

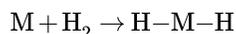
6.5: Organometallic Chemistry of d Block Metals (Part 2)

Small Molecule Complexes

Two or three atomic molecules, such as H_2 , N_2 , CO , NO , CO_2 , NO_2 , and H_2O , SO_2 , etc., are called **small molecules** and the chemistry of their complexes is very important not only for basic inorganic chemistry but also for catalyst chemistry, bioinorganic chemistry, industrial chemistry, and environmental chemistry. The complexes of small molecules other than water and carbon monoxide were synthesized comparatively recently. Dihydrogen complexes in particular were reported only in 1984.

Dihydrogen complexes

The oxidative addition reaction of a hydrogen molecule, H_2 , is one of the methods used to generate the M-H bond of a hydride complex. Schematically, the above reaction is written as



but it was believed that there must be an intermediate complex containing a coordinated dihydrogen. The first example of a stable complex of this sort, $[\text{W}(\text{CO})_3(\text{H}_2)(\text{P}^i\text{Pr}_3)_2]$, was reported by G. Kubas in 1984 (Figure 6.5.18). It was proved by the neutron diffraction that the H_2 is coordinated as an η^2 ligand by maintaining the bond between hydrogen atoms with an interatomic distance of 84 pm.

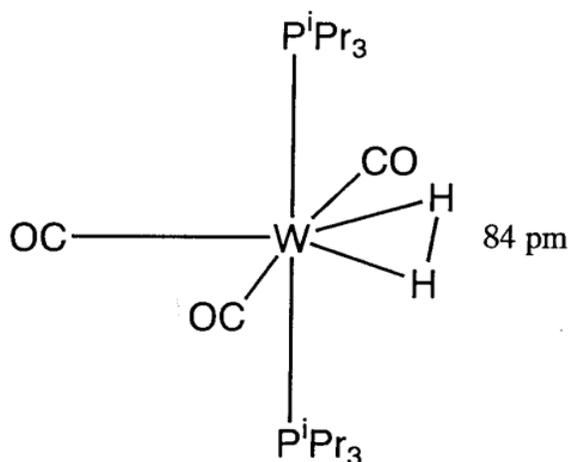


Figure 6.5.18: - Structure of $[\text{W}(\text{CO})_3(\text{H}_2)(\text{P}^i\text{Pr}_3)_2]$

Once this new coordination mode was established, new dihydrogen complexes have been prepared one after another, and dozens of dihydrogen complexes are now known. Dihydrogen complexes are interesting not only from the viewpoint of bond theory but they have also greatly contributed to the study of the activation process of the hydrogen molecule.

Dinitrogen complexes

Since N_2 is isoelectronic with CO , the possible stability of dinitrogen complexes analogous in structure to carbonyl complexes was the subject of speculation for many years. These compounds generated great interest because of the parallels with the interaction and activation of nitrogen molecules on the iron catalyst used in ammonia synthesis and the nitrogen fixing enzyme nitrogenase. However, the first dinitrogen complex, $[\text{Ru}(\text{N}_2)(\text{NH}_3)_5]\text{X}_2$, was prepared by A. D. Allen (1965) unexpectedly from the reaction of a ruthenium complex and hydrazine. Subsequently, it was discovered by chance that nitrogen gas coordinates to cobalt, and $[\text{CoH}(\text{N}_2)(\text{PPh}_3)_3]$ was prepared in 1967 (Figure 6.5.19). Many dinitrogen complexes have been prepared since these early beginnings.

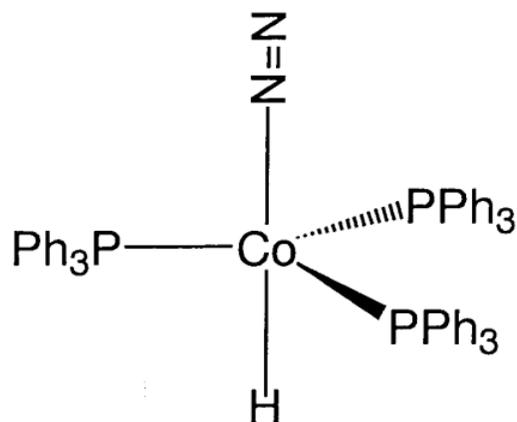
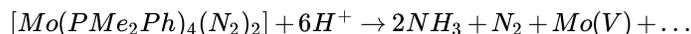


Figure 6.5.19: - Structure of $[\text{CoH}(\text{N}_2)(\text{PPh}_3)_3]$.

