Heteronuclear Cluster Compounds

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Phil. Trans. R. Soc. Lond. A 1982 **308**, 17-26
doi: 10.1098/rsta.1982.0142

Phil. Trans. R. Soc. Lond. A **308**, 17–26 (1982) [17]
Printed in Great Britain

Heteronuclear cluster compounds

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Several designed syntheses have been developed for heteronuclear organometallic cluster compounds. They involve step-by-step construction, fragment combination and metal exchange. The compounds obtained permit the study of the physical phenomena of electron distribution and chirality in the cluster frameworks. Prominent chemical phenomena are the weakness of some metal–metal bonds, the unsaturated nature of some clusters, and polarity due to heteronuclearity. They permit the study of basic cluster reactions like the unfolding of the clusters with nucleophiles, the addition of substrates without gross changes in the cluster framework and without ligand substitution, the capping of clusters by suitable ligands, and the reaction of different substrates at different locations in the cluster core.

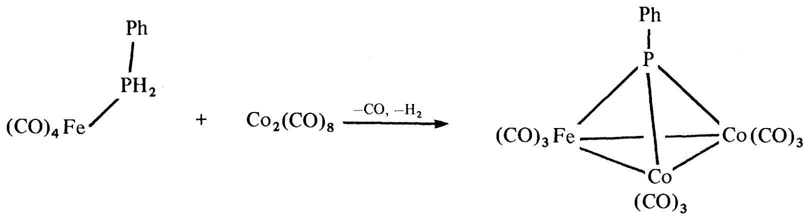
INTRODUCTION

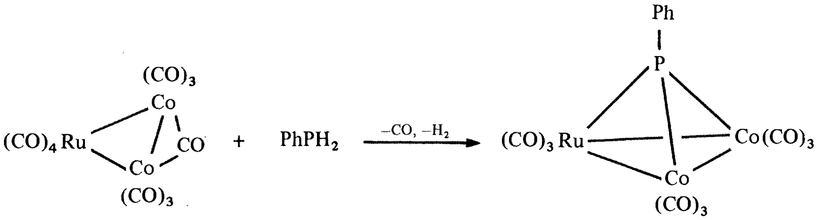
Organo-transition metal cluster chemistry has reached a point where systematization has begun to evolve. This is especially obvious for heteronuclear cluster compounds. Owing to the availability of suitable reagents and the polarity of hetero-metal–metal bonds their synthesis can be designed in several ways and their reactivity predicted, at least in part.

Our interest in cluster synthesis and reactivity is one part of our interest in the properties of metal–metal bonds (Vahrenkamp 1978). Therefore basic metal cluster reactions, as we understand them, involve the formation and rupture of metal–metal bonds, thereby changing the shape of the cluster core. In most cases we have performed the corresponding chemical reactions on heteronuclear clusters. This paper summarizes our recent results in this area.

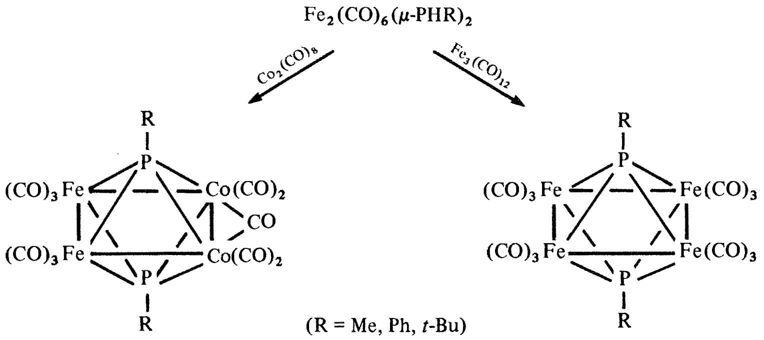
CLUSTER SYNTHESIS

The number of specifically designed cluster syntheses, i.e. those where each step in the cluster build-up is an identifiable product, is still very small. This results from the fact that each change in the metal atom framework is accompanied by the breaking and reforming of at least two or three bonds, processes that can even less easily be controlled than those involved in the construction of carbon-containing cage compounds. In some cases the introduction of multiply bridging main group elements as constituents of the cluster core improves the situation by holding the metal atoms together during the critical reactions. We have made use of this clamp effect in the synthesis and stabilization of compounds with two to four connected metal atoms. Two simple reactions exemplify this:



