

Tableau 1. Coordonnées atomiques relatives, facteurs de température équivalent (\AA^2) et écarts-type

	$U_{eq} = \frac{1}{3}(\text{trace } U)$			
	x	y	z	U_{eq}
Pd	0,0000	0,12684 (4)	0,2500	0,0383
Cl	0,2614 (1)	0,1290 (2)	0,2668 (2)	0,0569
N(1)	0,0000	-0,0040 (4)	0,2500	0,0417
N(2)	0,0000	0,2575 (4)	0,2500	0,0455
C(1)	0,0942 (6)	-0,0489 (4)	0,1559 (6)	0,0456
C(2)	0,0969 (6)	-0,1379 (4)	0,1547 (6)	0,0501
C(3)	0,0000	-0,1813 (5)	0,2500	0,0485
C(4)	0,0565 (7)	0,3011 (4)	0,1299 (6)	0,0492
C(5)	0,0570 (7)	0,3908 (4)	0,1278 (7)	0,0570
C(6)	0,0000	0,4352 (6)	0,2500	0,0581

Tableau 2. Distances (\AA) et angles ($^\circ$)

Pd—Cl	2,297 (1)	Pd—N(1)	2,024 (6)
Pd—N(2)	2,023 (6)	N(1)—C(1)	1,356 (6)
N(2)—C(4)	1,336 (6)	C(1)—C(2)	1,377 (8)
C(2)—C(3)	1,336 (7)	C(4)—C(5)	1,388 (8)
C(5)—C(6)	1,359 (8)		
Cl—Pd—Cl	178,3 (1)	N(1)—Pd—Cl	90,83 (7)
N(2)—Pd—Cl	89,17 (7)	C(1)—N(1)—Pd	120,8 (3)
C(1)—N(1)—C(1')	118,3 (7)	C(4)—N(2)—Pd	120,3 (3)
C(4)—N(2)—C(4)	119,4 (7)	C(2)—C(1)—N(1)	121,9 (6)
C(3)—C(2)—C(1)	118,4 (6)	C(2)—C(3)—C(2')	121,1 (8)
C(5)—C(4)—N(2)	121,1 (6)	C(6)—C(5)—C(4)	119,6 (6)
C(5)—C(6)—C(5)	119,3 (8)		

Code de symétrie: (i) $-x, y, \frac{1}{2} - z$.

1983). $R = 0,033$, $wR = 0,033$ ($w = 1$); $S = 2,6$; valeur maximum du $\Delta/\sigma = 0,1$; aucun résidu significatif sur la série de Fourier des différences. Angles entre les plans moyens: *BP7C* (Ito & Sugawara, 1983).

Fig. 1: programme *ORTEPII* (Johnson, 1976). Ordinateur MicroVAX II. Les coordonnées atomiques relatives sont rassemblées dans le Tableau 1, les distances interatomiques et les angles des liaisons dans le Tableau 2.* La Fig. 1 indique la numérotation utilisée pour désigner les atomes dans le complexe.

Littérature associée. Synthèse du *trans*-dichlorobis(pyridine)palladium(II) (Krauss & Brodkor, 1927). Formation du *trans*-dichlorobis(pyridine)palladium(II) par isomérisation thermique du *cis* (Kukushkin & Vlasova, 1983). Structures des *cis*- et

* Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des paramètres des atomes d'hydrogène, des distances C—H, des distances de van der Waals et des équations des différents plans moyens, et une vue stéréoscopique du contenu de la maille ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 55396: 11 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: DU1002]

trans-dichlorobis(pyridine)platine(II) (Colamarino & Orioli, 1975). Synthèse et structure cristalline du *trans*-dichloro(diméthyl sulfoxyde)ténonitrozole)platine(II) (Viossat, Nguyen-Huy, Lancelot & Robba, 1991).

