

CLUSTER CHEMISTRY

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Summary

Metal cluster chemistry is one of the most rapidly developing areas of inorganic and organometallic chemistry. Prior to 1960 only a few metal clusters were well characterized. However, shortly after the early development of boron cluster chemistry, the field of metal cluster chemistry began to grow at a very rapid rate and a structural and a qualitative theoretical understanding of clusters came quickly. Analyzed here is the chemistry and the general significance of clusters with particular emphasis on the cluster research within my group. The importance of coordinately unsaturated, very reactive metal clusters is the major subject of discussion.

Introduction

The first metal cluster reported in the literature probably was $\text{Ta}_6\text{Cl}_{14} \cdot 7 \text{H}_2\text{O}$, compositionally described in 1907 [1]. Structural characterization of a metal cluster did not come until the midcentury when an X-ray study [2] was made of aqueous $\text{Nb}_6\text{Cl}_{12}$ and $\text{Ta}_6\text{X}_{12}^{2+}$ aggregates and when a two-dimensional X-ray crystallographic analysis [3] was completed for $\text{Mo}_6\text{Cl}_8(\text{OH})_4 \cdot 14\text{H}_2\text{O}$ and $\text{Mo}_6\text{Cl}_{12} \cdot 2 \text{H}_2\text{O}$. Today, the class of metal halide clusters is modest in size; representative examples are listed in Table 1. Metal carbonyl clusters, presently the largest class of metal clusters, were not defined until relatively late in the twentieth century. First reported was $\text{Fe}_3(\text{CO})_{12}$ whose fine structural details were not resolved until much later because of intrinsic disorder in the crystals [7]. Then this field of study literally exploded in the sixties and seventies through the efforts of many and especially those of the research groups of Chini, Lewis and Johnson, and Dahl. Sizes of these carbonyl clusters now have the impressive range of from three to thirty-eight, the latter probably a number that has been exceeded or will soon be exceeded by the time this article is in print. A representative list of carbonyl clusters is given in Table 2. Cage clusters with an atom or atoms within the metal cluster polyhedron are

TABLE 1
MOLECULAR METAL HALIDE CLUSTERS ^a

Cluster size	Cluster	Cluster form
3	Re ₃ Cl ₁₂ ³⁻	Equilateral triangle
	(arene) ₃ Ta ₃ Cl ₆ ⁺	Triangle
6	Mo ₆ Cl ₁₄ ²⁻	Octahedron
	Nb ₆ Cl ₁₄	Octahedron
	Ta ₆ Cl ₁₂ (OH ₂) ₅ ²⁺	Octahedron
	Ta ₅ MoCl ₁₂ (OH ₂) ₆ ³⁺	Octahedron
	Nb ₆ I ₁₁	Octahedron
	Zr ₆ I ₁₂	Octahedron
	Zr ₆ Cl ₁₂ ³⁺	Octahedron
	Pt ₆ Cl ₁₂	Octahedron

^a See references 4–6 for general reviews of clusters of this type.

also known for a wide range of atoms including hydrogen, carbon, sulfur, phosphorus, antimony and transition metals (Table 3). There are clusters that contain no halide or carbonyl ligands but their number is presently so small that description by class is unrealistic. Examples include Ni₄(η⁵-C₅H₅)₄H₄, Co₄(η⁵-C₅H₅)₄H₃, Ni₄(CNR)₇, Ni₆[η⁵-C₅H₅]₆, Ni₄(CNR)₄(η³-RC₂R)₃, Pt₃(CNR)₆, gold and copper clusters like Au₆(PR₃)₆²⁺ and Cu₆H₆(PR₃)₆, the Mo₄Hg₄ cubane cluster in [C₅H₅Mo(CO)₃Hg]₄Mo₄ and Rh₃H₃[P(OCH₃)₃]₆ [8]. The third major class of metal clusters comprises the naked cluster ions, a class largely derived from the post transition elements of Groups III, IV, V and VI [10]. These

TABLE 2
METAL CARBONYL CLUSTERS ^a

Cluster Size	Cluster	Cluster Form
3	Os ₃ (CO) ₁₂	Equilateral triangle
4	Ir ₄ (CO) ₁₂	Regular tetrahedron
5	Os ₅ (CO) ₁₅	Trigonal bipyramid
6	Co ₆ (CO) ₁₄ ⁴⁻	Regular octahedron
	Pt ₆ (CO) ₁₂ ²⁻	D _{3h} -trigonal prism
7	Rh ₇ (CO) ₁₆ ³⁻	Capped octahedron
8	Ni ₈ (PR) ₆ (CO) ₈	Cube
9	Pt ₉ (CO) ₁₈ ²⁻	Stacked trigonal prisms
12	Pt ₁₂ (CO) ₂₄ ²⁻	Stacked trigonal prisms
13	Rh ₁₃ (CO) ₂₄ H ₃ ²⁻	D _{3h} -hexagonal close-packed
14	Rh ₁₄ (CO) ₂₅ ²⁻	C _{4v} -body-centered cubic
15	Pt ₁₅ (CO) ₃₀ ²⁻	Stacked trigonal prisms
17	Rh ₁₇ S ₂ (CO) ₃₂ ³⁻	Rh centered set of four
		staggered Rh ₄ squares
19	Pt ₁₉ (CO) ₂₂ ⁴⁻	Pt centered sets of staggered
		pentagons capped by platinum atoms at each end
26	Pt ₂₆ (CO) _x ²⁻	D _{3h} -hexagonal close-packed
38	Pt ₃₈ (CO) ₄₄ ²⁻	O _h -face-centered cubic-cuboctahedron

^a See reference 8 for a general review of carbonyl clusters.

