Synthesis and Spectroscopic Characterization of New Hydrido and Dihydrogen Complexes of Osmium and Ruthenium Stabilized by the Tris(pyrazolyl)borate Ligand

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The five-coordinate complexes $MHCl(CO)(P^iPr_3)_2$ (M = Os (**1**), Ru (**2**)) react with $Na[HBpz_3]$ in methanol at room temperature to give $M(\eta^2\text{-}HBpz_3)H(CO)(P^iPr_3)_2$ (M = Os (**3**), Ru (**4**)), which in toluene under reflux evolve into $M(\eta^3\text{-}HBpz_3)H(CO)(P^iPr_3)$ (M = Os (**5**), Ru (**6**)) by dissociation of triisopropylphosphine. The protonation with HBF_4 of **5** and **6** in dichloromethane yields the dihydrogen complexes $[M(\eta^3\text{-}HBpz_3)(\eta^2\text{-}H_2)(CO)(P^iPr_3)]BF_4$ (M = Os (**7**), Ru (**8**)), from which the dihydrogen ligand can be easily displaced by acetone to afford the solvate compounds $[M(\eta^3\text{-}HBpz_3)\{\eta^1\text{-}OC(CH_3)_2\}(CO)(P^iPr_3)]BF_4$ (M = Os (**9**), Ru (**10**)).

Introduction

We recently reported that the five-coordinate complexes $MHCl(CO)(P^iPr_3)_2$ (M = Os, Ru) react with cyclopentadiene to give the corresponding cyclopentadienyl derivatives $MH(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)$ (M = Os, Ru).[1] In dichloromethane-d_2, the protonation of $Os(\eta^5\text{-}C_5H_5)H(CO)(P^iPr_3)$ affords the dihydrido derivative $[Os(\eta^5\text{-}C_5H_5)(H)_2(CO)(P^iPr_3)]^+$ as a unique product,[1a] whereas under the same conditions the addition of HBF_4 to $Ru(\eta^5\text{-}C_5H_5)H(CO)(P^iPr_3)$ leads to the dihydrogen complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)(CO)(P^iPr_3)]^+$ in equilibrium with traces of the dihydrido tautomer $[Ru(\eta^5\text{-}C_5H_5)(H)_2(CO)(P^iPr_3)]^+$.[1b]

In recent years, the tris(pyrazolyl)borate ligand ($HBpz_3$) has found widespread uses in organometallic chemistry.[2] For the iron triad, numerous iron and ruthenium complexes containing this ligand have been reported.[2,3] On the other hand, the related osmium compounds are very scarce. The chemistry of the $Os(HBpz_3)$ unit is limited to the complexes $[Os(\eta^3\text{-}HBpz_3)(CO)_2]_2$, $Os(\eta^3\text{-}HBpz_3)Br(CO)_2$,[4] $Os(C^tBu)(CH_2{}^tBu)_2(\eta^3\text{-}HBpz_3)$,[5] and $Os(\eta^5\text{-}C_5H_5)(\eta^3\text{-}HBpz_3)$.[6] Although both tris(pyrazolyl)borate and cyclopentadienyl are five-electron donor ligands, there is a marked difference between them in the hydrido chemistry, the nitrogen-donor ligand having a higher tendency to stabilize the dihydrogen complexes than the cyclopentadienyl group.[3b,7]

The interest of the dihydrogen compounds containing nitrogen donor ligands[7,8] and the novelty of the osmium tris(pyrazolyl)borate chemistry prompted us to investigate the reactivity of the five-coordinate compounds $MHCl(CO)(P^iPr_3)_2$ (M = Os, Ru) toward $Na[HBpz_3]$. In this paper, we report the synthesis and spectroscopic characterization of new hydrido and dihydrogen derivatives of osmium and ruthenium stabilized by tris(pyrazolyl)borate. The osmium complexes are the first examples of OsH_x compounds containing this tridentate nitrogen donor ligand.

Results and Discussion

The five-coordinate complexes $MHCl(CO)(P^iPr_3)_2$ (M = Os (**1**), Ru (**2**)) react with 1 equiv of $Na[HBpz_3]$ in methanol at room temperature to afford the six-coordinate compounds **3** and **4** (Scheme 1) containing a bidentate tris(pyrazolyl)borate ligand. Complexes **3** and **4** were isolated in high yields (about 75%) as white solids.

