

## Ligand sphere reactivity of organometallic clusters

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**Abstract** - Designed synthesis of clusters with face bridging functional organic ligands has paved the way for reactivity studies. Simple multiply bonded substrates of the C=C, C=N, and N=N type have been attached to three metal atoms in bonding modes isoelectronic to the  $\mu_3$ -alkyne, the  $\mu_3$ -vinylidene and the  $\mu_3$ -alkylidyne fashion. The interconversions of the bonding modes and the cleavage of the multiple bonds have been investigated. Starting from the simple substrates the combination of organic fragments can form new organic molecules. The interconversions of phosphorus ylides in the ligand sphere of clusters shed some light on possible pathways between C atoms and CO resp. CH<sub>2</sub> groups on metal surfaces. Likewise, intermediates which are highly reactive in mononuclear complexes can be trapped as stable derivatives of clusters.

### INTRODUCTION

It has been demonstrated by many research groups (ref. 1) that organometallic clusters bearing organic substrates in a multicenter bonded fashion can serve as models for surface chemistry in the structural sense as well as in terms of reactivity. The author's research group has contributed to this field in the past by working on new methods of cluster synthesis (ref. 2) and by focusing on basic metal cluster reactions, i. e. those that affect the metal atom core (ref. 3). More recently, we have turned to the study of reactivity patterns in the ligand sphere and to attempts at finding organic products resulting from multicenter substrate attachment (ref. 4). This report will present some generalizations and extensions of the latter subject produced by the enthusiastic cluster group at the University of Freiburg.

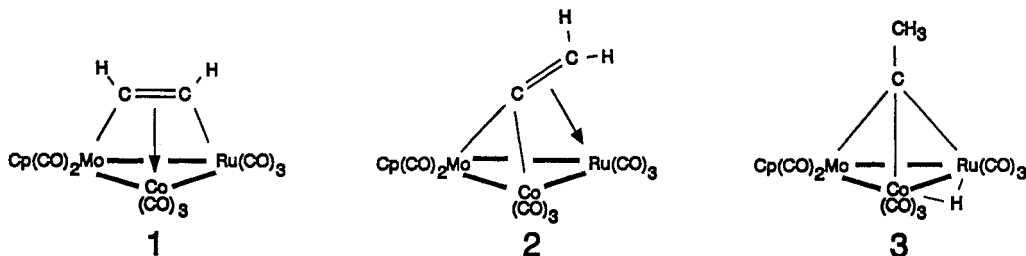
Despite the focus on ligand sphere reactivity, the basis of all our work is still the synthesis of reactive clusters. We have been working on the optimization of the three major approaches to substrate capped clusters, i. e. capping, cluster construction, and metal exchange. In the field of cluster capping we have been trying to use milder reaction conditions, for instance by resorting to highly reactive clusters like RuCo<sub>2</sub>(CO)<sub>11</sub> (ref. 5). In the area of cluster construction we have attempted to utilize mononuclear cluster building blocks in a more controlled fashion or with better reaction yields, for instance the Fe(CO)<sub>3</sub> and Ru(CO)<sub>3</sub> units (ref. 6). In the field of metal exchange we have tried to improve the metal replacement procedures (ref. 7), for instance to improve the availability of chiral clusters (ref. 8).

The synthetic cluster work has made it possible that most of the reactivity studies reported below could be performed on cluster compounds obtained by our own routes. This was so either because we could make the investigated cluster type more easily available or because we were able to introduce a very reactive substrate under conditions mild enough to prevent it from being degraded.

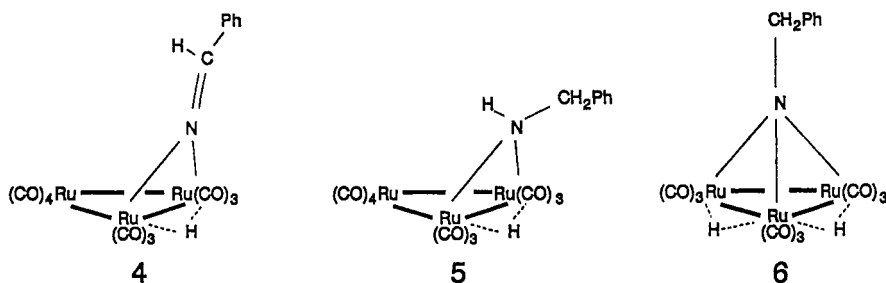
### ISOELECTRONIC C=C, C=N, AND N=N LIGANDS

