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Reactivity of Functionalized Halo-derivatives with Transition Metal Complexes. Synthesis and X-Ray Diffraction Study of $[Ph_3P(CH_2CH_2COCH_3)]^+[PdCl_3(PPh_3)]^-$ Obtained by Reaction of *trans*-$[PdCl_2(PPh_3)_2]$ with $CH_3COCH_2CH_2Cl$

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The complex $[PdCl_3(PPh_3)]^-[Ph_3P(CH_2CH_2COCH_3)]^+$ (I) was prepared by reacting trans-*$[PdCl_2(PPh_3)_2]$ with $CH_3COCH_2CH_2Cl$ in boiling ethanol. The i.r. spectrum of (I) shows a band of strong intensity at 1717 cm^{-1} for $\nu_{(C=O)}$ and bands attributable to $\nu_{(Pd-Cl)}$ at 343(s), 301(w) and 277(m) cm^{-1}.*

The crystal and molecular structure of complex (I) has been determined from three-dimensional X-ray diffractometer data. The complex crystallizes in the monoclinic space group $P2_1/n$. Cell parameters are as follows: $a = 18.849(9)$, $b = 21.301(9)$, $c = 9.156(7)$ Å, $\beta = 92.8(1)°$, $Z = 4$. Full-matrix least-squares refinement converged at $R = 0.063$ ($R_w = 0.055$). The anion $[PdCl_3(PPh_3)]^-$ has approximately square planar geometry. The cation $[Ph_3P(CH_2CH_2COCH_3)]^+$ shows the usual angular distortions from the tetrahedral value at the phosphorus atom.

Introduction

It is well known that halo-derivatives can interact with transition metal complexes to yield metal–alkyl–halo species *via* oxidative addition of the halo compound to the metal atom [1].

Our recent interest in the reactivity of functionalized halo-derivatives is mainly due to the possibility of synthesizing alkyl complexes which may present a singular reactivity when the functionalizing atom influences the M–C bond and/or interacts with the metal atom.

In the course of studying the reactivity of $CH_3COCH_2CH_2Cl$ with *trans*-$[PdCl_2(PPh_3)_2]$ we have isolated yellow-orange crystals of a complex whose elemental analysis corresponds to $(CH_3COCH_2CH_2)(3Cl)(Pd)(2PPh_3)$. Rather surprisingly, it has been found that the $(CH_2CH_2COCH_3)$ moiety is not bonded to the palladium atom but to a phosphorus atom to form the cation $[Ph_3P(CH_2CH_2COCH_3)]^+$ which is the counter ion of the anionic complex of palladium(II) $[PdCl_3(PPh_3)]^-$.

We present here the X-ray diffraction study of the resulting complex.

Experimental

Solvents were purged before use. *Trans*-$[PdCl_2(PPh_3)_2]$ and $[PdCl_2(PPh_3)]_2$ were prepared following the procedure reported in the literature [2].

Infrared spectra were recorded with a Perkin-Elmer spectrophotometer Mod. 683 using CsI windows, in nujol mulls.

Synthesis of $[PdCl_3(PPh_3)]^-[Ph_3P(CH_2CH_2COCH_3)]^+$ (I)

Trans-$[PdCl_2(PPh_3)_2]$ was treated with an excess of $CH_3COCH_2CH_2Cl$ in boiling EtOH for some hours. After cooling and standing, yellow-orange crystals of (I) separated out.

Complex (I) can be prepared also by treating phosphonium chloride $[Ph_3P(CH_2CH_2COCH_3)]^+Cl^-$ with the chloro-bridged dimer $[PdCl_2(PPh_3)]_2$ in EtOH. Anal. for $C_{40}H_{37}Cl_3OP_2Pd$: Calcd. C = 59.43, H = 4.61, Cl = 13.16. Found C = 59.31, H = 4.56, Cl = 13.23%.

Synthesis of $[Ph_3P(CH_2CH_2COCH_3)]^+Cl^-$ (III)

This was prepared following a procedure widely used for the synthesis of phosphonium compounds *via* quaternization of an organic halide with a tervalent phosphorus [3].

PPh_3, dissolved in ether, was treated with an excess of $CH_3COCH_2CH_2Cl$. A white precipitate of

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(III) forms after a few minutes. The i.r. spectrum of (III) shows $\nu_{(C=O)}$ at 1723 cm^{-1}. *Anal.* for $C_{22}H_{22}ClOP$: Calcd. C = 71.64, H = 6.01, Cl = 9.61. Found C = 71.76, H = 6.02, Cl = 9.43%.

