# Homogeneous Catalytic Hydrogenation. 6. Synthetic and Mechanistic Aspects of the Regioselective Reductions of Model Coal Nitrogen, Sulfur, and Oxygen Heteroaromatic Compounds Using the ($\eta^5$-Pentamethylcyclopentadienyl)rhodium Tris(acetonitrile) Dication Complex as the Catalyst Precursor[1]

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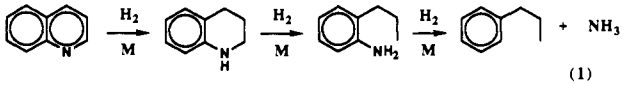
**Abstract:** The synthetic and mechanistic aspects of the regioselective hydrogenation of representative mono and polynuclear heteroaromatic nitrogen, sulfur, and oxygen model coal compounds such as 2-methylpyridine (**1**), *N*-methylindole (**2**), benzofuran (**3**), benzothiophene (**4**), quinoline (**5**), 2-methylquinoline (**6**), 5,6- and 7,8-benzoquinolines (7 and **8**), and acridine (**9**) were studied with a ($\eta^5$-pentamethylcyclopentadienyl)rhodium tris(acetonitrile) dicationic complex, $[Cp^*Rh(CH_3CN)_3]^{2+}$, as the catalyst precursor. The order of relative rates as a function of structure was found to be **8** >>> **9** > **5** > **7** > **6** > **4** ≫ **1**-**3**. Competitive hydrogenation experiments of **5** with other model coal compounds, **1**-**4**, **6**-**9**, pyridine (**10**), and isoquinoline (**11**) and its regioselective reduction product, 1,2,3,4-tetrahydroquinoline (**12**), showed the following effects on the initial hydrogenation rate of **5**: no effect (**2**-**4**), enhancement (**8**), and inhibition (**9**-**12**). In addition, 7,8-benzoquinoline (**8**) and its reduced product, 1,2,3,4-tetrahydro-7,8-benzoquinoline (**13**), were found to also enhance the initial hydrogenation rates of **2**, **6**, and **7**; a $[Cp^*Rh]^{2+}$-catalyzed transfer hydrogenation mechanism was invoked as one explanation for this rate enhancement by using **13**-$d_5$ in the presence of **5**, which showed deuterium atom transfer to provide **12**-$d_3$. Replacement of $H_2$ with $D_2$ provided information on several of the mechanistic aspects of these selective hydrogenation reactions and included reversibility in the N=C and C=C bond reductions of six-membered N heteroaromatic compounds (**1**, **5**-**9**), stereoselective reduction of the C=C bond in the five-membered N, S, and O heteroaromatic ring compounds (**2**-**4**), and exchange of aromatic ring and 2-methyl group hydrogens (**2**-**9**). The catalytic hydrogenation precursor Cp*Rh complexes for ligands **1** and **5**-**9** had the known structural formulas $[Cp^*Rh(\eta^1(N)\text{-ligand})(CH_3CN)_2]^{2+}$, while those for **2**-**4** are speculated to have $[Cp^*Rh(\eta^2\text{-ligand})(CH_3CN)_2]^{2+}$ structures, $\eta^2$ bonding of the C=C bond in the five-membered heteroaromatic ring to Cp*Rh. A partially hydrogenated pyridine intermediate, 1,2,5,6-tetrahydropyridine (**14**), bonded to $[Cp^*Rh]^{2+}$, $[Cp^*Rh(\eta^1(N)\text{-}1,2,5,6\text{-tetrahydropyridine})(CH_3CN)_2]^{2+}$ (**15**) was synthesized and reacted with $D_2$ gas to provide further evidence for a possible intermediate in the selective hydrogenation process. Moreover, thermal dehydrogenation of **15** was observed with formation of a $[Cp^*Rh(\eta^1(N)\text{-pyridine})(CH_3CN)_2]^{2+}$ complex. High-pressure NMR experiments were able to further verify the above-mentioned mechanistic pathways with quinoline (**5**) as an example, but the identity of intermediate $[Cp^*RhH\text{-quinoline}]^{2+}$ complexes was not successful. An overall mechanism for selective N, S, and O heteroaromatic ring hydrogenation will be presented.

The hydrodenitrogenation reaction (HDN), where nitrogen is removed from the heteroaromatic nitrogen ring of compounds found in coal and its products at high temperatures (400-600 °C) and high pressures of $H_2$ gas (2000 psi), is one of the most important and highly studied petroleum industrial processes.[3a,b] As well, hydrodesulfurization (HDS) and hydrodeoxygenation (HDO) are also significant industrial processes for removal of sulfur and oxygen, respectively.[3c]

The thermodynamics of the HDN process dictates that the nitrogen-containing ring be selectively hydrogenated prior to any carbon-nitrogen bond cleavage reactions. The subsequent nitrogen atom removal steps include metal-mediated hydrogenolysis of the alkylcarbon-nitrogen bond followed by a similar cleavage of the aromatic ring carbon-nitrogen bond; quinoline (**5**), a model coal compound, is shown in eq 1 as an example of the ideal HDN pathway.[4]




(1)

A decade ago, we discovered that a wide variety of soluble rhodium and ruthenium complexes were catalysts for the regioselective hydrogenation of polynuclear heteroaromatic nitrogen model coal compounds under $CO/H_2O$, $CO/H_2$, and $H_2$ reaction conditions; this being the first step in the above-mentioned HDN reaction (eq 1).[1a-e] Selective heteroaromatic ring hydrogenation has also been shown to be significant in HDS model studies[5] and, presumably, is also critical in the HDO process. Studies by other workers have also verified the selective nitrogen and sulfur heteroaromatic hydrogenation results with several homogeneous Fe, Mn, Rh, Os, Ru, and Ir systems under a similar variety of reaction conditions as mentioned above.[6]

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(2) (a) Lawrence Berkeley Laboratory. (b) Current address: Chevron Chemical Co., Kingwood, TX. (c) DOE Teacher Research Associate, June-Aug 1990. (d) DOE Undergraduate Research Associate, Sept-Dec 1990 (Dartmouth College, Hanover, NH). (e) Exxon Research and Engineering Co. (f) To whom correspondence should be addressed.

(3) (a) Schulz, 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. (b) Laine, R. M. *Catal. Rev. Sci. Eng.* **1983**, *25*, 459. (c) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979.

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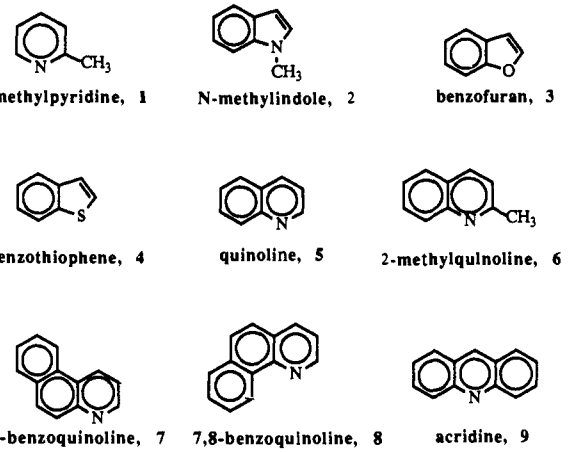
**Chart I.** Model Coal Nitrogen, Sulfur, and Oxygen Compounds, **1–9**




In recently reported bonding studies, we have been able to ascertain with a soluble ($\eta^5$-pentamethylcyclopentadienyl)rhodium dicationic complex, $[Cp^*Rh(CH_3CN)_3]^{2+}$, that initial $\eta^1$(N)-bonding of the six-membered ring nitrogen (N) ligands (**1**, **5–9**) to the organorhodium metal center was critical for N-ring reduction.[1e,7] However, it was also necessary that the previously mentioned $\eta^1$(N)-bonded complexes have the formula, $[Cp^*Rh(\eta^1(N)\text{-ligand})(CH_3CN)_2]^{2+}$, to be catalytically active; i.e., two replaceable $CH_3CN$ ligands were found to be necessary for catalysis to proceed.[1e,7]

In addition, our recently communicated selective hydrogenation studies also revealed that a sulfur heteroaromatic compound, benzothiophene (**4**), appears to bind in a $\eta^2$ (C=C) fashion with $[Cp^*Rh(CH_3CN)_3]^{2+}$ prior to selective reduction of the C=C double bond.[1e] This $\eta^2$-bonding mode for **4** has recently been verified by Angelici and co-workers with a $Cp^*Re(CO)_2(THF)$ complex and was found in be in equilibrium with its $\eta^1$(S) isomer.[8]

In this paper, we present the full account of our results on the synthetic and mechanistic aspects of these selective hydrogenation reactions as a function of N heteroaromatic ligand structure and, for comparison purposes, two other heteroatom compounds, one of sulfur (S) and one of oxygen (O) (compounds **1–9**, Chart I), using the $[Cp^*Rh(CH_3CN)_3]^{2+}$ dicationic complex as the catalyst precursor.

**Relative Rates of Hydrogenation and Factors That Enhance and Inhibit Selective Nitrogen, Sulfur, and Oxygen Ring Reduction.** The initial and relative rates (quinoline (**5**), designated as having a relative rate of 1.0), as well as number of turnovers (mmol of product/mmol of $[Cp^*Rh(CH_3CN)_3]^{2+}$) in the hydrogenation reaction of ligands **1–9** (Chart I) are shown in Table I using $[Cp^*Rh(CH_3CN)_3]^{2+}$ as the catalyst precursor.[1e] The order of relative rates as a function of N, O, and S ligand structure was found to be **8** >>> **9** > **5** > **7** > **6** > **4** ≫ **1–3**.

It was surprising to find that compound **8** is 11 times faster than **5** and 15 times faster than its 5,6-isomer, **7**, while compound **6** has a relative rate that is 2 times slower than that of **5**. In the case of ligand **1**, it is important to note that relatively few examples of pyridine derivatives have been reported to be hydrogenated under such mild homogeneous catalytic conditions, although **1** is 32 times slower than **5** and 15 times slower than **6**.

It appears that both steric and electronic effects exert control on the hydrogenation rates. The consequence of the 2-methyl group is shown by comparing **5** and **6**; the effect of the 2-methyl group in **6** lowers the relative rate by a factor of 2. The pyridine ring of **1** is more difficult to hydrogenate and we find that it is 15 times slower than **5**. Moreover, ligand **9** is 1.3 times faster than **5**, with the stipulation that it only takes 1 mol of $H_2$ to hydrogenate **9** and 2 mol for **5**. The sulfur heteroaromatic compound studied for comparison, **4**, was found to be 5 times slower than **5**, while the oxygen heterocyclic compound, **3**, was found to be 11 times slower than **5**.

