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(20) Abbreviations: 1-MeIm, 1-methylimidazole; 1,2-DiMeIm, 1,2-dimethylimidazole; OEP, octaethylporphyrin dianion; pip, piperidine, 3-pic, 3-methylpyridine.

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Contribution from the Chemistry Department,
University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

Reactions of Acetylenes Held Proximate to a Metal. Addition of Hydrogen Chloride to *cis*-Dichlorobis(3,3,3-trifluoropropynyldiphenylphosphine)palladium(II) and -platinum(II). X-Ray Structure of *trans*-$PdCl_2[Ph_2PCH{=}C(Cl)CF_3]_2$

N. J. TAYLOR, S. E. JACOBSON, and A. J. CARTY*

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The reaction of *cis*-$MCl_2(Ph_2PC{\equiv}CCF_3)_2$ (M = Pd, Pt) with HCl in nonaqueous solutions yields predominantly the complexes *trans*-$PdCl_2(Ph_2PCH{=}C(Cl)CF_3)_2$ and *cis*-$PtCl_2(Ph_2PCH{=}C(Cl)CF_3)_2$ via trans addition to the triple bonds. The compounds have been characterized by microanalysis, ir, ^1H, ^{19}F, and ^{31}P NMR spectroscopy. The palladium complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.202$ (3) Å, $b = 10.964$ (4) Å, $c = 14.943$ (5) Å, $\beta = 90.16$ (6)°, $Z = 2$, $d_{measd} = 1.61$ g cm^{-3}, and $d_{calcd} = 1.602$ g cm^{-3}. The structure has been solved by heavy-atom methods and refined by full-matrix least-squares techniques to a final R value of 0.040. All hydrogen atoms were located and refined. The principal structural features are the trans square-planar stereochemistry at palladium (Pd–P = 2.322 (1) Å; Pd–Cl(1) = 2.291 (1) Å) and the olefinic phosphine with H and Cl mutually trans across the double bond. A possible mechanism for the reactions is suggested.

Introduction

In the square-planar complex *cis*-$PdCl_2[Ph_2PC{\equiv}CCF_3]_2$ (I) and the platinum analog (II) (vide infra) the alkyne triple bonds are uncoordinated yet are held proximate to the coordination sphere of the metal and to one another.[1-5] The phosphorus-coordinated phosphinoacetylenes in these derivatives are activated and highly susceptible to nucleophilic attack at phosphorus or an alkyne carbon atom. These reactions have provided synthetic routes to the stabilized coordinated ligands $[R_2PO\cdots H\cdots OPR_2]^-$ and R_2POH via nucleophilic displacement at phosphorus,[6,7] to $R_2PCH{=}C(CF_3)O$ chelates and β-keto phosphines via acetylene hydration,[7] and to unsymmetrical diphosphines via base-promoted acetylene coupling[8] or R_2PH addition.[9] The apparent analogy of acetylene coupling in the formation of *cis*-$MCl_2(Ph_2PCH_2C(CF_3)CHPPh_2)$ (M = Pd, Pt) from I and II to the dimerization of adjacent alkyne groups in *o*-bis(phenylethynyl)benzene promoted by both electrophilic and nucleophilic reagents[10] together with the known[11,12] susceptibility of alkynes to electrophilic attack prompted us to investigate the addition of hydrogen chloride to I and II. Ionic additions of HCl and HBr to acetylenes appear to be strictly electrophilic reactions in which the intermediacy of vinyl carbonium ions has been adequately demonstrated.[13,14] In some cases proton-initiated alkyne dimerizations to cyclobutanes accompany simple addition to the triple bond.[13] The steric course of these reactions is very dependent on experimental conditions.[14] However, for tolan and propyne, addition is stereospecific, leading to the trans olefin.[15]

In this paper we describe the synthesis and characterization of *trans*-$PdCl_2[Ph_2PCH{=}C(Cl)CF_3]_2$ and *cis*-$PtCl_2[Ph_2PCH{=}C(Cl)CF_3]_2$ from the reactions of I and II with HCl. A single-crystal X-ray structure determination of the palladium derivative has revealed a trans addition of HCl to the phosphinoacetylene. The likely course of these reactions is discussed.

Experimental Section

Physical Measurements. Infrared spectra were measured as Nujol mulls on cesium iodide plates using a PE 180 spectrophotometer. ^1H NMR spectra in CD_2Cl_2 were obtained from a Varian HA100 spectrometer. Shifts (δ) are downfield of TMS as an internal standard. A Varian HA-60 operating at 58.3 MHz was utilized for ^{19}F measurements. Shifts are upfield of $CFCl_3$ as an internal standard. ^{31}P spectra were measured in the FT mode at 40.49 MHz on a JEOL-100 FTL instrument. Chemical shifts are upfield of external trimethyl phosphite in deuteriobenzene using dichloromethane as a solvent. Microanalyses and molecular weight measurements were carried out by Galbraith Laboratories, Knoxville, Tenn.

