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***trans*-Carbonyl[η^2 -dihydrobis(pyrazol-1-yl-*N*²)borato]hydridobis(triphenylarsine)-ruthenium(II) monohydrate**

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Abstract

The molecule of the title compound, [RuH(C₆H₈BN₄)-(C₁₈H₁₅As)₂(CO)]·H₂O, is a discrete monomeric complex which has the hydride, carbonyl and dihydrobis(pyrazol-1-yl)borate ligands in equatorial positions, and two *trans*-positioned AsPh₃ ligands. The geometry around the Ru^{II} atom is distorted octahedral. In addition to the water dimer formed by strong intermolecular hydrogen bonds, two possible weak intramolecular hydrogen bonds have been observed within the complex.

Comment

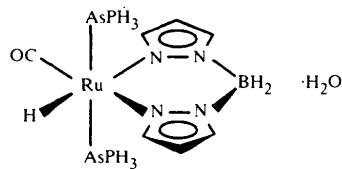
A variety of poly(pyrazol-1-yl)borates have been prepared and used in transition metal or main-group chemistry for three decades because of their versatile electronic and steric properties (Trofimenko, 1993). Most

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effort has been focused on the possible tridentate ligands [HB(pz^{*})₃][−] (pz^{*} is pyrazol-1-yl with various substituents at the 3, 4 or 5 positions). However, the study of Ru^{II} complexes with these ligands has been initiated only very recently. Furthermore, compounds of Ru^{II} with bidentate dihydrobis(pyrazol-1-yl)borates are very scarce.

We have been studying the reaction of bidentate dihydrobis(pyrazol-1-yl)borates with [RuHCl(CO)(PPh₃)₃]. Hydridocarbonyl–Ru^{II} complexes bearing several bidentate dihydrobis(pyrazol-1-yl)borates have been prepared by our group (Huh *et al.*, 1999); they are indefinitely air stable in the solid state. The crystal structures of two of them, namely [RuH(CO)(PPh₃)₂(η^2 -H₂Bpz₂)] and [RuH(CO)(PPh₃)₂{ η^2 -H₂B(4-Brpz₂)}] (pz is pyrazol-1-yl), have been solved. Unlike the latter compound, the former shows a high degree of hydrogen-bond interaction, in which four intramolecular and one intermolecular hydrogen bond can be accounted for. The two PPh₃ ligands adopt a staggered conformation based on the *ipso*-C atoms, while the latter compound shows an eclipsed conformation.

Stimulated by this interesting difference, we have synthesized one of the AsPh₃ analogues, [RuH(CO)-(AsPh₃)₂(η^2 -H₂Bpz₂)], (1), to compare its structure with the corresponding PPh₃ analogues. The title compound cocrystallizes with one solvent water molecule. Basically, the geometrical structures around the Ru^{II} metal centres are the same. However, we have observed only two probable hydrogen-bond interactions in (1) apart from the hydrogen bonds between two adjacent solvent water molecules. There are two possible weak hydrogen-bond interactions, C3—H3···N1 and C25—H25···N4; their respective donor–acceptor distances and angles at hydrogen are 3.413(9)/3.469(9) Å and 145/157°. Adjacent water molecules form a dimer by way of intermolecular hydrogen bonds, which must be disordered across an inversion centre. The title compound shows a staggered conformation of the two AsPh₃ ligands relative to the *ipso*-C atoms, similar to [RuH(CO)(PPh₃)₂(η^2 -H₂Bpz₂)].



(1)

The coordination geometry of (1) is distorted octahedral with two *trans*-positioned AsPh₃ in axial positions and the remaining ligands in equatorial positions. The Ru—As bond distances are almost the same, 2.4393(8) and 2.4485(7) Å. These bond lengths are longer than those of the PPh₃ analogue, which has Ru—P distances of 2.3576(12) and 2.3482(12) Å. These longer

distances can be explained by the greater radius of As relative to P. As a result, this difference may be related to the lower extent of intramolecular hydrogen-bond interactions within compound (1). The Ru1—H1 and Ru1—CO bond distances are normal, as is seen for other hydridocarbonyl—Ru^{II} complexes. The Ru1—N1 distance, 2.181(5) Å, is rather long relative to Ru1—N3, 2.138(5) Å. At first, this difference seems unreasonable because carbonyl usually shows a greater *trans* effect than hydride. Therefore, we conclude that this difference may result from the combined effect of crystal packing and the *trans* effect. This tendency has also been observed for [RuH(CO)(PPh₃)₂(η^2 -H₂Bpz₂)] and [RuH(CO)(PPh₃)₂{ η^2 -H₂B(4-Brpz)₂}].

