concentrations of DBA and DPA were of the first order for at least 3 half-lives and showed no dependence on amount or type of added fluorescer. The initial dioxetane concentrations were approximately 10^{-3} M or lower to avoid complications due to induced decomposition. First-order thermolyses with an upper limit (mixing and thermal equilibration) on k_1 of approximately 5×10^{-2} s^{-1} can be studied with this instrumentation.

The relative yields of excited states produced upon dioxetane thermolysis were determined at 50 °C by variation of the concentration of appropriate fluorescer at constant dioxetane concentration (DBA/DPA method). For the calculation of excited state yields for **2**, the value of Φ_{ET} was assumed to be 0.2. The method of calculation has been discussed in detail.[2] The instrument was calibrated by setting the yield of triplet products from the thermolysis of trimethyl-1,2-dioxetane[14] (DBA method) at 0.15.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, to the Camille and Henry Dreyfus Foundation, and to the GSU reseach fund.

Registry No. **1**, 92242-01-8; **2**, 185-19-3; **3**, 92242-02-9; **4**, 92242-03-0; **5a**, 92242-04-1; **5e**, 92242-05-2; **6**, 92242-10-9; **7**, 92242-06-3; **8**, 92242-07-4; **9**, 92242-08-5; **10**, 92242-09-6.

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Homogeneous Catalytic Hydrogenation. 2. Selective Reduction of Polynuclear Heteroaromatic Compounds Catalyzed by Chlorotris(triphenylphosphine)rhodium(I)

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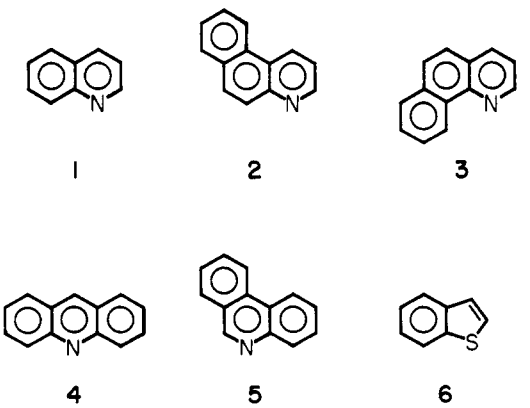
The selective reduction of polynuclear heteroaromatic nitrogen compounds such as quinoline, **1**, 5,6-benzoquinoline, **2**, 7,8-benzoquinoline, **3**, acridine, **4**, phenanthridine, and, and in one case, a sulfur heterocyclic compound, benzothiophene, **6**, with chlorotris(triphenylphosphine)rhodium(I), $(Ph_3P)_3RhCl$, provided under rather mild hydrogenation conditions the corresponding saturated nitrogen and sulfur heterocyclic analogues of the above-mentioned compounds in reasonable conversion rates and total percent yields. In addition, compounds that inhibit the initial rate of hydrogenation of **1** in the conversion to 1,2,3,4-tetrahydroquinoline, **10**, include pyridine, **7**, 3-methylpyridine, **8**, and **10** itself. These results are indicative of electronic effects in these competitive hydrogenation reactions, while 2-methylpyridine, **9**, slightly reduces the rate of hydrogenation of **1**, implicating a steric effect at the metal center. It was also observed that substrate **6**, indole, **11**, pyrrole, **12**, carbazole, **13**, thiophene, **14**, dibenzothiophene, **15**, and *p*-cresol, **16**, enhanced the initial rate of hydrogenation of **1** to **10** by an average factor of >1.5. The substitution of deuterium gas for hydrogen gas in the reduction of **1** provided information on the reversibility of the hydrogenation step, stereoselectivity in the reduction of the 3,4-double bond, and the implication of cyclometalation reactions which caused the exchange of H for D at the 8-position and possibly the 2-position. Similar deuteration data with compound **5** strengthened the concept of dehydrogenation in the hydrogenation step and in fact provided independent evidence for the facile dehydrogenation of 1,9,9,10-tetradeuterio-9,10-dihydrophenanthridine, **19**, catalyzed by $(Ph_3P)_3RhCl$. ^1H NMR and IR experiments also verify some of the postulated mechanistic aspects of these selective hydrogenation reactions.

Introduction

Recently, we discovered that the nitrogen heterocyclic ring incorporated in polynuclear heteroaromatic nitrogen compounds can be regioselectively reduced under a variety of homogeneous hydrogenation conditions.[1a,b] These results are important, since they have possible implications for the future synthetic fuel industry with regard to coal liquefaction and the upgrading of coal liquids and shale oils as well as the ultimate removal of nitrogen from these synthetic fuels.

In our quest for catalysts that could perform these reductions under rather mild conditions, we have discovered that chlorotris(triphenylphosphine)rhodium(I), $(Ph_3P)_3RhCl$, can selectively reduce the heterocyclic ring in polynuclear heteroaromatic nitrogen and sulfur model synthetic fuel compounds at reasonable initial rates and total percent yields.

