Structure of cis-Dichlorobis[(2-methylcyclopropylmethoxy)diphenylphosphine]platinum(II) Chloroform Solvate, [PtCl₂(C₁₇H₁₉OP)₂].CHCl₃

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Abstract. Mr = 926.0, monoclinic, P2₁/c, a = 11.628 (4), b = 18.274 (8), c = 17.266 (6) Å, β = 93.63 (2)°, U = 3662 Å³, Z = 4, Dc = 1.68 g cm⁻³, λ = 0.7093 Å, μ(Mo Kα) = 43.6 cm⁻¹, F(000) (with anomalous dispersion) = 1826, T = 118 K, R(F²) = 0.082, Rw(F²) = 0.111 for 4749 unique data including those with Fₒ < 0 and 407 variables, R(F) = 0.053, Rw(F) = 0.056 for 4156 reflections with Fₒ > 3σ(Fₒ). The structure contains a square-planar Pt⁺⁺ center coordinated by cis-chloro cis-phosphorus ligands. The Pt-Cl distances are 2.358 (2) and 2.369 (2) Å while the Pt-P distances are 2.222 (2) and 2.224 (3) Å. There is substantial tetrahedral distortion of the geometry about the Pt⁺⁺ center with deviations of atoms from the best, weighted Cl₂PtP₂ plane being Cl(1), 0.143 (2); Cl(2), -0.131 (2); P(1), 0.119 (2); P(2), -0.153 (2); and Pt, -0.025 (2) Å.

Introduction. The title compound was prepared in connection with an ongoing study of the interactions with transition-metal systems of chelated cyclopropanes (Youngs & Ibers, 1983a,b; Youngs, Mahood, Simms, Swepton, Ibers, Shang, Huang & Lu, 1983).

Experimental. A mixture of pyridine (4.72 g) and HO-CH₂-CH-CH₂-CH₂-CH₃ (5.15 g) was added to (C₆H₅)₂PCl (13.1 g) in diethyl ether at 273 K, allowed to warm to room temperature over a 12 h period, and then refluxed for 2 h. Distillation gave the final product, i.e., (C₆H₅)₂EP-O-CHE-/₂H-CHE-CH₂-CH₃. The latter compound (0.30 g) was added to cis-PtCl₂(PhCN)₂ (0.23 g) in a toluene-CH₂Cl₂ mixture and the solution was stirred for 12 h. The solvents were removed under vacuum and ethanol was added. Filtration gave a yellow filtrate and a white precipitate. The colorless crystals suitable for X-ray analysis were obtained from a toluene, diethyl ether, and chloroform mixture. Two prismatic crystals displaying faces of the {100} and {011} forms, 0.31 and 0.36 mm long, of cross-sections 0.26 × 0.33 mm and 0.22 × 0.32 mm, calculated volumes 0.0267 and 0.0258 mm³ respectively;

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The molecular structure contains a square-planar Pt\(^{II}\) center that shows a substantial tetrahedral distortion, evident both from the deviations of atoms from the Cl\(_2\)PtP\(_2\) plane and from the trans-P–Pt–Cl angles of 171.03 (8) and 172.55 (8)°. The deviations of atoms from the best weighted least-squares plane defined by atoms Cl(1), Cl(2), P(1), P(2) are 0.143 (2), −0.131 (2), 0.119 (2), and −0.153 (2) Å, respectively, and −0.025 (2) Å for the Pt atom. There are three angles around the Pt atom that are smaller than the idealized 90°: P(1)–Pt–Cl(2) = 87.82 (9), Cl(1)–Pt–Cl(2) = 88.05 (9), and Cl(1)–Pt–P(2) = 87.94 (9)°. The mutually cis P atoms subtend a rather large angle of 97.00 (9)°. These deformations arise from the steric interactions between bulky phosphine ligands and have been frequently observed in other structures that contain the cis-PtCl\(_2\)P\(_2\) entity (Table 3). It has been noted previously (Russell, Tucker & Wilson, 1976; Hitchcock, Jacobson & Pidcock, 1977) that in complexes of the cis-[PtCl\(_2\)L(PR\(_3\))] type, the Pt–P bond length shows a significant variation with L. The variation with L of the Pt–Cl bond lengths is smaller and in the opposite sense from the Pt–P bond lengths. The Pt–P and Pt–Cl bond lengths found in the present structure fit this correlation very well (Hitchcock, Jacobson & Pidcock, 1977, Fig. 2), in spite of the fact that the same groups are connected to both P atoms.
Examination of the external dimensions of the coordination figure shows it to be a twisted rectangle rather than a square. The respective distances are: Cl(1)...Cl(2) = 2.285 (4), P(1)...P(2) = 3.330 (3), P(1)...Cl(2) = 3.178 (3) and P(2)...Cl(1) = 3.190 (4) Å. The appropriate angles at P(1), P(2), Cl(1), and Cl(2) are 89.24 (8), 89.13 (9), 89.84 (8), and 90.16 (8)°, respectively. The portions of the molecule containing methylcyclopropane rings exhibit some apparent disorder, even though the data were collected at 118 K. This disorder affects bond lengths and angles within the cyclopropane rings. However, no useful model for such disorder was found from difference electron density syntheses. Owing to this disorder, the mean cyclopropane C-C distance, 1.44 (2) Å, is foreshortened, being smaller than the normal length in saturated hydrocarbons: 1.537 (5) Å (Sutton, 1965) and 1.510 (5) Å found from an electron diffraction study of cyclopropane (Bastiansen, Fritsch & Hedberg, 1964). The average angle is exactly 60° for both cyclopropane rings and the bond lengths opposite the smallest angles are the shortest ones. A similar arrangement was observed for trans-2,trans-3-dimethylcyclopropanecarboxylic acid (Luhan & McPhail, 1972). The remaining bond lengths and angles have typical values. There is a well defined molecule of chloroform present in the crystal structure. The closest contact between Pt complex and solvent is Cl(3)...C(16) = 3.3 Å.