Références

- COLAMARINO, P. & ORIOLI, P. L. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1656–1659.
- ITO, T. & SUGAWARA, Y. (1983). *Best Plane Program*, 3ième version. The Institute of Physical and Chemical Research, Wako-Shi, Saitama 351, Japon.
- JOHNSON, C. K. (1976). *ORTEPII*. Rapport ORNL-5138. Oak Ridge National Laboratory, Tennessee, EU.
- KRAUSS, F. & BRODKOR, B. (1927). *Z. Anorg. Allg. Chem.* **165**, 73–78.
- KUKUSHKIN, YU. N. & VLASOVA, R. A. (1983). *Zh. Obshch. Khim.* **53**, 948.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. de York, Angleterre, et de Louvain, Belgique.
- VIOSSAT, B., NGUYEN-HUY, D., LANCELOT, J. C. & ROBBA, M. (1991). *Chem. Pharm. Bull.* pp. 3023–3024.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.
- WATKIN, D. J., CARRUTHERS, J. R. & BETTERIDGE, P. W. (1988). *CRYSTALS*. Chemical Crystallography Laboratory, Univ. de Oxford, Angleterre.

Acta Cryst. (1993). **C49**, 85–87

$[\text{Rh}(\text{9}]\text{aneS}_3)(\text{CO})(\text{PPh}_3)]^+ \cdot \text{PF}_6^-$

BY ALEXANDER J. BLAKE,* MALCOLM A. HALCROW AND MARTIN SCHRÖDER

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

(Received 16 December 1991; accepted 30 April 1992)

Abstract. (Carbonyl)(triphenylphosphine-*P*)(1,4,7-trithiacyclononane-*S, S', S''*)rhodium hexafluoro-

phosphate, $[\text{Rh}(\text{C}_6\text{H}_{12}\text{S}_3)(\text{C}_{18}\text{H}_{15}\text{P})(\text{CO})]\text{PF}_6$, $M_r = 718,45$, orthorhombic, *Pnma*, $a = 12,4367$ (8), $b = 12,7190$ (6), $c = 18,0229$ (8) \AA , $V = 2850,9$ \AA^3 , $Z = 4$, $D_x = 1,674$ Mg m^{-3} , $\lambda(\text{Mo K}\alpha) = 0,71073$ \AA , $\mu =$

* Author to whom correspondence should be addressed.

Table 1. Atomic coordinates and isotropic or equivalent isotropic thermal parameters (Å²)

