ligand in cis-Pt(NH₃)(cyclobutylamine)Cl₂ (toxicity ~ 10 mg kg⁻¹) has also been observed (Rochon & Melanson, 1986). The crystal structure of cis-Pt-(cpa)₂Cl₂ could provide further information, but so far it has not been possible to obtain the compound in a suitable crystalline form.

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Structure of a Rh^I Complex of a Bis(2,3-quinolino)-annulated cis,syn,cis-Tricyclo[6.3.0.0³,⁷]undecane*

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Abstract. [Rh(cod)(bqtu)]BF₄ (2), $C_{33}H_{32}N_2Rh.BF_4$, $M_r = 646.35$, orthorhombic, Pcmn, $a = 8.793$ (2), $b = 14.957$ (2), $c = 20.665$ (3) Å, $V = 2717.7$ (6) Å³, $Z = 4$, $D_x = 1.580$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 6.59$ cm⁻¹, $F(000) = 1320$, $T = 294$ K, $R = 0.0546$ for 1829 reflections. The structure contains mononuclear ions with square-planar geometry about the Rh^I atom. The Rh^I atom is coordinated to the two double bonds of the 1,5-cyclooctadiene (cod) ligand and to two N atoms from the new bqtu ligand, (1). The two midpoints of the double bonds and the two N atoms form the square-planar geometry. The axial sites are shielded by H atoms from the two ligands. The heptacyclic bqtu ligand has cis-fusion to the central five-membered ring leading to a folded conformation resulting in a cleft between π-electron systems with a syn-orientation of N atoms. The angle between these two systems is 87·0 (8)°.
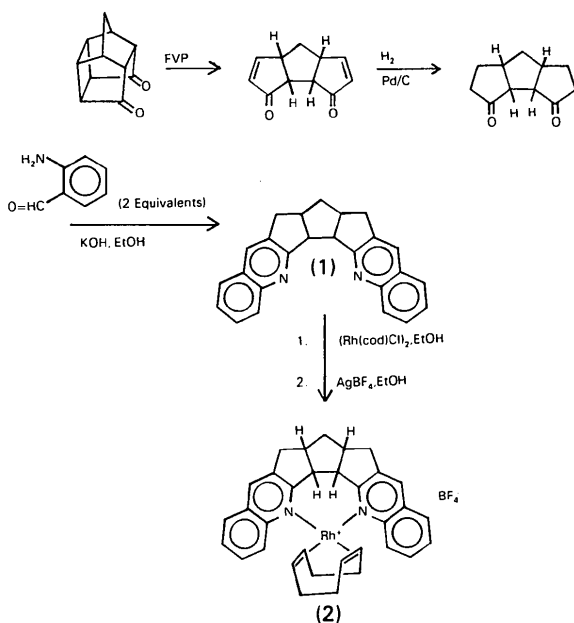
Introduction. Our research groups are interested in fused-ring systems which exhibit significant strain energies, strong intramolecular interactions, enhanced or unusual reactivities or unusual geometric shapes (Marchand, 1988; Watson, 1982; Vögtle, Müller & Watson, 1984). Recently, the heptacyclic ligand (1), a bis(2,3-quinolino) derivative of cis,syn,cis-tricyclo-

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|6.3.0.0^{3,7}|undecane, was prepared as indicated in the scheme (Marchand & Annapurna, 1988) and the crystal structure was determined (Marchand, Annapurna, Flippen-Anderson, Gilardi & George, 1988). Many potentially binucleating ligands such as 1,8-naphthyridine (Tiripicchio, Camellini, Uson, Oro, Ciriano & Viguri, 1984), 7-azaindole (Oro, Ciriano, Villarroya, Tiripicchio & Lahoz, 1984) and pyrazole and its derivatives (Uson, Oro, Ciriano, Carmona, Tiripicchio & Camellini, 1982) form complexes in which the ligand bridges binuclear Rh$_2$ units. In the case of amidinato complexes of Rh^I with cod (1,5-cyclooctadiene), tfbb (tetrafluorobenzo|5,6|bicyclo|2.2.2|-octa-2,5,7-triene) and nbd (norbornadiene) both mononuclear and binuclear Rh^I complexes can be prepared depending upon the nature of the two ligands and upon the resulting steric interactions (Lahoz, Tiripicchio, Camellini, Oro & Pinillos, 1985). In some cases monomer–dimer equilibria have been observed by NMR techniques (Knoth, 1973). In order to investigate the complexing properties of ligand (1) and the geometry and steric character, we have prepared the mononuclear Rh^I species (2) with cod and the tetrafluoroborate anion (see scheme).

