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Synthesis, Structure, Reactivity, and Solution Behavior of Bis{dicarbonyl[hydridotris(1,2,4-triazolyl)borato]ruthenium(I)}(*Ru–Ru*)

Kom-Bei Shiu* and Wei-Ning Guo

Department of Chemistry, National Cheng Kung University,
Tainan, Taiwan 70101, ROC

Shie-Ming Peng and Ming-Chu Cheng

Department of Chemistry, National Taiwan University,
Taipei, Taiwan 10764, ROC

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Metal–metal-bonded dinuclear compounds, especially those with multiple bonds,[1] are potential building blocks for metallic clusters.[2] Though scission of the σ, π, and δ bonds usually occurs when the dimers react with π-acids such as CO or isocyanides,[3] the metal–metal bonds of some carbonyl-containing dinuclear compounds may be stabilized owing to good σ-bonding. These compounds may serve as suitable models to help our understanding of the conversion of metal–metal multiply bonded dimers to other polynuclear compounds. Previously, we showed that the metal–metal bond of $[Ru_2(O_2CR)_2(CO)_4L_2]$ complexes displays weakening upon coordination of axial donors (L),[4] similar to that of the d^7–d^7 dimers, $[Rh_2(O_2CR)_4L_2]$,[5] or the d^4–d^4 compounds, $[Cr_2(O_2CR)_4L_2]$.[6] These diruthenium compounds, derived from polymeric *catena*-$[Ru(O_2CR)(CO)_2]$, can be viewed as possible intermediates to the conversion of the low-valent cluster compounds (LVCs), such as $[Ru_3(CO)_{12}]$, or the high-valent cluster compounds (HVCs), such as $[Ru_2(O_2CR)_4Cl]$, as defined by Cotton in 1983.[7] In this contribution, however, we wish to show that a slight variation, replacing 1-pyrazolyl (pz) with 1,2,4-triazolyl (tz), can lead to the unexpected results of a Ru–Ru and a Ru–L bond length reduction in $[Ru\{\eta^3\text{-}HB(tz)_3\}(CO)_2]_2$ as compared to its analogue, $[Ru\{\eta^3\text{-}HB(pz)_3\}(CO)_2]_2$.[8]

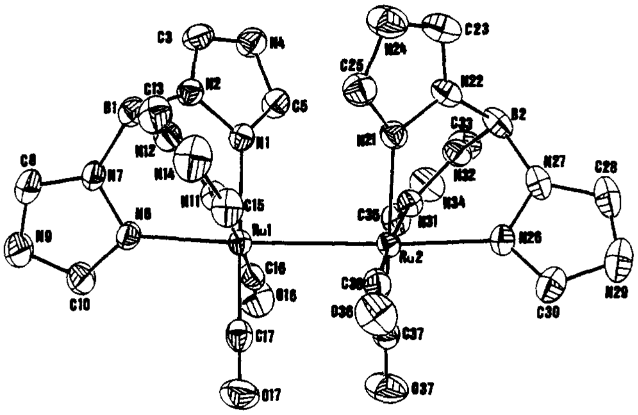

Figure 1. ORTEP drawing of complex $[Ru\{\eta^3\text{-}HB(tz)_3\}(CO)_2]_2$·(1) (50% probability ellipsoids).

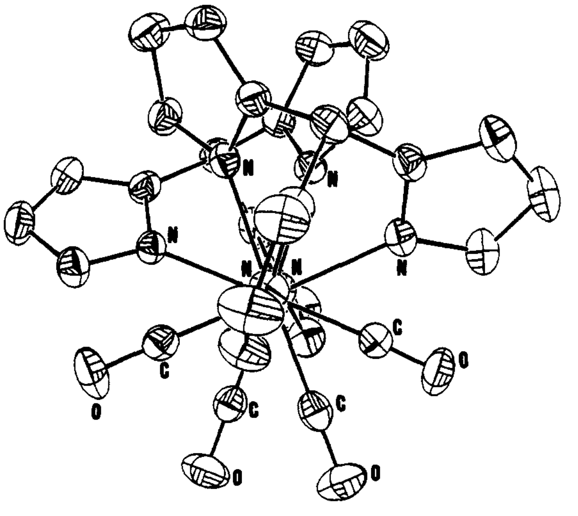

Figure 2. Projection of complex **1** down the Ru–Ru bond.

