Homogeneous Catalytic Hydrogenation. 4. Regioselective Reduction of Polynuclear Heteroaromatic Compounds Catalyzed by Hydridochlorotris(triphenylphosphine)ruthenium(II)

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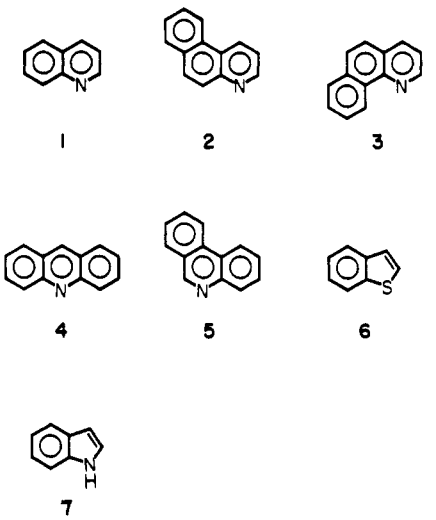
The selective reduction of polynuclear heteroaromatic nitrogen compounds such as quinoline, **1**, 5,6-benzoquinoline, **2**, 7,8-benzoquinoline, **3**, acridine, **4**, phenanthridine, **5**, and indole, **7**, and in one case the sulfur heterocycle benzothiophene, **6**, with hydridochlorotris(triphenylphosphine)ruthenium(II) as catalyst, under rather mild hydrogenation conditions, provided in each case the corresponding saturated nitrogen- or sulfur-containing ring compound with reasonable conversion rates and total yields. In addition, it was found that several compounds would inhibit the reduction of **1**, to 1,2,3,4-tetrahydroquinoline, **8**, including **8** itself, as well as **2**, **7**, **9** (2-methylpyridine), **10** (3-methylpyridine), and **11** (carbazole). Compounds **3** and **6** did not inhibit the rate of reduction. These inhibitions are seen as effects of competition for binding to the catalyst metal center, this competitive binding being affected by steric constraints and electronic effects such as basicity of the substrates. The substitution of deuterium gas for hydrogen gas in the reduction of **1** provided information on the reversibility of the hydrogenation step and implies a cyclometalation reaction is occurring leading to exchange of the 8-position of the product. Additional deuterium experiments starting with **8** instead of **1** indicate that the catalyst can partially dehydrogenate **8** to form an imine intermediate leading to deuterium exchange at the 2-position.

Introduction

We have recently reported on the regioselective hydrogenation of polynuclear heteroaromatic compounds using a variety of transition-metal complexes.[1a-c] The types of aromatic substrates we have investigated contain a single nitrogen or sulfur heteroatom in a two or three fused ring aromatic structure (Chart I) and are intended to model the types of compounds known to be in coal-derived liquids and shale oil. A better understanding of these reductions will hopefully lead to the improvement of the existing processes for refining and upgrading coal and other synthetic fuels using hydrogen gas.

In our previous studies,[1a-c] we found that ruthenium[1a,b] and rhodium[1c] complexes show the most activity toward selective reduction of the heteroaromatic ring in the types of substrates previously described when compared with Fe, Mn, and Co complexes also previously investigated.[1a,b] We have now found that hydridochlorotris(triphenylphosphine)ruthenium(II), formed in situ from dichlorotris(triphenylphosphine)ruthenium(II) and hydrogen gas, with the heterocycle acting as base, is an exceptionally active catalyst for the types of reactions described. Interestingly, it is more active by a factor of 3 than its rhodium analogue, $(PPh_3)_3RhH_2Cl$, in the regioselective reduction of polynuclear heteroaromatic nitrogen compounds, which we have previously investigated.[1c] This ruthenium complex is a well-known hydrogenation catalyst and has been used to reduce a variety of compounds, including olefins, aldehydes, ketones, and nitro compounds.[2a-e] To our knowledge, this is the first reported use of this catalyst in the selective reduction of polynuclear heteroaromatic compounds.

