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Key indicators

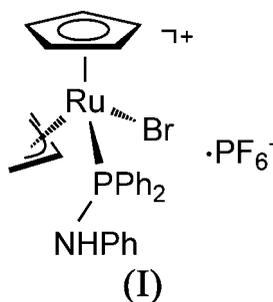
Single-crystal X-ray study
T = 123 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.023
wR factor = 0.056
Data-to-parameter ratio = 21.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**(η^3 -Allyl)bromo(η^5 -cyclopentadienyl)-
(phenylaminodiphenylphosphine- κP)-
ruthenium(IV) hexafluorophosphate**The title compound, $[\text{RuBr}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_3\text{H}_5)(\text{C}_{18}\text{H}_{16}\text{NP})]\text{PF}_6$, contains a half-sandwich cyclopentadienylruthenium(IV) complex with a three-legged piano-stool structure and an intramolecular N—H \cdots Br hydrogen bond.

Received 7 April 2006

Accepted 7 April 2006

Comment

Ruthenium complexes with cyclopentadienyl (Cp), pentamethylcyclopentadienyl (Cp*) or hydridotrispyrazolylborate (Tp) as ancillary ligand and phenylaminodiphenylphosphine (Ph₂PNHPh) as coligand have recently attracted attention because of a rich chemistry in stoichiometric or catalytic transformations of alkenes and alkynes (Pavlik *et al.*, 2003, 2006; Pavlik, Mereiter *et al.*, 2005; Pavlik, Jantscher *et al.*, 2005; Priya *et al.*, 2003; Jimenez-Tenorio *et al.*, 2005). For Cp, such compounds are accessible from the cationic complex $[\text{RuCp}(\text{Ph}_2\text{PNHPh})(\text{CH}_3\text{CN})_2]^+$ (Pavlik *et al.*, 2003), which behaves as a masked electron-deficient entity and reacts under mild conditions with unsaturated hydrocarbons. In order to evaluate further chemistry, the bis(acetonitrile) complex was reacted with allyl bromide. As indicated by NMR spectroscopy (see *Experimental*) and colour change, oxidative addition at the metal centre with replacement of both acetonitrile ligands took place. The resulting crystals contained the title cationic complex of tetravalent Ru, (I), shown in Fig. 1.



Complex (I) has a three-legged pseudo piano-stool structure with Cp as the seat and bromide, aminophosphine and the four-electron electron-donor allyl as the legs. The complex agrees in stereochemistry and orientation of the allyl group with several related compounds $[\text{RuCp}(\text{allyl})(\text{Br})(\text{EPh}_3)]\text{PF}_6$, where E = P, As and Sb but not Bi, and Ph = phenyl (Becker *et al.*, 2002). This is demonstrated in Fig. 2, which presents a superposition plot of (I) with $[\text{RuCp}(\text{allyl})(\text{Br})(\text{PPh}_3)]\text{PF}_6$ (Becker *et al.*, 2002). The bond lengths around Ru in this latter complex compare well with those in (I), except that the Ru—P bond to PPh₃ is longer by $\sim 0.04 \text{ \AA}$ because it is weaker π -

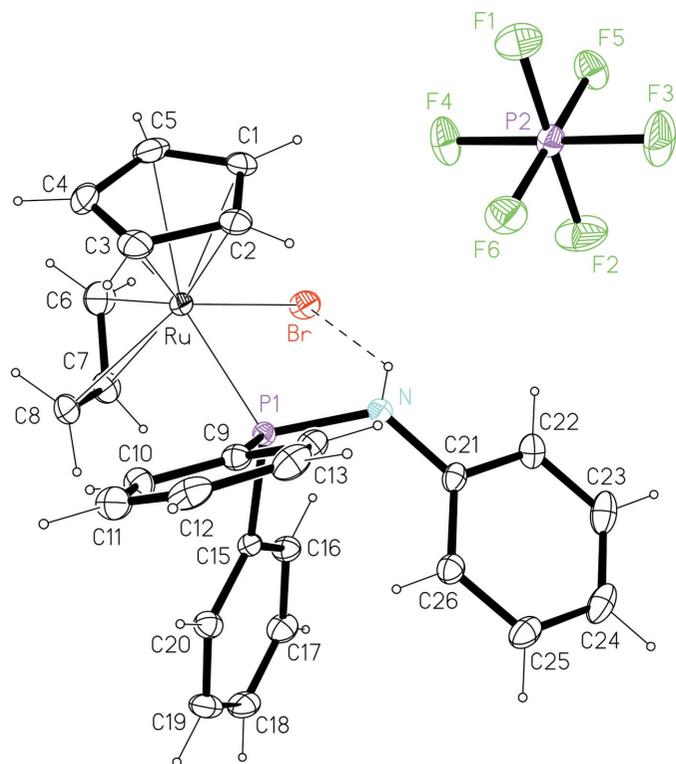


Figure 1
The molecular structure of (I), shown with 40% probability displacement ellipsoids. The broken line represents the intramolecular N–H...Br hydrogen bond.

