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Carbonyl[dihydrobis(pyrazol-1-yl-κN^2)borato]hydridobis(tri-*p*-tolylphosphine-κP)ruthenium(II)

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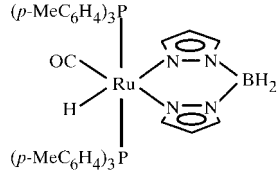
The title compound, $[RuH(C_6H_8BN_4)(C_{21}H_{21}P)_2(CO)]$, possesses two *trans*-disposed tri-*p*-tolylphosphines in axial positions and the remaining ligands in equatorial positions. The overall geometry of the Ru^{II} ion is a distorted octahedral structure. The P—Ru—P axis deviates from linearity by about 13°. This distortion arises mainly from the steric congestion between the bulky phosphine moieties and the tetrahedral dihydrobis(pyrazol-1-yl)borate ligands.

Comment

Our recent structural investigations of several hydrido–carbonyl–Ru^{II} complexes containing bidentate anionic dihydrobis(pyrazol-1-yl)borates, $[H_2B(pz^*)_2]^-$ (pz* = pyrazol-1-yl rings with various substituents), have revealed that these compounds often form novel cyclic dimers consisting of mutual intermolecular hydrogen bonds, namely Ru—C≡O···H, where the H atom belongs to a phenyl or pyrazolyl ring of a neighbouring molecule. We are interested in this type of hydrogen bonding because this motif can be a good candidate for crystal engineering of organometallic compounds. Both $[RuH(PPh_3)_2(\eta^2\text{-}H_2Bpz_2)(CO)]$, (II), and $[RuH(PPh_3)_2\{\eta^2\text{-}H_2B(4\text{-}Brpz)_2\}(CO)]$, (III), display intermolecular hydrogen-bond dimensions of Ru—C≡O···H_{Ph} 2.5834 Å and 144.56°, and Ru—C≡O···H_{pz} 2.5960 Å and 172.23°, where Ph and pz represent phenyl and pyrazolyl rings, respectively (Huh *et al.*, 2000). It is interesting to note that the sources of the hydrogen bonding (H-atom donor groups) are different in each of the compounds studied. Furthermore, such intermolecular hydrogen bonding leading to the dimeric motif was not observed when we prepared the compound $[RuH(AsPh_3)_2(\eta^2\text{-}H_2Bpz_2)(CO)]$, (IV), using $AsPh_3$ in place of PPh_3 (Huh *et al.*, 1999).

In the present study, an analogous Ru^{II} complex having substituted phenyl groups in the PPh_3 moieties has been prepared to test the effect of the structural variation in the PPh_3 moiety on the formation of the dimeric motif. Instead of PPh_3, we have chosen a tri-*p*-tolylphosphine, $P(p\text{-}C_6H_4CH_3)_3$, whose cone angle is also 145° (Tolman, 1977). This ligand has a methyl group at the *para* position of each phenyl ring. In our synthesis of the title compound, $[RuH\{P(p\text{-}C_6H_4CH_3)_3\}_2(\eta^2\text{-}H_2Bpz_2)(CO)]$, (I), we had anticipated obtaining another example of the novel cyclic dimer *via* mutual intermolecular hydrogen bonding. Quite unexpectedly, however, we have not been able to obtain the dimeric motif but only the monomeric form in (I).



(I)

Compound (I) shows the same ligand geometry as (II) and (III). Also, the two Ru—P bond distances are comparable with those of (II) and (III) [2.3578 (12)–2.3841 (12) Å]. However, in (I), Ru1—P2 is longer than Ru1—P1 by about 0.025 Å. Although the *para*-positioned methyl groups of the phosphines do not seem to affect the Ru—P bond distances

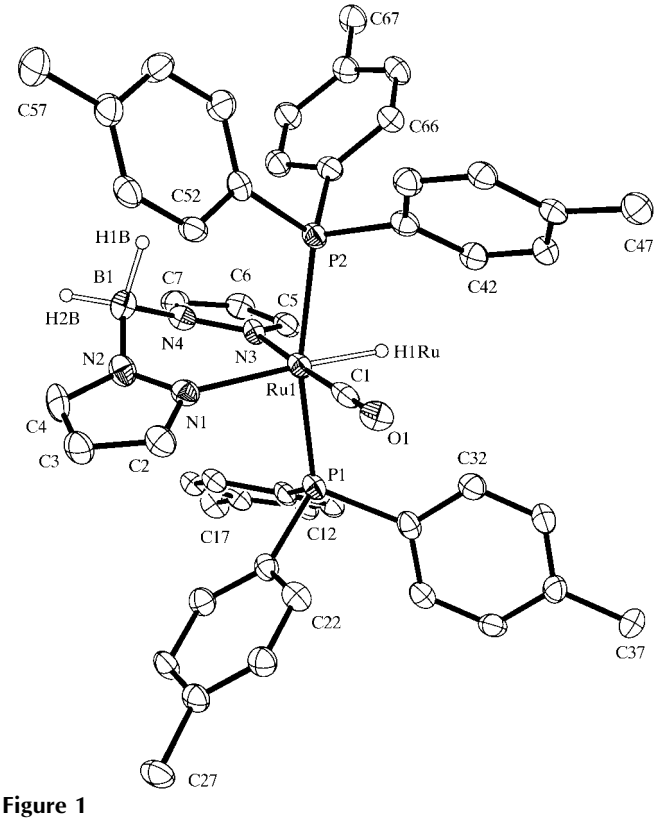


Figure 1
View of the molecule of (I) showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity, except those bonded to B and Ru, which are shown as spheres of arbitrary radii.