In order to establish what effect each of the ligands had on the initial rate of hydrogenation of **5** (standard), a series of competitive reactions with ligands **1**, **4–9**, pyridine (**10**), isoquinoline (**11**), and 1,2,3,4-tetrahydroquinoline (**12**) (1:1 molar ratio) were carried out (Table II). The results show that neither ligand **4** nor **7** affects the initial rate of hydrogenation of **5**, while **1**, **6**, or **9** decreases the rate by a factor of 2–4. Interestingly, **8** dramatically increased the initial rate of **5** by a factor of 9. Compounds **10** and **11** (not shown in Table II) totally inhibited the initial rate of **5**. It was

**Table I.** Regioselective Hydrogenation of Heteroaromatic Nitrogen, Sulfur, and Oxygen Model Coal Compounds with $[Cp^*Rh(CH_3CN)_3]^{2+}$ as the Catalyst Precursor: Initial Rates (IR), Relative Rates (Rel Rate), and Number of Turnovers (NOT)[a]

| substrate | product[b] | IR, %/min | rel rate | NOT (1 h) |
|---|---|---|---|---|
| **1** |  | 0.01 | 0.03 | <1 |
| **2** |  | 0.01 | 0.03 | <1 |
| **3** |  | 0.03 | 0.09 | <1 |
| **4** |  | 0.06 | 0.19 | 1 |
| **5** |  | 0.32 | 1.0[c] | 4 |
| **6** |  | 0.15 | 0.47 | 2 |
| **7** |  | 0.23 | 0.72 | 3 |
| **8** |  | 3.5 | 11 | 20[d] |
| **9** |  | 0.41 | 1.28 | 5 |

[a] Solvent: $CH_2Cl_2$; substrate/catalyst ratio = 20; temp, 40 °C; press, 500 psi of $H_2$; NOT = (mmol of product/mmol of $[Cp^*Rh(CH_3CN)_3]^{2+}$)/h. Reactions were run in a Parr kinetic apparatus (see ref 1c for details). [b] Analysis by GC and GC/MS. [c] Standard. [d] 30 min.

**Table II.** Competitive Hydrogenation of Quinoline (**5**) with Compounds **1**, **4**, and **6–9** and Its Reduction Product 1,2,3,4-Tetrahydroquinoline (**12**): Initial Rate, Relative Rate, Number of Turnovers, and Selectivity Factors

| quinoline IR | rel rate[a] | NOT (1 h) | competing substrate | IR | rel rate[b] | NOT[c] (1 h) | sel factor[e] |
|---|---|---|---|---|---|---|---|
| 2.80 | 8.8 | 33.6 | **8** | 0.66 | 0.2 | 10.7 | 4 |
| 0.41 | 1.3 | 4.9 | **4** | 0.03 | 0.5 | 0.4 | 14 |
| 0.32 | 1.0 | 4.0 | **5**[d] | | | | |
| 0.29 | 0.9 | 3.5 | **7** | 0.13 | 0.2 | 1.6 | 2 |
| 0.18 | 0.6 | 2.2 | **1** | 0.00 | 0.0 | 0.0 | |
| 0.13 | 0.4 | 1.6 | **6** | 0.08 | 0.5 | 0.9 | 2 |
| 0.13 | 0.4 | 1.6 | **9** | 0.23 | 0.6 | 2.7 | 0.6 |
| 0.11 | 0.3 | 1.3 | **12** | | | | |

[a] Conditions similar to those in Table I. Substrates to catalyst ratio are 1:1:0.050; rel rate, relative to initial rate of hydrogenation of quinoline alone. [b] Relative to initial rate of hydrogenation of substrate alone. [c] Number of Turnovers = (mmol of product/mmol of $[CpRh(CH_3CN)_3]^{2+}$)/h. [d] Standard for quinoline alone. [e] Quinoline IR/competitor IR.

(6) (a) Jardine, I.; McQuillin, F. J. *Chem. Commun.* **1970**, 626. (b) Derencsenyl, T. T.; Vermeulen, T. *Chem. Abstr.* **1980**, *93*, 188 929; LBL Report 9777, Sept 1979 (Ph.D. Thesis of T.T.D.). (c) Lynch, T. J.; Banah, M.; Kaesz, H. D.; Porter, C. R. *J. Org. Chem.* **1984**, *49*, 1266. (d) Murahashi, S.-I.; Imada, Y.; Hirai, H. *Tetrahedron Lett.* **1987**, *28*, 77. (e) Sanchez-Delgado, R. A.; Gonzalez, E. *Polyhedron* **1989**, *8*, 1431. (f) Laine, R. M. *New J. Chem.* **1987**, *11*, 543 and references therein. (g) Giandomenico, C. M.; Eisenstadt, A.; Fredericks, M. F.; Hirschon, A. S.; Laine, R. M. In *Catalysis of Organic Organic Reactions*; Augustine, R. L. Ed.; Marcel Dekker, Inc.: New York, 1985; p 73.

(7) (a) Fish, R. H.; Kim, H.-S.; Babin, J. E.; Adams, R. D. *Organometallics* **1988**, *7*, 2250. (b) Fish, R. H.; Baralt, E.; Kim, H.-S. *Organometallics* **1991**, *10*, 1965.

(8) Choi, M.-G.; Robertson, M. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 4005.

Table III. Competitive Hydrogenation of 7,8-Benzoquinoline (**8**) with Compounds **1**, **2**, **4**, **6**, and **7**: Initial Rate, Relative Rate, and Selectivity Factors

| 7,8-benzoquinoline IR | 7,8-benzoquinoline rel rate[a] | competing substrate | IR | rel rate[b] | sel factor[d] |
|---|---|---|---|---|---|
| 0.005 | 0.001 | **1** | 0.008 | 0.8 | 0.54 |
| 0.1 | 0.03 | **2** | | | |
| 3.5 | 11.0 | **8** (alone)[c] | | | |
| 0.5 | 0.2 | **4** | 0.01 | 0.2 | 43 |
| 0.5 | 0.2 | **6** | 2.26 | 15 | 0.24 |
| 0.95 | 0.3 | **7** | 1.44 | 6.3 | 0.7 |

[a] Conditions similar to Table I; substrates to catalyst ratio are 1:1:0.05, rel rate, relative to initial rate of hydrogenation of 7,8-benzoquinoline alone. [b] Relative to initial rate of hydrogenation of substrate alone. [c] Standard for 7,8-benzoquinoline. [d] 7,8-Benzoquinoline/competitor rate.

also determined that the regioselective reduction product of **5**, 1,2,3,4-tetrahydroquinoline (**12**), decreased the initial rate by a factor of 3. These above-mentioned results provided us with a selectivity factor in the competitive hydrogenation of **5** over other ligands and showed a factor of 4 over **8**, 14 over **4**, and 2 over **6** and **7**, while **9** was hydrogenated selectively over **5** by a factor of 1.7.

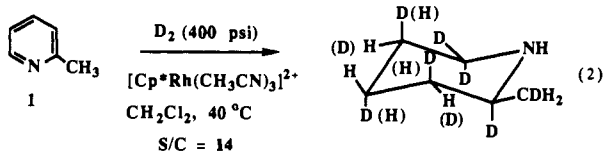
We also found that the rate enhancement produced by **8** in the hydrogenation of **5** was concentration dependent; i.e., as the molar concentration of **8**:**5** was varied from 0.5:1 to 1:1 there was a initial rate enhancement for **5** from a factor of 3 to that of 9, and even the hydrogenation product of **8**, 1,2,3,4-tetrahydro-7,8-benzoquinoline (**13**), enhanced the initial rate of **5** by a factor of 4 (1:1 molar ratio). Thus, **8** by itself is hydrogenated faster than **5** but then enhances the rate of hydrogenation of **5** in a mixture, and only after all of **5** is hydrogenated is **8** reduced. This result coincides with a previous result we found that **5** binds to $[Cp^*Rh]^{2+}$ in preference to **8**.[7b]

The rate enhancement of **5** by **8** was further studied in order to see what other ligands were affected similarly (Table III). It is interesting to note that the initial rate of **6** was increased by a factor of 15 and that of **7** by a factor of 6, while decreases in the initial rates of **1**, **2**, and **4** were observed. The initial hydrogenation rate of **8** was reduced dramatically by all ligands studied with the selectivity factor favoring **8** only in the case of **4** by a factor of 43.

It seems logical from these results that one possibility for the rate enhancement phenomena could emanate from the partial hydrogenation of **8** to 1,2-dihydro-7,8-benzoquinoline (**13a**), followed by a catalytic transfer hydrogenation reaction. Several years ago, we discovered that 9,10-dihydrophenanthridine readily transferred hydrogen to **5** and **9** to form their respective tetrahydro and dihydro analogues by using $(Ph_3P)_3RhCl$ and $(Ph_3P)_3RuCl_2$ as catalysts at 85 °C.[9a] While **13a** was difficult to prepare and isolate in a pure form, a control experiment with **13** and **5** in the presence of $[Cp^*Rh(CH_3CN)_3]^{2+}$ at 40 °C showed formation of 1,2,3,4-tetrahydroquinoline (**12**) (11%). Thus, catalytic transfer hydrogenation could be one plausible pathway to account for the increase in formation of reduced product with time for compounds **5**–**7**. Subsequent deuterium labeling experiments have further strengthened this concept and are reported in the following section.

**Deuterium Gas Studies with Compounds 1, 4–6, and 8**, several other mechanistic aspects of the selective hydrogenation reactions were obtained with the substitution of $D_2$ for $H_2$ using compound **1**, **4**–**6**, and **8** as examples.[1b-e] The results for **1** are depicted in eq 2.

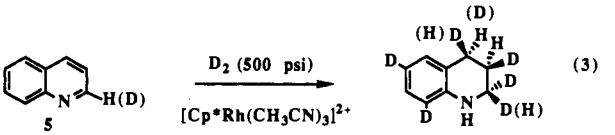
The product from the reaction of $D_2$ with compound **1** was analyzed by $^1H$ and $^{13}C$ NMR spectroscopy and GC/MS to



(2)

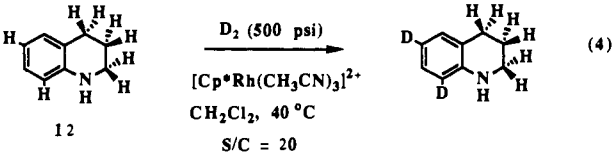
provide the following data. The $^1H$ NMR spectra were obtained at −50 °C to prevent fluxionality problems that would further complicate the results. The $^1H$ and $^{13}C$ NMR analysis, including decoupling experiments at −50 °C with the nondeuterated 2-methylpiperidine to assign the various protons, shows that all axial hydrogens have a substantial deuterium content and that all equatorial hydrogens also are partially or fully deuterated, with the 2- and 6-positions almost fully deuterated and the methyl group partially deuterated. For example, the signals at 2.89 and 2.49 ppm assigned to the equatorial and axial hydrogens, respectively, on carbon 6 and the axial hydrogen on carbon 2 at 2.43 ppm are >90% deuterated. The $^{13}C$ NMR also verifies that deuterium is present at every carbon atom. GC/MS analysis shows the deuterated product to be $d_{1-9}$, with parent ions at $m/z$ 100–109.

