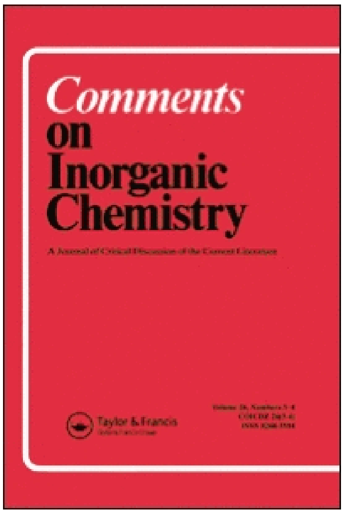
This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

# Metal Exchange in Organometallic Cluster Compounds

Heinrich Vahrenkamp[a]
[a] Institut für Anorganische und Analytische Chemie der Universität Freiburg, Freiburg, Federal Republic of Germany

**To cite this Article** Vahrenkamp, Heinrich(1985) 'Metal Exchange in Organometallic Cluster Compounds', Comments on Inorganic Chemistry, 4: 5, 253 — 267

**To link to this Article: DOI:** 10.1080/02603598508072266

**URL:** http://dx.doi.org/10.1080/02603598508072266

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Metal Exchange in Organometallic Cluster Compounds

In organometallic clusters with three, four, five, and six metal atoms metal–ligand fragments can be replaced by isolobal units. $Fe(CO)_3$ and $Co(CO)_3$ are good leaving groups. Organometallic units of the chromium, manganese, iron, cobalt, and nickel subgroups have been incorporated. The yields of the reactions can be remarkably high considering that during the replacement at least three bonds have to be broken and reformed. One-step and two-step reactions can be employed. Mechanistically, three reaction pathways have to be considered: fragmentation-reconstitution, elimination-addition, and addition-elimination. The new clusters obtained open up hitherto inaccessible aspects of cluster chemistry.

Downloaded At: 13:33 15 January 2011

## INTRODUCTION

Metal cluster chemistry was more an art than a science until about 10 years ago. Since then there has been a rapid development of synthetic methods enabling a better predictability of cluster stoichiometries and geometries. This is in part due to a tremendous number of crystal structure determinations but also to the fact that the buildup and breakdown of clusters can occur quite differently from classical organic or main-group-element cage framework reactions. This has allowed the use of seemingly unusual or unsystematic reaction conditions or reagents to build up or reconstitute clusters in short reaction sequences with remarkably high yields. For instance, the cluster $SFeCo_2(CO)_9$ is formed almost quantitatively from $Fe(CO)_5$, $Co_2(CO)_8$, and EtSH under synthesis gas[1] or from $S_2Fe_2Co_2(CO)_{11}$ and $Co_2(CO)_8$.[2]

---

*Comments Inorg. Chem.*
1985, Vol. 4, No. 5, pp. 253–267
0260-3594/85/0405-0253/$20.00/0

© 1985 Gordon and Breach,
Science Publishers, Inc. and OPA Ltd.
Printed in Great Britain

The main reason for the unconventionality (or ease) of cluster formation (or breakdown) is the lability of metal–ligand and, more important, metal–metal bonds. This allows the formation of organometal fragments which lack one to six electrons according to the 18 electron rule but which nevertheless persist in solution long enough to react with other such fragments and build up cluster frameworks with negligible decomposition. An early demonstration of the easy metal–metal bond breaking was provided by Dessy[3] in his electrochemical reductive cleavage of dinuclear organometallic compounds. We later found equilibrium reactions between dinuclear metal carbonyls which are most easily explained by the intermediate formation of 17-electron fragments,[4] and similar fragment exchange reactions were observed by Mackay[5] for fragments bound externally to clusters. Probably the most efficient advancement for the systematic thinking in terms of fragments came from R. Hoffmann's isolobal relationships.[6]

One aspect of the unconventional use of organometallic fragments as cluster building blocks is metal exchange, the subject of this Comment. Not only can fragments combine to put clusters together as in the formation of $Fe_3(CO)_{12}$ from $Fe(CO)_5$,[7] but fragments can also be taken out of clusters and replaced by other fragments as in the formation of $CpNiCo_3(CO)_9$ from $Co_4(CO)_{12}$ and $[CpNiCO]_2$ (see below). This is what we call metal exchange and it should not be confused with the replacement of one metal atom by another in the ligand sphere of a monometallic complex. Metal exchange in clusters was, to our knowledge, first observed in 1971/72[8,9] without it being explicitly recognized. But only recently[10] were systematic studies begun to elucidate the scope and variability of this reaction.

