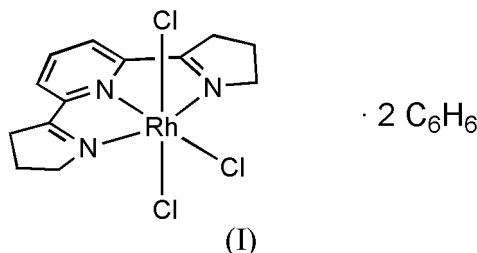


Amel Cabort, Bruno Therrien,  
Klaus Bernauer and Georg  
Süss-Fink\*Institut de Chimie, Université de Neuchâtel,  
Case postale 2, CH-2007 Neuchâtel, Switzer-  
landCorrespondence e-mail:  
georg.suess-fink@unine.ch

## Key indicators

Single-crystal X-ray study  
 $T = 153\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$   
 $R$  factor = 0.026  
 $wR$  factor = 0.059  
Data-to-parameter ratio = 15.9For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**[2,6-Bis(3,4-dihydro-2H-pyrrol-5-yl)pyridine]-  
trichlororhodium(III) dibenzene solvate**The structure of the mononuclear octahedral rhodium(III) complex,  $[\text{RhCl}_3(L)] \cdot 2\text{C}_6\text{H}_6$ , with  $L = 2,6\text{-bis}(3,4\text{-dihydro-}2H\text{-pyrrol-}5\text{-yl)pyridine}$  ( $\text{C}_{13}\text{H}_{15}\text{N}_3$ ), possesses a twofold axis passing through Rh, the equatorial Cl atom and the N atom pyridine ring.

## Comment

In the context of our study on hydrogenation reactions catalysed by transition metals, we have synthesized a rhodium complex containing the tridentate ligand 2,6-bis(3,4-dihydro-2H-pyrrol-5-yl)pyridine (Bernauer & Gretillat, 1989).  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  reacts with 2,6-bis(3,4-dihydro-2H-pyrrol-5-yl)pyridine ( $L$ ) in refluxing dichloromethane to afford in good yield  $[\text{RhCl}_3(L)] \cdot 2\text{C}_6\text{H}_6$ , (I). The coordination of  $L$  to the Rh atom can be monitored by  $^1\text{H NMR}$ ; a position inversion and a downfield shift of the pyridinyl H atoms are observed. Thus, free ligand  $H_{para} = 7.80$  p.p.m. and  $H_{meta} = 8.15$  p.p.m. may be compared with coordinated ligand  $H_{para} = 8.47$  p.p.m. and  $H_{meta} = 8.34$  p.p.m.The three N atoms of the tridentate ligand along with three Cl atoms form a distorted octahedral geometry around the metal atom in (I) (Fig. 1 and Table 1). Complex (I) crystallizes with two molecules of  $\text{C}_6\text{H}_6$  per asymmetric unit. The bond distances and angles are similar to other  $[\text{RhCl}_3(\eta^3\text{-}L)]$  complexes;  $L = \text{bis}(\text{oxazoliny})\text{pyridine}$  (Nishiyama *et al.*, 1991),  $L = \text{bis}(\text{pyrazolyl})\text{pyridine}$  (Christenson *et al.*, 1995),  $L = 2,6\text{-bis}(\text{ethylideneimino})\text{pyridine}$  (Haarman *et al.*, 1997),  $L = 2,3,6\text{-tris}(2\text{-pyridyl})\text{-}1,3,5\text{-triazine}$  (Paul *et al.*, 1998),  $L = 2,2':6',2''\text{-terpyridine}$  (Ziegler *et al.*, 1999; Kwong *et al.*, 2001).The formation of five-membered chelate rings imposes an important distortion around the Rh atom. The  $\text{N1}-\text{Rh1}-\text{N2}$  [ $79.54(5)^\circ$ ] and  $\text{N1}-\text{Rh1}-\text{N1}^i$  [ $159.07(10)^\circ$ ; symmetry code: (i)  $-x, y, -z + \frac{1}{2}$ ] angles are significantly smaller than the values of  $90$  and  $180^\circ$  expected for an ideal octahedral geometry. The equatorial plane formed by the atoms of  $L$  together with Rh1 and Cl2 is planar, with an average deviation of  $0.042\text{ \AA}$ ; only atoms C1 and C2 of the pyrrole fragment are out of plane, by  $-0.100(2)$  and  $0.088(2)\text{ \AA}$ , respectively. The distance between Rh1 and the central N2 atom of  $1.941(2)\text{ \AA}$  is shorter than the other  $\text{Rh1}-\text{N1}$  bond of  $2.031(2)\text{ \AA}$ .

In the crystal structure, there is no meaningful interaction between the complex and the two benzene molecules, one molecule being parallel to the equatorial plane of (I) [4.0 (5)°] and the other being almost perpendicular [67.9 (2)°].

## Experimental

To a dichloromethane solution (15 ml) of  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  (70 mg) was added dropwise a 5 ml solution of 2,6-bis(3,4-dihydro-2*H*-pyrrol-5-yl)pyridine (58 mg, 0.27 mmol). The mixture was stirred and refluxed for 2 h. After cooling to room temperature, a brown–orange precipitate was observed. The solid was filtered off and washed twice with cold  $\text{CH}_2\text{Cl}_2$  and once with diethyl ether to give  $[\text{RhCl}_3\{2,6\text{-bis}(3,4\text{-dihydro-2*H*-pyrrol-5-yl)pyridine}\}]$  in 65% yield [based on 2,6-bis(3,4-dihydro-2*H*-pyrrol-5-yl)pyridine]. To a small amount of  $[\text{RhCl}_3\{2,6\text{-bis}(3,4\text{-dihydro-2*H*-pyrrol-5-yl)pyridine}\}]$  dissolved in hot benzene was added diethyl ether. Crystals of (I) formed after a few days.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , p.p.m.): 8.47 (*t*, 1H), 8.34 (*d*, 2H), 4.16 (*m*, 4H), 3.50 (*m*, 4H), 2.50 (*m*, 4H). MS (ESI, *m/z*): 444;  $[\text{RhCl}_3(L)] + \text{Na}$ . Analysis calculated for  $\text{C}_{19}\text{H}_{21}\text{Cl}_3\text{N}_3\text{Rh}$ : C 45.58, H 4.23, N 8.39%; found: C 45.24, H 8.26, N 4.14%.

