signals that partially overlap the signals of IIIa with a free hydrogen bond.

Synthesis of IIb. Oxidation of 2.3 g (5.0 mmol) of Ib and chromatographic separation of the reactant Ib monoaldehyde and the mixture of dialdehydes were carried out as in ref 4. The mixture of dialdehydes was separated analogously to the mixture of the Ru analogues; yield of IIb 0.1 g (0.21 mmol, 4%). ^{1}H NMR: δ 2.07 (s, 6 H, α-Me), 1.82 (s, 3 H, β-Me), 1.76 (s, 15 H, γ-Me), 9.94 (s, 2 H, CHO). Anal. Found: C, 49.27; H, 5.23; Os, 38.99. Calcd for $C_{20}H_{26}O_2Os$: C, 49.16; H, 5.36; Os, 38.92.

Synthesis of IIIb. The reduction of 0.24 g (0.5 mmol) of IIb by the action of LiAlH(t-OBu)$_3$, analogous to the reduction of the monoaldehyde,[4] leads to 0.22 g (0.45 mmol, 90%) of IIIb. ^{1}H NMR: δ 1.79 (s, 6 H, α-Me), 1.71 (s, 3 H, β-Me), 1.78 (s, 15 H, γ-Me), 4.02 and 4.04 (AB q, $^2J_{HH} \leq 7$ Hz, 4 H, 2 CH_2). Anal. Found: C, 48.32; H, 6.16; Os, 38.28. Calcd for $C_{20}H_{30}O_2Os$: C, 48.75; H, 6.14; Os, 38.60.

Synthesis of Dications and Recording of ^{1}H and ^{13}C NMR Spectra. To a solution of IIIa (or IIIb) in CD_3NO_2 or CH_3NO_2 under an Ar atmosphere was added a small excess of CF_3SO_3H. This was transferred in an ampule to the NMR spectrometer. The results are given in Tables I and II.

Acknowledgment. We are grateful to the National Science Foundation for its support of this research through Grant CHE8912070.

Heteroaromatic Nitrogen Ligand Studies with the (η^5-Pentamethylcyclopentadienyl)ruthenium Cation: η^1(N) and $\eta^6(\pi)$ Bonding Modes and Factors That Influence a Nitrogen to π Rearrangement

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Summary: The reactions of the (η^5-pentamethylcyclopentadienyl)ruthenium tris(acetonitrile) cationic complex [Cp*Ru(CH_3CN)$_3$](OTf) with pyridine (**1**), 2-methylpyridine (**2**), and quinoline (**3**) were studied to ascertain bonding modes as a function of heteroaromatic nitrogen ligand structure. Ligand **1** bonds η^1(N) and forms mono- or tris(pyridine) complexes with [Cp*Ru(CH_3CN)$_3$]$^+$ depending on ligand concentration. Ligand **2** only forms an η^6 complex with [Cp*Ru(CH_3CN)$_3$]$^+$, while ligand **3** also forms an η^6 complex, but with the benzo ring not the nitrogen ring. In the presence of excess pyridine, the complexed CH_3CN ligands are fully displaced to form [Cp*Ru(η^1(*N*)-pyridine)$_3$]$^+$, while in the presence of excess **2** or **3** only the [Cp*Ru(η^1(*N*)-ligand)(CH_3CN)$_2$]$^+$ complexes are formed. The latter [Cp*Ru(η^1(*N*)-ligand)(CH_3CN)$_2$]$^+$ complexes with ligands **2** and **3** were not isolated; rather, they undergo a rapid nitrogen (N) to π rearrangement to the corresponding η^6 complexes, [Cp*Ru(η^6-2-methylpyridine or quinoline)]$^+$. The isolation of [Cp*Ru(η^1(*N*)-pyridine)(CH_3CN)$_2$]$^+$ and its conversion to [Cp*Ru(η^6-pyridine)]$^+$ clearly demonstrates the pathway to the η^6 complexes. Ligand-exchange reactions of [Cp*Ru(η^6-pyridine)]$^+$ with CD_3CN and pyridine-d_5 show facile replacement of the η^6-bonded pyridine, while the former result with CD_3CN ligand exchange proves that the N to π rearrangement is not reversible. Factors such as ligand steric effects and the propensity of the Cp*Ru$^+$ group to act as an arenophile will also be discussed.