The presence of the nitrogen-donor ligand in **3** and **4** is supported by the IR and ^1H NMR spectra of these

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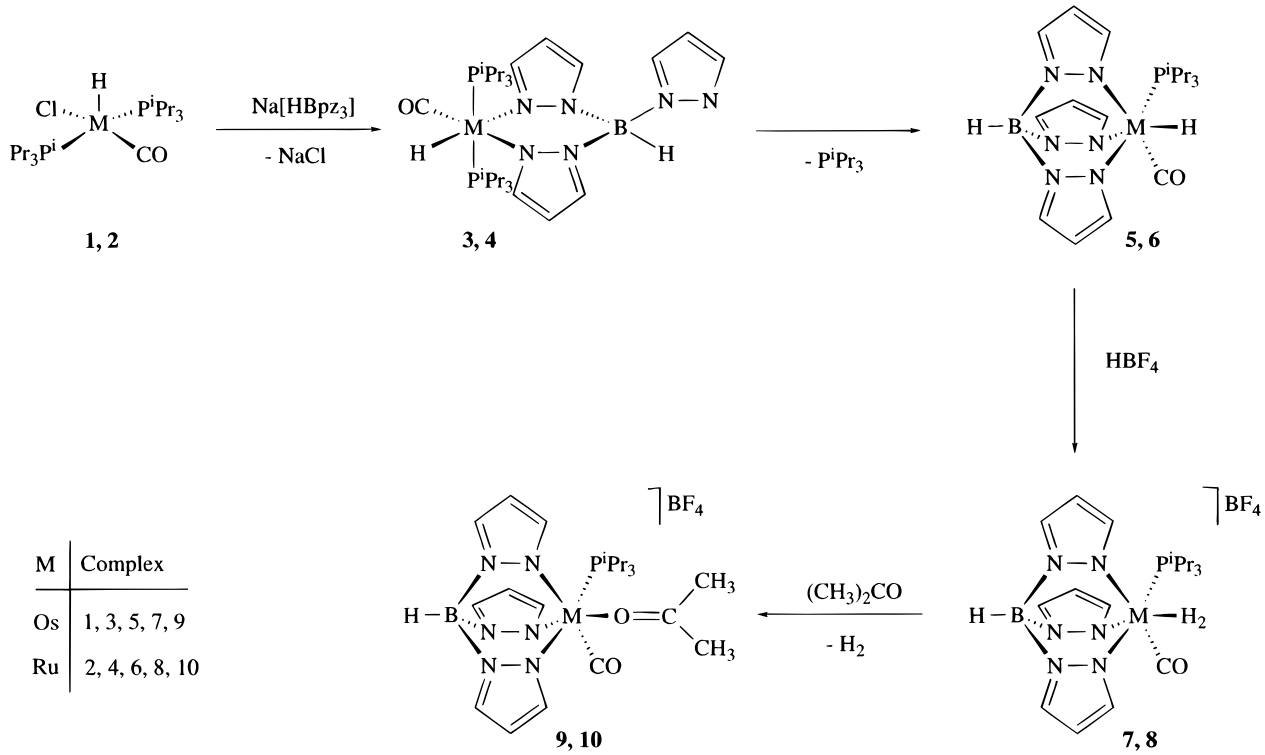
Scheme 1



compounds. The IR spectra in Nujol show bands at 2442, 2093, and 1894 (**3**) and 2440, 2002, and 1907 (**4**) cm^{-1}, corresponding to the ν(B−H), ν(M−H), and ν(C≡O) vibrations, respectively. The ^1H NMR spectra contain resonances due to the C−H protons of the tris(pyrazolyl)borate ligand between 8.04 and 5.82 ppm and in the high field region virtual triplets at −14.20 (**3**) and −13.10 (**4**) ppm, with P−H coupling constants of 18.6 and 22.0 Hz, respectively. In agreement with the structure proposed in Scheme 1, the $^{31}P\{^1H\}$ NMR spectra show AB spin systems. For complex **3**, the AB spin system is defined by $\delta_A = 23.9$, $\delta_B = 16.1$, and $J_{AB} = 261.4$ Hz, while for **4** the related parameters are $\delta_A = 52.9$, $\delta_B = 44.1$, and $J_{AB} = 277.4$ Hz.

In toluene under reflux, complexes **3** and **4** evolve into **5** and **6** by dissociation of a triisopropylphosphine ligand (Scheme 1). Complexes **5** and **6** were also isolated as white solids in 87% (**5**) and 70% (**6**) yields, respectively.