pyrazolyl rings are planar. The angle between these two rings is 139.1(2)°. The angles made by the Ru equatorial plane and the two pyrazolyl rings are 24.6(7) and 25.9(2)°. The Ru—N—N—B torsion angles are -6.0(8) (Ru1—N1—N2—B1) and 17.6(7)° (Ru1—N3—N4—B1). Other bond lengths and angles of the phenyl and pyrazolyl rings are normal.

The solvent water molecule is involved in an intermolecular hydrogen-bond interaction with its neighbouring centrosymmetrically related molecule to form a dimer. Although the water H atoms could not be located, the separation of the two O atoms is only 2.77(2) Å. This value is much less than that of the water dimer, 2.96 Å, formed by a hydrogen bond in the results of Odulota *et al.* (1979).

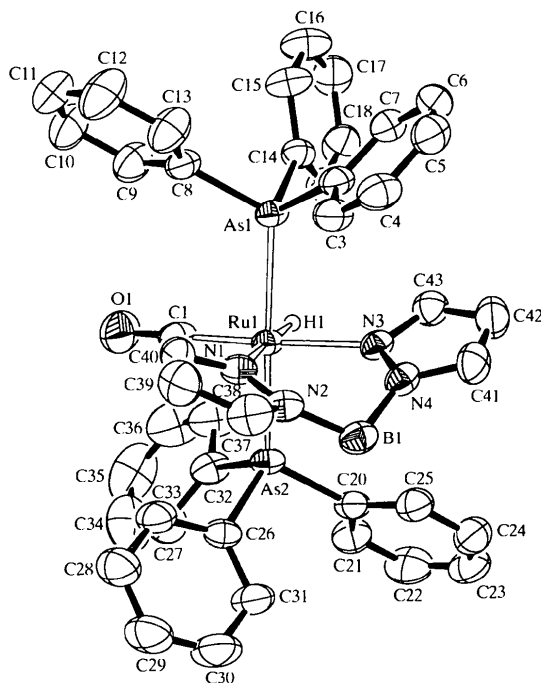


Fig. 1. View of compound (1). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms have been omitted, except for the hydride, which is represented with an arbitrary radius.

The distortion of the octahedral coordination is mainly due to the tetrahedral environment of the borate ligand and the small size of the hydride. The As1—Ru1—As2 angle of 171.53(3)° deviates from the ideal value of 180° by about 10°. The two AsPh₃ ligands lean toward the small hydride, as is seen from the two As—Ru1—H1 angles which are less than 90°. The tetrahedral environment of B1 is somewhat distorted. The angle with the greatest deviation from 109.5° is H44—B1—H45 of 118(5)°.

The five atoms Ru1, H1, C1, N1 and N3 are almost coplanar (r.m.s. deviation 0.0262 Å). The two

Experimental

The title compound was prepared according to literature methods (Huh *et al.*, 1999; Cartwright *et al.*, 1990). A suspension of [RuHCl(CO)(AsPh₃)₃] (520 mg, 0.5 mmol; Sánchez-Delgado *et al.*, 1990) and K[H₂Bpz₂] (130 mg, 0.7 mmol; Trofimenko, 1970) in dried toluene (30 ml) was heated under reflux for 15 h under a nitrogen atmosphere. The cooled solution was filtered to remove any insolubles and rotary evaporated to dryness. After dissolving the residue in a small amount of acetone (5 ml), the solution was set aside in air. Yellow crystals were obtained within a few hours by slow evaporation of the solvent. Crystallization of the product from acetone by slow evaporation in air produced yellow X-ray quality crystals. ¹H NMR (293 K, CDCl₃, TMS): δ (Ru—H) -12.4 (s) p.p.m.

