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TRANSITION-METAL-PROPARGYL COMPLEXES: VERSATILE REAGENTS IN SYNTHESIS

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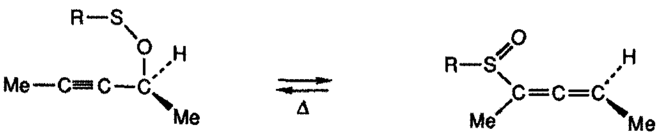
SUMMARY

The chemistry of transition-metal-propargyl complexes, $L_nMCH_2C{\equiv}CR$, is presented, with a particular focus on recent developments in the authors' laboratories. Included in the presentation are synthetic approaches to and reactions of these complexes. The latter are classified as (i) insertion into the M-CH_2 bond, (ii) electrophilic addition to the $C{\equiv}C$ bond, and (iii) addition of coordinatively unsaturated metal species to build complexes of higher nuclearity. The last-mentioned reactions (iii), which have resulted in the development of new synthetic methods for heterobinuclear and homo- and heterotrinuclear metal-μ-allenyl complexes, dominate the chemistry given in this account. Several modes of bonding of a bridging allenyl ligand to two and three metals have been demonstrated for these complexes, and conversions among them have been investigated. Possible pathways for these cluster-building reactions are considered.

INTRODUCTION

Transition-metal propargyls, $L_nMCH_2C{\equiv}CR$, and mononuclear allenyls, $L_nMCH{=}C{=}C(R^1)R^2$, present themselves as some of the most interesting metal-carbon-bonded complexes. Not only are they expected to participate in the usual reactions that characterize transition-metal-alkyl complexes (ref. 1), but they also have the capacity to engage in reactions analogous to those of organic acetylenes and allenes, and to undergo rearrangements of the two hydrocarbon fragments, i.e., propargyl to allenyl and allenyl to propargyl. Such rearrangements are well known in organic chemistry and include, among others, conversion of propargyl phosphites, phosphinates, sulfenates, and sulfites to the corresponding allenyl phosphonates, phosphine oxides, sulfoxides, sulfones, and sulfonates, respectively (refs. 2,3); see, for example, eqn. (1):



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Additionally, propargyl halides and esters are isomerized to the allenyl compounds by the action of metal salts. Several of the aforementioned reactions are reversible. Reduction of propargyl and allenyl halides can afford allenes and acetylenes, respectively.

Our interest in transition-metal-propargyl complexes developed in the late 1960's as a result of the observation that metal complexes containing structurally analogous allyl ligands tend to insert SO_2 with 1,3 inversion of that fragment (ref. 4):

$$L_nMCH_2CH{=}C(R^1)R^2 + SO_2 \rightarrow L_nMS(O)_2C(R^1)(R^2)CH{=}CH_2 \qquad (2)$$

To gain further insight into these rearrangement reactions, we endeavored to synthesize what were at that time unknown metal-propargyl complexes and examine their reactions with SO_2 and related electrophiles.

In this account are described our studies on the preparation and reaction chemistry of this interesting class of metal-carbon-bonded compounds. The discussion of the reaction chemistry will be first concerned with the additions to the propargylic C≡C bond (ref. 5), most of which were carried out independently in our (ref. 6) and Roustan's (ref. 7) laboratories a number of years ago. The latter part of the account will focus on our recent studies concerned with the development of new synthetic approaches to heteronuclear metal clusters by use of propargyl complexes and appropriate metal-ligand fragments. Consistent with the tradition of the Basolo school, mechanistic considerations permeate the discussion of our synthetic efforts in these areas.

SYNTHESIS OF METAL-PROPARGYL AND -ALLENYL COMPLEXES

Metal-propargyl complexes are conveniently prepared by using metal carbonylate anions in conjunction with propargyl halides (refs. 5-7):

$$L_n(CO)_mM^- + XCH_2C{\equiv}CR \rightarrow L_n(CO)_mMCH_2C{\equiv}CR \qquad (3)$$

When R = alkyl or aryl, only propargyl complexes have been isolated; however, when R = H, sometimes the corresponding metal allenyls, $L_n(CO)_mMCH{=}C{=}CH_2$, are obtained. Accordingly, reactions of $Cp(CO)_2M^-$ (M = Fe, Ru) with $XCH_2C{\equiv}CH$ afford $Cp(CO)_2MCH{=}C{=}CH_2$ (refs. 7a,8,9):

$$Cp(CO_2M^- + XCH_2C{\equiv}CH \rightarrow Cp(CO)_2MCH{=}C{=}CH_2 \qquad (4)$$

without any evidence of $Cp(CO)_2MCH_2C{\equiv}CH$. It has been suggested that such reactions proceed by an S_N2' mechanism, i.e., attack of the metal carbonylate at the terminal carbon atom (≡CH) with displacement of halide (ref. 8c). However, a recent study of the reaction of $Cp(CO)_3W^-$ with $BrCH_2C{\equiv}CH$ showed that the initial product is $Cp(CO)_3WCH_2C{\equiv}CH$, which then isomerizes to $Cp(CO)_3WCH{=}C{=}CH_2$ (ref. 10):

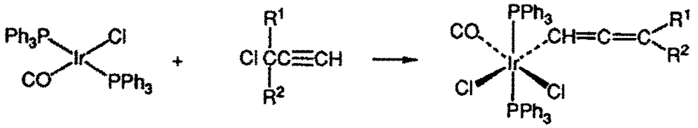
$$Cp(CO)_3W^- + BrCH_2C{\equiv}CH \rightarrow Cp(CO)_3WCH_2C{\equiv}CH \rightarrow Cp(CO)_3WCH{=}C{=}CH_2 \qquad (5)$$

Similarly, Johnson and coworkers reported that treatment of $(dmgH)_2(py)Co^-$ (dmgH = dimethylglyoximate, py = pyridine) with propargyl halides first yields $(dmgH)_2$-$(py)CoCH_2C{\equiv}CH$ and then, from this complex, $(dmgH)_2(py)CoCH{=}C{=}CH_2$, through an S_N2' displacement reaction by another Co(I) anion (ref. 11):

$$(dmgH)_2(py)Co^- + XCH_2C{\equiv}CH \rightarrow (dmgH)_2(py)CoCH_2C{\equiv}CH \xrightarrow{(dmgH)_2(py)Co^-} (dmgH)_2(py)CoCH{=}C{=}CH_2 \qquad (6)$$

Thus, the mechanism of formation of $L_n(CO)_mMCH{=}C{=}CH_2$ is still uncertain for at least some of these compounds.

Propargyl and allenyl complexes are also accessible by oxidative addition reactions of propargyl and allenyl halides to the appropriate lower-valent metal compounds. Accordingly, the halides $XC(R^1)(R^2)C{\equiv}CH$ or $XCH{=}C{=}C(R^1)R^2$ react with *trans*-$Ir(PPh_3)_2(CO)Cl$ and $Pt(PPh_3)_4$ to give the respective allenyl complexes (ref. 12), e.g.:



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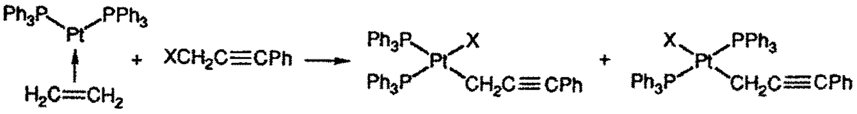
Recently, the first examples of 16-electron transition-metal-propargyl complexes were prepared by oxidative addition of $XCH_2C{\equiv}CPh$ to $Pt(PPh_3)_2(C_2H_4)$ (ref. 13):



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REACTIONS OF METAL-PROPARGYL COMPLEXES WITH NONMETALLIC REAGENTS

Insertion into the M-CH_2 bond.

Metal-propargyl complexes might be expected to undergo insertion of unsaturated species into the M-CH_2 bond in a manner similar to that observed for the corresponding metal alkyls (refs. 1,4,14). However, such a behavior is quite uncommon, presumably because of the following considerations: (i) the C≡C group appears to exert deactivating influence on the M-CH_2 bond and (ii) the presence of the C≡C bond in the propargyl ligand leads to a different, more facile reaction pathway. It is this latter type of reactivity that provides the focus for the chemistry discussed in this account.

