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New Bonding Modes, Fluxional Behavior, and Reactivity in Dinuclear Complexes Bridged by Four-Electron Donor Unsaturated Hydrocarbons

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Contents

I. Abbreviations

Cp	$-C_5H_5$ = cyclopentadienyl
Cp*	$-C_5Me_5$ = pentamethyl cyclopentadienyl
Fv	$C_5H_4-C_5H_4$ = fulvalene
THF	tetrahydrofuran
dppm	$CH_2(PPh_2)_2$
t-Bu	$-C(CH_3)_3$
Ph	$-C_6H_5$ = phenyl
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
bornyl	1,7,7-trimethylbicyclo[2.2.1]heptyl
fenchyl	1,3,3-trimethylbicyclo[2.2.1]heptyl
Cym	cymantrenyl
Fc	ferrocenyl
$[Co_2]$	$Co_2(CO)_6$
$[Mo_2]$	$Cp_2Mo_2(CO)_4$
[Mo]	$CpMo(CO)_2$
[Co]	$Co(CO)_3$
[W]	$CpW(CO)_2$
[Mo−Co]	$CpMo(CO)_2Co(CO)_3$
$[Co_2]$ propargylium ions	$[Co_2(CO)_6(\mu\text{-}\eta^2,\eta^3\text{-}R^1\text{-}C{\equiv}CCR^2R^3)]^+$

II. Introduction

The extensive and rapid development of the chemistry of dinuclear transition metal complexes bridged by unsaturated hydrocarbons is stimulated in part by their resemblance to the chemistry of metal−catalyst surfaces.[1] It is been hoped that carbon-rich C_nH_x fragments bridging a dinuclear frame in homogeneous systems serve as models to the understanding of the chemistry of reactive intermediates obtained during catalytic reactions like Fischer−Tropsch[2] in heterogeneous systems. Further it is well known that the coordination of an organic molecule to a metal center increases the stability of the whole system and activates the coordinated substrate toward specific reactions which may not be possible via the classical organic procedures.[3]

The purpose of this review is to highlight some of the most important recent developments in the chemistry of dinuclear carbonyl transition metal complexes which contain four-electron unsaturated hydrocarbon bridges. Two major categories will be considered (Chart 1) (a) neutral species including alkyne−dinuclear complexes (**I**), vinylidene (**II**), and allenylidene species (**III**), (b) charged derivatives including dinuclear metal-stabilized carbenium ions (**IV**), dinuclear heteroelement-cations (**V**), and dinuclear ylide complexes (**VI**).

These compounds may be heterodinuclear ($M \neq M'$) or homodinuclear ($M = M'$). We wish to establish a connectivity and/or a relationship among the different species present in Chart 1. In this respect we would like to outline the possible chemical transformation or isomerization processes that would transform them into each other. We also discuss a rich and interesting chemistry of a class of dinuclear carbonyl complexes anchored to the fulvalene ligand, which has not hitherto been reviewed.

The extensive review by Bruce[4] reported mainly the chemistry of vinylidenes and carbenes and hence will not be reviewed here. However we wish to outline the recent developments and describe the relationship between **I** and **II**. Further a recent review on $[Co_2]$ propargylium ions type **IV** has been reported by Nicholas et al.[5] The authors describe the use of these species and their applications in organic chemistry; thus, this area will not be investigated,

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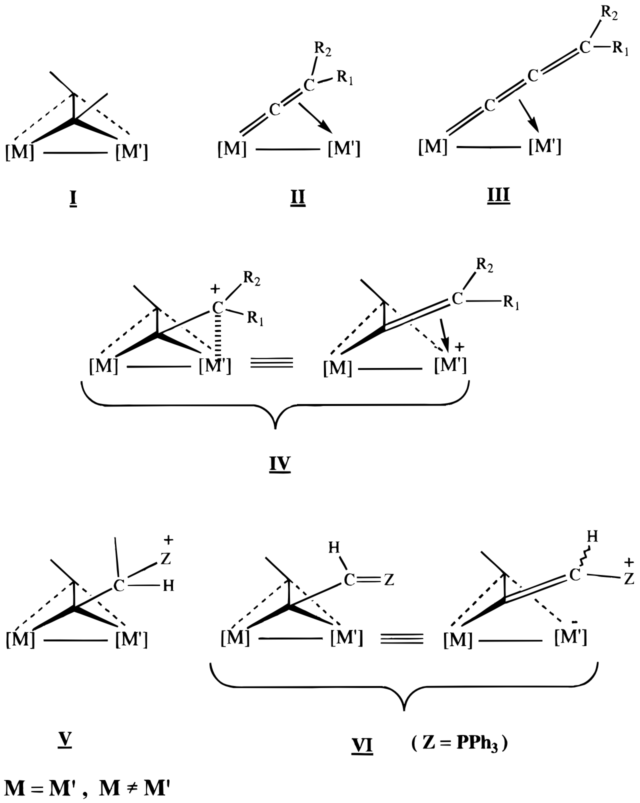
Hani El Amouri was born in Anapolis Goias (Brazil) and received his Ph.D. (1987) in transition metal chemistry in catalysis (hydrogenation) from Louis-Pasteur University (Strasbourg) under Professor J. A. Osborn. In 1988, he joined the group of H. Felkin ICSN, Gif-sur-Yvette, for a one year postdoctoral period, where he studied C–H activation of saturated hydrocarbons using polyhydride of transition metal complexes. In 1989 he joined the URA 403 (Unité de Recherche Associée), a C.N.R.S. research group within the Ecole Nationale Supérieure de Chimie de Paris directed by Professor G. Jaouen. In 1992, he spent one year at the University of California, Berkeley, where he joined the group of Professor K. P. C. Vollhardt and has been working on the synthesis of oligocyclopentadienyl metal complexes and their behavior as electron-transfer reagents. He is currently a “Chargé de Recherche in CNRS” at the URA 403. His research interests include synthesis and reactivity of dinuclear monocarbenium and dicarbenium complexes, organometallic ylide complexes as Wittig reagents, π-complexation of arenes with useful chains, and conjugated metallacyclopentadienyls in electron-transfer reactions.

Michel Gruselle is Directeur de Recherche at the Centre National de la Recherche Scientifique, born in Decazeville (France). He received his Masters Degree in Chemistry at Orsay University in 1968 and his Doctoral Degree in 1975. In 1969 he joined Bianca Tchoubar’s group at the C.N.R.S. Laboratory in Thiais, a suburb of Paris, where he worked on stereochemical problems in radical reactions. He then became interested in nitrogen activation and spent some time on this subject collaborating with Professor A. S. Shilov in Moscow. From 1986 to the present he has been a member of URA 403 (Unité de Recherche Associée), a C.N.R.S. research group within the Ecole Nationale Supérieure de Chimie de Paris directed by Professor G. Jaouen, where he began developing the chemistry of carbenium ions stabilized by bimetallic clusters.

but a complete review on the syntheses of the homo- and heterodinuclear propargylium ions (**IV**) will be presented. Further more the solution and fluxional behavior as a function of metal and ancillary ligands will be discussed. We also describe unexpected rearrangements of the bridging hydrocarbon ligand in these propargylium ions (**IV**). Several papers have been recently reported on complexes of type **IV**; hence, we wish to outline the recent development in this area.

Chart 1



Another interesting class of dinuclear species is type **V** they have been neglected in literature although they serve as synthetic equivalents of the propargylium ions, exhibiting attenuated reactivity toward nucleophiles. They also can be used to prepare polynuclear species exhibiting new reactivity. Further this class of compounds type (**V**) (Z = PPh_3) can be deprotonated to give the novel dinuclear ylide species type **VI** where the metal center stabilizes the corresponding zwitter ion form. This new generation of dinuclear ylide species (**VI**) may promote the Wittig reaction[6] to allow the preparation of enyne substrates, important molecules in organic syntheses. This review will also outline the recent development in the synthesis and coupling reactions involving presumably the dinuclear propargyl radicals as reactive intermediates.[7]

III. Neutral Dinuclear Species

A. Dinuclear Alkyne Complexes (I)

Dinuclear bridging alkyne complexes have been prepared for almost all transition elements from groups V to VIII.[8] These complexes display two types of bonding whether the alkyne group is perpendicular to the metal−metal bond (form I) or parallel to the metal−metal bond (form II) (see Figure 1).

In the latter case the ligand is two-electron donor. Such complexes are mostly encountered with group VIII. Form I is well known and has been largely investigated, the alkyne unit donates four electrons to the metal centers as described by the Dewar−Chatt−Duncanson model[9] (Figure 2).

In this orientation the bonding to each metal can be described as a combination of σ-donation and

Figure 1.

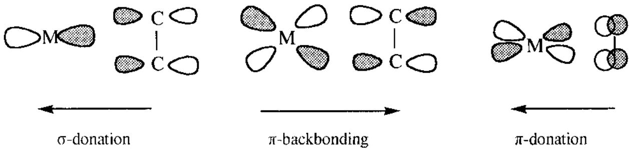


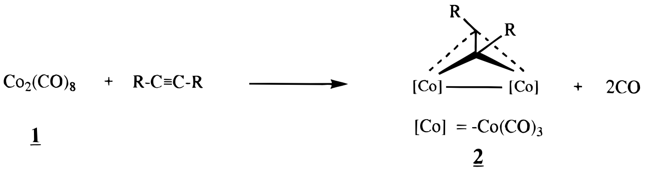
Figure 2.

π-back-bonding interactions with one of the orthogonal sets of π- and π*-orbitals bonding to each metal. X-ray crystallographic data of these species[10] have shown that the coordination of the alkyne unit to the dinuclear system increases the —C≡C— bond distance concomitant with a decrease in the X—C≡C— angle θ. These variations are influenced by the nature of the metal (oxidation states, whether rich or poor electron donor) as well as to the nature of the disubstituted acetylene unit.

Extended Huckel molecular orbital calculations carried out on the parallel and perpendicular alkyne bonding have been reported.[11] The authors suggest that the interconversion between the two modes requires high activation energy barrier and thus rotation of the alkyne unit in either type of complex should not readily occur. It is worth knowing that there are few examples where the bonding structure does not fit into either type of complex, where the alkyne unit is rotated by 31—35° away from the perpendicular position.[12]

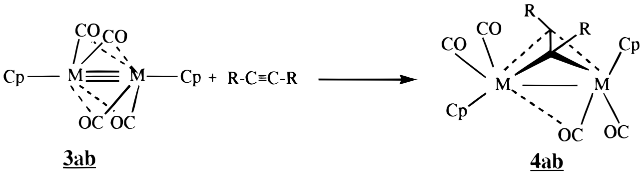
The synthetic approach to these dinuclear alkyne complexes consists of treating the dinuclear compounds with the alkyne unit. The most usual reaction is the substitution of two carbonyl groups in $Co_2(CO)_8$ (**1**) by an acetylenic molecule RC≡CR to yield the dinuclear alkyne complex $[Co_2(CO)_6(\mu\text{-}\eta^2,\eta^2\text{-}RC{\equiv}CR)]$ **2**[8f] (Scheme 1).

Scheme 1



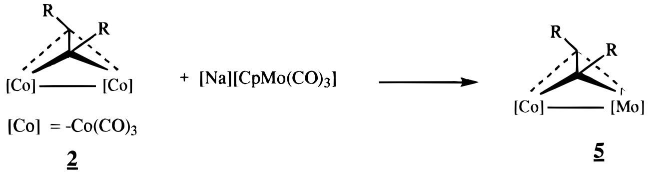
Further treatment of the tetracarbonyl dinuclear species $[Cp_2M_2(CO)_4]$ (M = Mo, W) **3ab** with the alkyne molecule affords the substituted dinuclear alkyne complex $[Cp_2M_2(CO)_4(\mu\text{-}\eta^2,\eta^2\text{-}RC{\equiv}CR)]$ **4ab** where the metal vertex $CpM(CO)_2$ is isolobal with the $-Co(CO)_3$ unit[13] (Scheme 2).

Scheme 2



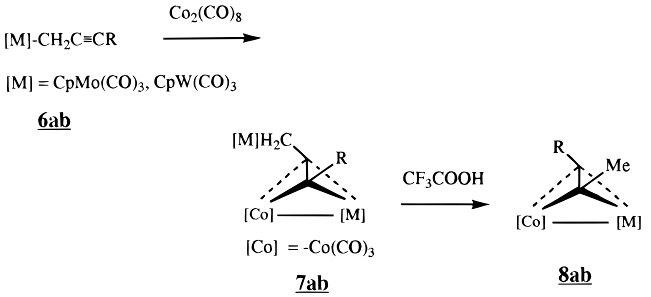
The isolobal relationship between $-CpMo(CO)_2$ and $-Co(CO)_3$ units makes it easy to replace one of the cobalt vertices in the dinuclear alkyne cobalt complex[14] and prepare the mixed heterobimetallic system $[Cp(CO)_2MoCo(CO)_3(\mu\text{-}\eta^2,\eta^2\text{-}RC{\equiv}CR)]$ **5** as demonstrated by Scheme 3.

Scheme 3



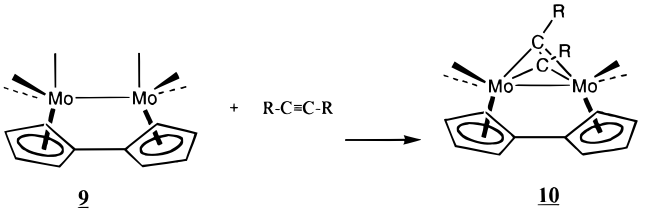
Another synthetic procedure to these heterodinuclear systems was described by Wojcicki and coworkers,[15] thus the pendant acetylenic functionality in $[M(CO)_3Cp(\eta^1\text{-}CH_2C{\equiv}CR)]$ **6ab** (M = Mo, W; R = Me, Ph) has been used as a template for the two-step synthesis of heterodinuclear μ-alkyne complexes **8ab** (Scheme 4). The presence of different metal centers is supposed to illicit different reactivity when compared to homobinuclear complexes.

Scheme 4



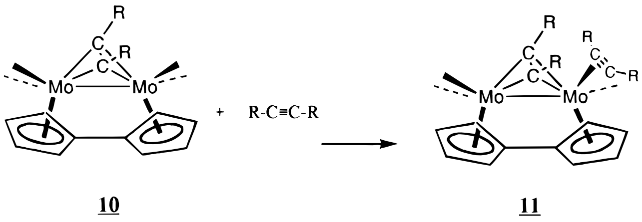
A new class of dinuclear complexes which has received less attention in the literature are the dinuclear fulvalene alkyne complexes $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^2\text{-}RC{\equiv}CR)]$ **10**, Fv = fulvalene.[16] The fulvalene ligand contains two connected Cp rings and hence they are forced to be always in cis geometry and hence it offers a different bonding structure when compared with analogous Cp systems. The intermetallic distance in a planar fulvalene system is 4 Å, and since simple M—M metal distances are less than 3.5 Å,[17] this situation results in creating a strain angle while the metal—metal bond becomes more reactive than the analogous Cp systems and hence different reactivities are expected to take place. Vollhardt and co-workers[18] have elegantly prepared these dinuclear fulvalene alkynes by irradiating the dinuclear fulvalene complex $FvMo_2(CO)_6$ (**9**) in the presence of the alkyne to give the dinuclear species $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^2\text{-}RC{\equiv}CR)]$ (**10**) (see Scheme 5).

Scheme 5



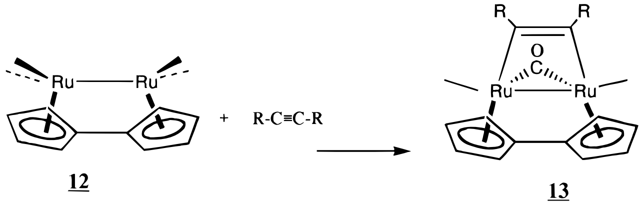
Further photolysis of [$FvMo_2(CO)_4(\mu$-η^2,η^2-RC≡CR)] in the presence of alkynes afforded [$FvMo_2(CO)_3(\mu$-η^2,η^2-RC≡CR)(η^2-RC≡CR)] (**11**) containing one terminal and one bridging alkyne (Scheme 6). The structure of one of these derivatives (R = $-CO_2Me$) was determined.[17] These species are unusual because the alkynes remain uncoupled, unlike those observed with the analogous Cp systems.

Scheme 6



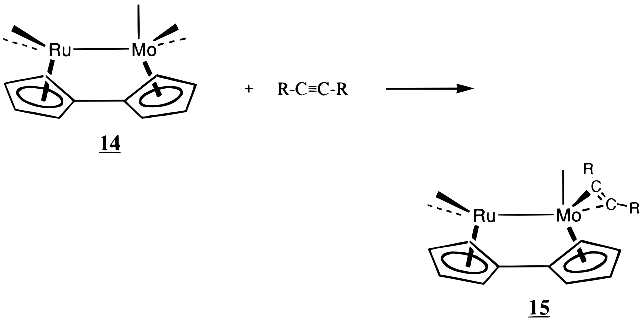
It is worth mentioning that photolysis of the fulvalene ruthenium dimer $FvRu_2(CO)_4$ (**12**), in the presence of alkynes,[19] afforded the dinuclear alkyne complex **13** where the alkyne unit is parallel to the Ru−Ru metal−metal bond, thereby acting as a two-electron donor (Scheme 7).

Scheme 7



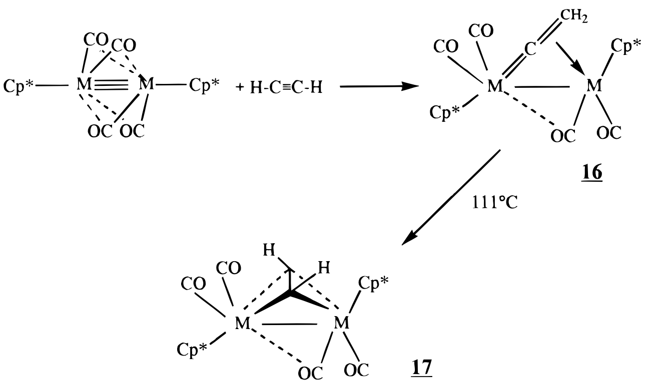
We have also found that refluxing of the dimer $FvMo_2(CO)_6$ with the alkyne unit in toluene affords the dimetal alkyne complex [$FvMo_2(CO)_4(\mu$-η^2,η^2-RC≡CR)] in good yield.[20] Vollhardt and co-workers have also reported a general synthetic procedure for the preparation of fulvalene heterodinuclear complexes[21] which show different reactivity to their analogous homodinuclear species. For instance complex FvRu−$Mo(CO)_5$ (**14**) reacts with alkyne to produce the dinuclear alkyne complex **15** with the alkyne unit only bonded to the molybdenum center (Scheme 8).