Collection and Reduction of X-ray Intensity Data

Suitable crystals for X-ray analysis of the complex were separated directly from the reaction media (in EtOH).

Approximate unit cell dimensions were obtained from preliminary Weissenberg and precession photographs. Systematic absence of the types h0l (h + l = 2n + 1) and 0k0 (k = 2n + 1) observed uniquely define the centrosymmetric, monoclinic space group $P2_1/n$ (C^5_{2h}, No. 14).

Intensity data were collected on a Philips PW 1100 four-circle diffractometer. Accurate unit cell dimensions and crystal orientation matrices, together with their estimated standard errors, were obtained from least-squares refinement of the 2ϑ, ω, χ and φ values of 20 carefully centered high-angle reflections. Details of the crystal data, experimental conditions and data collection method used are given in Table I.

Solution and Refinement

The structure was solved by conventional Patterson and Fourier syntheses. The refinement was carried out by the full-matrix least-squares using anisotropic temperature factors for Pd and Cl atoms and isotropic thermal parameters for the others. Hydrogen atoms could not be located from Fourier difference maps but their fixed contributions were included in the refinement (idealized position with C–H = 0.95 Å).

The function minimized was $\Sigma w\Delta^2$, ($\Delta = |F_o| - |F_c|$) and w was $[\sigma^2(F_o) + 0.000192\ F_o^2]^{-1}$. Weighting-scheme analysis showed no serious dependence of the mean $w\Delta^2$ as a function of either $|F_o|$ and $\lambda^{-1}\sin\vartheta$. Atomic scattering factors were taken from ref. [4]. Allowance was made for the anomalous scattering of palladium, chlorine and phosphorus atoms using values of $\Delta f'$ and $\Delta f''$ from reference [4]. The final conventional R value for the 2595 observed reflections ($I \geqslant 3\sigma(I)$) was 0.063 (R_w = 0.055).

Final atomic positional parameters are in Table II and a selection of functions derived from them are presented in Tables III–V. Torsion angles, final atomic thermal parameters and tables of structure factors are deposited as supplementary material. All calculations were carried out with the SHELX-76 program for crystal structure determination [5].

Results and Discussion

The i.r. spectrum of the complex $[PdCl_3(PPh_3)]^-[Ph_3P(CH_2CH_2COCH_3)]^+$ shows a band of strong intensity at 1717 cm^{-1} for $\nu_{(C=O)}$ and bands attributable to $\nu_{(Pd-Cl)}$ at 343(s), 301(w) and 277(m) cm^{-1}. The values of the low frequency infrared absorption bands are close to those reported for the same anionic complex dissolved in *cis*-1,2-dichloroethylene solution (348, 298, 271 cm^{-1}) [6].

TABLE I. Crystal and Experimental Data.

a (Å)	18.849(9)
b (Å)	21.301(9)
c (Å)	9.156(7)
β (°)	92.8(1)
Formula wt	808.73
ρ_{obsd} (g cm^{-3})	1.46 (by flotation)
ρ_{calcd} (g cm^{-3})	1.46
Z	4
Volume (Å^3)	3671.6
Space group	$P2_1/n$
Crystal dimensions (mm)	0.2 × 0.15 × 0.40
μ(cm^{-1})	8.32 (MoKα)
Radiation	MoKα, λ = 0.7107 (graphite monochromated)
Scan method	ϑ–2ϑ
Scan speed (° sec^{-1})	0.03
Scan width (°)	1.20
Total background time (sec)	20
Standard reflections	(2 4 1), (4 $\bar{1}$ $\bar{1}$) every 180 min
2ϑ scan limit (°)	2–46
No. of independent reflections	4569
No. of observed refl. ($I \geqslant 3\sigma(I)$)	2595
Final R (including unobs.)	0.088
Final R (omitting unobs.)	0.063
Final R_w (omitting unobs.)	0.055

Possibly, complex (I) forms as shown below,

$$2[PdCl_2(PPh_3)_2] \longrightarrow \underset{(II)}{[PdCl_2(PPh_3)]_2} + 2PPh_3$$

$$PPh_3 + CH_3COCH_2CH_2Cl \longrightarrow \underset{(III)}{[Ph_3P(CH_2CH_2COCH_3)]^+Cl^-}$$

$$1/2(II) + (III) \longrightarrow (I)$$

as may be suggested by the following facts:

i) by slurrying *trans*-$[PdCl_2(PPh_3)_2]$ in chloroform or dichloromethane, the chloro-bridged dimeric complex(II) forms;

ii) $CH_3COCH_2CH_2Cl$ promptly reacts with PPh_3, at r.t. in ether, yielding the phosphonium chloride (III);

iii) the dimer(II) reacts with (III) in EtOH yielding complex (I).

