomet. Chem., vol. 116.

[8] The use of hydrogen peroxide can be hazardous if some of the H_2O_2 remains in the product. On one occasion a sample of solid o-$C_6H_4(P(O)Ph_2)_2$ detonated with great violence whilst being dried on a vacuum line, almost certainly because it retained "hydrogen peroxide of crystallisation", i.e. the hydrogen peroxide co-crystallised with the phosphine oxide. A.R.J. Genge. Ph. D Thesis. Southampton University 1998.

[9] A.M. Aguiar, J. Beisler, J. Org. Chem., vol. 29.

[10] H.C.E. McFarlane, W. McFarlane, Polyhedron, vol. 2.