The presence of only one triisopropylphosphine ligand in these derivatives is mainly supported by the ^1H NMR spectra of the compounds, which show doublets at −14.05 (**5**) and −12.85 (**6**) ppm in the high-field region, with P−H coupling constants of 18.7 and 27.3 Hz, respectively. In contrast to the $^{31}P\{^1H\}$ NMR spectra of **3** and **4**, the $^{31}P\{^1H\}$ NMR of **5** and **6** contain singlets at 28.8 (**5**) and 72.9 (**6**) ppm. As for **3** and **4**, the most noticeable features of the IR spectra of **5** and **6** are three bands at 2466, 2061, and 1905 (**5**) and 2461, 1969, and 1919 (**6**) cm^{-1}, corresponding to the ν(B−H), ν(M−H), and ν(C≡O) vibrations, respectively. Complexes **5** and **6** are analogous to the half-sandwich cyclopentadienyl derivatives M(η^5-C_5H_5)H(CO)(P^iPr_3) (M = Os, Ru), which give rise to similar values for the ν(C≡O) vibration (1900 (Os) and 1920 (Ru) cm^{-1}). Although it has been suggested that the tris(pyrazolyl)borate is a better π-donor ligand than the cyclopentadienyl group,[9] we note that the electron-donating abilities of the two ligands are similar since the differences in ν(C≡O) are minimal, in agreement with that previously observed by Simpson.[10]

In spite of the fact that the electron density of the metallic centers of both systems appear to be similar, there is a marked difference in their reactivity toward HBF_4. Thus, while the addition of 1 equiv of HBF_4 to dichloromethane-d_2 solutions of Os(η^5-C_5H_5)H(CO)(P^iPr_3) affords the dihydrido [Os(η^5-C_5H_5)(H)$_2$(CO)(P^iPr_3)]$^+$,[1a] the reaction of the tris(pyrazolyl)borate compound **5** with HBF_4 leads to the dihydrogen derivative [Os(η^3-HBpz$_3$)(η^2-H_2)(CO)(P^iPr_3)]$^+$ (**7**, in Scheme 1). The ^1H NMR spectrum of **7** has the typical broad dihydrogen signal centered at −5.79 ppm. A variable-temperature 300-MHz T_1 study of this peak gives a T_1(min) of 9 ms at 203 K. This T_1(min) value corresponds to a hydrogen−hydrogen distance of 0.80 (fast spinning) or 1.00 Å (slow spinning).[11] The protonation of **5** in dichloromethane-d_2 with DBF_4 yields the partially deuterated dihydrogen derivative [Os(η^3-HBpz$_3$)(η^2-HD)(CO)(P^iPr_3)]$^+$ (**7-*d*$_1$**), which has a H−D coupling constant of 25.8 Hz at 203 K. According to eq 1,[12] this value allows one to calculate a hydrogen−hydrogen separation of 0.99 Å. The reaction for the formation of **7** is reversible in the presence of PPh_3. At 213 K, a value of 0.42 was determined by $^{31}P\{^1H\}$ NMR spectroscopy for the equilibrium constant of the reaction shown in eq 2. According to eq 3,[13] this

$$d(\mathrm{H-H}) = -0.0167J(\mathrm{HD}) + 1.42 \qquad (1)$$

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value allows one to estimate, at 213 K, a pK_a of 9.3 on the pseudo-aqueous scale for the dihydrogen complex.[14]