Chart I. Model Synthetic Fuel Compounds Used in Hydrogenation Reactions with $(Ph_3P)_3RhCl$



Although $(Ph_3P)_3RhCl$ has been one of the most extensively studied homogeneous hydrogenation catalysts known,[2a-f] to our knowledge, this is the first reported use

(1) (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.

0022-3263/84/1949-4500$01.50/0

Scheme I. Plausible Rhodium Complexes as Intermediates in the Catalytic Hydrogenation of Quinoline, 1

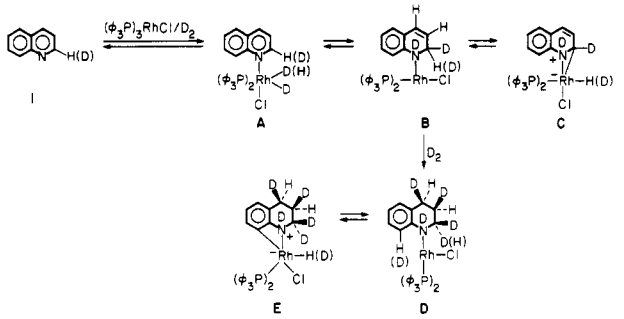


Table I. Relative Rates of Reduction of Compounds 1–6 under Hydrogenation Conditions with $(Ph_3P)_3RhCl$ as Catalyst[a]

substrate	product[b]	rate,[c] %/min	rel rate[d]
1	1,2,3,4-tetrahydroquinoline	0.079	1.0
2	1,2,3,4-tetrahydro-5,6-benzoquinoline	0.03	0.38
3	1,2,3,4-tetrahydro-7,8-benzoquinoline	0.013	0.16
4	9,10-dihydroacridine[e]	0.21	2.7
5	9,10-dihydrophenanthridine	>6	>76
6	2,3-dihydrobenzothiophene	0.12	1.5

[a] The solvent used was benzene and the substrate to metal ratio was 10:1. The partial pressure of hydrogen was 310 psi and the temperature was 85 °C. [b] Analysis by capillary gas chromatography and GC–EIMS (see Experimental Section). [c] Pseudo-zero-order rate that was followed to ~25% conversion (see Experimental Section for details). [d] The individual rates are relative to quinoline which was set to 1.0; i.e., each substrate rate was divided by 0.079%/min to obtain a relative rate. [e] Another product, 1,2,3,4-tetrahydroacridine (GC–EIMS), was also formed at a rate of 0.12%/min (relative rate 1.5) and represents 36% of total product (64% dihydroacridine).

of this catalyst for the selective hydrogenation of the types of model synthetic fuel compounds shown in Chart I under homogeneous conditions.[3] Additionally, we will demonstrate the usefulness of deuterium gas, in place of hydrogen gas, for understanding the various mechanisms involved in the reduction of polynuclear heteroaromatic compounds, including reversibility in the hydrogenation of the carbon–nitrogen double bond, i.e., dehydrogenation, as well as the implication of a cyclometalation reaction in the exchange of hydrogen for deuterium in the aromatic ring that is in proximity to the heterocyclic ring and the position α to the nitrogen atom. Furthermore, we have used 200-MHz ^1H NMR data as well as IR data to ascertain binding of quinoline to the preformed rhodium hydride, $(Ph_3P)_3RhClH_2$, that further corroborates an important mechanistic aspect in our proposed Scheme I. We have also attempted to define what potential inhibitory and enhancement effects others model synthetic fuel constituents would have on the initial rate of hydrogenation using compound 1 for these studies.

Table II. Selectivity Rates in the Reduction of 1 with Substrates 2, 3, and 6

added substrate	rel selectivity rate[a]
2	7.3
3	32
6	3.5

[a] Relative rates were obtained by dividing the quinoline initial rate by the substrate initial rate in a 1:1 mixture of reactants at 85 °C, 310 psi H_2 partial pressure (initial) at a substrate to catalyst ratio equal to 10.

Table III. Relative Rates of Hydrogenation of Compound 1 in the Presence of Other Added Substrates

added substrate[a]	rel hydrogenation rates	added substrate[a]	rel hydrogenation rates
none	1.0	12	1.5
7	0.00	13	1.5
8	0.004	14	1.5
9	0.047	15	1.8
6	1.5	16	2.5
11	1.5		

[a] 1 (1 mmol), 1 mmol of added substrate, and 0.1 mmol of $(Ph_3P)_3RhCl$ at 85 (±1) °C and 310 psi H_2 (initial) (see Experimental Section for details regarding calculations of relative rates).

