

New interconversions in the ligand sphere of clusters

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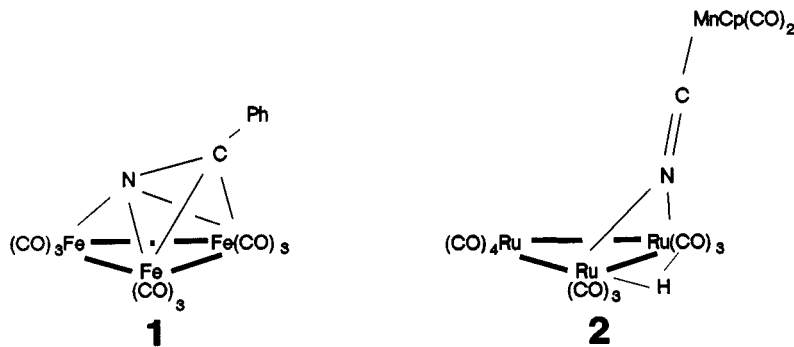
Abstract - Synthesis of organometallic cluster compounds has reached a stage where clusters of a desired composition can be made available for reactivity studies. Multiply bonded C-C, C-N, and N-N containing substrates can be attached in the μ_2 or μ_3 bonding mode. In the cluster derivatives so obtained the substrate as well as the metal part of the cluster may be labilized. As a consequence, various kinds of rearrangements are observed. After rearrangement, new kinds of substrates can be formed by addition of carbon nucleophiles or alkynes. The cluster-induced cleavage of C-C or N-N multiple bonds, the mechanism of which has been investigated, can produce new reactive cluster compounds which lend themselves to further reactivity studies.

INTRODUCTION

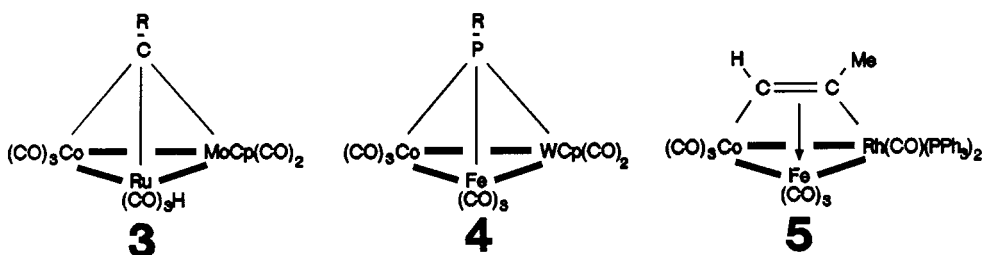
In the context of "New Chemistry Induced by Metal Coordination" organometallic cluster compounds offer a further dimension as compared to mononuclear complexes. This is the possibility of multicenter attachment and multicenter activation as well as the activation of different substrates at different metal sites in the cluster (ref.1). The reactivity consequences resulting from this have so far been investigated for quite a number of compounds, predominantly derived from the $M_3(CO)_12$ clusters of iron, ruthenium, and osmium (ref. 2, 3). In recent years the synthetic chemistry of cluster compounds has been advanced significantly by many research groups, such that now systematic ways to heterometallic clusters and controlled methods to attach labile substrates are available. On this basis it should now be possible to obtain the right combinations of metals and substrates for novel interconversions in the ligand sphere. This article based on thesis and postdoctoral work by E. Roland, W. Bernhardt, T. Jaeger, T. Albiez, H. Bantel, B. Oswald, R. Planalp, E. Wucherer, M. Tasi and Miss A. Powell summerizes our attempts to find systematic approaches in this field.

THE BASIS: CLUSTER CONSTRUCTION

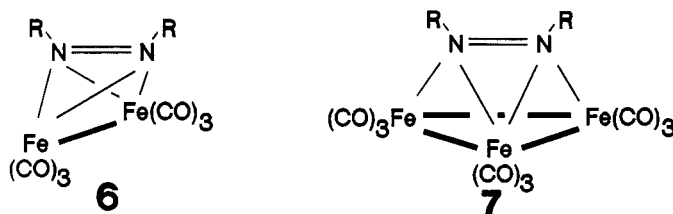
The simplest approach to making clusters with functional ligands, i.e. direct reaction between a simple cluster and a substrate, is still the most common one. If it leads to multicenter attachment, it can be called a capping reaction (ref. 1). We have found clusters that undergo capping under very mild conditions (ref. 1). Recently we could show that according to the electronic situation of the substrate the capping mode may change. With $C\equiv N$ containing substrates for instance, RCN produces the μ_3 -bridging cluster 1 while $[Cp(CO)_2Mn-CN]^-$ produces the μ_2 -bridging cluster 2.