TABLE 3
MOLECULAR CAGE CLUSTERS ^a

"Outer" cluster size	Cage atom	Cluster	Cluster form
6	H	HNb ₆ I ₁₁	Nb ₆ octahedron
	C	Ru ₆ C(CO) ₁₇	Ru ₆ octahedron
	C	Rh ₆ C(CO) ₁₅ ²⁻	Rh ₆ trigonal prism
	N	Rh ₆ N(CO) ₁₅ ²⁻	Rh ₆ trigonal prism
8	C	Co ₈ C(CO) ₁₈ ²⁻	Co ₈ square antiprism
	Au	Au ₉ (PR ₃) ₈ ³⁺	D _{2h} Au ₈ polyhedron
9	P	Rh ₉ P(CO) ₂₁ ²⁻	C _{4v} rhodium capped Rh ₄ square antiprism-Rh ₈ P square antiprismatic unit
12	Rh	Rh ₁₃ (CO) ₂₄ H ₃ ²⁻	Hexagonal close-packed with Rh ₁₂ Rh core of D _{3h} symmetry (reflected cuboctahedron)
13	Rh	Rh ₁₄ (CO) ₂₅ ⁴⁻	C _{4v} pentacapped cube (body-centered cubic) with Rh ₈ Rh central core
16	Rh, 2 S	Rh ₁₇ S ₂ (CO) ₃₂ ³⁻	Four staggered Rh ₄ squares (Rh ₄ SRh ₄ RhRh ₄ SRh ₄) separated by S or Rh atoms; Rh ₈ S square antiprismatic units
17	2 Pt	Pt ₁₉ (CO) ₂₂ ⁴⁻	End capped set of three staggered Pt ₅ pentagons (PtPt ₅ PtPt ₅ PtPt ₅ Pt) separated by Pt atoms, Pt ₁₀ Pt pentagonal antiprismatic units
23	Pt ₃ ^b	Pt ₂₆ (CO) _x ²⁻	D _{3h} -hexagonal close-packed ^c with central and enclosed Pt ₃ unit
32	Pt ₆ ^d	Pt ₃₈ (CO) ₄₄ ²⁻	O _h -face centered cubic with central and enclosed Pt ₆ octahedron

^a See references 8 and 9 for a general review of these clusters. ^b Enclosed Pt₃ equilateral triangle. ^c Number of carbonyl ligands is not established. ^d Contains an enclosed Pt₆ regular octahedron.

TABLE 4
NAKED CLUSTER IONS ^a

Cluster size	Cluster Ion	Cluster Form
4	Pb ₄ ⁴⁻	T _d -tetrahedron
	Te ₄ ²⁺	Square plane
	Hg ₄ ⁶⁻	Square plane
5	Bi ₄ ²⁻	Square plane
	Bi ₅ ³⁺	D _{3h} -trigonal bipyramid
	Sn ₅ ²⁻	D _{3h} -trigonal bipyramid
6	Pb ₅ ²⁻	D _{3h} -trigonal bipyramid
	Te ₆ ⁴⁺	Trigonal prism
7	Sb ₇ ³⁺	C _{3v} -capped octahedron
	Pb ₇ ⁴⁻	C _{3v} -capped octahedron
8	Bi ₈ ²⁺	Square antiprism
9	Bi ₉ ⁵⁺	D _{3h} -tricapped trigonal prism
	Sn ₉ ⁴⁺	C _{4v} -capped square antiprism
	Pb ₉ ⁴⁻	C _{4v} -capped square antiprism
	Ge ₉ ²⁻	Tricapped trigonal prism
	Ge ₉ ⁴⁻	~C _{4v} -capped square antiprism

^a See references 8 and 10 for a general review of these clusters.

TABLE 5
 DINUCLEAR METAL COMPLEXES

Complex	Bond order	M—M Bond distance (Å)	Reference
Mn ₂ (CO) ₁₀	1	2.93	43
(C ₅ H ₅) ₂ Cr ₂ (CO) ₆	1	3.28	44
(C ₅ H ₅) ₂ Cr ₂ (CO) ₄ [P(OCH ₃) ₃] ₂	1	3.34	45
(C ₅ H ₅) ₂ Mo ₂ (CO) ₆	1	3.24	46
(C ₅ H ₅) ₂ Cr ₂ (CO) ₄	3	2.22 (ave)	47
(C ₅ H ₅) ₂ Mo ₂ (CO) ₄	3	2.45	48
Mo ₂ [N(CH ₃) ₂] ₆	3	2.21 (ave)	49
Re ₂ Cl ₄ [P(C ₂ H ₅) ₃] ₄	3	2.23	50
[Re ₂ Cl ₈] ²⁻	4	2.24	51
[Mo ₂ Cl ₈] ⁴⁻	4	2.14	52
[Mo ₂ (CH ₃) ₈] ⁴⁻	4	2.15	53

