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

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Abstract

C86H78F12I2O2P4Pt2, triclinic, P1 (no. 2), a = 11.520(1) Å, b = 12.196(1) Å, c = 15.382(2) Å, α = 73.20(1)°, β = 75.18(1)°, γ = 86.81(1)°, V = 2000.1(4) Å³, Z = 1, Rgt(F) = 0.0631, wRref(F²) = 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.

Source of materials

The title compound [HC(PPh₃)₂][[(CF₃)₂Pt(μ-I₂)Pt(CF₃)₂]] was obtained as the only crystalline material from the reaction of the carbene C(PPh₃)₂ with [(CF₃)₂Pt(cod)] containing appreciable amounts of [I₂Pt(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...
Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

| Atom | x      | y      | z      | U(eq)/Ueq |
|------|--------|--------|--------|------------|
| 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 | 0.84938 | 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) | 0.7269 (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) | 0.5679 (9) | 0.049 (3)   |
| C11  | -0.354952 | -0.146692 | 0.538438 | 0.058*       |
| C12  | -0.2202 (12) | -0.1047 (12) | 0.5896 (9) | 0.054 (3)   |
| H111 | -0.163958 | -0.158928 | 0.571381 | 0.064*       |
| C13  | -0.1924 (12) | -0.0363 (12) | 0.6378 (10) | 0.056 (3)   |
| H121 | -0.117359 | -0.046378 | 0.653739 | 0.067*       |
| C14  | -0.2717 (10) | 0.0447 (10) | 0.6641 (8) | 0.041 (3)   |
| H131 | -0.250607 | 0.092627 | 0.697655 | 0.050*       |
| C15  | -0.4971 (9) | 0.2626 (9) | 0.5564 (7) | 0.032 (2)   |
| C16  | -0.5979 (11) | 0.3269 (10) | 0.5501 (8) | 0.045 (3)   |
| H151 | -0.664810 | 0.317548 | 0.602843 | 0.054*       |
| C17  | -0.6002 (12) | 0.4085 (11) | 0.4619 (9) | 0.051 (3)   |
| H161 | -0.669288 | 0.453492 | 0.455847 | 0.061*       |
| C18  | -0.5052 (12) | 0.4211 (12) | 0.3886 (9) | 0.052 (3)   |
| H171 | -0.507179 | 0.476429 | 0.331060 | 0.062*       |
| C19  | -0.4073 (13) | 0.3580 (14) | 0.3941 (9) | 0.061 (4)   |
| H181 | -0.340954 | 0.369456 | 0.304734 | 0.074*       |
| C20  | -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) | 0.6846 (9) | 0.045 (3)   |
| H211 | -0.733865 | -0.007747 | 0.639512 | 0.055*       |
| C22  | -0.8560 (11) | -0.1319 (11) | 0.6579 (10) | 0.049 (3)   |
| H221 | -0.862867 | -0.109377 | 0.594592 | 0.058*       |
| C23  | -0.9226 (12) | -0.2248 (12) | 0.7223 (11) | 0.057 (4)   |
| H231 | -0.974506 | -0.266314 | 0.703592 | 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  | -0.8570 (12) | -0.1977 (10) | 0.8410 (9) | 0.048 (3)   |
| H251 | -0.830763 | -0.221168 | 0.904103 | 0.058*       |
| C26  | -0.7587 (9) | -0.0350 (9) | 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*       |

with pentane. Small colorless crystals of [H(CPPh3)2][(CF3)2Pt(μ-μ1)(Pt(CF3)2)2]THF 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)3 reacts with traces of humidity under formation of the hydrolysis product Ph2PCHP(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 (1JF,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 [Co₂(CO)₈] and C(PPh₃)₂ in THF a nearly quantitative proton abstraction was found [4]; the same is true upon the reaction with [Mn₂(CO)₁₀] and MCl₂ compounds (M = Zn, Cd) [6]. This procedure is supported by a very high first proton affinity (PA) of the carbone C(PPh₃)₂ calculated as 280.0 kcal mol⁻¹ [7].

