Preparation of Benzylpalladium(II) Derivatives and their Reactions with Metal Acetates in Acetic Acid

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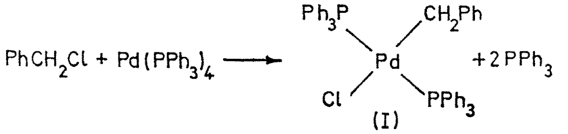
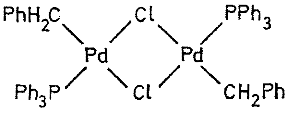
σ-BONDED BENZYLPALLADIUM(II) compounds have so far been inaccessible by conventional synthetic routes. Such compounds are of special interest as models for intermediates which might exist in selective benzylic oxidation by diacetatopalladium(II).[1]

We report the preparation of the first benzylpalladium(II) complex, benzylchlorobistriphenylphosphinepalladium(II), (I), and sone reactions of benzylpalladium compounds with silver acetate and potassium acetate in acetic acid.

Addition of benzyl chloride to a suspension of $Pd(PPh_3)_4$ in benzene at room temperature gave (I), (92%, m.p. ($MeCl-C_6H_{14}$) 147—151° (decomp.),† [ν (Pd–Cl) 275 cm.$^{-1}$]. Only one isomer was obtained, presumably the *trans*-form.[2]



The n.m.r. spectrum of (I) ($CDCl_3$) showed, in addition to signals for CH_2Cl_2, δ 6·6—8 (m, 38H, ArH) and 2·8 p.p.m. (S, 2H, benzylic H). No phosphorus coupling to the benzylic protons was observed, and recrystallization of (I) from chloroform–hexane gave a new complex, di-μ-chlorodibenzylbistriphenylphosphinedipalladium(II), (II).



(II)

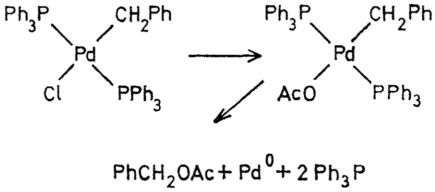
The isolation of (II) suggests the following equilibrium in solution. The free triphenylphosphine rapidly exchanges with the triphenylphosphine ligands of (I) causing the

$$2(I) \rightleftharpoons (II) + 2PPh_3$$

expected triplet due to the benzyl protons to collapse to the observed singlet.

Complexes (I) and (II) were treated with silver acetate and with potassium acetate in acetic acid at 100° (Table). Crude reaction mixtures were analysed by g.l.c. and no organic products other than benzyl acetate and benzylidene diacetate were observed.

The greater effectiveness of AgOAc than KOAc suggests that the formation of benzyl acetate probably proceeds by a mechanism involving the displacement of chloride from the co-ordination sphere of palladium by acetate, to give an aceto(benzyl)palladium(II) complex. In (II), acetate can be introduced into the co-ordination sphere of palladium by breaking the chlorine bridge. The increase in yield of benzyl acetate from (II) and KOAc, as compared to (I) and KOAc, suggests that bridge-breaking is an easier process than the displacement of chloride.



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† Both (I) and (II) gave satisfactory elemental analysis: (I) always contained $\frac{1}{2}CH_2Cl_2$ of recrystallization even after prolonged vacuum drying.

Reactions of (I) *and* (II) *with metal acetates in acetic acid**

Complex (0·002 mole)	MOAc (0·01 mole)	*t* (hr.)	$PhCH_2OAc$ (% Yield)†	$PhCH(OAc)_2$ (% Yield)†
[A]	Ag^+	10·5	24·0	7·0
	K^+	22·0	6·0	None
[B]	Ag^+	10·5	33·0	24·0
	K^+	22·0	22·0	None

* Carried out in 0·1 mole of acetic acid.
† Based on palladium.

Benzylidene diacetate may be a product derived only from (II), and the low yield formed when (I) is treated with AgOAc would then be due to the formation of a small amount of (II) in solution. This diacetate could result from hydride transfer from benzyl acetate before it leaves the metal co-ordination sphere. The (acetoxybenzyl)palladium intermediate thus formed could then undergo reductive elimination with co-ordinated acetate ion to yield benzylidene diacetate.

In the catalytic oxidation of toluene to benzyl acetate with palladium acetate in acetic acid,[3] benzylidene diacetate is formed with zero-order kinetics; this may be attributed to a mechanism such as that described above. At high conversions, the oxidation of unco-ordinated benzyl acetate to benzylidene diacetate occurs, and the overall rate of benzylidene diacetate formation increases.

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‡ The n.m.r. spectrum was recorded at 100 Mc./sec. using a Varian HA-100 Spectrometer. Chemical shifts are given in p.p.m. relative to tetramethylsilane. We thank Mr. C. B. Strow, jun. for this assistance in recording and interpreting this spectrum.

[1] D. R. Bryant, J. E. McKeon, and B. C. Ream, *Tetrahedron Letters*, 1968, 2371.

[2] The oxidative addition of other halogenocarbons to $Pd(PPh_3)_4$ has given only *trans*-isomers; P. Filton and J. E. McKeon, *Chem. Comm.*, 1968, 4.

[3] D. R. Bryant, J. E. McKeon, and B. C. Ream, *J. Org. Chem.*, in the press.