The deuterium results for **5** are shown in eq 3. The deuterated



(3)

1,2,3,4-tetrahydroquinoline-$d_5$ was analyzed by GC/MS to show $m/z$ values of 134–138 corresponding to a $d_1$–$d_5$ deuterium pattern. Analysis by 500-MHz $^1H$ NMR spectroscopy revealed ~1.5 d at position 2, ~1 d each at positions 3 and 4, ~1 d at position 8, and ~0.9 d at position 6. $^{13}C$ NMR was also performed to verify the deuterium positions. Previously, we reported a vicinal coupling for the 3,4-hydrogens of ~7.6 Hz from a measurement of the half-bandwidth and suggested it to be consistent with cis stereochemistry.[1c,e] To further help in this stereochemical analysis, the $^1H$ NMR analysis also was performed on the $[\eta^6$-Cp*Rh$]^{2+}$ complex (benzene ring) of 1,2,3,4-tetrahydroquinoline-$d_5$ to facilitate the separation of axial and equatorial protons on positions 3 and 4. We found that both the 4-axial and 4-equatorial protons had ~0.5 d each. The 3-axial proton appeared fully deuterated, while the 3-equatorial hydrogen was buried under the Cp*Rh signal at 2.12 ppm. These results, therefore, do not allow us to unequivocally assign a cis stereochemistry to the reduction of the 3,4-double bond and, in fact, rather supports a reversible reduction of the 3,4-double bond. The remaining **5** was analyzed as well by GC/MS and $^1H$ NMR to show quinoline-*2-d*. Furthermore, the aromatic ring deuterium exchange chemistry was found to occur from $[Cp^*Rh]^{2+}$-catalyzed deuteration of 1,2,3,4-tetrahydroquinoline under similar conditions as shown in eq 4; *only positions 6 and 8 undergo exchange (NMR), while the saturated nitrogen ring contains no deuterium* (eq 4). We also looked for



(4)

the formation of $HBF_4$ by NMR, but it was not evident in the ~11 ppm range, and this tends to eliminate an acid-catalyzed, rather than a highly electrophilic ($Cp^*Rh^{2+}$) metal-catalyzed, exchange mechanism for the aromatic ring protons.[1,6f]

Deuterium gas studies with 2-methylquinoline (**6**) showed a similar pattern of deuteration to that of **5**, except that the 2-methyl group at 2.06 ppm had been totally exchanged as evidenced by the $^1H$ and $^{13}C$ NMR spectra (eq 5). As in the analysis of the $[\eta^6$-Cp*Rh$]^{2+}$ complex of **12**-*d* for stereochemistry at the 3,4-C=C bond, the $[\eta^6$-Cp*Rh$]^{2+}$ complex of 1,2,3,4-tetrahydro-2-methylquinoline-$d_8$ (GC/MS analysis) showed similar NMR

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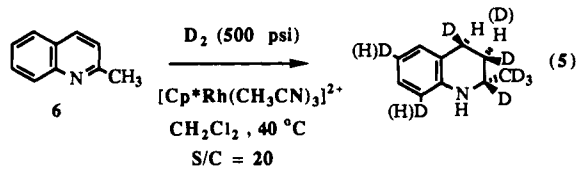
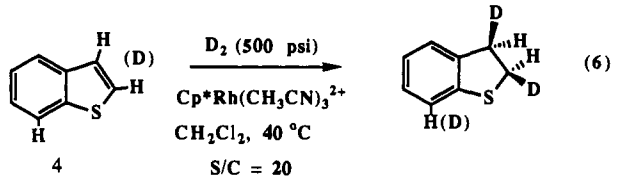



features and thus the reduction of the 3,4-C=C bond of **6** also appears to be reversible.

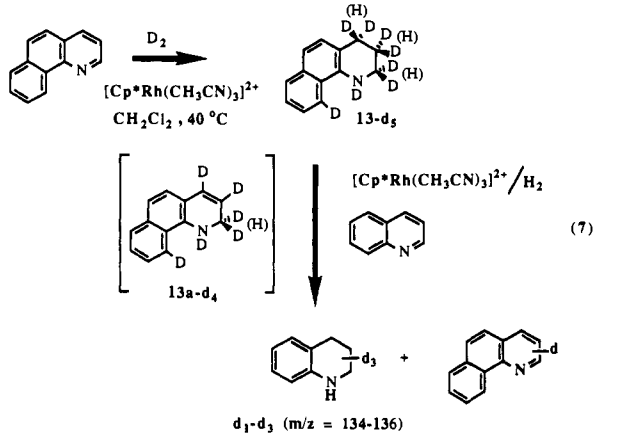
The results for **4** are depicted in eq 6 and what is interesting is that it appears that $\eta^2$, rather than $\eta^1$, S-bonding is predominant (as opposed to initial $\eta^1$, N-bonding for the six-membered nitrogen ligands) and kinetically controls the deuteration of the 2,3-C=C double bond. The stereoselective cis hydrogenation of the 2,3-




C=C bond is clearly evident by the $^1$H NMR spectrum to show two doublets at 3.22 and 3.30 ppm with $J_{2H-3H}$ = 7.0 Hz, while the $^{13}$C NMR spectrum shows a triplet at 37.56 ppm ($J$ = 21 Hz) for $C_2$ and 34.65 ppm ($J$ = 22 Hz) for $C_3$. The remaining **4** was found to have trace amounts of deuterium in the 2- and 3-positions (~0.1 d). This latter result might be indicative of some slight reversibility in the reduction of the 2,3-double bond. As well, minor amounts of deuterium (~0.1 d) were found in the 7-position of 2,3-dihydrobenzothiophene and exchange is thought to occur after the 2,3-C=C double bond is deuterated as was the case for compounds **5** and **6**.

As stated in the last section on the initial rate data, the use of **13**, the N-ring hydrogenation product of **8**, to also increase the rate of hydrogenation of **5** by a factor of 4 provided us with some clues for further experiments to elucidate the mechanism of this rate enhancement phenomena. Since **13** also enhanced the initial rate of hydrogenation of **5**, we surmised that one promising possibility for the rate enhancement emanated from a $[Cp^*Rh]^{2+}$-mediated catalytic transfer hydrogenation reaction that shuttled hydrogen from **13** or, more probably, the partially hydrogenated product 1,2-dihydro-7,8-benzoquinoline (**13a**) to **5**; this would effectively increase the production of **12** with time and thus the dramatic initial rate increase.

Therefore, we prepared the deuterated analogue of **13**, **13**-$d_5$, and reacted it with **5** under normal hydrogenation conditions. The reaction mixture was analyzed by $^1$H and $^{13}$C NMR spectroscopy as well as GC/MS and clearly showed that deuterium was transferred from **13**-$d_5$ or **13a**-$d_4$ to **5** to provide ~25% **12**-$d_3$ (eq 7). The $^1$H NMR spectrum of **12**-$d_3$ has the broad singlets we




usually see when deuterium is bonded to the N-ring carbons, while $^{13}$C NMR also shows that the N-ring has deuterium. However, complications of having very similar $^{13}$C NMR chemical shifts for the N-ring carbon atoms for **12**-$d_3$ and **13**-$d_5$ prevent us from differentiating between deuterium bonded to either compound. We can tentatively say that **13**-$d_5$ can transfer deuterium to **5** via a $[Cp^*Rh]^{2+}$-catalyzed transfer hydrogenation reaction.

**High-Pressure Nuclear Magnetic Resonance Spectroscopy Studies on the Catalytic Hydrogenation of Quinoline (5) with $[Cp^*Rh(CH_3CN)_3]^{2+}$.** The advent of the high-pressure NMR technique (HPNMR) allows homogeneous catalytic reactions to be studied in real time.[10] In order to further define the mechanism of this selective hydrogenation reaction (eq 1), we have utilized HPNMR with compound **5** as an example.

The complex from **5** and $[Cp^*Rh(CH_3CN)_3]^{2+}$, $[Cp^*Rh(\eta^1$-(N)-quinoline)$(CH_3CN)_2]^{2+}$, was formed in situ (drybox, $CD_2Cl_2$, s/c ratio = 14) in the sapphire HPNMR tube (10 mm) and the $^1$H NMR (300 MHz, 30 °C) recorded (Figure 1, 0 min) to show the Cp* signal at 1.78 ppm (singlet) for $[Cp^*Rh(\eta^1$(N)-quinoline)$(CH_3CN)_2]^{2+}$, the complexed $CH_3CN$ signal at 2.5 ppm, and the free quinoline signals at ~7.4–8.9 ppm.[7b] The HPNMR tube was pressurized to 500 psi with $D_2$ (or $H_2$ with $[Cp^*Rh(\eta^1$(N)-quinoline-$d_7$)$(CD_3CN)_2]^{2+}$) gas and the reaction monitored for 23 h (Figure 1). In the time it took to process the HPNMR data after $D_2$ pressurization (21 min), the signal at 1.78 ppm had disappeared with the concomitant formation of free $CH_3CN$ (2.05 ppm). As well, the 2-hydrogen at 8.9 ppm on quinoline (**5**) was almost all exchanged for deuterium, while the 8-hydrogen at 8.2 ppm and the 7-hydrogen at 7.88 ppm were also undergoing broadening, but were not exchanged. We also observe new signals at 0.85 and 0.7 ppm that eventually disappear as the reaction proceeds, but we could not determine their origin and can only speculate that they could possibly be associated with $Cp^*RhH$-$\eta^2$-C=N or C=C intermediates.[11]

At 21 min, 1,2,3,4-tetrahydroquinoline-*d* (**12**-*d*) is barely perceptible and continues to grow with time (6.4–7.0 ppm and 3.2, 2.7, and 1.9 ppm). Also evident is the small signal for $[Cp^*Rh(\eta^6$-1,2,3,4-tetrahydroquinoline)$]^{2+}$ at 2.12 ppm (871 min).[7] After 1361 min, all of **5** is reacted to form **12**-$d_4$. Isolation of the product 1,2,3,4-tetrahydroquinoline-$d_4$ by column chromatography and subsequent analysis by $^1$H and $^2$H NMR as well as GC/MS analysis provided ~1.5 d at the 2-position and ~1 d each at the 3- and 4-positions. Thus, it is obvious that exchange of hydrogen for deuterium at the 2-position on **5** occurs, while reversible hydrogenation–dehydrogenation of the N=C bond proceeds. We do not understand as yet the mechanism of the 7- and 8-hydrogen broadening process.

Further low-temperature (0–30 °C) HPNMR experiments (over a period of 31 h), to elucidate what occurs between 0 and 21 min in Figure 1, were carried out this time with the deuterated $CD_3CN$ ligand and show the disappearance of the signal for $[Cp^*Rh(\eta^1$(N)-quinoline)$(CD_3CN)_2]^{2+}$ at 1.78 ppm and the appearance new Cp* signals at 1.9 and 2.1 ppm (Figure 2). We believe that these new Cp* signals are due to intermediates in the reduction process and are associated with the hydrogenation of the N=C and C=C bonds. We attempted to isolate and identify the major product with the signal at 1.9 ppm that remains throughout the experiment, but, unfortunately, it was too unstable for isolation.

