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HOMOGENEOUS CATALYTIC HYDROGENATION. 3. SELECTIVE REDUCTIONS OF POLYNUCLEAR AROMATIC AND HETEROAROMATIC NITROGEN COMPOUNDS CATALYZED BY TRANSITION-METAL CARBONYL HYDRIDES.

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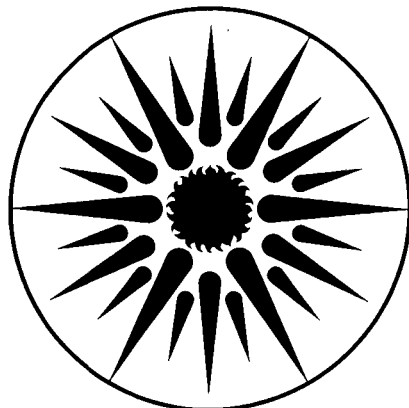
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Richard H. Fish

March 1983

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Homogeneous Catalytic Hydrogenation. 3.  
Selective Reductions of Polynuclear Aromatic and Heteroaromatic  
Nitrogen Compounds Catalyzed by Transition-Metal Carbonyl Hydrides

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ABSTRACT

The reductions of polynuclear aromatic and heteroaromatic nitrogen compounds with transition metal carbonyl catalysts (Fe, Mn, Co, Ru, W, Cr, Mo) under water gas shift (wgs) (CO, H<sub>2</sub>O, base) and synthesis gas (sg) (CO, H<sub>2</sub>, 1:1) conditions as well as strictly hydrogenation conditions (H<sub>2</sub> alone) were studied.

It was found that under either wgs or sg conditions, the linear polynuclear aromatic compound anthracene was more reactive than the corresponding bent aromatic compounds such as phenanthrene. In con-

trast, the polynuclear heteroaromatic nitrogen compounds were more reactive than the polynuclear aromatic compounds either under wgs or sg conditions with the nitrogen containing ring regioselectivity reduced in each case.

The reactions with ruthenium carbonyls were inhibited by carbon monoxide, and thus it appears that coordination of substrate to ruthenium is essential for reduction to occur.

The mononuclear ruthenium carbonyl  $\text{Ru}(\text{Cl})_2(\text{CO})_2(\text{P}_3)_2$  produced, regioselectively ( $\text{H}_2$  alone), the outer ring reduction product 1,2,3,4-tetrahydroanthracene from anthracene as well as the selective reduction of the nitrogen heterocyclic ring in such model synthetic fuel compounds as acridine and quinoline.

Reductions of the nitrogen heterocyclic rings in polynuclear heteroaromatic nitrogen compounds was also affected by  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ . In the latter reactions, polynuclear aromatic compounds were not reduced under the reaction conditions.

Homogeneous Catalytic Hydrogenation. 3. Selective Reductions of  
Polynuclear Aromatic and Heteroaromatic Nitrogen Compounds  
Catalyzed by Transition-Metal Carbonyl Hydrides<sup>1a,b</sup>

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Introduction

Many of the synthetic fuel processes, such as coal liquefaction and oil shale retorting, generate products that require additional hydroprocessing to reduce their nitrogen and sulfur content. Since these synthetic fuel products contain a wide variety of polynuclear aromatic and polynuclear heteroaromatic constituents, it becomes extremely important to understand the reactivity of model synthetic fuel compounds under various homogeneous catalytic hydrogenation conditions.

The recent reports by Pettit et al.<sup>2-4</sup> on the utilization of transition-metal carbonyl compounds as catalysts in the hydroformylation of olefins and the reduction of nitroarenes prompted us to study these catalysts with polynuclear aromatic and heteroaromatic nitrogen compounds that are known to be present in various synthetic fuels.

In addition, the intermediacy of transition-metal carbonyl hydrides from the corresponding transition-metal carbonyls was also postulated under water gas shift ( $\text{CO}$ ,  $\text{H}_2\text{O}$ ), synthesis gas ( $\text{CO}$ ,  $\text{H}_2$ ) and strictly hydrogenation conditions ( $\text{H}_2$  alone)<sup>5a-d</sup>, which further increased our interest in generating these hydrides for the purpose of testing their reactivities and selectivities with model synthetic fuel compounds

Previous studies on the reductions of polynuclear aromatic compounds, with transition-metal carbonyl hydrides as catalysts, dates back to the 1950's with the observations by Friedman et al.<sup>6</sup> They reacted a variety of polynuclear aromatic compounds under synthesis gas conditions ( $\text{CO}/\text{H}_2$ , 1:1, 3,000 psi, 135-200°C) with  $\text{Co}_2(\text{CO})_8$  as the catalyst. For example, anthracene is reduced to 9,10-dihydroanthracene (100%), while other polynuclear aromatics such as pyrene and phenanthrene were more difficult to hydrogenate. Other workers, for example, Taylor and Orchin<sup>7</sup> and Sweany et al.<sup>8</sup> reacted  $\text{HCo}(\text{CO})_4$  and  $\text{HMn}(\text{CO})_5$ , respectively, with 9,10-dimethylantracene to show both cis and trans 9,10-dihydro-9,10-dimethylantracene (~1:1) thus implicating a free radical process for these reductions.