The dimer $[Ru\{\eta^3\text{-}HB(tz)_3\}(CO)_2]_2$ (**1**) is prepared by a procedure analogous to that for $[Ru\{\eta^3\text{-}HB(pz)_3\}(CO)_2]_2$ (**2**).[8] The crystal structure of **1** (Figure 1) reveals that the Ru–Ru bond length of 2.8688(7) Å is significantly shorter than that of **2** (d(Ru–Ru) = 2.882(1) Å) though both compounds have a similar *cis* staggered geometry with torsional angles ranging from 36.2(1) to 49.2(1)° (Figure 2). (The asymmetry parameters, Ω,[9] are calculated to be 2.26 for C(16)O(16), 2.28 for C(17)O(17), 2.25 for C(36)O(36), and 2.27 for C(37)O(37). These carbonyls are consistent with semibridging carbonyls.) Contrary to the fact that the solid-state structure of **1** has approximate C_2 symmetry, only three carbon singlets responsible for the two types of carbon atoms located at the 3- and 5-triazolyl ring positions, and the carbonyl carbon atoms are observed at 298 K in the $^{13}C\{^1H\}$ NMR spectrum in CD_2Cl_2, indicating that the compound is fluxional in solution. By comparing the variable-temperature NMR spectra of **1** (Figure 3) and **2**,[8] it appears that the fluxional behaviors of these compounds are quite similar, but fluxional behavior should involve participation of the carbonyl groups in the compounds. In this revised mechanism, we propose that the two pairs of the semibridging carbonyls undergo pairwise exchange[10] with synchronous nondissociative rotation[11] of the tris(azolyl)borato group around the Ru---B bond, probably with more or less rotation about the Ru–Ru bond. The spectrum at 298 K of **1** shows two singlet resonances at 8.28 and 7.71 ppm for the two protons of the triazolyl rings (Figure 3), indicating

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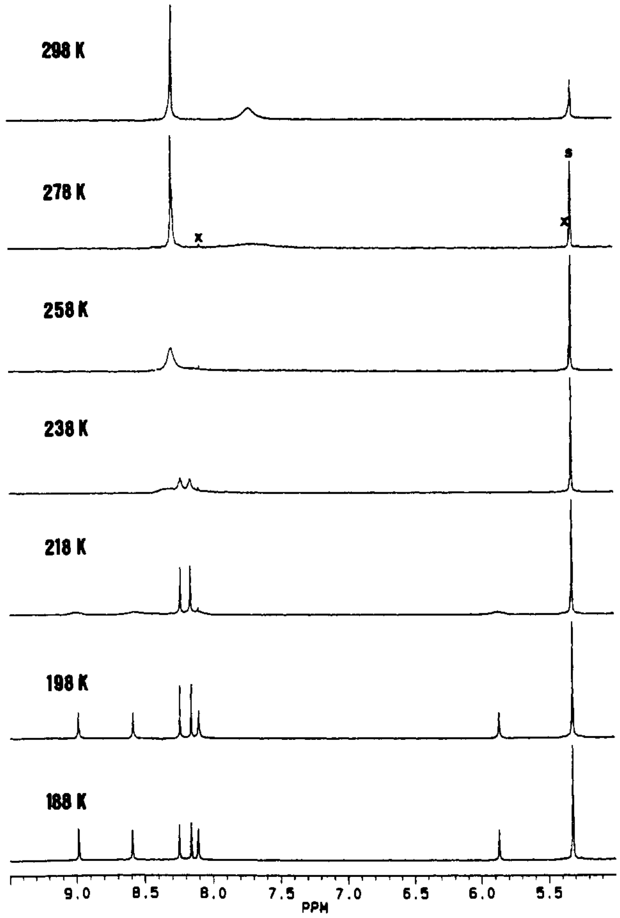

Figure 3. Variable-temperature 300-MHz ^1H NMR spectra of **1** in CD_2Cl_2. The resonances marked (×) are due to impurties and that marked (s) is due to the solvent.

