"Catalytic Arene Hydrogenation Using Early Transition Metal Hydride Compounds".

P.I.: Ian P. Rothwell

Since the beginning of this grant in August, 1992 considerable progress has been achieved in a number of areas. Four of these areas are highlighted below.

1. Development of Surface Supported Group 5 Metal Organometallic Compounds for Catalytic Arene Hydrogenation.

Our initial identification of Group 5 metal hydrido, aryloxy compounds as catalysts for the homogeneous hydrogenation of arene rings has led us to investigate the activity of oxide bound derivatives of niobium and tantalum for related reactivity. We have developed an extremely active hydrogenation catalyst by supporting the alkylidyne bridged compounds $[(\text{Me}_3\text{SiCH}_2)_2\text{M}(\mu\text{-CSiMe}_3)]$ ($\text{M}=\text{Nb}, \text{Ta}$) on silica surfaces. The resulting impregnated material will hydrogenate benzene and other aromatics at rates comparable to that found using the much more expensive platinum group metals.

On going work in this area involves determining the scope of the reactivity (e.g. heteroatom sensitivity), regiochemistry and the stereochemistry of various steps in the reaction. In conjunction with Prof. Ben Freiser's group we are investigating the use of gas-phase ion-molecule reactions to probe the stereochemistry of the hydrogenation products. Future work will focus on attempting to better characterize the nature of the surface bound catalyst precursors as well as the nature of the attached species present under catalytic conditions.

MASTER

2. Isolation and Reactivity of Possible Intermediates in Catalytic Arene Hydrogenation.

We have been able to isolate and structurally characterize a pair of η^4 -cyclohexadiene derivatives of niobium and tantalum containing aryloxy ligation. These new compounds, $[(\text{ArO})_3\text{M}(\eta^4\text{-C}_6\text{H}_8)]$ ($\text{M}=\text{Nb, Ta}$) will catalyze the disproportion of 1,3-cyclohexadiene exclusively to benzene and cyclohexene. Furthermore, in the presence of hydrogen, we have shown that 1,3-cyclohexadiene is hydrogenated preferentially over cyclohexene. This remarkable selectivity is being further investigated along with a combination of kinetics and labelling studies to attempt to map out the mechanistic pathway for the catalytic hydrogenation of benzene, 1,3-cyclohexadiene and cyclohexene.

3. Synthesis and Characterization of New d^0 -Metal Hydride Compounds.

Both our stoichiometric and catalytic reactivity studies implicate Group 5 metal hydride compounds as key elements in the hydrogenation of arene rings. We have now developed novel, high yield syntheses of a wide variety of hydride compounds of Ta(V) containing ancillary aryloxy ligation. Synthetic methods involve hydrogenolysis of metal-alkyls, reduction in the presence of H_2 and reaction of halide compounds with hydride sources. A particularly high yield synthesis has involved reaction of tantalum-chloro compounds with $\text{Bu}_3^{\text{n}}\text{Sn-H}$ in the presence of phosphine ligands; e.g.

Further work in this area will involve the synthesis and study of related hydride compounds to investigate whether their reactivity can be attenuated by varying the accompanying ligand set.

4. Stoichiometric Reactivity of d⁰ Metal Hydrido, Aryloxo Compounds.

The above synthetic methods have made available a range of new hydrido compounds for study. Their stoichiometric reactivity towards arenes, olefins and other unsaturated substrates is being investigated. The structure and reactivity of the products of the reaction with heteroatom containing small molecules are of particular interest. Preliminary work in this area has already shown that we can expect an extensive body of reactivity to be opened up. As an example, reaction of the simplest hydride we have [(ArO)₂TaCl₂(H)(PMe₂Ph)₂] with organic isocyanides leads to at least three different products depending on the bulk of the substrate. In the case of Bu^tNC, trimerization of three equivalents of isocyanide rapidly takes place.

Unexpended Balance

As of 2/28/93, the unexpended balance of the present DOE grant was \$33,196.12. No funds will be remaining at the end of this grant period (7/31/93).

Publications Acknowledging Support of D.O.E. Grant #ER14280

1. Surface Supported Group 5 Metal Organometallic Compounds for Catalytic Arene Hydrogenation, Profilet, R. D.; Rothwell, A. P.; Rothwell, I. P., *J. Chem. Soc. Chem. Com.*, **1993** 12, 42-44.
2. Crystal and Molecular Structure of Penta(4-methylbenzyl)Tantalum, $[\text{Ta}(\text{CH}_2\text{C}_6\text{H}_4\text{-4Me})_5]$, Piersol, C. J.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P., **1993**, 12, xxxx.
3. Structure of Niobium Bis(2,6-diisopropylphenoxide)bis-(dimethylphenylphosphine)dichloride, Nguyen, M. T.; Yu, J. S.; Fanwick, P. E.; Rothwell, I. P., *Acta. Cryst.*, submitted.
4. Structure of $[(2,6\text{-Ph}_2\text{C}_6\text{H}_3\text{O})(\text{Me}_3\text{SiCH}_2)\text{Nb}(\mu\text{-CSiMe}_3)]_2$, Torrez, E.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P., *Acta. Cryst.*, submitted.

END

DATE
FILMED

7 / 19 / 93