Scheme 8



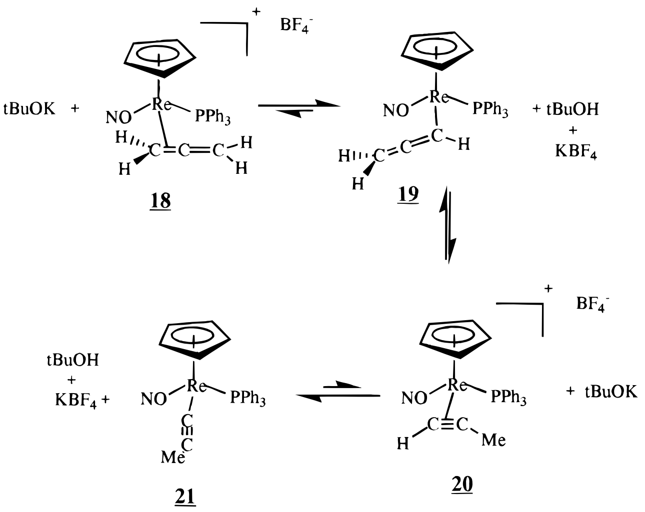
On the other hand the tetracarbonylmolybdenum dimer [$Cp^*_2Mo_2(CO)_4$] reacts with acetylene to yield the side-on vinylidene species **16** which upon warming to 111 °C rearranges to give the expected 1-alkyne dimolybdenum species [$Cp^*_2Mo_2(CO)_4(\mu$-η^2,η^2-HC≡CH)] **(17),** (Scheme 9).[22]

Scheme 9



Vinylidene complexes are known to isomerize to the corresponding 1-alkyne dinuclear complexes. Another example describing this phenomenon was reported by Gladysz and co-workers[23] but on a mononuclear system. Thus deprotonation of the η^2-bound allene precursor [CpRe(NO)(PPh_3)(η^2-CH_2=C=CH_2)]$^+$ (**18**) by *t*-BuOK gave the methylacetylide complex [CpRe(NO)(PPh_3)(η^1-C≡CMe)] (**21**). Further studies on these systems suggested that the first step in the above reaction consists of the formation of the σ-bound allenyl species [CpRe(NO)(PPh_3)(η^1-CH=C=CH_2)] (**19**), which exists in equilibrium with its corresponding η^2-boundalkyne complex [CpRe(NO)(PPh_3)(η^2-HC≡C-Me)]$^+$ (**20**), and subsequent deprotonation by *t*-BuOK affords the acetylide derivative **21** (Scheme 10).

Scheme 10



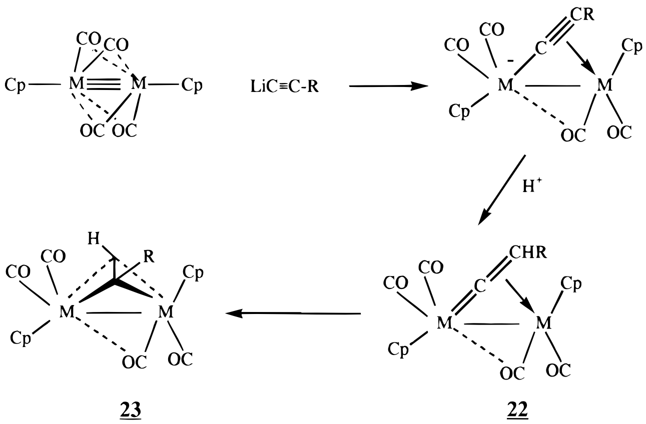
B. Dinuclear Vinylidene Complexes (II)

As mentioned previously, there are good reviews in this area and the last report was published in 1991 by Bruce.[4] We note that some papers have appeared in this area since 1991,[24] and hence, we will outline the recent development in dinuclear vinylidene derivatives and their relationships with the corresponding 1-alkyne species. These vinylidene complexes exist either as form A in which the unsaturated hydrocarbon bridges symmetrically the two metal centers and acts as a two-electron donor or form B adopting unsymmetrical a side-on fashion and providing four electrons to the metal centers (Figure 3).

Figure 3.

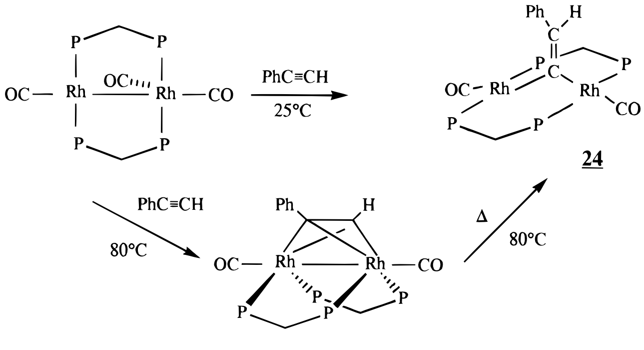
A general procedure for the preparation of these side-on vinylidene species consists of treating the tetracarbonyl dimer [Cp$_2$M$_2$(CO)$_4$] with lithium acetylides giving the anionic bridging acetylide dimers [Li][Cp$_2$M$_2$(CO)$_4$(μ,σ:η^2-C≡CR)].[25] Protonation or alkylation of the latter produces the corresponding side-on vinylidene species **22** (Scheme 11). The latter rearranges to give the 1-alkyne complex **23**.

Scheme 11



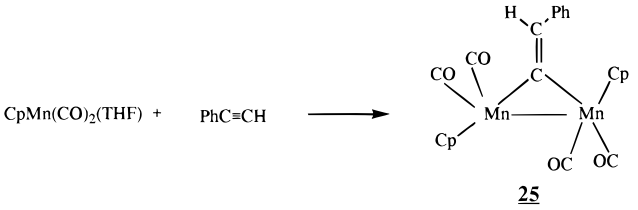
An X-ray structure of such vinylidene complex was reported in the literature.[26] Generally the side-on vinylidene derivative rearranges to give the corresponding dinuclear 1-alkyne species. Another example illustrating the relationship between 1-alkyne binuclear complexes and the corresponding carbene-species is shown by Scheme 12 for instance, treatment of [Rh$_2$(dppm)$_2$(CO)$_3$] with PhC≡CH gives the bridged alkyne species [Rh$_2$(μ-dppm)$_2$(CO)$_2$(μ-PhC≡CH)] which upon further heating is transformed to the symmetrical bridged vinylidene derivative **24**.[27]

Scheme 12



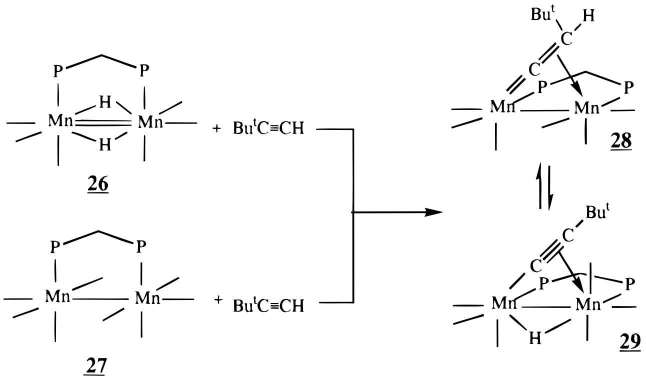
In a similar reaction it has been found that treatment of the mononuclear CpMn(CO)$_2$(THF) species with phenylacetylene affords the dinuclear complex **25** where the vinylidene unit bridges the dimanganese frame,[28] while acting as a two-electron donor (Scheme 13).

Scheme 13



Recently Riera et al.[29] have reported that 1-alkynes (HC≡CR, R = H, Ph,) react with dimanganese complexes **26** and **27** to afford the hydrido vinyl complexes while in the case of R = *t*-Bu, a mixture of side-on vinylidene dinuclear species [Mn$_2$(μ_2-η^1,η^2-C=CH*t*-Bu)(CO)$_6$(μ-dppm)] (**28**) and the bimetallic hydrido−alkynyl complex [Mn$_2$(μ-H)(μ_2-η^1,η^2-C≡C*t*-Bu)(CO)$_6$(μ-dppm)] (**29**) was obtained (Scheme 14). The authors have also observed[29] the spontaneous isomerization of the bridging vinylidene [Mn$_2$(μ_2-η^1,η^2-C=CH*t*-Bu)(CO)$_6$(μ-dppm)] (**28**) to give the hydrido−alkynyl complex [Mn$_2$(μ-H)(μ_2-η^1,η^2-C≡C*t*-Bu)(CO)$_6$(μ-dppm)] (**29**) (Scheme 14). Such a process has been considered to be disfavored on theoretical grounds. In this regard Sylvestre and Hoffmann[30] have carried out EHMO calculations on the possible rearrangement of the 1,2-hydrogen shift. Their conclusion suggests that hydrido alkynyl complexes could isomerize to give the corresponding vinylidene species while the reverse process in dinuclear systems is not possible.

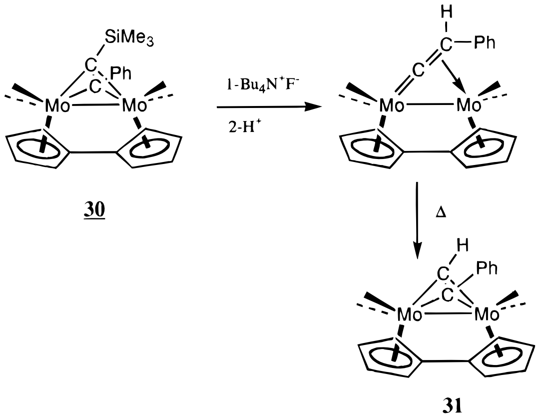
Scheme 14



An interesting class of dinuclear vinylidene complexes are those obtained with the fulvalene ligand. Huffmann[31] has reported the preparation of homo- and heterodinuclear vinylidene complexes. The author obtained the side-on vinylidene species [FvMo$_2$(CO)$_4$(μ-η^1,η^2-C=C(H)(Ph)] when the alkyne−molybdenum dimer **30** was protodesylilated. Upon warming [FvMo$_2$(CO)$_4$(μ-η^1,η^2-C=C(H)(Ph))] it isomerizes to the corresponding bridging 1-alkyne species **31** (Scheme 15).

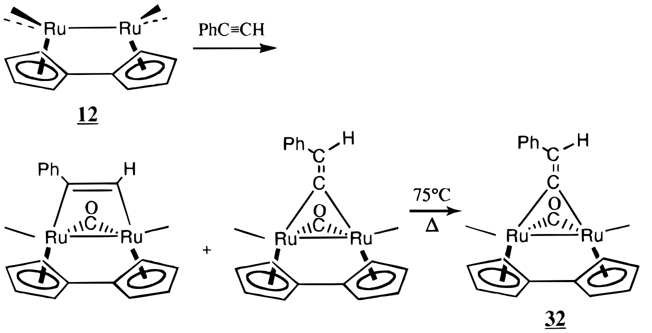
On the other hand photolysis of the ruthenium dimer **12** in the presence of phenylacetylene affords a mixture of the symmetric dinuclear vinylidene species [FvRu$_2$(CO)$_2$(μ-CO)(μ-η^2-C=C(H)(Ph))] and the parallel bridging alkyne derivative [FvRu$_2$(CO)$_2$(μ-CO)(μ-η^1,η^1-HC≡CPh)] in 3: 1 ratio. When the mixture was heated to 75 °C it was converted to

Scheme 15



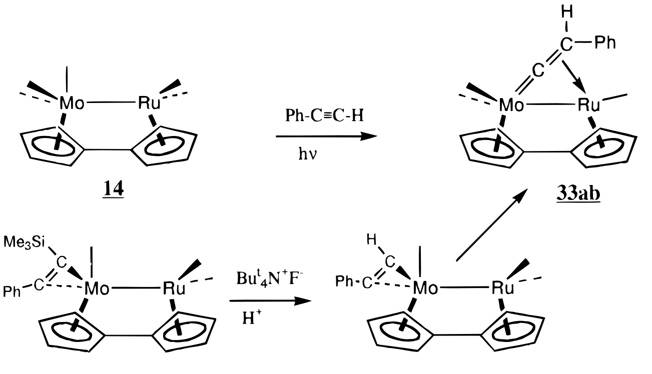
the corresponding symmetric vinylidene species **32** (Scheme 16).

Scheme 16



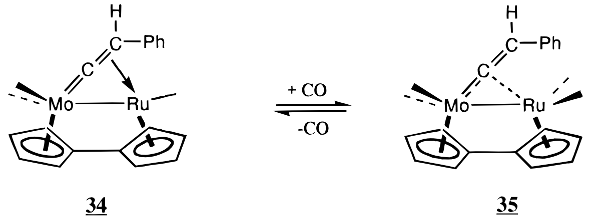
Vollhardt and co-workers[32] have also investigated the reactivity of heterodinuclear fulvalene complex FvRuMo(CO)$_5$ (**14**) with disubstituted and 1-alkynes. These systems appear to offer a richer chemistry than their homonuclear analogs. Thus photolysis of **14** with phenylacetylene gave a mixture of two isomers in (3.5:1) ratio of the side-on vinylidene derivatives **33ab** (Scheme 17). These species can also be obtained from protodesilylation of the alkyne complex [FvMoRu(CO)$_3$(Me$_3$SiC≡CPh)] which affords primarily the terminal-alkyne compound [FvMoRu(CO)$_3$(HC≡CPh)]. The authors have found[32] that the complex [FvMoRu(CO)$_3$(HC≡CPh)] undergoes a rapid isomerization process (alkyne−vinylidene side on) even at −40 °C.

Scheme 17



An important process has been disclosed by the same group[32] concerning the reversible conversion of a side-on vinylidene coordination mode in complex **34** to a semibridging vinylidene coordination mode in complex **35** by a carbonylation/decarbonylation process (Scheme 18). Such coordination mode remained unknown for the bridging vinylidene ligands; however, this mode of binding is well documented for other ligands especially CO.[32] The molecular structures of **35** was determined by X-ray analysis, thus confirming their spectroscopic and solution behavior.

Scheme 18



C. Dinuclear Allenylidene Complexes (III)

As a general trend, most of complexes containing C=C=C(R)(R′) ligands exhibit two modes of coordination[33] similar to that of the vinylidene species type **II**: (a) The symmetrical allenylidene complexes (A) where the bridging unsaturated carbene provides two electrons to the two metal centers (Figure 4). (b) The side-on allenylidene complexes (B) where the ligand acts as a four-electron donor.

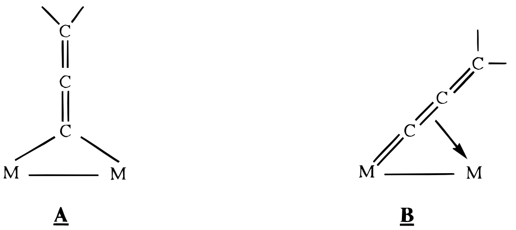


Figure 4.

Complexes of type **III** have been reviewed by Bruce in 1991.[4,33] The preparation of allenylidenes of type "A" involves treatment of the dinuclear carbonyl species with deprotonated alcohol $[C{\equiv}CCR_2O]^{2-}$ leading to the intermediate acetylide dianion $[M_2(CO)_9(C{\equiv}CCR_2O)]^{2-}$ further treatment with phosgene liberates CO$_2$ forming the symmetric allenylidene $[M_2(CO)_9(\mu\text{-}\eta^1,\eta^1\text{-}C{=}C{=}CR_2)]$ (M = Mn, Re).[33] Similarly the mononuclear allenylidene species $[W(CO)_5(C{=}C{=}CPh_2)]$ was prepared,[34] which upon further condensation with W(CO)$_6$ afforded the dinuclear $[(W(CO)_5)_2(\mu\text{-}\eta^1,\eta^1\text{-}C{=}C{=}CPh_2)]$. Allenylidenes of type "B" **37** can be obtained by addition of acetylides to

Scheme 19

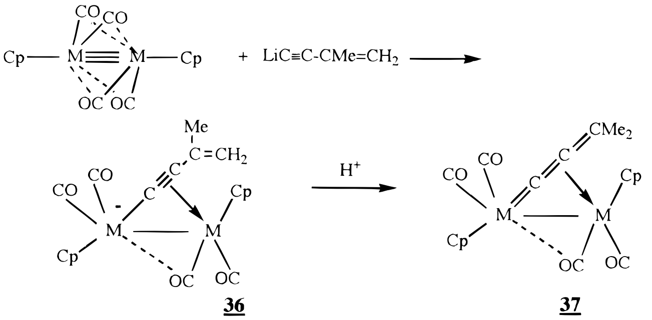
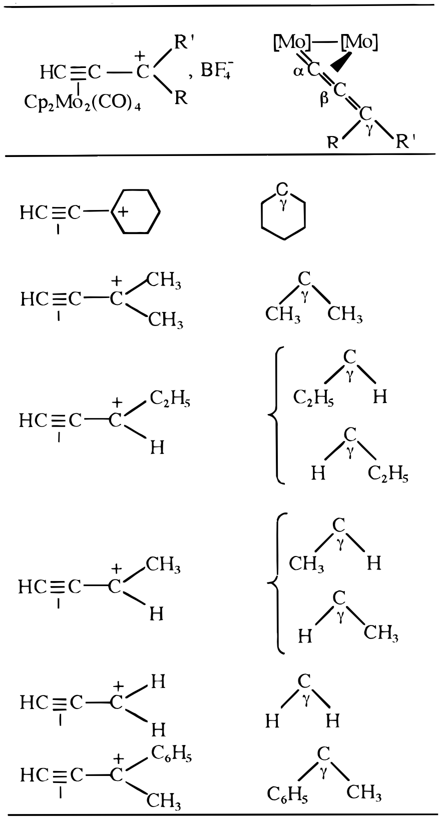


Table 1. μ-η^2,η^3-Allenyl and the Corresponding μ-η^2-Allenylidene Molybdenum Complexes

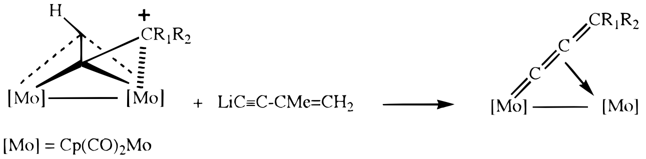


the tetracarbonyl dimers [$Cp_2M_2(CO)_4$] followed by protonation of the anionic intermediate **36**[35] (Scheme 19).

It is worth mentioning that during the last years a great number of papers on this topic were reported including a recent and efficient synthetic procedure for these allenylidene species.[36]

As presented previously in this review, we would like to stress the connectivity among these different types of dinuclear complexes; in this regard, an efficient method for the preparation of these allenylidene complexes relating type **III** and type **IV** has been published. Recently Kergoat and co-workers reported a general procedure for the preparation of side-on allenylidene complexes in high yields. The abstraction of the acetylenic proton of the dinuclear propargylium complexes **38** type **IV** by the acetilyde $LiC{\equiv}CC(CH_3){=}CH_2$ afforded the corresponding allenylidene complexes **39** type **III** in high yield (Scheme 20).