After many years of investigations into the controlled use of organo-transition metal fragments as building blocks we now have a pool of reactive compounds which serve as fragment sources. These can either be used to replace other fragments from existing clusters (metal exchange, ref. 4). Thereby, for instance, the chiral functional clusters 3, 4, and 5 are accessible, some of which are optically active.



Alternatively, the fragments can be used to enlarge existing clusters (cluster buildup, ref. 1). Very suitable building blocks, originating from various sources, are $\text{Fe}(\text{CO})_3$, $\text{Ru}(\text{CO})_3$, $\text{RhCp}(\text{CO})$, and $\text{IrCp}(\text{CO})$. By assembling a cluster around a substrate like in the formation of 7 via 6 by using azoalkanes and $(\text{C}_8\text{H}_{14})_2\text{Fe}(\text{CO})_3$ they provide access to clusters which are not available by capping or metal exchange.

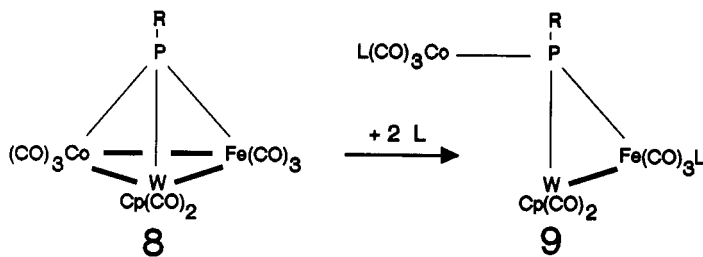


THE DRAWBACK: LABILITY

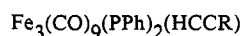
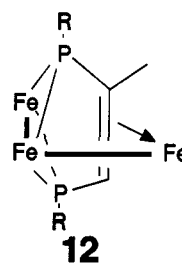
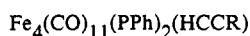
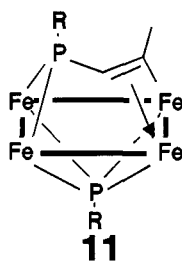
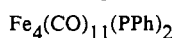
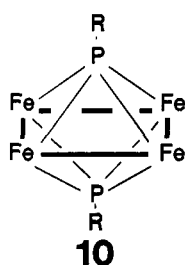
Not only with respect to the number of reactive sites do the clusters offer more possibilities than mononuclear compounds. This is also true for mobility and lability. Substrates can move around in the ligand sphere of clusters, and metal-metal bonds can be broken and re-formed. Viewed in a positive sense, this is one of the major aspects of cluster reactivity. But it also adds the risk of unwanted reactions and unnoticed multistep reactions to the substrate chemistry of clusters, especially those of the light transition elements.

We have experienced this risk in attempts to define a hierarchy of site reactivities for various metals in mixed metal clusters. Although the general sequence of substitution labilities seems to be $\text{Rh} > \text{Co} > \text{Ru} > \text{Fe}$, the product structures do not necessarily reflect this because the donor ligands can move to a different metal in the cluster after attachment to the most reactive one (ref. 5).

Whereas it is well-accepted that multicenter attachment to a cluster makes a substrate mobile and labile, it is only recently becoming obvious that this labilization can affect the cluster framework as well. We observed a pure case of framework mobility during studies of the optically active cluster 8 (ref. 6). 8 is racemized in the presence of donor substrates and of CO. Under mild conditions the intermediates 9 can be isolated which initially are optically active but then are inverted after which they can re-form the original cluster 8.



A typical case of mobility in the metal as well as in the ligand spheres is observed for the clusters **11** which are obtained by alkyne insertion into **10** (ref. 7). Not only is there an unusual insertion between two iron atoms and a phosphorus atom but also is there twofold lability: an equilibrium exists between two alkyne orientations, and oxidants or CO easily remove one iron carbonyl unit to form the clusters **12** with yet another mode of alkyne attachment.

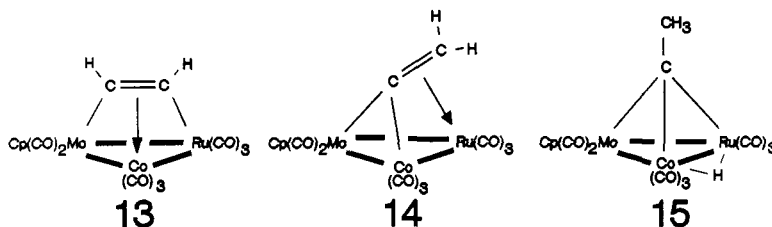


A similar case of fluxionality is observed for the cluster **21** (see below) with an azoalkane on one side and an alkyne on the other side of the metal triangle.