A control experiment was done to prove that no hydrogen for deuterium exchange with $[Cp^*Rh(\eta^6$-1,2,3,4-tetrahydroquinoline)$]^{2+}$ occurs under the reaction conditions. Thus, $[Cp^*Rh(\eta^6$-1,2,3,4-tetrahydroquinoline)$]^{2+}$ was dissolved in $(CD_3)_2CO$-$d_6$ in the HPNMR tube and then the tube was pressurized with 500 psi of $D_2$ gas and spectra were recorded for 16 h with no apparent exchange of either the 2-, 6-, or 8-hydrogens as occurred at 40 °C in a Parr apparatus (eq 4). We then added a 14-fold excess of **5** to this solution and catalysis proceeded, but at a slower rate when compared to using $[Cp^*Rh(CH_3CN)_3]^{2+}$ as the catalyst precursor. This result suggests that $[Cp^*Rh(\eta^6$-1,2,3,4-tetrahydroquinoline)$]^{2+}$ can be in the catalytic cycle;

(10) (a) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388. (b) Horvath, I. T.; Ponce, E. C. *Rev. Sci. Instrum.* **1991**, *62*, 1104. (c) For a review of the HPNMR technique, see: Horvath, I. T.; Millar, J. M. *Chem. Rev.* **1991**, *91*, 1339.

(11) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1989**, *111*, 8722.

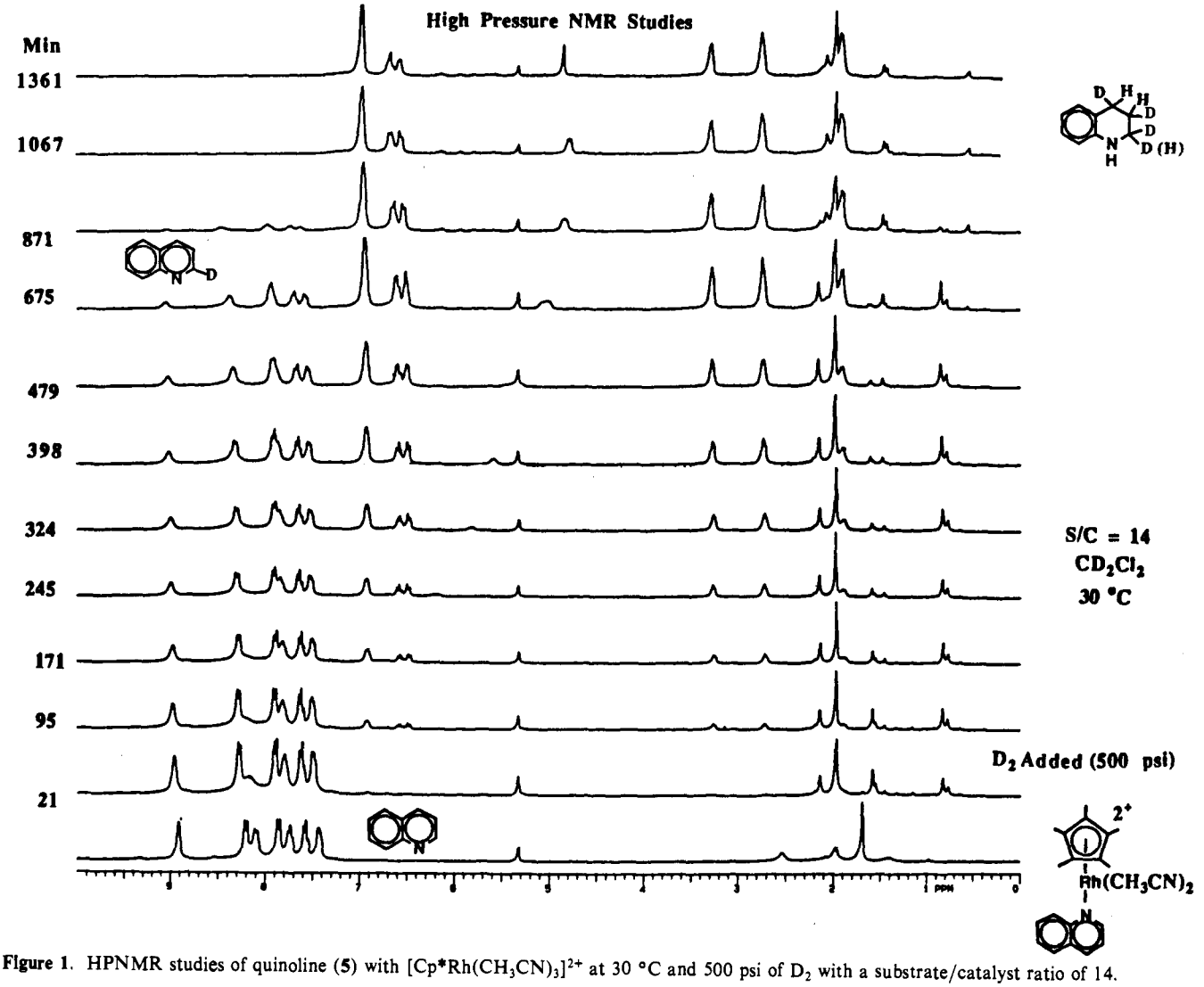
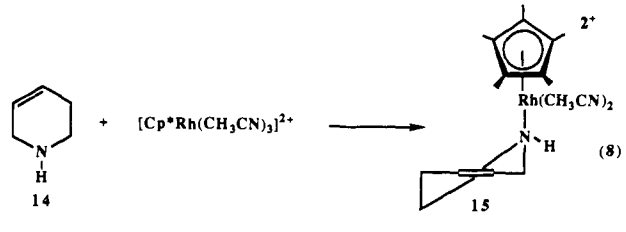



**Figure 1.** HPNMR studies of quinoline (**5**) with $[Cp^*Rh(CH_3CN)_3]^{2+}$ at 30 °C and 500 psi of $D_2$ with a substrate/catalyst ratio of 14.

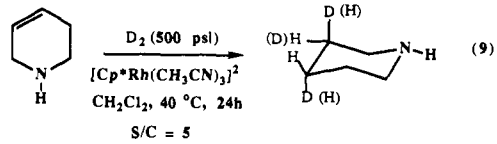
but, apparently, as the concentration of **12** increases the rate of hydrogenation of **5** decreases; this finding corroborates the initial rate data where **12** decreases the initial rate of hydrogenation of **5** by a factor of 3.

Attempts to identify the intermediate hydrides were undertaken with the following experiments. The $[Cp^*Rh(CH_3CN)_3]^{2+}$ was cooled to −60 °C in $CD_2Cl_2$ and then the sapphire NMR tube was pressurized with 1000 psi of $H_2$ gas. Interestingly, no hydrides were observed (2 h) as the temperature was raised up to ambient temperature (30 °C for 13 h); $[Cp^*Rh(CH_3CN)_3]^{2+}$ maintained its integrity at all temperatures. Similarly, as described above, an experiment with $[Cp^*Rh(\eta^1(N)\text{-quinoline})(CH_3CN)_2]^{2+}$ from −60 (14 h) to 0 °C (over 5 h) also showed no formation of hydrides or reduction product, **12**. However, as the solution was warmed from 0 to 30 °C (2 h) the reduction proceeded (continued for 29 h), but no hydrides could be detected even when the reaction was cooled back to −60 °C. Apparently, hydride transfer from Cp*Rh to complexed quinoline is extremely fast on the NMR time scale. In similar HPNMR experiments with compound **1**, we did observe several hydride signals in the −10 to −12 ppm range that appeared and then disappeared with time, but the spectra were too complicated for any rational analysis.

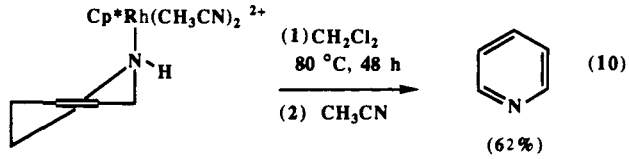
**Plausible Intermediates in the Reduction of a Pyridine Ring System and Its Dehydrogenation Reactions.** The selective hydrogenation reactions of these heteroaromatic compounds probably entails having N-bound, partially saturated intermediates present during reaction. Fortunately, we were able to synthesize and tentatively characterize by $^1H$ NMR spectroscopy $[Cp^*Rh(\eta^1\text{-}(N)\text{-}1,2,5,6\text{-tetrahydropyridine})(CH_3CN)_2]^{2+}$ (**15**) (eq 8) and use it to understand the plausible mechanism of reduction of the 3,4-C=C double bond and any dehydrogenation component during hydrogenation of 1,2,5,6-tetrahydropyridine (**14**).




Complex **15**, with an $\eta^1(N)$-bound 1,2,5,6-tetrahydropyridine ligand and two acetonitrile groups, provided us with a similar precursor as previously identified for such unsaturated ligands as **1** and **5–9** that is needed for reduction of the 3,4-double bond.[1e,7] In fact, reduction of **14** gave $^{13}C$ NMR results that showed two deuteriums on the 3- and 4-carbon atoms (3- and 4-carbon atoms at ~22 ppm, overlapping triplets) and no deuterium at the 2- and 6-positions (2- and 6-carbon atoms at 43.9 ppm, singlet), while carbon 5 was masked by the 3- and 4-carbon atoms. These deuterium results provide tentative evidence that the $[Cp^*Rh]^{2+}$ group migrates to the 3,4-C=C during the hydrogenation process and that apparently reversible C=N bond hydrogenation for **14** was negligible in contrast to results obtained for **1** (eq 9).



More importantly, thermal reaction of **15** at 80 °C in an NMR tube for 48 h in $CD_2Cl_2$ followed by $^1H$ NMR analysis showed a $[Cp^*Rh(\eta^1(N)\text{-pyridine})(CH_3CN)_2]^{2+}$ derivative ($Cp^*$ at 1.71 ppm) as compared to an authentically prepared sample. The pyridine ligand was liberated from the $[Cp^*Rh]^{2+}$ complex by addition of $CH_3CN$ and then quantified by GC/MS analysis (62%). This confirms the facile nature of the dehydrogenation reaction and is a graphic illustration of the reason that C–N bond cleavage for cyclic amines is not favored thermodynamically in comparison to rearomatization (eq 10).




(10)

## Discussion

Selective heteroaromatic ring hydrogenation is the first step in removal of the N, S, and presumably O heteroatoms from coal-derived products.[3-5] Our homogeneous hydrogenation results (Table I), with model coal compounds, **1–9**, show that six-membered mononuclear, N-ring compounds such as **1** are the least reactive in comparison to bi- and trinuclear N-ring compounds under our extremely mild reaction conditions. The five-membered ring binuclear S compounds, such as **4**, are slightly more reactive than similar N (**2**) and O (**3**) compounds; but again, they are dramatically slower than the bi- and trinuclear N-ring compounds. The bi- and trinuclear N-ring model coal compounds, **5–9**, show a trend where **8**, a trinuclear N-ring model, is far and above the most reactive compound studied and is 11 times faster than our standard, compound **5**, with an overall reactivity sequence of **8** >>> **9** > **5** > **7** > **6** > **4** ≫ **1–3**.

What is apparent is that the resonance stabilization energies for six-membered mononuclear, N-ring model coal compounds such as **1**, which are higher than for the bi- and trinuclear models, **5–9**, must be a barrier to N-ring hydrogenation.[1a] Consequently, initial N=C bond hydrogenation to disrupt the aromaticity in the six-membered N-ring is the most critical hydrogenation step in the overall reduction process. This step, the reduction of the N=C bond, is clearly reversible from our deuterium gas experiments. The second reduction step with six-membered mono- and polynuclear N-ring model coal compounds is C=C bond hydrogenation, which also appears reversible in **1**, **5**, **6**, and **8**.