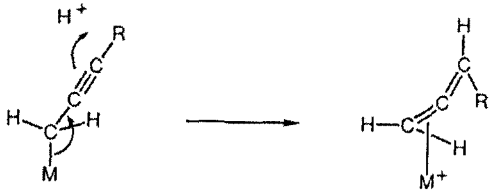
The only well established examples of insertion into the M-CH_2 bond of the metal propargyls are furnished by the reactions of $(PPh_3)(CO)_3CoCH_2C{\equiv}CR$ (R = Me, CH_2Cl, Ph) with CO (ref. 15):

$$(PPh_3)(CO)_3CoCH_2C{\equiv}CR + CO \rightarrow (PPh_3)(CO)_3CoC(O)CH_2C{\equiv}CR \qquad (9)$$

Since the corresponding alkyls $L(CO)_3CoR$ (L = tertiary phosphine) generally readily insert CO (ref. 16), this reactivity does not come as a surprise. The propargylcarbonyl products $(PPh_3)(CO)_3CoC(O)CH_2C{\equiv}CR$ undergo facile decarbonylation to regenerate the propargyl complexes.

Addition of electrophiles to the C≡C bond

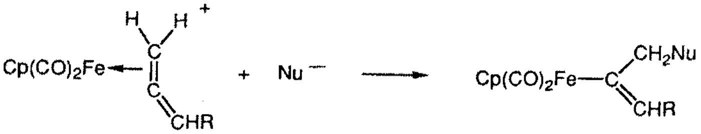
Reagents that are electrophilic in nature generally undergo addition to the C≡C bond of metal-propargyl complexes (refs. 5,17). The simplest of these reactions is protonation. Thus, treatment of $L_nMCH_2C{\equiv}CR$ with a strong acid such as HBF_4, HPF_6, or $HClO_4$ affords the corresponding cationic metal-η^2-allene complexes (refs. 18-20). The stereospecific formation of the syn isomer has been rationalized in terms of trans periplanar participation of the metal concerted with addition of H^+ (ref. 20):



(10)

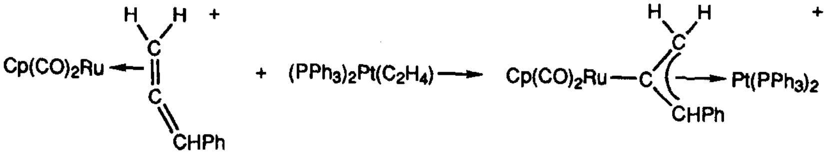
This product then converts to the more stable anti isomer (M and R trans).

The cationic allene complexes $[Cp(CO)_2Fe(\eta^2\text{-}CH_2{=}CHMe)]^+$ have been shown to react with a number of nucleophiles Nu^- (hydride, hydroxide, secondary amines, and tertiary phosphines) at the CH_2 carbon to afford iron-vinyl complexes (refs. 19,21):



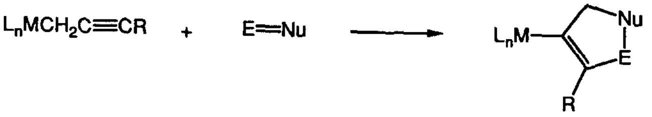
(11)

The role of the nucleophile Nu^- can be assumed also by $Pt(PPh_3)_2$ as illustrated by the recently studied reaction (ref. 22):



(12)

The aforementioned sequence of electrophilic and nucleophilic additions to metal-propargyl complexes apparently occurs in the course of the latter's reactions with a host of neutral unsaturated reagents. Electrophilic compounds such as SO_2, SO_3, PhNSO, RSO_2NSO, $(RSO_2N)_2S$, $ClSO_2NCO$, RSO_2NCO, $(CF_3)_2CO$, $R^1(R^2)CCO$, and $(CN)_2C{=}C(CN)_2$ (E=Nu; E = electrophilic atom, Nu = nucleophilic atom) undergo [3+2] cycloaddition reactions with the propargyl ligand of $L_nMCH_2C{\equiv}CR$ (refs. 5,7,17):



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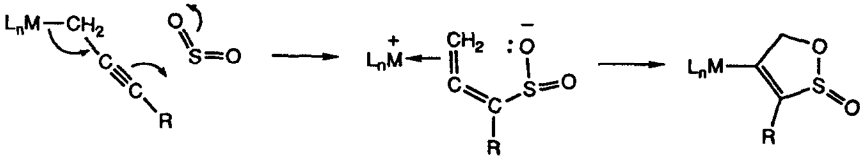
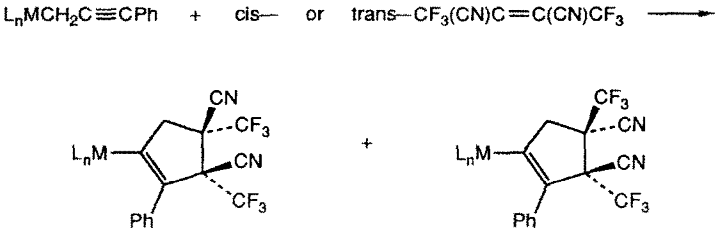
These reactions are conveniently carried out in various organic solvents and afford good to essentially quantitative yields of metal-vinyl derivatives with a five-membered ring. The proposed mechanism for this cycloaddition is depicted below for E=Nu being SO_2:



(14)

This mechanism receives support from a stereochemical study of the reaction shown in eqn. (15), in which a mixture of cis and trans CF_3,CN-substituted metal-cyclopentenyl complexes was obtained when starting with either *cis*- or *trans*-$CF_3(CN)C{=}C(CN)CF_3$. The observed loss of stereochemistry is incompatible with a concerted mechanism of the cycloaddition. However, it is consistent with a two-step pathway analogous to that in eqn. 14, with the loss of stereochemistry occurring at the negative terminus of the dipolar intermediate.

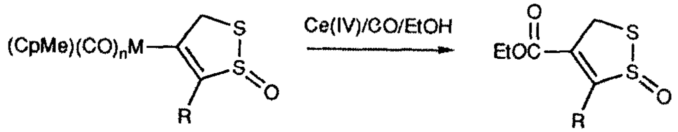
A kinetic study of the reaction of a series of metal propargyls $L_nMCH_2C{\equiv}CR$ with *p*-$MeC_6H_4SO_2NCO$ demonstrated a considerable range of reactivity of these



(15)

complexes (ref. 24). Second-order rate constants for this cycloaddition reaction are presented in Table 1. It is evident that replacement of a CO group with a stronger σ-bonding ligand such as $P(OPh)_3$ or, especially, PPh_3, leads to a substantial increase in the rate constant for the cycloaddition. This increase in reactivity may be ascribed to better stabilization of the incipient metal-η^2-allene bond in the zwitterion through greater π back-donation. The faster reaction of the methylpropargyl complexes (R = Me) than of the corresponding phenylpropargyl complexes (R = Ph) accords with both steric and electronic properties of the two substituents.

The [3+2] cycloadducts of metal-propargyl complexes and E=Nu represent potential precursors of various classes of organic ring compounds. However, their usefulness in synthesis depends on the efficacy of cleavage of the metal-carbon bond without destruction of the organic part. Efforts in that vein have been limited so far; one successful application is the preparation of esters of cyclic thiosulfinates (ref. 25):



(16)

REACTIONS OF METAL-PROPARGYL COMPLEXES WITH ORGANOMETALLIC COMPOUNDS

With dicobalt octacarbonyl

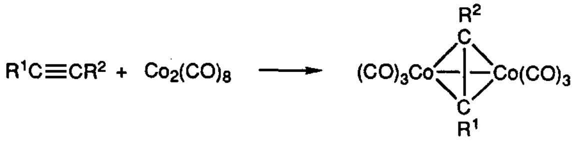
Dicobalt octacarbonyl reacts with terminal and internal alkynes to yield binuclear cobalt complexes that feature a transversely bridging alkyne ligand (ref. 26) (eqn.(17)). Analogous complexes have been synthesized by using several metal acetylides, $L_nMC{\equiv}CR$, in place of $R^1C{\equiv}CR^2$ (refs. 27-29). We thought that it would be of interest to extend these reactions of $Co_2(CO)_8$ with compounds containing C≡C bonds to

TABLE 1

Second-order rate constants for the cycloaddition reactions of $L_nMCH_2C{\equiv}CR$ with *p*-$MeC_6H_4SO_2NCO$ in CH_2Cl_2 at 25 °C.