One of the most common bonding types of small molecule substrates on trinuclear clusters is the  $\mu_3$ - $\eta^2$  type, exemplified by alkyne bridged clusters like 1. Isoelectronic ligands with C=N and N=N units can be formulated and

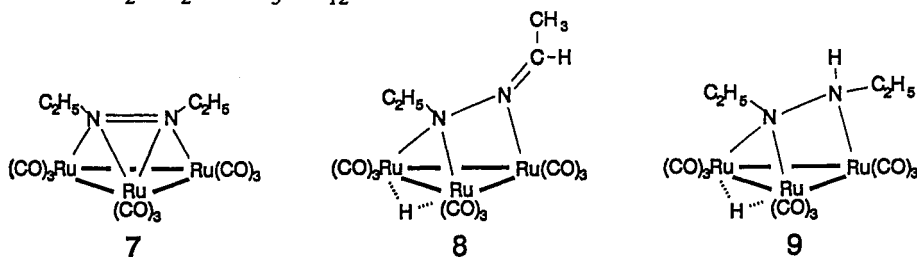
were first prepared for  $RC=NH$  by Kaesz (ref. 9) and for  $RN=NR$  by Kisch (ref. 10). We provided a different entry for the  $C=N$  case (ref. 11) and improved the synthesis of the  $N=N$  compounds (ref. 12). The bonding of the vinylidene ligand is also of the  $\mu_3-\eta^2$  type, though with a different orientation like in 2. Here, again, isoelectronic analogs exist for the  $C=N$  case with  $N=CHR$  ligands (ref. 9), whereas the analogous  $N=NHR$  ligand (hydrazinediyl) has not been attached to a cluster yet. The third alternative for bonding of a  $C_2$  unit to three metal atoms is the  $\mu_3-\eta^1$  type, like in the alkylidyne bridged cluster 3. Its analogs for the  $C-N$  case are the well-known  $\mu_3$ -nitrene bridged clusters, while again no such compound with a  $\mu_3-N-NH_2-R$  ligand is known.



In order to test the interconvertibility of the three bonding types, we investigated thermal rearrangements, hydrogenations, and dehydrogenations of the  $C=C$ ,  $C=N$ , and  $N=N$  ligated trinuclear clusters. For the  $C=C$  system one interconversion is definitely preferred. This is the alkyne  $\rightarrow$  vinylidene rearrangement as in  $1 \rightarrow 2$ . It occurs for all metal compositions upon mild heating, as long as terminal alkynes are present. In our hands it could be reverted in only one specific case, the treatment of 2 with  $NaMoCp(CO)_3$  as a base. In order to hydrogenate the vinylidene bridged clusters to the alkylidyne bridged clusters, again only a few very specific metal compositions of the clusters could be used, like in  $2 \rightarrow 3$ . On the other hand the dehydrogenation of type 3 clusters to type 2 clusters occurs readily upon heating, as long as a cluster-bound hydride ligand is present (ref. 13).



A sequence for the  $C=N$  system which is completely analogous to the 1 - 2 - 3 sequence and fully reversible has been provided by Kaesz (ref. 9) with  $CH_3CN$  as the starting point and  $H_2Fe_3(CO)_9(\mu_3-N-CH_2-CH_3)$  as the end point. We have investigated a similar system for  $Ru_3(CO)_{12}$  and benzonitrile. The first isolable product in this system is 4 which already contains a partially hydrogenated  $C-N$  ligand. Its thermal hydrogenation to 5 and the decarbonylation of 5 to 6 are reversible. Under very forcing conditions the nitrene ligand can be removed from the cluster yielding  $Ph-CH_2-NH_2$  and  $Ru_3(CO)_{12}$  (ref. 11).