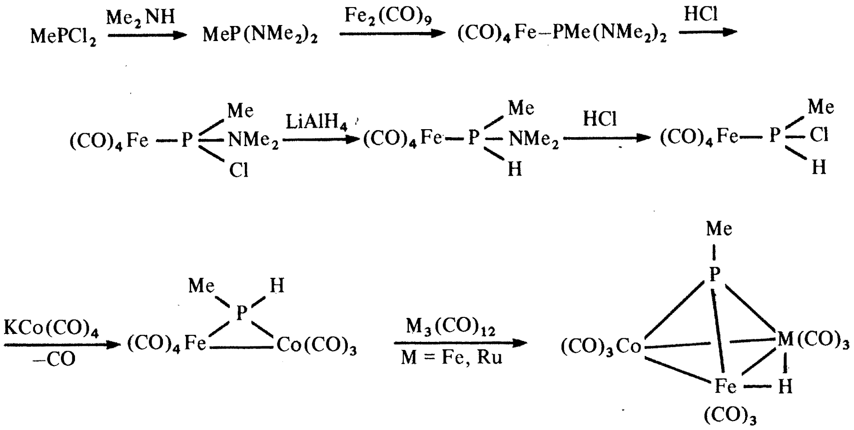


In both cases rather labile starting compounds are converted to rather inert reaction products. The expansion reaction employed in both cases is the metathetical reaction between main-group element hydride functions and metal carbonyl units leading to CO and H_2 evolution and main-group–transition-metal bond formation. This reaction seems to have been first performed by Harrod & Chalk (1965) between Si–H compounds and cobalt carbonyl but has only recently come to the attention of cluster chemists. We could show that it is also applicable for cluster construction from dinuclear starting materials:



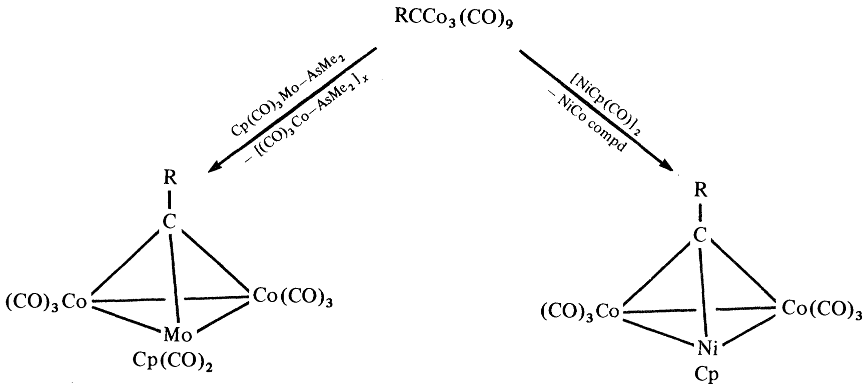
(R = Me, Ph, *t*-Bu)

And a real stepwise cluster synthesis with the P–H reaction as a crucial step is the following:

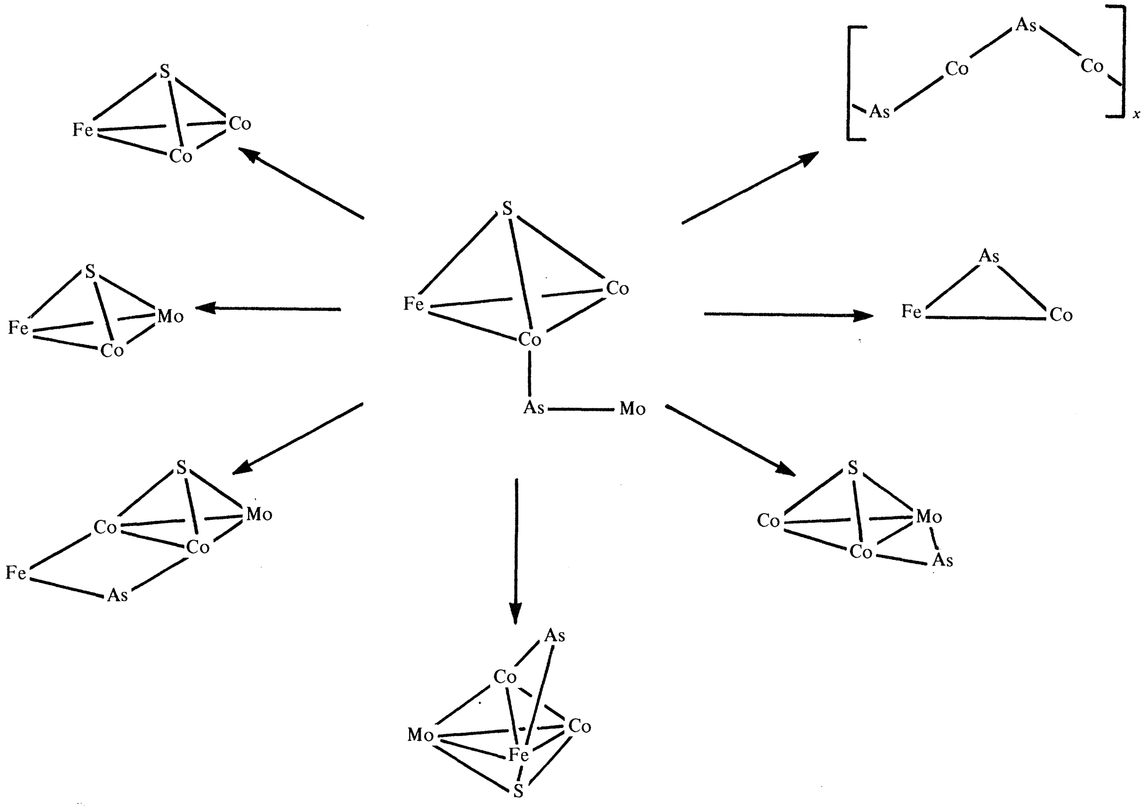


By variations of this procedure phosphinidene bridged clusters with one, two, or three different metal atoms can be obtained.

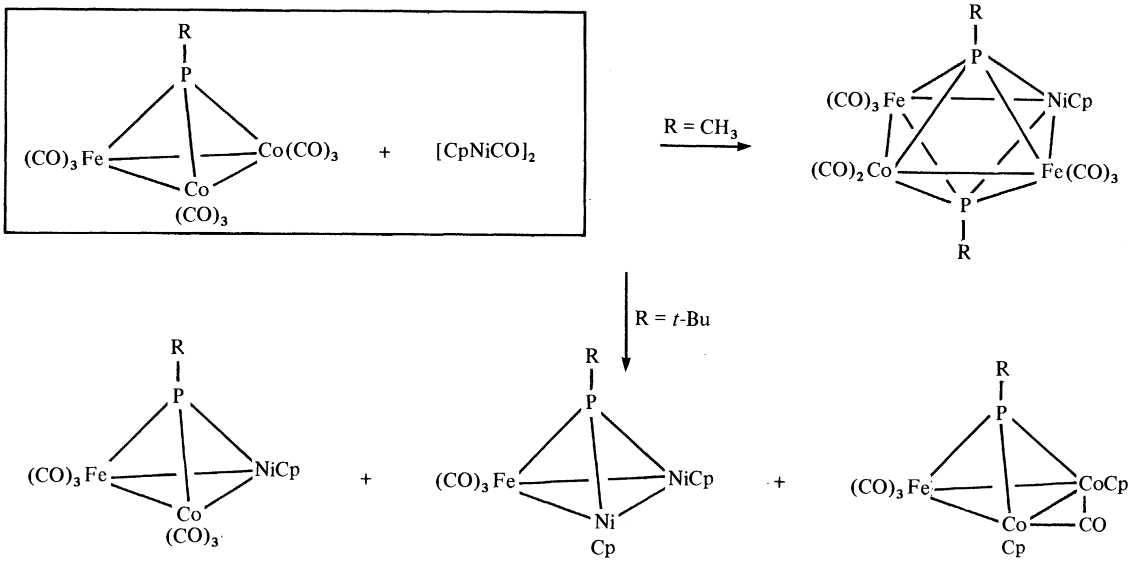
A growing number of mixed metal clusters is being prepared by using clusters as starting materials (Gladfelter & Geoffroy 1980). In most cases the reactions involve cluster expansion. Our contribution in this area is the metal-exchange reaction. It is based on the observation that arsenic-bridged dinuclear complexes (Müller & Vahrenkamp 1977) and simple dinuclear metal carbonyls (Madach & Vahrenkamp 1980) undergo fragmentation and equilibration reactions that can be explained by the intermediate formation of mononuclear metal carbonyl units. Applied to clusters this has allowed the exchange of cobalt for chromium, molybdenum, tungsten, manganese, iron, ruthenium and nickel in an extended range of tetrahedral cluster frameworks. These are composed of tetrametal units or trimetal units with μ_3 bridging CR, SiR, GeR, PR, AsR and S ligands. Among the first systems used for this reaction were the methylidyne tricobalt enneacarbonyls, e.g.:



It has turned out that these reactions must be mechanistically quite complex. Carefully controlled conditions are necessary to obtain good yields of the desired products. Otherwise a considerable range of alternative compounds can be formed whose structural features are indicated for two examples in schemes 1 and 2.



Scheme 1



SCHEME 2

These alternative reactions support the view that fragmentation is a major characteristic of such first-row transition metal clusters and that the reaction conditions have to limit the fragmentation to the desired amount. However, the large number of new clusters obtained in a predictable way justifies calling this procedure a directed synthesis.