Scheme 20

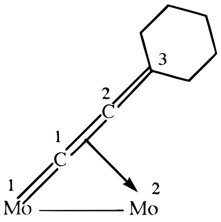


38 **39**

Table 1 presents some allenylidene complexes obtained via the new method.[36]

The X-ray structure of one compound [$Cp_2Mo_2(CO)_4(\mu$-η^2-$C{=}C{=}C_6H_{10})$] belonging to the allenylidene family was determined.[36] Some bond lengths and angles of this compound [$Cp_2Mo_2(CO)_4(\mu$-η^2-$C{=}C{=}C_6H_{10})$] are presented in Table 2.

Table 2. Some Bond Lengths and Angles of $Cp_2Mo_2(CO)_4(\mu$-η^2-$C{=}C{=}C_6H_{10})$



Mo1-Mo2	= 3.163(2)Å
Mo1-C1	= 1.190(1)Å
Mo2-C1	= 2.20(1)Å
Mo2-C2	= 2.26(1)Å
C1-C2	= 1.32(1)Å
Mo1-C1-C2	= 168.5(8)°
C1-C2-C3	= 146(1)°

The nature of the starting material cationic complexes (**IV**) affects the yield and the number of allenylidene species obtained.[36] For instance when the carbenium center possesses two different substituents, the authors observed the formation of two allenylidene isomers, in which the different substituents at "Cγ" adopt two opposite configurations. Only one isomer was obtained when one of the substituents at the "Cγ" was bulky. For steric reasons the bulky substituent is directed away from the metal center Figure 5.

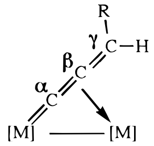
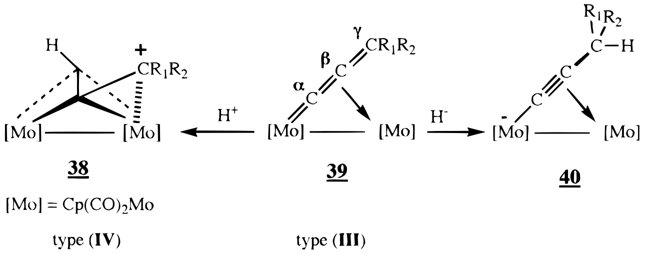


Figure 5.

It is also important to note that the acetylide reagent $LiC{\equiv}CC(CH_3){=}CH_2$ is very specific toward the abstraction of the acetylenic proton from the cationic species type **IV**. In this respect when the cations [$Cp_2M_2(CO)_4(\mu$-η^2,η^3-$HC{\equiv}CCMe_2)$][BF_4], M = Mo, W, were treated with other kinds of bases such as *t*-BuLi, MeLi, or DBU, different types of complexes were obtained.[36]

Green and co-workers[37] reported that treatment of dinuclear allenylidene complex [$Cp_2Mo_2(CO)_4(\mu$-η^2-$C{=}C{=}C(R^1)(R^2))$] **39** with an hydride afforded the corresponding acetylide anion **40**; the authors suggested that the nucleophilic attack is kinetically regiocontrolled and is occurring at the "Cγ" carbon (Scheme 21).

Scheme 21



38 **39** **40**

type (**IV**) type (**III**)

We also note that the side-on alkylidene complexes can be protonated at the Cα carbon by HBF_4/Et_2O to give the corresponding propargylium complexes **38** type **IV** (Scheme 21).

The chemical reversibility between complexes of type **III** and type **IV** represents one of the manuscript goals where a direct relationship can be established among the different dinuclear families presented in this review.

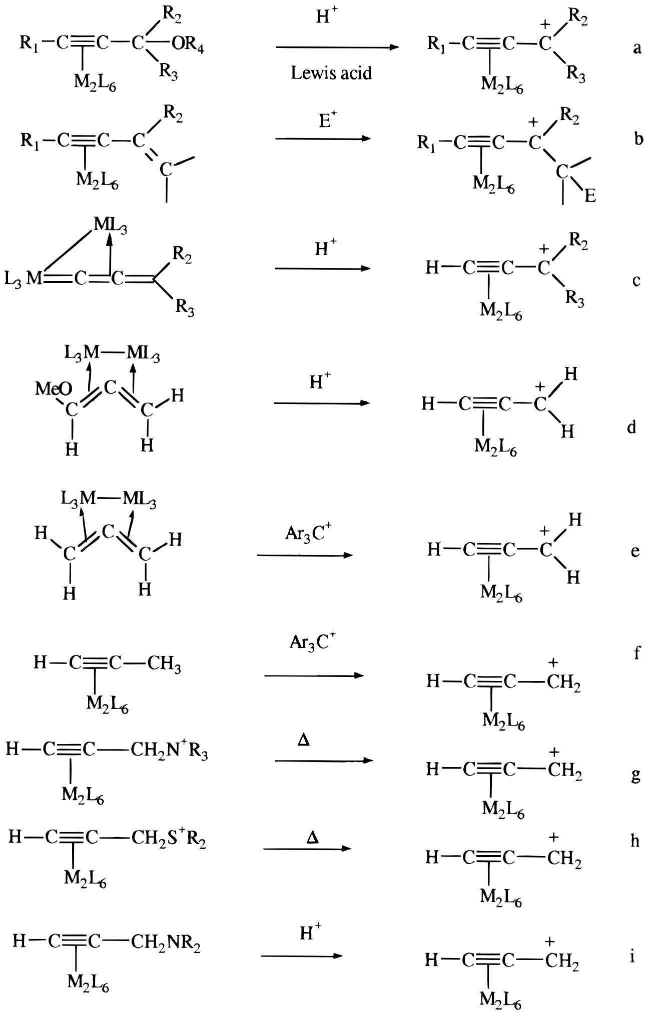
IV. Cationic Dinuclear Species

A. Dinuclear Propargylium Complexes (IV)

1. Synthesis

Dinuclear propargylium species were prepared using different routes as shown in Scheme 22 a–i.

Scheme 22. Synthetic Pathways To Obtain [M_2L_6]-Stabilized Propargylium Ions



The most useful pathway consists of the action of a Lewis or Brönsted acid on acetylenic ether or alcohol dinuclear complexes[38–39] (a). In general the reaction is performed in Et_2O solution; the cationic species formed, which is insoluble in this medium, appears as a red brown oil or a precipitate. By this technique, some homo ([Co_2], [Mo_2], or [W_2]) and hetero ([Co–Mo] or [Co–W]) propargylium ions were obtained. Others routes have been described in the literature using enyne[40] (b), allenylidene[38,41] (c), or allenic complexes[42] (d). Abstraction of a hydrogen by Ar_3C^+ from an acetylenic complexed hydrocarbon derivative was also described[42] (f).

Thermolysis of an ammonium complex leads also to carbenium ion species[43] (g). Other methods to generate dinuclear propargylium ions from sulfonium or amine derivatives are mentioned in the literature[44] (h and i).

Table 3. pKR⁺ Values for Several Carbonium Ions

compounds	pKR⁺	ref
triphenylmethyl	−6,6	38
α-ferrocenylmethyl	−1,5	38
α-[(benzene)chromiumtricarbonyl]methyl	−11,8	38
$[(HC{\equiv}CC(CH_3)_2)Co_2(CO)_6]^+$	−7,2	38
$[(HC{\equiv}CC(C_6H_5)_2)Co_2(CO)_6]^+$	−7,4	38
$[(HC{\equiv}CCH_2)Co_2(CO)_6]^+$	−6,8	38
$[(HC{\equiv}CCH_2)Mo_2Cp_2(CO)_4]^+$	+3,5	45
$[(HC{\equiv}CC_{19}H_{25}O)Mo_2Co_2(CO)_4]^+$	+2,7	45
$[(HC{\equiv}CC_{19}H_{25}O)Co_2(CO)_6]^+$	−7,3	45

2. Identification and Physical Characteristics

The [Mo_2], [W_2], or [Mo–Co] propargylium ions are much more stable than their corresponding [Co_2] propargylium ions; the latter in general are moisture sensitive. They can be isolated and identified as definite products.

pKR⁺ Measurements. The pKR⁺ values (Table 3) found for [Mo_2] propargylium ions are ~9 units higher than their [Co_2] equivalents.[45] For example, the pKR⁺ for $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH_2)]^+$ is +3.5 at 20 °C compared to −6.8 in case of the analogous cobalt–cation complex $[Co_2(CO)_6(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH_2)]^+$.[38,46] The pKR⁺ value is a direct indication of the thermodynamic stability of the carbonium center ($-C^+$). This implies that the molybdenum is much more efficient than cobalt at alleviating the positive charge located on the carbenium center.

The great stabilizing effect of molybdenum is illustrated by its capacity to counterbalance the withdrawing effect of α-CF_3 substituent, rendering possible the isolation of α-CF_3-secondary or -tertiary carbenium ions like $[CoMoCp(CO)_5(\mu\text{-}\eta^2,\eta^3\text{-}CH_3(CH_2)_4\text{-}C{\equiv}CCH(CF_3))]^+$ or $[CoMoCp(CO)_5(\mu\text{-}\eta^2,\eta^3\text{-}CH_3(CH_2)_4\text{-}C{\equiv}CC(CH_3)(CF_3))]^+$.[47] It should be mentioned that the synthesis of the free cations $[RC{\equiv}CCH(CF_3)]^+$ is known to be quite difficult.[48]

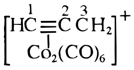
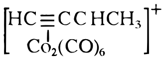
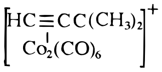
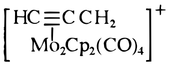
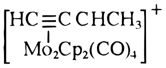
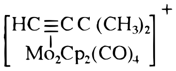
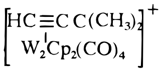
Electronic Absorption, Infrared, Raman, and NMR Measurements. *Electronic absorption* spectra were recorded for the complexed alcohol $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2,\eta^2\text{-}HC{\equiv}CCH_2OH)]$ and its corresponding cation $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH_2)]^+$. Two bands were found at 357 and 529 nm for the alcohol complex corresponding to $\sigma-\sigma^*$ and $d\pi-d\pi^*$ electronic transitions.[49] These bands are shifted to lower wave lengths at 348 and 485 nm for the corresponding cation $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH_2)]^+$.

Infrared and Raman Spectra. The IR spectra of $[Co_2(CO)_6(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCR^1R^2)^+$ (R^1 and R^2 are hydrogen or methyl groups) in CH_2Cl_2 indicate significant charge delocalization onto the cluster core (Table 4). The carbonyl absorptions of the alcohol complexes appear in the area 2010 −2090 cm^{-1}. These bands are shifted to higher wave lengths and appear around 2080–2130 cm^{-1} for the corresponding cation complexes.[38] The infrared spectra of $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH_2)]^+$ (**41**) were recorded in the solid state and in solution.[50,51] The spectra show that the four carbonyl vibrations are shifted to higher frequencies by a value of ~70 cm^{-1} relative to the parent complexed alcohol species. The lowest frequency

Table 4. IR Data for [Mo_2], [Mo−Co], and [Co_2] Propargylium Ions and Their Parent Alcohols

compounds		ν_{CO}, cm^{-1}	ref
$[(HC{\equiv}CCH_2OH)Co_2(CO)_6]$	CH_2Cl_2	2025, 2050, 2090	38
$[(HC{\equiv}CCH_2)Co_2(CO)_6]^+$	CH_2Cl_2	2085, 2105, 2130	38
$[(HC{\equiv}CCH_2OH)Mo_2Cp_2(CO)_4]$	KBr pellet	1986, 1903, 1829	49
$[(HC{\equiv}CCH_2)Mo_2Cp_2(CO)_4]^+$	KBr pellet	2042, 1994, 1982, 1984	49
$[(HC{\equiv}CCH(OH)(CH_3))MoCp(CO)_2Co(CO)_3]$	CH_2Cl_2	2050, 2000, 1980, 1942, 1888	52
$[(HC{\equiv}CCHCH_3)MoCp(CO)_2Co(CO)_3]^+$	CH_2Cl_2	2098, 2068, 2048, 2034, 2000, 1982, 1941	52
$[(CH_3C{\equiv}CCH_2OCH_3)FvMo_2(CO)_4]$	CH_2Cl_2	1992, 1920	20
$[(CH_3C{\equiv}CCH_2)FvMo_2(CO)_4]^+$	CH_2Cl_2	2049, 2022, 1955, 1950	20

Table 5. ^1H NMR Data of Several [Co_2], [Mo_2], and [W_2] Propargylium Ions

compound	solvent	H^1	H^3	CH_3	Cp	ref
		[Co_2]				
 $[\overset{1}{H}\overset{2}{C}{\equiv}\overset{3}{C}CH_2]^+$ $Co_2(CO)_6$	TFA	4.92−5.14	7.67			49
 $[HC{\equiv}CCHCH_3]^+$ $Co_2(CO)_6$	SO_2	6.6 d,q $J = 6\text{-}2$ Hz	8.2	2.2 d $J = 6$ Hz		38
 $[HC{\equiv}CC(CH_3)_2]^+$ $Co_2(CO)_6$	SO_2		7.6	2.2		38
		[Mo_2]				
 $[HC{\equiv}CCH_2]^+$ $Mo_2Cp_2(CO)_4$	$(CD_3)_2CO$	4.93−5.56	6.90		5.83−5.93	49
 $[HC{\equiv}CCHCH_3]^+$ $Mo_2Cp_2(CO)_4$	CD_2Cl_2	d $J = 2$ Hz 7.29	6.67	1.90	5.55−5.86	115
 $[HC{\equiv}CC(CH_3)_2]^+$ $Mo_2Cp_2(CO)_4$	CD_2Cl_2		6.29	2.07	5.64	37
		[W_2]				
 $[HC{\equiv}CC(CH_3)_2]^+$ $W_2Cp_2(CO)_4$	CD_2Cl_2		5.21	2.04	5.65	37

band has been attributed to a semibridged carbonyl ligand. The Mo−Cp vibration is also shifted in the same way by a value of about 20 cm^{-1}. These results indicate a decrease of the electronic density on the cluster core of the cationic complex compared to the starting alcohol. Surprisingly there is no variation observed in the frequency of the Mo−Mo vibrator at 180 cm^{-1}.[51] This implies that the delocalization of the positive charge onto the cluster affects the metal−ligands strengths but not the metal−metal bond, indicating that there is no electronic density variation on this metal−metal bond. Thus the metal appears to act just as a transferring medium of the electronic density from the ligands to the carbenium center. In the case of heterobinuclear cluster, $[CpMo(CO)_2Co(CO)_3(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CC(H)(CH_3)]^+$ the carbonyls absorptions' in solution were found at 1941, 1982, 2000, 2034, 2048, 2068, 2098 cm^{-1} compared to 1888, 1942, 1980, 2000, 2050 cm^{-1} in the starting secondary alcohol complex $[CpMo(CO)_2Co(CO)_3(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CC(H)(CH_3)OH)]$.[52]

^1H and ^{13}C nuclear magnetic resonance spectra were performed for a large variety of [M_2L_6] propargylium ions and provide some information about the distribution of the positive charge on the cluster and also on the geometry and symmetry of these complexed carbenium ions.[37,38,39a,46,50,53] For $[Co_2(CO)_6(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCR^1R^2)^+$ (R^1 and R^2 are hydrogen or methyl groups), the proton NMR spectra (Table 5) exhibited very small downfield shifts relative to the alcohols precursors.[38] The ^{13}C NMR (Table 6) spectra exhibit resonances which are only mildly deshielded relative to the alcohol−precursor complexes and dramatically shielded compared to those of free propargyl cations.[46] For [M_2L_6] = [$Mo_2Cp_2(CO)_4$] or [$W_2Cp_2(CO)_4$], the tendency is the same to that observed for [$Co_2(CO)_6$] propargylium ions. Curtis et al.[50] have reported the spectroscopic data (^1H, ^{13}C) of several acetylenic, allenic, and propargylic complexes with the dinuclear cluster [$Mo_2Cp_2(CO)_4$]. The authors correlated the chemical shifts and signals patterns to the chirality of the tetrahedral cluster [M_2C_2] core. For instance the chirality of the cluster core is determined by the diastereotopic feature displayed by the cyclopentadienyl ligands and by the hydrogens or substituents at the carbenium center. It is evident that this situation or chirality is a result of the bending of the carbenium center toward one of the metallic vertices.

X-ray structures were obtained for primary,[50] secondary,[54] and tertiary[45,55] homobimetallic complexed propargylium ions. The main characteristics of these ions in the solid state are the following: (1) The C_3R_3 ligand is unsymmetricaly bonded to the metallic atoms. (2) The molybdenum−molybdenum bond is single according to the interatomic distance dMo−Mo which is in the range of 2.90−3.00 Å (Table 7). (3) The cyclopentadienyl and carbonyl ligands are unsymmetrically arranged around the cluster core. (4) One of the carbonyl ligands is semibridging; the

Table 6. ^{13}C NMR Data of $[Co_2]$, $[Mo_2]$, and $[W_2]$ Propargylium Ions

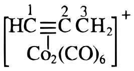
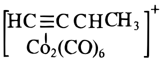
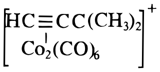
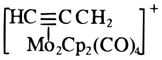
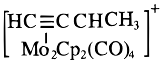
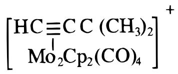
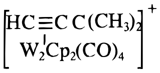
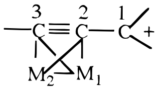
compound	solvent	C^1	C^2	C^3	CH_3	Cp	CO	ref
			$[Co_2]$					
 $\left[\begin{array}{l}H\overset{1}{C}\equiv\overset{2}{C}\overset{3}{C}H_2\\ \quad Co_2(CO)_6\end{array}\right]^+$	SO_2	79.5	122	80			192	46
 $\left[\begin{array}{l}HC\equiv CCHCH_3\\ \quad Co_2(CO)_6\end{array}\right]^+$	SO_2	107	117	79.5	21		193	46
 $\left[\begin{array}{l}HC\equiv CC(CH_3)_2\\ \quad Co_2(CO)_6\end{array}\right]^+$	SO_2	146	110	79.5	31−28		192	46
			$[Mo_2]$					
 $\left[\begin{array}{l}HC\equiv CCH_2\\ \quad Mo_2Cp_2(CO)_4\end{array}\right]^+$	$(CD_3)_2CO$	75.1	118.2	79.9		94.8−93.6	218−221.5	49
 $\left[\begin{array}{l}HC\equiv CCHCH_3\\ \quad Mo_2Cp_2(CO)_4\end{array}\right]^+$	CD_2Cl_2 (t = 193 K)	96.3	110.7	76.7	20.9	91.8−92.3	224-228 227.6−226.5	115
 $\left[\begin{array}{l}HC\equiv CC(CH_3)_2\\ \quad Mo_2Cp_2(CO)_4\end{array}\right]^+$	CD_2Cl_2 (t = 193 K)	143.7	104.2	76.7	28.8−36.2	92.8−93.7	217.9−217.1 227.2−227.1 216.9−217.7	115
			$[W_2]$					
 $\left[\begin{array}{l}HC\equiv CC(CH_3)_2\\ \quad W_2Cp_2(CO)_4\end{array}\right]^+$	CD_2Cl_2	151.9	93.2	54.2	33.1	90.7	205.7-209.2	37

Table 7. Crystallographic Bonds, Distances, and Angles for $[Mo_2]$ and, $[MoCo]$ and $[W_2]$ Propargylium Ions

	$d(M_1-C_1)$ Å	$d(M_1-M_2)$ Å	$\angle(C_1-C_2-C_3)$ deg	ref
$[(HC\equiv CCH_2)(Mo_2Cp_2(CO)_4)]^+$	2.444	3.022	133.85	49
$[(CH_3C\equiv CCH_2)(Mo_2Fv(CO)_4)]^+$	2.44	2.926	131.5	20
$[(CH_3C\equiv CCH_2)(Mo_2Fv(CO)_4)]^+$	2.55	2.926	140.6	20
$[(HC\equiv CCH_2)(Mo_2(CO)_4(C_5F_4Me)_2)]^+$	2.47	3.01	139	50
$[(HC\equiv CCH_2)(Mo_2(CO)_4(C_5F_4Me)_2)]^+$	2.47	3.02	137	50
$[(HC\equiv CCHMe)(Mo_2Cp_2(CO)_4)]^+$	2.613	3.007	130.5	7b
$[(CH_3CH_2CH_2C\equiv CCH$ferrocenyl$)(Mo_2Cp_2(CO)_4]^+$	2.63	2.963	141.1	116
$[(CH_3C\equiv CCH$bornyl$)(Mo_2Cp_2(CO)_4]^+$	2.915	2.960		55b
$[(HC\equiv C$mestranyl$)(Mo_2Cp_2(CO)_4]^+$	2.74	3.018	144	45
$[(HC\equiv CCMe_2)(Mo_2Cp_2(CO)_4]^+$	2.75	3.021	136.4	55a
$[(HC\equiv CCHMe)(MoCp(CO)_2CoCO)_3)]^+$	2.64	2.719	142.5	52
$[(CH_3C\equiv CCH$ferrocenyl$)(MoCp(CO)_2Co(CO)_3]^+$	2.726	2.715	140.2	118
$[(CH_3C\equiv CCH$cymanthrenyl$)(MoCp(CO)_2Co(CO)_3]^+$	2.66	2.715	133.4	118
$[(CH_3C\equiv CCH$fenchyl$)(MoCp(CO)_2Co(CO)_3]^+$	3.08	2.6781	146.6	57
$[(HC\equiv CCHMe_2)(W_2Cp_2(CO)_4)]^+$	2.837	2.943	136.1	37

other three are terminals. (5) The local symmetry for the C_2M_2 cluster core is C_{2v}.