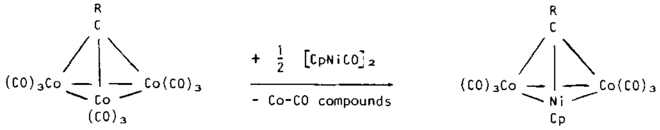
## ONE-STEP REACTIONS

Despite the fact that metal exchange reactions ought to be mechanistically complex (see below) quite a number of such reactions have been found to operate like one-step processes. Among these are the oldest examples which were not called metal exchange: the replacement of the $Os(CO)_4$ group in $Os_3(CO)_{12}$ via $M(CO)_5^-$ ($M = Mn$, $Re$) to form $MOs_2(CO)_{12}^-$ [9] and the replacement of $Fe(CO)_3$ and $Ru(CO)_3$ units in $M_3(CO)_{12}$ via cyclopentadienyl nickel reagents to form $Fe_2Ni$ and $Ru_2Ni$ clusters.[11]

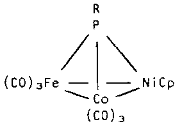
Downloaded At: 13:33 15 January 2011

Downloaded At: 13:33 15 January 2011

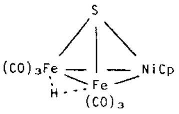
The first reagent to be used systematically for such purposes was probably $[CpNiCO]_2$.[12] It acts as a source of NiCp fragments if reacted with clusters containing $Co(CO)_3$ units, thereby replacing these. In the simplest formulation one nickel unit is needed to replace one cobalt unit as in the conversion of **1** to **2**.[12,13] Until now $[CpNiCO]_2$ has turned out to be one of the most versatile exchange reagents, and the $Co(CO)_3$ unit has been found to be the easiest leaving group. Conversions like **1** → **2** have worked for the $\mu_3$-bridged trinuclear clusters $RGeCo_3(CO)_9$,[14] $RPFeCo_2(CO)_9$,[15] $SFe_3(CO)_9H_2$,[16] $RCCo_2MoCp(CO)_8$,[13,17] and $(R_2C_2)RuCo_2(CO)_9$.[18] Representative products are **3**, **4**, and **5**. Similar, less clean reactions with $[CpNiCO]_2$ were observed for several alkyne-bridged trimetal clusters.[11,19] $NiCp_2$ sometimes works similarly.[11,20]



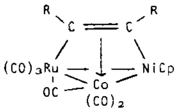
**1** **2**



**3**

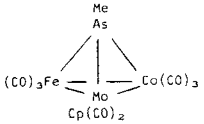


**4**

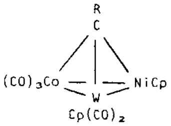


**5**

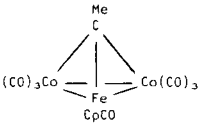
$[CpNiCO]_2$ is a representative of a whole range of dinuclear cyclopentadienyl metal carbonyls. $[CpMo(CO)_3]_2$, $[CpW(CO)_3]_2$, and $[CpFe(CO)_2]_2$ react similarly, but often less effectively in replacing $Co(CO)_3$ units.[13,14,17,21,22] Amongst others, the mixed metal clusters **6**, **7**, and **8** are accessible this way.



**6**



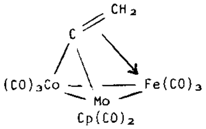
**7**



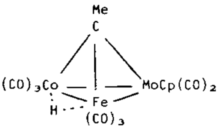
**8**

Downloaded At: 13:33 15 January 2011

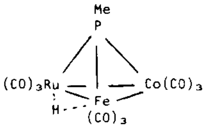
Next important as metal exchange reagents for trinuclear clusters are the anionic metal carbonyls. Sometimes the anions $MoCp(CO)_3^-$, $WCp(CO)_3^-$, and $FeCp(CO)_2^-$ are more effective in replacing $Co(CO)_3$ units than the corresponding dinuclear neutral complexes.[17,18,22,23] This holds especially for cases where the electron count of the clusters changes, e.g., when redox activation by electron-transfer catalysis has been applied.[24,25] The clusters **6**, **8**, and **9** can be obtained this way. Even more powerful in this respect are the dianions $Fe(CO)_4^{2-}$ [14,17,25,26] and $Ru(CO)_4^{2-}$.[27] They lead to the exchange of $Co(CO)_3$ for $M(CO)_3H$ (M = Fe, Ru) as in the formation of **10** and **11**. In all the anion reactions the expelled cobalt unit appears as $Co(CO)_4^-$.



**9**

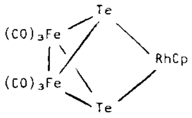


**10**

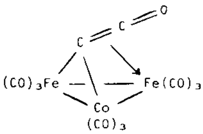


**11**

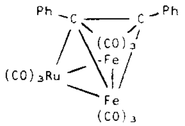
Although the $Co(CO)_3$ group is the most common leaving group in these systems, several reactions have been found which replace other groups, specifically $Fe(CO)_3$. Since this is an even electron species, it normally requires even electron fragments to replace it. Thus, starting from $Te_2Fe_3(CO)_9$ and $CpCo(CO)_2$, $CpRh(CO)_2$, or $(C_2H_4)Pt(PPh_3)_2$ exchange occurs to produce $Te_2Fe_2M'$ clusters.[28,29] However, during these reactions the 14-electron $Fe(CO)_3$ fragment is replaced by 16-electron fragments which means that the product clusters like **12** have one metal–metal bond less than the starting cluster. This change of the electron count does not occur in the $Fe(CO)_3/Co(CO)_3$ exchange from $Fe_3(CO)_9(CCO)^{2-}$ with $Co_2(CO)_8$ to form **13**[30] or in the conversion of $Fe_3(CO)_9(C_2Ph_2)$ with $Ru_3(CO)_{12}$ to form **14**.[31]