SPECTRAL CLUSTER PROPERTIES RELATED TO THE METAL FRAMEWORK

The accumulation of electrons in the heavy-atom core of transition metal clusters gives rise to electronic phenomena that exceed those of simpler inorganic or organic compounds. Spectral measurements give evidence for this. With the advent of a better theoretical understanding of cluster bonding they should provide a quantitative basis for bonding discussions.

The e.s.r. spectrum of a paramagnetic cluster has been used for a classical qualitative MO description: from an analysis of the 22 line e.s.r. signal of $SCo_3(CO)_9$ Strouse & Dahl (1969) derived the delocalized and metal–metal antibonding nature of the unpaired electron in this cluster. In cooperation with B. H. Robinson, Dunedin, New Zealand, we have extended such e.s.r. measurements to the anions of tetrahedral clusters with one, two and three cobalt atoms. In each case the hyperfine coupling of the electron spin with the cobalt nuclear spin is of the same magnitude indicating comparable electron delocalization, and in each case the fourth framework atom like phosphorus does not show up in the hyperfine structure, indicating the limitation of the h.o.m.o. to the metal region. Figure 1 shows three representative spectra.

Another indication of electron accumulation is given by the o.r.d. spectra of clusters with chiral frameworks. Such clusters were first obtained by us by the aforementioned metal exchange reactions and separated into their enantiomers by substitution with chiral phosphine ligands. As figure 2 shows for SFeCoMo clusters, the o.r.d. spectra of the enantiomers are mirror-symmetric. Those of the diastereoisomers are not, owing to the same configuration of the phosphine in both compounds. The dominance of the metal-containing framework in determining the optical rotation is obvious in several ways: the phosphine part of the diastereo-

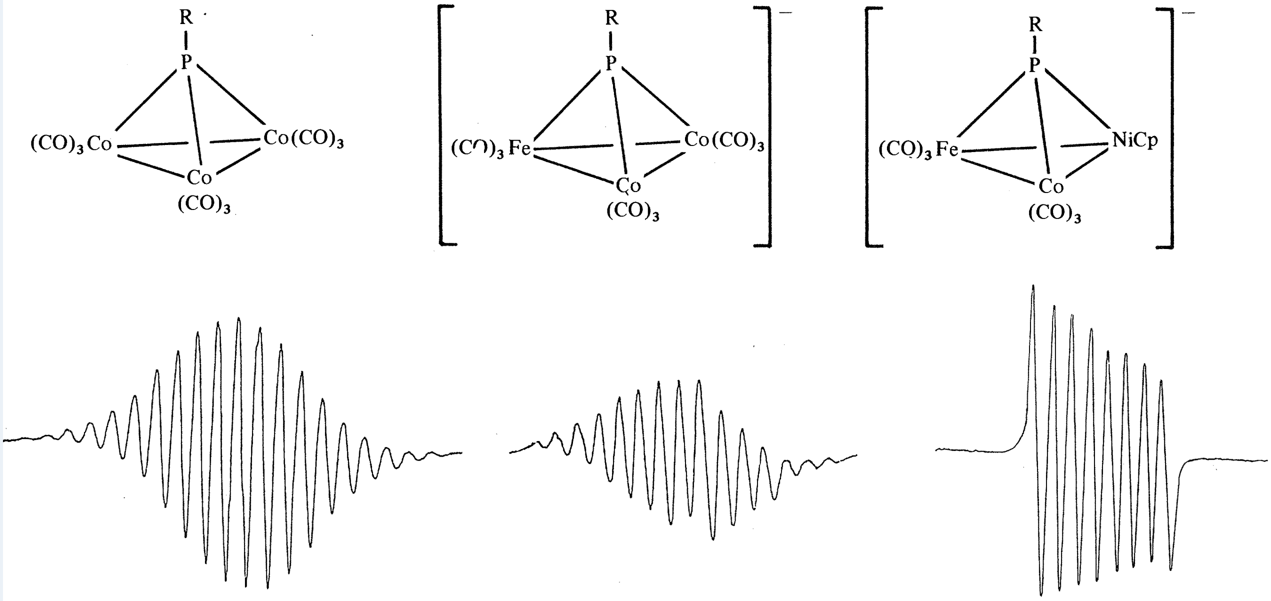


FIGURE 1. E.s.r. spectra of phosphinidene-bridged isoelectronic paramagnetic clusters with three, two, and one cobalt atoms ($I = \frac{7}{2}$), each with one electron in excess of a closed-shell electronic configuration. R = *t*-Bu, solvent THF, anions prepared electrolytically.

isomers only slightly disturbs the mirror symmetry of their o.r.d. spectra, the appearance of the o.r.d. spectra of the diastereoisomers and of the enantiomers is similar, and moreover the molar rotations are in the order of 10000–60000°. Similar cluster types show similar o.r.d. curves, and it is hoped that this can be used to correlate the absolute configurations of such clusters, one of which has been determined.

