Reactions of Tetrakis(triphenylphosphine)palladium(0) with Olefins bearing Electron-withdrawing Substituents

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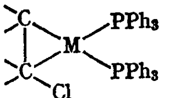
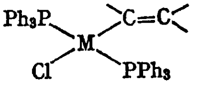
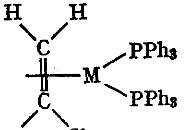
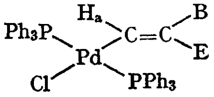
THE reaction of tetrakis(triphenylphosphine)-platinum(0) with chloro-olefins has been reported to give complexes of the general formula $Pt(PPh_3)_2$(chloro-olefin).[1] A structure of type (I; M=Pt) was suggested for these complexes, owing to the failure to detect an infrared band that could be assigned to a C=C stretching absorption.


(I)


(II)


(III)


(IV; B=Cl, E=Cl)
(V; B=Cl, E=H_b)
(VI; B=H_b, E=Cl)

In the palladium series we have found that the reaction of tetrakis(triphenylphosphine)-palladium(0) with chloro-olefins gives complexes of the type (II; M=Pd). However maleic anhydride and similar olefins did give complexes of type (I; M=Pd).

A suspension of $Pd(PPh_3)_4$ in benzene reacted readily at room temperature with tetracyanoethylene, maleic anhydride, and diethyl fumarate and at reflux with tetrachloroethylene, trichloroethylene, and *cis*- and *trans*-1,2-dichloroethylene to give excellent yields of stable monomeric complexes having the general formula $Pd(PPh_3)_2$-(olefin).†

The reaction of $Pd(PPh_3)_4$ with vinyl chloride at room temperature gave a new complex of palladium(0), $[Pd(PPh_3)_2]_x$, possibly by way of a labile π-complex with vinyl chloride.

A π-complex structure, such as type (III), is unlikely for the stable chloro-olefin complexes. Olefin ligands π-bonded to palladium would be expected to be displaced readily. $Pd(PPh_3)_2$-(trichloroethylene) did not exchange the olefin ligand when treated with a large excess of either tetrachloroethylene or phenylacetylene.

The spectrum of each of the chloro-olefin complexes possessed an intense band in the far-infrared attributable‡ to a Pd–Cl stretching absorption.[3] Only one isomer of each chloro-olefin complex was observed; it is undoubtedly the *trans*-form as shown. The systematic variation of ν(Pd–Cl) with the chlorine content of the halogenocarbon ligand shows that Cl is *trans* to that ligand rather than to triphenylphosphine. The configuration of the products does not necessarily reflect the stereochemistry of the oxidative addition. The *trans*-isomer is generally the more stable one in this type of palladium complex and isomerization

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† All the compounds described in this report gave satisfactory elemental analyses. Molecular weights were measured at 30° in $CHCl_3$ by the "Thermometric" technique.

‡ We thank Dr. M. P. Johnson for assistance in recording and interpreting the far-infrared spectra. These were run as mineral oil mulls on polyethylene plates using a Beckman IR-12 spectrophotometer.

TABLE 1

Complexes with the composition $Pd(PPh_3)_2$(olefin)

Olefin	M.p. (°c)	Yield (%)	ν(Pd–Cl) (cm.$^{-1}$)	Mol. wt. Calc.	Mol. wt. Found
Tetrachloroethylene	259—262 (d)	94	321, 305(sh)	797	869
Trichloroethylene	>300 (d)	93	315	762	745
trans-1,2-Dichloroethylene	272—277 (d)	73	292		—
cis-1,2-Dichloroethylene	279—283 (d)	85	291		—
Maleic anhydride	147—151 (d)	70	—		—
Diethyl fumarate	124—131 (d)	94	—	803	694
Tetracyanoethylene	256—257 (d)	83	—		—

(d) means decomposed.

