not show either *trans*-[Mo(≡CCH_2CMe_3)(CO){P(OMe)$_3$}$_2$(Cp)]$^{2+}$ or *trans*-[Mo(C=CHCMe_3)(OTf){P(OMe)$_3$}$_2$(Cp)] as intermediates, consistent with the view that decarbonylation of **9** occurs *before* the vinylidene ligand can rearrange to a η^2-alkyne. Carbon monoxide is labile in **9** because it must compete for metal π-electron density with the strongly π-acidic vinylidene ligand trans to it. Trapping of "[Mo(C=CHCMe_3){P(OMe)$_3$}$_2$(Cp)]$^+$" by triflate followed by a second protonation leads to **11**. In contrast, protonation of **8** with HOTf gives a stable vinylidene complex, *trans*-[Mo(C=CHCMe_3)(CO)(PMe_2Ph)$_2$(Cp)][OTf] (**10**). Tris(phosphite) alkynyl **12** is so basic that it was converted without isolation to its stable vinylidene cation [Mo(C=CHCMe_3){P(OMe)$_3$}$_3$(Cp)][BF_4] (**13**) by protonation on alumina (6% H_2O), followed by elution with CH_2Cl_2/MeOH.

Treatment of a CH_2Cl_2 solution of [Mo(HC≡$CCMe_3$)(PMe_2Ph)$_2$(Cp)][BF_4] (**6**) with 1 atm of CO at −78 °C, followed by warming to room temperature, transforms it into *trans*-[Mo(C=CHCMe_3)(CO)(PMe_2Ph)$_2$(Cp)][BF_4] (**10**). This is the first example of alkyne to vinylidene tautomerization on a d^4 metal center, starkly contrasting with the reverse transformation of vinylidene **9** into [Mo(HC≡$CCMe_3$){P(OMe)$_3$}$_2$(Cp)]$^+$ (**5**). This difference is attributed to varying electron density at molybdenum. In **5**, two weakly donating P(OMe)$_3$ ancillary ligands leave molybdenum electron-poor, so a η^2-alkyne ligand which is both a good σ- and π-donor is favored. In **10**, two strongly donating PMe_2Ph ligands create an electron-rich molybdenum, so CO and vinylidene ligands which are weak σ-donors but strong π-acceptors are favored. The stability of [Mo(C=CHCMe_3){P(OMe)$_3$}$_3$(Cp)][BF_4] (**13**) is similarly rationalized. The mild conditions for transformations **6** to **10** and **9** to **5** (Scheme II) suggest that the energy difference between η^2-alkyne and vinylidene tautomers must be small for divalent molybdenum. So far, only carbon monoxide promotes alkyne to vinylidene rearrangement. For example, excess P(OMe)$_3$ does *not* convert [Mo(HC≡$CCMe_3$){P(OMe)$_3$}$_2$(Cp)]$^+$ (**5**) into the stable vinylidene [Mo(C=CHCMe_3){P(OMe)$_3$}$_3$(Cp)]$^+$ (**13**). Perhaps both the σ-donor and π-acceptor abilities of CO are necessary to promote this rearrangement.

In closing, we have demonstrated that (1) deprotonation of coordinated alkynes provides a useful route to alkynyl complexes, (2) reprotonation of these alkynyls can lead to vinylidene, rather than alkyne, products, (3) electron density overwhelmingly determines the relative stability of η^2-alkyne versus vinylidene structures for d^4 molybdenum, and (4) tautomerization of a η^2-alkyne to a vinylidene ligand can be driven by the addition of carbon monoxide. Future reports will expand on these findings.

Acknowledgment. We thank the U.S. Department of Energy and the National Science Foundation (EPSCoR Program) for financial support.

Supplementary Material Available: Spectroscopic data for all new compounds and tables of positional and thermal parameters, bond distances, bond angles, and least-squares planes for the structure of **4** (12 pages); a listing observed and calculated structure factors for the structure of **4** (25 pages). Ordering information is given on any current masthead page.

