Hydrogenation of Iron(II) Cationic Complexes of Naphthalene and Methyl-Substituted Naphthalenes

Douglas S. Masterson, Christine M. Tratz, B. Anthony Behrens, and Daniel T. Glatzhofer*

Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Norman, Oklahoma 73019

Received September 20, 1999

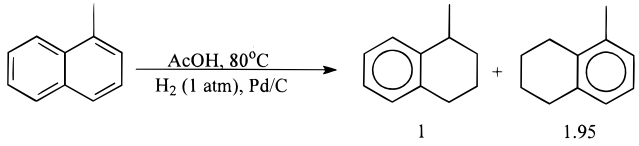
Complexation of one ring of naphthalene as an η^6-ligand by cyclopentadienyliron(II) cation significantly disrupts aromaticity in the noncomplexed ring, rendering it more "diene-like". This was demonstrated by a significant acceleration ($\gg 25\times$) of the hydrogenation (Pd/C, 1 atm. H_2, methanol, room temperature) of (η^5-cyclopentadienyl)(η^6-naphthalene)iron(II) hexafluorophosphate to its corresponding tetralin complex under mild conditions relative to analogous reduction of naphthalene to tetralin. Complexation of methyl- and dimethylnaphthalenes by cyclopentadienyliron(II) cations resulted in mixtures of isomers with the isomer having the iron on the methyl-substituted ring generally predominating. However, hydrogenation of these mixtures often demonstrated a remarkable selectivity with regard to the production of their corresponding tetralin complexes. Hydrogenation of a 1.5:1 mixture of (η^5-cyclopentadienyl)(η^6-1,4-dimethylnaphthalene)iron(II) hexafluorophosphate isomers gave a >26:1 mixture of the corresponding tetralin complexes at 88% conversion. Larger amounts of Pd catalyst lowered the selectivity. Results for the hydrogenation of 1-methyl-, 2-methyl-, 1,2-dimethyl-, 2,3-dimethyl-, and 1,4-dimethylnaphthalenes and their corresponding (η^5-cyclopentadienyl)iron(II) complexes are presented, and a mechanism by which the product selectivity occurs is proposed. In all cases complexation significantly facilitates the hydrogenation of the naphthalene ligands relative to the noncomplexed naphthalenes.

Introduction

Many biological and medicinal compounds contain a tetralin core structure. Compounds that contain a tetralin core are utilized as antidepressants,[1,2] cholesterol biosynthesis inhibitors,[3] and potential antimalarial drugs,[4] and many have shown potent anti-infective properties.[5] The tetralin core can be constructed by pathways such as acid-catalyzed cyclization[1] and by the reduction of appropriately substituted tetralone compounds.[6] These methods suffer from the harsh reaction conditions that are frequently employed. It would be advantageous if the tetralin core could be easily constructed from inexpensive starting materials in as few steps as possible under relatively mild reaction conditions.

The direct reduction of naphthalenes to tetralins is well-known.[7,8] Various reagents have been employed to perform the direct reduction of naphthalenes such as platinum- and palladium-catalyzed hydrogenation,[9] BF_3/Et_3SiH,[10] and borane-catalyzed hydrogenation.[11] Unfortunately direct reduction methods suffer significant reactivity, selectivity, and functional group tolerance problems. The platinum oxide-catalyzed reduction of naphthalene to tetralin requires elevated temperatures and pressures, which results in significant over-reduction to *cis*- and *trans*-decalin.[12] The palladium-catalyzed reduction of substituted naphthalenes in refluxing acetic acid suffers from a lack of regioselectivity in the reduction. For example, catalytic reduction of 1-methylnaphthalene results in approximately a 1:2 mixture of tetralin products[9] (see Scheme 1).

Scheme 1



Conceptually, many of the problems that are encountered in the catalytic reduction of naphthalenes could

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10.1021/om990738t CCC: $19.00
Publication on Web 12/31/1999

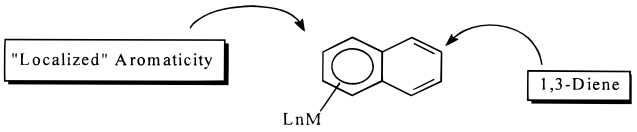

Figure 1.