Synthesis of Compounds. ***cis*-$PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ (I)** was prepared from *trans*-$PdCl_2(PhCN)_2$ and $Ph_2PC{\equiv}CCF_3$ as previously described.[2]

***cis*-Dichlorobis(3,3,3-trifluoropropynyldiphenylphosphine)platinum(II) (II).** Dichlorocyclooctadieneplatinum(II)[16] (1.67 g) was dissolved in dry benzene (50 ml), and $Ph_2PC{\equiv}CCF_3$ (2.49 g) in benzene (50 ml) was added. The solution was stirred for 0.5 hr and then filtered, and the volume was reduced to 10 ml. Addition of acetonitrile (5 ml) caused the deposition of colorless crystals of the product (1.45 g). Anal. Calcd for $PtCl_2(Ph_2PC_2CF_3)_2$: C, 43.81; H, 2.45; P, 7.53. Found: C, 43.62; H, 2.40; P, 7.46. The ir spectrum of this complex has ν(C≡C) at 2222 (m) cm^{-1} and ν(Pt–Cl) at 324 (s), 301 (s) cm^{-1}. This complex is thus entirely analogous to *cis*-$PtCl_2(Ph_2PC{\equiv}CR)_2$ (R = Ph, Et, *i*-Pr, *t*-Bu)[5] with the phosphinoacetylenes being coordinated in cis fashion.

Reaction of I with HCl. The complex I (0.5 g) was stirred in anhydrous methanol (25 ml) under nitrogen while anhydrous HCl was bubbled through the solution (0.5 hr). The compound had dissolved in this time to give an orange solution. The flow of HCl was halted and the solution stirred for a further 1 hr. On reducing the volume of solution on a rotary evaporator an orange solid (0.32 g) was precipitated. Recrystallization from dichloromethane–methanol gave 0.23 g of rhombohedral orange crystals. Anal. Calcd. for $PdCl_2(Ph_2PC_2CF_3)_2{\cdot}2HCl$: C, 44.67; H, 2.51; Cl, 17.57; P, 7.67; mol wt 807. Found: C, 44.52; H, 2.51; Cl, 17.46; P, 7.73; mol wt (osmometry in CH_2Cl_2) 820.

Similar experiments were carried out in the solvents tetrahydrofuran and dichloromethane with virtually identical results, yields of 0.32 and 0.35 g, respectively, being obtained from 0.5 g of I. Infrared spectra of the residues from these experiments were indistinguishable from the spectrum of the bis adduct above, there being no evidence of starting material (ν(C≡C) absent) or a higher adduct.

Reaction of II with HCl. Complex II (0.5 g) was dissolved in dry tetrahydrofuran (100 ml) and anhydrous HCl was bubbled through the solution for 0.5 hr. After 2 hr of stirring, the volume of solution was reduced, leaving a colorless oil. Addition of a few milliliters of dichloromethane and diethyl ether (50 ml) followed by cooling gave 0.12 g of white crystals. Anal. Calcd for $PtCl_2(Ph_2PC_2CF_3)_2{\cdot}2HCl$: C, 40.60; H, 2.48; P, 6.90; Cl, 15.88. Found: C, 41.03; H, 2.61; P, 6.91; Cl, 15.43.

The same compound was obtained from reactions carried out in methanol and dichloromethane. The residue from these reactions contained no starting material but bands other than those of the bis adduct were present in the infrared spectrum. Attempts to obtain further characterizable platinum containing solids from these residues were unsuccessful.

X-Ray Structure Determination

Collection and Reduction of X-Ray Data. Orange-yellow crystals were grown from methyl cyanide–methylene chloride solutions. Weissenberg and precession photographs were used to establish cell constants which were refined by least-squares methods from the 2θ values (Mo Kα) measured using a General Electric XRD-6 diffractometer for 24 reflections. Unit cell data: $C_{30}H_{22}Cl_4F_6P_2Pd$, mol wt 806.66; monoclinic, a = 10.202 (3) Å, b = 10.964 (4) Å, c = 14.943 (5) Å, β = 90.16 (6)°; V = 1671.45 Å^3; d_{measd} = 1.61 g cm^{-3} (by flotation), Z = 2, d_{calcd} = 1.602 g cm^{-3}; λ 0.7107 Å, μ(Mo Kα) = 10.2 cm^{-1}, F(000) = 800; space group $P2_1/n$ (C_{2h}^5, No. 14) from systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$.

A crystal of acute rhombic, prismatic habit with dimensions 0.28 × 0.23 × 0.22 mm was mounted on a glass fiber and aligned with b^* along the ϕ axis of a General Electric XRD-6 automatic diffractometer equipped with scintillation counter and pulse height analyzer. Zirconium-filtered Mo Kα radiation was employed. Intensities were measured by the θ–2θ scan technique with a scan speed of 2°/min. The scan width was determined by the equation $\Delta(2\theta) = (1.72 + 0.3 \tan\theta)$. Background counts of 20 sec were taken before and after a scan. The intensities of three standard reflections were monitored every 100 reflections. These standards varied by less than 5% during the course of data collection. From a total of 4773 independent reflections measured ($2\theta \leq 60°$), 2699 with intensities $\geq 3\sigma$ were considered observed and used in structure factor calculations. Lorentz and polarization factors were applied to the derivation of structure amplitudes. In view of the small value of μ and the equidimensional crystal used, no absorption correction was deemed necessary.