**12**



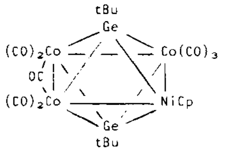
**13**



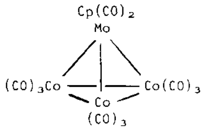
**14**

Downloaded At: 13:33 15 January 2011

Even less systematic than the replacements of $Fe(CO)_3$ units have been the observations on the one-step metal exchange in tetranuclear clusters. This is partly due to the fact that fewer attempts have been made. But the main reason may be that most tetranuclear clusters lack the significant stabilization of the trinuclear clusters mentioned so far in the form of the connecting main group element unit. This makes it understandable why, in contrast to the many successful exchanges at $ECo_3(CO)_9$ compounds with E = CR, GeR, PR, and S, only one such reaction could be performed for $E = Co(CO)_3$: the conversion of $Co_4(CO)_{12}$ with $[CpNiCO]_2$ to $CpNiCo_3(CO)_9$.[13] Similarly, the successful transformation of $(t\text{-}BuGe)_2Co_4(CO)_{11}$ into **15** with $[CpNiCO]_2$ [32] could be predicted. In accordance with the $Fe(CO)_3$ expulsion from anionic $Fe_3$ clusters by $Co_2(CO)_8$ [30] similar processes converted $Fe_4(CO)_{13}^{2-}$ and $Ru_4(CO)_{13}^{2-}$ to $Fe_3Co(CO)_{13}^{-}$ and $Ru_3Co(CO)_{13}^{-}$ [33]; and the exchange of metal units other than $Fe(CO)_3$ or $Co(CO)_3$ was observed in the $Fe_3W(CO)_{14}^{2-} \rightarrow Fe_3Co(CO)_{13}^{-}$ conversion[33] or during the reactions of $RuCo_3(CO)_{12}^{-}$ with $[Rh(CO)_2Cl]_2$ or $CpMo(CO)_3Cl$ which replace the $Ru(CO)_3$ unit by the heterometal unit as in **16**.[34]



**15**

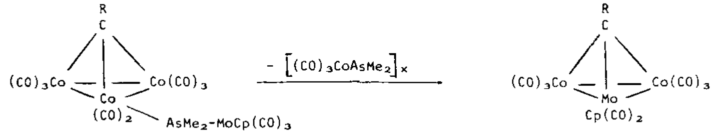


**16**

Clusters with more than four metal atoms have not been subjected to designed one-step metal exchange procedures. But since a number of such clusters exists which are stabilized by connecting main-group elements, e.g., $RPRu_5(CO)_{15}$ or $CFe_5(CO)_{15}$, it is likely that such reactions will also be found here.

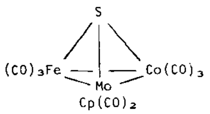
## TWO-STEP REACTIONS

The first discovery of a designed metal exchange was made for a two-step process. Initially intended to lead to cluster expansion by CO elimination, the thermolysis of **17** eliminated a cobalt arsenic unit thereby replacing cobalt by molybdenum in the cluster **18**.[35] The driving force for this reaction results mainly from the preferred formation of the very stable oligomeric compound of approximate composition $[(CO)_3CoAsMe_2]_x$. This became evident during attempts to incorporate $Mn(CO)_4$ units into the $RCCo_3$ clusters by reacting the compound which differs from **17** by an external $AsMe_2-Mn(CO)_5$ unit. In this case the starting cluster $RCCo_3(CO)_9$ was reformed while $[(CO)_4MnAsMe_2]_2$, which is also very stable, was eliminated.[35]

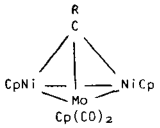


**17** **18**

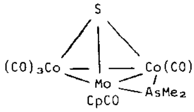
This Co–As elimination method is suitable to introduce chromium, molybdenum, and tungsten into triply bridged trinuclear clusters using the stable organometal dimethylarsenides $Cp(CO)_3M-AsMe_2$ (M = Cr, Mo, W) as reagents. It has been applied successfully to $RCCo_3(CO)_9$,[17,35] $SFeCo_2(CO)_9$,[36] $SRuCo_2(CO)_9$,[21] $RPFeCo_2(CO)_9$,[37] $RAsFeCo_2(CO)_9$,[22] and $RGeCo_3(CO)_9$.[38] It complements the one-step methods using $[CpM(CO)_3]_2$ or $CpM(CO)_3^-$, and at the moment it is not predictable which method works better. It has made available the first optically active cluster **19**[39] and, in combination with the one-step process, the cobalt-free alkylidyne bridged clusters **20**.[13,17] It works almost exclusively for $Co(CO)_3$ as a leaving group. But starting from $EFeCo_2(CO)_9$ (E = S, PR) the elimination of $Fe(CO)_3$ was a side reaction, producing, e.g., **21**.[36,37]



