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trans-(Isothiocyanato-*κN*)phenylbis(triphenylphosphine-*κP*)platinum(II)

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Key indicators

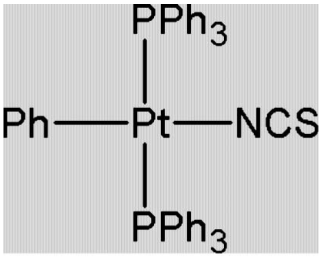
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.039
wR factor = 0.079
Data-to-parameter ratio = 25.8

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

The crystal structure of the title compound, *trans*-[Pt(C_6H_5)(NCS)($C_{18}H_{15}P$)$_2$], represents a typical example where steric crowding around the platinum metal centre induces *N*-coordination of the thiocyanate ligand. The compound crystallizes on a twofold rotation axis. Selected geometrical parameters are Pt—C = 2.019 (6) Å, Pt—P = 2.3007 (11) Å, Pt—N = 2.052 (6) Å, C—Pt—P = 92.47 (3)°, P—Pt—P′ = 175.06 (5)° and N—Pt—P = 87.53 (3)°. The compound represents a rare example of a *trans* bisphosphine complex of platinum(II) containing the NCS^- ligand.

Comment

As part of an extensive investigation into the structure and reactivity relationships of platinum(II) complexes, NCS^- was evaluated as ligand in systems with the general formula *trans*-[Pt*R*Cl(*L*)$_2$] (*R* = Me, Ph or H, and *L* = phosphine, arsine or stibine; Otto, 2000). Crystals of the title compound, (I), were obtained from a chloroform solution containing Bu_4N(NCS) and *trans*-[PtPhCl(PPh$_3$)$_2$] as a result of these studies.



(I)

Compound (I) (Fig. 1) crystallizes with a distorted square-planar geometry; a twofold rotation axis passes through Pt and the thiocyanate and phenyl ligands. The compound crystallizes with the two bulky PPh$_3$ ligands in the expected *trans* orientation with respect to each other. The NCS^- ligand is coordinated through the N atom, an indication of the steric strain induced by the PPh$_3$ ligands, making the electronically preferred S coordination mode energetically unfavourable. ^{31}P NMR studies confirmed that this was indeed the only isomer formed in solution. The packing in the unit cell is governed by van der Waals forces alone, with no significant intermolecular interactions.

The Pt1—P1 and Pt1—C1 bond distances within the square-planar coordination are within the expected ranges, at 2.3007 (11) and 2.019 (6) Å, respectively. The Pt1—N1 bond distance, of 2.052 (6) Å, is slightly elongated compared with that found in the related *trans*-[Pt(NCS)$_2$(PBz$_3$)$_2$] complex (see Table 2). This difference is mainly attributed to the large *trans* influence of the σ-bonded C atom of the phenyl ring. The Pt1—N1 bond distance is indeed similar to that found *trans* to the C atom of the ruthenocenyl group. With regards to the bond angles, the only significant distortion is the P1—Pt1—P1^i angle of 175.06 (5) Å. As expected, the phenyl ring is orientated almost perpendicular to the equatorial plane, as indicated by the C2—C1—Pt1—P1 torsion angle of 71.66 (19) Å.

It was noted previously (Johansson & Otto, 2000; Johansson *et al.*, 2000) for a series of structures of *trans*-$[PtCl_2(L)_2]$ (L = PPh_3 and $AsPh_3$) that tertiary phosphine and arsine ligands seem to have a preferred orientation as described by their rotation with respect to the coordination plane in square-planar complexes. Further investigation (Johansson *et al.*, 2002) in a series of structures with the general formula *trans*-$[PtX_2(PBz_3)_2]$ (X^- = Cl, I and NCS) showed that all of the PBz_3 ligands had one X—Pt—P—C torsion angle very close to zero (lying parallel to the coordination plane). In the case of X^- = Cl and I, the opposing PBz_3 ligand exhibited an *anti* conformation with respect to the first PBz_3 ligand. In the case of X^- = NCS, however, the two PBz_3 ligands exhibited a *gauche* conformation, as in the current study, where a *gauche* conformation for the phosphine ligands, in this case PPh_3, was observed.

Experimental

Crystals suitable for diffraction studies of the title compound were isolated by slow evaporation of a chloroform solution containing *trans*-$[PtPhCl(PPh_3)_2]$ (50 mg, 0.06 mmol) and $Bu_4N(NCS)$ (90 mg, 0.3 mmol). ^{31}P NMR /$CDCl_3$: 21.45 p.p.m. (t, $^1J_{Pt-P}$ = 3073 Hz). IR (KBr): ν(NCS) 2106 cm^{-1}.

