

Activation of Organic Substrates on Multi-Metallic Sites of Transition Metal Polyhydride Clusters Having C₅Me₅ Groups as Auxiliary Ligands

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Keywords: Cluster compounds / Hydride ligands / Iron / Ruthenium

An overview of the chemistry of the di- and trinuclear transition metal polyhydride complexes containing only C₅Me₅ groups as auxiliary ligands is presented. The synthesis of a series of η⁵-C₅Me₅ polyhydride clusters and their reactivities centered about some typical examples of "multi-metallic activation" including the cleavage of carbon–hydrogen bonds

of alkanes, carbon–carbon bond of cyclopentadiene, and carbon–carbon double bond of 1,1-disubstituted alkenes, achieved on the reaction site of the polyhydride-bridged clusters, are reported.

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1. Introduction

The reactivity of transition metal cluster complexes has been of special interest recently, in the area of organometallic chemistry, because of their potential applicability to organic synthesis.^[1] The advantageous properties of multi-metallic systems over a mono-metallic ones in the substrate activation step are their capability for multiple coordination of the substrate to the metal clusters, and the multi-electron transfer between the substrate and the cluster. Transition metal clusters have therefore been intensively investigated, in the quest to develop new and effective organic transformations achieved by the synergetic effect of the metal centers. A large number of studies on the reaction chemistry of clusters have been reported, to date using mostly carbonylmatal clusters. However, most of the metal clusters used in these studies have been binary carbonylmatal com-

plexes or clusters directly derived from them, M_m(CO)_n or L_kM_m(CO)_n, and it is hard to say that the reactions developed are really characteristic of the metal cluster. Although selectivity and efficiency of the reactions are modified in some cases, the mode of the reaction is sometimes similar to that achieved by using mononuclear metal complexes. In contrast, there have been a relatively small number of reported examples of metal polyhydride clusters – probably due to their instability. Furthermore, an effective synthetic method for obtaining polyhydride clusters that is applicable to the many ligand/metal combinations has not been developed thus far.

Electron density at the metal centers in the metal hydride cluster is most certainly higher than that in the polycarbonylmatal or polycarbonylmatal hydride clusters. The metal polyhydride clusters are, therefore, expected to be much more active than the carbonylmatal clusters toward oxidative addition of substrates. In addition, a metal polyhydride cluster, particularly a polyhydride-bridged cluster, is considered to be a suitable and versatile precursor of the active species for multi-metallic activation. We have used the term

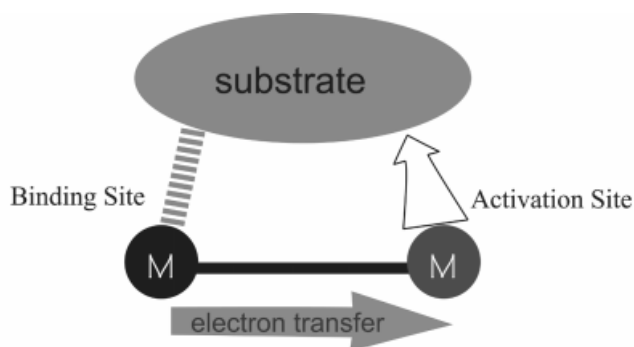
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Hiroharu Suzuki was born in Gifu, Japan, in 1948 and studied chemistry at Nagoya University. In 1976, he obtained his Ph.D. degree from Nagoya University on a study on organometal–nitrogen bonds, under the supervision of Prof. Yoshio Ishii. Upon graduation, he moved to the Research Laboratory of Resources Utilization at Tokyo Institute of Technology and was offered a position of Assistant Professor. After a post-doctoral stay with Prof. Tobin J. Marks at Northwestern University (1982–1983), he returned to Tokyo and became Associate Professor in 1984. In 1991, he was promoted to his current position of Professor. He is concurrently serving as Research Director of the "CREST Molecular Architecture of Metal Hydride Cluster" Project of Japan Science and Technology Corporation (JST). His research interests are concentrated on the chemistry of transition metal polyhydride clusters, in particular development of new synthetic methods for polyhydride clusters, and activation of unreactive substrates such as alkanes and dinitrogen on multimetallic sites.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

“multi-metallic activation” to refer to a mode of activation achieved as a result of cooperative action of many metal centers. Liberation of bridging hydride ligands from the metal cluster gives rise, spontaneously, to vacant coordination sites on the adjacent metal centers, and the substrate taken in the reaction site likely interacts with the resulting vacant metal centers all together. In such a situation, the metal centers probably cooperate in activating the substrate as a binding site and an activation site. This must be the origin of the cluster effect in the substrate activation.



There had been several reported examples of multinuclear polyhydride-bridged complexes having tertiary phosphanes as auxiliary ligands,^[2] while no polyhydride clusters having only cyclopentadienyl ligands as auxiliaries were known at the end of the 1980s. Unfortunately, the reaction chemistry of the phosphane polyhydride clusters is not as remarkable or unique as that of a polycarbonylmetal cluster.

A cyclopentadienyl ligand, especially the C_5Me_5 ligand, is strongly electron-releasing and almost inert towards substitution, unlike tertiary phosphanes. Introduction of C_5Me_5 groups into the cluster framework, therefore, increases the electron density at the metal centers and, as a result, makes the cluster much more reactive to oxidative addition. Even carbonyl clusters become highly reactive and therefore often reveal really unique reactivity when cyclopentadienyl ligands are introduced into the cluster framework.^[3] Introduction of cyclopentadienyl ligands affects not only the activity but also the selectivity. An empty space surrounded by the C_5Me_5 ligands becomes a reaction site in which substrates are activated in a shape-selective manner, due to the steric repulsion among the substrates and the C_5Me_5 groups.

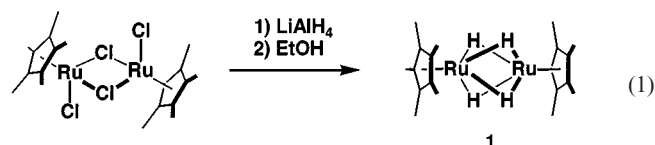
We now describe the synthesis of a series of $\eta^5-C_5Me_5$ polyhydride clusters and some typical examples of “bi- and trimetallic activation” achieved on the reaction site of the polyhydride-bridged clusters.

2. Synthesis of Transition Metal Polyhydride Clusters Having C_5Me_5 Groups

2.1 Synthesis and Structure of a Dinuclear Tetrahydride Complex of Ruthenium

Ruthenium is a fascinating metal from the standpoint of electron transfer between the substrate and the metal atom

because of its wide diversity of oxidation states, from -2 (d^{10}) to $+8$ (d^0). We therefore attempted to synthesize a new class of polyhydride complex having only C_5Me_5 groups as the auxiliary ligands.



A dinuclear tetrahydride-bridged complex of ruthenium $\{(C_5Me_5)Ru\}_2(\mu-H)_4$ (**1**) was synthesized by treatment of $\{(C_5Me_5)RuCl_2\}_2$ ^[4] with $LiAlH_4$ followed by workup with ethanol [Equation (1)].^[5] To the best of our knowledge, only two examples have been reported for the dinuclear tetrahydride-bridged complexes $L_mM(\mu-H)_4ML_n$,^[6] while related trihydride-bridged complexes such as $[(C_6Me_6)Ru]_2(\mu-H)_3^+$ are known.^[7] Complex **1** is the first dinuclear tetrahydride-bridged complex having no phosphane or arsane ligands.

An X-ray diffraction study of **1** showed that the four hydride ligands were essentially arrayed at the vertices of an approximate square, and were placed perpendicularly to the Ru–Ru vector (Figure 1). The average H–H distance of 1.46 Å and the T_1 value of 2.28 s were deemed to be sufficient to characterize the complex as a classical metal polyhydride.^[8] Although the short Ru–Ru distance [2.463(1) Å] and the 18-electron rule applied to the dimer **1** require a triple bond between the ruthenium atoms, a theoretical study performed by Morokuma et al. showed the absence of a direct metal–metal bond.^[9] The short Ru–Ru distance is most likely due to four $3c-2e$ M–H–M bonds.

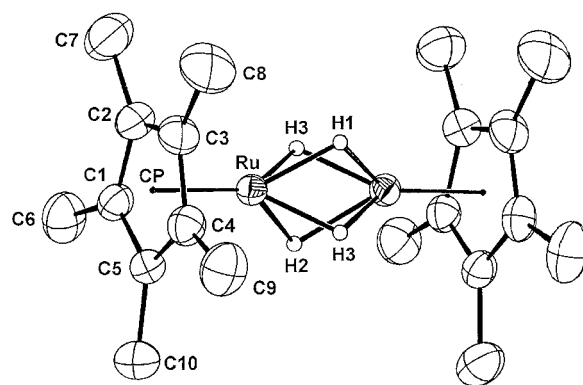
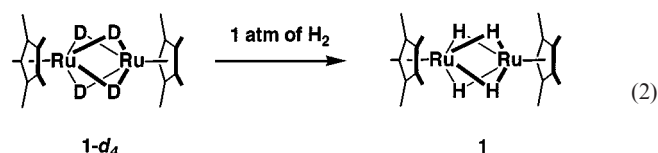
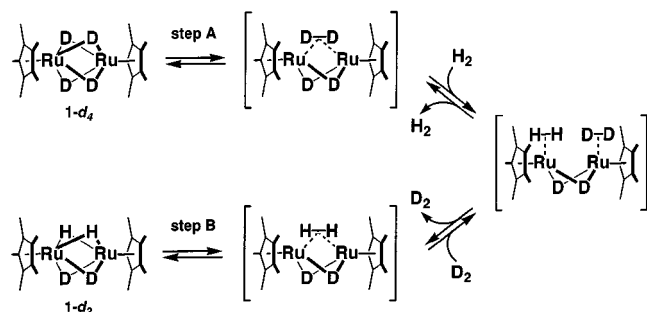


Figure 1. Molecular structure of $\{(C_5Me_5)Ru\}_2(\mu-H)_4$ (**1**)

The hydride ligands of **1** undergo an intermolecular exchange reaction with dihydrogen under mild conditions. Exposure of a toluene solution of an isotopomer **1**- d_4 to an atmospheric pressure of dihydrogen resulted in the quantitative exchange of the deuteride ligands for hydride, affording **1**- h_4 [Equation (2)].



