Public Health Service Research Grant (CA 13689-05) from the National Cancer Institute and the National Institutes of Health NMR Facilities for Biomedical Studies (RR-00292). We thank Drs. Mugio Nishizawa and Narihiko Fukamiya for many helpful discussions. We are indebted to Professor James A. Marshall for a sample gift of natural damsin and Professor Eloy Rodriquez for samples of natural ambrosin, psilostachyin C, and damsin.

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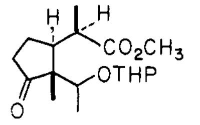

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(20) Fellow of the Alfred P. Sloan Foundation.

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Received June 20, 1977

Catalytic Homogeneous Hydrogenation of Arenes. 5.[1] The η^6-$C_6(CH_3)_6Ru$-η^4-$C_6(CH_3)_6$ Catalyst

Sir:

The pervasive cis stereochemistry of hydrogen addition to aromatic hydrocarbons elicited by the homogeneous η^3-$C_3H_5CoL_3$ (L = phosphite or phosphine) catalysts and the remarkable selectivity of these catalysts to arenes with respect to alkenes clearly have established the possibility of very selective and stereoselective catalysts for arene hydrogenation.[1-4] Unfortunately, the allylcobalt catalysts fail in a practical sense because of their relatively short lifetimes.[4] An intermediate postulated[3] in the cobalt system, η^1-$C_3H_5CoH_2$-$[P(OCH_3)_3](\eta^4$-$C_6H_6)$, as well as alternative η^6-C_6H_6-cobalt species have raised substantive questions about the susceptibility of π-bonded arenes to hydrogenation.[5-8] From a general investigation of metal arene complexes, we have now obtained fundamental mechanistic information about arene hydrogenation, demonstrated the hydrogenation of an η^6-arene–metal complex, and discovered a new homogeneous and long-lived arene hydrogenation catalyst system.

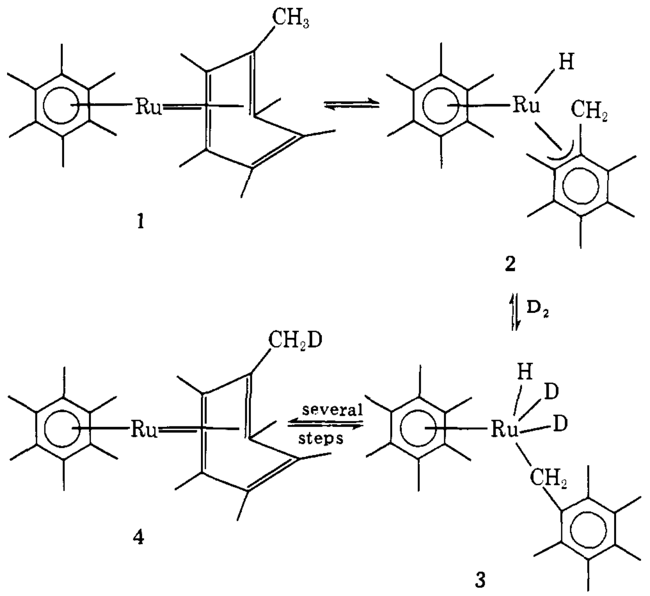
Hexahapto bonded arenes can be hydrogenated to cyclohexanes. η^6-$CH_3C_6H_5$-$Ru_6C(CO)_{14}$, which is thermally stable and does not undergo arene exchange with a benzene solvent at 150 °C, reacted with hydrogen at 150 °C (2–3 atm) to produce methylcyclohexane quantitatively, a black mirror that appeared to be ruthenium metal, and no recoverable toluene. The reaction effected with benzene as the solvent produced only traces of cyclohexane; the cyclohexane was produced by a ruthenium metal (formed in the initial hydrogenation reaction) catalyzed reaction. Although this reaction system was not catalytic, it does establish for the first time that η^6-arene–metal complexes can be hydrogenated. Attempts to stabilize this reaction system for a catalytic mode by addition of carbon monoxide led to complete suppression of the hydrogenation reaction suggesting that intermediates of the type arene–$Ru_6C(CO)_x$ with $x < 14$ are involved in the hydrogenation.[9] In sharp contrast, $(\eta^6$-$C_6H_6)_2Cr$ and $(\eta^6$-$CH_3C_6H_5)_2Mo$ underwent no hydrogenation in benzene solution at 150 °C (~5 atm). Under these conditions, there was no detectable arene exchange with the benzene solvent in the molybdenum system. Similarly, the η^6-$CH_3C_6H_5M(CO)_3$ (M = Mo, W) complexes were fully resistant to hydrogenation to 120 °C and arene exchange was observed only for the molybdenum complex at 120 °C. At 150 °C, there was gross thermal decomposition and no hydrogenation of the molybdenum carbonyl complex and arene exchange but no hydrogenation of the tungsten analogue.[10]