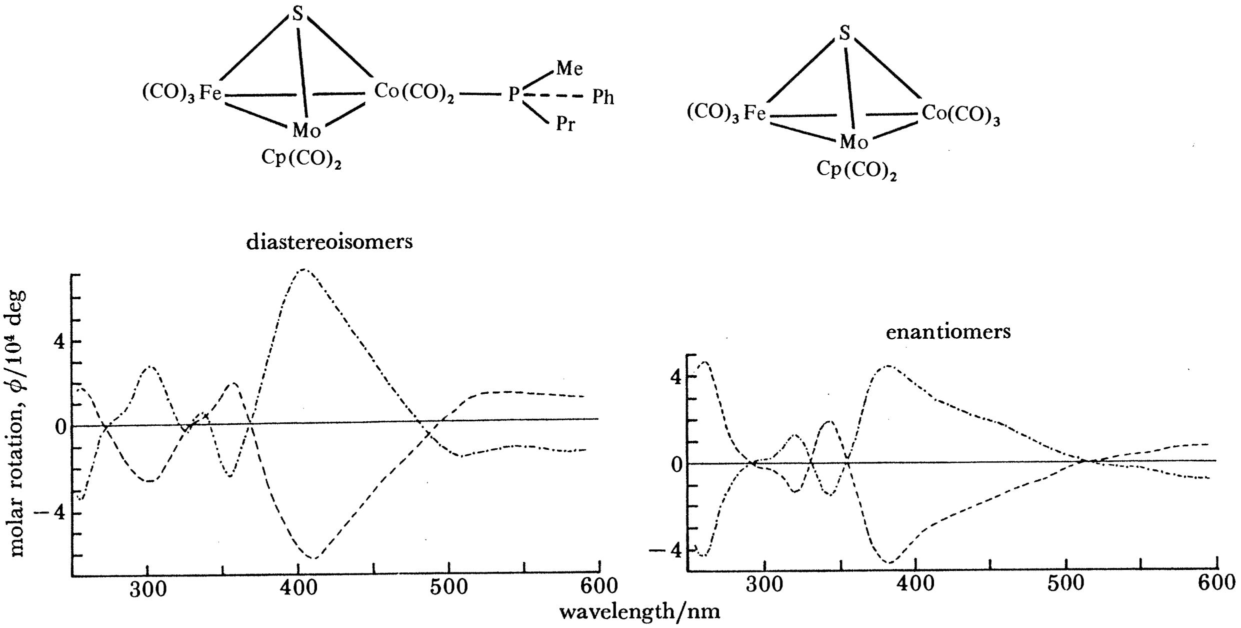
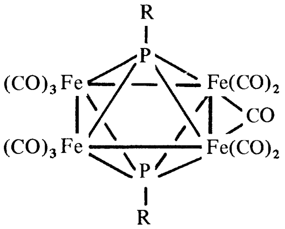
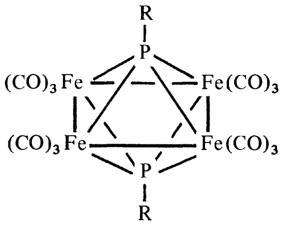


FIGURE 2. Optical rotation of the (+) and (−) isomers of diastereomeric and enantiomeric pairs of SFeCoMo clusters.

In organic chemistry, electron delocalization in ring compounds is indicated by unusual ^{1}H-n.m.r. chemical shifts. Effects of this kind have not yet been observed in metal-containing rings. We may have found a related phenomenon for the two following cluster types differing only by one CO ligand (R = Me, *t*-Bu, *p*-Tol):





Of these the $Fe_4(CO)_{12}(PR)_2$ compounds are saturated according to the 18-electron rule while the $Fe_4(CO)_{11}(PR)_2$ compounds lack two electrons. The bond lengths of the latter do not permit the location of a Fe–Fe double bond unambiguously, which means that they may be considered as Fe_4 rings with two delocalized π-electrons, i.e. members of the Hückel $4n+2$ series. Support for this comes from the n.m.r. spectra (see table 1). The PR groups located above the centres of the Fe_4 rings should feel a diamagnetic effect if there is a benzene-type ring current in the $Fe_4(CO)_{11}(PR)_2$ clusters. There is actually a high field shift for the methyl resonances in going from the saturated $(CO)_{12}$ clusters to the unsaturated $(CO)_{11}$ clusters. This shift becomes stronger the closer the observed methyl groups are to the Fe_4 ring.