The third  $M_3E_2$  cluster system to be interconverted was the  $Ru_3N_2$  cluster 7. It followed a different path of thermal rearrangement or hydrogenation. Thermal treatment resulted in  $C-H$  activation and formation of the hydrazone derivative 8. This could be hydrogenated to form the hydrazide derivative 9. So far it has not been possible to make these reactions reversible (ref. 14).

### MULTIPLE BOND CLEAVAGE ON CLUSTERS

The interconversions among the cluster triads 1-2-3, 4-5-6 and 7-8-9 represent one aspect of the cluster-surface analogy by demonstrating the ease of H atom mobility. Another aspect of this kind is the ease of multiple bond cleavage. Its occurrence for cluster-bound alkynes is well-documented, a classical case being the thermal rearrangement of  $\text{Cp}_3\text{Rh}_3(\text{CO})(\mu_3-\eta^2\text{-PhC}\equiv\text{CPh})$  to  $\text{Cp}_3\text{Rh}_3(\mu_3\text{-CPh})_2$  (ref. 15). The reversal of this reaction, the combination of two alkyldiyne ligands to form an alkyne ligand is less well known. It sometimes occurs in side reactions resulting from cluster fragmentation (ref. 16). Attempts at obtaining similar C-N cleavage reactions of cluster-bound nitriles or imides have not been successful yet. However, in one case the formation of a cluster-bound nitrile from an alkyldiyne ligand and the N atom of a diazoalkane has been observed, the product being  $\text{Fe}_3(\text{CO})_9(\mu_3-\eta^2\text{-MeCN})$  (ref. 17).

We have focused on the cleavage and formation of azo compounds in the ligand sphere of clusters, an area in which the groups of M. I. Bruce and W. L. Gladfelter are also active (refs. 18, 19). Using azoalkanes on the  $\text{Fe}_3$  cluster we observed the thermal transformation of  $\text{Fe}_3(\text{CO})_9(\mu_3-\eta^2\text{-RN=NR})$  into  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NR})_2$  (ref. 12). This reaction which was found to be of first order and intramolecular corresponds to the interconversion of two 7 SEP square pyramidal frameworks, as shown in Fig. 1. Such an interconversion, although theoretically feasible, is not in accord with the observed CO dependency of the reaction. It is therefore concluded that the first step is CO elimination, forming a 6 SEP trigonal bipyramidal  $\text{Fe}_3\text{N}_2$  framework, which may then undergo the characteristic pseudorotations until the two N atoms are separated, after which CO is added again to give the product cluster. Fig. 2 shows this presumed sequence of events (ref. 12).

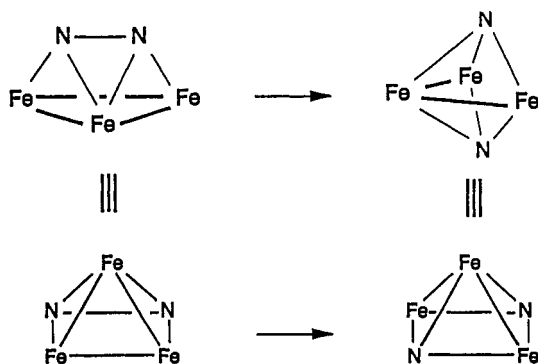


Fig. 1 Molecular frameworks of  $\text{Fe}_3(\text{CO})_9(\mu_3-\eta^2\text{-RN=NR})$  and  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NR})_2$

