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Hydrogenation of Anthracene and Nitrogen Heterocycles Catalyzed by Iron Pentacarbonyl under Water–Gas Shift Conditions

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Iron pentacarbonyl in the presence of H_2O, CO, base and a phase-transfer agent catalyzes the reduction of quinoline regiospecifically in the nitrogen-containing ring at temperatures between 150 and 300 °C. The best yield (87 turnovers) is obtained in the presence of 18-crown-6 ether as phase-transfer agent. Anthracene is reduced to 9,10-dihydroanthracene by the same system, which becomes catalytic (17 turnovers) with the addition of bipyridine or terpyridine and tetra-*n*-butylammonium iodide as phase-transfer agent. The phenanthrolines (4,7 or 1,10) are also regiospecifically reduced in one of the nitrogen-containing rings (71% or 50% yield, respectively, without optimization). With 9,10-dimethylanthracene, nearly equal amounts of both *cis*- and *trans*-9,10-dihydro-9,10-dimethylanthracene are obtained. Aromatic coal constituents such as pyrene, chrysene, or dibenzothiophene are not reduced under these conditions; a reduction potential >−2.0 V seems to be required to achieve hydrogenation in this system. An electron-transfer process is indicated.

Iron pentacarbonyl is an affordable organometallic reagent[2] that is capable of desulfurizing coal.[3] It has also been used as a constituent in coal liquefaction[4] under water–gas shift (WGS) conditions,[5] i.e., CO, H_2O, and base. Earlier studies had indicated that anthracene, representing an important constituent in coal,[4a] could be hydrogenated stoichiometrically by $[Et_4N][HFe(CO)_4]$.[6] In the case of acenaphthene, hydrogenation could be achieved catalytically by $[Et_4N][HFe(CO)_4]$ under WGS conditions.[6]

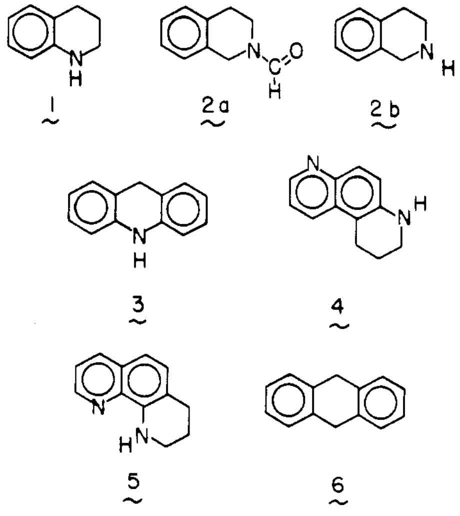
We undertook the present studies to examine the reactivity of various aromatic constituents in the $Fe(CO)_5$-modified coal liquefaction. We were led to modifications of the catalyst system, principally in the addition of phase-transfer catalysts, which markedly improved hydrogenation of anthracene and quinoline; our best conditions are summarized at the end of the discussion below. Such hydrogenations have been achieved both under heterogeneous[7] or homogeneous[8] conditions but heretofore not with iron pentacarbonyl; the synthetic utility of this reagent in organic synthesis is thus extended.[9] This work parallels studies of the action of $Co_2(CO)_8$[8c] or other transition-metal complexes[8d] on model coal compounds. A preliminary communication of our work has appeared.[10]

Table I. Reductions with $Fe(CO)_5$[a]

substrate	[sub]/[cat]	temp, °C	product	turnover
quinoline	55	150	1	37
	55	300	1	18
isoquinoline	55	150	2a	22
	55	300	2a 2b	14 21
acridine	28	150	3	24
4,7-Phen[b]	2	150	4	1.4
1,10-Phen[c]	2	150	5	1.0
anthracene	2	150	6	0.23
		300	6	0.32

[a] See Experimental Section for complete reaction conditions. [b] 4,7-Phenanthroline. [c] 1,10-Phenanthroline.

Chart I. Products from Nitrogen Heterocycles and Anthracene when Treated with $Fe(CO)_5$ under Water–Gas Shift Conditions



Results

Hydrogenations and Formylation. Products and yields from the treatment of several nitrogen heterocycles or anthracene with $Fe(CO)_5$ under WGS conditions are listed in Table I. Product structures are illustrated in Chart I. Conditions were selected to optimize either the WGS reaction at 150 °C[5] or coal liquefaction at 300 °C.[4a] Control experiments demonstrate that among all the

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[1] (a) University of California, Los Angeles. (b) Pentanyl Technologies.