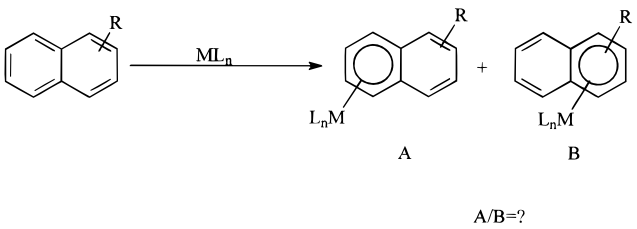

Figure 2.

be overcome by the η^6-coordination of a metal moiety to one ring of the naphthalene unit (see Figure 1). By choosing the appropriate metal moiety, it could be possible to view the naphthalene unit as two separate components: a 1,3-diene component and a 6π localized, by metal coordination, aromatic component. The hydrogenation of other metal-containing dinuclear aromatics is well-known in which the metal essentially protects a 6π, five-membered, aromatic ring.[13−15] If the metal moiety can effectively localize the aromatic system to a single ring of the naphthalene unit as depicted in Figure 1, the noncoordinated ring of the naphthalene should become activated toward catalytic hydrogenation under mild conditions since conjugated dienes can be catalytically reduced under mild conditions. One potential problem with the activation of substituted naphthalenes using a metal moiety is the selectivity of the complexation (see Figure 2). The selectivity of complexation could result in a problem with the selectivity of the reduction. If a mixture of naphthalene metal complexes are formed, one would expect a mixture of reduction products, the composition being directly related to the composition of the naphthalene complexes.

In 1994, Glatzhofer et al. reported the catalytic hydrogenation of a (η^5-cyclopentadienyl)(η^6- naphthalene)ruthenium(II) cationic complex under mild conditions.[16] Unfortunately, the ruthenium moiety that was employed involved several synthetic steps to make and was also relatively expensive. To avoid the disadvantages of the ruthenium moiety, use of the iron cyclopentadienyl moiety in place of the isoelectronic ruthenium moiety is a logical substitution.

The chemistry of iron cyclopentadienyl cationic complexes of naphthalenes has been explored. Sutherland et al. reported that the iron cyclopentadienyl cationic complex of naphthalene underwent conversion to the corresponding tetralin when formed from naphthalene and ferrocene in refluxing decalin.[17] Sutherland et al. also reported that the naphthalene iron complex did not undergo platinum-catalyzed reduction to the complexed tetralin.[17] We found it quite interesting that the ruthenium complex of naphthalene readily underwent catalytic reduction, but that the analogous iron complexes reportedly did not. Given our previous success with the ruthenium complexes, we decided to revisit the chemistry of the iron complexes. The utilization of iron over ruthenium has several advantages from a synthetic point of view. The iron complexes are synthesized in one step from readily available starting materials, the iron moiety is far less expensive than the ruthenium moiety, and although the reactions used here to synthesize the naphthalene complexes involve reaction with aluminum chloride at elevated temperatures, mild methods of complexation are known.[18] We wish to report here on the palladium-catalyzed reduction of several methyl- and dimethyl-substituted (η^5-cyclopentadienyl)(η^6-naphthalenyl)iron(II) hexafluorophosphate salts under mild conditions. In many instances, the regioselectivity of the catalytic reduction of the iron complexes proved to be extremely high even when the regioselectivity of the complex formation was not. We also report on initial experiments performed to help elucidate the mechanism of the catalytic reduction of the naphthalene complexes.

