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Crystal structure of bis[hydrido-hexaphenylcarbodiphosphoran][tetra-trifluoromethyl-(μ -diiodo)-diplatinat]

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Abstract

$C_{86}H_{78}F_{12}I_2O_2P_4Pt_2$, triclinic, $P\bar{1}$ (no. 2), $a = 11.520(1)$ Å, $b = 12.196(1)$ Å, $c = 15.382(2)$ Å, $\alpha = 73.20(1)^\circ$, $\beta = 75.18(1)^\circ$, $\gamma = 86.81(1)^\circ$, $V = 2000.1(4)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0631$, $wR_{ref}(F^2) = 0.1759$, $T = 193(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless small rods
Size:	0.14 × 0.07 × 0.04 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	4.42 mm ⁻¹
Diffractometer, scan mode:	IPDS II (Stoe)
θ_{max} , completeness:	26.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	19,972, 7988, 0.070
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 4844
$N(param)_{refined}$:	488
Programs:	STOE [1], SIR-92 [2], SHELX [3]

Source of materials

The title compound $[HC(PPh_3)_2]_2[(CF_3)_2Pt(\mu-I)_2Pt(CF_3)_2]$ was obtained as the only crystalline material from the reaction of the carbene $C(PPh_3)_2$ with $[(CF_3)_2Pt(cod)]$ containing appreciable amounts of $[I_2Pt(cod)]$. A 1:1 mixture in toluene was stirred for 10 h at room temperature to give an orange solution and an orange brown precipitate, which was treated with THF. A suspension formed and the colorless solid was filtered, dissolved in dichloromethane (DCM), and layered

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Pt1	−0.95928 (4)	0.39469 (5)	0.60822 (4)	0.04342 (16)
I1	−1.02017 (10)	0.37878 (9)	0.45797 (7)	0.0675 (3)
C1	−0.6286 (8)	0.1048 (9)	0.7262 (7)	0.034 (2)
H1	−0.692775	0.150920	0.708817	0.05 (3)*
P1	−0.4895 (2)	0.1612 (2)	0.66777 (18)	0.0298 (6)
C2	−0.4260 (9)	0.2449 (9)	0.7257 (7)	0.033 (2)
C3	−0.4832 (11)	0.2438 (10)	0.8173 (8)	0.042 (3)
H31	−0.554067	0.198351	0.849038	0.051*
C4	−0.4388 (12)	0.3071 (12)	0.8623 (9)	0.050 (3)
H41	−0.480333	0.307491	0.924129	0.061*
C5	−0.3337 (13)	0.3702 (12)	0.8181 (11)	0.057 (4)
H51	−0.301377	0.412107	0.850076	0.068*
C6	−0.2751 (10)	0.3726 (11)	0.7262 (9)	0.047 (3)
H61	−0.204006	0.417761	0.694594	0.057*
C7	−0.3215 (10)	0.3082 (10)	0.6815 (8)	0.040 (3)
H71	−0.280631	0.307856	0.619610	0.048*
C8	−0.3832 (9)	0.0555 (9)	0.6421 (7)	0.034 (2)
C9	−0.4092 (10)	−0.0153 (10)	0.5914 (8)	0.040 (3)
H91	−0.483191	−0.007233	0.573803	0.048*
C10	−0.3296 (12)	−0.0956 (11)	0.5671 (8)	0.049 (3)
H101	−0.349592	−0.144692	0.534843	0.058*
C11	−0.2202 (12)	−0.1047 (12)	0.5896 (9)	0.054 (3)
H111	−0.163958	−0.158928	0.571381	0.064*
C12	−0.1924 (12)	−0.0363 (12)	0.6378 (10)	0.056 (3)
H121	−0.117359	−0.044378	0.653739	0.067*
C13	−0.2717 (10)	0.0447 (10)	0.6641 (8)	0.041 (3)
H131	−0.250607	0.092627	0.696755	0.050*
C14	−0.4971 (9)	0.2626 (9)	0.5564 (7)	0.032 (2)
C15	−0.5979 (11)	0.3269 (10)	0.5501 (8)	0.045 (3)
H151	−0.664810	0.317548	0.602843	0.054*
C16	−0.6002 (12)	0.4085 (11)	0.4619 (9)	0.051 (3)
H161	−0.669288	0.453492	0.455847	0.061*
C17	−0.5052 (12)	0.4211 (12)	0.3886 (9)	0.052 (3)
H171	−0.507179	0.476429	0.331060	0.062*
C18	−0.4073 (13)	0.3580 (14)	0.3941 (9)	0.061 (4)
H181	−0.340954	0.369456	0.340734	0.074*
C19	−0.4015 (11)	0.2748 (12)	0.4778 (8)	0.050 (3)
H191	−0.333308	0.227648	0.480643	0.059*
P2	−0.6717 (2)	−0.0209 (2)	0.81099 (19)	0.0319 (6)
C20	−0.7686 (9)	−0.1032 (9)	0.7760 (8)	0.035 (2)
C21	−0.7793 (10)	−0.0713 (11)	0.6844 (9)	0.045 (3)
H211	−0.733865	−0.007747	0.639517	0.055*
C22	−0.8560 (11)	−0.1319 (11)	0.6579 (10)	0.049 (3)
H221	−0.862847	−0.109377	0.594952	0.058*
C23	−0.9226 (12)	−0.2248 (12)	0.7223 (11)	0.057 (4)
H231	−0.974506	−0.266314	0.703532	0.068*
C24	−0.9133 (12)	−0.2566 (12)	0.8129 (12)	0.061 (4)
H241	−0.959839	−0.319793	0.857276	0.073*
C25	−0.8370 (12)	−0.1977 (10)	0.8410 (9)	0.048 (3)
H251	−0.830763	−0.221168	0.904103	0.058*
C26	−0.7587 (9)	−0.0035 (10)	0.9215 (7)	0.035 (2)
C27	−0.7674 (10)	−0.0922 (10)	1.0056 (8)	0.040 (3)
H271	−0.721630	−0.159315	1.004970	0.047*

