The position of the Fe atom was determined by direct methods (MULTAN 78).[11] All other computations were carried out by use of the Universal Crystallographic Computation Program System, UNICS III.[12] Subsequent difference Fourier maps revealed the positions of the remaining non-hydrogen atoms. After all the non-hydrogen atoms had been refined isotropically, a series of refinements with anisotropic thermal parameters for all non-hydrogen atoms reduced R_1 ($\sum(|F_o| - |F_c|)/\sum|F_o|$) to 0.078 and R_2 ($[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$) to 0.081. All hydrogen atoms were placed at idealized positions. In the final stage, non-hydrogen atoms were refined anisotropically, including hydrogen atoms whose positions were fixed (B = 4.0 Å^2). In the final refinement R_1 converged to 0.064 and R_2 to 0.065: unit weighting was used. All atomic scattering factors were taken from Cromer and Weber.[13]

All the computations, including the ORTEP drawing,[14] were carried out by a HITAC M-680H computer at the Hiroshima University Information Processing Center.

Acknowledgment. We thank Mr. Akira Mizuno and Mr. Yoshihisa Toda at the Materials Science & Analysis Laboratories, Mitsui Petrochemical Industry, Ltd., for ^{31}P NMR measurements. We acknowledge financial support from the Ministry of Education under Grant No. 01470052 and 02640479.

Supplementary Material Available: Tables of calculated hydrogen atom parameters and anisotropic thermal parameters for 3 (Tables V and VI) (2 pages); a listing of observed and calculated structure factors (Table VII) (12 pages). Ordering information is given on any current masthead page.

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(13) Cromer, D. T.; Weber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72-79.

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Bonding Mode of Nitrogen Heterocyclic Ligands to (η^5-Cyclopentadienyl)ruthenium Cation and Reactivity Studies of the Nitrogen and π-Bonded Complexes: Mechanistic Aspects of a Nitrogen to π Rearrangement

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The nitrogen heterocyclic ligands pyridine (**1**), 2-methylpyridine (**2**), 2,4-dimethylpyridine (**3**), 2,4,6-trimethylpyridine (**4**), quinoline (**5**), isoquinoline (**6**), 2-methylquinoline (**7**), and 1,2,3,4-tetrahydroquinoline (**8**) were reacted with (η^5-cyclopentadienyl)ruthenium cation, $[CpRu(CH_3CN)_3](PF_6)$, to ascertain the mode of bonding as a function of structure, i.e., nitrogen (η^1(N)) versus π (η^6) bonding. Ligands **1**-**3**, **5**, and **6** formed N-bonded complexes, while **4**, **7**, and **8** only formed π-bonded complexes. Thus, it appears that steric and electronic effects influence the bonding mode of nitrogen heterocyclic compounds to $CpRu^+$. An interesting N (η^1) to π (η^6) rearrangement occurred with the N-bonded $CpRu^+$ complexes of ligands **2**, **3**, and **5**, and mechanistic aspects were studied by ^{1}H NMR spectroscopy. Crossover experiments with $[CpRu(\eta^1(N)\text{-2-methylpyridine})(CH_3CN)_2]^+$ (**11**) and $[MeCpRu(\eta^1(N)\text{-2-methylpyridine-}d_7)(CH_3CN)_2]^+$ (**21**-d_7) clearly show that N(η^1)-bonded complexes undergo ligand exchange much faster than the N to π rearrangement at 21 °C (NMR probe temperature). Furthermore, neither N- and π-bonded complexes nor π- and π-bonded complexes undergo ligand exchange with each other; however, both types of bonding modes did undergo facile exchange with free nitrogen ligand. These exchange reaction rates were found to be concentration-dependent. Consequently, our attempts to use the former result with N- and π-bonded complexes to prove the intramolecular nature of the N to π rearrangement, i.e., rearrangement of **11** in the presence of $[MeCpRu(\eta^6\text{-2-methylpyridine-}d_7)]^+$ (**22**-d_7), were not successful; exchange of any free **2** that might form, i.e., at low concentrations, with **22**-d_7 was found to be slower than the N to π rearrangement. The role of the acetonitrile ligand in the N to π rearrangement and in the displacement of η^1- and η^6-bonded nitrogen heterocyclic ligands will also be discussed.

The bonding mode of nitrogen heterocyclic ligands to rhodium and ruthenium complexes that act as homogeneous catalysts has been of considerable interest due to its pivotal role in the regioselective hydrogenation of the nitrogen-containing ring of these model coal compounds.[1] We recently communicated our initial results on the bonding mode of polynuclear heteroaromatic nitrogen ligands with (η^5-pentamethylcyclopentadienyl)rhodium dicationic complexes (Cp^*Rh^{2+}) and (η^5-cyclopentadienyl)ruthenium cationic complexes ($CpRu^+$), i.e., nitrogen (N) versus π bonding, and have shown that the regioselectivity of nitrogen ring reduction is in fact dependent on the ligand being N-bonded to the Rh or Ru metal centers.[2]

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(2) (a) Fish, R. H.; Kim, H.-S.; Babin, J. E.; Adams, R. A. *Organometallics* **1988**, *7*, 2250. (b) Fish, R. H.; Kim, H.-S.; Fong, R. H. *Organometallics* **1989**, *8*, 1375. (c) $[CpRu(CH_3CN)_3]^+$ was found to be a poor catalyst precursor for the selective hydrogenation of **5** to **8** in comparison to $[Cp^*Rh(CH_3CN)_3]^{2+}$. A preliminary account of the selective hydrogenation reactions of nitrogen heterocyclic compounds with $[Cp^*Rh(CH_3CN)_3]^{2+}$ as the catalyst precursor has appeared (Fish, R. H.; Baralt, E.; Smith, S. J. *Organometallics* **1991**, *10*, 54).

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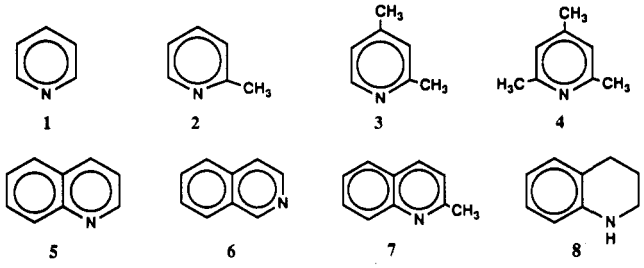
Chart I. Model Coal, Nitrogen Heteroaromatic Ligands Used in the Bonding Studies with $CpRu^+$



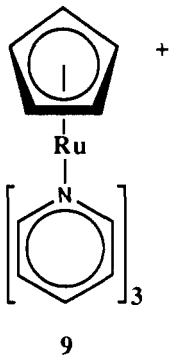
In this paper, we present the full details of our synthesis and bonding studies of (η^5-cyclopentadienyl)ruthenium tris(acetonitrile) cation[3] ($[CpRu(CH_3CN)_3]^+$) with a number of nitrogen heterocyclic ligands (1–8, Chart I). Prior to our initial report, the only previous nitrogen heterocyclic ligand bonding studies to $CpRu^+$ were those by Moriarty et al. with indole derivatives, and they observed π (η^6) bonding to the aromatic ring.[4] In addition, Chaudret and Jalon published some preliminary results on the bonding mode of pyridine and several methyl-substituted pyridine ligands with (η^5-pentamethylcyclopentadienyl)ruthenium cation (Cp^*Ru^+).[5] In all cases, they isolated π-bonded Cp^*Ru^+ complexes, while observing a pronounced solvent effect in acetone that provided a pyridine N-bonded complex ($(py)_6Ru^{2+}$), with a concomitant loss of Cp^*.