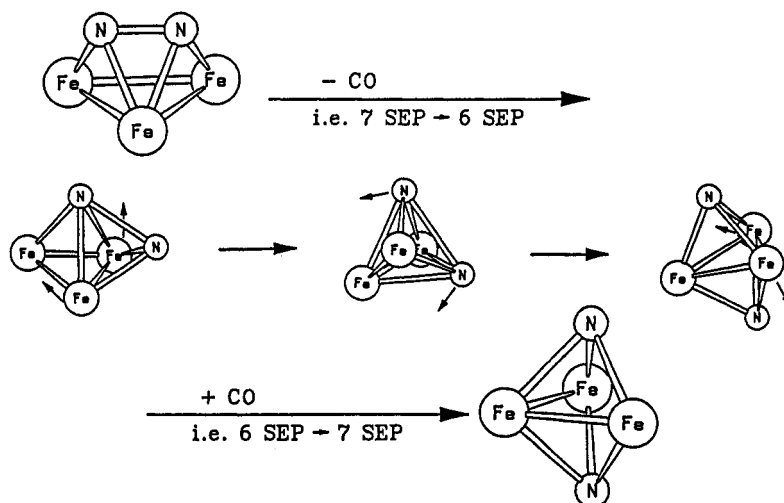
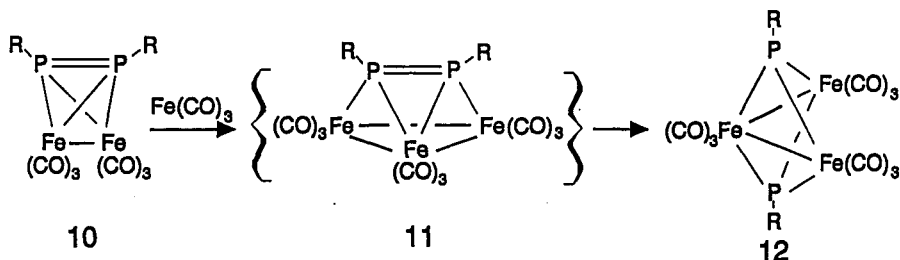


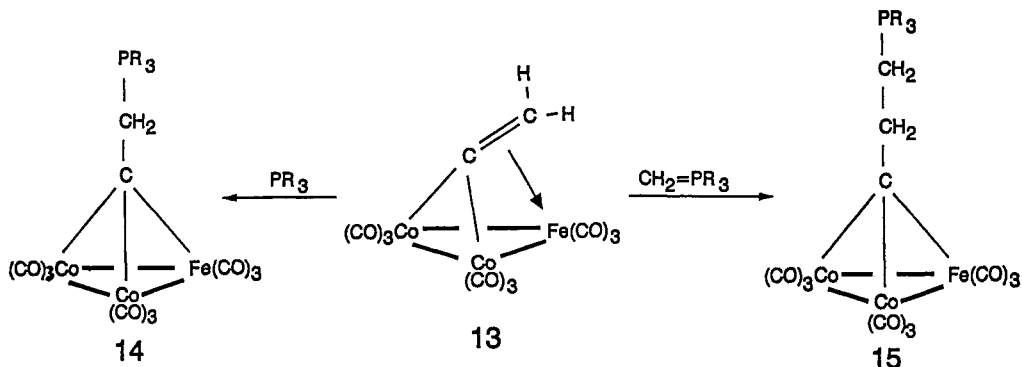
Fig. 2  $\text{Fe}_3\text{N}_2$  polyhedral rearrangement via 6 SEP intermediates

Two further observations have rounded off this reaction type which does not change the overall cluster composition. The cleavage of the azo compound is reversed when the nitrene bridged cluster  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NPh})_2$  is treated with oxidants. This treatment (originally done with  $\text{Me}_3\text{NO}$  in order to facilitate CO substitution) produces some decomposition compounds, some  $\text{Fe}_3(\text{CO})_{12}$ , and some  $\text{PhN=NPh}$ , thereby returning to the starting materials which upon heating will produce  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-NPh})_2$  again (ref. 14). Likewise, and expectedly, the cleavage of a diphosphene occurs much more easily than that of an azoalkane. Thus, attempts to do a cluster expansion reaction with the dinuclear complex 10 (ref. 20) did not yield the expected  $\mu_3\text{-}\eta^2$  bridged cluster 11 but instead its bis- $\mu_3$  bridged cleavage product 12 (R = t-Bu, ref. 14).

