comparison with the metal ion–benzene complexes is not yet possible.

Hettich et al. measured a bond strength of 57 kcal/mol for the $C_6H_6V^+$–C_6H_6 bond.[13] By analogy, the lower limit of 23 kcal/mol on the binding energy of the $M^+(TBC)_2$ complexes of the early-transition-metal ions is not at all surprising. What is striking is the low bond strengths of the $M^+(TBC)_2$ complexes of Cu, Ni, and Co, which are much weaker than any of the organometallic complexes reported by Hettich et al.

It may be suggestive to relate the drop-off in $M^+(TBC)_2$ complex formation, and the apparent associated drop-off in binding energy of the second ligand, to the valence electron count around the metal center. The $Fe^+(TBC)_2$ complex, which appears to lie at the dividing line between efficient and inefficient complex formation, has a 19-electron valence count. The inefficiently formed $M^+(TBC)_2$ complexes of Co^+, Ni^+, and Cu^+ exceed an 18-valence-electron count by two or more. The exception to this trend is $Ag^+(TBC)_2$, which has a formal electron count of 22.[8]

The inefficient formation of $M^+(TBC)_2$ by Co^+, Ni^+, and Cu^+ may stem from size factors rather than electron count. It is possible that the $M^+(TBC)$ complexes of Co^+, Ni^+, and Cu^+ have the metal in the pocket, whereas the other larger first-row M^+ ions and Ag^+ adopt an open-face sandwich structure. A metal encapsulated in the TBC ligand would be less likely to bind another large ligand such as TBC.

The ICR technique provides no direct structural information about the complexes. However, the ready formation and substantial bonding energy of the $M^+(TBC)$ complexes of Co^+, Ni^+, and Cu^+ and the ready formation of the $Ag^+(TBC)_2$ complex are features of the present results which are consistent with what we have observed in solution and the solid state. This is encouraging to the idea that gas-phase results may have predictive value for the formation of mononuclear compounds with other metal systems in the condensed phase.

It will be interesting to observe both the radiative association reactions of metallocyclyne ions with other ligands, as in

$$M^+(TBC) + L \rightarrow M^+(TBC)L$$

and also possible ligand displacement reactions such as

$$M^+(TBC)_2 + L \rightarrow M^+(TBC)L + TBC$$

which should clarify further the binding patterns and bond strengths of gas-phase metallocyclyne complexes and their interactions with small molecules of interest in catalytic chemistry, such as CO, CO_2, CH_4, and CH_3OH.

Acknowledgment. This work was supported in part by the National Science Foundation, by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Edison Sensor Technology Center at CWRU. We thank BP America for use of the FT-ICR instrument.

Homogeneous Catalytic Hydrogenation. 5. Regioselective Reductions of Mono- and Polynuclear Heteroaromatic Model Coal Compounds Using the (η^5-Pentamethylcyclopentadienyl)rhodium Tris(acetonitrile) Dication as the Catalyst Precursor[1]

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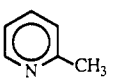
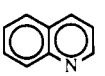
Summary: The regioselective hydrogenation of representative mono- and polynuclear heteroaromatic nitrogen and sulfur model coal compounds such as 2-methylpyridine (**1**), quinoline (**2**), 2-methylquinoline (**3**), 5,6- and 7,8-benzoquinolines (**4** and **5**), acridine (**6**), and benzothiophene (**7**) was studied with the dicationic complex (η^5-pentamethylcyclopentadienyl)rhodium tris(acetonitrile) ($Cp^*Rh(CH_3CN)_3^{2+}$) as the catalyst precursor. The order of relative rates as a function of structure was found to be **5** >>> **6** > **2** > **4** > **3** > **7** >> **1**. Replacement of H_2 with D_2 provided information on several of the mechanistic aspects of these selective hydrogenation reactions with compounds **2** and **7** as examples.