Chart I. Model Coal Compounds Used in Hydrogenation Reactions with $(Ph_3P)_3RuHCl$



In this paper, we report on the regioselective reductions of compounds **1–7**, with regards to the relative rate of hydrogenation of the substrates both individually and in a mixture with other substrates and model coal compounds. We will also present data on the reduction of one of these compounds, **1**, using deuterium gas in place of hydrogen gas. As well, we will establish the binding of **8** to the ruthenium hydride complex by NMR spectroscopy. We will then propose a reduction scheme (Figure 1) that accounts for our observed results.

Results and Discussion

Regioselective Hydrogenation. Table I contains the initial and relative rates for the selective reduction of the heterocyclic ring in compounds **1–7** (N-ring compounds **1–5**, **7**; S-ring compound **6**) catalyzed by $(PPh_3)_3RuHCl$ under a standard set of conditions. The catalyst was generated in situ from $(PPh_3)_3RuCl_2$ and hydrogen gas, and our substrates, which were basic enough to neutralize the HCl, formed during this reaction. The substrate to catalyst ratio was 10:1 in all cases, with initial turnover numbers

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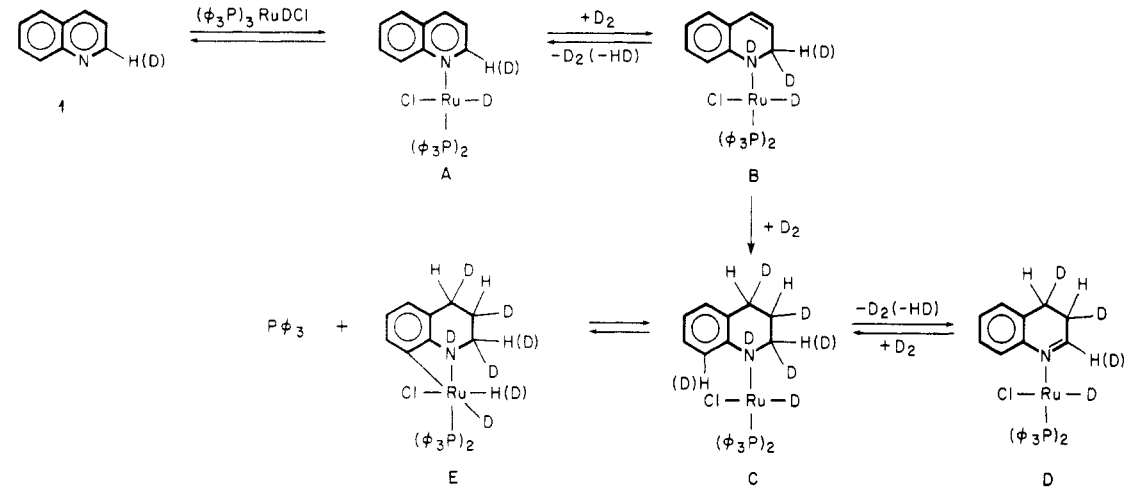


Figure 1. Postulated ruthenium complexes as intermediates in the catalytic hydrogenation of quinoline, 1.

Table I. Rates of Reduction of Compounds 1-7 under Hydrogenation Conditions Using $(PPh_3)_3RuHCl$ as Catalyst[a]

compd	product[b]	rate,[c] % min	rel rate[d]
1	1,2,3,4-tetrahydroquinoline	0.47	1.00
2	1,2,3,4-tetrahydro-5,6-benzoquinoline	0.059	0.12
3	1,2,3,4-tetrahydro-7,8-benzoquinoline	0.014	0.03
4	9,10-dihydroacridine	4.3	9.2
5	9,10-dihydrophenanthridine[e]	>11	>24
6	2,3-dihydrobenzothiophene	0.041	0.09
7	2,3-dihydroindole	0.085	0.18