Table 1. Crystal Data for $[Ru\{\eta^3\text{-}HB(tz)_3\}(CO)_2]_2$ (**1**)

formula	$C_{17}H_{16}B_2Cl_2N_{16}O_4Ru_2$
M_r	831.10
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
cell params at 296 K	
a, Å	8.9687(21)
b, Å	14.444(4)
c, Å	23.114(5)
β, deg	99.241(20)
V, Å^3	2955.5(12)
Z	4
D_{calc}, g cm^{-3}	1.868
λ	0.709 30
μ(Mo Kα), mm^{-1}	1.243
T_{min}, T_{max}	0.816–1.000
no. of unique obsd data	4467
R,[a] R_w[b]	0.026, 0.024

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table 2. Atomic Coordinates and B_{iso}[a] for **1**

atom	x	y	z	B_{iso}, Å^2
Ru(1)	0.34506(3)	0.185282(19)	0.053543(12)	1.774(11)
Ru(2)	0.19288(3)	0.276719(19)	−0.049443(12)	1.792(11)
B(1)	0.2783(5)	0.2052(3)	0.18790(18)	2.52(18)
B(2)	−0.1671(5)	0.3201(3)	−0.08890(20)	2.84(20)
N(1)	0.1360(3)	0.16929(18)	0.08689(12)	2.10(12)
N(2)	0.1358(3)	0.17567(19)	0.14602(12)	2.27(13)
C(3)	0.0004(4)	0.1502(3)	0.15640(16)	2.88(17)
N(4)	−0.0910(3)	0.12830(22)	0.10711(13)	3.07(15)
C(5)	−0.0022(4)	0.14133(25)	0.06609(15)	2.55(16)
N(6)	0.4499(3)	0.11530(19)	0.13337(12)	2.24(12)
N(7)	0.4007(3)	0.13196(19)	0.18505(12)	2.32(13)
C(8)	0.4800(4)	0.0767(3)	0.22488(16)	3.45(19)
N(9)	0.5799(4)	0.02613(23)	0.20259(15)	4.19(17)
C(10)	0.5578(4)	0.0529(3)	0.14595(17)	3.35(19)
N(11)	0.3797(3)	0.30497(18)	0.11138(12)	2.19(12)
N(12)	0.3364(3)	0.29750(19)	0.16582(12)	2.24(12)
C(13)	0.3721(4)	0.3770(3)	0.19387(16)	3.10(17)
N(14)	0.4362(4)	0.43687(21)	0.16163(14)	3.71(17)
C(15)	0.4390(4)	0.38884(25)	0.11209(16)	2.94(17)
C(16)	0.3179(4)	0.07783(24)	0.01030(15)	2.32(15)
O(16)	0.3085(3)	0.00892(17)	−0.01401(12)	3.90(13)
C(17)	0.5242(4)	0.20429(23)	0.02522(15)	2.45(16)
O(17)	0.6344(3)	0.21585(19)	0.00753(12)	4.05(14)
N(21)	0.0386(3)	0.34562(19)	−0.00087(13)	2.25(13)
N(22)	−0.1090(3)	0.35721(19)	−0.02705(13)	2.47(13)
C(23)	−0.1769(4)	0.4049(3)	0.01005(19)	3.46(19)
N(24)	−0.0857(4)	0.42608(23)	0.05926(15)	3.90(16)
C(25)	0.0448(4)	0.3880(3)	0.05018(17)	3.06(17)
N(26)	0.0758(3)	0.35568(19)	−0.12307(12)	2.39(12)
N(27)	−0.0774(3)	0.36679(19)	−0.13177(13)	2.60(13)
C(28)	−0.1117(4)	0.4189(3)	−0.17991(17)	3.60(19)
N(29)	0.0076(4)	0.44209(23)	−0.20288(15)	4.10(18)
C(30)	0.1203(4)	0.4015(3)	−0.16618(16)	3.23(19)
N(31)	0.0084(3)	0.18061(18)	−0.07544(12)	2.19(12)
N(32)	−0.1358(3)	0.21532(20)	−0.08999(13)	2.48(14)
C(33)	−0.2236(4)	0.1446(3)	−0.11060(17)	3.19(18)
N(34)	−0.1487(3)	0.06547(21)	−0.11063(15)	3.54(16)
C(35)	−0.0068(4)	0.09148(24)	−0.08936(17)	2.93(17)
C(36)	0.3441(4)	0.36330(24)	−0.03360(15)	2.45(15)
O(36)	0.4363(3)	0.41876(18)	−0.02942(12)	3.98(14)
C(37)	0.3143(4)	0.21218(25)	−0.09262(15)	2.58(16)
O(37)	0.3875(3)	0.17377(20)	−0.12105(13)	4.64(15)
C	0.8424(6)	0.3658(3)	0.2316(3)	6.9(3)
Cl(1)	1.01831(15)	0.33428(10)	0.27082(6)	6.24(7)
Cl(12)	0.71594(16)	0.27434(11)	0.23070(9)	9.18(11)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