Steric and electronic effects appear to mediate the initial rates of hydrogenation. For example, the differences in the initial rate ratio (Table I) of **5**/**6** of 2 must emanate from a predominating steric effect of the 2-methyl group in binding to the Rh metal center, since **6** ($pK_b$ = 8.03) is a stronger base than **5** ($pK_b$ = 9.52); in a competition experiment with **5** and **6** (Table II), the initial rate of **5** is reduced by a factor of 2.5 and that of **6** by a factor of 1.6, indicative of the influence of both steric and electronic effects. The basicity factor (binding to $[Cp^*Rh]^{2+}$) must also be prevalent in the other individual reduction reactions, where model compounds **2–4** are, for example, less basic than the six-membered nitrogen heterocyclic compounds and this is reflected in their slower initial rates of hydrogenation.

However, the dramatic rate enhancement for **8** alone and its role in enhancing the rate of hydrogenation of **5–7** has not been totally defined. The one possible explanation for this enhancement phenomena that we can invoke stems from catalytic transfer hydrogenation (deuterium gas) experiments, where 1,2-dihydro-(dideuterio)-7,8-benzoquinoline (**13a**) is proposed to shuttle hydrogen to **8** and, when present in other hydrogenation reactions, to **5–7**; compound **12**, 1,2,3,4-tetrahydroquinoline, has in fact been used as a hydrogen donor in coal liquefaction experiments.[9c] The catalytic transfer hydrogenation phenomena occurs in addition to selective ring hydrogenation and must involve an extremely complicated mechanism with the possibility that donor (**13a**) and acceptor (for example, **5**) are bonded to the same metal atom during hydrogen transfer.[9b] Since no other ring systems we studied showed this rate enhancement, we speculate that resonance stabilization energies that are similar or lower to that of **8** can accept hydrogen transfer, while those that have higher values cannot, i.e., thermodynamic control.

The competitive binding studies, where steric and electronic effects can be directly compared, were also very informative and showed, first using **5** as the competitor (Tables II), that the initial rates for all other model compounds were greatly reduced, while those for **5** were enhanced (**8**), not affected (**4**, **7**), or retarded (**1**, **6**, **9–11**). More importantly, the regioselective reduction product of **5**, compound **12** ($pK_b$ = 9.38), reduced the initial rate of **5** by a factor of 3; this clearly demonstrates the competitive binding power of the hydrogenation products with their model coal heteroaromatic analogues.[7b] The competitive binding studies with **8** as the competitor (Table III) also showed initial rate reductions for **8** with model compounds **1**, **2**, **4**, **6**, and **7**.

The deuterium gas studies in the Parr reactor and in HPNMR experiments were able to confirm that reversible reduction of N=C and C=C bonds in six-membered rings is universal, while C=C bonds in five-membered N, S, or O rings are considerably less likely to undergo reversible hydrogenation. The reason for this derives from the fact that the hydrogenated $CH_2$ positions in six-membered N rings are $\alpha$ to the N atom and are also allylic to C=C bonds. Thus, the reduced N=C bond, *NH—CH*$_2$C=C, is highly activated for metal-catalyzed dehydrogenation and, therefore, rearomatization of the N-heteroaromatic ring. In the absence of $H_2$ gas, dehydrogenation prevails as shown in eq 10 and, to reiterate, is the main reaction that occurs; no C–N bond cleavage is observed under these mild reaction conditions. Deuterium exchange is also observed in the aromatic ring (benzene) that is not reduced, particularly at the aromatic C–H positions $\beta$ to the heteroatom, and occurs only after the heteroaromatic ring is hydrogenated.

We can compare our deuterium results on the heteroaromatic nitrogen compounds with those obtained by Laine and co-workers with Os cluster complexes $H_2Os_3(CO)_{10}$ and $Os_3(CO)_{12}$.[6f,g] Laine et al. found with quinoline a very similar deuterium pattern in the 1,2,3,4-tetrahydroquinoline-*d* product as shown in eq 3, but with subtle differences. For example, they observe more deuterium in the 4-position and less in the 2-position then our results (eq 3). In addition, they also see small amounts of deuterium at the 4-position and one deuterium at the 2-position in the remaining quinoline, while we only see deuterium at the 2-position. As well, deuterium experiments with 1,2,3,4-tetrahydroquinoline and the Os cluster hydride gave a similar deuterium pattern in the aromatic ring (6- and 8-positions exchanged, eq 4), but they also saw small amounts of deuterium in the saturated nitrogen ring, where we see none. While differences in mechanistic interpretations are apparent for the Os cluster and mononuclear $[Cp^*Rh]^{2+}$ catalysts concerning pathways to the deuterium incorporation in the nitrogen ring, both metal complexes provide remarkably similar deuterium patterns.

As well, Laine et al. also compared their homogeneous Os cluster results to similar studies they performed with a heterogeneous HDN catalyst, CoMo, supported on alumina and presulfided.[6g] The deuterium incorporation studies for the CoMo catalyst, under similar reaction conditions, provided more deuterium in the 3- and 4-positions of the unreacted quinoline and more deuterium at the 3-position of 1,2,3,4-tetrahydroquinoline in comparison to the homogeneous Os cluster hydride. In addition, studies with 1,2,3,4-tetrahydroquinoline as the starting substrate showed only trace deuterium in the nitrogen ring and a similar deuterium pattern in the 6- and 8-positions of the aromatic ring as with the homogeneous results.

Laine et al. suggest that reversible N=C hydrogenation, as we propose for incorporation of ~2 deuteriums in the 2-position of 1,2,3,4-tetrahydroquinoline and 1 deuterium in the remaining quinoline, does not correlate with their results and rather they postulate that oxidative addition of the Os cluster to the C–H bonds in quinoline and 1,2- and 1,4-hydrogenation of quinoline provide a better rationale for their data. We suggest that differences in mechanistic pathways between an Os cluster hydride

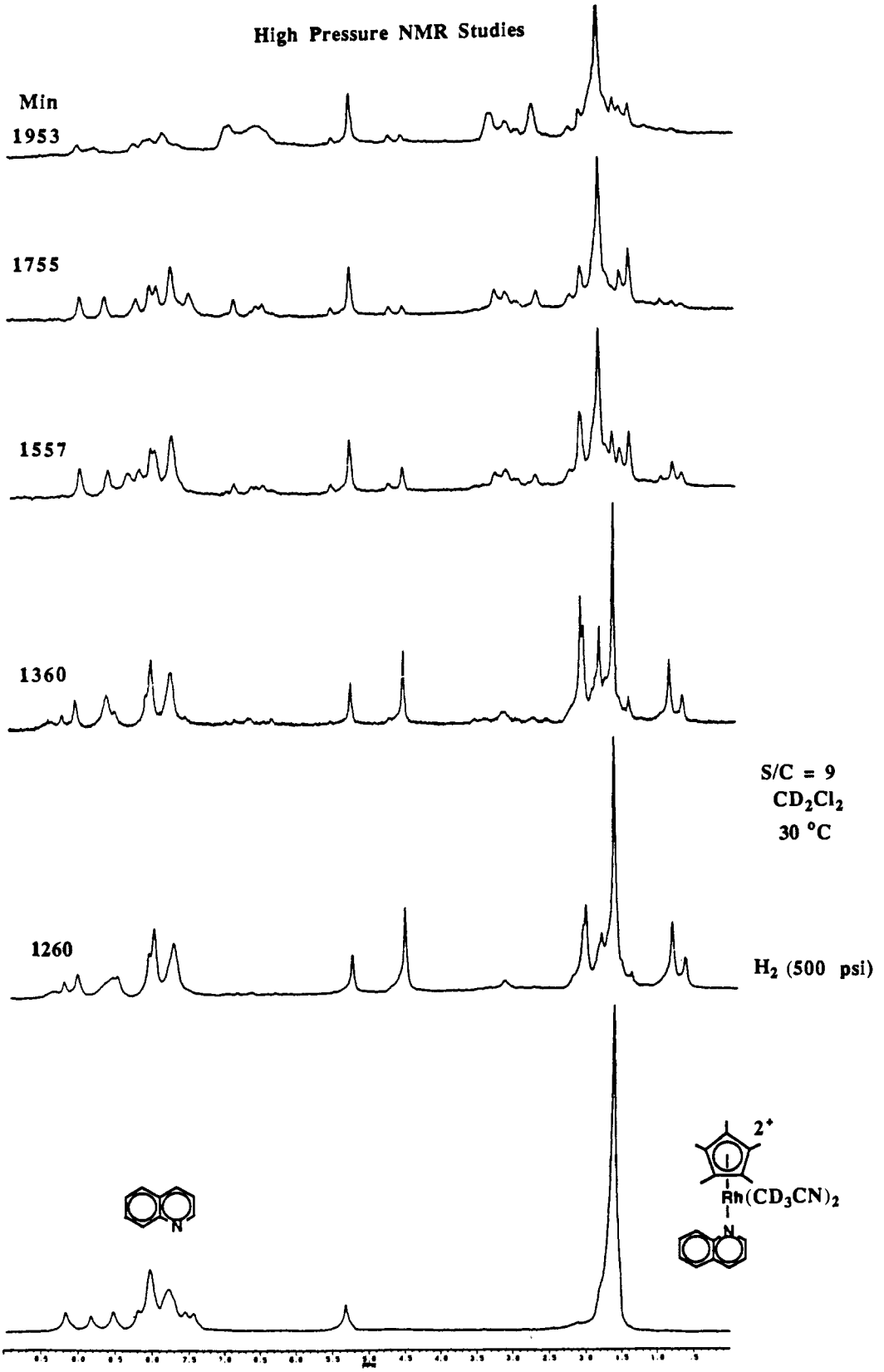
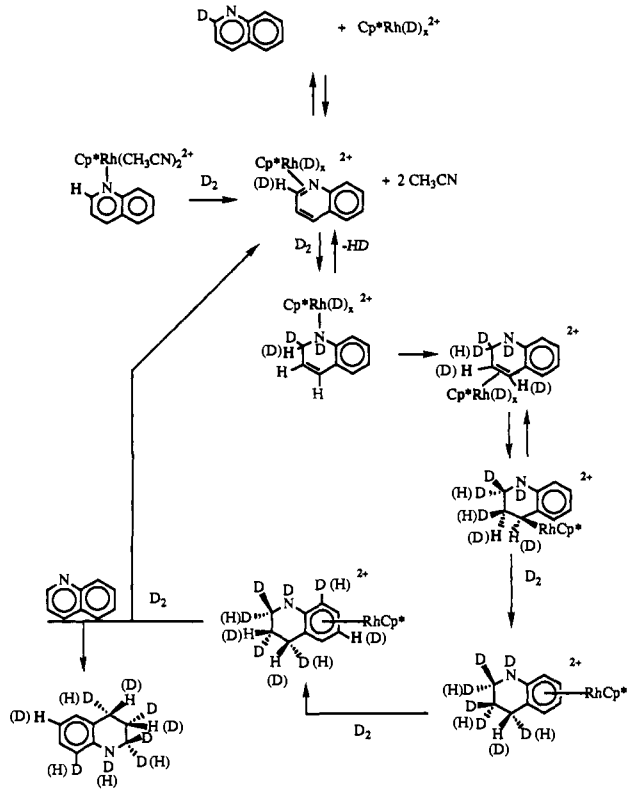



**Figure 2.** HPNMR studies of **5** with $[Cp^*Rh(CD_3CN)_3]^{2+}$ at 0–30 °C and 500 psi $H_2$ with a substrate/catalyst ratio of 9.

