The Insertion of Alkynes into Metal–Metal Bonds and Organic Chemistry of the Dimetallated Olefin Complexes

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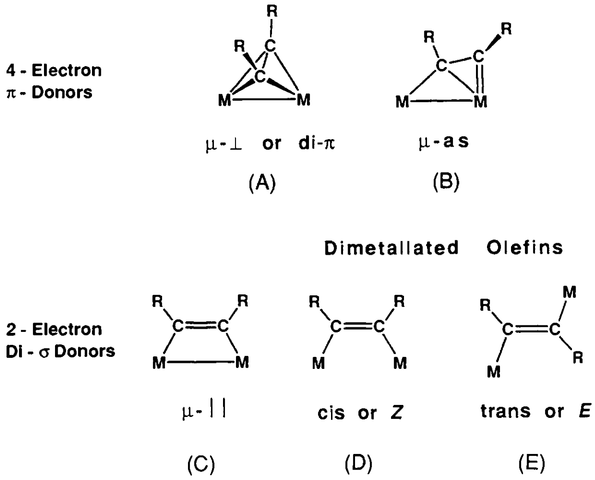
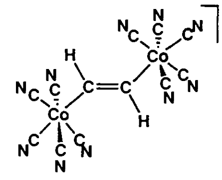
1 Introduction

The activation of alkynes through complexation to metal atoms has played an important role in the development of the organic chemistry of these molecules.[1,2] Recently, there has been much interest in the coordination and reactivity of alkynes in polynuclear metal complexes.[3] Alkynes have been found to coordinate to the metal atoms in binuclear metal complexes in several different ways. By far the most common mode is the μ-⊥ or di-π in which the ligand donates electrons from both of its π-bonds to the two metal atoms, **A**.[4] The direction of the C–C bond is perpendicular to the M–M bond. In these complexes the alkyne ligand serves as a four-electron donor. There are a few examples where the alkyne is coordinated in a skewed 'asymmetric' bridging mode, **B**.[2b,5]

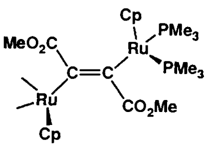
There are a number of examples where the alkyne is coordinated to the metal atoms through σ-like bonds with one carbon bonded to each metal atom. In these cases the alkyne serves as a two-electron donor. Two basic geometries are possible. In one both metal atoms lie *cis*- or *Z*-positioned relative to the C=C double bond, **C** and **D**. The metal atoms may be bonded or not. This coordination mode is also referred to as μ-||. In the other case the metal atoms lie *trans*- or *E*- to the C=C double bond, **E**. The two structural types, **D** and **E**, in which the metal atoms are not mutually bonded are often referred to as dimetallated olefins.[6]



The first example of a dimetallated olefin complex, $[(NC)_5Co(\mu\text{-}HC{=}CH)[Co(CN)_5]^{6-}$ was made by Wilkinson from the reaction of HC≡CH with $K_6[Co_2(CN)_{10}]$.[7] A structure having *Z*-stereochemistry, **E**, was proposed[7] and established many years later through an *X*-ray crystallographic analysis of the dicarboxylate-substituted derivative.[8] Since $[Co_2(CN)_{10}]^{6-}$ is well-known to split into monomeric $[Co(CN)_5]^{3-}$ fragments in solution, it seems most likely that the *E*-stereochemistry of these products is a consequence of the approach of the two $[Co(CN)_5]^{3-}$ groups from opposite sides of the alkyne. Recently, Beck and co-workers have prepared the *E*-dimetallated olefin complex $[CpRu(PMe_3)_2(\mu\text{-}Z\text{-}MeO_2CC{\equiv}CCO_2Me)[Ru(CO)_2Cp]$, (2) by the addition of the organometallic anion $[CpRu(CO)_2]^-$ to the alkyne ligand in the cationic complex $[CpRu(PMe_3)_2(MeO_2CC{\equiv}CCO_2Me)]^+$.[9]

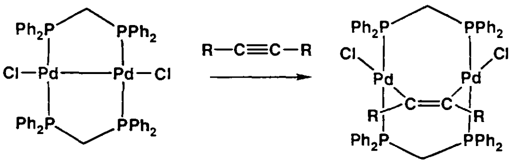


(1)



(2)

