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AROMATIC AND POLYNUCLEAR HETEROAROMATIC
NITROGEN COMPOUNDS CATALYZED BY RUTHENIUM
CARBONYL HYDRIDES

Richard H. Fish, Arne Thormodsen,
and Gregg A. Cremer

January 1982

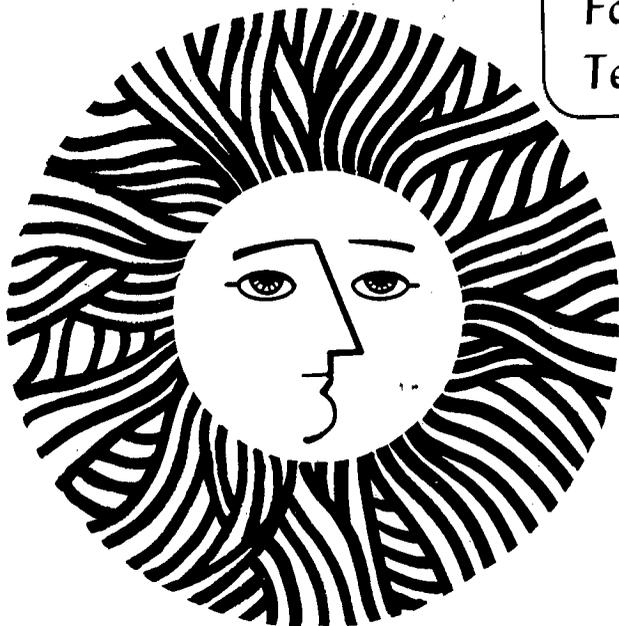
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HOMOGENEOUS CATALYTIC HYDROGENATIONS, 2:
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Homogeneous Catalytic Hydrogenations, 2: Regiospecific Reductions of
Polynuclear Aromatic and Polynuclear Heteroaromatic Nitrogen Compounds
Catalyzed by Ruthenium Carbonyl Hydrides.

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The various synthetic fuel products derived from coal or oil shale require additional hydroprocessing to minimize their nitrogen and sulfur content and therefore the selective hydrogenation of polynuclear heteroaromatics becomes critically^{1a-c}. Thus, it is extremely important to have a basic understanding of which polynuclear aromatic and polynuclear heteroaromatic compounds are hydrogenated in these complex fossil fuel matrices.

We have reported, in the previous paper², our results on utilizing carbon monoxide with either water or hydrogen, in the presence of transition metal carbonyls as catalysts, for the reduction of polynuclear aromatic and polynuclear heteroaromatic nitrogen compounds. In that study, we found that several of the transition metal carbonyl compounds did not catalyze the reduction of the above mentioned synthetic fuel models. The major factors in their inability to provide reduced products was the thermal stability of the generated transition metal carbonyl hydrides and a pronounced carbon monoxide inhibition. When carbon monoxide was removed from these reactions, several possible consequences of this removal were immediately obvious. First, several of the transition metal carbonyls such as those of Fe, Mn, Co, W, Cr, Mo etc. appeared to be unstable under the reaction conditions, and secondly, a dramatic increase in reduced product resulted when ruthenium carbonyls were used as catalysts.

In this communication, we wish to report our results on the regio-specific catalytic reduction of polynuclear aromatic and heteroaromatic nitrogen compounds with ruthenium carbonyl hydrides. Chart 1 shows the model synthetic fuel compounds, 1-8, used in this study.

In initial experiments, we utilized $\text{RuCl}_2(\text{CO})_2(\phi_3\text{P})_2$, 9, as a catalyst. We found, interestingly, with compound 9 that we needed both hydrogen and base for the reduction of compound 1³. No reaction occurred in the presence of carbon monoxide or in the absence of base. The reduction of 1 was highly regiospecific and gave exclusively 1,2,3,4-tetrahydroanthracene, 10⁴, in 30% yield. A control experiment was performed to establish that 9,10-dihydroanthracene, 11, was not the initial product formed, which then rearranged to compound 10. We reacted 11 under similar reaction conditions and found that it did not produce compound 10 and hence no rearrangement occurred.