Structure of Complex (I)

The stereochemical arrangement of the complex is shown in Fig. 1.

TABLE II. Fractional Atomic Positional Parameters (×10^4) with the E.s.d.s in Parentheses.

Anion				Cation			
Atom	x	y	z		x	y	z
Pd	8393(1)	3294(1)	7168(1)	P(2)	8424(1)	642(2)	3416(4)
C1(1)	7164(2)	3324(2)	7555(4)	C(7)	8269(6)	783(6)	5307(14)
C1(2)	8536(2)	4163(2)	8605(5)	C(8)	7501(7)	839(6)	5688(15)
C1(3)	8219(2)	2425(2)	5690(5)	C(9)	7392(9)	753(8)	7329(19)
P(1)	9564(2)	3235(2)	6794(3)	C(10)	6664(12)	847(10)	7839(27)
				O(1)	7909(6)	647(6)	8124(13)
Phenyl ring 1				Phenyl ring 4			
C(1)	9747(6)	3076(5)	4909(13)	C(4)	8008(6)	−83(5)	2825(13)
C(11)	9340(6)	3372(6)	3817(13)	C(41)	7881(6)	−553(6)	3803(14)
C(12)	9482(7)	3304(7)	2357(14)	C(42)	7624(7)	−1127(7)	3287(16)
C(13)	10034(8)	2915(7)	1995(18)	C(43)	7510(8)	−1214(7)	1816(17)
C(14)	10446(7)	2605(6)	3043(15)	C(44)	7627(7)	−761(7)	851(18)
C(15)	10297(6)	2689(6)	4503(14)	C(45)	7885(7)	−174(6)	1320(15)
Phenyl ring 2				Phenyl ring 5			
C(2)	10016(6)	2618(5)	7878(13)	C(5)	8062(6)	1258(6)	2305(13)
C(21)	10717(7)	2666(6)	8325(14)	C(51)	7336(7)	1273(6)	1963(15)
C(22)	11056(8)	2186(7)	9154(16)	C(52)	7045(7)	1730(7)	1014(15)
C(23)	10675(9)	1680(9)	9485(18)	C(53)	7489(7)	2179(7)	463(16)
C(24)	9980(9)	1601(8)	9085(17)	C(54)	8202(8)	2177(7)	787(16)
C(25)	9630(7)	2090(7)	8242(16)	C(55)	8503(7)	1721(7)	1723(14)
Phenyl ring 3				Phenyl ring 6			
C(3)	10106(6)	3930(5)	7173(13)	C(6)	9365(6)	594(5)	3230(13)
C(31)	10391(6)	4285(6)	6070(14)	C(61)	9633(7)	164(7)	2263(15)
C(32)	10800(7)	4813(6)	6442(15)	C(62)	10359(8)	163(7)	2081(17)
C(33)	10931(7)	4988(6)	7864(15)	C(63)	10809(7)	568(7)	2809(15)
C(34)	10660(7)	4654(6)	8943(16)	C(64)	10549(8)	977(7)	3795(17)
C(35)	10239(7)	4122(6)	8609(15)	C(65)	9825(8)	1001(7)	4042(17)

TABLE III. Bond Lengths (Å) and Angles (°) with E.s.d.s in Parentheses.

Anion		Cation	
Distance		Distance	
Pd–C1(1)	2.362(3)	P(2)–C(4)	1.802(11)
Pd–C1(2)	2.279(3)	P(2)–C(5)	1.775(11)
Pd–C1(3)	2.307(3)	P(2)–C(6)	1.794(11)
Pd–P(1)	2.255(3)	P(2)–C(7)	1.796(12)
P(1)–C(1)	1.809(11)	C(7)–C(8)	1.51(1)
P(1)–C(2)	1.832(11)	C(8)–C(9)	1.54(2)
P(1)–C(3)	1.822(11)	C(9)–C(10)	1.48(2)
		C(9)–O(1)	1.21(2)
Angle		Angle	
C1(1)–Pd–C1(2)	88.9(1)	C(4)–P(2)–C(5)	108.2(5)
C1(1)–Pd–C1(3)	89.9(1)	C(4)–P(2)–C(6)	109.9(5)
C1(2)–Pd–C1(3)	178.5(1)	C(4)–P(2)–C(7)	110.1(5)
C1(1)–Pd–P(1)	178.4(1)	C(5)–P(2)–C(6)	109.9(5)
C1(2)–Pd–P(1)	92.5(1)	C(5)–P(2)–C(7)	110.6(5)
C1(3)–Pd–P(1)	88.8(1)	C(6)–P(2)–C(7)	108.1(5)
C(1)–P(1)–C(2)	106.1(5)	P(2)–C(7)–C(8)	116.1(9)
C(1)–P(1)–C(3)	101.7(5)	C(7)–C(8)–C(9)	113(1)
C(2)–P(1)–C(3)	103.8(5)	C(8)–C(9)–C(10)	117(1)