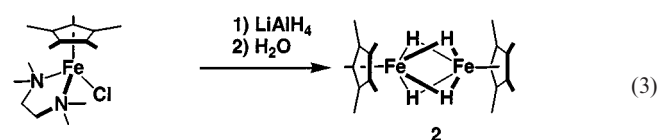
The mechanism shown in Scheme 1 possibly accounts for the H/D exchange reaction of **1** with H₂, which presumably involves a dihydride/dihydrogen equilibrium (step A and step B). With regard to the chemistry of η²-dihydrogen complexes, such an equilibrium is proposed on the basis of VT-¹H NMR studies.^[10]



Scheme 1

2.2 Synthesis and Structure of Dinuclear Tetrahydride Complex of Iron

According to the vertical trends associated with the transition elements, the metal–metal and metal–ligand bond enthalpies decrease up a period and the complexes become substitutionally active. The iron analogue of diruthenium tetrahydride **1** is, therefore, expected to be much more reactive than **1**.



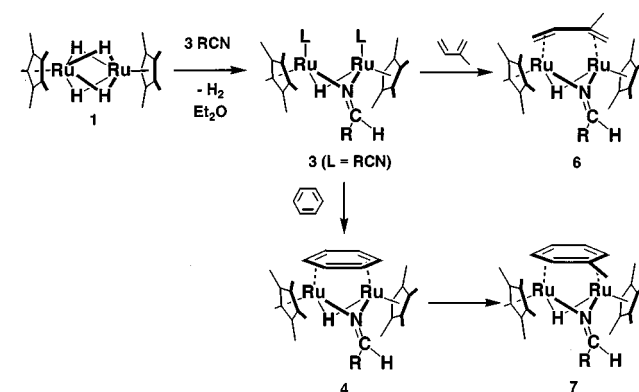
Treatment of (C₅Me₅)FeCl(tmeda)^[11] with LiAlH₄, followed by workup with H₂O, gave the dinuclear iron tetrahydride {(C₅Me₅)Fe}₂(μ-H)₄ (**2**) [Equation (3)].^[12] The X-ray analysis clearly showed structural identity between **1** and **2**. The presence of four bridging hydride ligands are probably responsible for the short Fe–Fe distance of 2.202(1) Å.

We concluded that compound **2** was a classical metal hydride similar to **1** on the basis of the long H–H distance (av. 1.60 Å) and the large *T*₁ value of 0.63 s (–80 °C) for the hydride ligands. The iron tetrahydride **2** has also been shown to undergo H/D exchange between hydride ions and added dihydrogen. As anticipated, the reaction proceeded much faster than that of the corresponding ruthenium analogue. Since tetrahydride **2** is stable enough in solution not to release dihydrogen even under reduced pressure, the H/D exchange must be an associative process.

2.3 Dinuclear Polyhydride Clusters Bridged by a Ligand Containing a Heteroatom

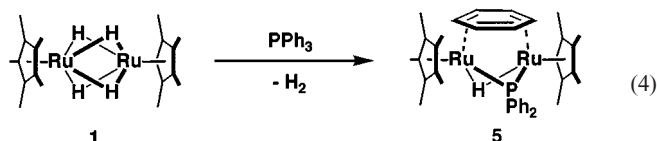
Introduction of a bridging ligand containing a heteroatom into a dinuclear complex possibly affects the electronic and steric environment of the bimetallic reaction sites and, therefore, modifies the complex with regard to both reactivity and selectivity.

A dinuclear μ-alkylideneamide complex {(C₅Me₅)Ru}₂(NC–R)₂(μ-N=CHR) (**3**) was exclusively generated in the reaction of **1** with R–CN in diethyl ether, as a result of insertion of the nitrile into an Ru–H bond (Scheme 2).^[13] The coordinated nitrile molecule in **3** was readily replaced with arene to form an (alkylideneamide)(η²:η²-arene) complex {(C₅Me₅)Ru}₂(μ-η²:η²-arene)(μ-N=CHR) (**4**). Complex **4** was directly synthesized by the reaction of **1** with nitrile in an appropriate arene solution.

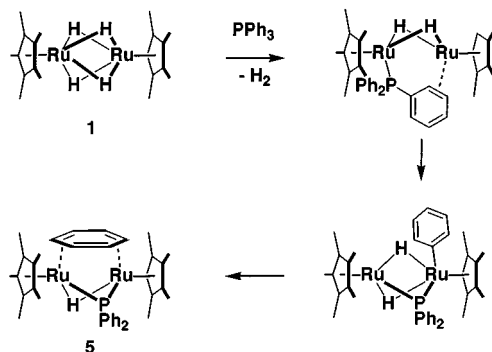


Scheme 2

A phosphide-bridged dinuclear complex {(C₅Me₅)Ru}₂(μ-η²:η²-C₆H₆)(μ-PPh₂) (**5**) was prepared by applying a P–C(aromatic) bond cleavage reaction to PPh₃. Treatment of **1** with PPh₃ in toluene led to the formation of **5** as a result of the P–C bond cleavage [Equation (4)].^[14]



The formation of **5** is reasonably elucidated by a sequence of reactions depicted in Scheme 3. Coordination of PPh₃ and reductive elimination of H₂ would form an intermediary (dihydrido)(monophosphane) complex {(C₅Me₅)Ru}₂(H)₂(PPh₃). Cleavage of a P–C bond of the coordinated PPh₃ ligand by one of the ruthenium centers would be expected to yield a μ-phosphido species that would then undergo reductive elimination of benzene and subsequent coordination of the benzene molecule in a μ-η²:η² mode to give **5**. For the cluster-mediated P–C bond cleavage of tertiary phosphane, a similar mechanism has been proposed.^[15]

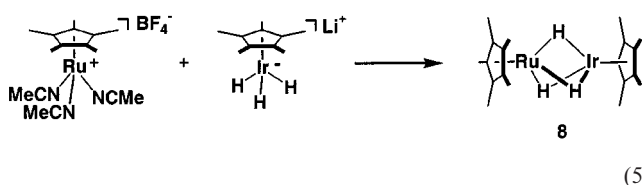


Scheme 3

A series of dinuclear μ -phosphido complexes $\{(C_5Me_5)Ru\}_2(\mu-\eta^2:\eta^2-C_6H_6)(\mu-PRR')$ were synthesized in a similar manner.^[16] As a result, modification of the electronic environment of the bimetallic reaction sites might be achieved by changes in the substituents on the bridging phosphido ligand. It is noteworthy that arene molecules coordinated both in **4** and **5** were readily replaced by the added organic substrates and therefore, they are considered to be a suitable precursor of the active species for bimetallic activation. For example, addition of isoprene to a solution of **4** in tetrahydrofuran resulted in the exclusive formation of a $(\mu\text{-alkylideneamide})(\eta^2\text{-}\eta^2\text{-isoprene})$ complex $\{(C_5Me_5)Ru\}_2(\mu-\eta^2:\eta^2\text{-isoprene})(\mu-N=CHR)$ (**6**). Similarly, the coordinated benzene was substituted with toluene to yield $\{(C_5Me_5)Ru\}_2(\mu-\eta^2:\eta^2\text{-toluene})(\mu-N=CHR)$ (**7**) when **5** was heated at 60 °C in toluene.