The macrocyclic C atoms [C(2), C(3), C(5), C(12), C(13) and C(15)] are all half-occupied. The F atoms on the mirror plane [F(1)–F(4)] all have occupancies of 0.25, while for those in general positions, F(5)–F(7) are half-occupied and F(7), F(8) one-quarter-occupied. F atoms with occupancies less than 0.5 have isotropic thermal parameters. Remaining non-H atoms were refined anisotropically; $U_{eq} = (1/3)\sum_i U_{ij} a_i^* a_j^* a_j$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} / <i>U</i> _{eq}
Rh	0.10867 (7)	0.2500	0.13271 (4)	0.0445 (5)
S(1)	0.2894 (3)	0.2500	0.16778 (17)	0.0637 (16)
C(2)	0.3541 (3)	0.3442 (7)	0.1054 (4)	0.0543 (22)
C(12)	0.3326 (6)	0.3778 (4)	0.1320 (5)	0.0637 (23)
C(3)	0.2758 (6)	0.4322 (4)	0.0872 (5)	0.0677 (23)
C(13)	0.30573 (22)	0.3853 (8)	0.0500 (4)	0.0737 (23)
S(4)	0.15987 (18)	0.37829 (17)	0.03763 (13)	0.0654 (12)
C(5)	0.2304 (9)	0.30018 (10)	-0.0323 (5)	0.1238 (25)
C(15)	0.1678 (10)	0.30013 (10)	-0.04745 (19)	0.0464 (21)
P	-0.07076 (23)	0.2500	0.10245 (16)	0.0411 (14)
C(21)	-0.2535 (4)	0.3784 (3)	0.11301 (25)	0.0698 (23)
C(22)	-0.3128 (4)	0.4624 (3)	0.14139 (25)	0.0952 (24)
C(23)	-0.2651 (4)	0.5326 (3)	0.19091 (25)	0.1079 (24)
C(24)	-0.1582 (4)	0.5188 (3)	0.21205 (25)	0.1060 (24)
C(25)	-0.0989 (4)	0.4349 (3)	0.18368 (25)	0.0731 (23)
C(26)	-0.1465 (4)	0.3646 (3)	0.13415 (25)	0.0484 (22)
C(31)	-0.0935 (5)	0.3436 (3)	-0.0364 (3)	0.0529 (22)
C(32)	-0.0953 (5)	0.3428 (3)	-0.1138 (3)	0.0684 (23)
C(33)	-0.0966 (5)	0.2500	-0.1520 (3)	0.0718 (24)
C(34)	-0.0923 (5)	0.2500	0.0025 (3)	0.0414 (23)
C	0.0719 (9)	0.2500	0.2309 (6)	0.0654 (24)
O	0.0521 (7)	0.2500	0.2921 (4)	0.0920 (23)
P(1)	0.0478 (3)	0.2500	-0.39792 (24)	0.0773 (18)
F(1)	-0.0533 (19)	0.2500	-0.4265 (18)	0.373 (3)
F(2)	0.1549 (13)	0.2500	-0.4343 (14)	0.186 (3)
F(3)	-0.0644 (13)	0.2500	-0.3638 (11)	0.153 (3)
F(4)	0.0916 (18)	0.2500	-0.3174 (9)	0.171 (3)
F(5)	0.0038 (16)	0.1405 (13)	-0.3933 (14)	0.264 (3)
F(6)	0.1302 (14)	0.1607 (13)	-0.4068 (12)	0.219 (3)
F(7)	0.0203 (15)	0.1896 (15)	-0.4668 (8)	0.247 (3)
F(8)	0.0115 (20)	0.1809 (19)	-0.3279 (16)	0.1618 (25)
F(9)	0.0991 (18)	0.1744 (19)	-0.3531 (14)	0.1292 (25)

Table 2. Bond lengths (Å), bond angles (°) and torsion angles (°)

Primed atoms are related to their unprimed equivalents by the mirror plane at $y = \frac{1}{2}$.

Rh–S(1)	2.335 (3)	C–O	1.129 (11)
Rh–S(4)	2.4504 (23)	P–C(26)	1.828 (5)
Rh–P	2.2972 (24)	P–C(34)	1.822 (5)
Rh–C	1.828 (9)		
S(1)–Rh–S(4)	86.51 (8)	Rh–S(4)–C(13)	101.8 (3)
S(1)–Rh–P	178.03 (9)	Rh–S(4)–C(5)	104.2 (3)
S(1)–Rh–C	88.8 (3)	Rh–S(4)–C(15)	103.8 (3)
S(4)–Rh–S(4')	83.50 (8)	C(3)–S(4)–C(5)	99.3 (4)
S(4)–Rh–P	94.96 (8)	C(13)–S(4)–C(15)	94.3 (4)
S(4)–Rh–C	137.9 (3)	Rh–P–C(26)	115.26 (18)
P–Rh–C	89.2 (3)	Rh–P–C(34)	112.18 (18)
Rh–C–O	178.0 (8)	C(26)–P–C(26')	105.83 (23)
Rh–S(1)–C(2)	104.88 (25)	C(26)–P–C(34)	103.54 (23)
Rh–S(1)–C(12)	100.8 (3)	P–C(26)–C(21)	120.4 (3)
C(2)–S(1)–C(12)	103.6 (3)	P–C(26)–C(25)	119.4 (3)
C(12)–S(1)–C(2')	103.6 (3)	P–C(34)–C(31)	120.1 (3)
Rh–S(4)–C(3)	96.47 (24)	P–C(34)–C(31')	119.0 (3)
C(12')–S(1)–C(2)–C(3)	138.8 (5)	C(26')–P–C(26)–C(21)	-57.6 (4)
C(2)–S(1)–C(12)–C(13)	53.9 (6)	C(26)–P–C(26)–C(25)	118.2 (4)
S(1)–C(2)–C(3)–S(4)	-63.1 (5)	C(34)–P–C(26)–C(21)	50.9 (4)
S(1)–C(12)–C(13)–S(4)	63.0 (6)	C(34)–P–C(26)–C(25)	-133.3 (4)
C(2)–C(3)–S(4)–C(5)	-48.7 (5)	C(26)–P–C(34)–C(31)	39.1 (4)
C(12)–C(13)–S(4)–C(15)	-142.4 (5)	C(26)–P–C(34)–C(31')	-148.7 (4)
C(3)–S(4)–C(5)–C(15')	144.0 (5)	C(22)–C(21)–C(26)–P	175.8 (4)
C(13)–S(4)–C(15)–C(5')	56.9 (6)	C(24)–C(25)–C(26)–P	-175.8 (4)
S(4)–C(5)–C(15)–S(4')	-61.8 (6)	C(32)–C(31)–C(34)–P	171.3 (3)
S(4)–C(15)–C(5)–S(4')	61.8 (6)	C(32)–C(31')–C(34)–P	-171.4 (3)

