Research Interests

1. Semi-Sandwich Metallacarboranes Derived from \([nido-C_2B_9H_{12}]^{+}\) Isomers and Other Metallacarboranes with Smaller-Cage Dicarbon Carboranes.

This area covers many aspects of modern transition metal metallacarborane chemistry. The complexes under investigation can be divided into two groups:

1) 12-vertex closo- and pseudocloso-metallacarboranes with metal-coordinated carbocyclic ligands derived from diene hydrocarbons (these are planned to be logically extended to open-chain alkene, acetylene and diene hydrocarbons),

2) closo-metallacarboranes of 11-12-vertex \{MC_2B_9\} and \{MC_2B_8\} cluster structure with terminal non-hydrocarbon ligands at metal centers (i.e. halogen, phosphine and hydride/dihydride).

Both these groups are represented by a number of unique complexes. Of these one group is agostic (C-H...M) fluxional species served as ideal models for investigations of complicated exchange or hydrogen migration processes in metal-coordinated hydrocarbon ligands. One of the specific goals is the development of efficient routes to enantiomerically pure platinum metal metallacarboranes (including an elucidation of their absolute configuration and the study of their chiroptical properties) which might find utility as catalysts for diastereo- and/or enantiocontrolled organic processes. Specifically, these are of interest for the synthesis of biologically active natural products or their precursors.

A series of 16-electron chlorohydrido-Os(IV) exo-nido complexes [exo-nido-10,11-{(Ph\textsubscript{3}P)\textsubscript{2}OsHCl}-10,- 11-(\textmu-H)2-7,R-7,9-C\textsubscript{2}B\textsubscript{9}H\textsubscript{8}] (R = H; R = Ph) as well as [exo-nido-10,11-{(Ph\textsubscript{3}P)\textsubscript{2}OsH\textsubscript{2}}]-10,11-(\textmu-H)2-7,9-C\textsubscript{2}B\textsubscript{9}H\textsubscript{8}] has been prepared starting from [OsCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}] and the K\textsuperscript{+}-salts of the [nido-7,9-C\textsubscript{2}B\textsubscript{9}H\textsubscript{12}]\textsuperscript{-} anion and its C-phenylated derivative either in benzene or ethanol, respectively. Structures of both complexes with unsubstituted cage ligand have been unambiguously confirmed by single-crystal X-ray diffraction studies. Thus, they represent the first structurally characterized exo-nido-metallacarboranes based on meta-dicarbollide-type ligands. These studies also revealed that nido-carboranes in these species function as a bidentate dicarbollide ligands [nido-7,9-C\textsubscript{2}B\textsubscript{9}H\textsubscript{10}]\textsuperscript{-} linked to the Os(IV) center via two B-H \cdots Os bonds involving adjacent B-H vertices in the upper CBCBB belt of the carborane cage. Variable-temperature \textsuperscript{1}H and \textsuperscript{31}P\{\textsuperscript{1}H\} NMR experiments indicate that dehydrido complex [exo-nido-10,11-{(Ph\textsubscript{3}P)\textsubscript{2}OsH\textsubscript{2}}]-10,11-(\textmu-H)2-7,9-C\textsubscript{2}B\textsubscript{9}H\textsubscript{8}] is fluxional in solution showing an unusual exchange between terminal Os-(H)\textsubscript{2} and bridging [B-H]\textsubscript{2} \cdots Os hydrogen atoms and could irreversibly be converted to its closo isomer [2,2-(PPh\textsubscript{3})2-2,2-H\textsubscript{2}-closo-2,1,7-OsC\textsubscript{2}B\textsubscript{9}H\textsubscript{11}].

