Structure of carbonylchloro(η^1-cyclopentadienyl)(methyldiphenylphosphine)platinum

Ronald J. Cross, Louis J. Farrugia and Karl E.A. Kuma

Chemistry Department, Glasgow University, Glasgow G12 8QQ (UK)

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Abstract

The molecular structure of the title compound shows the cyclopentadienyl ring to be near planar, η^1-bonded, and *trans* to the tertiary phosphine. Compounds of this geometry react with Ag^+ to produce $[Pt(\eta^5\text{-}C_5H_5)(CO)(PR_3)]^+$; these in turn regenerate the same isomers of the η^1-C_5H_5 complexes on subsequent halide treatment. Reasons for the failure to observe other geometries for compounds $[PtCl(\eta^1\text{-}C_5H_5)(CO)(PR_3)]$ are discussed.

Key words: Crystal structure; Platinum; Cyclopentadienyl; Carbonyl

1. Introduction

The reactions of *cis*-$[PtCl_2(CO)L]$ (L = tertiary phosphine) with $Tl(C_5H_5)$ or $Hg(C_5H_5)_2$ have been shown to produce the isomers of $[PtCl(C_5H_5)(CO)L]$ (**1**) with C_5H_5 *trans* to L [1]. The compounds decomposed in solution by a bimolecular reaction and attempted purifications have mostly been unsuccessful. The complexes with L = PPh_3 and PMe_2Ph were obtained as powders by freeze-drying their benzene solutions.

The complexes $[PtCl(C_5H_5)(CO)L]$ are fluxional, and on the basis of their cyclopentadienyl ^1H NMR parameters ($J(PH) \sim 4$ Hz; $J(PtH) \sim 30$ Hz), it was suggested they contained η^1-cyclopentadienyl ligands [1,2]. The values of $J(PtP)$ were less than 1800 Hz. Recently Boag and coworkers produced pentamethylcyclopentadienyl analogues from the action of L on $[PtCl(\eta^5\text{-}C_5Me_5)(CO)]$ [3]. The η^1-bonding of the C_5Me_5 groups in $[PtCl(C_5Me_5)(CO)L]$ was proved by their low-temperature ^{13}C NMR spectra. The values of J (PtP) of the η^1-C_5Me_5 complexes (*ca.* 1400 Hz) are considerably lower than those found in our C_5H_5 analogues. In view of the great variety of bonding modes available to fluxional cyclopentadienyl complexes, we have further examined our compounds and report here the crystal structure of $[PtCl(C_5H_5)(CO)(PMePh_2)]$.

2. Results and discussion

The complexes *cis*-$[PtCl_2(CO)(PMePh_2)]$ and *cis*-$[PtCl_2(CO)(PPh_3)]$ both reacted smoothly with $Tl(C_5H_5)$ to form the respective cyclopentadienylplatinum complexes, **1**. Careful crystallisation from an ether/pentane mixture at −78° gave the pure compounds as pale yellow micocrystals. Their ^1H and ^{31}P NMR spectroscopic data confirmed their identities. The cyclopentadienyl proton signals remained sharp down to −80°C in CD_2Cl_2, indicating a low energy-barrier to the ring fluxionality.

The molecular structure of $[PtCl(C_5H_5)(CO)(PMePh_2)]$ is depicted in Fig. 1. Table 1 lists fractional atomic coordinates and Table 2 the salient bond lengths and angles. The coordination geometry is close to square planar. The bond lengths to platinum can be compared with those in *cis*-$[PtCl_2(CO)(PPh_3)]$ [4]. The main difference is the lengthened Pt–P distance of 2.338(2) Å, compared to 2.282(2) Å in the dichloro complex. This undoubtedly reflects the markedly greater *trans*-influence of the C_5H_5 ligand than of the Cl ligand. The Pt–Cl distance [2.299(2) Å] is somewhat longer than the bond to the chlorine-*trans* to CO in *cis*-$[PtCl_2(CO)(PPh_3)]$ [2.276(1) Å], but the Pt–C(O)

Correspondence to: Dr. R.J. Cross.