It was surprising to find that polynuclear heteroaromatic nitrogen compounds had not been studied, under homogeneous hydrogenation conditions, to any significant extent. These studies were limited to the hydrogenation of quinoline and under either synthesis gas (CO/H<sub>2</sub>)<sup>9</sup> with Mn(CO)<sub>8</sub>(Bu<sub>3</sub>P)<sub>2</sub>, or H<sub>2</sub> conditions with RhCl<sub>2</sub>Py<sub>2</sub>(dmf)BH<sub>4</sub> as catalyst,<sup>10</sup> 1,2,3,4-tetrahydroquinoline was formed.

Recently, we communicated on the homogeneous hydrogenation of a wide variety of polynuclear aromatic and heteroaromatic nitrogen compounds under wgs, sg and H<sub>2</sub> (alone) conditions using transition-metal carbonyl hydrides as catalysts.<sup>1a</sup> In addition, we also discovered that Wilkinson's Catalyst, (PPh<sub>3</sub>)<sub>3</sub>RhCl, was also an excellent catalyst for the hydrogenation of polynuclear heteroaromatic compounds<sup>1b</sup> and Lynch et al.<sup>11</sup> reported similar results with Fe(CO)<sub>5</sub> as the catalyst under wgs conditions.

In this paper, we will amplify on our initial studies<sup>1a</sup> with transition-metal carbonyl hydrides and their reactivity with both polynuclear aromatic and heteroaromatic nitrogen compounds (Chart 1).



## Results

A wide variety of transition-metal carbonyl compounds were used to generate, in situ, the corresponding transition-metal carbonyl hydrides under wgs ( $\text{CO}$ ,  $\text{H}_2\text{O}$ , base) conditions with anthracene, phenanthrene and pyrene as substrates.

Figure 1 details the mechanism of formation of transition-metal carbonyl hydrides under wgs conditions from the corresponding carbonyls.<sup>5a-c</sup> Our hope was that the carbonyl hydrides would transfer hydrogen to the model synthetic fuel compounds rather than reductively eliminate  $\text{H}_2$  gas. Table 1 demonstrates the results with the above named polynuclear aromatic substrates and clearly shows that anthracene, a linear polynuclear aromatic, is reduced to 9,10-dihydroanthracene but in poor yields. The bent polynuclear aromatics, pyrene and phenanthrene, were totally unreactive under wgs conditions.

In contrast, we found that the polynuclear heteroaromatic nitrogen compounds were more reactive than their carbon analogues under wgs conditions. Table 2 provides the data to show this reactivity trend and also demonstrates the regioselectivity of the reductions, where only the nitrogen heterocyclic ring is reduced. Under these

wgs conditions only Fe, Mn and Co carbonyls gave products with the model synthetic fuel compounds studied, while those carbonyls of W, Cr, Ru, Rh, Re, Mo and Os gave  $\text{CO}_2$  and  $\text{H}_2$  (wgs reaction), but gave no reduced products.

We then turned our attention to sg condions ( $\text{CO}/\text{H}_2=1$ ). We found that both Mn and Co carbonyls exhibited greater reactivity when water was removed and replaced with hydrogen gas. Again, anthracene was far more reactive than pyrene or phenanthrene, which were unreactive under sg conditions. In turn, the polynuclear heterocyclic nitrogen compounds demonstrated far greater reactivity than their carbon analogues. Figure 2 illustrates the reactivity of both polynuclear aromatics and heteroaromatic nitrogen compounds with  $\text{Co}_2(\text{CO})_6(\phi_3\text{P})_2$  as the catalyst under sg conditions ( $200^\circ\text{C}$ , 1 hour, 350 psi  $\text{H}_2$ , 350 CO,  $\text{CO}/\text{H}_2=1$  Sub/cat=20:1). Again, as under wgs conditions, the reductions under sg conditions provide high regioselectivity for the nitrogen heterocyclic ring.

Mechanistically, we found that the rate of hydrogenation of polynuclear aromatic and heteroaromatic nitrogen compounds with Fe, Co and Mn carbonyls as catalysts was independent of the partial pressure of CO. This suggests that substrate does not need to coordinate to these metal centers for hydrogenation to proceed.

In experiments to define the role of carbon monoxide, base and  $\text{H}_2$  alone, we found that removal of carbon monoxide had a profound effect on the reductions of the model synthetic fuel compounds in the presence of ruthenium carbonyls. We can illustrate this with

quinoline using  $H_4Ru_4(CO)_{12}$  as the catalyst and varying the CO partial pressure from 0 psi to 350 psi with the  $H_2$  partial pressure remaining constant at 350 psi (Figure 3). A similar effect of carbon monoxide inhibition was also found in the hydrogenation of ethylene with  $H_4Ru_4(CO)_{12}$  as the catalyst.<sup>12</sup>

It is interesting to note that anthracene is reduced to 1,2,3,4-tetrahydroanthracene; however, only in the presence of base and hydrogen gas with ruthenium carbonyl catalyst, i.e.,  $RuCl_2(CO)_2(\phi_3P)_3$  and  $Ru_3(CO)_6(\phi_3P)_6$ .

The speculation is that base (KOH) is required to open up coordination sites on the ruthenium metal center by forming  $CO_2$ . Consequently, anthracene must bind via four haptic coordination and this results in selective outer ring hydrogenation. A similar regioselectivity was shown by a ruthenium anion hydride in the reduction of anthracene with  $H_2$  alone.<sup>13</sup>

With the polynuclear nitrogen heterocyclic compounds, selective reduction also occurred at the nitrogen heterocyclic ring and can be illustrated with  $H_4Ru_4(CO)_{12}$  as the catalyst <sup>( $H_2$ , alone)</sup> (Figure 4).