Experimental Section

General. THF was distilled from sodium/benzophenone under a nitrogen atmosphere prior to use. All other solvents were used as received unless otherwise noted. Ammonium hexafluorophosphate was prepared by neutralizing an aqueous solution of hexafluorophosphoric acid with ammonium hydroxide. $AlCl_3$ was obtained from Aldrich Chemical Co. and used as received. All naphthalene iron complexes were prepared using known literature procedures, substituting cyclohexane for methylcyclohexane as solvent, using standard Schlenk and glovebox techniques, and ^{1}H NMR spectra were consistent with published values.[19] All naphthalene iron complexes were dried at 80 °C in vacuo for 5 h. ^{1}H NMR spectra of the resulting iron complexes were obtained using either a Varian unity 400 or a 300 XL spectrometer using acetone-d_6 as solvent with reference to residual solvent proton concentration. NMR data assigned to the complexes with the iron cyclopentadienyl moiety on the substituted ring are denoted by an * next to the chemical shift. Variable-temperature (VT) NMR was performed on a Varian 300 XL spectrometer from −50 °C to room temperature (10 °C increments) allowing ∼15 min equilibration at each temperature setting. 1-Methylnaphthalene was obtained from Aldrich Chemical Co. and distilled under reduced pressure prior to use. 2-Methylnaphthalene was obtained from Aldrich Chemical Co. and was recrystallized from benzene and dried under vacuum prior to use. 1,4-Dimethyl-[20] and 1,2-dimethylnaphthalene[21] were prepared by LAH reduction of the corresponding bromomethylmethylnaphthalenes.[22] 2,3-Dimethylnaphthalene was obtained from Aldrich Chemical Co. and recrystallized from ethanol. Naphthalene and ferrocene were recrystallized from methanol prior to use. 10% Pd/C was obtained from Aldrich Chemical Co. and used as received. All hydrogenation reactions were performed at ambient temperature and pressure using a hydrogenation

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apparatus which consisted of a column of water as the hydrogen reservoir. FAB MS were recorded on a VG ZAB-E mass sprectrometer using 3-nitrobenzyl alcohol as the matrix. Decomplexation of the 1-methyltetralin iron complex was performed in a Pyrex beaker using acetone as solvent in a Rayonet photochemical reactor.

Catalytic reduction of naphthalene iron complexes (typical procedure). (η^5-Cyclopentadienyl)(η^6-naphthalene)-iron(II) hexafluorophosphate (80−90 mg) was dissolved in 6 mL of fresh methanol and added to a 10 mL round-bottom flask that was previously charged with 16−20 mg of 10% Pd/C and a stir bar. The charged flask was attached to a hydrogen reservoir and flushed three times with hydrogen. The mixture was allowed to stir at ambient temperature and pressure for 18 h. The reaction mixture was removed from the hydrogen atmosphere and filtered through filtering agent to remove the Pd/C to give a yellow solution. The solvent was removed under reduced pressure to give a yellow solid. ^{1}H NMR and mass spectra of the solid were consistent with literature values[17] and were identical to an authentic sample of (η^5-cyclopentadienyl)(η^6-tetralin)iron(II) hexafluorophosphate (**1**), which was prepared from commercially available tetralin. ^{1}H NMR (300, acetone-d_6): δ 2.75−2.90 (m, 4H), 3.05−3.20 (m, 4H), 5.1 (s, 5H Cp), 6.30 (s, 4H).

1,4-Dimethyltetralin Iron Complexes (2). The 1,4-dimethyltetralin complex mixture (**2**) was obtained in a manner similar to that described for the tetralin complex. FAB MS gave a *m*/*z* of 281.0 ($C_{17}H_{21}Fe$). ^{1}H NMR (400, acetone-d_6): δ 1.61 (d, J =7.2 Hz, 6H), 2.25* (s, 6H), 2.7−3.3 (m, 14H), 4.9* (s, 5H Cp), 5.2 (s, 5H Cp), 6.21 (s, 2H), 6.35−6.45 (m, 4H). The integration of the Cp protons and methyl protons for each diastereomer is in agreement with the given assignment.

2,3-Dimethyltetralin Iron Complexes (3). The 2,3-dimethyltetralin complex mixture (**3**) was obtained in a manner similar to that described for the tetralin complex. FAB MS gave a *m*/*z* of 281.0 ($C_{17}H_{21}Fe$). ^{1}H NMR (400, acetone-d_6): δ 1.20 (d, 6H), 2.50* (s, 6H), 2.7−3.2 (m, 14H), 4.9* (s, 5H Cp), 5.15 (s, 5H Cp), 6.2 (s, 2H), 6.4 (s, 4H). The integration of the Cp protons and methyl protons for each diastereomer is in agreement with the given assignment.