In most dinitrogen complexes, N_2 is coordinated to the metal by one nitrogen atom. That is to say, the $\text{M}-\text{N}\equiv\text{N}$ bond is common and there are few complexes in which both nitrogen atoms bond to the metal in the η^2 coordination mode. In 1975, the coordinated dinitrogen in a molybdenum complex was discovered to be protonated by mineral acids to form ammonia, as described in the following reaction. The electrons required for the reduction are supplied by the molybdenum in a low oxidation state as this reaction shows.



In spite of attempts to prepare ammonia and organic nitrogen compounds from various dinitrogen complexes, no nitrogen fixation system which is equal to biological systems has yet been discovered. Ammonia synthesis is a long-established industrial process, and its parameters have been extensively studied and little room for improvement remains. However, elucidating the mechanism of the biological nitrogen fixation reaction at ordinary temperatures and pressures remains one of the major challenges of bio-inorganic chemistry.

Dioxygen complexes

Although it has long been recognized that schiff base complexes of cobalt absorb oxygen, the discovery that **Vaska's complex**, $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$, coordinates dioxygen reversibly to form $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{O}_2)]$ was very significant. In this complex, two oxygen atoms bond to iridium (side-on), and dioxygen has a peroxide character (O_2^{2-}). However, many superoxide (O_2^-) complexes in which only one oxygen atom is bonded to the metal are known. There are also binuclear dioxygen complexes in which O_2 bridges two metals. The relation between reversible coordination of dioxygen and its reactivity is important in relation to the behavior of dioxygen in living systems (refer to [Section 8.2 \(a\)](#)).

(e) Metal-metal bonds

The concept of the formation of a coordinate bond between ligands and a central metal proposed by A. Werner was the basis for the development of the chemistry of complexes. The bonding mode and structures of known complexes have become the guidepost of the preparation of a much larger number of new complexes. For most of the dinuclear or polynuclear complexes that contain two or more metals in a complex, it was sufficient to take into consideration only the bonds between the metal and ligands.

The concept of direct bonds between metals was born of the necessity of explaining the structural chemistry of the dinuclear metal carbonyls that have a partial structure with an odd number of electrons. Two $\text{Mn}(\text{CO})_5$ units in $\text{Mn}_2(\text{CO})_{10}$ are connected by a direct Mn-Mn bond (Figure 6.5.20) without the help of bridge ligands. According to X-ray structural analysis (1963), the Mn-Mn distance of 292 pm was significantly longer than twice that of the metal radius of 127 pm but a Mn-Mn direct bond was envisaged in the absence of a bridge carbonyl ligand. This compound's diamagnetism indicates a structure with an even number of electrons (18 electrons) by sharing electrons between two d^7 -Mn (17 electrons) moieties, each with five carbonyl ligands.

Similarly, it can be concluded that $\text{Co}_2(\text{CO})_8$, with two bridging carbonyl ligands, should have a direct Co-Co bond to be compatible with its diamagnetism.

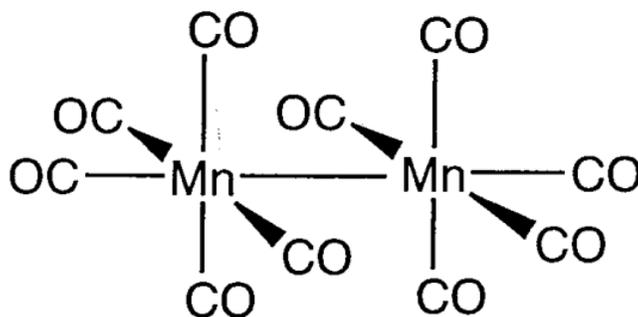


Figure 6.5.20: - Structure of $\text{Mn}_2(\text{CO})_{10}$.

The concept of the single bond between metals introduced for dinuclear metal carbonyl compounds is also very useful in explaining the structure of cluster carbonyl compounds containing two or more metals. The metal-metal bond has been established today as one of the common bonding modes, together with the metal-ligand bond, present in coordination complexes. However, it is not always clear to what extent the interaction between metals exists in the polynuclear complexes which have bridging ligands. As a criterion, the bond order can be evaluated from the bond distance in standard metals (for example, in bulk metals). However, even if the bond distance between metals analyzed by X-ray is sufficiently short, this does not prove the existence of a bond between metals unless the orbital conditions to account for such bonds are also fulfilled.