Experimental. Reaction of an ethanol solution of (1) with an ethanol solution of rhodium(cod)chloride dimer at ambient temperature followed by addition of AgBF$_4$ (Yamamoto, Watanabe, Chikamatsu, Okamoto & Yoshida, 1987) afforded the Rh^I complex (2) as a pale orange microcrystalline solid, m.p. 513–518 K. Recrystallization from ethanol yielded a sample suitable for X-ray investigations.

A yellow-orange crystal 0.10 × 0.25 × 0.25 mm; Nicolet R3m/μ update of a P2$_1$ diffractometer; data collected in the ω-scan mode ($3 \leq 2\theta \leq 50°$), scan rate 4 to 29.3° min^{-1}, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($30.39 \leq 2\theta \leq 36.91°$); systematic absences ($hk0, h+k = 2n+1; 0kl, l = 2n+1$) and Laue symmetry mmm consistent with space group Pcmn; monitored reflections (0,0,10 and 361) showed only statistical variations in intensities; 2505 unique reflections measured ($0 \leq h \leq 10, 0 \leq k \leq 17, 0 < l \leq 24$), $1829 \geq 3\sigma(I)$; Lorentz–polarization corrections applied, ψ-scan empirical absorption correction (transmission factors 0.873 to 0.951), structure solved by direct methods, block-cascade least-squares refinement, H atoms located in a difference map but atoms allowed to ride at fixed distances from attached C atoms with an isotropic thermal parameter refined for each of the organic moieties; final $R = 0.0546$, $wR = 0.0336$ for 196 parameters and 1829 reflections ($R = 0.0829$ and $wR = 0.0375$ for all 2505 reflections), $S = 1.415$, $(\Delta/\sigma)_{max} = 0.008$; largest peaks in the final difference map of +0.63 and −0.70 e Å^{-3} located near the Rh atom; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/\sigma^2(F_o)$; isotropic extinction correction $F = F_c/|1 + 0.002xF_c^2/\sin(2\theta)|^{0.25}$ applied with x refined to 0.00008 (2). All computer programs supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configuration (Nicolet Instrument Corporation, 1986); atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Table 1 lists atomic positional parameters and U_{eq} values while Table 2 lists interatomic distances and valence angles. Fig. 1 is a drawing of the title compound.*

Discussion. The Rh^I complex contains isolated mononuclear ions having crystallographic C_s symmetry. The Rh^I atom, the two N atoms and the midpoints (MP) of the two double bonds form an approximate square-planar array (r.m.s.d. = 0.03 Å) with two Rh^I–N distances of 2.084 (4) Å and two Rh–MP distances of 2.033 (6) Å. The N–Rh–N, N–Rh–MP and MP–Rh–MP angles are 81.9 (2), 95.3 (2) and 87.1 (2)°, respectively and the N···N separation is 2.734 (6) Å which may be compared with the values of 3.19 and 3.54 Å observed for two independent molecules of the uncomplexed ligand (1) (Marchand, Annapurna, Flippen-Anderson, Gilardi & George, 1988). The axial sites of the Rh^I ion are shielded effectively by H(10), H(13), H(15), H(16) and the mirror-related H atoms. The Rh–N, Rh–MP and Rh–C distances |2.150 (6) and 2.145 (5) Å| are consistent with the values reported