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Studies on the Bonding of Polynuclear Heteroaromatic Nitrogen Ligands to (Pentamethylcyclopentadienyl)rhodium Dication: The Role of Nitrogen versus π-Complexation on the Regioselective Hydrogenation of the Nitrogen Ring

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Summary: The reactions of quinoline (**1**), isoquinoline (**2**), 1,2,3,4-tetrahydroquinoline (**3**), and 2-methylquinoline (**4**) with (pentamethylcyclopentadienyl)rhodium dication [Cp*Rh(acetone)$_3^{2+}$, Cp*Rh(acetonitrile)$_3^{2+}$, or Cp*Rh(*p*-xylene)$^{2+}X_2$; X = PF_6 or BF_4] were studied to ascertain nitrogen (N) versus π-bonding. Ligands **1** and **2** were found to form N-bonded rhodium complexes, while ligand **3** preferred π-coordination (η^6). Ligand **4** was found to provide both π- and N-bonded complexes. A single-crystal X-ray structural analysis of a derivative of Cp*Rh(quinoline)(acetonirile)$_2^{2+}$, [Cp*Rh(quinoline)(μ-hydroxo)]$_2^{2+}$, verified the N-bonding of ligand **1** to the rhodium metal center. It was also found that the above-mentioned Cp*Rh^{2+} synthetic precursors were excellent catalysts or catalyst precursors for the selective hydrogenation of **1**, **2**, and **4** to their corresponding tetrahydro derivatives. This latter result defines the important role of N-bonding for regioselective nitrogen ring reduction.

In recent studies on the regioselective hydrogenation of polynuclear heteroaromatic nitrogen compounds with mononuclear rhodium and ruthenium homogeneous catalysts, it was evident that the substrate nitrogen compound binds to the catalyst metal center prior to hydrogen transfer.[2a,b] The mode of bonding of the nitrogen heterocyclic compound to the metal center, we speculated, was pivotal for the selective hydrogenation of the nitrogen-containing ring. Therefore, in order to determine more unequivocally the nature of this substrate bonding, i.e., nitrogen (N) versus π-bonding, we have initiated studies on the reactions of several representative polynuclear heteroaromatic nitrogen ligands with (pentamethylcyclopentadienyl)rhodium dication (Cp*Rh^{2+}).

A previous study showed that reaction of Cp*Rh^{2+} with indole provided a π-bonded complex (η^6) to the benzene ring.[3] To our knowledge, no other complexes with polynuclear heteroaromatic nitrogen ligands and Cp*Rh^{2+} have been reported. In this communication, we report preliminary findings that show that the structure of the nitrogen ligand and availability of nonbonding electrons on the nitrogen atom determines N-versus π-bonding to Cp*Rh^{2+}.

(1) (a) Lawrence Berkeley Laboratory. (b) University of South Carolina.

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(3) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* 1977, 1654. Another synthetic procedure that we found useful for the preparation of complexes **5**–**9** was reaction of Cp*Rh(*p*-xylene)$(BF_4)_2$ with ligands **1**–**4**. This ligand exchange reaction provided good yields of **5**–**9**, while circumventing the use of silver salts that often made purification of product more difficult.

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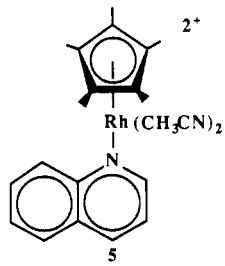
We also demonstrate the catalytic activity of several of the Cp^*Rh^{2+} complexes in the selective hydrogenation of 1, 2, and 4 to their tetrahydro derivatives, and this result defines the critical role of N-bonding for the regioselective nitrogen ring reduction.

The general synthetic reaction procedures that were followed are shown in eq 1.[3]

$$[Cp^*RhCl_2]_2 + AgX \xrightarrow{S} Cp^*Rh(S)_3X_2 \xrightarrow{\text{"N"}} Cp^*Rh(p\text{-xylene})X_2 \xrightarrow[\text{"N"}]{} Cp^*Rh(N)_{1,3}X_2 \quad (1)$$

X = BF_4 or PF_6; S = CH_3CN or $(CH_3)_2CO$; "N" = ligands 1-4

The reaction of quinoline (1) with $Cp^*Rh(S)_3^{2+}$ (S = acetonitrile) provided a monoquinoline rhodium complex containing two acetonitrile molecules. The ^{13}C NMR spectrum indicated that the quinoline ligand was N-bound to rhodium by the lack of Rh–C coupling[3] and allowed us to assign the structure as **5**.[4]



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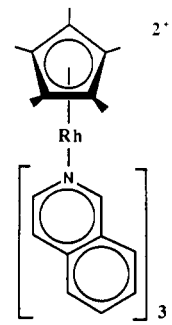
However, we found that when the previous reaction was carried out in either acetone or acetonitrile containing traces of water only a crystalline derivative, $[Cp^*Rh(quinoline)(\mu\text{-hydroxo})]_2(BF_4)_2$ (**5a**) was obtained. A single-crystal X-ray analysis of **5a**[5] provided the ORTEP drawing shown in Figure 1. The structure consists 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 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.