The X-ray structure of the most simple complexed $[Mo_2]$ carbenium ion $[Cp_2Mo_2(CO)_4(\mu,\eta^2,\eta^3\text{-}HC\equiv CCH2)]$-$[BF_4]$ (**41a**) which illustrates these properties is shown in Figure 6.

The distance between the interacting molybdenum atom and carbenium center determines the strength of the stabilizating interaction. This distance increases from 2.45 to 2.63 and then 2.74 Å for primary,[50] secondary,[54] and tertiary,[45,55a] cations. For tertiary $[W_2]$ propargylium ions, this distance was found to be 2.83 Å[37] (Table 7). In the case of a fulvalene ligand the structures of primary and tertiary cations were also determined.[20,56] Figure 7 shows the X-ray structure of the fulvalene tertiary carbenium ion $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC\equiv CCMe_2)]$-$[BF_4]$ (**41b**).

The structure displays a partial C_{2v} symmetry not only for the C_2Mo_2 core but also for the fulvalene and carbonyl ligands. We also note the absence of a semibridging carbonyl as usually found in the analogous cyclopentadienyl system $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC\equiv CCH_2)][BF_4]$ (Figure 6).

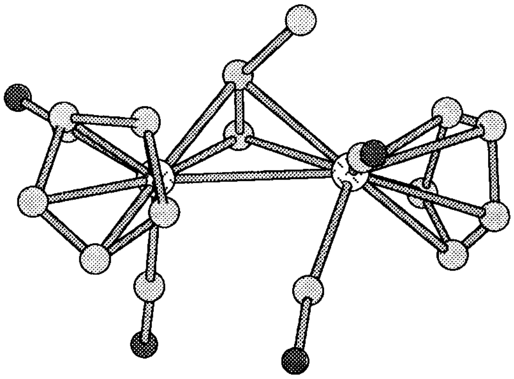


Figure 6. View of the cation $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC\equiv CCH_2)]^+$ (**41a**).

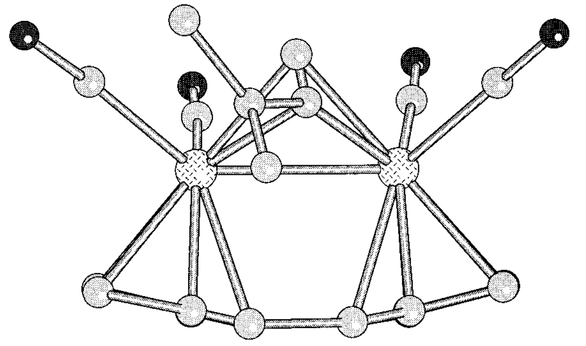


Figure 7. X-ray molecular structure of $[FvMo_2(CO)_4(\mu$-η^2,η^3-$HC{\equiv}CCMe_2)]^+$ (**41b**).

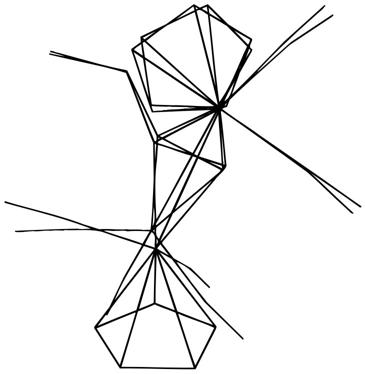


Figure 8. Superimposed view of $(Mo_2Cp_2(CO)_4)[HC{\equiv}CCH(CH_3)]^+$ and $(MoCp(CO)_2Co(CO)_3)[HC{\equiv}CCH(CH_3)]^+$.

Some X-ray structures were resolved for heterobimetallic [Mo−Co] propargylium ions (Table 7).

A comparison between the solid-state structures of homobinuclear cluster $[Mo_2Cp_2(CO)_4(\mu$-η^2,η^3-$HC{\equiv}CCH(CH_3))][BF_4]$ and heterobinuclear cluster $[CpMoCo(CO)_5(\mu$-η^2,η^3-$HC{\equiv}CCH(CH_3))][BF_4]$[52] demonstrates that the carbenium center is bent toward one of the molybdenum atom, the interatomic $Mo{-}C^+$ distances are very close at 2.64 and 2.613 Å, respectively. The remarkable similarity between these two cations is emphasized in Figure 8, in which the two structures are superimposed. This illustrates the power and utility of the isolobal analogy. Other heterobimetallic cationic structures were described in the bicyclo[2.2.1] series.[55b,57]

3 Dicationic Species

Barinov et al. have first demonstrated by ^1H and ^{13}C NMR spectroscopy the existence of the dication $[Mo_2Cp_2(CO)_4(\mu$-$\eta^3,\eta^3CH_2C{\equiv}CCH_2)]^{2+}$ produced by the action of tetrafluoroboric acid on the complexed acetylenic diol. A C_2 symmetry was proposed for this species, according to the NMR data.[58] Recently Curtis et al.[59a] obtained the X-ray structure of this dicationic salt and confirmed that the molecular symmetry is nearly C_2 with the bridging C_2H_4 ligand adopting a μ-η^3,η^3-coordination mode. The metal−carbenium distance of 2.45 Å is very close to that found for a primary monocation, 2.44 Å.[59a] We have recently reported the synthesis and spectroscopic characterization of the novel dicarbenium fulvalene complex $[FvMo_2(CO)_4(\mu$-$\eta^3,\eta^3CH_2C{\equiv}CCH_2)][BF_4]_2$[59b] (see Figure 9). This species appears to be more reactive than the analogous dicarbenium cyclopentadienyl complex $[Mo_2Cp_2(CO)_4(\mu$-$\eta^3,\eta^3CH_2C{\equiv}CCH_2)]$.$^{2+}$ Indeed the dicarbenium fulvalene complex reacts with weak nucleophiles to give the corresponding monocarbenium derivatives, while with strong nucleophiles double nucleophilic additions to both carbenium centers were observed.[59b]

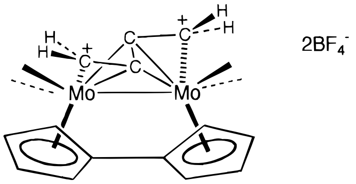


Figure 9. Proposed structure for the dicarbenium fulvalene complex $[FvMo_2(CO)_4(\mu$-$\eta^3,\eta^3CH_2C{\equiv}CCH_2)][BF_4]_2$.

Other dicationic species were described in the literature[60] one of them possesses a ferrocenyl function between the two carbenium centers.[61]

4. EHMO Calculations

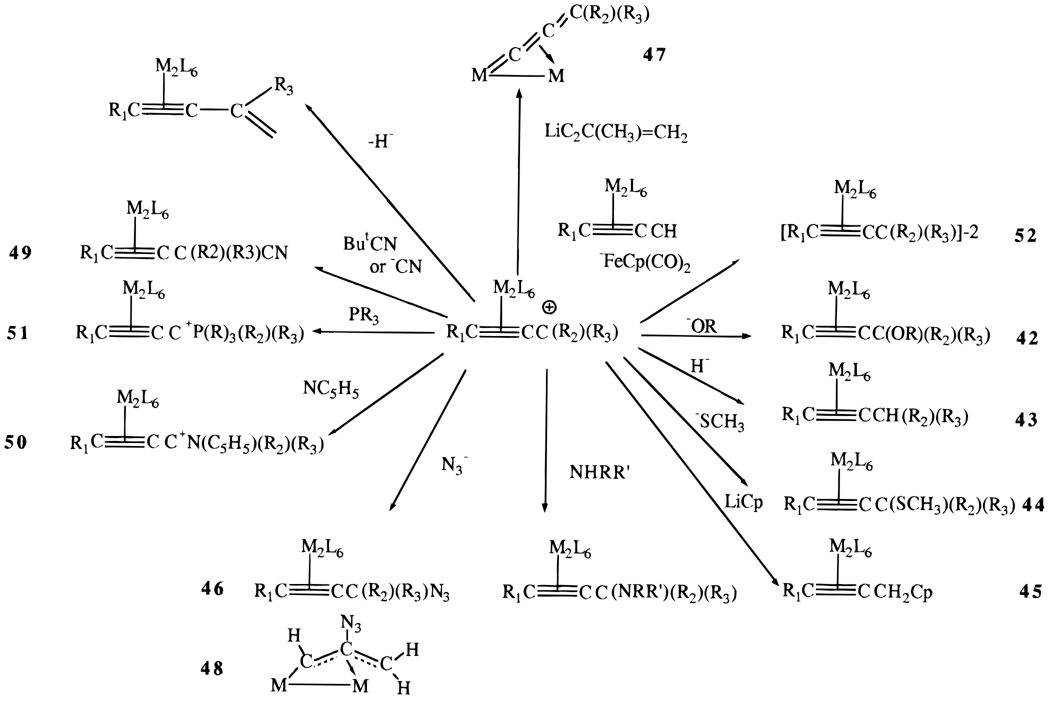
EHMO calculations have been performed on the homo- and heterobimetallic stabilized cations,[49] as well as on the dicationic species.[59] All these calculations have been done according to the fractional methodology.[62]

The π-acceptor character of the propargylium fragment was found to increase relative to the π-donor character, compared to the starting neutral acetylenic complex. An important electronic transfer from the metallic group to the propargylium fragment was found. Metallic and propargylium orbitals of good symmetry, directionality, and energy to interact were pointed out. Curtis et al.[59] analyzed the situation in the dication $[Mo_2Cp_2(CO)_4(\mu$-$\eta^3,\eta^3H_2CC{\equiv}CCH_2)]^{2+}$ and concluded that all the positive charge of the carbenium ion is transferred to the metal atom and suggested that the carbon atoms of the bridging carbenium ion carry a negative charge. In these conditions the regioslectivity of nucleophilic addition to these cationic complexes is frontier orbital controlled.[63]

5. Reactivity

The chemistry attached to dinuclear $[Mo_2]$ or [Mo−Co] propargylium ions is less rich compared to their $[Co_2]$ isolobal equivalents. The main reason for this is the greater thermodynamic stability of $[Mo_2]$ propargylium ions than the $[Co_2]$ propargylium ions. The reactivity of this ion has been extensively reviewed by K. M. Nicholas.[64] The sensitivity to moisture illustrates this difference in reactivity, whereas $[Co_2]$ propargylium ions are very sensitive to water, the isolobal $[Mo_2]$ propargylium ions are in general unreactive under the same conditions. Thus it is possible to obtain $[Mo_2Cp_2(CO)_4(\mu$-η^2,η^3-$HC{\equiv}CCH_2)][BF_4]$ using HBF_4 aqueous solution in ether. The insolubility and unreactivity of this salt in water was used to introduce propargylic fragment into water soluble amines under biphasic conditions.[65] Reactions with charged nucleophiles, ^-OR, ^-H, ^-SMe, LiCp, $^-N_3$ (Scheme 23), lead to the corresponding addition products **42**−**46**, in the case of tertiary cations possessing a hydrogen adjacent to the carbenium center, some elimination reactions were observed.[45,50,66]

Scheme 23. Reactivity of $[M_2L_6(R_1CCC(R_2)(R_3))]^+$ with $M_2L_6 = Mo_2Cp_2(CO)_4$, $W_2Cp_2(CO)_4$, or $MoCoCp(CO)_5$



With the acetylenic hydrogen of a propargylium ligand, reactions were observed at this position, thus addition of $LiC{\equiv}CC(CH_3){=}CH_2$ to $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH_2)][BF_4]$ afforded the allenylidene complexed compound **47**.[36] With N_3^- the formation of an allylic complex **48** was observed.[61] The action of sodium cyanide or *t*-BuCN leads to the complexed propargyl nitriles **49**.[50] Pyridine and phosphine react to form pyridinium **50** and phosphonium salts **51**.[44b]

Reducing reagents like $^-FeCp(CO)_2$, Na/Hg, or Zn were found to react with primary and secondary homo-$[Co_2]$, -$[Mo_2]$ and hetero-[Mo−Co] propargylium ions leading to the reduced and/or coupled products **52**.[7a,50,52]

All the above reactions of $[M_2L_6(R^1C{\equiv}CR^2R^3)][BF_4]$ cations $M_2L_6 = Cp_2Mo_2(CO)_4$, $Cp_2Mo_2(CO)_4$, and $CpMoCo(CO)_5$ are summarized in Scheme 23.

Recently an interesting synthesis of aza-ferrocene derivatives starting from dicationic species was reported.[61]

The stereochemical course of the coupling reaction was studied for secondary cations.[67] A difference in reactivity was observed for mono- and dications. This result was discussed on the basis of EHMO calculations.[59]

This difference in reactivity was interpreted by Curtis et al.,[59] assuming that for dicationic species the LUMO is primarily M-CO π-bonding and the M−M antibonding. Upon reduction of dication, the added electron would be expected to occupy this orbital. Since this orbital places no electron density on the $[\mu\text{-}\eta^3,\eta^3CH_2C{\equiv}CCH_2]^{2+}$ ligand, it is not surprising that reduction of this dication does not lead to C−C coupled product, as reported in case of monocation or dication where the two carbenium centers are separated by a ferrocenyl group. In the latter case the two carbenium centers can be considered as noninteracting functions.

6. Ionization Process, Stereochemical Course of the Nucleophilic Reactions

It is well known that with monometallic complexes, such as ferrocenyl or arene tricarbonyl chromium alcohols derivatives, the ionization process is metal-assisted and leads to carbenium ions with inversion of the configuration due to the formation of a metal−C^+ bond.[68]

In a bimetallic system the situation is rather different because two metallic centers can contribute to the ionization process.

The diastereoselective formation of a binuclear secondary [W−Co] propargylium ion in solution, starting from diastereomerically pure secondary alcohol but with unknown relative configuration,[69] has been established.

Nicholas[70] has described a second generation of carbenium ion complexes with chiral metal cluster $[(CO)_3Co{-}Co(CO)_2PPh_3]$. Thus a mixture of these diastereomeric alcohol complexes have been prepared.[70] The protonation of either isomer leads to the same mixture (syn/anti) of diastereomeric carbenium complexes $[Co_2(CO)_5PPh_3(\mu\text{-}\eta^2,\eta^3\text{-}R^1C{\equiv}CCR^2R^3)][BF_4]$ in which the major isomer adopts the anti configuration. Surprisingly the ratio of syn/anti isomers gradually evolves in an acetone solution, approaching the value of nearly one at equilibrium which suggests the kinetic control for the ionization process. Recently Nicholas et al. have prepared another type of carbenium complexes with chiral metal clusters by using tris (1,1,1,3,3,3-hexafluoroisopropyl)phosphine instead of triphenylphosphine which possesses a strongly π-accepting character.[71] This system behaved differently relative to the precedent $[Co_2(CO)_5PPh_3(\mu\text{-}\eta^2,\eta^2\text{-}R^1C{\equiv}CC(R^2)(R^3)(OH))]$ model, displaying higher reactivity toward carbon-centered nucleophiles. In both cases reactions were stereoselective, determined by the configuration of the tetrahedral cluster core, but nonstereospecific,

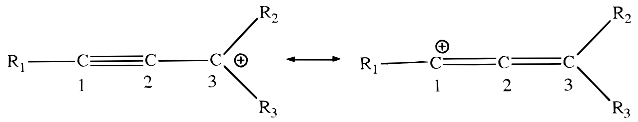


Figure 10. Acetylenic allenic resonance in the free ligand.

different diastereomers lead to identical product mixtures.

Starting from each diastereomerically pure secondary complexed alcohols [CoMoCp(CO)$_5$(μ-η^2,η^2-HC≡CCH(CH$_3$)(OH))] we have found that the action of HBF$_4$/Et$_2$O leads to a 85/15 mixture of the anti/syn corresponding cations.[52] This ratio is not time dependent.

