(1,3-Dimesityldihydroimidazol-2-ylidene)(2-peroxidopropan-2-olato-κ²O,O)(triphenylphosphine-κP)platinum(II) benzene-d₆ disolvate

Huub Kooijman, Jeroen W. Sprengers, Cornelis J. Elsevier and Anthony L. Spek
(1,3-Dimesityldihydroimidazol-2-ylidene)-(2-peroxidopropan-2-olato-κ²O,O’)(triphenylphosphine-κP)platinum(II) benzene-d₆ disolvate

The title compound, [Pt(C₃H₆O₃)(C₂₁H₂₆N₂)(C₁₈H₁₅P)]·2C₆D₆, displays a rare platinacycle formed by a peroxoacetoacetate (2-peroxidopropan-2-olate) ligand and the Pt ion. The platinacycle adopts a half-chair conformation, with the local twofold rotation axis running through the Pt atom. The dihydroimidazol-2-ylidene deviates significantly from planarity.

Comment

Transition-metal peroxo complexes have been proposed as key intermediates in metal-catalysed oxidation reactions. For example, metal complexes containing a ketone-peroxy-chelate moiety, (I), can serve as model compounds for intermediates in the metal-catalysed Baeyer–Villiger oxidation of ketones (Strukul, 1998). However, only a few crystal structures of transition metal complexes are known which contain a ketone peroxo-metallacycle (Cambridge Structural Database, July 2004 update; Allen, 2002). Ugo et al. (1968) reported the crystal structure of (triphenylphosphine)₂(O,O’-peroxo-acetacetate)platinum(II). The only other reported structure containing a peroxoacetate ligand is an antimony complex (Bordner et al., 1986). Pizzotti et al. (1991) published two structures which contain two triphenylphosphines and a peroxo-platinacycle involving one of the carbonyl groups of p-benzoquinone and 1,4-naphthoquinone, respectively. The structures of two rhodium complexes (Dahlenburg & Prengel, 1984, 1986) and one iron complex (Hashimoto et al., 2002) containing a peroxocarbonate moiety have also been reported. Finally, the structures of a rhodium and an iridium complex have been published which contain an oxygen adduct of 9,10-phenanthrenequinone (Dutta et al., 2000; Barbaro et al., 1991, 1992).
In this paper, we report the crystal structure of (1,3-dimesityldihydroimidazol-2-ylidene)(2-peroxidopropan-2-olato-κ²O,O')(triphenylphosphine-κP)platinum(II) benzene-d₆ disolvate, (II). This is the first structure of a platinum complex containing 1,3-dimesityldihydroimidazol-2-ylidene; a complex with the unsaturated 1,3-dimesitylimidazol-2-ylidine has been reported earlier by Arduengo et al. (1994).

The structure of (II) is shown in Fig. 1. Selected bond lengths and angles have been compiled in Table 1. The observed geometry of the structure is very similar to that of bis(triphenylphosphine)_2(O,O'-peroxoacetone)platinum(II) (Ugo et al., 1968) and the platinum complexes with benzoquinone- and naphthoquinone-based metalloccycles reported by Pizzotti et al. (1991).

The geometry at the platinum centre is square-planar. Triphenylphosphine and 1,3-dimesityldihydroimidazol-2-ylidene are orientated in a cis arrangement, with the peroxo moiety in a cis position with respect to 1,3-dimesityldihydroimidazol-2-ylidene. The five-membered peroxoacetate platincycle adopts a somewhat distorted half-chair conformation, with the local twofold axis running through atom Pt1 (see Fig. 2). The Cremer & Pople (1975) puckering parameter ϕ is 276.87 (16)° (ideal value is 270°); the lowest asymmetry parameter (Duax & Norton, 1975) is ΔC₂[Pt1] = 4.51 (13)° (ideal value is 0°).

The bond lengths in the peroxoacetonate moiety indicate a partial double-bond character for O1—C41 and a single-bond character for O2—C41 and O2—O3. The Pt—C1 bond length is short compared to (1,3-dimesityl-dihydroimidazol-2-ylidene)(allyl)(Cl)palladium (Viciu et al., 2004). The short bond lengths indicates a strong coordination of the carbene ligand to the platinum ion. The five-membered dihydroimidazol-2-ylidene ring displays small deviations from planarity. The maximum deviation from the least-squares plane through the ring atoms is 0.134 (2) Å. The deviations follow the pattern of a half-chair conformation with the atom-numbering scheme. The two benzene-6 molecules and all H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 1**
Atomic displacement plot (Spek, 2003) of the title compound, showing the atom-numbering scheme. The two benzene-d₆ molecules and all H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**
Partial view of the title compound, showing the conformation of the platincycle.

**Experimental**

The title compound was synthesized by heating [Pt(1,3-dimesityldihydroimidazol-2-ylidine)(dimethyl fumarate)]₂ (67 μmol) (Duin et al., 2003) with 1 equivalent of triphenylphosphine (67 μmol) and 10 equivalents of HSiEt₃ (0.67 mmol) at 373 K in toluene (6 ml) for 1 h under a nitrogen atmosphere. The solvent was evaporated and acetone (10 ml) was added, after which the solution was slowly reduced in volume by evaporation in air. The resulting solid was dissolved in benzene-d₆. After several days, a few colourless crystals of the title compound were obtained from this solution.

**Crystal data**

<table>
<thead>
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<th>Parameter</th>
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<tr>
<td>μ</td>
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<tr>
<td>T</td>
<td>150 K</td>
</tr>
<tr>
<td>Block, colourless</td>
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</table>

**Data collection**

Nonius KappaCCD area-detector diffractometer

9970 reflections with I 2σ(I)

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<td>k</td>
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<tr>
<td>l</td>
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</table>

**Refinement**

Refinement on F²

R(F²) = 0.018

wR(F²) = 0.041

10600 independent reflections

10600 reflections

558 parameters

H-atoms parameters constrained

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**Table 1**

<table>
<thead>
<tr>
<th>Parameter</th>
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<td>Fmin</td>
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<td>Fmax</td>
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<tr>
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<tr>
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<td>2.0–25.0°</td>
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<td>μ</td>
<td>3.10 mm⁻¹</td>
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<tr>
<td>T</td>
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**Figure 1**

Atomic displacement plot (Spek, 2003) of the title compound, showing the atom-numbering scheme. The two benzene-d₆ molecules and all H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

Partial view of the title compound, showing the conformation of the platincycle.
Methyl groups were refined as rigid groups, allowing for rotation around the C–C bond. H-atom isotropic displacement parameters were set at 1.5 or 1.2 times the equivalent isotropic displacement parameter of the carrier atom for methyl H atoms and other H atoms, respectively. The highest peak residual density peak was located at 0.9 Å from atom H27. The C–H distances were fixed at 0.95, 0.98 or 0.99 Å for aromatic, methylene and methyl H atoms, respectively.

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO; data reduction: DENZO; program(s) used to solve structure: DIRDIF (Beurskens et al., 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

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References