1,2-Dimethyltetralin Iron Complexes (4). The 1,2-dimethyltetralin complex mixture (**4**) was obtained in a manner similar to that described for the tetralin complex. FAB MS gave a *m*/*z* of 281.2 ($C_{17}H_{21}Fe$). ^{1}H NMR (400, acetone-d_6): δ 1.1(d, 3H), 1.6 (d, 3H), 2.49* (s, 3H), 2.54* (s, 3H), 2.7−3.2 (m, 14H), 4.96* (s, 5H Cp), 5.08 (s, 5H, Cp), 6.0−6.2 (m, 6H). The integration of the Cp protons and methyl protons is in good agreement with the given assignments.

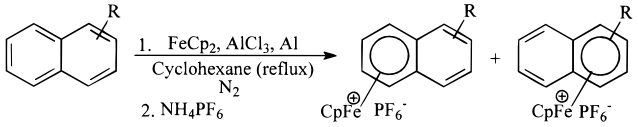
1-Methyltetralin Iron Complexes (5). The 1-methyltetralin iron complex mixture (**5**) was obtained in a manner similar to that of the tetralin complex. FAB MS gave a *m*/*z* of 267.1 ($C_{16}H_{19}Fe$). ^{1}H NMR (400, acetone-d_6): δ 1.61 (d, J = 6.9, 3H), 2.55* (s, 3H), 2.7−3.2 (m, 15H), 5.01* (s, 5H Cp), 5.20 (s, 5H Cp), 6.2−6.5 (m, 7H). The integration of the Cp protons and methyl protons is in good agreement with the given assignments.

2-Methyltetralin Iron Complexes (6). The 2-methyltetralin iron complex mixture (**6**) was obtained in a manner similar to that of the tetralin complex. FAB MS gave a *m*/*z* of 267.1 ($C_{16}H_{19}Fe$). ^{1}H NMR(300, acetone-d_6): δ 1.16 (d, J = 6.1, 3H), 2.45* (s, 3H), 2.7−3.2 (m, 15H), 5.08* (s, 5H Cp), 5.14 (s, 5H Cp), 6.21−6.40 (m, 7H). The integration of the Cp protons and the methyl protons is in good agreement with the given assignments.

Stop Reduction Experiment. The procedure for the stop experiment was essentially the same as for the reduction of the 1,4-dimethylnaphthalene iron complexes except the reaction was removed from the hydrogen atmosphere after ∼50−60% conversion (about 8−10 h).

Palladium Isomerization Experiment. Isomerization experiments were performed in a manner similar to the catalytic reduction of the 1,4-dimethylnaphthalene iron complexes except nitrogen was used as the atmosphere and the reaction apparatus was thermostated.

Scheme 2. Formation of Naphthalene Iron Complexes



Results

The cationic iron cyclopentadienyl complexes were synthesized using a literature procedure.[17] The products of this procedure were approximately 1:1 mixtures of complexed substituted naphthalenes (see Scheme 2 and Table 1).The complexation of both mono- and dimethylnaphthalenes occurs with a slight preference for the iron moiety to attach to the substituted ring when a substituent is placed in the 1 or 4 position. A lesser preference was observed for the substituted ring by the iron moiety when a substituent was placed in the 2 or 3 position. The observed preference for substitution to the more or less substituted ring is probably due to electronic differences between the substituted and unsubstituted rings with the placement of the substituent.[19] Attempted chromatographic separation of these mixtures (silica gel) proved difficult, and they were used without any further workup in the subsequent hydrogenation reactions.