Starting from the K\textsuperscript{+}-salt of the [7,8-(4'-MeC\textsubscript{6}H\textsubscript{4})\textsubscript{2}-7,8-nido-C\textsubscript{2}B\textsubscript{9}H\textsubscript{10}]\textsuperscript{-} monoanion and the COD-metal \textmu-chloride complexes [(\textnu\textsuperscript{4}-COD)\textsubscript{2}M\textsubscript{2}(\textmu-Cl)\textsubscript{2}] in benzene two new 16-electron complexes [3-{(1-3-\textnu\textsuperscript{3})-C\textsubscript{8}H\textsubscript{13}}-1,2-(4'-MeC\textsubscript{6}H\textsubscript{4})\textsubscript{2}-3,1,2-pseudocloso-MC\textsubscript{2}B\textsubscript{9}H\textsubscript{6}] (M = Rh\textsuperscript{III}; M = Ir\textsuperscript{III}), have been prepared and studied by single-crystal X-ray diffraction as well as by a combination of spectroscopic methods. The major rhodium complex is formed along with a small amount of an unusual dimeric rhodacarborane [(\textnu\textsuperscript{6}-MeC\textsubscript{6}H\textsubscript{4})Rh(C\textsubscript{2}B\textsubscript{9}H\textsubscript{3}C\textsubscript{6}H\textsubscript{4}Me)Rh(\textnu\textsuperscript{4}-C\textsubscript{8}H\textsubscript{12})]\textsubscript{2}, which, as found from X-ray structure determinations, is composed of two distorted \{4,9,1,10-Rh\textsubscript{2}C\textsubscript{2}B\textsubscript{9}\} cluster units joined together through \textnu\textsuperscript{6} coordination of the 4-tolyl cage substituent of one unit to one of the rhodium atoms of the second unit and vice versa.
Reactions of \([3,3-(\text{PPh}_3)_2-3-\text{Cl}-3-\text{H}-3,1,2-\text{closo-RuC}_2\text{B}_9\text{H}_{11}]\) and its \textit{exo-nido} isomer \([\text{exo}-5,6,10-\{\text{Ru(Ph}_3\text{P})_2\text{Cl}\}-5,6,10-(\mu-\text{H})_3-10-\text{H}-7,8-\text{nido-C}_2\text{B}_9\text{H}_8]\) with \(\text{NH}_4\text{PF}_6\) in methanol or ethanol solution followed by heating in the presence of an excess of phenylacetylene have been showed to afford a mixture of two isomeric \textit{closo} species \([3,3-\{(1'-3'-\eta^3):(5',6'-\eta^2)-\text{ortho-C}_6\text{H}_4\text{PPh}_2\text{CHC(Ph)CHCHPh}\}-8-(\sigma-\text{CH}=\text{CHPh})-3,1,2-\text{closo-RuC}_2\text{B}_9\text{H}_{10}]\) and \([3,3-\{(1'-3'-\eta^3):(5',6'-\eta^2)-\text{ortho-C}_6\text{H}_4\text{PPh}_2\text{CHC(Ph)CHCHPh}\}-4-(\sigma-\text{CH}=\text{CHPh})-3,1,2-\text{closo-RuC}_2\text{B}_9\text{H}_{10}]\). In these complexes boron vertexes in \(\beta\) - and \(\alpha\)-sites with respect to the cage carbons bear the \((E)-\text{CH}=\text{CHPh}\) group. The X-ray diffraction study of the first one together with the multinuclear NMR data for both revealed that such an unusual \(\eta^3:\eta^2\)-phosphacarbocyclic ligand in the isomers is formed by specific insertion of the initially metal-bound \text{PPh}_3\) group into the chain of two alkyne molecules coupled in a “head-to-tail” fashion around the metal vertex.

