

## *trans*-Tetrachloridobis(diphenylacetonitrile)platinum(IV)

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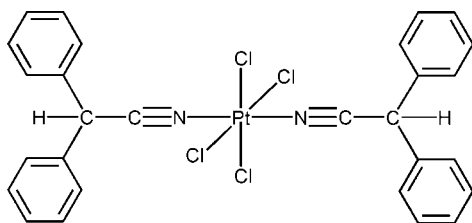
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.011$  Å;  $R$  factor = 0.038;  $wR$  factor = 0.099; data-to-parameter ratio = 19.4.

In the title compound,  $[\text{PtCl}_4(\text{C}_{14}\text{H}_{11}\text{N})_2]$ , the Pt atom lies on an inversion center and has a distorted octahedral environment. The main geometric parameters are Pt–N = 1.960 (5) Å, and Pt–Cl = 2.3177 (12) and 2.3196 (12) Å. The N≡C bond is a typical triple bond [1.137 (7) Å]. The Pt–N≡C–C unit is almost linear, with Pt–N–C and N–C–C angles of 174.6 (4) and 177.1 (6)°, respectively.

### Related literature

For background literature, see: Kukushkin & Pombeiro (2002); Luzyanin *et al.* (2002); Pombeiro & Kukushkin (2004). For related structures, see: Allen *et al.* (1987); Eysel *et al.* (1983); Johansson *et al.* (1998); Kritzenberger *et al.* (1994); Orpen *et al.* (1989); Scollard *et al.* (2001); Svensson *et al.* (1995); Yagyu *et al.* (2002).



### Experimental

#### Crystal data

$[\text{PtCl}_4(\text{C}_{14}\text{H}_{11}\text{N})_2]$   
 $M_r = 723.37$   
Triclinic,  $P\bar{1}$   
 $a = 5.7980$  (3) Å

$b = 10.8650$  (6) Å  
 $c = 11.2200$  (7) Å  
 $\alpha = 92.236$  (3)°  
 $\beta = 101.601$  (4)°

$\gamma = 98.565$  (4)°  
 $V = 682.91$  (7) Å<sup>3</sup>  
 $Z = 1$   
Mo  $K\alpha$  radiation

$\mu = 5.55$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.33 \times 0.09 \times 0.06$  mm

#### Data collection

Nonius KappaCCD diffractometer  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 2008a)  
 $T_{\min} = 0.255$ ,  $T_{\max} = 0.717$   
13055 measured reflections  
3096 independent reflections  
3076 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.048$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.099$   
 $S = 1.09$   
3096 reflections  
160 parameters  
36 restraints  
H-atom parameters constrained  
 $\Delta\rho_{\max} = 4.19$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -2.02$  e Å<sup>-3</sup>

Data collection: *COLLECT* (Hooft, 2008); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008b); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2142).

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**supplementary materials**

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## ***trans*-Tetrachloridobis(diphenylacetonitrile)platinum(IV)**

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### **Comment**

In the past decade, a Pt<sup>IV</sup> center was recognized as one of the most efficient electrophilic activators of the C≡N bond in nitriles (Pombeiro & Kukushkin, 2004; Kukushkin & Pombeiro, 2002). Within the framework of our project focused on reactivity of metal-activated nitriles, a novel platinum(IV) complex, *i.e.* *trans*-[PtCl<sub>4</sub>(N≡CCHPh<sub>2</sub>)<sub>2</sub>], (I), was synthesized and characterized by single-crystal X-ray diffraction. It should be mentioned that only few structures of platinum(IV) nitrile complexes are known, *e.g.* (Yagyu *et al.*, 2002; Johansson *et al.*, 1998; Scollard *et al.*, 2001). Probably the small number of examples is related to the high reactivity of various (nitrile)Pt<sup>IV</sup> species, where nitrile ligands are subject to facile nucleophilic attack even by weak nucleophiles or H<sub>2</sub>O in wet solvents.

The complex (I) crystallized in the centrosymmetrical P $\bar{1}$  space group wherein the Pt atom lies on an inversion center and it has an octahedral environment and nitrile ligands have the mutual *trans* orientation (Fig. 1). The angles N1—Pt1—Cl2, N1—Pt1—Cl1, Cl2—Pt1—Cl1 are close to the ideal 90°. The Pt1—Cl bond distances (2.3177 (12) and 2.3196 (12) Å) are similar within 3 $\sigma$  with many other Pt—Cl bond lengths (2.323 (38) Å) in related Pt<sup>IV</sup> complexes (Orpen *et al.*, 1989). The Pt1—N distances (1.960 (5) Å) are common for (nitrile)Pt complexes bearing two *trans*-coordinated nitriles, *e.g.* 1.943 (11)–1.978 (3) Å in Pt<sup>II</sup> complexes (Eysel *et al.*, 1983; Kritzenberger *et al.*, 1994; Svensson *et al.* 1995).