[2] Porter, C. R.; Kaesz, H. D.; Leto, J. L.; Giordano, T. J.; Haas, W. R.; Johnson, E.; Berry W. H., Jr. *Coal Process. Technol.* **1981**, *7*, 135.

[3] (a) Hsu, G. C. U.S. Patent 4 146 367, 1979; *Chem. Abstr.* **1979**, *90*, 189630c. (b) Porter, C. R.; Kaesz, H. D. U.S. Patent Appl. 189 087 1980; U.S. Patent Appl. 207 714, 1980.

[4] (a) Whitehurst, D. D.; Mitchell, T. O.; Farcasiu, M. "Coal Liquefaction"; Academic Press: New York, 1980. (b) Porter, C. R.; Kaesz, H. D. U.S. Patent 4 325 802, 1982. (c) Suzuki, T.; Yamada; O.; Fujita, K.; Takegami, Y.; Watanabe, Y. *Chem. Lett.* **1982**, 1467–1468.

[5] (a) King A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 1028–1032. (b) Pearson, R. G.; Mauermann, H. *J. Am. Chem. Soc.* **1982**, *104*, 500–504. (c) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 31–37.

[6] (a) Sumner, C. E. Ph.D. Dissertation, The University of Texas, Austin, TX, 1981. (b) Pettit, R.; Cann, K.; Cole, T.; Mauldin, C. H.; Slegeir, W. *Adv. Chem. Ser.* **1979**, *173*, 121–130.

[7] (a) Freifelder, M. *Adv. Catal.* **1963**, *14*, 203–253. (b) Freifelder, M. "Practical Catalytic Hydrogenation: Technique and Applications"; Wiley-Interscience: New York, 1971; pp 582–608. (c) Augustine, R. L., "Catalytic Hydrogenation"; Marcel Dekker: New York, 1965; pp 104–107. (d) Rylander, P. N. "Catalytic Hydrogenation over Platinum Metals"; Academic Press: New York, 1967; pp 375–387.

[8] (a) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973; pp 64–72, 349–353. (b) Alper, H.; Paik, H. N. *J. Org. Chem.* **1977**, *42*, 3522–3524. (c) Friedman, S.; Metlin, S., Svedi, A.; Wender, I. *J. Org. Chem.* **1959**, *24*, 1287. (d) Fish, R. H.; Thormodson, A. D.; Cremer, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 5234–5237.

[9] (a) Alper, H. In "Organic Synthesis via Metal Carbonyls"; Wender, I., Pino, P. Eds.; Wiley: New York, 1977; Vol. II, pp 545–593.

[10] Lynch, T. J.; Banah, M.; McDougall, M.; Kaesz, H. D.; Porter, C. R. *J. Mol. Catal.* **1982**, *17*, 109–112.

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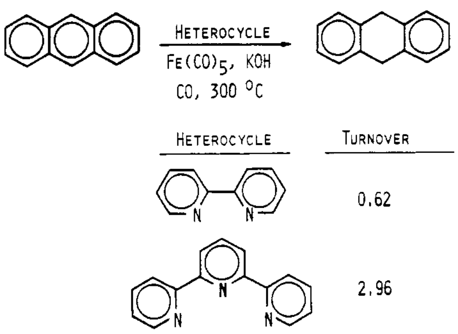
Scheme I



compounds, only acridine yields the reduction product in the absence of iron pentacarbonyl. Only experiments utilizing an excess of the organic substrate (i.e., with a catalytic quantity of $Fe(CO)_5$) are shown in Table I. Products **1**, **2a**,**b**, **4**, and **5** represent the incorporation of 2 mol of H_2, while **3** and **6** incorprate 1 mol of H_2. Notably, at 150 °C, isoquinoline is converted exclusively to **2a** while at 300 °C both the simple hydrogenation product (tetrahydroisoquinoline, **2b**) as well as the hydrogenated *and* formylated product, **2a**, are observed. We have not investigated conditions to optimize formation of **2b**. By independent experiments, we established that **2b** can be carbonylated quantitatively to give **2a** at 150 °C (55 turnovers).