Some *Z*-dimetallated olefins have been prepared by the addition alkynes to dinuclear metal complexes by a formal 'insertion' of the alkyne into a metal–metal bond. Prior to our studies all examples of these reactions have involved dinuclear metal complexes that are bridged by two chelating phosphine ligands, *e.g.* equation 1.[10]



(1)

The dimetallated olefin complexes formally contain a double bond between the two carbon atoms. Accordingly, it is expected that the **D**⇄**E**, or *Z*⇄*E*, isomerization should have a high energy barrier. Theoretical treatments have indicated that this isomerization barrier should exceed 60 kcal mol^{-1}.[6b]

In this review we will summarize the results of our recent studies on synthesis and reactivity of dimetallated olefin complexes of the manganese subgroup. The parent carbonyl complexes $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ serve as the starting points for these studies. Ditechnetium complexes have not yet been investigated. The decacarbonyl complexes are relatively unreactive to alkynes under mild conditions. Mays has reported that $Re_2(CO)_{10}$ will react with internal alkyl and aryl alkynes at 190 °C by the addition and coupling of the alkynes to form alkyne oligomers that bridge the two rhenium atoms.[11]

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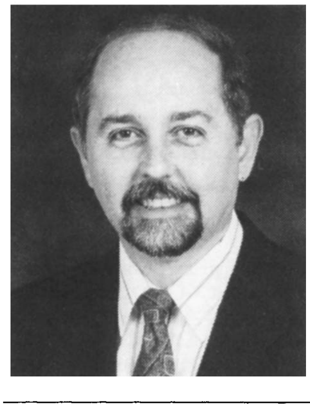
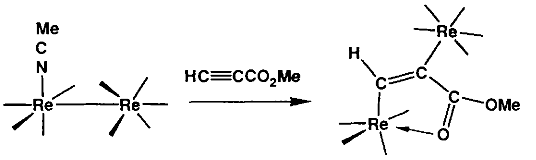


2 The Insertion of Alkynes into Re–Re and Mn–Mn Bonds

To enhance the reactivity of the decarbonyl compounds, they are routinely converted into their acetonitrile derivatives $Re_2(CO)_9(NCMe)$ (3) and $Mn_2(CO)_9(NCMe)$ (4) by the decarbonylation with Me_3NO in the presence MeCN.[12,13] The MeCN ligand in these complexes is readily displaced and bonding interactions between the alkyne and the metal atoms can be formed under mild conditions. All of the alkynes that we have studied contain at least one electron-withdrawing carboxylate group or an OEt group.

The first reaction of an alkyne with (3) that we studied involved the terminal alkyne $HC{\equiv}CCO_2Me$ at 68 °C. The product obtained in 81% yield was shown to be the *E*-dimetallated olefin complex $Re(CO)_4[\mu\text{-}E\text{-}HC{=}C(CO_2Me)]Re(CO)_5$ (5) (see equation 2) and the structure was established by a single crystal *X*-ray diffraction analysis.[12]

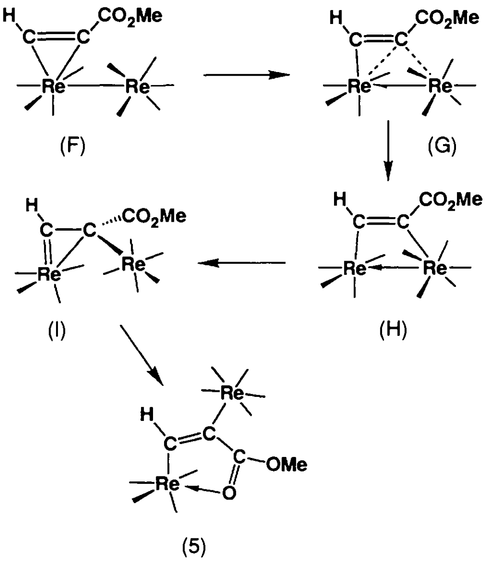


(2)

(5)