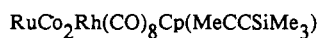
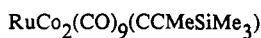
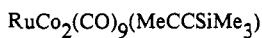
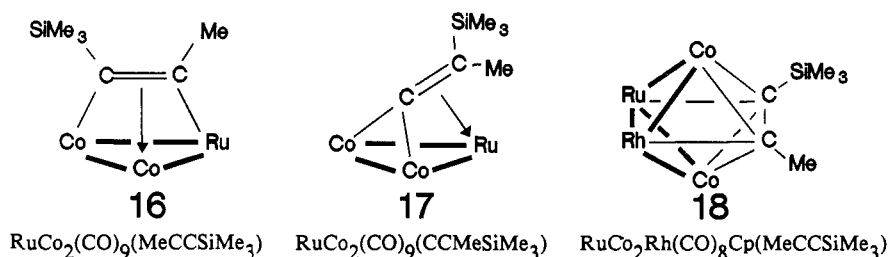
A USEFUL CASE OF TRIMETAL ACTIVATION: THE ALKYNE-VINYLDENE REARRANGEMENT

Alkynes are the most easily usable substrates for activation by clusters, and many studies have been done with internal alkynes (ref. 8). Until we found very mild conditions for cluster buildup and substrate capping reactions, terminal alkynes and acetylene itself could not as such be attached to clusters. One reason for this is the facile hydrogen migration converting the alkyne ligand to a vinylidene ligand (ref. 9). Since both alkyne and vinylidene are four electron ligands the composition of the cluster does not change during this rearrangement.

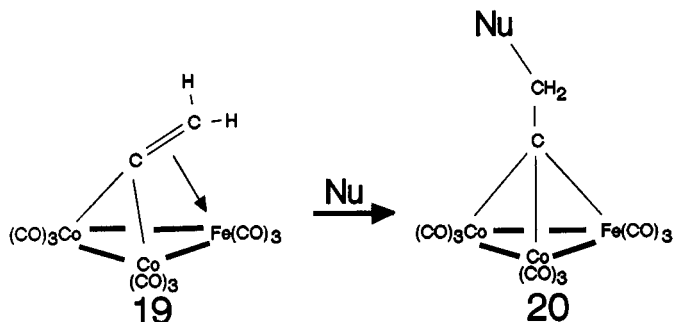
In trying to exploit the reactivity of the vinylidene ligand, we first found that on electron rich clusters it can be hydrogenated to the alkylidyne ligand, one hydrogen atom from H_2 ending up as a cluster-bound hydride ligand. Thereby a $\text{C}\equiv\text{C} \rightarrow \text{C}=\text{C} \rightarrow \text{C}-\text{C}$ sequence was realized on a cluster face, like in the reaction **13** \rightarrow **14** \rightarrow **15**. Of the three members in this series, **14** is the thermally most stable compound, and this seems to be generally true for the vinylidene bonding mode on trimetal clusters. Thus **15** is thermally reconverted to **14**, and of all the alkyne-vinylidene interconversions studied by us only one, namely **13** \rightarrow **14**, could be reversed.



Two further aspects of the alkyne-vinylidene rearrangement are noteworthy. Firstly, a silyl group of a silyl-substituted alkyne migrates just as easily as a hydrogen atom, cf. **16** \rightarrow **17**, thereby making a new functional group available on cluster bound vinylidene ligands. Secondly, the vinylidene bonding mode seems to be the less preferred one on tetrametal clusters: cluster expansion like in **17** \rightarrow **18** converts normal and silyl substituted vinylidene ligands back to alkyne ligands.



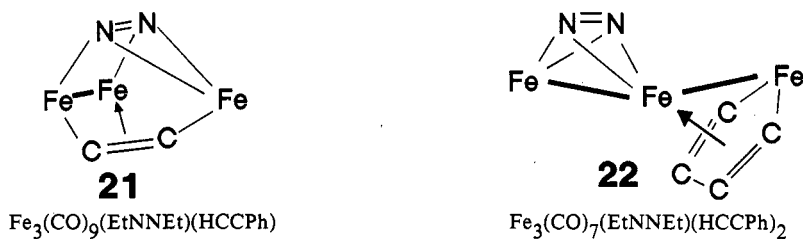
The hydrogenation of the vinylidene system can be called a H^- addition to the outer C atom followed by a H^+ addition to the metals. Justification for this comes from the isoelectronic relation between Seyferth's cluster-stabilized carbocation system $[Co_3(CO)_9(\mu_3-CCH_2)]^+$ (ref. 10) and our neutral cluster **19** (ref. 11). We have now realized the electrophilic nature of the CH_2 group in **19** by addition of soft bases to form the series of clusters **20**. The nucleophile Nu in **20** can be an alkyl substituted phosphine, a dialkyl sulphoxide, an anion like SCN^- or I^- , or the anion of malonic ester. Using phosphine ylides or the anion of cyano-acetic ester an equilibrium mixture results containing the C-C coupled product **20** and the two starting compounds.