The catalytic reduction of the naphthalene iron complexes was performed at ambient temperature and pressure. The resulting tetralin complexes were characterized by characteristic ^{1}H NMR resonances and by FAB mass spectrometry. The mass spectra of all tetralin complexes clearly indicated the addition of four hydrogen atoms to the parent naphthalene complex. ^{1}H NMR of the known (η^5-cyclopentadienyl)(η^6-tetralin)iron(II) hexafluorophosphate was used as a comparison. The disappearance of the upfield Cp signals of the (η^5-cyclopentadienyl)(η^6-naphthalene)iron(II) hexafluorophosphate (4.7, s, 5H) was observed with new Cp signals appearing downfield for the corresponding tetralin complex (5.1, s, 5H). The appearance of aliphatic resonances in the 2.6−3.2 range are observed at the expense of aromatic signals (as is seen in the hydrogenation of the naphthalene complex). The aromatic upfield multiplets located at ∼7.5 and 6.6 coalesce into an apparent singlet at ∼6.3, and the aromatic absorptions of the noncomplexed ring (∼8.0 ppm) disappear. Comparison of the methyl signals and the Cp signals of the methyl-substituted tetralin complexes (**2**−**6**) were used to assign the location of the iron moiety. The results of the hydrogenation reactions are shown in Table 1.

From Table 1 it is clear that the uncomplexed naphthalenes are difficult to reduce to tetralins under mild conditions. The catalytic reduction of naphthalene results in a 32% conversion to the corresponding tetralin after several days exposure to 1 atm hydrogen, even with a large excess of palladium catalyst (by weight). This difficulty is attributed to the aromatic character of the naphthalene nucleus.[12] By complexing naphtha-

Table 1

Hydrogenation of Substituted Naphthalenes[a]

entry	naphthalene	rxn time[b]	% conversion[c]
1	naphthalene	2	32
2	1-methylnaphthalene	2	0
3	2-methylnaphthalene	2	0
4	1,2-dimethylnaphthalene	2	64
5	1,4-dimethylnaphthalene	2	0
6	2,3-dimethylnaphthalene	2	0

Hydrogenation of Iron Cationic Naphthalene Complexes[d]

entry	naphthalene complex	complex[e] ratio	% conversion[f]	tetralin ratio[e]
7	naphthalene		100	
8	1-methylnaphthalene	1:1.31	80	1:4.9[g]
9	1-methylnaphthalene	1:1.31	100[h]	1:1.7
10	2-methylnaphthalene	1:1.20	100	1:1
11	1,2-dimethylnaphthalene	1:1.26	77	1:13.9
12	1,4-dimethylnaphthalene	1:1.46	88	1:26.2
13	1,4-dimethylnaphthalene	1:1.46	100[h]	1:2.7
14	2,3-dimethylnaphthalene	1.97:1	100	1.9:1

[a] Using 1 atm H_2 and 1 equiv of 10% Pd/C (by weight) at room temperature. [b] Reaction time in days. [c] Based on ^{1}H NMR. [d] Using 1 atm H_2 and ~16 mg of 10% Pd/C per 80−90 mg complex at room temperature for 18 h. [e] Ratio refers to iron moiety on unsubstituted ring:substituted ring and was measured by ^{1}H NMR of the Cp region. [f] Based on ^{1}H NMR of Cp region. [g] Ratio determined by GC integration of decomplexed material. [h] Using a 3-fold excess (by weight) of 10% Pd/C.

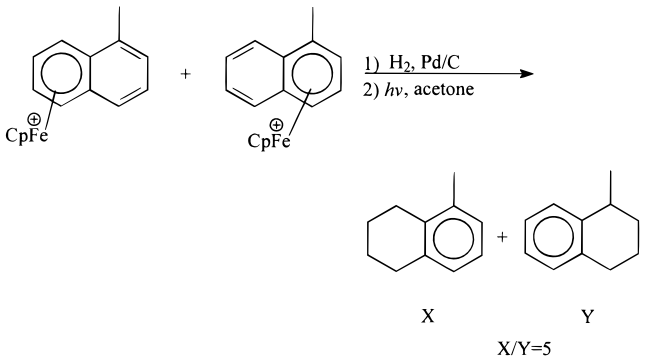
lene with the iron cyclopentadienyl cation, the reactivity toward catalytic reduction dramatically increases. An in-situ competition experiment between uncomplexed naphthalene and complexed naphthalene was performed which did not give reliable data due to the fact that the naphthalene iron complex was completely reduced before any detectable naphthalene reduction took place (by NMR). The reduction of the iron-complexed naphthalene essentially goes to completion (by ^{1}H NMR), and over-reduction to decalin is not observed.