TABLE 2

N.m.r. absorptions of chloro-olefin complexes

Chloro-olefin complex	H_a (p.p.m.)	H_b (p.p.m.)	J_{ab} (c./sec.)	J_bP (c./sec.)
(IV)	5·03 (s)	—	—	—
(V)	4·45 (d)	5·7 (ot)	14	7·5
(VI)	5·18 (d)	6·08 (ot)	5·5	5·0

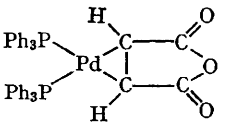
s = singlet, d = doublet, ot = overlapping triplets

is easy, particularly in the presence of excess triphenylphosphine.[4]

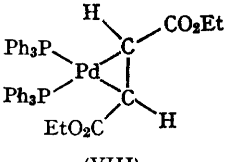
The n.m.r. spectra of the chloro-olefin complexes support the assignment of structures (IV), (V), and (VI) to the products from trichloroethylene, *trans*-1,2-dichloroethylene, and *cis*-1,2-dichloroethylene, respectively.§

In all three complexes, the chemical shift of the methine proton H_a is approximately the same; the small variation is due to the differences in the substitution at the other end of the double bond. In (V) and (VI), H_a appears as a doublet because of coupling to the other proton, H_b. The coupling constants [J for (V) = 14 and for (VI) = 5·5 c./sec.] are of the order that one would expect for *trans*- and *cis*-AB coupling respectively across a double bond, showing that the configuration of the original olefin has been retained in its palladium-complex. The proton H_b appears as a pair of overlapping triplets in (V) and (VI) and is coupled to the two phosphorus nuclei as well as to H_a.

The n.m.r. spectra of the maleic anhydride and diethyl fumarate complexes are consistent with structures (VII) and (VIII), respectively,



(VII)



(VIII)

In the maleic anhydride complex (VII), the aromatic protons appear as a complex multiplet at 7·28—7·68 p.p.m. (30 protons), and the two methine protons are identical and appear as a doublet at 4·0 p.p.m. (2 protons) due to coupling (J = 5·5 c./sec.) to the phosphorus nucleus *trans* to the carbon to which they are attached. The two methine protons in the complex (VIII) are non-identical and appear as an AB-type resonance multiplet (4 lines), which is centred at 4·17 p.p.m. The *trans*-vicinal coupling constant is 11 c./sec. and the coupling constant to phosphorous is 1 c./sec. The asymmetry of the molecule results in the geminal methylene hydrogens (of the ester groups) being nonequivalent. Each methylene group produces an identical AB coupling pattern (J = 11 c./sec.). These four lines are further split by coupling to the methyl group (J = 7 c./sec.) to give a total of sixteen lines centred at 3·3 and 3·7 p.p.m. The methyl protons appear as a triplet at 0·8 p.p.m.

The non-identity of the two methine protons in the diethyl fumarate complex indicates some deviation from a square-planar configuration with the plane of the olefinic ligand perpendicular to the square plane. The rather low value obtained for the molecular weight of the fumarate complex may indicate some dissociation in solution.

The tetracyanoethylene complex, $Pd(PPh_3)_2$-(C_6N_4) is probably of structural type (I) also. The infrared spectrum of this material showed a

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§ All n.m.r. spectra of solutions in $CDCl_3$ were recorded at 100 Mc./s. using a Varian HA-100 Spectrometer. Chemical shifts are given in p.p.m. relative to tetetramethylsilane. We thank Mr. C. B. Strow, jun., for his assistance in recording and interpreting these spectra.

single $-C\equiv N$ stretching band at 2230 cm.$^{-1}$, with no evidence of a $Pd-C\equiv N$ band.

When vinyl chloride was bubbled through a solution of $Pd(PPh_3)_4$ in methylene chloride at room temperature, removal of the solvent and trituration with ether gave a yellow compound, $[Pd(PPh_3)_2]_x$. No reliable molecular weight data have yet been obtained. The complex could be monomeric or may have a structure similar to that suggested for $[Pt(PPh_3)_2]_3$.[5] When bis-(triphenylphosphine)palladium(0) was treated with trichloroethylene an adduct identical with (IV) was formed. When $[Pd(PPh_3)_2]_x$ was exposed to air it was rapidly converted to a brown solid which gave elemental analyses corresponding to $[Pd(PPh_3)_2,\frac{3}{2}O_2]$.

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[1] W. T. Bland and R. D. W. Kemmitt, *Nature,* 1966, **211**, 963.

[2] C. D. Cook and G. S. Jauhal, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 31.

[3] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963). 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 halogenocarbon should fall in the former range since the halogenocarbon ligand should exhibit a strong σ-*trans* effect.

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

[5] R. P. Gillard, R. Ugo, F. Cariati, and F. Bonati, *Chem. Comm.*, 1966, 869.