Clusters as Ligands – Large Assemblies of Transition Metal Clusters

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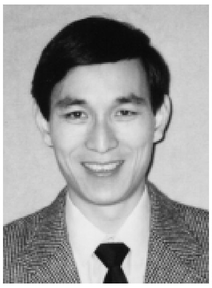
A strategy of using functionalized clusters as ligands for cationic metal centers facilitates the construction of designed transition metal cluster assemblies. Examples of cluster metal carboxylates with conventional as well as novel structures are given and an application of these large molecular species to the generation of heterogeneous hydrogenation catalysts with unusual activities and selectivities is described.

The synthesis of complex species for defined chemical roles is one common goal of both organic and inorganic chemistry. In the latter area, the synthesis of complex extended solid-state structures from the elements under thermodynamic control, e.g., zeolites, provides an impressive example of the power of synthesis. Many of these subdisciplines are covered in the interdisciplinary area known supramolecular chemistry.[1]

Interest in the construction of large, complex inorganic species is driven by an eclectic set of applications which include molecular electronics[2], photochemically driven electron transfer[3], liquid crystalline materials[4], host-guest chemistry[5], cryptate chemistry[6], nanocluster borderline solids[7], chemical sensors[8], ferrimagnetic solids[9], and others. The structures involved range from one dimensional chains of clusters[10], to cluster aggregates[11], to rigid-rod polymers[12], to metal spheres[13], to supramolecular chiral networks[14], to supported clusters[15], to dendritic systems[16][17], and more. The synthetic approaches are equally varied and include step-wise formation of oligomers[18],



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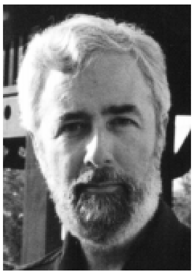

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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modular assembly of rings[19][20], polymerization[21], development of molecular tinkertoys[22] and carborods.[23] Another synthetic approach, the use of functionalized main group[24][25][26], transition metal complexes[27][28] or clusters,[29][30][31][32] is of particular relevance to this contribution.

Our interest in large assemblies of clusters was piqued when we found that $(CO)_9Co_3(\mu_3\text{-}C(CH_2)_nOH$, a major product of the decomposition of $(CO)_4CoBH_2\cdot THF$ above 0°C, crystallized in hexagonal columns with the hydrophilic hydrogen-bonded OH groups at the columnar axes and the hydrophobic metal carbonyl clusters on the surfaces (Scheme 1).[33] Even in solution this cluster derivative forms small aggregates reflecting its ambiphilic behavior. At the time, and still, the organization of metal clusters on various supports, principally for the generation of new catalysts, commanded considerable attention[34] and we wondered if suitably functionalized clusters would self-organize. This would eliminate the need for a complex substrate and, in doing so, introduce more uniformity into the cluster arrays.

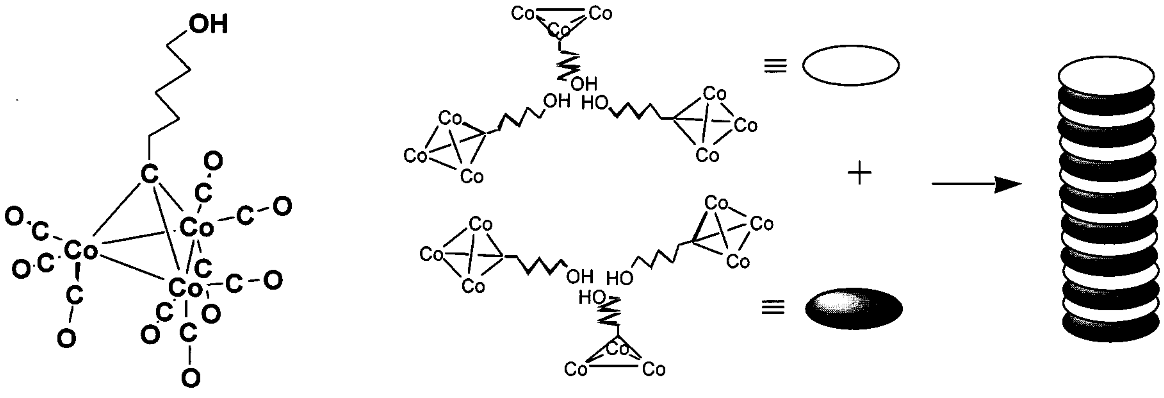
As the weak forces holding $(CO)_9Co_3[\mu_3\text{-}C(CH_2)_nOH]$ molecules together seemed inadequate for our purposes, we sought functionalization that would permit a cluster to serve as a ligand in a classical Werner coordination compound, i.e., the metal cluster would simply replace the usual organic foliage of the typical ligand. These coordination compounds would constitute cluster assemblies in which the central metal cationic moiety would determine both the number of clusters (coordination number) and the spatial array of clusters (coordination geometry). In a sense, the relatively small, well-defined cationic metal center would replace the large substrate of the typical supported cluster.

The idea of cluster coordination compounds presented a number of attractive aspects. First, by using the established principles of coordination chemistry, we could construct a predetermined cluster array from monofunctional clusters. In principle, these cluster building blocks could be made di- and trifunctional in order to construct chains and nets as well. Indeed the Schauer group has made considerable progress in this direction by using bidentate cluster ligands in which main group atoms in the cluster itself act as ligating sites.[18][35][36][37] Curiously, monodentate clusters of the same type form trimeric rings by an intermolecular ligand displacement reaction on the cluster itself.[38] Second, metal clusters are very different from a typical organic substituent, e.g., CH_3R vs $(CO)_9Co_3(\mu_3\text{-}CR)$.[39][40][41][42][43][44][45][46][47] In terms of electronic effects, the metals within the clusters plus their ancillary ligands constitute electron reservoirs capable of donating or accepting electron density. The fact that even the smallest clusters have a substantial steric bulk must affect the products formed in cluster coordination reactions. Consequently, we expected to find significant differences between the coordination chemistry of a cluster ligand and that of a typical main group ligand.

Perhaps the most attractive aspect of an externally functionalized metal cluster is that cluster size, composition as well as ligand type and extension are quantities that can, in principle, be varied.[48] Unfortunately, cluster synthetic chemistry, although continuously developing, is in a rudimentary state relative to, e.g., organic ligand synthesis. Many cluster types are derived from reactions that are unselective thereby requiring tedious separations resulting in modest yields.[48] Much of the interesting structural chemistry[49] is based on metals such as Os and Rh which put an economic damper on thoughts of gram scale syntheses from low yield reactions. Thus, little of the cluster derivative chemistry in the literature was suitable for our purposes.