2.4 Synthesis of Heterobimetallic Polyhydride Complexes

As an extension to multimetallic activation by homonuclear cluster complexes, we focused our attention on the synthesis of a heterometallic polyhydride cluster, thereby making the reaction sites electronically anisotropic. Enhancement of the anisotropic character of the reaction sites likely causes changes in regioselectivity at the stage of substrate activation. Although a number of heterobimetallic polyhydride cluster complexes have been synthesized,^[17] there have only been a few reported examples of successful achievement of heterobimetallic activation of organic substrates.^[18]

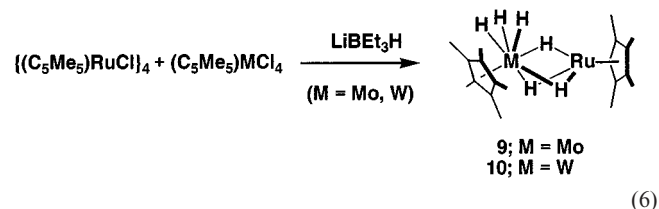


(5)

The reaction of $[(C_5Me_5)Ru(CH_3CN)_3](BF_4)$ ^[19] with an anionic iridium hydride complex $Li[(C_5Me_5)IrH_3]$ ^[20] led to a new heterobimetallic hydride cluster $(C_5Me_5)Ru(\mu-H)_3Ir(C_5Me_5)$ (**8**) [Equation (5)].^[21]

The longitudinal relaxation time T_1 for the hydride ligands was determined to be 3.34 s at -80 °C, which is suffi-

cient to characterize the complex as a classical trihydride complex. The hydride ligands of **8**, as well as the methyl group of the C_5Me_5 ligand coordinated to iridium, underwent an intermolecular H/D exchange reaction with C_6D_6 . Interestingly, the H/D exchange of the bridging hydride ions preceded that of the methyl hydrogen atoms of the C_5Me_5 group, and the H/D exchange of the methyl hydrogen atoms selectively occurred on the C_5Me_5 ligand bound to the iridium center. The H/D exchange between the bridging hydride ions and that of the methyl hydrogen atoms on the C_5Me_5 group likely proceed via an intermediary $\eta^2\text{-}C_6D_6$ complex and an $\eta^6\text{-}1,2,3,4\text{-tetramethylfulvene}$ or $\eta^1\text{-}\eta^6\text{-tetramethylcyclopentadienylmethyl}$ intermediate, respectively. The latter process is proposed for the reversible hydrogen shift from a ring methyl group to the titanium center in $(C_5Me_5)_2Ti$.^[22]



(6)

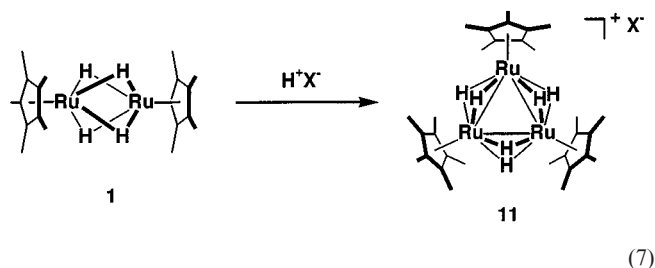
Heterobimetallic polyhydride complexes containing ruthenium and electron-deficient group-6 metal atoms, $(C_5Me_5)MH_3(\mu-H)_3Ru(C_5Me_5)$ (**9**; M = Mo; **10**; M = W), were obtained by the treatment of a 1:1 mixture of $\{(C_5Me_5)RuCl\}_4$ ^[19] and $(C_5Me_5)MCl_4$ ^[23] with $LiBEt_3H$ [Equation (6)].^[24]

The X-ray diffraction studies of **9** and **10** clearly establish the dinuclear structure with 3 terminal hydride ions and the three bridging hydride ions. The signals for the six hydride ions of **10** were observed to be equivalent above -40 °C due to a rapid exchange of the hydride ions among the terminal sites on the molybdenum center and the bridging sites. The hydride ligands of **9** were more mobile than those of the tungsten analogue **10**, and the signal for the terminal and the bridging hydride ions de-coalesced at -110 °C. On the basis of the T_1 value, both **9** and **10** were concluded to be the classical hydride complexes.

Heterobimetallic polyhydride clusters with different metal/metal combinations, such as Ru/Rh,^[25] Ru/Os,^[26] and Ru/Re^[27] were also synthesized and characterized.

2.5 Synthesis of a Trinuclear Polyhydride Cluster of Ruthenium

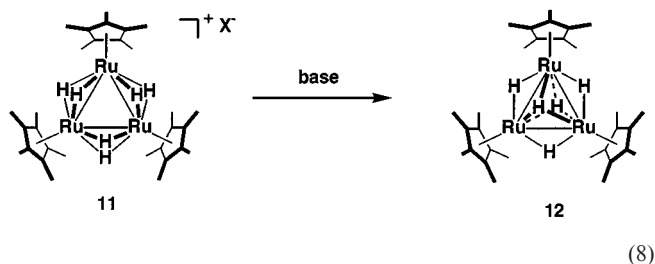
The reactivity of a cluster complex most probably depends on the ease of the electron transfer between complex and substrate. The number of transferable electrons between the cluster complex and the substrate must be changed by the nuclearity of the cluster: the more nuclei there are in the cluster, the more effectively electrons are transferred. As an extension of bimetallic activation, the trimetallic polyhydride cluster has attracted some attention.



A cationic triruthenim hexahydride cluster $\{[(C_5Me_5)Ru(\mu-H)_2]_3(X)\}$ (**11**) was obtained by the reaction of **1** with an acid HX in excellent yields [Equation (7)].^[28,29] Compound **11** is stable enough to be stored in chloroform for several hours without decomposition.

The T_1 value of 0.387 s for the hydride resonance of **11** lies within the range of those for the classical hydride complexes. This result is consistent with the relatively long distance (average 1.81 Å) between the two hydrogen atoms bridging the same Ru–Ru bond observed in the X-ray structure.

Treatment of the cationic cluster **11** with an appropriate base such as sodium methoxide afforded a neutral pentahydride cluster $\{(C_5Me_5)Ru\}_3(\mu-H)_3(\mu_3-H)_2$ (**12**) [Equation (8)].^[29]



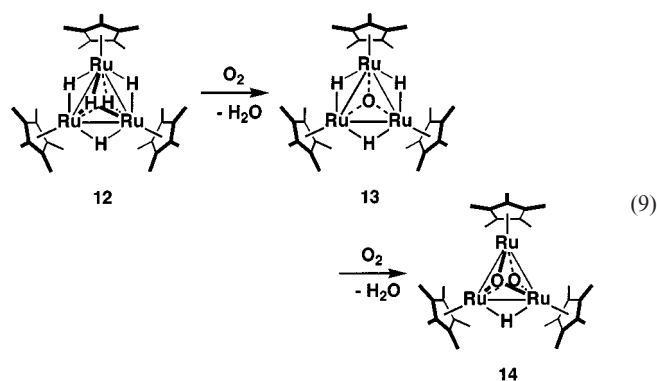
The VT-¹H NMR study has shown the rapid exchange of the hydride ions among the coordination sites, on an NMR timescale in the temperature range from 20 to –120 °C. The T_1 value of 2.55 s (–80 °C) for the hydride signal of **12** is significantly large in comparison with that of the hydride signal of the cationic cluster **11**. Cluster **12** was also concluded to be a classical hydride complex based on this T_1 value.

Triruthenium pentahydride **12** is an unsaturated 44-electron cluster and is able to capture a weakly coordinating substrate such as dihydrogen or benzene in a triangular reaction site. As a result, **12** readily underwent an H/D exchange reaction between the hydride ligands and D₂ or C₆D₆.

Unlike the cationic cluster **11**, the neutral cluster **12** is much more reactive because of high electron density at the metal center to activate even a chemically inert alkane molecule (vide infra).

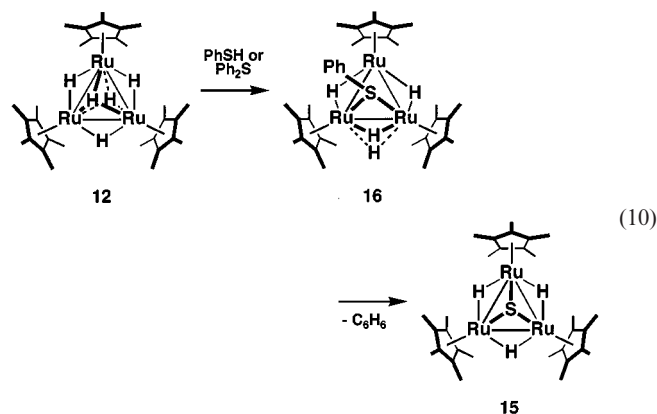
2.6 Trinuclear Polyhydride Clusters with a Triply Bridged Ligand Containing a Heteroatom

Introduction of a triply bridging ligand on to the Ru₃ core allowed control over the reactivity of the cluster due to change in the electronic environment of the reaction site. It is of utmost importance to introduce one bridging ligand onto one side of the Ru₃ core. If both faces of the Ru₃ plane are covered with the two bridging ligands, there is no space for the substrate activation on the Ru₃ plane. Cluster **12** is stable enough not to undergo fragmentation of the Ru₃ framework even in the reaction with various reactive small molecules such as dioxygen and pressurized dihydrogen. A new class of trinuclear polyhydride cluster with a triply bridging ligand has therefore been synthesized by using pentahydride **12** as the starting material.

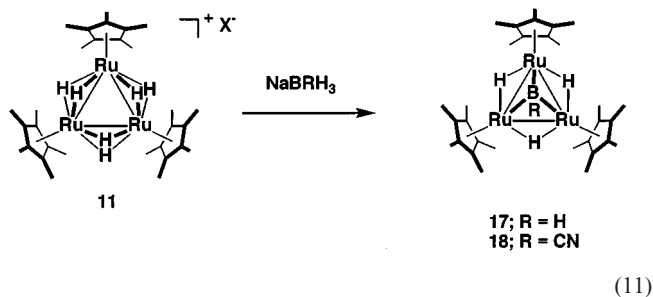


Cluster **12** was converted into a mono- μ_3 -oxo complex $\{(C_5Me_5)Ru\}_3(\mu_3-O)(\mu-H)_3$ (**13**) and a di- μ_3 -oxo complex $\{(C_5Me_5)Ru\}_3(\mu_3-O)_2(\mu-H)$ (**14**), successively, by the reaction with dioxygen at low temperature [Equation (9)].^[29] The mono- μ_3 -oxo complex was isolated in high yield by controlling the reaction conditions such as the O₂/12 ratio and the temperature.