equilibration of the three triazolyl rings by rotation about the Ru---B bond. No BH proton is observed due to broadening by the quadruple moment of the boron isotopes. As temperature decreases, both resonances broaden with the latter one gradually unseen. The barrier to rotation about the Ru---B bond in **1** and **2** is similar as reflected by a similar T_c of *ca.* 258 K with $\Delta G^{\ddagger}$ = 12.7 kcal/mol at this temperature. (Knowing that T_c depends on the observing frequency and that T_c shifts upward by *ca.* 10 K when doubling the frequency,[12a] the T_c values used for **2** were estimated from the published spectra of this compound.[8]) The singlet at 8.28 ppm then decomposes at 238 K into one broad resonance at 8.16 ppm and one broader peak at 8.30 ppm with an integration ratio of 1:2, while the singlet at 7.71 ppm decomposes into only one observed peak at 8.23 ppm (Figure 3). A second T_c is shown at *ca.* 220 K ($\Delta G^{\ddagger}$ = 10.2 kcal/mol) for **1**, much lower than that of *ca.* 236 K for **2**. The broad singlet at 8.30 ppm then decomposes at 218 K into two singlets at 8.11 and 8.59 ppm. Finally, the spectrum at 188 K represents the low-temperature limiting spectrum, containing six singlets at 8.98, 8.59, 8.24, 8.16, 8.11, and 5.87 ppm, and corresponds to the solid-state structure. Apparently, the lower T_c (*i.e.*, the faster pairwise exchange of semibridging carbonyls) observed for **1** is compatible with the shorter Ru–Ru bond found in **1**, compared to that in **2**. (Impurity resonances appear pronounced due to the low solubility of **1**. The low solubility in the usual organic solvents precluded variable-temperature measurements of $^{13}C\{^1H\}$ spectra for further confirmation of the fluxional mechanism.)

Each ruthenium in **1** (Figure 1) has a distorted octahedral geometry with three 2-N nitrogen atoms of the hydridotris(1,2,4-triazolyl)borato anion occupying two equatorial (N_e) sites and one axial (N_a) site (octahedral angles around the Ru atom range from 81.30(10) to 100.10(7)°). The other octahedral positions are occupied by the other Ru atom and two semibridging carbonyl carbon atoms, each situated *trans* to the N_e atoms. Like **2**,[8] the carbonyls lean slightly toward the metal–metal bond whereas the equatorial nitrogen atoms are pulled toward the boron atom,

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Table 3. Selected Bond Lengths (Å) and Bond and Torsion Angles (deg) for **1**