In the course of our bonding studies of mono- and polynuclear heteroaromatic nitrogen ligands with the (η^5-pentamethylcyclopentadienyl)rhodium dication (Cp*Rh^{2+})[1a] and the (η^5-cyclopentadienyl)ruthenium cation (CpRu$^+$),[1b] Chaudret and co-workers recently published some results on the bonding mode of pyridine, several methyl-substituted pyridine ligands, and quinoline with the (η^5-pentamethylcyclopentadienyl)ruthenium cation (Cp*Ru$^+$).[2] In all cases, they isolated $\eta^6(\pi)$-bonded Cp*Ru$^+$ complexes, while observing a pronounced solvent effect in acetone that provided a pyridine N-bonded complex (py$_6$Ru^{2+}), with a concomitant loss of Cp*.

Since our bonding results with [Cp*Rh(CH_3CN)$_3$]$^{2+}$ and [CpRu(CH_3CN)$_3$]$^+$ as starting complexes were dramatically different for similar mono- and polynuclear heteroaromatic nitrogen ligands, i.e., η^1(N)- not η^6-bonding,[1a,b] we decided to examine the reactions of [Cp*Ru(CH_3CN)$_3$](OTf), a conveniently prepared starting material,[3] with pyridine (**1**), 2-methylpyridine (**2**), and quinoline (**3**) to ascertain bonding modes as a function of heteroaromatic nitrogen ligand structure. We also wanted to determine whether any η^6 complexes that formed with **1**–**3** and [Cp*Ru(CH_3CN)$_3$]$^+$ emanated from our recently reported N to π rearrangement that appears to be general for complexes that have a [CpRu(η^1(*N*)-ligand)(CH_3CN)$_2$]$^+$ structure.[1b,4]

Results and Discussion

The reaction of excess pyridine (**1**) and [Cp*Ru(CH_3CN)$_3$](OTf) in CH_2Cl_2 at ambient temperature provided only [Cp*Ru(η^1(*N*)-pyridine)$_3$]$^+$ (**4**) in 87% yield; no corresponding η^6 complex was observed. The 500-MHz ^{1}H NMR spectrum (CD_2Cl_2) of **4** provided clear evidence for the η^1(N)-bonding mode with signals at 8.3, 7.73, and 7.34 ppm that were shifted downfield from free pyridine,[1b,4] while the Cp* resonance was found at 1.29 ppm. A similar product was also observed when $(CH_3)_2CO$ was substituted for CH_2Cl_2 as the solvent. This latter result is in contrast

(1) (a) Fish, R. H.; Kim, H.-S.; Babin, J. E.; Adams, R. D. *Organometallics* **1988**, *7*, 2250. (b) Fish, R. H.; Kim, H.-S.; Fong, R. H. *Organometallics* **1989**, *8*, 1375.

(2) (a) Chaudret, B.; Jalon, F. A. *J. Chem. Soc., Chem. Commun.* **1988**, 711. (b) Chaudret, B.; Jalon, F. A.; Perez-Manrique, M.; Lohoz, F.; Plou, F. J.; Sanchez-Delgado, R. *New J. Chem.* **1990**, *14*, 331.

(3) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

(4) Fish, R. H.; Kim, H.-S.; Fong, R. H. *Organometallics* **1991**, *10*, 770.