$C_{33}H_{32}N_2Rh.BF_4$

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq}^*
Rh	1404 (1)	2500	1141 (1)	28 (1)
C(1)	−1350 (11)	2500	−1096 (4)	52 (3)
C(2)	−374 (7)	3305 (4)	−931 (2)	45 (2)
C(3)	−1314 (7)	4145 (3)	−778 (2)	47 (2)
C(4)	−1481 (7)	4136 (3)	−53 (3)	39 (2)
C(5)	−2386 (7)	4627 (4)	347 (3)	44 (2)
C(6)	−2279 (6)	4505 (3)	1016 (3)	40 (2)
C(7)	−3243 (7)	4948 (4)	1463 (3)	59 (2)
C(8)	−3146 (7)	4782 (4)	2098 (3)	62 (3)
C(9)	−2095 (7)	4183 (4)	2344 (3)	55 (2)
C(10)	−1117 (6)	3741 (4)	1934 (3)	45 (2)
C(11)	−1196 (6)	3889 (3)	1265 (2)	36 (2)
N	−249 (5)	3414 (3)	849 (2)	30 (1)
C(12)	−450 (6)	3525 (3)	214 (2)	30 (2)
C(13)	432 (6)	3036 (3)	−291 (2)	34 (2)
C(14)	4581 (8)	2992 (4)	744 (3)	79 (3)
C(15)	3229 (6)	3434 (4)	1012 (3)	45 (2)
C(16)	2804 (7)	3438 (4)	1657 (3)	48 (2)
C(17)	3677 (9)	2996 (4)	2183 (3)	89 (3)
B	507 (15)	2500	3748 (6)	59 (5)
F(1)	−12 (7)	3203 (3)	4062 (3)	154 (3)
F(2)	2017 (7)	2500	3719 (4)	147 (4)
F(3)	−40 (10)	2500	3179 (3)	228 (7)

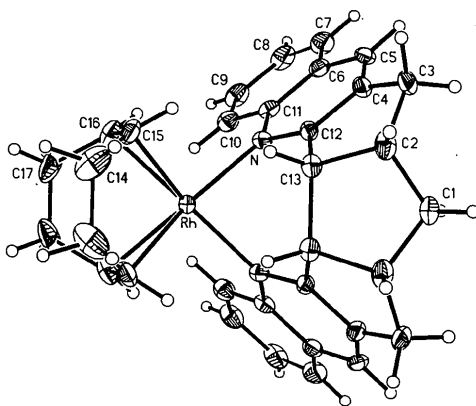* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Fig. 1. Drawing of compound (2) with thermal ellipsoids drawn at the 25% probability level. H atoms represented by spheres of arbitrary size.

Table 2. Bond lengths (Å) and angles (°)

A refers to atoms related by the mirror plane.

Rh—N	2·084 (4)		Rh—C(15)	2·145 (5)
Rh—C(16)	2·150 (6)		Rh—N(A)	2·084 (4)
Rh—C(15A)	2·145 (5)		Rh—C(16A)	2·150 (6)
C(1)—C(2)	1·518 (8)		C(1)—C(2A)	1·518 (8)
C(2)—C(3)	1·537 (8)		C(2)—C(13)	1·553 (7)
C(3)—C(4)	1·506 (7)		C(4)—C(5)	1·363 (8)
C(4)—C(12)	1·400 (7)		C(5)—C(6)	1·398 (8)
C(6)—C(7)	1·417 (8)		C(6)—C(11)	1·422 (7)
C(7)—C(8)	1·339 (10)		C(8)—C(9)	1·384 (9)
C(9)—C(10)	1·375 (8)		C(10)—C(11)	1·403 (7)
C(11)—N	1·391 (6)		N—C(12)	1·333 (6)
C(12)—C(13)	1·491 (7)		C(13)—C(13A)	1·605 (9)
C(14)—C(15)	1·468 (9)		C(14)—C(14A)	1·473 (12)
C(15)—C(16)	1·386 (8)		C(16)—C(17)	1·486 (9)
C(17)—C(17A)	1·483 (13)		B—F(1)	1·318 (9)
B—F(2)	1·329 (15)		B—F(3)	1·270 (14)
B—F(1A)	1·318 (9)			