[a] Conditions: 1 mmol of compounds 1-7, 0.1 mmol of $(PPh_3)_3RuCl_2$, 310 psi of H_2 (initial), 20 mL of benzene as solvent, temp = 85 °C (±0.5 °C). The active catalyst $(PPh_3)_3RuHCl$ is formed in situ from $(PPh_3)_3RuCl_2$ and hydrogen, with the substrate acting as base. [b] Analysis by capillary gas chromatography (see Experimental Section). [c] Pseudo-zero-order rate, followed to approximately 20% conversion (see Experimental Section). [d] Rates are relative to quinoline; i.e., each reduction rate was divided by the rate for quinoline (0.47) to obtain the values given. [e] Phenanthridine was reduced too rapidly to determine a rate using our technique. Reduction was complete within 9 min, and thus the value given for this rate is a lower bound.

(per Ru/h) varying from >66 to 0.08. The order of individual reduction rates was **5** > **4** >> **1** > **7** > **2** > **6** > **3**, reflecting both steric and electronic effects. For the reduction of **1**, and its two benzo derivatives **2** and **3**, steric effects are clearly important. Compound **3**, which is the most sterically hindered at the nitrogen, is reduced at the slowest rate, while compound **1**, with the least hindrance, is reduced the fastest. However, a comparison of the reduction rates of **6** and **7** show that other effects are in operation. Since these two molecules differ only in the identity of the heteroatom, the rate differences cannot be sterically caused. Electronic effects are most likely to be the cause of the differing rates, either concerning the complexing ability of the heteroatom or the electron density on the adjacent double bond.

Inhibition Studies. Since the rate differences given in Table I seem to partly reflect steric and electronic requirements in the binding of compounds 1-7 to the ruthenium metal center, experiments were carried out in which **1** was reduced in the presence of an equimolar amount of another compound that could potentially compete with **1** for binding to the ruthenium metal center. Table II clearly shows that the reduction of **1** was inhibited by compounds **2**, **7**, **8**, **9**, **10**, and **11** but was unaffected by **3** and **6**. There were no enhancements in rate such as we have observed with the rhodium analogue.[1c] The effects of compounds **3** (7,8-benzoquinoline) and **9** (2-methylpyridine), when compared to the effect of **2** (5,6-benzoquinoline) and **10** (3-methylpyridine), provide insight into the steric requirements for binding to the ruthenium metal center. Compounds **2** and **10** should have less hindrance at the nitrogen than the corresponding isomers **3** and **9**. In both cases, the less sterically hindered **2** and **10** show greater inhibition, indicative of more effective competition with **1** for catalyst metal centers than shown by **3** and **9**. Compounds **6** (benzothiophene) and **11** (carbazole) indicate the importance of basicity in determining strength of binding, since both of these molecules are less basic than **1**, suggesting that they should not compete with **1** for the catalyst. Both these compounds show little or no effect on the reduction rate of **1**, consistent with the assumption that they do not competitively bind. Compound **8** (1,2,3,4-tetrahydroquinoline) is the product of reduction of **1** and strongly inhibits its reduction by a factor of 0.34. This indicates that product inhibition may be an important factor in many of these reductions, in which the products are often stronger bases than the reactants. In the case of compounds **2**, **3**, **6**, and **7**, these compounds were reduced

Table II. Relative Rates of Reduction of 1 in the Presence of Other Compounds[a]

added compd	rel rate[b]	added compd	rel rate[b]
none	1.0	**8**	0.34
2[c]	0.79	**9**	0.85
3[c]	0.98	**10**	0.00
6[c]	1.0	**11**	0.89
7[c]	0.66		

[a] Conditions: 1 mmol of **1**, 1 mmol of added compound, 0.1 mmol of $(PPh_3)_3RuCl_2$, 310 psi of H_2 (initial), 20 mL of benzene as solvent, temp = 85 °C (±0.5 °C). [b] Rates are relative to rate of reduction of **1** alone (0.47, see Table I). [c] In these cases, the added substrate was reduced along with **1**, see Table III and discussion.