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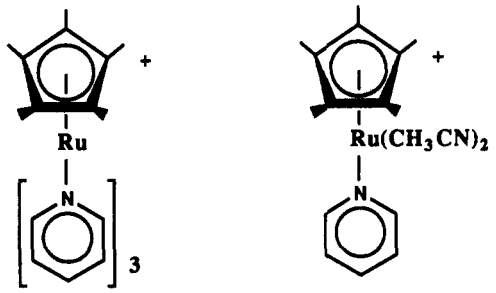
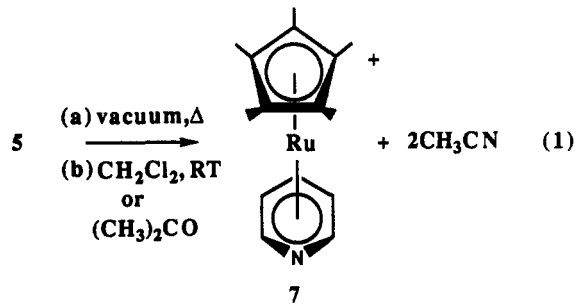


4 5

to the reported results of Chaudret and co-workers using $[Cp^*RuCl]_n$ in $(CH_3)_2CO$; loss of the Cp* ligand was observed.[2] Attempts to prepare $[Cp^*Ru(\eta^1(N)\text{-pyridine})(CH_3CN)_2]^+$ (**5**) were successful when 1 equiv of pyridine was utilized, but only in the presence of small amounts of CH_3CN and with short reaction times (5 min) and cooling. The purified product, **5** (>95%, NMR, Cp* at 1.48 ppm) still contained <5% of $[Cp^*Ru(\eta^1(N)\text{-pyridine})_2(CH_3CN)]^+$ (**6**) (Cp* at 1.41 ppm), which was difficult to separate.

Previously, we reported on a facile N to π rearrangement for complexes with the structure $[CpRu(\eta^1(N)\text{-ligand})(CH_3CN)_2]^+$.[1b,4] In order to verify a similar mechanism for the Cp*Ru analogue, **5**, we carried out the following experiments. Thus, solid complex **5** (contaminated with <5% of **6**) was heated at 80 °C under vacuum for 12 h to provide only $[Cp^*Ru(\eta^6\text{-pyridine})]^+$ (**7**)[2] (eq 1). The

