## **Ready Cleavage of Triphenylphosphine**

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DURING attempts to prepare bis(triphenylphosphine)palladium (I)<sup>1</sup> from tetrakis(triphenylphosphine)palladium (II) by the use of palladium dichloride (III) as a potential scavenger of triphenylphosphine, a rapid reaction occurred to give products<sup>†</sup> resulting from a cleavage of the phosphorus-aryl bond:

$$\begin{array}{ccc} 6\mathrm{Pd}(\mathrm{PPh}_3)_4 + 7\mathrm{PdCl}_2 \rightarrow 3(\mathrm{PPh}_3)_2\mathrm{PdCl}_2 + \\ (\mathrm{II}) & (\mathrm{III}) & (\mathrm{IV}) \\ \\ 4\text{-trans-}(\mathrm{PPh}_3)_2\mathrm{Pd}(\mathrm{Ph})\mathrm{Cl} + 2(\mathrm{PPh}_3)_3(\mathrm{PPh}_2)_2\mathrm{Pd}_3\mathrm{Cl}_2 \\ (\mathrm{V}) & (\mathrm{VI}) \end{array}$$

The reaction could be effected in high yield in dimethyl sulphoxide solution by rapidly adding a solution of (III) to a saturated solution of (II) at ca. 130°<sup>+</sup> under nitrogen. Immediate distillation under reduced pressure gave a residue which was extracted with ether to remove residual solvent. The residue was then extracted with benzene leaving crude (IV) (ca. 90% yield). Evaporation of the benzene extract gave a residue (R), which was washed with methanol and recrystallized from methylene chloride by addition of methanol, to afford (V) as colourless needles, m.p. 240.5° (decomp.) (ca. 75% yield). An authentic sample of (V) was prepared by treating (II) with an excess of refluxing chlorobenzene;<sup>2</sup> the latter was evaporated, and the residue extracted with ether. The infrared absorption found at 290 cm.-1 and assigned to the Pd-Cl stretching mode supports the trans-configuration of this compound.<sup>2</sup>

The residue (R) was washed with methanol to give a red-brown syrup, which was crystallized by dissolution in methylene chloride followed by addition of ether, to form red-violet platelets of (VI) (ca. 85% yield), m.p. 149.5-150°, which contained 0.2 mole equiv. of ether, retainable under vacuum.

A solution of (VI) in methylene chloride gave  $53 \pm 3$  wt. % (calc. 50.4 %) of triphenylphoshine and  $21 \pm 3$  wt. % (calc. 23.8%) of diphenylphosphine on treatment with an excess of aqueous potassium cyanide. Results of ebullioscopic molecular weight measurements in methylene chloride suggested a monomeric structure (Found: M, 1450-1628; calc. 1547). A <sup>31</sup>P n.m.r. spectra§ (CHCl<sub>3</sub>) confirmed the PPh3: PPh2 ratio (Found  $2.80 \pm 0.2$ ;  $2.0 \pm 0.1$ ; calc. 3:2) and revealed a simple splitting pattern, suggestive of an A<sub>2</sub>M system,<sup>3</sup> composed of bands at  $\delta -11.6$  (t, J 90 c./sec.) and -19.1 (d, J 90 c./sec.). A singlet at  $\delta - 110$  was assigned to the PPh<sub>2</sub> groups.

The stability of (VI) towards recrystallization



† Satisfactory elemental analyses were obtained for compounds (V) and (VI). ‡ A temperature of *ca.* 130° was used only to increase the solubility of (II). It was found that the reaction proceeded rapidly at room temperature as well.

<sup>§</sup> The <sup>31</sup>P n.m.r. spectra was run at 40.5MH<sub>2</sub> with 85% H<sub>3</sub>PO<sub>4</sub> as an external reference.

from solutions containing triphenylphosphine suggests the presence of a co-ordinatively saturated

(III) to (II) followed by an internal cleavage of the resulting intermediate:



system. This apparent stability towards triphenylphosphine, together with the previous evidence, suggests that (VI) exists as a cluster formation, *i.e.* (VIII). A definite structural assignment, however, must await additional information.

Although one can only speculate on a detailed mechanism at this point, it is felt that a reasonable pathway would involve the oxidative addition of The triphenylphosphine arising from these reactions could react with (III) to account for the formation of (IV).

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<sup>1</sup> P. Fitton and J. E. McKeon, Chem. Comm., 1968, 4.

<sup>2</sup> P. Fitton, M. P. Johnson, and J. E. McKeon, *Chem. Comm.*, 1968, 6. These authors report an analogous preparation of (PPh<sub>3</sub>)<sub>2</sub>Pd(Ph)I.

<sup>9</sup> D. R. Eaton and S. Suart, J. Amer. Chem. Soc., 1968, 30, 4170.