3·28 (7) Å; C(43)—H(432)···Pd 119 (3)°]. Short intermolecular contacts include the interaction H(442)···I [1−x, ½+y, ½−z] 2·90 (1); C(44)···I 3·926 (8) Å; C(44)—H(442)···I 158·8 (6)°.

A slight skeletal deformation of the benzene rings of the triphenylphosphine ligands in the title compound is observed. It may be described in terms of an average decrease of 2·3° from 120° of the endocyclic bond angle, opposite to the P atom. Domenicano, Vaciago & Coulson (1975) explain this in terms of hybridization effects and valence-shell electron-pair repulsions.

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Structure of {2,6-Bis[(dimethylamino)methyl]phenyl}iodoplatinum(II)

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Abstract. $[PtI(C_{12}H_{19}N_2)]$, $M_r = 513·28$, monoclinic, $I2/a$, $a = 17·044$ (6), $b = 9·259$ (3), $c = 18·44$ (1) Å, $\beta = 96·65$ (4)°, $V = 2890$ (2) Å^3, $Z = 8$, $D_x = 2·359$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 119·1$ cm^{-1}, $F(000) = 1888$, $T = 294$ K, $R = 0·0301$ for 2635 observed reflections with $I > 2\sigma(I)$. Pt is square-planar (within 0·013 Å) coordinated by C(1), I, N(1) and N(2). The molecule has approximate twofold axial symmetry along the Pt—I axis.

Introduction. Recently it appeared that the title compound [=PtI(NCN)] readily forms a very stable complex with I_2 (van Beek, van Koten, Smeets & Spek, 1986). The resulting PtI(NCN)(η^1-I_2) compound is the first example of a complex mimicking the initial stage of the oxidative addition of halogens at d^8 metal centres.

PtI(NCN)(η^1-I_2) has a distorted square-pyramidal coordination with an end-on bonded I_2 molecule occupying the apical position. Two of the NMe groups are located on the opposite side of the η^1 bonded I_2 molecule and seem to shield that side from further attack by I_2.

In order to study this aspect in more detail the structure of the parent compound PtI(NCN) was determined.

Experimental. Transparent yellow prismatic crystal 0·48 × 0·29 × 0·13 mm glued on top of a glass fibre. Enraf–Nonius CAD-4F diffractometer, Zr-filtered Mo $K\alpha$ radiation, cell constants from the angular settings of 12 reflections with $11·5 < \theta < 14·0°$. Intensity data of 3512 unique reflections were collected within a quarter of the reflection sphere; $-21 \le h \le 22$, $0 \le k \le 12$, $-23 \le l \le 0$; $(\sin\theta/\lambda)_{max} = 0·649$ Å^{-1};

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ω–2θ scan mode with $\Delta\omega = (0{\cdot}55 + 0{\cdot}35\tan\theta)°$. Three reference reflections [400 (e.s.d. = 0·8%), 040 (e.s.d. = 0·7%), 004 (e.s.d. = 1·0%)], measured every hour showed a linear decay of 1·6% during the 67·1 h of X-ray exposure time. The intensities were corrected for this decay, Lorentz and polarization effects and for absorption using a Gaussian integration method (grid: 8 × 6 × 12; corrections in the range 2·728 to 6·703), resulting in 2636 observed reflections with $I > 2\sigma(I)$. Standard deviations in the intensities were increased according to an analysis of the variance of the reference reflections: $\sigma^2(I) = \sigma^2(I)_{cs} + (0{\cdot}017I)^2$ (McCandlish, Stout & Andrews, 1975). Space group $I2/a$ derived from systematic absences [hkl ($h + k + l = 2n + 1$) and $h0l$ ($h, l = 2n + 1$)] and discriminated from Ia during the structure determination process. Structure solved by Patterson (*SHELX*84; Sheldrick, 1984) and subsequent difference Fourier methods. H atoms introduced on calculated positions (C—H = 0·98 Å) and included in weighted, blocked full-matrix refinement (on F) riding on their carrier atom. All non-H atoms were refined with anisotropic thermal parameters, H atoms refined with one isotropic temperature factor. The 002 reflections with a $\Delta F/\sigma(F)$ ratio of 24·9 was excluded from the final refinement cycles. Convergence with 159 parameters was reached at $R = 0{\cdot}0301$, $wR = 0{\cdot}0310$, $w = 1/\sigma^2(F)$, $S = 1{\cdot}90$, $(\Delta/\sigma)_{max} = 0{\cdot}094$, max. and min. residual densities 0·88 and −1·46 e Å^{-3} near the heavy atoms. The crystal exhibited some secondary extinction for which the F_c values were corrected by refinement of an emperical isotropic extinction parameter $X[=1{\cdot}0\ (1) \times 10^{-8}]$: $F_c' = F_c[1-(XF^2/\sin\theta)]$.

