Nucleophilic Attack on Co-ordinated Phosphinoacetylenes: Products from the Hydrolysis of *cis*-$PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ and the *X*-Ray Structure of a 1-Diphenylphosphino-3,3,3-trifluoropropen-2-olato Complex

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Summary The hydrolysis of *cis*-$PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ proceeds *via* nucleophilic attack at both phosphorus and alkyne sites yielding novel complexes containing 1-diphenylphosphino-3,3,3-trifluoropropen-2-olato, diphenylethoxyphosphine, diphenylphosphinous acid, and β-keto phosphine ligands; a 1-diphenylphosphino-3,3,3-trifluoropropen-2-olato species has been fully characterised by an *X*-ray structure determination.

SYNTHETIC routes to many important inorganic and organometallic compounds have been developed from reactions of nucleophiles with co-ordinated ligands.[1] We have found that the phosphinoacetylene complexes *cis*-$MCl_2(Ph_2PC{\equiv}CCF_3)_2$ (M = Pd, Pt) are susceptible to nucleophilic attack at phosphorus and at the unco-ordinated triple bonds, providing rich sources of novel inorganic compounds. Here we describe the characterisation of some 1-diphenylphosphino-3,3,3-trifluoropropen-2-olato complexes including an *X*-ray structure determination of chloro(1-diphenylphosphino-3,3,3-trifluoropropen-2-olato)-(ethoxydiphenylphosphine)palladium(II). Mild hydrolysis of *cis*-$PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ (I) also provides a useful route to derivatives containing co-ordinated diphenylphosphinous acid (Ph_2POH) and β-keto phosphine ligands.

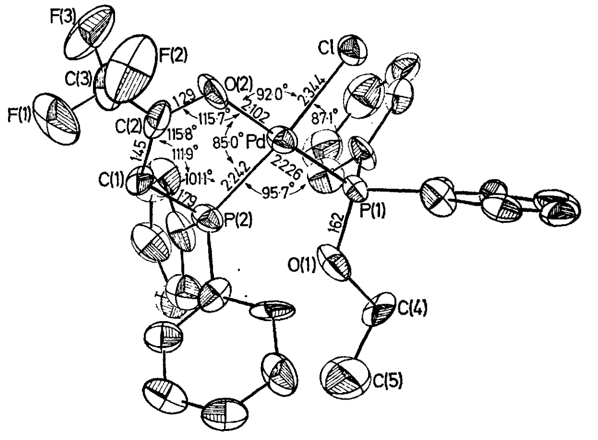
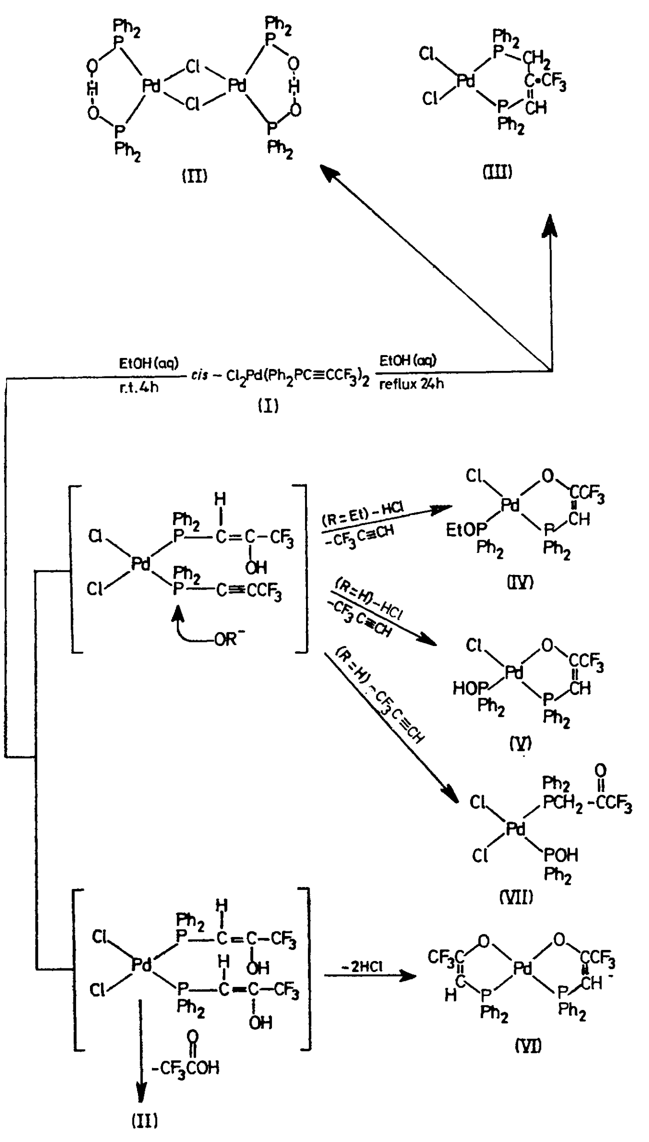


FIGURE. A view of the molecular structure of $PdCl(PPh_2OEt)$-$[Ph_2PCHC(CF_3)O]$ (IV) showing the atomic numbering and pertinent distances and angles.



