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Note

Synthesis and structural analysis of *trans*-Cp$(CO)_2(PPh_3)$WHgCl

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Abstract

The title compound was prepared by reaction of $[Cp(CO)_3W]_2Hg$ with PPh_3 in the presence of chlorinated solvents. The compound was characterized by IR, ^1H and ^{31}P NMR, high resolution mass spectrometry, and X-ray crystallography. The subject compound crystallizes in the monoclinic space group $P2_1/n$ (No. 14, C_{2h}^5) with $Z=4$ and $a=9.807(2)$, $b=17.854(2)$, $c=14.449(1)$ Å and $\beta=96.28(1)°$. The final least-squares full-matrix refinement based on 2141 unique reflections yielded a reliability factor of 0.037. Bond lengths and angles are internally consistent and the van der Waals interactions are normal. Important geometric details are tabulated.

Keywords: Crystal structures; Tungsten complexes; Cyclopentadienyl complexes; Carbonyl complexes; Mercury complexes

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1. Introduction

We have recently reported a detailed mechanism for the oxidative cleavage of the Mo–Hg bonds in $[Cp(CO)_2(PPh_3)Mo]_2Hg$ ($Cp=\eta$-C_5H_5) [1]. That mechanism involved a postulated pentametallic intermediate, assigned the formula $\{[Cp(CO)_2(PPh_3)Mo]_3Hg_2\}^+$ based upon its IR spectrum and the stoichiometry of its thermal decomposition. Since that intermediate could not be isolated for complete characterization, we recently attempted (unsuccessfully) to synthesize the tungsten-containing analog. The synthesis was to have begun with the tungsten analog of the preceding complex, $[Cp(CO)_2(PPh_3)W]_2Hg$. While the corresponding phosphite complexes, $[Cp(CO)_2P(OR)_3W]_2Hg$ (R = Me, Ph), have been reported [2,3], the substitution of phosphines for CO on $[Cp(CO)_3W]_2Hg$ has not. Our attempts to replace CO with PPh_3 using the approaches which work for phosphines on Mo and phosphites on W failed. However, in the course of attempting this synthesis, we did produce very low yields of a heretofore unreported tungsten complex, *trans*-$Cp(CO)_2(PPh_3)$-WHgCl (**1**). We now wish to report the details of the synthesis and characterization of **1** as well as its X-ray crystal structure.

2. Experimental

2.1. Physical measurements

IR spectra were obtained using a Mattson Instruments Cygnus 100 FTIR and ^1H and ^{31}P NMR spectra were obtained on a Bruker AMX 360 NMR spectrometer. High resolution mass spectra were obtained on a Fisons ProSpec 3000 double focusing spectrometer.

2.2. Preparation of trans-Cp$(CO)_2(PPh_3)$WHgCl (1)

The complex $[Cp(CO)_3W]_2Hg$ was prepared according to the literature procedure [4]. A mixture of $[Cp(CO)_3W]_2Hg$ (1.06 g, 1.22 mmol) and PPh_3 (1.92 g, 7.32 mmol) in 75 ml of 1-propanol was refluxed under argon for 72 h. The solution was then cooled to −10 °C for 12 h. The resulting precipitate was separated by filtration. To the filtrate was added 50 ml of CH_2Cl_2 and 50 ml of heptane. The solvents were then removed under reduced pressure until an oily red precipitate formed on the walls of the flask. The remaining milky yellow solution was decanted, 10 ml of Et_2O added, and then the mixture was dried under vacuum. The resulting red solid was dissolved in 25 ml of CH_2Cl_2 and neutral alumina (5 g) was added. The alumina was separated by filtration and washed with CH_2Cl_2. Ethanol (20 ml) was added and the CH_2Cl_2

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was removed under reduced pressure to yield a yellow solid. The yellow solid was collected, dissolved in 3.5 ml of CH_2Cl_2 and then chromatographed on a silica gel preparative TLC plate using 3:1 dichloroethane/hexane as the eluent. The second of three bands was collected, washed from the silica with CH_2Cl_2, and then precipitated with ethanol. Yield = 73.2 mg (3.6% based on W). IR (CH_2Cl_2): ν_{max} (cm^{-1}) (CO) 1921s, 1846vs. NMR ($CDCl_3$): δ_H 7.4 [15H, m, PPh_3] and 5.09 [5H, d, J(PH) 1.4, Cp]; δ_P 33.5 [s, J(WP) 273, J(HgP) 401, PPh_3]. HRMS calc. for $C_{25}H_{20}ClHgO_2PW$ (M^+) 804.0105, found m/e 804.0193. Single crystals for X-ray analysis were prepared by layering ethanol over a solution of **1** in CH_2Cl_2.