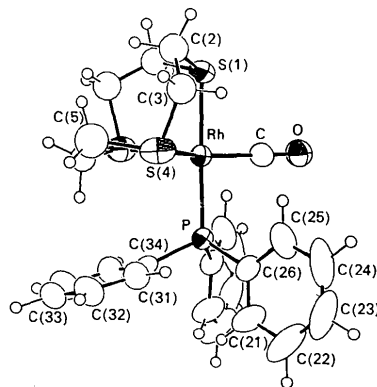


Fig. 1. A general view of the cation showing the atom-numbering scheme. Only one orientation of the disordered macrocycle is shown. Thermal ellipsoids are drawn at the 30% probability level, except those of the H atoms which have artificial radii of 0.10 Å for clarity.

0.968 mm⁻¹, $F(000) = 1448$, $T = 298$ K, $R = 0.0498$ for 1401 unique observed reflections. The Rh^I centre is five-coordinate, with the donor atoms conferring a distorted trigonal bipyramidal environment in which the carbonyl group and two of the three thia donors are equatorial and the remaining thia donor and the phosphine are axial.

Experimental. The title compound was prepared by reaction under N₂ of [RhCl(CO)(PPh₃)₂] with [9]aneS₃ and NH₄PF₆ in CH₂Cl₂. Crystals were obtained from CH₂Cl₂/hexane. A yellow columnar crystal, 0.65 × 0.15 × 0.12 mm, was used for data collection on a Stoe Stadi-4 four-circle diffractometer with graphite-monochromated Mo K α radiation. Cell parameters were determined from 2 θ values of 39 reflections measured at $\pm \omega$ (28 < 2 θ < 30°). Data were collected at $T = 298$ K, using ω -2 θ scans with ω -scan width (0.99 + 0.35tan θ)°, to 2 $\theta_{max} = 45$ °, and over $h 0 \rightarrow 11$, $k 0 \rightarrow 13$, $l 0 \rightarrow 19$. Three standard reflections showed no significant crystal movement or decay. 2028 unique reflections were measured giving 1401 with $F \geq 6\sigma(F)$ for structure solution (from a Patterson synthesis followed by iterative cycles of least-squares refinement and difference

Fourier synthesis) and refinement [using full-matrix least squares on F (SHELX76; Sheldrick, 1976)]. A crystallographic mirror plane, about which the tri-thiacyclononane is disordered, also passes through the metal, the axial S atom, the CO group, the P atom and one phenyl ring. This disorder was modelled using two alternative orientations and constraints to S–C and C–C distances and S–C–C angles, while disorder in the anion required alternative positions for some of the F atoms. Refinement included anisotropic thermal parameters for all non-H atoms except F with occupancies less than 0.5, phenyl rings constrained to have D_{6h} symmetry,

