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MONOMERS, POLYMERS AND TRANSITION METAL COMPLEXES BASED UPON CA--ETC(U)
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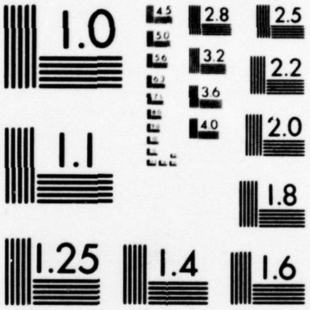
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LEVEL II ⑫
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⑥ MONOMERS, POLYMERS AND TRANSITION METAL COMPLEXES BASED UPON CARBORANES

⑨ FINAL REPORT,

⑮ ONR #N00014-75-C-0301 Task No. NR 053-481

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Recently our research interests have turned to metallocarborane complexes with more reactive ligands in a search for catalytic systems. Over the past year we have had considerable success.

In addition to the recently reported catalyst,[1] [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (I), we have now synthesized the iridium analog (II) and a related ruthenium compound, [*closo*-3,3-$(PPh_3)_2$-3,3-$(H)_2$-3,1,2-$RuC_2B_9H_{11}$] (III) by reaction of [*nido*-7,8-$C_2B_9H_{12}]^-$ with $RhCl(PPh_3)_3$, $IrCl(PPh_3)_3$, and $RuHCl(PPh_3)_3$ respectively. The isomers of (I), (II), and (III) in which the carbons in the bonding face of the carborane ligand are separated (the 2,1,7 isomers) have also been prepared.

An X-ray crystal structure determination of (I) confirms the presence of a rhodium-bound hydride as opposed to the alternative, a rhodium-boron bridging hydride; and an X-ray crystal structure determination of (III) is substantially complete and indicates a formally seven-coordinate ruthenium.

We have also prepared compounds similar to (I), (II) and (III) with other carboranes. Reaction of [*arachno*-$C_2B_7H_{12}]^-$ with $RhCl(PR_3)_3$ gives [*closo*-$(PR_3)_2$-$HRhC_2B_7H_9$] (IV). For R=Ph, no metal-bound hydride resonance is found in the ^1H NMR spectrum, probably due to extensive phosphine dissociation. With a more basic phosphine (R=p-tolyl), however, the hydride resonance has been found. (IV) (R=Ph) has been found to catalyze olefin isomerization and hydrogenation, and preliminary results indicate the kinetics of these reactions for (IV) are significantly different from those of (I). This is being investigated further.

$IrCl(PPh_3)_3$ reacts with [*nido*-$C_2B_8H_{11}]^-$ to produce [*closo*-1,1-$(PPh_3)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$] (V), and $RuHCl(PPh_3)_3$ reacts with [*arachno*-$C_2B_7H_{12}]^-$ to give [*closo*-6,6-$(PPh_3)_2$-6,2,3-$RuC_2B_7H_9$] (VI). (VI) is an electron-deficient complex which has been found to catalyze the hydrogenation of 1-octene and react reversibly with activated olefins such as ethyl acrylate. (VI) also reacts with hydrogen to produce [closo-6,6-$(PPh_3)_2$-6,6-$(H)_2$-6,2,3-$RuC_2B_7H_9$] (VII). The hydride ligands can be removed from (VII) and from (III) by subjecting them to high vacuum at 120°C. The existence of these pairs of compound suggests the following as a possible mechanism for olefin hydrogenation for the ruthenium catalysts:

$$\begin{tikzcd}
\mathrm{RuH_2(PPh_3)_2(C_2B_nH_{n+2})'} + \text{olefin} \arrow[r] & \mathrm{RuH(alkyl)(PPh_3)_2(C_2B_nH_{n+2})} \arrow[d] \\
 & \mathrm{Rh(PPh_3)(C_2B_nH_{n+2})} + \text{alkane} \arrow[ul, "H_2"']
\end{tikzcd}$$

We have begun work on the modification of the basic metallocarborane catalysts to see what effects different co-ligands have. A compound now well-characterized as [closo-3-PPh_3-3-CO-3-H-3,1,2-$RhC_2B_9H_{11}$] (VIII) can be prepared by the following route:

$$\begin{tikzcd}
\mathrm{(PPh_3)_2HRhC_2B_9H_{11}} \arrow[r, "\text{KOH/EtOH}"] \arrow[d, "\text{KOH/EtOH}", "\text{CO}"'] & \mathrm{K[(PPh_3)_2RhC_2B_9H_{11}]} \arrow[d, "\mathrm{Me_4N^+}"] \\
\text{orange solid} \arrow[dr, "H+"] & \text{green solid} \arrow[l, "\text{CO}"'] \arrow[ul, "H+"'] \\
 & \mathrm{(PPh_3)(CO)HRhC_2B_9H_{11}}
\end{tikzcd}$$

We anticipate that (VIII) may show some very interesting catalytic behavior.

We have also done the preliminary work on the preparation of analogs of (I) with phosphite ligands in place of triphenylphosphine. It is hoped that the more labile phosphite ligands will enhance catalytic activity.

Additionally, we are beginning the investigation of the effects various substituents on the carborane cage may have. The pyridine carborane adduct $C_5H_5N\text{-}C_2B_9H_{11}$, in which the pyridine is bound to a boron in the top belt of the carborane, reacts with sodium hydride to give $Na[C_5H_5NC_2B_9H_{10}]$ which produces [<u>closo</u>-3,3-$(PPh_3)_2$-4-C_5H_5N-3,1,2-$RhC_2B_9H_{10}$] (IX) from $RhCl(PPh_3)_3$. It is expected that this rhodium(I) complex will show some interesting differences from (I) which is a rhodium(III) complex. (IX) reacts readily with carbon monoxide, hydrogen chloride, methyl iodide, hydrogen, and carbon tetrachloride. These products are under investigation. (I) does not show analogous reactions.