TABLE III *(continued)*

Angle		Angle	
Pd–P(1)–C(1)	112.9(4)	C(8)–C(9)–O(1)	118(1)
Pd–P(1)–C(2)	112.9(3)	O(1)–C(9)–C(10)	124(2)
Pd–P(1)–C(3)	118.0(4)		

TABLE IV. Some Mean Planes with the Distances (Å) of the Atoms to the Plane.

Plane 1: $-0.0969X + 0.5904Y - 0.8013Z = -2.6127$

Pd	0.001(2)	Cl(2)	0.021(4)
P(1)	−0.015(3)	Cl(3)	0.016(4)
Cl(1)	−0.019(4)		

Plane 2: $-0.1857X - 0.9820Y - 0.0335Z = -4.3912$
P(2)–C(7)–C(8)–C(9)–C(10)–O(1)

Plane 3: $0.0268X + 0.9821Y - 0.1863Z = 6.0863$
Pd–P(1)–C(1)

Plane 4: $-0.1511X - 0.6524Y - 0.7426Z = -11.7865$
Pd–P(1)–C(2)

Plane 5: $0.1276X - 0.3074Y + 0.9430Z = 6.0023$
Pd–P(1)–C(3)

TABLE V. Some Twist and Dihedral Angles (°).

a) Twist angle (°)* between the plane of the phenyl ring and the corresponding Pd–P–C plane;

Pd–P(1)–C(1)	and	C(1)–C(15)	40°
Pd–P(1)–C(2)	and	C(2)–C(25)	29°
Pd–P(1)–C(3)	and	C(3)–C(35)	71°

b) Dihedral angles (°) between the phenyl rings.

C(1)–C(15)	and	C(2)–C(25)	77.8(4)
C(1)–C(15)	and	C(3)–C(35)	86.0(3)
C(2)–C(25)	and	C(3)–C(35)	117.0(4)
C(4)–C(45)	and	C(5)–C(55)	65.6(4)
C(4)–C(45)	and	C(6)–C(65)	104.8(4)
C(5)–C(55)	and	C(6)–C(65)	80.8(4)

*The twist angle is here taken to be the acute dihedral angle between the Pd–P–C plane and the corresponding phenyl ring.

The structure consists of discrete $[PdCl_3(PPh_3)]^-$ anions and $[PPh_3(CH_2CH_2COCH_3)]^+$ cations separated by van der Waals contacts. The closest Pd–Pd and Pd–P^+ approaches are 9.156(4) and 6.613(4) Å respectively: all other intermolecular contacts agree with those predicted from radii-sum rules.

In the anion a distorted square plane about the metal atom is defined by the phosphorus atom of triphenylphosphine ligand and three chlorine atoms. Individual atoms are displaced by $\leqslant$0.02 Å from the coordination plane of the Pd atom (Table IV).

In the two triphenylphosphine groups (ligand and cation), corresponding bond lengths, valence angles and conformation agree well. The interbond angles at the phosphorus atoms show the usual departures from the tetrahedral value. In many transition-metal complexes containing coordinated PPh_3 groups [7] it is found that the plane of one of the phenyl rings essentially contains the metal–phosphorus vector, the second phenyl ring is twisted *ca.* 90° about its P–C bond with respect to the first ring, while the third phenyl ring is in an intermediate orientation. The anionic moiety of this compound does not conform to this stereochemistry. Of the phenyl groups attached to P(1), the ring C(3)–C(35) lies roughly at right angle to the plane Pd–P(1)–C(3), while the other two rings C(2)–C(25) and C(1)–C(15) form angles of *ca.* 29° and 40° with respect to their corresponding Pd–P–C planes.