2.3. X-ray analysis

A clear yellow single crystal (0.26×0.41×0.62 mm) selected on the basis of optical homogeneity was mounted on an Enraf-Nonius CAD4-F autodiffractometer (Mo K$\bar{\alpha}$, λ_{mean} = 0.71073 Å, 292 K). Table 1 summarizes the crystal data and experimental processing parameters. Intensities were measured within the limits of $3.0 < 2\theta < 40.0°$ (h: $0 \rightarrow 9$, k: $0 \rightarrow 17$, l: $-13 \rightarrow 13$). The crystal stability and electronic hardware reliability were verified by two check reflections (every 2 h, <0.3% dev.). Lorentz, polarization and empirical absorption (max., min. factors = 0.9976, 0.5961) corrections were applied to the data [5]. Systematic absences of $0k0$ where $k = 2n+1$ and $h0l$ where $h+l = 2n+1$ were consistent with space group $P2_1/n$. Additional examination of the data using an N(Z) analysis (cumulative prob-

Table 1
Experimental and statistical summary of compound **1**

Molecular formula [a]	$C_{25}H_{22}O_3PClHgW$
Formula weight [a]	821.3
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14, C^5_{2h})
a (Å)	9.807(2)
b (Å)	17.854(2)
c (Å)	14.449(1)
β (°)	96.28(1)
V (Å^3)	2514.8(6)
Z	4
D_{calc} (Mg m^{-3})	2.168
μ(Mo K$\bar{\alpha}$) (mm^{-1})	10.96
F(000) (e$^-$)	1528
2θ Range (°)	3.0–40.0
$\Delta\omega$ (ω–2θ) (°)	$1.15 + 0.34 \tan\theta$
R_{int}	0.031
R (R_w, R_{all})	0.037 (0.048, 0.042)
Unique reflections	2141
Extinction correction (e^{-2})(×10^{-4})	5.6(6)
No. variable parameters	290
Goodness-of-fit	1.31

[a] Includes one water of crystallization.

Table 2
Fractional atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (×10^3) with e.s.d.s in parentheses for non-hydrogen atoms of compound **1**

Atom	x	y	z	U_{eq} [a] (Å^2)
W	2548(1)	4277(1)	6006(1)	32(1)
C(1)	3326(17)	4606(9)	7519(11)	66(3)
C(2)	4092(18)	5076(9)	6948(13)	66(3)
C(3)	3143(16)	5527(10)	6417(11)	63(3)
C(4)	1835(17)	5358(7)	6645(10)	57(3)
C(5)	1962(15)	4830(8)	7328(10)	51(3)
Hg	2182(1)	4913(1)	4327(1)	43(1)
Cl	2083(4)	5419(2)	2795(3)	53(1)
C(6)	761(15)	3886(7)	5455(10)	47(3)
O(6)	−336(10)	3654(5)	5202(7)	60(3)
C(7)	3894(14)	3854(7)	5269(10)	43(3)
O(7)	4742(12)	3634(6)	4848(9)	78(3)
P	2679(3)	2986(2)	6624(2)	28(1)
C(11)	1718(11)	2264(7)	5945(8)	36(3)
C(12)	1928(12)	2179(8)	5015(10)	42(3)
C(13)	1277(13)	1587(8)	4477(11)	57(3)
C(14)	403(14)	1132(8)	4900(9)	60(3)
C(15)	244(15)	1196(7)	5835(9)	69(3)
C(16)	891(12)	1762(6)	6357(9)	46(3)
C(21)	4364(12)	2546(5)	6834(9)	32(3)
C(22)	5579(13)	2958(7)	6944(9)	40(3)
C(23)	6835(14)	2632(7)	7119(10)	54(3)
C(24)	6955(15)	1867(8)	7233(12)	69(3)
C(25)	5755(14)	1432(8)	7106(11)	53(3)
C(26)	4534(14)	1784(6)	6932(10)	44(3)
C(31)	2064(13)	2919(8)	7764(9)	39(3)
C(32)	2858(13)	2670(7)	8556(9)	37(3)
C(33)	2315(15)	2700(9)	9412(11)	57(3)
C(34)	978(15)	2888(7)	9475(10)	46(3)
C(35)	170(12)	3125(7)	8686(10)	45(3)
C(36)	666(14)	3145(8)	7836(11)	51(3)
O(1)	1390(14)	5051(8)	−160(11)	115(3)