$$\mathbf{7} + PPh_3 \rightleftharpoons \mathbf{5} + [HPPh_3]^+ \quad (2)$$

$$pK_a(\eta^2\text{-}H_2) = pK_{eq} + pK_a\{[HPPh_3]^+\} \quad (3)$$

The ruthenium tris(pyrazolyl)borate complex **6** reacts with HBF_4 in a similar manner to that of the osmium compound **5**. Thus, the addition of 1 equiv of HBF_4 to a dichloromethane-d_2 solution of **6** affords the dihydrogen derivative **8** (Scheme 1). In contrast to the reaction of the half-sandwich cyclopentadienyl complex Ru(η^5-C_5H_5)H(CO)(P^iPr_3) with HBF_4, the formation of a trace amount of a dihydrido tautomer, in equilibrium with **8**, was not observed. The characteristic dihydrogen signal of **8** was observed in the ^{1}H NMR spectrum at −7.61 ppm as a broad resonance. In this case, the variable-temperature 300-MHz T_1 study gives a T_1(min) of 6 ms at 193 K, which corresponds to a hydrogen−hydrogen distance of 0.75 (fast spinning) or 0.95 Å (slow spinning). Similar to **6**, the protonation of **5** with DBF_4 gives the partially deuterated dihydrogen derivative [Ru(η^3-$HBpz_3$)(η^2-HD)(CO)(P^iPr_3)]$^+$ (**8-*d*$_1$**), which has a H−D coupling constant of 28.0 Hz at 193 K. According to eq 1, this value allows one to calculate a hydrogen−hydrogen separation of 0.95 Å, which is similar to that calculated for the analogous cyclopentadienyl cation [Ru(η^5-C_5H_5)(η^2-H_2)(CO)(P^iPr_3)]$^+$ (0.94 Å), in agreement with the similar electron-donating abilities of both ligands, tris(pyrazolyl)borate and cyclopentadienyl. However, the hydrogen−hydrogen distance in **8** is 0.04 Å shorter than that obtained for the osmium tris(pyrazolyl)borate complex **7**, suggesting that in **7** the M(η^2-H_2) bond is stronger than in **8**. In accordance with this, we have also observed that the addition of 1 equiv of $[HPPh_3]BF_4$ to dichloromethane-d_2 solutions of **6** produces the loss of molecular hydrogen and the formation of [Ru(η^3-$HBpz_3$)(CO)(PPh_3)(P^iPr_3)]BF_4 (eq 4). In this context, it should be noted that ruthenium is a poorer π-back-bonder than osmium, because the osmium valence orbitals have better overlap with the ligand orbitals.[15]

$$Ru(\eta^3\text{-}HBpz_3)H(CO)(P^iPr_3) + [HPPh_3]BF_4 \rightarrow H_2 + [Ru(\eta^3\text{-}HBpz_3)(CO)(PPh_3)(P^iPr_3)]BF_4 \quad (4)$$

The addition of acetone to dichloromethane-d_2 solutions of **7** and **8** produces the displacement of the dihydrogen ligand of these compounds and the formation of the solvate complexes **9** and **10** (Scheme 1), which can be isolated as yellow solids in 51% (**9**) and 78% (**10**) yields by protonation of **5** and **6** with HBF_4 in acetone and the subsequent addition of diethyl ether.

In the IR spectra of **9** and **10** in Nujol, the most noticeable features are the absorption due to the $[BF_4]^-$ anion with T_d symmetry centered at 1058 (**9**) and 1030 (**10**) cm^{-1}, indicating that the anion is not coordinated to the metallic centers, and the ν(C═O) band of the carbonyl group of the acetone ligand at 1657 (**9**) and 1665 (**10**) cm^{-1}, suggesting that the acetone molecule coordinates to the metal atoms by the oxygen atom.[16] In agreement with this, the ^{13}C{^{1}H} NMR spectra of **9** and **10** show singlets at 228.3 (**9**) and 229.3 (**10**) ppm, corresponding to the carbon atom of the carbonyl group of the acetone.

The higher tendency of the tris(pyrazolyl)borate ligand to stabilize dihydrogen compounds in comparison with the cyclopentadienyl group merits some additional comment. Often differences in steric and electronic properties as well as in symmetry have been argued to explain the tendency of the cyclopentadienyl ligand to afford higher coordination numbers than the tris(pyrazolyl)borate. Comparison of the ν(C≡O) IR data for **5** and **6** and the analogous cyclopentadienyl complexes suggests that the electron-donating abilities of the two ligands are similar, so in our case, the electronic factors do not appear to play a significant role. Furthermore, it is not reasonable to think that the size of the tris(pyrazolyl)borate and cyclopentadienyl groups can affect the coordination mode of the smallest known ligand. However, it should be noted that the symmetry of the M(η^3-$HBpz_3$) fragment, determined by the N−M−N angles (87° for VIII group),[17] affects the coordination mode of the other ligands of the complex rather than the symmetry of the M(η^5-C_5H_5) unit. In this context, it has been suggested[3a] that the [Ru(η^3-$HBpz_3$)]$^+$ unit is strongly hybrid-biased to preferentially bind three additional ligands for an octahedral six-coordinate structure to be obtained and maintained. The diffuse electron clouds of the cyclopentadienyl ligand are rather ineffective in promoting strongly directional frontier orbitals. As a consequence, processes involving coordination number increase (e.g., the homolytic cleavage of the dihydrogen ligand at the metal center) are less likely for the tris(pyrazolyl)borate ligand.