The bonding results we present with $CpRu^+$ are dramatically different from those of the bonding study reported for pyridine and substituted analogues with Cp^*Ru^+, and furthermore, we report full mechanistic details on the recently discovered nitrogen (η^1(N)) to π (η^6) rearrangement for N-bonded complexes [CpRu(η^1(*N*)-2-methylpyridine)$(CH_3CN)_2]^+$ (**11**), [CpRu(η^1(*N*)-2,4-dimethylpyridine)$(CH_3CN)_2]^+$ (**12**), and [CpRu(η^1(*N*)-quinoline)$(CH_3CN)_2]^+$ (**16**) to their π-bonded analogues.[2b] A similar rearrangement was previously reported by Morris and Ressner for a (η^1(*N*)-pyridine)bis(dinitrogen)bis(methyldiphenylphosphine)molybdenum complex.[6] Additionally, the critical role of acetonitrile in the N to π rearrangement and its ability to displace η^1- and η^6-bonded nitrogen ligands will be discussed.

During the course of our studies, we have investigated several important criteria that influence the bonding mode of nitrogen heterocyclic ligands to $CpRu^+$, i.e., steric and electronic effects, which control the availability of lone-pair electrons on the nitrogen atom and affect the lability of the Ru–N bond. More importantly, several new exchange reactions of N- and π-bonded ligands with free nitrogen ligands and ligand-exchange reactions between different N-bonded $CpRu^+$ complexes were established.

Results

Pyridine and Methylpyridines. The reaction of excess pyridine (1) with $[CpRu(CH_3CN)_3]^+$ for 30 min at room temperature in CH_2Cl_2 provided complex **9**, which from ^1H and ^{13}C NMR and elemental data was clearly tris N-bound. Notably, the characteristic Cp resonance at 4.24 ppm and the downfield shifts of the pyridine protons in the ^1H NMR spectrum, compared to free pyridine, were similar for all of the N-bonded complexes we report and

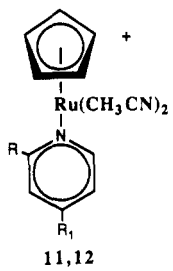


9

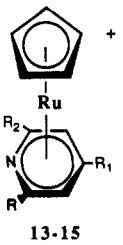
corroborate the structure of **9**.

Alternatively, reaction in CH_3CN provided the bis(pyridine), N-bonded complex [CpRu(η^1(*N*)-pyridine)$_2$-$(CH_3CN)]^+$ (**10**), as well as small amounts of **9**. In fact, reaction of **9** with CD_3CN by ^1H NMR analysis shows the formation of **10**-d_3 and free **1**. These N-bonded results contrast with those obtained for Cp*Ru and pyridine,[5] in which η^6 bonding is prevalent, and are representative of the role of the acetonitrile ligand in the mechanism of ligand replacement. In addition, coordinatively saturated **9** is thermally stable (prolonged heating (12 h) of **9** in 1,2-dichloroethane at 80 °C). Even heating **10** in 1,2-dichloroethane only provided **9**, with no π-bonded pyridine complexes observed.

The reaction of 2-methylpyridine (**2**) and 2,4-dimethylpyridine (**3**) with $[CpRu(CH_3CN)_3]^+$ in CH_2Cl_2 also resulted in the formation of N-bonded complexes **11** and **12** (R = CH_3, R_1 = H; R, R_1 = CH_3) by ^1H NMR analysis, but in these cases only one acetonitrile ligand was displaced. The N-bonded complexes were successfully iso-



11,12



13-15

lated by using short reaction times (5 min at room temperature in CH_2Cl_2), followed by addition of diethyl ether and crystallization (−30 °C). Interestingly, initial attempts to isolate these N-bonded complexes by use of longer reaction times (20 h at room temperature in CH_2Cl_2) followed by solvent removal only resulted in the isolation of the π-bonded complexes **13** and **14** (R = CH_3, R_1, R_2 = H; R, R_1 = CH_3, R_2 = H), which had characteristic Cp signals at 5.70 and 5.64 ppm, respectively, and upfield shifts of the pyridine ring protons compared to the free ligand; these findings are similar for all of the π-bonded complexes we report. This result was the first indication that the monosubstituted, N-bonded complexes with two acetonitrile ligands were capable of undergoing an N to π rearrangement.

Alternatively, it is interesting to note that 2,4,6-trimethylpyridine (**4**) only provided the π-bonded complex **15**, an indication that steric crowding around nitrogen may prevent the isolation of the N-bonded complex.[7]

Quinoline Derivatives. The polynuclear heteroaromatic nitrogen ligand quinoline (**5**) and its isomer iso-

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(4) For an excellent review of the η^6 complexation of arenes, including substituted indole ligands, with $CpRu^+$, see: Moriarty, R. M.; Gill, U. S.; Ku, Y. Y. *J. Organomet. Chem.* **1988**, *350*, 157 and references therein.

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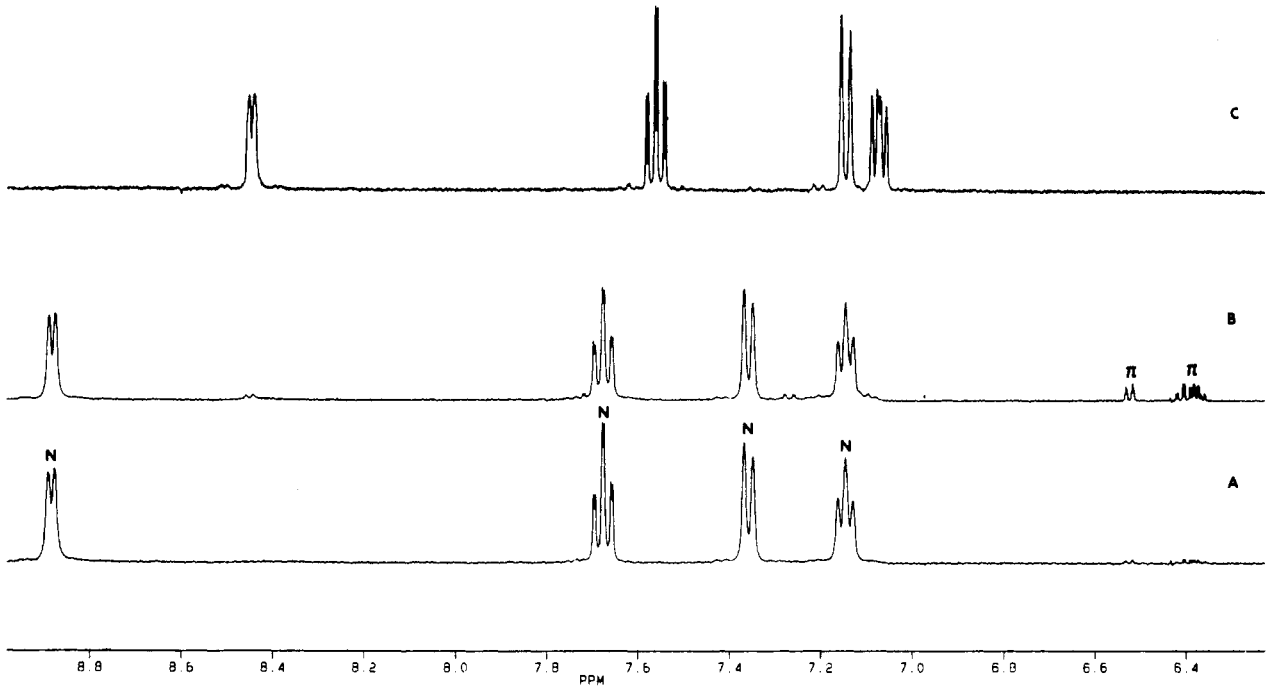
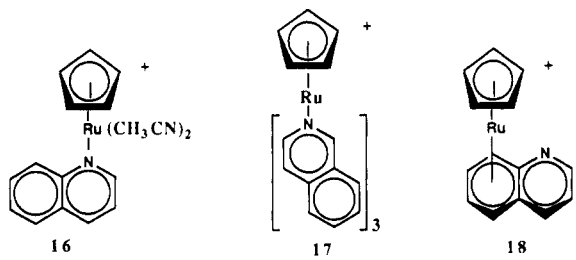


Figure 1. N to π rearrangement of 11 at room temperature: (A) ^{1}H NMR spectrum of 11 in CD_2Cl_2 after 30 min; (B) ^{1}H NMR spectrum of 11 after 24 h; (C) ^{1}H NMR spectrum of 2-methylpyridine in CD_2Cl_2.