naked cluster ions, which have no peripheral ligands, are illustrated by the listing in Table 4. Dinuclear metal complexes are excluded from the cluster group by definition but their chemistry, particularly the chemistry associated with the metal—metal bond, is obviously relevant to cluster chemistry and, in fact, study of these dinuclear systems is important to the complete development and understanding of metal cluster chemistry. The dinuclear species may have single or multiple metal bonds of widely varying bond distances and bond strengths which is selectively illustrated in Tables 5 and 6. Table 6 lists metal—metal bond distances for a set of dinuclear manganese complexes having on the basis of electron count a formal bond order of one. For the set illustrated, the bond distance range is ~2.5 to 3.2 Å [12]. Factors that increase the bond distance are increased formal oxidation state of the manganese atoms and large steric bulk in the ligand. In clusters, bridging ligands affect the separation of the metal centers. Metal—metal bond distances generally are shorter and longer where carbon monoxide and hydride hydrogen atoms, respectively, are bridging ligands than for unbridged separations. Doubly and triply hydride hydrogen atom bridged metal—metal bonds typically are substantially shorter than unbridged separations.

 TABLE 6
 VARIATION IN METAL—METAL BOND DISTANCES IN "SINGLY BONDED" DINUCLEAR METAL COMPLEXES: THE MANGANESE SYSTEM ^a

Complex	Mn—Mn distance (Å)	<i>d</i> ^x
Mn—Mn[Mn(c)] ^b	2.74	<i>d</i> ⁷
Mn ₂ (CO) ₁₀	2.92	<i>d</i> ⁷
Mn ₂ (CO) ₈ (μ ₂ -N ₂ C ₆ H ₅) ₂	3.23	<i>d</i> ⁷
Mn ₂ (CO) ₈ [μ ₂ -Si(C ₆ H ₅) ₂] ₂	2.87	<i>d</i> ⁶
Mn ₂ (CO) ₄ (C ₅ H ₅) ₂ (μ-CH ₂)	2.78	<i>d</i> ⁵
Mn ₂ (CO) ₂ (NO) ₂ (η ⁵ -C ₅ H ₅) ₂ ^c	2.57	<i>d</i> ⁵

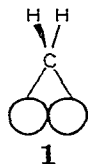
^a See reference 12. ^b Value adjusted for a coordination of 12. ^c There are two bridging ligands but their identities were not established in the crystallographic studies.

There is a beauty and an order to clusters and cluster structures that provide sufficient aesthetic and intellectual content for justification of molecular metal cluster research be it theory, structure analysis or exploratory synthesis. As to the future scientific and technological values of metal clusters, they probably will lie in areas not anticipated today. The very difficulty in this type of prediction is a strong point in favor of an unfettered prosecution of fundamental and exploratory research in molecular metal clusters. From a contemporary view, I have been interested in the relationships between molecular metal clusters and metal surfaces with respect to chemisorption and catalytic processes. A detailed analysis of clusters and surfaces has been completed using the surface chemisorption state as the surface reference point [8]. There are similarities between clusters and surfaces especially in the context of structure and stereochemistry for the molecule or molecular fragment interaction with surface metal atoms and peripheral cluster metal atoms and also in thermochemistry, i.e., average metal-metal and metal-ligand bond energies. Similarities are enhanced if the comparison is made between the larger metal clusters and small metal particles rather than between small clusters and flat metal single crystals; this is especially notable in the context of the mechanistic features of ligand migration processes [8,13]. However, significant variances are evident [8]; variances that arise from obvious differences between molecular clusters and metal surfaces and differences that should affect chemistry in a significant fashion.

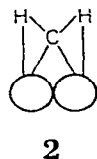
I see the most fundamental differences between clusters and surfaces in the context of the coordination features of the peripheral (surface) metal atoms [8]. The metal-metal coordination number of the peripheral metal atoms in molecular clusters ranges from two in 3-atom clusters to four in octahedral clusters to six in $\text{Pt}_{38}(\text{CO})_{44}^{2-}$ whereas the coordination number for flat metal surfaces is typically in the range of nine to six although it is as low as four for the (100) face of a body-centered cubic metal structure [8]. Metal-ligand coordination numbers for peripheral metal atoms in clusters are typically much larger than for the surface atoms in metals on which chemisorbed molecules or molecular fragments are present [8]: The metal-ligand coordination numbers are four in $\text{Os}_3(\text{CO})_{12}$, three in $\text{Ir}_4(\text{CO})_{12}$, three in $\text{Os}_6(\text{CO})_{18}$, and an average of ~ 1.16 in $\text{Pt}_{38}(\text{CO})_{44}^{2-}$ in sharp contrast to the surface metal-ligand coordination numbers which generally are less than one. Obviously, the disparity in values for these two types of coordination numbers decreases as molecular cluster size increases and metal particle size decreases and the crude analogy should be more useful for the large cluster-small metal particle comparisons. The features of the largest structurally established [14] molecular cluster, $\text{Pt}_{38}(\text{CO})_{44}^{2-}$, nicely illustrate this point since this cluster has cuboctahedral form with exposed faces of (111) and (100) character. For comparison, vapor deposition of platinum metal tends to yield cuboctahedral crystals again with (111) and (100) faces although typically the crystals prepared in this fashion are larger ($\sim 50 \text{ \AA}$) than the Pt_{38} cluster [15].