Ru(1)–Ru(2)	2.8688(7)	Ru(1)–N(1)	2.151(3)
Ru(1)–N(6)	2.180(3)	Ru(1)–N(11)	2.177(3)
Ru(1)–C(16)	1.841(3)	Ru(1)–C(17)	1.850(4)
Ru(2)–N(21)	2.160(3)	Ru(2)–N(26)	2.174(3)
Ru(2)–N(31)	2.170(3)	Ru(2)–C(36)	1.838(3)
Ru(2)–C(37)	1.844(4)	C(16)–O(16)	1.139(4)
C(17)–O(17)	1.140(4)	C(36)–O(36)	1.144(4)
C(37)–O(37)	1.144(4)		
Ru(2)–Ru(1)–N(6)	177.14(7)	Ru(2)–Ru(1)–N(1)	91.20(7)
Ru(2)–Ru(1)–C(16)	86.21(11)	Ru(2)–Ru(1)–N(11)	98.39(7)
Ru(1)–Ru(2)–N(21)	92.29(8)	Ru(2)–Ru(1)–C(17)	87.86(11)
Ru(1)–Ru(2)–N(31)	92.29(8)	Ru(1)–Ru(2)–N(26)	175.38(8)
Ru(1)–Ru(2)–C(37)	88.44(11)	Ru(1)–Ru(2)–C(36)	84.86(11)
N(1)–Ru(1)–N(11)	84.94(10)	N(1)–Ru(1)–N(6)	85.94(10)
N(21)–Ru(2)–N(26)	84.03(11)	N(6)–Ru(1)–N(11)	81.30(10)
N(26)–Ru(2)–N(31)	82.40(10)	N(21)–Ru(1)–N(31)	85.12(10)
Ru(1)–C(17)–O(17)	179.7(3)	Ru(1)–C(16)–O(16)	175.6(3)
Ru(2)–C(37)–O(37)	177.7(3)	Ru(2)–C(36)–O(36)	173.4(3)
N(1)–Ru(1)–Ru(2)–N(31)	–49.2(1)	N(1)–Ru(1)–Ru(2)–N(21)	36.2(1)
N(11)–Ru(1)–Ru(2)–C(36)	46.6(1)	N(11)–Ru(1)–Ru(2)–N(21)	–48.8(1)
C(16)–Ru(1)–Ru(2)–C(37)	–46.7(1)	C(16)–Ru(1)–Ru(2)–N(31)	44.0(1)
C(17)–Ru(1)–Ru(2)–C(37)	42.3(1)	C(17)–Ru(1)–Ru(2)–C(36)	–46.2(1)

with similar averaged Ru–Ru–C angles = 86.8° in **1** and 87.2° in **2** and the Ru–Ru–N_e angles = 95.5° in **1** and 94.8° in **2**. However, the N_a atoms in the two compounds differ in dispositions with respect to the Ru–Ru bond ((Ru–N_a, ∠Ru–Ru–N_a) = 2.180(3) Å, 177.14(7)°; 2.174(3) Å, 175.38(8)° in **1** (Table 2) and 2.191(4) Å, 175.1(1)°; 2.199(4) Å, 175.8(1)° in **2**[8]). *A short Ru–Ru bond in 1 is observed despite a short Ru–axial ligand bond.* Such a feature is quite the reverse to what we observed from dinuclear compounds such as $[Rh_2(O_2CR)_4L_2]$[5] or $[Cr_2(O_2CR)_4L_2]$.[6] On the basis of the detailed MO calculation results for bridged and unbridged $M_2L'_{10}$ complexes (M = transition-metal atoms; L′ = donor or acceptor)[13] and those of $HBpz_3^-$ and cyclopentadienyl anion,[10] it is probably true that the level ordering in **1** and **2** is *different* from that in $[Ru_2(O_2CR)_2(CO)_4L_2]$, though the same filled orbitals of σ, π, δ, δ^*, and π^* are involved. The stronger π acidity of $HBtz_3^-$ or $HBpz_3^-$, relative to the acetate and phosphine (L) groups, and the longer Ru–Ru distances in **1** and **2**, compared with those, in a range between 2.637 and 2.741 Å, in $[Ru_2(O_2CR)_2(CO)_4L_2]$ with a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ configuration,[4] may make the σ orbital to be the HOMO in **1** and **2**. We believe that the improved electron acceptor, $HB(tz)_3^-$, in place of $HB(pz)_3^-$, may increase Ru→N_a back-bonding and shorten the Ru–N_a bond length, while the stronger Ru–Ru π^* (or δ^*) back-bonding to the equatorial semibridging carbonyls,[14] as reflected by the smaller averaged Ru–Ru–C angles, helps to increase the Ru–Ru bond order and reduce the Ru–Ru distance. The σ-character of the HOMO in **1** and **2**, as well as the apparently increased Ru–Ru bonding in **1** from that in **2**, is also found to be compatible with the stronger resistance to oxidation, either electrochemically or chemically toward diiodine. (Both compounds exhibit irreversible oxidation waves with $E_{p,a}$ = 633 mV for **1** and 312 mV for **2**. Bulk electrolysis experiments at E = 830 mV for **1** and 670 mV for **2** indicate that the oxidation process involves one-electron transfer.)