As shown in Table I, the two phenanthroline isomers are hydrogenated essentially in stoichiometric amount at 150 °C despite the presence of excess of these in the reaction mixture. Anthracene, which is less reactive, is hydrogenated in less than stoichiometric yield. This provided us with an opportunity to search for methods in which the iron pentacarbonyl based hydrogenations could be improved, which are described below.

Unreactive Substrates. A number of compounds representing other coal constituents were found to be unreactive at 300 °C under conditions described in the Experimental Section. These are dibenzothiophene, dibenzyl, *p*-(benzyloxy)phenol, 2,4-dimethylquinoline, 2,2′-bipyridine, 1-hydroxynaphthalene, 2,3-benzofuran, and diphenyl sulfide. Benzothiophene is only marginally reactive, yielding 2% of product hydrogenated in the heteroatom ring.

Cocatalysis in Hydrogenation of Anthracene: Effect of Nitrogen Heterocycles. The contrast between the catalytic yields obtained in hydrogenation of nitrogen heterocycles as compared to the low yield in hydrogenation of anthracene led us to combine these two substrates in one experiment to determine whether the nitrogen heterocycles were modifying the catalyst. The yield of 9,10-dihydroanthracene, **6**, is in fact enhanced in the presence of nitrogen heterocycles. The best results are presented in Scheme I.

Yields of **6** are significantly improved over that shown in Table I. Smaller increases in the yield of **6** are realized in the presence of quinoline and 1,10-phenanthroline.[9] Experiments with other chelating ligands such as bis(1,2-diphenylphosphino)ethane and tetramethylethylenediamine or with the complex (terpy)$Fe(CO)_2$ (terpy = terpyridine) in place of $Fe(CO)_5$ as loaded form of the catalyst did not lead to increased yields of **6**.

Phase-Transfer Effects in Hydrogenation of Anthracene. Interpretations of the iron carbonyl catalyzed WGS reaction[5] suggest that the major catalytic species may be anionic. Contact of such a catalyst with a hydrophobic substrate such as anthracene would then be minimal. We were thus led to explore the effects of phase-transfer agents.[11] Results of these experiments are summarized in Table II.

Table II. Effect of Phase-Transfer Agents and 2,2′-Bipyridine with Phase-Transfer Agents on Hydrogenation of Anthracene to 6[a]

phase-transfer agent	turnover	
	b	*c*
none	0.32	0.62
$(PhCH_2)Et_3NCl$		1.3
$Me_3(C_8H_{17})NCl$		2.9
Me_4NCl	1.00	3.0
Bu_4NI	14.2	17.1
18-crown-6	16.9	4.7
$Me_4N(OH)$	0.54	

[a] Temperature, 300 °C; see Experimental Section for details. [b] Phase-transfer agent alone. [c] Phase-transfer agent with bipyridyl (2,2′-bipyridine).

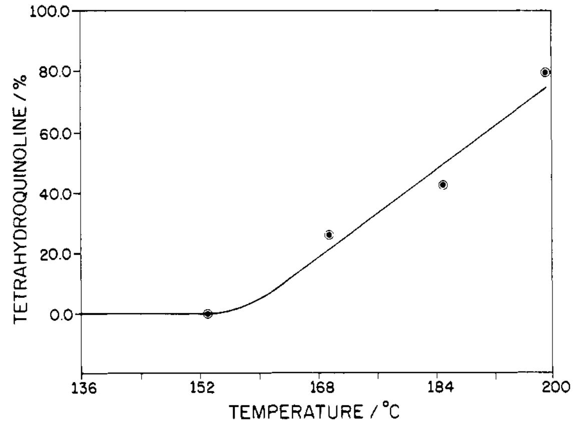


Figure 1. Temperature profile for hydrogenation of quinoline; the data points represent temperatures at which samples were extracted from the autoclave.

The salt, $[Bu_4N][I]$, is the most effective catalyst of the tetraalkylammonium halides (R_4NX) as expected from its superior ability to solubilize $[OH]^-$ in an organic solvent.[11b] The crown ether is more effective than $[Bu_4N][I]$ when either of these agents is used alone; combining bipyridine with the tetraalkylammonium salt produces an enhancement in hydrogenation while addition of bipyridine to the crown ether leads to an attenuation in the yield. To see if the requirements for base in the mixture could be combined with the effects of a phase-transfer agent, we investigated the reaction with $[Me_4N][OH]$, the last entry in Table II; we used 1 molar equiv of this agent and no other source of base. This proves to be more effective per mole of base compared to the first entry, which includes 42 molar equiv of KOH.