Complex		k x 10^2,[a]	Ref.
L_nM	R	M^{-1} s^{-1}	
$(PPh_3)(CO_4Mn$	Me	≥ 20[b]	24
$Cp(CO)_2Fe$	Me	6.3	24
$Cp(PPh_3)(CO)_2Mo$	Ph	3.3	24
$Cp(CO)_3Mo$	Me	2.1	24
$(PPh_3)(CO)_4Mn$	Ph	0.77	24
$Cp[P(OPh)_3](CO)_2Mo$	Ph	0.66	24
$Cp(CO)_2Ru$	Ph	0.27	22
$Cp(CO)_2Fe$	Ph	0.21	24
$Cp(CO)_3Mo$	Ph	0.070	24
$Cp(CO)_3W$	Ph	0.027	24
$(CO)_5Mn$	Ph	0.0061	24

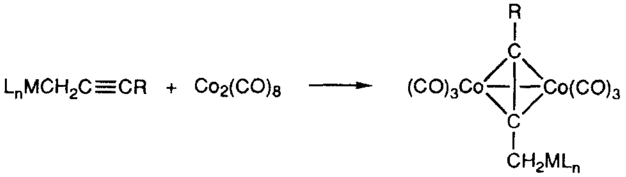
[a] ± 10% or better.
[b] Estimated value.



(17)

various metal-propargyl complexes. In addition to the likelihood of obtaining trinuclear metal compounds (Co_2M) which might serve as precursors of heteronuclear metal clusters, the propensity of the propargyl group to undergo rearrangement to an allenyl structure suggested some interesting chemistry of such reaction systems.

Indeed, facile reactions occurred between $Co_2(CO)_8$ and $L_nMCH_2C{\equiv}CR$ (L_nM = $Cp(CO)_2Fe$, $(CO)_5Mn$, $Cp(CO)_3Mo$, $Cp(CO)_3W$, $Cp(CO)_2Ru$; R = Me, Ph) to give expected trinuclear metal compounds, **1** (refs. 22,30):



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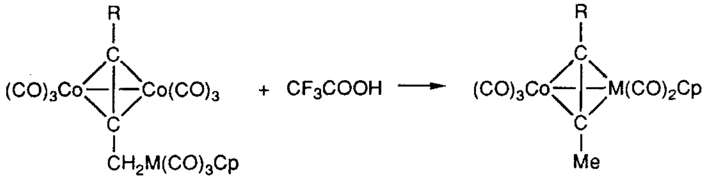
(18)

The chemistry of some of these products toward protic acids proved to be most unusual. Whereas the iron-, ruthenium-, and manganese-containing complexes **1** reacted with CF_3CO_2H or alumina in a normal manner, by cleavage of the M-CH_2 bond and formation of $(CO)_3Co(\mu\text{-PhC}{\equiv}\text{CMe})Co(CO)_3$, the molybdenum- and tungsten-containing complexes **1** displayed completely different behavior (ref. 30):

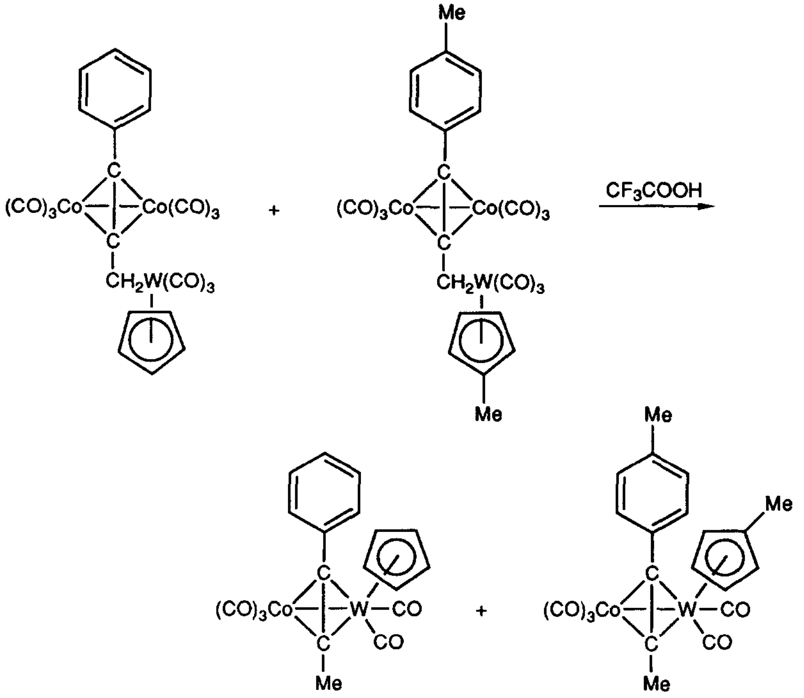


1 **2**

(19)

The products of these reactions turned out to be heterobinuclear CoMo and CoW acetylene complexes, **2**, that are structurally similar to $(CO)_3Co(\mu\text{-}R^1C{\equiv}CR^2)Co(CO)_3$. Several such heterobinuclear acetylene compounds are now reported in the literature, including examples of CoNi, CoMn, and CoRh combinations (refs. 31-34); however, all were prepared by different routes. The chemistry of these compounds has not yet been much explored.

The mechanism of the interesting transformation shown in eqn. (19) is certainly intriguing. We demonstrated by use of CF_3CO_2D that the additional hydrogen in the Me group of **2** indeed derives from the acid (ref. 30). Furthermore, it was shown by a crossover experiment (ref. 35):

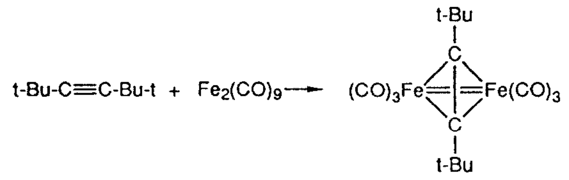


(20)

that the reaction is intramolecular, viz., that cleavage of the W-CH$_2$ bond with hydrogen from the CF$_3$CO$_2$H does not separate CpW- and acetylene-containing fragments deriving from the trinuclear metal complex 1. Instead, these fragments remain together in an intermediate that continues to react to give the final products. The nature of this intramolecular pathway is not obvious, and further studies by NMR were precluded by the formation of a paramagnetic species.

Molybdenum and tungsten propargyls with iron and ruthenium carbonyls

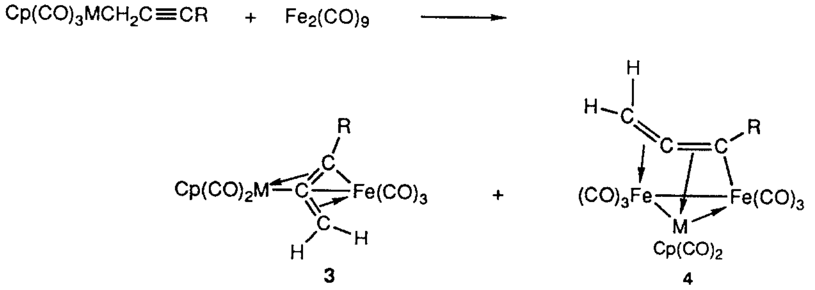
The successful synthesis of the trinuclear complexes Co$_2$M (1) and, when M = Mo and W, also the binuclear complexes CoM (2) suggested a possible extension of this chemistry from cobalt to analogous iron systems. Reactions of alkynes with iron carbonyls have been extensively investigated and have resulted in the isolation of numerous organometallic products whose nature depends on the reaction conditions employed (ref. 36). η^4-Cyclobutadiene, cyclic ketone, quinone, and ferrole complexes represent some of those products. However, the reaction that attracted our attention in the context of the present study is that between *t*-BuC≡CBu-*t* and Fe$_2$(CO)$_9$ (ref. 37):



(21)

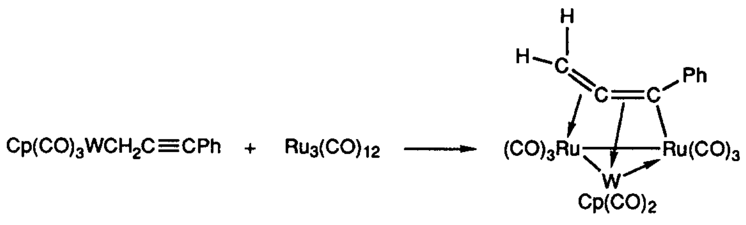
The diiron acetylene product was shown by X-ray crystallography to adopt a structure very similar to that of $(CO)_3Co(\mu\text{-}R^1C{\equiv}CR^2)Co(CO)_3$ (except for a double bond between the iron atoms) which provides each metal with a full complement of 18 valence electrons. Therefore, we thought that reactions of $Cp(CO)_2MCH_2C{\equiv}CR$ (M = Mo, W) with $Fe_2(CO)_9$ might broaden the scope of the already described chemistry of metal propargyls by furnishing FeM complexes analogous to **1**.