A facile ligand-exchange method based on the direct reaction of either three-bridge \textit{exo-nido} complex \([\text{exo}-5,6,10-\{\text{Cl(Ph}_3\text{P})_2\text{Ru}\}-5,6,10-(\mu-\text{H})_3-10-\text{H}-7,8-\text{C}_2\text{B}_9\text{H}_8]\) or its \textit{closo} isomer \([3,3-(\text{PPh}_3)_2-3-\text{Cl}-3-\text{H}-3,1,2-\text{closo-RuC}_2\text{B}_9\text{H}_{11}]\) with chelating N,N-donor ligands was employed to synthesize N,N-diamine-\textit{closo}-ruthenacarborane complexes \([3,3-\{\kappa^2-4,4'-\text{R}_2-2,2'-(\text{C}_6\text{H}_3\text{N})_2\}-3-\text{PPh}_3\text{-}\text{closo}-3,1,2-\text{RuC}_2\text{B}_9\text{H}_{11}\] (\(R = \text{H, Bu}^t\)) and \([3,3-\{\kappa^2-\text{phen}\}-3-\text{PPh}_3\text{-}\text{closo}-3,1,2-\text{RuC}_2\text{B}_9\text{H}_{11}\].
Reactions of \([\text{exo-5,6,10-}{\text{Cl(Ph}_3\text{P})}_2\text{Ru}]\)-5,6,10-(\(\mu\)-H)\_3-10-H-nido-7,8-C\_2B\_9H\_8\] with 1,5-bis(diphenylphosphino)pentane in benzene either at ambient temperature for ca 2 days or under gently reflux for 30 min in anaerobic conditions both proceed with the replacement of PPh\(_3\) ligands on the ruthenium center with the diporphine to form diamagnetic (18-electron) closo complex \([3,3-[\kappa_2^{\text{2}}-\{\text{Ph}_2\text{P(\text{CH}_2\text{)}_5\text{PPh}_2}\}]-3-\text{Cl}-3-H-closo-3,1,2-RuC\_2B\_9H\_11\] ). The latter complex on heating in benzene in the presence of a small amount of CCl\(_4\) affords stable paramagnetic (17-electron) species \([3,3-[\kappa_2^{\text{2}}-\text{Ph}_2\text{P(\text{CH}_2\text{)}_5\text{PPh}_2}]\)-3-Cl-closo-3,1,2-RuC\_2B\_9H\_11\]. By thermal treatment of either the abovementioned diamagnetic or paramagnetic under more severe conditions in toluene at 110 °C ortho-phenylene-cycloboronated closo complex \([3-\text{Cl}-3,3,7,8-[\kappa_2^{\text{2}}-\text{Ph}_2\text{P(\text{CH}_2\text{)}_5\text{PPh}_2}]\)-closo-3,1,2-RuC\_2B\_9H\_10\] was prepared in high yields. Thermolysis of the latter in boiling toluene in the presence of a small amount of CCl\(_4\) afforded the new paramagnetic complex \([3-\text{Cl}-3,3,7,8-[\kappa_2^{\text{2}}-\text{Ph}_2\text{P(\text{CH}_2\text{)}_5\text{PPh}_2}]\)-closo-3,1,2-RuC\_2B\_9H\_9\], featuring bis(ortho-cycloboronation) of both P-phenyl groups located at the same phosphorus atom of the ruthenium bound dppt ligand. All new closo-ruthenacarboranes obtained were characterized by a combination of analytical, multinuclear NMR (for even-electron species) or EPR (for odd-electron species) data and, in addition, by single-crystal X-ray diffraction studies of three selected paramagnetic complexes.

A series of new agostic (CH\(_3\)···Rh) (η-allyl)-closo-rhodacarboranes (η-allyl = 1,1-dimethylallyl, 1,2-dimethylallyl, 1,1,2-trimethylallyl, 1,2,3-trimethylallyl), stable in the solid state, have been synthesized via one-pot reactions between the K\(^-\) salts of the [7-R-8-R’-7,8-nido-C\_2B\_9H\_10\]\(^-\) monoanions (R = R’ = Me; R,R’ = \(\mu\)-(o-xylylene); R,R’ = \(\mu\)-(CH\(_2\))\(_3\)) and the di-\(\mu\)-chloro cyclooctene rhodium dimer \([\eta_2^{}-\text{C}_8\text{H}_{14}]_2\text{Rh}_2(\mu-\text{Cl})_2\] in the presence of a 3-fold excess of the conjugated 1,3-dienes 2-methylbuta-1,3-diene.
(isoprene), 2,3-dimethylbuta-1,3-diene, and 3-methylpent-1,3-diene. The agostic structures of \([3\{-\{(1-3-\eta^3)-1,1\text{-dimethylallyl}\}-1,2-(\text{CH}_3)_2-3,1,2\text{-closo-RhC}_2\text{B}_9\text{H}_9\}]\) and \([3\{-\{(1-3-\eta^3)-1,1,2\text{-trimethylallyl}\}-1,2-(\text{CH}_3)_2-3,1,2\text{-closo-RhC}_2\text{B}_9\text{H}_9\}]\) have been unambiguously confirmed by single-crystal X-ray diffraction studies. Two of these \(\pi\) allyl complexes prepared were evaluated for their efficacy in hydroformylation of the model alkenes under syngas (CO/H\(_2\)) using supercritical carbon dioxide (scCO\(_2\)) as the solvent, and both display excellent conversion and high regioselectivity in the formation of aldehyde products.