Crystal data

[RuH(C₆H₈BN₄)-(C₁₈H₁₅As)₂(CO)]·H₂O
M_r = 907.52
 Triclinic
P $\bar{1}$
a = 9.569(1) Å
b = 12.023(1) Å
c = 19.556(1) Å
 α = 103.82(1)°
 β = 91.43(1)°
 γ = 110.25(1)°
V = 2035.3(3) Å³
Z = 2
D_x = 1.481 Mg m⁻³
D_m not measured

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 9.29–12.28°
 μ = 2.039 mm⁻¹
T = 293(2) K
 Block
 0.50 × 0.45 × 0.40 mm
 Yellow

Data collection

Enraf-Nonius CAD-4 MACH3 diffractometer
 2 θ - ω scans
 Absorption correction: none
 7617 measured reflections
 7147 independent reflections
 5397 reflections with *I* > 2 σ (*I*)

*R*_{int} = 0.015
 θ _{max} = 25.01°
h = 0 → 11
k = -14 → 13
l = -23 → 23
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.153$
 $S = 1.118$
 7147 reflections
 490 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2 + 6.2199P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.715 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.636 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ru1—C1	1.823 (7)	C1—O1	1.159 (8)
Ru1—N3	2.138 (5)	N1—N2	1.360 (7)
Ru1—N1	2.181 (5)	N2—B1	1.544 (10)
Ru1—As2	2.4393 (8)	N3—N4	1.359 (7)
Ru1—As1	2.4485 (7)	N4—B1	1.540 (9)
Ru1—H1	1.78 (6)		
C1—Ru1—N3	177.0 (2)	C1—Ru1—H1	88 (2)
C1—Ru1—N1	94.1 (3)	N3—Ru1—H1	90.8 (19)
N3—Ru1—N1	87.60 (19)	N1—Ru1—H1	178 (2)
C1—Ru1—As2	88.09 (19)	As2—Ru1—H1	83 (2)
N3—Ru1—As2	94.12 (13)	As1—Ru1—H1	89 (2)
N1—Ru1—As2	96.46 (13)	O1—C1—Ru1	178.9 (6)
C1—Ru1—As1	91.13 (19)	N2—N1—Ru1	123.8 (4)
N3—Ru1—As1	86.39 (13)	N1—N2—B1	123.0 (5)
N1—Ru1—As1	92.01 (13)	N4—N3—Ru1	123.6 (4)
As2—Ru1—As1	171.53 (3)	N3—N4—B1	123.4 (5)

H atoms bonded to Ru1 and B1 were refined freely; others were constrained with a riding model. The H atoms of the water molecule were not located; they are presumably disordered. The largest residual peak is 1.14 Å from O2 of the water molecule.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *CAD-4-PC Software*. Data reduction: *XCAD4* (Harms, 1997). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1291). Services for accessing these data are described at the back of the journal.

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Di- μ -chloro-bis{chloro[(4a,5,6,7,8,8a- η^6)-1,2,3,4-tetrahydronaphthalene]-ruthenium(II)}

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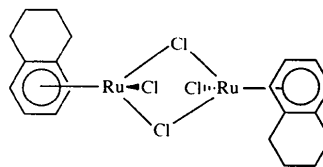
(Received 30 July 1998; accepted 3 March 1999)

Abstract

The title compound, $[\{\text{RuCl}(\eta^6\text{-C}_{10}\text{H}_{12})\}_2(\mu\text{-Cl})_2]$ or $[\text{Ru}_2\text{Cl}_4(\text{C}_{10}\text{H}_{12})_2]$, has the expected edge-sharing bi-octahedral geometry, in which two crystallographically related [(4a,5,6,7,8,8a- η^6)-1,2,3,4-tetrahydronaphthalene]RuCl₂ moieties are asymmetrically bridged by two symmetry-related Cl atoms, with Ru— μ -Cl bond lengths of 2.438 (1) and 2.440 (1) Å, and a terminal Ru—Cl bond length of 2.397 (1) Å.

Comment

In the course of investigations into transition metal stabilized *o*-xylylene (*o*-quinodimethane) complexes (Bennett *et al.*, 1992, 1995; Bennett, Bown & Byrnes, 1998; Bennett, Bown, Hockless *et al.*, 1998; McGrady *et al.*, 1996), we synthesized the chloro-bridged arene-ruthenium dimer $[\text{RuCl}_2\{(4a,5,6,7,8,8a\text{-}\eta^6)\text{-1,2,3,4-tetrahydronaphthalene}\}]_2$, (I). The diffraction analysis was undertaken to investigate the conformation of the (4a,5,6,7,8,8a- η^6)-1,2,3,4-tetrahydronaphthalene (η^6 -tetralin) ligand.



(I)