In conclusion, in spite of the fact that the electron-donating abilities of the tris(pyrazolyl)borate and cyclopentadienyl ligands are similar between the complexes M(η^3-$HBpz_3$)H(CO)(P^iPr_3) and M(η^5-C_5H_5)H(CO)(P^iPr_3) (M = Os, Ru), there is a marked difference in reactivity toward HBF_4. Thus, while the tris(pyrazolyl)borate compounds react with HBF_4 to give the dihydrogen derivatives [M(η^3-$HBpz_3$)(η^2-H_2)(CO)(P^iPr_3)]$^+$ (M = Os, Ru), protonation of the osmium−cyclopentadienyl complex Os(η^5-C_5H_5)H(CO)(P^iPr_3) affords dihydrido [Os(η^5-C_5H_5)$(H)_2$(CO)(P^iPr_3)]$^+$ as a unique reaction product and protonation of the ruthenium−cyclopentadienyl complex Ru(η^5-C_5H_5)H(CO)(P^iPr_3) leads to dihydrogen [Ru(η^5-C_5H_5)(η^2-H_2)(CO)(P^iPr_3)]$^+$ in equilibrium with trace amounts of the dihydrido tautomer [Ru(η^5-C_5H_5)$(H)_2$(CO)-(P^iPr_3)]$^+$.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Nicolet 550

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spectrometer. NMR spectra were recorded on a Varian UNITY 300, Varian GEMINI 2000, 300 MHz, or on a Bruker ARX 300. ^{1}H and ^{13}C{^{1}H} chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. ^{31}P{^{1}H} chemical shifts are reported relative to H_3PO_4 (85%). T_1 relaxation measurements were carried out on a Varian UNITY 300 spectrometer with a standard 180°−τ−90° pulse sequence. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectra analyses were performed with a VG AutoSpec instrument. The ions were produced, FAB$^+$ mode, with the standard Cs$^+$ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

Synthesis. All reactions were carried out with exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon. Sodium hydridotris(1-pyrazolyl)borate[18] and the complexes RuHCl(CO)(P^{i}Pr$_3$)$_2$ and OsHCl(CO)(P^{i}Pr$_3$)$_2$were prepared according to the literature procedures.[19]

Preparation of Os(η^2-HBpz$_3$)H(CO)(P^{i}Pr$_3$)$_2$ (3). A suspension of OsHCl(CO)(P^{i}Pr$_3$)$_2$ (**1**) (400 mg, 0.70 mmol) in 15 mL of methanol was treated with 164 mg (0.70 mmol) of sodium hydridotris(1-pyrazolyl)borate. The mixture was stirred for 20 min at room temperature, and a white solid was obtained. It was separated by decantation, washed with methanol, and dried in vacuo: yield 397 mg (75%). IR (Nujol, cm^{-1}): ν(B−H) 2442 (m), ν(Os−H) 2093 (m), ν(C≡O) 1894 (vs). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.04, 7.99, 7.81 (all d, 1H each, H^3), 7.68, 7.09, 6.92 (all d, 1H each, H^5), 6.34, 6.03, 5.82 (all t, 1H each, H^4), 2.38 (m, 3H, PCH), 1.96 (m, 3H, PCH), 1.14 (dd, 9H, J(HH) = 6.9 Hz, J(PH) = 12.9 Hz, PCCH$_3$), 0.98 (dd, 18H, J(HH) = 7.2 Hz, J(PH) = 12.0 Hz, PCCH$_3$), 0.92 (dd, 9H, J(HH) = 7.2 Hz, J(PH) = 11.7 Hz, PCCH$_3$), −14.20 (t, 1H, J(PH) = 18.6 Hz, OsH); all coupling constants for the pyrazolyl proton resonances were about 2 Hz. ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 23.9, 16.1 (AB system, J_{AB} = 261.4 Hz). Anal. Calcd for $C_{28}H_{53}BN_6OOsP_2$·CH_3OH: C, 44.37; H, 7.33; N, 10.70. Found: C, 43.81; H, 6.40; N, 9.67. MS (FAB$^+$): *m*/*e* 754 (M$^+$).