Most molecular metal clusters are coordinately saturated and do not display the high reactivity of metal surfaces which, even with chemisorbed molecules or molecular fragments, do not have coordinately saturated surface metal atoms especially if the metal surface crystallography is relatively flat and close-packed

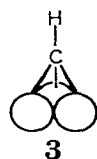
in character. These electronic features alone can lead to substantive differences in the stereochemistry of the bound molecule or molecular fragment. For example, methylene (CH_2) ligands in molecular dinuclear or cluster species always have the stereochemical arrangement shown in **1** with the CH_2 plane normal to the $\text{M}-\text{M}$ vector. However, a configuration like **1** appears to be less



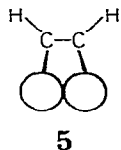
stable than **2** for a relatively bare $\text{Ni}(111)$ surface because of optimal $\text{Ni}-\text{H}$



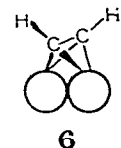
interactions in **2** where the CH_2 plane contains the $\text{M}-\text{M}$ vector. These assessments are based on EHMO calculations for the surface case [16]. Interestingly, the energy difference between **1** and **2** falls as other molecules, e.g., carbon monoxide, are added to the surface, i.e., as the degree of surface coordination saturation increases. Similar considerations prevail for the methylidyne (CH) species on nickel (111): the pervasive configuration, **3**, found for methylidyne



based clusters like $\text{HCCO}_3(\text{CO})_9$, is found by calculation to be less stable than **4** [16] and ultrahigh vacuum spectroscopic studies suggest that for chemisorbed CH on $\text{Ni}(111)$ the $\text{C}-\text{H}$ vector is tipped from the surface normal [17]. In cluster chemistry, there is an established example of a $\mu_4-\eta^2-\text{CH}$ ligand: The cluster, $\text{HFe}_4(\text{CH})(\text{CO})_{12}$, has a CH ligand bound through both the C and H atoms to a butterfly array of iron atoms (Figure 1) [18] (see later discussion). Also, Shustorovich and Baetzold [19] have noted the greater stability of **5**



with respect to **6** for a Pt_2 bare "cluster" complex with an acetylene ligand;



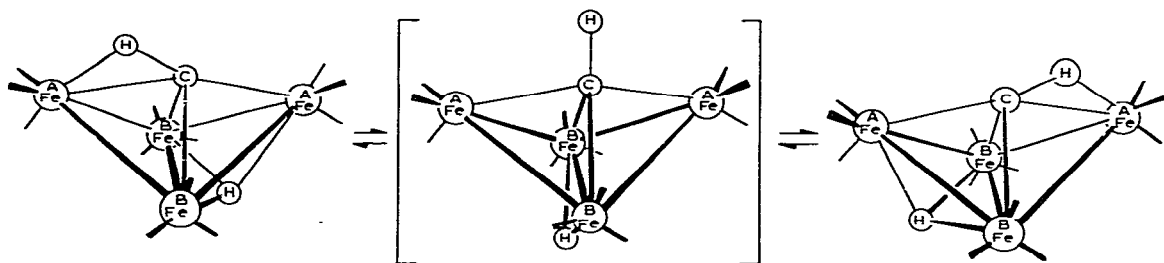
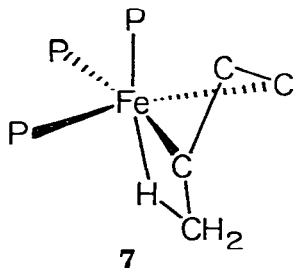


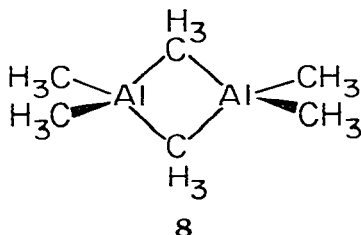
Fig. 1. Skeletal framework in the cluster $\text{HFe}_4(\eta^2\text{-CH})(\text{CO})_{12}$ with the CH ligand bound through both the carbon and hydrogen atoms to iron atoms. Hydrogen atom exchange between CH and Fe_xH sites occurs in this molecule and the three structures illustrated here might represent *part* of the hydrogen atom (CH and Fe_xH) migration process [18]. Recently completed X-ray and neutron diffraction studies have established the solid state structure of this cluster as illustrated above except that the hydride hydrogen atom bridges the two basal iron atoms, Fe^{B} [18].

form 6 is the invariant one [8] for molecular dinuclear metal acetylene complexes.