[a] U_{eq} is the equivalent isotropic thermal parameter and is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

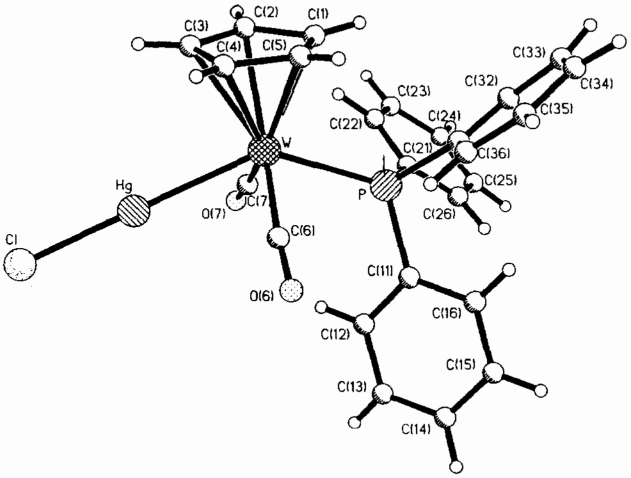

Fig. 1. The *trans*-Cp(CO)$_2$(PPh$_3$)WHgCl molecule with the atom numbering scheme shown. Small circles represent hydrogen atoms.

Table 3
Selected interatomic bond lengths (Å) and angles (°) for compound **1**

W–Hg	2.667(1)	Hg–Cl	2.382(4)
W–P	2.471(3)	C(1)–C(2)	1.44(2)
W–C(1)	2.31(2)	C(1)–C(5)	1.40(2)
W–C(2)	2.39(2)	C(2)–C(3)	1.40(2)
W–C(3)	2.37(2)	C(3)–C(4)	1.39(2)
W–C(4)	2.28(1)	C(4)–C(5)	1.36(2)
W–C(5)	2.28(2)	P–C(11)	1.82(1)
W–C(6)	1.97(1)	P–C(21)	1.83(1)
W–C(7)	1.94(1)	P–C(31)	1.82(1)
C(6)–O(6)	1.17(2)		
C(7)–O(7)	1.15(2)		
W–Hg–Cl	173.8(1)	W–P–C(11)	117.6(4)
Hg–W–P	136.3(1)	W–P–C(21)	118.2(4)
Hg–W–C(6)	76.1(4)	W–P–C(31)	112.3(4)
Hg–W–C(7)	72.4(4)	C(11)–P–C(21)	100.9(5)
C(6)–W–C(7)	105.6(6)	C(11)–P–C(31)	103.8(6)
C(6)–W–P	79.8(4)	C(21)–P–C(31)	101.9(6)
C(7)–W–P	79.8(4)	W–C(6)–O(6)	174.4(13)
		W–C(7)–O(7)	176.2(12)

Ring	Distance (Ph)		Angle (Ph)	
	Mean	Range	Mean	Range
C(11)–C(16)	1.39(2)	1.37–1.42	120.0(13)	117.5–121.9
C(21)–C(26)	1.38(2)	1.35–1.41	120.0(33)	114.7–125.0
C(31)–C(36)	1.39(3)	1.37–1.44	120.0(12)	118.9–122.0

ability distribution test) provided further evidence of a centrosymmetric system [6].