For these reasons we decided to focus on the well studied tricobalt akylidyne cluster system and began our exploration of cluster coordination chemistry using $(CO)_9Co_3(\mu_3\text{-}CCOOH)$ as a precursor to the corresponding cluster carboxylate ligand, $[(CO)_9Co_3(\mu_3\text{-}CCOO)]^-$.[40][41] This is a fortunate choice as metal carboxylate chemistry is a mature area of coordination chemistry of considerable interest.[50] Importantly, this cluster ligand precursor can be prepared in good yield from commercially available $Co_2(CO)_8$ and $Cl_3CC(O)OR$ on a multigram scale by undergraduates. Its main drawback, and one that figures in its chemistry, is cluster degradation which is facile under basic conditions. For this reason, simple salts of the free ligand $[(CO)_9Co_3(\mu_3\text{-}CCOO)]^-$ are unavailable and only efficient coordination reactions lead to simple chemistry. However, this cluster ligand is selective and metal carboxylate formation reactions are usually clean giving good to excellent yields even for obviously complex reaction pathways. In the following we highlight the varied coordination chemistry of

Scheme 1



the $[(CO)_9Co_3(\mu_3\text{-}CCOO)]^-$ ligand established in our laboratory over the last few years.

Cluster Metal Carboxylate Chemistry

Organic carboxylate anions (RCO_2^-) have been known for over a hundred years as versatile ligands capable of forming metal carboxylates with almost all the metal elements in the periodic table. The resulting metal carboxylates exhibit a variety of core structures, coordination modes, and coordination numbers depending on the properties of the elements used.[50] Recently the chemistry of transition metal carboxylates has drawn renewed attention as such compounds can serve as precursors for the synthesis nanometer-sized polynuclear aggregates with unusual structural and magnetic properties. These compounds may also help to further improve our understanding of the transition from the molecular to the solid state in the biomineralization process or in the development of molecular magnets.[51][52][53]

Likewise, the chemistry of alkylidynetricobalt nonacarbonyl cluster compounds, $(CO)_9Co(\mu_3\text{-}CR)$, has been extensively investigated since the appearance of the first member of this class of compounds, $(CO)_9Co_3(\mu_3\text{-}CCH_3)$ in 1958.[41][54] These complexes are all deeply colored and most are air-stable in solution and in the solid state. In general the alkylidynetricobalt nonacarbonyls undergo degradation by oxidizing agents, bases, and nucleophiles. For example, reactions of potassium permanganate or water with $(CO)_9Co(\mu_3\text{-}CR)$ complexes lead to evolution of carbon monoxide, the formation of inorganic cobalt salts and carboxylic acids derived from the apical organic substituents. Fortunately from the point of view of the work described here, most alkylidynetricobalt nonacarbonyl complexes are soluble in organic solvents, stable toward protonic and Lewis acids, and possess an extensive chemistry.[34][41][42][48][55][56] Our interest in cluster assemblies joins these two fields, i.e. the carboxylic acid derivative of the alkylidynetricobalt nonacarbonyl complex, $(CO)_9Co(\mu_3\text{-}COOH)$, is used as a cluster carboxylate ligand precursor to synthesize cluster metal carboxylates.

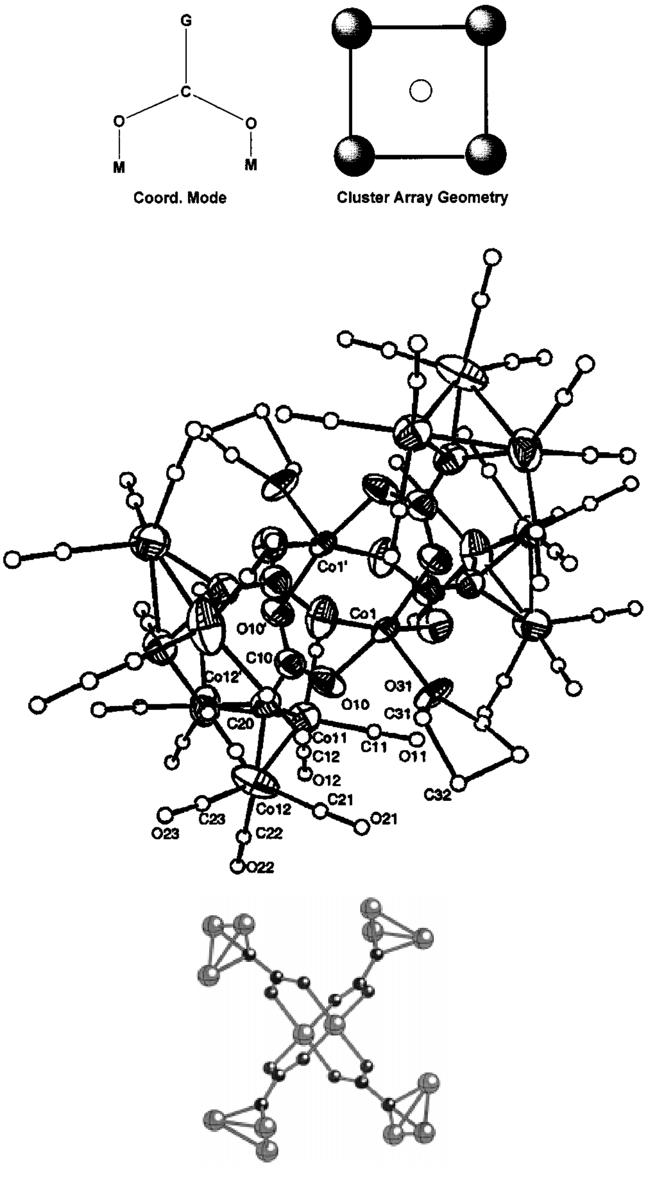
Structures of the Cluster Metal Carboxylates

The principal means of characterization of the cluster metal carboxylates was single crystal X-ray diffraction. In all cases, the bond distances and angles of the tricobalt cluster substituents are unchanged within experimental error from those of free tricobalt clusters. In some cases, the cluster acid functions just like an organic carboxylic acid and analogs of known metal carboxylates are obtained. In other cases the combination of steric and electronic properties associated with the cluster substituent on the acid made novel structural types accessible. The compounds featured below illustrate analogs of organic carboxylates, unusual metal carboxylate structural types, and varied spatial arrangements of the tricobalt cluster assemblies. As will be seen, the cluster carboxylate ligand exhibits the same variety of coordination modes as organic metal carboxylates but also generates some novel structures.

Cluster Carboxylate Mimics of Known Metal Carboxylates

$[M_2\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_4L_2]$ (M = Co, L = THF; M = Mo, L = $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$):[57][58] As an example, the structure of $[Co_2\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_4(THF)_2]$ is shown in Scheme 2. In this first scheme the complete structure from the crystallographic results is shown, and below, for clarity, a simplified structure. As some of the succeeding structures are considerably more cluttered, the representations have been simplified principally by removing the carbonyl ligands of the cobalt clusters. As with similar organic carboxylate analogs,[59] the cluster carboxylate ligands symmetrically bridge two cobalt centers. Consequently, the four tricobalt clusters are arranged in a square

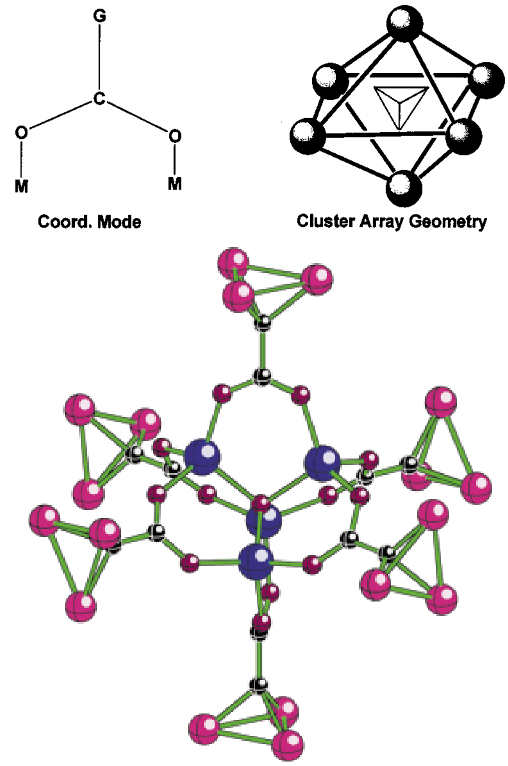
Scheme 2



planar array perpendicular to Co−Co bond axis. Each metal atom is coordinated in the equatorial positions by four oxygen atoms from the four carboxylate ligands and in an axial position by one from the THF solvent.