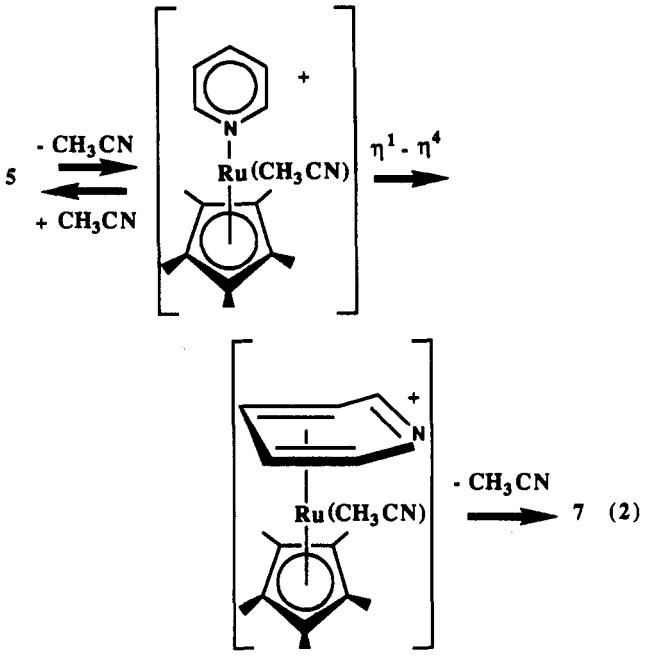


(a) vacuum, Δ; (b) CH_2Cl_2, RT or $(CH_3)_2CO$

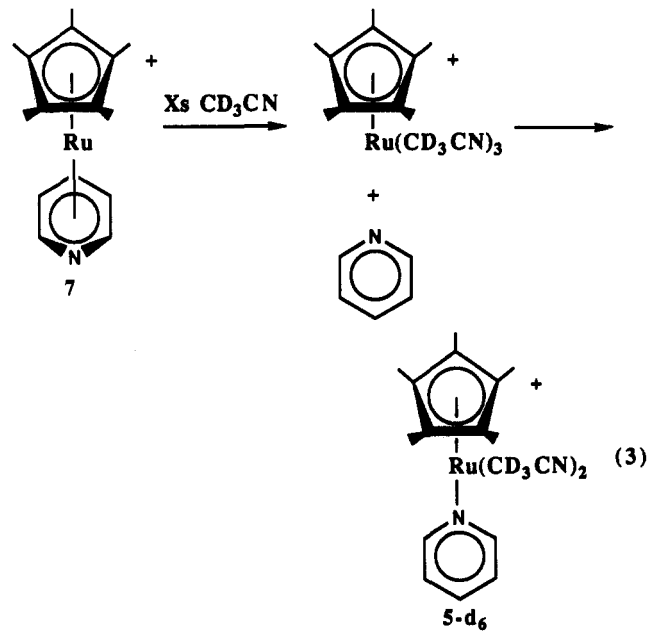
7

structure of complex **7** was verified by 500-MHz ^1H NMR spectroscopy (CD_2Cl_2) with signals at 6.83, 6.26, and 6.19 ppm for the η^6-bound pyridine protons and 2.04 ppm for the Cp* signal. The N to π rearrangement was more conveniently followed by NMR spectroscopy. Thus, **5** in CH_2Cl_2 was followed by NMR spectroscopy (CD_2Cl_2) for 11 days or, more preferably, in $(CH_3)_2CO$ over a 48-h period (NMR, $(CD_3)_2CO$) of time at ambient temperature to be totally converted to **7**.

The mechanism of the N to π rearrangement, an irreversible process, was extensively studied in the $CpRu^+$ system[4] and was thought to occur by an initial dissociation of a CH_3CN ligand followed by an η^1–η^4–η^6 slip-fold process; the driving force being the formation of the thermodynamically more stable $\eta^6(\pi)$-bonded complex (eq 2). The irreversible nature of the rearrangement lies in the fact that the η^6 ligand displacement reaction, i.e., reaction of CH_3CN with **7**, is concentration dependent *but does not directly form the* $\eta^1(N)$*-bonded starting complex*. At the low concentrations of CH_3CN that are formed in the rearrangement, no displacement reaction occurs, as observed by NMR spectroscopy.[4] One can displace the η^6-bonded pyridine ligand in complex **7**, presumably via η^6–η^4–η^2-pyridine coordination (associative process), by conducting the reaction (NMR analysis) using CD_3CN as the solvent. After 1 h, we observe a 1:1 ratio of $[Cp^*Ru(CD_3CN)_3](OTf)$ to **7** along with free pyridine; however, complex **5**-d_6, as stated above, is not directly formed in this process.[4]



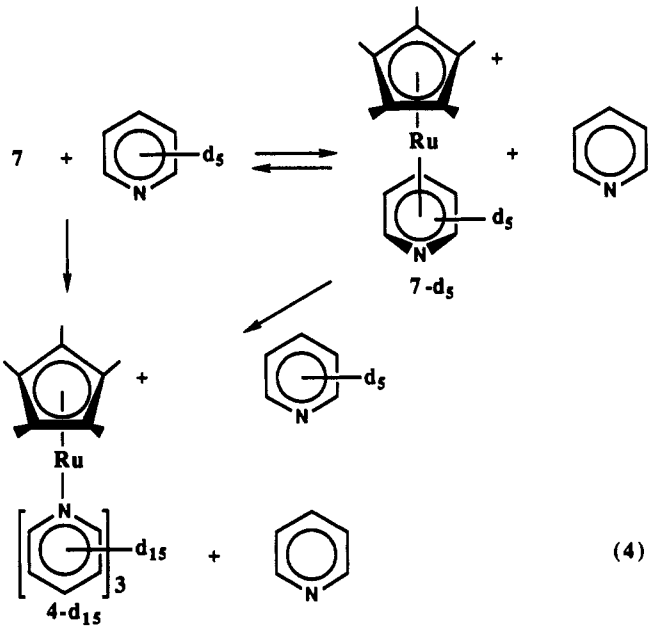
Complex **5**-d_6 was the only complex evident (NMR analysis) after 24 h, when free pyridine (1 equiv) reacted with $[Cp^*Ru(CD_3CN)_3](OTf)$ (eq 3).