Determination and Refinement of the Structure. A Patterson map, calculated using the $|F_o|^2$ data, readily revealed the positions of the coordinated chlorine and phosphorus atoms relative to the palladium atom. The Patterson function also indicated unambiguously that the correct special position for the heavy atom was at the origin. A Fourier synthesis phased with these three atoms then yielded the locations of all remaining nonhydrogen atoms. Three cycles of full-matrix least-squares refinement of atomic positional parameters with the inclusion of an isotropic temperature factor for palladium gave an agreement factor R of 0.203. Inclusion of anisotropic thermal parameters for palladium and isotropic coefficients for P, Cl, C, and F atoms in a cycle of full-matrix refinement reduced R to 0.121. After three further cycles of refinement with anisotropic thermal parameters for all nonhydrogen atoms the R value was 0.060. At this stage a difference Fourier synthesis revealed the positions of all 11 hydrogen atoms. These hydrogens were included in subsequent refinement with isotropic temperature coefficients. Two further cycles of refinement yielded an R value of 0.042. Finally a Cruickshank type weighting scheme with $w^{-1} = 40.0 + |F_o| + 0.001|F_o|^2$ was introduced and a final cycle of refinement gave convergence at R = 0.040 with the weighted residual of 0.047. No nonhydrogen atom parameter was observed to shift by more than one quarter of its estimated standard deviation. A final difference Fourier synthesis exhibited no peaks greater than 0.5 e Å^{-3}.

Table I

(a) Nonhydrogen Fractional Atomic Coordinates × 10^4

Atom	x	y	z
Pd	0	0	0
Cl(1)	1214 (1)	−1602 (1)	533 (1)
Cl(2)	−1820 (1)	2147 (1)	1896 (1)
P	1047 (1)	1218 (1)	1053 (1)
F(1)	−2144 (4)	4652 (4)	1045 (3)
F(2)	−1372 (6)	4791 (4)	2325 (4)
F(3)	−191 (4)	5181 (3)	1222 (5)
C(1)	471 (4)	2791 (4)	1151 (3)
C(2)	−654 (4)	3137 (4)	1477 (3)
C(3)	−1075 (6)	4445 (6)	1512 (5)
C(11)	1132 (4)	697 (4)	2202 (3)
C(12)	1930 (4)	1290 (4)	2829 (3)
C(13)	1956 (5)	879 (5)	3709 (4)
C(14)	1209 (5)	−89 (5)	3973 (4)
C(15)	413 (6)	−676 (5)	3367 (4)
C(16)	356 (5)	−287 (4)	2472 (4)
C(21)	2706 (4)	1457 (4)	643 (3)
C(22)	2850 (5)	2091 (5)	−157 (4)
C(23)	4086 (6)	2272 (6)	−510 (4)
C(24)	5176 (5)	1815 (5)	−73 (5)
C(25)	5043 (4)	1160 (5)	708 (4)
C(26)	3801 (4)	969 (4)	1078 (3)

(b) Hydrogen Fractional Atomic Coordinates × 10^3 and Isotropic Temperature Factors

Atom	x	y	z	B_{iso}, Å^2
H(1)	104 (4)	338 (4)	87 (3)	5.4 (9)
H(12)	224 (4)	196 (4)	263 (3)	5.5 (9)
H(13)	247 (4)	126 (4)	415 (3)	5.9 (9)
H(14)	120 (4)	−32 (4)	465 (3)	7.8 (11)
H(15)	−13 (4)	−135 (4)	347 (3)	7.7 (10)
H(16)	−14 (4)	−69 (4)	196 (3)	6.6 (9)
H(22)	207 (4)	244 (4)	−47 (3)	5.1 (9)
H(23)	421 (4)	263 (4)	−112 (3)	7.5 (10)
H(24)	603 (4)	196 (4)	−37 (3)	6.7 (10)
H(25)	584 (4)	83 (4)	101 (3)	7.0 (10)
H(26)	372 (4)	53 (4)	162 (3)	4.8 (9)

Atomic scattering factors for neutral atoms were used[17] and the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion of the palladium atom were included. The atomic scattering factors for hydrogen were taken from ref 18.

The final atomic positional coordinates are listed in Table I together with isotropic temperature coefficients for hydrogen atoms while Table II gives anisotropic parameters for all nonhydrogen atoms.

Computer programs used include revised versions of least squares (Doedens and Ibers), Fourier (Zalkin), and Ranger (Corfield). The plotting program ORTEP II (Johnson) was used for perspective plots of the molecule. Other programs used were developed at Waterloo. Calculations were carried out on an IBM 360/75 computer in the University of Waterloo Computing Center.

Table II. Anisotropic Thermal Parameters ($\times 10^4$)[a]