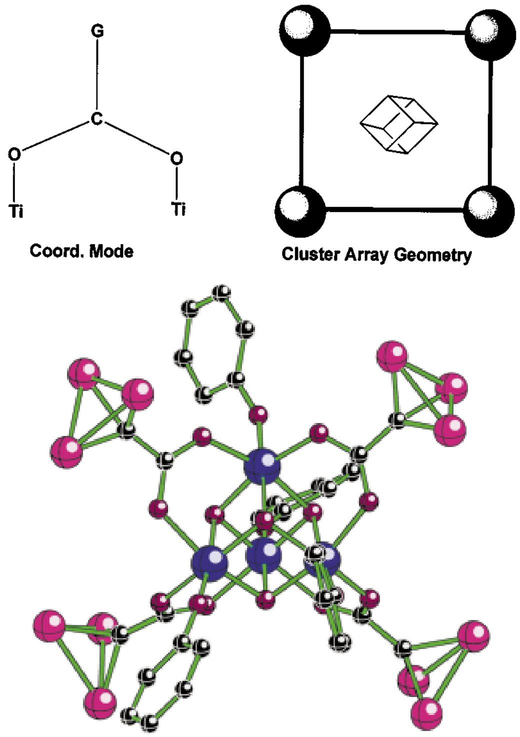
$[M_4O\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_6]$ (M = Zn, Co): [60][61][62] As shown in Scheme 3, the core structure of the cluster zinc carboxylate consists of an M_4 tetrahedron with a centered oxygen atom. The six carboxylate moieties bridge the six metal-metal edges, resulting an octahedral spatial distribution of the tricobalt clusters. These cluster metal carboxylates are direct analogs of classical $M_4O(RCO_2)_6$ "basic" metal carboxylates which are known for M = Be, Zn, Co.[50]

Scheme 3



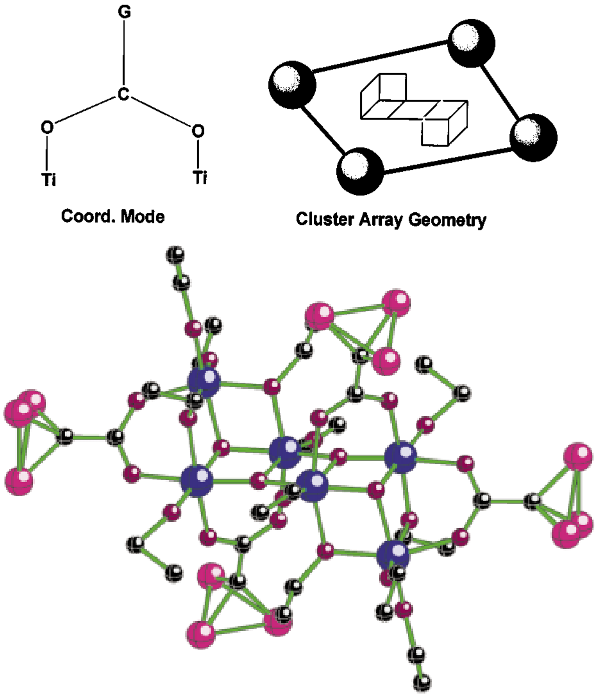
$[Ti_4O_4(OR)_4\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_4]$ (R = $CH(Me)_2$, $(CH_2)_3CH_3$, C_6H_5, 2,6-$(CH_3)_2$-C_6H_3):[63] The structure of the phenoxide derivative is shown in Scheme 4. The core is a distorted Ti_4O_4 cube with titanium and oxo oxygen atoms occupying alternate vertices. As expected, the coordination sphere of each Ti atom contains six oxygen atoms in a distorted octahedral arrangement. The cluster carboxylates bridge four of the six edges of the Ti_4 tetrahedron and the four tricobalt clusters lie roughly in a plane with one transoid pair being above and the other below the plane which results in a slightly distorted square-shape as indicated in Scheme 4. There is considerable open space in the structures, but this decreases with increasing size of the R group. One organic analog has been reported.[64]

Scheme 4

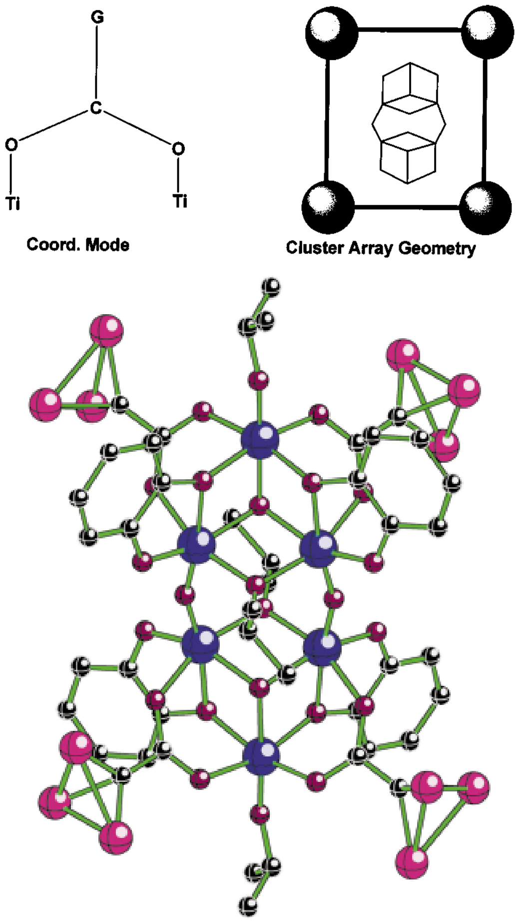


$[Ti_6O_4(OCH_2CH_3)_{12}\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_4]$ and $[Ti_6O_4(OCH(CH_3)_2)_4(1,2\text{-}O_2C_6H_4)_4\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_4]$:[63]The structure of the first cluster metal carboxylate (Scheme 5) shows that it is a dimer of two Ti_3O_4 units linked together by TiO edges oriented so that the