\[\begin{align*}
\text{[}\{\eta^2\text{-C}_{8}\text{H}_{14}\}_4 \text{Rh}_{2}(\mu-\text{Cl})_2\}, \quad 1,3\text{-diene; C}_6\text{H}_6, 20^\circ\text{C} \end{align*}\]


### 2. Chemistry of exo-nido-Metallacarboranes of Platinum Metals.

Systematic work in this area includes the development of practical synthetic methods that would result in the formation of novel exo-nido-metallacarboranes, in which metal-containing moiety is attached to the cage of anionic nido-carborane through a multiple two-electron three-center (B-H)\(_n\)...M bonds. These zwitter-ionic species of the \(d\)-block metals are known to play an important role in the field, frequently representing efficient precatalysts for homogeneous organic reactions. Other important studies concern the development of the chemistry of these systems.

Some of “three-bridge” exo-nido-metallacarboranes could be used as precursors in the generation of “exo-metalladicarbollide ions” which could further serve as new building-blocks for the design of novel mixed-metal and mixed-ligand exo-closo-bimetallacarboranes wherein transition metals (including earlier transition metals) will have different electronic configurations (i.e. from 16 to 18e). Such species may have multifunctional applications in chemistry and catalyses.
Among complexes containing carbocyclic ligands, homonuclear bimetallacarborane clusters having both symmetrical and nonsymmetrical bimetal cores have not been studied extensively. Herein we report the results of the room-temperature reactions of the mononuclear iridium(III) complex \([3-\{(1-3)-\eta^3-\text{C}_8\text{H}_{13}\}-1,2-(\text{CH}_3)_2-3,1,2-\text{closo}-\text{IrC}_2\text{B}_9\text{H}_9]\) with air or oxidizing reagent such as \([\text{C}_6\text{H}_5\text{CO}_2]_2\), which unexpectedly produced \(\eta^1,\eta^4\)-COD-ligated biiridacarboranes with multiple metal-metal bond, \([\text{Ir}(\eta^1,\eta^5-1,n-(\text{CH}_3)_2\text{C}_2\text{B}_9\text{H}_9)(\eta^1,\eta^4-\text{C}_8\text{H}_{12})\text{Ir}(\eta^5-1,2-(\text{CH}_3)_2\text{C}_2\text{B}_9\text{H}_9)]\), isolated as \(3,1,2\) \((n = 2)\) and \(2,1,8\) \((n=8)\) isomers. Both isomers were carefully studied by NMR spectroscopic and X-ray diffraction methods.

Much of the work in this area is focused on the synthesis and reactivity studies of monocarbon metallacarboranes based on structurally different monocarbon archno-, nido- or closo-carboranes.

We are interested in the design of new productive approaches for their synthesis and structural investigations, as well as dynamic behaviour in solution, by modern physical methods: multinuclear/low-temperature/exchange NMR spectroscopy, X-ray diffraction etc.

We are currently developing novel synthetic methodology on the use of simple transition metal complexes (for example, [RuCl₂(PPh₃)₃]) as promoters of an extensive polyhedral contraction reactions of 8-11-vertex monocarbon carboranes to form smaller-cage metallacarboranes with specific electronic and cluster structures, especially complexes which do not obey Wade’s electron counting rules.