## Discussion

Our results clearly indicate that polynuclear heteroaromatic nitrogen compounds are more reactive under wgs, sg or H<sub>2</sub> (alone) conditions than their polynuclear aromatic counterparts. More importantly, the high regioselectivity in the reduction of the nitrogen heterocyclic ring in polynuclear heteroaromatic nitrogen compounds has important implications in the use of the transition-metal carbonyls for synthetic fuel applications such as hydroprocessing of coal liquids and shale oils as well as hydrodenitrogenation.

It is of interest to emphasize the mechanistic differences between Fe, Mn and Co carbonyls and those of Ru mononuclear and cluster carbonyls. Under either wgs or sg conditions, the Fe, Mn and Co carbonyls reduce both polynuclear aromatic and heteroaromatic compounds, while other transition-metal carbonyls were unreactive. Additionally, Fe, Mn, and Co carbonyl were found to be poor water-gas shift catalysts, while those of Rh, Ru, Cr, Mo and W were more active shift catalysts.<sup>1a</sup>

This implies that with Fe, Mn and Co carbonyl hydrides transfer of hydrogen is either by electron transfer<sup>4</sup> or hydrogen radical transfer<sup>14</sup> with coordination of substrate to metal not an important

rate determining step. Alternatively, substrate coordination to ruthenium mononuclear and cluster carbonyls must be an important rate determining step as evidenced by the inhibition of hydrogenation of substrate in the presence of carbon monoxide. In agreement with the proposed mechanism for ethylene hydrogenation, catalyzed by  $H_4Ru_4(CO)_{12}$ , where coordination of ethylene to coordinatively unsaturated  $H_4Ru_4(CO)_{11}$  occurs prior to intramolecular hydrogen transfer,<sup>12</sup> we can speculate on a similar mechanism for the hydrogenation of quinoline. Figure 5 incorporates all the features of the ethylene hydrogenation mechanism,<sup>12</sup> including an intramolecular addition to the carbon-nitrogen double bond.

We are in the process of trying to isolate these complexes as well as clarify many of the other mechanistic details with deuterium gas experiments as well as the evaluation of other catalysts.<sup>1b</sup>

Finally, we have recently heterogenized, on divinylbenzene/polystyrene, homogeneous catalysts  $H_4Ru_4(CO)_{12}$ ,  $(\phi_3P)_3RhCl$  and  $RuCl_2(\phi_3P)_3$  and have found, under strictly  $H_2$  conditions, excellent activity for these heterogenized homogeneous catalysts in the selective reductions of polynuclear heteroaromatic nitrogen compounds.<sup>15</sup> These latter results provide further definitive evidence for the potential utilization of these catalysts in future synthetic fuel processes.

### Experimental

The reactions were conducted in Parr minireactors (45 ml) constructed of stainless steel and equipped with a 2000 psi pressure gauge, 2000 psi rupture disc with a magnetic stirring bar and either a septum attachment for sampling under pressure and temperature or a set-up without this assembly, and a needle valve for controlling pressurization and flushing of gases. The reactors are placed in a constant temperature bath ( $\pm 1^\circ\text{C}$ ). After reaction, the reactor body was cooled in water and the reaction mixture worked up in a standard manner.

Gases were analyzed by transferring to a gas cylinder and using a CEC model 21103 mass spectrometer to ascertain  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2$  concentrations.

The reaction mixtures were analyzed by capillary gas chromatography (12m x 0.1 mm OV 101) using the HP 5880A gas chromatograph. We identified products by GC-MS analysis and isolation by Florisil chromatography followed by 250 MHz  $^1\text{H}$  NMR spectroscopy. Tables 1 and 2 define concentrations of catalyst and substrates as well as reaction conditions including  $\text{CO}$  and  $\text{H}_2$  partial pressures.

### Acknowledgements

The experimental work reported in this paper was performed by Dr. Gregg A. Cremer and Arne D. Thormosen. We wish to thank Dr. Heinz Heinemann of LBL for encouragement and support of this research project. This study was jointly supported by the Director, Office of

Energy Research, Office of Basic Energy Science, Chemical Sciences Division, and the Assistant Secretary of Fossil Energy, Office of Coal Research, Liquefaction Division of the U.S. Department of Energy through the Pittsburgh Energy Technology Center under Contract No. DE-AC03-76SF00098.

## REFERENCES

- (1) a) Part 1. FISH, R.H., A.D. THORMODSEN, & G.A. CREMER. 1982. J. Am. Chem. Soc. 104:5234.
- b) Part 2. FISH, R.H. & A.D. THORMODSEN. 1983. J. Am. Chem. Soc. Submitted for publication.
- (2) KANG, H.G., C.H. MAULDIN, T. COLE, W. SLEGEIR; K. CANN, & R. PETTIT. 1977. Ibid. 99:8323.
- (3) CANN, K., T. COLE, W. SLEGEIR, & R. PETTIT. 1978. Ibid. 100:3969.
- (4) COLE, T., R. RAMAGE, K. CANN, & R. PETTIT. 1980. Ibid. 102:6182.
- (5) a) GRICE, N., S.C. KAO, & R. PETTIT. 1979. Ibid. 101:1627.
- b) DARENSBOURG, D.J., B.J. BALDWIN, & J.A. FROELICH. 1980. Ibid. 102:4688.
- c) FORD, P.C. 1981. Acc. Chem. Res. 14:31.
- d) KAESZ, H.D., & SAILLANT. 1972. R.B. Chem. Rev. 72:231 and references therein.