Preparation of Ru(η^2-HBpz$_3$)H(CO)(P^{i}Pr$_3$)$_2$ (4). This complex was synthesized analogously to **3**, starting from **2** (200 mg, 0.41 mmol) and Na[HBpz$_3$] (100 mg, 0.42 mmol): white solid; yield 199 mg (73%). IR (Nujol, cm^{-1}): ν(B−H) 2440 (m), ν(Ru−H) 2002 (m), ν(C≡O) 1907 (vs). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.01, 7.97, 7.84 (all d, 1H each, H^3), 7.61, 7.21, 7.05 (all d, 1H each, H^5), 6.35, 6.11, 5.91 (all t, 1H each, H^4), 2.26 (m, 3H, PCH), 1.87 (m, 3H, PCH), 1.14 (dd, 9H, J(HH) = 7.2 Hz, J(PH) = 12.9 Hz, PCCH$_3$), 0.98 (dd, 18H, J(HH) = 7.2 Hz, J(PH) = 12.3 Hz, PCCH$_3$), 0.94 (dd, 9H, J(HH) = 7.2 Hz, J(PH) = 12.0 Hz, PCCH$_3$), −13.10 (t, J(PH) = 22.0 Hz, RuH); all coupling constants for the pyrazolyl proton resonances were about 2 Hz. ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 52.9, 44.1 (AB system, J_{AB} = 277.4 Hz). Anal. Calcd for $C_{28}H_{53}BN_6OP_2Ru$·CH_3OH: C, 50.06; H, 8.27; N, 12.08. Found: C, 50.06; H, 8.31; N, 12.44.

Preparation of Os(η^3-HBpz$_3$)H(CO)(P^{i}Pr$_3$) (5). A solution of **3** (390 mg, 0.52 mmol) in 10 mL of toluene was heated under reflux for 2 h. The resulting solution was filtered through Kieselguhr and concentrated to dryness. Addition of pentane precipitated a white solid, which was separated by decantation, washed with pentane, and dried in vacuo: yield 265 mg (87%). IR (Nujol, cm^{-1}): ν(B−H) 2466 (m), ν(Os−H) 2061 (m), ν(C≡O) 1905 (vs). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 8.06, 7.84, 7.74 (all d, 1H each, H^3), 7.49, 7.36, 7.26 (all d, 1H each, H^5), 5.93, 5.75, 5.67 (all t, 1H each, H^4), 2.13 (m, 3H, PCH), 1.05 (dd, 18H, J(HH) = 7.1 Hz, J(PH) = 12.1 Hz, PCCH$_3$), −14.05 (d, 1H, J(PH) = 18.7 Hz, OsH); all coupling constants for the pyrazolyl proton resonances were about 2 Hz. ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 28.8 (s). Anal. Calcd for $C_{19}H_{32}BN_6OOsP$: C, 38.59; H, 5.47; N, 14.21. Found: C, 39.06; H, 5.82; N, 13.90.

Preparation of Ru(η^3-HBpz$_3$)H(CO)(P^{i}Pr$_3$) (6). This complex was prepared analogously to **5**, with **4** (200 mg, 0.30 mmol) as the starting material: white solid; yield 107 mg (70%). IR (Nujol, cm^{-1}): ν(B−H) 2461 (m), ν(Ru−H) 1969 (m), ν(C≡O) 1919 (vs). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.95, 7.76, 7.69 (all d, 1H each, H^3), 7.54, 7.46, 7.34 (all d, 1H each, H^5), 6.01, 5.83, 5.75 (all t, 1H each, H^4), 2.07 (m, 3H, PCH), 1.03 (dd, 18H, J(HH) = 6.9 Hz, J(PH) = 12.3 Hz, PCCH$_3$), −12.85 (d, 1H, J(PH) = 27.3 Hz, RuH); all coupling constants for the pyrazolyl proton resonances were about 2 Hz. ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 72.9 (s). Anal. Calcd for $C_{19}H_{32}BN_6OPRu$: C, 45.67; H, 6.42; N, 16.70. Found: C, 46.09; H, 6.74; N, 16.21.

Preparation of [Os(η^3-HBpz$_3$)(η^2-H$_2$)(CO)(P^{i}Pr$_3$)]BF$_4$ (7). A solution of **5** (29.0 mg, 0.049 mmol) in 0.5 mL of CD_2Cl_2 in an NMR tube was treated with a stoichiometric amount of tetrafluoroboric acid (6.7 μL, 0.049 mmol, 54% in diethyl ether). The NMR tube was sealed under argon, and the measurement was initiated immediately. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.04, 7.97, 7.91 (all br, 1H each, H^3), 7.83, 7.69, 7.66 (all br, 1H each, H^5), 6.46, 6.36, 6.29 (all br, 1H each, H^4), 2.52 (m, 3H, PCH), 1.18 (dd, 9H, J(HH) = 7.2 Hz, J(PH) = 14.4 Hz, PCCH$_3$), 1.13 (dd, 9H, J(HH) = 7.2 Hz, J(PH) = 14.4 Hz, PCCH$_3$), −5.79 (br, 2H, Os(η^2-H$_2$)); all coupling constants for the pyrazolyl proton resonances were about 2 Hz. T_1 (Os(η^2-H$_2$), 300 MHz, CD_2Cl_2): 25 ms (293 K), 11 ms (233 K), 8.9 ms (213 K), 8.7 ms (203 K), 9 ms (193 K). T_1(min): 8.7 ms (203 K). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 19.4 (s).