The value of the N1≡C1 bond (1.137 (7) Å) is typical for the triple bonds in Pt<sup>II</sup>-coordinated (1.129 (9)–1.154 (18) Å in *trans*-[PtCl<sub>2</sub>(NCR)<sub>2</sub>] (Eysel *et al.*, 1983; Kritzenberger *et al.*, 1994; Svensson *et al.* 1995), in Pt<sup>IV</sup>-bound (1.09 (4)–1.157 (12) Å) (Yagyu *et al.*, 2002; Johansson *et al.*, 1998; Scollard *et al.*, 2001), and in uncomplexed (1.136 (10) Å (Allen *et al.*, 1987) nitriles. The value of the C1—C2 bond (1.469 (7) Å) agrees well with those reported for C<sub>sp</sub>–C<sub>sp</sub><sup>3</sup> single bonds (1.470 (13) Å) (Allen *et al.*, 1987). The Pt1/N1/C1/C2 moiety is almost linear with Pt1—N1≡C1 and N1≡C1—C2 angles of 174.6 (4) and 177.1 (6)°, correspondingly. The angle C3—C2—C9 (114.7 (5)°) is larger than 109° probably due to steric repulsion between two phenyl rings.

### **Experimental**

Diphenylacetonitrile (8.5 mg, 0.044 mmol; purchased from Aldrich) was added to a suspension of *trans*-[PtCl<sub>4</sub>(EtCN)<sub>2</sub>] (9.7 mg, 0.022 mmol) (Luzyanin *et al.*, 2002) in CDCl<sub>3</sub> (1 ml) and the reaction mixture was left to stand for 2 d at 323 K in an NMR tube, whereupon orange–yellow crystals were formed on walls of the tube. The crystals were mechanically separated.

### **Refinement**

The phenyl ring C3–C8 was slightly disordered. However, no disordered model was used in the final refined but the C atoms on phenyl ring C3–C8 were restrained with effective standard deviation 0.1 so that its  $U_{ij}$  components approximate to isotropic behavior. All H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H =

# supplementary materials

0.95 and 1.00 Å, for methine and aryl H atoms, respectively, and  $U_{\text{iso}} = 1.2U_{\text{eq}}$ (parent atom). The residual electron density in the final difference map could be attributed to insufficient absorption correction as well as twinning, which could not be corrected.

## Figures

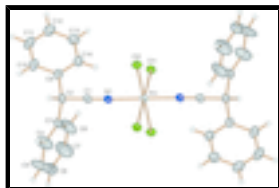


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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### Crystal data

[PtCl<sub>4</sub>(C<sub>14</sub>H<sub>11</sub>N)<sub>2</sub>]

$M_r = 723.37$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 5.7980$  (3) Å

$b = 10.8650$  (6) Å

$c = 11.2200$  (7) Å

$\alpha = 92.236$  (3)°

$\beta = 101.601$  (4)°

$\gamma = 98.565$  (4)°

$V = 682.91$  (7) Å<sup>3</sup>

$Z = 1$

$F_{000} = 350$

$D_x = 1.759$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 30861 reflections

$\theta = 1.0$ – $27.5$ °

$\mu = 5.55$  mm<sup>-1</sup>

$T = 100$  K

Needle, yellow

$0.33 \times 0.09 \times 0.06$  mm

### Data collection

Nonius KappaCCD  
diffractometer

3096 independent reflections

Radiation source: fine-focus sealed tube

3076 reflections with  $I > 2\sigma(I)$

Monochromator: horizontally mounted graphite crystal

$R_{\text{int}} = 0.048$

Detector resolution: 9 pixels mm<sup>-1</sup>

$\theta_{\text{max}} = 27.4$ °

$T = 100$  K

$\theta_{\text{min}} = 1.9$ °

$\varphi$  scans and  $\omega$  scans with  $\kappa$  offset

$h = -6 \rightarrow 7$

Absorption correction: multi-scan  
(SADABS; Sheldrick, 2008a)

$k = -13 \rightarrow 14$

$T_{\text{min}} = 0.255$ ,  $T_{\text{max}} = 0.717$

$l = -14 \rightarrow 14$

13055 measured reflections

### Refinement

Refinement on  $F^2$

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.038$$

$$wR(F^2) = 0.099$$

$$S = 1.09$$

3096 reflections

160 parameters

36 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2 + 0.3244P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 4.19 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -2.02 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

### Special details

**Experimental.** IR spectrum in KBr, selected bonds,  $\text{cm}^{-1}$ : 2340 s  $\nu(\text{C}\equiv\text{N})$ .  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$ ,  $\delta$ : 5.85 (s, 1H, CH), 7.42 (m, 10H, Ph).