### Crystal data

$[\text{RhCl}_3(\text{C}_{13}\text{H}_{15}\text{N}_3)] \cdot 2\text{C}_6\text{H}_6$   
 $M_r = 578.76$   
 Monoclinic,  $C2/c$   
 $a = 11.434$  (2) Å  
 $b = 10.630$  (2) Å  
 $c = 20.948$  (4) Å  
 $\beta = 100.12$  (3)°  
 $V = 2506.5$  (8) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.534$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 8000 reflections  
 $\theta = 2.6\text{--}25.9^\circ$   
 $\mu = 1.02$  mm<sup>-1</sup>  
 $T = 153$  (2) K  
 Block, yellow  
 $0.5 \times 0.4 \times 0.1$  mm

### Data collection

Stoe IPDS diffractometer  
 $\varphi$  oscillation scans  
 Absorption correction: multi-scan (Blessing, 1995)  
 $T_{\min} = 0.495$ ,  $T_{\max} = 0.824$   
 8616 measured reflections  
 2341 independent reflections

1964 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.049$   
 $\theta_{\text{max}} = 25.9^\circ$   
 $h = -12 \rightarrow 14$   
 $k = -12 \rightarrow 13$   
 $l = -24 \rightarrow 25$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.059$   
 $S = 0.98$   
 2341 reflections  
 147 parameters

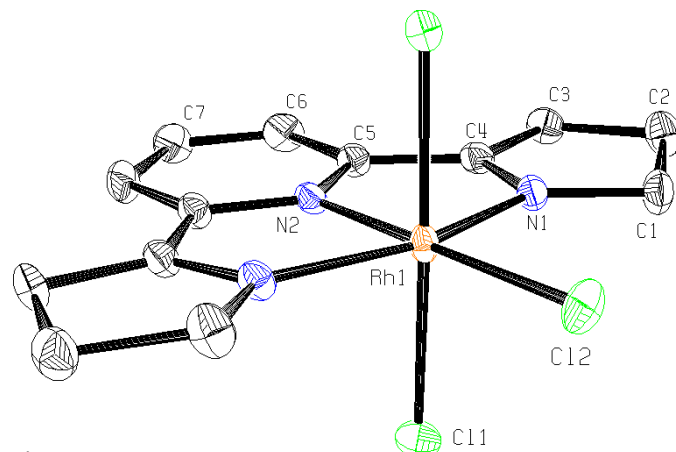
H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0361P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.89$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.89$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

N1–Rh1	2.031 (2)	Cl1–Rh1	2.3424 (9)
N2–Rh1	1.941 (2)	Cl2–Rh1	2.3618 (8)
N2–Rh1–N1	79.54 (5)	N1 <sup>i</sup> –Rh1–Cl1 <sup>i</sup>	90.93 (5)
N1–Rh1–N1 <sup>i</sup>	159.07 (10)	Cl1 <sup>i</sup> –Rh1–Cl1	177.36 (3)
N2–Rh1–Cl1 <sup>i</sup>	88.678 (14)	N1–Rh1–Cl2	100.46 (5)
N1–Rh1–Cl1 <sup>i</sup>	88.59 (5)	Cl1–Rh1–Cl2	91.322 (14)

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



**Figure 1**

The molecular structure of (I) (Farrugia, 1997). The  $\text{C}_6\text{H}_6$  molecules and H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

H atoms were included in calculated positions and treated in the riding-model approximation.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Swiss National Science Foundation (grant No. 20-61227-00). The authors thank Professor H. Stoeckli-Evans for helpful discussions and free access to X-ray facilities.

## References

- Bernauer, K. & Gretillat, F. (1989). *Helv. Chim. Acta*, **73**, 477–481.  
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.  
 Christenson, D. L., Tokar, C. J. & Tolman, W. B. (1995). *Organometallics*, **14**, 2148–2150.  
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
 Haarman, H. F., Ernsting, J. M., Kranenburg, M., Kooijman, H., Veldman, N., Spek, A. L., van Leeuwen, P. W. N. M. & Vrieze, K. (1997). *Organometallics*, **16**, 887–900.  
 Kwong, H.-L., Wong, W.-L., Lee, W.-S., Cheng, L.-S. & Wong, W.-T. (2001). *Tetrahedron Asymmetry*, **12**, 2683–2694.  
 Nishiyama, H., Kondo, M., Nakamura, T. & Itoh, K. (1991). *Organometallics*, **10**, 500–508.  
 Paul, P., Tyagi, B., Bilakhiya, A. K., Bhadbhade, M. M., Suresh, E. & Ramachandraiah, G. (1998). *Inorg. Chem.* **37**, 5733–5742.  
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.  
 Stoe & Cie (2000). *IPDS Software*. Stoe & Cie GmbH, Darmstadt, Germany.  
 Ziegler, M., Monney, V., Stoeckli-Evans, H., Von Zelewsky, A., Sasaki, I., Dupic, G., Daran, J.-C. & Balavoine, G. G. A. (1999). *J. Chem. Soc. Dalton Trans.* pp. 667–675.