Generally for these chiral clusters, the reaction of a nucleophile occurs on the cation by an anti attack relative to the metallic atom position, under these conditions, the diastereomixture ratio of the resulting products is the same as that found for the starting cations.[52] For homobimetallic [Mo$_2$] clusters and their isolobal [Co$_2$] compounds,[72] the carbenium center acts, in most cases, as a prochiral carbon.[73]

7. Rearrangement Processes

Propargylium ions are formed starting from propargylic alcohols when dissolved in a strong acidic medium.[74] The major resonance contributors for these ions are the allenic structures (Figure 10). The positive charge is delocalized onto the carbon C$_1$ and C$_3$ as provided by spectroscopic NMR data,[74] confirmed by theoretical calculations[75] and by the nature of the resulting products of a nucleophilic attack on these ions. Electron-donating substituents should stabilize the propargylium structure.[75,76] Furthermore, *N*,*N*-dialkylpropyne iminium salts with only weakly nucleophilic anions (e.g. CF$_3$SO$_3^-$, ClO$_4^-$) can be isolated.[77] Recently, Maas et al. have obtained [Co$_2$] complexes of these iminium salts.[78]

One interesting effect of the complexation of an acetylenic function by a bimetallic moiety is to prevent the allenic isomerization. This property was largely used in syntheses, mainly when the metallic group is Co$_2$(CO)$_6$. This property of dinuclear alkyne complexes was first described by Seyferth[79] and developed by Nicholas[80] and other groups.[81]

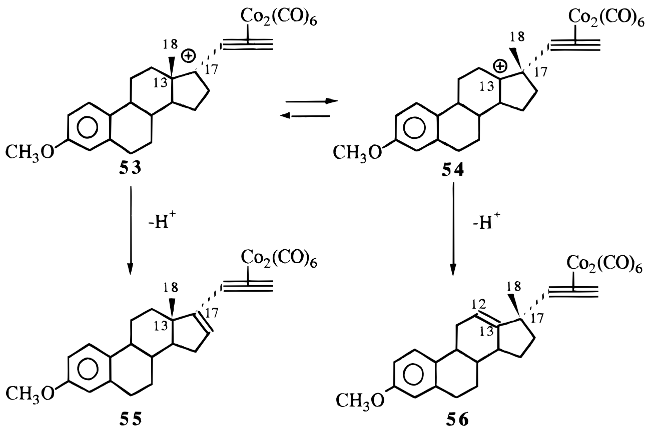
Due to the stabilization of the carbenium ion by the bimetallic cluster, it was not expected to observe rearrangements, like spinal migration of a methyl group in steroidal structures[82] or Wagner–Meerwein[83] and Nametkin[84] isomerization in bicyclo[2.2.1] systems.

Turuta[85] reported the synthesis of an enyne–steroidal derivative from [Co$_2$(CO)$_6$]–ethynylestradiol complex in the presence of a Lewis acid (BF$_3$), followed by hydrolysis. The author observed in addition to the expected 16δ-enyne **55** an unidentified product (Scheme 24).

In the acidic hydrogenolysis of [Co$_2$(CO)$_6$]–ethynylmestranol using trifluoroacetic acid in the presence of NaBH$_4$, Nicholas,[72a] has postulated the formation, as intermediate, of a carbenium ion in the C$_{17}$ position, but did not observe any isomerization products.

Our own experiments[45] have confirmed the results found by Turuta. We were successful to identify the second major olefin complex **56** obtained by action of HBF$_4$/Et$_2$O on the [Co$_2$(CO)$_6$]–ethynylmestranol, followed by water hydrolysis (Scheme 24). Our results suggest that after initial formation of the C$_{17}$ carbenium ion **53**, the latter quickly isomerizes by migration of the methyl group from the C$_{13}$ to the C$_{17}$ position to give the C13 carbenium complex **54**, as shown in Scheme 24. Subsequent elimination of HBF$_4$ from these carbenium ion give the corresponding 16δ-enyne **55** and 12δ-enyne **56** complexes, respectively.

Scheme 24. Migration of the Methyl Group from the 13 to the 17 Position and Subsequent Elimination Reaction



The isolation and structural determination of the isolobal [Mo$_2$Cp$_2$(CO)$_4$]–steroidal carbenium ion **57** demonstrates that the molybdenum cluster strongly stabilizes the carbenium center at C$_{17}$ preventing further isomerization (Figure 11).

Surprisingly, in the solid state, the stabilization of the C$^+$ center occurs by the β face of the steroid, which is known to be the most hindered.[86]

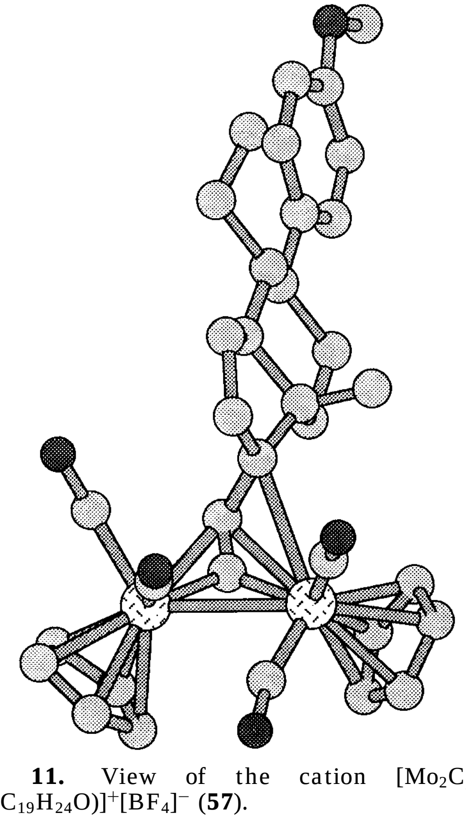
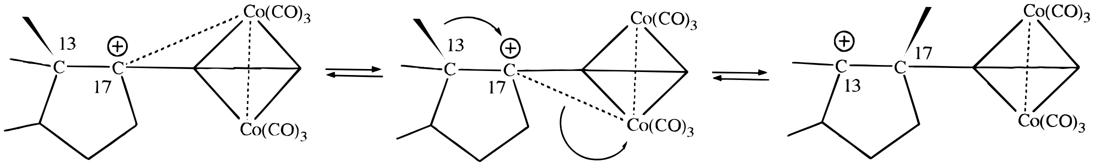


Figure 11. View of the cation [Mo$_2$Cp$_2$(CO)$_4$(HC≡CC$_{19}$H$_{24}$O)]$^+$[BF$_4$]$^-$ (**57**).

Scheme 25. Rearrangement Process Occurring via Inversion of the Configuration on C17



Assuming that the isolobal [Co_2] and [Mo_2] propargylium ions have the same structural pattern, the relative situation of the C^+ and the stabilizing metal in the solid state structure is not favorable to a migration process. Nevertheless we have to take into consideration the fluxional properties of these ions in solution. NMR experiments[87] have shown that **57** is fluxional even at room temperature and two of the four diastereomers in equilibrium have the right configuration to illicit the skeletal methyl migration from C_{13} to C_{17}. The mechanism of migration of the methyl group assisted by the cluster is shown in Scheme 25.

The results obtained in the steroidal series have stimulated some work on the bicyclo[2.2.1] systems, which are very well known as a center of rearrangement processes discovered by Wagner.[83] Studies of Wagner−Meerwein rearrangements of terpenoid skeletons have greatly enhanced our understanding of the factors contributing to the relative stabilities of these carbocations.[88] It has long been known that camphenyl chloride undergoes self-ionization in nitromethane to yield the tertiary carbocation which rearranges to the secondary cation, the final product being isobornyl chloride.

On protonation, 2-ethynylborneol, undergoes Wagner−Meerwein rearrangement in the opposite sense to that exhibited by the camphenyl chloride/isobornyl chloride system[89] as shown in Scheme 26a.

It is evident that the ethynyl group destabilizes the neighboring cationic center sufficiently to force it to rearrange to the sterically less favored camphenyl cation.

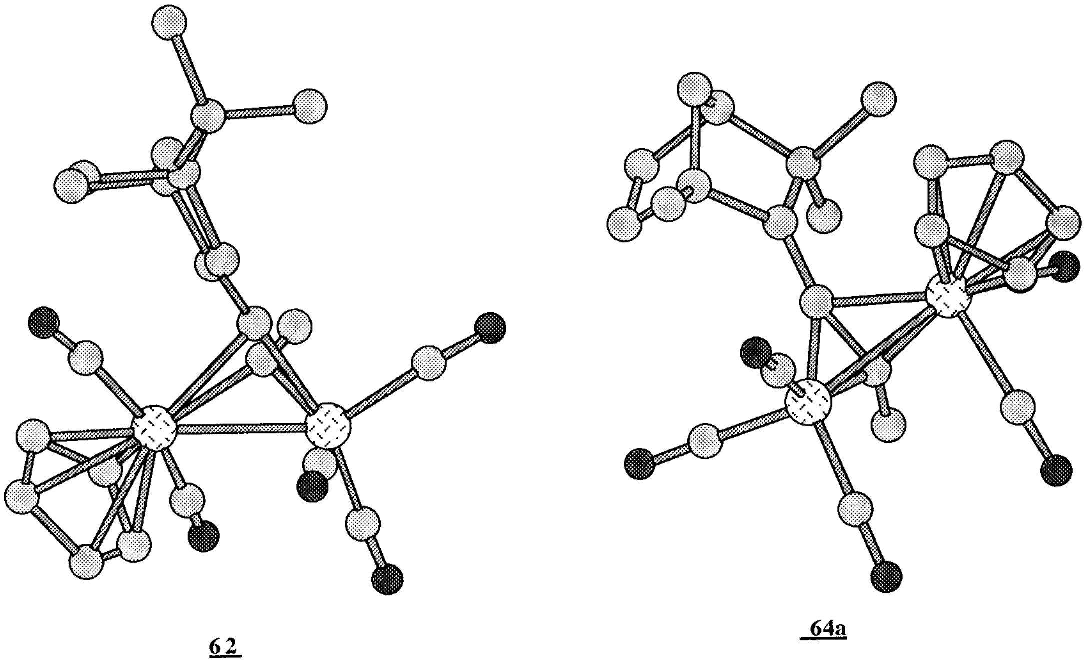
In a preliminary work[90] it was demonstrated, that the coordination of the alkyne linkage in 2-*endo*-propynylborneol to either $Co_2(CO)_6$ or $Cp_2Mo_2(CO)_4$ unit yields the tetrahedral clusters [Co_2]-**58** and [Mo_2]-**59**, respectively, which have been characterized crystallographically. Moreover, protonation of [Co_2]-**58** and [Mo_2]-**59** leads to the cationic species **60** and **61**, respectively, which ^{13}C NMR spectra reveal that, in contrast to the behavior of the free ligand, the bornyl skeleton has not suffered rearrangement[69] (Scheme 26b).

Confirmation of this result is obtained from the crystallographic determination of the structure of **61** and **62** which is the mixed cluster [Mo−Co] and clearly reveals that the methyl substitution pattern remains unchanged from that of the original 2-propynylborneol, suggesting that no Wagner−Meerwein skeletal rearrangement had occurred[55b] (Figure 12).

Once again, it is apparent that in **62** the 2-bornyl cation leans toward the molybdenum vertex rather than the cobalt. In these two cases the cluster core is located on the endo face of the terpenoid skeleton. The bulk of the dimethyl bridge makes the formation of an exo isomer rather improbable.

^{13}C and ^{1}H NMR studies[91] reveal that the fluxional properties of **61** in solution are quite dependent on the steric effect of the C_7 dimethyl substituent group and leads to the conclusion that it is very difficult for the cluster to be in the exo position.

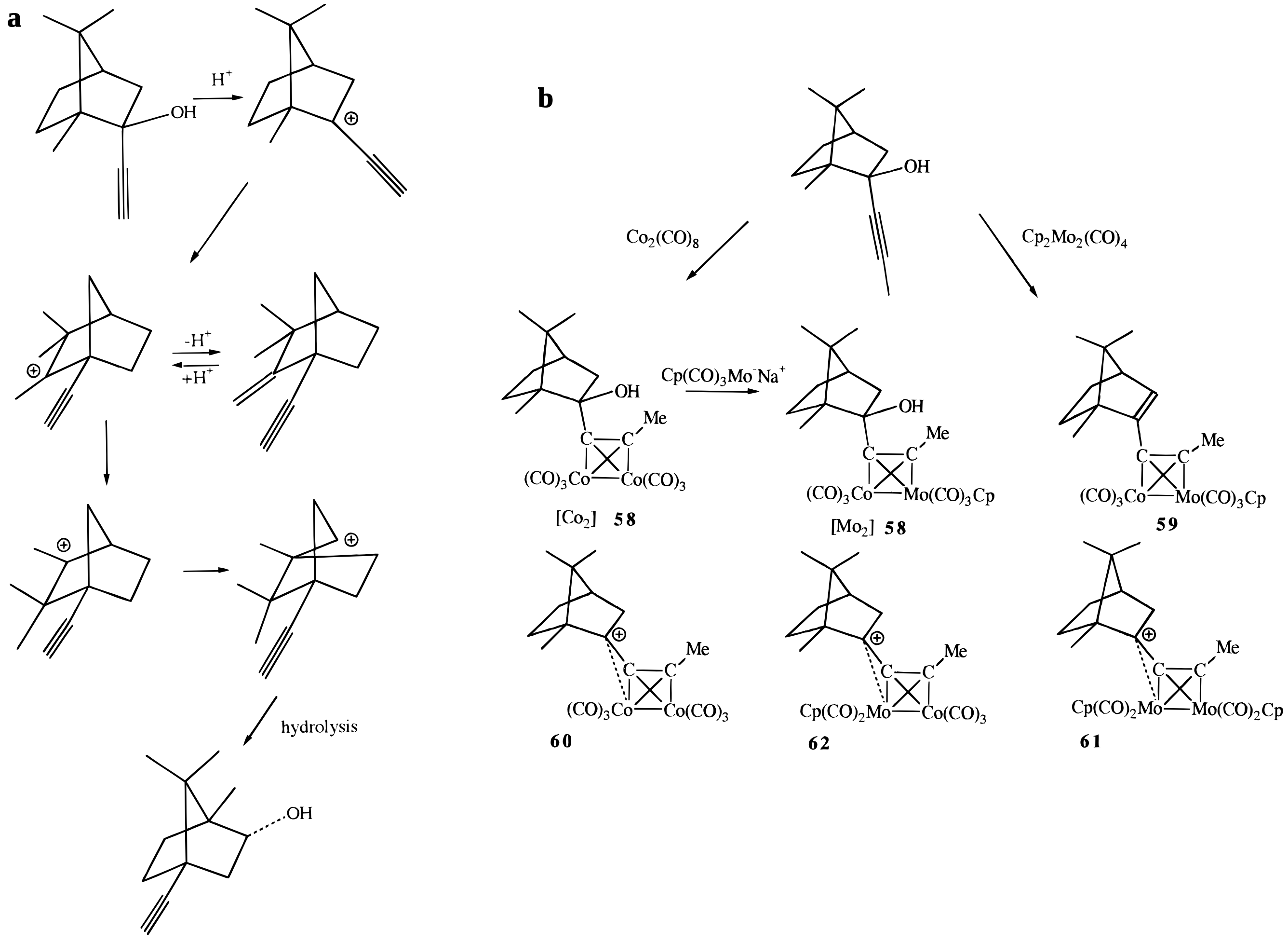
However, the question arises as to whether such cations will be sufficiently metal stabilized so as to be able to resist Wagner−Meerwein rearrangement


62

64a

Figure 12. Comparison between the bornyl and fenchyl cation structures.

Scheme 26. (a) Rearrangement of the 2-Ethynylbornyl Cation and (b) No Rearrangement Observed for the Metal-Stabilized 2-*endo*-Propynylbornyl Cation



when placed in a situation of considerable steric stress.

Results with [$(Co_2(CO)_6)$(propynylfenchol)] complexes provide new interesting information about this problem of rearrangement in the bicyclo[2.2.1] series.

When the [$Co_2(CO)_6$(*exo*-propynylfenchol)] (**63**) was treated with HBF_4/Et_2O the [$Co_2(CO)_6$(2-propyl-2-fenchyl)] cation, [Co_2] **64**, was readily produced. After hydrolysis three major products have been identified: two alkenes **65** and **66** and the [(*endo*-propynylfenchol)($Co_2(CO)_6$)] (**67**). As shown in Scheme 27a these products are yielded from two isomeric cations **63** and **68**.

The conversion of the relatively unstable initially formed cluster, **63**, into its epimer **67**, in which the cluster is endo, is readily rationalized in terms of the intermediacy of the cation **64** which is subsequently quenched by attack of water on the less hindered *endo* face. The alkenes **65** and **66** are evidently produced by a Wagner–Meerwein rearrangement to yield primarily the bornyl-type cation **68** which, upon subsequent deprotonation in either of two ways affords the corresponding alkene complexes **65** and **66**.

Considering the observed relative yields of the two alkenes (**65** and **66**) and the alcohol **67**, one might suspect that the equilibrium constant relating the cations [Co_2] **64** and [Co_2] **68** is close to unity.

The facile interconversion of the cations [Co_2] **64** and [Co_2] **68** in the fenchyl system contrasts markedly with the behavior of the analogous cobalt-complexed bornyl cation **60**.