Results and Discussion

Selective Hydrogenation. Table I contains the initial and relative rate data for the selective reduction of compounds 1–5 for the nitrogen heterocyclic ring, and in one case, 6, a sulfur heterocyclic ring, catalyzed by $(Ph_3P)_3RhCl$ under a standard set of conditions. We made no effort to study the variation of substrate to metal ratio but found that turnover numbers per metal atom ranged from ~35 to ~0.1 per hour with the 10:1 substrate/metal ratio used. We also varied the stirring rate and found no effect on the initial rate of reduction of substrate 1. The order of individual relative rates was shown to be **5** ≫ **4** > **6** > **1** > **2** > **3** reflecting both steric and electronic effects as contributing factors in these selective reductions. In only one case (4) did we see a change in the regioselectivity. We found that at the 10:1 substrate to catalyst ratio a substantial amount of 1,2,3,4-tetrahydroacridine (36%) was formed along with 9,10-dihydroacridine, although at half the initial rate of the latter product.

Several substrates, **2**, **3**, and **6**, were competed with **1** in order to determine a selectivity for various nitrogen and sulfur ring systems. Table II demonstrates the high selectivity for quinoline in the presence of **2**, **3**, or **6**. This selectivity is exemplified by the result of **6** and **1**, individually and in competition, with the former situation giving approximately similar initial rates and the latter providing a 3.5-fold relative selectivity rate increase with a preference for **1**. These results parallel those obtained by Candlin and Oldham[2e] in the hydrogenation of olefins and acetylenes with $(Ph_3P)_3RhCl$ as a catalyst.

While total yields for all substrates were not studied, we did, however, show that **1** was quantitatively converted to **10** in approximately 60 h. Compound **5** could be quantitatively reduced in less than 1 h and reflects the large initial rate differences between the two substrates. Finally, total conversion times for the other substrates we did not study, **2**, **3**, **4**, and **6**, can be easily estimated from the initial rate data.

Inhibition and Enhancement Rate Studies. As stated, we wanted to learn about other potential synthetic

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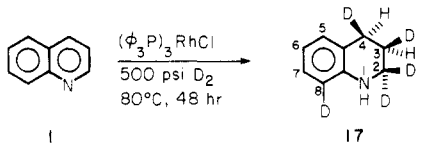
(3) A preliminary account of the work was presented at the 3rd International Symposium on Homogeneous Catalysis, Milano, Italy, Aug 30 – Sept 3, 1982, Abstr C33, p 105, the Pacific Conference on Chemistry and Spectroscopy, San Francisco, CA, Oct 27–29, 1983, Abstr 208, p 96, and the New York Academy of Sciences Conference on Catalytic Transition Metal Hydrides, New York, NY, Nov 15–17, 1982, Abstr 24. Also see: Lynch, T. J.; Banah M.; McDougall, M.; Kaesz, H. D.; Porter, C. R. *J. Mol. Catal.* **1982**, *17*, 109.

fuel compounds that might inhibit or enhance the initial rate of these hydrogenation reactions. Quinoline, **1**, was chosen as the model compound, and interestingly we found that the initial rate of hydrogenation was totally quenched by pyridine, **7**, and 3-methylpyridine, **8**,[4] (1:1 molar ratio of **7** and **8** to **1**). In addition, 2-methylpyridine, **9**, slightly retarded the rate as did the product 1,2,3,4-tetrahydroquinoline, **10**. However, the initial rate of hydrogenation of **1** was enhanced by benzothiophene, **6**, indole, **11**, pyrrole, **12**, carbazole, **13**, thiophene, **14**, dibenzothiophene, **15**, and *p*-cresol, **16**, by an average factor of greater than 1.5 (see Table III).

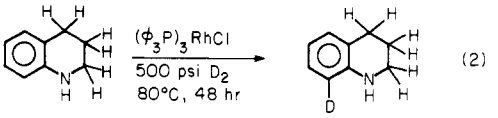
It appears that competitive binding of the added substrates, **7–10**, to the rhodium metal center, is a highly critical parameter that encompasses both steric and electronic effects. For example, **7** (pk_b 8.42) and **10** ($pk_b \sim$ 9.38) are stronger bases than **1** (pk_b 9.52) with **7** quenching and **10** retarding the rate of hydrogenation of **1**. It is interesting to note that **7** and **8** quench, but 2-methylpyridine, **9**, (pk_b 8.03) slightly retards the hydrogenation rate of **1**, and this clearly must be a consequence of a steric effect in the competitive binding of **9** at the rhodium metal center.[5,2d] At this time, we have no definitive reason why compounds **6** and **11–16** enhance the initial hydrogenation rate of **1**, other than the possibility of assisting in the dissociation of triphenylphosphine from the rhodium metal center and thus permitting a more facile pathway for quinoline, **1**, coordination to rhodium.[2d,e] Another viable possibility is that these compounds act as ligands to stabilize an electron deficient rhodium metal center.[2e]

Deuterium Gas Experiments. The substitution of deuterium gas (D_2) for hydrogen gas (H_2) has been shown to be helpful in elucidating mechanisms and stereochemistry in homogeneous hydrogenation reactions.[2c,d] The reaction of **1** with D_2 gas (500 psi) and $(Ph_3P)_3RhCl$ at 80 °C for 48 h (10:1 substrate to metal ratio) followed by analysis by gas chromatography–mass spectrometry (GC–MS) and 400-MHz ^1H nuclear magnetic resonance spectroscopy (NMR) provided the results depicted in eq 1.