Experimental Section

All operations were performed by the usual Schlenk techniques, using deoxygened, dry solvents and gases. IR spectra, calibrated with polystyrene, were recorded on a Hitachi Model 270-30 instrument with the following abbreviations: s, strong; m, medium; w, weak. NMR spectra were obtained on a Bruker AM-200 (^1H, 200 MHz) or a Varian VXR-300 (^1H, 300 MHz; ^{13}C, 75 MHz) FT-NMR spectrometer. Chemical shifts (δ in ppm) are positive downfield or negative upfield relative tointernal $SiMe_4$ (TMS) standard. Elemental analysis results were obtained by the staff of the Microanalytical Service of the Department of Chemistry, National Cheng Kung University.

The compounds *catena*-$[Ru(O_2CMe)(CO)_2]$,[15] $[Ru\{\eta^3\text{-}HB(pz)_3\}(CO)_2]_2$ (**2**),[8] and $K^+HB(tz)_3^-$ [16] were prepared by using published procedures. The variable-temperature ^1H NMR measurements of **1** were recorded on the Varian machine, and the energy barriers (ΔG^*) at T_c were calculated from the Eyring equation by assuming first-order reversible site exchange.[12b,17]

Cyclic voltammograms of $[Ru\{\eta^3\text{-}HB(tz)_3\}(CO)_2]_2$ and $[Ru\{\eta^3\text{-}HB(pz)_3\}(CO)_2]_2$ were obtained for MeCN solutions that contained 0.5 mM dimers and 0.1 M Bu_4NPF_6 as the supporting electrolyte. Ferrocene (0.1 mM) was used as the internal standard. A BAS 100B electrochemical analyzer was used to collect CV data and to perform the bulk electrolysis, equipped with a three-electrode geometry (Pt working electrode, Pt auxiliary electrode, and $Ag/AgNO_3$ (0.1 M) reference electrode).

Preparation of 1. A suspension of *catena*-$[Ru(O_2CMe)(CO)_2]$ (0.65 g, 3.0 mmol) and $K^+HB(tz)_3^-$ (1.28 g, 5.0 mmol) in MeOH (30 mL) was heated under reflux for 35 min. The yellow crystalline product, formed as a precipitate, was collected. Recrystallization from $CH_2Cl_2/MeOH$ gave 0.80 g (64%) of $[Ru\{\eta^3\text{-}HB(tz)_3\}(CO)_2]_2\cdot CH_2Cl_2$. Anal. Calcd for $C_{17}H_{16}B_2Cl_2N_{18}O_4Ru_2$: C, 24.57; H, 1.94; N, 30.34. Found: C, 24.23; H, 1.89; N, 30.06. ^1H NMR (188 K, CD_2Cl_2, 300 MHz): hydrogen atoms at the ring-3 and -5 positions, δ 8.98 (s, 2 H), 8.59 (s, 2 H), 8.24 (s, 2 H), 8.16 (s, 2 H), 8.11 (s, 2 H), 5.87 (s, 2 H). $^{13}C\{^1H\}$ NMR (298 K, CD_2Cl_2, 75 MHz): carbon atoms at the ring-3 and -5 position, δ 149.44 (s, 6 C), 155.87 (s, 6 C); carbonyl carbon atoms, 204.69 (s, 4 C). IR (CH_2Cl_2): ν_{CO} 2044 s, 1996 m, 1966 s cm^{-1}. IR (KBr): ν_{BH} 2528 w cm^{-1}; ν_{CO}, 2040 s, 1996 m, 1962 s, 1942 s cm^{-1}.