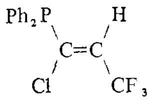
Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	63.6 (4)	63.7 (3)	57.3 (3)	−0.4 (4)	−11.0 (2)	−2.0 (3)
Cl(1)	146.4 (16)	86.9 (11)	79.1 (9)	40.3 (11)	−39.3 (9)	−9.7 (8)
Cl(2)	92.6 (12)	146.0 (17)	92.5 (10)	−4.2 (12)	18.7 (9)	3.6 (11)
P	59.8 (8)	66.2 (8)	53.5 (6)	−6.1 (7)	−4.0 (5)	−2.3 (6)
F(1)	188 (5)	169 (5)	152 (4)	69 (4)	−59 (4)	−1 (3)
F(2)	412 (11)	193 (6)	119 (3)	119 (7)	−18 (5)	−73 (4)
F(3)	179 (5)	83 (4)	302 (8)	12 (4)	42 (5)	3 (4)
C(1)	79 (4)	74 (4)	64 (3)	−2 (3)	−6 (2)	−3 (3)
C(2)	88 (4)	86 (4)	60 (3)	4 (3)	13 (3)	−13 (3)
C(3)	111 (6)	115 (6)	103 (5)	37 (5)	−18 (4)	−34 (5)
C(11)	72 (3)	73 (4)	53 (2)	−3 (3)	0 (2)	−3 (2)
C(12)	97 (4)	88 (4)	55 (2)	−7 (3)	0 (3)	−14 (3)
C(13)	138 (6)	104 (5)	53 (3)	10 (5)	−4 (3)	−11 (3)
C(14)	146 (6)	108 (5)	60 (3)	26 (5)	4 (3)	8 (4)
C(15)	151 (7)	96 (5)	75 (4)	−19 (5)	9 (4)	16 (4)
C(16)	102 (5)	90 (5)	69 (3)	−18 (3)	−2 (3)	8 (3)
C(21)	67 (3)	71 (4)	59 (2)	−12 (3)	4 (2)	−11 (2)
C(22)	112 (5)	100 (5)	59 (3)	−11 (4)	5 (3)	−2 (3)
C(23)	146 (7)	120 (6)	69 (3)	−28 (5)	34 (4)	−5 (4)
C(24)	107 (6)	120 (6)	93 (4)	−36 (5)	41 (4)	−34 (4)
C(25)	72 (4)	114 (5)	93 (4)	−1 (4)	5 (3)	−28 (4)
C(26)	75 (4)	86 (4)	67 (3)	0 (3)	−1 (3)	−15 (3)

[a] Thermal parameters are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

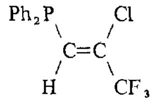
Observed and calculated structure amplitudes are available.[19]

Results and Discussion

Orange crystals of an adduct analyzing as $PdCl_2(Ph_2PC_2CF_3)_2 \cdot 2HCl$ are obtained from the reaction of I with HCl in methanol, tetrahydrofuran, and dichloromethane. This crystalline complex has a single strong ν(Pd–Cl) band in the far-infrared region at a frequency (362 cm^{-1}) characteristic of a trans square-planar stereochemistry.[20,21] The new ligands in this complex exhibit a medium-intensity infrared band at 1618 cm^{-1} which we attribute to ν(C═C), strong ν(C—F) bands in the region 1150–1300 cm^{-1}, and a γ(C—H) absorption at 823 cm^{-1}. In the ^{1}H NMR spectrum the expected resonance of the vinyl proton in the olefinic phosphine ligands $Ph_2PCH{=}C(Cl)CF_3$ is obscured by a complex phenyl proton resonance (δ 7.72 m; 7.39 m). The ^{19}F spectrum has two multiplets at δ −67.3 ppm (relative intensity 1) and δ −77.3 ppm (relative intensity 4). This spectrum could be interpreted in terms of the coexistence of trans and cis square-planar complexes in the ratio 4:1, respectively, or alternatively, in terms of cis–trans rotational isomerism about the olefinic double bonds of the phosphines. The former assignment seems more likely for the following reasons. (a) The chemical shift difference between the CF_3 multiplets is ~10 ppm. This is larger than the shift differences for perfluoroalkyl fluorine resonances in *cis*- and *trans*-1-fluoro-2-(perfluoroisopropyl)ethylene and related fluoroalkenes.[22] (b) The ^{31}P spectrum of $PdCl_2(Ph_2PCH{=}C(Cl)CF_3)_2$ in CH_2Cl_2 consists of two singlets (δ +124.93 and +130.84 ppm) upfield from external trimethyl phosphite, with a chemical shift difference compatible with values for cis and trans square-planar palladium isomers.[23,24] We assign the more intense higher field line to the trans isomer. The absence of observable ^{31}P–^{19}F coupling in the ^{31}P spectrum under high-resolution conditions (instrumental resolution 2.44 Hz) indicates that $J_{P\text{-}CF_3}$ is very small. This must also be true for $J_{H\text{-}CF_3}$ since the width at half-height for the intense ^{19}F multiplet is only 2.5 Hz. The small magnitude of the H–^{19}F coupling constant (<2 Hz) supports attachment of the hydrogen atom to the α carbon of the original alkyne since by analogy with *cis*- and *trans*-$(CF_3)_2CFCH{=}CHF$,[22] $^3J_{H\text{-}CF_3}$ in the ligand



should be large compared to $^4J_{H\text{-}CF_3}$ in



This is the expected manner of addition of HCl to the triple bonds of I in view of the strong electron-withdrawing properties of the coordinated PPh_2 group.

The available data are thus consistent with addition of HCl to I in the expected sense, giving an olefinic phosphine complex with a trans square-planar configuration in the solid state. A small amount of isomerization to a cis square-planar complex occurs on dissolution in CH_2Cl_2. An X-ray analysis of the adduct has confirmed the solid-state structure and revealed that in the phosphinoolefin H and Cl are mutually trans (vide infra).