**19**



**20**



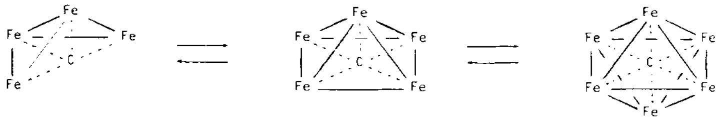
**21**

The best system to be exploited for two-step metal exchange reactions has been the series of tetra-, penta-, and hexanuclear iron carbide clusters **22**–**24**. These clusters can be prepared independently

Downloaded At: 13:33 15 January 2011

and then interconverted by using $Fe_2(CO)_9$ for cluster expansion or oxidative methods for cluster degradation.[40,41] All three are anionic and therefore well suited for cluster expansion with electrophilic monometallic reagents. This was performed starting from **22** and **23** with Cr, Mo, W, Fe, Rh, Ir, Ni, Pd, and Cu complexes, in each case producing the corresponding $Fe_4M$ or $Fe_5M$ cluster,[41] two examples being **26** and **27**. This sequence is completed by the $Fe_3M$ clusters like **25**, which are accessible from $Fe_3(CO)_9(CCO)^{2-}$ and Cr, W, Mn, and Rh containing reagents.[30,42] The clusters **25**–**27** again are interconvertible which was demonstrated for oxidative degradations like **27** → **26** and similar Fe/Mo, Fe/W, and Fe/Rh systems[41] and which should work with $Fe_2(CO)_9$ for the expansions. Thereby a complete sequence of mixed-metal iron carbide clusters has been accessible either by the expansion-degradation or by the degradation-expansion route, the $Fe_4M$ compounds finally resulting from **23** and the $Fe_5M$ compounds from **24**; and there is no reason to assume that a second and third heterometal might not be introduced by the same procedures.

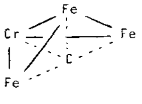
Downloaded At: 13:33 15 January 2011



$Fe_4C(CO)_{12}^{2-}$ **22**

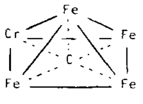
$Fe_5C(CO)_{14}^{2-}$ **23**

$Fe_6C(CO)_{16}^{2-}$ **24**



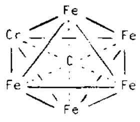
$Fe_3CrC(CO)_{13}^{2-}$

**25**



$Fe_4CrC(CO)_{15}^{2-}$

**26**

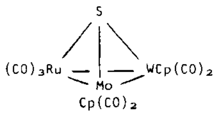


$Fe_5CrC(CO)_{17}^{2-}$

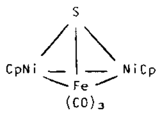
**27**

## REPEATED EXCHANGE

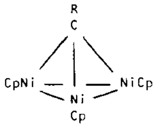
Several of the examples for metal exchange given so far have produced clusters with three different metal atoms. This mostly means that readily accessible clusters with two different kinds of metals were used as starting materials. In the formation of **7**, **10**, and **20**, however, two metal-exchange steps were involved starting from $RCCo_3(CO)_9$. This demonstrates the high leaving tendency of the $Co(CO)_3$ groups: both the one-step and the two-step exchange methods can be used repeatedly or in combination to replace two $Co(CO)_3$ groups from $RCCo_3(CO)_9$,[13,17] $RGeCo_3(CO)_9$,[14,38] $RPCo_3(CO)_9$,[25] $SFeCo_2(CO)_9$, and $SRuCo_2(CO)_9$,[43] a further typical example being **28**. Similarly, it has been possible to replace two $Fe(CO)_3$ groups, e.g., in forming $Te_2FeMo_2(CO)_7$ [44] or **29**[16] from the corresponding $Fe_3$ clusters.



**28**



**29**



**30**

The cluster **20** provides an example of a product in which all three $Co(CO)_3$ units of the starting cluster have been replaced. The alkylidyne bridged trinuclear clusters are the only ones so far for which triple exchange has been investigated. It was found that stepwise replacement of all three cobalt atoms by molybdenum- or nickel-containing units is possible with progressively lower yields, producing, e.g., compound **30**.[17] There is a clean progression in colors, thermal stabilities, reactivities, and molecular geometries for such series of compounds starting from the $RCCo_3(CO)_9$ parent. The high number of methods applicable to the synthesis and conversion of $RCM_3$ clusters has actually resulted in the existence of almost every transition element as a constituent in this class of compounds.