Temperature Profile for Hydrogenation of Quinoline. We undertook this series of studies to determine an optimum temperature for the hydrogenation of quinoline in the presence of $[Bu_4N][I]$ and bipyridyl. Samples of the reaction mixture were extracted as the temperature was elevated to 200 °C at a rate of about 1°/min. The results are shown in Figure 1.

Proton NMR of the aliquots revealed that essentially no reaction occurrs below 150 °C and that reaction is 80% complete at 200 °C over 1 h.

Temperature Stability of Catalyst and Effect of Base. If quinoline is injected into a solution of the catalyst preheated to 225 °C for 15 min, only 2% conversion is

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(11) (a) Starks, C. M.; Liotta, C. "Phase Transfer Catalysis: Principles and Techniques"; Academic Press: New York, 1978. (b) Reference 11a, p 18.

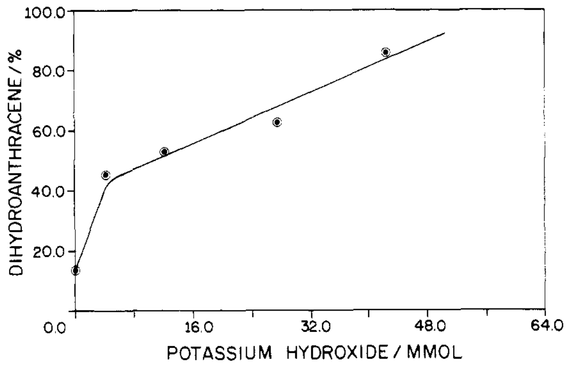


Figure 2. Hydrogenation of anthracene as a function of added KOH in 2.5 mL of aqueous phase.

Table III. Comparison of Iron Complexes as Catalysts for the Hydrogenation of Anthracene to 6[a]

complex	turnover
$Fe(CO)_5$	17.1[b]
$Fe_2(CO)_9$	8.8
$Fe_3(CO)_{12}$	3.4
$[PPN][HFe(CO)_4]$[c]	12.3
$[Et_3NH][HFe_3(CO)_{11}]$	11.2
$Fe(C_8H_8)(CO)_3$	0.7[d]
$Fe(terpy)(CO)_2$	0.8

[a] Temperature, 300 °C, with bipyridyl added; see Experimental Section for further details. [b] Turnover 14.2 without bipyridyl. [c] $[PPN^+] = [(Ph_3P)_2N^+]$. [d] Turnover 7.1 without bipyridyl.

observed, representing 0.2 turnover to tetrahydroquinoline. This remains unchanged even after 12 h.

In order further to understand the catalytically active $Fe(CO)_5$ system, the dependence of the activity of the catalyst was explored relative to concentration of base, see Figure 2. Even in the absence of KOH some reduction is seen. This low background yield must result from hydrolysis of quinoline, generating hydroxide, i.e., $[quinolineH^+][OH^-]$. The first addition of base leads to a sharp increase in activity which is then followed by a more gradual dependence of hydrogenation on base concentration. The latter is therefore an integral factor of this catalyst system.

Principal Iron Species in Solution under Reaction Conditions. Several studies have identified the $[HFe(CO)_4]^-$ ion as the major iron species in basic solution both at room temperature and above 160 °C (eq 1).[12] We

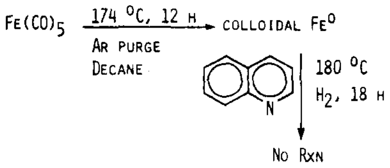
$$Fe(CO)_5 + KOH \rightarrow HFe(CO)_4^- \qquad (1)$$

corroborate these results on an aliquot taken 15 min after the start of a reaction at 175 °C. The infrared spectrum is taken ca. 2 min after removal of the aliquot.