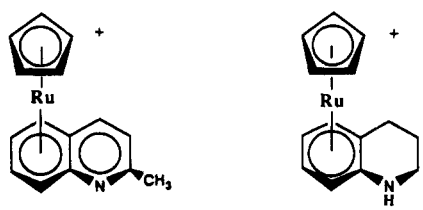
quinoline (6) provided insight into steric effects as a function of the nitrogen ligand structure. The reaction of $[CpRu(CH_3CN)_3]^+$ with 5, in either CH_2Cl_2 or CH_3CN at short reaction times, gave the mono(quinoline), N-bonded complex 16 (Cp at 4.29 ppm and downfield shifts of quinoline protons compared to the free ligand). However,



16 17 18

reaction with 6 gave the tris N-bonded complex 17 in CH_2Cl_2, while in CH_3CN $[CpRu(\eta^1(N)\text{-isoquinoline})_2(CH_3CN)]^+$ could also be formed. As with the N-bonded methylpyridine complexes 11 and 12, complex 16 rearranged to $[CpRu(\eta^6\text{-quinoline})]^+$ (18) with longer reaction times and complete solvent removal. The ^{13}C NMR spectrum clearly indicated that $CpRu^+$ was bonded in an η^6 fashion to the benzene ring and not the pyridine ring.[2b]

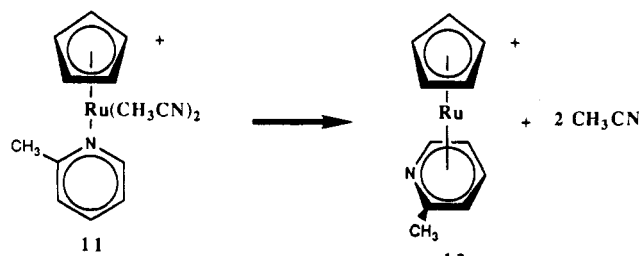
Two other ligands, 2-methylquinoline (7) and 1,2,3,4-tetrahydroquinoline (8), reacted with $[CpRu(CH_3CN)_3]^+$ in CH_2Cl_2 to provide only π-bonded (η^6, benzene ring) complexes, 19 and 20.



19 20

Mechanism of the N to π Rearrangement. The synthetic reaction conditions (kinetic or thermodynamic control), aside from certain ligand-imposed steric and electronic effects, dictated to some extent whether N or π products were formed. The synthetic results show that isolated N-bonded complexes 11, 12, and 16, with two labile acetonitrile ligands, undergo an N to π rearrangement with longer reaction times, with higher temperatures, or under high vacuum (solvent removal).

Initial experiments to elucidate various mechanistic aspects of this interesting rearrangement focused on studying the thermal stability of 11 and 16 by variable-temperature (VT) ^{1}H NMR analysis. For example, complex 11 clearly showed (500-MHz ^{1}H NMR in 1,2-dichloroethane-d_4) that as the temperature was raised from 23 to 70 °C over a 1.5-h period, the formation of complex 13 was apparent (ratio of 11/13 = 6/1 at 70 °C, monitoring of Cp resonances at 4.18/5.47 ppm and CH_3 resonances at 2.80/2.57 ppm, respectively), *without the observation of free ligand* 2 (eq 1). When the temperature was

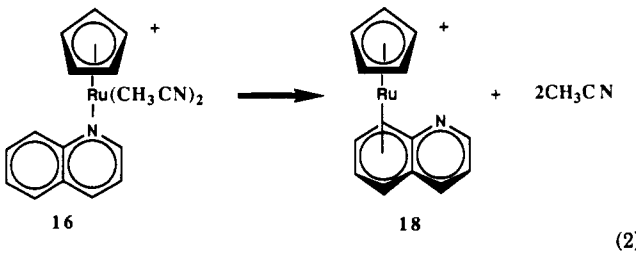


11 13 (1)

brought back to 23 °C, the ratio of 11/13 did not change appreciably, an indication that the rearrangement was not an equilibrium nor was it undergoing, to any significant extent, a displacement process with acetonitrile. Figure 1 demonstrates the ease by which the rearrangement of 11 to 13 can be followed via ^{1}H NMR spectroscopy. Figure 1A shows the spectrum of 11 in CD_2Cl_2 after 30 min at ambient temperature, and after 24 h, complex 13 is evident from the upfield shifts of the η^6-2-methylpyridine ligand (Figure 1B) without the observation of free ligand 2 (Figure 1C).

The N to π rearrangement of 16 to 18 was much more facile than that of 11 to 13 and occurred on immediate

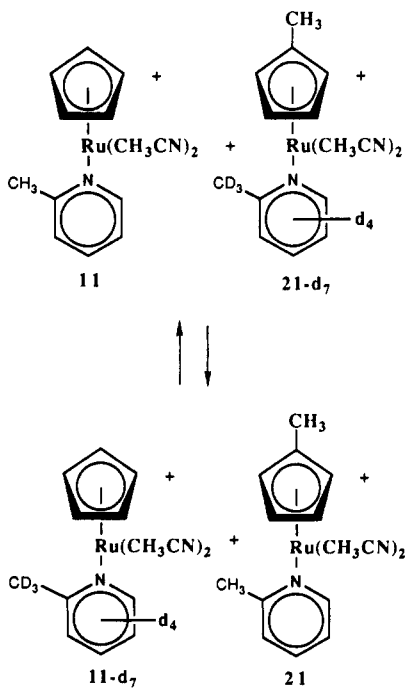
dissolution of pure **16** in 1,2-dichloroethane-d_4. Upon heating the mixture of complexes **16** and **18** (**16**/**18** = 7/3, monitoring of Cp, 4.27/5.03 ppm) in an NMR tube (500-MHz ^{1}H NMR spectroscopy, 1,2-dichloroethane-d_4) from 23 to 70 °C over a 1.5-h period, we found that the ratio of **16**/**18** at 70 °C became 1/9 (eq 2). As in the VT NMR



(2)

experiment with complex **11**, we saw no free ligand **5** in the N to π rearrangement of **16** to **18**. Again, we lowered the temperature back to 23 °C but saw no significant change in the ratio of **16**/**18**, an indication that eq 2 was not an equilibrium. Figure 2 demonstrates the conversion of **16** to **18** at ambient temperature in $C_2D_4Cl_2$. Within 30 min, **16** has already undergone considerable rearrangement at ambient temperature (Figure 2A), and after 24 h, complex **18** is dominant from its characteristic upfield shifts (Figure 2B), with no observation of free ligand **5** (Figure 2C).

In order to completely elucidate the mechanism of this rearrangement, we wanted to conduct double-labeling crossover experiments to define unequivocally whether the rearrangement was an intra- or intermolecular process. Synthesis of [(η^5-methylcyclopentadienyl)Ru(η^1(*N*)-2-methylpyridine-d_7)(CH_3CN)$_2$]$^+$ (**21**-d_7) provided an opportunity to answer this important question. However, a 1/1 reaction of **11** with **21**-d_7 in $C_2D_4Cl_2$ at 23 °C immediately provided scrambling of the ligands to give [CpRu(η^1(*N*)-2-methylpyridine-d_7)(CH_3CN)$_2$]$^+$ (**11**-d_7) and [MeCpRu(η^1(*N*)-2-methylpyridine)(CH_3CN)$_2$]$^+$ (**21**) in a ~1/1 ratio, prior to any substantial N to π rearrangement (eq 3). This mixture then further rearranged to a 1/1



(3)

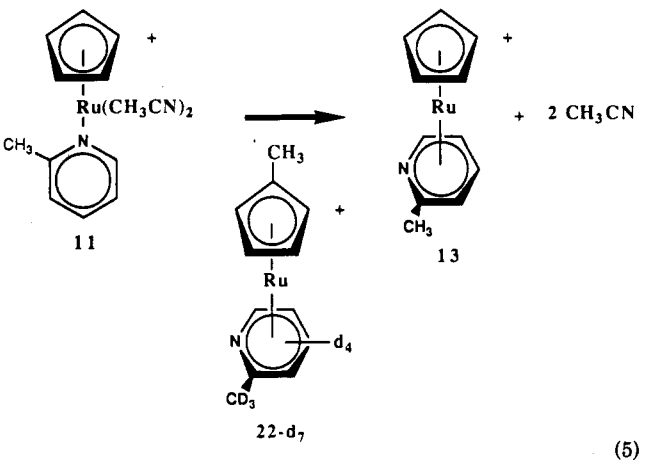
mixture of the π-bonded complexes **13** and [MeCpRu(η^6-2-methylpyridine)]$^+$ (**22**). A control experiment between the π-bonded complexes **13** and **22**-d_7 in CD_2Cl_2 at 23 °C indicated no exchange of the π-bonded ligands.