M-M multiple bonds

There are many dinuclear compounds in which the metal atoms are bound by multiple bonds with bond orders of 2 to 4. The M-M quadrupole bond was proposed first for $\text{Re}_2\text{Cl}_8^{2-}$, and this remains the best-known example (Figure 6.5.21). The Re-Re distance in this compound is only 224 pm, which is unusually short compared with the Re-Re distance of 275 pm in rhenium metal. Another unusual feature is that the ReCl_4 units assume an **eclipsed** configuration (chlorine atoms overlap along the direction of the Re-Re bond) even though the **staggered** configuration (in which chlorine atoms do not overlap along the Re-Re bond direction) should be more stable because the distance between ReCl_4 units is very short, resulting in the distances between the chlorine atoms being very short (experimental value of 332 pm). As a result, the repulsive interaction between the chlorine atoms becomes strong.

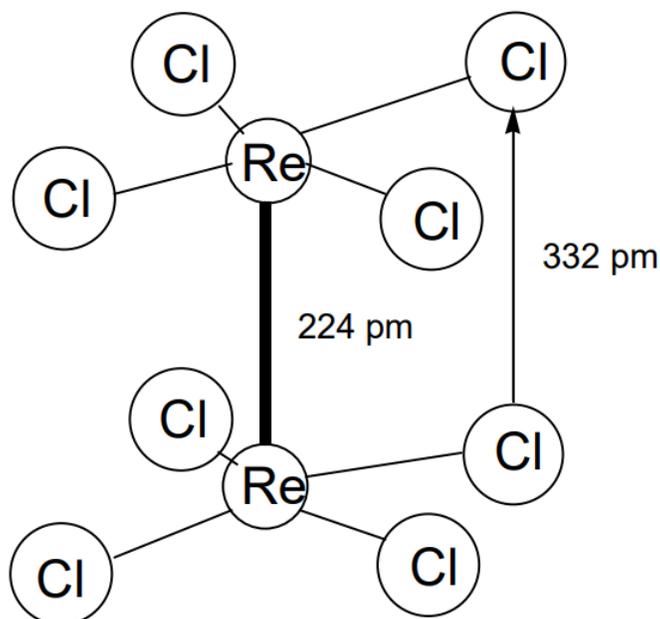


Figure 6.5.21: - Structure of $\text{Re}_2\text{Cl}_8^{2-}$.

F. A. Cotton explained this anomaly by introducing the concept of the delta bond between metals in 1964. Namely, if one takes the z-axis in the direction of the Re-Re bond, a σ bond is formed between the d_{z^2} , the π bonds between d_{yz} and d_{xz} orbitals and the δ bond between d_{xy} orbitals among the five d orbitals. $d_{x^2-y^2}$ is mainly used for the Re-Cl bond. The delta bond is formed by a weak sideways overlap of d_{xy} orbitals, when they are located perpendicular to the direction of the metal-metal bond axis and become

eclipsed (Figure 6.5.22). Therefore, although the δ bond is relatively weak among bonding interactions, it is sufficient to maintain the chlorine ligands in their eclipsed positions.

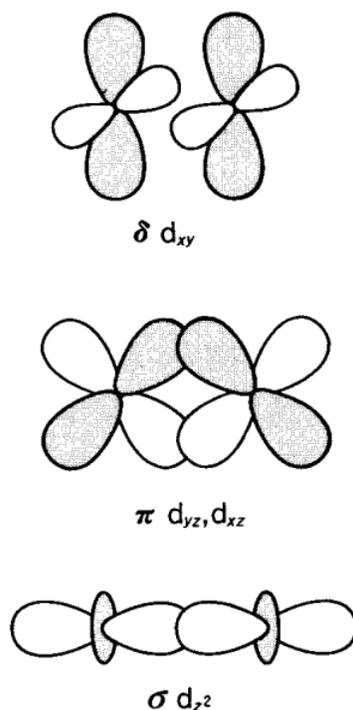


Figure 6.5.22: - Overlap of d orbitals in $\text{Re}\equiv\text{Re}$ quadrupole bond.

