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(1,3-Dimesityldihydroimidazol-2-ylidene)-(2-peroxidopropan-2-olato-κ^2O,O')(triphenyl-phosphine-κP)platinum(II) benzene-d_6 disolvate

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.018
wR factor = 0.041
Data-to-parameter ratio = 19.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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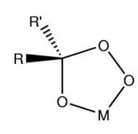
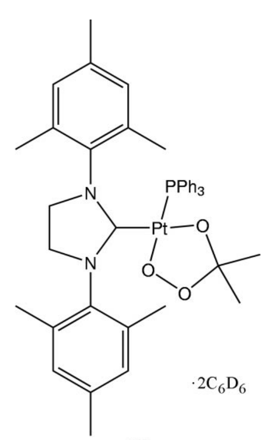
The title compound, $[Pt(C_3H_6O_3)(C_{21}H_{26}N_2)(C_{18}H_{15}P)]\cdot 2C_6D_6$, displays a rare platinacycle formed by a peroxoacetonate (2-peroxidopropan-2-olate) ligand and the Pt ion. The platinacycle adopts a half-chair conformation, with the local twofold rotation axis running through the Pt 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-acetonate)platinum(II). The only other reported structure containing a peroxoacetonate 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 an 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).



(I)



(II)

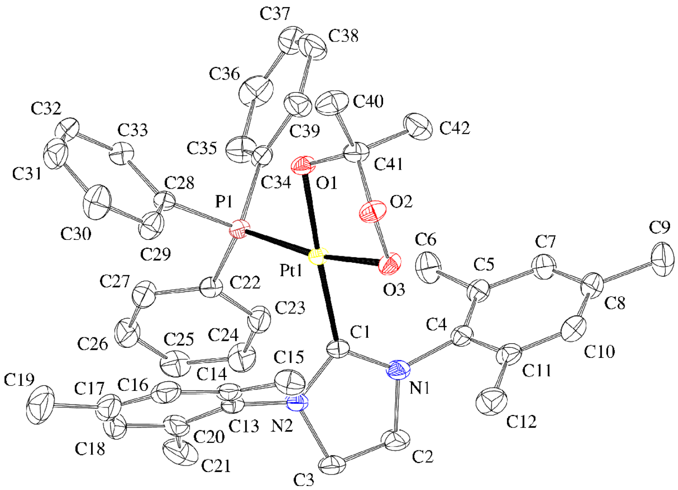


Figure 1
Atomic displacement plot (Spek, 2003) of the title compound, showing the atom-numbering scheme. The two benzene-d_6 molecules and all H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

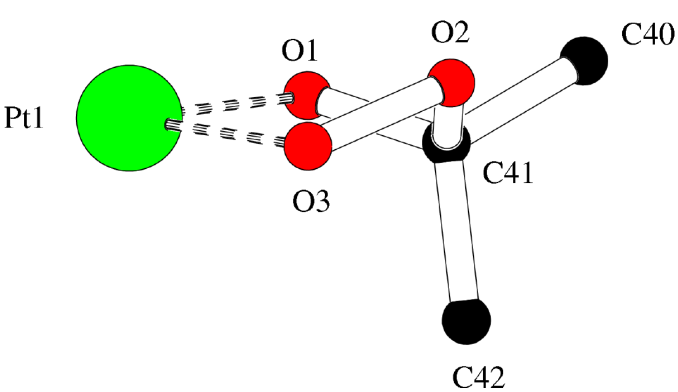


Figure 2
Partial view of the title compound, showing the conformation of the platinacycle.

In this paper, we report the crystal structure of (1,3-dimesityldihydroimidazol-2-ylidene)(2-peroxidopropan-2-olato-κ^2O,O')(triphenylphosphine-κP)platinum(II) benzene-d_6 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-ylidene 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'-peroxoacetonate)platinum(II) (Ugo *et al.*, 1968) and the platinum complexes with benzoquinone- and naphthoquinone-based metallocycles 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 peroxoacetonate platinacycle 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 ΔC_2[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 Pt1—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 local twofold axis running through atom C1 (asymmetry parameter: ΔC_2[C1] = 1.3 (2)°, ideal is 0°; Cremer & Pople parameter: φ = 127.7 (6)°, ideal is 126°).

Experimental

The title compound was synthesized by heating [Pt(1,3-dimesityldihydroimidazol-2-ylidene)(dimethyl fumarate)$_2$] (67 µmol) (Duin *et al.*, 2003) with 1 equivalent of triphenylphosphine (67 µmol) and 10 equivalents of $HSiEt_3$ (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-d_6. After several days, a few colourless crystals of the title compound were obtained from this solution.

Crystal data

[Pt($C_3H_6O_3$)($C_{21}H_{26}N_2$)-($C_{18}H_{15}P$)]·2C_6D_6
M_r = 1022.11
Triclinic, $P\overline{1}$
a = 11.5582 (10) Å
b = 12.6032 (10) Å
c = 17.605 (2) Å
α = 69.96 (3)°
β = 86.70 (4)°
γ = 74.80 (3)°
V = 2323.5 (7) Å^3
Z = 2
D_x = 1.461 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 574 reflections
θ = 2.0–25.0°
μ = 3.10 mm^{-1}
T = 150 K
Block, colourless
0.25 × 0.25 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*PLATON/MULABS* ; Spek, 2003)
T_{min} = 0.494, T_{max} = 0.629
57354 measured reflections
10600 independent reflections
9970 reflections with I 2σ(I)
R_{int} = 0.041
θ_{max} = 27.5°
h = −14 → 14
k = −16 → 16
l = −22 → 22

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.041
S = 1.07
10600 reflections
558 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0131P)^2 + 1.2P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.83 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—P1	2.2517 (6)	O1—C41	1.388 (3)
Pt1—O1	2.0238 (14)	O2—O3	1.495 (2)
Pt1—O3	2.0231 (14)	O2—C41	1.432 (2)
Pt1—C1	1.9726 (19)		
P1—Pt1—O1	87.72 (6)	O1—Pt1—O3	83.02 (7)
P1—Pt1—O3	170.40 (6)	O1—Pt1—C1	171.66 (8)
P1—Pt1—C1	99.85 (7)	O3—Pt1—C1	89.55 (8)
O3—Pt1—O1—C41	11.95 (13)	C41—O2—O3—Pt1	−44.14 (15)
O1—Pt1—O3—O2	17.73 (10)	O3—O2—C41—O1	58.02 (18)
Pt1—O1—C41—O2	−41.44 (18)		

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* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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