Interestingly, reaction of isoquinoline (2) with $Cp^*Rh(S)_3^{2+}$ or $Cp^*Rh(p\text{-xylene})^{2+}$ provided an air-stable, tris(isoquinoline), dicationic complex, **6**.[6] The structure of



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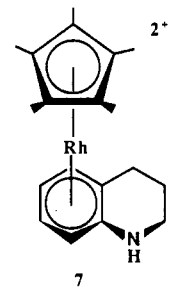
complex **6** was verified by ^{13}C NMR, which indicates no Rh–C coupling and thus confirms N-bonding to the rhodium metal center. This result suggests that differences in the steric requirements at the Rh metal center and possible differences in the electronic effects of ligands 1 and 2 control Rh–N complex lability.

We anticipated that ligand 3, 1,2,3,4-tetrahydroquinoline, the regioselective reduction product of 1, would also bond to rhodium in a similar fashion; however, this was not the case. Ligand 3 reacted with Cp^*Rh^{2+} to form a dicationic complex, **7**,[7] that was π-bonded to the benzene ring (η^6). Therefore, it appears that the nonbonding electrons on the nitrogen atom in 1 and 2, which are or-



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(4) Complex **5** (air and moisture sensitive): BF_4, 78%; ^1H NMR (500 MHz, CD_3NO_2, δ) Me_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), Me_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), 129.8 (s), 128.7 (s), 124.6 (s). Anal. Calcd for $C_{23}H_{28}N_3Rh(BF_4)_2$: C, 44.34; H, 4.53; N, 6.75. Found: C, 44.52; H, 4.51; N, 6.62.

(5) Complex **5a**: BF_4, 83%; mp 173–175 °C dec; ^1H NMR (250 MHz, CD_2Cl_2, 5 °C, δ) Me_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 15:2:1:1:1:2:1:1; $^{13}C\{^1H\}$ NMR (500 MHz, CD_3NO_2, -20 °C, δ) C_5, 93.2 (d, J_{Rh-C} = 8.2 Hz), Me_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, 48.44; H, 4.88; N, 2.97. Found: C, 48.45; H, 4.89; N, 2.97. The solid-state structure shows the N-bound quinoline ligands to be cis to each other, while ^1H and ^{13}C NMR solution spectra of **5a** 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. Crystals of **5a** were obtained from the reaction mixture in acetone at 5 °C: space group $P2_1/c$, a = 11.092 (1) Å, b = 18.958 (2) Å, c = 18.426 (2) Å, β = 96.10 (2)°, Z = 4. The structure was solved by direct methods and was refined (4053 reflections) to the final values of the residuals R = 0.027 and R_w = 0.035. The structure consists of well-separated ions of $[Cp^*Rh(quinoline)(\mu\text{-OH})]_2^{2+}$ and BF_4^-. Selected intramolecular distances (Å) and angles (deg) are as follows: Rh(1)···Rh(2) = 3.322 (1); Rh(1)–O(1) = 2.102 (3); Rh(1)–O(2) = 2.084 (3); Rh(2)–O(1) = 2.086 (2); Rh(2)–O(2) = 2.112 (3); Rh(1)–N(1) = 2.160 (3); Rh(2)–N(2) = 2.149 (4); O(1)–Rh(1)–O(2) = 75.1 (1); O(1)–Rh(2)–O(2) = 74.8 (1). Diffraction data were collected on a Rigaku AFC6 diffractometer. Structure solving programs were obtained from the Molecular Structure Corp., College Station, TX.

(6) Complex **6**: BF_4, 87%, mp 164–166 °C dec; PF_6, 94%, mp 188–90 °C dec; ^1H NMR (200 MHz, $(CD_3)_2CO$, δ) Me_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(7), 7.87 (t, J = 7.2 Hz), H(8), 8.33 (d, J = 8.2 Hz), ratio 15:1:1:3:1:1; $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ) C_5, 100.2 (d, J_{Rh-C} = 8.6 Hz), Me_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, 48.54; H, 3.96; N, 4.59. Found: C, 48.38; H, 4.03; N, 4.50. Anal. Calcd for $C_{37}H_{36}N_3Rh(BF_4)_2$: analysis of C, H, N within 0.5%.