Preparation of $[Ru\{\eta^3\text{-}HB(tz)_3\}(CO)_2Br]$. Both $[Ru\{\eta^3\text{-}HB(pz)_3\}(CO)_2Br]$[18] and $[Ru\{\eta^3\text{-}HB(tz)_3\}(CO)_2Br]$ can be obtained readily by bromination of **2** and **1**, respectively, as follows. To a stirred solution of **1**·CH_2Cl_2 (0.19 g, 0.23 mmol) dissolved in 20 mL of CH_2Cl_2, was added 1.2 mL (*ca.* 0.28 mmol) of a Br_2 solution (0.112 g of Br_2 in 30 mL of CH_2Cl_2) dropwise. The solution was stirred for 3 h after complete addition of the Br_2 solution, and the solvent was then removed under vacuum. Recrystallization from $CH_2Cl_2/MeOH$ gave 0.10 g (96%) of the pale yellow product. Anal. Calcd for $C_8H_7BBrN_9O_2Ru$: C, 21.21; H, 1.56; N, 27.83. Found: C, 21.06; H, 1.70; N, 27.80. ^1H NMR (298 K, $CDCl_3$, 200 MHz): hydrogen atoms at the ring-3 and -5 position, δ 8.50 (s, 2 H), 8.43 (s, 1 H), 8.40 (s, 2 H), 8.12 (s, 1 H). IR (CH_2Cl_2): ν_{CO} 2084 s, 2032 s cm^{-1}. IR (KBr): ν_{BH} 2554 w cm^{-1}; ν_{CO} 2074 s, 2014 s cm^{-1}.

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Preparation of [Ru{η^3-HB(tz)$_3$}(CO)$_2$I]. Although [Ru{η^3-HB(pz)$_3$}(CO)$_2$I][18] can be obtained readily by using a procedure analogous to that for [Ru{η^3-HB(tz)$_3$}(CO)$_2$Br], [Ru{η^3-HB(tz)$_3$}(CO)$_2$I] cannot be obtained from the mixture of **1**·CH_2Cl_2 and I_2 in CH_2Cl_2 even under reflux for 1 h. An alternative preparation is described as follows. The solution of **1**·CH_2Cl_2 (83 mg, 0.10 mmol) and I_2 (28 mg, 0.11 mmol) in 30 mL of MeCN was heated at 82 °C for 3 h. The solvent was then removed under vacuum, giving a brown residue. The pure product was obtained by eluting a solution of the residue through a silica gel column, using acetone as the elutent. The removal of acetone from the elutent resulted in the formation of the yellow brown solid (44 mg, 88%). Anal. Calcd for $C_8H_7BIN_9O_2Ru$: C, 19.22; H, 1.41; N, 25.21. Found: C, 19.27; H, 1.40; N, 25.20. ^{1}H NMR (298 K, acetone-*d*$_6$, 200 MHz): hydrogen atoms at the ring-3 and -5 position, δ 8.77 (s, 1 H), 8.76 (s, 1 H), 8.72 (s, 2 H), 8.63 (s, 2 H). IR (CH_2Cl_2): υ_{CO} 2080 s, 2028 s cm^{-1}. IR (KBr): υ_{BH} 2548 w cm^{-1}; υ_{CO} 2072 s, 2012 s cm^{-1}.

X-ray Diffraction Study of 1. The single crystals of **1** were grown from CH_2Cl_2/hexane at room temperature. General procedures and listings of programs were previously given.[12a] Except for **1**, a single molecule of CH_2Cl_2 was also found in the asymmetrical unit of the crystal used. An absorption correction was performed on the structure using ψ scans. Related crystal data, final coordinates of the non-hydrogen atoms, and selected bond lengths, bond angles, and torsion angles are reported in Tables I-III.

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Supplementary Material Available: Tables of fractional atomic coordinates for hydrogen atoms, anisotropic thermal displacement coefficients, and complete bond lengths and angles for complex **1** (5 pages). Ordering information is given on any current masthead page.

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