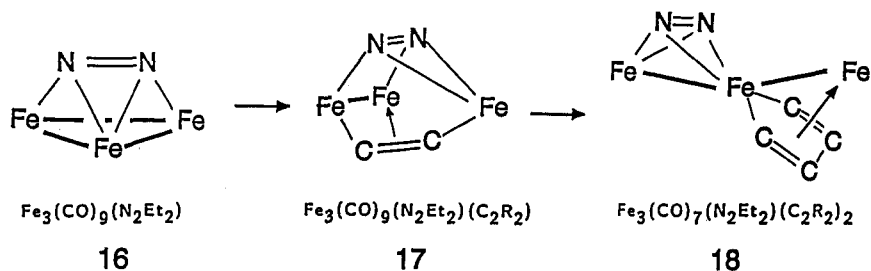


### USE OF INTERCONVERTED SUBSTRATES

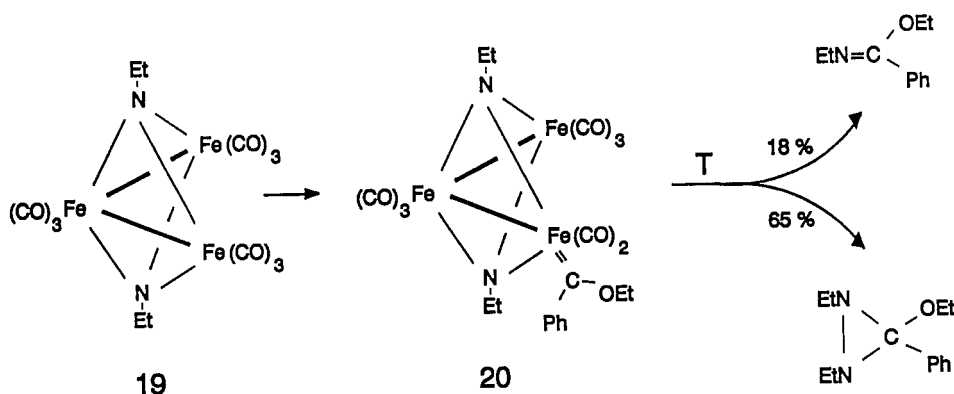
Multicenter attachment can alter the reactivity of metal-bound substrates as well as allowing the assembly of several substrates for a reaction. Both possibilities were realized for the  $\mu_3$  ligands of the C=C and N=N types. Since the reactivity of cluster-bound alkyne molecules is well investigated we put emphasis on the investigation of the vinylidene ligand. It turned out that, contrary to the chemistry of vinylidene ligands in mono- or dinuclear complexes, the  $\mu_3\text{-}\eta^2\text{-C}=\text{CH}_2$  unit is electrophilic at the outer C atom. All kinds of soft nucleophiles can be added, two simple examples being a phosphine or a phosphorus ylide as in the formation of 14 and 15 from 13 (refs. 21, 22).



Of the ligands of the N=N type the azoalkane as well as its cleavage product, the nitrene unit, could be released in the form of new organic products. For the azoalkane- $\text{Fe}_3$  cluster 16 a stepwise incorporation of alkyne ligands could be observed leading via 17 to 18 (ref. 23). The cluster type 18, also accessible from  $\text{Fe}_3(\text{CO})_8(\mu\text{-}\eta^4\text{-C}_4\text{R}_4)$  and  $\text{R}_2\text{N}_2$ , could then be degraded by irradiation, releasing tetra- or hexasubstituted dihydropyridazines in which the cyclic cotrimerization of two alkynes and one azoalkane is realized (ref. 14).

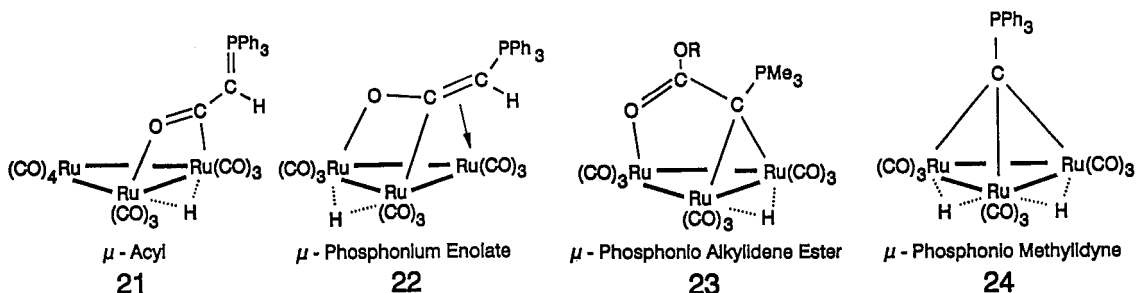


Starting from the nitrene bridged cluster **19**, the rearrangement product of **16** (see above), a further organic fragment could be introduced by the Fischer carbene route. The resulting cluster **20** could then be induced by heating to release the carbene and nitrene units, either 1 + 1 to yield an iminoester, or 1 + 2 to yield a diaziridine (ref. 14).