Of special interest to us has been the arene complexes in which an arene is *tetrahapto* bonded to a metal as in the presumed allylcobalt intermediates.[2] Within this class, the η^6-$C_6(CH_3)_6Ru$-η^4-$C_6(CH_3)_6$[11] complex proved to be a long-lived homogeneous catalyst for the hydrogenation of arenes with turnover rates of ~1/12 min at 90 °C (2–3 atm) for benzene. The reaction solution was clear orange to orange-red. No free hexamethylbenzene was detected in the reaction residues and the ruthenium catalyst was recovered quantitatively after 10-h reaction periods. Hydrogenation rates decreased with increased alkyl substitution on the arene as was observed for the allylcobalt catalyst. Hexamethylbenzene was not hydrogenated;[12] thus, the ruthenium catalyst has no reducible ligand, a critical element for a long-lived catalyst.

There are important differences as well as similarities between the ruthenium and allylcobalt systems. The exceptional cis character of the hydrogen additions in the cobalt catalyst is not present in the ruthenium catalyst where cis to trans ratios in the dimethylcyclohexanes produced from *o*- and *p*-xylenes were 9:1 and 9:2, respectively. These ratios more closely approximate reported stereochemistries with solid state, metallic catalysts. Cyclohexenes were significant products; the percentage of cyclohexenes in the total hydrogenation product were ~5, 40, and 55% for benzene? *o*-xylene, and *p*-xylene, respectively, whereas none is produced from these arenes with the allylcobalt catalyst[1-4] nor with Maitlis' $\{Rh[\eta^5$-$C_5(CH_3)_5]Cl_2\}_2$ catalyst.

The most dramatic distinguishing feature between the ruthenium and allylcobalt catalysts was the verv extensive H–D exchange observed for the former catalyst in arene-D_2 and perdeuterioarene-H_2 reactions. Cyclohexanes from d_0 through

Scheme I



d_{12} were obtained from $C_6D_6 + H_2$ and $C_6H_6 + D_2$ with $C_6H_6D_6$ the major species in both reactions. Both the benzene recovered in the $C_6H_6 + D_2$ reaction and the hexamethylbenzene ligands in recovered catalyst contained deuterium. Most unexpectedly, the recovered xylenes from a D_2 hydrogenation reaction contained large amounts of deuterium and primarily consisted of the d_0 and d_1-d_6 species with relatively minor amounts of the d_7-d_{10} xylenes. A similar result was observed with the recovered toluene from a toluene-D_2 reaction system where the d_0 and the d_1-d_3 species predominated. Clearly, H-D exchange in the methyl groups is fast with respect to that of the aromatic hydrogen atoms. The distribution of deuterium in the hexamethylbenzene ligands of the recovered catalyst was unexceptional with $[d_0] > [d_1] > [d_2]$ and so on through $[d_{18}]$.