Interestingly, the carbonyl oxygen atom of the carboxylate group was coordinated to one of the metal atoms to form a five-membered ring. The complex (5) was formed formally by the insertion of the alkyne into the Re–Re bond in (3). The question of mechanism was addressed immediately. In particular, did the insertion occur by a non-dissociative 'intramolecular' process or did the complex somehow dissociatively split into mononuclear fragments which subsequently recombined? The latter process would easily explain the formation of the observed *E*-stereochemistry. Radical scavengers, light, and polar solvents had no detectable effect on the reaction which suggested that the process was instead intramolecular; but the most convincing evidence was that provided by an intermolecular crossover test. In this experiment a mixture of unlabelled $Re_2(CO)_9(NCMe)$ and fully ^{13}C-labelled (99%) $Re_2(^{13}CO)_9(NCMe)$ was allowed to react with the $HC{\equiv}CCO_2Me$ to form the product (5). If the reaction was occurring *via* the intermediacy of fully dissociated mononuclear fragments, then a statistical distribution of the four products: $Re(CO)_4[\mu\text{-}E\text{-}HC{=}C(CO_2Me)]Re(CO)_5$ (5a), $Re(^{13}CO)_4[\mu\text{-}E\text{-}HC{=}C(CO_2Me)]Re(CO)_5$ (5b), $Re(CO)_4[\mu\text{-}E\text{-}HC{=}C(CO_2Me)]Re(^{13}CO)_5$ (5c), and $Re(^{13}CO)_4[\mu\text{-}E\text{-}HC{=}C(CO_2Me)]Re(^{13}CO)_5$ (5d) should be formed. The non-dissociative mechanism should lead to the products (5a) and (5d) only. A mass spectrum of the products from this reaction showed the formation of (5a) and (5d) only. Accordingly, it is believed that the insertion of the alkyne into the metal–metal bond occurs without a splitting of the molecule into mononuclear fragments. Further evidence was obtained from the reaction of (3) with $EtO_2CC{\equiv}CCO_2Et$, see below.

It remained to explain how a product with *E*-stereochemistry was formed under such mild conditions, if the $Z \rightleftarrows E$ transformation has a high energy barrier as predicted theoretically.[6b] The mechanism shown in Scheme 1 was proposed. It is expected that the reaction proceeds initially by the displacement of the MeCN ligand by the alkyne to produce an intermediate **F** in which the alkyne is π-bonded to one of the rhenium atoms in the usual fashion. An interaction subsequently develops between the second rhenium atom and the carboxylate-substituted end to the coordinated alkyne, **G**. In the process the Re–Re bond begins to develop a heteropolar character. In the limit **H**, the metal–metal bond has a full heteropolar character. The next step is probably the slowest step and involves a spontaneous cleavage of the metal–metal bond with both electrons in the bond shifting to the $Re(CO)_5$ grouping. This would reduce the number of valence electrons at the $Re(CO)_4$ group to sixteen. This unfavourable condition could be alleviated by a conversion of the $HC{=}C(CO_2Me)Re(CO)_5$ grouping into an η^2-coordination to the $Re(CO)_4$ group through a 90° twist of the $C(CO_2Me)$ $Re(CO)_5$ grouping to form the intermediate **I**. This η^2-$HC{=}C(CO_2Me)Re(CO)_5$ grouping would serve as a three-electron donor to the $Re(CO)_4$ group. Recently, a number of complexes containing related η^2-alkenyl ligands have been isolated and structurally characterized.[14] The intermediate **I** may be a transition state that is subsequently converted into the product (5) by a further 90° rotation of the $C(CO_2Me)Re(CO)_5$ grouping and a coordination of the carbonyl oxygen atom to the $Re(CO)_4$ group.



Scheme 1

Evidence to support this mechanism was obtained from the reaction of (3) with the internal alkyne $EtO_2CC{\equiv}CCO_2Et$.[13] The product $Re(CO)_4[\mu\text{-}Z\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$, (6), was structurally characterized and found to have the a *Z*-stereochemistry of the two metal atoms, Figure 1. This complex could be formed directly from a species analogous to **H** by cleavage of the heteropolar metal–metal bond and a stabilization of the intermediate by the coordination of the oxygen atom of the proximate carbonyl group which results in the formation of the four-membered metallacyclic ring. Compound (6) can be converted into an *E*-species $Re(CO)_4[\mu\text{-}E\text{-}(EtO_2C){=}C(CO_2Et)]$ $Re(CO)_5$ (7), analogous to (5), but more forcing conditions are required. This is reasonable because the complex (6) is stabilized