### ATTACHMENT AND INTERCONVERSION OF PHOSPHORUS YLIDES

The successful use of phosphorus ylides for cluster-mediated C-C bond formation (see **15** above) prompted us to exploit the use of salt-free ylides as substrates to be attached to and interconverted on clusters. The preliminary results for ruthenium carbonyls are promising (ref. 24), as are those obtained simultaneously by Deeming et al for osmium carbonyls (ref. 25). The ylides  $\text{R}_3\text{P}=\text{CHX}$  with  $\text{X} = \text{H}$  or  $\text{OR}$  react under rather mild conditions with  $\text{Ru}_3(\text{CO})_{12}$ . The major isolable products are **21-24**.

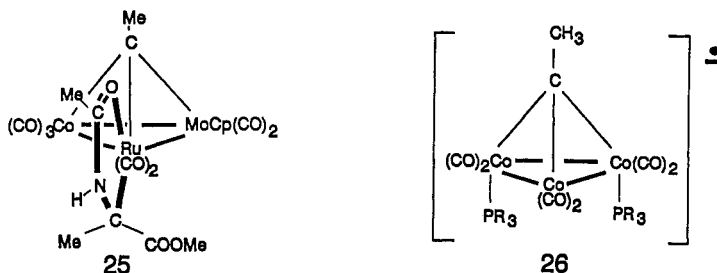


The clusters **21-23** result from a nucleophilic attack of the ylide at the CO carbon atom. As shown by Deeming (ref. 24), the cluster **21** which is an unstable intermediate for the  $\text{Ru}_3$  system can also be called the product of oxidative addition of the aldehyde  $\text{Ph}_3\text{P}=\text{CH}-\text{CHO}$  to the cluster. CO elimination from **21** results in **22**. Further rearrangement with group transfer from the the ylide carbon to the carbonyl carbon yields **23**, while CO elimination from **22** with migration of the H atom to the metals yields **24**. **24** is the product of double oxidative addition of  $\text{Ph}_3\text{P}=\text{CH}_2$  to  $\text{Ru}_3(\text{CO})_{12}$ .

Composition and structure of the clusters **21-24** bear some significance related to the fate of CO,  $\text{H}_2$ , and  $\text{CH}_2$  on metal surfaces in syngas reactions. Cluster **24** contains a ligand stabilised carbon atom. The reaction sequence links this to  $\text{Ph}_3\text{P}=\text{CH}_2$  which can be called a ligand stabilized  $\text{CH}_2$  unit. The intermediates **21** and **22** contain ligand stabilized CH units, and the H atoms move between the C atom and the metals. In syngas chemistry the "ligand" will be CO which can be assumed without difficulty since the cluster  $\text{Ru}_3(\text{CO})_9(\mu_3\text{C}\cdot\text{CO})^{2-}$ , a CO/ $\text{PPh}_3$  analog of **24**, is readily available (ref. 26), and CO-ligated  $\text{CH}_2$  is ketene which is known to be a ligand on clusters. Furthermore replacement of the  $\text{PR}_3$  group in **22-24** by H atoms would generate clusters with the  $\mu_3$ -bridging units  $\text{CH}_2\text{CO}$ ,  $\text{CHC}(\text{OR})\text{O}$ , and  $\text{CH}$  respectively, which are all known for  $\text{Ru}_3$  frameworks. The cluster sequence **21-24**, despite being derived from the unusual starting materials  $\text{R}_3\text{P}=\text{CHX}$ , thus helps to understand possible pathways between the building blocks C,  $\text{CH}_2$ , and CO in stoichiometric or catalytic reactions.

### PASSIVATION INSTEAD OF ACTIVATION

The product sequence  $21 \rightarrow 24$  cannot be fully realized for a single phosphorus ylide, nor can it be reversed. This points to the fact that the stabilization of unusual substrates, which is an asset of cluster chemistry, may also be a liability in that it may prevent reaction sequences from going to completion. Quite often, therefore, the phenomenon of "passivation instead of activation" occurs which fixes an otherwise very labile reaction intermediate as a cluster-bound species. Two typical examples for this phenomenon are **25** and **26**.