Compounds 2 and 3 were unreactive under the reaction conditions and is consistent with previous findings of bent aromatic compounds greatly unreactive versus the linear aromatics such as 1². The polynuclear heteroaromatic nitrogen compounds, 4-8, were reacted under similar conditions to produce poor to moderate yields of reduced product (Table 1). However, we found that the removal of base (KOH) in the reactions of 4-8, with 9 as a catalyst, provided a dramatic increase in the yields of reduced products (Table 1). For example, compound 5 provided no reduced product with base present, while affording a 72% yield of 1,2,3,4-tetrahydro-7,8-benzoquinoline in the absence of base. Additionally, as with compound 1, carbon monoxide totally inhibited reduced product formation in the reactions of 4-8 with 9 as catalyst.

Mechanistically, these latter results strongly suggest a coordination of the substrate to the ruthenium as a prerequisite for reaction to occur and further accounts for the high regioselectivity for the nitrogen heterocyclic ring. Thus, carbon monoxide inhibites by competing with the substrate for a vacant ruthenium coordination site. The role of the KOH must be important in opening coordination sites on the ruthenium metal center in the reduction of the outer ring in compound 1. This might be achieved by hydroxide attack on coordinated carbon monoxide providing carbon dioxide and a ruthenium carbonyl hydride anion. There is ample precedent in the recent literature for this type of reaction^{5a-c}. In contrast to the beneficial use of base with 1, the reactivity of compounds 4-8 is greatly inhibited by base being present and possibly reflects the mechanistic differences in hydride formation and substrate coordination between the two sets of reaction conditions.

In concurrent experiments, we discovered that tetrahydridotetra-ruthenium dodecacarbonyl ($H_4Ru_4(CO)_{12}$)^{6a,b}, 12, was also^{or} an excellent catalyst for the hydrogenation of compounds 4-8. Compound 12 was not the initial catalyst used; rather, we pursued the catalytic activity of triruthenium dodecacarbonyl, 13, ($Ru_3(CO)_{12}$). We found that under our reaction conditions 12 readily formed (IR and MS analysis) by reaction of 13 with hydrogen gas (eq. 1)^{6b}.



Under the latter reaction conditions, reduction of 4-8 was evident; however, catalytic activity increased dramatically if 12 was formed prior to substrate addition. In this process CO was flushed from the system. Evidently, even a small partial pressure of CO (~ 10 psi CO

was generated in the formation of 12 from 13) was sufficient to cause inhibition of substrate coordination to ruthenium and greatly reduced product yield. For example, compound 13 provided a 7% yield of 1,2,3,4-tetrahydro, -5,6-benzoquinoline from 4, while 12 produced the same product in 75% yield.

Compound 12 has been previously described as a hydrogenation catalyst for olefins, carboxylic acids and ketones ^{7a,b}, but to our knowledge, never for polynuclear heteroaromatic nitrogen compounds. Table 2 shows the results of these catalytic hydrogenations with 12 and indicates again, as with 9, the high regioselectivity for the nitrogen heterocyclic ring. The order of reactivity with 12 as the catalyst, in this series of polynuclear nitrogen heterocycles, is interesting with $\underline{7} \sim \underline{8} > \underline{4} \gg \underline{5} \sim \underline{6}$. It is not totally clear whether steric or electronic effects make quinoline more reactive than 5,6-benzoquinoline. However, the reactivity differences between the 5,6 and 7,8-benzoquinoline could be due to a steric affect, which hinders the 7,8 isomer's ability to coordinate to the ruthenium. This steric effect could also be invoked to explain the lowered reactivity of compound 6.

We attempted to react 12 with polynuclear aromatic compounds, 1-3, however, we observed, at the higher temperatures needed (200°C) for reduction to proceed, a decomposition of the hydride to ruthenium metal. This type of result does not allow one to differentiate between homogeneous and heterogeneous catalysis. In fact, we find, not surprisingly, ruthenium metal to be active in the reduction of polynuclear aromatics under our conditions⁸. This decomposition was not evident at 150°C, and furthermore infrared analysis^{6b} of the reaction solutions of the nitrogen compounds, 4-8, clearly shows 12 still present after reaction.

