Crystal and Molecular Structure of Chloro[1-(diphenylphosphino)-3,3,3-trifluoropropen-2-olato](ethoxydiphenylphosphine)palladium(II)–Dichloromethane

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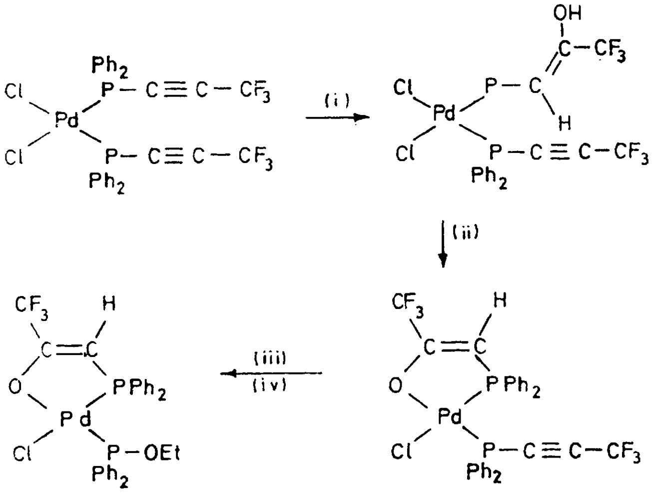
Crystals of the title compound formed *via* the controlled hydrolysis of *cis*-[$PdCl_2(Ph_2PC{:}CCF_3)_2$] are orthorhombic, space group *Pbca* with a = 16.982(11), b = 18.312(12), c = 20.774(15) Å, Z = 8. The structure was determined from diffractometer data by Patterson and Fourier syntheses and refined by full-matrix least-squares methods to R 0·058 for 3 799 observed reflections. The palladium atom is co-ordinated in distorted square-planar fashion by a chloride ion, an ethoxydiphenylphosphine, and the phosphorus and oxygen atoms of deprotonated [1-(diphenylphosphino)-3,3,3-trifluoropropen-2-ol]. The diphenylethoxyphosphine phosphorus is *trans* to the oxygen atom of the chelating ligand. Metal–ligand bond distances are: Pd–Cl(1) 2.356(2), Pd–P(1) 2.222(2), Pd–P(2) 2.246(2), and Pd–O(2) 2.099(5) Å. Delocalisation over the PC_2O fragment of the chelate ring is indicated by the distances: P(2)–C(1) 1.776(8), C(1)–C(2) 1.36(1), and C(2)–O(2) 1.313(9) Å.

COMPLEXES of the type *cis*-[$MCl_2(Ph_2PC{:}CCF_3)_2$] (M = Pd or Pt) are susceptible to nucleophilic attack at the unco-ordinated but activated triple bonds and at the co-ordinated phosphorus.[1,2] The controlled hydrolysis of the above palladium complex has provided synthetic routes to several unusual inorganic derivatives.[3,4] We describe here the molecular structure of chloro[1-(diphenylphosphino)-3,3,3-trifluoropropen-2-olato] (ethoxydiphenylphosphine)palladium(II) as determined by single-crystal *X*-ray diffraction. This compound is derived from *cis*-[$PdCl_2(Ph_2PC{:}CCF_3)_2$] by hydration of one acetylene, intramolecular elimination of hydrogen chloride, and nucleophilic displacement of $CF_3{\cdot}C{:}C^-$ from phosphorus by ethoxide (see Scheme). A preliminary account of the *X*-ray structure determination has been published.[1]



SCHEME

Reagents: i, H_2O; ii, −HCl; iii, EtOH; iv, $-CF_3{\cdot}C{:}CH$

EXPERIMENTAL

The compound was synthesised as described in ref. 2 and recrystallised as yellow plates from dichloromethane–light petroleum. These crystals were for preliminary photographic work to determine unit-cell and space-group data. The initial structure solution [1] was based on 2 020 intensity data collected from a hexagonal plate. A second set of data of much improved quality was obtained from a larger prism grown by slow evaporation of a dichloromethane solution. The following results refer only to the latter measurements.