Other Iron Complexes or Colloidal Iron as Reagent or Catalyst Precursor. In attempts to learn more about the actual form of the catalyst, we investigated several iron compounds that could be expected to be produced under reaction conditions in the hydrogenation of anthracene. These results are presented in Table III. All of the iron complexes exhibited some activity but none were as effective as $Fe(CO)_5$ itself.

It is known that $Fe(CO)_5$ is decomposed to colloidal iron at temperatures comparable to those used in this study.[13] This form of Fe(0) is expected to be unstable under reaction conditions. Nevertheless we felt it necessary to test such material as a control experiment. These experiments are summarized in Scheme II. Iron pentacarbonyl was pyrolyzed in refluxing decane and combined with quinoline under H_2 or with H_2O and N_2; no material other than starting material was found at the end of 18 h. This rules out the possibility that iron(0) prepared in this manner is a reagent and/or the active form of the catalyst.

Scheme II



Hydrogenation of 9,10-Dihydro-9,10-dimethylanthracene. This was performed to assist in choosing between several reaction paths, as discussed below. The experiment was identical with that for anthracene at 300 °C (Table I). A 52:48 cis:trans ratio is found, the same as obtained in the Birch reduction of this compound[14] and in independent tests using $Mn_2(CO)_{10}$.[8d] A control experiment indicated that the 9,10-dihydro-9,10-dimethylanthracene isomers do not interconvert under these reaction conditions.

Discussion

The reaction mixture consists of an aqueous phase and an organic phase. Except for the possible formation of some colloidal iron (which we already know not to be an effective catalyst), the catalyst probably remains in solution under reaction conditions. Upon cooling and venting, the reaction mixtures are observed to contain solids but these are not active in catalysis. These solids presumably[5a] contain formate, carbonate, and related salts of the alkali metal hydroxide originally employed, as well as Fe(II)-decomposition products.

The present catalyst is not unique in showing selectivity for hydrogenation of pyridinoid rings in polynuclear heteroaromatics.[7,8a,d] It may, however, offer advantages in the low cost of the iron carbonyl (to compare to other homogeneous catalysts)[8b] or in biocompatibility of iron as compared to the supported, heterogeneous noble-metal based systems.[7]

Mechanistic Considerations. Hydrogenation of Acridine under the Control Conditions. This reduction being observed in the absence of $Fe(CO)_5$ in glass-lined equipment must have come about through the action of formate salts, which are produced by contact of CO with base under reaction conditions of this study.[5a] None of the other substrates tested here gave similar reaction under the control conditions.

Speculations on the Iron-Based Catalyst. By IR studies, Wada and Matsuda[12] have shown the anion $[HFe(CO)_4]^-$ to be prevalent in mixtures of iron pentacarbonyl and amines at temperatures in the range we have used in our studies. We confirm their observations for our reaction mixtures.

The improvements in yield when phase-transfer agents are employed suggests a water-soluble form of the active catalyst. We also note that iron pentacarbonyl was the most effective form of the loaded catalysts (Table III). We thus postulate some hydrido species of iron, possibly $[HFe(CO)_4]^-$, as a working model of the iron-based catalyst. There are numerous paths by which a metal hydride can cause hydrogenation of a substrate.[8a,15] We discuss only

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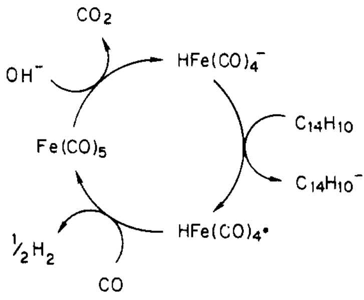
(12) Wada, F.; Matsuda, T. *J. Organomet. Chem.* **1973**, *61*, 365.
(13) Carlton, H. E.; Oxley, J. H. *AIChE J.* **1965**, *11*, 79–84.
(14) Harvey, R. G.; Arzadon, L.; Grant, J.; Urberg, K. R. *J. Am. Chem. Soc.* **1969**, *91*, 4535–4541.
(15) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319–406.

Scheme III



those about which we have some information.

Hydride Transfer. The anion $[HFe(CO)_4]^-$ has not as yet been characterized as a hydride-transfer agent such as has been shown for $[Ru_3[\mu\text{-}H,\alpha\text{-}(CO)](CO)_{10}]^-$.[16] Furthermore, the substrates investigated in this work do not respond to hydrogenation to well-established hydride donors such as $[BH_4]^-$;[17] we have in fact checked the reaction of anthracene with $NaBH_4$ and confirm that it is not affected under this treatment.