Scheme 5



Scheme 6



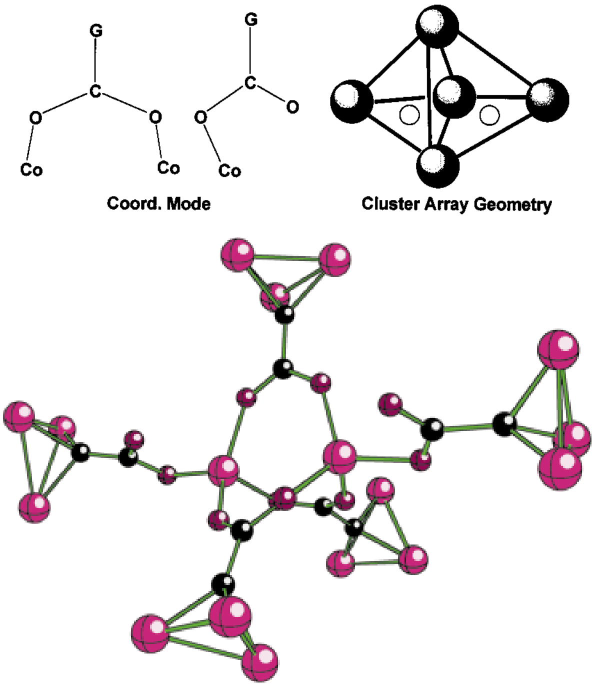
Ti_3O_4 units are related to each other by a crystallographic inversion center. Each Ti_3O_4 unit is bridged by two cluster ligands and the remaining coordination positions are occupied by six ethoxy ligands, two of which are bridging. The cluster carboxylates symmetrically bridge Ti centers, resulting a rhombic arrangement of the four tricobalt clusters elongated in the direction of the ladder-like Ti_6 core.

The structure of the second compound (Scheme 6) reveals that it is an isomeric form of the first resulting from different interconnects between the two Ti_3O_4 units. The catechol ligand uses one oxygen to bridge two Ti atoms and the other to coordinate to one of the two Ti centers in a terminal fashion. Each cluster carboxylate symmetrically bridges two Ti centers resulting a rectangular arrangement of the tricobalt clusters in the direction of the ladder-like Ti_6 core. Both cluster metal carboxylates have structurally characterized organic analogs[65][66][67][68]

Unique Cluster Metal Carboxylates

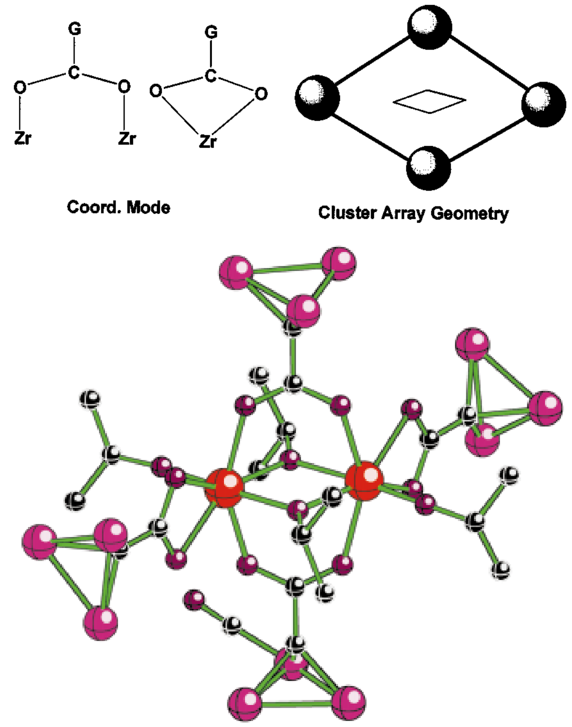
$[C_{10}H_6(NMe_2)_2][Co_2\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_5]$:[69] As shown in Scheme 7, this anionic cluster metal carboxylate consists of two tetrahedral Co centers with very long Co–Co separation [3.47(4)Å]. The two Co atoms are held together by three bridging cluster ligands while the two remaining cluster ligands are terminally coordinated to each Co center in a unidentate fashion thereby generating a tetrahedral ligand environment for each Co atom and a triangular bipyramidal geometry for the spatial distribution of the five tricobalt clusters.

Scheme 7



$[Zr_2(OCHMe_2)_4\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_4]$:[63] This compound represents the first example of a structurally

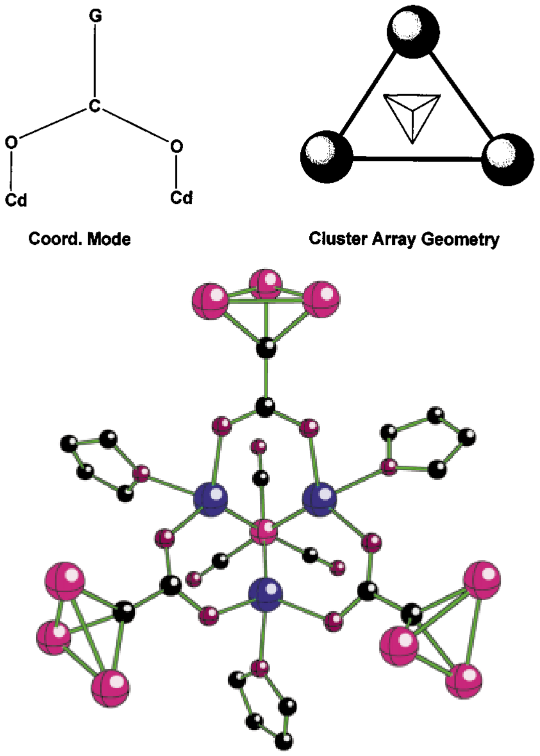
Scheme 8



characterized zirconium alkoxy carboxylate. The structure (Scheme 8) reveals that there are two kinds of coordination modes for the cluster ligands, bridging and chelating. The coordination sphere of each zirconium atom is a slightly distorted pentagonal bipyramid in which the five equatorial positions are occupied with two oxygen atoms from a chelating cluster ligand, two from bridging cluster ligands, and one from a bridging isopropoxy group. The apical positions are occupied with oxygen atoms from one terminal and one bridging isopropoxy group. The spatial distribution of the four tricobalt clusters is a rhombic shape within which the rhombic Zr_2O_2 core is located.