(7) Complex **7**: BF_4, 74%, mp 270–2 °C dec; PF_6, 80%, mp 248–250 °C dec; ^1H NMR (250 MHz, CD_3NO_2, δ) Me_5, 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 (CD_3NO_2, δ) C_5, 110.5 (d, J_{Rh-C} = 7.9 Hz), Me_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 = 6.0 Hz), 85.7 (d, J = 7.6 Hz, 85.5 (d, J = 1.7 Hz), 101.5 (d, J = 3.9 Hz); FABS-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. Anal. Calcd for $C_{19}H_{26}NRh(PF_6)_2$; analysis of C, H, N within 0.5%

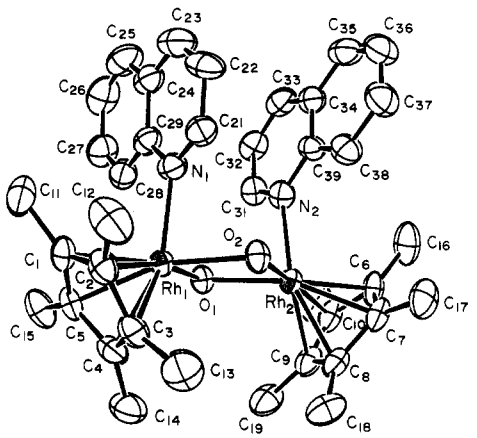
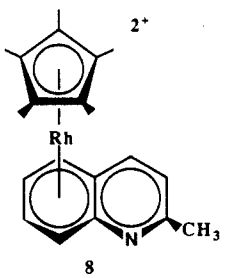


Figure 1. An ORTEP diagram of the dimer $[Cp^*Rh(quinoline)(\mu\text{-}OH)]_2^{2+}$ (**5a**) showing 50% probability thermal ellipsoids.

thogonal to the π-electrons of the aromatic ring, are readily available for bonding to rhodium. The opposite situation can exist for **3**, where the nonbonding 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.[8]

By sterically hindering the nitrogen nonbonding electrons in **1** with a methyl group in the 2-position, we hoped to force the formation of a π-complex. Indeed, the apparent steric effect of the methyl group in ligand **4** allows π-complexation to take place as well as N-bonding, interestingly, to give **8** and **9** (~1:1 ratio).[9] The rhodium



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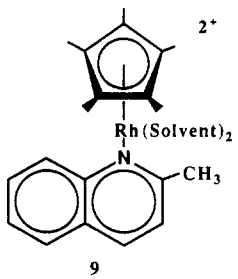

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metal center appears by ^{13}C NMR, in complex **8** to be bonded to the π-system of the benzene ring rather than the nitrogen-containing ring. Although complex **9** was difficult to isolate, we assign **9** as N-bonded from the chemical shifts of the ligands in the ^1H NMR spectrum and, as well, from the lack of Rh–C coupling in the ^{13}C NMR spectrum. These NMR results are consistent with the other two characterized N-bonded Cp^*Rh^{2+} complexes, **5** and **6**.

The results we presented show that Cp^*Rh^{2+} bonding to nitrogen heterocyclic ligands is a function of ligand structure with steric effects and nitrogen nonbonding electron availability being important parameters. The relative order of reactivity of polynuclear heteroaromatic nitrogen ligand with Cp^*Rh^{2+}, defined in competitive experiments, was **2** (N) > **3** (π) > **4** (π) > **1** (N).[10] This order of reactivity appears to be a consequence of N-bonding more favorable than π-bonding, but only if steric effects permit; i.e., $Cp^*Rh(quinoline)(solvent)_2^{2+}$ lability should provide a facile mechanism for ligand exchange with **2–4**. The π-bonding order **3** > **4** appears to reflect the ability of the N atom to increase electron density in the aromatic ring.