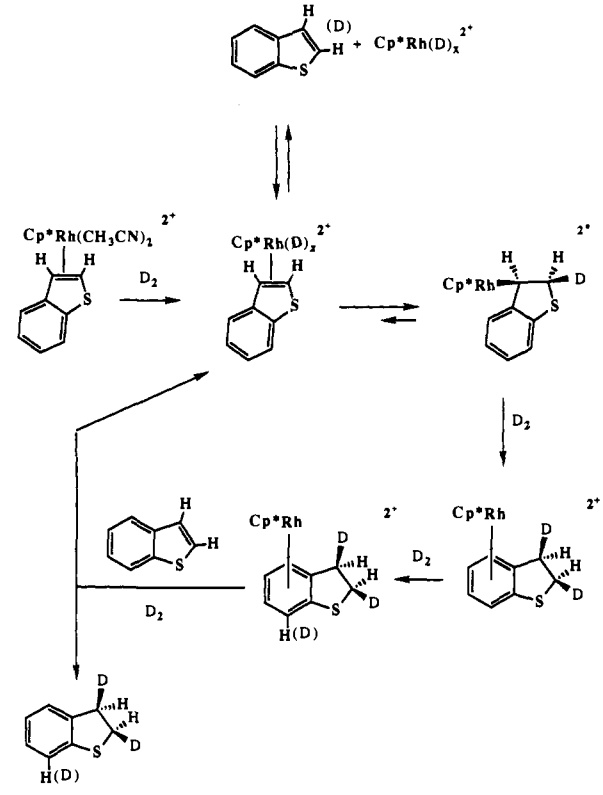
and a $[Cp^*Rh]^{2+}$ cationic complex for deuterium incorporation possibly exist due to cluster versus mononuclear metal bonding modes and temperature (145 °C [Os] versus 40 °C [Cp*Rh]) as well as steric and electronic requirements.

Nitrogen heteroaromatics were the real focus of our present studies, while compound **4**, benzothiophene, provided some intriguing bonding, stereochemical, and C–H exchange results. It is clear that $\eta^2$-bonding precedes selective cis hydrogenation of the 2,3-C=C bond and that there is slight reversibility in that step evidenced by the trace amounts of deuterium at the 2- and 3-positions in the remaining **4**. The aromatic C–H(7), $\beta$ to the sulfur, also appears to have a slight amount of deuterium. Angelici and co-workers studied the base-catalyzed ($OH^-/CH_3OD$) hydrogen for deuterium exchange of $[CpRu(\eta^6\text{-benzothiophene}]^+$

**Scheme I.** Postulated Mechanism for Selective Hydrogenation of Quinoline (**5**) to 1,2,3,4-Tetrahydroquinoline (**12**)



**Scheme II.** Postulated Mechanism for Selective Hydrogenation of Benzothiophene (**4**) to 1,2-Dihydrobenzothiophene



and found that the C–H(2) and the C–H(7) hydrogens were readily exchanged with the rate of C–H(2) > C–H(7);[12] this verifies that the aromatic C–H(7) is exchangeable under varying reaction conditions.

The overall results we described in this and other papers, i.e., bonding studies, deuterium gas experiments, and HPNMR studies, allow us to postulate an overall mechanism for the hydrogenation of six-membered N rings with the conversion of **5** to **12** as an example. Scheme I, for conversion of **5** to **12**, reveals the following logical sequence of events: (a) $\eta^1$, N-bonding of the N ligand to $[Cp^*Rh(CH_3CN)_3]^{2+}$, followed by the formation of a hydride with loss of complexed $CH_3CN$; (b) reversible 1,2-N=C bond reduction, which is a pathway to H(2) exchange on **5** and placing more than one deuterium at the 2-position of **12**; (c) migration of Cp*Rh from nitrogen to form an $\eta^2$-olefin complex; (d) reversible 3,4-C=C bond reduction; (e) Cp*Rh complexation to the aromatic ring followed by aromatic C–H exchange at the 6- and 8-positions; (f) formation of the $[Cp^*Rh(\eta^6$-1,2,3,4-tetrahydroquinoline$)]^{2+}$ complex followed by ligand exchange with **5** to continue the catalytic cycle.

The postulated mechanism for the five-membered ring N, O, and S compounds is as follows (Scheme II): (a) The five-membered ring N, O, and S compounds such as **2–4** may initially bind $[Cp^*Rh]^{2+}$ via the heteroatom but then rapidly rearrange to form the $\eta^2$-2,3-C=C bond complex.[8,11] (b) This is followed by selective cis hydrogenation of the 2,3-C=C bond (proven only in the case of compound **4**) with a small amount of reversibility evident. (c) The next step is formation of the $[Cp^*Rh(\eta^6$-dihydrobenzothiophene$)]^{2+}$ complex followed by a small amount of aromatic C–H ring exchange at position 7 in the benzo ring. (d) The final step is ligand exchange with **4**.

## Conclusions

In conclusion, we have found that five- and six-membered aromatic ring N compounds and five-membered aromatic ring S and O compounds can be regioselectively hydrogenated in the heteroaromatic ring under extremely mild conditions with $[Cp^*Rh(CH_3CN)_3]^{2+}$ as the catalyst precursor. Catalytic activity depends upon initial $\eta^1$, N-binding of N ligands and the role of two replaceable $CH_3CN$ ligands to the rhodium metal center for six-membered aromatic N-ring compounds and presumably $\eta^2$-bonding for **2–4**; ligand **4** was found to bind $\eta^6$ to $[Cp^*Rh]^{2+}$ under thermodynamic conditions[13] but $\eta^2$ with a $Cp^*Re(CO)_2(THF)$ complex.[8] Steric and electronic effects appear to be dominating factors controlling the relative rates of hydrogenation of ligands **1–9**.

The competitive binding, influenced by both steric and electronic effects, of the various N ligands to $[Cp^*Rh]^{2+}$ appears to be responsible for the differences in the initial rates of hydrogenation of **5**, while the interesting rate enhancement phenomena found for 7,8-benzoquinoline (**8**) in separate experiments and in a mixture with **5–7** can be explained to some extent by a catalytic transfer hydrogenation mechanism. We have also demonstrated the usefulness of the HPNMR technique in helping to verify mechanisms in complex catalytic hydrogenation reactions in real time.

The results presented in this study clearly define homogeneous metal catalysts as viable models for the first step in the heterogeneously catalyzed HDN reaction and for the role of nitrogen compounds as hydrogen donor solvents in coal liquefaction. The overall results also suggest that $[Cp^*Rh(CH_3CN)_3]^{2+}$ can be a highly efficient and selective, homogeneous hydrogenation catalyst precursor for many N, S, and O heteroaromatic compounds of interest in organic synthesis. In the future, we will focus on the second and third steps of the HDN reaction that involve C–N bond cleavage reactions (eq 1) with the hope that we can overcome the dehydrogenation reaction and find a soluble metal complex that will oxidatively add to C–N single bonds.

## Experimental Section

**Instrumentation and Materials.** $^1H$ and $^{13}C$ NMR spectroscopy were performed on a Bruker AM either 400- or 500-MHz instrument with deuterated solvents as internal locks and reference with respect to TMS.

(12) Huckett, S. C.; Angelici, R. J.; Ekman, M. E.; Schrader, G. L. *J. Catal.* **1988**, *113*, 36.

(13) Huckett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686.

The instruments are located in the Department of Chemistry, University of California, Berkeley, CA. The $^1$H HPNMR experiments at Exxon were performed on a Bruker 300-MHz instrument. The sapphire HPNMR tube was designed and constructed at Exxon; see ref 10b for the design of the titanium pressure head. All the Parr kinetic apparatus procedures were done under argon in a Vacuum Atmospheres glovebox equipped with a −30 °C freezer. The Parr kinetic apparatus was described elsewhere.[1c] Elemental analysis were performed by the microanalytical laboratory located in the Department of Chemistry, University of California, Berkeley, CA. Gas chromatographic analyses were performed on a Hewlett-Packard 5580A instrument with an FID detector and a 30 m ×0.25 mm J & W DB5 Carbowax capillary column, while GC/MS analyses were performed on a Hewlett-Packard 5971A MSD instrument in the EI mode with the same capillary column. 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. $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ was prepared according to the literature procedure.[14] The $^1$H and $^{13}$C NMR spectral analyses of deuterated products were assigned on the basis of their nondeuterated analogues.[1,12] The errors in measurement of the deuterium content of signals in the $^1$H NMR is ~5–10%. Verification of the presence of deuterium on carbon was found by $^{13}$C NMR spectral analysis of deuterated products.

**A Typical Rate Experiment Procedure.** To the 45-mL reactor cup of the Parr kinetic apparatus, inside a drybox, was added 26.7 mg (0.05 mmol) of $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ and 129.0 mg (1.0 mmol) of compound **5** (substrate to catalyst molar ratio 1.0:0.05) in 15 mL of $CH_2Cl_2$ along with a stirring bar. The reactor was brought outside of the drybox and connected to a hydrogen line. Then it was purged with hydrogen gas three times. The reactor was pressurized with hydrogen gas to 500 psi in a thermostated oil bath (40.0 °C). At regular intervals samples were removed for capillary gas chromatography analysis (0.25 mm × 30 m J & M DB5 capillary column. A plot of percent conversion (determined by digital integration of area of product and starting material) versus time (to ~30% conversion) gave a straight line, whose slope provided the initial rate of quinoline hydrogenation, 0.32%/min (least-squares regression analysis).[15] We have previously shown that the reactor cup, cleaned properly, does not act as a catalyst for the observed hydrogenation reactions.[1]

**A Typical Competition Experiment Procedure.** To the 45-mL reactor cup, inside the drybox, was added 129.0 mg (1.0 mmol) of compound **5**, 179 mg (1.0 mmol) compound **8**, and 26.7 mg (0.05 mmol) of $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ (substrates to catalyst molar ratio 1.0:1.0:0.05) in 15 mL of $CH_2Cl_2$ along with a stirring bar. The reactor was brought outside of the drybox and connected to a hydrogen line and purged with hydrogen gas three times. The reactor was pressurized with hydrogen gas to 500 psi in a thermostated oil bath (40.0 °C). At regular intervals samples were removed for capillary gas chromatography analysis (0.25 mm × 30 m J & W DB5 capillary column). Plots of percent conversion versus time (to ~30% conversion) gave straight lines, whose slopes provided the initial rate of quinoline hydrogenation, 2.56%/min (least-squares regression analysis), and that of **8**, 0.66%/min (least-squares regression analysis).