## MECHANISTIC INTERPRETATION

If, in a tetrahedral framework as is present in most of the clusters mentioned so far, one vertex is to be replaced, at least three bonds have to be broken and reformed. It is unlikely that this process of metal exchange proceeds by the simplest route, i.e., by the extrusion of one vertex, persistence of the remaining cluster fragment until the

Downloaded At: 13:33 15 January 2011

reagent is encountered, and then incorporation of the reagent. If cluster fragmentation occurs, total fragmentation is more likely and, to visualize the elimination-incorporation nature of metal exchange, it is more realistic to assume multistep mechanisms.

In fact there is evidence for all three possible reaction pathways. The first of these is total fragmentation followed by fragment recombination. If one realizes how readily $Fe_3(CO)_{12}$ or $Co_4(CO)_{12}$ are completely degraded by donor ligands one must accept the possibility of similar degradations during $Co(CO)_3$ or $Fe(CO)_3$ fragment exchange reactions. This is borne out by the observations of how easily Fe–Rh clusters can be interconverted between the 2 : 1 and 1 : 5 atom ratios,[45] and by mass spectroscopic evidence for the scrambling of $Fe(CO)_4$ and $Ru(CO)_4$ units upon mixing of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$.[46] Of the metal exchange procedures, especially those involving alkyne bridged clusters were found to yield product mixtures containing combinations of all possible fragments,[11,19] and clean reactions could rarely be achieved.[18] Breakdown of starting clusters is frequently observed.[13,15,17,25,28,29] An extreme case is the conversion of $SFeCo_2(CO)_9$ into **19** where the reaction, if not carefully controlled, produces a mixture of nine di-, tri-, and tetranuclear complexes.[36] It may well be that many of the reported reactions between clusters and other organometallic compounds proceed by the fragmentation/reconstitution pathway, but only in a limited number of favorable cases can products be formed which result from a net metal exchange.

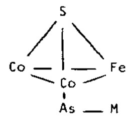
A more obvious reaction pathway consists in the controlled elimination of a monometallic fragment to form a reasonably stable intermediate followed by addition of the incoming fragment. This mechanism is not very likely for odd-electron fragments like $Co(CO)_3$ since the remaining unit would also have to be odd numbered. But there is ample evidence that clusters can be increased or decreased by even-numbered fragments like $Fe(CO)_n$ units. This has been shown already in the sequences of reactions interrelating the clusters **22** to **24** and **25** to **27**.[40–42] There are similarly easy interconversions between $Fe_3(CO)_9(PR)_2$ and $Fe_4(CO)_{12}(PR)_2$,[47] as are between $Ru_4N(CO)_{12}^-$, $Ru_5N(CO)_{14}^-$, and $Ru_6N(CO)_{16}^-$.[48] As a mechanistic interpretation the elimination-addition sequence has been used to explain the conversion of $Te_2Fe_3(CO)_9$ to clusters like **12** by the intermediacy of $Te_2Fe_2(CO)_6$. And it is easy to imagine the formation of **14** from $Fe_3(CO)_9(Ph_2C_2)$

Downloaded At: 13:33 15 January 2011

such that first $Fe(CO)_3$ elimination produces $Fe_2(CO)_6(Ph_2C_2)$, the tertiary butyl analoque of which has been described as a stable compound, and then $Ru(CO)_3$ addition leads to the product.[31]

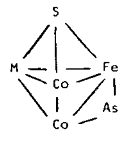
The most evidence has been accumulated for the addition-elimination sequence of metal exchange. Again the series **22**–**27** provides examples[40,41] of which the sequence **23** → **27** → **26** has been mentioned. Certain monometallic reagents which are useful as metal exchange reagents are also readily added to clusters and removed again under different conditions. For instance, the clusters $RPRuCo_2(CO)_9$ add CpRhCO fragments resulting from $CpRh(CO)_2$ reversibly to form $RPRuCo_2RhCp(CO)_{10}$[49]; and the mechanism of the $Co(CO)_3/HFe(CO)_3$ exchange by means of $Fe(CO)_4^{2-}$ [26] as in the formation of **10** becomes obvious from the fact that $Fe(CO)_4^{2-}$ adds to $M_3(CO)_{12}$ ($M$ = Fe, Ru, Os) to form the tetrahedral clusters $FeM_3(CO)_{13}^{2-}$ which after protonation are readily degraded by CO with reformation of $M_3(CO)_{12}$.[50] In one case it has been possible to analyze the step-by-step nature of an addition-elimination cycle: the metal exchange reagents $Cp(CO)_3M{-}AsMe_2$ ($M$ = Cr, Mo, W) first substitute CO as in **17** (see above). Starting from $SFeCo_2(CO)_9$ this leads to a framework like **31**.[36] Heating of **31** in vacuum results in aggregation to form the tetrahedral framework **32**.[51] If **32** is briefly treated with CO it is unfolded to **33**. Under more forcing conditions **33** is finally fragmented, eliminating $[(CO)_3Co{-}AsMe_2]_x$ and leaving behind the metal exchange product **19**.[52]

Downloaded At: 13:33 15 January 2011



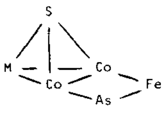
$SFeCo_2(CO)_8{-}AsMe_2MCp(CO)_3$

**31**



$SFeCo_2M(AsMe_2)Cp(CO)_8$

**32**



$SFeCo_2M(AsMe_2)Cp(CO)_{10}$

**33**

Detailed as it is, this sequence may still not be complete since the three metal atoms bridged by the sulfur atom change along the series. This reemphasizes that metal exchange is complicated despite its frequent facile occurrence.