- (6) FRIEDMAN, S., S. METLIN, A. SV EDI, & I.WENDER. 1959. J. Org. Chem. 24:1287.
- (7) TAYLOR, P.D. & M. ORCHIN. 1972. J. Org. Chem. 37:3913.
- (8) SWEANY, R., S.C. BUTLER, & J. HALPERN. 1981. J. Organometal. Chem. 213:487.
- (9) DERENCSENZI, T.T. & T. VERMUELEN. 1980. Chem. Abst. 93:188929; and LBL Report 9777, September 1979 (Ph.D. Thesis of T.T.D.).
- (10) JARDINE, I. & F.J. MCGUILLIN. 1970. Chem. Commun. 626.
- (11) LYNCH, T.J., M. BANAH, M. McDOUGALL, H.D. KAESZ, & C.R. PORTER. 1982. J. Mol. Catal., 17, 109.
- (12) DOI, Y., K. KOSHIZUKA, & T. KEII. 1982. Inorg. Chem. 21:2732.
- (13) GREY, R.H., G.P. PEZ, & A.H. WALL. 1980. J. Am. Chem. Soc. 102:5948 and references therein.
- (14) FEDER, H.M. & J. HALPERN. 1975. J. Am. Chem. Soc. 97:7186.
- (15) FISH, R.H., A.D. THORMODSEN, R.S. TANNOUS, & H. HEINEMANN. 1983. Organometallics. Submitted for publication.

TABLE CAPTIONS

- (1) Hydrogenation of Polynuclear Aromatics Under Water Gas Shift Conditions
- (2) Reductions of Polynuclear Heteroaromatic Nitrogen Compounds Under Water Gas Shift Conditions

Table 1  
Hydrogenation of Polynuclear Aromatics  
Under Water Gas Shift Conditions<sup>a</sup>

Catalyst	Temp (°C)	Substrate	Product
Rh <sub>6</sub> (CO) <sub>16</sub>	180	Anthracene	None
Ru <sub>3</sub> (CO) <sub>12</sub>	180	Anthracene	None
Os <sub>3</sub> (CO) <sub>12</sub> , Cr(CO) <sub>6</sub> Mo(CO) <sub>6</sub> , W(CO) <sub>6</sub> , Re <sub>2</sub> (CO) <sub>10</sub>	200	Anthracene	None
Co <sub>2</sub> (CO) <sub>6</sub> (PPh <sub>3</sub> ) <sub>2</sub>	160	Anthracene	3% 9,10-Dihydro- anthracene
Fe(CO) <sub>4</sub> (PBu <sub>3</sub> )	200	Anthracene	8% 9,10-Dihydro- anthracene
Mn <sub>2</sub> (CO) <sub>8</sub> (PBu <sub>3</sub> ) <sub>2</sub>	160	Anthracene	4% 9,10-Dihydro- anthracene
Mn <sub>2</sub> (CO) <sub>8</sub> (PBu <sub>3</sub> ) <sub>2</sub>	180	Anthracene	8% 9,10-Dihydro- anthracene
Mn <sub>2</sub> (CO) <sub>8</sub> (PBu <sub>3</sub> ) <sub>2</sub>	200	Anthracene	13% 9,10-Dihydro- anthracene
Mn <sub>2</sub> (CO) <sub>8</sub> (PBu <sub>3</sub> ) <sub>2</sub>	200	Phenanthrene	None

Table 1 continued

Table 1 continued

Catalyst	Temp (°C)	Substrate	Product
$\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$	200	Pyrene	None
$\text{Mn}_2(\text{CO})_{10}$	180	Anthracene	6% 9,10-Dihydro- anthracene
$\text{Mn}_2(\text{CO})_6(\text{PBu}_3)_4$	180	Anthracene	7% 9,10-Dihydro- anthracene
$\text{Mn}_2(\text{CO})_4(\text{PBu}_3)_6$	180	Anthracene	9% 9,10-Dihydro- anthracene
$\text{Mn}_2(\text{CO})_2(\text{PBu}_3)_8$	180	Anthracene	7% 9,10-Dihydro- anthracene

(a)  $P_{\text{CO}} = 350$  psi; 12 ml THF; 3 ml 0.2M KOH; substrate/catalyst ratio ,20:1.

Table 2

Reductions of Polynuclear Heteroaromatic Nitrogen Compounds  
Under Water-Gas Shift Conditions<sup>a</sup>

Substrate	Catalyst	Sub/Cat	Temp (°C)	Time (h)	Product (%) <sup>c</sup>
5,6-benzoquinoline	$\text{Mn}_2(\text{CO})_5(\text{Bu}_3\text{P})_2$	20	200	2	1,2,3,4-tetrahydro-5,6-benzoquinoline(4)
5,6-benzoquinoline	$\text{Fe}(\text{CO})_4\text{Bu}_3\text{P}$	10	180	5	1,2,3,4-tetrahydro-5,6-benzoquinoline(1)
7,8-benzoquinoline	$\text{Mn}_2(\text{CO})_8(\text{Bu}_3\text{P})_2$	20	200	2	No product
Phenanthridine	$\text{Mn}_2(\text{CO})_8(\text{Bu}_3\text{P})_2$	20	200	2	9,10-dihydrophenanthridine(1)
Acridine	$\text{Fe}(\text{CO})_5$ <sup>b</sup>	10	180	2	9,10-dihydroacridine(100)
Acridine	$\text{Mn}_2(\text{CO})_8(\text{Bu}_3\text{P})_2$	10	200	2	9,10-dihydroacridine(38)
Quinoline	$\text{Mn}_2(\text{CO})_8(\text{Bu}_3\text{P})_2$	20	200	5	1,2,3,4-tetrahydroquinoline(4)