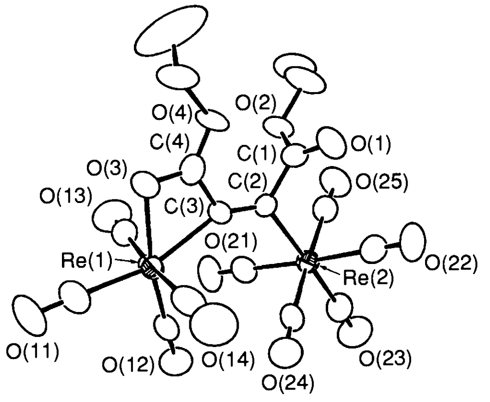
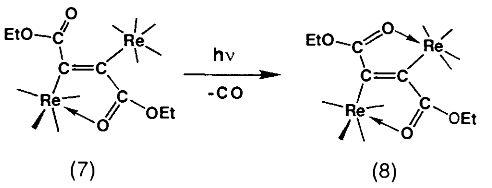


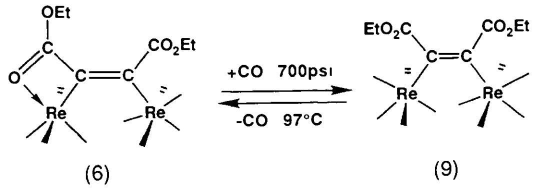
Figure 1 An ORTEP diagram of the molecular structure of the dimetallated olefin complex $Re(CO)_4[\mu\text{-}Z\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$ (2). Selected intramolecular bond distances (Å) are as follows: Re(1)–C(3) = 2.193(8), Re(2)–C(2) = 2.228(8), C(1)–C(2) = 1.49(1), C(2)–C(3) = 1.34(1), C(3)–C(4) = 1.46(1); Re(1)–O(3) = 2.214(6). (Reproduced with permission from *Organometallics*, 1994, **13**, 1264.)

relative to the species traversed *en route* to (5) Compound (7) can be decarbonylated when heated to yield the *E*-complex $Re(CO)_4[\mu\text{-}E\text{-}(MeO_2C)C{=}C(CO_2Me)]Re(CO)_4$ (8) that contains two five-membered rings formed by the coordination of the carbonyl oxygen atoms from both carboxylate groups, equation 3 [13]



(3)

Interestingly, complex (6) adds CO reversibly to yield the *Z*-dimetallated olefin complex $Re(CO)_5[\mu\text{-}Z\text{-}(MeO_2C)C{=}C(CO_2Me)]Re(CO)_5$, (9), having two $Re(CO)_5$ groups, equation 4 [13]



(4)

The irradiation of $Mn_2(CO)_{10}$ in the presence of $EtO_2CC{\equiv}CCO_2Et$ yields the compound $Mn(CO)_4[\mu\text{-}Z\text{-}(EtO_2C)C{=}C(CO_2Et)]Mn(CO)_5$ (10), which is structurally analogous to (6), in 36% yield in a matter of minutes A small amount of the two-ring compound $Mn(CO)_4[\mu\text{-}E\text{-}(MeO_2C)C{=}C(CO_2Me)]Mn(CO)_4$ (11), analogous to (8), is also formed Interestingly, compound (10) slowly isomerizes to the compound $Mn_2(CO)_8[\mu\text{-}(EtO_2C)C{=}C(CO_2Et)C{=}O]$ (12) by an insertion of a CO ligand into the metal–carbon bond of the $Mn(CO)_5$ group The oxygen atoms of the inserted CO grouping and one of the carboxylate groupings are coordinated to the manganese atoms to form five-membered rings, Figure 2 The reaction of $Mn_2(CO)_9(NCMe)$ with $EtO_2CC{\equiv}CCO_2Et$ proceeds slowly (hours) to yield (12) directly, presumably *via* the intermediacy of (10) CO coupling to the alkynes is an important difference between the chemistry of the rhenium and manganese dimetallated olefins It is the norm in the manganese chemistry and quite rare in the rhenium chemistry