1 17 (1)

The reaction product, **17**, had 1.6 D at position 2, 1.0 D each at positions 3 and 4, and 0.7 D at position 8. The deuterium on the nitrogen atom (N–D) gets readily exchanged due to traces of water in the sample preparation procedures for both GC–EIMS and NMR analysis. The high-field ^1H NMR spectrum at 400 MHz also provided information concerning the stereochemistry of deuteriums at positions 3 and 4. The line width for multiplets at 1.90 ppm, assigned to H-3, and 2.73 ppm, assigned to H-4, were both 12.1 Hz, clearly, indicative of a cis configuration[6] for the hydrogens on carbons 3 and 4[2a,c,d] (eq 1), i.e., a 3,4-cis deuteration of the 3,4-double bond. More importantly, when compound **10** was subjected to the same deuteration condition as shown in eq 1, no exchange of the saturated nitrogen ring hydrogens was observed by 250-MHz ^1H NMR spectroscopy. However, exchange of the aromatic hydrogen (position 8) that is β to the nitrogen readily occurs with incorporation of 0.7 D as evidenced by the decrease in the area of the doublet at 6.42 ppm, assigned to the proton on C-8 of compound **18** (eq 2).



10 18 (2)

The experiment defined in eq 1 also showed by GC–EIMS that the remaining quinoline (~2%) was monodeuterated [$M^{+\cdot}$, *m/e* 130 (100% RA)]. Furthermore, if the reduction of **1** with deuterium gas (eq 1) was allowed to proceed to only a 50% conversion of the deuterated tetrahydroquinoline, the remaining isolated **1** had deuterium incorporation exclusively at C-2 as evidenced by its 250-MHz ^1H NMR spectrum (8.9 ppm, doublet of doublets, 0.3 D). A GC–EIMS analysis showed a *m/e* 130 ion for quinoline-2-*d*, but in approximately 10% relative abundance. This strongly implies that the second deuterium incorporation at C-2 (i.e., **17**) comes predominately, but not exclusively, by deuteration of quinoline-2-*d*. This is substantiated by GC–EIMS and NMR analyses of the deuterated tetrahydroquinoline formed in the incomplete reduction (~50%), which indicates mainly 1,2,3,4-tetrahydroquinoline-d_3 rather than the d_4 compounds formed in the quantitative conversion, i.e., one deuterium at C-2 rather than 1.6 D.

Plausible Mechanistic Pathways in the Hydrogenation of 1. The above-stated deuterium results can be accommodated by several plausible rhodium intermediates as shown in Scheme I. Intermediate B can occur via intramolecular addition of deuterium (or hydrogen) to the carbon–nitrogen double bond via intermediate A. Exchange of the hydrogen on the carbon that is α to nitrogen and allylic to the 3,4-double bond can occur by two conceivable pathways: (1) oxidative addition (cyclometallation) to give C or the apparently more predominate mechanism (2) where intermediate B can exchange hydrogen for deuterium by being in equilibrium with A and quinoline-2-*d*. The latter compound can then recycle to B. Reduction of the 3,4-double bond must have a comparable rate to the dehydrogenation step, i.e., B $\rightleftarrows$ A $\rightleftarrows$ 1 as evidenced by the partial deuterium incorporation at position 2 in compound **1**, but its reduction effectively eliminates any exchange at position 2. We, however, do not know whether the stereospecific reduction of the 3,4-double bond is intermolecular or intramolecular. It could conceivably occur via the complexation of the 3,4-double bond to another rhodium metal center (intermolecular) as is known for olefin reduction,[2a] but Dreiding models provide some insight into a plausible intramolecular addition of hydrogen from the rhodium binding to the nitrogen atom. Further studies to clarify this point are needed. The cyclometalation reaction (oxidative addition) at position 8 (intermediate E) will allow exchange of that aromatic hydrogen.

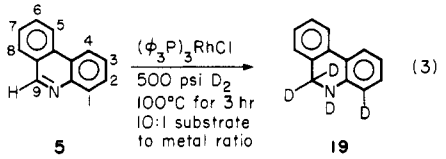
In order to provide information on the binding, 1 $\rightleftarrows$ A, we did several 200-MHz ^1H NMR experiments *and found interestingly that quinoline did indeed bind to the rhodium metal center, however, only after the rhodium hydride was preformed.* Thus, **1** did not appear to bind to $(Ph_3P)_3RhCl$ in the absence of hydrogen. These important NMR observations, which show downfield chemical shifts of 0.13 ppm for the 2-proton and 0.09 ppm for the 8-proton upon addition of **1** to presumably $(Ph_3P)_3RhClH_2$,[8] clearly

