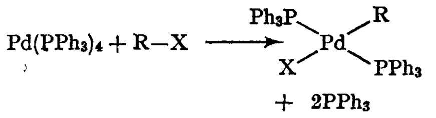
Oxidative Additions to Palladium(0)

By P. FITTON,* M. P. JOHNSON, and J. E. MCKEON

(*Research and Development Department, Union Carbide Corporation, Chemicals and Plastics, South Charleston. West Virginia* 25303)

THE oxidative addition of chloro-olefins to palladium(0)–phosphine complexes, described in the preceding Communication, has now been extended to other organic compounds which contain a carbon–halogen bond, and has been found to be a general method for the preparation of palladium(II) complexes, difficult to prepare by other methods.

The products were obtained in good yield by the addition of the halogenocarbon to a suspension of $Pd(PPh_3)_4$ in benzene at room temperature. Removal of benzene *in vacuo* gave a solid which was triturated with ether to remove triphenylphosphine. Recrystallization of the residue from methylene chloride–hexane gave the pure complexes.†



When tetrakis(triphenylphosphine)palladium(0) was used in the oxidative addition reaction only one isomer of each compound was observed; it is, with little doubt, the *trans*-form.[1] The variation in ν(Pd–Cl) indicates that, at least in the chloro-complexes, the halogen is *trans* to R. A similar variation of ν(Pd–Cl) was noted in the complexes derived from chloro-olefins.[2] The *trans*-configuration of the products does not illuminate the stereochemistry of the oxidative addition. The *cis*-isomers are generally the less stable forms in the palladium series and isomerization is easy, particularly in the presence of excess triphenylphosphine.[3]

When methyl iodide was added to bis(triphenylphosphine)palladium(0)[2] the product after recrystallization was identical with that obtained when $Pd(PPh_3)_4$ was used. This complex (I) gave an n.m.r. spectrum consistent with the proposed structure; the methyl protons appear at 0·18 p.p.m., split into a 1 : 2 : 1 triplet by coupling to two phosphorus nuclei ($J = 5{\cdot}0$ c./sec.). Occasionally the reaction of methyl iodide and $[Pd(PPh_3)_2]_x$ gave an adduct, the n.m.r. spectrum of which contained, in addition to the usual triplet at 0·18, a second 1 : 2 : 1 triplet of comparable intensity at −0·10 p.p.m. ($J = 5{\cdot}0$ c./sec.). This was at first attributed to the presence of some of the *cis*-isomer which had survived the work-up in the absence of excess phosphine or other isomerization catalyst. However, the changes in the n.m.r. spectrum caused by the addition of triphenylphosphine to the $CDCl_3$ solution were inconsistent with such an explanation; both triplets collapsed to singlets at 0·18 and −0·10 p.p.m.,

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† Compounds (I) through to (V) gave satisfactory elemental analyses. Far-infrared spectra were run as Nujol mulls on polyethylene plates using a Beckman IR-12 spectrophotometer. Mr. C. B. Strow made all n.m.r. measurements at 100 Mc./s. using a Varian HA-100 spectrometer. Chemical shifts in $CDCl_3$ were recorded in p.p.m. from tetramethylsilane.

TABLE

Products of oxidative addition of R–X

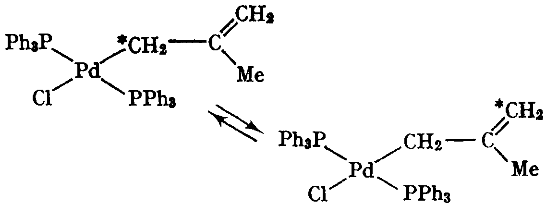
R–X	Product	M.p. (°C)	ν(Pd–Cl)(cm.$^{-1}$)	ν_{CO} (cm.$^{-1}$)
MeI	(I; R=Me, X=I)	151—154 (d)	—	—
$CH_2:CMe\cdot CH_2Cl$	(II; R=C_4H_7, X=Cl)	121—143 (d)	282	—
MeCOCl	(III; R=Ac, X=Cl)	166—172 (d)	327	1680
EtO·COCl	(IV; R=EtOCO, X=Cl)	232—237 (d)	337	1650
PhI	(V; R=Ph, X=I)	171—186 (d)	—	—

(d) means decomposed.

but one singlet was not converted to the other, even on long standing. The n.m.r. spectrum of the ordinary *trans*-isomer showed only one singlet at 0·18 p.p.m. in the presence of excess triphenylphosphine. The nature of the irregular product is being investigated.

The oxidative addition of halogenocarbons to tetrakis(triphenylphosphine)platinum(0) has recently been reported.[4] It was suggested, but not established, that the platinum products had the *cis*-configuration.

Compound (II) is of special interest. An intense infrared band at 282 cm.$^{-1}$ can be assigned to a Pd–Cl stretching absorption in the crystalline solid. The n.m.r. spectrum contains singlets at 3·62 (4 protons) and 1·88 p.p.m. (3 protons). The integration of the spectrum and the absence of coupling between the allylic protons and the phosphorus nuclei is consistent with a σ-bonded methallylic ligand undergoing rapid isomerization as shown below.



The n.m.r. spectrum of (II) in $CDCl_3$ is essentially identical to that obtained by Powell, Robinson, and Shaw after the addition of two moles of triphenylphosphine to a solution of the π-allylic compound $[Pd_2Cl_2(C_4H_7)_2]$ in chloroform, and deduced to be due to the presence of a species which could be formulated as (II).[5]

The methyl protons of (III) appear as a singlet at 1·4 p.p.m. in the n.m.r. spectrum.

Products have also been isolated from the reaction of allyl bromide, cyanogen bromide, toluene-*p*-sulphonyl chloride and several alkyltin halides with $Pd(PPh_3)_4$. These products have not yet been fully characterized and will be reported at a later date.

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[1] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, 421. These authors give the range 269–335 cm.$^{-1}$ for ν(Pd–Cl) when Cl is *trans* to a phosphine and 353—359 cm.$^{-1}$ for Cl *trans* to Cl. In the present case ν(Pd–Cl) for Cl *trans* to carbon should fall in the former range since R$^-$, like the phosphines, should exhibit a strong *trans*-effect.

[2] P. Fitton and J. E. McKeon, preceding Communication.

[3] G. Calvin and G. E. Coates, *J. Chem. Soc.*, 1960, 2008.

[4] C. D. Cook and G. S. Jauhal, *Canad. J. Chem.*, 1967, **45**, 301; J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705.

[5] J. Powell, S. D. Robinson, and B. L. Shaw, *Chem. Comm.*, 1965, 78.