The sulfur analogue of **13**, $\{(C_5Me_5)Ru\}_3(\mu_3-S)(\mu-H)_3$ (**15**), was selectively synthesized by the reaction of **12** with an equimolar amount of thiophenol or diphenyl sulfide [Equation (10)].^[30] An intermediary μ -(phenyl sulfide) complex $\{(C_5Me_5)Ru\}_3(\mu-SPh)(\mu-H)_4$ (**16**) was isolated in the reaction, which underwent S–C(aromatic) bond cleavage to afford **15**.



Reaction of **12** with excess diphenyl sulfide yielded a bi-capped cluster $\{(C_5Me_5)Ru\}_3(\mu_3-S)_2(\mu-H)$, which was almost inactive toward various unsaturated hydrocarbons because both faces of the Ru_3 core were covered with the μ_3-S groups.

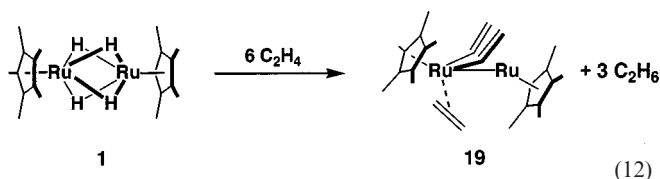


Bridging ligands containing not only an electronegative element but also an electropositive one were introduced into the Ru_3 core. The reaction of a cationic polyhydride cluster **11** with $NaBH_4$ resulted in the exclusive formation of $\{(C_5Me_5)Ru\}_3(\mu_3-BH)(\mu-H)_3$ (**17**) [Equation (11)].^[31] A cluster having a μ_3-BCN ligand, $\{(C_5Me_5)Ru\}_3(\mu_3-BCN)(\mu-H)_3$ (**18**), was similarly prepared by using $NaB(CN)H_3$.^[31] Complexes **17** and **18** are both an unprecedented type of a μ_3 -borylene cluster, namely, "single-faced μ_3 -borylene cluster", having a spacious reaction site on the reverse side of the μ_3 -borylene ligand with respect to the Ru_3 plane.

3 Multimetallic Activation of Hydrocarbon Molecules on the Reaction Site of a Polyhydride Cluster

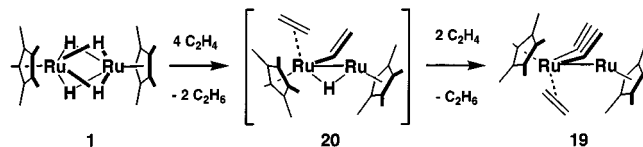
3.1 Reactions of a Dinuclear Polyhydride Cluster with Ethylene and Diphenylacetylene

The reaction of **1** with ethylene under atmospheric pressure proceeded at ambient temperature to form a dinuclear di- μ - $\eta^1:\eta^2$ -vinyl complex $\{(C_5Me_5)Ru\}_2(CH_2CH_2)(\mu-CHCH_2)_2$ (**19**) in excellent yield [Equation (12)].^[5b] The GLC analysis of the gas phase of the reaction revealed the formation of ca. 270% of ethane together with a small amount of 1-butene. This result suggests that the coordinatively unsaturated sites are generated on **1** by way of a hydride transfer from the ruthenium center to the ethylene ligand, i.e., hydrogenation of ethylene.



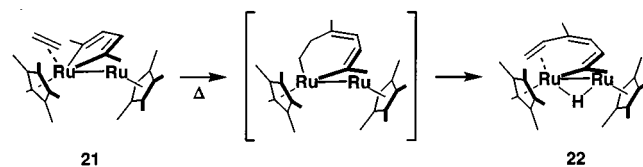
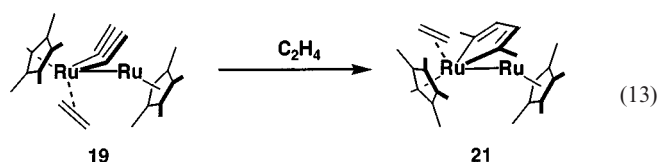
Monitoring the reaction by NMR spectroscopy showed the formation of an intermediary mono- μ -vinyl complex $\{(C_5Me_5)Ru\}_2(CH_2CH_2)(\mu-CHCH_2)(\mu-H)$ (**20**). Monovinyl

complex **20** was highly reactive owing to coordinative unsaturation at the metal centers and could be readily converted into **19** in the presence of excess amounts of ethylene (Scheme 4).



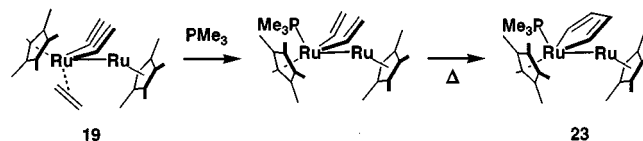
Scheme 4

Subsequent reaction proceeded to yield a 2,5-dimethylruthenacyclopentadiene complex **21** when **19** was heated in the presence of ethylene under atmospheric pressure [Equation (13)]. Ruthenacycle **21** was further converted into a μ - $\eta^2:\eta^2:\eta^2$ -5-methylhepta-2,4,6-trien-2-yl complex **22** (Scheme 5). The formation of **22** is reasonably elucidated by the mechanism involving an insertion of the coordinated ethylene ligand into one of the $Ru-C$ σ bonds of **21**. Subsequent β -H elimination from the resulting intermediary ruthenacycloheptadiene would yield **22**.



Scheme 5

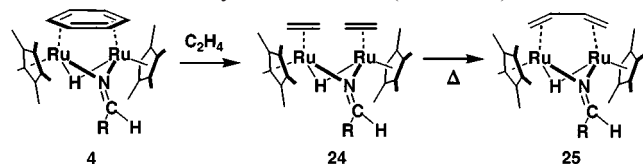
Interestingly, dinuclear divinyl complex **19** underwent dehydrogenative C–C coupling between the terminal carbon atoms of the bridging vinyl groups to generate a ruthenacyclopentadiene complex **23** upon heating in the presence of trimethylphosphane (Scheme 6).^[32]



Scheme 6

Introduction of a bridging ligand onto the bimetallic reaction site caused changes in reactivity due to changes in the electronic and steric environment around the metal centers. The (μ -alkylidene)(amide) complex **4** could easily open a pair of vacant coordination sites in solution to generate an active species for bimetallic activation. The reaction of **4** with 1 atm of ethylene proceeded at ambient temperature

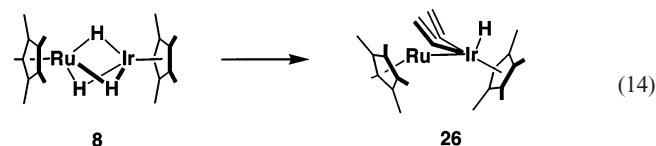
to give a bis(η^2 -ethylene)ruthenium complex **24**.^[13] When **24** was heated at 80 °C, a μ - η^2 : η^2 -*s-cis*-butadiene complex **25** was exclusively formed by a dehydrogenative coupling of the coordinated ethylene molecule (Scheme 7).



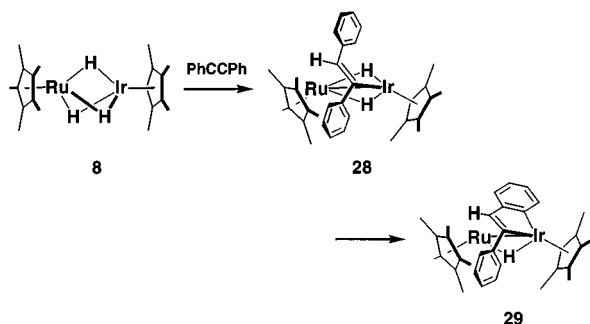
Scheme 7

The butadiene complex **25** could be directly synthesized from **4** by treatment with 1 atm of ethylene in refluxing toluene.

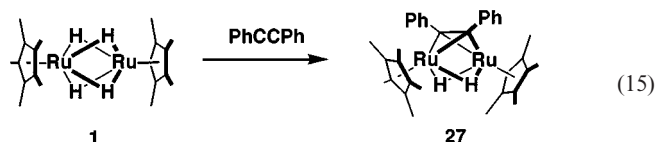
The reaction of the heterobimetallic complex **8** with ethylene revealed the site selectivity of the heterobimetallic system toward an organic substrate. The reaction of **8** with ethylene led to the exclusive formation of a di- μ - η^1 : η^2 -vinyl complex **26** [Equation (14)].^[21] A notable feature of this reaction is the site selectivity in which C–H bond cleavage exclusively took place at the iridium center. The ruthenium center most likely plays the role of a coordination site.



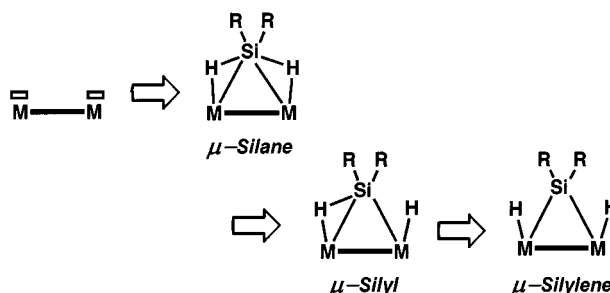
The reactivity of the heterobimetallic cluster **8** is significantly different from that observed for homonuclear cluster **1**. While the reaction of **1** with diphenylacetylene resulted in the formation of a dinuclear complex bridged by a perpendicularly coordinated diphenylacetylene, $\{(C_5Me_5)Ru\}_2(\mu-\eta^2:\eta^2-PhCCPh)(\mu-H)_2$ (**27**) [Equation (15)],^[33] complex **8** smoothly reacted with diphenylacetylene to produce a μ - η^1 : η^2 -alkenyl complex, $(C_5Me_5)Ir\{\mu-\eta^1:\eta^2-(Z)-CPh=CHPh\}(\mu-H)_2Ru(C_5Me_5)$ (**28**) (Scheme 8).^[21] The formation of **28** is most likely due to an initial μ - η^2 : η^2 -alkyne coordination perpendicular to the Ir–Ru vector and subsequent *trans*-addition of Ir and a hydride ion to the carbon–carbon triple bond. The bridging alkenyl complex **28** was quantitatively converted into a dinuclear benzoiridacyclopentadiene complex **29**, as a result of intramolecular activation of the C(*ortho*)–H bond, upon heating at 80 °C.