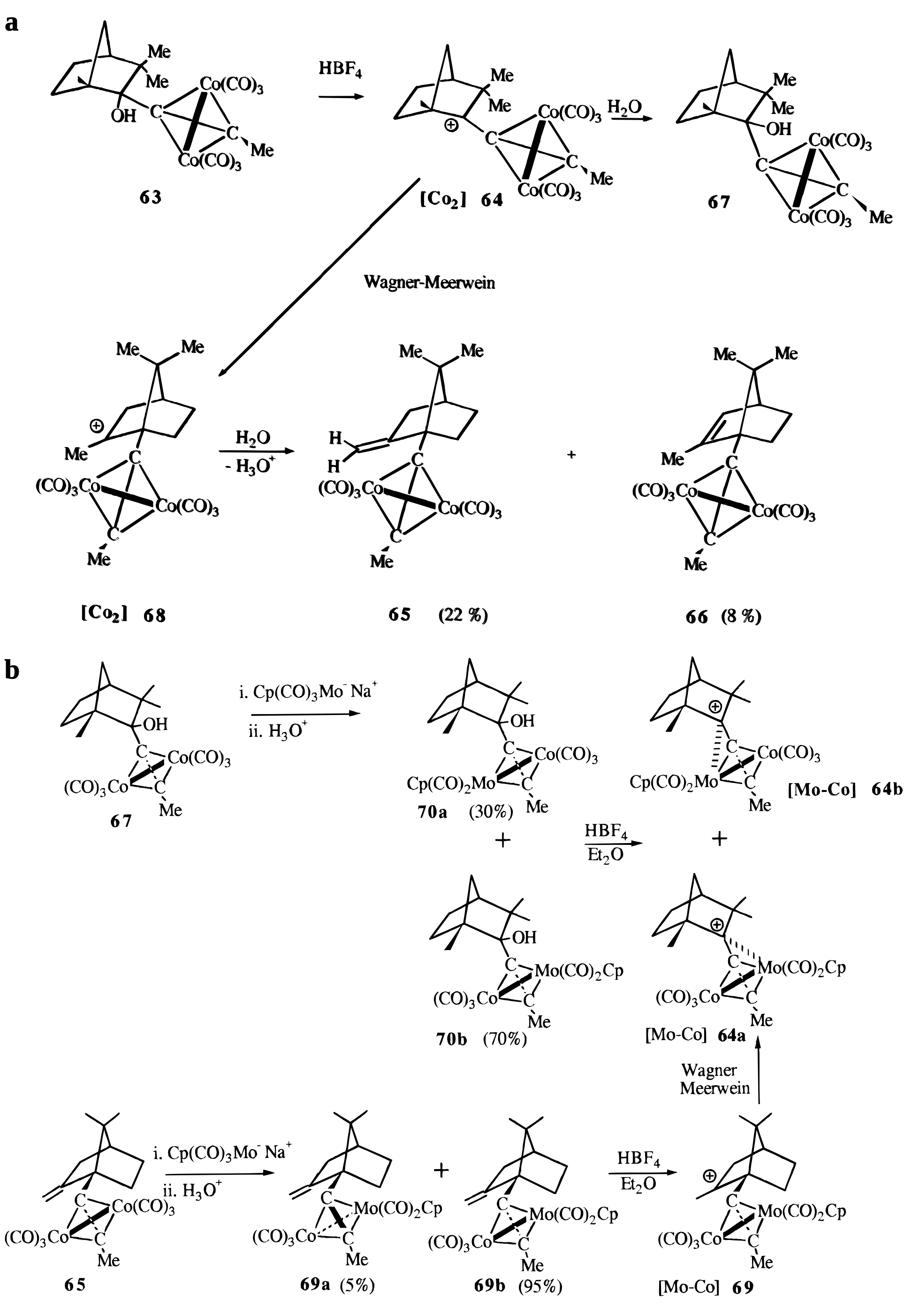
Protonation of the mixed clusters **69ab** and **70ab** obtained from **65** and **67** respectively by replacing one $Co(CO)_3$ vertex by a $MoCp(CO)_2$ fragment leads to the formation of fenchyl cations [Mo–Co] **64a** and [Mo–Co] **64b** (Scheme 27b)

The crystallographic structure of [Mo–Co] **64a** has been determined[57] (Figure 12). As shown in Figure 12, it is immediately evident that it is a fenchyl-type cation **64a** in which the cluster core stabilizes the cation from the exo position, while in the bornyl cation **62** the cluster stabilizes the carbonium center from the endo position.

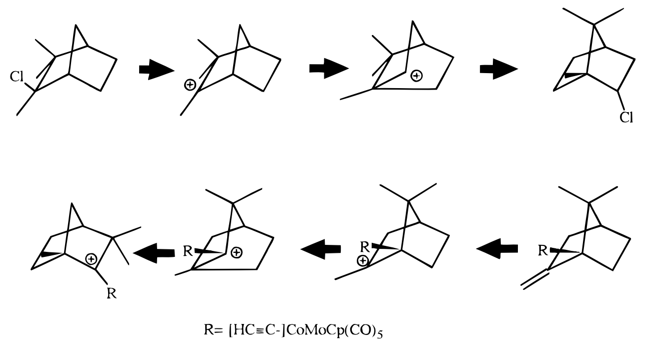
The reaction sequence leading to the fenchyl-type cation is shown in Scheme 28, it corresponds to the reverse of the classical rearrangement of camphenyl chloride to isobornyl chloride. In the conversion of the [Mo–Co] **69** cation to [Mo–Co] **64a**, the metal-assisted electronic stabilization of the latter must overcome the steric hindrance associated with the fenchyl skeleton.

We have commented that the Wagner–Meerwein rearrangement which interconverts the [Co_2] **64** and [Co_2] **68** cations should proceed preferentially through the *exo*-conformation of the complexed cation [Co_2]

Scheme 27



Scheme 28. Wagner–Meerwein Rearrangement Occurring on the Opposite Direction for Complexed and Noncomplexed Cations



64. It is therefore not unreasonable to suppose that the reverse process which takes the [Mo–Co]-bornyl type cation **69** back to the fenchyl system [Mo–Co] **64a** should generate the *exo* cation, as indeed it does!

It is interesting that the structures of the fenchyl-*exo*-[Mo–Co] cation, **64a**, and the bornyl-*endo*-[Mo–Co] cation **62**, parallel the behavior of nucleophiles attacking fenchone and camphor, respectively. In fenchone, the sp^2 center accepts electron density from a nucleophile *exo* attacking while for camphor the nucleophile approaches from the *endo* face. It may be the case that since the *exo*-stabilized bornyl cation is disfavored by the presence of the dimethyl substituents on C_7 of the bicyclo unit, the transition state for Wagner–Meerwein is less readily accessible.

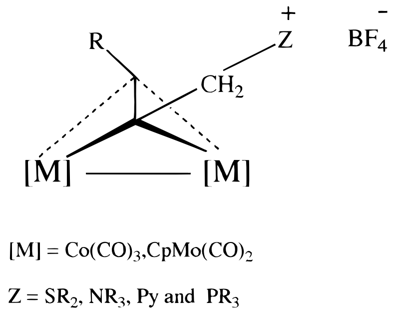


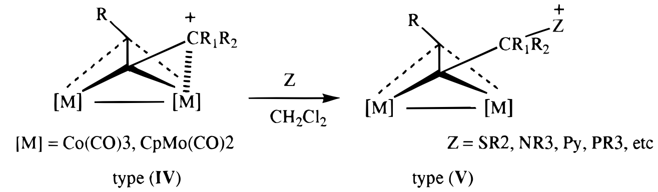
Figure 13.

B. Dinuclear Propargylic Derivatives (V)

1. Synthesis

Dinuclear complexes of type **V** can be prepared in high yields by treating the $[Co_2]$− and $[Mo_2]$propargylium cations type **IV** with nucleophiles (Z = SR_2, NR_3, Py, PR_3,etc.)[44b] (Scheme 29).

Scheme 29



These cationic derivatives are stable under argon for a long period of time. Figure 13 shows a schematic drawing for this kind of compound, where several X-ray structures of the phosphonium $[Co_2]$ and $[Mo_2]$ derivatives (Z = PR_3) were reported in the literature.[44b] It is worth mentioning that these complexes were more investigated for the $[Co_2]$ derivatives relative to the $[Mo_2]$ species due to the higher reactivity of $[Co_2]$ propargylium ions compared to their $[Mo_2]$ isolobal propargylium ions.

Table 8. IR Values of the Carbonyl Bands for Dichloromethane Solution of $[(HC{\equiv}CCH_2)Co_2(CO)_6][BF_4]$, $[(HC{\equiv}CCH_2OH)Co_2(CO)_6]$, and Derivatives

compounds	ν_{CO},[a,b] cm^{-1}		
$[(HC{\equiv}CCH_2)Co_2(CO)_6]BF_4$	2130 (m)	2105 (s)	2085 (s)
$[(HC{\equiv}CCH_2OH)Co_2(CO)_6]$	2090 (m)	2050 (s)	2025 (s)
$[(HC{\equiv}CCH_2SEt_2)Co_2(CO)_6]BF_4$	2103 (m)	2066 (s)	2035 (s)
$[(HC{\equiv}CCH_2PEt_3)Co_2(CO)_6]BF_4$	2101 (m)	2062 (s)	2037 (s)
$[(HC{\equiv}CCH_2Py)Co_2(CO)_6]BF_4$	2103 (m)	2067 (s)	2025 (s)

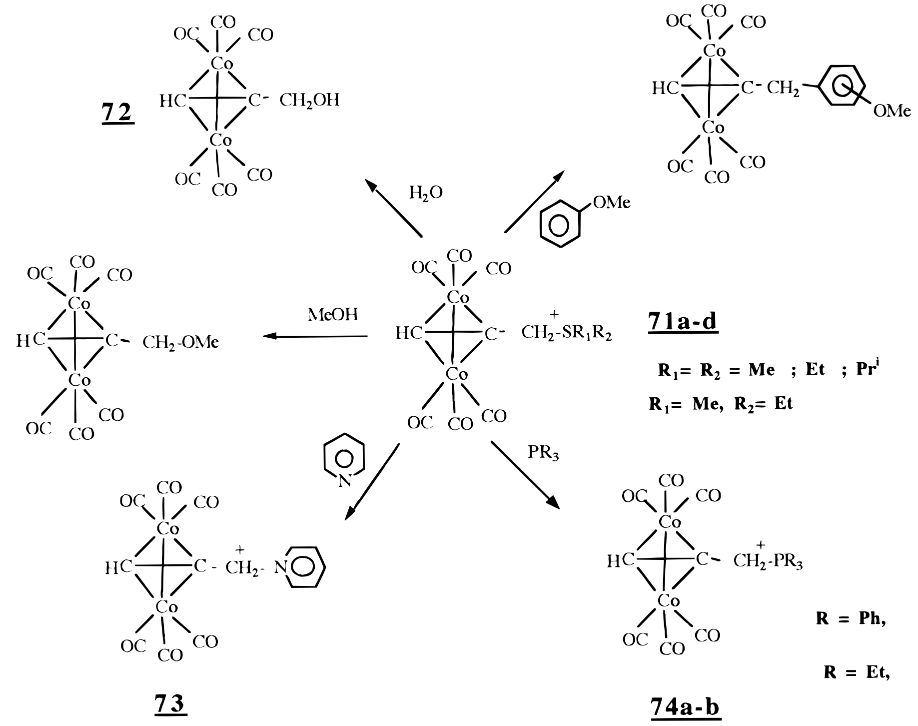
[a] m = medium; s = strong. [b] Reference 44b.

The major difference between the cationic derivative type **V** and the propargylium dinuclear complex type **IV** is the absence of any anchimeric assistance from the metal to the positive charge, which is now greatly located on the heteroatom. Another important feature displayed by this class of compounds comes from their infrared spectra. Thus the values of the carbonyl stretching bands lie in between those of the alcohol parent molecule and the starting material type **IV** (Table 8). This implies that coordination of the carbonium center ($-C^+-$) by a heteroatom generates a new class of complexes where the charge density on the cluster moiety is between the dinuclear propargylic alcohol complex and the propargylium complexes type **V**.

2. Reactivity

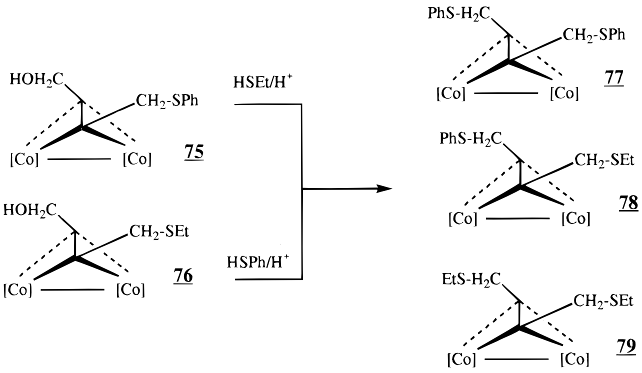
Among these complexes are the $[Co_2]$ sulfonium derivatives **71a**−**d** which seem to offer an attenuated reactivity but a higher stability compared to the propargylium complex.[44b] We have found that $[Co_2]$ sulfonium series $[Co_2(CO)_6(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH_2SR^1R^2)][BF_4]$ (**71a**−**d**) react with various nucleophiles as shown in Scheme 30.

Scheme 30

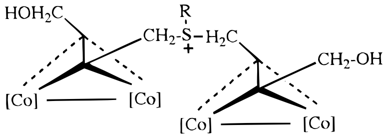


They are also sensitive toward hydrolysis providing the corresponding [Co_2]−propargyl alcohol complex **72**. The pyridinium **73** and the phosphonium complexes **74ab** are less reactive. Went and co-workers,[60,66] have studied the reaction of thiols with dicationic [Co_2]−propargyl compounds prepared in situ. The authors observed the formation of mono- and disubstituted thioether complexes depending on the amount of thiol used. During an attempt to prepare mixed thioether complexes from [$Co_2(CO)_6(\mu$-η^2,η^2-HOC≡$CCH_2SR)$] with R = Ph (**75**), Et, (**76**) (Scheme 31) and in the presence of H^+/HSR, a mixture of products was obtained **77**−**79**.

Scheme 31



To explain the thioether scrambling from the previous reaction, the authors proposed the initial formation of the cation thioether dimer **80** as an intermediate (Figure 14). The latter undergoes thioether transfer to give the desired compounds when exposed to nucleophiles (HSR). Whereby the original thioether bridge "C−SR−C^{+1}" is cleaved by the attacking nucleophile.



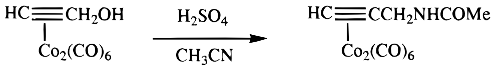
80

[Co] = $Co(CO)_3$

Figure 14.

Treatment of the [Co_2] and [Mo_2] propargylium ions with secondary amines in the presence of a hindered base gave respectively bis- and monopropargylated tertiary amines in good yield.[65] Clearly the intermediates for the previous reaction are the ammonium species type **V** which get deprotonated to give the final compounds. An interesting reaction observed with the [Co_2] propargylium ions is the Ritter reaction[92] which converts CH_3CN into the $Co_2(CO)_6$ complex of *N*-propargylacetamide (**81**, Scheme 32).

Scheme 32



$$\underset{Co_2(CO)_6}{HC\equiv CH_2OH} \xrightarrow[CH_3CN]{H_2SO_4} \underset{Co_2(CO)_6}{HC\equiv CCH_2NHCOMe}$$

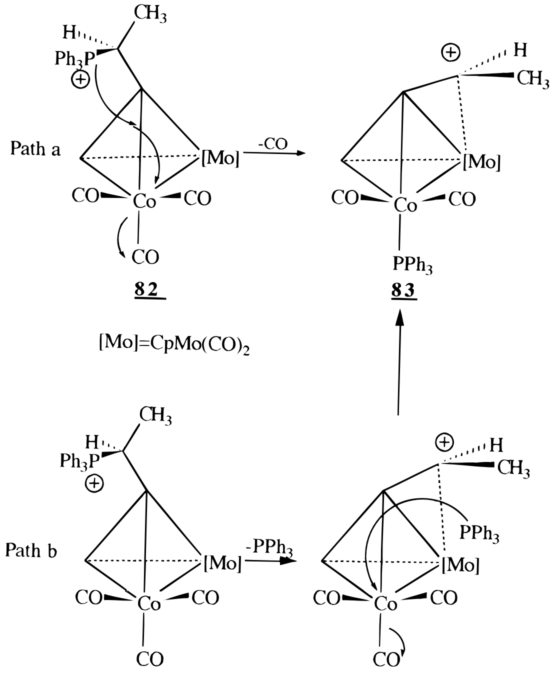
81

Curtis and co-workers[50] have found that reaction of a [Mo_2] propargyl derivative with *t*-BuNC gives primarily the cation derivative type **V** which subsequently loses isobutene and H^+ to give the [Mo_2]-complexed propargyl nitrile.

In attempt to prepare the heterodinuclear phosphonium derivative [(μ-η^2,η^2-HC≡$CCHCH_3PPh_3$)-$CoMoCp(CO)_5$][BF_4] (**82**) from the secondary propargylium complex [(μ-η^2,η^3-HC≡$CCH(CH_3)$)CoMoCp-$(CO)_5$][BF_4] and PPh_3, we obtained unexpectedly the phosphinated propargylium complex [(μ-η^2,η^3-HC≡$CCH(CH_3)$)$CoMoCp(CO)_4PPh_3$][BF_4] (**83**) by CO substitution at Co-center, the X-ray structure of the latter was determined.[52]

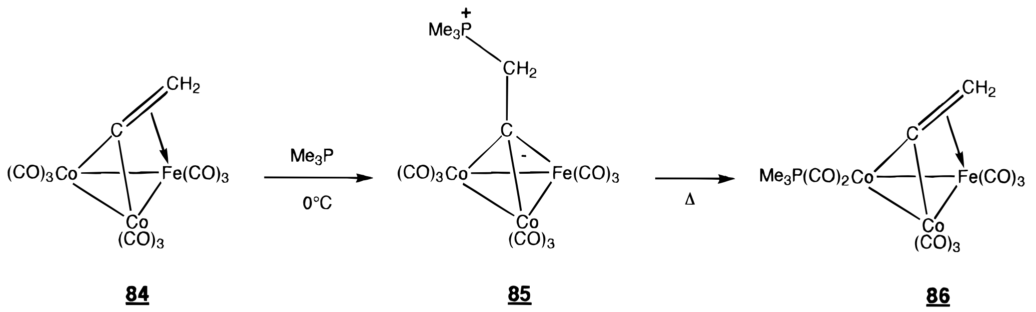
Further analysis of this reaction suggested that the attack at the electrophilic carbonium center (CHMe) is kinetically stereocontrolled and gives primarily the phosphonium species [(μ-η^2,η^2-HC≡$CCH(CH_3)(PPh_3)$)-$CoMoCp(CO)_5$][BF_4] (**82**), which rearranges to provide the thermodynamic stable carbenium ion [(μ-η^2,η^3-HC≡$CCH(CH_3)$)$CoMoCp(CO)_4PPh_3$][BF_4] (**83**) with the phosphine ligand bonded to the Co center (Scheme 33). This is a rare example where the nucleophilic attack preferably occurs at the metal center (thermodynamic factors) rather than the electrophilic carbonium center (CHMe). Vahrenkamp and co-workers[93] reported that the neutral μ_3-vinylidene cluster [$Co_2Fe(\mu_3$-$CCH_2)(CO)_9$] (**84**) reacts with PMe_3 to give a zwitterionic complex **85** where an attack at the electrophilic C_β occurs. Upon heating, complex **85** is converted to compound **86** by phosphine migration and CO substitution at the Co center (Scheme 34).

Scheme 33



An interesting example of a dinuclear propargylic derivative in which the cationic center does not receive any anchimeric assistance from the metal center was recently reported by Maas and co-workers.[78] The authors reported the synthesis and X-ray structure of the $Co_2(CO)_6$ complexed propyne iminium cation **87** as well as its uncomplexed **88** counterpart. The latter shows a highly localized π-bond system with no contribution from the corresponding allenylic form. In a similar fashion the Co_2-

Scheme 34



(CO)$_6$ complexed propyne imminium **87** derivative is fully comparable to complexes of neutral alkynes where no charge delocalization onto the metal fragment occurs (see Figure 15).

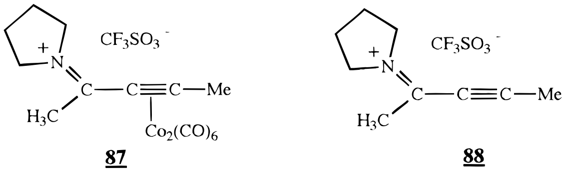


Figure 15.

V. Dinuclear Stabilized Ylides (VI)

A. Synthesis and Structural Identification

This type of complex **VI** (Figure 16) is not well known in the literature, but can be easily obtained by deprotonation of the phosphonium derivative **V** with the appropriate base.[94]

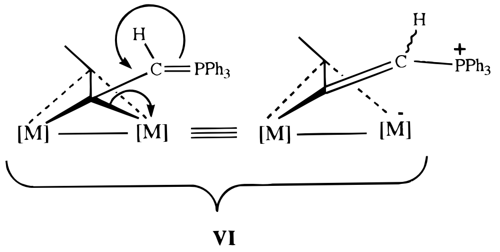


Figure 16.