# USE OF METAL EXCHANGE PRODUCTS

All metal exchange products are mixed-metal clusters. The advantages of these have been treated in several review articles,[10,53,54] the most important ones being metal–metal bond polarity, site-specific reactivity, multimetal reactivity, low symmetry, and ease of spectroscopic investigation. Although in principle every mixed-metal cluster synthesis can lead to these properties there are several which up to now have only been reached by metal exchange.

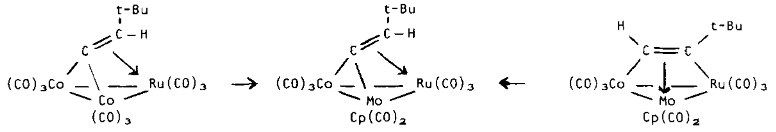
The most prominent physical property of mixed-metal clusters is optical activity. So far only metal exchange products, namely **7**,[17] **19**[39] (and similar compounds), $SRuCoMoCp(CO)_8$,[21] and $RPFeCoWCp(CO)_8$ [37] have been separated into their enantiomers. All these compounds are deeply colored and have extreme optical rotations. The record value in the visible range is Φ(molar) = 43,000 degrees at 436 nm. All these compounds represent the hitherto unknown case of "asymmetric tetrahedron" where the chirality center is not located on an atom but in the interstice between the vertices. This opens up new possibilities for the racemization mechanism which has not been investigated yet.

Along with the asymmetry of the mixed-metal clusters goes the possibility for selective metal–ligand interactions.[55] An example of this is the comparison between $FeCo_2(CO)_9(\mu\text{-}R_2C_2)$ and $RuCo_2(CO)_9(\mu\text{-}R_2C_2)$ of which the former has the alkyne parallel to the Co–Co bond[56] and the latter parallel to the Ru–Co bond.[57] Metal exchange is possible for both compounds, so far being the only reasonable way to chiral alkyne-bridged clusters.[18] In products like **5** there are now three different possible orientations of the alkyne ligand. Investigation of such systems will lead to a better understanding of the interactions between unsaturated systems and several metal atoms as well as of their reactivity. The same holds for other types of mixed-metal clusters obtainable this way.

Metal exchange opens another gate to cluster chemistry which has not been used yet: that to the investigation of stereocontrol. One example may underline this. The vinylidene-bridged cluster **35** is obtained by metal exchange from the precursor **34** or by rearrangement from the metal exchange product **36**.[18] Both reactions lead to only one of the two isomers differing by the orientation of the H

Downloaded At: 13:33 15 January 2011

and *t*-Bu substituents. The structure of **35** has not been determined yet but it seems that repulsion between the bulky *t*-Bu and MoCp(CO)$_2$ units determines the geometry of the product cluster.



**34** **35** **36**

Several clusters obtained by metal exchange have been used for cluster catalysis.[58-60] But the promise they hold has not been fulfilled yet, namely the definite proof of cluster catalysis. In all cluster-catalyzed processes studied so far it cannot be excluded that it is not the cluster but fragments thereof that are the real catalyst. If, however, a physical property which only the cluster but none of its possible fragments can possess is transferred during the catalytic process to the substrate, the proof is obtained. Optical activity is such a property, and therefore the optically active clusters would be valuable as catalysts. Until now, however, in each case studied (hydrosilylation, hydroformylation, hydrogenation) the conditions needed to perform the catalytic reactions (irradiation, high temperature, CO pressure) were such that racemization of the clusters took place. Here the advantage of the metal exchange reaction, the lability of the metal–metal bonds, becomes a disadvantage for purposes where rigidity of the cluster framework is required. Finally, a general feature of mixed-metal clusters may best be achieved by way of metal exchange. This is the fine tuning of properties. For instance, the clusters RCCo$_3$(CO)$_9$ are easily and reversibly reduced but not oxidized[61] whereas the reverse is true for the clusters RCRu$_3$Cp$_3$(CO)$_3$ which has a pronounced effect on the reactivity of the $\mu_3$-CR ligand.[62] In this case a rather electron-poor and a very electron-rich cluster are compared. Quite often, however, the interesting chemistry occurs between the extremes, and quite often metal exchange as shown above is the method of choice to attain such intermediate situations starting from homonuclear clusters.