Several years ago, we discovered that a variety of rhodium and ruthenium complexes were catalysts for the regioselective hydrogenation of polynuclear heteroaromatic nitrogen model coal compounds, this being the first step in the highly important hydrodenitrogenation reaction.[1]

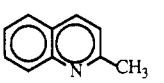
Chart I



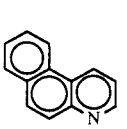
2-methylpyridine, 1



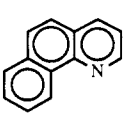
quinoline, 2



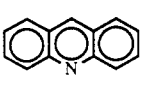
2-methylquinoline, 3



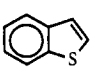
5,6-benzoquinoline, 4



7,8-benzoquinoline, 5



acridine, 6



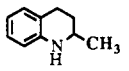
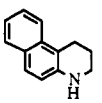
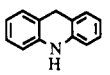
benzothiophene, 7

(1) For previous papers in this series see: (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.

(2) DOE Teacher Research Associate, June–August 1990.

0276-7333/91/2310-0054$02.50/0

Table I. Regioselective Hydrogenation of Heteroaromatic Nitrogen and Sulfur 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		0.32	1.0[c]	4
3		0.15	0.47	2
4		0.23	0.72	3
5		3.5	11	20[d]
6		0.41	1.28	5
7		0.06	0.19	1

[a] Conditions: solvent CH_2Cl_2; substrate:catalyst ratio 20; temperature 40 °C; pressure 500 psi of H_2. 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.

Other workers have also verified these results with several homogeneous Fe, Mn, Rh, Os, Ru, and Ir systems under a similar variety of reaction conditions.[3] More recently, we have been able to ascertain with a (η^5-pentamethylcyclopentadienyl)rhodium dicationic complex, $Cp^*Rh(CH_3CN)_3^{2+}$, that initial η^1(N) bonding of the nitrogen (N) ligand to the organorhodium metal center was critical for N ring reduction.[4] However, it was also necessary that the previously mentioned η^1(N)-bonded complexes have the formula $Cp^*Rh(\eta^1,N)(CH_3CN)_2^{2+}$ to be catalytically active; i.e., two replaceable CH_3CN ligands were found to be necessary for catalysis to proceed.[4,5]

In this communication, we present our preliminary results on the relative rates of hydrogenation as a function of ligand structure (compounds 1–7, Chart I) with $Cp^*Rh(CH_3CN)_3^{2+}$ as the catalyst precursor and steric and electronic effects apparently being important factors. These results also include a rare example of a homogeneous catalytic hydrogenation of a pyridine derivative (1) and, furthermore, shows the effect of ligand structure (1, 3–7) on the initial rate of quinoline (2) hydrogenation in competitive experiments. Several mechanistic pathways for these selective reductions are also presented that are derived from deuterium gas experiments (D_2).

The initial and relative rates (quinoline (2) designated as having a relative rate of 1.0) as well as the number of turnovers in the hydrogenation reactions of ligands 1–7 (Chart I) are shown in Table I with $Cp^*Rh(CH_3CN)_3^{2+}$ as the catalyst precursor.[6] The order of relative rates as a function of ligand structure was found to be **5** >>> **6** > **2** > **4** > **3** > **7** >> **1**. What is striking in Table I is that compound **5** is 11 times faster than **2** and 15 times faster than its 5,6-isomer **4**, while compound **3** has a relative rate that is 2 times slower than that of **2**. In the case of ligand **1**, it is interesting 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 **2** and 15 times slower than **3**.[7,8]

Thus, it is apparent that steric and electronic effects control the hydrogenation rates. The consequence of the 2-methyl group is shown by comparing **2** and **3**; the steric effect of the 2-methyl group in **3** lowers the relative rate by a factor of 2. The higher resonance stabilization energy of the nitrogen ring for **1** over that of **3** could be one reason that **1** is 15 times slower than **3**. Moreover, ligand **6** is 1.3 times faster than **2**, with the stipulation that it only takes 1 mol of H_2 to hydrogenate **6** and 2 mol for **2**. The only sulfur heteroaromatic compound studied for comparison, **7**, was found to be 5 times slower than **2**. The reason for the dramatic hydrogenation rate enhancement for ligand **5** over all the compounds studied was not entirely clear but could possibly emanate from a steric acceleration effect, with the 8-hydrogen being involved or some electronic effect.