Preparation of [Ru(η^3-HBpz$_3$)(η^2-H$_2$)(CO)(P^{i}Pr$_3$)]BF$_4$ (8). This complex was prepared analogously to **7**, with **6** (27.6 mg, 0.049 mmol) and HBF$_4$·Et$_2$O (7.5 μL, 0.049 mmol) as the starting materials. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 8.14, 8.02, 7.97 (all d, 1H each, H^3), 7.79, 7.64, 7.29 (all d, 1H each, H^5), 6.49, 6.23, 6.18 (all t, 1H each, H^4), 2.47 (m, 3H, PCH), 1.20 (dd, 9H, J(HH) = 7.2 Hz, J(PH) = 14.1 Hz, PCCH$_3$), 1.15 (dd, 9H, J(HH) = 7.5 Hz, J(PH) = 13.8 Hz, PCCH$_3$), −7.61 (br, 2H, Ru(η^2-H$_2$)); all coupling constants for the pyrazolyl proton resonances were about 2 Hz. T_1 (Ru(η^2-H$_2$), 300 MHz, CD_2Cl_2): 22 ms (293 K), 16 ms (273 K), 12 ms (253 K), 8.5 ms (233 K), 6 ms (213 K), 5.7 ms (203 K), 5.6 ms (193 K). ^{31}P{^{1}H} NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 45.3 (s).

Preparation of [Os(η^3-HBpz$_3$)(η^2-HD)(CO)(P^{i}Pr$_3$)]BF$_4$ (7-*d*$_1$). A solution of **5** (32 mg, 0.05 mmol) in 0.5 mL of CD_2Cl_2 in an NMR tube was treated with a stoichiometric amount of DBF$_4$ (11 μL, 0.05 mmol) (prepared by adding 0.4 mL of D_2O into 1 mL of 54% HBF$_4$·Et$_2$O). The NMR tube was sealed under argon, and the measurements were initiated immediately. ^{1}H NMR (300 MHz, 216 K): δ −5.84 (1:1:1, t, 1H, J(HD) = 25.8 Hz, Os(η^2-HD)).

Preparation of [Ru(η^3-HBpz$_3$)(η^2-HD)(CO)(P^{i}Pr$_3$)]BF$_4$ (8-*d*$_1$). This complex was prepared analogously to **9**, with **6** (33 mg, 0.066 mmol) and a DBF$_4$ solution (13.5 μL, 0.066 mmol). The NMR tube was sealed under argon, and the measurements were initiated immediately. ^{1}H NMR (300 MHz, 193 K): δ −7.56 (1:1:1, t, 1H, J(HD) = 28.0 Hz, Ru(η^2-HD)).

Reaction of 5 with [HPPh$_3$]BF$_4$. Complex **5** (24.3 mg, 41.1 μmol) and [HPPh$_3$]BF$_4$ (14.3 mg, 40.9 μmol) were dissolved in 0.5 mL of CD_2Cl_2. Integration of the signals of **5**, **7**, PPh$_3$, and [Ph$_3$PH]$^+$ in the ^{31}P NMR spectrum of the solution at 213 K gave a K_{eq} value of 0.42 for the reaction shown in eq 2.

Reaction of 6 with [HPPh$_3$]BF$_4$. Complex **6** (12.5 mg, 24.8 μmol) and [HPPh$_3$]BF$_4$ (8.5 mg, 24.5 μmol) were dissolved in 0.5 mL of CD_2Cl_2 in an NMR tube. The NMR tube was sealed under argon, and the ^{31}P NMR spectrum was measured immediately. The results showed the exclusive formation of [Ru(η^3-HBpz$_3$)(CO)(PPh$_3$)(P^{i}Pr$_3$)]BF$_4$. ^{31}P NMR (CD_2Cl_2, 293 K): δ 31.6, 29.7 (AB system, J_{AB} = 24.5 Hz).