It turned out that such compounds did not form; however, the chemistry observed and subsequently developed proved to be much more interesting than that expected. Young noted that the reaction between equimolar amounts of various $Cp(CO)_3MCH_2C{\equiv}CR$ (M = Mo, W; R = Me, Ph, p-Tol) and $Fe_2(CO)_9$ in pentane at ambient temperatures affords two heteronuclear metal complexes (ref. 38):



(22)

the binuclear **3** being the major product. With an excess of the metal-propargyl complex, **3** becomes the only isolated product, whereas by employing $Fe_3(CO)_{12}$ in benzene at reflux in place of $Fe_2(CO)_9$, **4** is obtained exclusively. Complexes **3** afford no detectable **4** when heated or irradiated alone in solution; however, **3** can be converted to **4** in low yield by treatment with $Fe_2(CO)_9$. Reaction between $Cp(CO)_3WCH_2C{\equiv}CPh$ and $Ru_3(CO)_{12}$ gave the Ru_2W analogue of **4**, **5**:



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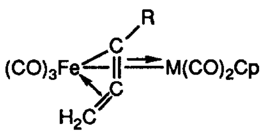
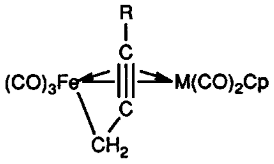
(23)

there being no evidence for a heterobinuclear complex similar to **3**.

An X-ray structural analysis of **3** (M = W; R = p-Tol) showed it to be a novel heterobinuclear metal-μ-η^2,η^3-allenyl complex, with the most acute allenyl C-C-C bond angle (128.9 (6)°) yet reported in metal complexes (ref. 38). The structure of **3** may receive some contribution from the resonance representation (B), in addition to the contribution from (A), the latter being considered more important based on the



A



B

value of the NMR coupling constant $^1J_{CH}$ of the allenyl CH_2 group (164 Hz). Products **3** represent the first well characterized heterobinuclear metal-allenyl complexes of this type[1]; however, one homobinuclear (Mo_2) analogue has been previously prepared, but by a different route (ref. 40).

Complexes **4** (M = W, R = Ph) and **5** were also structurally characterized to show the presence of a μ_3-η^1,η^2,η^2-allenyl ligand bridging a triangular arrangement of Fe_2W and Ru_2W atoms, respectively. Here the allenyl C-C-C bond angle is less strained (144.3 (3) and 138 (2)°, respectively) than in **3**, as would be expected. The new products were the first examples of heterotrinuclear μ_3-η^1,η^2,η^2-allenyl complexes, and the first such trinuclear compounds lacking ancillary bridging ligands.[2]

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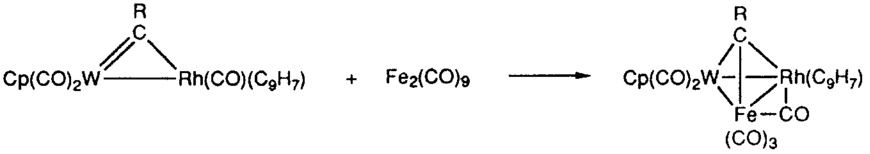
[1] A possible exception is $FeCo(CO)_5L(\mu\text{-}R^1C{=}C{=}CR^2{}_2)$(L = CO, PPh_3; R^1 = Me, Et, CH_2OH; $R^2{}_2$ = H_2, HMe, Me_2), which could not be accurately characterized by X-ray crystallography (ref. 39).

[2] However, homotrinuclear μ_3-η^1,η^2,η^2-allenyl complexes with ancillary bridging ligands have been reported (ref. 41).

Although only a limited number of reactions have been tried to date, complexes **3-5** appear to be rather unreactive, failing to give products with such reagents as protic acids, lithium alkyls, metal hydrides, alkynes, and diazomethane. This is especially surprising for **3** where the bridging allenyl ligand is rather severely twisted. However, treatment of **3** (M = Mo, R = Me) with iodine removes the allenyl group as $R(I)C{=}C{=}CH_2$, whereas addition of PPh_3 to **3** (M = W, R = p-Tol) in the presence of Me_3NO affords the phosphine-disubstituted (at Fe) analogue of the starting complex (ref. 42).

The reactions shown in eqns. (22) and (23) represent a new methodology of metal cluster synthesis. Whereas the use of unsaturated compounds for the formation of higher nuclearity clusters has been practiced for some time, such a method has been generally limited to complexes with metal-metal and metal-carbon multiple bonds (refs. 43, 44). Stone and coworkers have applied this approach to the preparation of many novel metal clusters; an example is given in eqn. (24) (ref. 45):



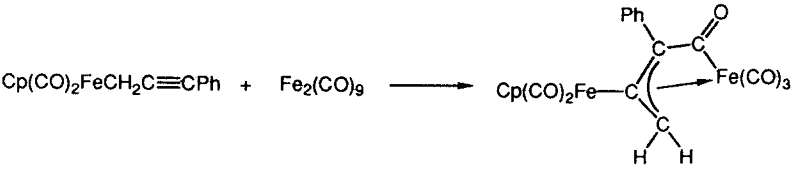
(24)

Our approach differs from Stone's in that the unsaturation is contained entirely within the attached ligand (i.e., C≡C); furthermore, this ligand displays a remarkable propensity to undergo rearrangement. Thus, different reaction chemistry is to be expected from the use of our "propargyl strategy."

Iron propargyl with diiron nonacarbonyl

At this point of our study it was important to ascertain whether the aforementioned chemistry of the molybdenum and tungsten propargyls extends to similar complexes of other transition metals. With regard to this question, the iron-propargyl complex brought a real surprise, as its behavior toward $Fe_2(CO)_9$ appears to differ considerably from that of the molybdenum and tungsten counterparts.

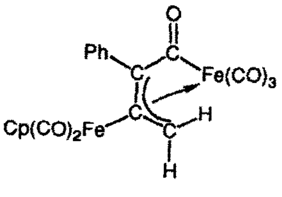
Reaction between $Cp(CO)_2FeCH_2C{\equiv}CPh$ and $Fe_2(CO)_9$ in pentane at ambient temperatures affords one major product, $(CO)_3Fe[\eta^4\text{-}C(O)C(Ph){-}{-}C(Fe(CO)_2Cp){-}{-}CH_2]$, **6** (ref. 9):



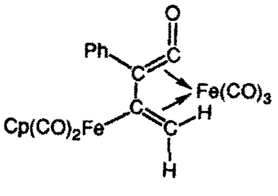
(25)

6

An X-ray structural investigation revealed that molecules of **6** consist of an allylcarbonyl ligand that is η^4-bonded to $Fe(CO)_3$ through the CO and the three allyl carbons and η^1-attached to $Fe(CO)_2Cp$ through its central allyl carbon (representation A). However, a vinylketene representation (B) probably also contributes to the



A



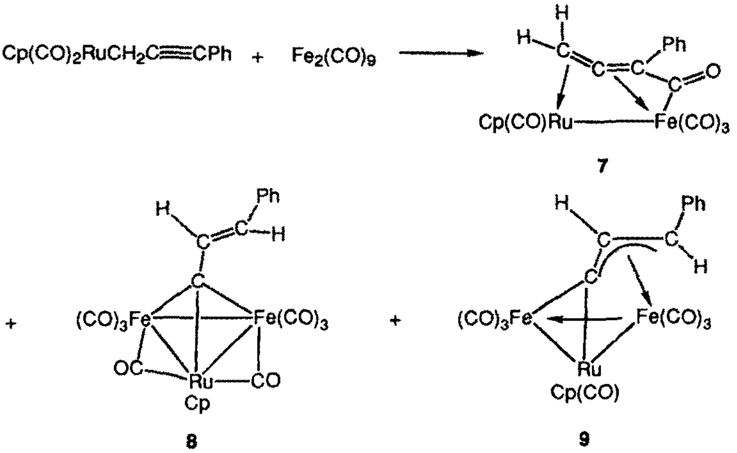
B

bonding description of **6**. There is no Fe-Fe linkage. Organoiron complexes with a similar η^4-allylcarbonyl - η^4-vinylketene dual bonding description are known (refs. 46,47); however, they were prepared by different methods.