In order to overcome the scrambling dilemma, we discovered that both N- and π-bonded complexes undergo facile ligand exchange with free nitrogen ligands. Reaction of **11** with **2**-d_7 (1/1) in CD_2Cl_2 immediately showed the formation of free 2-methylpyridine (**2**). Likewise, **13** rapidly exchanged in CD_2Cl_2 with 2-methylpyridine-d_7 (**2**-d_7; 1/1) to also provide free **2** (eq 4). *Moreover, we found*

$$\mathbf{13} + \mathbf{2}\text{-}d_7 \rightleftharpoons \mathbf{13}\text{-}d_7 + \mathbf{2} \qquad (4)$$

that the rate of exchange in eq 4 was concentration-dependent. At a 13/1 concentration ratio of **13** to **2**-d_7, only 5% of **2** was evident after 24 h (^{1}H NMR). Thus, at low concentrations of free **2**-d_7, very slow exchange with π-bonded **2** was observed.

Accordingly, if the exchange of free ligand **2** with the π-complexed ligand were rapid, then an intermolecular N to π rearrangement of **11** in the presence of **22**-d_7 would result in the formation of **22**. Conversely, if the rearrangement were intramolecular, then there would be no observation of **22** in the ^{1}H NMR spectrum. Therefore, we studied complex **11** in the presence of **22**-d_7 (CD_2Cl_2) and found no formation of **22** after 24 h and ~15% conversion of **11** to **13** (eq 5). *Unfortunately, the fact that*



(5)

no formation of **22** *was observed still does not allow us to unequivocally assign an intramolecular mechanism to the N to π rearrangement, due primarily to the slow exchange at low concentrations of free* **2** *with π-complexed* **2**.

The kinetics of the N to π rearrangement were studied by NMR spectroscopy at 35 °C (±1 °C) in CD_2Cl_2 with complex **11**, by monitoring the disappearance of the Cp signal. The reaction was studied at two different concentrations of **11**, 1.68×10^{-2} and 9.50×10^{-3} M. First-order kinetics of the initial rates (first 30–40 min) gave $k_1 = 2.92 \times 10^{-3}$ and 5.12×10^{-3} s^{-1}, respectively. However, as the N to π rearrangement proceeds, the rates are slowed in both cases. We believe that this result is due to the role of free CH_3CN in that as its concentration increases during the N to π rearrangement, it causes the reaction rate to slow down by competing for the ruthenium center with the rearranging complexed nitrogen ligand. This was further verified by preparing complex **11** in situ in an NMR tube with CD_3CN as solvent; *no N to π rearrangement of* **11** *to* **13** *was observed.* We also determined (NMR), qualitatively, that when CD_2Cl_2 was replaced as the solvent with $(CD_3)_2CO$ the rate of rearrangement of **11** to **13** increased markedly.

Displacement Reactions of N- and π-Bonded Nitrogen Ligands with CH_3CN. As we have just shown, the role of free CH_3CN in the N to π rearrangement ap-

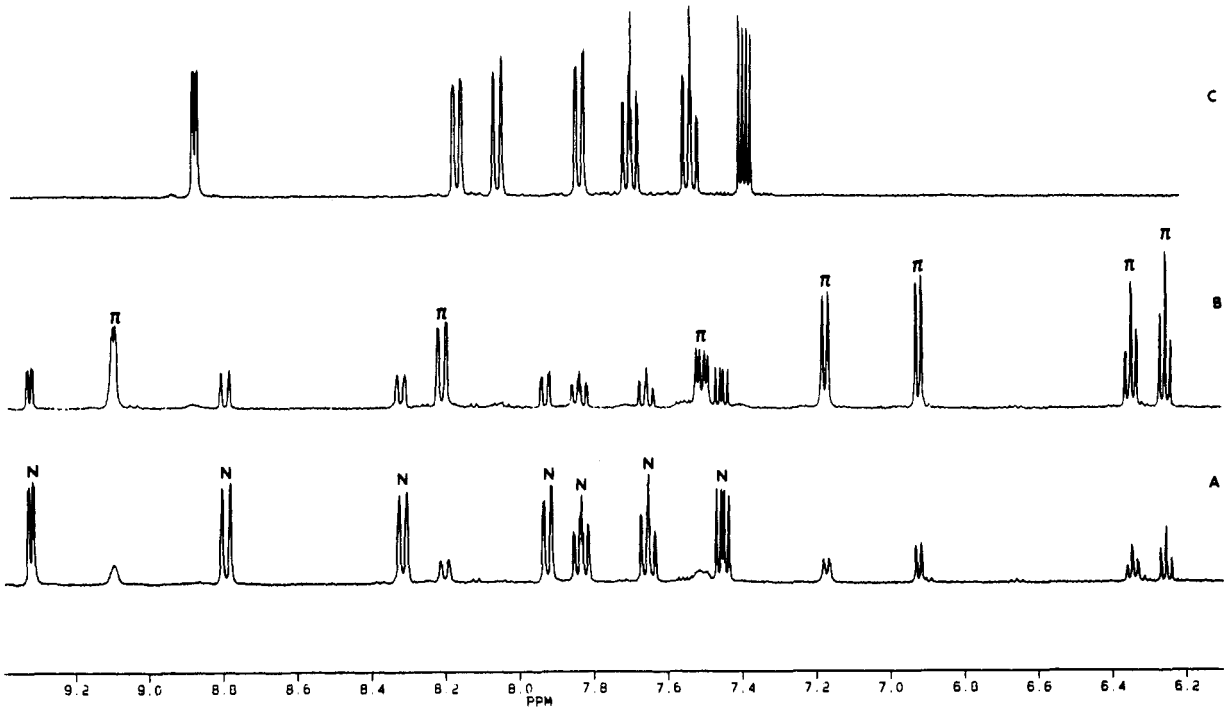


Figure 2. N to π rearrangement of **16** at room temperature: (A) ^{1}H NMR spectrum of **16** in $C_2D_4Cl_2$ after 30 min; (B) ^{1}H NMR spectrum of **16** after 24 h; (C) ^{1}H NMR spectrum of quinoline in $C_2D_4Cl_2$.

pears to be that of slowing this reaction; therefore, we decided to study the displacement reactions of both **11** and **13** by ^{1}H NMR spectroscopy with CD_3CN as the solvent. Reaction of **11** in CD_3CN (0.02 M) shows formation of free **2** and $[CpRu(CD_3CN)_3]^+$ (ratio of $[CpRu(CD_3CN)_3]^+/11 = 6$). The reaction of **13** in CD_3CN also gives free **2** and $[CpRu(CD_3CN)_3]^+$ without the formation of **11** (1 h); however, upon further reaction, the free **2** reacts with the formed $[CpRu(CD_3CN)_3]^+$ to give $[CpRu(\eta^1(N)\text{-}2\text{-methylpyridine})(CD_3CN)_2]^+$; *this provides further evidence that the N to π rearrangement is not reversible but that CH_3CN fully displaces π-complexed nitrogen ligands before N-complexed nitrogen ligands can form.*

Additionally, Mann et al.[8] have shown that the rates of the $[CpRu(\eta^6\text{-aromatic})]^+$ displacement reactions with CH_3CN are concentration-dependent (associative process); therefore, in the case of the N to π rearrangements, any displacement reaction with N- or π-bonded complexes by the relatively low concentration of free CH_3CN should be extremely slow in both $C_2D_4Cl_2$ and CD_2Cl_2, as is observed.