Concerted Addition to the Unsaturated Center. This type of reaction would involve a 9,10-addition of FeH on dimethylanthracene. Our observation of a 52:48 mixture of *cis*:*trans*-9,10-dihydro-9,10-dimethylanthracene rules this possibility out as a major path for the reaction. Such a mechanism would further require the hydrogenation to be accompanied by a significant amount of carbonylation under the atmosphere of CO employed in our studies. The absence of such hydroformylation products, except for the single case of the *N*-formyltetrahydroisoquinoline that we observed, seems further to rule out the concerted addition path.[18]

Hydrogen Atom or Electron-Transfer Pathways. Having ruled out the possibility of a concerted process, we need to consider pathways such as electron-transfer (followed by protonation) or hydrogen-atom transfer.[19] The fact that we observe hydrogenation of only one ring of polycyclic derivatives responding to these reactions suggests the former.[20]

With respect to the electron-transfer path, we note a correlation between reduction potentials of substrates and their ability or resistance to undergo hydrogenation in this study. Substrates such as the heteroaromatics that are easy to hydrogenate have low reduction potentials ($E_{1/2}$, V, SCE ref):[21a] acridine, −1.68; quinoline, −2.08; isoquinoline, −2.15; and phenanthroline, −2.17. The unreactive substrates such as dipyridyl, chrysene, phenanthrene, naphthalene, pyridine, dibenzthiophene, and diphenyl ether all have reduction potentials more negative than −2.25 V. Anthracene is borderline in its reactivity yet shows a low reduction potential of −1.93 V; this may be due to its immiscibility in the aqueous media employed in this reaction. Its improved response in the presence of phase-transfer agents is consistent with this interpretation.

The participation of an anionic hydride reagent in a catalytic cycle involving an unpaired electron path is suggested in Scheme III. The participation of aromatic substrates in such electron-transfer paths and their conversion to hydrogenated products has been extensively discussed elsewhere.[21b] The oxidation potential of the $[HFe(CO)_4^-]$ ion has been measured at 0.64 V (vs. Ag/AgCl; 0.59 V vs. SCE).[22,23] Thus this anion is not in itself capable of reducing the aromatic substrates in question. It is possible that some species derived from this anion (perhaps one in which one or more carbonyl groups are replaced by less π-acidic ligands) would raise the oxidation potential sufficiently for the electron transfer to take place. Perhaps this is the role of the nitrogen ligands discussed below.

Table IV. Effect of Terpyridine (terpy) and Phase-Transfer Agents on the Reduction of Quinoline at 180 °C[a]

added agent(s)	turnover
	8.6
Bu_4NI	51
Bu_4NI + terpy	42
18-crown-6	87

[a] Using $Fe(CO)_5$ as catalyst under WGS conditions, see Experimental Section.

Possible Causes for Formylation. Before the nitrogen bases are N-formylated they must first be hydrogenated.[24] The preference for N-formylation of isoquinoline in contrast to quinoline likely derives from greater basicity of nitrogen of **2b** as compared to **1**. At 300 °C we observe a mixture of **2a,b** by contrast to only the formylated product **2a** at 150 °C. This indicates a reduced lifetime at 300 °C of the catalytic species responsible for carbonylation. In support of the intermediate role of **2b** in the formation of **2a**, we find the latter can be obtained directly from the former at 150 °C.

Activation by Heterocycles. There are several ways in which this activation may be interpreted. First, this result might be derived from an electrochemical modification caused by substitution of the hetereocycles for carbon monoxide on the catalyst (see Discussion above). We prepared $Fe(terpy)(CO)_2$ and used it in place of $Fe(CO)_5$ in a typical experiment for anthracene reduction. Little or no anthracene is however hydrogenated to **6**. This result does not preclude in situ formation of a terpyridine substitution product *after* formation of the anion $[HFe(CO)_4^-]$; it could well be that an initially substituted complex such as $Fe(terpy)(CO)_2$ might be less susceptible to nucleophilic attack and thus less susceptible to conversion to an anionic active form of the catalyst.