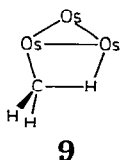
Carbon—hydrogen—metal bonding interactions as depicted in 2 and 4 are not generated from coordinately saturated metal complexes but are from coordinately unsaturated metal clusters and also mononuclear metal complexes. For example, protonation of $(\eta^4\text{-diene})\text{Fe}(\text{PX}_3)_3$ complexes must yield an intermediate 16-electron complex $(\eta^3\text{-allyl})\text{Fe}(\text{PX}_3)_3^+$ species which transforms then to a more stable 18-electron complex of structural form 7 with a multicenter



Fe-H-C bond [20,21]. Similarly, in $(\text{CH}_3)\text{HOs}_3(\text{CO})_{10}$, a conventional symmetrical CH_3 bridging ligand, as found in the trimethylaluminum dimer, 8, would yield a coordinately unsaturated complex. In fact, this methyl-osmium



cluster has an unsymmetrically bridging methyl ligand, analogous to 7 and partially shown in 9, whereby a higher degree of coordination saturation is



achieved [22]. Facile scission of carbon–hydrogen bonds occurs in molecular coordination complexes only if the complex is coordinately unsaturated as in the ubiquitous ortho metalation reaction of aryl phosphine or phosphite metal complexes that are coordinately unsaturated and in coordinately unsaturated trialkylphosphine metal complexes like $\text{Fe}[\text{P}(\text{CH}_3)_3]_4$ which transforms to $\text{HFe}[\eta^2\text{-CH}_2\text{P}(\text{CH}_3)_2][\text{P}(\text{CH}_3)_3]_3$ [21].

As another example of a strikingly different electronic and stereochemical mode of binding for a molecule between the cluster and surface regimes consider the case of the benzene molecule. Presently, the stereochemical mode of benzene binding on a flat close-packed surface is not rigorously established. Our ultrahigh vacuum studies of the $\text{Ni}(111)\text{-C}_6\text{H}_6$ state have established that benzene chemisorption on this surface is associative or molecular in character; no C–H or C–C bonds are broken at 25–100°C [23]. Also, the data are most consistent with a configuration in which the benzene molecule is in a plane above and parallel to the (111) surface [23]. Because of the variance in the Ni–Ni and C–C bond distances, there can be no precise registry of the carbon and the nickel atoms. Our EHMO analyses [16] suggest that Ni–H interactions are also important for this surface hydrocarbon binding and we note that there can be nearly perfect registry of the benzene hydrogen atoms with nickel atoms in the (111) surface plane. No such multi-metal atom interaction with an aromatic molecule is in fact known for a molecular metal cluster. All arene complexes of metal clusters have the arene bound in an η^6 fashion with a single cluster metal atom. Examples of seven and eight member rings bound to three metal atoms in an η^7 and η^8 fashion respectively, are established e.g., $\text{Ru}_3(\text{CO})_9[\mu_3\text{-SC}(\text{CH}_3)_3](\mu_3\text{-}\eta^7\text{-C}_7\text{H}_7)$ and $\text{Ni}_3(\text{CO})_3(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\mu_3\text{-}\eta^8\text{-C}_8\text{H}_8)$ [24,25]. Interestingly, $\text{RCCO}_3(\text{CO})_6(\eta^6\text{-C}_6\text{H}_6)$ with benzene bound to a single cobalt atom reacts with C_8H_8 to yield $\text{RCCO}_3(\text{CO})_6(\mu_3\text{-}\eta^6\text{-C}_8\text{H}_8)$ with the cyclooctatetraene bound to three metal atoms [26]. We are presently seeking μ_x -arene cluster chemistry through the use of coordinately unsaturated molecules and of clusters with polydentate ether ligands where the ether oxygen atoms are bound at axial coordination sites of a cluster triangular face. Benzene is known to react with the coordinately unsaturated clusters, $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and with $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ to give a σ bound (to two osmium atoms) and π bound (to one osmium atom) benzyne ligand as shown in Figure 2 [27,28] a type of surface reaction that may be operating with the more electropositive metals.

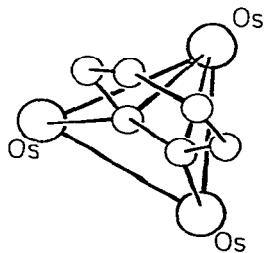


Fig. 2. Benzene reacts with $\text{H}_2\text{Os}_3(\text{CO})_{10}$ or $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ to form $\text{H}_2\text{Os}_3(\text{CO})_9\text{C}_6\text{H}_4$. As illustrated above, the C_6H_4 unit is σ bound to two osmium atoms and π bound to the third [27,28].

For the reasons cited above, I see the virtually unknown area of coordinately unsaturated molecular metal clusters to be a major and exciting new area of cluster chemistry. Firstly, the enhanced reactivity of such clusters will generate a broad and diverse cluster chemistry. Some such clusters should be reactive catalysts or catalyst precursors and will present a new phase of catalytic chemistry. Secondly, this new aspect of cluster chemistry should yield better structural models, albeit still crude models, of chemisorbed metal surface states than do saturated metal clusters. Thirdly, new vistas of cluster chemistry should be evident. For these reasons, my research is directed to the synthesis of coordinately unsaturated clusters and I describe below preliminary results of this research. Also, I note further compelling arguments for the elaboration of coordinately unsaturated cluster synthesis and chemistry. In coordinately saturated clusters, the metal–metal average bond energies are comparable to or less than the metal–ligand average bond energies. Consequently, the chemistry of these clusters may be based on a first step that comprises metal–metal bond breaking and a chemistry that may be based on mononuclear metal complexes; for surfaces, the very process of chemisorption reduces the surface metal atom metal–metal bond order but rarely leads to generation of mononuclear metal fragments. Fragmentation reactions should be less significant for coordinately unsaturated metal clusters.