Downloaded At: 13:33 15 January 2011

## OUTLOOK

The first review on mixed-metal clusters, although written only five years ago did not recognize metal exchange.[53] In the meantime several fertile approaches have been found to this class of compounds, metal exchange being only one of them. This also means that the future value of metal exchange will not just lie in the production of more mixed-metal clusters. Beyond this it has the potential of becoming a method for reactivity control in the cluster field. The simple variation of terminal ligands often does not change the properties of clusters very much. Metal exchange, however, brings about a significant variation of the electronic and/or steric situation. This in turn will affect other parts of the cluster with respect to metal-based as well as ligand-based reactions. The fine tuning of $C_mH_n$ ligands mentioned above is an example. Very few of the possibilities involved have been realized yet: there is just one example of stereocontrol (see **34**, **35**, **36**), cluster chirality has hardly been exploited, and electronic effects due to the mixed-metal nature of clusters have much more often been discussed[55] than found.

In order to make such efficient use of metal exchange the method itself will have to be improved. So far the number of types of usable clusters is small, there is no predictable choice of exchange reagents, and leaving groups other than $Fe(CO)_n$ and $Co(CO)_n$ are not well explored. In order to bring metal exchange to textbook level a systematization will have to be achieved including as the most important aspect a hierarchy of entering and leaving groups. This will require some effort, but the potential value should be worth it.

### Acknowledgments

The work described in this text was done by a team of multiskilled, enduring, and dedicated co-workers whose names are given in the references. Financial support by the University of Freiburg, the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Wissenschaftliche Gesellschaft Freiburg, the Deutscher Akademischer Austauschdienst, and the Alexander-von-Humboldt-Stiftung is gratefully acknowledged.

Downloaded At: 13:33 15 January 2011

HEINRICH VAHRENKAMP
*Institut für Anorganische*
*und Analytische Chemie der Universität Freiburg,*
*Albertstr. 21, D-7800 Freiburg,*
*Federal Republic of Germany*

## References

1. L. Markó (private communication), cf. E. Roland and H. Vahrenkamp, Chem. Ber. **117**, 1039 (1984).
2. H. Vahrenkamp and D. Wolters (unpublished), cf. H. Vahrenkamp and E. J. Wucherer, Angew. Chem. **93**, 715 (1981); Angew. Chem. Int. Ed. Engl. **20**, 680 (1981); S. A. Khattab, L. Markó, G. Bor and B. Markó, J. Organomet. Chem. **1**, 373 (1964).
3. R. L. Dessy and L. Bares, Acc. Chem. Res. **5**, 415 (1972).
4. T. Madach and H. Vahrenkamp, Chem. Ber. **113**, 2675 (1980).
5. J. A. Christie, D. N. Duffy, K. M. Mackay and B. K. Nicholson, J. Organomet. Chem. **226**, 165 (1982).
6. R. Hoffmann, Angew. Chem. **94**, 725 (1982); Angew. Chem. Int. Ed. Engl. **21**, 711 (1982).
7. J. Dewar and H. O. Jones, Proc. Roy. Soc. (London) A **76**, 558 (1905); **79**, 66 (1906).
8. A. T. Hsieh and M. J. Mays, J. Organomet. Chem. **26**, 125 (1971).
9. J. Knight and M. J. Mays, J. Chem. Soc. Dalton Trans. 1022 (1972).
10. cf. H. Vahrenkamp, Adv. Organomet. Chem. **22**, 169 (1983).
11. cf. E. Sappa, A. M. Manotti Lanfredi and A. Tiripicchio, J. Organomet. Chem. **221**, 93 (1981) and references cited therein.
12. H. Beurich and H. Vahrenkamp, Angew. Chem. **93**, 128 (1981); Angew. Chem. Int. Ed. Engl. **20**, 98 (1981).
13. H. Beurich, R. Blumhofer and H. Vahrenkamp, Chem. Ber. **115**, 2409 (1982).
14. P. Gusbeth and H. Vahrenkamp, Chem. Ber. **118**, 1770 (1985).
15. M. Müller and H. Vahrenkamp, Chem. Ber. **116**, 2765 (1983).
16. K. Fischer, W. Deck, M. Schwarz and H. Vahrenkamp, Chem. Ber. (in press).
17. R. Blumhofer, K. Fischer and H. Vahrenkamp, Chem. Ber. (in press).
18. C. v. Schnering, E. Roland and H. Vahrenkamp (unpublished).
19. E. Sappa, A. Tiripicchio and P. Braunstein, Chem. Rev. **83**, 203 (1983).
20. M. Mlekuz, P. Bougeard, M. J. McGlinchey and G. Jaouen, J. Organomet. Chem. **253**, 117 (1983).
21. E. Roland and H. Vahrenkamp, Chem. Ber. **117**, 1039 (1984).
22. W. R. Dietrich and H. Vahrenkamp, J. Chem. Research (in press).
23. C. Mahe, H. Patin, J.-Y. Le Marouille and A. Benoit, Organometallics **2**, 1051 (1983).
24. S. Jensen, B. H. Robinson and J. Simpson, J. Chem. Soc. Chem. Commun. 1081 (1983).
25. U. Honrath and H. Vahrenkamp, Z. Naturforsch. **39b**, 559 (1984).
26. R. A. Epstein, H. W. Withers and G. L. Geoffroy, Inorg. Chem. **18**, 942 (1979).
27. D. Mani and H. Vahrenkamp (unpublished).
28. L. E. Bogan, D. A. Lesch and T. B. Rauchfuss, J. Organomet. Chem. **250**, 429 (1983).