The platinum atom in the analogous platinum complex $PtCl_2(Ph_2PC_2CF_3)_2 \cdot 2HCl$ is coordinated in cis fashion by two chlorides (ν(Pt—Cl) 319 (s), 298 (s) cm^{-1}) and two phosphorus atoms of the newly synthesized olefinic phosphines (ν(C═C) 1615 (m)). In the ^{1}H NMR spectrum (δ 7.37 m (phenyl H), 6.96 d (vinyl H), 6.82 d (vinyl H), the two vinyl resonances have intensities close to 3:1, respectively. The separation of the components of the doublets is 6.5 Hz in each case. One interpretation of this spectrum is that both ^{31}P–^{1}H and ^{19}F–^{1}H couplings are present, the spectrum being a 1:3:3:1 quartet of doublets with two components hidden under the phenyl proton resonance. For this assignment $J_{P\text{-}H}$ = 6.5 Hz and $J_{F\text{-}H}$ = 14 Hz. An alternative explanation is that the $(HCl)_2$ adduct is contaminated with ca. 25% of the monoadduct. This would still agree satisfactorily with the analytical results and would account for the less intense vinyl proton doublet, with the same H–^{31}P coupling constant as the bis adduct. The ^{31}P Fourier transform NMR spectrum of $PtCl_2(Ph_2PC_2CF_3)_2 \cdot 2HCl$ lends support to the latter supposition. The dominant features of this spectrum are an intense singlet at δ 141.94 ppm with attendant satellites due to ^{31}P–^{195}Pt coupling at δ 96.41 and 187.33 ppm, respectively. The value of $J_{Pt\text{-}P}$ (3682 Hz) can be compared with coupling constants of 3520 and 3504 Hz for $^1J_{Pt\text{-}P}$ in *cis*-$PtCl_2(PEt_3)_2$[25] and *cis*-$PtCl_2(PBu_3)_2$,[26] respectively. These values are characteristic of cis square-planar $PtCl_2(PR_3)_2$ species whereas $^1J_{Pt\text{-}P}$ in trans complexes is much smaller.[24,26] In addition to these resonances, two doublets of ca. one-third of the satellite intensity are apparent. These

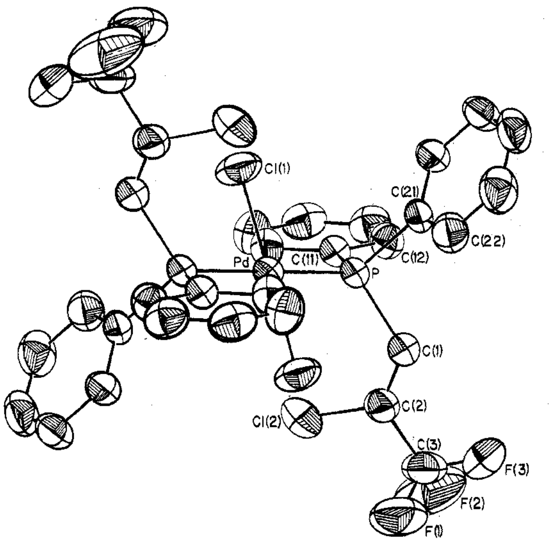


Figure 1. Perspective view of the molecular structure of *trans*-$PdCl_2[Ph_2PCH{=}C(Cl)CF_3]_2$ drawn by the program ORTEP.

doublets probably arise from the two inequivalent phosphorus atoms in the complex *cis*-$PtCl_2(Ph_2PC{\equiv}CCF_3)(Ph_2PCH{=}C(Cl)CF_3)$. The coupling in these doublets is 15 Hz which is typical of the small $^2J_{P-P}$ values for cis complexes.[24] In agreement with this assignment the infrared spectrum of the crystalline material shows a weak, residual ν(C≡C) peak at 2120 cm^{-1}. These results suggest that the addition of HCl to II gives mainly the bis adduct $PtCl_2(Ph_2PCH{=}C(Cl)CF_3)_2$ which has a cis stereochemistry at platinum. By analogy with the palladium complex, a trans addition of HCl to the acetylenes is likely.

Description of the Structure of *trans*-$PdCl_2(Ph_2PCH{=}C(Cl)CF_3)_2$. An ORTEP diagram of the molecular structure is given in Figure 1 together with the atomic numbering scheme. A stereoscopic packing diagram is shown in Figure 2. Interatomic distances and angles are listed in Table III. The equations for several least-squares planes and the displacements of atoms from these planes are presented in Table IV.

Table III. Intramolecular Bond Distances (Å) and Angles (deg)