Table III. Selectivity for the Reduction of 1 in Competition with Other Reducible Substrates

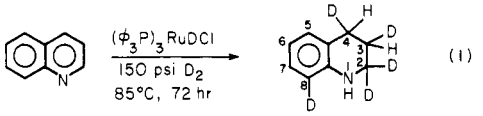
compd	rel rate in[a] separate reductions	rel rate[b] in mixture
2	8.0	11
3	33.6	42
6	11.5	43
7	5.5	8.2

[a] Values derived from data in Table I (separate reductions) by dividing the initial rate of reduction of **1** by the initial rate of reduction of the other compound. [b] Conditions: 1 mmol of **1**, 1 mmol of added compound, 0.1 mmol of $(PPh_3)_3RuCl_2$, 310 psi of H_2 (initial), 20 mL of benzene as solvent, temp = 85 °C (±0.5 °C). Figures obtained by dividing the initial rate of reduction of **1** by the initial rate of reduction of added compound.

along with 1, providing addition insight into binding effect and rates.

Binding and Selectivity in Competitive Reductions. Table III contains data derived from the experiments described in the previous two sections. The first column of rates are derived by dividing the individual reduction rate of 1 by the individual reduction rates of 2, 3, 6, and 7, respectively (data taken from Table I), to provide a ratio representing the rate of reduction of 1 relative to each other compound. The second column of rates are calculated in the same manner, except that the rate data used are for the competitive reduction of 1 in the presence of an equimolar amount of 2, 3, 6, and 7, respectively. In all four cases, the relative rate for the reduction of 1, vs. the other compounds, is greater in the mixture, indicating a selectivity toward the reduction of 1. The most dramatic example is for compound 6 (benzothiophene). Compound 1 is reduced 11.5 times faster than 6 when the reductions are carried out separately but is reduced 43 times faster than 6 when the reduction is carried out on a mixture of the two. In the second case, the more basic 1 can compete for catalyst more effectively than 6, resulting in a higher relative rate. It is interesting to note that 1 is reduced 3.5 times faster than 6 in the analogous competition experiment with $(PPh_3)_3RhH_2Cl$.[1c] This indicates a stronger binding of 6 to the rhodium complex than to the ruthenium complex and is consistent with the fact that 6 was the only compound reduced faster by rhodium than by ruthenium in the individual relative rate experiments.

Deuterium Gas Experiments. In previous studies,[1c,3,4] the substitution of deuterium gas for hydrogen gas in catalytic reductions has been found to provide useful mechanistic information. Compound 1 was reduced for 72 h at 85 °C, 10:1 substrate:catalyst ratio, providing a 100% yield of deuterated 1,2,3,4-tetrahydroquinoline. Analysis of this product by 200-MHz ^1H NMR provides the results depicted in eq 1.



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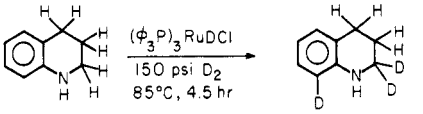
The product had 1.8 deuteriums at position 2, 1.0 deuterium each at positions 3 and 4, and 0.8 deuterium at position 8. The nitrogen was not observed to be deuterated due to the rapid exchange of this position with traces of water during workup.

When this same reduction was carried out for 150 min, to approximately 50% conversion, the deuterium substitution pattern was much the same as in the case of complete reduction. The 2-position was substituted with 1.85 deuteriums, the 3- and 4-positions had 1.0 deuterium each, and 0.2 deuterium was found at position 8. The unreduced quinoline was also observed in the NMR spectrum and showed 0.5 deuterium substitution at the 2-position.

Finally, compound 8 (1,2,3,4-tetrahydroquinoline) was reacted with deuterium and the ruthenium catalyst under the same conditions used to reduce 1. After 4.5 h the reaction product was analyzed by 200-MHz ^1H NMR to give the results in eq 2.

The 2-position was substituted with 1.8 deuteriums, and the 8-position was substituted with 0.1 deuterium. A mass spectrum was also obtained for this compound, giving m/e



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135 for the base (M − 1) peak, and indicated d_1, d_2, and d_3 products.