SCHEME

Reaction of(I) with aqueous ethanol proceeds according to the Scheme. Under reflux conditions the major product is the symmetrical hydrogen bonded species $[PdCl\{(Ph_2PO)_2H\}]_2$ (II).[2] The unsymmetrical diphosphine complex *cis*-$PdCl_2(Ph_2PCH_2C(CF_3)CHPPh_2)$ (III)[3] is present in smaller amounts. With short reaction times at room temperature four other products (IV)—(VII) have been characterised. Pale-yellow crystals of a dichloromethane solvate of (IV) gave i.r. spectra [mull; ν(Pd–Cl) 306 cm^{-1}; ν(P–O) 945 cm^{-1}; ν(C=C) + ν(C–O) 1563s, 1579s, 1590s, cm^{-1}] indicating the absence of –C≡C– bonds, the presence of P–OR groups, and co-ordinated carbonyl or olefin moieties. An *X*-ray structure determination revealed the nature of the new ligands formed.

Crystal data: $PdCl[PPh_2OEt][Ph_2PCHC(CF_3)O]CH_2Cl_2$, orthorhombic crystals, space group *Pbca*, $a = 20{\cdot}774(19)$, $b = 18{\cdot}312(18)$, $c = 16{\cdot}982(22)$ Å, $Z = 8$, $D_m = 1{\cdot}56, D_c = 1{\cdot}543$ g cm^{-3}. The structure was solved by the heavy-atom method using 2020 observed reflections [$I \geqslant 3{\cdot}0\,\sigma(I)$] measured on a GEXRD 6 diffractometer and refined by least-squares techniques to the present *R* value of 0·085. An ORTEP drawing of the structure is shown in the Figure.

The palladium atom is co-ordinated by a chloride, a diphenylethoxyphosphine, and a deprotonated 1-diphenylphosphino-3,3,3-trifluoropropen-2-ol (Dptpo) bidentate ligand. The complex is one of relatively few having Pd–O bonds since Pd^{II} has a low affinity for oxygen donors. The two phosphorus atoms are mutually *cis* with Pd–P(1) [2·226(5) Å] marginally (3σ) shorter than Pd–P(2) [2·242(5) Å]. The $\overline{\text{Pd–P–C–C–O}}$ ring is almost planar with C(1)–C(2) [1·446(26) Å] and C(2)–O(2) [1·290(22) Å] distances, indicative of some degree of delocalisation between C(1) and C(2). The Pd–O(2) distance of 2·102(13) Å compares with an average Pd–O bond length of 2·02 Å in $Pd[C_5(CO_2Me)_4(CO_2Me)C(CO_2Me)Cl](acac)$.[4] The formation of the Dptpo ligand in (IV) can be envisaged in terms of addition of H_2O to the triple bond of one phosphinoacetylene followed by intramolecular HCl elimination, while the phosphite is derived from co-ordinated $Ph_2PC{\equiv}CCF_3$ by nucleophilic attack of OEt^- at phosphorus.

Complexes (V)—(VII) are assigned the structures shown on the basis of i.r., n.m.r., and *X*-ray [for (VI)] data.

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[1] See, for example J. P. Collman, *Transition Metal Chem.*, 1966, **2**, 1; D. A. White, *Organometallic Chem. Rev.*, 1968, **3**, 497; J. P. Candlin, K. A. Taylor, and D. T. Thompson, 'Reactions of Transition Metal Complexes,' Elsevier, Amsterdam, 1968.

[2] The *X*-ray structure of this complex has recently been completed: D. V. Naik, G. J. Palenik, S. Jacobson, and A. J. Carty, *J. Amer. Chem. Soc.*, 1974, **96**, 2286.

[3] S. Jacobson, R. T. Simpson, A. J. Carty, M. Mathew, and G. J. Palenik, *J.C.S. Chem. Comm.*, 1973, 388.

[4] D. M. Roe, C. Calvo, N. Krishnamachan, K. Moseley, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1973, 436.