The uncomplexed monomethylnaphthalenes did not undergo catalytic reduction under mild conditions, even after several days exposure to a hydrogen atmosphere and a large excess of palladium catalyst (by weight). In contrast, the complexed monomethylnaphthalenes underwent smooth conversion to the monomethyltetralin complexes under mild catalytic reduction conditions. Interestingly, under certain circumstances, the monomethylnaphthalene complexes experienced a selectivity in the reduction which did not correspond to the ratio of the starting complex. When the 1-methylnaphthalene iron cyclopentadienyl complex (mixture of isomers) underwent catalytic reduction to 80% conversion, a ~1:5 selectivity was observed for **5** (by GC of the uncomplexed material) in favor of the more substituted ring being protected by the iron moiety (entry 8, Table 1) (Scheme 3).

When the reduction of the 1-methylnaphthalene iron complex was carried out with an excess of palladium catalyst, the reduction went to completion within 2−3 h and a much lower selectivity was observed (entry 9, Table 1). The catalytic reduction of the 2-methylnaphthalene iron complex produced a mixture of tetralin complexes that was essentially in the same ratio as the starting 2-methylnaphthalene iron complex (entry 10, Table 1).

The uncomplexed dimethylnaphthalenes were also difficult to reduce under mild conditions. Reduction of 1,4- and 2,3-dimethylnaphthalene did not occur under mild conditions, although the reduction of 1,2-dimethylnaphthalene[23] was observed to have taken place in 64% yield (using a excess of Pd by weight). The catalytic

Scheme 3



reduction of the 1,2-dimethylnaphthalene iron cyclopentadienyl complex mixture underwent conversion to the tetralin complexes in 77% with high selectivity of ~1:14 (by ^{1}H NMR) in favor of the more substituted ring being protected by the iron moiety. Even more dramatic results were observed for the 1,4-dimethylnaphthalene iron cyclopentadienyl complex in both conversion and selectivity. Interestingly, when the 1,4-dimethylnaphthalene iron cyclopentadienyl complex was reduced in the presence of a large excess of palladium catalyst, the reaction was essentially complete within 2−3 h and a much lower selectivity of ~1:2 was observed. The catalytic reduction of the 2,3-dimethylnaphthalene iron cyclopentadienyl complex produced a mixture of tetralin complexes that was essentially in the same ratio as the starting 2,3-dimethylnaphthalene complex.

Discussion

In all cases presented the complexation of the aromatic naphthalene unit with a cationic iron moiety significantly increases the rate of hydrogenation and protects the complexed ring from reduction. This suggests that the iron moiety is capable of localizing the aromaticity of the naphthalene nucleus to the complexed ring.

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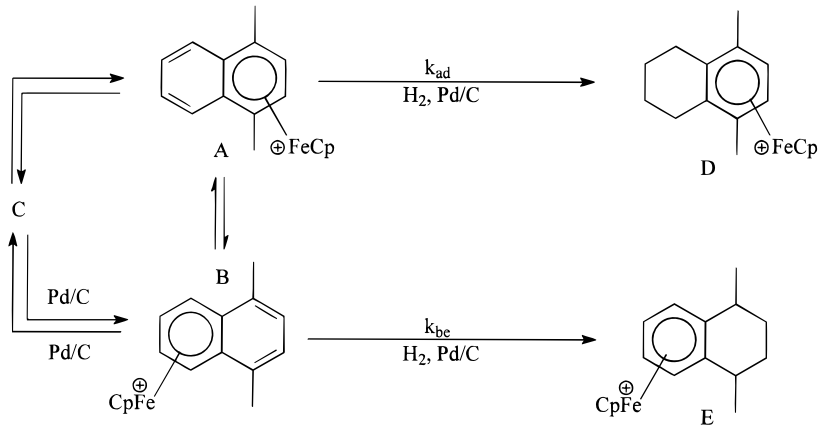
Scheme 4. Proposed Reaction Pathway