Discussion

Ligand Structure and Reactivity with $CpRu^+$. The structures of the nitrogen heterocyclic ligands have a profound effect on the product being N-bound and either mono or tris substituted. This is reflected in several cases; namely, **1** and **2**, with the steric effect of the 2-methyl group in **2** the possible reason that the mono(2-methylpyridine) complex **11** is preferred, while with ligand **1**, the tris(pyridine) complex **9** is favored. Similarly, with ligand **5**, the benzo group apparently creates a steric effect that favors the mono(quinoline) complex, **16**, while with its less sterically demanding isomer **6**, the tris(isoquinoline) complex **17** was preferred.

In addition, steric effects can contribute to a change in the bonding mode that favors π-bonding, rather than N-bonding. For example, ligand **4**, with methyl groups in the 2- and 6-positions, forms the η^6 complex **15**. It is possible that the initial product is the unstable, kinetic N-bonded product that undergoes a facile N to π rearrangement, a consequence of a weakened CpRu–N bond due to the steric effects of the methyl groups on the 2- and 6-positions.[9] In a similar fashion, ligands **7** and **8** preferentially form the π-bonded complexes, **19** and **20**, respectively. Again, as in the case of **4**, ligand **7** has the steric effect associated with the 2-methyl group and the benzo group that then favors π-bonding. The increased electron availability in the aromatic ring for **8**, due to nonbonding nitrogen electron overlap with the π orbitals of the aromatic ring, apparently makes η^6 bonding more favorable with this ligand.

The role of $CpRu^+$ obviously must enter the discussion due to its propensity for being a good π donor; however, we believe that the basicity of the lone-pair electrons on the nitrogen atom overrides that of the π electrons of the nitrogen ring. Thus, if steric effects prevent or weaken the Ru–N interaction, the subsequent π-bonded complex that forms is stabilized by back-bonding from filled metal orbitals to π^* orbitals of the nitrogen ligand.

Plausible Ligand-Exchange Mechanisms between η^1- or η^6-CpRu–N^+ Complexes and Free CH_3CN or Nitrogen Ligands. The pathways for ligand exchange for both $[CpRu(\eta^1\text{- and } \eta^6(N))]^+$ complexes with free CH_3CN or nitrogen ligands can be related to those known for other CpMR (examples are M = Ru, Mn and R = CO, aromatic) systems.[10,11] The associative mechanism (ligand concentration dependent) could be invoked as one process to explain our results in the $\eta^1(N)$-bonded cases. For example, Cp ring slippage, $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$, could be one pathway to account for $[CpRu(\eta^1(N))]^+$ exchange with free CH_3CN or nitrogen ligands. The ring-slippage mechanism would conserve the 18-electron count, therefore bypassing the higher energy 20-electron intermediate or transition

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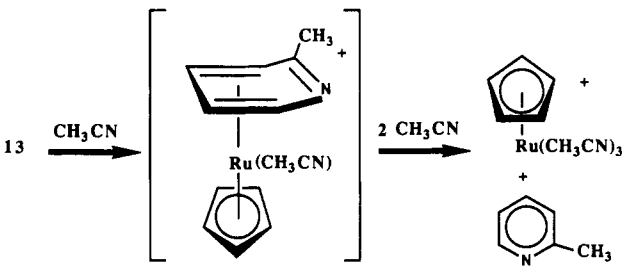
state, where electrons reside on the metal rather than the ligand.[11] We favor the associative mechanism for these concentration-dependent exchange reactions, while a future detailed kinetic study might help differentiate between this pathway and their interchange mechanism counterparts.[12]

Alternatively, the η^6-bonded nitrogen ligand could undergo the slip-fold mechanism, $\eta^6 \rightarrow \eta^4$, in the displacement reaction with free CH_3CN or nitrogen ligands (eq 6). This



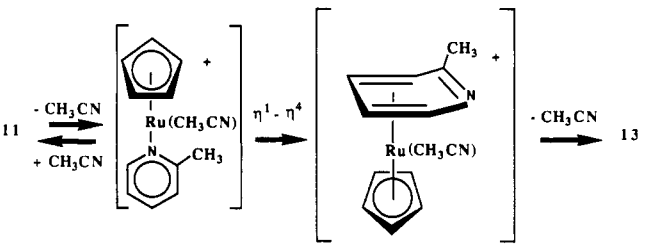
(6)

explanation has been invoked by Mann and coworkers as one pathway for the displacement of $[CpRu(\eta^6\text{-polyaromatic})]^+$ complexes with CH_3CN, a reaction that is directly related to eq 6.[8] In fact, Basolo and co-workers have recently shown that $(\eta^5\text{-pyrrole})Mn(CO)_3$ complexes react faster than their carbon analogues in the displacement of CO ligands via the ring-slippage pathway; they speculate that the driving force is related to the greater electronegativity of the nitrogen ligand.[13]

Factors Controlling the N to π Rearrangement. In 1983, Morris and Ressner reported on a facile N to π rearrangement with a $(\eta^1(N)\text{-pyridine})$bis(dinitrogen)bis(methyldiphenylphosphine)molybdenum complex.[6] They obtained the η^6-bonded complex from the η^1 complex by removal of the N_2 ligands under vacuum at 25 °C. They also suggested that this rearrangement was intramolecular from the fact that no aromatic solvent was incorporated during the rearrangement process. In addition, Rauchfuss and co-workers discovered an S to π rearrangement for a $[CpRu(\eta^1(S)\text{-thiophene})(Ph_3P)_2]^+$ complex but did not determine the mechanism of this process.[14]

Recently, there has been a tremendous amount of interest in slip-fold mechanisms with arene ligands, since this type of process has been implicated in homogeneous catalysis mechanisms (arene ring hydrogenation)[15] and exchange reactions[8,16,17] and from the fact that η^2- and η^4-bonded arene and nitrogen heterocyclic ligands have been isolated.[18-20] We postulate that the mechanism of the N to π rearrangement is an example of an $\eta^1 \rightarrow \eta^4 \rightarrow \eta^6$ slip-fold process with the rate-limiting step being the dissociation of the first complexed CH_3CN ligand and a weakened Ru–N bond that can be related to steric effects. Furthermore, the initial rates were dependent on the $CpRu(\eta^1(N))^+$ complex concentration; i.e., the higher the concentration the slower the initial rate, this being a consequence of the higher free CH_3CN concentration associated with slowing the initial rate of the rearrangement. Accordingly, the N to π rearrangement can be totally suppressed by running the reaction in acetonitrile, thereby further supporting the concept of CH_3CN dissociating being the first step in the reaction. The steric effect of a weakened Ru–N bond is observed by a comparison of the N to π rates of **11** and **16**; qualitatively, **16** rearranges much faster than **11**. It is also possible that higher electron density (aromaticity) in the benzo group of quinoline further promotes the N to π rearrangement of **16** due to the greater thermodynamic stability of this product.

This 16-electron intermediate provides access to the η^4-bonding mode (18-electron), presumably by a rapid (on the NMR time scale no free ligand is observed) N-bond-breaking/η^4-bond-making process, and, as well, to the η^6 complex with loss of the second complexed CH_3CN ligand (eq 7). The π-donating $CpRu^+$ group can stabilize the η^4



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intermediate by overlap of filled metal orbitals with ligand π^* orbitals. The 18-electron η^4 intermediate can then rapidly form the thermodynamically more stable η^6 complex by loss of the second CH_3CN ligand.