The formation of structurally different products, **1**, **3**, **4**, and **6**, by reaction of metal-propargyl complexes with the binuclear metal carbonyls $Co_2(CO)_8$ and $Fe_2(CO)_9$ raises an important question with regard to mechanism of these reactions. This question will be approached after some additional propargyl chemistry is considered, viz., that of $Cp(CO)_2RuCH_2C{\equiv}CPh$.

Ruthenium propargyl with iron and ruthenium carbonyls

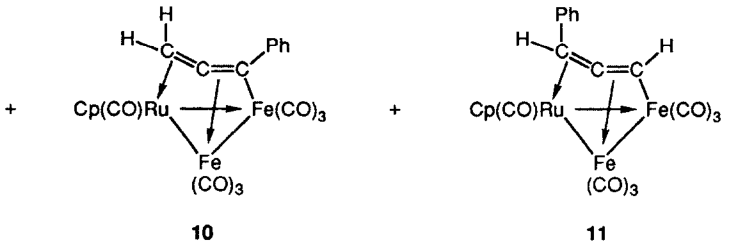
Surprisingly, the propargyl complex $Cp(CO)_2RuCH_2{\equiv}CPh$ shows a completely different, more complex chemistry when reacting with $Fe_2(CO)_9$ than does the congeneric $Cp(CO)_2FeCH_2C{\equiv}CPh$. Five heteronuclear iron-ruthenium products, **7-11**, have been isolated and characterized from these reactions (refs. 9,22):



7

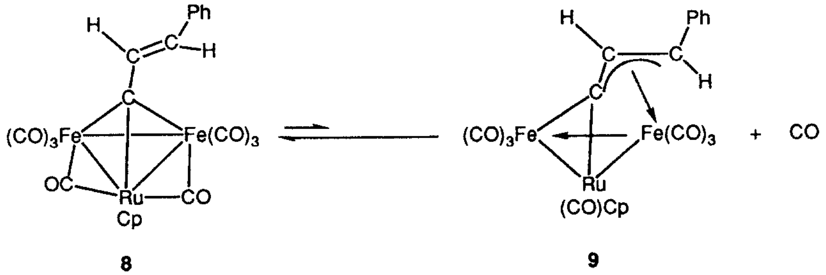
8

9



(26)

Complexes **8** and **9** slowly attain equilibrium in solution, with **8** predominating 4:1 when the solvent is $CHCl_3$:



(27)

When the equilibrium is approached from the right-hand side, the necessary CO probably comes from partial decomposition of **9**, which is appreciably less stable than **8**.

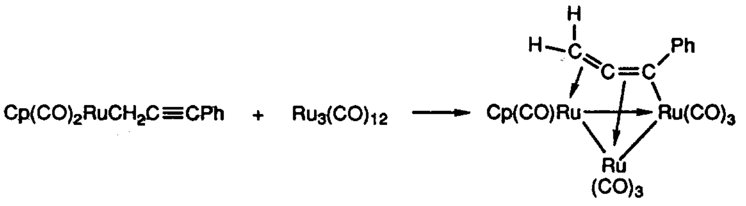
The binuclear FeRu product **7** is obtained in highest yield by using THF at 0 °C and terminating the reaction before it reaches completion, since the trinuclear products begin to form in substantial amounts after a while. Its structure, determined by X-ray analysis by Calligaris (ref. 9), shows a novel bridging allenylcarbonyl ligand, η^4-$C(O)C(Ph){=}C{=}CH_2$, which is attached to Fe through the CO carbon and the internal C=C bond, and to Ru through the terminal C=C bond. The different connectivity of the double bonds of the allenyl fragment to the metals in **7** compared to **3** (ref. 38) undoubtedly stems from the presence of an intervening CO in the bridging ligand of the former complex. This reduces the strain in the allenyl group (C-C-C bond angle of **7** = 145 (1)°) and allows the internal C=C to coordinate to iron.

A number of experiments were performed to elucidate whether the trinuclear clusters **8-11** derive from **7** either through decomposition or by reaction with an iron carbonyl species, or whether they arise via an independent pathway (ref. 22). Results of these studies (which are too involved to be discussed specifically in this account) suggest that **10** originates substantially or entirely from **7**. Complexes **8-9** may derive in part from **7**; however, complex **11** appears to be formed by a different pathway in the overall reaction given in eqn. (26). Also, each of the Fe_2Ru clusters **10** and **11** remains intact after an attempted reaction with $Fe_2(CO)_9$, and therefore does not seem to be involved in the formation of the other trinuclear clusters.

Complexes **10** and **11**, like **4**, represent trinuclear metal-μ_3-η^1,η^2,η^2-allenyl clusters Fe_2M. Both were characterized by X-ray crystallography (refs. 9,48) and shown to differ from **4** (ref. 38) in one rather important structural detail. Complex **10** contains metal-to-allenyl C=C bond connectivity that is the opposite of that in **4**; viz., the internal C=C is bonded to Fe and the terminal C=C to the metal from the propargyl complex (Ru for **10**). The connectivity in **10** may be rationalized in terms of the allenylcarbonyl ligand attachment in **7**, from which **10** is derived. Thus, dissociation of the internal C=C bond from the iron atom in **7** would allow it to be coordinated to an $Fe(CO)_{3 \text{ or } 4}$ fragment in the course of formation of **10**. By contrast, the connectivity in **11**, although of the same type as in **10**, involves a modified allenyl bridging ligand. This ligand η^1-bonds to iron through its CH carbon and η^2-coordinates to ruthenium through its terminal C=CHPh double bond. Most likely, such a rearranged structure resulted from hydrogen scrambling that occurred via intermediates with bridging hydride ligands.

The "capped" cluster **8** is a member of the class of trinuclear metal complexes with a triple-bridging alkylidyne ligand, of which various compounds $Co_3(CO)_9(\mu_3\text{-}CR)$ are well known examples (ref. 49). The related complex **9** represents an intramolecular substitution derivative of **8**, with the vinyl C=C bond replacing a carbonyl group on iron. A process analogous to the conversion of **8** to **9** has been recently reported for a Mo_3 complex (ref. 50). It is easy to see how **8** and **9** could represent possible precursors of the rearranged allenyl complex **11**; however, it is uncertain whether such a reaction pathway is actually operative.

A homonuclear metal cluster analogous to **10** is formed as the only major product when $Cp(CO)_2RuCH_2C{\equiv}CPh$ and $Ru_3(CO)_{12}$ react in hexane at reflux (ref. 22):

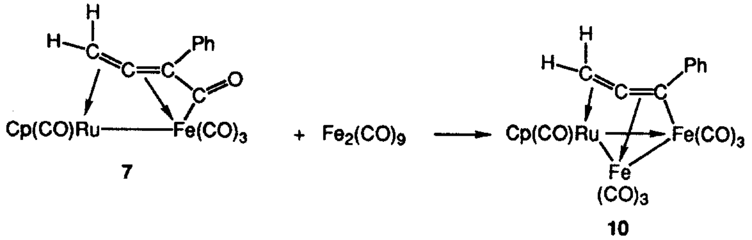


12

(28)

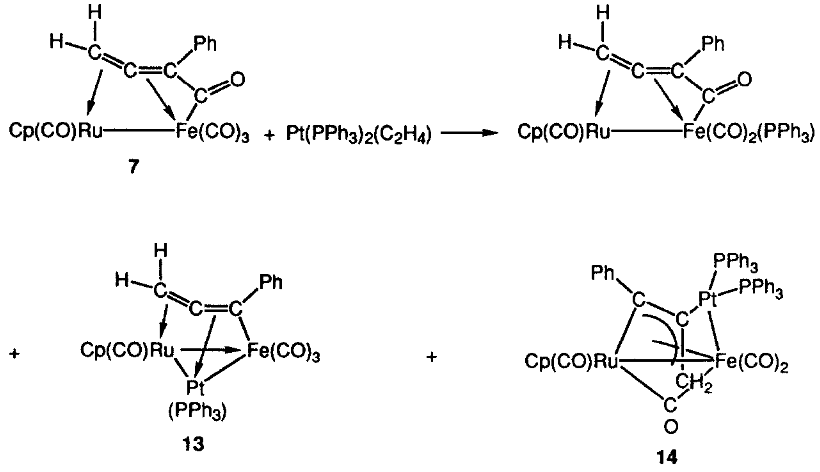
The connectivity of the allenyl bridge to Ru_3 in **12** parallels that in **10** but is different from that in the Ru_2W complex **5** (ref. 38), as discussed earlier for **10** vs. **4**.