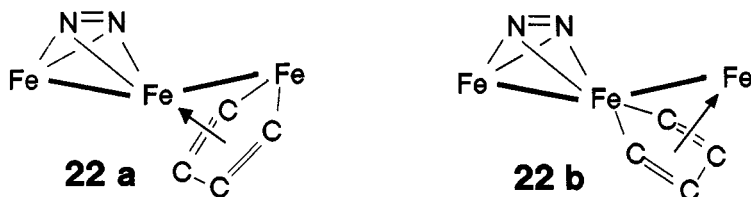
Thus, a new variant of C-C coupling has been found on the face of trinuclear clusters. It remains to be explored which types of functional groups can be incorporated in the new organic ligand and how it can be released from the cluster.

A CASE OF METAL-METAL AND LIGAND-LIGAND BONDING CHANGES: ALKYNE ADDITIONS TO $Fe_3(CO)_9(R_2N_2)$

The now readily available clusters **7** contain the azoalkane ligand which is quite reactive in the free state. It is therefore tempting to look for variations of its reactivity in the $\mu_3-\eta^2$ bonding mode. Alkynes again seemed appropriate as reagents to test for possible C-N couplings. Although we have not been able yet to perform such couplings we observed the stepwise incorporation of two equivalents of phenyl acetylene to form **21** and **22**.



In the formation of **21** from **7** the alkyne is added without loss of CO, which means opening of two metal-metal bonds. **21** picks up the second alkyne molecule very quickly. In the resulting formation of **22** CO is eliminated, one iron-iron bond is re-formed, and C-C coupling producing a ferracyclopentadiene system occurs. Furthermore, **22** forms the two interconvertible isomers **22a** and **22b** thereby providing yet another type of cluster rearrangement.

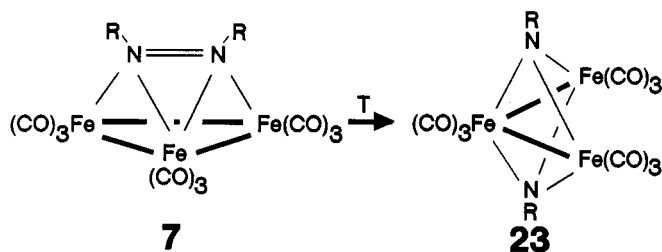


It seems realistic to assume that other unsaturated substrates will give rise to further novel fragment combinations and molecular shapes starting from the rather symmetrical cluster **7**.

THE DRASTIC EFFECT OF MULTICENTER ATTACHMENT: C≡C AND N=N BOND CLEAVAGE

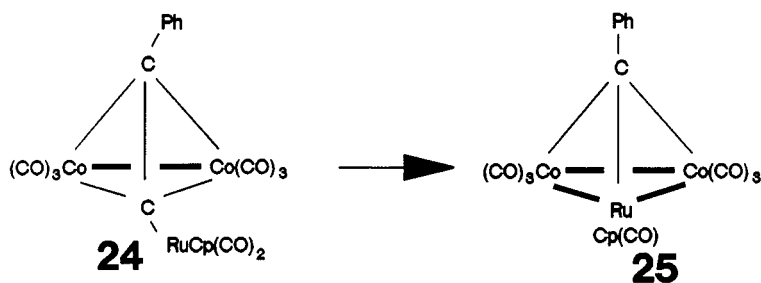
When unsaturated ligands are coordinated to transition metals in the π bonding mode, their multiple bond is lengthened. For alkynes it was observed that this lengthening is the more pronounced the more metal atoms are associated with the C-C triple bond (ref. 8). It is not unexpected, therefore, that η^2 -bound alkynes can be cleaved thermally to form two η^1 -bound alkylidyne ligands, a well-investigated case being the conversion of $\text{Cp}_3(\text{CO})\text{Rh}_3(\mu_3-\eta^2-\text{C}_2\text{R}_2)$ to $\text{Cp}_3\text{Rh}_3(\mu_3-\text{CR})_2$ (ref. 12).

