Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: NA1254). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dicyano(2,9-dimethyl-1,10-phenanthroline-*N*,*N'*)(η^2-ethene)platinum(II)

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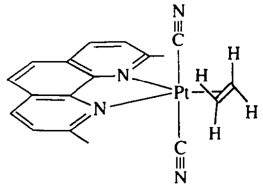
Abstract

In the title compound, $[Pt(CN)_2(C_2H_4)(C_{14}H_{12}N_2)]$, the Pt atom has a trigonal-bipyramidal coordination geometry, with the phenanthroline and ethene ligands in the equatorial plane and the cyano ligands axial. A *trans* configuration of cyano ligands in such five-coordinate Pt^{II} complexes is unprecedented.

Comment

A recent report of the synthesis of coordinatively saturated Pt^{II} complexes suitable as precursors of organometallic polymers (Giordano, Panunzi, Roviello & Ruffo, 1995) included the title compound, (I), or the oxidative addition of $(CN)_2$ to $(dmphen)Pt(C_2H_4)$ (where dmphen is 2,9-dimethyl-1,10-phenanthroline). Analytical and spectroscopic data indicated the formula $[(dmphen)Pt(C_2H_4)(CN)_2]$ and a trigonal-bipyramidal (TBP) geometry, with axial cyano ligands attached through their C atoms and ethene being considered as occupying a single equatorial site. Such an axial arrangement of the cyano ligands is unprecedented for 18-electron TBP-Pt^{II} complexes and provides potential for the linking of metal ions. We have confirmed the proposed structure of (I) by X-ray crystallographic analysis.



(I)

The Pt coordination geometry is indeed TBP, with equatorial chelating dmphen and ethene ligands and with axial cyanides (Fig. 1). The Pt atom lies on a twofold rotation axis bisecting the ethene ligand and the overall molecular symmetry is approximately C_{2v} (*mm*2). The N—C—Pt—C—N unit is essentially linear, with angles of 177.6 (1) at platinum and 178.9 (4)° at carbon. The Pt—C [2.007 (5) Å] and C—N [1.130(7) Å] bond lengths are comparable to corresponding values in square-planar complexes having *trans*-CN^- ligands (Ebihara, Imai & Kawamura, 1995; Staples, Khan, Wang & Fackler, 1992). The dmphen ligand is essentially planar, with a maximum deviation of 0.039 (5) Å for

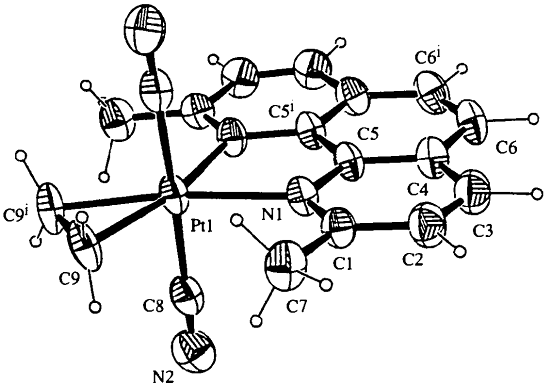


Fig. 1. The molecular structure of (I) with ellipsoids at the 50% probability level. H atoms are drawn as small circles of arbitrary radii.

the C3 atom from the mean plane, excluding H atoms. The Pt atom lies in this plane (required by symmetry) and C9 lies only 0.019 (6) Å from it, so the dmphen and coordination equatorial planes are essentially coincident. The Pt—N [2.215 (3) Å], ethene C—C [1.441 (5) Å] and Pt—C [2.103 (4) Å] bond lengths are typical of TBP-Pt^{II} complexes having these ligands (Albano *et al.*, 1992; Albano, Castellari, Ferrara, Panunzi & Ruffo, 1994).

Intermolecular contacts for non-H atoms are all greater than 3.4 Å. Molecules are arranged with dmphen ligands stacked parallel to one another.