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Pt1	0.0000	0.0000	0.0000	0.01907 (11)
Cl1	-0.1642 (2)	0.18164 (11)	-0.02653 (11)	0.0242 (3)
Cl2	0.1559 (2)	0.03117 (12)	-0.17314 (11)	0.0259 (3)
N1	0.2869 (8)	0.0989 (4)	0.1023 (4)	0.0219 (9)
C1	0.4426 (9)	0.1634 (5)	0.1627 (5)	0.0223 (10)
C2	0.6350 (10)	0.2492 (5)	0.2438 (5)	0.0244 (10)
H2	0.7905	0.2282	0.2306	0.029*
C3	0.6198 (10)	0.2260 (6)	0.3764 (5)	0.0304 (12)
C4	0.7693 (19)	0.1559 (9)	0.4421 (7)	0.060 (2)
H4	0.8855	0.1233	0.4068	0.072*
C5	0.751 (3)	0.1322 (10)	0.5624 (8)	0.083 (4)
H5	0.8513	0.0808	0.6067	0.100*
C6	0.5929 (16)	0.1807 (9)	0.6164 (7)	0.058 (2)
H6	0.5877	0.1677	0.6992	0.069*
C7	0.442 (2)	0.2487 (14)	0.5495 (9)	0.084 (3)
H7	0.3263	0.2819	0.5849	0.101*
C8	0.4554 (18)	0.2700 (12)	0.4286 (8)	0.071 (3)
H8	0.3468	0.3164	0.3825	0.085*

## supplementary materials

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C9	0.6217 (10)	0.3826 (5)	0.2100 (5)	0.0253 (11)
C10	0.8298 (11)	0.4709 (6)	0.2383 (6)	0.0335 (13)
H10	0.9758	0.4464	0.2767	0.040*
C11	0.8249 (13)	0.5941 (6)	0.2106 (7)	0.0415 (15)
H11	0.9671	0.6535	0.2298	0.050*
C12	0.6130 (13)	0.6299 (6)	0.1552 (7)	0.0396 (14)
H12	0.6094	0.7139	0.1355	0.047*
C13	0.4058 (12)	0.5434 (6)	0.1285 (6)	0.0352 (13)
H13	0.2597	0.5691	0.0919	0.042*
C14	0.4085 (11)	0.4201 (5)	0.1543 (5)	0.0297 (12)
H14	0.2656	0.3612	0.1342	0.036*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Pt1	0.02018 (16)	0.01738 (16)	0.01892 (16)	0.00369 (10)	0.00211 (10)	0.00008 (10)
C11	0.0285 (6)	0.0191 (6)	0.0254 (6)	0.0078 (5)	0.0035 (5)	0.0017 (5)
C12	0.0321 (7)	0.0243 (6)	0.0224 (6)	0.0052 (5)	0.0078 (5)	0.0018 (5)
N1	0.022 (2)	0.023 (2)	0.022 (2)	0.0071 (17)	0.0047 (17)	0.0036 (17)
C1	0.025 (3)	0.021 (2)	0.023 (2)	0.008 (2)	0.005 (2)	0.002 (2)
C2	0.023 (2)	0.024 (3)	0.024 (2)	0.002 (2)	0.002 (2)	-0.002 (2)
C3	0.027 (3)	0.037 (3)	0.023 (2)	0.001 (2)	-0.001 (2)	0.001 (2)
C4	0.084 (5)	0.059 (4)	0.041 (4)	0.035 (4)	0.007 (3)	0.002 (3)
C5	0.150 (11)	0.072 (7)	0.033 (4)	0.057 (7)	0.002 (5)	0.014 (4)
C6	0.066 (5)	0.072 (5)	0.027 (3)	-0.008 (4)	0.001 (3)	0.007 (3)
C7	0.078 (6)	0.139 (8)	0.046 (4)	0.037 (6)	0.024 (4)	0.019 (5)
C8	0.063 (5)	0.123 (7)	0.039 (4)	0.046 (5)	0.013 (3)	0.019 (4)
C9	0.028 (3)	0.024 (3)	0.025 (2)	0.003 (2)	0.008 (2)	-0.002 (2)
C10	0.030 (3)	0.029 (3)	0.039 (3)	-0.001 (2)	0.007 (2)	-0.006 (2)
C11	0.040 (4)	0.028 (3)	0.055 (4)	-0.004 (3)	0.015 (3)	-0.001 (3)
C12	0.046 (4)	0.025 (3)	0.049 (4)	0.004 (3)	0.014 (3)	0.001 (3)
C13	0.040 (3)	0.028 (3)	0.040 (3)	0.011 (2)	0.008 (3)	0.004 (2)
C14	0.030 (3)	0.024 (3)	0.034 (3)	0.003 (2)	0.005 (2)	-0.001 (2)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Pt1—N1 <sup>i</sup>	1.960 (5)	C6—C7	1.360 (15)
Pt1—N1	1.960 (5)	C6—H6	0.9500
Pt1—C12	2.3177 (12)	C7—C8	1.400 (12)
Pt1—C12 <sup>i</sup>	2.3178 (12)	C7—H7	0.9500
Pt1—C11	2.3196 (12)	C8—H8	0.9500
Pt1—C11 <sup>i</sup>	2.3196 (12)	C9—C14	1.394 (8)
N1—C1	1.137 (7)	C9—C10	1.398 (8)
C1—C2	1.469 (7)	C10—C11	1.389 (9)
C2—C9	1.522 (8)	C10—H10	0.9500
C2—C3	1.536 (8)	C11—C12	1.379 (10)
C2—H2	1.0000	C11—H11	0.9500
C3—C8	1.348 (11)	C12—C13	1.383 (9)