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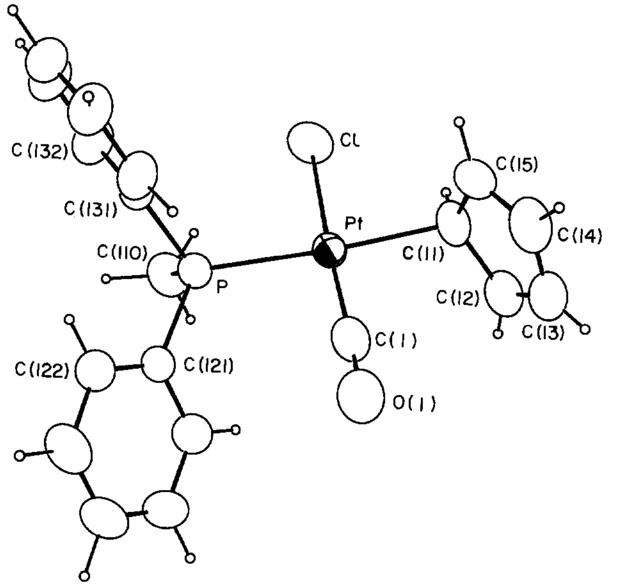

Fig. 1. Molecular structure and atomic labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radius.

bond is marginally shorter [1.835(6) Å] in our compound compared to that in the dichloro complex [1.858(7) Å].

TABLE 1. Fractional Coordinates and Isotropic Displacement Parameters (Å^2). The isotropic displacement parameter is given by

$$U=\frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*\left(\vec{a}_i.\vec{a}_j\right)$$

	x	y	z	V
Pt	0.20830(2)	0.11215(3)	0.11696(1)	0.037
P	0.05430(12)	0.29539(21)	0.15585(4)	0.038
Cl	0.35127(17)	0.05617(29)	0.18123(5)	0.067
O(1)	0.0264(5)	0.1702(9)	0.0331(2)	0.085
C(1)	0.0991(6)	0.1470(9)	0.0645(2)	0.054
C(11)	0.3643(5)	−0.0556(9)	0.0862(2)	0.051
C(12)	0.3682(6)	0.0143(11)	0.0421(2)	0.063
C(13)	0.3192(7)	−0.1371(13)	0.0147(2)	0.069
C(14)	0.2822(6)	−0.3149(12)	0.0381(2)	0.066
C(15)	0.3125(6)	−0.2745(10)	0.0804(2)	0.055
C(110)	0.1451(5)	0.5115(9)	0.1874(2)	0.053
C(121)	−0.0957(5)	0.4236(8)	0.1232(2)	0.040
C(122)	−0.2367(6)	0.3850(10)	0.1280(2)	0.058
C(123)	−0.3454(6)	0.4881(13)	0.1017(2)	0.073
C(124)	−0.3163(7)	0.6294(11)	0.0714(2)	0.071
C(125)	−0.1798(7)	0.6691(10)	0.0662(2)	0.061
C(126)	−0.0693(6)	0.5667(9)	0.0916(2)	0.053
C(131)	−0.0198(5)	0.1253(8)	0.1936(2)	0.042
C(132)	0.0133(6)	0.1519(10)	0.2377(2)	0.058
C(133)	−0.0411(6)	0.0145(13)	0.2657(2)	0.068
C(134)	−0.1306(7)	−0.1463(11)	0.2503(2)	0.072
C(135)	−0.1646(7)	−0.1749(10)	0.2069(2)	0.066
C(136)	−0.1085(6)	−0.0437(9)	0.1783(2)	0.055

TABLE 2. Selected bond lengths (Å) and angles (°)

Pt–P	2.338(2)	Pt–Cl	2.299(2)
Pt–C(1)	1.835(6)	Pt–C(11)	2.157(5)
P–C(110)	1.820(6)	P–C(121)	1.824(5)
P–C(131)	1.810(6)	O(1)–C(1)	1.132(7)
C(11)–C(12)	1.459(9)	C(11)–C(15)	1.456(9)
C(12)–C(13)	1.319(10)	C(13)–C(14)	1.404(10)
C(14)–C(15)	1.346(9)	C(15)–H(15)	0.97(7)
P–Pt–Cl	87.3(1)	P–Pt–C(1)	95.4(2)
P–Pt–C(11)	174.9(2)	Cl–Pt–C(1)	177.2(2)
Cl–Pt–C(11)	87.7(2)	C(1)–Pt–C(11)	89.6(3)
Pt–P–C(110)	111.3(2)	Pt–P–C(121)	114.8(2)
Pt–P–C(131)	112.8(2)	Pt–C(1)–O(1)	176.8(6)
Pt–C(11)–C(12)	113.1(4)	Pt–C(11)–C(15)	105.5(4)
Pt–C(11)–H(11)	92.8(42)	C(12)–C(11)–C(15)	102.5(6)
C(11)–C(12)–C(13)	110.6(6)	C(12)–C(13)–C(14)	108.5(7)
C(13)–C(14)–C(15)	109.6(7)	C(11)–C(15)–C(14)	108.7(6)