Scattering factors from Cromer & Mann (1968); anomalous-dispersion factors from Cromer & Liberman (1970). Calculations performed with *SHELX*76 (Sheldrick, 1976) and the *EUCLID* package (geometry calculations and illustrations) (Spek, 1982) on the CDC Cyber-855 of the University of Utrecht.

Discussion. Fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 1.* The molecular structure with the adopted atom numbering is shown in Fig. 1. Bond distances and angles are listed in Table 2.

The monoclinic unit cell contains eight discrete molecules of the title compound. The Pt atom has a distorted square-planar coordination by N(1), N(2), I and C(1). These atoms are coplanar with Pt within 0·013 Å. The distortion from regular square-planar coordination is illustrated by the deviation of the

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Pt	0·16958 (1)	0·61977 (3)	0·37491 (1)	0·0369 (1)
I	0·07875 (3)	0·37817 (7)	0·37017 (3)	0·0746 (2)
N(1)	0·2762 (3)	0·5235 (6)	0·3541 (3)	0·041 (2)
N(2)	0·0840 (3)	0·7687 (6)	0·3981 (3)	0·047 (2)
C(1)	0·2339 (3)	0·7921 (7)	0·3788 (3)	0·041 (2)
C(2)	0·2055 (4)	0·9184 (7)	0·4033 (4)	0·049 (2)
C(3)	0·2519 (4)	1·0418 (8)	0·4051 (4)	0·060 (3)
C(4)	0·3270 (4)	1·0342 (9)	0·3849 (5)	0·065 (3)
C(5)	0·3562 (4)	0·9064 (8)	0·3596 (4)	0·061 (3)
C(6)	0·3089 (3)	0·7835 (8)	0·3558 (3)	0·047 (2)
C(7)	0·3266 (3)	0·6362 (8)	0·3254 (4)	0·050 (2)
C(8)	0·2691 (4)	0·4035 (8)	0·3015 (4)	0·064 (3)
C(9)	0·3144 (3)	0·4697 (8)	0·4255 (4)	0·049 (2)
C(10)	0·1260 (4)	0·9065 (8)	0·4305 (4)	0·063 (3)
C(11)	0·0298 (4)	0·7200 (9)	0·4506 (4)	0·061 (3)
C(12)	0·0369 (4)	0·808 (1)	0·3289 (4)	0·077 (3)

Table 2. *Bond distances* (Å) *and angles* (°) *for the non-hydrogen atoms*

Pt–I	2·716 (2)	N(2)–C(12)	1·472 (9)
Pt–N(1)	2·099 (5)	C(1)–C(2)	1·363 (9)
Pt–N(2)	2·087 (5)	C(1)–C(6)	1·395 (7)
Pt–C(1)	1·933 (6)	C(2)–C(10)	1·50 (1)
N(1)–C(7)	1·487 (9)	C(2)–C(3)	1·39 (1)
N(1)–C(8)	1·471 (9)	C(3)–C(4)	1·38 (1)
N(1)–C(9)	1·486 (9)	C(4)–C(5)	1·39 (1)
N(2)–C(10)	1·549 (9)	C(5)–C(6)	1·39 (1)
N(2)–C(11)	1·484 (9)	C(6)–C(7)	1·52 (1)
I–Pt–N(1)	98·4 (2)	C(10)–N(2)–C(12)	108·2 (6)
I–Pt–N(2)	98·1 (2)	C(11)–N(2)–C(12)	108·8 (5)
I–Pt–C(1)	179·6 (2)	Pt–C(1)–C(2)	119·9 (4)
N(1)–Pt–N(2)	163·4 (2)	Pt–C(1)–C(6)	118·5 (5)
N(1)–Pt–C(1)	81·8 (2)	C(2)–C(1)–C(6)	121·5 (6)
N(2)–Pt–C(1)	81·6 (2)	C(1)–C(2)–C(10)	114·6 (6)
Pt–N(1)–C(7)	108·4 (4)	C(1)–C(2)–C(3)	119·4 (6)
Pt–N(1)–C(8)	115·8 (4)	C(3)–C(2)–C(10)	125·9 (6)
Pt–N(1)–C(9)	106·3 (4)	C(2)–C(3)–C(4)	119·8 (7)
C(7)–N(1)–C(8)	107·6 (5)	C(3)–C(4)–C(5)	121·1 (7)
C(7)–N(1)–C(9)	109·8 (5)	C(4)–C(5)–C(6)	119·1 (6)
C(8)–N(1)–C(9)	109·0 (5)	C(1)–C(6)–C(5)	118·9 (6)
Pt–N(2)–C(10)	108·7 (4)	C(1)–C(6)–C(7)	113·1 (6)
Pt–N(2)–C(11)	115·8 (4)	C(5)–C(6)–C(7)	127·9 (5)
Pt–N(2)–C(12)	108·0 (4)	N(1)–C(7)–C(6)	110·6 (5)
C(10)–N(2)–C(11)	107·1 (5)	N(2)–C(10)–C(2)	109·0 (6)