The relationship of these bonding results to our previous homogeneous hydrogenation studies with similar substrates[2a,b] corroborates our contention that N-bonding to the rhodium or ruthenium metal center, as in **1**, **2**, and **4**, provides a driving force for the regioselective reduction of the nitrogen ring. In fact, we have now found that $Cp^*Rh(acetonitrile)_3^{2+}$ and $Cp^*Rh(p\text{-xylene})^{2+}(BF_4)_2$ are excellent homogeneous hydrogenation catalysts or catalyst precursors for the conversion of **1** to **3**, while **2** and **4** were selectively hydrogenated to 1,2,3,4-tetrahydroisoquinoline and 1,2,3,4-tetrahydro-2-methylquinoline, respectively, with $Cp^*Rh(p\text{-xylene})^{2+}$ as the catalyst precursor.[11] Thus, the product of the regioselective reduction of **1**, ligand **3**, π-bonds to the rhodium metal center and this may provide an explanation for it not being further reduced as well as being able to retard the relative rate of hydrogenation of **1** as was observed previously with $(Ph_3P)_3RhCl$.[2a]

We are presently evaluating Cp^*Rh^{2+} derivatives as hydrogenation catalysts for other polynuclear heteroaromatic nitrogen compounds, studying the direct reactions of **5–9** with hydrogen gas and hydride ion, and also studying the bonding of ligands **1–4** with cyclopentadienylruthenium cation ($CpRu^+$) and their catalytic properties.

Acknowledgment. The synthetic and catalysis studies at LBL and the single-crystal X-ray study at USC were both supported by the Director, Office of Energy Research, Office of basic Energy Science, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098 (LBL) and DEFG84ER 13296 (USC).

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and ansiotropic thermal parameters (11 pages); a listing of structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

(8) The reaction of phenol with Cp^*Rh^{2+} gave η^6-phenol and η^5-oxocyclohexadienyl complexes. See: White, C.; Thompson, S. J.; Maitlis, P. M. *J. Organomet Chem.* **1977**, *127*, 415.

(9) Complex **8**: BF_4, 67%, mp 243–245 °C dec; PF_6, 55%; ^1H NMR (500 MHz, CD_3NO_2, δ) Me_5, 2.23 (s), CH_3, 2.22 (s), H(3–8), 6.7 (m), 7.1 (m), ratio 15:3:6; $^{13}C\{^1H\}$ NMR (500 MHz, CD_3NO_2, δ) C_5, 111.3 (d, J_{Rh-C} = 7.9 Hz), Me_5, 10.6 (s), CH_3, 10.3 (s), C(3–8), 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); FAB-MS, ligand **4** was replaced by sulfolane. Anal. Calcd for $C_{20}H_{24}NRh(BF_4)_2$: C, 43.29; H, 4.32; N, 2.52. Found: C, 42.25; H, 4.44; N, 2.59. Complex **9** was difficult to isolate, but ^1H NMR (250 MHz, CD_3NO_2, δ) suggested a structure similar to **5**, i.e., H(3–8), 9.09 (d), 8.35 (d); 8.33 (d); 8.15 (t); 8.06 (d); 7.94 (t); CH_3, 3.04 (s); CH_3CN, 2.58 (s), Me_5, 1.68 (s), ratio 1:1:1:1:1:1:3:6:15.

(10) An example of a competitive reaction is described as follows: $Cp^*Rh(acetone)_3^{2+}(BF_4)_2$ (0.162 mmol) was prepared in situ in 10 mL of acetone. To this solution was added dropwise **3** (0.49 mmol) and **2** (0.49 mmol) dissolved in 2 mL of acetone and then reacted for 10 min. Analysis by ^1H NMR showed only **6** and **3** being present, while **7** was absent. In another procedure, we showed that **2** reacted with **7** to provide **6** and **3**, while the reverse reaction did not occur. Both procedures gave the same order of ligand reactivity.

(11) The catalytic hydrogenation reactions of **1**, **2**, and **4** were carried out in a Parr kinetic apparatus with $Cp^*Rh(acetonitrile)_3^{2+}$ or $Cp^*Rh(p\text{-xylene})^{2+}(BF)_2$ as the catalysts. Thus, **1**, **2**, or **4** (1.93 mmol) and the above-mentioned catalysts (0.04 mmol) in 25 mL of anhydrous methanol were reacted with 500 psi of hydrogen gas at 80 °C to give, with 100% regioselectivity, the corresponding tetrahydro derivatives (capillary column GC analysis). The relative rates (based on **1** as the standard with an initial rate of 1%/min) were 1.0 (**1**), 0.03 (**2**), and 0.43 (**4**) at a substrate/catalyst ratio of 50.