Bonding Differences between $CpRu^+$ and Cp^*Ru^+ for Pyridine and Methylpyridine Ligands. The dramatic differences between our pyridine bonding results and Chaudret and Jalon's[5] may be a consequence of possible electronic differences between Cp and Cp*. For example, Cp* places higher electron density on Ru than Cp, making Cp^*Ru^+ a better π donor, and this may make N-bonding less likely, while strongly favoring π-bonding (arenophilicity) at Cp^*Ru^+ as is observed for arene and heteroaromatic compounds.[4,5,8,21] However, as we pointed out earlier, the lone-pair electrons on nitrogen are far more basic than the π electrons of the nitrogen heteroaromatic ring, which then kinetically controls the initial product; *it is our thought that all π-bonded complexes of $CpRu^+$ and Cp^*Ru^+ with nitrogen heterocyclic ligands proceed first via the $\eta^1(N)$ complex and that the facile rearrangement to the $\pi(\eta^6)$ complex is predicated on a variety of steric, electronic, and lability effects of the surrounding ligands.*[22]

Conclusions

We have shown that the structure of the nitrogen heterocyclic ligand has a profound effect on whether the mode of bonding to $CpRu^+$ occurs in an N or π manner, with steric and electronic effects being important contributing factors. The complexes with the formula $[CpRu(\eta^1$-

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(22) In preliminary experiments with $[Cp^*Ru(CH_3CN)_3]^+$ and excess pyridine, we found that the only product formed was $[Cp^*Ru(\eta^1(N)\text{-pyridine})_3]^+$. However, at a 1/1 ratio of $[Cp^*Ru(CH_3CN)_3]^+$ and pyridine, we obtained $[Cp^*Ru(\eta^1(N)\text{-pyridine})(CH_3CN)_2]^+$, which rearranged under vacuum or by heating in solution to $[Cp^*Ru(\eta^6\text{-pyridine})]^+$ (Fish, R. H.; Fong, R. H.; Tran, A.; Baralt, E. *Organometallics*, in press).

(N))$(CH_3CN)_2]^+$ rearrange to the $[CpRu(\eta^6)]^+$ complexes. Facile ligand exchange was found to occur between different η^1(N)-bonded complexes as well as between free nitrogen ligand and both η^1(N)- and η^6-bonded complexes, while acetonitrile was able to displace both N- and π-bonded ligands, their rates being concentration-dependent. We are continuing our studies on the bonding and catalytic activity of organorhodium and ruthenium cationic complexes with nitrogen heterocyclic compounds.

Experimental Section

Instrumentation and Materials. ^1H and ^{13}C NMR spectra were obtained on either a Bruker AM 400- or 500-MHz instrument located at 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 at 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 and acetonitrile were purchased from Aldrich Chemical Co., and diethyl ether was distilled from Na/benzophenone ketyl. $[CpRu(CH_3CN)_3](PF_6)$ was prepared according to the literature procedure.[3]

Preparation of [CpRu(pyridine)$_3$](PF$_6$) (9). A 100-mg (0.23-mmol) amount of $[CpRu(CH_3CN)_3](PF_6)$ and 0.5 mL (6.2 mmol) of pyridine were reacted in 10 mL of CH_2Cl_2. After 30 min, the solvent was removed and the resulting solid washed with diethyl ether and then vacuum-dried to give **9** as a light orange-yellow solid in 81% yield. ^1H NMR ($(CD_3)_2CO$, δ): Cp, 4.24 (s); H(2), 8.72 (dd, J = 6.4, 1.5 Hz); H(3), 7.46 (dd, J = 6.4, 7.5 Hz); H(4), 7.96 (tt, J = 1.5, 7.5 Hz); ratio 5/6/6/3. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ): Cp, 70.90; C(1), 155.91; C(2), 126.52; C(3), 138.14. Anal. Calcd for $C_{20}H_{20}N_3Ru(PF_6)$: C, 43.80; H, 3.68; N, 7.66. Found: C, 43.53; H, 3.54; N, 7.40.

Preparation of [CpRu(pyridine)$_2$(CH$_3$CN)](PF$_6$) (10). A 100-mg (0.23-mmol) amount of $[CpRu(CH_3CN)_3](PF_6)$ and 0.5 mL (6.2 mmol) of pyridine were reacted in 10 mL of CH_3CN for 30 min. The volume was reduced to approximately 5 mL, and then 7 mL of diethyl ether was added. The solution was then cooled to −30 °C overnight to give yellow-orange crystals. The crystals were collected, washed with diethyl ether, and vacuum-dried to give **10** in 66% yield. ^1H NMR (CD_2Cl_2, δ): Cp, 4.24 (s); H(2), 8.48 (dd, J = 6.4, 1.5 Hz); H(3), 7.28 (dd, J = 6.4, 7.5 Hz); H(4), 7.78 (tt, J = 1.5, 7.5 Hz); CH_3CN, 2.50 (s). $^{13}C\{^1H\}$ NMR (CD_3CN, δ): Cp, 70.68; C(1), 155.75; C(2), 138.09; C(3), 126.22. Anal. Calcd for $C_{17}H_{18}N_3Ru(PF_6)$: C, 40.01; H, 3.55; N, 8.23. Found: C, 40.12; H, 3.55; N, 8.12.

Preparation of [CpRu(CH$_3$CN)$_2$(2-methylpyridine)](PF$_6$) (11). A 50-mg (0.12-mmol) amount of $[CpRu(CH_3CN)_3](PF_6)$ and 0.013 mL (0.13 mmol) of 2-methylpyridine were reacted in 5 mL of CH_2Cl_2 for 5 min with vigorous stirring. A 15-mL portion of diethyl ether was then added and the solution cooled to −30 °C overnight. The bright orange-yellow crystals were filtered off, washed with diethyl ether, and vacuum-dried for 10 min to give **11** in 73% yield. ^1H NMR (CD_2Cl_2, δ): Cp, 4.20 (s); H(6), 8.88 (d, br, J = 6.2 Hz); H(4), 7.68 (dt, br, J = 7.7, 1.6 Hz); H(3), 7.36 (d, br, J = 7.7 Hz); H(5), 7.15 (t, br, J = 6.2 Hz); CH_3, 2.83 (s, br); CH_3CN, 2.40 (s, br); ratio 5/1/1/1/1/3/6. $^{13}C\{^1H\}$ NMR (1,2-$C_2D_4Cl_2$, δ): Cp, 68.92; C(2), 163.70; C(6), 155.14; C(4), 137.37; C(3), 126.11; C(5), 121.81; CH_3, 27.56; CH_3CN, 3.99. Anal. Calcd for $C_{15}H_{18}N_3Ru(PF_6)$: C, 37.04; H, 3.73; N, 8.64. Found: C, 37.40; H, 3.80; N, 8.49.

Preparation of [CpRu(CH$_3$CN)$_2$(2,4-dimethylpyridine)](PF$_6$) (12). The procedure was the same as that for **11**. The complex was obtained as a orange-yellow solid in 100% yield. ^1H NMR (CD_2Cl_2, δ): Cp, 4.19 (s, br); H(6), 8.68 (s, br); H(3), 8.18 (s, br); H(5), 7.18 (s, br); 2-CH_3, 2.76 (s, br); CH_3CN, 2.46 (s, br); 4-CH_3, 2.35 (s, br); ratio 5/1/1/1/3/6/3. Correct analytical data for **12** could not be obtained, because of its instability.

Preparation of [CpRu(2-methylpyridine)](PF$_6$) (13). A 50-mg (0.12-mmol) amount of $[CpRu(CH_3CN)_3](PF_6)$ and 0.3 mL (3.0 mmol) of 2-methylpyridine were reacted in 10 mL of CH_2Cl_2 for 20 h followed by solvent removal. The solid was washed with diethyl ether and then dried overnight on a high-vacuum line. The resulting white solid was recrystallized from CH_2Cl_2/diethyl ether (1/1) at −30 °C to give white crystals of **13** in 75% yield. ^1H NMR (CD_2Cl_2, δ): Cp, 5.52 (s); H(6), 7.13 (dt, br, J = 3.6, 1.2 Hz); H(3), 6.52 (d, br, J = 6.0 Hz); H(4,5), 6.38 (m); CH_3, 2.62 (s); ratio 5/1/1/2/3. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ): Cp, 83.45; C(2), 121.83; C(6), 104.84; C(4), 89.79; C(3), 88.31; C(5), 85.18; CH_3, 22.60. Anal. Calcd for $C_{11}H_{12}NRu(PF_6)$: C, 32.68; H, 2.99; N, 3.46. Found: C, 32.74; H, 2.89; N, 3.27.