(4) Several examples of inhibition of olefin hydrogenation by pyridine and other coordinating substrates have been reported: See ref 2a and 2e.
(5) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.
(6) Fish, R. H.; Broline, B. M. *J. Organometal. Chem.* **1978**, *159*, 255.
(7) For several examples of cis addition of deuterium to olefins with $(Ph_3P)_3RhCl$ see: St. Jacques, M.; Prod'homme, R. *Tetrahedron Lett.* **1970**, 4833. Slack, D.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1974**, 701. Gaghaire, A.; Voltero, P. *Bull. Soc. Chem. Fr.* **1970**, 164. Hussey, A. S.; Takeuchi, Y. *J. Org. Chem.* **1970**, *35*, 643 and ref 2d, pp 220–226, and 2a.

indicate the "hydride route"[2a-f] as being operative in these selective reduction reactions. The NMR spectra also establishes the presence of Rh–H with signals at –8.8, –9.2 and –16.9 ppm (multiplets).[9] Additionally, we have done IR studies to further confirm the binding with Rh–H stretching frequencies at 2110 (sh) and 2040 cm^{-1} for the rhodium hydride that shift to 2122 and 2065 cm^{-1} upon addition of **1**, and this result is consistent with the findings of Yoshida et al.[9] for bipyridine–rhodium(I) hydride complexes.

Although at this stage in our studies, we do not have definitive data for all intermediates we do know that intermediates C and E (Scheme I) have some precedents in the literature. For example, Stone et al.[10a,b] reported on several orthometalation reactions with Os and Ru carbonyls and compound **3** (Chart I) to provide the five-membered ring equivalent to intermediate E (Scheme I), and Yin and Deeming[11] have observed metalation of carbon atoms α to a nitrogen atom in several aromatic imine (PhC=N—) derivatives. Kaesz et al.[12a,b] have reported on a cyclometalated product, which had a metalaazacyclopropane structure, as established by single-crystal X-ray crystallography, and represents a model for intermediate C (Scheme I). Laine et al. have also postulated these metalaazacyclopropane intermediates in deuterium exchange reactions with trialkylamine compounds as substrates and rhodium cluster carbonyls as catalysts.[13] Moreover, the homogeneous catalytic activation of C–H bonds for hydrogen–deuterium exchange has been reviewed extensively by Parshall[14] and Dehand and Pfeiffer.[15]

Dehydrogenation Step in Hydrogenation of 5. In further experiments to provide more support for the dehydrogenation sequence, B $\rightleftarrows$ A $\rightleftarrows$ 1 (Scheme I), we studied the deuteration of compound **5** and found, by GC–EIMS (*m/e* 184, 32% RA) and 250-MHz ^1H NMR spectroscopy, two deuteriums at position 9 (absence of an NMR signal at 4.4 ppm, singlet) and approximately 0.3 D at position 1 (7.66 ppm, doublet) for compound **19**. Again, as in the deuterium gas experiments with **1**, the N–D group gets exchanged to some extent upon workup (eq 3). This



5 19 (3)

results supports the fact that activation of hydrogen on the carbon atom α to the nitrogen atom is a prerequisite for exchange, i.e., benzylic or allylic carbon positions. Furthermore, reaction of compound **19** with catalytic amounts of $(Ph_3P)_3RhCl$ readily provided the dehydrogenated product (25 °C, 1 h), phenanthridine-d_2, with deuteriums at the 9- and 1-positions as determined by GC–EIMS and 250-MHz ^1H NMR spectroscopy (absence of a singlet at 9.3 ppm assigned to the proton on carbon 9).

Clearly, from the above-stated results, the dehydrogenation step by a plausible intermediate such as B (Scheme I) to deuterated **1**, via intermediate A, definitely occurs under the hydrogenation conditions.[15] Obviously, the isolation and spectroscopic studies of complexes such as B–E (Scheme I) would help to understand these rather complicated hydrogenation reactions and such studies are underway to clarify these points.

Conclusions

Our results show the mechanistic complexities in the hydrogenation of polynuclear heteroaromatic nitrogen compounds; but clearly, several plausible reaction pathways have been elucidated. Namely, the reduction of the carbon–nitrogen double bond, i.e., **1**, **2**, **3**, and **5**, is the initial product of hydrogen transfer from rhodium to the complexed substrate. This is followed by a reversible dehydrogenation step, which was proven via deuterium experiments with **1** and **5**, that must have a comparable rate to the stereospecific reduction of the 3,4-double bond in compounds such as **1–3**. However, in the hydrogenation of compounds such as **5** the metal-catalyzed dehydrogenation step must be extremely facile due to the benzilic nature of the methylene group α to the nitrogen atom. In addition, cyclometalation reactions play a role in not only the exchange of aromatic hydrogens[14,15] but conceivably also in the exchange of hydrogens on the carbon α to the nitrogen.

It was also observed that both steric and electronic effects control the initial hydrogenation rates of our substrates in the presence of compounds that can competitively bind to the rhodium metal center as well as those substrates that enhance initial rates of hydrogenation. This type of data will be highly useful in attempting to define the reactivity and selectivity of these model coal compounds in very complex matricies such as coal liquids and shale oils.