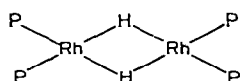
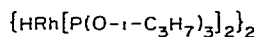
Synthesis tactics

One direct approach to the generation of coordinately unsaturated clusters is synthesis of saturated complexes in which labile ligands are present. For example, the replacement of carbonyl ligands in metal carbonyl clusters by weak field ligands like acetonitrile yields complexes that are reactive because of facile acetonitrile ligand dissociation. However, to form a cluster in which there are reactive sites at more than one metal site (to fully exploit the reactive potential of a cluster) a multi-substituted cluster must be prepared. Only two classes are known. One is based on $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ [29] and $\text{Os}_3(\text{CO})_{10}(\text{olefin})_2$ [29] which are reactive and have substantial synthesis value and have the weak field ligands associated with different metal atoms. The other is based on $\text{Fe}_3(\text{PC}_6\text{H}_3)_2(\text{CO})_7^-(\text{NCCH}_3)_2$ which is highly reactive but with both acetonitrile ligands bound to the same iron atom [30]. We seek metal complexes in which at least three coordination sites, ideally a set normal to a triangular metal face, are occupied by a weak field ligand like nitrile, an ether or a ketone. To date, this synthetic tack has not been extensively examined.

In an alternative synthetic approach, we have attempted the generation of clusters that are de facto coordinately unsaturated. Here we have had some success with dinuclear and trinuclear rhodium complexes that possess very high reactivity yet an impressive resistance to fragmentation.

The polynuclear rhodium hydrides

Reaction of $\eta^3\text{-C}_3\text{H}_5\text{Rh}[\text{P}(\text{OR})_3]_2$ with hydrogen largely yields a class of reactive polynuclear rhodium hydride complexes of the form $\{\text{HRh}[\text{P}(\text{OR})_3]_2\}_n$ with $n = 2$ or 3 [31–34]. With the phosphite substituent, R, either methyl or ethyl, the nuclearity, n , is three and with R isopropyl, the nuclearity is two. All



Rh-Rh	2 650(2) Å
Rh-H	1.66(23) Å
Rh-P	2.167(15) Å
P-Rh-P	96.0(2)°
Rh-H-Rh'	105°
H-Rh-H'	75°

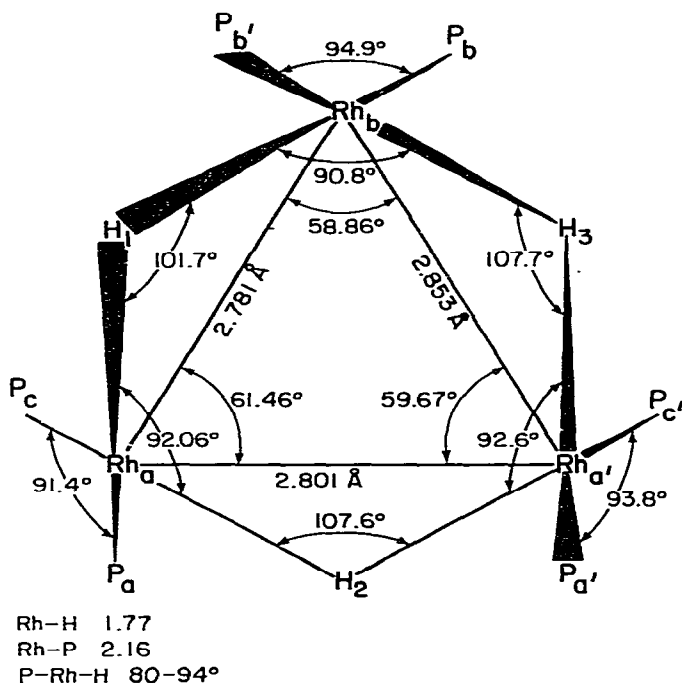
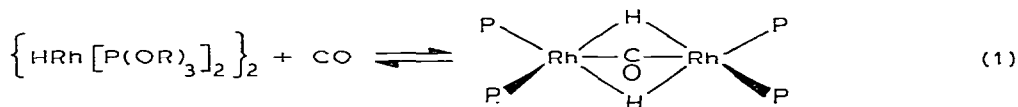


Fig. 3. Illustrated is the skeletal structure of $\text{H}_2\text{Rh}_2[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ which has a near coplanar array of hydridic hydrogen atoms, the two rhodium atoms, and the four phosphorus atoms. Each rhodium atom has an effective d^8 -square planar electronic and structural environment [32,34].

Fig. 4. A representation of the structure of $\text{H}_3\text{Rh}_3[\text{P}(\text{OCH}_3)_3]_6$. The three rhodium atoms describe a nearly equilateral triangle and each edge is bridged by a hydrogen atom. Individual rhodium atoms have a near square planar coordination environment, H_2RhP_2 [33].

essentially have square planar metal coordination sites. The dimer consists of a coplanar set of rhodium, hydrogen and phosphorus atoms (Figure 3). An edge-bridged set of three square planar Rh coordination spheres is found in the trimer as shown in Figure 4 for the crystallographically established $\{\text{HRh}[\text{P}(\text{OCH}_3)_3]_2\}_3$ complex.