The three ions are connected by weak F⋯H-C bridges to the CH proton with F/C distances of 3.33 Å. The four membered PtIPtI ring is planar and the midpoint 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(CF₃) bond lengths are 1.98(1) and 2.02(1) Å and are appreciably shorter than in the dianion [Pt(CF₃)₂]²⁻ (mean value 2.050(4) Å) [8] and in the anion [Pt(CF₃)₂CO]⁻ (mean value 2.068(4) Å) [9]. Relative to the values in the dianion [I₂Pt(μ-I₂)PtI₂] where the ring Pt–I bond lengths amount to 2.600 Å (mean value) [10], whereas the related bond lengths in the title dianion are longer with 2.642(1) and 2.674(1) Å. The parameters of the cations exhibit no special characteristics relative to the previously reported [HC(PPh₃)₂]⁺ ion [11].

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References
1. STOE & Cie. X-AREA (version 1.18) and X-RED (version 1.04); Stoe & Cie: Darmstadt, Germany, 2002.
2. Altomare A., Cascarano G., Giacovazzo C., Guagliardi A., Burla M. C., Polidori G., Camalli M. SIR-92; Altomar: Rome, 1992.
3. Sheldrick G. M. SHELXL-2016/6, Program for the Refinement of Crystal Structures; University of Goettingen: Goettingen, Germany, 2016.
4. Petz W., Wenc K., Neumüller B. On the reaction of C(PPh₃)₂ with [Co₂(CO)₈]: formation and structure of an unusual tetranuclear cluster. Z. Naturforsch. 2007, 62b, 413–418.
5. Petz W., Öxler F., Ronge R., Neumüller B. An unusual product from the reaction of C(PPh₃)₂ with [Mn₂(CO)₁₀]: formation and crystal structure of [Mn(OPPh₃)₂{O₂CC(PPh₃)₂}]₂[Mn(CO)₅]₂. Z. Anorg. Allg. Chem. 2008, 634, 1415–1420.
6. Petz W., Neumüller B. Reaction of C(PPh₃)₂ with MCl₂ compounds (M = Zn, Cd) – formation and crystal structures of [I₂Zn(C(PPh₃)₂)], [(I₂Cd(C(PPh₃)₂)]₂ and the salt-like compounds (HC(PPh₃)₂) [M₁₂(THF)] and (HC(PPh₃)₂)₂[Zn₄]. Eur. J. Inorg. Chem. 2011, 4889–4895; https://doi.org/10.1002/ejic.201100646.
7. Tonner R., Heydenrych G., Frenking G. First and second proton affinities of carbon bases. ChemPhysChem 2008, 9, 1474–1481.
8. Menjón B., Martínez-Salvador S., Gómez-Saso M. A., Forniés J., Falvello L. R., Martín A., Tsipis A. Oxidative addition of halogens to homoleptic perfluoromethyl or perfluorophenyl derivatives of platinum(II): a comparative study. Chem. Eur J. 2009, 15, 6371–6382.
9. Martínez-Salvador S., Menjón B., Forniés J., Martín A., Usón I. Trapping a difluorocarbone-platinum fragment by base coordination. Angew. Chem. 2010, 122, 4382–4385.
10. Eliseeva A. A., Ivanov D. M., Novikov A. S., Rozhkov A. V., Kornyakov I. V., Dubovtsev A. Yu., Kukushkin V. Yu. Hexaiododiplatinate(II) as a useful supramolecular synthon for halogen bond involving crystal engineering. Dalton Trans. 2020, 49, 356–367.
11. Petz W., Neumüller B. Reaction of (PPh₃)₂C—CO₂ with halogenated hydrocarbons; formation and crystal structure of a cationic ester with 1, 2-dichloroethane. Z. Anorg. Allg. Chem. 2012, 638, 987–991.