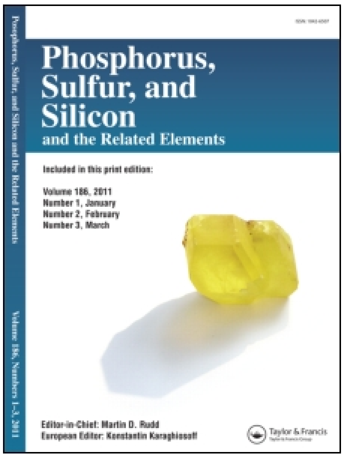

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# $[PMe_3(CH_2CH(OMe)Ph)]$ A PHOSPHONIUM SALT WITH AN ASYMMETRIC CARBON ATOM SYNTHESIZED BY REACTION OF PHENYLACETYLENE WITH $COBr(PMe_3)_3$ IN METHANOL. STRUCTURAL CHARACTERIZATION

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# $[PMe_3(CH_2CH(OMe)Ph)]^+$ A PHOSPHONIUM SALT WITH AN ASYMMETRIC CARBON ATOM SYNTHESIZED BY REACTION OF PHENYLACETYLENE WITH $CoBr(PMe_3)_3$ IN METHANOL. STRUCTURAL CHARACTERIZATION

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Reaction of HC≡CPh in excess with a mixture of $CoBr(PMe_3)_3/NaBPh_4$ in methanol gave rise in 40% yield to the cationic phosphonium salt $[PMe_3(CH_2CH(OMe)Ph)]BPh_4$. It has been characterized in the solid state by X-ray diffraction and in solution by $^1H$ and $^{31}P$ NMR.

*Key words:* cobalt(I) complex; trimethylphosphine; phenylacetylene; phosphonium salt; X-ray structure; methanol.

Recently we reported the synthesis of novel alkyne-trimethylphosphine cobalt complexes by reaction of terminal and internal alkynes with $CoBr(PMe_3)_3$.[1] These compounds were precipitated at $BPh_4$ salts from methanol solutions. Surprisingly, when HC≡CPh was used, the cobalt complex $CoH(C_2Ph)_2(PMe_3)_3$ was isolated but the major reaction product was the phosphonium salt $[PMe_3(CH_2CH(OMe)Ph)]BPh_4$, **1**, obtained in 40% yield.[2]

$$CoBr(PMe_3)_3 + 3HC{\equiv}CPh \xrightarrow[-NaBr]{+NaBPh_4,\ PMe_3,\ +MeOH} [PMe_3(CH_2CH(OMe)Ph)]BPh_4 + CoH(C_2Ph)_2(PMe_3)_3$$

**1**

Our interest in this compound arises because, to our knowledge, the reaction of alkynes with tertiary phosphines gives rise to phosphonium salts bearing an alkenyl susbstituent.[3] These species are usually stabilized by dimerization or in acidic media.

However, reaction of transition metal coordinated alkynes toward nucleophilic addition of amine or phosphine has already been observed: for example in iron, tungsten or ruthenium complexes. In every case, vinylphosphonium metal complexes have been isolated.[4] Such a cobalt complex has not been observed. Surprisingly, the phosphonium salt **1** precipitated at room temperature when excess HC≡CPh was allowed to react with an equimolecular mixture of

$CoBr(PMe_3)_3$ and $NaBPh_4$ in methanol.[5] It has been characterized by elementary analysis, $^1H$ and $^{31}P$ NMR spectroscopy[6] and a single crystal X-ray structural determination has been carried out.

## CRYSTAL DATA

Orthorhombic, space group Pna21; $a = 19.070(4)$; $b = 15.750(3)$; $c = 10.191(3)$; $Z = 4$. Least-squares refinement based on 1033 observed independent reflections with $(I) < 3\sigma(I)$ measured on a CAD 4 diffractometer converged at $R = 0.0489$. The phosphonium and tetraphenylborate ions have been refined as independent blocks by using the SHELX program.[7] The molecular structure is shown in Figure 1. The phosphorus atom is approximately tetrahedral, the C–P–C values being in the range 107.6(6) and 110.7(6)°. The phosphorus-carbon distances (1.79(1) Å av.) lie in the usual range (1.790 Å in $[PPh_3(CH_2Ph)]^+$)[8] and are not significantly different. The C–C and C–H distances are as expected.[9] A particular feature of this structure is the difference between the two C–O (1.32(1) and 1.40(1) Å) and the two C4–C5 and C5–C51 distances (1.47(2) and 1.55(2) Å). Thus, only the *s*-conformer is present in the crystal.