Scheme 8



The reaction of **1** with various organosilanes provided evidence for the concerted activation of the Si–C and Si–H bonds, in which the two ruthenium atoms cooperatively affect the silane molecule. In the reaction of **1** with secondary silanes, a stepwise transformation of the silane from the μ -silane complex to a μ -silylene complex by way of the μ -silyl complex was observed, and each metal center mutually took the role of a binding site and an activation site (Scheme 9).^[12,34]

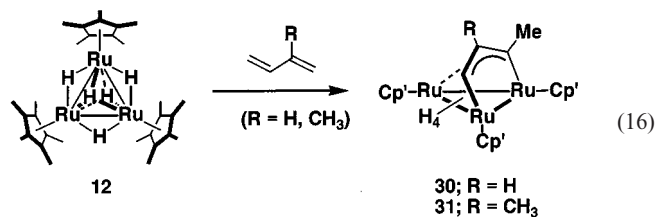


Scheme 9

3.2 Reactions of a Trinuclear Polyhydride Cluster with Acyclic 1,3-Dienes

The reaction of **12** with acyclic conjugated dienes such as butadiene and isoprene affords a novel trinuclear μ_3 - η^2 : η^2 -*s-cis*-1,3-diene complexes having an agostic Ru–H–C interaction.

Treatment of **12** with excess butadiene (1 atm) in tetrahydrofuran led to the formation of a trinuclear 1-methyl-1,3-dimetalloallyl complex $\{(C_5Me_5)Ru\}_3(H)_4\{\mu_3-\eta^3-C(Me)-CHCH\}$ (**30**).^[35] The reaction of **12** with isoprene proceeded in a similar manner at ambient temperature to form the corresponding μ_3 -dimetalloallyl complex **31** [Equation (16)].

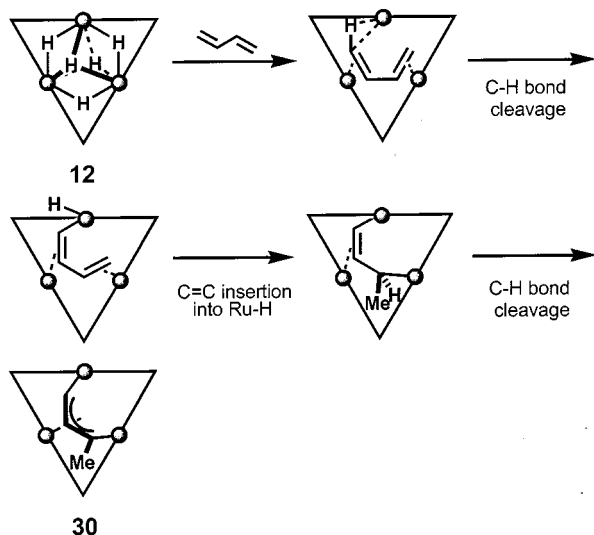


The molecular structure of **30** was proven by X-ray crystallography. Monitoring the reaction of **12** with 1 equiv. of isoprene in [D₆]benzene at room temperature by ¹H and ¹³C NMR spectroscopy showed the formation of an intermediary trinuclear μ_3 - η^2 : η^2 -*s-cis*-isoprene complex **33** in the initial stage of the reaction. Complex **33** involved an agostic interaction among the terminal carbon and hydrogen atoms and one of the ruthenium atoms. The small C(sp²)–H

coupling constant ($J_{\text{CH}} = 107 \text{ Hz}$) and the upfield shift ($\delta = -9.33$) of the resonance for the terminal methylene proton of the diene ligand in **33** lie within the range of structurally well-established agostic complexes and unambiguously indicate the presence of a three-center two-electron $\text{Ru}-\text{H}-\text{C}$ interaction.^[18d,36] An intermediary agostic complex **32** was similarly detected in the reaction of **12** with butadiene by means of NMR spectroscopy.

The intermediates **32** and **33** underwent activation of the agostic $\text{C}-\text{H}$ bond to ultimately form the 1,3-dimetallallyl complexes **30** and **31**, respectively. These results show that 2 of the 3 ruthenium centers in **12** act as coordination sites, and the third metal atom takes the role of an activation site by agostic interaction in the reaction with 1,3-diene. This is a typical example showing the activation process performed by the concerted action of three metal centers.

Formation of the $\mu_3\text{-}\eta^2\text{:}\eta^2\text{-}s\text{-cis}$ -1,3-diene complexes **32** and **33** suggests the mechanism shown in Scheme 10 for the reaction of **12** with acyclic conjugated dienes leading to the exclusive formation of the μ_3 -1,3-dimetallallyl complexes. When the 1,3-diene is incorporated into the triangular reaction site, the diene ligand is forced to adopt the *s-cis* conformation to minimize the steric repulsion between the substrate and the C_5Me_5 groups. The agostic intermediate likely undergoes activation of the carbon-hydrogen bond to form a $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2$ -dienyl complex. Insertion of the terminal carbon-carbon double bond into an adjacent $\text{Ru}-\text{H}$ bond followed by carbon-hydrogen cleavage at the allylic position of the resulting dimetallo-cyclopentene would give the μ_3 -1,3-dimetallallyl complex as a final product.



Scheme 10

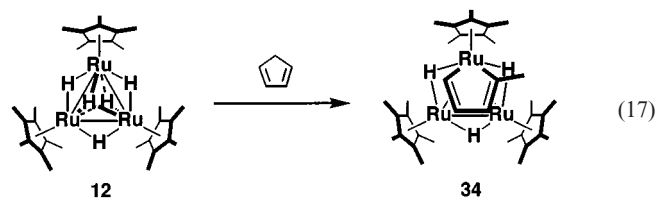
As the trimetallic reaction site of **12** is surrounded by the three C_5Me_5 groups, steric repulsion between the C_5Me_5 ligand and the substrate strongly influences the incorporation step of the substrate into the trimetallic site. As a result, remarkable shape selectivity for the incorporation of the substrate was observed in the reaction of **12** with a series of substituted 1,3-diene. While complex **12** readily reacted with monosubstituted 1,3-butadienes such as isop-

rene, 1,3-pentadiene, and 1,3-hexadiene to generate the corresponding μ_3 -1,3-dimetallallyl complexes exclusively, the reaction of **12** with disubstituted butadiene such as 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, and 2,4-hexadiene resulted in the recovery of the starting complex **12** and the diene.

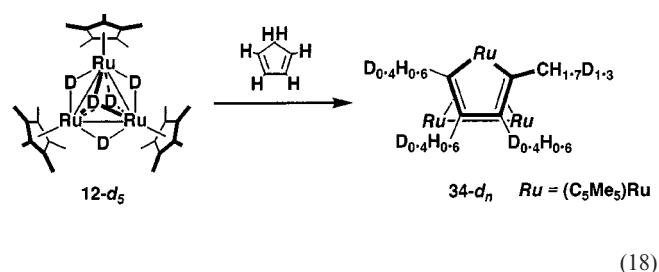
3.3 Reactions of a Trinuclear Polyhydride Cluster with Cyclic 1,3-Dienes

The size and shape of cyclopentadiene fit well with those of the reaction site of **12**. Whereas $\text{C}-\text{H}$ bond cleavage took place at the terminal carbon atom of the diene in the reaction of **12** with acyclic 1,3-diene, the reaction of **12** with cyclopentadiene resulted in selective $\text{C}-\text{C}$ bond cleavage in cooperation with the three metal centers.

The reaction of **12** with cyclopentadiene in tetrahydrofuran at room temperature led to the quantitative formation of the trinuclear 2-methylruthenacyclopentadiene $\{(\text{C}_5\text{Me}_5)\text{Ru}\}_3(\mu\text{-H})_3\{\mu_3\text{-}\eta^4\text{-C}(\text{Me})=\text{CHCH}=\text{CH}\}$ (**34**) as a result of the $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$ bond cleavage of the cyclopentadiene [Equation (17)].^[37] To the best of our knowledge, this is the first example of the selective activation of an unactivated carbon-carbon bond in cooperation with three metal centers. Kinetic parameters of $\Delta H^\ddagger = 12.7(3) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -30.0(10) \text{ cal mol}^{-1} \text{ K}^{-1}$ for this reaction indicate that incorporation of the cyclopentadiene into the trimetallic reaction site is the rate-determining step.