Crystal data

$[Pt(C_6H_5)(NCS)(C_{18}H_{15}P)_2]$
$M_r = 854.81$
Monoclinic, $C2/c$
$a = 25.317 (5)$ Å
$b = 13.762 (3)$ Å
$c = 11.542 (2)$ Å
$\beta = 114.26 (3)°$
$V = 3666.2 (13)$ Å^3
$Z = 4$
$D_x = 1.549$ Mg m^{-3}
$D_m = 1.525$ Mg m^{-3}

D_m measured by flotation in NaI/H_2O
Mo $K\alpha$ radiation
Cell parameters from 6384 reflections
$\theta = 2.0$–$27.4°$
$\mu = 4.00$ mm^{-1}
$T = 293 (2)$ K
Prism, colourless
$0.10 \times 0.05 \times 0.02$ mm

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min} = 0.662$, $T_{max} = 0.923$
18254 measured reflections
5693 independent reflections

3249 reflections with $I > 2\sigma(I)$
$R_{int} = 0.088$
$\theta_{max} = 31.8°$
$h = -37 \rightarrow 32$
$k = -18 \rightarrow 19$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.079$
$S = 0.87$
5693 reflections
221 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.80$ e Å^{-3}
$\Delta\rho_{min} = -1.20$ e Å^{-3}

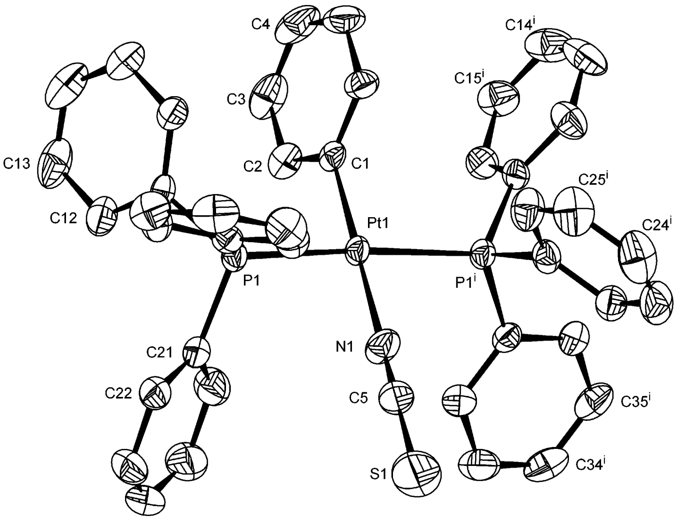


Figure 1
A view of the structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. All H atoms have been omitted for clarity. The phenyl rings of the PPh_3 ligands are numbered with the first digit referring to the number of the ring (1–3) and the second digit referring to the number of the C atom within the ring (1–6). [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

Table 1
Selected geometric parameters (Å, °).

Pt1—C1	2.019 (6)	P1—C11	1.807 (4)
Pt1—N1	2.052 (6)	P1—C31	1.809 (4)
Pt1—P1	2.3007 (11)	S1—C5	1.630 (8)
P1—C21	1.803 (4)	C5—N1	1.092 (8)
C1—Pt1—N1	180	C21—P1—Pt1	108.52 (14)
C1—Pt1—P1	92.47 (3)	C11—P1—Pt1	117.65 (13)
N1—Pt1—P1	87.53 (3)	C31—P1—Pt1	115.12 (14)
C21—P1—C11	105.43 (19)	N1—C5—S1	180
C21—P1—C31	106.1 (2)	C5—N1—Pt1	180
C11—P1—C31	103.06 (18)		
P1—Pt1—C1—C2	−71.66 (19)	N1—Pt1—P1—C21	−53.05 (15)
N1—Pt1—P1—C11	−172.54 (15)	N1—Pt1—P1—C31	65.64 (15)

Table 2
Comparative X-ray data for trans-$[Pt(X)(NCS)(L)_2]$ complexes.

X	L	Pt—X (Å)	Pt—N (Å)	Pt—L_{ave} (Å)
NCS^i	PBz_3	1.966 (5)	2.014 (5)	2.3221 (14)
Ph^{ii}	PPh_3	2.019 (6)	2.052 (6)	2.3007 (11)
Rc^{iii}	PEt_3	2.031 (8)	2.055 (8)	2.309 (3)

Notes: (i) Johansson *et al.* (2002); (ii) this work; (iii) Rc = ruthenocenyl, all bonds averaged for two independent molecules (Yoshida *et al.*, 1999).

All H atoms were placed in geometrically idealized positions (C—H = 0.93 Å) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. The minimum and maximum residual electron density are located within 1.3 Å of the Pt atom, indicating no physical meaning.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXL97*.

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