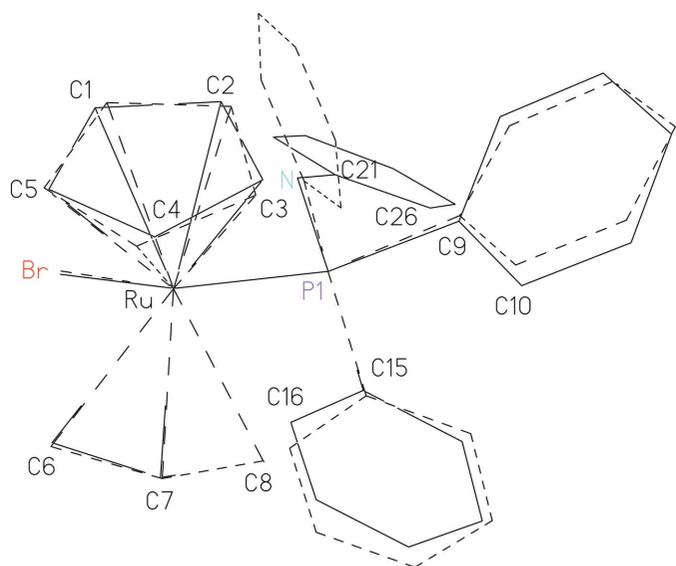


Figure 2
Superposition plot of the Ru complexes in (I) (full lines) and [RuCp(allyl)(Br)(PPh₃)]PF₆ (broken lines; Becker *et al.*, 2002). Weighted r.m.s. deviation of the fitted atoms Ru, Br, P1, C6, C7, and C8 is 0.040 Å.

acceptor than Ph₂PNHPh. A typical behaviour of the amino-phosphine complexes is the formation of a distinctly bent intramolecular hydrogen bond to Br (Fig. 1 and Table 2).

Experimental

The synthesis of (I) was carried out as follows. To a solution of [RuCp(PPh₂NHPh)(CH₃CN)₂]PF₆ (100 mg, 0.15 mmol) in CH₂Cl₂ (10 ml), allyl bromide was added (26 µl, 0.30 mmol) and the mixture was stirred for 2 h at room temperature. After evaporation of the solvent, (I) was obtained as a yellow solid, which was washed with diethyl ether (3 × 5 ml) and dried *in vacuo* (yield 87 mg, 82%). Spectroscopic analysis: ¹H NMR (acetone-*d*₆, 293 K, δ, p.p.m.): 7.84–7.30 [*m*, 10H, Ph(P)], 7.06–6.87 [*m*, 2H, Ph(NH)], 6.84–6.66 [*m*, 1H, Ph(NH)], 6.63–6.48 [*m*, 2H, Ph(NH)], 5.92 (5H, Cp), 4.80 (*dd*, ³*J*_{HH} = 10.7 Hz, ²*J*_{HH} = 2.7 Hz, 1H, CH₂CHCH₂), 4.52–4.38 (*m*, 1H, CH₂CHCH₂), 4.10–3.90 (*m*, 1H, CH₂CHCH₂), 3.86–3.69 (*m*, 1H, CH₂CHCH₂), 3.61 (*d*, ³*J*_{HHtrans} = 10.6 Hz, CH₂CHCH₂). The NH proton could not be detected. ¹³C{¹H} NMR (acetone-*d*₆, 273 K, δ, p.p.m.): 141.8–119.0 [Ph(P), Ph(NH)], 97.0 (CH₂CHCH₂), 95.2 (Cp), 62.1 (CH₂CHCH₂), 54.7 (CH₂CHCH₂). ³¹P{¹H} NMR (acetone-*d*₆, 273 K, δ, p.p.m.): 49.8 (PPh₂), –144.2 (¹*J*_{FP} = 706.5 Hz, PF₆). Crystals of (I) for X-ray structure analysis were obtained by crystallization using vapour diffusion of diethyl ether into a solution of the compound in CH₂Cl₂ at room temperature.