Reduction Mechanism. The deuterium exchange results presented above can be accounted for by several plausible intermediates, incorporated together in our proposed reduction scheme (Figure 1).

The overall reduction occurs in order $1 \rightleftharpoons A \rightleftharpoons B \rightleftharpoons C$. The first step, $1 \rightleftharpoons A$, is the necessary prior coordination of 1 to the ruthenium metal catalyst. At this stage, as we have shown in our competitive rate results, coordination can be inhibited by competititon by another coordinating substrate, slowing the overall rate of hydrogenation.

After coordination, the reversible reduction of the C–N double bond occurs, step $A \rightleftharpoons B$. It is the reversibility of this step which accounts for the incorporation of deuterium into the 2-position of the unreduced quinoline. It accounts as well for some of the exchange at the 2-position of the product. However, not all of the exchange at this position on the product can occur by this mechanism. When the reduction was carried out to 50% completion, the unreduced 1 was substituted with 0.5 deuterium at the 2-position, while the product was substituted with 1.85 deuteriums. If all the exchange had occurred through this reversible step, no more than 1.5 deuteriums would have been found at the 2-position of the product.

The next and final step in the reduction is the irreversible reduction of the 3,4 double bond. This step is shown as irreversible, since only 1.0 deuterium was found at the 3- and 4-positions on the product, and also because no 1 was ever observed being formed from 8 by dehydrogenation, under reducing conditions. However, our techniques are not sufficient to rule out a small amount of reversibility. We have found that $(PPh_3)_3RuCl_2$ will catalyze the dehydrogenation of 8 to 1 to a small extent (3%) under nitrogen in refluxing benzene, suggesting the possibility of a fully reversible pathway from 1 to 8. As well, we do not know if the reduction of the 3,4 double bond is inter- or intramolecular. It may proceed by an intramolecular addition of hydrogen from the nitrogen bound ruthenium, or, as is more likely, it may occur by an intermolecular coordination of a ruthenium to the 3,4 double bond, as with an olefin.[2a]

In order to provide more information about the complex C, a 1:1 mixture of 8 and preformed $(PPh_3)_3RuHCl$ was prepared in an NMR tube, and its 200-MHz ^1H NMR spectrum taken. All of the signals for 8 were found and were shifted from the signals of the free compound, with the relative areas of the peaks remaining the same. Thus binding to the metal center has occurred. The largest shift (2.4 ppm) occurred at the 1-position, consistent with coordination to the nitrogen. The next largest shifts were 0.2 (H-2) and 0.25 ppm (H-8), consistent with the close proximity of these positions to the nitrogen binding site.

To account for the exchange of deuterium found when starting with 8 the imine intermediate D is proposed. $(PPh_3)_3RuCl_2$ is known to be an active catalyst for alkyl amine chain scrambling and deuterium exchange at carbons adjacent to nitrogen in amines.[3,5a,b] This type of reactivity is generally explained by proposing hydrido-

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chlororuthenium–imine complexes formed by dehydrogenation of amines. Such an imine intermediate has in fact been observed by Garrou et al.[3] We are proposing that the reversible formation and reduction of the imine intermediate D accounts for the exchange of deuterium found on 8, as well as part of the exchange found on the product when reducing 1. Such an intermediate and the imine itself would be unstable both to oxidation and reduction as well as being present in only small quantities. This would explain why we have failed to observe free imine in these reactions.

It is also possible that deuterium exchange occurs through a oxidative addition and reductive elimination mechanism, rather than by a reversible dehydrogenation/hydrogenation, at the 2-carbon position. If the metal–nitrogen bond remains intact then this intermediate would be a metallaazacyclopropane (not shown in Figure 1). Such compounds have been reported by Kaesz et al.[6a,b] and have been postulated by Laine et al.[4] to explain their results with deuterium exchange reactions on tertiary alkylamines catalyzed by rhodium clusters.