In 1994 we reported[94] the first dinuclear [Mo$_2$]-stabilized ylide complexes **90ab** by treating the [Mo$_2$] phosphonium derivative **89** type **V** with DBU in CH$_3$-CN (Scheme 35).

This reaction provides two ylide isomers **90ab** in a (2/1) ratio, the X-ray structure of the major species **90a** was determined (see Figure 17).

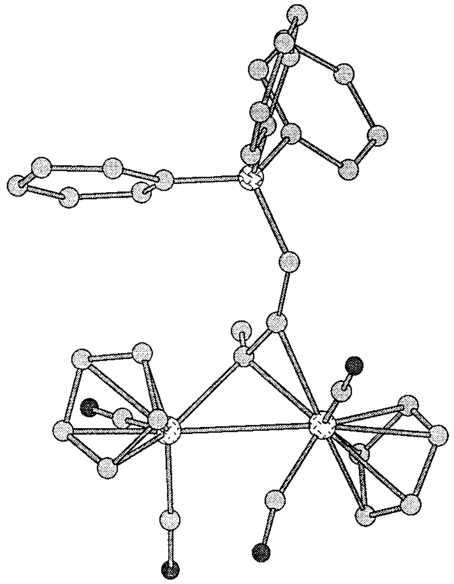
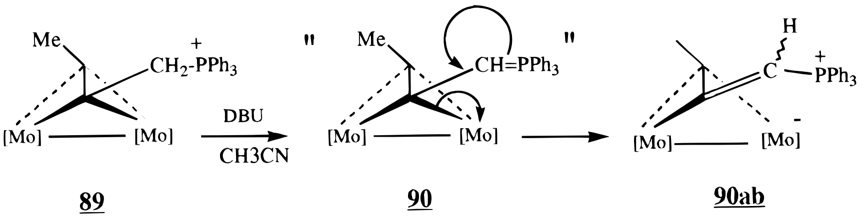


Figure 17. X-ray molecular structure of [Cp$_2$Mo$_2$(CO)$_4$ (μ-η^2,η^1-MeC≡CC(H)(PPh$_3$)].

The two isomers arise from the relative configuration of the two substituents (PPh$_3$) and (H) at the Cγ. The major isomer is the one where the PPh$_3$ adopts a configuration distal from the metal—metal bond and due to steric factors, evidently the minor isomer has the reverse configuration. The term metal-stabilized ylide is basically related to the zwitterionic form of the dinuclear species as confirmed by its X-ray structure, whereby the hydocarbyl unit is bonded in a μ-η^2,η^1- mode and hence a significant stabilization of the negative charge by delocalization onto the metal cluster is suggested. This situation resembles the well-known carbonyl-substituted P-ylides **91ab** in which the negative charge is delocalized onto the oxygen atom (Scheme 36).

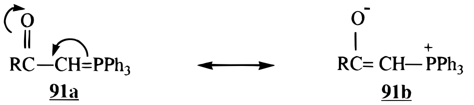
We feel that these complexes offer a new bonding structure and a rich and potentially fascinating chemistry. These species may promote the Wittig

Scheme 35



[Mo] = CpMo(CO)$_2$

Scheme 36

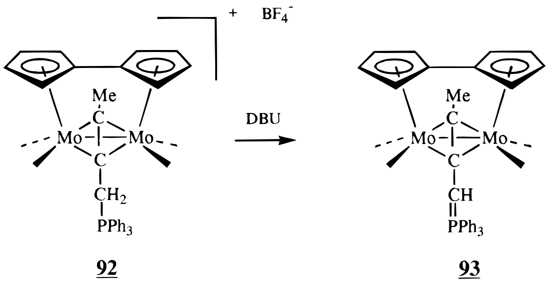


reaction, which provides after metaloxidation the enyne substrates ($-C{\equiv}C-C{=}C-$) important species in organic syntheses.

B. Reactivity

When the phosphonium−fulvalene complex $[FvMo_2(CO)_4(Me\text{-}C{\equiv}CCH_2PPh_3)][BF_4]$ (**92**) was deprotonated by DBU only one species was identified as the novel $[Mo_2]$ fulvalene ylide complex **93** (Scheme 37). The spectroscopic data suggested that the major contributor to the structure of this novel ylide is the neutral form and not the zwitterion form as observed with the cyclopentadienyl system.[95]

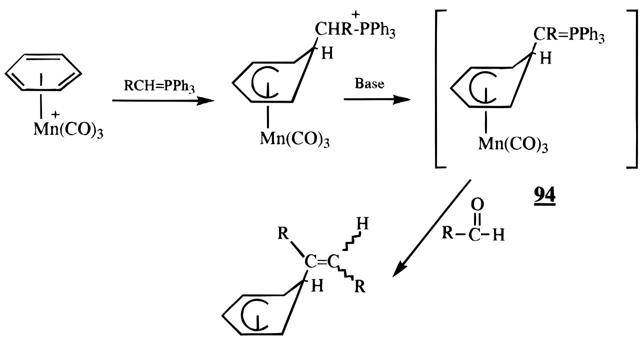
Scheme 37



The deprotonation procedure to prepare ylide complexes can also be applied to the $[Co_2(CO)_6(Me\text{-}C{\equiv}CCH_2PPh_3)][BF_4]$ derivatives. The latter appears to be less stable than their isolobal $[Mo_2]$ counterparts. Preliminary results[95] on the reactivity of the $[Cp_2Mo_2(CO)_4]$ ylide complexes to promote the Wittig reaction has been so far unsuccessful. However we feel that the $[Co_2]$ analogue and $[FvMo_2(CO)_4]$ derivatives appear to be more reactive.

It should be mentioned however that Shin's group[96] has prepared the organotransition metal-substituted ylide complex **94** but it was not isolated (Scheme 38).

Scheme 38



The latter reacts as a Wittig olefination of aldehydes and eliminates the phosphine oxide unit. Although the Mn−ylide system shows that metal-stabilized ylides are potentially interesting precursors for organic syntheses, however we feel the latter system remains restricted to only arenes functionalization.

VI. Metal–Ligand Dynamics

A. Tetrahedral Bimetallic Clusters

Tetrahedral alkyne bimetallic clusters possess different symmetry properties from C_{2v} through C_s to C_1 as shown in Figure 18.

The change in symmetry from C_{2v} to C_1 can be obtained by using an unsymmetrical alkyne and one of the following: two different isolobal metallic groups such as $[MoCp(CO)_2\text{-}Co(CO)_3]$,[97] $[Co(CO)_3\text{-}NiCp]$,[98] $[MoCp(CO)_2\text{-}Re(CO)_5]$,[99] $[WCp(CO)_2\text{-}Co(CO)_3]$,[15a,100] $[Mn(CO)_5\text{-}Co(CO)_3]$,[101] $[NiCp\text{-}Mn(CO)_5]$,[102] $[MoCp(CO)_3\text{-}NiCp]$;[103] or two nonequivalent vertices possessing the same metallic atom with different ligands such as $[Co(CO)_3\text{-}Co(CO)_2PR_3]$,[70,71,104] $[Co(CO)_3\text{-}Co(CO)_2SR_2]$.[105]

When the symmetry is C_1 the cluster is intrinsically chiral. Thus, it is possible to observe the diastereotopic feature of methylene or isopropyl groups adjacent to the cluster.[106]

This property is lost when the cluster isomerizes on the time scale of spectroscopic measurements as demonstrated for $[(Co(CO)_3\text{-}NiCp)(\mu\text{-}\eta^2,\eta^2\text{-}PhC{\equiv}CCO_2\text{-}CH(Me)_2)]$.[107] A mechanism for this cluster core isomerization has been proposed,[106] considering the tetrahedral cluster as a nidotrigonal bipyramid with a vacant coordination site on the surface of the polyhedron and may be regarded as coordinatively unsaturated.[108] The activation energy for this isomerization process was found to be 21 kcal mol^{-1} in the example cited.

1. Uncharged Bimetallic Acetylenic Complexes

According to X-ray crystallographic data,[110] the unsymmetrical disposition of the ligands around the tetrahedral cluster core was clearly demonstrated even in homobimetallic acetylenic cluster of C_{2v} symmetry.

Thus, in $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2,\eta^2\text{-}RC{\equiv}CR)]$ complexes, the two cyclopentadienyl and the four carbonyl ligands are nonequivalent; one of the CO appears as semibridging. At room temperature, the C_{2v} symmetry is a consequence of a rapid exchange mechanism. Cotton et al.[109] have elegantly demonstrated by variable-temperature NMR studies that the complex $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^2\text{-}PhC{\equiv}CPh)]$ (**95**) is fluxional in solution. Two processes ($\Delta G^{\#} = 8$ kcal mol^{-1} and 10 kcal mol^{-1}) are observed (i) first the carbonyl ligands switch between terminal and semibridging positions and (ii) a higher energy process where the metal vertex $CpMo(CO)_2$ rotates about the metal−metal bond. These two processes are depicted in Scheme 39.

Kergoat et al.[67] have synthesized the racemic (*SS*,*RR*) neutral complex $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2,\eta^2\text{-}HC^1{\equiv}C^2C^3(Et)HC^4(Et)HC^5{\equiv}C^6H)]$. The authors assumed the existence in solution at low temperature of an equilibrium between some conformers resulting from strained rotation about the C^3-C^4 bond.[61]

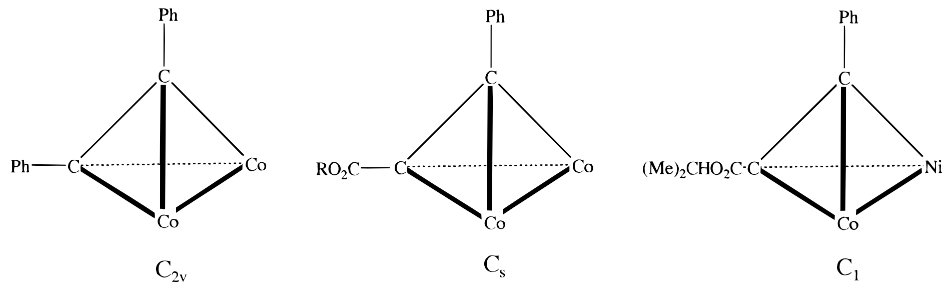
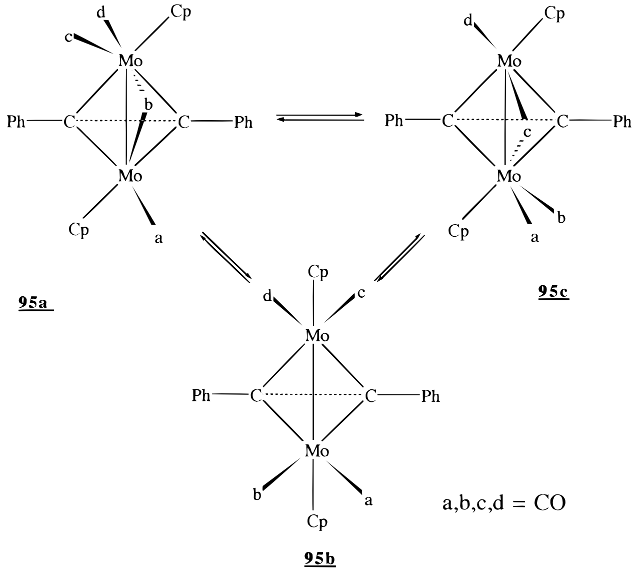


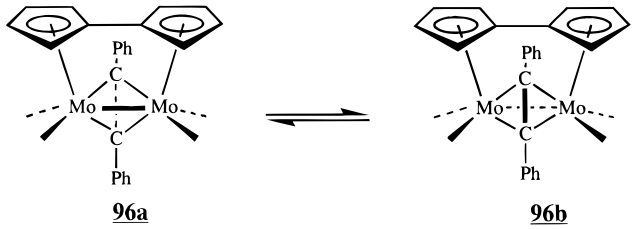
Figure 18. Tetrahedral alkyne bimetallic clusters.

Scheme 39



The situation is quite different when the cyclopentadienyl groups cannot individually exchange their relative position, as is the case of the fulvalene ligands.[17] Vollhardt and co-workers have synthesized the alkyne-[FvMo$_2$(CO)$_4$] derivatives. They found that these complexes exhibit temperature-dependent ^{1}H NMR spectra, indicating the occurrence of a fluxional process. A variable-temperature study of the [FvMo$_2$(CO)$_4$(μ-η^2,η^2-PhC≡CPh)] (**96**) demonstrated coalescence of the four sharp fulvalene multiplets into two broad signals. The coalescence temperature ($T = 308$ K) was used to calculate the activation free energy $\Delta G^{\#}$ of 15.0 kcal mol^{-1}. The authors interpret this fluxional behavior as the result of a rapid interconversion between two isomeric species **96a**,**b** (Scheme 40).

Scheme 40



This fluxional process is similar to that of lower energy observed by Cotton *et al.*[109] assuming the rotation of the fulvalene ligand and carbonyl about the Mo–Mo bond.

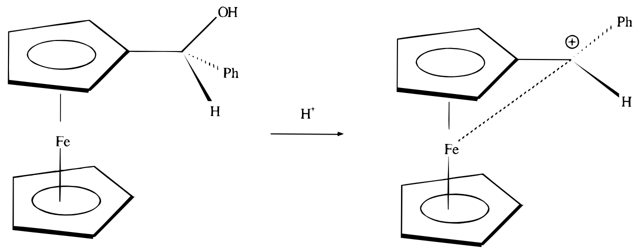


Figure 19. Obtention of a configurationally stable carbenium ion.

2 Carbenium Ions Stabilized by Acetylenic Bimetallic Cluster

Homobimetallic Clusters. Carbenium ions are important species in organic synthesis. This property has stimulated chemists to study and investigate their solution and dynamic behavior, particularly the configuration and stability of the carbenium center and the dinuclear cluster.

It is very well known that carbenium ions adjacent to a metallic group are not only more stable than the corresponding free cation but also, in many cases, they are configurationally stable, due to a strong interaction between the electron-rich metallic and the electron-poor carbenium centers (Figure 19).

This property, together with the enantioselective formation of the carbenium ion, is largely used in enantioselective syntheses.[110] Generally the reaction occurs with retention of configuration at the carbon center through a double inversion mechanism.[111]

In the case of monometallic-stabilized carbenium ions, change in configuration at the carbenium center can occur just by a simple rotation about the C$^+$–C bond.[112] The situation is much more complicated for bimetallic systems.

We have shown *vide supra* that the simplest carbenium ion [Mo$_2$Cp$_2$(CO)$_4$(μ,η^2,η^3-HC≡CCH$_2$)][BF$_4$] (**41a**) adopts a chiral structure in the solid state, due to a specific interaction between the carbenium center and one of the metallic vertices. Under these conditions the two metallic atoms are not equivalent and the cluster core becomes chiral. The description of this chirality is shown in Figure 20.

Spectroscopic NMR data at room temperature are consistent with a chiral structure in solution in the time-scale of NMR measurements, for [Mo$_2$Cp$_2$(CO)$_4$(μ-η^2,η^3-HC≡CCH$_2$)][BF$_4$].[42] Curtis et al. who have studied the ^{1}H and ^{13}C NMR temperature-dependent spectra for [Mo$_2$Cp$'_2$(CO)$_4$(μ-η^2,η^3-HC≡CCH$_2$)][BF$_4$] with Cp$'$=C$_5$H$_4$CH$_3$ have observed that the signals for CH$_3$ and C$_5$H$_4$CH$_3$ broaden and coalesce at 338 K ($\Delta G^{\#} = 16.9$ kcal mol^{-1}). Upon this basis Curtis et al.[50] have proposed a dynamic process which inter-

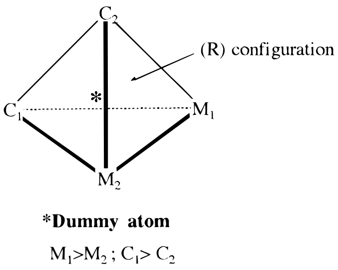


Figure 20.

converts enantiomers **97a** and **97b** via intermediate **97c**, as shown in Scheme 41.

Schreiber et al.[72c] from NMR results for $[(Co_2(CO)_6)(\mu\text{-}\eta^2,\eta^3\text{-}Me_3SiC{\equiv}CC(Me)(CH(Me)_2)][BF_4]$ have proposed an explanation for the dynamic behavior of this ion on the basis of the competition between three processes. One of them is an enantiomerization process while the other two are diastereomerization processes. These processes also occur for the analogous $[Mo_2]$ propargylium ions as shown by Scheme 42 for the compound.$[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH_2)][BF_4]$ (**41a**).

The enantiomerization process occurs by an antarafacial migration of the carbenium center from one metallic vertex to the other.

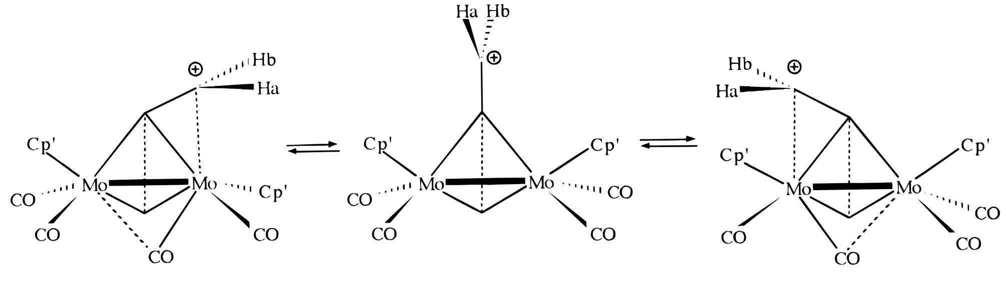
The diastereomerization processes can be (1) a suprafacial migration of the carbenium center from one metallic atom to the other, or (2) a simple rotation about the C^+—cluster bond.

One can imagine that it is very difficult to separate these three processes because the different relative configurations of the cluster and the carbenium center can be exchanged concurrently by each process or by a succession of two different mechanisms.

In general the enantiomerization can be distinguished from the diastereomerization because this mechanism operates at a lower energy than the others.