Crystal Data.—[$PdCl\{Ph_2PCHC(CF_3)O\}\{Ph_2P(OEt)\}$]·$CH_2Cl_2$, M = 752.26, Orthorhombic, a = 16.982(11), b = 18.312(12), c = 20.774(15) Å, U = 6 460.2 Å^3, D_c = 1.546 Z = 8, D_m = 1.56 g cm^{-3}, $F(000)$ = 3 024. Mo-K_α radiation, λ = 0.710 7 Å; μ(Mo-K_α) = 9.56 cm^{-1}. Space group *Pbca*, from systematic absences: $0kl$ for $k \neq 2n$, $h0l$ for $l \neq 2n$, and $hk0$ for $h \neq 2n$.

A prism of dimensions 0.30 × 0.35 × 0.30 mm was mounted on a glass fibre and aligned with the b^* axis parallel to the ϕ axis of a General Electric XRD 6 automatic diffractometer equipped with scintillation counter and pulse-height analyser. Zirconium-filtered Mo-K_α radiation was employed and the θ—2θ scan method used. Background was measured for 10 s before and after each scan. The intensities of three standard reflections monitored every 100 reflections diminished by 6% during data collection, and were used to scale data to a common level. Standard deviations were estimated from counting statistics. Of 7 396 independent reflections measured ($2\theta \leqslant 55°$), 3 799 with intensities $I > 3\sigma(I)$ were considered observed and used for the structure determination. Lorentz and polarisation factors were applied to the derivation of structure amplitudes. Scattering factors were taken from ref. 5.

Structure Solution and Refinement.—The palladium atom co-ordinates were determined from a three-dimensional Patterson map. An initial Fourier map revealed the positions of the phosphorus and chlorine atoms together with those of the majority of the lighter atoms. Remaining non-hydrogen atoms, including those of the solvent molecule, were located from a subsequent Fourier map. With all atoms having isotropic thermal parameters, the structure was refined by full-matrix least-squares methods to R 0.104.

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[5] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

The structure was then refined with anisotropic temperature factors to R 0.061. An empirical weighting scheme of the form $w^{-1} = 2.007\,9 - 0.014\,2|F| + 0.000\,18|F|^2$ with coefficients derived from the computer programme Ranger was introduced to obtain constant errors in the various ranges of $|F_o|$ values. Final refinement gave convergence at R 0.058 with a weighted residual R' of 0.071. In the last cycle, no parameter was observed to shift by $> 0.1\ \sigma$. Final positional parameters are listed in Table 1. Thermal parameters and observed and calculated structure factors are listed in Supplementary Publication No. SUP 21614 (24 pp., 1 microfiche).*

TABLE 1

Atomic fractional co-ordinates (× 10^4), with estimated standard deviations in parentheses