The energy levels of the molecular orbitals of σ , π , and δ bonds decrease in this order, and the energy difference between the bonding and antibonding delta orbitals is small. Therefore, even if one electron is removed (oxidation) from $\text{Re}_2\text{Cl}_8^{2-}$, which has a quadruple bond, or one electron is added (reduction) to it, the Re-Re distance should hardly change.

The Mo(II) compound $[\text{Mo}_2(\text{CH}_3\text{COO})_4]$ which is isoelectronic with Re (III) has a Mo-Mo quadruple bond. $[\text{W}_2\text{Cl}_9]^{3-}$ and $[\text{W}_2(\text{NMe}_2)_6]$ are examples of compounds which have the metal-metal triple bonds. Although the issue of whether such metal-metal multiple bonds really exist has been argued many times, the concept has now been established and hundreds of dinuclear compounds with metal-metal multiple bonds are known at present. Metal-metal distances determined by X-ray analysis are most useful in determining whether a metal-metal bond is a multiple one, but as in the case of metal-metal single bonds, the bond distance alone cannot be the absolute determiner and it is necessary to draw conclusions from molecular orbital calculations.

(f) Metal cluster compounds

Analysis of the structures of newly prepared polynuclear complexes that contain two or more metals was, until recently, very difficult. However, with the progress of single crystal X-ray structural analysis, our understanding of the chemistry of polynuclear complexes is progressing quickly. Metal-cluster complexes are polynuclear complexes built by three or more transition-metal atoms with bonds between the metals coordinated by ligands to form polyhedral frames, such as a triangle, a regular tetrahedron, a regular octahedron, and an icosahedron. Even if there is no strong bond between metals, as long as there is some bonding interaction, they may be included as cluster compounds.