Preparation of [CpRu(2,4-dimethylpyridine)](PF$_6$) (14). The procedure was the same as that for **13**. After workup, white crystals of the complex **14** were obtained in 73% yield. ^1H NMR ($(CD_3)_2CO$, δ): Cp, 5.64 (s); H(6), 7.27 (dd, J = 3.8, 0.7 Hz); H(3), 6.83 (s); H(5), 6.61 (dd, J = 0.7, 3.8 Hz); 2-CH_3, 2.62 (s); 4-CH_3, 2.39 (s); ratio 5/1/1/1/3/3. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ): Cp, 83.46; C(2), 121.20; C(4), 106.80; C(6), 104.23; C(3), 87.77; C(5), 86.23; 2-CH_3, 22.38; 4-CH_3, 19.80. Anal. Calcd for $C_{12}H_{14}NRu(PF_6)$: C, 34.46; H, 3.37; N, 3.35. Found: C, 34.01; H, 3.55; N, 3.47.

Preparation of [CpRu(2,4,6-trimethylpyridine)](PF$_6$) (15). The procedure was the same as that for complex **13**. After workup, white crystals of **15** were obtained in 63% yield. ^1H NMR ($(CD_3)_2CO$, δ): Cp, 5.57 (s); H(3,5), 6.68 (s); 2- and 6-CH_3, 2.60 (s); 4-CH_3, 2.36 (s); ratio 5/2/6/3. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ): Cp, 83.47; C(2,6), 119.78; C(4), 106.20; C(3,5), 86.23; 2- and 6-CH_3, 22.31; 4-CH_3, 19.63. Anal. Calcd for $C_{13}H_{16}NRu(PF_6)$: C, 36.12; H, 3.73; N, 3.24. Found: C, 35.90; H, 3.61; N, 3.06.

Preparation of [CpRu(CH$_3$CN)$_2$(quinoline)](PF$_6$) (16). A 100-mg (0.23-mmol) amount of $[CpRu(CH_3CN)_3](PF_6)$ and 0.03 mL (0.25 mmol) of quinoline were reacted in 5 mL of CH_2Cl_2. After 5 min, 10–15 mL of diethyl ether was added and the solution cooled to −30 °C overnight. The resulting orange-yellow crystals were filtered off, washed with diethyl ether, and vacuum-dried for 10 min. The complex was obtained in 60% yield. ^1H NMR (CD_2Cl_2, δ): Cp, 4.29 (s): H(2), 9.35 (d, J = 5.1 Hz); H(3), 7.48 (dd, J = 5.1, 8.1 Hz); H(4), 8.32 (d, J = 8.1 Hz); H(5), 7.93 (d, J = 8.1 Hz); H(6), 7.66 (t, J = 8.5 Hz); H(7), 7.85 (t, J = 8.0 Hz); H(8), 8.81 (d, J = 8.8 Hz); CH_3CN, 2.35 (s); ratio 5/1/1/1/1/1/1/6. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): Cp, 69.35; C(2), 157.39; C(3), 121.62; C(4), 138.53; C(5), 130.80; C(6), 127.55; C(7), 129.13; C(8), 131.09; C(9), 150.12; C(10), 129.83; CH_3CN, 4.08. Anal. Calcd for $C_{18}H_{18}N_3Ru(PF_6)$: C, 41.39; H, 3.47; N, 8.04. Found: C, 41.10; H, 3.43; N, 8.04.

Preparation of [CpRu(isoquinoline)$_3$](PF$_6$) (17). A 100-mg (0.23-mmol) amount of $[CpRu(CH_3CN)_3](PF_6)$ and 0.5 mL (4.2 mmol) of isoquinoline were reacted in 10 mL of CH_2Cl_2. After 30 min, the solvent was evaporated and the solid washed with diethyl ether and vacuum-dried overnight to give the yellow complex in 86% yield. ^1H NMR (CD_2Cl_2, δ): Cp, 4.33; H(1), 9.18 (s); H(3), 8.48 (d, J = 6.5 Hz); H(5), 7.93 (d, J = 8.6 Hz); H(6,8), 7.82 (m); H(4,7), 7.69 (m). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ): Cp, 71.62; C(1), 158.99; C(3), 148.50; C(4), 122.93; C(5 or 8), 133.0; C(6 or 7), 128.63; C(6 or 7), 127.35; C(5 or 8), 129.43; C(9), 130.36; C(10), 136.08. Anal. Calcd for $C_{32}H_{26}N_3Ru(PF_6)$: C, 55.02; H, 3.76; N, 6.01. Found: C, 55.25; H, 3.66; N, 5.80.

Preparation of [CpRu(quinoline)](PF$_6$) (18). A 100-mg (0.23-mmol) amount of $[CpRu(CH_3CN)_3](PF_6)$ and 0.03 mL (0.25 mmol) of quinoline were reacted in 5 mL of CH_2Cl_2. After 1 h, the solvent was removed and the resulting solid washed with diethyl ether and vacuum-dried overnight to give the light yellow complex in 100% yield. ^1H NMR ($(CD_3)_2CO$, δ): Cp, 5.24; H(2), 9.19 (dd, J = 1.7, 3.8 Hz); H(3), 7.66 (dd, J = 3.8, 8.9 Hz); H(4), 8.46 (dd, J = 1.1, 8.9 Hz); H(5), 7.24 (d, J = 5.9 Hz); H(6), 6.52 (dt, J = 0.6, 6.0 Hz); H(7), 6.63 (dt, J = 0.9, 6.0 Hz); H(8), 7.34 (d, J = 6.1 Hz), ratio 5/1/1/1/1/1/1. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ): Cp, 81.21; C(2), 161.62; C(3), 126.34; C(4), 140.54; C(5), 88.43; C(6), 86.33; C(7), 84.87; C(8), 87.31; C(9), 94.05; C(10), 114.34. Anal. Calcd for $C_{14}H_{12}NRu(PF_6)$: C, 38.19; H, 2.75; N, 3.18. Found: C, 38.04; H, 2.76; N, 3.25.

Preparation of [CpRu(2-methylquinoline)](PF$_6$) (19). A 100-mg (0.23-mmol) amount of $[CpRu(CH_3CN)_3](PF_6)$ and 0.3 mL (2.2 mmol) of 2-methylquinoline were reacted in 10 mL of CH_2Cl_2. After 30 min, 20 mL of diethyl ether was added and the solution cooled to −30 °C overnight. The resulting light yellow crystals were filtered, washed with diethyl ether, and vacuum-dried to give the complex in 85% yield. ^1H NMR (CD_2Cl_2, δ): Cp, 5.03;

H(3), 7.37 (d, J = 9.0 Hz); H(4), 8.07 (d, 9.0 Hz); H(5), 7.05 (d, J = 6.3 Hz); H(6), 6.30 (dt, J = 1.0, 5.9 Hz); H(7), 6.19 (dt, J = 0.7, 6.1 Hz); H(8), 6.86 (d, J = 5.8 Hz); 2-CH_3, 2.68 (s); ratio 5/1/1/1/1/1/1/3. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ): Cp, 80.93; C(2), 171.10; C(3), 127.87; C(4), 140.0; C(5), 88.07; C(6), 85.60; C(7), 84.50; C(8), 86.66, C(9), 114.7; C(10), 92.09; 2-CH_3, 26.38. Anal. Calcd for $C_{15}H_{14}NRu(PF_6)$: C, 39.66; H, 3.11; N, 3.08. Found: C, 39.58; H, 3.11; N, 3.04.