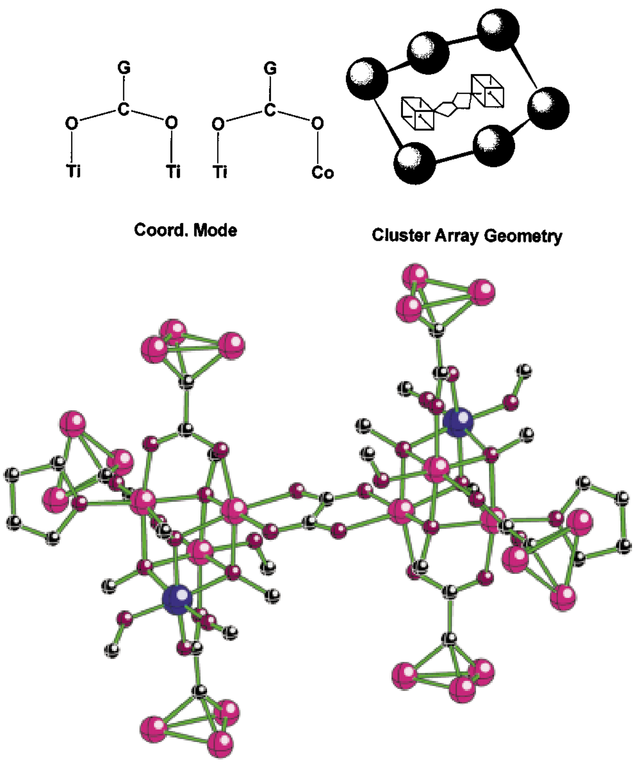
$[\{Co(CO)_3\}Cd_3\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_3(THF)_3]$:[70] This unusual hybrid compound consists of an equilateral triangle of Cd atoms capped with a $Co(CO)_3$ fragment with each Cd−Cd edge bridged by a cluster ligand (Scheme 9). In addition, each Cd atom is coordinated to a THF molecule. Although the bonding of the Cd_3Co core is very interesting, in terms of the spatial distribution of the clusters, the compound can be described as an equilateral triangle of tricobalt clusters in which an equilateral triangle of Cd atoms capped by a $Co(CO)_3$ fragment is inscribed.

Scheme 9

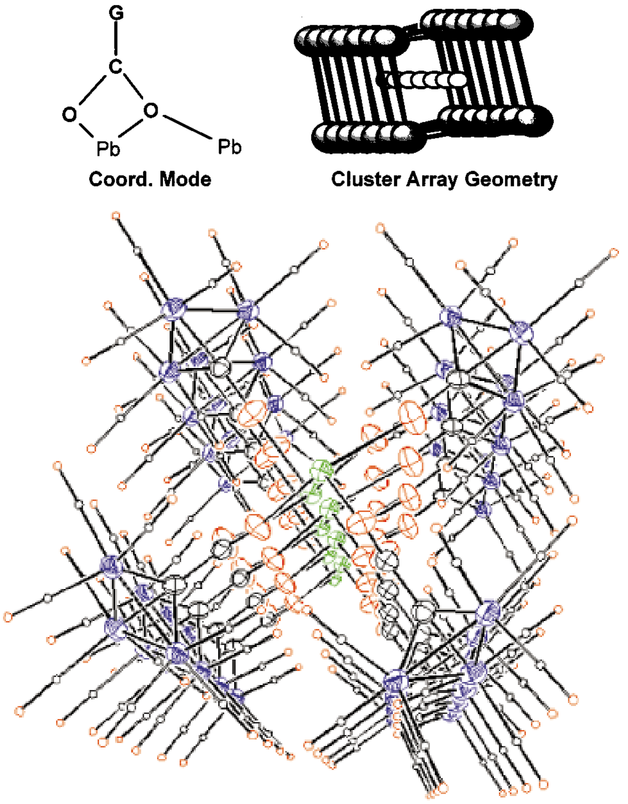


$[\{Co_3Ti(OMe)_6(HOMe)(THF)\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_3\}_2\text{-}(O_2CCO_2)]$:[63] The structure (Scheme 10) consists of two complete $Co_3Ti(OMe)_4$ cubes, related by a inversion center, and joined by a bridging tetradentate oxalate ligand. The coordination environments of both the Ti and core Co atoms are both nearly octahedral. For a single cube, the three tricobalt clusters lie in an approximate plane, but the cluster planes of each cube are displaced with respect to each other, resulting a chair-like arrangement of the six tricobalt clusters. The coordination modes of the cluster ligands fall into two groups: homonuclear bridging and heteronuclear bridging.

Scheme 10



Scheme 11



$[Pb\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_2]_n$:[71] Each Pb atom is primarily coordinated by two cluster carboxylates but secondary Pb−O interactions occur between an oxygen atom of each chelating carboxylate and its adjacent Pb^{II} thereby generating a chainlike structure (Scheme 11) and unusual, solvent free six-coordinate Pb centers.[72] The three distinct Pb−O distances differ considerably. Viewed along the Pb−Pb direction, the tricobalt clusters generate an infinite square columnar array.

Synthetic Routes

The differences between the cluster acid and an organic acid originate in the instability of the metal framework, the capability of the cluster acting as either an electron donor or acceptor, and the steric bulk of the cluster. Consequently, some methods used to prepare organic metal carboxylates are not applicable to these cluster metal carboxylates, e.g., reactions involving carboxylate salts. Some of the successful approaches used for the metal cluster substituted acids are set out below.

Spontaneous Reaction: The cluster acid, $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$, is soluble in polar solvents such as ether, THF, CH_2Cl_2, acetone, and methanol. However, when exposed to air, the solutions spontaneously precipitate the cluster oxo tetrametal carboxylate, $Co_4O\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_6$ (Scheme 3) in high yield (Eq. 1).[61]

$$22\ (CO)_9Co_3(\mu_3\text{-}CCO_2H) + 7\ O_2 \rightarrow Co_4O\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_6 + 44\ CO + 11\ H_2O \quad (1)$$

The origin of the Co^{II} ions is the tricobalt cluster which illustrates how the intrinsic lability of the metal cluster can control the coordination chemistry observed. Unless suitable precautions are taken, this reaction competes with all the other reactions described and generates unusable mixtures of products.

Reactions with Metal Alkyls: The preparation of anhydrous metal carboxylates using the elimination of an alkane from a metal alkyl as the driving force has been effectively used for the formation or organic metal carboxylates. Unlike the organic acids, $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ reacts with $ZnEt_2$ in ether giving a cluster oxo tetrametal carboxylate, $Zn_4O\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_6$ (Scheme 3). A pathway involving formation of a cluster ester is postulated as shown in Eq. 2.[61]

$$8\ (CO)_9Co_3(\mu_3\text{-}CCO_2H) + 4\ ZnEt_2 \rightarrow Zn_4O\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_6 + \{(CO)_9Co_3(\mu_3\text{-}CCO)\}_2O \quad (2)$$

Although the reaction of $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ and $CdMe_2$ under similar conditions may yield a simple cluster metal carboxylate, heating the reaction mixture in toluene at 70°C resulted in the formation of an unexpected product, $[\{(\mu_3\text{-}Co(CO)_3)\}Cd_3\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_3(THF)_3]$ (Scheme 9) in good yield. Note that $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ also serves as a source of the $Co(CO)_3$ fragment that caps the Cd_3 triangle thereby demonstrating another way in which the metal cluster can participate in the reaction.