The monocarbon carborane [Cs][nido-7-CB₁₀H₁₃] reacts with the 16-electron [RuCl₂(PPh₃)₃] in a solution of benzene/methanol in the presence of N,N,N′,N′-tetramethylnaphthalene-1,8-diamine as the base to give a series of 12-vertex monocarbon arene-biruthenacarborane complexes of two types: [closo-2-{7,11-exo-RuClIPPh₃(μ,η⁵-C₆H₅PPh₂)}-7,11-(μ-H)₂-2,1-RuCB₁₀H₈R] (R = H; R = 6-MeO; R = 3-MeO)
and \([\text{closo-2-}(\eta^6-\text{C}_6\text{H}_6)-10,11,12-[\text{exo-RuCl}(\text{PPh}_3)_2]-10,11,12-(\mu-\text{H})_3-2,1-\text{RuCB}_{10}\text{H}_2\text{R}^1]\) (R^1= 6-MeO; R^1= 3-MeO as inseparable mixture of isomers) along with trace amounts of 10-vertex mononuclear hypercloso/isocloso-type complexes \([2,2-(\text{PPh}_3)_2-2-\text{H}-3,9-(\text{MeO})_2-2,1-\text{RuCB}_8\text{H}_7]\) and \([2,5-(\text{Ph}_3\text{P})-2-\text{Cl}-2-\text{H}-3,9-(\text{MeO})_2-2,1-\text{RuCB}_8\text{H}_6]\) have been prepared by the reaction of \([\text{Cs}]\text{nido-7-CB}_{10}\text{H}_{13}\) with the 16-electron \([\text{RuCl}_2(\text{PPh}_3)_3]\) in a solution of benzene/methanol in the presence of the Proton Sponge. Binuclear ruthenacarborane clusters of both series were characterized by a combination of analytical and multinuclear NMR spectroscopic data and by single-crystal X-ray diffraction studies of three selected complexes. In solution, some isomers have been shown to undergo the isomerization process through the scrambling of the exo-[RuCl(\text{PPh}_3)_2]-fragment about two adjacent triangular cage boron faces B(7)B(11)B(12) and B(8)B(9)B(12).

Two isomeric monocarbon (\(\eta\)-dicyclopentenyl)-closo-rhodacarborane complexes, differing in hapticity of the carbocyclic ligand, \(\text{viz.}\ [2,2-((2',3'-\eta^2):(5'-\eta^1)-\text{C}_{10}\text{H}_{13})-1-(\text{Me}_3\text{N})-2,1-\text{closo-RhCB}_{10}\text{H}_{10}]\) and \([2-((1'-3'-\eta^3)-\text{C}_{10}\text{H}_{13})-1-(\text{Me}_3\text{N})-2,1-\text{closo-RhCB}_{10}\text{H}_{10}]\) were prepared by the reaction of the dianion \([7-\text{Me}_3\text{N}-\text{nido-7-CB}_{10}\text{H}_{10}]^{2-}\) (assumed to be formed \textit{in situ} during the treatment of a neutral \([7-\text{Me}_3\text{N}-\text{nido-7-CB}_{10}\text{H}_{10}]\) with two molar equivalent of Proton Sponge) with \([(\eta^4-\text{C}_{10}\text{H}_{12})_2\text{Rh}_2(\mu-\text{Cl})_2]\) in benzene–ethanol solution. Isomeric rhodium compounds thus prepared were characterized by analytical, multinuclear NMR spectroscopic data as well as by single-crystal X-ray diffraction study, which revealed the existence of an agostic C–H⋯Rh interaction in both these species.
4. Catalytically active metallacarboranes in homogeneous catalysis and polymerization.

We are also interested in the design of new catalytically active metallacarboranes of transition metals and, in particular, those derived from platinum group metals. Approaches for their synthesis and dynamic behaviour in solution, as well as catalytic investigations for the most important organic processes includes enantio- and diastereoselective reactions which are exemplified below. These works we usually perform in the frame of collaboration with other groups who are actively involved in the transition metal catalysis including polymerization of vinyl monomers.