TABLE 1. ^{1}H-N.M.R. DATA (MILLIONTHS, $CDCl_3$, INT. TMS) FOR THE METHYL GROUPS OF THE PR LIGANDS IN Fe_4 CLUSTERS

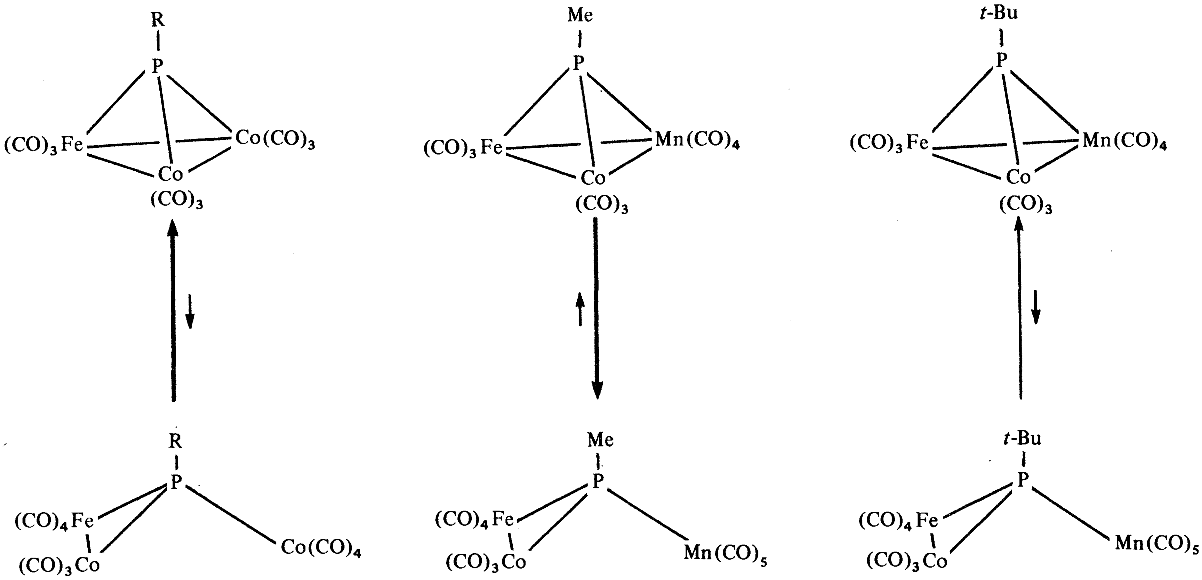
R	$Fe_4(CO)_{12}(PR)_2$	$Fe_4(CO)_{11}(PR)_2$
p-Tol	2.52	2.20
t-Bu	2.06	0.70
Me	3.34	0.98

It may be too early to call these n.m.r. shifts a ring-current phenomenon. But irrespective of this it cannot be overlooked that the metal atom accumulations do, as might have been predicted, give rise to enhanced n.m.r. effects.