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significantly, they do affect the P1—Ru1—P2 bond angle, whose value is 166.69 (5)°.

The two phosphine ligands are tilted toward the small hydride ligand and this is evident from the H1Ru—Ru1—P1 and H1Ru—Ru1—P2 angles of 85.1 (17) and 81.8 (17)°, respectively. This significant deviation from linearity can be attributed to the steric repulsions between the phosphines and the tetrahedral BN_2H_2 moiety, as shown in Fig. 1. The interligand angles of the equatorial donor atoms lie in the range 87.6 (15)–92.36 (19)° and these values are only slightly different from 90°. The bond distances of Ru1 and the other donor atoms are not significantly different from those of complexes (II) and (III). Moreover, the five atoms Ru1, H1Ru, C1, N1 and N3 are almost coplanar; the r.m.s. deviation of these five atoms from the best plane is only 0.035 Å. The angle between the two pyrazolyl rings is 152.2 (4)° and this value is very similar to that in (III).

There are two short intramolecular H···N contacts, C62—H62*A*···N3 and C62—H62*A*···N4, with H···N distances of 2.55 and 2.51 Å, and C—H···N angles of 118 and 149°, respectively.

Experimental

[RuHCl{P(*p*-$C_6H_4CH_3$)$_3$}$_3$(CO)] (324 mg, 0.3 mmol; Stephenson & Wilkinson, 1966) was reacted with K[H_2Bpz$_2$] (74 mg, 0.4 mmol; Trofimenko, 1970) in boiling toluene (30 ml) solution under a nitrogen atmosphere for 18 h, resulting in a green solution. After being cooled and filtered, the clear filtrate was evaporated to dryness on a rotary evaporator. The resultant residue was dissolved in a small amount of acetone (5 ml) and this solution was set aside in air. Colourless crystals were obtained in a few days by slow evaporation of the solvent. X-ray quality crystals were collected from the mother liquor, washed with *n*-hexane and dried in air. Spectroscopic analysis: IR (cm^{-1}, KBr): ν(BH) 2396, 2344, 2294, ν(CO) 1932; ^{1}H NMR (293 K, $CDCl_3$, TMS, Bruker 500 MHz, p.p.m.): δ(Ru—H) −11.8 (*t*, ^2J = 21.5 Hz).

Crystal data

[RuH($C_6H_8BN_4$)($C_{21}H_{21}P$)$_2$(CO)]
M_r = 885.76
Triclinic, $P\overline{1}$
a = 13.3445 (2) Å
b = 13.7089 (2) Å
c = 14.2471 (2) Å
α = 106.644 (7)°
β = 116.816 (8)°
γ = 90.965 (7)°
V = 2195.85 (6) Å^3
Z = 2
D_x = 1.340 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 686 reflections
θ = 4.19–25.10°
μ = 0.471 mm^{-1}
T = 100.0 (1) K
Block, pale yellow
0.25 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offset scans
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.891, T_{max} = 0.954
14 686 measured reflections
7547 independent reflections
4669 reflections with $I > 2\sigma(I)$
R_{int} = 0.103
θ_{max} = 25.10°
$h = 0 \rightarrow 15$
$k = -16 \rightarrow 16$
$l = -16 \rightarrow 14$

Table 1
Selected geometric parameters (Å, °).

Ru1—C1	1.837 (6)	Ru1—P2	2.3699 (17)
Ru1—N1	2.173 (4)	Ru1—H1Ru	1.62 (4)
Ru1—N3	2.132 (4)	O1—C1	1.164 (6)
Ru1—P1	2.3448 (17)		
C1—Ru1—N1	92.36 (19)	N1—Ru1—P2	102.26 (14)
C1—Ru1—N3	177.85 (19)	N3—Ru1—P1	90.53 (14)
C1—Ru1—P1	90.02 (19)	N3—Ru1—P2	90.99 (14)
C1—Ru1—P2	88.00 (18)	N3—Ru1—N1	89.71 (16)
N1—Ru1—P1	90.98 (14)	P1—Ru1—P2	166.69 (5)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.152
S = 0.965
7547 reflections
541 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −0.99 e Å^{-3}

All H atoms were included in calculated postions and treated as riding, except for those bonded to B and Ru which were refined with isotropic displacement parameters.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JA1005). Services for accessing these data are described at the back of the journal.

References

Huh, S., Kim, Y., Park, S., Park, T.-J. & Jun, M.-J. (1999). *Acta Cryst.* C**55**, 850–852.
Huh, S., Kim, Y., Park, Y. J., Youm, K.-T., Choi, M.-G. & Jun, M.-J. (2000). In preparation.
Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1998). *SHELXTL/PC*. Version 5.1. Windows NT Version. Bruker AXS Inc., Madison, Wisconsin, USA.
Stephenson, T. A. & Wilkinson, G. (1966). *J. Inorg. Nucl. Chem.* **28**, 945–956.
Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.
Trofimenko, S. (1970). *Inorg. Synth.* **12**, 100–101.