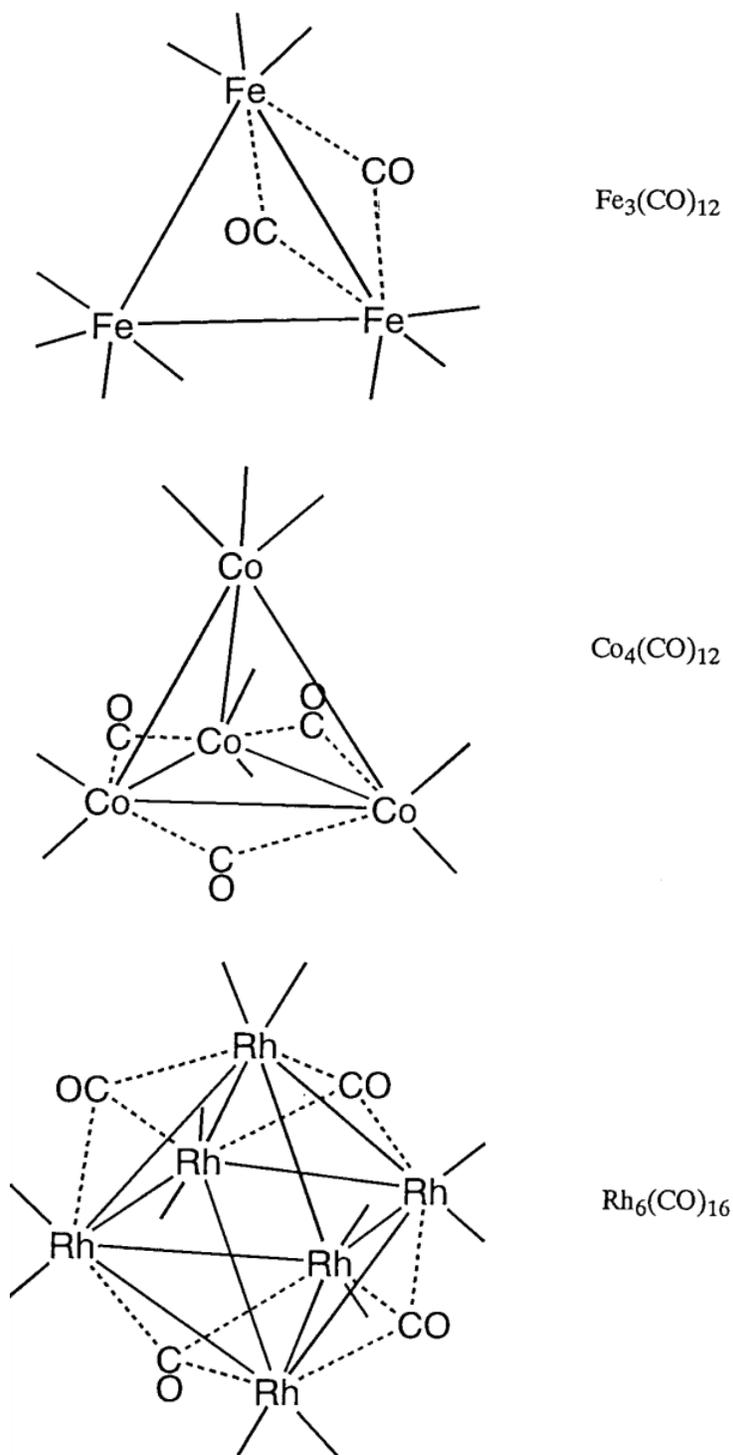


Figure 6.5.23: - Examples of metal cluster carbonyls (terminal carbonyl ligands are omitted for clarity).

Metal cluster complexes may be broadly classified into groups according to the general character of the associated ligands. They are low oxidation state metal clusters with π -acceptor ligands like carbonyls (CO), isonitriles (RNC) or phosphines (PR_3) and with π -donor ligands like oxygen (O), sulfur (S), chlorine (Cl) or alkoxides (OR). Many carbonyl cluster and sulfur cluster compounds have been synthesized. Carbonyl cluster compounds are obtained by heating or irradiating mononuclear carbonyl compounds. The chemical properties of cluster compounds such as $\text{Fe}_3(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$, $\text{Co}_4(\text{CO})_{12}$, $\text{Ir}_4(\text{CO})_{12}$ or $\text{Rh}_6(\text{CO})_{16}$ have been studied in detail (Figure 6.5.23).

Since $\text{Os}_3(\text{CO})_{12}$ forms many kinds of cluster compounds by pyrolysis, it has been used to study the skeletal structures of osmium cluster compounds and their relationship to skeletal electron numbers. A M-M bond is satisfactorily described by the 2 center 2 electron bond and the 18 electron rule is also applicable to each metal for small clusters such as a triangle and a regular tetrahedron. When clusters become large, the Wade rule that describes the relation between the structures of boranes and skeletal electron numbers, or the Lauher rule that draws the number of the bonding metal-metal orbitals for various metal polyhedral structures from the molecular orbital calculations of bare rhodium clusters without ligands, are more applicable. The relationship between the number of cluster valence electrons and the cluster's polyhedral shape as shown in Table 6.5.8 has contributed much to the theory of cluster chemistry.

Table 6.5.8 Metal frameworks and cluster valence electrons in metal cluster carbonyl compounds

Metal framework	Cluster valence electron	Example
Triangle	48	$\text{Fe}_3(\text{CO})_{12}$
Tetrahedron	60	$\text{Co}_4(\text{CO})_{12}$
Butterfly	62	$[\text{Fe}_4(\text{CO})_{12}\text{C}]^{2-}$
Trigonal bipyramid	72	$\text{Os}_5(\text{CO})_{16}$
Square pyramid	74	$\text{Fe}_5\text{C}(\text{CO})_{15}$
Octahedron	86	$\text{Rh}_6(\text{CO})_{16}$
Trigonal prism	90	$[\text{Rh}_6\text{C}(\text{CO})_{15}]^{2-}$

Monovalent anions such as halogens, alkoxides, carboxylate ions, and divalent anions such as oxygen and sulfur stabilize the cluster frameworks by helping metals assume oxidation states suitable for cluster formation and connect metal fragments by bridging. Since neutral ligands such as phosphines, carbonyl, or amines can also be coordinated to metals, a variety of cluster complexes have been prepared.

The halide clusters of molybdenum, Mo_6X_{12} , tungsten, W_6X_{12} , niobium, Nb_6X_{14} , and tantalum, Ta_6X_{14} , are solid cluster compounds that have been known for many years. The octahedral metal frameworks were shown by X-ray structure analysis more than 50 years ago. The molecular cluster complexes were prepared in the 1960s from solid-state halide clusters by the reaction of ligands such as amines and phosphines, and these cluster compounds generated considerable interest for some time. New halide cluster compounds with octahedral structures have again been prepared recently and they are being studied from new perspectives. The molecular cluster complex $[\text{Mo}_6\text{S}_8\text{L}_6]$ (where L is PEt_3 , py, etc.), which has similar Mo_6 frameworks with those of the superconducting Chevrel phase compounds MxMo_6S_6 and their tungsten and chromium analogs have been prepared and the relationships between their structures and physical properties attract great interest (Figure 6.5.24).