	x	y	z
Pd	1 821.7(3)	1 983.3(3)	1 756.7(3)
Cl(1)	1 610(1)	717(1)	1 858(1)
Cl(2) *	1 564(4)	−175(3)	−29(2)
Cl(3) *	783(4)	1 236(4)	−109(3)
P(1)	880(1)	2 139(1)	2 486.9(9)
P(2)	2 168(1)	3 165(1)	1 699.1(9)
F(1)	4 348(4)	1 864(4)	683(3)
F(2)	4 133(5)	2 873(4)	262(4)
F(3)	3 539(4)	1 941(5)	−53(3)
O(1)	688(3)	2 988(3)	2 578(2)
O(2)	2 722(3)	1 814(3)	1 081(2)
C(1)	2 999(5)	3 094(4)	1 183(4)
C(2)	3 122(4)	2 410(4)	949(3)
C(3)	3 782(5)	2 281(5)	447(4)
C(4)	36(6)	3 253(5)	2 993(5)
C(5)	−40(9)	4 075(7)	2 896(8)
C(6) *	1 227(21)	589(13)	260(11)
C(11)	−45(5)	1 711(4)	2 265(4)
C(12)	−240(5)	1 669(5))	1 608(4
C(13)	−985(6)	1 418(6)	1 425(5)
C(14)	−1 526(6)	1 170(5)	1 909(5)
C(15)	−1 322(5)	1 182(5)	2 558(5)
C(16)	−582(4)	1 454(5)	2 730(4)
C(21)	1 171(4)	1 820(4)	3 274(3)
C(22)	1 110(5)	1 074(5)	3 456(4)
C(23)	1 383(6)	852(6)	4 058(4)
C(24)	1 711(6)	1 366(6)	4 482(4)
C(25)	1 781(6)	2 090(7)	4 305(5)
C(26)	1 506(5)	2 319(5)	3 700(4)
C(31)	1 535(4)	3 852(4)	1 342(3)
C(32)	1 845(5)	4 550(4)	1 236(4)
C(33)	1 378(6)	5 086(5)	932(4)
C(34)	616(6)	4 919(5)	737(4)
C(35)	306(5)	4 214(6)	840(5)
C(36)	765(5)	3 676(5)	1 145(4)
C(41)	2 496(4)	3 530(4)	2 471(4)
C(42)	3 076(5)	3 122(5)	2 801(4)
C(43)	3 315(6)	3 336(5)	3 417(4)
C(44)	2 975(6)	3 940(5)	3 709(5)
C(45)	2 407(7)	4 340(5)	3 379(4)
C(46)	2 161(5)	4 136(5)	2 752(4)

* Atoms of dichloromethane of crystallisation.

RESULTS AND DISCUSSION

The structure consists of discrete units of chloro-[1-(diphenylphosphino)-3,3,3-trifluoropropen-2-olato]-(ethoxydiphenylphosphine)palladium(II) separated by normal van der Waals distances and packed in the lattice with dichloromethane molecules of crystallisation. A perspective view of the molecule is shown in the Figure. Bond distances and angles are listed in Table 2, and some relevant least-squares planes in Table 3.

The Figure shows that the palladium atom is co-ordinated in distorted square-planar fashion by a chloride ion, an ethoxydiphenylphosphine ligand, and the phosphorus and oxygen atoms of a chelating deprotonated 1-(diphenylphosphino)-3,3,3-trifluoropropen-2-ol ligand.

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances

Pd–Cl(1)	2.356(2)	O(1)–C(4)	1.48(1)
Pd–P(1)	2.222(2)	C(4)–C(5)	1.52(2)
Pd–P(2)	2.246(2)	C(1)–C(2)	1.36(1)
Pd–O(2)	2.099(5)	C(2)–C(3)	1.55(1)
P(1)–O(1)	1.600(5)	C(2)–O(2)	1.313(9)
P(1)–C(11)	1.815(8)	C(3)–F(1)	1.32(1)
P(1)–C(21)	1.804(7)	C(3)–F(2)	1.30(1)
P(2)–C(31)	1.814(7)	C(3)–F(3)	1.28(1)
P(2)–C(41)	1.824(8)	C(6)–Cl(2)	1.63(3)
P(2)–C(1)	1.776(8)	C(6)–Cl(3)	1.60(3)