Finally, we have also carried out similar hydrogenation experiments with substrates **1–6** by using the heterogenized form of $(Ph_3P)_3RhCl$ bonded to phosphinated polystyrene–divinylbenzene (2% or 20% crosslinked, 1-2% loading) and have found the same regioselectivity and excellent product conversions we observed in this present study.[17] Subsequent manuscripts will also detail catalytic-transfer hydrogenation results that exploit the above-mentioned metal-catalyzed dehydrogenation of 9,10-dihydrophenanthridine.[18]

Experimental Section

Materials and Instrumentation. The benzene (HPLC grade) was distilled from sodium benzophenone ketal 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**, and **6** were analyzed by capillary column gas chromatography and found to have >99% purity (Aldrich). The chlorotris(triphenylphosphine)rhodium (I) was either purchased from Alfa Inorganics or Strem Chemical or was provided as a gift from Englehard 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

(8) Meakin, P.; Jesson, J. P.; Tolman, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 3240.
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(14) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113.
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(16) For a review of isomerization (dehydrogenation) of olefins under H_2 or D_2 conditions with Rhodium catalysts see ref 2d, Chapter XI, p 198.
(17) Fish, R. H.; Thormodsen, A. D.; Heinemann, H. *J. Mol. Catal.*, in press.
(18) Fish, R. H.; Thormodsen, A. D.; Ausban, A., manuscript in preparation.

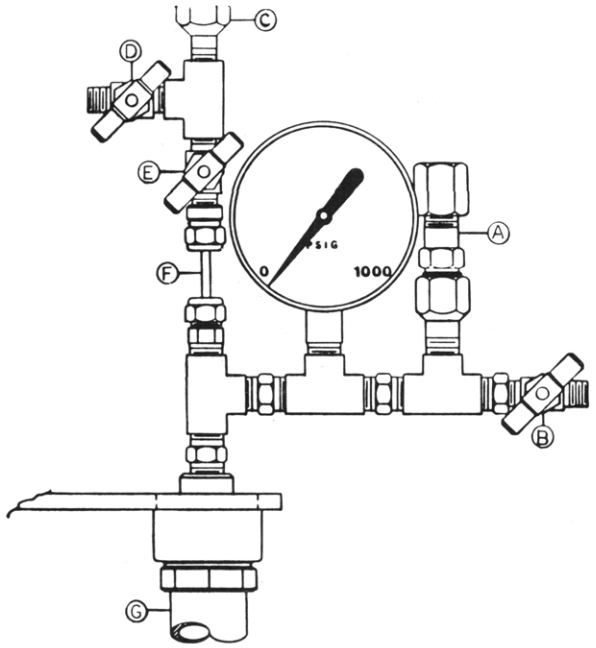

Figure 1. Schematic diagram of the Parr kinetic apparatus for use in hydrogenation rate studies: (A) rupture disk; (B) outlet valve; (C) septum port; (D) inlet valve; (E) dip tube valve; (F) dip tube; (G) reactor cup.

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 45–300 °C at 4 °C/min.

The NMR spectrometers used for ^{1}H NMR spectra were homemade (R. Nunlist) 250-MHz and 200-MHz instruments with Nicolet computers located in the Department of Chemistry, University of California, Berkeley, CA, and a 400-MHz Bruker NMR spectrometer located at the NBS-NML laboratory Gaithersburg, MD.

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. Figure 1 shows a schematic of the apparatus setup used to follow the initial rates of our hydrogenation reactions.

Procedure for Following Rates of Hydrogenation of Compounds 1–6 with Chlorotris(triphenylphosphine)rhodium(I). The 1991 ACK kinetic apparatus in Figure 1 can be used as follows in a typical rate experiment. To the 45-mL reactor cup was added 0.1 mmol (92.5 mg) of chlorotris(triphenylphosphine)rhodium(I) and 1 mmol of compound **1–6** dissolved in 20 mL of benzene along with a stirring bar. The reactor cup, G (Figure 1), was attached to the sample head. The hydrogen gas line was attached to valve D and with valves E and B open; the system was purged with hydrogen gas for 60 s. The reactor was pressured with H_2 gas to 310 psi (valve B closed), the cup (G) placed in a thermostatted oil bath (85 ± 1.0 °C), and the temperature allowed to equilibrate for 5 min. At regular intervals samples were removed for capillary gas chromatography analysis. For ease of sampling we followed a procedure in which valve E was opened and a sample was removed by previously inserting a syringe into the septum (C) with the barrel cut in half. Thus, approximately 100 μL of sample flowed into the cut off barrel to be readily sampled for GC analysis via a 10 μL syringe. After removal of the cut off syringe from the septum, valve D is opened along with valve E (cautiously) and the hydrogen gas forces the liquid back into the reactor. The pressure in the reactor can be readjusted to its initial reading by closing valve E and bleeding H_2 gas out of valve B. The entire sampling operation can be conveniently carried out in 1.5 min and at intervals of 30 min to 1 h depending on the rate of the reaction and GC analysis time. In this manner, five data points were obtained and analyzed graphically on an Apple II Plus computer with plotting routines, while linear least-squares analysis of the plots of percent conversion vs. time provided slopes that gave pseudo-zero-order rates (%/min) at low conversions (linear for conversion up to 25%).