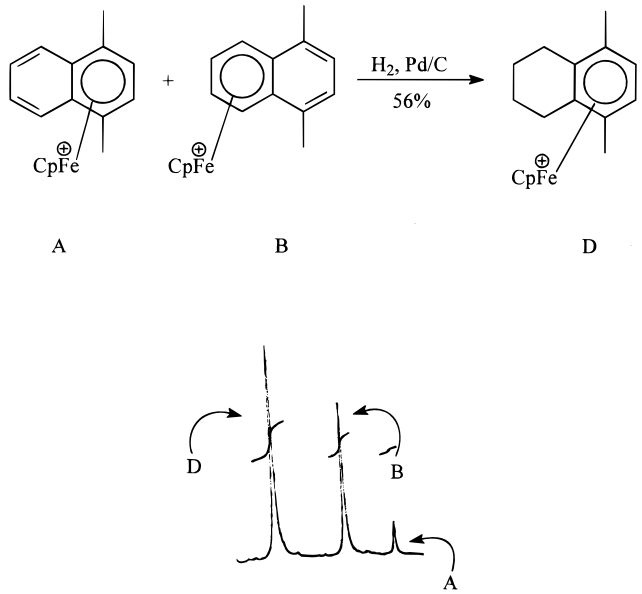


Figure 3. ^{1}H NMR of the Cp region after stop experiment.

The selectivity that was observed in the reduction of the 1-methyl-, 1,2-dimethyl-, and 1,4-dimethylnaphthalene iron cyclopentadienyl complexes was not expected. To account for the observed selectivity, we invoked a model, using the 1,4-dimethylnaphthalene complex as an example, depicted in Scheme 4.

Scheme 4 illustrates two possible pathways by which the selectivity in the reduction of the methyl-substituted naphthalenes could take place. Initially it was hypothesized that $k_{ad} \gg k_{be}$ and either an equilibration between A and B was occurring or an intermediate C was formed from B, which was then converted to A. The equilibration of A and B in solution was discounted on the basis of results obtained from both a stop (see Experimental Section) experiment and a VT NMR experiment. The stop experiment was performed by stopping the hydrogenation at ~56% conversion and performing ^{1}H NMR analysis on the reaction mixture. It was evident from this stop experiment that complex A (iron on more substituted ring) had indeed hydrogenated almost exclusively to form product D with complex B (iron on less substituted ring) largely unreacted (see Figure 3).

This observation confirmed the initial hypothesis that $k_{ad} \gg k_{be}$. Continued observation of this sample by ^{1}H NMR over several days revealed no re-equilibration between A and B, which was consistent with the absence of equilibration in the VT NMR results.

Given that both the VT NMR and the stop experiment were consistent with a mechanism that excluded a direct equilibration of A and B, it would seem likely that the palladium catalyst was necessary for the formation of an intermediate C, which could account for the conversion of B to A. Forming a 16-electron intermediate could allow for a ring slip, which would account for the conversion of B to A. As shown in Scheme 5, hydrogen could be added to compound B across the 2,3-bond, creating a ortho-quinodimethane type 16-electron intermediate.

The initially formed 16-electron intermediate shown in Scheme 5 could then undergo a ring slip to the more electron-rich diene, producing a more stabilized 16-electron intermediate. The data in Table 1 (entries 12 and 13) suggest that the ring slip is indeed a relatively slow process given that a large excess of palladium dramatically reduces the observed selectivity. Indeed the palladium was necessary for the isomerization to proceed, and it is hypothesized that the initial isomerization is due to residual hydrogen on the palladium catalyst, which allows the formation of the proposed 16-electron intermediate. Following ring slip, the η^4 16-electron species can then be re-aromatized by removal of H_2 by the palladium catalyst,[24] which would represent the formal conversion of B to A, as shown in Scheme 5, or the less substituted double bonds could be hydrogenated followed by re-aromatization. A process that involves a ring-to-iron migration of a hydrogen atom, which could possibly account for the re-aromatization, cannot be excluded. Control experiments were performed in which nitrogen was substituted for the hydrogen gas in hopes of determining if the palladium catalyst was playing a vital role in the isomerization. The 1,4-dimethylnaphthalene iron complex did undergo slow isomerization in the presence of the palladium catalyst, but this trend reached a maximum of approximately 68%, in favor of the more substituted ring, after 10 h exposure to the palladium catalyst in acetone solvent.