Preparation of [CpRu(1,2,3,4-tetrahydroquinoline)](PF_6) (20). A 100-mg (0.23-mmol) amount of [$CpRu(CH_3CN)_3$](PF_6) and 0.3 mL (2.4 mmol) of 1,2,3,4-tetrahydroquinoline were reacted in 10 mL of CH_2Cl_2. After 10 min, 10 mL of diethyl ether was added and the solution cooled to −30 °C overnight. The resulting yellow crystals were filtered, washed with diethyl ether, and vacuum-dried to give the complex in 91% yield. ^1H NMR (CD_2Cl_2, δ): Cp, 5.14 (s); H(2), 3.3(m); H(3,ax), 1.84 (m); H(3,eq), 2.08 (m); H(4,ax), 2.48 (m); H(4,eq), 2.67 (m); H(8), 5.78 (d, J = 5.5 Hz); H(7,5), 5.68 (m); H(6), 5.56 (dt, J = 1.0, 5.7 Hz); ratio 5/2/1/1/1/1/2/1. ^{13}C NMR (CD_3CN, δ): Cp, 79.87; C(2), 41.15; C(3), 21.47; C(4), 27.00; C(5–10), 81.20, 83.50, 85.15, 86.00, 86.89, 125.70. Anal. Calcd for $C_{14}H_{16}NRu(PF_6)$: C, 37.85; H, 3.63; N, 3.15. Found: C, 37.88; H, 3.61; N, 3.08.

Preparation of [MeCpRu(CH_3CN)$_2$(2-methylpyridine)](PF_6) (21). The procedure was the same as that for **11**. ^1H NMR (CD_2Cl_2, δ): Me*Cp*, 4.13, 3.88 (m, br); H(6), 8.88 (d, br, J = 6.1 Hz); H(4), 7.67 (dt, br, J = 7.7, 1.5 Hz); H(3), 7.36 (d, br, J = 7.7 Hz); H(5), 7.15 (t, br, J = 6.1 Hz); CH_3, 2.85 (s, br); *Me*Cp, 1.55; CH_3CN, 2.37 (s, br). All $MeCpRu^+$ complexes were >95% pure by NMR spectroscopy and were contaminated with <5% of the $CpRu^+$ analogue. Thus, we made no attempt to purify these complexes or obtain elemental analyses.

Preparation of [MeCpRu(2-methylpyridine)](PF_6) (22). The procedure was the same as that for **13**. ^1H NMR (CD_2Cl_2, δ): Me*Cp*, 5.46, 5.38 (m, br); H(6), 7.10 (dt, br, J = 3.6, 1.2 Hz); H(3), 6.43 (d, br, J = 6.1 Hz); H(4,5), 6.34 (m); CH_3, 2.58; *Me*Cp, 2.04.

Reaction of [CpRu(CH_3CN)$_2$(2-methylpyridine)](PF_6) (11) and [MeCpRu(2-methylpyridine-d_7)](PF_6) (22-d_7). A 5-mg (0.11-mmol) amount of **11** and 5 mg (0.01 mmol) of **22**-d_7 were mixed together and dissolved in approximately 0.6 mL of CD_2Cl_2. The reaction was monitored by ^1H NMR spectroscopy. After 24 h, 15% conversion of **11** to its π-bonded analogue had occurred with no sign of any signals due to the crossover product [MeCpRu(2-methylpyridine)](PF_6) (**22**).

Reaction between [CpRu(pyridine)$_3$](PF_6) (9) and Pyridine-d_5 (1-d_5). A 5-mg (0.11-mmol) amount of **9** was dissolved in approximately 0.6 mL of CD_2Cl_2, and then 0.01 mmol of 1-d_5 was added. ^1H NMR spectroscopy after 1 h showed a 1/1 ratio of coordinated ligand and free ligand. No further changes were observed after 24 h.

Reaction of [CpRu(CH_3CN)$_2$(2-methylpyridine)](PF_6) (11) and [MeCpRu(CH_3CN)$_2$(2-methylpyridine-d_7)](PF_6) (21-d_7). A 10-mg (0.02-mmol) amount of **11** and 10 mg (0.02 mmol) of **21**-d_7 were mixed together and dissolved in approximately 0.6 mL of $C_2D_4Cl_2$. The reaction was monitored by ^1H NMR spectroscopy. An NMR spectrum taken immediately after dissolution showed that complete exchange of the 2-methylpyridine and 2-methylpyridine-d_7 ligands had occurred before any substantial rearrangement to the π-bonded complexes.

Reaction of [CpRu(2-methylpyridine)](PF_6) (13) and [MeCpRu(2-methylpyridine-d_7)](PF_6) (22-d_7). A 5-mg (0.012-mmol) amount of **13** and 5 mg (0.012 mmol) of **22**-d_7 were mixed together and dissolved in approximately 0.6 mL of CD_2Cl_2. The reaction was monitored by ^1H NMR spectroscopy. After 24 h, no sign of any complex due to exchange between the π-bonded ligands was observed, i.e., complex **22**.

Reaction between [CpRu(2-methylpyridine)](PF_6) (13) and 2-Methylpyridine-d_7. A 5-mg (0.012-mmol) amount of **13** was dissolved in approximately 0.6 mL of CD_2Cl_2. A slight excess of 2-methylpyridine-d_7 (2-d_7; 1.1 equiv) was then added and the reaction monitored by ^1H NMR spectroscopy. Immediate observation of free 2-methylpyridine in the ^1H NMR spectrum indicated that exchange between π-bonded 2-methylpyridine with 2-methylpyridine-d_7 occurred. A similar experiment was performed at a 13/1 ratio of **13**/2-d_7, and the results clearly show that the rate of exchange was greatly decreased; i.e., after 24 h only 5% of **2** was evident and 10% after 72 h.

Reaction between [CpRu(CH_3CN)$_2$(2-methylpyridine)](PF_6) (11) and 2-Methylpyridine-d_7. A 5-mg (0.01-mmol) amount of **11** was dissolved in approximately 0.6 mL of CD_2Cl_2. A slight excess of 2-methylpyridine-d_7 (1.1 equiv) was then added and the reaction monitored by ^1H NMR spectroscopy. Immediate observation of free 2-methylpyridine in the ^1H NMR spectrum indicated that exchange between N-bonded 2-methylpyridine and 2-methylpyridine-d_7 occurred.

Reaction of [CpRu(CH_3CN)$_2$(2-methylpyridine)](PF_6) (11) in CD_3CN. A 5-mg (0.01-mmol) amount of **11** was dissolved in approximately 0.6 mL of CD_3CN and the reaction monitored by ^1H NMR spectroscopy. Within 1 h, displacement of 2-methylpyridine occurred to give free 2-methylpyridine and [$CpRu(CD_3CN)_3$](PF_6).

Reaction of [CpRu(2-methylpyridine)](PF_6) (13) in CD_3CN. A 5-mg (0.012-mmol amount) of **13** was dissolved in approximately 0.6 mL of CD_3CN and the reaction monitored by ^1H NMR spectroscopy. After 1 h, free 2-methylpyridine and [$CpRu(CD_3CN)_3$](PF_6) (15%) were observed with no formation of any N-bonded complex **11**. After 24 h, complex **13** is essentially gone, and complex **11** had formed.

Reaction of [CpRu(CH_3CN)$_3$](PF_6) with Excess 2-Methylpyridine in CD_3CN. A 5-mg (0.012-mmol) amount of [$CpRu(CH_3CN)_3$](PF_6) was dissolved in approximately 0.6 mL of CD_3CN, and a 15-fold excess of 2-methylpyridine was added. ^1H NMR spectroscopy indicated that only the N-bonded complex **11** had formed (35%) with no formation of any π-bonded complex **13**.

Kinetics of N to π Rearrangement. All samples were made up inside the glovebox in CD_2Cl_2. One microliter of dichloroethane was added as an internal standard. The samples were then transferred to an NMR tube and placed in an NMR probe at 35 ± 1 °C. Rates of starting material disappearance (N-bonded) were determined by measuring the disappearance of the Cp ligand. The rearrangement of **11** to **13** was studied at two concentrations, 0.0168 and 0.0095 M. Data points were taken approximately ever 10 min.

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