The $^1H\{^{31}P\}$NMR spectrum shown in Figure 2 (the resonances of the methyl, methoxy and phenyl groups are omitted) is in accord with the solid state structure. It consists of three distinct resonances ABC for the three non-equivalent methylene and methyne protons of the $CH_2CH(OMePh)$ substitutent. The hydrogens of the $CH_2$ group (AB) appeared as a 8 lines signal at 3.13 ppm: H41 ($J_{H41H42} = 14$ Hz; $J_{H41H5} = 11$ Hz; $J_{H41P} = 12$ Hz) and 3.02 ppm: H42 ($J_{H42H41} = 14$ Hz; $H_{42H5} = 4$ Hz; $H_{42P} = 12$ Hz). The H5 hydrogen (C) gives rise to a 16 lines signal centered at 6.3 ppm ($J_{H5H42} = 4$ Hz; $J_{H5H41} = 11$ Hz; $J_{H5P} = 4$ Hz). Only one signal is observed at 31 ppm in the $^{31}P$ NMR spectrum which is in the range of a quaternary phosphorus atoms.[10]

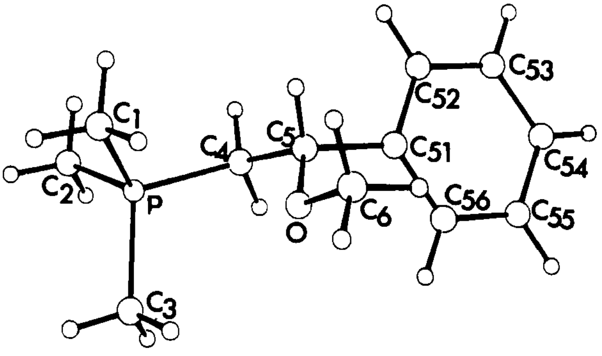

FIGURE 1 ORTEP drawing of the cation $[PMe_3(CH_2CH(OMe)Ph)]^+$. The main bond distances (Å) and angles (°) values are: P–C1, 1.75(1); P–C2, 1.78(1); P–C3, 1.80(1); P–C4, 1.82(1); C4–C5, 1.47(2); C5–C51, 1.55(2); C5–O, 1.32(1); C6–O, 1.40(1).; C1–P–C2, 108.6(6); C1–P–C3, 110.7(6); C1–P–C4, 110.5(6); C2–P–C3, 110.5(6); C2–P–C4, 107.6(6); C3–P–C4, 109.3(6); O–C5–C4, 114(1); O–C5–C51, 114(1); C4–C5–C51, 111(1); C5–O–C6, 119(1).

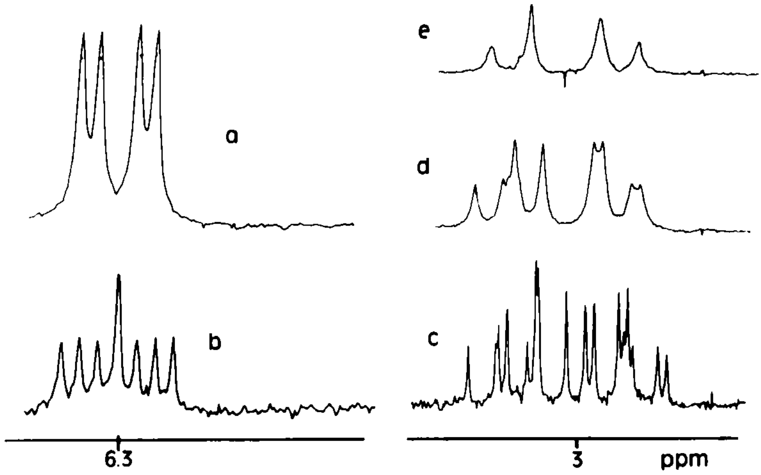

FIGURE 2 $^1$H NMR Spectra of $[PMe_3(C\underline{H}_2C\underline{H}(OMe)Ph)]^+$ in $(CD_3)_2CO$ at 293 K. (a) CH group $^1H\{^{31}P\}$, (b) CH group $^1$H, (c) CH2 group $^1$H, (d) CH2 group $^1$H, CH decoupling, (e) CH2 group $^1H\{^{31}P\}$, CH decoupling.

## SUPPLEMENTARY MATERIAL AVAILABLE

Tables of final fractional coordinates, refined temperature factors, fixed coordinates of the hydrogen atoms; a listing of observed and calculated structure factors amplitudes. Complete bond distances and angles values.

## ACKNOWLEDGEMENT

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5. A typical process consists in reacting phenylacetylene (13.2 mmol, 1.5 ml) with $CoBr(PMe_3)_3$ (3.3 mmol, 1.22 g) dissolved in methanol (15 ml). A small excess of $PMe_3$ is added. An acetonitrile solution of 3.3 mmol (1.13 g) of $NaBPh_4$ is added. After stirring for 2 h, yellow crystals of **1** precipitate. Yield: 40%.
6. RMN spectra were recorded on a Bruker 250 spectrometer using (CD3)2CO as solvent. Chemical shifts were referenced to the residual solvent signal: $\delta_H = 2.17$ ppm for acetone $d_6$.

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