Preparation of [Os(η^3-HBpz$_3$)(CO){η^1-OC(CH$_3$)$_2$}(P^{i}Pr$_3$)]BF$_4$ (9). A solution of **5** (265 mg, 0.45 mmol) in 10

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mL of acetone was treated with tetrafluoroboric acid (61.2 μL, 0.45 mmol, 54% in diethyl ether). Immediately, the color turned to yellow and the solution was concentrated almost to dryness. Addition of diethyl ether caused the precipitation of a yellow solid. The solid was washed with diethyl ether and dried in vacuo: yield 170 mg (51%). IR (Nujol, cm^{-1}): ν(B−H) 2519 (m), ν(C≡O) 1960 (vs), ν(C═O) 1657 (vs), $\nu(BF_4)$ 1058 (br). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.96, 7.94, 7.78 (all d, 1H each, H^3), 7.70, 7.58, 7.49 (all d, 1H each, H^5), 6.52, 6.30, 6.27 (all t, 1H each, H^4), 2.53 (m, 3H, PCH), 2.41 (s, 6H, {η^1-OC$(CH_3)_2$}), 1.16 (dd, 9H, J(HH) = 6.9 Hz, J(PH) = 13.5 Hz, $PCCH_3$), 1.06 (dd, 9H, J(HH) = 7.2 Hz, J(PH) = 13.5 Hz, $PCCH_3$); all coupling constants for the pyrazolyl proton resonances were about 2 Hz. ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$, 293 K): δ 3.69 (s). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 293 K): δ 228.3 (s, {η^1-O*C*$(CH_3)_2$}), 182.0 (d, J(PC) = 8.7 Hz, CO), 148.9 (d, J(PC) = 5.6 Hz, C^3), 143.9 (d, J(PC) = 7.8 Hz, C^3), 143.4 (d, J(PC) = 3.7 Hz, C^3), 138.9 (d, J(PC) = 7.3 Hz, C^5), 137.7 (d, J(PC) = 7.8 Hz, C^5), 136.4 (d, J(PC) = 5.9 Hz, C^5), 108.3 (s, C^4), 107.9 (s, C^4), 107.7 (s, C^4), 32.7 (s, {η^1-OC-(*C*$H_3)_2$}), 24.8 (d, J(PC) = 27.7 Hz, PC), 19.4 (d, J(PC) = 0.9 Hz, PC*C*H_3), 19.0 (d, J(PC) = 1.3 Hz, PC*C*H_3). Anal. Calcd for $C_{22}H_{37}B_2F_4N_6O_2OsP$: C, 35.88; H, 5.07; N, 11.41. Found: C, 35.87; H, 5.30; N, 11.31.

Preparation of [Ru(η^3-HBpz$_3$)(CO){η^1-OC$(CH_3)_2$}(P^{i}Pr$_3$)]-BF_4 (10). This complex was prepared analogously to **11**, with **6** (336 mg, 0.29 mmol) and tetrafluoroboric acid (91.2 μL, 0.29 mmol, 54% in diethyl ether) in 12 mL of acetone. A yellow solid was obtained: yield 354 mg (78%). IR (Nujol, cm^{-1}): ν-(B−H) 2525 (m), ν(C≡O) 1983 (vs), ν(C═O) 1665 (vs), $\nu(BF_4)$ 1030 (br). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.98, 7.90, 7.70 (all d, 1H each, H^3), 7.64, 7.53, 7.41 (all br, 1H each, H^5), 6.51, 6.25, 6.21 (all t, 1H each, H^4), 2.45 (m, 3H, PCH), 2.08 (s, 6H, {η^1-OC$(CH_3)_2$}), 1.19 (dd, 9H, J(HH) = 7.4 Hz, J(PH) = 14.0 Hz, $PCCH_3$), 1.09 (dd, 9H, J(HH) = 6.9 Hz, J(PH) = 13.2 Hz, $PCCH_3$); all coupling constants for the pyrazolyl proton resonances were about 2 Hz. ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$, 293 K): δ 44.56 (s). ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$, 293 K): δ 229.3 (s, {η^1-O*C*$(CH_3)_2$}), 203.0 (d, J(PC) = 14.2 Hz, CO), 147.7 (s, C^3), 144.4 (s, C^3), 143.1 (s, C^3), 138.8 (s, C^5), 137.1 (s, C^5), 135.9 (s, C^5), 107.7 (s, C^4), 107.5 (s, C^4), 107.1 (s, C^4), 32.0 (s, {η^1-OC(*C*$H_3)_2$}), 23.9 (d, J(PC) = 21.6 Hz, PC), 19.2 (s, PC*C*H_3), 18.9 (s, PC*C*H_3). Anal. Calcd for $C_{22}H_{37}B_2F_4N_6O_2PRu$: C, 40.82; H, 5.76; N, 12.98. Found: C, 40.54; H, 5.66; N, 12.97.

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