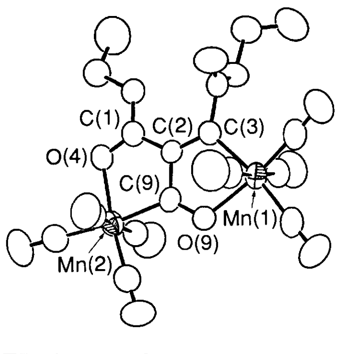


Figure 2 An ORTEP diagram of the molecular structure of the complex $Mn_2(CO)_8[\mu\text{-}(EtO_2C)C{=}C(CO_2Et)C{=}O]$ (12)
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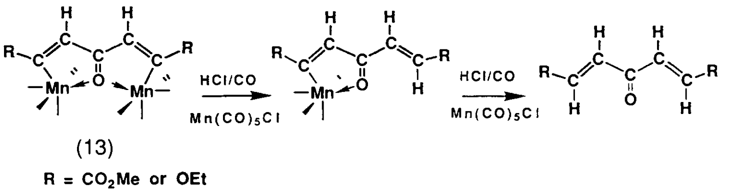
The reaction of the terminal alkyne $HC{\equiv}CCO_2Me$ with $Mn_2(CO)_9(NCMe)$ yields the compound $Mn_2(CO)_8\{\mu\text{-}O{=}C[C(H){=}C(CO_2Me)]_2\}$ (13) as the major product formed by the addition of two alkynes and their coupling to a single CO ligand [15] This same product can be obtained by the UV irradiation of $Mn_2(CO)_{10}$ in the presence of $HC{\equiv}CCO_2Me$ in a slightly lower yield [16] The reaction of $Mn_2(CO)_9(NCMe)$ with $HC{\equiv}CCOEt$ yields the analogous product, $Mn_2(CO)_8\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$ [17] In these compounds the oxygen atom of the alkyne-coupled carbonyl group is coordinated to two metal atoms The metal groupings can be sequentially cleaved from the organic ligand by reaction with a mixture of HCl and CO, Scheme 2 [15 17]



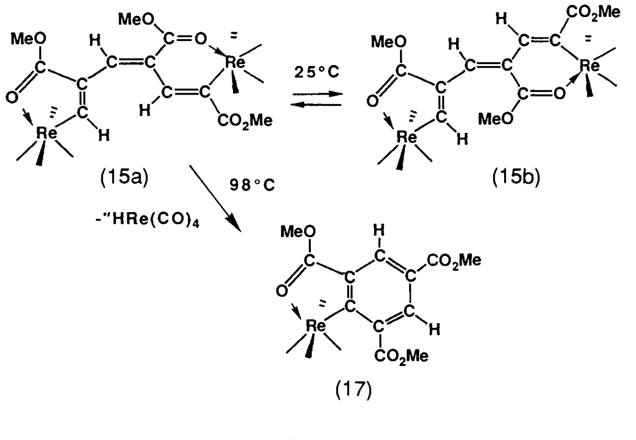
Scheme 2

The coupling of a CO ligand to one[18] and two[19] molecules of alkyne has been observed on many previous occasions, but the accompanying coordination of the oxygen atom of the carbonyl group as found in the compounds (12) and (13) appears to be unique to the manganese complexes

3 The Organic Chemistry of Dimetallated Olefin Complexes

Most of our investigations of the organic chemistry of dimetallated olefins have been derived from the compound (5) In its original form compound (5) is fairly unreactive to organic reagents, however, it can be activated by conversion into its MeCN derivative $Re(CO)_4[\mu\text{-}E\text{-}HC{=}C(CO_2Me)]Re(CO)_4(NCMe)$ (14) by treatment with Me_3NO in MeCN In this form it is quite reactive and number of interesting reactions have been studied

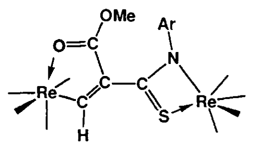
The reaction of (14) with $HC{\equiv}CCO_2Me$ results in an oligomerization of the alkyne through the addition and head-to-tail coupling of two equivalents of the alkyne to the existing alkyne ligand in (14) [20] The product $(OC)_4Re[C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_4$ (15) exists in solution as a mixture of isomers (15a) and (15b) that differ by their stereochemistry at the C=C double bond, see Scheme 3 Isomer (15a) was characterized crystallographically The coupling steps probably occur by displacement of the MeCN ligand in (14) followed by a series of two alkyne addition and insertion sequences at the adjacent metal–carbon bond When the reaction is performed under an atmosphere of CO, the CO-stabilized complex $(CO)_4Re[\mu\text{-}C(H){=}C(CO_2Me)C(H){=}C(CO_2Me)]Re(CO)_5$ (16) containing only two coupled alkyne groupings was isolated When heated to 98 °C the mixture of (15a) and (15b) was converted into the new compound $Re(CO)_4[C_6H_2(CO_2Me)(CO_2Me)_2]$, (17) by the elimination of one of the rhenium-containing fragments