**Hydrogenation of 2-Methylpyridine (1) with $D_2$ Gas.** To a 45-mL reaction cup, inside of the drybox, was added 65.1 mg (0.70 mmol) of 2-methylpyridine and 26.7 mg (0.05 mmol) of $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ in 15 mL of $CH_2Cl_2$. The reactor was sealed, brought out of the drybox, and pressurized to 400 psi of $D_2$ at 40.0 °C for 11 days (54% conversion). The reaction mixture was filtered through Celite to remove the catalyst and then the solvent was removed via distillation to give a solid. This solid was a mixture of the desired 2-methylpiperidine-*d* hydrochloride, presumably from the presence of HCl generated from the solvent, and the hydrochloride of the starting material, 2-methylpyridine. The solid, 260 mg, was dissolved in 2 mL of aqueous NaOH and the aqueous layer extracted thrice with diethyl ether (15 mL). The ether layer was dried over anhydrous $MgSO_4$ and the ether removed by distillation. The 2-methylpiperidine-*d* was purified by a dry column technique using silica gel. Elution with pentane (no compounds detected by GC analysis), pentane/ether (1:1, 2-methylpyridine-*d*) and finally 100% diethyl ether provided pure 2-methylpiperidine-$d_9$ by GC/MS analysis ($m/z$ 100–109, $d_1$–$d_9$). $^1$H NMR (400 MHz, $CD_2Cl_2$, −50 °C, ppm) analysis with decoupling experiments to assign $H_{axial}/H_{equatorial}$ positions provided the following data: $CH_3$, 0.91 (d, $J$ = 6 Hz, 2 H, 1 d); $H(2_{ax})$, 2.43 (m, $J$ = 30 Hz, half-bandwidth, 0.9 d; $H(3_{ax})$, 1.47 (t of d, $J$ = 12, 3 Hz, 1 H, 1 d); $H(3_{eq})$, 1.64 (m, 0.2 d); $H(4_{ax})$, 0.91 (buried under the $CH_3$ group); $H(4_{eq})$, 1.23 (buried under $H(5_{ax})$); $H(5_{ax})$, 1.23 (t, $J$ = 9 Hz, 1.6 H, 0.4 d); $H(5_{eq})$, 1.47 (buried under $H(3_{ax})$); $H(6_{ax})$, 2.49 (t of d, $J$ = 12, 3 Hz, 0.9 d); $H(6_{eq})$, 2.89 (d of d, $J$ = 12, 3 Hz, 0.9 d).

**Hydrogenation of Quinoline (5) with $D_2$ Gas.** To a 45-mL reaction cup, inside of the drybox, was added 130.0 mg (1.0 mmol) of quinoline and 26.7 mg (0.05 mmol) of $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ to 15 mL of $CH_2Cl_2$. The reactor was sealed, brought out of the drybox, and pressurized to 500 psi of $D_2$ at 40.0 °C for 4.5 h (50% conversion by GC analysis). Then the solution was filtered using a Florisil column (0.2 × 0.5 cm); the solvent was removed under vacuum. $^1$H NMR spectrum of a sample of the resulting oil reveals total H/D exchange at the H(2) position in quinoline (GC/MS data, $m/z$ 130). Then the remaining sample of the oil was passed through a Florisil column (0.2 × 4 cm). The deuterated product, **12**-*d*, was eluted from the column using 90% pentane/10% diethyl ether as solvents. Then the solvent was removed under vacuum and **12**-*d* was analyzed by $^1$H and $^{13}$C NMR. $^1$H NMR (ppm): H(8), 6.40 (0.05 H); H(6), 6.51 (0.10 H); H(7, 5), 6.82 (2 H); H(2) 3.25 (0.5 H); 2.72 (1.0 H); H(3), 1.89 (0.95 H). $^{13}$C NMR (ppm): C(8), 113.5 (t, $J$ = 23.3 Hz); C(6), 116.4 (t, $J$ = 23.3 Hz); C(7), 128.0 (s); C(5), 129.4 (s); bridgehead carbons, 121.3 and 145.2. The product was also analyzed by GC/MS to show **12**-$d_{1-5}$ ($m/z$ 134–138).

**Isolation of $[Cp^*Rh(\eta^6$-1,2,3,4-tetrahydroquinoline$)]^{2+}$ from the Deuterium Gas Experiment with Quinoline.** To isolate the $[Cp^*Rh(\eta^6$-1,2,3,4-tetrahydroquinoline-$d_5)]^{2+}$ complex for $^1$H NMR analysis from the previous experiment, the 1,2,3,4-tetrahydroquinoline-$d_5$ was dissolved in 1 mL of $CH_2Cl_2$ and then 53.5 mg (0.1 mmol) of $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ was added. After 30 min, a yellow precipitate was formed. The solution was decanted and the precipitate was vacuum dried. $^1$H NMR of $[Cp^*Rh(\eta^6$-1,2,3,4-tetrahydroquinoline-$d_5)]^{2+}$ in $CD_3NO_2$ (ppm): NH, 7.18 (br s); H(7), 6.84 (s); H(5), 6.80 (s); H(6), 6.72 (t, $J$ = 5.86 Hz); H(8), 6.44 (d, $J$ = 6.99 Hz); $H(2_{eq})$, 3.65 (m); $H(2_{ax})$, 3.55 (m); $H(4_{eq})$, 2.66 (m); $H(4_{ax})$, 2.66; signals for $H(3_{ax})$ and $H(3_{eq})$ are masked by the Cp* signal at 2.12 (s). See text for analysis.

**Aromatic C–H Bond Exchange with 1,2,3,4-Tetrahydroquinoline (12) and $D_2$ Gas.** Inside a drybox, 133.0 mg (1.0 mmol) of 1,2,3,4-tetrahydroquinoline was added to a solution of 15 mL of $CH_2Cl_2$ containing 26.7 mg (0.05 mmol) of $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ in a 45-mL reaction cup. The reactor was sealed, brought out of the drybox and pressurized to 500 psi of $D_2$ at 40.0 °C for 4.5 h. The solution was filtered by using Florisil (0.2 × 0.5 cm). The solvent was removed under vacuum and the resulting oil, compound **12**, was analyzed by NMR. $^1$H NMR ($C_2D_4Cl_2$, 500 MHz, ppm): H(7, 5), 6.82 (2 H, s); H(6), 6.55 (0.3 d, t, $J$ = 0.64 Hz); H(8), 6.44 (0.72 d, d, $J$ = 6.90 Hz); H(2), 3.24 (2 H, t, $J$ = 5.37 Hz); H(4), 2.70 (2 H, $J$ = 6.37 Hz); H(3), 1.95 (2 H, quintet, $J$ = 6.22 Hz). $^{13}$C NMR ($C_2D_4Cl_2$, 500 MHz, ppm): C(2), 42.27 (s); C(4), 27.34 (s); C(3), 22.59 (s), C(8), 114.25 (s and t, $J$ = 23.33 Hz); C(6), 116.91 (s and t, $J$ = 23.33 Hz); C(7), 126.69 (s); C(5), 129.69 (s); bridgehead carbon, 145.36 and 121.66.

**Hydrogenation of 2-Methylquinoline (6) with $D_2$ Gas.** To 144.0 mg (1.0 mmol) of 2-methylquinoline and 26.6 mg (0.05 mmol) of $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ was added 15 mL of $CH_2Cl_2$ and then the reactor was pressurized with $D_2$ to 400 psi for 48 h at 70 °C (~100% reduction). To this solution was added 5 mL of diethyl ether and a yellow precipitate formed. The solution was decanted and the precipitate was vacuum dried. The $^1$H NMR spectrum in $CD_3NO_2$ shows an organometallic complex with the Cp* ring deuterated (area ~1.16 H's). The deuterated 1,2,3,4-tetrahydro-2-methylquinoline-*d* was removed from the Cp*Rh complex by dissolving in acetonitrile. Then the solvent was removed and the $^1$H and $^{13}$C NMR were recorded. $^1$H NMR ($CDCl_3$, 400 MHz, ppm): H(7), 6.67 (1 H, d, $J$ = 6.70 Hz); H(5), 6.64 (1 H, t, $J$ = 6.67 Hz); H(6), 6.54 (1 H, t, $J$ = 6.06 Hz); H(8), 6.22 (0.70 H, $J$ = 5.51 Hz); H(4), 2.78 (1 H, m); H(3), 1.91 (0.95 H, m); $CH_3$, 1.16 (1.86 H, br s). $^{13}$C NMR ($CDCl_3$, 400 MHz), $CH_3$, 22.53 (m); C(3), 26.42 (m); C(4), 29.65 (m); C(2), 47.00 (m); C(8), 113.92 (s), C(6), 116.86 (s); (C5), 126.62 (s); C(7), 129.20 (s); bridgehead carbons, 120.95 (s) and 144.75 (s).

In another procedure, 143 mg (1.0 mmol) of 2-methylquinoline and 26.7 mg (0.05 mmol) of $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ were dissolved in 15 mL of $CH_2Cl_2$, pressurized at 500 psi with $D_2$ at 40.0 °C for 16 h to provide ~89% of 1,2,3,4-tetrahydro-2-methylquinoline-*d*. GC/MS data indicate a range of $d_3$–$d_7$ compounds ($m/z$ 150–154), with $d_3$ ($m/z$ 150, 48%) and $d_4$ ($m/z$ 151, 17%) being the most abundant.

**Reduction of Benzothiophene (4) with $D_2$ Gas.** To 134.2 mg (1.0 mmol) of benzothiophene and 26.7 mg (0.05 mmol) of $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ was added 15 mL of $CH_2Cl_2$ and the reactor was

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(15) We found that the reaction mixtures were clear solutions with no evidence of a heterogeneous component. As a further test for homogeneity, we attempted to see if Hg metal had an effect on the initial rate of hydrogenation of **2**, but it appeared to react with $[Cp^*Rh(CH_3CN)_3]^{2+}$ prior to hydrogen addition (see: Anton, D. R.; Crabtree, R. *Organometallics* **1983**, *2*, 855).

pressurized with $D_2$ gas to 500 psi at 40.0 °C for 4 days (~65% reduction; GC/MS data for the remaining benzothiophene-*d*, *m/z* 134, $d_0$, 60%; *m/z* 135, 136, $d_1$, 18%, $d_2$, 22%; the product, 2,3-dihydrobenzothiophene-$d_3$, *m/z* 138, $d_2$, 85%; *m/z* 139, 140, $d_3$, 12%, $d_4$, 3%). Then, to this solution, 10 mL of *n*-hexane was added. The solution was filtered by using Celite and the solvent volume was reduced to 0.1 mL. Then it was passed through Florisil (solvent *n*-hexane/diethyl ether; 1:1). The 2,3-dihydrobenzothiophene-$d_3$ was isolated and the $^1H$ and $^{13}C$ NMR spectra were recorded. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): H(2), 3.32 (0.9 H, d, $J$ = 7.08 Hz); H(3), 3.22 (0.9 H, d, $J$ = 7.03 Hz); H(4, 7), 7.16 (1.95 H, d, $J$ = 7.77 Hz); H(5), 7.07 (1 H, t, $J$ = 7.30 Hz); H(6), 6.97 (1 H, t, $J$ = 7.14 Hz). $^{13}C$ NMR ($CD_2Cl_2$, 400 MHz): C(2), 37.56 (t, $J_{C-D}$ = 20.05 Hz); C(3), 34.65 (t, $J_{C-D}$ = 21.85 Hz); C(4), 128.99 (s); C(5), 126.19 (s); C(7), 125.79 (s); C(6), 123.67 (s). $^1H$ NMR of the unreacted benzothiophene ($CD_2Cl_2$, 400 MHz, ppm): 7.88 H(7) (1.0 H, d, $J$ = 7.08 Hz); H(4), 7.83 (1 H, d, $J$ = 6.91 Hz); H(2), 7.66 (0.9 H, d, $J$ = 7.48 Hz); H(3), 7.44 (0.9 H, d, $J$ = 7.48 Hz); H(5, 6) 7.33 (2 H, m).