(*b*) Angles

Cl(1)–Pd–P(1)	87.4(0)	C(31)–P(2)–C(1)	105.9(3)
Cl(1)–Pd–P(2)	173.3(0)	C(41)–P(2)–C(1)	108.4(3)
Cl(1)–Pd–O(2)	91.5(1)	P(1)–O(1)–C(4)	122.6(4)
P(1)–Pd–P(2)	95.8(0)	O(1)–C(4)–C(5)	108.1(5)
P(1)–Pd–O(2)	178.5(1)	P(2)–C(1)–C(2)	113.9(3)
P(2)–Pd–O(2)	85.1(1)	C(1)–C(2)–C(3)	119.5(4)
Pd–P(1)–C(11)	113.2(2)	C(1)–C(2)–O(2)	127.7(3)
Pd–P(1)–C(21)	112.3(2)	C(3)–C(2)–O(2)	112.8(3)
Pd–P(1)–O(1)	110.6(1)	Pd–O(2)–C(2)	113.2(3)
C(11)–P(1)–C(21)	109.1(3)	C(2)–C(3)–F(1)	111.3(4)
C(11)–P(1)–O(1)	105.8(3)	C(2)–C(3)–F(2)	113.9(4)
C(21)–P(1)–O(1)	105.2(2)	C(2)–C(3)–F(3)	112.8(4)
Pd–P(2)–C(31)	122.3(2)	F(1)–C(3)–F(2)	105.1(4)
Pd–P(2)–C(41)	112.7(2)	F(1)–C(3)–F(3)	104.8(4)
Pd–P(2)–C(1)	99.8(2)	F(2)–C(3)–F(3)	108.4(5)
C(31)–P(2)–C(41)	106.6(3)	Cl(2)–C(6)–Cl(3)	128.8(3)

(*c*) Mean dimensions in phenyl rings

Ring (1)	C–C 1.41,	C–C–C 120.0,	P–C–C 120.2
Ring (2)	C–C 1.40,	C–C–C 120.0,	P–C–C 120.3
Ring (3)	C–C 1.41,	C–C–C 120.0,	P–C–C 119.6
Ring (4)	C–C 1.40,	C–C–C 120.0,	P–C–C 119.6

TABLE 3

Equations of least-squares planes in fractional co-ordinates and displacements (Å; in square brackets) of atoms therefrom

Plane (1): Pd, P(2), C(1), C(2), O(2)
$0.6232x - 0.1633y + 0.7648z + 4.0897 = 0$
[Pd 0.0361, P(2) −0.0421, C(1) 0.0386, C(2) 0.0014, O(2) −0.0340]

Plane (2): C(11)—(16)
$-0.3794x + 0.9226y + 0.0696z - 3.2146 = 0$

Plane (3): C(21)—(26)
$0.9027x - 0.1798y - 0.3909z - 1.4591 = 0$

Plane (4): C(31)—(36)
$-0.3494x + 0.2936y + 0.8898z + 3.6389 = 0$

Plane (5): C(41)—(46)
$0.7132x + 0.5786y - 0.3957z + 4.7347 = 0$

The angles subtended by the donor atoms at palladium differ significantly from one another and from the ideal value (90°) for a square-planar stereochemistry as a result of the 'bite' of the chelating ligand and the steric bulk of the two *cis*-phosphine ligands. Thus the O(2)–Pd–P(2) angle [85.1(1)°] corresponds to a relatively small 'bite' [2.942(5) Å], while non-bonded repulsions between the phenyl substituents on P(2) and the ethoxy-group of P(1) are responsible in part for the magnitude of the P(2)–Pd–P(1) [95.8(0)°] and the very large Pd–P(2)–C(31)

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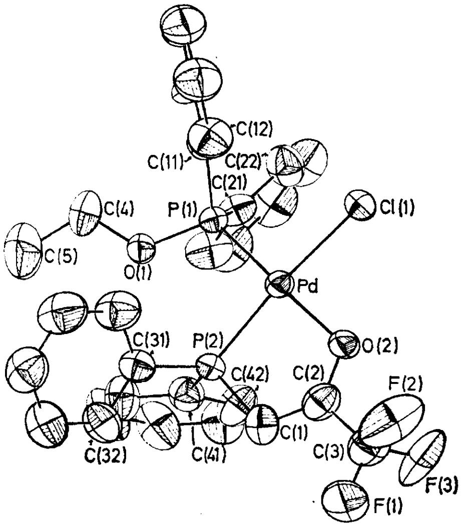
* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, issue.

angles [122.3(2)°]. By contrast the Pd–P(2)–C(41) [112.7(2)°], Pd–P(1)–C(11) [113.2(2)°], and Pd–P(1)–C(21) [112.3(2)°] angles are normal for co-ordinated phenylphosphines.