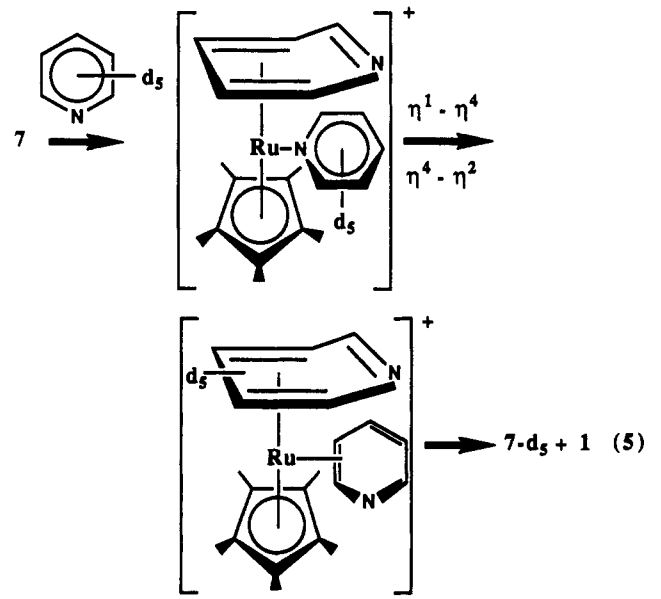


5-d_6

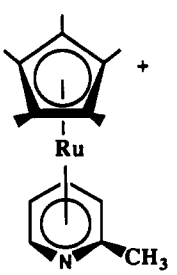
The reaction of complex **7** with pyridine-d_5 (**1**-d_5) as the solvent was also studied by NMR spectroscopy. It was observed that **7**-d_5 was rapidly formed with **4**-d_{15} in a ~1:1 ratio (1 h) along with free **1**, while after 24 h only **4**-d_{15} was present (eq 4).

Apparently, the η^6-bonded pyridine ligand, **7**, can readily exchange with free **1**-d_5 to give the η^6-bonded pyridine-d_5, **7**-d_5, as was previously shown for the CpRu analogue.[4] However, it can also, in a slower process, react to provide the tris N-bonded complex, **4**-d_{15}. The mechanism of the η^6 to η^6 ligand exchange (**7** to **7**-d_5) with free **1**-d_5 is not totally evident, but might occur via a η^1,η^4 intermediate. Thus, free pyridine-d_5 initially bonds η^1 to Ru, while η^6-complexed pyridine becomes η^4. The process then reverses by a facile N to π rearrangement to give pyridine-d_5 as η^4 and, by loss of η^2-bound pyridine, the η^6-bonded pyridine-d_5 (eq 5).





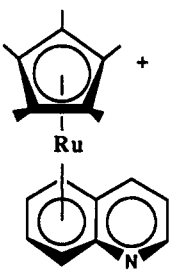
The dramatic effect on the bonding mode of placing a methyl group at the 2-position of pyridine was studied by reaction of ligand **2** with $[Cp^*Ru(CH_3CN)_3](OTf)$. The only product isolated (84%) was $Cp^*Ru(\eta^6$-2-methylpyridine) + (**8**), with no observation of its precursor, $[CpRu(\eta^1(N)$-2-methylpyridine$)(CH_3CN)_2]^+$ (**9**).



8

Clearly, the steric effect of the methyl group weakened the Ru–N bond in **9** and provides one driving force for the facile N to π rearrangement to form **8**. The steric effect of the methyl group cannot be the sole determining factor for the ready conversion of **9** to **8**, since kinetic products in the $CpRu^+$ series with the general formula $[CpRu(\eta^1$-(N)-ligand$)(CH_3CN)_2]^+$ were readily isolated. It appears that the Cp* ligand must also influence the N to π rearrangement due to its powerful electron-donating ability, which makes the soft Ru metal center a better π donor and thus able to stabilize the η^6-bonded complex by back-bonding from filled metal orbitals to π^* orbitals of the nitrogen ligand.