N—Rh—C(15)	93·4 (2)		N—Rh—C(16)	96·6 (2)
C(15)—Rh—C(16)	37·6 (2)		N—Rh—N(A)	81·9 (2)
C(15)—Rh—N(A)	155·9 (2)		C(16)—Rh—N(A)	166·1 (2)
C(16)—Rh—C(15A)	93·4 (2)		C(15)—Rh—C(15A)	81·3 (3)
C(16)—Rh—C(16A)	81·5 (3)		C(2)—C(1)—C(2A)	105·0 (7)
C(15A)—Rh—C(16A)	37·6 (2)		C(1)—C(2)—C(13)	104·1 (5)
C(1)—C(2)—C(3)	113·0 (5)		C(2)—C(3)—C(4)	104·4 (4)
C(3)—C(2)—C(13)	106·4 (4)		C(3)—C(4)—C(12)	109·7 (5)
C(3)—C(4)—C(12)	130·9 (5)		C(4)—C(5)—C(6)	119·3 (5)
C(5)—C(4)—C(12)	119·4 (5)		C(5)—C(6)—C(11)	119·2 (5)
C(5)—C(6)—C(7)	122·9 (5)		C(6)—C(7)—C(8)	120·9 (6)
C(7)—C(6)—C(11)	117·9 (5)		C(8)—C(9)—C(10)	120·2 (6)
C(7)—C(8)—C(9)	121·5 (6)		C(6)—C(11)—C(10)	119·4 (5)
C(9)—C(10)—C(11)	120·0 (5)		C(10)—C(11)—N	119·9 (4)
C(6)—C(11)—N	120·6 (4)		Rh—N—C(12)	117·3 (3)
Rh—N—C(11)	125·0 (3)		C(4)—C(12)—N	123·7 (4)
C(11)—N—C(12)	117·6 (4)		N—C(12)—C(13)	123·9 (4)
C(4)—C(12)—C(13)	112·3 (4)		C(2)—C(13)—C(13A)	105·0 (3)
C(2)—C(13)—C(12)	103·4 (4)		C(15)—C(14)—C(14A)	116·8 (3)
C(12)—C(13)—C(13A)	119·4 (3)		Rh—C(15)—C(16)	71·4 (3)
Rh—C(15)—C(14)	111·0 (4)		Rh—C(16)—C(15)	71·0 (3)
C(14)—C(15)—C(16)	125·7 (5)		C(15)—C(16)—C(17)	124·3 (5)
Rh—C(16)—C(17)	111·6 (4)		F(1)—B—F(2)	111·6 (7)
C(16)—C(17)—C(17A)	116·4 (3)		F(2)—B—F(3)	109·7 (10)
F(1)—B—F(3)	109·0 (7)		F(2)—B—F(1A)	111·6 (7)
F(1)—B—F(1A)	105·9 (10)			

for similar complexes (Tiripicchio, Camellini, Uson, Oro, Ciriano & Viguri, 1984; Oro, Ciriano, Villarroya, Tiripicchio & Lahoz, 1984; Lahoz, Tiripicchio, Camellini, Oro & Pinillos, 1985).

The central five-membered ring of ligand (1) is in an envelope conformation with the C(1) flap pointed away from the H-atom side. The other five-membered rings are in flattened envelope conformations and are cis-fused to the central ring. The mean planes through the central and adjacent five-membered rings make an angle of 53·4 (8)°, and the cis-fusion of the two outside five-membered rings results in a folded conformation with a molecular cleft between the π-electron systems.