In order to establish what effect each of the ligands had on the initial rate of hydrogenation of **2**, a series of competitive reactions (1:1 molar ratio) were carried out.[9] The results show that neither ligand **4** nor **7** affects the initial rate of hydrogenation of **2**, while **1** or **3** decreases the rate by a factor of 2–2.5. To our surprise, **5** dramatically increased the initial rate of **2** by a factor of 8, while **6** totally inhibited the initial rate (a similar total inhibition was observed with pyridine and isoquinoline). It was also determined that the regioselective reduction product of **2**, 1,2,3,4-tetrahydroquinoline, decreased the initial rate by a factor of 3; the product can also compete for the rhodium metal center.

We also found that the rate enhancement produced by **5** in the hydrogenation of **2** was concentration-dependent; i.e., as the molar concentration of **5**:**2** was varied from 0.5:1

(3) (a) Jardine, I.; McQuillin, F. J. *J. Chem. Soc. D* **1970**, 626. (b) Derencsenyl, T. T.; Vermeulen, T. *Chem. Abstr.* **1980**, *93*, 188929; 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.

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

(5) Fish, R. H.; Baralt, E.; Kim, H.-S. Submitted for publication.

(6) A typical hydrogenation procedure is as follows: The Parr kinetic apparatus was described elsewhere.[1c] To the 45-mL reactor cup, inside a Vacuum Atmospheres glovebox, 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 **2** (substrate to catalyst molar ratio 1.0:0.05 or 20:1) in 15 mL of CH_2Cl_2 along with a stirring bar. The reactor was brought outside of the drybox, 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 × 15 m J&W DB-5 capillary column). A plot of percent conversion vs time (to ~30% conversion) gave a straight line, whose slope provided the initial rate of quinoline hydrogenation, 0.32%/min (least-squares regression analysis).

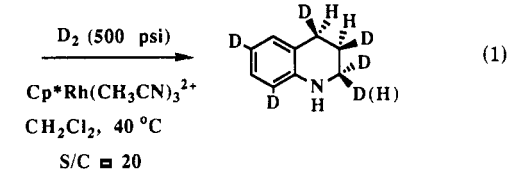
(7) Laine, R. M.; Thomas, D. W.; Cary, L. W. *J. Org. Chem.* **1979**, *44*, 4964.

(8) We also found that both pyridine and isoquinoline were not hydrogenated to any significant extent due to the formation of their $Cp^*Rh(\eta^1(N))_3^{2+}$ complexes (in situ), which are catalytically inactive. Also, we could not hydrogenate pyrrole; again, this is probably due to the in situ formation of $Cp^*Rh(\eta^5\text{-pyrrole})^{2+}$.

(9) A typical competition experiment was as follows: To the 45-mL reactor cup, inside a Vacuum Atmospheres glovebox, was added 26.7 mg (0.05 mmol) of $[Cp^*Rh(CH_3CN)_3][BF_4]_2$, 129.0 mg (1.0 mmol) of compound **2**, and 179 mg (1.0 mmol) of compound **5** (substrate to catalyst molar ratio 1.0:1.0:0.05 or 20:20:1) in 15 mL of CH_2Cl_2 along with a stirring bar. The reactor was brought outside of the drybox, 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 × 15 m J&W DB-5 capillary column). A plot of percent conversion vs time (to ~30% conversion) gave a straight line, whose slope provided the initial rate of quinoline hydrogenation, 2.56%/min (least-squares regression analysis).

to 1:1 there was a initial rate enhancement for **2** from a factor of 3 to that of 9, and even the hydrogenation product of **5**, 1,2,3,4-tetrahydro-7,8-benzoquinoline, enhanced the initial rate of **2** by a factor of 4 (1:1 molar ratio). Thus, **5** by itself is hydrogenated faster than **2** but then enhances the rate of hydrogenation of **2** in a mixture (only after all of **2** is hydrogenated is **5** reduced) and this result coincides with a previous result where we found that **2** binds to Cp^*Rh^{2+} in preference to **5**.[5] The origin of the initial rate increase of **2** by **5** is at this time not apparent.