Experimental

The title compound was synthesized according to the method of Giordano *et al.* (1995). Crystals suitable for X-ray analysis were obtained by slow evaporation of a 1:1 methylene chloride/acetone solution.

Crystal data

[$Pt(CN)_2(C_2H_4)(C_{14}H_{12}N_2)$]
$M_r = 483.45$
Monoclinic
$C2/c$
$a = 15.265 (3)$ Å
$b = 11.115 (2)$ Å
$c = 10.178 (2)$ Å
$\beta = 109.70 (1)°$
$V = 1626 (7)$ Å^3
$Z = 4$
$D_x = 1.975$ Mg m^{-3}
$D_m = 1.87$ Mg m^{-3}
D_m measured by flotation in aqueous K_2HgI_4 solution

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.52–11.21°$
$\mu = 8.72$ mm^{-1}
$T = 295$ K
Prism
0.25 × 0.13 × 0.05 mm
Pale orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.320$, $T_{max} = 0.753$
1791 measured reflections
1606 independent reflections

1462 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.017$
$\theta_{max} = 28°$
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 13$
1 standard reflection frequency: 120 min intensity decay: 0.1%

Refinement

Refinement on F
$R = 0.019$
$wR = 0.028$
$S = 1.093$
1458 reflections
106 parameters
H atoms riding
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = 0.22$ e Å^{-3}
Extinction correction: Stout & Jensen (1989)
Extinction coefficient: 2.3219×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pt1	1/2	0.16560 (2)	3/4	0.0353 (1)
N1	0.4358 (3)	0.3232 (3)	0.6199 (4)	0.037 (1)
N2	0.6587 (4)	0.1591 (3)	0.6188 (5)	0.060 (1)
C1	0.3727 (3)	0.3200 (3)	0.4914 (5)	0.041 (1)
C2	0.3361 (3)	0.4300 (4)	0.4214 (5)	0.051 (1)
C3	0.3626 (3)	0.5377 (4)	0.4818 (5)	0.052 (1)
C4	0.4315 (3)	0.5440 (4)	0.6169 (4)	0.044 (1)
C5	0.4662 (3)	0.4339 (3)	0.6837 (4)	0.037 (1)
C6	0.4668 (4)	0.6519 (3)	0.6855 (6)	0.054 (1)
C7	0.3432 (4)	0.2025 (5)	0.4233 (5)	0.052 (1)
C8	0.6009 (3)	0.1619 (3)	0.6648 (5)	0.041 (1)
C9	0.4645 (4)	−0.0122 (3)	0.6820 (5)	0.051 (1)

Table 2. *Selected geometric parameters (Å, °)*

Pt1—N1	2.215 (3)	C2—C3	1.343 (7)
Pt1—C8	2.007 (5)	C3—C4	1.423 (6)
Pt1—C9	2.103 (4)	C4—C5	1.412 (6)
N1—C1	1.338 (6)	C4—C6	1.401 (6)
N1—C5	1.396 (5)	C5—C5^i	1.397 (4)
N2—C8	1.130 (7)	C6—C6^i	1.363 (6)
C1—C2	1.431 (6)	C9—C9^i	1.441 (5)
C1—C7	1.476 (6)		
N1—Pt1—C8	90.4 (2)	C8—Pt1—C8^i	177.6 (1)
N1—Pt1—C9	122.2 (2)	C9—Pt1—C9^i	40.1 (1)
N1—Pt1—N1^i	75.5 (1)	Pt1—C8—N2	178.9 (4)
C8—Pt1—C9	89.3 (2)	Pt1—C9—C9^i	70.0 (2)

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

H atoms were constrained using a riding model and were given U_{iso} values equal to those of the carrier atoms.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *SDP* (Enraf–Nonius, 1985). Data reduction: *SDP*. Program(s) used to solve structure: Patterson function of *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Unexpected Trimethylstannylpyrrole from a Stannylated Derivative of Tosylmethyl Isocyanide (TosMIC) and Chalcone