The reaction of a polynuclear heteroaromatic nitrogen ligand, **3**, with $[Cp^*Ru(CH_3CN)_3](OTf)$ provided $[Cp^*Ru(\eta^6$-quinoline$)]^+$ (**10**), with no observation of its η^1(N)-bonded precursor.[2b] The structure of **10** was established by ^1H and ^{13}C NMR spectroscopy and was consistent with the fully characterized CpRu analogue.[1b,4]



10

Conclusions

The dramatic differences between our pyridine results and those of Chaudret and co-workers[2] must arise from the starting Cp^*Ru^+ derivatives. In our case, Cp^*Ru^+ can back-bond from filled metal orbitals to π^* orbitals of the CH_3CN ligand, making it less labile, while they appear to form a $[Cp^*Ru(THF)_3]^+$ complex in situ; THF is not able to back-bond and is sterically more demanding than CH_3CN, allowing it to dissociate more rapidly. Therefore, with the THF derivative, the N to π rearrangement is perhaps faster than further THF displacement from the Ru metal center with pyridine. The opposite conclusion appears true when the CH_3CN derivative is used: displacement faster than rearrangement. In fact, we have observed a dramatic solvent effect on the rate of the N to π rearrangement with the $[CpRu(\eta^1(N)$-ligand$)(CH_3CN)_2]^+$ complexes[4] as well as the present conversion of **5** to **7** in $(CH_3)_2CO$; there is a substantial rate increase presumably by replacement of complexed CH_3CN with $(CH_3)_2CO$, which is a better leaving group.

The steric effect of a methyl group, ligand **2**, or a benzo group, ligand **3**, and the arenophilicity of Cp^*Ru^+ favors the formation of the η^6- over the η^1(N)-bonded complex; however, when the steric effect is absent, i.e., ligand **1**, η^1(N)-bonding is favored with $[Cp^*Ru(CH_3CN)_3](OTf)$ as the starting material. The π-bonded pyridine ligand replacement with excess CD_3CN was also shown to presumably occur by an associative η^6–η^4–η^2-pyridine mechanism followed by formation of $[Cp^*Ru(CD_3CN)_3](OTf)$ and free pyridine; this result proves the irreversible nature of the N to π rearrangement. The π-bonded pyridine ligand exchange with excess free pyridine-d_5 provided both η^6-d_5 and tris η^1(N)-d_{15} complexes.

We are continuing our Cp^*Ru^+ bonding studies with other heteroaromatic nitrogen compounds and also initiating reactivity studies. For example, $[Cp^*Ru(CH_3CN)_3](OTf)$ was found to be a rather poor catalyst precursor for the selective hydrogenation of **3** to 1,2,3,4-tetrahydroquinoline because of the facile formation of **10**; initial η^1(N)-bonding is critical for selective nitrogen ring reduction.[1a,5]

(5) Fish, R. H.; Baralt, E.; Smith, S. J. *Organometallics* **1991**, *10*, 54.

Experimental Section

Instrumentation and Materials. ^1H and ^{13}C NMR analyses were performed on either a Bruker AM 400- or 500-MHz instrument located in the Department of Chemistry, University of California, Berkeley, CA. All the reactions were done under argon in a Vacuum Atmospheres glovebox equipped with a −30 °C freezer. Elemental analyses were performed by the microanalytical laboratory located in the Department of Chemistry, University of California, Berkeley, CA. All nitrogen heterocyclic ligands were purchased from Aldrich Chemical Co. and redistilled before use. Anhydrous methylene chloride, acetone, and acetonitrile were purchased from Aldrich Chemical Co., while diethyl ether was distilled from Na/benzophenone ketyl. [Cp*Ru(CH_3CN)$_3$](OTf) was prepared according to the literature procedure.[3]

