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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The syntheses of metallacycles from metallacarborane carbonyl anions [closo-3-PPh_3-3-(CO)-3,1,2-$MC_2B_9H_{11}]^-$ (M = Ir, Rh) and [closo-2-PPh_3-2-(CO)-2,1,7-$RhC_2B_9H_{11}]^-$ and a number of pentamethylcyclopentadienyl and cyclopentadienyl complexes of Co, Rh and Ir of the type $(\eta^5-C_5R_5)LM(CO)$ (R = H, Me; L = PPh_3, PMe_3, CO) and the metal carbonyl anions $M(CO)_5^-$ (M = Mn, Re) have been achieved. The thermolysis products of $(\eta^5-C_5Me_5)(CO)Ir[\eta^2-C(p-ClC_6H_4)NOC(=O)-]$ (1) and $(\eta^5-C_5Me_5)(PMe_3)Rh[\eta^2-C(p-FC_6H_4)NOC(=O)-]$ (2) have been shown to activate C-H bonds under relatively mild conditions. The thermolysis of (1) has been shown to proceed via the side-bonded nitrile intermediate $(\eta^5-C_5Me_5)(CO)Ir(\eta^2-NCC_6H_4Cl)$ (3) which was isolated, characterized and shown to independently activate benzene C-H bonds at 50°C. Complexes (1) and (3) can also be readily decomposed under mild photochemical conditions in benzene or cyclohexane to yield the C-H activation products, $(\eta^5-C_5Me_5)Ir(CO)(H)(C_6H_5)$ and $(\eta^5-C_5Me_5)Ir(CO)(H)(C_6H_{11})$ in high yield.

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OFFICE OF NAVAL RESEARCH
FINAL REPORT
PUBLICATION/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

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"Monomers, Polymers and Transition Metal Complexes Based Upon Carboranes"

Period Covered: March 3, 1986 - February 28, 1989
Principal Investigator: Professor M. Frederick Hawthorne
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Part I

a. Papers Submitted to Refereed Journals: none

b. Papers Published in Refereed Journals:

1. "The Formation of η^2-Side-bonded Aryl Nitrile Complexes," Peter A. Chetcuti, Carolyn B. Knobler and M.F. Hawthorne *Organometallics* **1988**, 7, 650.

2. "Synthesis of Metallacycles by [3 + 2] Cycloaddition Reactions Between Low Valent Metal Carbonyl Complexes and Nitrile-N-oxides," Peter A. Chetcuti, John A. Walker, Carolyn B. Knobler and M.F. Hawthorne *Organometallics* **1988**, 7, 641.

3. "Activation of C-H Bonds with Intermediates Produced by Mild Thermal and Photochemical Decomposition of Metallacycle $(\eta^5\text{-}C_6H_5)Ir[C(p\text{-}ClC_6H_4)=NOC(=O)]CO$ in Hydrocarbon Solvent" Peter A Chetcuti and M.F. Hawthorne *J. Am. Chem. Soc.* **1987**, 109, 942.

4. "Intramolecular Conversion of a 5-Membered Iridacycle to a 3-Membered Counterpart by CO_2 Extrusion" Peter A. Chetcuti, Carolyn B. Knobler and M.F. Hawthorne *Organometallics* **1986**, 5, 1913.

c. Books Submitted for Publication: none

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f. Patents Filed: none

g. Patents Granted: none

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i. Contributed Presentations at Scientific/Technical Society Conferences: none

j. Honors/Awards/Prizes: none

k. Number of Graduate Students Receiving Full or Partial Support on ONR Contract: three

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Part II

a. Principal Investigator: Professor M. Frederick Hawthorne

b. Cognizant ONR Scientific Officer: Dr. Harold E. Guard

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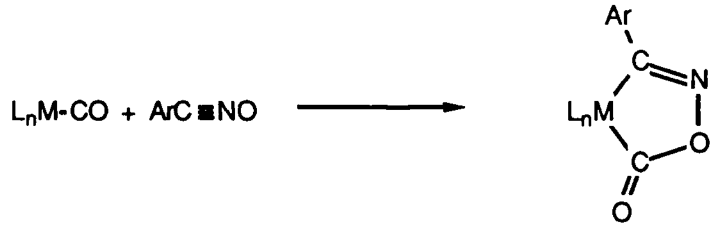
d. Brief Description of Completed Project:

Our research for the Chemistry Division of ONR has involved studies of the reactions of low valent metal carbonyl complexes with arylnitrile oxides resulting in the [3 + 2] cycloaddition of the arylnitrile oxide to the M-CO bond of the metal carbonyl complex. A number of metallacycles have been synthesized in good yield by this route, establishing the generality of this reaction.

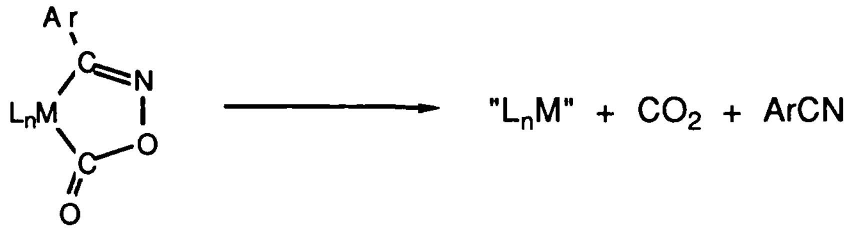


(1)

Recent studies have been concerned with the nature and synthetic utility of the products resulting from the thermolysis of rhodium- and iridium-containing metallacycles. We have recently reported the accomplishment of an important goal of this project, the metallacycle-promoted thermal activation of C-H bonds of saturated hydrocarbons. This accomplishment has attracted considerable interest from other workers in this field. In short, the thermolysis of selected metallacycles results in the loss of arylnitrile and CO_2 to genrate a coordinatively and electronically unsaturated metal fragment which is highly reactive.

Carbon [illegible]

[illegible] Cyclic Compounds, [illegible]
[illegible] Iridium Compounds, Rhodium Compounds, [illegible] Metal Complexes. (AU)



(2)

Thermolysis of the appropriate metallacycle provides a low energy pathway to the generation of a metal fragment which is sufficiently reactive to add into the C-H bonds of hydrocarbons. The extension of the [3 + 2] cycloaddition reaction of arylnitrile-N-oxide to other metal complexes was attempted. The reactions of $[W(CO)_3(C_2B_9H_{11})][PPN]_2$, $Rh(PPh_3)_2(Cl)(CS)$ or $RhCp(PPh_3)(NO)$ with p-fluorobenzonitrile-N-oxide and attempts using nitrones, instead of arylnitrile-N-oxides, as the 1,3-dipolar reagent in the reaction with metal carbonyls generated unpromising results.

In another area, recent research efforts have been directed towards an examination of the chemistry of ruthenium-containing metallacarboranes with regard to their potential for catalytic behavior. This chemistry has precedence in the synthesis of the active and highly stable rhodacarborane catalyst [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] and its derivatives. Previous work by us involving *ruthenacarboranes has* led to the discovery of two hydride complexes that show catalytic activity for the hydrogenation of activated olefins such as ethyl acetate, as well as, the isomerization of terminal olefins. In addition, the eleven vertex complex [*hyper-closo*-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_9$] has previously been shown to be an active catalyst precursor for the hydrogenation of alkenes, and the icosahedral cluster [*closo*-3,3,3-$(PPh_3)_3$-3-H-3,1,2-$RuC_2B_9H_{11}$] facilitates the activation of carbon monoxide, promoting reactions with various nucleophiles. Our recent studies in this area have involved the synthesis and structural characterization of various metal- and carborane cage-substituted ruthenacarborane complexes in an attempt to obtain new ctalytic species having high selectivity.