The cyclopentadienyl ligand is clearly η^1-bonded in the solid phase. The C_5 ring is almost planar, with C(11) lying 0.052(5) Å out of the mean plane defined by C(12)–C(15). This is similar to the structure of [PtMe(η^1-C_5H_5)(cod)] [5] and [PtP^tBu_2-(CMe_2CH_2)(η^1-C_5H_5)(PPh_3)] [6] and many η^1-cyclopentadienyls of other metals [7]. The Pt atom is bent out of the ring plane at the pseudotetrahedral carbon atom. The Pt–C(11) distance of 2.197(5) Å is essentially the same as the analogous distance in [PtMe(η^1-C_5H_5)(cod)] (2.151(8) Å), in which the cyclopentadienyl is *trans* to alkene. An interesting feature is the angle Pt–C(11)–H(11) of only 93(4)°. This brings this α-hydrogen closer to Pt than would be expected [Pt–H(11) = 2.37(6) Å], although the e.s.d's are quite high.

It is noteworthy that the isomers of [PtX(η^1-C_5H_5)(CO)L] with C_5H_5 *trans* to L are the only ones observed. Transfer of cyclopentadienyl from Tl(C_5H_5), Hg$(C_5H_5)_2$, or other Pt(η^1-C_5H_5) species invariably produces this geometry [1]. Moreover when the cyclopentadienyl is transferred from *cis*-[Pt$(\eta^1$-$C_5H_5)_2$(CO)L′], the geometry of both platinum species is this same isomer, [1] indicating the operation of an easy isomerisation path which is not observed with other organic groups [8].

The same isomer configuration is found for the pentamethylcyclopentadienyl complexes [PtX(η^1-C_5Me_5)(CO)L], produced from [Pt(η^5-C_5Me_5)X(CO)] and L [3]. These η^1-pentamethylcyclopentadienyls revert to η^5-bonding by elimination of CO or X^-, and this process may be the key to easy isomerisation of η^1-cyclopentadienyls. Reversible elimination of X^-, CO or L from any of the three isomers of [PtX(η^1-C_5H_5)(CO)L] could readily lead to only the most stable isomer remaining in solution. We observe that treatment of [PtCl(η^1-C_5H_5)(CO)($PMePh_2$)] with

$AgSO_3CF_3$ quantitatively produces [Pt(η^5-C_5H_5)(CO)($PMePh_2$)]SO_3CF_3 [ν(CO) 2056 cm^{-1}: ^1H NMR; C_5H_5 δ 6.06, J(Pt–H) 13.50 Hz, J(P–H) 1.26 Hz; ^{31}P NMR δ −12.3, J(Pt–P) 3838 Hz]. When this compound is heated with [Et_4N]Cl it regenerates the same isomer of [PtCl(η^1-C_5H_5)(CO)($PMePh_2$)] with C_5H_5 *trans* to $PMePh_2$, compatible with the above hypothesis.

3. Experimental section

NMR spectra were recorded in $CDCl_3$ solutions on a Bruker AM200 spectrometer operating in Fourier transform mode. IR spectra were recorded as KBr discs on a Perkin-Elmer 16PC FTIR spectrophotometer. The starting materials Tl(C_5H_5) and *cis*-[$PtCl_2$(CO)(PR_3)] were prepared and purified by standard methods [9,10].

3.1. [PtCl(η^1-C_5H_5)(CO)($PMePh_2$)]

A mixture of *cis*-[$PtCl_2$(CO)($PMePh_2$)] (1.0 g, 2.02 mmol) and Tl(C_5H_5) (0.543 g,2.02 mmol) in ether (17 ml) was stirred under N_2 for 1 h. After filtration to remove TlCl, the orange solution was cooled to −78°C and pentane added at the same temperature, producing, after 20 h, microcrystalline [PtCl(η^1-C_5H_5)(CO)($PMePh_2$)] (0.3 g,30%). Found C, 43.68; H, 3.44; calc. for $C_{19}H_{18}ClOPPt$ C, 43.55; H, 3.44%. ν(CO), 2076 cm^{-1}. ^1H NMR: C_5H_5 δ 6.25, J(Pt–H) 30.3 Hz, J(P–H) 4.4 Hz; P(CH_3)Ph_2 δ 2.25, J(Pt–H) 20.9 Hz, J(P–H) 10.75 Hz. ^{31}P NMR δ 6.29, J(Pt–P) 1762 Hz.