The chemistry of these polynuclear rhodium hydrides is rather surprising. Although addition of excess phosphite ligand is an explicable fast and irreversible generation of the very stable mononuclear $\text{HRh}[\text{P}(\text{OR})_3]_4$ complex [31-34], carbon monoxide reacts in a rather unexpected and complex fashion [35] to reversibly generate a series of metal complexes; e.g., the dimer reacts as in equations 1 and 2. * Hydrogen reacts instantly with the polynuclear



* The structures of the carbonyl complexes are not established but an X-ray crystallographic study of the dicarbonyl has been initiated. A tetracarbonyl derivative is not very stable and reverts to the dicarbonyl when the CO atmosphere is removed.

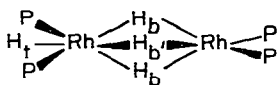
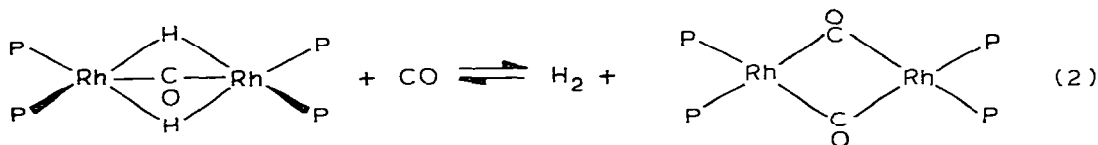
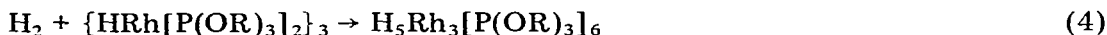
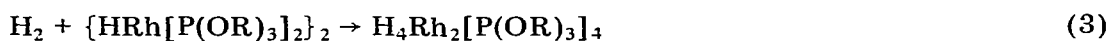


Fig. 5. The catalytic intermediate $\text{H}_4\text{Rh}_2[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ has the structure illustrated above with three bridging hydride ligands [31].

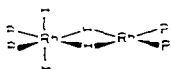


hydrides to form not mononuclear $\text{H}_3\text{Rh}[\text{P}(\text{OR})_3]_2$ complexes but rather polynuclear rhodium polyhydrides, equations 3 and 4.



Nuclear magnetic resonance studies of these polynuclear polyhydrides have established for the dimer the tris(hydrido) bridged dimer structure illustrated in Figure 5.

Both the trimeric and dimeric rhodium hydrides are very active olefin hydrogenation catalysts. Turnover rates at 20°C are between 1 and 100 per second. Reaction of the complexes with olefins is slow and complex whereas the reaction with hydrogen as noted above is virtually instantaneous. Hence the polyhydride is the first key intermediate in the catalytic cycle for the dimeric $\{\text{HRh}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_2\}_2$ species. The tetrahydride is a fluxional structure, and a key intermediate form implicated by DNMR studies is **10** (see Figure 6). This is the structure that is presumed to interact



10

with the olefin in the completion of the catalytic cycle shown in Figure 7. Thus, this dinuclear species shows the elements of effective hydrogen addition to one metal atom and olefin addition to a second, contiguous metal atom; the first demonstrated example in a polynuclear complex wherein catalytic chemistry involving different metal atoms occurs. Analogous chemistry is evident in the $\{\text{HRh}[\text{P}(\text{OCH}_3)_3]_2\}_3$ catalyzed olefin hydrogenation reactions.

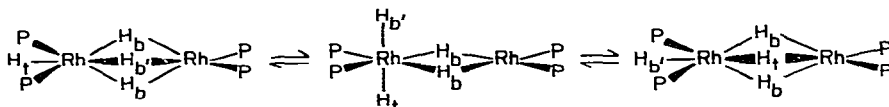


Fig. 6. The tetrahydride $\text{H}_4\text{Rh}_2[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ is a fluxional molecule. DNMR studies suggest that the structure shown in the center of the drawing above is an intermediate in the intramolecular exchange process. This intermediate structure is proposed to react with olefins in the olefin hydrogenation cycle illustrated in Figure 7.

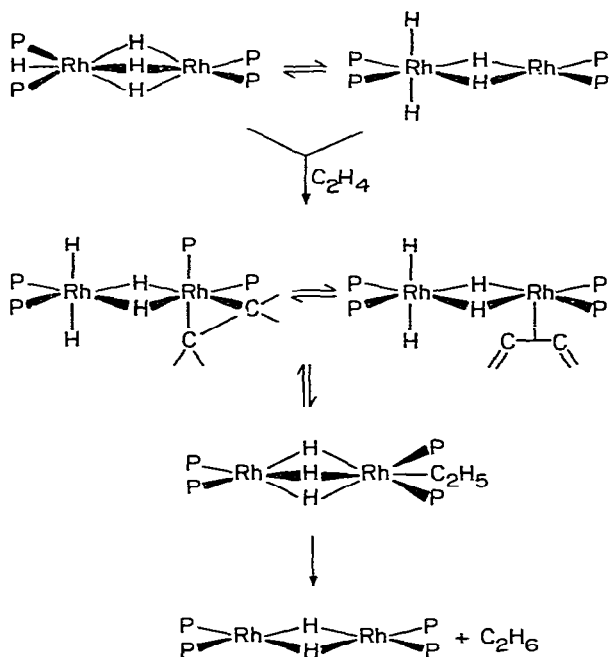


Fig. 7. Representation of the catalytic cycle for the olefin hydrogenation cycle catalyzed by $\text{H}_2\text{Rh}_2[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ [31].