As well, we have successfully bound a metallocarborane to polymer beads using a boron-carbon bond as follows:

$$\begin{tikzcd} \textcircled{P}\text{-}C_6H_4\text{-}CH_2Cl + KNa[C_2B_9H_{11}] \arrow[r] & {[\textcircled{P}\text{-}C_6H_4\text{-}CH_2\text{-}C_2B_9H_{11}]^-} \arrow[dl, "RhCl(PPh_3)_3"] \\ \textcircled{P}\text{-}C_6H_4\text{-}CH_2\text{-}C_2B_9H_{10}RhH(PPh_3)_2 & \end{tikzcd}$$

These polymer-bound catalyst beads were found to isomerize 1-octene and hydogenate 3-methyl-3-phenyl-1-butene at a rate comparable to similar non-polymer bound compounds.

A second major area of interest is the preparation of polymetallocarboranes. The possibilities of cooperative behavior in catalytic reactions when two or more metal atoms are present in one catalyst molecule make this area very promising. We have already prepared part of a series of bimetallic metallocarboranes of the general form $(PPh_3)_2M(PPh_3)_2M'H_xC_2B_nH_{n+2}$ for M=Ni,Pd,Pt; M'=Ru,Os,Rh,Ir; $6\leq n\leq 9$. The most promising route to this type of compound is as follows:

$$\begin{tikzcd}
\underline{\text{closo}}\text{-1,6-}C_2B_8H_{10} \arrow[r, "2e^-"] & {[\underline{\text{nido}}\text{-}C_2B_8H_{10}]^{2-}} \arrow[d, "(PPh_3)_2MCl_2"] \\
{[\underline{\text{nido}}\text{-}(PPh_3)_2MC_2B_8H_{11}]^-} \arrow[dr, "(PPh_3)_3M'Cl"'] & {[\underline{\text{closo}}\text{-1,1-}(PPh_3)_2\text{-1,2,3-}MC_2B_8H_{10}]} \arrow[l, "NaBH4"'] \\
 & {[\underline{\text{closo}}\text{-}(PPh_3)_2M(PPh_3)_2M'H_xC_2B_8H_{10}]}
\end{tikzcd}$$

We have also prepared the first trimetallocarborane containing nickel by direct insertion of three transition metal vertices into a nido carborane. An x-ray structure determination of this compound, $(CpNi)_3CB_5H_6$, revealed a nido structure which apparently consists of a Ni(III)-Ni(III)-Ni(IV) mixed valence system.[2]

Polyhedral expansion of $CpFeC_2B_9H_{11}$ leads to formation of $(CpFe)_2C_2B_9H_{11}$ (X), which is an electron-deficient compound containing two formally d^5 Fe(III) vertices. Preliminary x-ray structural data on this diamagnetic compound indicate that the metals are non-adjacent. This implies long range metal-metal communication in the thirteen vertex polyhedron.

The unusual properties displayed by complexes of early transition metals led us to prepare a number of carborane complexes of them. Reaction of early transition metal chlorides ($TiCl_4$, $ZrCl_4$, $HfCl_4$, VCl_3CrCl_3) with $[\underline{\text{nido}}\text{-}C_2B_{10}H_{12}]^{2-}$ gave bis-dicarbollyl complexes of the form $[M(C_2B_{10}H_{12})_2]^{2-}$.[3] Titanacarboranes with cyclopentadienyl and cyclooctatetraenyl co-ligands were also prepared.[4] The compounds $C_8H_8TiC_2B_nH_{n+2}$ (n=9,10) are the first metallocarboranes to incorporate a η^8-C_8H_8 ligand.

Unlike some similar titanium cyclopentadienyl compounds, $[CpTiC_2B_{10}H_{12}]^-$ (XI) does not react with nitrogen, apparently due to different electronic and steric requirements. We have shown that electron-donating substituents (i.e. CH_3) on the carborane cage increase the stability of complexes like (XI). It is probable that electron-withdrawing groups will enhance the electrophilic nature of the metal and may permit the formation of dinitrogen complexes.

Finally, we have synthesized a number of closo and nido metalloboranes[5,6] such as [closo-$CpNiB_9H_9]^-$, [closo-$CpNiB_{11}H_{11}]^-$, [closo-$(CpNi)_2B_{10}H_{10}]$, [closo-$(CpNi)(CpCo)B_{10}H_{10}]^-$, [nido-$CpNiB_{10}H_{12}]^-$, [nido-$CpNiB_{10}H_{13}]$, and [nido-CpCo-$B_{10}H_{13}NEt_3]$. The closo compounds show the extreme thermal and oxidative stability associated with the parent closo-borane anions, $B_nH_n^{2-}$.

Two isomers of the compound $[CpNiB_9H_9]^-$ have been observed, one with the nickel in an apical site of the bicapped square antiprism, and one with the nickel in an equatorial site. The equatorial isomer which is formed initially isomerizes thermally and photochemically to the apical isomer. The isomerization appears to be acid catalyzed.

The equatorial isomer, $[2\text{-}(CpNi)B_9H_9]^-$, reacts smoothly with chlorine under mild conditions to give the perchloro compound, $[2\text{-}(CpNi)B_9Cl_9]^-$ which also rearranges thermally to the apical isomer. However, photochemically the apical isomer is partially converted to the equatorial isomer.

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