This study has focused on the potential of homogeneous catalysts as viable candidates for use in the hydroprocessing of fossil fuels as well as important insights into compound reactivity in these complex matrices. In order to further determine the utility of these ruthenium carbonyl hydrides, we are in the process of "heterogenizing" these homogeneous catalysts to see if this form is still active. Additionally, we are continuing our model synthetic fuel compound studies in order to ascertain the role of other polynuclear heterocyclic compounds and hope to elucidate the more important mechanistic aspects of these highly interesting catalytic reactions⁹.

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We wish to thank Professors P. Vollhardt, R. Bergman and T. Vermeulen for helpful comments concerning this research project. We also wish special thanks to Dr. H. Heinemann of LBL for encouragement and support of this project.

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References and Notes

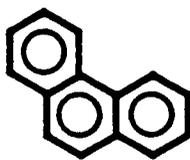
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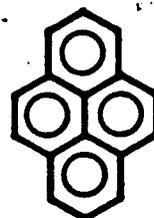
Chart 1. Model Synthetic Fuel Compounds Used in the Catalytic Hydrogenations with Ruthenium Carbonyl Hydrides.



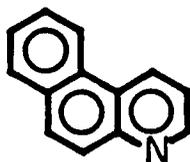
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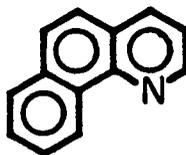
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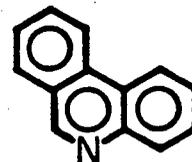
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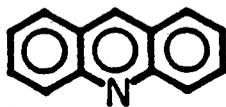
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5



6



7



8

Table 1. Reductions of Compounds 1-8 with $\text{Ru}(\text{Cl})_2(\text{CO})_2(\text{P}_3\text{P})_2$ as Catalyst

<u>Substrate</u>	<u>Product(%) with base a,b</u>	<u>Product (%) without base b,c</u>
<u>1</u>	1,2,3,4-Tetrahydroanthracene (30)	(0)
<u>2</u>	No product	No product
<u>3</u>	No product	No product
<u>4</u>	1,2,3,4-tetrahydro-5,6-benzoquinoline (10)	(92)
<u>5</u>	1,2,3,4-tetrahydro-7,8-benzoquinoline (0)	(72)
<u>6</u>	9,10-dihydrophenanthradine (5)	(15)
<u>7</u>	9,10-dihydroacridine (100)	(74)
<u>8</u>	1,2,3,4-tetrahydroquinoline (42) 5,6,7,8-tetrahydroquinoline (5)	(100) (0)

-
- a) Experiments were performed in a 45 ml Parr mini-reactor containing 1 mmole of substrate, 0.1 mmol $\text{Ru}(\text{Cl})_2(\text{CO})_2(\text{P}_3\text{P})_2$ in THF (12 ml), 0.2 M KOH (3 ml), 180°C, 350 psi H_2 for 5 hrs, 1-7, 2 hrs, 8.
- b) Identified by capillary column GC-MS analysis and quantitated by integration of starting material and product.
- c) 180°C, THF (12 ml), 0.1 mmole $\text{RuCl}_2(\text{CO})_2(\text{P}_3\text{P})_2$, 1 mmole substrate, 350 psi H_2 for 2 hrs.

Table 2. Reductions of Polynuclear Heteroaromatic Nitrogen Compounds, 4-8, Catalyzed by $H_4Ru_4(CO)_{12}^a$.

<u>Compound</u>	<u>Product (%)^b</u>
<u>4</u>	1,2,3,4-tetrahydro-5,6-benzoquinoline (75)
<u>5</u>	1,2,3,4-tetrahydro-7,8 benzoquinoline (8)
<u>6</u>	9,10-dihydrophenanthridine (10)
<u>7</u>	9,10-dihydroacridine (100)
<u>8</u>	1,2,3,4-tetrahydroquinoline (100)

(a) Experiments were performed in a 45 ml Parr mini-reactor containing 1 mmole of substrate, 0.1 mmole $H_4Ru_4(CO)_{12}$ (10:1 substrate to catalyst ratio) in 15 ml of cyclohexane with 350 psi H_2 for 2 hr. at 150°C.

(b) Analyzed by gas chromatography on a 12m x 0.1 mm i.d. fused silica capillary column (OV101) using a HP-5880A instrument with flame ionization and digital integration. Products were isolated by column chromatography (florisil) and identified by GC-MS and nmr spectroscopy (1H , 250MHz).

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