From the slope of the plots of % conversion vs. time, we obtained an initial rate of hydrogenation (% conversion/min), which was used to calculate the relative rates (compound **1** set to 1.0) by simply dividing the quinoline rate into the rates of the other substrates studied.

Inhibition Rate Studies. The inhibition rate studies were carried out in the above-mentioned reactor with 92.5 mg (0.1 mmol) of $(Ph_3P)_3RhCl$, 118 μL (1 mmol) of quinoline, **1**, and 1 mmol of the compound being studied as the inhibitor or enhancer of the initial hydrogenation rate (Table III) of **1** all dissolved in 20 mL of benzene. The reactor was pressurized to 310 psi H_2 and heated to 85 ±1 °C. Five data points, as before, were plotted and analyzed by linear least-square analysis (% conversion vs. time).

Deuteration of Compound 1. $(Ph_3P)_3RhCl$ (92 mg, 0.1 mmol) and 118 μL (1 mmol) of compound **1** dissolved in 20 mL of benzene was placed in a Parr minireactor (45 mL). The minireactor was pressurized to 500 psi with deuterium gas and heated at 80 °C in a constant temperature oil bath for 10 h. The reaction mixture was analyzed by capillary column gas chromatography and showed 100% conversion to deuterated tetrahydroquinoline. The reaction mixture was filtered through a 10-cm Florisil column to remove the catalyst and the solvent was removed on a rotary evaporator. The capillary column GC–EIMS results provided evidence for tetrahydroquinoline-d_4, m/e 137, while the 400-MHz ^{1}H NMR spectrum (benzene-d_6) gave multiplets at 1.90 (H-3), 2.73 (H-4), 3.24 (H-2), 6.42 (H-8), 6.55 (H-5), and 6.93 (H-6, H-7) ppm with areas of 1:1:0.4:0.6:1:2, respectively, clearly defining the positions of deuteration.

A small amount (~2%) of compound **1** that remained after reduction was also analyzed by GC–EIMS to show m/e 130 (100% RA) indicative of deuterium incorporation in the starting material. To verify this result, we ran the deuteration of **1** to partial completion (~50% THQ) and after workup by filtering through a 10-cm Florisil column and eluting with benzene–acetone (9:1), quinoline-2-d_1 was found by 250-MHz ^{1}H NMR (8.9 ppm, d, d, 0.3 D) and GC–EIMS (m/e 130 ~10% RA).

Deuteration of Compound 10. $(Ph_3P)_3RhCl$ (92.5 mg, 0.1 mmol) and 120 μL (1 mmol) of 1,2,3,4-tetrahydroquinoline, **10**, dissolved in 20 mL of benzene was placed in the 45-mL Parr minireactor. The reactor was pressurized to 500 psi with D_2 gas and heated at 80 °C for 20 h. The catalyst was removed by passing the reaction mixture through a 10-cm column of Florisil and the benzene was removed by rotary evaporation. The GC–EIMS analysis showed the m/e 134 ion (44% RA) indicative of 1,2,3,4-tetrahydroquinoline-d_1. The 250-MHz ^{1}H NMR spectrum ($CDCl_3$, Me_4Si) provided clear evidence for deuterium exchange at C8 (6.42 ppm, doublet, ~0.7 D) and no deuterium incorporation at carbons C_1–C_4.

Deuteration of Compound 5. $(Ph_3P)_3RhCl$ (92.5 mg, 0.1 mmol) and 100 mg (0.56 mmol) of **5** dissolved in 20 mL of purified benzene was placed in a Parr minireactor (45 mL). The reactor was pressurized to 350 psi with deuterium gas and heated at 80 °C for 2 h. After reaction, the catalyst was removed by passing the reaction mixture through a column of Florisil (10 cm) and the benzene removed by rotary evaporation.

A ^{1}H 250-MHz NMR spectrum of the product, **19**, provided unequivocal evidence for total deuteration at C-2 with the absence of the singlet for the methylene group α to the nitrogen atom at 4.4 ppm. The doublet (J_{ortho} = 4.7 Hz, J_{meta} = 2 Hz) at 7.66 ppm assigned to C-1 was reduced in area by about 30% (0.3 D). A GC–EIMS analysis of **19** indicated dihydrophenanthridine-d_3 with m/e 184 (32% RA).