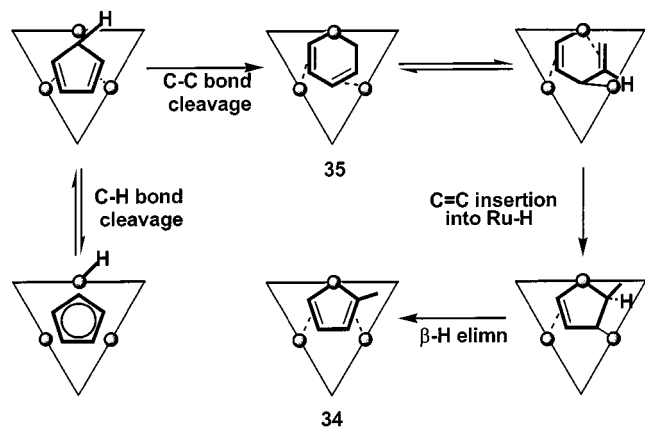
Monitoring the reaction of **12** with 5 equiv. of cyclopentadiene in $[\text{D}_8]\text{tetrahydrofuran}$ at room temperature by ^1H NMR spectroscopy showed the formation of an intermediary ruthenacyclohexadiene **35** during the initial stage of the reaction. Although **35** could not be isolated, it was unambiguously characterized by means of NMR spectroscopy.



To elucidate the reaction mechanism, a labeling experiment was performed by use of triruthenium pentadeuteride complex **12-d₅**. The reaction of **12-d₅** with cyclopentadiene-*h*₆ smoothly proceeded at room temperature to give an iso-

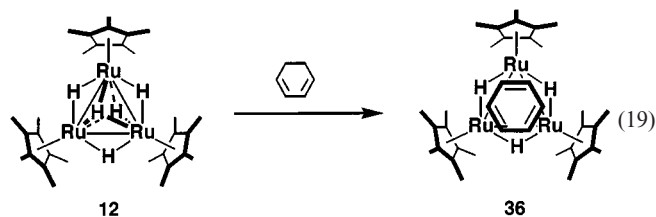
topomer of the 2-methylruthenacyclopentadiene **34-d_m**, in which the deuterium atoms were uniformly scrambled over the ruthenacycle [Equation (18)]. This result indicates that the activation of the carbon–hydrogen bond at the allylic position of cyclopentadiene leading to a μ_3 -cyclopentadienyl intermediate takes place prior to the carbon–carbon bond cleavage.

One plausible reaction mechanism involving a pre-equilibrium between a μ_3 - η^2 : η^2 -cyclopentadiene complex and a μ_3 - η^5 -cyclopentadienyl complex is illustrated in Scheme 11. Cyclopentadiene incorporated into the Ru₃ core is bound to two of the three ruthenium centers of **12** through μ - η^2 : η^2 coordination to form the μ_3 -cyclopentadiene complex. In the intermediary μ_3 -cyclopentadiene complex, both the allylic C–H bond and the C(sp³)–C(sp²) bond are nicely oriented towards the third metal atom for the bond cleavage. Ruthenacyclohexadiene formed as a result of the C(sp³)–C(sp²) bond cleavage is in equilibrium with a μ_3 -penta-1,4-diene-1,3-diyl complex, which undergoes insertion of the carbon–carbon double bond into Ru–H to yield a μ_3 -5-methylruthenacyclopent-2-ene complex.



Scheme 11

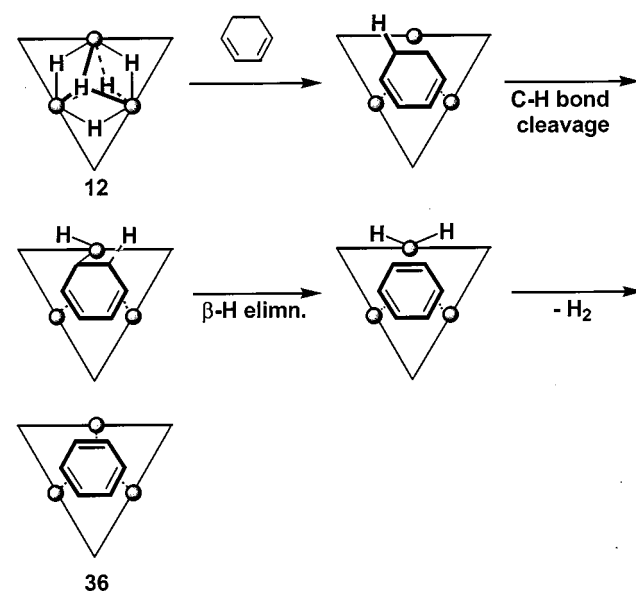
The space of the triangular reaction site in **12** is large enough to accommodate a C₆-ring compound. The reaction of **12** with 5 equiv. of 1,3-cyclohexadiene in tetrahydrofuran resulted in the quantitative formation of a face-capping benzene complex $\{(\text{C}_5\text{Me}_5)\text{Ru}\}_3(\mu\text{-H})_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)$ (**36**) by C–H bond cleavage at the allylic carbon atoms [Equation (19)].^[38]



The shift of the ¹H and ¹³C NMR resonances for the coordinated benzene ligand, respectively, are much higher than those observed in the carbonyl clusters Ru₃(CO)₉(μ_3 - η^2 : η^2 : η^2 -C₆H₆)^[39] and Os₃(CO)₉(μ_3 - η^2 : η^2 : η^2 -C₆H₆)^[40]

The μ_3 - η^2 : η^2 : η^2 coordination of the benzene ring was unequivocally confirmed by an X-ray diffraction study. The reaction of **12** with 1,3-cyclohexadiene to give **36** is first-order in both **12** and cyclohexadiene [$k_{\text{obs}} = 2.7(1) \times 10^{-3} \text{ mol}^{-1} \text{ s}^{-1}$ at 66 °C] with $\Delta H^\ddagger = 13.5(8) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -30.6(3) \text{ cal mol}^{-1} \text{ K}^{-1}$. The value of the activation entropy is similar to that for the reaction of **12** with cyclopentadiene, as mentioned above. The negative large value of ΔS^\ddagger and the relatively small value of ΔH^\ddagger indicate that fitting into the size and shape between the substrate and the reaction site surrounded by the three C₅Me₅ groups is essential for the progress of the reaction.

In an attempt to observe intermediates by NMR spectroscopy, the reaction was performed in an NMR tube at 0 °C. Although no resonance signal except for those attributable to **12**, **36**, and H₂ was observed, the reaction most likely proceeds via an intermediary μ_3 - η^2 : η^2 -cyclohexadiene complex. One plausible reaction mechanism for the reaction of **12** with cyclohexadiene leading to the μ_3 - η^2 : η^2 -cyclohexadiene complex **37** is illustrated in Scheme 12. In the present reaction, two of the three metal centers in **12** act as coordination sites, and the third metal atom plays the role of an activation site to cleave an allylic C–H bond as observed in the reaction of **12** with butadiene or isoprene.

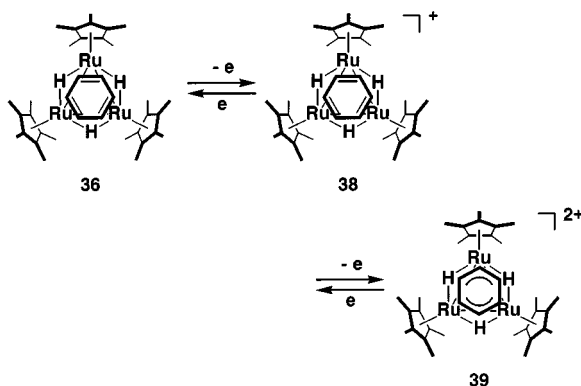


Scheme 12

In the trimetallic reaction site of the triruthenium pentahydride **12**, conjugated dienes with the appropriate size and shape could be effectively activated due to the concerted action of the three metal centers. The reaction of **12** with 1,4-cyclohexadiene or 1,3-cycloheptadiene, however, required heating at 60–100 °C to complete, because the orientation of two carbon–carbon double bonds or the ring size of the substrate is not suitable for the coordination to the Ru₃ site.

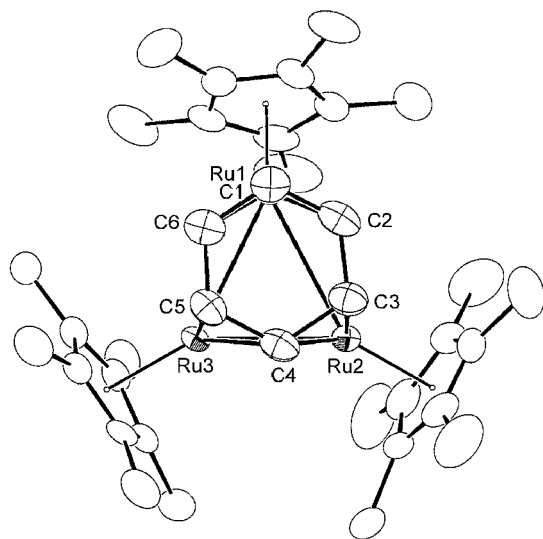
It is noteworthy that oxidation of the face-capping C₆H₆ complex **36** induces change in the coordination mode of the benzene ligand. The electrochemistry of **36** displays two

reversible one-electron oxidations at -490 and -224 mV vs. Ag/AgCl. To examine changes in the coordination mode of the face-capping benzene ligand due to changes in the oxidation state, oxidation of **36** with a ferricinium salt was examined (Scheme 13).