(a) Reactions run in THF (12 ml) with 0.2M KOH (3 ml), 350 psi CO

(b) 800 psi CO

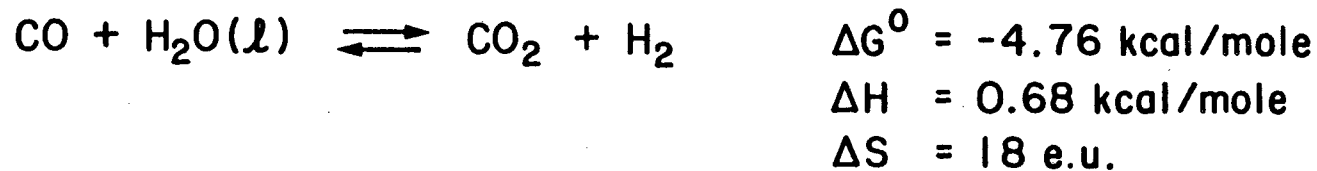
(c) Determined by capillary GC using a digital integration (HP5880A). Isolated by column chromatography (Florisil) and identified by GC-MS and <sup>1</sup>H, 250 MHz NMR spectroscopy.

## FIGURE CAPTIONS

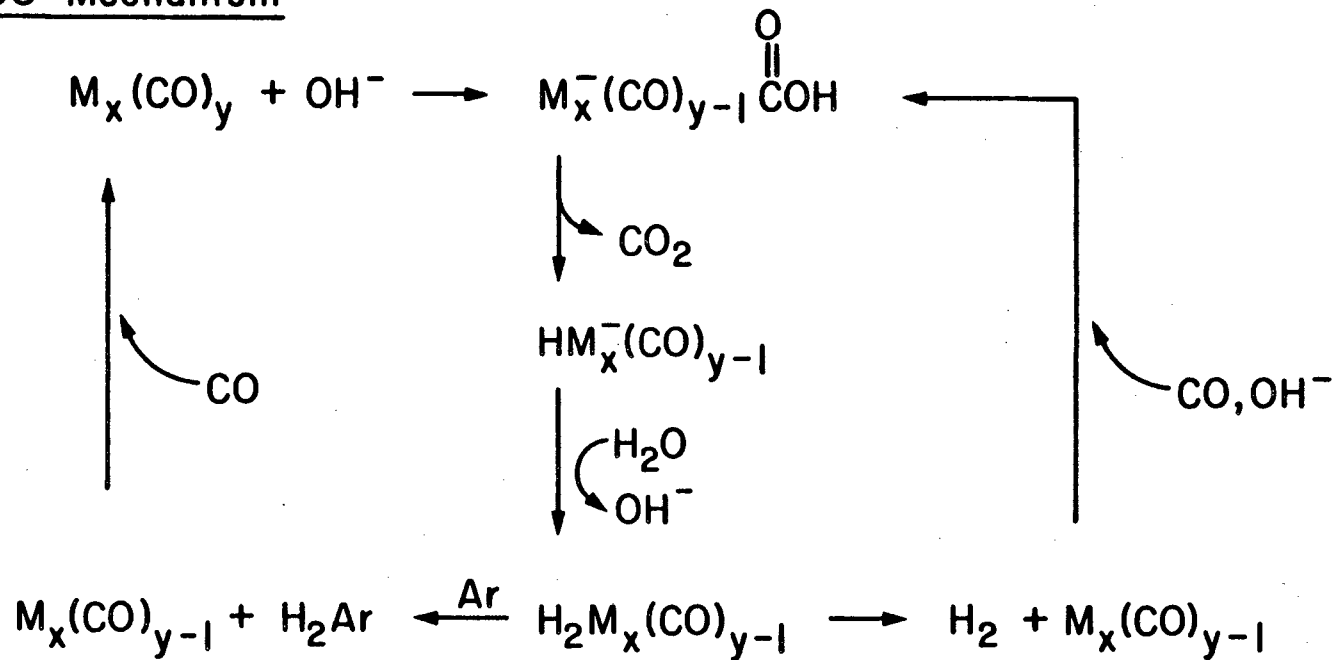
- (1) Mechanism of the WGS Reaction for the Formation of Transition-Metal Carbonyl Hydrides
- (2) Percent Conversion in the Homogeneous Hydrogenation of Model Synthetic Fuel Compounds by  $\text{Co}_2(\text{CO})_6(\text{Ph}_3\text{P})_2$  at  $200^\circ\text{C}$ , for 1 hr,  $\text{CO}/\text{H}_2=1$ , sub/cat=20:1
- (3) Effect of CO Partial Pressure on  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  Catalyzed Hydrogenation of Quinoline
- (4) Percent Conversion in the Homogeneous Hydrogenation of Model Synthetic Fuel Compounds by  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  at  $150^\circ\text{C}$  for 1hr, 350psi,  $\text{H}_2$ , sub/cat=10:1
- (5) Proposed Mechanism for the  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  Catalyzed Hydrogenation of Quinoline