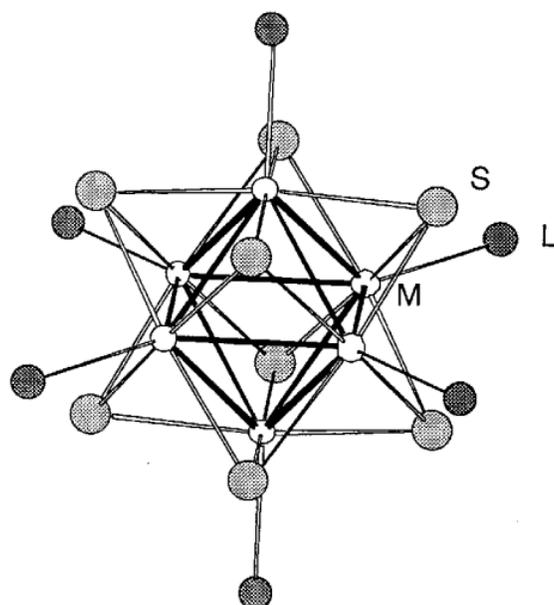


Figure 6.5.24: - Structure of $[\text{Mo}_6\text{S}_8\text{L}_6]$.

As will be described in the Chapter on bioinorganic chemistry, clusters such as Fe_4S_4 are contained in nitrogenase, the nitrogen-fixing enzyme, and also in the active center of ferredoxins, and they play important roles in the activation of dinitrogen or multi-electron transfer reactions. Since R. H. Holm synthesized the $\text{Fe}_4\text{S}_4(\text{SR})_4$ cluster (Figure 6.5.25), our understanding of the chemistry of the iron-sulfur cluster has developed considerably.

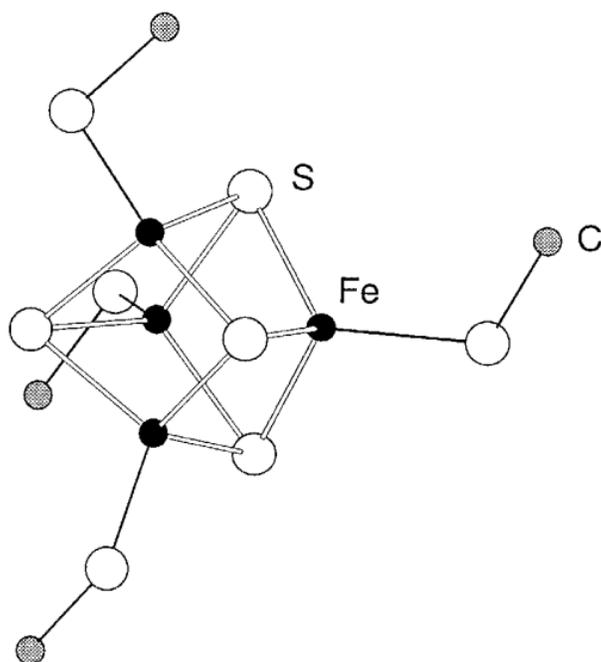


Figure 6.5.25: - Structure of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$.

As the metal species of metal cluster carbonyls are in near-zero valence oxidation states, they had been expected to play a role in specific catalysis. Although many organic syntheses using metal cluster compounds as catalysts have been attempted and some interesting reactions were discovered, in most cases the clusters decomposed during the reactions and they turned out to be false cluster catalysts. Despite this, there have been some examples of reactions that pass through several elementary reaction stages on the metal of the cluster. Hence, it is likely that catalytic reactions that employ the **multi-center coordination** and **multi-electron transfer** abilities of cluster compounds will be developed in the future.

Metal clusters have been helpful as models of the surfaces of bulk metals, metal oxides, or metal sulfides, and they have been useful in the study of chemisorption and successive reactions on solid surfaces. The fine metal grains which maintain the basic cluster frameworks are deposited by the pyrolysis of metal carbonyl cluster compounds chemically bonded to carriers such as silica and alumina. If used in solid catalysis, it is expected that analysis of the catalytic reaction on a metal cluster framework will be possible.

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