Table 2: (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C28	−0.8430 (11)	−0.0821 (11)	1.0899 (8)	0.046 (3)
H281	−0.851643	−0.143258	1.146006	0.055*
C29	−0.9048 (10)	0.0182 (11)	1.0904 (8)	0.044 (3)
H291	−0.954126	0.027287	1.147528	0.053*
C30	−0.8953 (10)	0.1048 (11)	1.0084 (9)	0.044 (3)
H301	−0.939879	0.172481	1.009888	0.053*
C31	−0.8228 (9)	0.0964 (10)	0.9237 (8)	0.037 (2)
H311	−0.816932	0.157640	0.868073	0.044*
C32	−0.5452 (9)	−0.1064 (10)	0.8370 (7)	0.036 (2)
C33	−0.5094 (10)	−0.1961 (11)	0.8003 (9)	0.050 (3)
H331	−0.553689	−0.217617	0.763383	0.060*
C34	−0.4053 (13)	−0.2566 (13)	0.8182 (12)	0.067 (4)
H341	−0.380406	−0.320436	0.794851	0.080*
C35	−0.3417 (11)	−0.2223 (15)	0.8689 (10)	0.066 (5)
H351	−0.269808	−0.260643	0.878099	0.080*
C36	−0.3779 (11)	−0.1344 (14)	0.9071 (9)	0.060 (4)
H361	−0.333073	−0.114643	0.944572	0.072*
C37	−0.4799 (10)	−0.0733 (11)	0.8917 (8)	0.043 (3)
H371	−0.504823	−0.011159	0.917274	0.051*
C38	−0.9456 (9)	0.2230 (11)	0.6510 (10)	0.047 (3)
F1	−0.9135 (9)	0.1750 (8)	0.7335 (6)	0.075 (2)
F2	−1.0442 (8)	0.1669 (8)	0.6673 (9)	0.095 (3)
F3	−0.8579 (9)	0.1848 (7)	0.5932 (6)	0.077 (3)
C39	−0.9185 (13)	0.4087 (12)	0.7217 (10)	0.055 (3)
F4	−0.8116 (7)	0.3654 (9)	0.7376 (6)	0.076 (3)
F5	−0.9967 (8)	0.3518 (9)	0.8070 (6)	0.077 (2)
F6	−0.9164 (12)	0.5126 (9)	0.7332 (8)	0.105 (4)
O1	0.1439 (12)	0.4149 (12)	0.0106 (11)	0.124 (5)
C40	0.1738 (17)	0.5154 (12)	0.0336 (11)	0.080 (5)
H401	0.165423	0.497758	0.101867	0.096*
H402	0.119402	0.578688	0.014989	0.096*
C41	0.300 (2)	0.5487 (17)	−0.0189 (10)	0.123 (10)
H411	0.357308	0.506266	0.016532	0.148*
H412	0.314422	0.631966	−0.032565	0.148*
C42	0.3121 (17)	0.5149 (15)	−0.1098 (10)	0.114 (9)
H421	0.292825	0.579933	−0.159485	0.137*
H422	0.394319	0.489275	−0.132787	0.137*
C43	0.2199 (19)	0.4159 (18)	−0.0806 (11)	0.139 (10)
H431	0.171104	0.427760	−0.126931	0.167*
H432	0.261471	0.342090	−0.077274	0.167*