Pd–Cl(1)	2.291 (1)	C(2)–C(3)	1.498 (8)
Pd–P	2.322 (1)	C(2)–Cl(2)	1.729 (5)
P–C(1)	1.828 (4)	C(3)–F(1)	1.313 (8)
P–C(11)	1.812 (4)	C(3)–F(2)	1.308 (9)
P–C(21)	1.820 (4)	C(3)–F(3)	1.287 (8)
C(1)–C(2)	1.305 (6)		
Cl(1)–Pd–P	87.6 (0)	C(1)–C(2)–Cl(2)	124.0 (2)
Pd–P–C(1)	116.7 (1)	C(3)–C(2)–Cl(2)	113.0 (2)
Pd–P–C(11)	118.8 (1)	C(2)–C(3)–F(1)	112.6 (2)
Pd–P–C(21)	106.3 (1)	C(2)–C(3)–F(2)	112.2 (3)
C(1)–P–C(11)	103.6 (1)	C(2)–C(3)–F(3)	112.8 (3)
C(1)–P–C(21)	101.0 (1)	F(1)–C(3)–F(2)	104.4 (3)
C(11)–P–C(21)	108.8 (1)	F(1)–C(3)–F(3)	107.1 (3)
P–C(1)–C(2)	126.0 (2)	F(2)–C(3)–F(3)	107.2 (3)
C(1)–C(2)–C(3)	123.0 (3)		
Phenyl Rings			
C(11)–C(12)	1.399 (6)	C(21)–C(22)	1.392 (7)
C(12)–C(13)	1.389 (7)	C(22)–C(23)	1.383 (8)
C(13)–C(14)	1.366 (8)	C(23)–C(24)	1.382 (8)
C(14)–C(15)	1.374 (8)	C(24)–C(25)	1.378 (9)
C(15)–C(16)	1.405 (8)	C(25)–C(26)	1.399 (6)
C(16)–C(11)	1.398 (6)	C(26)–C(21)	1.397 (6)
P–C(11)–C(12)	121.0 (1)	P–C(21)–C(22)	117.5 (2)
P–C(11)–C(16)	119.4 (2)	P–C(21)–C(26)	122.1 (1)
C(16)–C(11)–C(12)	119.6 (2)	C(26)–C(21)–C(22)	120.3 (2)
C(11)–C(12)–C(13)	119.5 (2)	C(21)–C(22)–C(23)	119.9 (3)
C(12)–C(13)–C(14)	121.1 (3)	C(22)–C(23)–C(24)	120.1 (3)
C(13)–C(14)–C(15)	120.1 (3)	C(23)–C(24)–C(25)	120.5 (3)
C(14)–C(15)–C(16)	120.5 (3)	C(24)–C(25)–C(26)	120.3 (3)
C(15)–C(16)–C(11)	119.1 (2)	C(25)–C(26)–C(21)	118.9 (2)
Carbon–Hydrogen Distances			
C(1)–H(1)	0.96 (4)	C(22)–H(22)	0.99 (4)
C(12)–H(12)	0.95 (4)	C(23)–H(23)	1.00 (4)
C(13)–H(13)	0.94 (4)	C(24)–H(24)	0.99 (5)
C(14)–H(14)	1.04 (5)	C(25)–H(25)	0.99 (4)
C(15)–H(15)	0.94 (4)	C(26)–H(26)	0.94 (4)
C(16)–H(16)	1.02 (4)		

In the centrosymmetric structure, the palladium atom is coordinated in square-planar fashion by two chloride ligands and the phosphorus atoms of two 2-chloro-3,3,3-trifluoropropenyldiphenylphosphine molecules. The Pd–P distance of 2.322 (1) Å is almost identical with the Pd–P bond length (2.326 (3) Å) in *trans*-$Pd(SCN)_2(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$[27] suggesting that the ligands $Ph_2PCH{=}C(Cl)CF_3$ and $Ph_2PC{\equiv}C\text{-}t\text{-}Bu$ have very similar structural trans influences. By contrast a recent compilation of Pd–P distances[28] shows that in cis complexes where the phosphines are trans to weakly trans-directing halide or nitrogen donors the Pd–P bond lengths are on the average ca. 0.07 Å shorter. From a comparison of available data for trans complexes[28,29] it is apparent that Pd–P bond lengths vary within the narrow range of 2.306 (3)

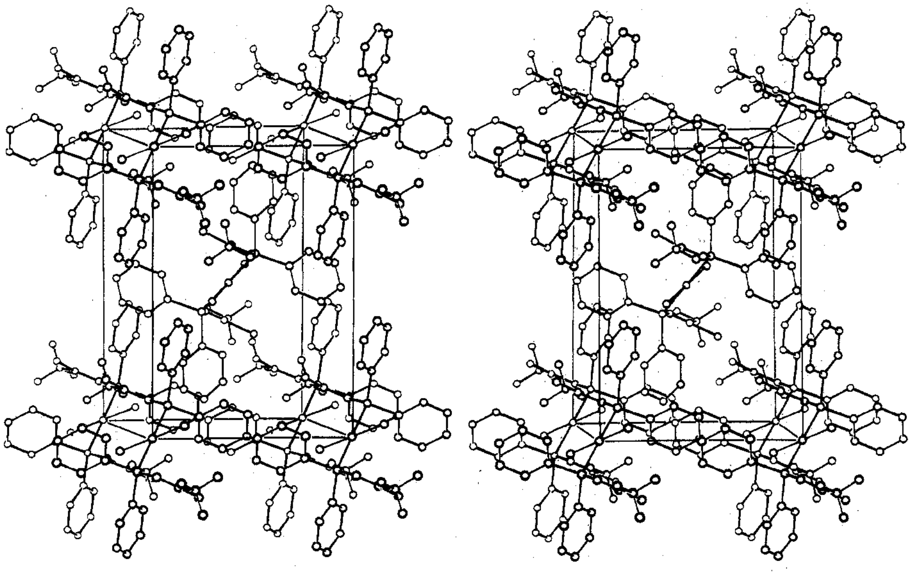


Figure 2. Stereoscopic packing diagram. The outline of one unit cell containing two molecules in the asymmetric unit is shown. The *z* axis is vertical, the *x* axis horizontal, and the *y* axis points out of the plane of the paper. The H atoms have been omitted for clarity.