Scheme 13

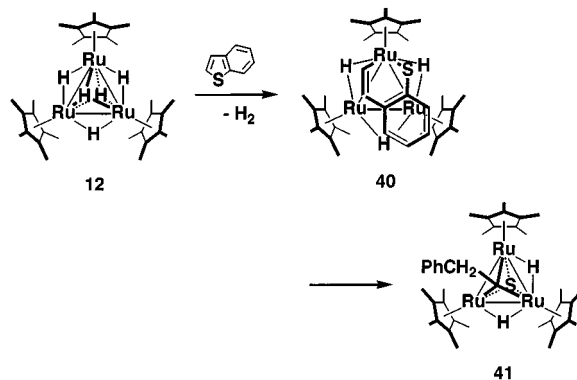
Treatment of **36** with 1 equiv. of $[(C_5H_5)_2Fe]PF_6$ in toluene quantitatively yielded a paramagnetic monocationic complex $[(C_5Me_5)Ru]_3(\mu-H)_3(\mu_3-\eta^2:\eta^2:C_6H_6)]PF_6$ (**38**). The X-ray diffraction study established the $\mu_3-\eta^2:\eta^2$ coordination of benzene in **38**. As was anticipated from the electrochemical study, a diamagnetic complex $[(C_5Me_5)Ru]_3(\mu-H)_3(\mu_3-\eta^3:\eta^3-C_6H_6)](PF_6)_2$ (**39**) was obtained by two-electron oxidation of **36**. The most striking structural feature of **39** is the $\mu_3-\eta^3:\eta^3$ coordination of the C_6 ring (Figure 2). Thus far, there have been a few precedents of trinuclear $\mu_3-\eta^3:\eta^3-C_6H_6$ complexes.^[41] Complex **36** is, however, the first example that exhibits the hapticity change in the face-capping benzene ligand induced by a redox process.

Figure 2. Molecular structure of $[(C_5Me_5)Ru]_3(\mu-\eta^3:\eta^3-C_6H_6)]^{2+}$ (**39**)

3.4 Reactions of a Trinuclear Polyhydride Cluster with Benzothiophene and Dibenzothiophene

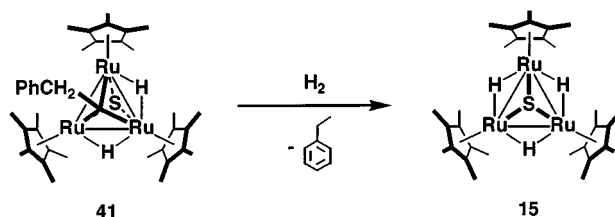
Cleavage of the C–S bond of thiophenes by transition metal complexes has attracted the attention of many inorganic and organometallic chemists in connection with hydrodesulfurization (HDS) from petroleum feedstock. While there is a vast chemistry of organosulfur–transition metal complexes, successful examples of C–S bond cleavage of benzothiophene and dibenzothiophene by mono- and dinuclear transition metal complexes have been limited.^[42]

Interestingly, the trimetallic hydride cluster **12** could effectively activate benzothiophene and dibenzothiophene to cleave their C–S bonds selectively. The reaction of **12** with benzothiophene in toluene quantitatively afforded a $(\mu_3\text{-phenethylidene})(\mu_3\text{-sulfido})$ complex $\{[(C_5Me_5)Ru]_3(\mu-H)_2(\mu_3-S)(\mu_3-CCH_2Ph)\}$ (**41**) as a result of the successive cleavage of two C–S bonds (Scheme 14).^[43]



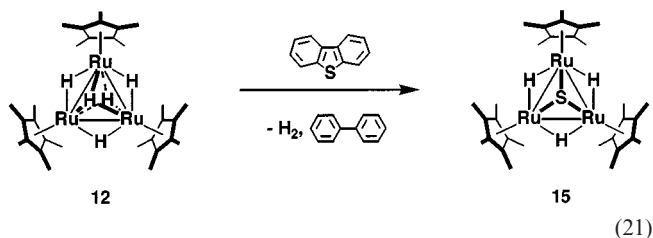
Scheme 14

Monitoring the reaction by means of 1H NMR spectroscopy revealed formation of an intermediary thiaruthenacyclohexadiene complex **40**, which was isolated from the resulting mixture at -30 °C. The structure of the intermediary thiaruthenacyclohexadiene **40** was confirmed in comparison with that of the analogous thiaruthenacycle derived by the reaction of μ_3 -borylene complex **17** with benzothiophene.^[31] Complex **41** underwent hydrogenolysis by treatment of **41** with dihydrogen (7.2 atm) to produce ethylbenzene and the μ_3 -sulfido complex **15** [Equation (20)].



(20)

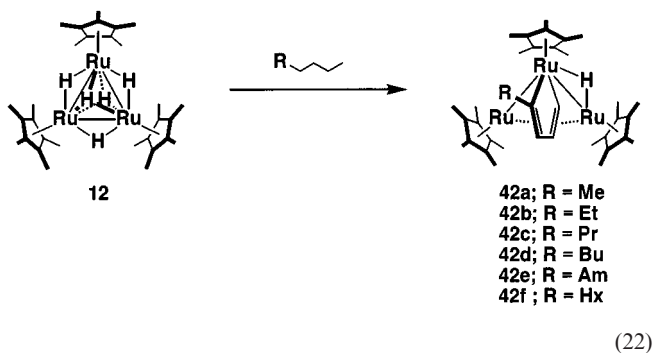
Complex **12** shows reactivity for the cleavage of the C–S bonds in dibenzothiophene. The reaction of **12** with dibenzothiophene proceeded at 110 °C to form **15** and biphenyl in high yield [Equation (21)].



3.5 Reactions of a Trinuclear Polyhydride Cluster with Alkanes

Activation of an alkane C–H bond mediated by late transition metal complexes has been the focus of recent studies in organometallic chemistry because of its potential applicability to the functionalization of alkanes.^[44] We have dealt with C–H bond activation of alkanes on the multimetallic site and found that trinuclear clusters **12** and **15** effectively activated alkanes in a thermal reaction.

Heating a solution of **12** in various alkanes at 170 °C resulted in the formation of novel trinuclear *closo*-ruthenacyclopentadiene complexes **42** (**a**: R = Me; **b**: R = Et; **c**: R = Pr; **d**: R = Bu; **e**: R = Am; **f**: R = Hx) in reasonable yield [Equation (22)].^[45]

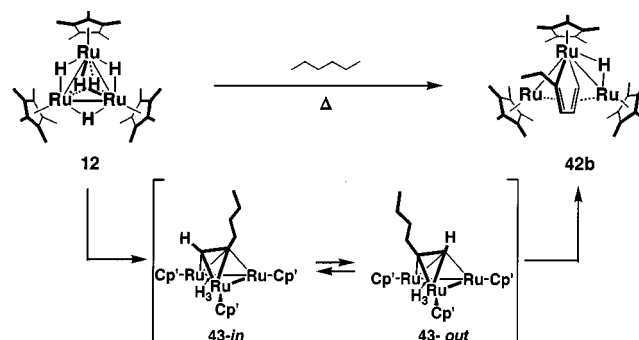


It is clear that the carbon framework of 2-alkylruthenacyclopentadiene in **42** originates from the *n*-alkane used as the solvent. In this reaction, six C–H bonds of the alkanes were successively cleaved on the trimetallic site, and these results strongly suggest the potential applicability of transition metal cluster complexes, especially polyhydrido metal clusters, to the functionalization of alkanes.

The *n*-alkane molecule is most likely incorporated into the triangular reaction site from one of the methyl termini at the initial stage of the reaction. This was confirmed through the H/D exchange between the hydride ligands in **12** and the deuterated methyl group in octane-*d*₁₈ observed in the temperature range of 140–160 °C.

Monitoring the reaction by means of ¹H NMR spectroscopy showed signals for several reaction intermediates. They finally converged into thermodynamically stable products **42**. When the reaction of **12** with hexane was monitored at 170 °C by ¹H NMR spectroscopy, formation of an equilibrated mixture of perpendicularly coordinated μ₃-hexyne complexes, {(C₅Me₅)Ru}₃(μ-H)₃{μ₃-η¹:η²:η²-

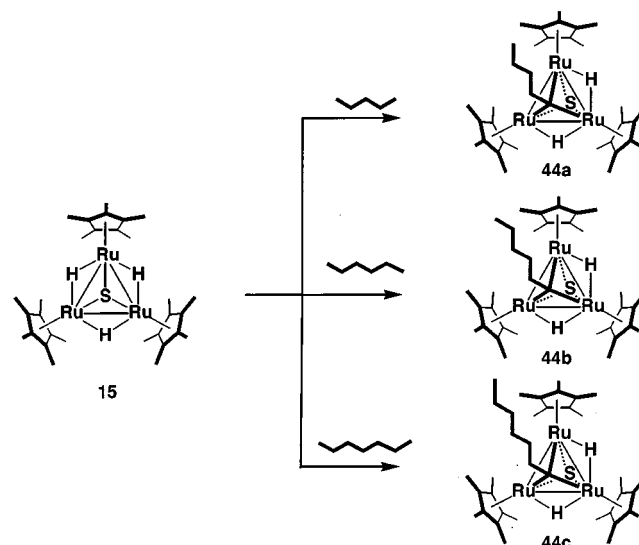
HCCCC₄H₉} (**43-in**) and {(C₅Me₅)Ru}₃(μ-H)₃{μ₃-η¹:η²:η²-C₄H₉CCH} (**43-out**), was detected in a complex mixture of intermediates (Scheme 15). The intermediacy of the alkyne complex **43** was confirmed by use of an authentic complex independently prepared by treatment of **12** with 1-hexyne.