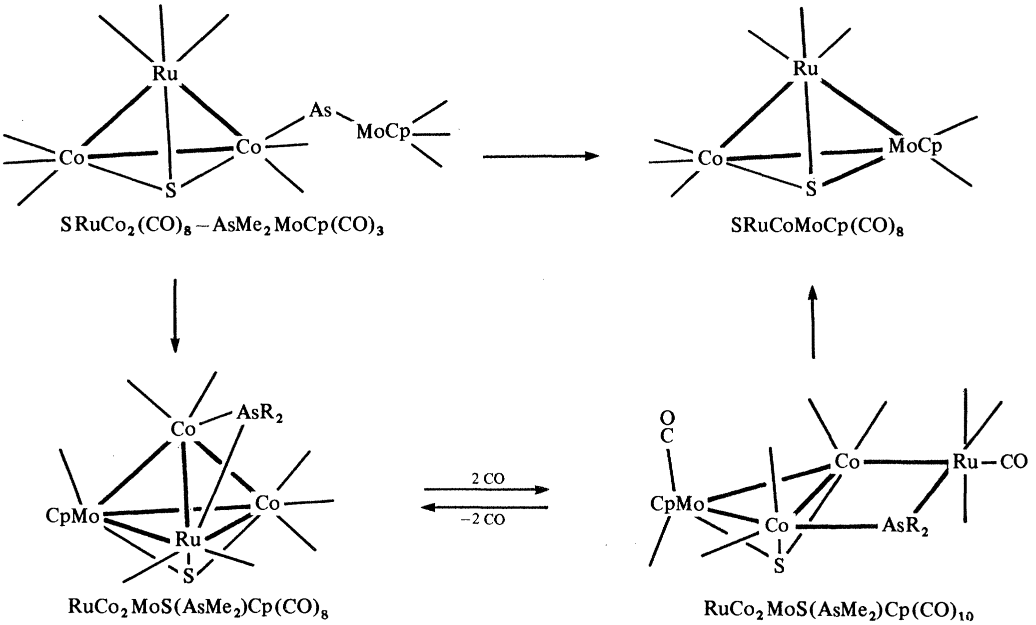
CLUSTER REACTIVITY

Owing to the potential application of cluster compounds in catalysis, many reactions of organic substrates with metal clusters have been investigated. From an inorganic viewpoint most of these reactions are variations of the cluster ligand sphere. Comparatively little work has been performed on the basic cluster reactions, i.e. those that change the geometry or the bonding in the cluster core. Heteronuclear clusters lend themselves to such reactions owing to their lower symmetry and their polar metal–metal bonds. We have found examples for several types of basic cluster reactions.

A very common reaction of first-row transition metal clusters is destruction by strong nucleophiles causing the rupture of all metal–metal bonds. The reason for this is that for light transition elements metal–ligand bonding liberates more energy than metal–metal bonding. For application-oriented considerations it means that the rupture of metal–metal bonds can provide coordination sites for the activation of substrates. If main-group elements bridge the cluster metal atoms the identity of the cluster ought not get lost during such an opening of its framework. We (Langenbach & Vahrenkamp 1979) have investigated this in detail for dinuclear arsenic-bridged complexes and found that, even with the simplest nucleophile, CO, reversible opening and closing of the metal–metal bonds are possible. Scheme 3 shows corresponding interconversions for μ_3-PR bridged clusters upon addition or removal of CO. It is obvious that the steric requirements of the metal–ligand units as well as of the PR ligands influence the formation of the preferred compounds. The situation in scheme 4 is somewhat more complicated. Besides demonstrating the reversible unfolding of a tetranuclear cluster it also shows its formation by aggregation and its degradation by Co–As fragment elimination, which all seem to be steps in the above mentioned metal exchange reaction.



SCHEME 3



SCHEME 4

Another basic cluster reaction is the addition of nucleophiles to unsaturated clusters without gross changes in the cluster framework and without ligand substitution. We found an entry into the field of unsaturated clusters from the following isoelectronic series of $(\mu_4\text{-PR})_2M_4$ clusters of which the Fe_4 and Fe_2Co_2 compounds have been mentioned above, and of which the Co_4 compound was known before (Ryan *et al.* 1980):

$$(RP)_2Co_4(CO)_{10},\quad (RP)_2Fe_2Co_2(CO)_{11},\quad (RP)_2Fe_4(CO)_{12}.$$

In these clusters steric crowding is extensive in the $Fe_4(CO)_{12}$ compound, noticeable in the $Fe_2Co_2(CO)_{11}$ compound and absent in the $Co_4(CO)_{10}$ compound. Relief of the crowding would involve a loss of CO ligands, leading to unsaturation, as in the following clusters:

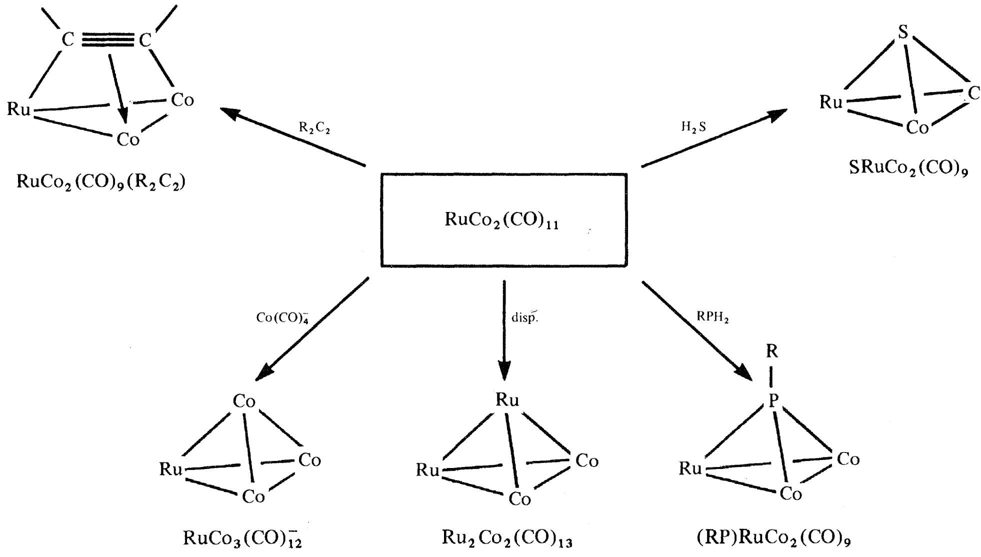
$$(RP)_2Fe_2Co_2(CO)_{10},\quad (RP)_2Fe_4(CO)_{11}.$$