with pentane. Small colorless crystals of [HC(PPh₃)₂]₂[(CF₃)₂Pt(μ-I)₂Pt(CF₃)₂].2THF were obtained. The salt crystallizes with two molecules of THF. The proton of the cation stems from the solvent THF. A signal at δ = 20.3 ppm was attributed to the cation. Water as proton source can be excluded, because C(PPh₃)₂ reacts with traces of humidity under formation of the hydrolysis product Ph₃PCHP(O)Ph₂ with release of benzene; no signals of this compound was found in the ³¹P NMR spectra. In the ¹⁹F NMR spectrum a signal at δ = −23.2 ppm (²J_{Pt,F} = 824 Hz) was recorded.

Experimental details

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 cell contains two molecules of THF without nearer contacts to cation or anion.

Comment

A proton transfer from the solvent THF is quite common in the carbon chemistry. For instance with $[Co_2(CO)_8]$ and $C(PPh_3)_2$ in THF a nearly quantitative proton abstraction was found [4]; the same is true upon the reaction with $[Mn_2(CO)_{10}]$ [5] or MCl_2 compounds ($M = Zn, Cd$) [6]. This procedure is supported by a very high first proton affinity (PA) of the carbene $C(PPh_3)_2$ calculated as $280.0 \text{ kcal mol}^{-1}$ [7]. The three ions are connected by weak $F \cdots H-C$ bridges to the CH proton with $F \cdots C$ distances of $3.33 \text{ \AA}$. The four membered PtIPtI ring is planar and the mid point is the inversion center of symmetry; the Pt atoms are in a planar environment. The sum of the angles in the four membered ring amounts to 360° , as well as the sum of the angles at the Pt(II) atom. The Pt-C(CF_3) bond lengths are $1.98(1)$ and $2.02(1) \text{ \AA}$ and are appreciably shorter than in the dianion $[Pt(CF_3)_4]^{2-}$ (mean value $2.050(4) \text{ \AA}$) [8] and in the anion $[Pt(CF_3)_3CO]^-$ (mean value $2.068(4) \text{ \AA}$) [9]. Relative to the values in the dianion $[I_2Pt(\mu-I_2)PtI_2]^{2-}$ where the ring Pt-I bond lengths amount to $2.600 \text{ \AA}$ (mean value) [10], whereas the related bond lengths in the title dianion are longer with $2.642(1)$ and $2.674(1) \text{ \AA}$. The parameters of the cations exhibit no special characteristics relative to the previously reported $[HC(PPh_3)_2]^+$ ion [11].

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