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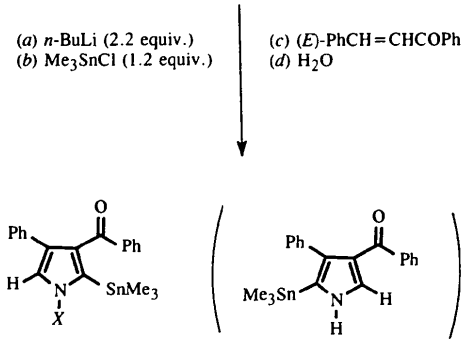
Abstract

The structure of the title compound, *tert*-butyl 3-benzoyl-4-phenyl-2-(trimethylstannyl)pyrrole-*N*-carboxylate, [$Sn(CH_3)_3(C_{22}H_{20}NO_3)$], is one of the first in which the stannyl group is attached to a C atom of the pyrrole ring. There appears to be an intramolecular interaction between the Sn atom and the carbonyl O atoms of both the benzoyl and the *tert*-butoxycarbonyl substituents. The compound was prepared by a base-induced cycloaddition of a stannylated derivative of tosylmethyl isocyanide to chalcone.

Comment

(Trialkylstannyl)pyrroles are of use in palladium-catalyzed cross-coupling reactions (Stille, 1986) for the preparation of oligo- and polypyrroles (Martina, Enkelmann, Wegner & Schlütter, 1992). We are presently engaged in developing new routes to stannylated azoles using tosylmethyl isocyanide [TosMIC; (1)] and trialkylstannyl halides. In one case, a stannylated synthon was prepared *in situ* by double deprotonation of TosMIC, followed by addition of one equivalent of trimethylstannyl chloride in tetrahydrofuran (THF) at 203 K (see reaction scheme). Chalcone (*E*)-PhCH═CHCOPh was then added at the same temperature to give a pyrrole, (2), which was converted to a stable crystalline *N*-*tert*-butoxycarbonyl (Boc) derivative, (3), using Boc_2O (Grehn & Ragnarsson, 1984). Compound (3) was crystallized from petroleum ether (b.p. 313–333 K).

$Tos—CH_2—N{=}C$ (1)



X=H (2)
X=Boc (3)

(4)

So far, trisubstituted pyrroles prepared by the same approach (from Michael acceptors and monosubstituted derivatives of TosMIC) always carry the third substituent (introduced *via* monosubstituted TosMIC) at the position β to the electron-withdrawing group of the Michael acceptor (Possel & van Leusen, 1977; van Leusen & van Leusen, 1995*a*). By extrapolation, the initial reaction product of the reaction scheme was expected to be 4-benzoyl-3-phenyl-2-(trimethylstannyl)pyrrole, (4), rather than 3-benzoyl-4-phenyl-2-(trimethylstannyl)pyrrole, (2), through regiospecific cycloaddition of $TosCLi(SnMe_3)N{\equiv}C$, (5). To confirm the inconclusive spectroscopic evidence for (4), the X-ray structure of the *N*-Boc derivative was determined, which surprisingly proved to be compound (3) and not the *N*-Boc derivative of (4). This means that stannylation of dilithio–TosMIC probably leads to reaction at the isocyano C atom (unlike all previously known alkylations) to give $TosCLi{=}N^+{=}C^-—SnMe_3$, (6), as the synthon prepared *in situ*. Alternative explanations, such as a reversal of the regioselective addition of (5) or a migration of the trimethylstannyl group in (4), seem much less likely. The actual structure of the corresponding silylated TosMIC derivative, so far considered to be $TosCLi(SiMe_3)N{\equiv}C$ (van Leusen & Wildeman, 1982), remains to be seen. Trisubstituted pyrroles similar to (2), with Ph, Me, MeO and MeS substituents in place of Me_3Sn, have been prepared previously using different synthons of the *N*-tosylmethyliminocarbonate and *N*-tosylmethylthiobenzimidate types, for example, $TosCH_2N{=}C(SMe)Ph$ (Houwing & van Leusen, 1981; van Leusen & van Leusen, 1995*b*).