The compound **25** is a product of olefin insertion into the Ru-H function of the cluster  $\text{HRuCoMoCp}(\text{CO})_8(\mu_3\text{-CMe})$  (ref. 27). The olefin is 2-acetamido acrylic acid methyl ester which upon stereocontrolled hydrogenation would form a derivative of the amino acid alanine. The cluster, though catalytically active for olefin hydrogenations and chiral, does not catalyze this hydrogenation but yields **25** in a stoichiometric reaction. **25**, however, contains important general information. It is a model of the last step of an asymmetric hydrogenation before the release of the product. This last step can hardly be traced in catalytic systems due to its lability. Here it is the end-point of the reaction containing all the stereochemical information of the inaccessible final product.

The radical ion cluster **26** likewise models an otherwise inaccessible intermediate in a catalytic process (ref. 28). This time the process is the electron transfer catalyzed ligand substitution in metal complexes. The reaction chain is  $\text{ML}_n \rightarrow [\text{ML}_n]^\ddagger \rightarrow [\text{ML}_{n-1}]^\ddagger \rightarrow [\text{ML}_{n-1}\text{L}']^\ddagger \rightarrow \text{ML}_{n-1}\text{L}'$ . The most labile species in this chain is the electron deficient complex  $[\text{ML}_{n-1}]^\ddagger$ . By investigating electrochemically such ligand substitutions for cobalt clusters we observed that starting from  $\text{Co}_3(\text{CO})_6(\text{PR}_3)_3(\mu_3\text{-CMe})$  the cluster **26** could be enriched in solution. **26** results from electron transfer and  $\text{PR}_3$  elimination, thus lacking one electron for a closed-shell electronic configuration and corresponding to  $[\text{ML}_{n-1}]^\ddagger$ . In the catalytic reaction  $\text{PR}_3$  will be replaced by CO. This is the first direct experimental evidence for such an intermediate. It owes its stability to the delocalized nature of the unpaired electron which is equally associated with all three metal atoms, thus making the cluster nature of **26** the basis for the accessibility of this radical ion.

### OUTLOOK

This review has mostly dealt with the chemistry of C=C, C=N, and N=N bonded substrates, and the subject of C=O bonded substrates has briefly been touched with the ylide reactions. There is, however, a much wider range of multiply bonded substrates on trimetal clusters. For each of them some unique reactivity patterns have been observed (ref. 1). Many further reactions have yet to be found, and even a few more simple substrates have yet to be attached in the  $\mu_3\text{-}\eta^3$  mode. This opens many prospects for cluster chemistry. Fig. 3 is intended to present these prospects like viewing from a lookout point in space. The approaching "spaceships" are the frameworks of trimetal

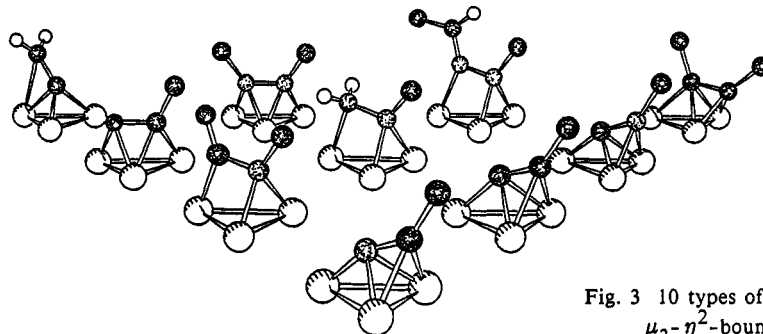


Fig. 3 10 types of cluster frameworks with  $\mu_3\text{-}\eta^2$ -bound substrates (see text)

clusters capped by  $\mu_3\text{-}\eta^2$ -bonded substrates. From left to right and row by row the substrates are: (first row) nitrile, acetylide, isonitrile, alkyne; (second row) isocyanate, hydrazide, hydrazone; (third row) acyl, azoalkane; (fourth row) vinylidene. We are optimistic that in addition to the systems mentioned in this report the nitrile, isonitrile, and acyl substrates will provide us with a fertile derivative chemistry.