The observation that the binuclear complex **7** reacts with $Fe_2(CO)_9$ to furnish the trinuclear complex **10** (refs. 9,22):



(29)

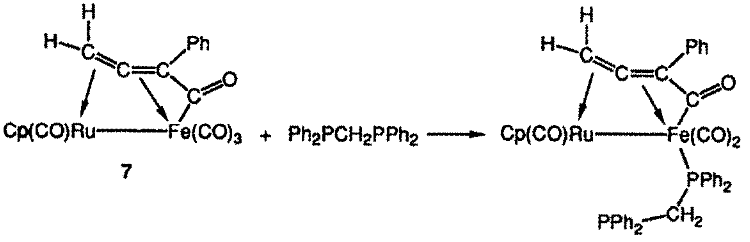
suggested that **7** might be a suitable reagent for the formation of heterotrinuclear clusters FeRuM. One approach that seemed particularly attractive in this context focused on further studies of reactions between **7** and coordinatively unsaturated metal complexes or metal complexes that undergo fragmentation into such species. Thus, we examined the reaction of **7** with $Pt(PPh_3)_2(C_2H_4)$ in THF at 0 °C, which afforded two new FeRuPt clusters, besides a PPh_3-substitution derivative of **7** (refs. 9,22):



(30)

Complex **13** appears to be structurally analogous to **10**, although an X-ray analysis is needed to check this assignment. Its formation may be rationalized similarly to that of **10** from **7** and $Fe_2(CO)_9$. By contrast, complex **14**, whose structure was recently determined by Rheingold (ref. 51), comes as a complete surprise. It is evident at this early stage of the investigation that the chemistry of such reacting systems can be unpredictable and quite complex.

The other approach exploited by us takes advantage of the ability of **7** to readily undergo substitution of one CO by a phosphine ligand. Accordingly, reaction of **7** with $Ph_2PCH_2PPh_2$ affords a monosubstituted derivative of the former, with one phosphorus donor atom remaining uncoordinated (ref. 22):

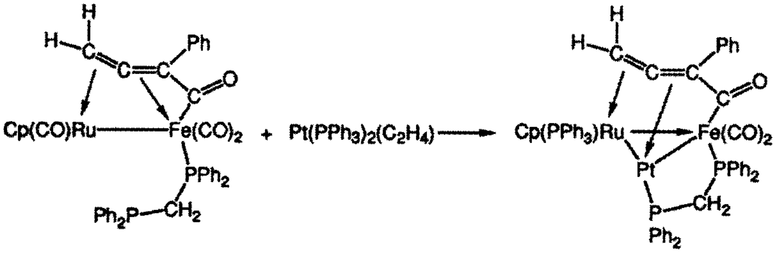


7

15

(31)

Complex **15** undergoes a facile reaction with $Pt(PPh_3)_2(C_2H_4)$ to give an FeRuPt cluster, **16**:



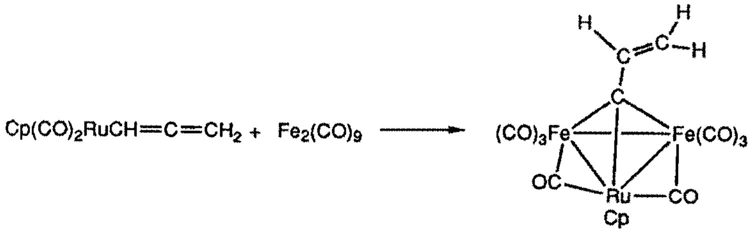
15

16

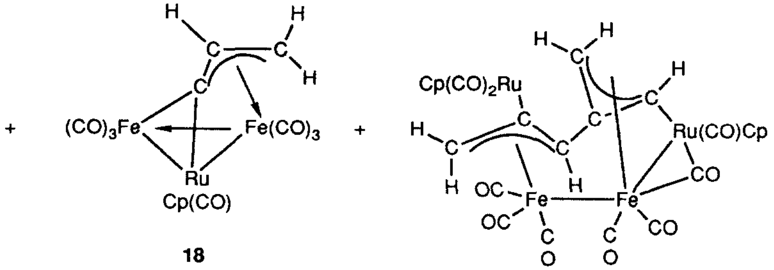
(32)

and another heterotrinuclear complex which requires structural characterization. This approach utilizes the availability of a free phosphorus donor atom to bring a reactive, coordinatively unsaturated metal fragment into the proximity of the Fe and Ru centers. However, general applicability of this method to synthesis still needs to be explored.

In a study that was undertaken to complement the foregoing investigations, we also examined reactions of $Cp(CO)_2RuCH{=}C{=}CH_2$ with $Fe_2(CO)_9$. Although this work has not yet been completed, three products have been fully characterized, **17**, **18**, and a tetranuclear Fe_2Ru_2 cluster (refs. 22, 52, 53):



17



18

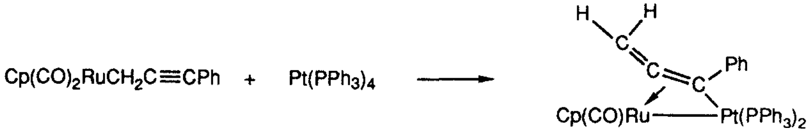
(33)

Complexes **17** and **18** are the respective analogues of "capped" **8** and its equilibrium partner **9**, with the Ph group being replaced by the hydrogen in each. They also exist together in solution as an equilibrium mixture. Another major reaction product, a heteronuclear cluster, is under structural investigation. It is not clear at this point how **17** and **18** are formed and what similarities exist between reactions in the $Cp(CO)_2RuCH{=}C{=}CH_2$ - $Fe_2(CO)_9$ system and those in the $Cp(CO)_2RuCH_2C{\equiv}CPh$ - $Fe_2(CO)_9$ system.

Ruthenium propargyl with platinum(0) complexes

The behavior of the ruthenium propargyl complex $Cp(CO)_2RuCH_2C{\equiv}CPh$ toward $Fe_2(CO)_9$ is characterized by complexity and dependence on the reaction conditions employed. In an attempt to simplify the chemistry of $Cp(CO)_2RuCH_2C{\equiv}CPh$ in cluster-building reactions, we examined the use of $Pt(PPh_3)_2$-containing compounds in place of $Fe_2(CO)_9$ as the substrate. Such compounds generally react to give metal clusters with only one platinum atom (refs. 43,44).

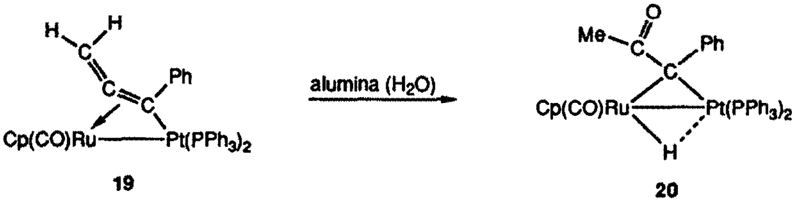
Reaction between $Cp(CO)_2RuCH_2C{\equiv}CPh$ and $Pt(PPh_3)_4$ in THF at reflux affords a RuPt allenyl product, **19** (ref. 22):



19

(34)

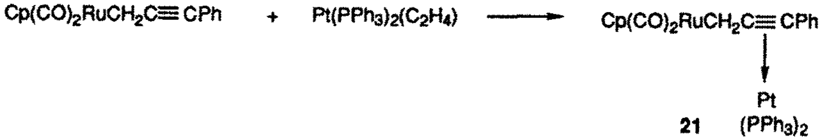
This complex was observed to react with alumina during an attempt at chromatography to yield a binuclear metal-μ-alkylidene μ-hydride, **20**:



(35)

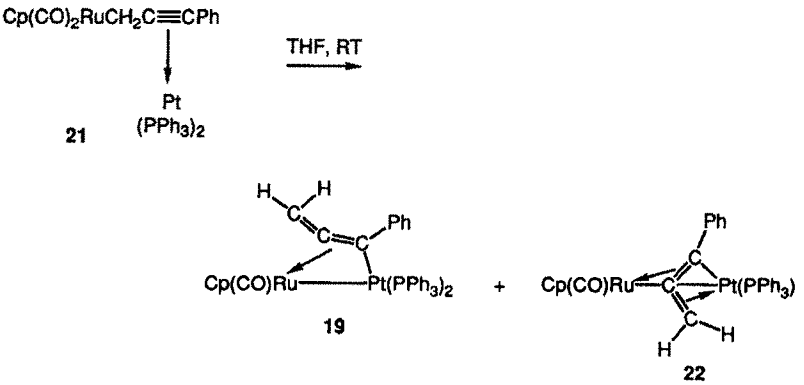
presumably by addition of H_2O to the central allenyl carbon atom. The structures of close analogues of **19** and **20**, differing by replacement of the Ph group with the hydrogen (**23** and **24**, *vide infra*), were elucidated by X-ray crystallographic analyses (ref. 54). A μ-η^1,η^2 mode of bonding that features coordination of the internal allenyl C=C bond (as in **19** and **23**) is precedented in homobinuclear metal chemistry (ref. 55), but had been unknown for heterobinuclear complexes.