The two N atoms are in a syn-orientation. The angle between the two planar halves forming the cleft is 87·0 (8)°. The pyridyl and phenyl rings are each planar (0·015 and 0·004 Å r.m.s.d., respectively) and the pyridyl ring makes an angle of 5·4 (8)° with the adjacent five-membered ring and 3·7 (8)° with the phenyl ring.

The bite angle N—Rh—N of ligand (1) in the complex is 81·9 (2)° with the lone pairs pointing almost directly toward the Rh^I ion $|C(5)-N-Rh = 175·1 (2)°|$. Unlike the naphthyridine ring in which the lone pairs have a parallel relationship and pyrazole in which the lone pairs point away from each other, the ligand (1) is probably best suited for chelating a single ion rather than bridging. Binuclear bridges would also encounter considerable steric congestion with the cod ligands. Replacement by CO should remove these steric constraints and test the binuclear complexing ability of ligand (1).

The cyclooctadiene ring exhibits a tub conformation with the four-atom segments being planar and exhibiting an interplanar angle of 56·9 (6)°.

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Bis(méthanesulfonate) de Tétraammine-*trans*-dichloroplatine(IV) Monohydrate

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Abstract. $[PtCl_2(NH_3)_4].2CH_3SO_3.H_2O$, $M_r = 542\cdot3$, monoclinic, $C2/m$, $a = 19\cdot406$ (2), $b = 7\cdot482$ (1), $c = 12\cdot456$ (2) Å, $\beta = 122\cdot84$ (1)°, $V = 1519\cdot5$ (9) Å³, $Z = 4$, $D_x = 2\cdot37$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0\cdot7107$ Å, $\mu = 9\cdot98$ mm⁻¹, $F(000) = 1040$, $T = 294$ (1) K, $R = 0\cdot020$ for 1389 independent reflections. The structure consists of CH_3SO_3 anions, $[PtCl_2(NH_3)_4]^{2+}$ cations and water molecules. Each independent Pt atom is at a centre of symmetry and has an octahedral environment. All molecular parameters are similar to those obtained for other related compounds. Numerous O—H···O, N—H···O and N—H···Cl hydrogen bonds take part in the cohesion of the structure.

Introduction. Le bis(méthanesulfonate) de tétraammine-*trans*-dichloroplatine(IV) monohydrate a été préparé à la température ambiante, en ajoutant un excès de peroxyde d'hydrogène et d'acide chlorhydrique, pris l'un et l'autre en solutions concentrées, à un mélange de bis(méthanesulfonate) de tétraammineplatine(II) et d'acide méthanesulfonique en solution aqueuse.

L'évaporation lente de cette solution a donné un résidu incolore dans lequel a été prélevé le cristal soumis à l'analyse structurale. Celle-ci a été entreprise dans le cadre de l'étude des dérivés formés par le platine avec l'ammoniac et les polyamines aliphatiques. Elle a eu pour objectif de déterminer la nature des entités chimiques qui constituent le produit étudié.

Partie expérimentale. Cristal parallélépipédique: $0,10 \times 0,22 \times 0,40$ mm. Diffractomètre Enraf–Nonius CAD-4. Dimensions de la maille déterminées avec 25 réflexions telles que $6,59 \le \theta \le 15,13°$. $0,039 \le (\sin\theta)/\lambda \le 0,650$ Å⁻¹; $-25 \le h \le 20$, $0 \le k \le 9$, $0 \le l \le 16$. Balayage $\theta/2\theta$ d'amplitude $s(°) = 0,80 + 0,35$tgθ. Réflexions de contrôle des intensités: $11\overline{4}$, $\overline{6}04$ et $73\overline{6}$. 1883 réflexions indépendantes mesurées, 494 réflexions inobservées [$I < 2\sigma(I)$]. $\sigma(I)/I$ moyen (contrôle) = 0,0030. Corrections d'absorption (Walker & Stuart, 1983). Valeurs maximale et minimale du coefficient de correction: 1,251 et 0,853. Méthode de l'atome lourd; H non localisés avec certitude. Affinement basé sur les