One final result to be explained is the exchange of the aromatic C–H bond at the 8-position. A means for this exchange to occur is through the formation and cleavage of a four-membered cyclometalated ring, intermediate E. This complex is similar to five-membered rings prepared from 3 and osmium and ruthenium clusters by Stone.[7a,b] Loss of triphenylphosphine must occur as indicated to provide an 18-electron species after oxidative addition to the C–H bond.

The mechanism we have proposed here is somewhat similar to the hydrogenation mechanism previously proposed for $(PPh_3)_3RhH_2Cl$.[1c] Both these catalysts show the exchange behavior indicated in intermediates 1, A, B, C, and E. However, only the ruthenium catalyst will exchange deuterium at the 2-position of 8, as accounted for by intermediate D. This is consistent with the fact that the ruthenium catalyst is known to show special reactivity toward amines, as described, while the rhodium catalyst does not.

Conclusions

The complexity of the mechanism of hydrogenation of polynuclear heteroaromatics using $(PPh_3)_3RuHCl$ is apparent from our results; nevertheless several plausible reduction pathways for 1 may be inferred. The reduction must incorporate an initial reversible step (A ⇌ B) as well as a post-reduction reversible step (C ⇌ D) to account for the exchange of deuterium found at the 2-position of both reactant and product. The existence of intermediate C is indicated by NMR data, and imine intermediates such as D have been reported in similar systems.[3] The irreversibility of the reduction of the 3–4 double bond (B → C) is indicated by the presence of only one deuterium at each carbon, but could not be absolutely established. Cyclometalated intermediate E is proposed to explain the deuterium incorporation at position 8, while cyclometalated intermediates may also play a role in exchange at the 2-position.

The hydrogenation rates of the various substrates investigated depend on a variety of factors, some of which have been elucidated from competitive hydrogenation experiments. The ability of a substrate to bind to the catalyst, as determined by steric and electronic factors, is of clear importance to the overall rate of reduction. This type of information is valuable when trying to predict the reactivity of chemically complex coal liquids and shale oils.

Experimental Section

Materials and Instrumentation. The benzene (HPLC grade) was distilled from sodium benzophenone ketyl and stored under nitrogen before use. Compound 1 (Aldrich) was distilled from 4A molecular sieves, while compound 3 (Aldrich) was purified by sublimation. Compounds 2, 4, 5, 6, and 7 were analyzed by capillary column gas chromatography and found to have >99% purity (Aldrich). Dichlorotris(triphenylphosphine)ruthenium(I) was provided as a gift from Engelhard Industries. The capillary gas chromatography analyses were performed on a HP5880A instrument with a 15 m × 0.035 mm DB-5 (J&W) capillary column and flame-ionization detection with the following condition: 50–200 °C with 1.5-min initial hold at 50 °C and 10 °C/min to 200 °C with a 10-min hold at 200 °C.

The GC–MS analyses were performed on a Finnigan 4023 quadrupole mass spectrometer with a 30 m × 0.031 mm DB-5 (J&W) capillary column and temperature programmed from 45 to 300 °C at 4 °C/min.

The NMR spectrometers used for ^1H NMR spectra were homemade (R. Nunlist) 250- and 200-MHz instruments with Nicolet computers located in the Department of Chemistry, University of California, Berkeley, CA.

The kinetic apparatus (1991 ACK kinetic apparatus) was designed by us and built by Parr Instrument Co. to facilitate sampling of our reaction mixtures under the pressure and temperature conditions of the reaction.