Several mechanistic aspects of the selective hydrogenation reaction were obtained by the substitution of D_2 for H_2 with compounds **2** and **7** as examples.[1c] The results for **2** are depicted in eq 1. The deuterated 1,2,3,4-tetra-

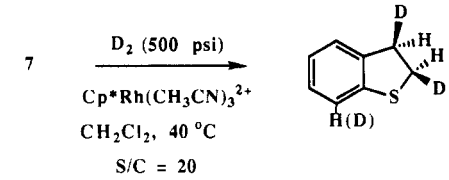


(1)

hydroquinoline (eq 1) 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 (^{13}C NMR was also performed to verify the deuterium position) 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. ^1H NMR analysis also showed a vicinal coupling for the 3,4-hydrogens of 7.6 Hz, consistent with cis stereochemistry. The remaining **2** was analyzed as well by GC–MS and NMR methods to show quinoline-2-*d*. The aromatic ring deuterium exchange chemistry was found to occur from Cp^*Rh^{2+}-catalyzed deuteration of 1,2,3,4-tetrahydroquinoline under conditions similar to those shown in eq 1; only positions 6 and 8 undergo exchange (NMR), while the saturated nitrogen ring contains no deuterium.

These deuterium gas results provide an overall view of the mechanism of hydrogenation of compound **2** and were surprisingly quite similar to those results we previously found with $(Ph_3P)_3RhCl$ as the catalyst precursor:[1c] (a) the 1,2-N=C bond was reversibly deuterated; (b) this was followed by cis deuteration of the 3,4-C=C double bond; (c) after this, aromatic ring H for D exchange at the 6- and 8-positions occurs.

The results for **7** are depicted in eq 2, and what is interesting is that it appears that initial η^2 or η^3 rather than any η^1(S) bonding is predominant (as opposed to initial η^1(N) bonding for the nitrogen ligands) and kinetically controls the stereoselective cis deuteration of the 2,3-C=C double bond, while the remaining **7** was found to have small amounts of deuterium in the 2- and 3-positions (~0.1 *d*). This latter result is indicative of some reversibility in the reduction of the 2,3-double bond. In addition, minor amounts of deuterium (~0.1 *d*) were found in the 7-position and exchange is thought to occur after the 2,3-C=C double bond is deuterated, this being similar to aromatic



(2)

C–H exchange with 1,2,3,4-tetrahydroquinoline.

It is important to note that several of the above-mentioned steps may also be pertinent in the selective hydrogenation of the other nitrogen model coal compounds studied, but differences did exist. For example, we found that the 2-methyl group for **3** was deuterated after nitrogen ring reduction, which implies a possible exchange of the methyl group hydrogens by a cyclometalation reaction. The intricate details of the role of Cp^*Rh^{2+} in each of the above-mentioned steps are presently being elucidated by high-pressure NMR experiments, and those details will be forthcoming.[10]

In conclusion, we have found that a variety of nitrogen heteroaromatic compounds and one sulfur compound can be regioselectively hydrogenated in the heteroaromatic ring under extremely mild conditions with $Cp^*Rh(CH_3CN)_3^{2+}$ as the catalyst precursor.[11] The importance of initial η^1(N) binding to the rhodium metal center (and presumably η^2 or η^3 bonding in a kinetic sense for **7**; ligand **7** was found to bind η^6 to Cp^*Rh^{2+} under thermodynamic conditions)[12] for catalytic activity was clearly demonstrated, as was the role of two replaceable CH_3CN ligands. Steric and electronic effects appear to be dominating factors controlling the relative rates of hydrogenation of ligands **1**–**7**. The competitive binding of the various N ligands to Cp^*Rh^{2+} appears to be responsible for the differences in the initial rates of hydrogenation of **2**, while the interesting rate enhancement phenomena found for 7,8-benzoquinoline (**5**), in separate experiments and in a mixture with **2**, cannot be readily explained at this time. We are continuing our studies in this fascinating area of homogeneous catalysis to further understand the mechanisms involved, but the present results suggest that $Cp^*Rh(CH_3CN)_3^{2+}$ can be a highly efficient and selective homogeneous hydrogenation catalyst precursor for many heteroaromatic compounds of interest in organic synthesis.

Acknowledgment. The catalysis studies at LBL were supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

(10) Fish, R. H.; Baralt, E.; Horvath, I. T. Manuscript in preparation.

(11) 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 reduction (see: Anton, D. R.; Crabtree, R. *Organometallics* **1983**, *2*, 855).

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