Bonding of Mono- and Polynuclear Heteroaromatic Nitrogen Ligands to the (η^5-Pentamethylcyclopentadienyl)rhodium Dication: Structure–Reactivity Relationships in the Formation of Nitrogen (η^1) versus π (η^5,η^6) Complexes and Competition Studies of the Ligands for the Rhodium Metal Center

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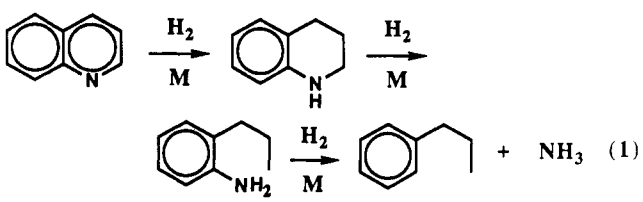
The reactions of 4-methylpyridine (**1**), 3-methylpyridine (**2**), 2-methylpyridine (**3**), 3,5-dimethylpyridine (**4**), 2,4-dimethylpyridine (**5**), 2,4,6-trimethylpyridine (**6**), *N*-methylpyrrole (**7**), quinoline (**8**), isoquinoline (**9**), 2-methylquinoline (**10**), 1,2,3,4-tetrahydroquinoline (**11**), *N*-methylindole (**12**), acridine (**13**), phenanthridine (**14**), 5,6-benzoquinoline (**15**), and 7,8-benzoquinoline (**16**) with (η^5-pentamethylcyclopentadienyl)rhodium dicationic complexes $[Cp^*Rh(CH_3CN)_3](X_2)$ or $[Cp^*Rh((CH_3)_2CO)_3](X_2)$ (X = PF_6 or BF_4) were studied to ascertain how structure influenced the reactivity of ligands, **1–16**, to provide nitrogen (N) versus π-bonded Cp^*Rh^{2+} complexes. Ligands **1–5**, **8**, **9**, and **13–16** were found to form N(η^1)-bonded rhodium complexes, while ligands **6**, **7**, **11**, and **12** preferred π(η^5,η^6)-coordination. Ligand **10** formed the N(η^1)-bonded complex with $[Cp^*Rh(CH_3CN)_3]^{2+}$ and a ~1:1 mixture of N(η^1)- and π(η^6)-bonded complexes with the $(CH_3)_2CO$ derivative. $[Cp^*Rh(\eta^1(N)\text{-2-methylquinoline})((CH_3)_2CO)_2]^{2+}$ was the only complex isolated that was found to undergo a N(η^1)–π(η^6) rearrangement under vacuum, while its CH_3CN analogue was unreactive. The order of competitive reactivity with ligands **3**, **6**, **8–11**, and **14–16** for the rhodium metal center was found to be **9** (N) > **11** (π) > **8** (N) > **3** (N) > **10** (N) > **14** (N) > **15**(N) ~ **16** (N) > **6**(π) ~ **7**(π). The steric and electronic factors that favor N or π bonding to Cp^*Rh^{2+} and similar factors that provide the competitive bonding order will be discussed.

Introduction

The hydrodenitrogenation reaction (HDN) with heterogeneous catalysts ideally involves the regioselective hydrogenation of the nitrogen-containing ring of the polynuclear heteroaromatic nitrogen compounds, which is followed by metal-catalyzed C–N bond cleavage to eventually provide ammonia and the aromatic hydrocarbon (eq 1).[1] The mode of bonding of the nitrogen heterocyclic



(1)

compounds to the metal centers of heterogeneous catalysts would appear to be pivotal for the selective hydrogenation of the nitrogen-containing ring and the subsequent bond cleavage reactions; however, this important aspect is difficult to study effectively with the heterogeneous surfaces.[2]

Previous studies in our laboratory have shown that homogeneous transition-metal catalysts can selectivity hydrogenate polynuclear heteroaromatic model coal compounds and, therefore, can provide information on the first step of the HDN reaction with soluble organometallic model complexes.[3] In order to determine uneqiuvocally the nature of this substrate bonding, i.e., nitrogen (N) versus π-bonding, we have initiated a program on the reactions of representative mono and polynuclear heteroaromatic nitrogen ligands, as model coal compounds, with the (η^5-pentamethylcyclopentadienyl)rhodium dication (Cp^*Rh^{2+}), (η^5-cyclopentadienyl)ruthenium cation ($CpRu^+$), and (η^5-pentamethylcyclopentadienyl)ruthenium cation (Cp^*Ru^+) to develop a structure–reactivity relationship.[4-6]

Indeed, we have found that the initial mode of bonding of the nitrogen heterocyclic compounds to the metal centers of homogeneous organorhodium and ruthenium catalysts is critical for the regioselective hydrogenation of the nitrogen-containing ring.[4,5] Prior to our initial communication on the synthesis, structure, order of reactivity, and catalytic properties of Cp^*Rh^{2+} complexes with nitrogen ligands,[4] the only other report on bonding of nitrogen heterocyclic ligands to Cp^*Rh^{2+} concerned indole, where coordination was found to occur η^6 (benzene ring) to rhodium, and that of pyrrole, where bonding was found to occur η^5 (nitrogen ring).[7] Other recently reported studies with $CpRu^+$ and Cp^*Ru^+ complexes and heteroaromatic nitrogen compounds, including indole (η^6, benzene ring),[8a] pyridine derivatives (η^6), and quinoline (η^6, benzene ring),[8b,c] have also shown a similar propensity for π-bonding.

In this paper, we report the full account of our synthetic studies of the reactions of the above-mentioned nitrogen

(1) For recent reviews of the HDN reaction see: (a) Laine, R. M. *Catal. Rev.—Sci. Eng.* **1983**, *25*, 459. (b) Schultz, H.; Schon, M.; Rahman, N. M. In *Studies in Surface Science and Catalysis*; Cerveny, L., Ed.; Elsevier: Amsterdam, 1986; Vol. 27, Chapter 6, p 201.

(2) Fish, R. H.; Michaels, J. M.; Moore, R. S.; Heinmann, H. *J. Catal.* **1990**, *123*, 74 and references therein.

(3) (a) Fish, R. H.; Thormodsen, A. D.; Cremer, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 5234. (b) Fish, R. H. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 292. (c) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *J. Org. Chem.* **1984**, *49*, 4500. (d) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *Organometallics* **1985**, *4*, 1743.

(4) Fish, R. H.; Kim, H.-S.; Babin, J. E.; Adams, R. A. *Organometallics* **1988**, *7*, 2250.

(5) (a) Fish, R. H.; Kim, H.-S.; Fong, R. H. *Organometallics* **1989**, *8*, 1375. (b) Fish, R. H.; Kim, H.-S.; Fong, R. H. *Organometallics* **1991**, *10*, 770.

(6) Fish, R. H.; Fong, R. H.; Tran, A.; Baralt, E. *Organometallics* **1991**, *10*, 1209.

(7) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654.

(8) (a) For an excellent review of the η^6 complexation of arenes with $CpRu^+$, including substituted indole ligands, see: Moriarty, R. M.; Gill, U. S.; Ku, Y. Y. *J. Organomet. Chem.* **1988**, *350*, 157 and references therein. (b) Chaudret, B.; Jalon, F. A. *J. Chem. Soc., Chem. Commun.* **1988**, 711. (c) Chaudret, B.; Jalon, F. A.; Perez-Manrique, M.; Lohoz, F.; Plou, F. J.; Sanchez-Delgado, R. *New J. Chem.* **1990**, *14*, 331.