Formally 16-electron \textit{closo}- and \textit{pseudocloso}-(\eta^3\text{-cyclooctenyl}) rhodacarboranes of the general formula \([3-{(1-3\text{-}\eta^3\text{-C}_8\text{H}_{13}})-1,2-R,R’-3,1,2-\text{RhC}_2\text{B}_9\text{H}_9}] \) (\textit{closo}: \( R, R’ = \mu\text{-1’2’-CH}_2\text{C}_6\text{H}_4\text{CH}_2; \) \textit{pseudocloso}: \( R = R’ = \text{PhCH}_2 \)) coupled in situ with the chiral phosphoramidite \((S)\)-PipPhos were found to catalyze an asymmetric hydrogenation of functionalized olefins (enamides) with enantioselectivities as high as 97-99.7\% and with 92-100\% conversions. The key catalyst precursor \([3,3-{(S)\text{-PipPhos}}2-3\text{-H}_1,2-\text{(o-xylylene)}\text{-closo}-3,1,2-\text{RhC}_2\text{B}_9\text{H}_9}] \), independently prepared by the stoichiometric reaction of the same reagents in benzene, was found to show of enantioselectivities and conversions upon the hydrogenation of prochiral enamides at the same levels as those observed for the relevant precursor formed \textit{in situ}. The structure of this catalyst precursor has been established on the basis of analytical and multinuclear NMR data as well as a single-crystal X-ray diffraction study. In contrast, the above \textit{pseudocloso} complex reacts with \((S)\)-PipPhos to afford the unstable hydrido_rhodium species \([3,3-{(S)\text{-PipPhos}}2-3\text{-H}_1,2-(\text{PhCH}_2)2-3,1,2-\text{RhC}_2\text{B}_9\text{H}_9}] \), the formation of which and further conversion into the salt \([3\text{-}(\text{PipPhos})4\text{Rh}]^+\text{[7,8-(PhCH}_2)2\text{-nido}-7,8-\text{C}_2\text{B}_9\text{H}_10}] \) was detected by time-dependent \(^1\text{H} \) NMR spectra. Some conclusions regarding the catalysis mechanistic pathway, which is consistent with that generally accepted for the rhodacarborane-catalyzed alkene hydrogenation, are made.

Novel ruthenium complexes with carborane ligands were employed as efficient catalysts for controlled polymer synthesis via Atom Transfer Radical Polymerization (ATRP) mechanism. The ability of carborane ligands to stabilize high oxidation states of
transition metals allows the proposed catalysts to be more active than their cyclopentadienyl counterparts. The proposed catalysts do not require additives such as aluminium alkoxides. It was shown that introduction of amine additives into the polymerization mixture leads to a dramatic increase of polymerization rate leaving polymerization controlled. The living nature of polymerization was proved via post-polymerization and synthesis of block copolymers.

A series of new paramagnetic (17-electron) and diamagnetic (18-electron) closo-ruthenacarboranes: [3,3-(dppb)-3-Cl-closo-3,1,2-RuC2B9H11], [3-Cl-3,3,8-[Ph2P(CH2)4PPh-μ-(C6H4-ortho)]-closo-3,1,2-RuC2B9H10], [3,7-Cl-3,3,7,8-[Ph2P(CH2)4P-μ-(C6H4-ortho)2]-closo-3,1,2-RuC2B9H9] and [3,3-(dppb)-3-H-3-Cl-closo-3,1,2-RuC2B9H11] have been prepared by thermolysis of diamagnetic complex at different temperature (80-110 °C). Several paramagnetic closo-ruthenacarboranes featured mono- or bis(ortho-cycloboronation) of P-phenyl groups at the same phosphorus atom of the ruthenium-bound dppb ligand. All ruthenacarboranes studied display high efficiency as catalyst precursors for the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) with the best catalyst performance in terms of polydispersity index (Mw/Mn) of the polyMMA samples as low as 1.15.