and H atoms in fixed calculated positions. At final convergence, $R = 0.0498$, $wR = 0.0691$, $S = 1.252$ for 202 parameters; $(\Delta/\sigma)_{\max}$ in the final cycle was less than 0.10; maximum and minimum residues in the final ΔF synthesis were 1.53 and $-0.80 \text{ e } \text{\AA}^{-3}$, respectively. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000373F^2$ gave satisfactory agreement analyses. Scattering factors were inlaid (Sheldrick, 1976) except for Rh (Cromer & Mann, 1968). Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, while selected bond lengths, bond angles and torsion angles appear in Table 2.* The atom-numbering scheme for the cation is shown in Fig. 1, which was generated using the interactive version of ORTEPII (Johnson, 1971) included in the GX crystallographic program system (Mallinson & Muir, 1985). Molecular geometry calculations were performed using CALC (Gould & Taylor, 1985).

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55418 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0111]

Acta Cryst. (1993). **C49**, 87–89

(Diisopropylthiocarbamato-*S,S'*)- (1,3-diphenyl-1,3-propanedithionato-*S,S'*)nickel(II)

BY IAN H. ANDERSON, ALEXANDER J. BLAKE* AND GRAHAM A. HEATH†

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland

(Received 24 March 1992; accepted 18 May 1992)

Abstract. $[\text{Ni}(\text{C}_7\text{H}_{14}\text{NS}_2)(\text{C}_{15}\text{H}_{11}\text{S}_2)]$, $M_r = 490.4$, monoclinic, $P2_1$, $a = 11.415(5)$, $b = 11.185(5)$, $c = 9.075(4) \text{ \AA}$, $\beta = 96.93(3)^\circ$, $V = 1150 \text{ \AA}^3$, $Z = 2$, $D_x = 1.416 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$, $\mu = 1.204 \text{ mm}^{-1}$, $F(000) = 512$, $T = 298 \text{ K}$, $R = 0.0537$ for 1915 unique observed reflections. The metal atom is in a distorted square-planar coordination; the Ni atom is coplanar with the four S atoms, but successive S—Ni—S angles are 77.49 (8) (within the dithiocarbamate ligand), 87.12 (9), 102.70 (9) (within the 1,3-dithionate ligand) and 92.57 (9)°. Despite its potential mirror symmetry, the molecule possesses no crystallographically imposed symmetry and shows inequivalent Ni—S distances to both ligands.

* Author to whom correspondence should be addressed.

† Present address: Research School of Chemistry, Australian National University, GPO Box 4, Canberra ACT 2601, Australia.

Related literature. This is a rare example of a trigonal bipyramidal complex containing the [9]aneS₃ macrocycle. Other examples are $[\text{Rh}(\text{[9]aneS}_3)(1,5\text{-cyclo-octadiene})]^+$ (Blake, Halcrow & Schröder, 1991) and $[\text{Pt}(\text{[9]aneS}_3)(\text{PPh}_3)_2]^{2+}$ (Blake, Roberts & Schröder, 1992).

We thank the SERC and ICI Organics Division for support, and Johnson Matthey PLC for generous loans of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$.

References

- BLAKE, A. J., HALCROW, M. A. & SCHRÖDER, M. (1991). *J. Chem. Soc. Chem. Commun.* pp. 253–256.
BLAKE, A. J., ROBERTS, Y. V. & SCHRÖDER, M. (1992). Unpublished results.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
GOULD, R. O. & TAYLOR, P. (1985). *CALC*. Program for molecular geometry calculations. Univ. of Edinburgh, Scotland.
JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794, 2nd revision. Oak Ridge National Laboratory, Tennessee, USA.
MALLINSON, P. D. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Experimental. The title compound $[\text{NiL}^1\text{L}^2]$ was prepared by refluxing $[\text{NiL}^1]$ and $[\text{NiL}^2]$ in toluene for 15 h; crystals were obtained from CH_2Cl_2 /petroleum spirit (333–353 K boiling range). A red acicular crystal, $1.50 \times 0.24 \times 0.14 \text{ mm}$, was used for data collection on a Stoe Stadi-2 two-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell