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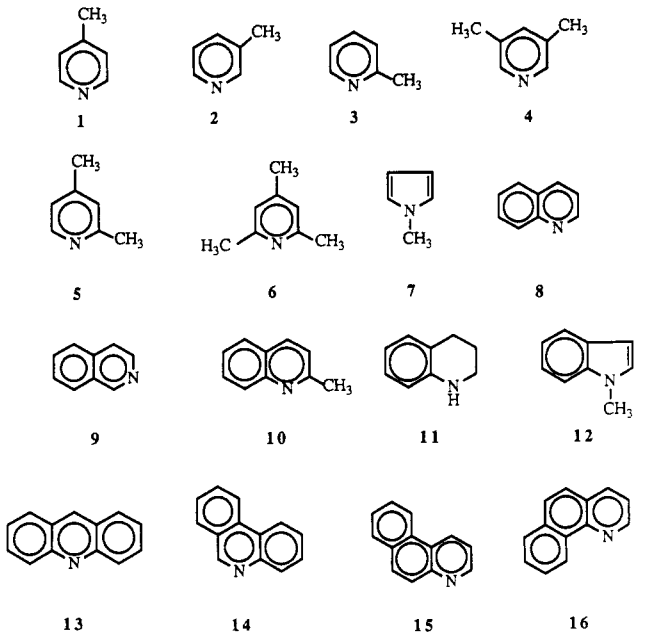
Chart I. Model Coal Nitrogen Compounds



ligands with Cp^*Rh^{2+} and, as well, we demonstrate that steric effects and the availability of lone pair electrons on the nitrogen ligands have a profound effect on the ability of the these ligands to bond N or π to the Rh metal center. We also provide information, with one example, on the mechanism of the formation of π-bonded complexes from N(η^1)-bonded complexes via an N(η^1)–$\pi(\eta^6)$ rearrangement. In addition, we will also address the competitive order of N ligand reactivity for the Rh metal center as it relates to the selective hydrogenation chemistry we are pursuing in tandem.

Results

The general synthetic reaction procedures followed are shown in eq 2, while the structures for all the model coal compounds are shown in Chart I.

$$[Cp^*RhCl_2]_2 + AgX \xrightarrow{S} Cp^*Rh(S)_3X_2$$

$$Cp^*Rh(S)_3X_2 \xrightarrow{\text{"N"}} Cp^*Rh(N)_{1,3}X_2 \qquad (2)$$

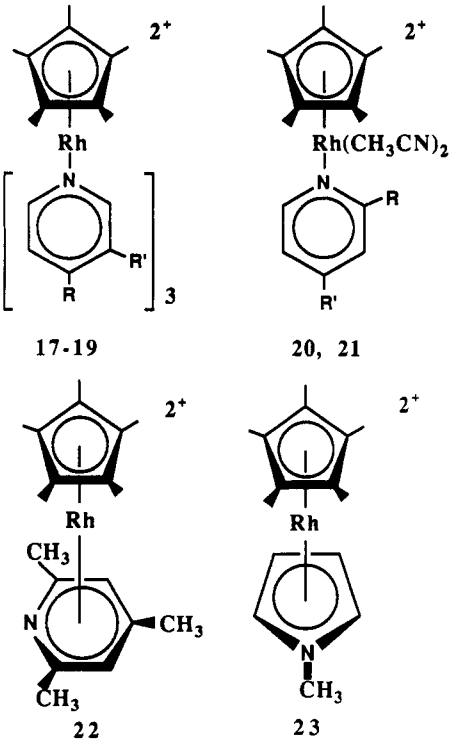
X= BF_4 or PF_6

S = CH_3CN or $(CH_3)_2CO$

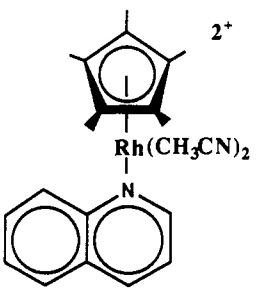
"N" = Ligands 1-16

Methyl-Substituted Pyridine and Pyrrole Complexes. The steric and electronic effects of the methyl-substituted pyridine ligands 1–6 and the *N*-methylpyrrole ligand 7 were probed, when reacted with $[Cp^*Rh(CH_3CN)_3]^{2+}$, to verify the degree of displacement of coordinated CH_3CN and formation of η^1(N)- or $\pi(\eta^5,\eta^6)$-bonded complexes. The structures of the Cp^*Rh^{2+} complexes were verified by ^1H and ^{13}C NMR spectroscopy and, when possible, FAB mass spectroscopy as well as elemental analyses. All the η^1(N)-bonded ligands had ^1H NMR spectra that showed that ligand protons were shifted *downfield* from the free ligand and ^{13}C NMR spectra that showed a *lack of Rh–C coupling*, while all η^5,η^6-bonded complexes had ^1H NMR spectra that showed ligand protons were shifted *upfield* from the free ligand and ^{13}C NMR spectra that showed *Rh–C coupling*.

Ligands 1, 2, and 4 provided tris-η^1, N-bonded complexes **17** (R = 4-methyl; R′ = H), **18** (R′ = 3-methyl; R = H), and **19** (R, R′ = 3,5-dimethyl), while ligands 3 and 5 provided mono-η^1,N-bonded complexes **20** (R = 2-methyl; R′ = H) and **21** (R = 2-methyl; R′ = 4-methyl). Ligand 6, with methyl groups that sterically hindered the nitrogen atom, gave the $\pi(\eta^6)$-bonded complex **22**, while a pyrrole derivative, ligand 7, provided the $\pi(\eta^5)$-bonded complex **23**.[7]

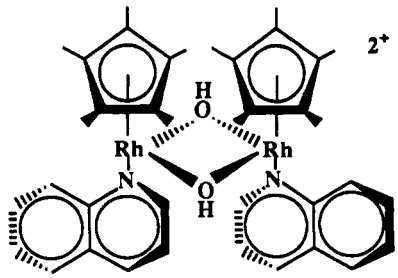


Quinoline and Indole Complexes. A similar study, as described above, was conducted with polynuclear nitrogen ligands 8–12. The reaction of quinoline, 8, with $[Cp^*Rh(CH_3CN)_3]^{2+}$ provided a η^1(N)-bonded mono-quinoline complex **24**; similar in structure to the 2-methyl-substituted pyridine complexes **20** and **21**.



We tried to obtain a single-crystal X-ray analysis on complex **24** to further prove the N-bonding mode, but all attempts failed due to its air and moisture sensitivity. Fortuitously, we found that when the previous reaction was carried out in either acetone or acetonitrile containing traces of water, only a crystalline derivative, $[Cp^*Rh(quinoline)(\mu\text{-hydroxo})]_2(BF_4)_2$ (**25**), was obtained.

A single-crystal X-ray analysis of **25** was published in our preliminary communication[4] and consisted of two Cp^*Rh(quinoline) groups joined by two bridging OH^- ligands with the $Rh_2(\mu\text{-}OH)_2$ group planar. Since the Rh atoms possess 18e configurations, there is no need for a Rh–Rh metal bond and it is consistent with the observation of the nonbonding Rh···Rh distance of 3.322 (1) Å. The quinoline ligands are cis to each other with respect to the $Rh_2(\mu\text{-OH})$ plane and are also in an anti conformation.



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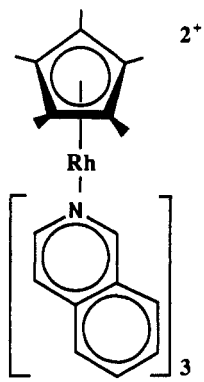
While the solid-state structure shows the N-bound quinoline ligands to be cis to each other, the ^1H and ^{13}C NMR solution spectra of **25** at ambient temperature tentatively indicate the possibility of some fluxional process taking place with broadening of both quinoline and Cp* signals. Since only one Cp* resonance was observed at low temperature (^1H, 5 °C; ^{13}C, −20 °C), we speculate that hindered internal rotation of both quinoline and Cp* ligands accounts for the fluxionality and not a cis–trans isomerization of both ligands around the Rh metal centers.

Interestingly, reaction of isoquinoline, **9**, with $[Cp^*Rh(CH_3CN)_3]^{2+}$ or $[Cp^*Rh(p\text{-xylene})]^{2+}$ provided an air-stable, tris(isoquinoline), dicationic complex **26**. This result suggests that differences in the steric requirements at the Rh metal center and possible differences in the electronic effects of ligands **8** and **9** control Rh–N complex lability.



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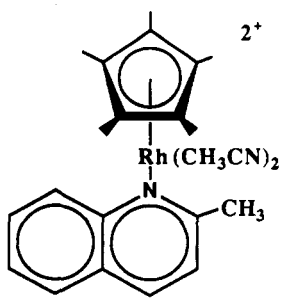
By sterically hindering the nitrogen nonbonding electrons in **8** with a methyl group in the 2-position, ligand **10**, we hoped to force the formation of a π-complex, as was shown with ligand **6**. However, reaction of $[Cp^*Rh(CH_3CN)_3]^{2+}$ with **10** (~1:1) in CH_2Cl_2 at ambient temperature provided the mono-η^1,N-bonded complex **27**, together with only trace amounts of a π-complex. Indeed, the apparent steric effect of the methyl group in ligand **10** does appear to provide somewhat of a driving force for the formation of the π-complex, but it also depends on the lability of the complexed solvent ligand. Alternatively, if the reaction was run with $[Cp^*Rh((CH_3)_2CO)_3]^{2+}$ added to excess ligand **10** in acetone, then a ~1:1 mixture of an η^1(N)-bonded **27A** and a π-bonded complex **28** was formed



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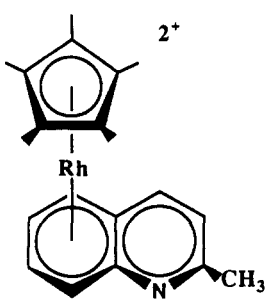

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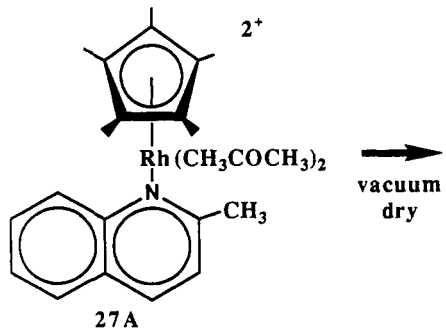
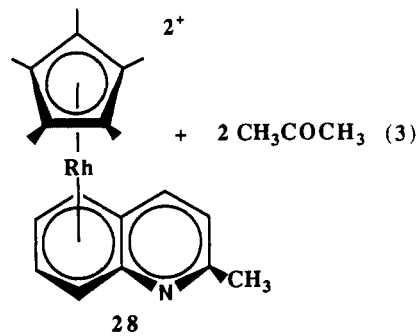
(NMR data), which were separated by solubility differences. We assign **27** as N-bonded from the chemical shifts of the ligands in the ^1H NMR spectrum and, as well, from the lack of Rh–C coupling in the ^{13}C NMR spectrum. The structure of the π-bonded complex, **28**, was confirmed by ^1H and ^{13}C NMR spectroscopy; the latter clearly showing Rh–C couplings in the benzo group only.

$[Cp^*Rh(\eta^1(N)\text{-2-methylquinoline})((CH_3)_2CO)_2]^{2+}$ (**27A**) could be converted to **28** via an N–π rearrangement by vacuum drying for several hours at ambient temperature (eq 3).[5] It is interesting to note that **27A** provided the



27A



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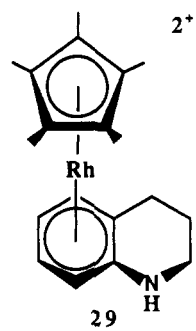
only example of a N–π rearrangement we were able to demonstrate; no complexed CH_3CN derivatives were found to undergo this rearrangement including complex **27**.

We anticipated that ligand **11**, 1,2,3,4-tetrahydroquinoline, the regioselective hydrogenation product of **8**, would also bond η^1(N) to rhodium; however, this was not the case. Ligand **11** reacted with $[Cp^*Rh(CH_3CN)_3]^{2+}$ or the acetone complex to form a dicationic complex **29**, that



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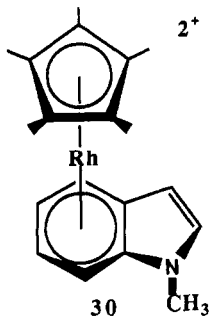
was $\pi(\eta^6)$-bonded to the benzene ring (^{13}C NMR spectrum). Therefore, it appears that the lone pair electrons on the nitrogen atoms in **8** and **9**, which are orthogonal to the π-electrons of the aromatic ring, are readily available for bonding to rhodium. The opposite situation can exist for **11**, where the lone pair electrons can overlap with the π-electrons of the aromatic ring, thereby increasing electron availability in the aromatic ring and providing a driving force for π-complexation.

Ligand **12** with $[Cp^*Rh(CH_3CN)_3]^{2+}$ also provided the π-bonded complex **30**, which, similarly to ligand **11**, is bound to the benzo group not the *N*-methylpyrrole ring;

lone pair electrons on nitrogen overlap with the π orbitals of the aromatic ring and the C=C double bond in the pyrrole ring.



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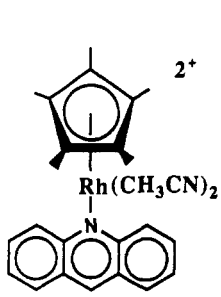
Tricyclic Heteroaromatic Nitrogen Complexes. Tricyclic heteroaromatic nitrogen ligands **13–16** all provided η^1(N)-bonded complexes **31–34** upon reaction with $[Cp^*Rh(CH_3CN)_3]^{2+}$.



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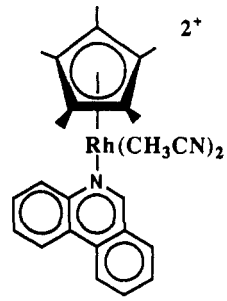

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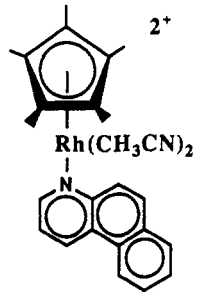

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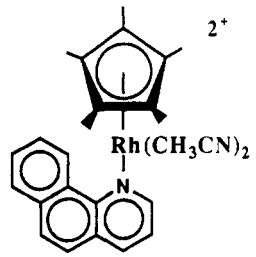

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Competitive Binding Studies: Ligands 3, 6, 8–11, and 14–16. The results just presented for a wide range of nitrogen heteroaromatic compounds indicate that η^1-(N)-bonding to Cp^*Rh^{2+} is predominant and can be directly related to the results on the regioselective hydrogenation of the nitrogen-containing ring that were recently reported with $[Cp^*Rh(CH_3CN)_3]^{2+}$ as the catalyst precursor.[4,9] Namely, initial η^1(N)-bonding of the nitrogen ligand to Cp^*Rh^{2+} and complexes specifically with the formula $[Cp^*Rh(\eta^1(N)\text{-ligand})(CH_3CN)_2]^{2+}$ are prerequisites for catalysis to proceed.

Therefore, competitive bonding studies are important to pursue in that they would allow one to predict in the selective hydrogenation of a mixture of nitrogen ligands what the order of reactivity might be and also provide information on the inhibition aspects of these important homogeneous catalysis reactions. Several methods were used to define the relative order of ligand reactivity and included reaction of a 1:1 molar ratio of free ligands competing for a deficient amount of Cp^*Rh^{2+} and, secondly, a method that entailed reaction of a complexed ligand with an excess of the competing ligand. The first method was accomplished by using NMR spectroscopy to identify the Cp^*Rh^{2+} complex formed, which was then isolated for confirmation. The second method was accomplished as well by NMR analysis. Thus, the relative order of reactivity of heteroaromatic nitrogen ligands, **3**, **6–11**, and **14–16**, with Cp^*Rh^{2+}, defined in the above-mentioned competitive experiments, was found to be: **9** (N) > **11** (π) > **8** (N) > **3** (N) > **10** (N) > **14** (N) > **15**(N) ~ **16** (N) > **6**(π) ~ **7**(π).

Discussion

The most important mode of bonding of nitrogen heteroaromatic ligands to the hard Cp^*Rh^{2+} metal center is via the lone pair of electrons on the nitrogen atom. For example, ligands **1–5**, **8–10**, and **13–16** all exhibit η^1(N)-bonding to Cp^*Rh^{2+}. Steric effects can limit the degree of displacement of solvent molecules from the rhodium metal center and also effect the availability of lone pair electrons on nitrogen for bonding to the Rh metal center. This was demonstrated by comparing ligands **1**, **3**, and **6**, and those of **8**, **9**, and **10**. Ligand **1** forms the tris-η^1-(N)-bonded complex **17**, while ligand **3** the monosubstituted η^1(N) complex **20**. By sterically hindering the nitrogen atom lone pair electrons further, i.e., ligand **6**, the bonding totally changes to the $\pi(\eta^6)$-bonded complex **22**. Similarly, **8** and **9** provide monosubstituted η^1(N) complex **24** and tris-η^1(N)-bonded complex **26**, respectively, as seen for **1** and **3**.

Ligand **10** was the only ligand we studied that gave both the η^1(N)- and the $\eta^6(\pi)$-bonded complexes **27** and **28**, respectively, depending on reaction parameters. Consequently, the acetone substituted complex **27A** was the only example of an N–π rearrangement we were able to study; all other ligands with a formula $[Cp^*Rh(\eta^1(N))(S)_2]^{2+}$ (where S = acetone) would not undergo this reaction and none with the CH_3CN ligand. However, complex **27A** did this rearrangement only reluctantly (vacuum drying for hours) and this clearly demonstrates the highly electrophilic Rh metal center's demand for lone pair nitrogen atom electrons.

We also speculate that all π-bonded complexes such as **22**, **23**, and **28–30** emanate from their weakly N-bonded, kinetic complexes with the formula $[Cp^*Rh(\eta^1(N))(S)_2]^{2+}$ via this rearrangement. The nature of the weakened Rh–N bond in these latter complexes stems from the steric effects we mentioned (ligands **6** and **10**) but also from delocalization of the lone pair of electrons on nitrogen into the aromatic or nitrogen rings, as demonstrated by ligands **7**, **11**, and **12**. The propensity of this N–π rearrangement to occur with organoruthenium complexes,[5,6] having similar structures, has also been studied by our group and the order of reactivity was found to be $Cp^*Ru^+ >> CpRu^+ >>> Cp^*Rh^{2+}$. The Ru metal center is soft and a better π-donor than the corresponding Rh metal center and is thus able to back-bond from filled metal orbitals to the π^* orbitals of the nitrogen ligand in a more facile manner.

With individual ligands, we have addressed various parameters that affect the binding to the Rh metal center. Thus, the competitive order of reactivity brings together the parameters of ligand steric effects and the availability of the lone pair of electrons on nitrogen and provides a method to compare their importance when two free ligands vie for the same Rh metal center or in displacement reactions with one free and the other ligand complexed.

The order of reactivity reaffirms, with ligand **11** the only exception, that nonbonding electron availability on nitrogen dictates the predominant N-bonding mode and that steric effects mediate this availability. Ligand **9** (and presumably **1**, **2**, and **4**) will dominate other ligands for the

(9) Fish, R. H.; Baralt, E.; Smith, S. J. *Organometallics*, in press.

Rh metal center regardless of the competitive method used. Placing one methyl group in the adjacent position to nitrogen, as in ligands **3** (and presumably **5**) and **10**, or other aromatic rings, as in ligands **14–16**, causes a decrease in binding strength to Rh but does not change the bonding mode.

Apparently, with ligand **11**, the high electron density in the aromatic ring from delocalization of the lone electron pair on the N atom, which also decreases its basicity, overrides other factors and allows it to compete effectively with all the ligands studied except **9**. However, both **6** and **7**, which π-bond to Rh, appear to be strongly affected by the steric effects of the methyl groups that may prevent bonding orbitals of the Rh atom in close proximity to the ligand π orbitals.

We can also extend this mode of bonding to the catalytic activity[9] of these complexes in the selective hydrogenation of the nitrogen ring. Ligands **1**, **2**, **4**, and **9** all form tris-substituted complexes, $[Cp^*Rh(\eta^1(N)\text{-ligand})_3]^{2+}$, and these tris-substituted complexes were found to be catalytically inactive when formed in situ during selective hydrogenation experiments. Ligands **6**, **7**, **11**, and **12** all provided π-bonded complexes with the formula $[Cp^*Rh(\eta^6(N)\text{-ligand})]^{2+}$ that were also found to be catalytically inactive. Ligands **1**, **2**, **4**, and **9** also have been shown to inhibit selective nitrogen ring reduction of **8**, and this we now know from our present results occurs by competitive bonding to the Rh metal center. Interestingly, ligands **3**, **8**, **10**, and **13–16** all form monosubstituted complexes, $[Cp^*Rh(\eta^1(N)\text{-ligand})(CH_3CN)_2]^{2+}$, which are catalytically acitve for selective nitrogen ring reduction. However, the order in relative reactivity for the selective hydrogenation reaction is quite different from the competitive bonding order just presented and turns out to be **16** >>> **13** > **8** > **15** > **10** >>> **3**.[9] This latter order reflects factors other than just initial binding of the substrate ligand to the metal center as important for selective hydrogenation and possibly includes effective hydrogen transfer to the N ring and product inhibition by competitive binding to the Rh metal center. The latter product inhibition can be demonstrated with **8** and **11**. For example, **11**, which is the regioselective reduction product of **8**, was just shown in this study to bind more effectively to the Rh metal center and was also recently shown (1:1 ratio) to inhibit the hydrogenation rate of **8** by a factor of 3.[9]

Conclusion

The Cp^*Rh^{2+} moiety has been shown to possess an exceptionally electrophilic Rh metal center that has a high affinity for nitrogen atom lone pair electrons. This is then the dominant mode of bonding (η^1(N)) we have seen in using the nitrogen ligands **1–5**, **8–10**, and **13–16** with the degree of displacement from the starting complex $[Cp^*Rh(S)_3]^{2+}$ being principally mediated by steric effects. Ligands **6** and **7** provided the only examples of Cp^*Rh^{2+} π-bonding to the nitrogen ring, while ligands **10–12** provided π-bonding to the benzo ring because of the higher electron density in that ring.

The only example of an N–π rearrangement was found for complex **27A** being converted to **28**, and this result proves tentatively that all π-bonded complexes emanate from their kinetically unstable $[Cp^*Rh(\eta^1(N)\text{-ligand})(S)_2]^{2+}$ derivatives. The competitive binding order of the nitrogen ligands to Cp^*Rh^{2+}, using several procedures, clearly demonstrated that availability of nitrogen lone pair electrons by either steric or resonance effects was the important factor contributing to this sequence.

Finally, our nitrogen ligand bonding results have been able to explain some important criteria for selective nitrogen ring hydrogenation with $[Cp^*Rh(S)_3]^{2+}$ as the catalyst precursor, namely, initial η^1(N)-bonding with a formula $[Cp^*Rh(\eta^1(N)\text{-ligand})(S)_2]^{2+}$ and inhibition by competitive binding.[9] The inhibition also includes the products from these reactions such as ligand **11**, the selective hydrogenation product of ligand **8**. We are continuing to exploit these Cp^*Rh^{2+} complexes for interesting reactivity and will report these results in the future.

Experimental Section

Instrumentation and Materials. ^1H and ^{13}C NMR spectroscopy were performed on either a Bruker AM 400- or 500-MHz instrument using deuterated solvents as internal locks and reference with respect to TMS. The instruments are 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, or Galbraith Laboratory, Inc. All nitrogen heterocyclic ligands were purchased from Aldrich Chemical Co. and redistilled or sublimed before use. Anhydrous methylene chloride and acetonitrile were purchased from Aldrich Chemical Co., and diethyl ether was distilled from Na/benzophenone ketyl. $[Cp^*Rh(p\text{-xylene})](X_2)$ and $[Cp^*RhS_3](X_2)$ (S = CH_3CN, $(CH_3)_2CO$; X = BF_4, PF_6) were prepared according to the literature procedure.[7]

$[Cp^*Rh(4\text{-picoline})_3](BF_4)_2$ (17). $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ (63.0 mg, 0.12 mmol) was dissolved in 5 mL of CH_2Cl_2, then 0.1 mL of 4-picoline was added, and the solution was stirred for 15 min. The resulting pale yellow solution was filtered through Celite. Solvent was reduced to 2 mL, and a yellow solid formed upon addition of diethyl ether (5 mL). The solid was washed with diethyl ether (3 × 5 mL) and recrystallized from CH_2Cl_2/diethyl ether (1:1 mL) at −30 °C (100% yield by ^1H NMR analysis), mp 182–185 °C. ^1H NMR (400 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 1.48 (s); CH_3, 2.50 (s); H(3,5), 7.48 (d, J = 6.01 Hz); H(2,6), 8.07 (d, J = 6.42 Hz); ratio 15:9:6:6. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 8.20 (s); CH_3, 21.11 (s); C(2,5), 154.37 (s); C(4), 152.19 (s); C(3,5), 129.05 (s); $(CH_3)_5C_5$, 9.80 (J_{Rh-C} = 8.01 Hz). Anal. Calcd for $C_{28}H_{36}N_3Rh[BF_4]_2$: C, 48.66; H, 5.25; N, 6.07. Found: C, 48.40; H, 4.99; N, 5.77.

$[Cp^*Rh(3\text{-methylpyridine})_3](BF_4)_2$ (18). $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ (38.1 mg, 0.07 mmol) was dissolved in 5 mL of CH_2Cl_2, then an excess (0.20 mL, 2.1 mmol) of 3-methylpyridine was added, and the solution was stirred for 20 min. The reaction solvent was evaporated, and the resulting yellow powder was washed with ether (3 × 5 mL). The resulting yellow powder was vacuum-dried to give 48.3 mg of the complex (100% yield), mp 102–105 °C. ^1H NMR (400 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 1.45 (s); CH_3, 2.37 (s); H(6), 8.25 (d, J = 5.52 Hz); H(2), 8.01 (s); H(4), 7.87 (d, J = 7.23 Hz); H(5), 7.64 (t, J = 7.51 Hz); ratio 15:9:3:3:3:3. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 9.07 (s); CH_3, 18.46 (s); C(6), 152.32 (s); C(2), 150.65 (s); C(4), 141.72 (s); C(3), 139.46 (s); C(5), 128.21 (s); $(CH_3)_5C_5$, 99.70 (J_{Rh-C} = 7.92 Hz). Anal. Calcd for $C_{28}H_{36}N_3Rh[BF_4]_2$: C, 48.66; H, 5.25; N, 6.07. Found: C, 48.21; H, 5.13; N, 5.97.

$[Cp^*Rh(3,5\text{-dimethylpyridine})_3](PF_6)_2$ (19). $[Cp^*Rh(CH_3CN)_3](PF_6)_2$ (80.0 mg, 0.12 mmol) was dissolved in 10 mL of CH_2Cl_2, an excess of 3,5-dimethylpyridine was added (0.3 mL, 2.63 mmol), and the solution was stirred at room temperature for 40 min. The solvent volume was reduced to 2 mL, and a yellow solid formed upon addition of 10 mL of diethyl ether. The solvent was decanted, and the solid was washed with 2 × 5 mL of diethyl ether. Then the product was recrystallized at −30 °C overnight (72.2 mg, 85 % yield), mp 200–205 °C. ^1H NMR (400 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 1.45 (s); CH_3, 2.34 (s); H(4), 7.69 (s); H(2,5), 7.79 (s); ratio 15:18:3:6. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 9.07 (s); CH_3, 18.43 (s); C(2,5), 149.71; C(4), 142.65 (s); C(3,5), 138.83 (s); $(CH_3)_5C_5$, 99.68 (d, J_{Rh-C} = 7.88 Hz). Anal. Calcd for $C_{31}H_{42}RhN_3[PF_6]_2$: C, 43.83; H, 4.98; N, 4.95. Found: C, 43.95; H, 4.97; N, 5.00.

$[Cp^*Rh(2\text{-picoline})(CH_3CN)_2](BF_4)_2$ (20) (Air and Moisture Sensitive). $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ (52.0 mg, 0.1 mmol) was dissolved in 5 mL of CH_2Cl_2, then 0.01 mL (0.1 mmol) of 2-picoline was added, and the solution was stirred for 15 min. The

reaction solvent was evaporated, and the resulting yellow powder was washed with diethyl ether. The solid was redissolved in 2 mL of CH_2Cl_2 and filtered through Celite. Ether was added until the solution turned cloudy (2 mL) and was then cooled at −30 °C overnight. The resulting yellow powder was vacuum-dried to give 41.5 mg of the complex (61% yield), mp 105–110 °C. ^1H NMR (400 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 1.68 (s); CH_3CN, 2.51 (bs); CH_3, 2.97 (s); H(6), 8.63 (d, J = 5.60 Hz); H(4), 7.94 (t, J = 6.63 Hz); H(3), 7.57 (d, J = 7.41 Hz); H(5), 7.53 (t, J = 6.46 Hz); ratio 15:6:3:1:1:1:1. $^{13}C\{^1H\}$ NMR (400 Hz, CD_2Cl_2), δ: C(2), 163.06 (s); C(6) 155.36 (s); C(4), 141.55 (s); C(3), 129.94 (s); (C5), 125.55 (s); $C_5(CH_3)_5$, 102.07 (d, J_{Rh-C} = 8.05 Hz); $(CH_3)_5$, 9.60 (s); CH_3, 27.34 (s), $NCCH_3$, 3.70 (b s). Anal. Calcd for $C_{20}H_{28}N_3Rh[BF_4]_2$: C, 40.92; H, 4.81; N, 7.16. Found: C, 40.57; H, 4.61; N, 6.91.

[Cp*Rh(2,4-dimethylpyridine)(CH_3CN)$_2$](PF_6)$_2$ (21) (Air and Moisture Sensitive). [Cp*Rh(CH_3CN)$_3$](PF_6)$_2$ (50.1 mg, 0.076 mmol) was dissolved in 5 mL of CH_2Cl_2, 0.012 mL (0.1 mmol) of 2,4-dimethylpyridine was added, and the solution was stirred at room temperature for 10 min. The solvent volume was reduced to 2 mL, 0.5 mL of diethyl ether was added, and the flask was left at −30 °C. Small yellow crystals formed after 1 week. The solvent was decanted, and the solid was washed with 3 × 5 mL of diethyl ether. The resulting yellow powder was vacuum-dried to give 19.0 mg of the complex (29% yield). ^1H NMR (500 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 1.68 (s); CH_3, 2.48 (s); CH_3CN, 2.52 (b s); CH_3, 2.66 (s); H(5), 7.36 (d, J = 5.67 Hz); H(3), 7.39 (s); H(5), 8.45 (d, J = 5.99 Hz); ratio 15:3:6:3:1:1:1. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 10.81 (s); CH_3CN, 5.33 (b s); CH_3(4), 22.61 (s); CH_3(2), 28.27 (s); $(CH_3)_5C_5$, 102.09 ($^1J_{Rh-C}$ = 8.58 Hz); C(5), 127.83 (s); CN, 128.93 (s); C(3), 131.03 (s); C(6), 154.39 (s); C(4), 154.85 (s); C(4), 161.62 (s). Anal. Calcd for $C_{21}H_{30}N_3Rh[PF_6]_2$: C, 35.16; H, 4.21; N, 5.85. Found: C, 35.34; H, 4.66; N, 5.76.

[Cp*Rh(2,4,6-trimethylpyridine)](BF_4)$_2$ (22) (Air and Moisture Sensitive). [Cp*Rh(CH_3CN)$_3$](BF_4)$_2$ (53.3 mg, 0.1 mmol) was dissolved in 5 mL of CH_2Cl_2, then 0.01 mL (0.1 mmol) of 2,4,6-trimethylpyridine was added, and the solution was stirred for 4 h. The solvent was reduced to 1 mL under vacuum, and a yellow precipitate formed after addition of 10 mL of diethyl ether. The solvent was decanted, and the solid was washed with ether (3 × 5 mL). The resulting yellow powder was vacuum-dried to give 33.1 mg of the complex (41% yield). ^1H NMR (400 MHz, $(CD_3)_2CO$), δ: $(CH_3)_5$, 1.90 (s); H(3,5), 7.51 (s); CH_3, 2.74 (s); CH_3, 2.59 (s); ratio 15:2:6:3. $^{13}C\{^1H\}$ NMR (400 Hz, $(CD_3)_2CO$), δ: C(2,6), 120.21 (d, J = 3.6 Hz); C(4), 107.10 (d, J = 3.7 Hz); C(3,5), 87.91 (d, J = 2.5 Hz); C_5, 100.85 (d, J_{Rh-C} = 7.75 Hz); $(CH_3)_5$, 9.6 (s); CH_3, 23.91 (s); CH_3, 20.21 (s). Anal. Calcd for $C_{18}H_{26}RHN[BF_4]_2$: C, 41.88; H, 4.81; N, 2.57. Found: C, 41.55; H, 4.42; N, 2.82.

[Cp*Rh(*N*-methylpyrrole)](BF_4 or PF_6)$_2$ (23). Prepared similarly to **22**: BF_4, 70%, mp 289–91 °C dec; PF_6, 83%, mp 266–8 °C dec. ^1H NMR (200 MHz, CD_3NO_2), δ: $(CH_3)_5$, 2.25 (s); N–CH_3, 4.01 (s); H(2,5), 7.68 (d, J_{Rh-H} = 0.9 Hz); H(3,4), 6.71 (d, J = 0.9 Hz), ratio 15:3:2:2. $^{13}C\{^1H\}$ NMR, δ: C_5, 109.9 (d, J_{Rh-C} = 8.8 Hz); $(CH_3)_5$, 10.7 (s); NCH_3, 41.2 (s); 109.7 (d, J = 4.6 Hz); 97.1 (d, J = 5.5 Hz). FAB-MS (sulfolane): m/e 406 (M − BF_4). Anal. Calcd for $C_{15}H_{22}NRh[PF_6]_2$: C, 29.61; H, 3.62; N, 2.30. Found: C, 29.76; H, 3.48; N, 2.13.

[Cp*Rh(quinoline)(CH_3CN)$_2$](BF_4)$_2$ (24) (Air and Moisture Sensitive). Prepared similarly to **21**: BF_4, 78%. ^1H NMR (500 MHz, CD_3NO_2), δ: $(CH_3)_5$, 1.75 (s); CH_3CN, 2.48 (s); H(2–8), 9.23 (d, J = 5.0 Hz); 8.72 (d, J = 8.0 Hz); 8.29 (d, J = 8.7 Hz); 8.20 (d, J = 8.0 Hz); 8.10 (d, J = 7.2 Hz); 7.87 (d, J = 7.5 Hz); 7.81 (d, J = 5.0 Hz); ratio 15:6:1:1:1:1:1:1:1. $^{13}C\{^1H\}$ NMR (500 MHz,CD_3NO_2), δ: C_5, 102.2 (d, J_{Rh-C} = 8.0 Hz); $(CH_3)_5$, 9.6 (s); CH_3, 3.7 (s); CN, 128.0 (s); C(2–9), 157.8 (s); 147.5 (s); 143.0 (s); 133.9 (s); 132.42 (s); 131.4 (s); 131.4 (s); 129.8 (s); 128.7 (s); 124.6 (s). Anal. Calcd for $C_{23}H_{28}N_3Rh[BF_4]_2$: C, 44.33; H, 4.50; N, 6.75. Found: C, 44.52; H, 4.51; N, 6.62.

[Cp*Rh(quinoline)(μ-OH)]$_2$(BF_4)$_2$ (25). Prepared similarly to complex **21** using CH_2Cl_2 containing traces of water: BF_4, 83%. Alternatively, exposing compound **24** to air forms complex **25** quantitatively; mp 173–175 °C dec. ^1H NMR (250 MHz, CD_2Cl_2, 5 °C), δ: $(CH_3)_5$, 1.45 (s); μ-OH, 2.12 (s); H(2–8) 8.5 (d, J = 5.5 Hz); 8.38 (d, J = 8.7 Hz); 7.9 (m); 7.55 (d, J = 3.5 Hz); 7.49 (d, J = 8.1 Hz); 6.24 (m); ratio 15:2:1:1:1:2:2:1:1; $^{13}C\{^1H\}$ NMR (500 MHz, CD_3NO_2, −20 °C), δ: C_5, 93.2 (d, J_{Rh-C} = 8.2 Hz); $(CH_3)_5$, 8.9 (s); C(2–10), 121.8 (s); 128.7 (s); 130 (s); 130.2 (s); 132 (s); 139.2 (s); 140.8 (s); 146.2 (s); 154.9 (s); 185.3 (s). FAB-MS (sulfolane): m/e 855 (M − BF_4). Anal. Calcd for $C_{38}H_{46}N_2O_2Rh_2[BF_4]_2$: C, 48.84; H, 4.96; N, 2.91. Found: C, 48.45; H, 4.89, N, 2.97.

[Cp*Rh(isoquinoline)$_3$](BF_4 or PF_6)$_2$ (26). Prepared similarly to 17: BF_4, 87% yield, mp 164–6 °C dec); PF_6, 94%, mp 188–90 °C dec. ^1H NMR (200 MHz, $(CD_3)_2CO$), δ: $(CH_3)_5$, 1.77 (s); H(1), 9.82 (s); H(3), 8.44 (d, J = 6.6 Hz); H(4–6), 8.2–7.9 (m); H(97), 7.87 (t, J = 7.2 Hz); H(8), 8.33 (d, J = 8.2 Hz); ratio 15:1:1:3:1:1:1:1:1; $^{13}C\{^1H\}$ NMR (500 MHz, $(CD_3)_2CO$), δ: C_5, 100.2 (d, J_{Rh-C} = 8.6 Hz); $(CH_3)_5$, 8.6 (s); C(1–10) 157.9 (s); 144.8 (s); 130 (s); 129.4 (s); 127.1 (s); 125.6 (s); 134.7 (s); 130.6 (s); 136.7 (s). FAB-MS (sulfolane): m/e 712 (M − BF_4) or m/e 770 (M − PF_6). Anal. Calcd for $C_{37}H_{36}N_3Rh[PF_6]_2$: C, 48.53; H, 3.93; N, 4.59. Found: C, 48.38; H, 4.03; N, 4.50.

[Cp*Rh(2-methylquinoline)(CH_3CN)$_2$](PF_6)$_2$ (27) (Air and Moisture Sensitive). [Cp*Rh(CH_3CN)$_3$](PF_6)$_2$ (65.1 mg, 0.1 mmol) and 0.014 mL (0.11 mmol) of 2-methylquinoline were stirred in 5 mL of CH_2Cl_2 for 4 h. The yellow solution was filtered through Celite, and a yellow solid was formed upon addition of 1 mL of *n*-hexane. Recrystallization from CH_2Cl_2/*n*-hexane (1/0.5 mL) at −30 °C gave 16.2 mg of the complex (21% yield). ^1H NMR (400 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 1.79 (s); CH_3CN, 2.49 (bs); CH_3, 3.09 (s); H(8), 8.81 (d, J = 8.5 Hz); H(3), 8.37 (d, J = 8.1 Hz); H(5), 8.14 (m); H(7), 8.14 (m); H(6), 7.91 (t, J = 8.0 Hz); H(4), 7.75 (d, J = 8.3 Hz); ratio 15:6:3:1:1:1:1:1:1. $^{13}C\{^1H\}$ NMR (400 Hz, CD_2Cl_2), δ: C(3–10), 148.4 (s); 146.2 (s); 136.6 (s); 131.1 (s); 130.6 (s); 124.8 (s); 121.0 (s); C_5, 101.2 (d, $^1J_{Rh-C}$ = 8.4 Hz); $(CH_3)_5$, 9.5 (s); 27.34 (s); $NCCH_3$, 4.10 (b s). Anal. Calcd for $C_{24}H_{30}N_3Rh[PF_6]_2$: C, 38.31; H, 4.02; N, 5.59. Found: C, 38.24; H, 4.36; N, 5.62.

Preparation of [Cp*Rh(2-methylquinoline)](BF_4)$_2$ (28). To a solution of 2-methylquinoline (0.15 mL, 1.0 mmol) in 5 mL of acetone was added dropwise 50.1 mg (0.09 mmol) of [Cp*Rh-$((CH_3)_2CO)_3$](BF_4)$_2$ in 5 mL of acetone. The solution turned green and was stirred for 20 min, after which 15 mL of diethyl ether was added and the flask left at −30 °C overnight. A yellow-green precipitate formed and was washed with diethyl ether (3 × 5 mL) and vacuum-dried for 3 h. The precipiate was recrystallized from CH_2Cl_2 (2 mL) to give a green powder, **28**. The solution contains compound **27A** ([Cp*Rh(2-methylquinoline)$((CH_3)_2CO)_2$](BF_4)$_2$), as observed by NMR analysis. This compound can be converted into compound **28** by further vacuum drying to yield 24.4 mg (44%). ^1H NMR (500 MHz, CD_3NO_2), δ: $(CH_3)_5$, 2.23 (s); CH_3, 2.22 (s); H(3–8), 6.7–7.1 (m); ratio 15:3:6. $^{13}C\{^1H\}$ NMR (500 Hz, CD_3NO_2), δ: C(2–10), 169.17 (s); 127.9 (s); 111.5 (d, J = 8.3 Hz); 105.9 (d, J = 5.3 Hz); 105.4 (d, J = 4.3 Hz); 95.6 (d, J = 5.4 Hz); 87.4 (d, J = 4.4 Hz); 83.2 (d, J = 4.6 Hz); C_5, 111.3 (d, J_{Rh-C} = 7.9 Hz); $(CH_3)_5$, 10.6 (s); CH_3, 10.3 (s). FAB-MS (sulfolane): m/e 458 (M −BF_4). Anal. Calcd for $C_{20}H_{24}NRh[BF_4]_2$: C, 43.32; H, 4.33; N, 2.52. Found: C, 41.54; H, 4.32; N, 2.51.

[Cp*Rh(1,2,3,4-tetrahydroquinoline)](BF_4 or PF_6)$_2$ (29). Prepared similarly to **22**: BF_4, 74%, mp 270–2 °C dec; PF_6, 80%, mp 248–50 °C dec. ^1H NMR (250 MHz, CD_3NO_2), δ: 2.19 (s); N–H, 7.10 (br); H (2–5), 3.63 (m); 1.87 (m); 2.75 (m); 6.33 (dd, J = 1.0 Hz, 7.0); H (6–8) 6.73 (m); ratio 15:1:2:2:2:1:3; $^{13}C\{^1H\}$ NMR (500 MHz, CD_3NO_2), δ: C_5, 110.5 (d, J_{Rh-C} = 7.9 Hz); $(CH_3)_5$, 9.4 (s); C(2–10), 41.0 (s); 18.6 (s); 24.1 (s); 104.6 (d, J_{Rh-C} = 5.4 Hz); 103.7 (d, J = 3.9 Hz); 94.1 (d, J = 60 Hz); 85.7 (d, J = 7.6 Hz); 85.5 (d, J = 1.7 Hz); 101.5 (d, J = 3.9 Hz). FAB-MS (sulfolane): m/e 458 (M − BF_4). Anal. Calcd for $C_{19}H_{26}NRh[BF_4]_2$: C, 41.88; H, 4.81; N, 2.57. Found: C, 41.25; H, 4.66; N, 2.52.

[Cp*Rh(*N*-methylindole)](BF_4 or PF_6)$_2$ (30). Prepared similarly to **22**: BF_4 78%, mp 271–3 °C dec; PF_6, 79%, mp 236–8 °C dec. ^1H NMR (250 MHz, CD_3NO_2), δ: $(CH_3)_5$, 2.03 (s); N–CH_3, 4.06 (s); H(2–7), 8.42 (d, J_{H-H} = 3.3 Hz); 6.92 (d, J = 3.3 Hz); 7.69 (d, J = 6.5 Hz); 6.93 (br t, J = 6.5 Hz); 7.04 (t, J = 6.9 Hz); 7.76 (br d, J = 6.9 Hz); ratio 15:3:1:1:1:1:1:1:1. $^{13}C\{^1H\}$ NMR (500 MHz, CD_3NO_2), δ: C_5, 110.4 (d, J_{Rh-C} = 8.3 Hz); $(CH_3)_5$, 10.0 (s); N–CH_3, 35.3 (s); C(2–9), 148.6 (s); 102.7 (s); 100.6 (d, J_{Rh-C} = 4.5 Hz); 98.9 (d, J = 5.5 Hz); 98.2 (d, J = 5.4 Hz); 91.3 (d, J = 4.4 Hz); 111.8 (d, J = 2.9 Hz); 120.8 (d, J = 2.3 Hz). FAB-MS (sulfolane): m/e 456 (M − BF_4). Anal. Calcd for $C_{19}H_{24}NRh[BF_4]_2$: C, 42.03; H, 4.42; N, 2.58. Found: C, 41.61; H, 4.45; N, 2.54.

[Cp*Rh(acridine)(CH_3CN)$_2$](BF_4)$_2$ (31). [Cp*Rh-(CH_3CN)$_3$](BF_4)$_2$ (26.9 mg) and 34.1 mg of acridine were dissolved in 5 mL of CH_2Cl_2 for 4 h, and then 10 mL of *n*-hexane was added and the flask left at −30 °C. Small yellow crystals formed after

2 days. The solution was decanted, and the crystals were washed with ether (3 × 5 mL). Yield: 19.6 mg (58%). ^{1}H NMR (400 MHz, CD_2Cl_2), δ: H(10), 9.79 (s); H(2,9), 8.12 (d, J = 8.1 Hz); H(5,6), 8.06 (d, J = 8.9 Hz); H(3,8), 7.60 (t, J = 7.9 Hz); H(4,7), 7.21 (t, J = 8.1 Hz); CH_3, 2.33 (b s); $(CH_3)_5$, 1.57 (s); ratio 1:2:2:2:6:15. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2), δ: C(10), 148.92; C(2,9), 136.01; bridging head, 130.01; C(5,6), 129.27; C(4,7), 128.12; bridging head, 126.48; C(3,7), 125.60; C_5, 93.98 (d, J_{Rh-C} = 9.92 Hz); $(CH_3)_5$, 10.1 (s); CH_3, 3.06 (b s). Analytical data for this compound could not be obtained due to complex instability.

[Cp*Rh(phenanthridine)$(CH_3CN)_2$]$(PF_6)_2$ (32) (Air and Moisture Sensitive). [Cp*Rh$(CH_3CN)_3$]$(PF_6)_2$ (80.1 mg, 0.12 mmol) and 28.0 mg (0.14 mmol) of phenanthridine were stirred in 10 mL of CH_2Cl_2 for 40 min. The yellow solution was filtered through Celite. Solvent volume was reduced to 1 mL and a yellow solid was formed upon addition of 1 mL of *n*-hexane. The solid was washed with *n*-hexane (3 × 5 mL). Recrystallization from CH_2Cl_2/*n*-hexane (2/0.5 mL) at −30 °C gave 65.0 mg of the complex (85% yield), mp 150–152 °C. ^{1}H NMR (400 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 1.79 (s); CH_3CN, 2.50 (b s); H(2–10), 9.85 (s); 8.80 (d, J = 8.24 Hz); 8.72 (d, J = 7.78 Hz); 8.70 (d, J = 8.74 Hz); 8.30 (d, J = 8.13 Hz); 8.10 (t, J = 7.94 Hz); 7.95 (t, J = 7.20 Hz); 7.92 (t, J = 7.51 Hz); 7.90 (t, J = 7.88 Hz); ratio 15:6:1:1:1:1:1:1:1:1:1:1. $^{13}C\{^1H\}$ NMR (400 Hz, CD_2Cl_2), δ: C(2–14), 162.09 (s); 141.19 (s); 135.37 (s); 133.56 (s); 132.11 (s); 130.89 (s); 129.89 (s); 129.60 (s); 128.60 (s); 127.77 (s); 127.24 (s); 124.34 (s); 122.01 (s); CN, 127.01 (b s); C_5, 101.20 (d, $^1J_{Rh-C}$ = 8.39 Hz); $(CH_3)_5$, 9.5 (s); CH_3, 4.10 (b s). Anal. Calcd for $C_{27}H_{30}N_3Rh(PF_6)_2$: C, 41.08; H, 3.83; N, 5.32. Found: C, 41.43; H, 3.77; N, 5.51.

[Cp*Rh(5,6-benzoquinoline)$(CH_3CN)_2$]$(PF_6)_2$ (33) (Air and Moisture Sensitive). [Cp*Rh$(CH_3CN)_3$]$(PF_6)_2$ (64.9 mg, 0.1 mmol) and 15.0 mg (0.08 mmol) of 5,6-benzoquinoline were stirred in 3 mL of CH_2Cl_2 for 20 min. The yellow solution was filtered through Celite, and a yellow solid was formed upon addition of 1 mL of *n*-hexane. Recrystallization from CH_2Cl_2/*n*-hexane (1/0.5 mL) at −30 °C gave 40.1 mg of the complex (50% yield), mp 130–132 °C. ^{1}H NMR (400 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 1.79 (s); CH_3CN, 2.50 (b s); H(2–10), 9.20 (d, J = 5.91 Hz); 9.04 (d, J = 7.81 Hz); 8.92 (d, J = 8.01 Hz); 8.21 (d, J = 8.47 Hz); 8.17 (t, J = 5.25 Hz); 8.15 (t, J = 5.27 Hz); 7.99 (d, J = 5.76 Hz); 7.94 (t, J = 7.66 Hz); 7.91 (d, J = 9.04 Hz); ratio 15:6:1:1:1:1:1:1:1:1:1. $^{13}C\{^1H\}$ NMR (400 Hz, CD_2Cl_2), δ: C(2–14), 210.01 (s); 155.44 (s); 148.03 (s); 136.21 (s); 135.45 (s); 132.19 (s); 129.50 (s); 129.53 (s); 129.42 (s); 129.34 (s); 124.14 (s); 124.97 (s); 123.44 (s); CH_3CN, 127.00 (b s); C_5, 100.52 (d, $^1J_{Rh-C}$ = 8.05 Hz); $(CH_3)_5$, 9.60 (s); 27.34 (s); $NCCH_3$, 3.70 (bs). Anal. Calcd for $C_{27}H_{30}N_3Rh[PF_6]_2$: C, 41.08; H, 3.83; N, 5.32. Found: C, 40.67; H, 3.75; N, 4.88.

[Cp*Rh(7,8-benzoquinoline)$(CH_3CN)_2$]$(PF_6)_2$ (34) (Air and Moisture Sensitive). [Cp*Rh$(CH_3CN)_3$]$(PF_6)_2$ (61.1 mg, 0.093 mmol) and 22.1 mg (0.12 mmol) of 7,8-benzoquinoline were stirred in 5 mL of CH_2Cl_2 for 60 min. The yellow solution was filtered through Celite, and a yellow solid was formed upon addition of 5 mL of diethyl ether. Recrystallization from CH_2Cl_2/*n*-hexane (1/0.5 mL) at −30 °C gave 40.1 mg of the complex (38% yield), mp 130–132 °C. ^{1}H NMR (400 MHz, CD_2Cl_2), δ: $(CH_3)_5$, 1.70 (s); CH_3CN, 2.51 (b s); H(2–10)m 9.38 (d, J = 8.49 Hz); 9.18 (d, J = 5.26 Hz); 8.78 (d, J = 8.15 Hz); 8.41 (d, J = 9.59 Hz); 8.11 (d, J = 7.93 Hz); 8.00 (t, J = 5.63 Hz); 7.97 (d, J = 9.46 Hz); 7.89 (t, J = 8.57 Hz); 7.84 (t, J = 8.38 Hz); ratio 15:6:1:1:1:1:1:1:1:1:1. $^{13}C\{^1H\}$ NMR (400 Hz, CD_2Cl_2), δ: C(2–14), 157.44 (s); 149.45 (s); 138.19 (s); 137.54 (s); 133.99 (s); 131.91 (s); 131.85 (s); 131.67 (s); 129.36 (s); 127.12 (s); 126.51 (s); 125.64 (s); CH_3CN, 127.96 (b s); C_5, 101.77 (d, $^1J_{Rh-C}$ = 7.69 Hz); $(CH_3)_5$, 9.60 (s); 27.34 (s); $NCCH_3$, 3.70 (b s). Anal. Calcd for $C_{27}H_{30}N_3Rh[PF_6]_2$: C, 41.08; H, 3.83; N, 5.32. Found: C, 40.55; H, 3.64; N, 5.77.

Example of General Procedures A–C for the Competition Experiments. A. [Cp*Rh$(CH_3CN)_3$]$(BF_4)_2$ (0.05 mmol) was dissolved in 5 mL of CH_2Cl_2. To this solution was added dropwise a mixture of quinoline, **8** (1.0 mmol), and isoquinoline, **9** (1.0 mmol), that were reacted for 10 min. Then 15 mL of diethyl ether was added, and the flask was left at −30 °C overnight. A yellow solid formed, and analysis by ^{1}H NMR spectroscopy showed only [Cp*Rh(isoquinoline)$_3$]$(BF_4)_2$ (**26**).

B. Another example of a competitive reaction is described as follows: [Cp*Rh(acetone)$_3$]$(BF_4)_2$ (0.162 mmol) was prepared in situ in 10 mL of acetone. To this solution was added dropwise **11** (0.49 mmol) and **9** (0.49 mmol) dissolved in 2 mL of acetone; the resulting solution was then reacted for 10 min. Analysis by ^{1}H NMR spectroscopy showed only **26** and **11** being present, while **29** was absent.

C. In yet another procedure, we showed that **9** reacted with **29** to provide **26** and **11**, while the reverse reaction did not occur. *All three procedures gave the same order of ligand reactivity.*

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