Exchange Reactions with Metal Carboxylates The exchange reactions between lower metal carboxylates and carboxylic acids have been used in the preparation of higher carboxylates. The lower carboxylic acid generated can be removed azeotropically from the reaction mixture when suitable solvents are employed. The reaction of binuclear carboxylates, $M(CH_3CO_2)_2$, (M = Cr, Mo,W, Cu) with $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ afforded a series of cluster carboxylates with the formula $[M_2(CH_3CO_2)_{4-n}\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_nL_2]$ (L = the axial coordination ligand) via Eq. 3 with structures based on that illustrated in Scheme 2.[57][73][74]

$$n\ (CO)_9Co_3(\mu_3\text{-}CCO_2H) + [M(CH_3CO_2)_2]_2 \rightarrow [M\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_n(CH_3CO_2)_{2-n}]_2 + n\ CH_3COOH \quad (3)$$

Although solvents often play an important role and are found coordinated in the product cluster metal carboxylates, this is not always the case. Organic lead carboxylates have a notable tendency to pick up water, but no coordinated or uncoordinated water is found in the crystal lattice of chain-like $[Pb\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}]_n$ (Scheme 11) even though present in the reaction system.[71]

Reactions with Metal Alkoxides and Aryloxides: The advantage of the reactions of metal alkoxides with carboxylic acids is that a variety of mixed alkoxide-carboxylate complexes can be produced by simply changing the stoichiometric ratios of the reactants.[67][68][75][76][77] The reaction of the cluster acids and group 4 alkoxides afforded cluster alkoxycarboxylates (Eqs. 4 and 5):

$$4\ (CO)_9Co_3(\mu_3\text{-}CCO_2H) + [Zr(OCHMe_2)4\cdot HOCHMe2]_2 \rightarrow [Zr_2\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_4(OCHMe_2)_4] + 6\ HOCHMe_2 \quad (4)$$

$$4\ (CO)_9Co_3(\mu_3\text{-}CCO_2H) + Ti(OR)_4 \rightarrow [Ti_4O_4\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_4(OR)_4] + 4\ ROH + 4\ ROR \quad (5)$$

Complex, Competitive Degradation: Some of the cluster carboxylates are unstable in the solution and undergo complicated redox reactions assisted by either the center metal or solvents to yield new cluster metal carboxylates. The exchange reaction of $Hg(CH_3CO_2)_2$ and $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ in CH_2Cl_2 led to $Hg\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_2$ which is soluble in THF. Crystallization attempts in acetone led to the oxotetracobalt cluster, $[Co_4O\{(CO)_9Co_3(\mu_3\text{-}CCO_2\}_6]$ and mercury metal whereas crystallization in THF afforded $[Co_2\{(CO)_9Co_3(\mu_3\text{-}CCO_2\}_4(THF)_2]$ (Scheme 2) as well as mercury metal. It is believed that in solution a slow redox reaction takes place resulting in precipitation of either $[Co_4O\{(CO)_9Co_3(\mu_3\text{-}CCO_2\}_6]$ or $[Co_2\{(CO)_9Co_3(\mu_3\text{-}CCO_2\}_4(THF)_2]$. It is important to note that the direct reaction of cobalt acetate with $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ only generates the cluster oxo tetracobalt carboxylate.

With similar complexity, the reactions of $[M^{II}\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_2]$ (M = Mn, Fe) with MeOH gave rise to $[M^{III}{}_2Co_2(MeO)_6(MeOH)_2\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_4]$ with cubane-like cores.[78] Further, when $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ was treated with $Ti(OMe)_4$ in THF, a heteronuclear octameric species, $[\{Co_3Ti(OMe)_6(HOMe)(THF)\{(CO)_9Co_3(\mu_3\text{-}$

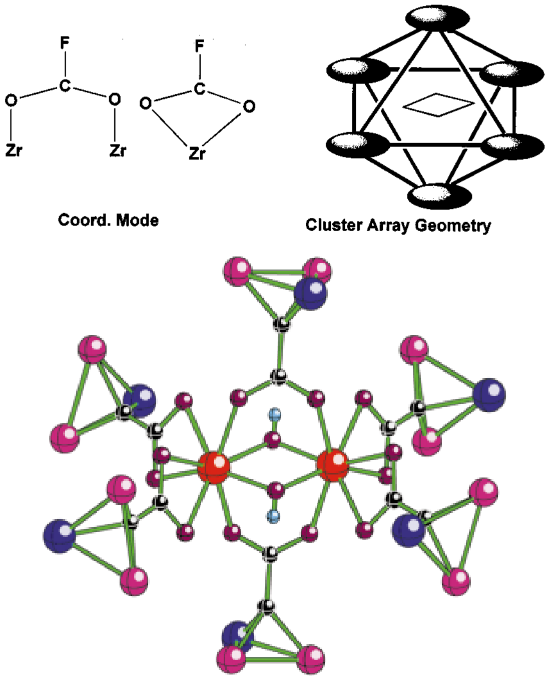
$CCO_2)\}_3\}_2(O_2CCO_2)]$ was isolated in good yield (Scheme 10). Both the Co^{II} ions and oxalate ligand arise from the degradation of the tricobalt cluster in situ.

Modified Cluster Acids and Their Reactivities

The $CpM(CO)_2$ (M=Mo, W) fragment can be substituted for one of the $Co(CO)_3$ fragments in $(CO)_9Co_3(\mu_3\text{-}CR)$ to yield $CpM(CO)_2Co_2(CO)_6(\mu_3\text{-}CR)$.[79] This method works well on a gram scale provided the acid group is protected as an ester from which the acid can be regenerated after metal fragment exchange.[80] The reaction of the heterometal cluster acids with Ti and Zr alkoxides was examined in order to directly compare their chemistry with that of $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$. The compounds structurally characterized are $Zr_2(OH)_2\{CpMo(CO)_2Co(CO)_6(\mu_3\text{-}CCO_2)\}_6$ and $Ti_4O_4(OR)_4\{CpMo(CO)_2Co(CO)_6(\mu_3\text{-}CCO_2)\}_4$.[80] The former exhibits two bridging cluster ligands, four chelating cluster ligands, and two hydroxyl groups, generating a Zr_2O_{14} core and a coordination number of eight for each Zr center with an octahedral spatial distribution of the six modified clusters (Scheme 12). The Ti clusters show the same structural motif as those of tricobalt cluster ligands, i.e., that shown in Scheme 4.

Interestingly, the Cp rings of the $CpM(CO)_2$ moieties in all the compounds are proximal (Cp ring adjacent to the capping carbon) rather distal (Cp ring positioned away from the capping carbon) and the $CpM(CO)_2$ carbonyls are semibridging to the Co atoms. The exclusive presence of the proximal isomer of the coordinated cluster ligand relative to the more stable distal isomer for the uncoordinated cluster[81][82][83] reflects the existence of a cluster electronic effect in the coordination properties of the carboxylic group.

Scheme 12



Reactivity and Physical Properties Imparted by the Cluster Substituent

Cluster substituted carboxylic acids are weaker acids than acetic acid and are expected to form more basic carboxylates.[61][80] It is not surprising, then, that the cluster substituent can alter the chemical selectivity of the carboxylate moiety. Thus, the reactions of the cluster acids with group 4 metal alkoxides exhibit significantly different chemistry than that of organic acids. For example, in contrast to acetic acid[68], the cluster carboxylate observed does not depend on the reaction stoichiometry. That this is a cluster effect is established by the reactivity of the modified cluster ligands, $CpM(CO)_2Co_2(CO)_6(\mu_3\text{-}CCO_2H)$. These are of similar size to the tricobalt cluster but under same reaction conditions the products from the reaction of the cluster acids with zirconium isopropoxide are different.