Promotion by Phase-Transfer Agents. Not all the tetraalkylammonium halides used gave good results (Table II). These are known to undergo Hoffmann degradation at temperatures we have used in this study. The crown ether shows superior catalysis. Its higher thermal stability may in part be responsible for the better yields obtained with this as a promoter. The R_4N^+ ions have a higher affinity for halide extraction into an organic phase than hydroxide so that R_4NOH-type catalysts in the absence of halide are expected to be more effective than the R_4NX catalysts. The role of the phase-transfer catalysts is believed to be the same as in other phase-transfer catalyzed systems.[11] That is, the hydroxide ion is rendered more soluble in the organic phase, increasing its concentration and therefore increasing the rate of hydroxide attack on $Fe(CO)_5$. In addition, the phase-transfer cations further solubilize the anionic iron hydride formed during catalysis

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[16] Bricker, J. C.; Nagel, C. C.; Shore, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1444–1445.

[17] House, Herbert O. "Modern Synthetic Reactions"; W.A. Benjamin: Menlo Park, CA, 1972; pp 45–49, 62–65.

[18] Feder, H. M.; Halpern, J. *J. Am. Chem. Soc.* **1975**, *97*, 7186.

[19] Chanon, M. *Bull. Soc. Chim. Fr.* **1982**, 197–238.

[20] Reference 17, pp 190–205.

[21] "Handbook Series in Organic Electrochemistry", Meites, L., Zuman P., Eds.; CRC Press: Cleveland, OH, 1977; Vol. 1, (a) Table I; (b) Table III.

[22] Bond, A. M.; Dawson, P. A.; Peake, B. M.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1977**, *16*, 2199–2206.

[23] El Murr, N.; Chaloyard, A. *Inorg. Chem.* **1982**, *21*, 2206–2208.

[24] Dombek, B. D.; Angelici, R. J. *J. Catal.* **1977**, *48*, 433.

in the organic phase; see mechanistic aspects discussed above.

Optimum Conditions for Hydrogenation. Having experimented with variations in the catalyst (Table III), reaction temperature (Figure 1), and catalyst promoters (Table II and Scheme I), we put together a reaction at optimum conditions. Results are summarized in Table IV. With these conditions we achieve a turnover of 87 in the regiospecific hydrogenation of quinoline.

In conclusion, iron pentacarbonyl is a catalytic precursor in the hydrogenation of polynuclear pyridinoid rings under water–gas shift conditions. The system shows the usual regioselectivity observed for these substrates. Iron pentacarbonyl can also be activated to reduce the middle ring of anthracene catalytically. These observations combined with the low cost of iron pentacarbonyl and biocompatibility of the Fe(II)-degradation products may be useful in applications in organic synthesis and in treatment of solid carbonaceous fuels.

Experimental Section

Materials. Iron pentacarbonyl and the model coal compounds were obtained from the Aldrich Chemical Co. (4,7-phenanthroline from ICI-KK). The complexes $Fe_2(CO)_9$,[25a] $Fe_3(CO)_{12}$,[25b] $(Et_3HN)HFe_3(CO)_{11}$,[25b] $Fe(terpy)(CO)_2$,[26] and $Fe(C_8H_8)(CO)_3$[27] were prepared by literature methods. The hydride $[PPN][HFe(CO)_4]$ was prepared by modification of a procedure described by Sumner.[6a] $Fe(CO)_5$ (2.0 mL, 15 mmol) is added under nitrogen to a degassed solution of KOH (2.4 g, 43 mmol) and bis(triphenylphosphine)iminium chloride (PPNCl, 20 mmol) in 45% aqueous ethanol (20 mL). After stirring for 1 h, degassed H_2O (20 mL) is added. A precipitate develops and the mixture is stirred for another 10 min. The air-sensitive precipitate is filtered, washed with H_2O, and dried under vacuum (90% yield).

Reactions with model coal compounds were performed in the glass insert of a 0.3-L copper-lined autoclave which was agitated in a temperature-controlled rocker. Experiments in which aliquots were removed were performed in the glass insert of a magnetically stirred, 128-mL Parr autoclave. This was equipped with a thermowell and dip tube that was heated with a 1000-W copper immersion heater.