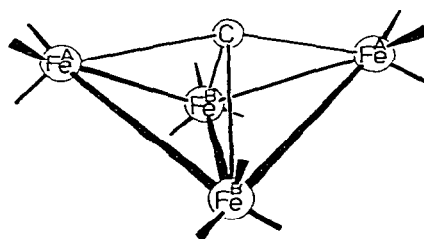


Fig. 8. The probable skeletal array for the related carbide cluster ions $[\text{HFe}_4(\mu_4\text{-C})(\text{CO})_{12}]^{2-}$ and $[\text{Fe}_4(\mu_4\text{-C})(\text{CO})_{12}]^{2-}$ [18]. The position of the hydride ligand in the former cluster has not been established.

Acetylene hydrogenation to *cis*-olefins is also catalyzed by the $\{\text{HRh}[\text{P}(\text{OR})_3]_2\}_x$ complexes. Rates are substantially lower than for olefin hydrogenation yet if these complexes are presented with a mixture of olefin, acetylene, and hydrogen only the acetylene hydrogenation to *cis*-olefin reaction is observed. The reason a selective hydrogenation of acetylenes to olefins occurs is that acetylene competes more effectively for the dimeric or trimeric $\{\text{HRh}[\text{P}(\text{OR})_3]_2\}_x$ complex than does hydrogen. Unlike the olefin hydrogenation cycle, the acetylene hydrogenation cycle comprises a first step of acetylene complexation followed by a relatively slow step of hydrogen addition, hydrogen migration or olefin displacement. The acetylene complex intermediates can and have been isolated. Crystallographic studies are not completed yet but solution state NMR studies of the dimeric complex clearly establish this intermediate to be $\text{H}(\text{RCH}=\text{CR})\text{Rh}_2[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_4$ with the vinyl ligand bridging both rhodium atoms. [35].

Unsaturated carbidic carbon centers in clusters

Another class of reactive metal clusters that we have sought is a carbide metal cluster in which the carbidic carbon atom * has a significant chemical

* A carbidic carbon in a cluster is defined as a carbon atom that is bonded (within bonding distance) only to cluster framework atoms [9].

reactivity. Previously, metal carbide clusters had been distinguished by a lack of reactivity centered on the carbide carbon atom. This lack of reactivity is understandable for the cage [9] carbide clusters that have a coordinately saturated carbon atom fully shielded (enclosed) by a polyhedron of metal atoms because reaction at the carbide site must be preceded by some type of cluster fragmentation. Peripheral carbide clusters have a partially exposed carbide carbon atom [9] and bear some negative charge and consequently should be directly subject to electrophilic attack. However, no such peripheral carbide reaction is documented [9]; for example, the exposed carbide carbon atom in $\text{Fe}_5\text{C}(\text{CO})_{15}$ is not protonated by strong acids [36]. Until our recent synthesis efforts, the lowest coordination number for a carbidic carbon atom in a molecular metal cluster was five as in the aforementioned $\text{Fe}_5\text{C}(\text{CO})_{15}$ [37]. The significance of low-coordinate carbidic carbon atoms in molecular metal clusters is their formal relevance to surface carbidic carbon atoms which are unlikely to have a metal atom coordination number greater than four and which have been shown to be very reactive intermediates in Fischer-Tropsch synthesis reactions [38]. These surface carbides, formed from dissociative chemisorption of CO on relatively electropositive metals like iron, react with hydrogen at room temperatures to yield hydrocarbons [39,40].

We have prepared recently [18] two clusters with four-coordinate carbide carbon atoms, $[\text{HFe}_4(\mu_4\text{-C})(\text{CO})_{12}]^-$ and $[\text{Fe}(\mu_4\text{-C})(\text{CO})_{12}]^{2-}$ in which the carbide carbon atoms nestles into a butterfly array of four iron atoms as in Figure 8. Protonation of the latter cluster instantaneously yields the former cluster and addition of a second equivalent of acid instantaneously leads to protonation of the carbidic carbon atom to form $\text{HFe}_4(\eta^2\text{-CH})(\text{CO})_{12}$ a cluster in which the CH hydrogen atom bridge bonds between the carbon atom and one of the wing iron atoms in a three center C—H—Fe bonding array (Figure 1). This neatly illustrates the potential high reactivity of low-coordinate and exposed carbidic carbon atoms in metal clusters. In addition, the methyne derivative points to an important bonding and structural point for CH fragments on metal surfaces. Unlike the $\eta^1\text{-CH}$ ligands in the coordinately saturated clusters like $\text{HCCO}_3(\text{CO})_9$ [41], the CH group may interact through both the carbon and the hydrogen atoms with surface metal atoms in the surface case and also with cluster metal atoms in nominally unsaturated regimes. All these very recent experimental results with clusters are fully consistent with this potential and with projections presented earlier in this discussion. It is important to note that in the very crude surface—cluster analogy that comparisons for the diverse aspects of cluster framework structure, the stereochemistry of ligand binding, ligand migration process, and of chemistry it is unlikely that a single cluster will exhibit close similarities to a surface chemisorption state for all these aspects. Rather a collage of clusters and their properties must be selected with due consideration of coordination principles and of metal surface features of crystallography and of surface composition.

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