## REFERENCES

1. For a compilation of reviews, see M. I. Bruce in D. F. Shriver, H. D. Kaesz, and R. D. Adams (Eds.), The Chemistry of Metal Cluster Complexes, p. 367, VCH Publishers, Weinheim (1990).
2. H. Vahrenkamp in A. Müller and E. Diemann (Eds), Transition Metal Chemistry, p. 35, Verlag Chemie, Weinheim (1981).
3. H. Vahrenkamp, Adv. Organomet. Chem. **22**, 169 (1983).
4. H. Vahrenkamp in H. Werner and G. Erker (Eds.), Organometallics in Organic Synthesis 2, p. 235, Springer, Berlin (1989).
5. E. Roland and H. Vahrenkamp, Chem. Ber. **119**, 2566 (1986); *ibid.* **118**, 2858 (1985).
6. H. Bantel, B. Hansert, A. K. Powell, M. Tasi, and H. Vahrenkamp, Angew. Chem. **101**, 1084 (1989); Angew. Chem. Int. Ed. Engl. **28**, 1059 (1989).
7. H. Vahrenkamp, Comments on Inorg. Chem. **4**, 253 (1985).
8. H. Vahrenkamp, J. Organomet. Chem. **370**, 65 (1989).
9. M. A. Andrews and H. D. Kaesz, J. Am. Chem. Soc. **101**, 7238 (1979).
10. A. Albin and H. Kisch, Top. Curr. Chem. **65**, 105 (1976).
11. W. Bernhardt and H. Vahrenkamp, Z. Naturforsch. **43b**, 643 (1988).
12. E. J. Wucherer, M. Tasi, B. Hansert, A. K. Powell, M. T. Garland, J. F. Halet, J. Y. Saillard, and H. Vahrenkamp, Inorg. Chem. **28**, 3564 (1989).
13. W. Bernhardt, H. T. Schacht, and H. Vahrenkamp, Z. Naturforsch. **44b**, 1060 (1989).
14. M. Tasi, B. Hansert, and H. Vahrenkamp, unpublished.
15. A. D. Clauss, J. R. Shapley, C. N. Wilker, and R. Hoffmann, Organometallics **3**, 619 (1984).
16. cf. H. T. Schacht and H. Vahrenkamp, Chem. Ber. **122**, 2239 (1989).
17. D. Nuel and R. Mathieu, J. Organomet. Chem. **307**, C5 (1986).
18. M. I. Bruce, M. G. Humphrey, O. bin Shawkataly, M. R. Snow, and R. T. Tiekink, J. Organomet. Chem. **336**, 199 (1987).
19. J. A. Smieja, J. E. Gozum, and W. L. Gladfelter, Organometallics, **6**, 1311 (1987).
20. R. L. De, D. Wolters, and H. Vahrenkamp, Z. Naturforsch. **41b**, 283 (1986).
21. T. Albiez and H. Vahrenkamp, Angew. Chem. **99**, 561 (1987); Angew. Chem. Int. Ed. **26**, 572 (1987).
22. D. Heineke and H. Vahrenkamp, Organometallics **9**, 1697 (1990).
23. M. Tasi, A. K. Powell, and H. Vahrenkamp, Angew. Chem. **101**, 327 (1989); Angew. Chem. Int. Ed. Engl. **28**, 318 (1989).
24. D. Heineke and H. Vahrenkamp, Angew. Chem. **102** (1990), in print.
25. A. J. Deeming, D. Nuel, N. I. Powell, and C. Whittaker, J. Chem. Soc. Chem. Commun. **1990**, 68.
26. M. J. Sailor and D. F. Shriver, Organometallics **4**, 1476 (1985).
27. D. Mani, H. T. Schacht, A. K. Powell, and H. Vahrenkamp, Chem. Ber. **122**, 2245 (1989).
28. K. Hinkelmann, J. Heinze, H. T. Schacht, J. S. Field, and H. Vahrenkamp, J. Am. Chem. Soc. **111**, 5078 (1989).