Synthesis of [Cp*Ru(η^1(*N*)-pyridine)$_3$](OTf) (4). A 100.0-mg (0.197 mmol) sample of [Cp*Ru(CH_3CN)$_3$](OTf) was dissolved in 5 mL of CH_2Cl_2, and the solution was stirred at room temperature. An excess of pyridine was added (0.24 mL, 2.95 mmol), and the resulting mixture was stirred for 60 min. Then, 20 mL of diethyl ether was added and the solution cooled to −30 °C. The orange solid was filtered off, washed with diethyl ether, and vacuum-dried to give 107 mg of the complex (87% yield). ^1H NMR (400 MHz, CD_2Cl_2, ppm): 1.29 (s, Me_5), 7.34 (t, br, H(4), J = 6.9 Hz), 7.78 (t, br, H(3,5), J = 7.6 Hz), 8.30 (d, br, H(2,4), J = 5.0 Hz), ratio 15:1:2:2. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, ppm): 154.92 (s, C(2,4)), 137.50 (s, C(3,5)), 126.46 (s, C(4)), 77.72 (s, C_5Me_5), 8.71 (s, C_5Me_5), 122.44 (q, CF_3, J = 322 Hz). Anal. Calc for $C_{28}H_{30}F_3N_3O_3RuS$: C, 50.15; H, 4.86; N, 6.75. Found: C, 50.07; H, 4.59; N, 6.52.

Synthesis of [Cp*Ru(η^1(*N*)-pyridine)(CH_3CN)$_2$](OTf) (5). A 100.0-mg (0.197 mmol) sample of [Cp*Ru(CH_3CN)$_3$](OTf) was dissolved in 5 mL of CH_2Cl_2 with 200 μL of CH_3CN added, and then the reaction flask was cooled to −30 °C. Pyridine (1 equiv) was then added, and the reaction was stirred at room temperature for 5 min. A 30-mL aliquot of diethyl ether was added, and the solution was placed in a freezer at −30 °C overnight. The resulting yellow-orange crystals were filtered off, washed with hexane, and then vacuum-dried to give 96 mg of product (81% yield). ^1H NMR (400 MHz, CD_2Cl_2, ppm): 1.48 (s, Me_5), 2.45 (s, br, CH_3), 7.35 (t, br, H(3,5), J = 7.0 Hz), 7.77, (tt, H(4), J = 1.6, 6.0 Hz); 8.56 (dd, H(2,6), J = 1.6, 6.5 Hz), ratio 15:6:2:1:2. Analytical data could not be obtained due to complex instability (also contaminated with <5% of Cp*Ru(η^1(*N*)-pyridine)$_2$(CH_3CN)$^+$ (6), Cp* at 1.41 ppm).

Synthesis of [Cp*Ru(η^6-pyridine)](OTf) (7). An 80.0-mg (0.12 mmol) sample of [Cp*Ru(η^1(*N*)-pyridine)(CH_3CN)$_2$](OTf) (5) was dissolved in 10 mL of $(CH_3)_2CO$, and the solution was stirred at room temperature for 48 h and vacuum-dried for 4 h to give 56 mg of product (100% yield). ^1H NMR of the dark green solid indicated complete conversion to 7. Alternatively, the complex can be formed by heating 5 as a solid under vacuum at 80 °C for 12 h. ^1H NMR (400 MHz, CD_2Cl_2, ppm): 2.04 (s, Me_5), 6.45 (t, H(4), J = 5.3 Hz), 6.81 (t, H(2,6), J = 3.60 Hz), 6.34 (t, H(3,5), J = 5.59 Hz), ratio 15:2:1:2. Anal. Calc for $C_{16}H_{20}F_3NO_3RuS$: C, 41.36; H, 4.34; N, 3.01. Found: C, 41.46; H, 4.79; N, 2.93.