The Pd–P(1) bond length, 2.255(3) Å, is shorter than the sum of the single bond covalent radii, 2.41 Å (assuming for Pd^{II} a covalent radius of 1.31 Å and 1.10 Å for the covalent radius of phosphorus) [8]. This fact has been used as evidence for a Pd–P double bond character (d_π–d_π bonding from the non-bonding d orbitals on metal to the empty phosphorus d orbitals) [9].

The Pd–Cl bonds are 2.279(3), 2.307(3) and 2.368(3) Å: while two of these fall within the normal range, 2.25–2.33 Å, for terminal Pd–Cl bond lengths [10], the third agrees with those normally found

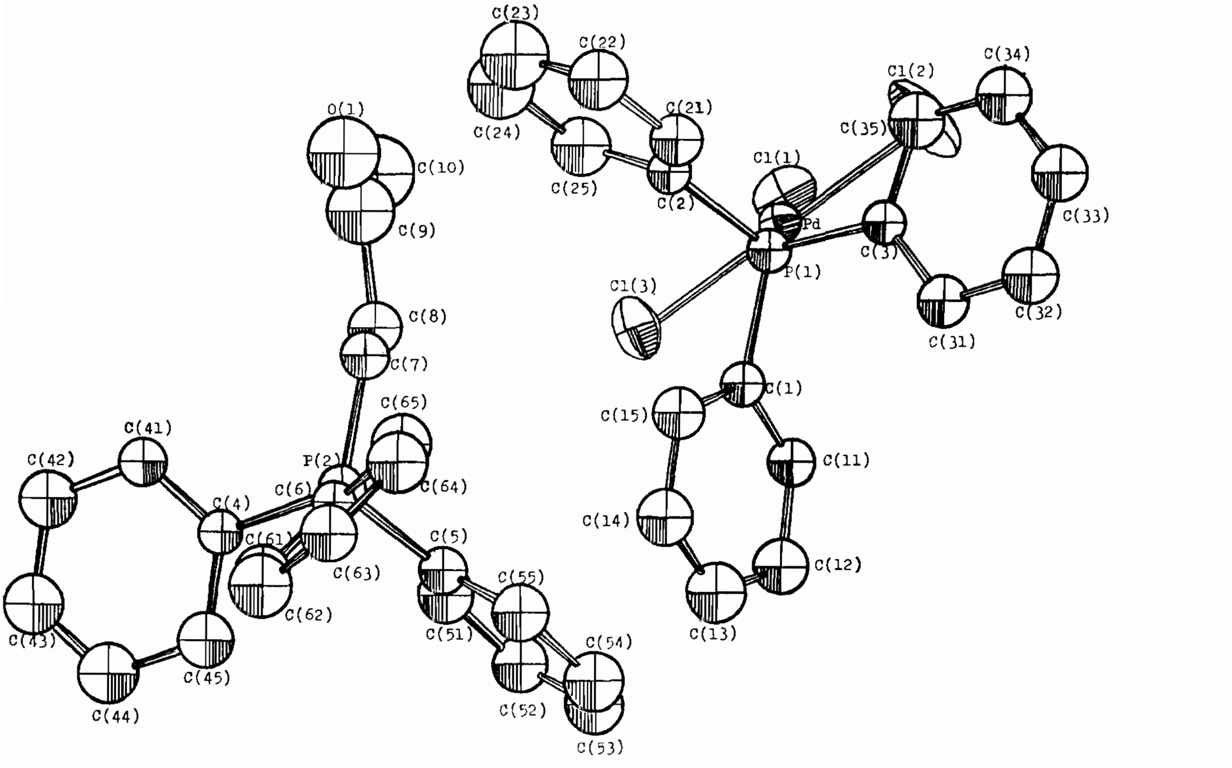

Fig. 1: Molecular structure of $[Ph_3P(CH_2CH_2COCH_3)]^+[PdCl_3(PPh_3)]^-$ with the numbering scheme.

when *trans* to a phosphine ligand (2.36–2.39 Å) [11].

In the cation, the P–C acyclic bond (1.796(12) Å) is shorter than the sum, 1.87 Å, of the covalent radii (1.10 Å is the covalent radius of phosphorus, 0.77 Å is the covalent radius of C(sp^3)) [8]. This would indicate the formation of a strong bond between the phosphorus ion and the acyclic C.

The mean C_{sp^3}–C_{sp^3} bond distance is 1.51(2) Å.

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