Figure 1

Water Gas Shift

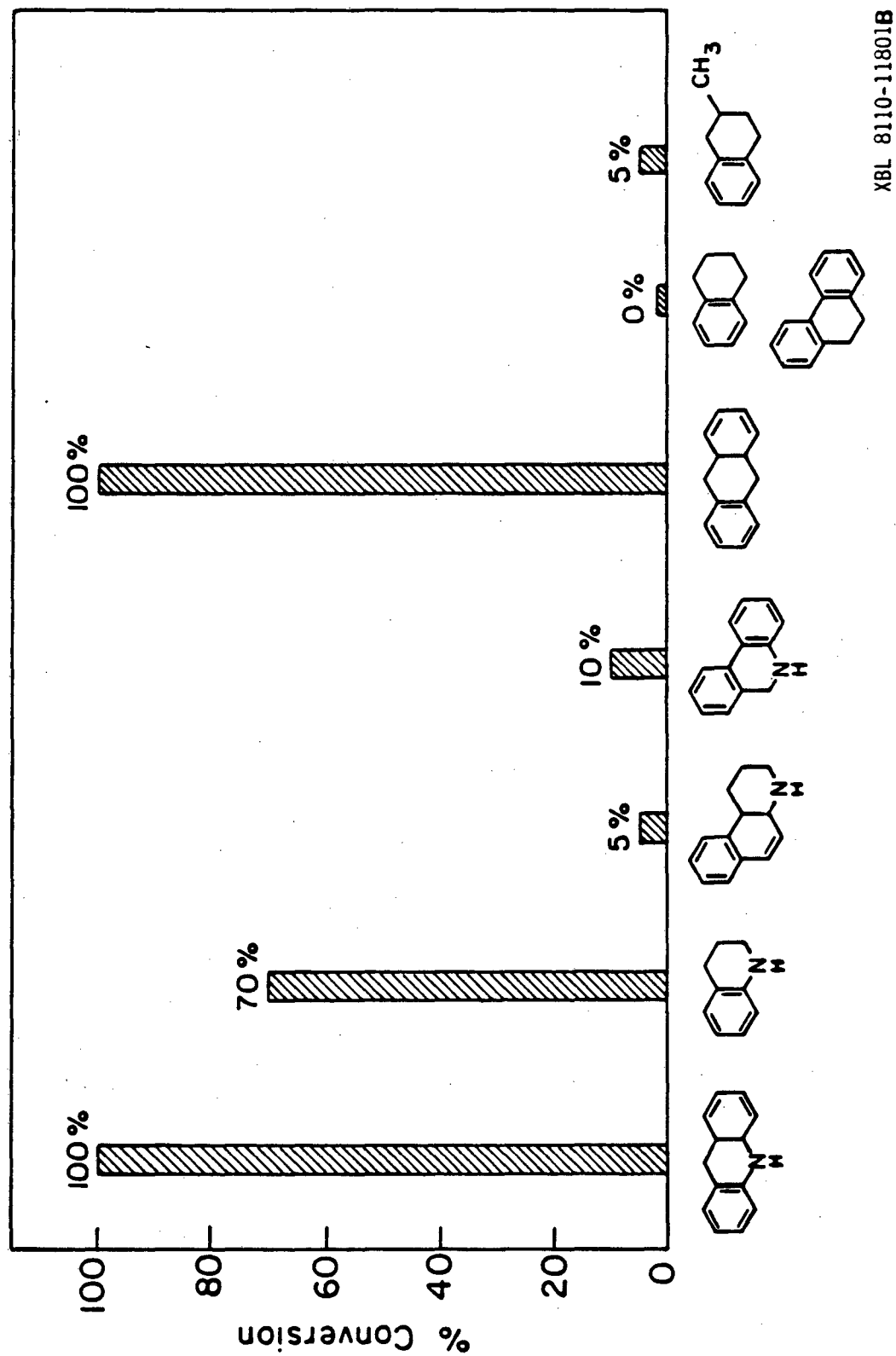


WGS Mechanism



M = Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir

Figure 2





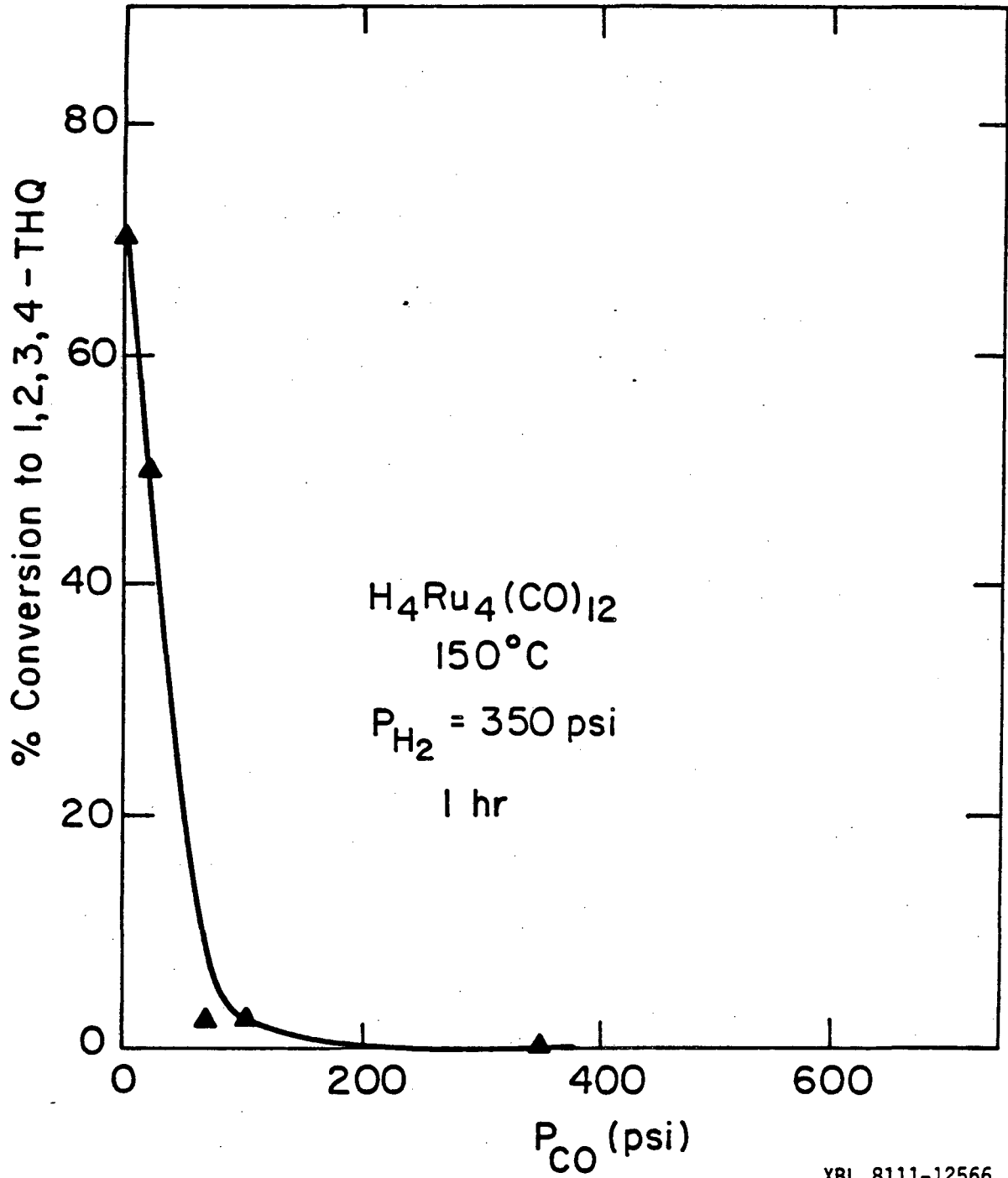


Figure 4

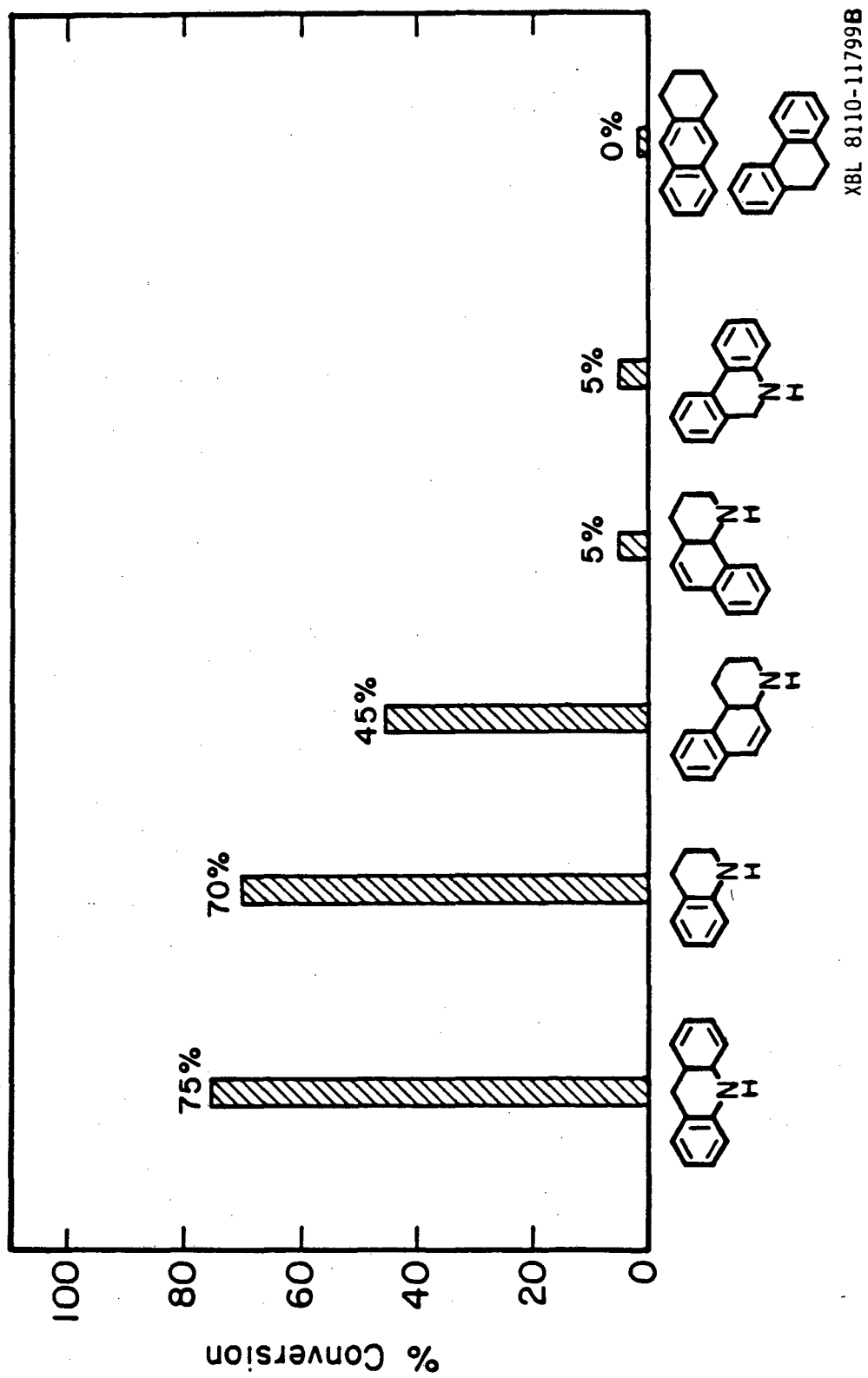
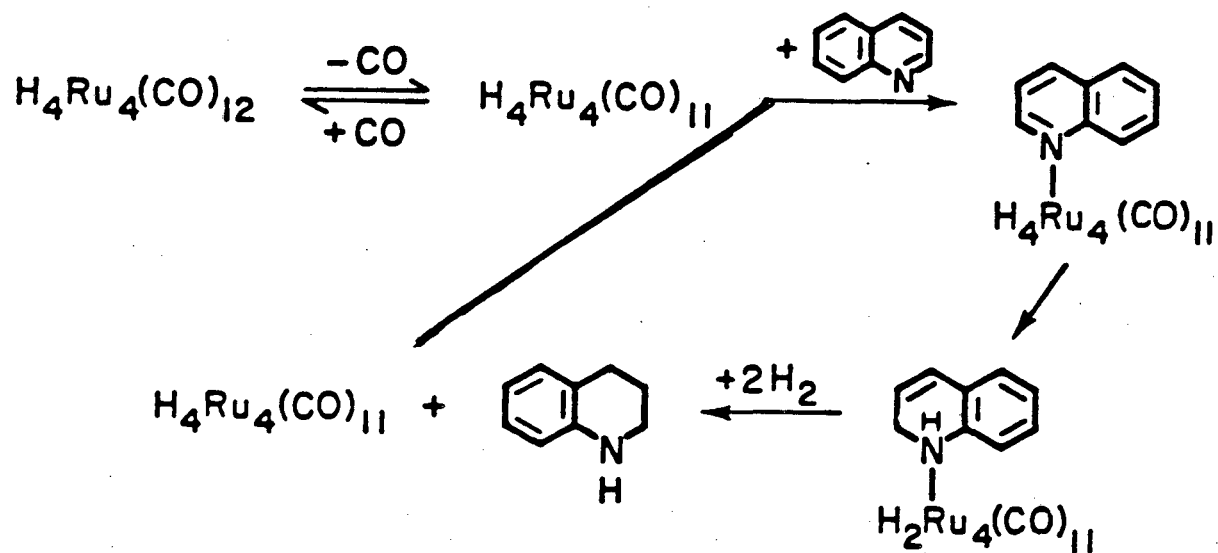


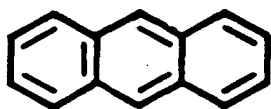
Figure 5



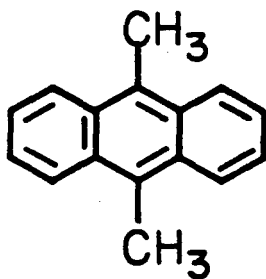