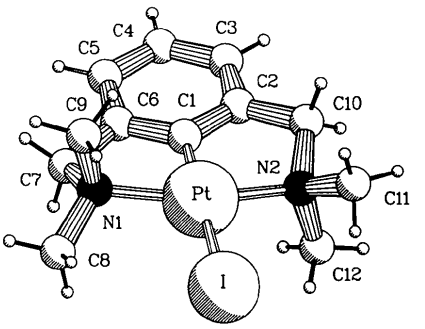

Fig. 1. *PLUTO* (*EUCLID* version: Spek, 1982) drawing of the title compound with the adopted atom numbering.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and geometrical data concerning H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43506 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

relevant angles from 90 or 180°: N(1)—Pt—N(2) and I—Pt—C(1) being 163·4 (2) and 179·6 (2)° respectively with a range of 81·6 (2)–98·4 (2)° for the four remaining angles. The angle between the coordination plane and the phenyl ring is 9·5 (3)°. The molecule shows approximate twofold symmetry along the line through Pt and C(1); this is illustrated by the ΔC_2[Pt—C(1)] asymmetry parameter for the eight-membered ring C(1)—C(2)—C(10)—N(2)—Pt—N(1)—C(7)—C(6) that amounts to 4·2 (6)° (Duax, Weeks & Rohrer, 1976). The molecular twofold axis is also present in the octahedral $PtCl_3$(NCN) complex (Terheijden, van Koten, de Booys, Ubbels & Stam, 1983) in which the angle between the coordination plane and the phenyl ring is 16·3 (5)° and the ΔC_2[Pt—C(1)] parameter is 4·9 (7)°. Some structural features of PtI(NCN) are comparable with those of the PtI(NCN)(η^1-I_2) complex (van Beek, van Koten, Smeets & Spek, 1986) which has a distorted square-pyramidal coordination with an I_2 molecule occupying the apical position, whereas the other coordinating atoms are the same as in the present structure. The geometry of the NCN ligand compares favourably with the geometries found in the studies of $PtCl_3$(NCN) and PtI(NCN)(η^1-I_2). The Pt—C(1) distances are nearly equal: 1·933 (6) Å in the present PtI complex and 1·937 (9) Å in the PtI(η^1-I_2) structure. The Pt—I distance and the averages of the Pt—N distances are slightly different; 2·716 (2) and 2·093 (6) Å respectively in PtI(NCN) and 2·727 (1), 2·111 (8) Å in PtI(NCN)(η^1-I_2).

Characteristic differences between the PtI and PtI(η^2-I_2) complexes include the position of the Pt atom with respect to the coordination plane [I(1), N(1), N(2), C(1)] which is included in the plane in the present PtI compound and lifted 0·18 (2) Å out of this plane in the square-pyramidal PtI(η^1-I_2) complex. The molecular symmetry of PtI(η^1-I_2) is also different, the molecule having an approximate mirror plane through the Pt—I—C(1) atoms, perpendicular to the phenyl ring. The different molecular symmetry can also be seen from the signs of the C—C—C—N torsion angles with values of −23·0 (7) and −20·5 (8)° for N(1) and N(2) in PtI(NCN) and −26 (1), 25 (1)° for the corresponding angles in the PtI(η^1-I_2) complex, indicating the different conformations of the side chains.

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Structure of the Organic Semiconducting Radical Cation Salt Bis[2,3:6,7-bis(methylenedioxydibenzofuran)]* Hexafluoroarsenate

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Abstract. $(C_{14}H_8O_5)_2^+.AsF_6^-$, $M_r = 701·33$, monoclinic, $C2/c$, $a = 9·564$ (1), $b = 13·899$ (2), $c = 19·364$ (3) Å, $\beta = 92·63$ (1)°, $V = 2571·4$ (6) Å^3, $Z = 4$, $D_x = 1·81$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 15·1$ cm^{-1}, $F(000) = 1404$, $T = 298$ K. Final $R = 0·035$ for 2047 unique reflexions. Dimers consisting of $(bMDODBF)_2^+$ molecules ($C_{14}H_8O_5$ = bMDODBF) form stacks along the [110] and [1$\bar{1}$0] directions and are surrounded by AsF_6^- ions. Interplanar distances are 3·19 (2) Å within the dimers and 3·25 (2) Å between the dimers in the stacks. Adjacent dimers have poor molecular overlap, giving rise to semiconducting electronic properties.

* 1′,3′-Benzodioxolo[5′,6′:3,2]benzofuro[6,5-*d*][1,3]dioxole.

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