The unusual rhodacarborane complex $[Rh(\eta^5\text{-}C_2B_9H_{11})(CO)(PPh_3)(Tl)]$ (**1**), was prepared as a result of attempts to develop an alternative one-step route to the important rhodacarborane anion complex $[Rh(\eta^5\text{-}C_2B_9H_{11})(CO)(PPh_3)]^-$, the precursor to the rhodacarborane metallacycle $[(PPh_3)(\eta^5\text{-}C_2B_9H_{11})Rh\{\eta^2\text{-}C(Ar){=}NOC({=}O)\text{-}\}]$. Complex (**1**) is very interesting since it possesses a very short rhodium-thallium interatomic distance of 2.954 Å. In order to gain a greater understanding of the metal-metal interaction, thallium-205 NMR spectroscopy was attempted. Unfortunately, no signal was observed in the NMR spectrum. The reason for this is unclear, since resonances of similarly bond thallium in other complexes have been observed. The variation of the carbonyl stretching frequency, ν(CO), in the infrared spectrum of (**1**) was studied as a function of solvent. In non-coordinating solvents the carbonyl stretching frequency varied only slightly from that of the solid. This indicates that there is still a strong interaction between rhodium and thallium in non-coordinating solvents. However, in coordinating solvents there was significant variation in the carbonyl stretching frequency. This indicates the formation of a solvent-seperated ion pair or free ion in coordinating solvents. Several attempts to form heterobimetallic compounds by reaction with metal halides yielded purple or red, amorphous, decomposition products and reaction with $(CH_3)_4NCl$ resutled in the formation of $\{Rh(PPh_3)_2(CO)\text{-}3,1,2\text{-}C_2B_9H_{11}\}^-[(CH_3)_4N]^+$, with TlCl precipitation. The iridium complex, $Ir(PPh_3)(CO)(Tl)[3,1,2\text{-}C_2B_9H_{11}]$, was synthesized from Vaska's complex, $Ir(PPh_3)_2(CO)Cl$, via its reaction with Tl[*closo*-3,1,2-$TlC_2B_9H_{11}$]. The analytically pure, yellow microcrystalline product was fully characterized and shown to possess a strong iridium-thallium interaction, similar to that found in (**1**).

The reaction of $(PPh_3)_3RuHCl$ with $[(CH_3)_3NH][7,8\text{-}C_2B_9H_{12}]$ and with $Tl_2[7,8\text{-}C_2B_9H_{11}]$ in the presence of $(C_2H_5)_4NCl$ yields $[(C_2H_5)_4N]$[*closo*-3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RuC_2B_9H_{11}$] (**2**) and $[(C_2H_5)_4N]$[*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RuC_2B_9H_{11}$] (**3**), respectively. Complex (**3**) has been shown to catalyze the isomerization of 1-hexene to cis and trans 2-hexene, however, the rate of this catalytic reaction is slow. The molecular structures of both (**2**) and (**3**) have been determined by X-ray diffraction studies. The reaction of $(PPh_3)_3RuHCl$ with $Na[9\text{-}NC_5H_5\text{-}7,8\text{-}C_2B_9H_{10}]$ yields the previously known complex [*closo*-3,3-$(PPh_3)_2$-3-H-7-NC_5H_5-3,1,2-$RuC_2B_9H_{11}$], which has also been shown to slowly catalyze olefin hydrogenation and isomerization. Acidification of solutions of (**3**) in ethanol and in acetonitrile yields [*closo*-3,3-(PPh_3)2-3,3-$(H)_2$-3,1,2-$RuC_2B_9H_{11}$] (**4**) and [closo-3,3-$(CH_3CN)_2$-3-(PPh_3)-3,1,2-$RuC_2B_9H_{11}$] (**5**), respectively. The molecular structures of (**4**) and (**5**) have been determined by single crystal X-ray diffraction studies.

The rhodacarborane catalyzed cleavage of alkenyl carboxylates concommitant with the activation of C-H and Si-H has been previously demonstrated. As an extension of our C-H activation project, we undertook a study aimed at determining the potential for activation of arene C-H bonds by a rhodium catalyst. The rhodium complex $[Rh(P(CH_3)_3)_2Cl]_2$ was chosen as a candidate for initial catalytic screening. Attempts with vinyl acetate and isopropenyl acetate did not result in the hoped for alkene formation; and the use of aldehydes as hydrogen sources also gave negative results.