Downloaded At: 13:33 15 January 2011

29. D. A. Lesch and T. B. Rauchfuss, Inorg. Chem. **22**, 1854 (1983).
30. J. W. Kolis, E. M. Holt, J. A. Hriljak and D. F. Shriver, Organometallics **3**, 496 (1984).
31. V. Busetti, G. Granozzi, S. Aime, R. Gobetto and D. Osella, Organometallics **3**, 1510 (1984).
32. P. Gusbeth and H. Vahrenkamp, Chem. Ber. **118**, 1746 (1985).
33. C. P. Horwitz, E. M. Holt and D. F. Shriver, Organometallics **4** (1985).
34. J. Rosé and P. Braunstein (private communication).
35. H. Beurich and H. Vahrenkamp, Chem. Ber. **115**, 2385 (1982).
36. F. Richter and H. Vahrenkamp, Chem. Ber. **115**, 3224 (1982).
37. M. Müller and H. Vahrenkamp, Chem. Ber. **116**, 2748 (1983).
38. P. Gusbeth and H. Vahrenkamp, Chem. Ber. **118**, 1758 (1985).
39. F. Richter and H. Vahrenkamp, Chem. Ber. **115**, 3243 (1982).
40. M. Tachikawa and E. L. Muetterties, J. Am. Chem. Soc. **102**, 4541 (1980).
41. M. Tachikawa, R. L. Geerts and E. L. Muetterties, J. Organomet. Chem. **213**, 11 (1981).
42. J. A. Hriljak, P. N. Swepston and D. F. Shriver, Organometallics **4**, 158 (1985).
43. F. Richter, E. Roland and H. Vahrenkamp, Chem. Ber. **117**, 2429 (1984).
44. L. E. Bogan and T. B. Rauchfuss, Inorg. Chem. (in press).
45. A. Ceriotti, G. Longoni, R. Della Pergola, B. T. Heaton and D. O. Smith, J. Chem. Soc. Dalton Trans. 1433 (1983).
46. S. Aime, G. Nicola, S. Pellegrino and D. Osella (private communication).
47. H. Vahrenkamp, E. J. Wucherer and D. Wolters, Chem. Ber. **116**, 1219 (1983).
48. M. L. Blohm and W. L. Gladfelter, Organometallics **4**, 45 (1985).
49. D. Mani and H. Vahrenkamp, Angew. Chem. **97** (1985); Angew. Chem. Int. Ed. Engl. **24** (1985).
50. J. R. Fox, W. L. Gladfelter and G. L. Geoffroy, Inorg. Chem. **19**, 2574 (1980).
51. F. Richter, H. Beurich, M. Müller, N. Gärtner and H. Vahrenkamp, Chem. Ber. **116**, 3774 (1983).
52. F. Richter, M. Müller, N. Gärtner and H. Vahrenkamp, Chem. Ber. **117**, 2438 (1984).
53. W. L. Gladfelter and G. L. Geoffroy, Adv. Organomet. Chem. **18**, 207 (1980).
54. H. Vahrenkamp, Phil. Trans. Roy. Soc. London A **308**, 1 (1983).
55. E. Sappa, A. Tiripicchio and P. Braunstein, Chem. Rev. (in press).
56. S. Aime, L. Milone, D. Osella, A. Tiripicchio and A. M. Manotti Lanfredi, Inorg. Chem. **21**, 501 (1982).
57. E. Roland, W. Bernhardt and H. Vahrenkamp, Chem. Ber. (in press).
58. C. U. Pittman, M. G. Richmond, M. Absi-Halabi, H. Beurich, F. Richter and H. Vahrenkamp, Angew. Chem. **94**, 805 (1982); Angew. Chem. Int. Ed. Engl. **21**, 780 (1982).
59. D. Mani and H. Vahrenkamp, J. Mol. Cat. **29**, 305 (1985).
60. F. Sistig, W. Keim, R. Blumhofer and H. Vahrenkamp (unpublished).
61. A. M. Bond, B. M. Peake, B. H. Robinson, J. Simpson and D. H. Watson, Inorg. Chem. **16**, 410 (1977).
62. N. G. Connelly, N. J. Forrow, S. A. R. Knox, K. A. Macpherson and A. G. Orpen, J. Chem. Soc. Chem. Commun. 16 (1985).

Downloaded At: 13:33 15 January 2011