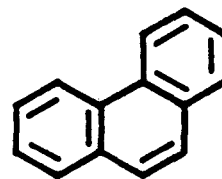
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**CHART CAPTION**

**(1) Model Synthetic Fuel Compounds Used in the Homogeneous Catalytic Hydrogenation Reactions**



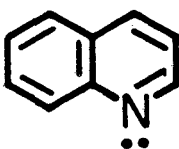
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9,10-Dimethyl-  
anthracene

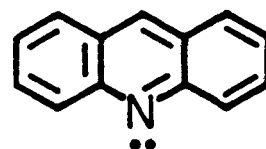
Phenanthrene



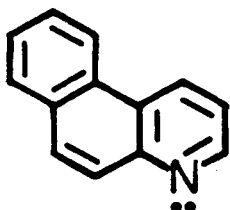
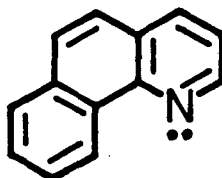
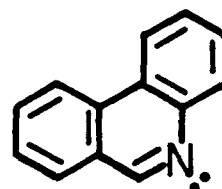
Pyridine



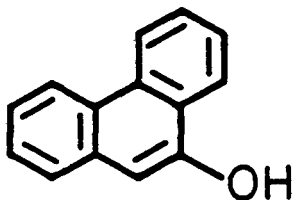
Quinoline



Acridine

5,6-Benzo-  
quinoline7,8-Benzo-  
quinoline

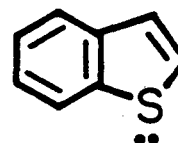
Phenanthridine



Phenanthrol



Thiophene



Benzothiophene

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