More reactive than $Pt(PPh_3)_4$ toward $Cp(CO)_2RuCH_2C{\equiv}CPh$ is $Pt(PPh_3)_2(C_2H_4)$, which at -20 °C in THF affords an unstable species thought to be a product of replacement of the C_2H_4 ligand with the propargyl C≡C bond:



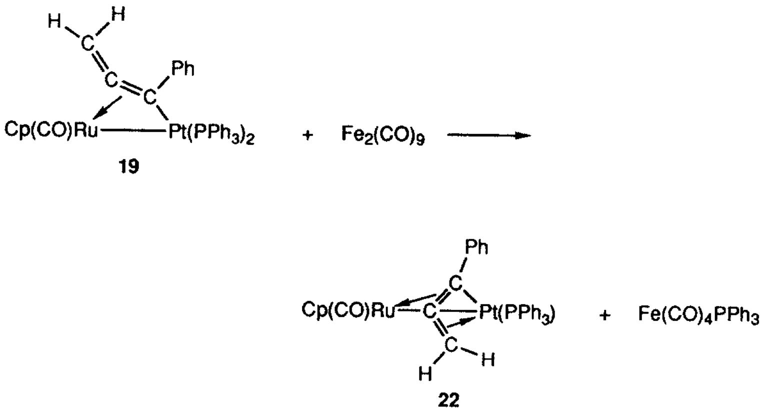
(36)

Continued reaction, at room temperature, furnishes two isolable heterobinuclear products, **19** and **22**:



(37)

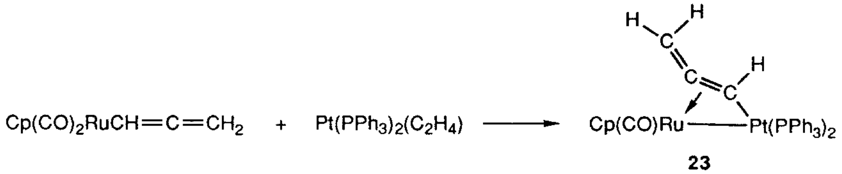
the latter appearing to be (from spectroscopic and analytical data) structurally analogous to the FeMo and FeW μ-η^2,η^3-allenyl complexes **3**. Significantly, conversion of **19** to **22** can be effected by using $Fe_2(CO)_9$, which acts as a scavenger of one PPh_3 ligand from the former RuPt complex, giving $Fe(CO)_4PPh_3$:



(38)

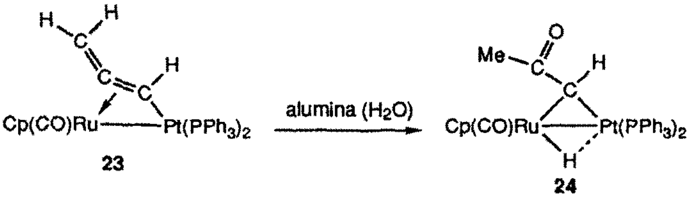
This transformation represents the first example of conversion of a μ-η^1,η^2-allenyl ligand to a μ-η^2,η^3-allenyl ligand bridging a binuclear metal complex framework. Moreover, looking back at the reaction of $Cp(CO)_2RuCH_2C{\equiv}CPh$ with $Pt(PPh_3)_4$ (eqn. 34), the observed lack of formation of **22** undoubtedly derives from the presence of an excess of PPh_3 in solution (from $Pt(PPh_3)_4$) which impedes conversion of **19** to **22**.

Reaction of the allenyl complex $Cp(CO)_2RuCH{=}C{=}CH_2$ with $Pt(PPh_3)_2(C_2H_4)$ proved to be as simple as that of the propargyl complex; it is most interesting that essentially the same chemistry takes place (ref. 22):



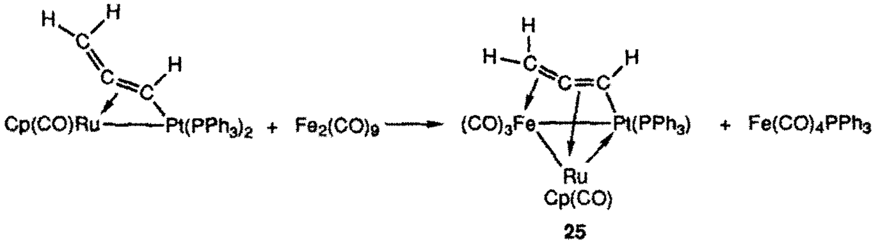
(39)

Complex **23** is transformed in the course of chromatography on alumina to a μ-alkylidene μ-hydride, **24**, a strict analogue of **20**:



(40)

Surprisingly however, its reaction with $Fe_2(CO)_9$ did not yield a μ-η^2,η^3-allenyl complex similar to **22** in sufficient amount for unambiguous characterization; instead, an FeRuPt cluster, **25**, was obtained as the major product:



(41)

It is not clear at this time why the reactions of $Cp(CO)_2RuCH_2C{\equiv}CPh$ and $Cp(CO)_2RuCH{=}C{=}CH_2$ with $Pt(PPh_3)_2(C_2H_4)$ are so much alike. Perhaps the allenyl complex exists in equilibrium with a small amount of reactive propargyl complex, or the reaction of $Pt(PPh_3)_2(C_2H_4)$ (or $Pt(PPh_3)_2$) proceeds by insertion into the Ru-CH bond of $Cp(CO)_2RuCH{=}C{=}CH_2$, or yet another mechanism is operative.

Mechanistic considerations

In this section, we wish to consider how the various binuclear and trinuclear metal-allenyl and related complexes may be formed from the metal propargyls and appropriate organometallic substrates. Since many of the systems synthetically examined in this investigation are quite complex, and since no mechanistic studies have been carried out on related reactions, the proposed pathways should be considered only as reasonable possibilities. Furthermore, we will not deal here with the formation of metal-cluster products of such unexpected or complex structures as those of **8**, **9**, **11**, and **14**. Reactions of metal-allenyl complexes will not be discussed either, since not enough is known about them at this time.

Possible reaction pathways are summarized in Fig. 1. Included here are the reactions of the propargyl complexes of molybdenum, tungsten, iron, and ruthenium with iron carbonyls and platinum(0) compounds. The reactions of these metal propargyls with $Co_2(CO)_8$ to give the trinuclear complexes **1** almost certainly proceed in a manner comparable to that of the reactions between acetylenes and $Co_2(CO)_8$ (ref. 26). They are also left out of the scheme in Fig. 1.

Substitution reactions of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ and of $Pt(PPh_3)_4$ and $Pt(PPh_3)_2(C_2H_4)$ with various ligands L can lead to the formation of appropriate mononuclear metal complexes (refs. 56,57). It is therefore proposed that the interactions between metal propargyls and these iron and platinum compounds initially give metal-acetylene-like complexes of $Fe(CO)_4$ and $Pt(PPh_3)_2$ (M^2). One complex, **21**, is assigned such a structure from spectroscopic evidence. These acetylene complexes then undergo rearrangement to dipolar metal-η^2-allene species by paths 1 or 2, the latter being possible only if M^2 contains CO. In path 2, the zwitterion collapses by attack of the negative $M^2 = Fe(CO)_3$ either at the coordinated allene (for $L_nM^1 = Cp(CO)_2Fe$) or at the L_nM^1 with loss of L (for $L_nM^1 = Cp(CO)_2Ru$). The observed selectivity may be due to the relative strength of the incipient M^1-M^2 bond, the susceptibility of $Cp(CO)_2M^1$ to attack by the negative $Fe(CO)_3$, the propensity of $Cp(CO)_2M^1$ to decarbonylation, or a combination of these factors. The binuclear allenylcarbonyl complex **7** reacts with (additional) M^2 to afford the trinuclear complexes **10** and **13**.