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References


Bis(μ-ethylthio-S)-bis[carbonyl(η⁵-cyclopentadienyl)iron](Fe-Fe) Chlorate, C₁₆H₂₀Fe₂O₂S₂⁺ClO₇⁻

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Abstract. \( M_r = 503-6 \), tetragonal, \( P_{4}2_{1}2_{1} \), \( a = 9.180 (5), \ c = 24.156 (5) \ \AA, \ V = 2036 (6) \ \AA^3 \), \( Z = 4 \), \( D_m = 1.70 (5), \ D_x = 1.643 (5) \ \text{Mg} \ \text{m}^{-3} \), \( \lambda(\text{Mo Kα}) = 0.7107 \ \text{Å}, \ \mu = 1.056 \ \text{mm}^{-1} \), \( F(000) = 1028 \), \( T = 295 \ \text{K} \), final \( R = 0.078 \) for 862 observed reflections.

The Fe-Fe distance of 2.957 (4) Å corresponds to an overall one-electron interaction; S-Fe = 2.240 (4), etc.

Both the cation and the chlorate anion exhibit crystallographic twofold symmetry; this symmetry imposes disorder on the latter.

Introduction. We are currently attempting to synthesize the mixed-metal complex \( [(\text{cp})\text{Fe(CO)}₂(\text{μ-SEt})(\text{CO})₂\text{Mn(Mecp)}]^+ \) (cp = \( \eta^5 \)-cyclopentadienyl, Mecp = \( \eta^5 \)-methylcyclopentadienyl). This complex is a hybrid of the known cations \( [(\text{cp})\text{Fe(CO)}₂(\text{SEt})]⁺ \) (English, Nassimbeni & Haines, 1978) and \( [(\text{Mecp})\text{Mn(CO)}₂(\text{SEt})]₂ \). (Burckett-St. Laurent, Caira, English, Haines & Nassimbeni, 1977); the latter compound has an Mn–Mn bond while there is no Fe–Fe interaction in the former. The degree of interaction between Fe and Mn in the hybrid would therefore be of interest. However, in the course of an attempt to prepare this compound by reacting \( [(\text{cp})\text{Fe(CO)}₂(\text{SEt})] \) (Ahmad, Bruce & Knox, 1966) with \( [(\text{Mecp})\text{Mn(CO)}₃(\text{SEt})] \) (thf = tetrahydrofuran) (Strohmeier, von Hobé, Schönauer & Laporte, 1962), the title complex was obtained when AgClO₄ was added to the reaction mixture. The complex was initially characterized as the perchlorate salt; however, as a referee has pointed out, the model used for the anion in the X-ray structure analysis was incompatible with ClO₄⁻ and closer investigation of difference maps of the electron density round Cl confirmed the presence of ClO₄⁻. The mechanism whereby ClO₄⁻ is reduced to ClO₇⁻ in this particular reaction is not clear: however, thf is susceptible to oxidation at the α-carbon position (Robertson, 1948) and perchloric acid is of course a powerful oxidizing agent. As the thf was not dried before use, it seems likely that this oxidation, with corresponding reduction of ClO₄⁻ to ClO₇⁻, was the source of ClO₇⁻. ¹H NMR spectra of thf solutions of AgClO₄ support this hypothesis.

With hindsight it would seem that the reaction
\[ [(\text{cp})\text{Fe(CO)}₂(\text{SEt})] + [(\text{Mecp})\text{Mn(CO)}₂(\text{thf})] \rightarrow [(\text{cp})\text{Fe(CO)}₂(\text{SEt})(\text{CO})₂\text{Mn(Mecp)}] + \text{thf} \]
is in fact in equilibrium and in the presence of Ag⁺ and excess thf the competing reaction
\[ 2[(\text{cp})\text{Fe(CO)}₂(\text{SEt})] + \text{Ag}⁺ \rightarrow [(\text{cp})\text{Fe(CO)}(\text{SEt})]⁺ + \text{Ag} + 2\text{CO} \]
which has not been hitherto reported, results in the formation of the title compound. While the structure of the methylthio analogue of this compound as the tetrafluoroborate salt has been communicated (Cannell & Dahl, 1970), a subsequent full report on the crystallographic analysis has not appeared. An X-ray analysis was therefore carried out on \( [(\text{cp})\text{Fe(CO)}(\text{SEt})]₂ \) ClO₄, which could be obtained in suitable crystaline form.

Experimental. When an excess of AgClO₄ (1.0 g, 4.8 mmol) was added to a thf solution of \( [(\text{cp})\text{Fe(CO)}₂(\text{SEt})] \) (0.3 g, 1.3 mmol) and \( [(\text{Mecp})\text{Mn(CO)}₃(\text{SEt})] \) formed \textit{in situ} by UV irradiation of a thf solution of \( [(\text{Mecp})\text{Mn(CO)}₃] \) (0.3 g, 1.4 mmol), the