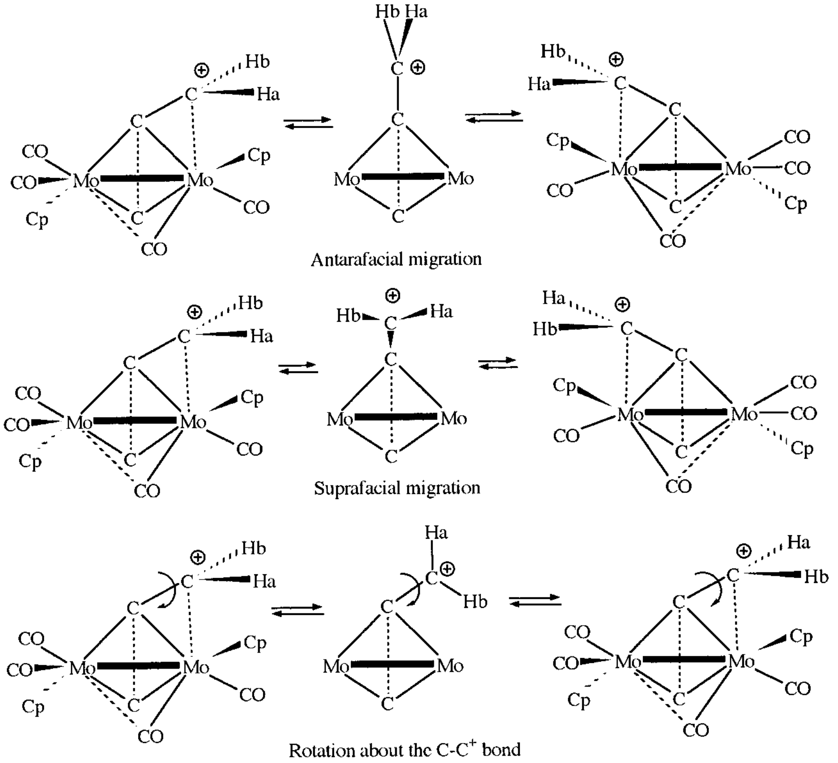
In one case,[113] an internal rotation about the C^+—cluster bond was postulated from studies of the ^{13}C CP-MAS NMR spectra of the solid complexes $[M_2Cp_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCMe_2)][BF_4]$ where $[M_2] = [W_2]$ or $[Mo_2]$. This motion was compared to that found in dimethyl sulfone which has been shown to perform 180° flips about its main C_2 molecular axis in the solid state.[114]

Scheme 41



97a 97c 97b

Scheme 42



The ability to isomerize is clearly related to the interatomic distance found in the solid state, between the metal alleviating the positive charge and the carbenium center.

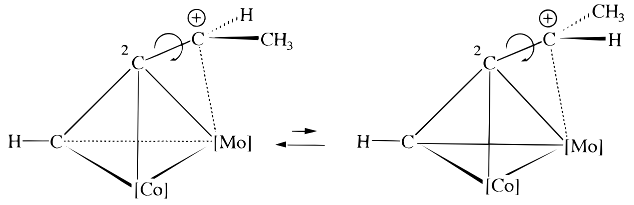
Thus the free energy for the fluxional processes decreases as the distance $d(\mathrm{M-C^+})$ increases. From primary to tertiary $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CC(R_1R_2))][BF_4]$ ($R_1 = R_2 = H$; $R_1 = H$, $R_2 = CH_3$; $R_1 = R_2 = CH_3$) cations the distances $d(\mathrm{M-C^+})$ were found to be 2.47, 2.63, and 2.74 Å, respectively, while the corresponding free activation energies were determined as $\Delta G^{\#} = 17$, 14, and 10 Kcal/mol, respectively.[115]

Although there is no crystallographic data reported for $[Co_2]$ isolobal cations, their structures, however, were proposed on the basis of NMR analysis.[72]

For secondary or tertiary cations possessing nonequivalent or achiral substituents two parameters should be considered to determine the chirality of the species: (a) the chirality of the cluster core, and (b) the chirality of the carbenium center as a consequence of the metal carbenium C^+ interaction leading to a tetrahedral carbon.

In this case it is possible to formalize the problem by considering an equilibrium between two enantiomeric diastereomers. Some examples provide that the position of this equilibrium is dependent on the nature of the groups borne by the carbenium center.[116] The relative position of the two substituents on the carbenium center was determined by X-ray diffraction. For instance, in a secondary cation the bigger substituent (Me) is located just above the metal−metal bond[52] as shown in Scheme 43.

Scheme 43



98a 98b

The ^{13}C NMR data obtained for $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCR_1R_2)][BF_4]$, (with $R_1 = R_2 = H$; $R_1 = CH_3$, $R_2 = H$; $R_1 = R_2 = CH_3$) in solid state and in solution at low temperature allow the unambiguous determination of the chemical shifts for the carbons in each diastereomer.[115]

$[Mo_2]$ propargylium ions possessing chiral ligands, for instance ethynylmestranol[87] or propynylborneol,[91] were also investigated. In these cases it was demonstrated by ^1H NMR analysis that the diastereomeric ratio is influenced by steric factors.

Froom and co-workers[37] have studied the dynamic behavior in solution of the tertiary cation $[W_2Cp_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CC(CH_3)_2)][BF_4]$. They found that a dynamic process averages the environment of the cyclopentadienyl and methyl resonances with a free activation energy measured as 10 kcal mol^{-1}. The mechanism of this process was compared to the disrotatory correlated rotation achieving circumambulation of the Co_3 triangle by the CH_2 group in the isolobal $[Co_3(CO)_9\text{-}(CCH_2)]^+$ cation.[117]

Fluxional properties of primary and tertiary complexed $[Mo_2]$ carbenium ions possessing a fulvalene ligand have been studied.[20,56] An advantage of studying this kind of complexes, is that the relatively rigid nature of the bridging fulvalene ligand obviates the spectral complications attributable to the presence of "CpMo−MoCp" rotamers at low temperature. Indeed, these systems are admirably suited to a study and compare the relative activation energy values of the antarafacial migration and rotation processes. For the primary carbenium ion R = H, $[FvMo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}CH_3C{\equiv}CC(R)_2)][BF_4]$, the energy barriers of the migration and rotation processes are 17.7 and 19.1 kcal mol^{-1} respectively, (these values were determined from 2D-EXSY experiment).[20] While the corresponding values for tertiary carbenium ion R = Me are much lower, 9.5 and 10.2 kcal mol^{-1} with $T_c = 195$ and $T_c = 215$ K, respectively.[56]

Heterobimetallic Clusters. In heterobimetallic cluster like $[MoCp(CO)_2Co(CO)_3](\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CC\text{-}R_1R_2)][BF_4]$ or in homobimetallic cluster, possessing nonequivalent ligands on each vertex $[Co(CO)_2\text{-}PPh_3Co(CO)_3](\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCR_1R_2)][BF_4]$, the problem of the fluxionality is simplified compared to homobimetallic systems. Indeed, the chirality of these clusters is not the result of the metal carbenium interaction, but is an intrinsic property of the tetrahedral structure. For this reason, just the rotation about the $C^+{-}C^2$ bond can operate leading to the diastereomerization of the secondary or tertiary $[M_2L_6]$ complexed carbenium ions. Scheme 43 illustrates this process for the secondary [MoCo] propargylium ions **98ab**.

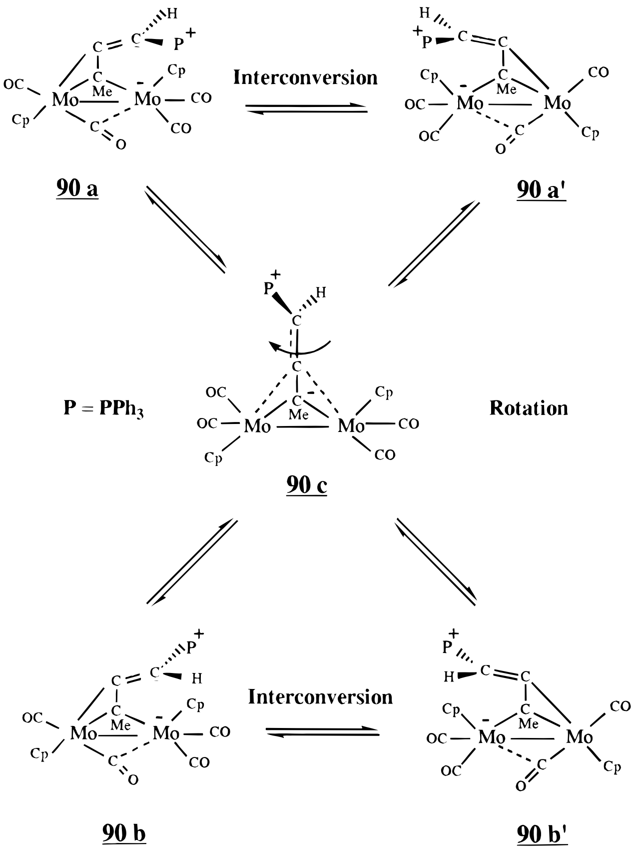
It was found, in the solid state[55b] and confirmed by EHMO calculations that, in the case of [Mo−Co] cluster, the molybdenum atom alleviates the positive charge rather than the cobalt atom. Starting from a pure diastereomeric alcohol $[Co(CO)_3WCp(CO)_2(\mu\text{-}\eta^2,\eta^2\text{-}HC{\equiv}CCH(Et)(OH))]$, McGlinchey and co-workers[69] have found that in acidic medium a mixture of diastereomeric cations is formed which do not isomerize on the time scale of NMR measurements. In contrast, Nicholas and co-workers have shown that secondary or tertiary complexed $[Co(CO)_3\text{-}Co(CO)_2PR_3]$ propargylic alcohols provide, in the presence of strong acid, a mixture of diastereotopic cations; the isomerization of the latter in solution depends on the nature of the phosphine attached to the cobalt atom.[71] In the [Co−Mo]-stabilized cations the free activation energy attached to the isomerization process depends on the nature of the substituents borne by the carbenium center and decreases in the order: R = CH_3, Cym, Fc, CF_3). We also note that in heterobimetallic clusters [Mo−Co] the bigger substituent at the carbenium center is situated above the Co−Mo metal−metal bond.[118]

A complete trajectory for the migration process in this class of dinuclear carbenium complexes has been proposed.[119] The authors used the Bürgi−Dunitz approach to establish this trajectory combined with EHMO calculations on the fulvalene primary propargylium complex $[FvMo_2(CO)_4(MeC{\equiv}CCH_2)][BF_4]$ as the appropriate model and crystallographic data of several primary, secondary, and tertiary $[Mo_2]$ propargylium complexes.

B. Dinuclear Ylide Complexes

The dinuclear ylide compound [Mo$_2$Cp$_2$(CO)$_4${μ-η^2:η^1-MeC=C=C(H)(PPh$_3$)}] was found to be fluxional in solution.[94] Two mechanisms were proposed to explain the variable-temperature ^{1}H, ^{13}C, and ^{31}P NMR spectra. One of them, the lower in energy 12.5 kcal mol^{-1} at 263 K, was attributed to an interconversion of the ylide ligand from one metallic atom to the other, the second process is higher in energy, 14.8 kcal mol^{-1} at 315 K, was considered as a simple rotation about the C−C(H)(PPh$_3$) bond, as shown in Scheme 44.

Scheme 44



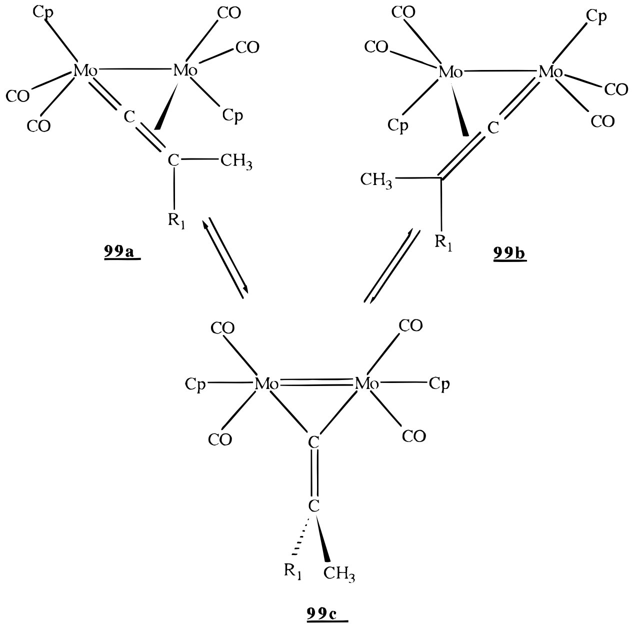
C. Dinuclear Vinylidene Complexes

Upon addition of trifluoroacetic acid, the complex [Mo$_2$Cp$_2$(CO)$_4${μ-σ:η^2-(4e)-C=CH$_2$}], leads to the bridged μ-vinyl complex [Cp$_2$Mo$_2${OC(O)CF$_3$}{μ-CH=CH$_2$)}(CO)$_4$].[120] In solution this species and the related methyl-substituted one show a dynamic behavior on the NMR time scale resulting in equilibrating of the two anti- and two syn-protons of the allyl ligand.[121] The mechanism for this process was established by deuterium-labeled experiments and EHMO calculations. As in dinuclear ylide complexes, the fluxional process is a combination between a rotation about the C−C$^+$ bond and an interconvertion of the μ-allyl ligand between the two metallic centers occurring by a symmetric transition state.

D. Dinuclear Allenylidene Complexes

The crystal structures of the allenylidene compounds [Mo$_2$Cp$_2$(CO)$_4$(−C=C=C$_6$H$_{10}$)] and [Mo$_2$Cp$_2$(CO)$_4$(−C=C=C(CH$_3$)$_2$)] were determined and reveal a close geometry for both complexes. These molecules are chiral; the two cyclopentadienyl groups and the four carbonyl ligands are disposed in a trans position. The allenylidene ligand is bridged asymmetrically toward the two molybdenum atoms. Kergoat et al.[41,61,121] have demonstrated in several examples the fluxional behavior of such [Mo$_2$] allenylidene complexes. Thus ^{1}H NMR spectra of [Mo$_2$Cp$_2$(CO)$_4$(−C=C=C(R^1)(R^2))] (where R^1 = R^2 = CH$_3$; R^1 = C$_6$H$_5$, R^2 = H; R^1 = Et, R^2 = H) are temperature dependent in toluene-d_8 or dimethyl sulfoxide-d_6. The free activation energy associated with the dynamic process is found to be 18 kcal mol^{-1}. The proposed mechanism is related with the balancing of the allenylidene ligand from one metallic atom to the other through a symmetrically transition state **99c**. Scheme 45 illustrates this mechanism for the allenylidene complex **99ab**.

Scheme 45



The transition state proposed in this mechanism is familiar for this class of compounds. It should be mentioned that several symmetrical structures were reported for the dinuclear allenylidene complexes of Fe **100**, Mn **101**, and W **102** (Figure 21).[4]

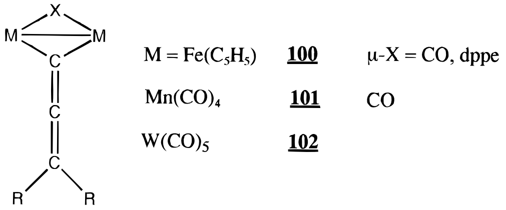
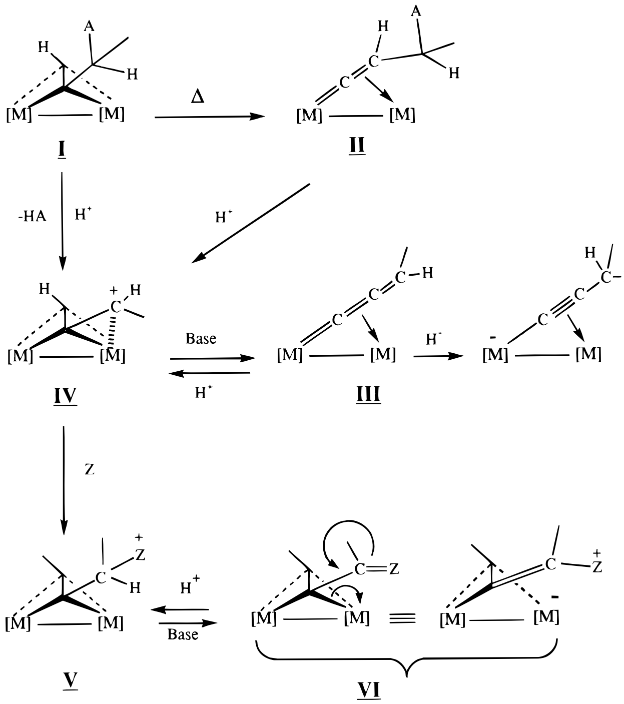


Figure 21.

In conclusion, the dynamic behavior observed in binuclear uncharged or charged complexes possessing a 4-electron donor hydrocarbon ligand presents a great similarity and can be related to: (a) the migration of a part of the bridging hydrocarbyl ligand from one metallic atom to the other, (b) the rotation about carbon−carbon bond, and (c) the internal isomerization of the dinuclear cluster.

Chart 2



A = Leaving group; -OH, -OMe

Z = PPh_3

VII. Outlook of Future Developments

Throughout this review we presented several types (**I**−**VI**) of dinuclear complexes where bridging hydrocarbyl unit exhibits different coordination modes. We have also stressed the connectivity among these dinuclear class of compounds as well as their fluxional and solution behavior. Chart 2 depicts the relationship among these types of dinuclear complexes where possible chemical transformation or isomerization processes take place.

It is important to note that in these dinuclear systems (**I**−**VI**), the bridging allenyl fragments change their mode of coordination (μ-η^1,η^1-; μ-η^1,η^2-; μ-η^2,η^2-; μ-η^2,η^3-; etc.) when moving from one system to the other. Thus, they can be considered as intermediates to alkyne transformation on metal surfaces. In this regard Casey and co-workers have reported[122] very recently on the reaction of acetylene with [$Cp^*Co_3(\mu^2\text{-}H)_3(\mu^3\text{-}H)$] to give bis(ethylidene)tricobalt cluster [$Cp^*_3Co_3(\mu^3\text{-}CCH_3)_3$]; this system provides an example of the possible intermediates in the conversion of acetylene to ethylidene ligand on metal Pt(III) surface. Another area which may be expected to develop rapidly is the chemistry of dinuclear propargylium complexes of type **IV**. They provide interesting reactions and applications in synthetic organic chemistry. Furthermore the recent detection of radical intermediates in this class of compounds has allowed the preparation of compounds of higher nuclearity via coupling reactions of such radicals. In this respect, the preparation in high yield of cyclic enediynes has been recently reported.[123] This area is very promising especially for the preparation of organometallic polymers involving the coupling of several dinuclear radical units.

We feel that the novel dinuclear ylid complexes type **VI** represent a new challenge in this area providing a new example of bonding and reactivity such as their possible use as Wittig reagents for the preparation of enynes, important substrates for organic synthesis. The presence of heteroatoms in these dinuclear complexes are destined to play an important role in developing our knowledge of the reactivity of the dinuclear cluster-bound molecule.

Finally we would expect to see a continuing expansion of this exciting and rich area of chemistry over the coming decade, with emphasis on reactivity and synthetic applications; furthermore their use as models to elucidate catalytic processes on heterogeneous systems remain vital and determinent to understand these chemical transformations.

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