C3—C4	1.363 (10)	C12—H12	0.9500
C4—C5	1.406 (13)	C13—C14	1.383 (9)
C4—H4	0.9500	C13—H13	0.9500
C5—C6	1.350 (15)	C14—H14	0.9500
C5—H5	0.9500		
N1 <sup>i</sup> —Pt1—N1	180.0	C6—C5—H5	119.2
N1 <sup>i</sup> —Pt1—Cl2	88.94 (13)	C4—C5—H5	119.2
N1—Pt1—Cl2	91.06 (13)	C5—C6—C7	118.4 (8)
N1 <sup>i</sup> —Pt1—Cl2 <sup>i</sup>	91.06 (13)	C5—C6—H6	120.8
N1—Pt1—Cl2 <sup>i</sup>	88.94 (13)	C7—C6—H6	120.8
Cl2—Pt1—Cl2 <sup>i</sup>	180.0	C6—C7—C8	120.2 (10)
N1 <sup>i</sup> —Pt1—Cl1	91.31 (13)	C6—C7—H7	119.9
N1—Pt1—Cl1	88.69 (13)	C8—C7—H7	119.9
Cl2—Pt1—Cl1	89.95 (5)	C3—C8—C7	121.4 (9)
Cl2 <sup>i</sup> —Pt1—Cl1	90.05 (5)	C3—C8—H8	119.3
N1 <sup>i</sup> —Pt1—Cl1 <sup>i</sup>	88.69 (13)	C7—C8—H8	119.3
N1—Pt1—Cl1 <sup>i</sup>	91.31 (13)	C14—C9—C10	119.1 (6)
Cl2—Pt1—Cl1 <sup>i</sup>	90.05 (5)	C14—C9—C2	122.2 (5)
Cl2 <sup>i</sup> —Pt1—Cl1 <sup>i</sup>	89.95 (5)	C10—C9—C2	118.7 (5)
Cl1—Pt1—Cl1 <sup>i</sup>	180.0	C11—C10—C9	120.5 (6)
C1—N1—Pt1	174.6 (4)	C11—C10—H10	119.7
N1—C1—C2	177.1 (6)	C9—C10—H10	119.7
C1—C2—C9	109.6 (4)	C12—C11—C10	119.8 (6)
C1—C2—C3	108.4 (5)	C12—C11—H11	120.1
C9—C2—C3	114.7 (5)	C10—C11—H11	120.1
C1—C2—H2	107.9	C11—C12—C13	120.0 (6)
C9—C2—H2	107.9	C11—C12—H12	120.0
C3—C2—H2	107.9	C13—C12—H12	120.0
C8—C3—C4	118.8 (7)	C12—C13—C14	120.8 (6)
C8—C3—C2	121.4 (6)	C12—C13—H13	119.6
C4—C3—C2	119.8 (6)	C14—C13—H13	119.6
C3—C4—C5	119.6 (9)	C13—C14—C9	119.8 (6)
C3—C4—H4	120.2	C13—C14—H14	120.1
C5—C4—H4	120.2	C9—C14—H14	120.1
C6—C5—C4	121.6 (8)		

Symmetry codes: (i)  $-x, -y, -z$ .

Fig. 1