Reactions of Model Coal Compounds at 150 °C, Table I. Potassium hydroxide (4.8 g, 85 mmol), distilled H_2O (10 mL), methanol (30 mL), and the substrates were combined in the glass liner and deaerated with argon. Iron pentacarbonyl (0.10 mL, 0.76 mmol) was then added to the mixture by syringe under an inert atmosphere. The glass liner was placed into the autoclave, flushed three times with CO (300 psi), pressurized (500 psi), and heated/aggitated for 15 h. Reaction temperature was reached in 1 h. The autoclave was cooled and the glass liner contents were shaken with H_2O and CCl_4; the CCl_4 layer was isolated and dried with $MgSO_4$ and concentrated on a rotary evaporator.

Reactions at 300 °C, Tables I–III, were performed in a fashion similar to the reactions at 150 °C but without methanol. These were initially pressurized to 400 psi (reaching 1000 psi at 300 °C) and held at reaction temperature for 1 h. Typically, KOH (2.4 g, 42 mmol), distilled H_2O (3.0 mL), and a model coal constituent were combined n the glass liner and deaerated with argon. Iron pentacarbonyl (0.10 mL, 0.76 mmol) or another iron complex was then added. The glass liner was loaded into the autoclave, flushed three times with CO (300 psi), pressurized, and heated for 1 h at reaction temperature.

The constituents 2,2′-bipyridyl, 2,2′,2″-terpyridyl, or a phase-transfer agent were introduced before deaerating the reaction mixture and in the same molar amount as $Fe(CO)_5$.

Reaction of Quinoline at 180 °C, Table IV. Reaction mixtures were prepared in the same manner as those at 300 °C by using the following quantities of reagents: KOH (2.4 g, 42 mmol), H_2O (4.0 mL, 222 mmol), quinoline (11.1 mL, 94 mmol), $Fe(CO)_5$ (0.10 mL, 0.76 mmol). Terpyridyl, 18-crown-6, or Bu_4NI was introducted in the same molar amount as $Fe(CO)_5$.

Reaction of anthracene (0.67 g, 3.7 mmol) with $NaBH_4$ (0.14 g, 3.7 mmol) was carried out in methanol (10 mL) under CO (400 psi at 25 °C) at 180 °C for 1 h; no **6** was produced.

Analysis. Characterization and quantitation of substrates and their reduction products were performed by standard methods using the following instrumentation: Hewlett-Packard 5880A gas chromatograph fitted with a 12-m OV-101 capillary column (anthracene, dimethylanthracene, and their reduction products); Jeol FX-90Q and Bruker WP200 NMR spectrometers; Kratos GC-MS25 spectrometer (nitrogen heterocycles and their reduction products). An authentic sample of **2a** was prepared by an alternate route.[28]

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Registry No. $(PhCH_2)Et_3NCl$, 56-37-1; $Me_3(C_8H_{17})NCl$, 10108-86-8; Me_4NCl, 75-57-0; Bu_4NI, 311-28-4; Me_4NOH, 75-59-2; $Fe(CO)_5$, 13463-40-6; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8; $[PPN][HFe(CO)_4]$, 56791-54-9; $[Et_3NH][HFe_3(CO)_{11}]$, 56048-18-1; $Fe(C_8H_8)(CO)_3$, 12093-05-9; $Fe(terpy)(CO)_2$, 15320-77-1; 18-crown-6, 17455-13-9; quinoline, 91-22-5; isoquinoline, 119-65-3; acridine, 260-94-6; 4,7-phenanthroline, 230-07-9; 1,10-phenanthroline, 66-71-7; anthracene, 120-12-7; 9,10-dimethylanthracene, 781-43-1; 2,2′-bipyridine, 366-18-7; 2,2′,2″-terpyridine, 1148-79-4.

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(25) (a) Braye, E. H.; Hübel, W. *Inorg. Synth.* **1966**, *8* 178–181. (b) McFarlane, W.; Wilkinson, G. *Ibid.* **1966**, *8*, 181–183.

(26) Behrens, H.; Feilner, H. D.; Lindner, E. *Z. Anorg. Allg. Chem.* **1971**, *385*, 321–324.

(27) Shvo, Y.; Hazam, E. *J. Chem. Soc., Chem. Commun.* **1975**, 829–830.

(28) Blicke, F. F.; Lu, C. J. *J. Am. Chem. Soc.* **1952**, *74*, 3933–3934.