3.2. [PtCl(η^1-C_5H_5)(CO)(PPh_3)]

This was prepared as above from *cis*-[$PtCl_2$(CO)(PPh_3)] (0.45 g, 0.81 mmol) and Tl(C_5H_5) (0.22 g, 0.81 mmol) in ether (8 ml). Found C, 49.53; H, 3.52; calc. for $C_{24}H_{20}ClOPPt$ C, 49.20; H, 3.44%. ν(CO) 2085 cm^{-1}. ^1H NMR: C_5H_5 δ 6.30, J(Pt–H) 31.05 Hz, J(P–H) 4.4 Hz. ^{31}P NMR δ 18.63, J(Pt–P) 1786 Hz.

TABLE 3. Experimental details of crystallographic study

Compd formula	$C_{19}H_{18}ClOPPt$
M_r	523.9
space group	$P2_1/n$ (No 14, C_{2h}^5)
cryst system	monoclinic
a(Å)	9.531(1)
b(Å)	6.245(1)
c(Å)	31.443(2)
β(deg)	98.126(6)
V(Å^3)	1852.7(4)
θ range for acc. cell(deg)	$17.5 < \theta < 22$
Z	4
D_{cald}(g cm^{-3})	1.88
F(000)	1000
μ(Mo Kα)(cm^{-1})	78.8
T(K)	298
scan mode	$\theta/2\theta$
θ range(deg)	$2 < \theta < 30$
cryst size(mm)	0.33×0.2×0.06
range of trans coefficient correlation	0.70–0.136
no. of data collected	5936
no. of unique data	5377
hkl range	$-13 \Rightarrow 13$; $-8 \Rightarrow 0$; $-44 \Rightarrow 0$
R_{merge}	0.021
std reflcns	(2, 0, −16) (4, 1, 2) (−1, 3, −1)
observability criterion n $I > n\sigma(I)$	2.0
no. of data in refinement	3880
no. of refined parameters	226
final R	0.032
R_w	0.035
goodness of fit S	1.31
largest remaining feature in electron dens map/(e Å^{-3})	+0.89(max)–1.13(min)
shift/esd in last cycle	0.009 (max), 0.001 (av)

3.3. Crystal structure determination

Details of data collection procedures and structure refinement are given in Table 3. Crystals were obtained as yellow rectangular prisms from hexanes/CH_2Cl_2. Data were collected on an Enraf-Nonius Turbo-CAD4 diffractometer, running under CAD4-Express software and with graphite monochromated X-radiation (λ = 0.71069 Å). Accurate unit cell parameters were determined by refinement of the setting angles of 25 reflections. Standard reflections were measured every 2 h during data collection, and a decrease in intensities of *ca.* 3% over the data collection period of 40 h was noted, and a linear decay correction was applied. Corrections were also applied for Lorentz-polarization and absorption (DIFABS) effects [11]. The structure was solved for the Pt atom by heavy atom methods. Subsequent difference syntheses gave all the other non-H atomic positions. All non-H atoms were allowed anisotropic thermal motion. Hydrogen atoms on the cyclopentadienyl group and two of the methyl hydrogens were observed in difference Fourier maps, the remaining methyl hydrogen and the phenyl hydrogens were included at calculated positions [C–H = 1.0 Å]. The positional parameters of the methyl and phenyl hydrogens were allowed to ride on their attached C atoms and they were assigned group isotropic thermal parameters (one for the methyl, one for the phenyl and one for the cyclopentadienyl hydrogens). The positional parameters for the cyclopentadienyl hydrogens were refined without constraint. Refinement was by full-matrix least-squares, with the function $\Sigma w(|F_o| - |F_c|)$ minimized, and with the weighting scheme $w =$

$[\sigma^2(F_o)]^{-1}$ used and judged satisfactory. $\sigma(F_o)$ was estimated from counting statistics. Neutral atom scattering factors were taken from ref. 12 with corrections for anomalous dispersion. All calculations were carried out on a Micro VAX 3600 computer using the Glasgow GX suite of programs [13].

Full lists of bond lengths and angles and a table of thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

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