Table IV. Some Relevant Least-Squares Planes, Equations to the Planes, and Atomic Displacements(Å)

Plane 1		Plane 2		Plane 3	
P	0.0028	C(11)	0.0062	C(21)	0.0120
H(1)	−0.0374	C(12)	−0.0033	C(22)	−0.0079
C(1)	0.0340	C(13)	−0.0008	C(23)	−0.0027
C(2)	0.0162	C(14)	0.0019	C(24)	0.0091
C(3)	0.0048	C(15)	0.0011	C(25)	−0.0049
Cl(2)	−0.0203	C(16)	−0.0051	C(26)	−0.0057

Equations

(1) $0.4256X + 0.0865Y + 0.9008Z + 1.9827 = 0$

(2) $0.7482X - 0.6242Y - 0.2249Z - 0.3659 = 0$

(3) $0.0876X + 0.8491Y + 0.5209Z + 2.0862 = 0$

Å for *trans*-Pd(H)Cl$(PEt_3)_2$[30] to 2.333 (7) Å in *trans*-$PdI_2(PMe_2Ph)_2$[31] despite the fact that the range of complexes encompasses phosphorus ligands of different steric and electronic properties as well as cis ligands at opposite extremes of the trans-influence series. Hence if the various phosphines have measurably different trans influences, they are not manifested in these Pd–P distances. In addition, it is clear that very accurate X-ray data will be required if the cis structural influence of ligands is to be estimated from Pd–P bond lengths in *trans*-PdX_2L_2 (X = halide, L = phosphine) complexes when L is held constant and X varies.[32]

The Pd–Cl bond length of 2.291 (1) Å is as expected considerably shorter than the corresponding distances in the cis phosphine complexes *cis*-$PdCl_2(PMe_2Ph)_2$[33] (2.362 (2) Å) and *cis*-$PdCl_2(Ph_2PN(Et)PPh_2)$ (2.37 (0.005) Å[34]) and also shorter than the Pd–Cl bond length in *trans*-Pd(H)(Cl)$(PEt_3)_2$ (2.427 (5) Å) presumably due to the strong trans structural influence of a hydride ligand in the latter.

The major feature of interest is the olefinic substituent on phosphorus, synthesized via HCl addition to the coordinated phosphinoacetylene. The hydrogen and chlorine atoms are mutually trans across the olefinic double bond. The C(1)–C(2) bond length of 1.305 (6) Å is slightly shorter than the normal olefin C═C distance (1.334 (6) Å)[35] whereas the P–C(1) length (1.828 (4) Å) is in excellent agreement with other accurate $P-C_{sp^2}$ values.[36] The bond angles around C(2) all deviate significantly from the ideal of 120° with the angle Cl(2)–C(2)–C(3) between the bulky CF_3 and Cl substituents considerably smaller than either of the other angles. These values may reflect a tendency for carbon s-orbital character to concentrate in the C(1)–C(2) bond rather than the bonds to the electronegative Cl and CF_3 groups. Table IV illustrates that the atoms P, C(1), H(1), C(2), Cl(2), and C(3) are virtually coplanar, deviations from the least-squares plane 1 being slight.

The hydrogen atom positions are sufficiently accurate that all of the C–H distances lie within the range 0.94–1.04 Å. There are no apparent inter- or intramolecular nonbonding contacts of sufficient importance to justify a discussion.

Conclusion

The predominant product formed in the addition of HCl to I is a centrosymmetric complex of the olefinic phosphine $Ph_2PCH{=}C(Cl)CF_3$ in which hydrogen and chlorine are mutually trans across the double bond. The reaction is clean and the coordinated olefinic phosphine is resistant to further attack. There is no evidence for the acetylene coupling which occurs when I is subject to attack by nucleophilic reagents. Reaction of HCl with the platinum analog II appears to proceed similarly although more slowly than for palladium since there is evidence for an intermediate 1:1 adduct containing olefinic and acetylenic phosphines.

Although there is no direct mechanistic evidence, the simplicity of the present reactions compared to the complexity of reactions between I and nucleophiles strongly suggests that addition of HCl to I occurs via an initial electrophilic attack at the α-carbon atoms of the alkynes followed by quenching of the carbonium ion by chloride. This mechanism is entirely analogous to that proposed for addition of hydrohalic acids to tolan and propyne.[13–15]

The specificity of these reactions for the addition of 1 mol of HCl to phosphinoacetylenes may be of synthetic utility in the synthesis of coordinated unsymmetrical diphosphines of the type $R_2PCH{=}CR'PR''_2$, a possibility which is actively being pursued.

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Registry No. *trans*-$PdCl_2[Ph_2PCH{=}C(Cl)CF_3]_2$, 56258-70-9; *cis*-$PtCl_2[Ph_2PCH{=}C(Cl)CF_3]_2$, 56258-71-0; I, 41043-47-4; II, 53426-08-7; dichlorocyclooctadieneplatinum(II), 12080-32-9.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC501717-11-75.

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Contribution from the Departments of Chemistry, University of Southern California, Los Angeles, California 90007, and Brookhaven National Laboratory, Upton, New York, 11973

Neutron Diffraction Study of the Structure of Zeise's Salt, $KPtCl_3(C_2H_4)\cdot H_2O$[1]

RICHARD A. LOVE,[2a] THOMAS F. KOETZLE,*[2b] GRAHEME J. B. WILLIAMS,[2b] LAWRENCE C. ANDREWS,[2b] and ROBERT BAU*[2a,c]