The proposed mechanism of a 16-electron intermediate is consistent with the results as shown in Table 1. Those compounds that contain a substituent in the 1 or 4 position show high selectivity as a result of the rate

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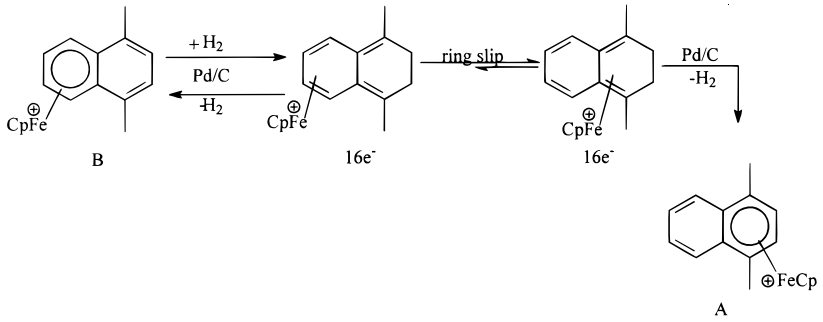
Scheme 5



difference in the hydrogenation of the two compounds and the formation of the η^4 16-electron intermediate, which can ring slip to the more electron-rich diene to produce a more stabilized 16-electron intermediate. Those compounds that contain a substituent in the 2 or 3 position have these sites blocked such that hydrogen cannot readily add across the 2,3 bond, similar to the difficulty in hydrogenating highly substituted alkenes, required in generating the η^4 16-electron species suspected to be the active isomerization intermediate.

Conclusion

Coordination of the naphthalene nucleus with the iron cyclopentadienyl cation has been shown to increase the rate of reduction of the naphthalene nucleus to tetralin. It is well-known that the catalytic reduction of aromatic compounds requires harsh reaction conditions of temperature and pressure.[7] It has also been well established that under harsh conditions naphthalenes are readily hydrogenated, often resulting in over-reduction to *cis*- and *trans*-decalins.[12] Coordination of the naphthalene nucleus with the iron cyclopentadienyl cation allows the reduction to proceed under extremely mild conditions and protects the naphthalene from over-reduction.

In many instances the reductions presented in Table 1 showed remarkable selectivity. If the substituents are appropriately placed (i.e., the 1 or 4 position), a single reduction product is produced almost exclusively favoring the iron protecting the more substituted ring. Amazingly the substituents need not be strongly electron donating to affect the observed selectivity. Product selectivity can be controlled by judicious choice of substrate/catalyst ratio.

A mechanism has been proposed that accounts for the observed selectivity. Unfortunately, due to the heterogeneous nature of the reaction, the suspected intermediate could not be directly detected. Even though the η^4 16-electron intermediate has not been detected, the results of all reductions reported herein are consistent with this intermediate.

In the future we hope to obtain ΔH_{red} data to help better understand the effect the iron cyclopentadienyl cation has on the naphthalene nucleus. Preliminary semiempirical calculations performed in our laboratories suggest that the coordination of the iron moiety increases the ΔH_{red} for the naphthalene system. We will report on ongoing efforts to expand the scope of this reaction to additionally substituted naphthalenes.

Acknowledgment. D.S.M. and B.A.B. would like to thank the Department of Education for GAANN Fellowship support. D.S.M. would also like to thank the National Science Foundation (NSF EPSCOR Cooperative Agreement EPS-9720651) and the University of Oklahoma for support of this work. We would also like to thank Dr. K. N. Nicholas (University of Oklahoma) and Dr. T. Baker (Los Alamos National Laboratory) for helpful discussions.

Supporting Information Available: FAB MS for the iron tetralin complex mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990738T