Crystal Structure of [Dihydrido-hexaphenylcarbodiphosphoran][chlorid]-[trichlorido-triphenylphosphino-platinat]

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The crystal structure of the salt [dihydrido-hexaphenylcarbodiphosphoran][chlorid][trichlorido-triphenylphosphino-platinat] was determined by X-ray crystallography. The title compound crystallizes in the monoclinic space group with the cell parameters $a = 38.858(3)\text{Å}$, $b = 10.851(1)\text{Å}$, $c = 27.666(2)\text{Å}$, $\alpha = 90^\circ$, $\beta = 109.07(1)^\circ$, $\gamma = 90^\circ$, $V = 11025(2)\text{Å}^3$, $Z = 8$. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1 = 0.0771$ and $wR2$ (all data) = 0.1732, $T = 100(2)\text{K}$.

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The title compound (Fig 1) was obtained in minor amounts upon attempts to synthesize a cationic platinum olefin complex by reacting the dicationic olefin complex $[(\text{PPh}_3)_2\text{C}=\text{CH}_2]\text{Br}_2^{1-}$ (an addition product of the carbene $\text{C}(\text{PPh}_3)_2$ at the four electron species CH_2^{2+}) with $\text{PtI}_2(\text{cod})$ in DCM solution. No spontaneous reaction sets in. After one day of standing at room temperature, orange crystals separated. A complex reaction occurred and the ^{31}P NMR spectrum of the solution exhibits 6 signals from which the signal at 19.6, 25.7 and 28.4 ppm could be assigned to the dication $[\text{H}_2\text{C}(\text{PPh}_3)_2]^{2+}$, $[(\text{PPh}_3)_2\text{C}=\text{CH}_2]^{2+}$ (starting material), and the anion $[\text{Cl}_3\text{Pt}(\text{PPh}_3)]^-$, respectively. Further signals at 30.6, 38.4, and 39.9 ppm could not be assigned so far. The unexpected formation of the salt can only be explained by the participation of the solvent CH_2Cl_2 . Finally, this leads to a total exchange of the halogen molecules of the starting materials by chloride. Concerning that the chemistry of $[(\text{PPh}_3)_2\text{C}=\text{CH}_2]\text{Br}_2$ only provides little information, the above reaction was one of the first attempts to shed light on it. The splitting off PPh_3 from the cation to form the PPh_3 and platinum containing anion is an important hint for further studies.

Pale-yellow plate crystals of the title compound were obtained from THF/pentane. The structure was solved by direct methods and refined with the SHELX crystallographic software package. The hydrogen atoms were placed at calculated positions and refined with common displacement parameters. The molecular structures are shown in Fig. 2, and the crystal

data are summarized in Table 1. The crystals were rather small and there was a weak diffraction behavior. Therefore, the ratio of the reflections ($>4\sigma$)/parameters was about 0.5 for a full refinement of the carbon atoms. With our used technique concerning the displacement parameters, we could perform an anisotropic refinement for all carbon atoms.

The cell contains a heavily disordered THF molecule: therefore, the SQUEEZE function of PLATON⁴ was applied. The SQUEEZE procedure omitted about $15.0\text{ e}/\text{pm}^3 \cdot 10^{-6}$. These remaining electron densities could be assembled to two strongly disordered THF molecules: one of them with an occupation parameter of 1.0 and the other with an occupation parameter of

Fig. 1 Chemical diagram of the title compound.

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Table 1 Crystal and experimental data

Chemical formula: $\text{C}_{55}\text{H}_{47}\text{Cl}_4\text{P}_3\text{Pt}$	
Formula weight: 1137.72	
$T = 100(2)\text{K}$	
Crystal system: monoclinic	Space group: $C2/c$ (No. 15)
$a = 38.858(3)\text{Å}$	$\beta = 109.07(1)^\circ$
$b = 10.851(1)\text{Å}$	
$c = 27.666(2)\text{Å}$	
$V = 11025(2)\text{Å}^3$	
$D_x = 1.371\text{ g}/\text{cm}^3$	
Radiation Mo $K\alpha$ ($\lambda = 0.71073\text{ Å}$)	
$\mu(\text{Mo } K\alpha) = 28.59\text{ cm}^{-1}$	$F(0\ 0\ 0) = 4544$
Crystal size = $0.15 \times 0.07 \times 0.07\text{ mm}^3$	
No. of reflections collected = 16974	
No. of independent reflections = 10197	
θ range for data collection: 2.172 to 25.959°	
Limiting indices: $-47 > h > 39$, $0 > k > 13$, $-30 > l > 32$	
Data/Restraints/Parameters = 10195/0/209	
Goodness-of-fit on $F^2 = 0.632$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0771$, $wR2 = 0.1403$	
R indices (all data): $R1 = 0.2203$, $wR2 = 0.1732$	
Measurement: IPDS II (Stoe)	
Program system: Sir-92 ² , SHELXL-2016/6 ³	
Structure determination: Direct methods (Sir-92)	
Refinement: SHELXL-2016/6	
CCDC deposition number: 1966049

Fig. 2 Partial ORTEP drawing of the title compound, showing thermal ellipsoids at the 40% probability level. Hydrogen atoms are omitted for clarity.

Table 2 Selected bond distances (Å) and angles (°) in $[\text{Cl}_3\text{PtPPh}_3]^-$

Pt-Cl1	2.366(4)	Pt-Cl2	2.313(5)
Pt-Cl3	2.291(5)	Pt-P3	2.222(5)
P3-Pt-Cl1	177.4(2)	Cl3-Pt1-Cl2	174.1(2)
P3-Pt1-Cl3	93.2(2)	P3-Pt1-Cl2	88.5(2)
Cl3-Pt1-Cl1	89.2(2)	Cl2-Pt1-Cl1	89.3(2)

Several further compounds with the structural motif $\text{Cl}_3\text{PtPPh}_3$ but with Pt(IV) and the platinum atom in an octahedral environment are found in the literature. These compounds exhibit similar Pt-Cl, but appreciably longer Pt-P bond lengths; a mean value of 2.326 Å from nine compounds was recorded. The latest publication in this field stems from Amico *et al.*, including earlier reports.¹²

0.5. The center of the void is localized at 0.06961 0.28765 0.20244.

A series of compounds with the dication $[\text{H}_2\text{C}(\text{PPh}_3)_2]^{2+}$ are described in the literature, which exclusively forms upon proton abstraction from the solvent CH_2Cl_2 by the carbene $\text{C}(\text{PPh}_3)_2$ and an appropriate Lewis acid. As anions acted $[\text{BeCl}_4]^{2-}$,⁵ 2 Cl^- ,⁶ $2 [\text{InCl}_4]^-$,⁷ and $[\text{AlCl}_4]^-/\text{Br}^-$,⁸ the $[\text{FeCl}_4]^-$ salt was obtained upon reacting FeCl_3 with PPh_3 in CHCl_3 .⁹ The yields range between quantitative and minor amounts. With Cl^- and $[\text{Cl}_3\text{PtPPh}_3]^-$ the title compound contains two different anions, the latter of which has not been structurally characterized so far. For a comparison, the structures of neutral Pt(II) complexes with a $\text{Cl}_2\text{Pt}(\text{Olefin})\text{PPh}_3$ core can be pulled up.¹⁰ The only compound with a similar $\text{Cl}_3\text{PtPPh}_3$ arrangement, as in the anion of the title complex, is found in *trans*-bis(μ_2 -chloro)-dichlorobistriphenylphosphine)-di-platinum(II) mentioned in a review.¹¹

The parameters of the dication $[\text{H}_2\text{C}(\text{PPh}_3)_2]^{2+}$ exhibit no special characteristics relative to those previously reported (see Supporting Information, Table S2). Close contacts to the chloride ion and one of the protons of the dication exist (C1-H2-Cl4, 3.49(2) Å; C1-H1-Cl4a, 3.64(2) Å). No closer contacts to the second platinum containing anion are found. Table 2 contains selected parameters of the complex anion. The Pt(II) atom is in a planar-four coordinate environment; the sum of the angles at Pt amounts to 360.2°. All of Pt-Cl distances are different (Pt-Cl1 2.366(4), Pt-Cl2 2.313(5), Pt-Cl3 2.291(5) Å), and the longest one belongs to Cl1 opposite to the PPh_3 group. Similar values were recorded for the olefin complexes.¹⁰ The title compound exhibits a remarkable short Pt-P bond length of 2.222(5) Å, while the related bond lengths in the olefin complexes are longer (2.2610(7) and 2.2517(8) Å).¹⁰

Supporting Information

A CIF format file, Tables S1 and S2, Figs. S1 and S2. These materials are available free of charge on the Web at <http://www.jsac.or.jp/xraystruct/>.

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