A crystallographic analysis (direct methods) of the reduced and averaged data employing Siemens SHELXTL-PC [7] located the heavy atoms (W and Hg) and electron density calculations revealed all other non-hydrogen atoms. The hydrogen atoms associated with the water of crystallization were located by difference Fourier mapping and thereafter constrained at 0.85 Å ($U_{iso}=0.08$ Å^2). All other hydrogen atoms were obtained with idealized geometry and were constrained (at 0.96 Å from the carbon atoms) to ride on their respective bonding atoms with isotropic temperature factors fixed arbitrarily at $U_{iso}=0.08$ Å^2. Several cycles of varying the anisotropic thermal parameters of the non-hydrogen atoms and applying a secondary extinction correction to the data yielded the final *R* values found in Table 1. A final electron density map revealed a maximum peak of 1.47 e$^-$ Å^{-3} in the area of the Hg atom which is quite normal for compounds containing heavy metal atoms. Atomic scattering factors and anomalous dispersion corrections were obtained from the usual source [8]. Table 2 lists the final fractional atomic coordinates according to the labeling scheme in Fig. 1 and the isotropic equivalent thermal parameters. Table 3 gives selected bond distances and angles.

3. Results and discussion

It has been known that the substitution of phosphines for carbonyl in tungsten complexes is substantially more difficult than in the analogous molybdenum complexes [9]. Consequently, there are few examples of complexes of the type $Cp(CO)_2LWX$ and $Cp(CO)_2LWHgX$, and to date only one X-ray crystal structure of an organometallic complex containing a W–Hg bond has been reported [10]. Thus the synthesis of $Cp(CO)_2(PPh_3)$-WHgCl, even in low yields, is significant. As would be expected from literature accounts of phosphite substitutions on $Cp(CO)_3W$-containing complexes, the reaction of $[Cp(CO)_3W]_2Hg$ with PPh_3 led to considerable decomposition and several unidentified products. But, low yields of complex **1** could be reproducibly obtained by the procedure given in Section 2. The details of its formation are unclear, but the chlorine atom of **1** probably originates with the CH_2Cl_2 used in the purification procedure, possibly through reaction with the intended product, $[Cp(CO)_2(PPh_3)W]_2Hg$.

The IR spectrum of **1** in CH_2Cl_2 follows the pattern observed with other $Cp(CO)_2LMX$ complexes [11]. Two carbonyl stretching bands are observed, with the lower frequency band being more intense. This pattern has been shown to be characteristic of *trans* isomers. Also in agreement with compound **1** being a *trans* isomer is its ^1H NMR spectrum [11], in which the Cp resonance is a doublet with *J*(PH) = 1.4 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 33.5 ppm with satellites due to coupling to ^{183}W and ^{199}Hg. The coupling constants (*J*(WP) = 273 Hz and *J*(HgP) = 401 Hz) are in agreement with values observed in similar complexes [3,12].

The crystallographic data of **1** best fit the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The lack of any additional symmetry was verified by the program MISSYM [13]. A perspective view of compound **1** (see Fig. 1) shows the tungsten atom coordinated to the η^5-cyclopentadienyl ring, the triphenylphosphine group, the Hg chloride group and to two carbonyl groups which are *trans*-oriented. The crystal also contained one water of crystallization per molecule of **1**, which has been omitted from Fig. 1. The arrangement of the functional groups about the Mo atom can be seen as a distorted square pyramid with the Cp ring at the apex of the pyramid forming a 'four-legged piano stool' which serves basically as a model for these types of organometallic complexes. The *trans* orientation of the carbonyl groups is in agreement with the data obtained from solution spectroscopy (both IR and NMR).

The average W–CO bond distance is 1.96(2) Å and the C(6)–W–C(7) angle is 105.6(6)°, both of which are in good agreement with values found in the Cambridge Structure Database [14]. Likewise, the W–Hg, Hg–Cl, W–P and the average C≡O bond lengths are in accord with published literature values [14]. The average C–P bond length of 1.82(1) Å is in direct agreement with observed results found in other structures containing triphenylphosphine groups [11,15,16] and in BIDICS [17]. The average W–P–C and C–P–C bond angles of 116.0 and 102.2°, respectively, are quite reasonable when comparing such angles to those published in the Cambridge Database [14]. The mean C–C bond lengths and the mean C–C–C bond angle in each phenyl ring can be considered ideal [18]. Planarity of the η^5-cyclopentadienyl ring and each of the phenyl rings was verified by employing a least-squares planes program [5]. The mean W–C bond length, dealing with the η^5-C_5H_5 ligand, is 2.33(4) Å and the mean C–C bond distance and C–C–C bond angle are 1.40(2) Å and 108.0°, respectively.

4. Supplementary material

Structure factors, anisotropic thermal parameters, hydrogen atom parameters, and complete bond distances and angles are available from the authors.

Acknowledgements

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