Since it is easy to see isoelectronic relations between μ_3 -alkyne and μ_3 -azoalkane bridged clusters we were attracted to look for similar cases of N-N bond lengthening and cleavage. This was the main reason for developing a synthesis for **7** (see above), the isoelectronic equivalent of the easily accessible cluster $\text{FeCo}_2(\text{CO})_9(\mu_3-\eta^2-\text{C}_2\text{R}_2)$. Whereas the structure determinations of **6** (N-N = 137 pm) and **7** (N-N = 139 pm) did not indicate an increased weakening of the N-N bond upon multicenter coordination, the reactivity of **7** did: under rather mild conditions (70–100°) a nearly quantitative conversion **7** → **23** occurs in complete analogy to the alkyne splitting.



By finding a first order rate law and by making crossover experiments with mixtures of $\text{Fe}_3(\text{CO})_9(\text{N}_2\text{Et}_2)$ and $\text{Fe}_3(\text{CO})_9(\text{N}_2\text{Pr}_2)$ it was established that the N-N splitting is an intramolecular reaction. Since it is completely inhibited in a CO atmosphere and since it leads to total decomposition in a vacuum it can be concluded that CO is eliminated during the reaction which has to be added again afterwards since the reaction does not change the net composition of the compound. Taking into account all the metal-metal bond cleavage reactions we have observed before we also do not exclude a reaction sequence involving a fragmentation and recombination of the Fe_3 unit.

Alkyne cleavage on a trimetal cluster need not only lead to two alkylidyne ligands. Alternatively chemical reagents may attack the cluster bound alkyne with subsequent C-C bond splitting (refs. 2, 3, 8). We observed such a splitting during attempts at cluster construction using metallo-alkynes as ligands, like $\text{Cp}(\text{CO})_2\text{Ru}-\text{C}\equiv\text{CPh}$ as a ligand in **24**. Treatment of **24** with controlled amounts of pure oxygen converts it to the cluster **25** (ref. 13). In this reaction the α -carbon of the acetylide is oxidatively removed, one CO is eliminated, and the product **25** can be considered as the $\text{Co}_2(\text{CO})_6$ adduct of the remaining metalla-alkyne $\text{Cp}(\text{CO})\text{Ru}\equiv\text{CPh}$.



Mechanistic insight into this reaction was possible by selective ^{13}C labelling of the α -carbon position of **24** and subsequent EI mass spectrometry of **25**. The mass spectrum with its typical CO elimination sequence shows that seven ninths of the ^{13}C content of **24** are present in the form of CO ligands in **25**. This means that the carbonyl function produced by attaching an oxygen atom to the α -carbon atom of **24** becomes equivalent immediately to all CO ligands thereby making a total of nine CO's. Since **25** has seven CO's and the nine CO's of oxidized **24** are seemingly indistinguishable, the unique ^{13}C CO of them has a 2/9 chance of being eliminated leading to 7/9 of one ^{13}C being present on the average in **25**.

Both the N-N cleavage of **7** and the oxidative decarbonation of **24** provide arguments to the discussion of the cluster-surface analogy. In both cases multicenter attachment provides the conditioning of the reactive substrate, but in both cases the metal framework also has to be realigned in order to make the reaction go. This is in complete accordance with modern understanding of catalytic activity on surfaces: it is not the flat surface where the activity is located but the steps and faults, and the metal atom arrangement on the surface is not static but mobile itself and thereby adapting to the changing electronic environment due to the reacting substrate.

THE CHALLENGE: MAKING USE OF UNSYMMETRICAL CLUSTERS

Mixed metal clusters not only provide electronic variations to reactions already known from homometallic clusters. They also offer the possibility of hetero-site reactivity and steric control due to cluster asymmetry. Both possibilities have not yet been put to use satisfactorily. Our conflicting results in searching for a hierarchy of site reactivities (ref. 5) have been mentioned above. Other research groups have encountered similar problems. Likewise, the challenge to use chiral clusters for catalytic optical induction has not yet been met with success. Although we do have catalytically active chiral clusters (ref. 14) and we can observe completely diastereospecific olefin reactions on clusters (ref. 9, 15), the lability of the cluster framework under catalysis conditions (ref. 6) or the inaccessibility of the optically active clusters (ref. 15) has so far prevented the exploitation of this promising area of cluster research.

Irrespective of this, cluster chemistry will continue providing insights into metal-mediated reaction pathways which are novel and which cannot be elucidated so conclusively by any other chemical system.

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