Individual Reduction Rates. The reactions were run in a Parr 1991 ACK pressure reactor.[1c] To the 45-mL reactor cup was added 0.1 mmol (95.9 mg) of dichlorotris(triphenylphosphine)-ruthenium(II) and 1 mmol of compounds 1–7, dissolved in 20 mL of dry, deaired benzene, along with a stirring bar. The reactor was pressurized to 310 psi with hydrogen gas and placed in a stirred thermostated oil bath (85 °C ± 0.5 °C) and the temperature allowed to equilibrate (5 min typically). The starting time of the reaction was taken to be the time midway to equilibrium. The dichloro complex reacted rapidly with hydrogen to form the red-violet hydridochlorotris(triphenylphosphine)ruthenium(II) (presumed to be the active catalyst) in the presence of all substrates except 6, in which case 0.1 mmol of triethylamine was added to effect formation of the hydride. This reaction was rapid enough that no induction period was apparent on the time scale of our measurements. Typically five samples were removed from the reactor at regular intervals of 30–60 min and were analyzed by capillary gas chromatography (HP5880 instrument with 15 m × 0.035 mm DB-5 (J&W) capillary column, FID detection, programmed from 50 °C to 200 °C at 10 °C/min with a 1.5-min hold at 50 °C and a 10-min hold at 200 °C). The conversion vs. time data were plotted, and for conversions of under 20% the plots were linear, providing a pseudo-zero-order rate by least-squares analysis. At the end of a run the reaction mixture was transferred to a vial and inspected for signs of decomposition or heterogeneity. Solutions were all visibly homogeneous at the temperatures and pressures used in this work, although decomposition was occasionally observed at higher temperatures (>100 °C).

Rate of Reduction of Mixtures of 1 with Other Substrates. These rate studies were carried out in the above-mentioned reactor with 0.1 mmol (95.9 mg) of dichlorotris(triphenylphosphine)ruthenium(II), 1 mmol (118 μL) of 1, and 1 mmol of the compound being investigated, all dissolved in 20 mL of dry, deaired benzene. The reactor was pressured to 310 psi with hydrogen and placed in the oil bath at 85 °C (±0.5 °C). Data was obtained as previously described, with both the reduction of 1 as well as the reduction of the added compound, when it occurred, being followed.

Complete Reduction of 1 with Deuterium. A 0.1-mmol sample of $(PPh_3)_3RuCl_2$ and 1 mmol (118 μL) of 1 were placed in the reactor with 20 mL of dry, deaired benzene. The system was pressurized to 150 psi with deuterium gas (lower pressures used with D_2 to conserve material) and placed in the oil bath at

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85 °C (±0.5 °C). The reaction proceeded for 72 h at which time GC analysis showed 100% reduction to deuterated tetrahydroquinoline. The reaction mixture was then passed through a 10-cm Florosil column to remove the catalyst (along with traces of unreduced 1) and the solvent removed on a rotary evaporator. The sample was redissolved in $CDCl_3$ and its 200-MHz ^1H NMR spectrum taken, giving multiplets at 1.95 (H-3), 2.75 (H-4), 6.50 (H-8), 6.62 (H-5), and 7.00 ppm (H-6,7). The H-2 signal was observed at 3.25 ppm as a small peak superimposed on the broad H-1 signal (the one position is initially deuterated but exchanges D for H rapidly during workup). The areas of these peaks (normalized) were as follows: H-2, 0.18; H-3, 1.0; H-4, 1.0; H-5, 1.0; H-6,7, 2.0; H-8, 0.22. These data indicate 1.0 deuterium each at positions 3 and 4, an average of 1.8 deuteriums at position 2, and an average of 0.8 deuterium at position 8.

Partial Reduction of 1 with Deuterium. The experimental conditions were the same as those described in the previous experiment. The reaction was stopped after 150 min, at approximately 50% conversion. Hydrogen chloride gas was bubbled through the reaction mixture to precipitate the unreduced quinoline and the product tetrahydroquinoline. The reaction mixture was then extracted with 50 mL of water; the water extract was make alkaline with excess KOH and extracted with benzene. The benzene extract was dried with anhydrous sodium sulfate and the solvent removed by rotary evaporation. The resulting mixture of quinoline and tetrahydroquinoline was dissolved in $CDCl_3$ and its 200-MHz ^1H NMR spectra taken.