The reactions of the molybdenum and tungsten propargyl complexes with $Fe_2(CO)_9$ to give **3** and **4** are not as clear-cut as those of the iron and ruthenium propargyls. To keep the scheme in Fig. 1 as simple as possible, we propose similar pathways for these and the already considered transformations. Either path 1 or 2 may be followed to yield a binuclear metal-μ-η^1,η^2-allenyl complex in which the terminal C=C bond is ligated. Complexes with such an allene coordination have not yet been reported. They may isomerize to the corresponding allenyl complexes in which the internal C=C bond is attached to M^1, and thence proceed to the isolable binuclear (**3**) and trinuclear (**4**) products.

The last steps in the proposed formation of **3** and **4** are known for the analogous RuPt and FeRuPt complexes (i.e., conversions of **19** to **22** and of **23** to **25**, respectively). If $Cp(CO)_2RuCH_2C{\equiv}CPh$ reacts with $Pt(PPh_3)_2$-containing complexes by a sequence of steps outlined in Fig. 1, then path 1 would be followed similarly to the reactions of $Cp(CO)_3MCH_2C{\equiv}CR$ (M = Mo, W) with $Fe_2(CO)_9$. However, there appears to be less tendency for the Ru-Pt reacting system to proceed to trinuclear metal clusters, and the binuclear μ-allenyl complexes **19** and **22** are obtained as the sole products. Over a longer period of time, a different metal-ligand fragment ($Fe(CO)_3$) undergoes addition to **23** to give a heterotrinuclear FeRuPt complex, **25**.

The overall reaction scheme does correlate the observed behavior of a number of metal-propargyl complexes toward iron carbonyls and platinum(0) compounds. Furthermore, it has some features in common with the mechanism proposed for the cycloaddition reactions of $L_nMCH_2C{\equiv}CR$ (refs. 5,17). However, it needs to be tested

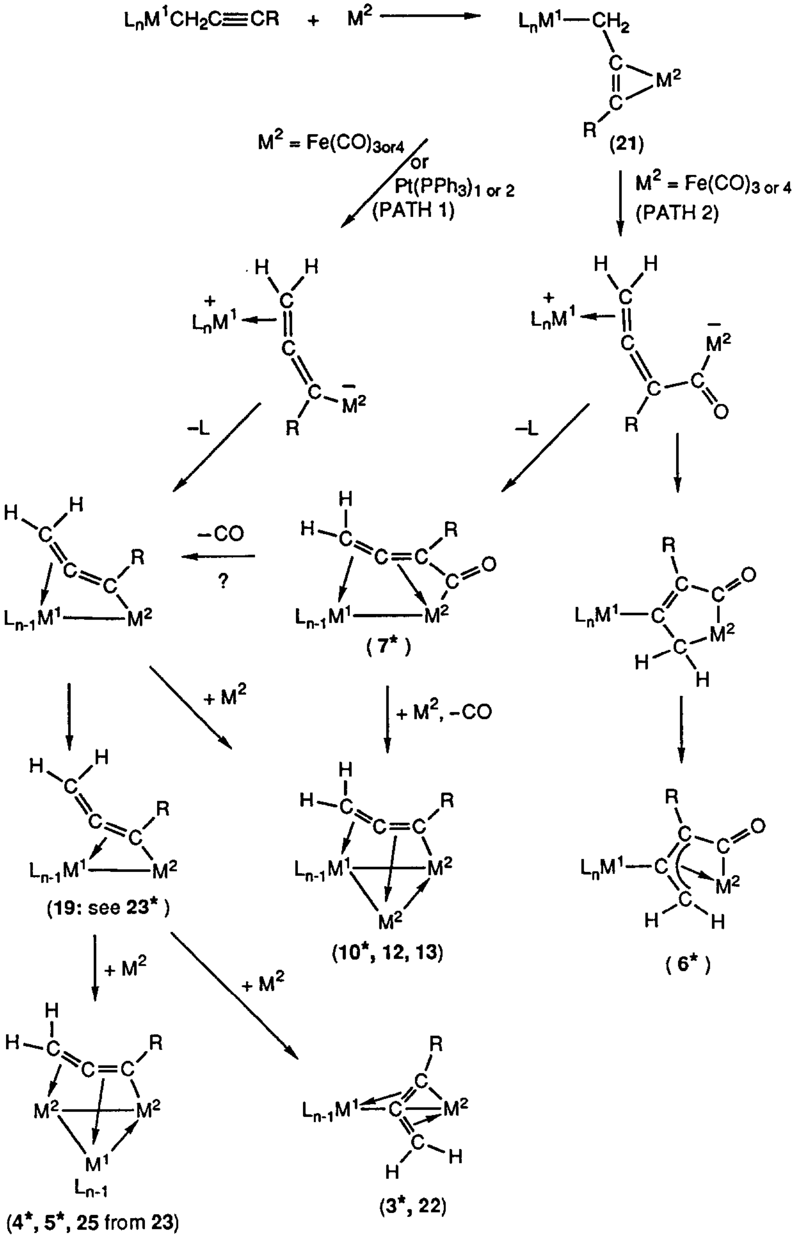


Fig. 1. A general scheme for the reactions of transition-metal-propargyl complexes with coordinatively unsaturated metal-ligand fragments, M^2. The composition of M^2 may change in the course of a given reaction, e.g., $Fe(CO)_4$ to $Fe(CO)_3$ or $Pt(PPh_3)_2$ to $Pt(PPh_3)$. Examples of complexes of various structures are given below the drawings. An asterisk indicates that the structure was determined by X-ray crystallography.

on a relatively simple reacting system, possibly such as $Cp(CO)_2RuCH_2C{\equiv}CR$ and $Pt(PPh_3)_2(C_2H_4)$ or a related substrate.

CONCLUDING REMARKS

This account focuses on the use of transition-metal-propargyl complexes in the synthesis of a variety of organometallic compounds. By utilizing different reagents one can obtain metal-η^2-allene complexes, metal complexes with five-membered homocyclic and heterocyclic organic rings, and binuclear and trinuclear complexes, virtually all of which are metal-metal-bonded and contain various combinations of metal atoms. In that last category, the synthesis of metal-μ-allenyl complexes is particularly noteworthy. Although several binuclear and trinuclear metal-μ-allenyl complexes had been reported at the start of our investigation, there was no general preparative route to such compounds, and no heteronuclear metal allenyls were known. Reactions of metal-propargyl complexes with compounds that readily generate coordinatively unsaturated metal species (e.g., $Fe_2(CO)_9$ and $Pt(PPh_3)_2(C_2H_4)$) provide the first general method of synthesis of heteronuclear metal allenyls. Moreover, with a proper choice of reactant, this method can be applied to both homonuclear and heteronuclear compounds. Metal-μ-allenyl complexes that have been obtained in this manner include: (i) the heterobinuclear allenyls in which either the internal C=C bond or both C=C bonds are ligated and (ii) the homotrinuclear and heterotrinuclear ($M^1M^2M^3$ or $M^1{}_2M^2$) allenyls in which both C=C bonds are coordinated. At this time, more needs to be learned about the chemistry of such compounds and its possible relevance to metal-assisted stoichiometric and catalytic reactions of unsaturated hydrocarbons.

ACKNOWLEDGEMENTS

This account of our studies in metal-propargyl chemistry is dedicated to Professor Fred Basolo on the occasion of his 70th birthday. His very high professional standards, love and enthusiasm for chemistry and teaching, and warm personal relationships with others have made profound impact not only on his students and associates, but also on many other chemists, in the U.S. and abroad. One of the authors and a former student of F. B. (A. W.), in particular, wishes to acknowledge the great impact that Fred has had on his professional career. It is also A. W.'s pleasure to acknowledge the contributions to this study of many coworkers whose names appear among the references. We are especially appreciative of the X-ray crystallographic analyses performed in the laboratories of Professors M. Calligaris, M. R. Churchill, and A. L. Rheingold. This research has been supported by the National Science Foundation and The Ohio State University.

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