In the ruthenium system, the H-D exchange that involves the methyl substituents of the arenes would seem to require an intermediate similar to that postulated by Weber and Brintzinger[13] for thermal reactions of the analogous but less stable iron complex $[C_6(CH_3)_6]_2Fe$. This is illustrated in Scheme I. The η^1-benzyl form, **3**, for hexamethylbenzene might be much less stable because of steric factors than the analogue from *o*-xylene which then might account for the faster deuterium introduction in the methyl groups of the xylenes than in those of hexamethylbenzene. The H-D exchange of ring protons can be readily accounted for by a kinetically significant reversibility in some of the initial hydrogen addition steps in the hydrogenation cycle. Mechanistically, the hydrogenation cycle could be formally analogous to the allylcobalt system, and, in fact, the benzylruthenium-arene species **2** and **3** are very similar to the postulated allylcobalt-arene intermediates.[1-4] However, note that hydrogen transfer to the σ or π benzyl ligand in the ruthenium system does not lead to catalyst destruction as does hydrogen transfer to the allyl ligand in the allylcobalt system.

The scope and kinetic features of this catalytic arene hydrogenation system are under investigation. Further studies of arene-metal complexes in their reactions with hydrogen may provide the key identification of intermediates in this type of reaction.[14] For arene hydrogenations by coordination catalysis, there may be a commonality[15] in reaction mechanism with allylic or benzylic species as key intermediates. Thus? for catalyst longevity, permethylarenes or -cyclopentadienyls[16] should be optimal ligands since these ligands, which can yield benzylic or benzylic-like complexes, are very resistant to hydrogenation.

Acknowledgment. We wish to sincerely thank the National Science Foundation for support of this research.

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(9) The arene–$Ru_6C(CO)_{14}$ complexes are obtained in low yield from the high temperature reaction of $Ru_3(CO)_{12}$ with an arene. Under present study is the reaction of $Ru_6C(CO)_{17}$ and $Ru_6C(CO)_{16}(PR_3)$ with arenes. Crucial to a catalytic system in this cluster system may be a facile arene exchange capability in some $Ru_6C(CO)_xL_y$ species. A catalytic hydrogenation of arenes with ruthenium carbonyls has been reported to proceed at 100 °C (100 atm): P. Frediani, M. Bianchi, and F. Piacenti, *Chim. Ind.* (*Milan*), **53,** 80 (1971). Our investigations of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ as arene hydrogenation catalysts showed no hydrogenation to 150 °C (5 atm). Above this temperature, ruthenium metal was formed and hydrogenation then proceeded: K. G. Caulton, M. G. Thomas, B. A. Sosinsky, and E. L. Muetterties, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 4274 (1976); E. L. Muetterties and J. W. Johnson, unpublished data.
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(15) At least there may be one dominant type of reaction mechanism.
(16) It would be of interest to determine whether the methyl groups of $C_5(CH_3)_5$ ligands in the rhodium catalyst, described by Maitlis, et. al.,[6] incorporate deuterium in the $C_6D_6 + H_2$ reaction.
(17) NSF Energy Related Postdoctoral Fellow, 1976–1977.

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Received July 28, 1977

A Novel Acylation of Some Activated Olefins by an Electroreductive Method[1]

Sir:

Owing to its wide potentiality in organic syntheses, the generation of acyl anion or its chemical equivalents, though most of them are rather complex species, has attracted much attention in recent years.[2] On the other hand, electrochemical reduction has been known as a powerful tool in the generation of active species which may difficultly be formed by conventional chemical methods.[3] Although the electroreductive acylation of heteroatoms has been studied extensively,[4] only few have been known in the acylation of carbon atom.[5]

We wish to report herein a novel electrochemical acylation of activated olefins **1**, **2**, and **3**, in which the products, γ-keto esters **4** and **5** and nitriles **6**, are just the same as those formed from the addition of acyl anion to the activated olefins, though this electrochemical reaction may not involve the acyl anion itself as the active species.

In view of its simplicity and generality, the electroreductive