The physical properties of the cluster metal carboxylates show some interesting differences from those of their organic analogs. The presence of the carbonyl clusters has a large effect on the intermolecular interactions. For example, $[Ti_4O_4(OR)_4\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_4]$ with molecular weights of ca. 2500 are soluble in hexane. All compounds are deeply colored, and their absorption spectra are similar to that of $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ with extinction coefficients roughly proportional to the number of the tricobalt units in the cluster arrays. Exceptions are $[M_2\{(CO)_9Co_3(\mu_3\text{-}CCO_2)\}_4]$ (M = Cr, Mo, W) which show intense absorption in the visible range, presumably due to the charge transfer from M center to the tricobalt units.[73]

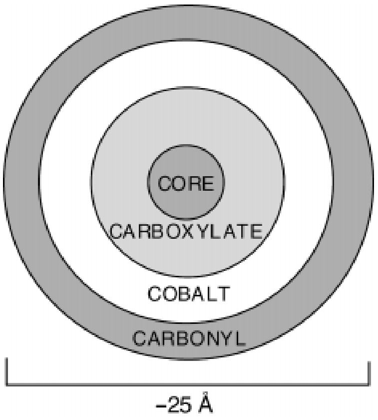
As with organic metal carboxylates the IR bands associated with the $-CCO_2$ moiety provide useful fingerprints to distinguish and identify new compounds.[50] In the cluster metal carboxylates the carbonyl ligand stretching bands 1900 to 2200 cm^{-1} are also useful, albeit less sensitive, probes of coordination. These two regions provide useful fingerprints to distinguish and identify new compounds. In general, the deprotonation and coordination of a cluster acid results in a reduction of the number of carbonyl bands and the frequencies of the antisymmetrical and symmetrical stretching modes of the COO^- group are significantly decreased.

Cluster Arrays as Catalyst Precursors

Metal clusters are attractive catalysts or catalyst precursors[34][84] and the use of supported metal clusters potentially provides a catalyst with homogeneous set of multimetal active sites. Such a heterogeneous catalyst would preempt one of the most attractive aspects of homogenous catalysts while retaining those of heterogeneous catalysts. Indeed, recent work has been very promising.[15][85]

As already indicated in the introductory paragraphs, our approach is to limit the "support" to a minimal metal core thereby producing identical nanosized cluster assemblies with different shapes but related compositions. Indeed these cluster metal carboxylates may be considered as layered particles as shown in Scheme 13 with shapes ranging from

Scheme 13



spheres to less symmetric solids. For the spherical particle, a cationic core is covered with a set of carboxylate moieties attached to a set of carbyne carbons, then a set of cobalt atoms, and, on the outside, a layer of carbonyl groups. In several of the compounds, one finds the 20 to 30 Å diameter molecular assemblies in a close-packed array in the solid state.

Ideally it was our intention to activate these species for catalysis by removing some or all of the external carbonyl ligands thereby forming reactive cobalt-covered nanoparticle spheres. Several issues had to be resolved experimentally. These included the relative lability of the outer Co−CO links vs the inner CCO_2−M links, the ease of metal diffusion resulting in Co crystallite formation (sintering), the surface areas of the active materials, and, most importantly, the catalytic activities and selectivities for selected reactions. In the following we describe the nature of the solid produced from the cluster assemblies by thermolysis, the catalytic properties of the solids in a standard hydrogenation reaction, and the unique properties of these catalysts for the selective hydrogenation of an α,β-unsaturated aldehyde to an unsaturated alcohol.

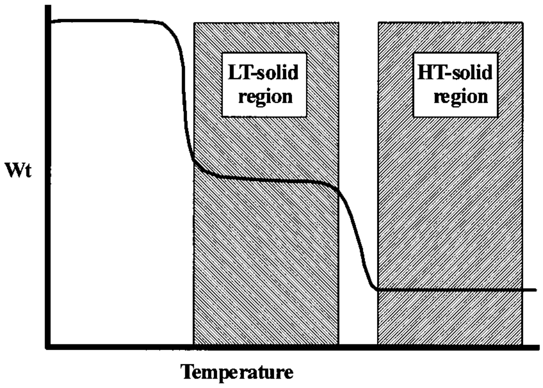
Properties of Solids Formed from Cluster Metal Carboxylates

The behavior of single crystals of cluster metal carboxylates on heating gave us the first indication of the special properties of these molecular cluster carboxylate solids.[86] For example, a single, well formed, shiny, dark colored crystal that diffracted X-rays was converted into a single smaller, but similarly shaped, apparent crystal with a metallic luster. The product did not, however, diffract X-rays and a close examination of the faces of the product showed extensive pitting. Indeed, density measurements revealed a substantial void volume in the product solid. Additional preliminary experiments also showed considerable hydrogenation activity and, thus, we set out to characterize the nature of these solids as well as their catalytic properties.

As long-range order in the molecular solids was lost on pyrolyzing the cluster carboxylates, unambiguous structure determination was out of the question. Further it appeared clear that there was some dependence of material properties on the activation procedure. Hence, the first efforts were directed towards establishing the nature of the chemical conversion of precisely characterized, but inactive, molecular precursors to amorphous, but active, solids.[87]

Thermal gravimetric analyses usually showed two stable regimes, i.e., a constant mass over a certain temperature range, depending on carboxylate structure type. Scheme 14 (labeled low temperature, LT, ca. 100−200°C: high temperature, HT, > ca. 200°C). Mass spectrometry showed that in the LT regime mainly CO loss occurred and CO_2 loss was predominant in the HT regime. Actual mass loss and gas composition suggested loss of the outer CO layer to reach to first regime and loss of the carboxylate links to reach the second regime. In situ IR measurements (DRIFTS) corroborated this interpretation in that the terminal carbonyl bands of the tricobalt disappeared followed by loss of the carboxylate bands as the temperature was raised.

Scheme 14

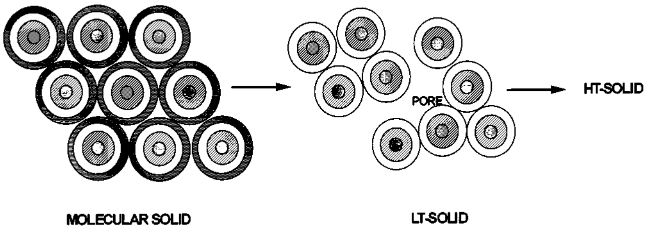


To say that only and all CO links are broken to reach the LT solids would be an oversimplification but it does appear that in the HT solids only the carbyne carbon remains in the amorphous product. This remaining carbon content is viewed as important in the same sense that main group elements are important in stabilizing amorphous metal alloys relative to crystallization.[88] This stability sustains the Co metal dispersion as well as the porous nature of the solid. However, there are limits and heating to 300°C and higher led to diffusion of the Co metal and the formation of α-Co crystallites detectable by X-ray diffraction.

The surface areas of the LT- and HT-solids ranged from 50 to 250 m^2/g which is well within usable range for catalytic purposes.[89] Heating to 300°C and higher led to loss of surface area which is consistent with the formation of the metal crystallites observed by X-ray diffraction. Transmission electron microscopy of cast thin films of the precursor, annealed to various temperatures, confirmed the porous nature of the solid implied by the density and surface area measurements. Electron diffraction of films heated to 300°C and higher showed cobalt crystallites of average size 100 Å. In the X-ray photoelectron spectroscopic experiments, the shift to lower binding energy on formation of the LT-, HT-solids is consistent with conversion of cobalt carbonyl fragments to cobalt metal and reveals that both the LT- and HT-solids have cobalt metal on exposed surfaces.