Dehydrogenation of Dihydrophenanthridine-d_3 with Chlorotris(triphenylphosphine)rhodium(I). Dihydrophenanthridine-d_3 (1 mmol) and $(Ph_3P)_3RhCl$ (0.1 mmol) were dissolved in 20 mL of benzene and allowed to remain at room temperature (25 °C) for 48 h. The catalyst was removed via Florisil chromatography and a 250-MHz ^{1}H NMR spectrum revealed phenanthridine-d_2 with the pertinent absence of a signal at 9.3 ppm (singlet) for the proton at carbon 9. GC analysis also showed only phenanthridine and no dihydrophenanthridine and GC–EIMS analysis provided the m/e 181 (63% RA) and 182 (10%) indicative of d_1 and d_2 compounds.

NMR and IR Binding Experiments of 1 with $(Ph_3P)_3RhClH_2$. NMR Experiment. In a flask was placed 18.4 mg (0.02 mmol) of $(Ph_3P)_3RhCl$ dissolved in 4 mL of deoxygenated benzene-d_6. To this solution was added hydrogen gas, via bubbling, for about 1 h with the solution turning a golden yellow. Compound 1 (2.4 μL, 0.02 mmol) was then added to the rhodium hydride, $(Ph_3P)_3RhClH_2$, and allowed to stir for 20 min. An aliquot was then placed in an NMR tube under nitrogen. The ^1H NMR spectra were taken on a 200-MHz FT instrument and provided downfield shifts at 8.92 (d, C-2) and 8.42 ppm (d, C-8) of 0.13 and 0.09 ppm, respectively, from the uncomplexed 1. The high-field spectra shows Rh–H signals at −8.8, −9.2, and −16.9 ppm.

IR Experiment. In a flask was placed 200 mg of $(Ph_3P)_3RhCl$ in 5-mL of dry tetrahydrofuran. Hydrogen gas was bubbled in for 1 h and the IR spectra of an aliquot was run in a solution cell (0.2 mm, NaCl windows) with a Perkin-Elmer 598 Grating IR spectrometer. This provided Rh–H stretching frequencies at 2110 (sh) and 2040 (b) cm^{-1}. Addition of 500 μL of 1 to the reaction mixture and then taking a sample for IR analysis provided Rh–H stretching frequencies at 2122 (sh) and 2065 (b) cm^{-1} consistent with a binding of 1 to the rhodium metal center, i.e., a shift of ~25 cm^{-1} would be expected from other complexes of rhodium hydrides with nitrogen heterocyclic ligands.[9]

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Evidence for Single Electron Transfer in the Reduction of Organic Halides by Lithium Triethylborohydride

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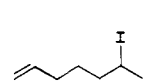
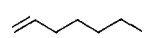
Product studies involving the reduction of cyclizable alkyl iodides and bromides, trapping of intermediate radicals by dicyclohexylphosphine, and direct EPR observation of radicals have been used to detect the occurrence of a single electron transfer pathway in the reduction of these halides by lithium triethylborohydride.

One of the most important synthetic methods in organic chemistry involves the hydrogenolysis of carbon–halogen bonds.[1] A number of different complex metal hydrides can be used for the reduction of organic halides;[2] however, the most powerful reducing agent is lithium triethylborohydride ($LiEt_3BH$), which rapidly reduces primary, secondary, allylic, benzylic, and neopentyl halides to the corresponding hydrocarbons.[3] In a recent detailed mechanistic study, Brown and Krishnamurthy proposed a S_N2 mechanistic pathway to describe the reduction of alkyl halides by $LiEt_3BH$.[4] On the other hand, we recently reported that lithium aluminum hydride ($LiAlH_4$) and aluminum hydride (AlH_3) react with organic halides (particularly iodides) in part or completely by a single electron transfer (SET) pathway.[5,6] Since the above hydrides react with alkyl bromides and iodides by SET, we were anxious to determine if $LiEt_3BH$ also reacts by a similar pathway. In this connection the following studies were carried out: (1) spectroscopic observation of a stable radical intermediate by EPR, (2) use of new alkyl halides containing a cyclizable radical probe, and (3) radical trapping reactions with dicyclohexylphosphine (DCPH).[7] The results are presented herein.

Table I. Rate-Profile Study of 0.1 M 6-Iodo-1-heptene (1) with 0.2 M $LiEt_3BH$ in THF at 0 °C

		% yield			
expt	time, min				
1	10	64	1.8	35	<1
	30	50	2.8	50	<1
	60	42	1.5	55	1.2
	120	14	1.4	87	1.5
	240	6	<1	97	2.2
2	360	5	0	94	4.3[a] (4.3)[b]

[a] This reaction was carried out from −78 °C to room temperature. [b] Cis/trans ratio of 1,2-dimethylcyclopentane.

Results and Discussion

EPR Study. When $LiEt_3BH$ (0.02 M) and trityl bromide (0.02 M) were combined in THF at room temperature, a yellow color appeared immediately and the solution was shown to be EPR active. The EPR spectrum was well resolved and was identical with the EPR spectrum of the trityl radical $[Ph_3C\cdot]$[8] reported earlier[8] (eq 1). This

$$Ph_3CBr + LiEt_3BH \rightarrow [Ph_3CBr]^{-}\cdot \rightarrow Ph_3C\cdot + Br^- \quad (1)$$

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