The 200-MHz ^1H NMR spectrum revealed signals for tetrahydroquinoline at 1.95 (H-3), 2.75 (H-4), 3.25 (H-2), 6.44 (H-8), 6.61 (H-5), and 6.97 ppm (H-6,7). The areas of these peaks (normalized) were as follows: H-2, 0.15; H-3, 1.0; H-4, 1.0; H-5, 1.0; H-6,7. 2.0; H-8, 0.80. These data indicate 1.0 deuterium each at positions 3 and 4, an average of 1.8 deuteriums at position 2, and an average of 0.2 deuterium at position 8.

The signals for quinoline, all of which were downfield of tetrahydroquinoline, were not as well resolved. Signals that could be unambiguously assigned, by decoupling, were at 7.36 (H-3), 7.53 (H-4), and 8.91 ppm (H-2). These signals were in the ratio of 1:1:0.5, indicating an average of 0.5 deuterium at position 2.

Deuteration of 8. A 0.1-mmol sample of $(PPh_3)_3RuCl_2$ and 1.0 mmol (125 μL) of 8 were placed in the reactor with 20 mL of benzene. The system was pressurized to 150 psi with deuterium gas and placed in the oil bath at 85 °C (±0.5 °C). The reaction proceeded for 270 min, followed by passing the reaction mixture through a 10-cm Florosil column to remove the catalyst, and the solvent was removed on a rotary evaporator. The sample was redissolved in $CDCl_3$ and its 200-MHz ^1H NMR spectrum taken, giving multiplets at 1.95 m (H-3), 2.75 (H-4), 3.28 (H-2), 6.49 (H-8), 6.62 (H-5), and 6.98 ppm (H-6,7). The areas of these peaks (normalized) were as follows: H-2, 0.17; H-3, 2.0; H-4, 2.0; H-5, 1.0; H-6,7, 2.0; H-8, 0.89. These data indicate an average of 1.8 deuteriums at position 2 and 0.11 deuterium at position 8. A mass spectrum was also obtained for this compound, with a base peak of m/e 135, and indicated d_1, d_2, and d_3 products.

NMR of Mixture of $(PPH_3)_3RuHCl$ and 8. A 0.80-g (0.83-mmol) sample of $(PPh_3)_3RuHCl$, which was prepared by standard methods,[8a,b] was dissolved in 0.4 mL of dry $CDCl_3$ in an NMR tube, followed by addition of 0.1 mL (0.83 mmol) of 8, while under an argon atmosphere. An immediate color change from red-violet to brown occurred upon the addition of 8, the NMR tube was warmed to 35 °C for several hours to ensure completion of any reaction. A 200-MHz ^1H NMR of this sample was obtained, giving signals for 8 at 1.91 (pentuplet, H-3), 2.73 (t, H-4), 3.25 (t, H-2), and 5.03 ppm (br, H-1). In the aromatic region signals for 8 were found at 6.53 (d, H-8), 6.63 and 6.82 (both t, H-6,7), and 6.93 ppm (d, H-5). Signals for triphenylphosphine were found in the region from 7.0 to 7.3 ppm. There were no signals observed upfield of Me_4Si.

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Reactions of Chromium Carbene Complexes with 1-Azirines. Synthesis of *N*-Vinylimidates

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Sunlight irradiation of pentacarbonyl(methoxymethylcarbene)- and pentacarbonyl(methoxyphenylcarbene)chromium(0) complexes in the presence of a number of 2-phenyl-1-azirines produced *N*-vinylimidates in fair to good yield.

Introduction

A variety of transition metals are reactive toward aryl azirines effecting ring-opening processes and producing larger ring heterocycles. Group 6 metal carbonyls dimerize 1-azirines to 1,4-pyrazines or their dihydro derivatives,[1] as does $[CpFe(CO)_2]_2$.[2] Azirines having formyl, imino, or vinyl groups undergo ring expansion reactions to form five-membered heterocycles when treated with molybdenum hexacarbonyl.[3] This same complex catalyzes the addition of dimethyl acetylenedicarboxylate to aziridines to give pyrroles.[4] Both $Co_2(CO)_8$[5] and $[Rh(CO)_2Cl]_2$[6]

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