A model for the chemical conversion of the molecular cluster metal carboxylates into the two solids based on these data is shown in Scheme 15. Loss of the external CO ligands reduces the size of the cluster assemblies which are still supported by internal core−cluster carboxylate bonds. Formation of inter-assembly metal−metal bonds follows thereby opening channels and generating an amorphous, high surface area, porous solid. Further heating leads to the destruction of the internal metal carboxylate bonding and the formation of larger metal aggregates of indeterminate structure, albeit with retention of significant surface area for the solid as a whole. These are the two meta-stable, amorphous, high surface area solids that were tested as catalysts.

Scheme 15



In order to establish the level of catalytic activity as well as to compare catalysts prepared from the different types of cluster metal carboxylates under a variety of conditions, the hydrogenation of 1,3-butadiene was used as a benchmark reaction.[90][74][89] This reaction was selected because the molecule is easily hydrogenated and high conversions can be achieved with small amounts of catalysts and relatively low temperatures. In addition, the reaction has been thoroughly studied with other transition and noble metal catalysts and a substantial literature exists for comparative purposes. In the event, the LT- and HT-solids tested were sufficiently active catalysts so that a gas phase, steady state flow system could be used for evaluation. This permitted a wide range of conditions to be expeditiously explored.

The activities and selectivities of the LT-solids produced from a variety cluster metal carboxylates showed similar, if not identical, behaviors. 1-Butene is the main product at low conversions whereas butane becomes the main product at high conversions.. On the other hand, the activities and selectivities of the HT-solids are markedly different from those of the LT-solids as well different among themselves. Core dependence appears to be important only for the HT-solids consistent with the model of solid formation summarized above. Importantly, these catalysts were stable (4−7 days on stream) and reproducible.

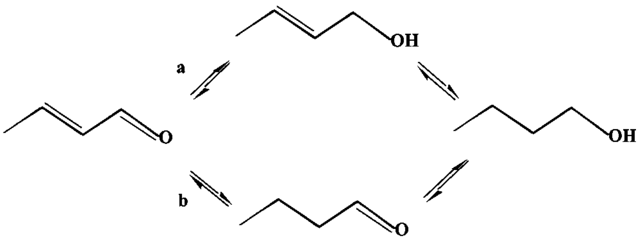
The catalytic behavior of solids produced from the tricobalt cluster alone and of conventional supported cobalt metal under identical conditions is very different from that of catalysts derived from the cluster arrays. This confirms that the catalytic behavior observed for the activated cluster assemblies is due in large part to properties derived from the cluster metal carboxylate precursors. Some carry over of structure from precursor to catalyst must take place in that octahedral and square planar cluster assemblies, both possessing cobalt cores, yield significantly different catalytic behaviors. The latter demonstrates structural as opposed to compositional control of activity and selectivity.

These studies suggest that carbonyl loss (outer cluster decomposition) before carboxylate ligand disruption is important and that core properties can modulate catalytic behavior but only for the HT-solids in which the cores are exposed. Chemical tests of these deductions were carried out. First, cluster metal carboxylates were synthesized using the very thermally stable 1,2-$C_2B_{10}H_{12}$ carborane as the external cluster. Thermolysis of these carboxylates resulted initially in the loss of CO_2 plus some free, intact carborane. This was followed by complex chemistry. The solids produced were of little use and clearly in this case the loss of the core-cluster bonding resulted in total collapse of the cluster assembly.[91] Second, a cluster lead carboxylate with an infinite chain-like structure was used as a catalyst precursor.[71] The LT-solid was an active catalyst with properties similar to any of the catalysts derived from tricobalt cluster metal carboxylates. However, the HT-solid was totally inactive and X-ray photoelectron spectroscopy showed the surface to be severely poisoned by lead metal. These observations are consistent with the model in which the LT-solid possesses an intact assembly core and the HT-solid a disrupted core.

Selective Hydrogenation of Crotonaldehyde

The selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols (path a, Scheme 16) is a challenging reaction for heterogeneous catalysis as C=C double bond reduction is thermodynamically favored at high temperatures and typical metal hydrogenation catalysts also favor C=C double bond reduction over the C=O double bond, i.e., path b in Scheme 16. For this reason a useful catalyst must have high activity at low temperatures as well as high selectivity for path a. As the catalytic solids derived from the cluster metal carboxylates expressed unusual activities and selectivity for the hydrogenation of butadiene, we were drawn to an investigation of the catalytic reduction of crotonaldehyde (2-butenal).[92][93][94]

Scheme 16



The catalyst activities and 2-butenol selectivities observed were good and depended on the type of metals in the core as well as the precursor structure. For cobalt core metals the highest yield (28%) of 2-butenol resulted from the HT-solid produced from an octahedral cobalt cluster assembly with a cobalt core whereas the highest selectivity (100%) resulted from the HT-solid produced from a square planar cluster assembly also with a cobalt core. The activity and regioselectivity of the former material give the highest yield for a heterogeneously catalyzed reaction reported in the open literature. Results of kinetic studies show that this high regioselectivity resides in increased barrier heights for the various reaction steps. The simultaneous high activity requires the active participation of a large fraction of sites on the catalyst. That is, these solids show the behavior expected for catalysts that possess sites having a narrow activity distribution. This, in turn, is in accord with the model of these solids drawn from the spectroscopic as well as chemical studies.

The activities and selectivities of these catalysts are constant for periods of times that are several fold higher than those reported with supported catalysts and the materials do not show deactivation up to 50 hours of time on stream. Catalysts derived from tricobalt cluster assemblies with heterometal cores give uniformly poorer results relative to the homometallic systems of the same structure type. Solids produced from the tricobalt cluster alone were less active with poor selectivity.

Summary

We have demonstrated the coordination of cluster-substituted carboxylates to cationic metals as a successful strategy for the assembly of large transition metal cluster arrays. In terms of the coordination modes of the cluster carboxylate ligand, most exhibited by organic metal carboxylates have been observed. In terms of core structure, rhombic, tetrahedral, cubane-like, ladder-like, double cubane-like, as well as chain-like geometries have been generated. In terms of the spatial arrangement of the clusters, triangular, square, triangular bipyramidal, octahedral, chair-like, and column-like types have been observed. The observed compounds reveal the unique properties of the functionlized clusters as ligands over convertional organic carboxylates. These studies also show that the catalytic properties of solids produced from molecular cluster metal carboxylates depend on the molecular composition and structure of the cluster assembly. Further, the detailed catalytic behavior suggests that the high activities and unusual selectivities observed are derived from a high number of uniform active sites. Both conclusions are consistent with catalytic solids that “remember” their molecular origins. Although no practical catalyst has been uncovered for the selective crotonaldehyde reduction, only small changes in relative reaction barrier heights are needed to do so. In turn this suggests that relatively minor changes in precursor structure and composition are required. It remains to experimentally define these changes. This requires the continued development synthetic cluster chemistry in order to produce additional useful cluster ligands.

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