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The molecular structure of Zeise's salt, $KPt(C_2H_4)Cl_3\cdot H_2O$, has been studied by single-crystal neutron diffraction techniques. The $PtCl_3$ moiety forms a nearly planar group with the platinum atom 0.03 Å from the least-squares plane through the $PtCl_3$ group. The Pt–Cl bond trans to the ethylene group [2.340 (2) Å] is significantly longer than the cis Pt–Cl bonds [2.302 (2) and 2.303 (2) Å]. This difference, which is 19 times its standard deviation, is probably attributable to the trans-directing influence of the ethylene ligand. The carbon atoms are approximately equidistant from the platinum atom [2.128 (3) and 2.135 (3) Å], and the distance from the midpoint of the C–C bond to the platinum atom is 2.022 Å. The C–C distance, 1.375 (4) Å, is 0.038 Å longer than the value found in free ethylene, indicating some $d\pi$–$p\pi^*$ back-bonding from the platinum atom to C_2H_4. Back-bonding is also indicated by a bending of the four hydrogen atoms away from the platinum atom: the carbon atoms are at an average distance of 0.164 Å from the plane of the four hydrogen atoms, and the angle between the normals to the methylene planes (the α angle) is 32.5°. Both the magnitude of α and the C–C bond lengthening are considerably smaller in Zeise's salt than in metal complexes of C_2F_4 and $C_2(CN)_4$, suggesting that the amount of metal–ligand back-bonding may be greater in these complexes than in those involving ethylene. Crystallographic details: space group $P2_1/c$, with $a = 11.212$ Å, $b = 8.424$ Å, $c = 9.696$ Å, $\beta = 107.52°$, $V = 873.4$ Å^3, and $Z = 4$. Data were collected using a θ–2θ step-scan procedure with neutrons of wavelength λ 1.021 Å at the Brookhaven high-flux beam reactor. The final agreement factor R (based on F) for the 1210 reflections with $I > 3\sigma(I)$ is 0.070.

Introduction

In 1825, William Zeise set into reflux a mixture of $PtCl_4$ and $PtCl_2$ in ethyl alcohol, treated the resultant black solid with KCl and HCl, and isolated cream-lemon crystals.[3] The report of the crystals' composition, $KPtCl_3(C_2H_4)\cdot H_2O$, immediately ignited a lengthy controversy between Zeise and Liebig, who believed that the salt contained an intact ethoxy moiety.[4] Accepted proof of Zeise's formulation came 13 years later when Birnbaum isolated the complex from a solution of platinic acid, $H_2PtCl_6\cdot 6H_2O$, treated with ethylene.[5]

Zeise's platinum–ethylene complex, later referred to as Zeise's salt in the literature, was the first organometallic compound to be isolated in pure form. This discovery spawned a tremendous growth in organometallic chemistry[6] and still serves as the simplest example of transition metal–olefin complexation.

Zeise's salt has become one of the most cited examples of the Dewar–Chatt–Duncanson model for metal–olefin complexation[7,8] where a σ bond is formed by overlap of the π orbital of the olefin with a $5d6s6p^2$ hybrid orbital of the platinum atom, and a π back-bond is formed by overlap of a filled 5d6p orbital with the antibonding π^* orbital of the olefin. Although the gross features of this model are now generally accepted, there is still some disagreement on the relative importance of the π back-bonding in stabilizing the platinum–ethylene interaction.

Both X-ray photoelectron spectroscopic[9] and ^{35}Cl nuclear quadrupole resonance[10] studies on Zeise's salt indicate considerable back-donation to the olefin in agreement with the Dewar–Chatt–Duncanson model. They also show electron shift to the trans chlorine atom relative to the cis chlorine atoms which is consistent with the trans influence of ethylene. These studies then imply that $d\pi$–$p\pi^*$ back-bonding is important. On the other hand, nuclear magnetic resonance[11] and neutron inelastic scattering[12] experiments indicate that the coordinated ethylene undergoes a large-amplitude rotational oscillation, an observation which appears to argue against the presence of strong $d\pi$–$p\pi^*$ bonding. Various molecular orbital calculations[13-15] give different estimates of the relative strength of $d\pi$–$p\pi^*$ back-bonding.

It has been realized for some time that a knowledge of the detailed structure of Zeise's salt would be useful in resolving some of the questions regarding the bonding in this compound. If $d\pi$–$p\pi^*$ back-bonding were important, the ethylene π^* orbitals would become partially occupied. This would in turn lead to (a) a lengthening of the C–C bond and (b) a loss of planarity of the ethylene molecule, as the carbon atoms assume some sp^3 character.

In 1953, Wunderlich and Mellor reported the first X-ray study of Zeise's salt.[16] Their study assumed space group $P2_1$, and the structure was solved from two Patterson projections (010, 001) and a single electron density projection (010). Their data were only sufficient to locate the positions of the $PtCl_3$ moiety and the potassium cation. Later they published an improved study in which the ethylene carbon atoms were located and the trans Pt–Cl bond was determined to be abnormally long.[17] Bokii and Kukina in 1957 recollected data on Zeise's salt by the precession method as part of a study on divalent haloplatinum complexes.[18] Again, data were limited to two-dimensional projections, and the space group was assumed to be $P2_1$. These early studies on Zeise's salt supported Chatt's thesis that the ethylenic C–C bond in the complex is perpendicular to the $PtCl_3$ plane.[8]

In 1969, Black, Mais, and Owston reported the first three-dimensional X-ray structural determination of Zeise's salt.[19] Their results showed that the trans influence of the ethylene was not as large as previously described. Also in 1969, Hamilton, Klanderman and Spratley reported a neutron diffraction study of Zeise's salt in space group $P2_1$.[20] In this latter study, the hydrogen atoms were located and found to