Scheme 15

To modify the regioselectivity of the triruthenium cluster mediated alkane C–H bond activation, a triply bridging sulfido ligand was introduced into the Ru₃ core by the reaction of **12** with thiophenol. The μ₃-sulfido group introduced was expected to reinforce the Ru₃ framework and to prevent Ru–Ru bond cleavage in the course of the reaction with the alkane.

Heating a solution of **15** in hexane at 170 °C for 107 h led to the quantitative formation of a μ₃-hexylidyne complex {(C₅Me₅)Ru}₃(μ₃-S)(μ-H)₂{μ₃-C(CH₂)₄CH₃} (**44b**) as a result of C–H bond cleavage at the terminal carbon atom while the reaction of **12** with hexane afforded a *closo*-ruthenacyclopentadiene complex **42**.^[46] The results of the reactions of **15** with a series of alkanes are summarized in Scheme 16.

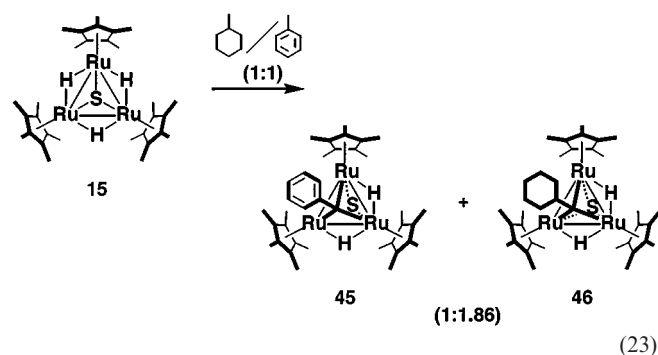


Scheme 16

A notable feature of the reaction is its regioselectivity such that no metal insertion products into the secondary C–H bonds were detected in spite of the clear advantage

over that of the primary C–H bonds, judging from the bond dissociation energy, ca. 95 kcal/mol vs. ca. 98 kcal/mol. The steric repulsion between the substrates and the C_5Me_5 fences surrounding the reaction site would be responsible for the highly primary-selective C–H bond activation because it impedes the access of the secondary C–H bonds to the metal center. The oxidative addition of the C–H bond at the less-hindered methyl group exclusively took place in the reaction with a 5-methylhexane to yield a 5-methylhexylidyne complex despite the statistical disadvantage.

Complex **15** was active toward cleavage of both aromatic and benzylic C–H bonds of toluene. When complex **15** was heated in $[D_8]$ toluene at 130 °C, H/D exchange took place among the hydride ligands of **15** and the aromatic C–D bonds of $[D_8]$ toluene. However, a tolyl intermediate resulting from the aromatic C–D bond cleavage could not be detected because it is presumably unstable due to the steric repulsion with the C_5Me_5 group. Heating a toluene solution of **15** at 170 °C, however, led to the exclusive formation of a thermally stable μ_3 -benzylidyne complex $\{(C_5Me_5)Ru\}_3(\mu_3-S)(\mu-H)_2(\mu_3-CC_6H_5)$ (**46**) as a result of C–H bond cleavage at the benzylic carbon.



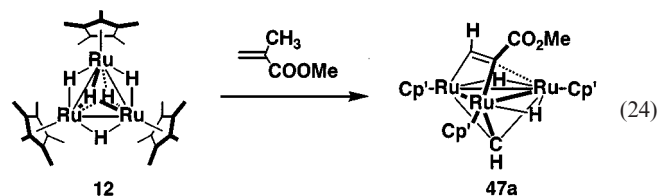
A competition experiment with a 1:1 mixture of toluene and methylcyclohexane was carried out to elucidate the mechanism. While the accessibility of the methyl group of these two substrates to the reaction site seem to be of similar extent in terms of the steric bulk of the substrate, the C(methyl)–H bond dissociation energy of toluene (ca. 88 kcal/mol) is much smaller than that of methylcyclohexane (ca. 98 kcal/mol). From a thermodynamic point of view, the μ_3 -benzylidyne complex should be exclusively formed if the reaction proceeded via homolysis of the C–H bond. In spite of this, heating a solution of **15** in the mixed solvent at 170 °C for 142 h resulted in the formation of **45** and **46** in the ratio of 1:1.86 [Equation (23)]. This result implies that a radical mechanism seems unlikely for these reactions.

3.5 Reactions of a Trinuclear Polyhydride Cluster with 1,1-Disubstituted Alkenes

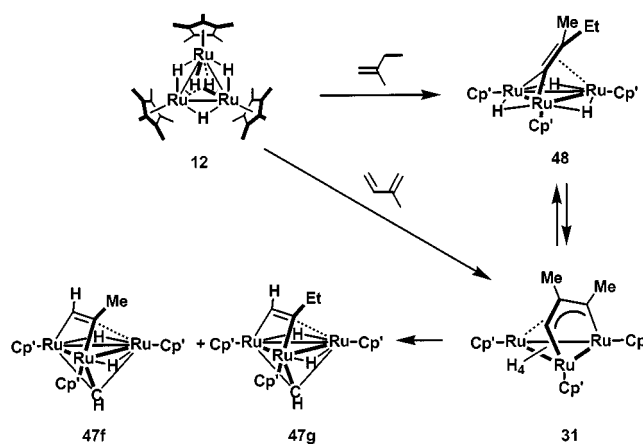
In comparison with the C–H bond cleavage reaction, there have been a relatively small number of successful examples of C–C bond cleavage mediated by mononuclear transition metal complexes.^[44h,47] However, the remarkable

properties of a multimetallic system, namely its capability of multiple coordination and multi-electron transfer, enabled us to activate not only a C–C single bond^[37,48] but also a double bond.

The reaction of **12** with excess methyl methacrylate at 80 °C resulted in the quantitative formation of $\{(C_5Me_5)Ru\}_3(\mu_3-\eta^2:\eta^2-CH=CCO_2Me)(\mu_3-CH)(\mu-H)_2$ (**47a**) [Equation (24)].^[49] The reaction of **12** with a 1,1-disubstituted alkene such as α -methylstyrene, methylenecyclopentane, methylenecyclohexane, and α -methylene- γ -butyrolactone proceeded similarly, leading to the exclusive formation of the corresponding $(\mu_3\text{-alkyne})(\mu_3\text{-methylidyne})$ complexes **47b–47e**.



Formation of **47** evidently shows that the C–C double bond is cleaved, and the resulting two fragments are converted into the μ_3 -methylidyne and the μ_3 -alkyne moieties. When the reaction of **12** with the alkene was conducted under milder conditions, formation of an intermediary μ_3 -vinylidene complex **48** was detected. Interestingly, heating a solution of the dimetalloallyl complex **31** derived from isoprene resulted in the formation of a 1:1 mixture of **47f** and **47g** by way of the μ_3 -vinylidene complex. These observations are consistent with the reaction path involving a reversible isomerization between the μ_3 -vinylidene complex and the μ_3 -1,3-dimetalloallyl complex, followed by C–C bond cleavage that is likely associated with metal–metal bond cleavage and recombination (Scheme 17).



Scheme 17

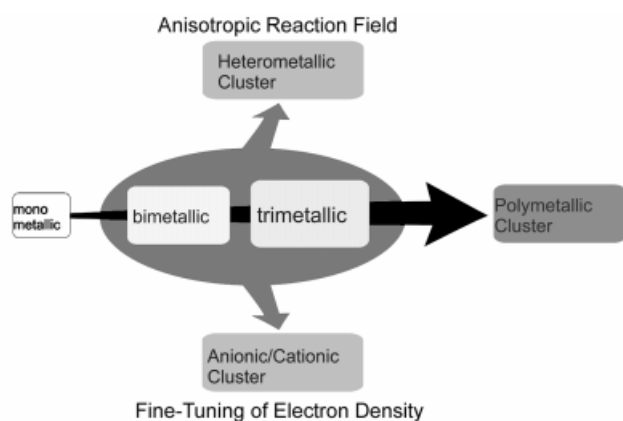
4. Conclusion

The reaction chemistry of metal polyhydride clusters has been a relatively unexplored field in comparison with that

of polycarbonyl clusters. However, the newly developed cyclopentadienylmetal polyhydride system has brought about several great changes in the reactivity of the clusters. Metal polyhydride clusters, especially those having C₅Me₅ groups, reveal remarkable reactivity, that is, an unprecedented mode of C–C bond cleavage, C–C double bond cleavage of terminal alkenes, alkane C–H bond cleavage, and so on.

Among the intrinsic properties of metal clusters, their capability of multi-electron transfer and multiple coordination discriminate their reactivity from that of mononuclear metal complexes. Particularly, the latter is most probably essential for the multimetallic activation. The metal–metal distances of the polyhydride clusters appearing in this review are in the range of 2–3 Å, and these metal–metal separations would be suitable for cooperation of multiple metal atoms in the activation step of the substrate. In the above-mentioned polyhydride clusters, metal centers are tightly bound to each other by multiple bridging hydride ions and, therefore, the clusters are stable enough not to undergo fragmentation during the reaction. As a result, each metal center mutually takes the role of a binding site and an activation site and activates the substrate concertedly.

We are now exploring the following three subjects: (1) synthesis of clusters with higher nuclearity, (2) modification of the electronic and steric environment of the reaction site by introducing a variety of bridging ligands into the core of the cluster, and (3) synthesis of heterometallic polyhydride clusters.



Systematic, namely both experimental and theoretical studies of the multimetallic activation would be a shortcut to the successful development of really new and versatile methods of transformation of the organic substrates.

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Received September 2, 2001
[I01388]