Palladium–ligand bond lengths would be expected to reflect the relative *trans*-directing influences of the co-ordinated ligands. Accordingly Pd–P(2) [2.246(2) Å] is similar to Pd–P(*trans* to Cl) [2.260(2) Å] in *cis*-[PdCl$_2$(PhPMe$_2$)],[6] but markedly shorter than in *trans*-[PdCl$_2${Ph$_2$P·CH:C(Cl)CF$_3$}$_2$] [2.322(1) Å],[7] where phosphorus is *trans* to a strongly *trans*-directing phosphine ligand. Likewise the Pd–Cl(1) bond length [2.356(2) Å] reflects the high *trans*-influence of phosphorus [6,7] and the difference in the Pd–P(1) and Pd–P(2) bond lengths (0.024 Å) reflects the relative positions of anionic oxygen donors and chloride ion in the structural *trans*-influence series.[8,9]



Perspective view of the molecule drawn by use of ORTEP; dichloromethane of solvation is not shown

The $\overline{\text{Pd–PC}_2\text{O}}$ ring is almost planar and maximum deviations from a best least-squares plane are given in Table 3. Within this ring the Pd–O bond length [2.099(5) Å] is significantly longer than any of the Pd–O distances in the compound [Pd{–CCl(CO$_2$Me)$_4$·C$_5$(CO$_2$Me)·C(OMe):O}(acac)] [10] [Pd–O(*trans* to O) mean 2.024 Å, Pd–O(*trans* to C) 2.024(11) Å] even though one of the co-ordinated oxygen atoms in the latter complex is *trans* to carbon. However, the present Pd–O bond length more closely resembles Pd–O(*trans* to Me$_2$PhP) (mean 2.128 Å) in [(Me$_2$PhP)ClPd(OAc)]$_2$.[11] Thus it appears, from the limited data available, that tertiary phosphines exert a particularly strong bond-lengthening influence on Pd–O bonds.

The present complex is an example of one of very few ionic *O,P*-chelating ligands.[12] A comparison of bond lengths within the P(2)–C(1)–C(2)–O(2) portion of the five-membered ring with parameters for other M:$\overline{(\text{X}\cdots\text{O})}$ (X = O, N, S) rings is thus of interest. The C(2)–O(2) distance [1.313(9) Å] is considerably shorter than the standard shortened C–O bond length in carboxylic acids [1.36(1) Å] but much longer than the mean literature values for aldehydes, ketones, and esters [1.23(1) Å].[13] However C(1)–C(2) [1.360(10) Å] is only slightly longer (Δ/σ 2.3) than the accepted C–C distance in alkenes [1.337(6) Å]. Thus there appears to be a small degree of delocalisation over the C(1)–C(2)–O(2) fragment of the ring. These bond lengths do not differ substantially from the mean C–O and C–C distances (1.274 and 1.390 Å) in metal–acetylacetonates [14] or mean C–O distance in the five-membered MO$_2$C$_2$ rings of metal–tropolonates [1.285(3) Å].[15] Structural data for five-membered $\overline{\text{M–NC}_2\text{O}}$ chelate rings are sparse, although there are many *X*-ray studies of Schiff-base chelates with N,O$^-$ donor sets, and a typical mean C–O bond length is 1.312 Å.[16] Hence it appears that the present C–O bond length is fairly typical for anionic chelate ligands.

The P(2)–C(1) distance [1.776(8) Å] is significantly shorter than the mean of the P–C(Ph) distances (1.814 Å), indicating possibly that delocalisation extends from phosphorus to oxygen over the PC$_2$O fragment of the chelate ring. Distances and angles within the phenyl rings (Table 3) are as expected.[17] The heavy atoms of the dichloromethane molecule of crystallisation have rather large amplitudes of thermal vibration. Similar thermal motion has been shown for chloroform of solvation in bis(salicylaldehyde)ethylenedi-iminecobalt(II) chloroformate.[18] The C–Cl bond lengths (mean 1.62 Å) are artificially shortened by this extreme thermal motion.

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