Synthesis of [Cp*Ru(η^6-2-methylpyridine)](OTf) (8). A 100-mg (0.197 mmol) sample of [Cp*Ru(CH_3CN)$_3$](OTf) was dissolved in 5 mL of CH_2Cl_2, and the solution was stirred at room temperature. An excess of 2-methylpyridine was added (0.05 mL, 0.59 mmol), and the resulting mixture was stirred for 30 min. The reaction was evaporated to dryness, and the resulting white solid was washed with *n*-hexane, filtered off, and vacuum-dried. Recrystallization from CH_2Cl_2/*n*-hexane (1/0.5 mL) at −30 °C gave 80.0 mg of the product (84% yield). ^1H NMR (400 MHz, CD_2Cl_2, ppm): 1.98 (s, Me_5), 2.00 (s, CH_3), 6.78 (d, br, H(6), J = 3.7 Hz), 6.21 (dt, H(5), J = 1.4, 6.1 Hz), 6.11 (m, H(4,3)), ratio 15:3:1:1:2. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, ppm): 119.74 (s, C(2)), 106.41 (s, C(6)), 91.45 (s, C(4)), 86.98 (s, C(3)), 86.81 (s, C(5)), 20.80 (s, CH_3), 98.90 (s, C_5Me_5), 10.33 (s, C_5Me_5), 122.35 (q, CF_3, J = 322 Hz). Anal. Calc for $C_{17}H_{22}F_3N_3O_3RuS$: C, 42.55; H, 4.63; N, 2.93. Found: C, 42.55; H, 4.42; N, 2.89.

Synthesis of [Cp*Ru(η^6-quinoline)](OTf) (10). A 100.0-mg (0.197 mmol) sample of [Cp*Ru(CH_3CN)$_3$](OTf) was dissolved in 5 mL of CH_2Cl_2. An excess of quinoline was added (0.07 mL, 0.59 mmol), and the solution was stirred for 30 min. Then 40 mL of ether was added to the resulting pale yellow solution, and the solution was cooled to −30 °C overnight. The light yellow solid was filtered off, washed with diethyl ether, and vacuum-dried to give 85 mg of 10 (84% yield). ^1H NMR (400 MHz, CD_2Cl_2, ppm): 1.69 (s, Me_5), 6.09 (m, br, H(8)), 6.63 (m, br, H(6)), 6.67 (m, br, H(7)), 7.60 (dd, H(4), J = 3.8, 8.8 Hz), 8.11 (d, H(3), J = 8.8 Hz), 9.15 (dd, H(2), J = 1.7, 3.8 Hz), ratio 15:1:1:1:1:1:1; $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, ppm): 9.66 (s, Me_5), 122.44 (q, CF_3, J = 322.0 Hz), 160.01 (s, C(2)), 139.13 (s, C(4)), 126.02 (s, C(3)), 113.16 (s, C(10)), 95.49 (s, C(9)), 91.13 (s, C(5)), 90.03 (s, C(8)), 88.21 (s, C(6)), 86.64 (s, C(7)), 93.87 (s, Me_5C_5). Anal. Calc for $C_{20}H_{22}F_3NORuS$: C, 46.69; H, 4.31; N, 2.72. Found: C, 45.90; H, 4.04; N, 2.60.

Reaction of Complex 7 with CD_3CN: NMR Study. A 5-mg (0.01 mmol) sample of 7 was dissolved in 0.6 mL of CD_3CN, and the reaction was monitored by ^1H NMR spectroscopy. After 1 h, a 1:1 ratio of 7 and [Cp*Ru(CD_3CN)$_3$]$^+$ was observed at 2.04 and 1.57 ppm, respectively, with the appearance of free pyridine. After 24 h, complex 7 and [Cp*Ru(CD_3CN)$_3$]$^+$ are not evident and 5-d_6 (1.48 ppm) is the only complex in solution.

Reaction of Complex 7 with Pyridine-d_5: NMR Study. A 3.9-mg (0.008 mm) sample of 7 was dissolved in 0.6 mL of pyridine-d_5. ^1H NMR spectroscopy indicated that after 1 h a 2:1:1 ratio of complex 4-d_{15} at 1.15 ppm, complex 7-d_5 at 1.88 ppm, and unreacted complex 7 (1.78 ppm) was observed. After 24 h, only complex 4-d_{15} was observed in solution.

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