Crystal data

| | |
|--|---|
| [RuBr(C ₅ H ₅)(C ₃ H ₅)(C ₁₈ H ₁₆ NP)]-PF ₆ | Z = 8 |
| <i>M_r</i> = 709.40 | <i>D_x</i> = 1.787 Mg m ⁻³ |
| Orthorhombic, <i>Pbca</i> | Mo Kα radiation |
| <i>a</i> = 15.384 (2) Å | <i>μ</i> = 2.29 mm ⁻¹ |
| <i>b</i> = 17.603 (2) Å | <i>T</i> = 123 (2) K |
| <i>c</i> = 19.469 (2) Å | Block, orange |
| <i>V</i> = 5272.4 (11) Å ³ | 0.38 × 0.31 × 0.25 mm |

Data collection

| | |
|--|---|
| Bruker SMART CCD area-detector diffractometer | 59992 measured reflections |
| <i>ω</i> scans | 7663 independent reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | 6108 reflections with <i>I</i> > 2σ(<i>I</i>) |
| <i>T</i> _{min} = 0.458, <i>T</i> _{max} = 0.564 | <i>R</i> _{int} = 0.037 |
| | <i>θ</i> _{max} = 30.0° |

Refinement

| | |
|---|---|
| Refinement on <i>F</i> ² | <i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0224 <i>P</i>) ² + 3.5883 <i>P</i>] |
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.023 | where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3 |
| <i>wR</i> (<i>F</i> ²) = 0.056 | (Δ/σ) _{max} = 0.002 |
| <i>S</i> = 1.04 | Δρ _{max} = 0.50 e Å ⁻³ |
| 7663 reflections | Δρ _{min} = –0.28 e Å ⁻³ |
| 352 parameters | |
| H atoms treated by a mixture of independent and constrained refinement | |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|----------|-------------|----------|-------------|
| Ru–C1 | 2.243 (2) | Ru–P1 | 2.3754 (5) |
| Ru–C2 | 2.218 (2) | Ru–Br | 2.5298 (3) |
| Ru–C3 | 2.189 (2) | C6–C7 | 1.402 (3) |
| Ru–C4 | 2.196 (2) | C7–C8 | 1.400 (3) |
| Ru–C5 | 2.233 (2) | P1–C9 | 1.815 (2) |
| Ru–C6 | 2.220 (2) | P1–C15 | 1.814 (2) |
| Ru–C7 | 2.175 (2) | P1–N | 1.6714 (15) |
| Ru–C8 | 2.243 (2) | N–C21 | 1.419 (2) |
| C7–Ru–P1 | 94.68 (6) | C6–C7–C8 | 116.6 (2) |
| C7–Ru–Br | 87.06 (6) | P1–N–C21 | 127.17 (13) |
| P1–Ru–Br | 85.053 (15) | | |

Table 2
Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------|----------|-------------|-------------|---------------|
| $N-H\cdots Br$ | 0.77 (2) | 2.65 (2) | 3.2206 (16) | 132 (2) |

H atoms attached to cyclopentadienyl and phenyl groups were placed in calculated positions and constrained to ride on their parent atoms with C–H distances of 0.95 Å. The positions of allyl and N-bound H atoms were refined freely. The isotropic displacement parameters of all H atoms were set at $U_{iso}(H) = 1.2U_{eq}(C,N)$ of their carrier atoms.

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

Financial support by the FWF Austrian Science Fund is gratefully acknowledged (project No. P16600-N11).

References

- Becker, E., Slugovc, C., Rüba, E., Standfest-Hauser, C., Mereiter, K., Schmid, R. & Kirchner, K. (2002). *J. Organomet. Chem.* **649**, 55–63.
- Bruker (1999). *SAINT* (Version 6.01), *SMART* (Version 5.054) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Jimenez-Tenorio, M., Puerta, M. C. & Valerga, P. (2005). *Eur. J. Inorg. Chem.* pp. 2631–2640.
- Pavlik, S., Jantscher, F., Dazinger, G., Mereiter, K. & Kirchner, K. (2006). *Eur. J. Inorg. Chem.* pp. 1006–1021.
- Pavlik, S., Jantscher, F., Mereiter, K. & Kirchner, K. (2005). *Organometallics*, **24**, 4899–4901.
- Pavlik, S., Mereiter, K., Puchberger, M. & Kirchner, K. (2005). *Organometallics*, **24**, 3561–3575.
- Pavlik, S., Mereiter, K., Schmid, R. & Kirchner, K. (2003). *Organometallics*, **22**, 1771–1774.
- Priya, S., Balakrishna, M. S., Mobin, S. M. & McDonald, R. (2003). *J. Organomet. Chem.* **688**, 227–235.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.