Our experiments indicate that the $Fe_2Co_2(CO)_{10}$ compound is very difficult to obtain, whereas the $Fe_4(CO)_{11}$ compound forms easily and quantitatively in vacuum. The unsaturated nature of the latter shows up in the ease of formation of the $Fe_4(CO)_{12}$ compound with CO and the fast addition of other donor ligands. Subsequently another CO ligand can be eliminated and another donor ligand added. For instance, with $L = P(OMe)_3$ the following sequence has been established:

$$(RP)_2Fe_4(CO)_{11} \longrightarrow (RP)_2Fe_4(CO)_{11}L \longrightarrow (RP)_2Fe_4(CO)_{10}L \longrightarrow (RP)_2Fe_4(CO)_{10}L_2.$$

Rather than steric crowding as against unsaturation, electron counting may be invoked to explain the ready interconversions of these Fe_4 clusters: the saturated clusters have the correct electron count according to the 18-electron rule whereas the unsaturated clusters have the correct electron count for *closo* octahedral systems according to Wade's rules.

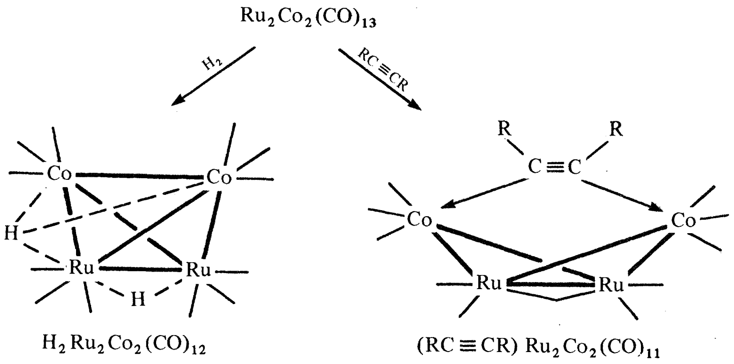
The two basic cluster reactions described so far provided coordination sites for binding of ligands to one metal atom each. The unique possibilities of clusters, however, rest on their ability to attach one substrate to several metal atoms. Normally clusters have faces of three metal atoms, which may be capped by units with μ_3 bonding ability, i.e. those isolobal with the CH fragment. The basic reaction is then the capping of an M_3 unit to form a tetrahedral framework. We have prepared the cluster $RuCo_2(CO)_{11}$, whose electrophilic nature allows



SCHEME 5

capping reactions under very mild conditions. Scheme 5 summarizes the results. The reagents used for capping range from simple four-electron ligands (RC≡CR) over a series of H_2E compounds (RPH_2, $RAsH_2$, SH_2, SeH_2) and metal carbonyl anions to simple metal carbonyl fragments like $Ru(CO)_n$ resulting from partial decomposition of the starting cluster. None of these reactions requires heating, and most of them give good yields. Capping undoubtedly is an elemental step in cluster build-up reactions, but the number of cases where simple capping products could be isolated is still relatively small.

Finally, multimetal reactivity should be considered. One of the advantages of heteronuclear clusters is their ability to activate different substrates at different metal atoms. This gives rise to the hope of the specific catalysis of complicated organic reactions. Again the number of examples to underline this is quite small. During our studies of ruthenium–cobalt clusters we found a partial approach to a result of this type. The two reactions are:



The affinity of cobalt carbonyl compounds for acetylenes has long been known, and butterfly-shaped (RC≡CR) $Co_4(CO)_{10}$ was prepared more than 20 years ago (Hübel *et al.* 1959). Conversely, ruthenium carbonyls react easily with hydrogen (Knox *et al.* 1975). Both properties are combined in $Ru_2Co_2(CO)_{13}$: acetylenes insert between the cobalt atoms, and hydrogen is added at the ruthenium atoms. Both reactions require mild conditions and produce essentially one compound. The continuation of the idea, however, is not simple: either the acetylene cluster and hydrogen or the hydrogen cluster and acetylenes react to produce mixtures that have not been separated so far.

The basic cluster reactions here, which also include the metal-exchange reaction, are just a beginning. The immense number of clusters synthesized so far offers many more possibilities, which have yet to be realized.

This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. It was performed by a team of hard-working graduate students: E. Keller, H. J. Langenbach, E. Röttinger, T. Madach, H. Beurich, F. Richter, U. Honrath, M. Müller, E. Roland, K. Fischer, P. Gusbeth and R. Blumhofer. The cooperation with Professor B. H. Robinson, Dunedin, New Zealand, and his research group is gratefully acknowledged.

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