**Preparation of [Cp*Rh($\eta^1$-1,2,5,6-tetrahydropyridine)$(CH_3CN)_2$]$(BF_4)_2$ (15).** To 12.1 mg (0.14 mmol) of 1,2,5,6-tetrahydropyridine (**14**) was added 53.5 mg (0.10 mmol) of [Cp*Rh$(CH_3CN)_3$]$(BF_4)_2$ dissolved in 5 mL of $CH_2Cl_2$. After 5 min, the solution was cooled to −30 °C and enough diethyl ether was added to turn the solution cloudy (~2 mL). The precipitate was vacuum dried, and $^1H$ NMR indicates complete conversion to the tetrahydropyridine complex. Small yellow crystals came out after 6 days but were not suitable for single-crystal X-ray analysis. NMR analysis for **15**. $^1H$ NMR (400 MHz, $CD_2Cl_2$); 5.98 (m, 1 H); 5.75 (m, 1 H); 5.12 (m, 2 H); 3.79 (t, $J$ = 6.1 Hz, 4 H); 2.45 (s, 6 H); 2.02 (s, 15 H). $^{13}C$ NMR (400 MHz, $CD_2Cl_2$): $CH_3CN$, 5.20 (s); $(CH_3)_5$, 9.04 (s); $NCH_2$, 21.87 (s); $4CH_2C{=}C$, 42.54 (s); $4CH_2C{=}C$, 43.34 (s); C(5), 98.02 (d, $J$ = 8.5 Hz); C=, 119.65 (s); C=, 126.03 (s). Due to compound instability, satisfactory analytical data could not be obtained for complex **15**. The $^1H$ and $^{13}C$ NMR spectra of **14**, for comparison to **15**, are as follows. $^1H$ NMR (400 MHz, $CD_2Cl_2$): 5.71 (m, 1 H); 5.66 (m, 1 H); 3.22 (m, 2 H); 2.85 (m, 2 H); 1.97 (m, 2 H). $^{13}C$ NMR (400 MHz, $CD_2Cl_2$); $NCH_2$, 26.08 (s); $CH_2C{=}C$, 43.21 (s); $CH_2C{=}C$, 45.12 (s); C=, 125.80 (s); C=, 127.40 (s).

**Thermal reaction of [Cp*Rh($\eta^1$-1,2,5,6-tetrahydropyridine)$(CH_3CN)_2$]$^{2+}$ (15).** [Cp*Rh($\eta^1$-1,2,5,6-tetrahydropyridine)$(CH_3CN)_2$]$(BF_4)$ (**15**) (6.0 mg, 0.12 mmol) was dissolved in 0.6 mL of $CD_2Cl_2$ in a 5-mm NMR tube. The NMR tube was then sealed and heated to 80 °C. After 48 h, new resonances at 8.65, 8.19, and 7.8 ppm for the pyridine ring signals and 1.71 ppm for Cp* appeared in the $^1H$ NMR. The resonances correspond to coordinated pyridine of the known [Cp*Rh($\eta^1$-pyridine)$(CH_3CN)_2$]$^{2+}$ complex prepared as follows: 56 mg (0.104 mmol) of [Cp*Rh$(CH_3CN)_3$]$(BF_4)_2$ and 10 μL of pyridine (0.1 mmol) were reacted for 20 min. The reaction mixture was vacuum dried and then washed thrice with 5 mL of diethyl ether. $^1H$ NMR ($CD_2Cl_2$, 400 MHz, ppm) of this unstable compound provided H(2, 6), 8.79; H(4), 8.04; H(3, 5), 7.74; $CH_3CN$, 2.54; and Cp*, 1.71. GC/MS analysis, after addition of $CH_3CN$ to release the pyridine ligand from the above-mentioned complex, confirms the presence of free pyridine (~62%). In another procedure, 6.0 mg (0.12 mmol) of the complex was dissolved in 0.6 mL of acetone-$d_6$ and heated to 40 °C for 16 h. $^1H$ NMR indicates formation of complexed pyridine, [Cp*Rh($\eta^1$-pyridine)$(CH_3CN)_2$]$^{2+}$ (Cp*, 1.71 ppm). After addition of $CH_3CN$ to release the pyridine ligand, GC/MS showed a conversion to pyridine of 36%.

**Reaction of 1,2,5,6-Tetrahydropyridine (14) with $D_2$ Gas.** To 28.0 mg (0.33 mmol) of 1,2,5,6-tetrahydropyridine dissolved in 2.0 mL of $CD_2Cl_2$ inside of a reactor cup was added 53.5 mg (0.1 mmol) of [Cp*Rh$(CH_3CN)_3$]$(BF_4)_2$. After 20 h, the deuteration is complete as shown by $^1H$ NMR spectroscopy. GC/MS data show predominantly piperidine-$d_2$ (*m/z* 86) and only traces of $d_3$ (*m/z* 87). Room temperature $^{13}C$ NMR of the crude reaction product shows H–D coupling on the Cp* methyl groups of the catalyst at 9.46 ppm, indicating H/D exchange. Also, the Cp* carbons show coupling with the Rh atom (93.82 ppm, $J$ = 8.39 Hz). Then 1 mL of the sample was filtered through Florisil (0.2 × 0.5 cm) into a NMR tube to remove the catalyst. The low-temperature $^{13}C$ NMR was recorded at −70 °C (400 MHz, $CD_2Cl_2$) to show a broad intense singlet at 43.82 ppm for C(2) and C(6); the signals for C(3), C(4), and C(5) are overlapping triplets at ~22 ppm, which indicates that there is deuterium incorporation at these positions.

**Catalytic Transfer Hydrogenation Reaction of 1,2,3,4-Tetrahydro-7,8-benzoquinoline-*d* with Quinoline.** The 179 mg (1.0 mmol) of 7,8-benzoquinoline was deuterated to 1,2,3,4-tetrahydro-7,8-benzoquinoline-$d_4$ by using 26.7 mg (0.05 mmol) of [Cp*Rh$(CH_3CN)_3$]$(BF_4)_2$ at 40.0 °C and 500 psi of $D_2$ for 1 h in 15 mL of $CH_2Cl_2$. GC analysis shows 100% 1,2,3,4-tetrahydro-7,8-benzoquinoline, while GC/MS analysis shows $d_3$, *m/z* 186, and $d_4$, *m/z* 187. Isolation and $^1H$ NMR (400 MHz, $CD_2Cl_2$, ppm) analysis shows deuterium at C(3), 1.98 (1.5 d); C(4), 2.88 (1.5 d); and C(2), 3.44 (1.6 d). Then 129.0 mg (1.0 mmol) of quinoline was added to the 15 mL of methylene chloride, and the mixture was stirred for 24 h. GC analysis shows 9% of quinoline has been deuterated with *m/z* 135 for $d_3$, 136 for $d_4$. The remaining 91% quinoline at *m/z* 130 has ~40% $d_1$, and 26.6% of the 1,2,3,4-tetrahydro-7,8-benzoquinoline-$d_4$ was dehydrogenated and formed 7,8-benzoquinoline-*d*.

**Catalytic Transfer Hydrogenation Reaction of 1,2,3,4-Tetrahydro-7,8-Benzoquinoline-$d_4$ and Quinoline in the Presence of $H_2$ Gas.** The 7,8-benzoquinoline (**8**) (179 mg, 1.0 mmol) was deuterated at 40.0 °C and 500 psi of $D_2$ for 1 h by using 26.7 mg (0.05 mmol) of [Cp*Rh$(CH_3CN)_3$]$(BF_4)_2$ to provide 1,2,3,4-tetrahydro-7,8-benzoquinoline-$d_4$. The reaction mixture was filtered through Florisil (0.2 × 1.0 cm), vacuum dried, and analyzed by $^1H$ NMR ($CD_2Cl_2$) to show 100% conversion. Then, 129.0 mg (1.0 mmol) of quinoline, 26.7 mg (.05 mmol) of [Cp*Rh$(CH_3CN)_3$]$(BF_4)_2$, and 1.0 mmol of 1,2,3,4-tetrahydro-7,8-benzoquinoline-$d_4$ were dissolved in 15 mL of $CH_2Cl_2$ and pressurized to 500 psi with $H_2$ for 4 h. GC/MS analysis showed *m/z* 134–136 for **12**-$d_{1-3}$. After GC/MS analysis, the solvent volume was reduced to 5 mL, 15 mL of *n*-pentane was added, and the solution was filtered using Celite and vacuum dried. The $^1H$ NMR ($CD_2Cl_2$) was recorded to provide conversion to **12**-$d_{1-3}$ with broad signals at 1.91 (C(3)), 2.8 (C(4)), and 3.3 (C(2)) ppm, showing deuterium incorporation.

**High-Pressure NMR Experiments with Quinoline (5).**[10b] In an $N_2$-filled Vacuum Atmospheres glovebox was added, into a 10-mm sapphire NMR tube with a titanium pressure head, 60 mg (0.11 mmol) of [Cp*Rh$(CH_3CN)_3$]$(BF_4)_2$ and 160 mg (1.54 mmol) of quinoline dissolved in 2.5 mL of $CD_2Cl_2$. After recording the $^1H$ NMR (300 MHz) spectrum at 30 °C for formation of [Cp*Rh($\eta^1$(N)-quinoline)$(CH_3CN)_2$]$(BF_4)_2$, the tube was pressurized with 500 psi of $D_2$ gas and the spectra were recorded at various time intervals (Figure 1). The 0–30 °C HPNMR experiment (Figure 2) to ascertain what occurs between 0 and 21 min in the previous experiment (Figure 1) was accomplished with 84 mg of [Cp$(Rh(CD_3CN)_3]$$(BF_4)_2$ and 16 μL of quinoline in 2.5 mL of $CD_2Cl_2$. See the text for details of the hydride experiment.

**High-Pressure NMR Experiments with [Cp*Rh($\eta^6$-1,2,3,4-tetrahydroquinoline)]$^{2+}$.** The aromatic ring hydrogen exchange experiment was accomplished with 110 mg of [Cp*Rh($\eta^6$-1,2,3,4-tetrahydroquinoline)]$^{2+}$ in 3.0 mL of $(CD_3)_2CO$. The 10-mm sapphire NMR tube was then pressurized with 500 psi of $D_2$. The reaction was monitored by $^1H$ NMR (300 MHz) for 20 h without changes in the aromatic region.

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