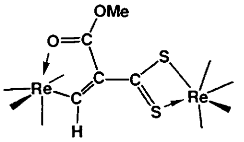
Scheme 3

The chain of alkynes was cyclized and a 2,4,6-tricarboxylate-substituted phenyl ring was formed in which one of the carboxylate groups was coordinated to the remaining metal atom. The cyclization process must have involved the cleavage of the C—H bond on the five-membered ring and elimination of the hydrogen atom with a Re(CO)$_4$ grouping.

Compound (14) also reacts with the heterocumulenes, ArN=C=S[21] and CS$_2$,[22] by displacement of the MeCN ligand and insertion of the heterocumulene into the metal–carbon bond. The compounds [Re(CO)$_4${*E*-HC=C(CO$_2$Me)C=N(C$_6$H$_4$-*p*-Me)S}Re(CO)$_4$ (18, Ar = Ph, *p*-tolyl, and *p*-C$_6$H$_4$Cl) and [Re(CO)$_4${*E*-HC=C(CO$_2$Me)CS$_2$}Re(CO)$_4$] (19), respectively, were formed in good yields. Compound (18) undergoes a remarkable photo-induced cyclization to yield products containing quinoline-2-thiolate ligands. The major product is the mononuclear metal complex Re(CO)$_4$(2-*S*,3-CO$_2$Me,6-*R*,NC$_9$H$_4$) (20, R = H, Me, Cl) in which the quinolinethiolate ligand is chelated to the metal atom.



(18)



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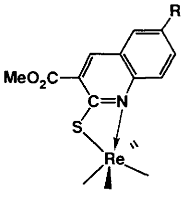
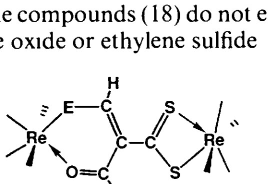


(20, R = H, Me, or Cl)

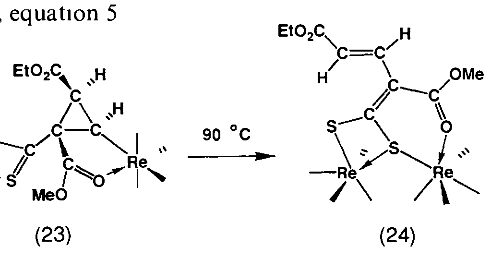
The cyclization to form (20) involves an activation of a C—H bond on the aryl ring at a position *ortho* to the nitrogen atom, a coupling of the ring carbon atom to the hydrogen-substituted carbon atom of the olefinic group, and elimination of a 'HRe(CO)$_4$' grouping.

Compound (19) undergoes an unusual reaction with pyridine oxide or ethylene sulfide in which the oxygen or sulfur atom is transferred and inserted into the remaining metal–carbon bond to yield the compounds (OC)$_4$Re[EC(H)C(CO$_2$Me)C(S)S]Re(CO)$_4$ (21, E = O) and (22, E = S). Compound (22) was characterized crystallographically.[22] The result of the sequence of two reactions, CS$_2$ plus pyridine oxide or ethylene sulfide, with (14) is that the alkyne has been derivatized at both ends. Curiously, the compounds (18) do not engage in such a reaction with pyridine oxide or ethylene sulfide.



(21, E = O)
(22, E = S)

Ethyldiazoacetate reacts with compound (19) by transfer of a carbene grouping to the olefinic site. Two compounds the metallated cyclopropane complex (OC)$_4$Re[C$_3$H$_2$(CO$_2$Me)(CO$_2$Et)C(S)S]Re(CO)$_4$ (23) and Re$_2$(CO)$_8$[SC(S)C(CHCHCO$_2$Et)C(OMe)O] (24) were formed. The cyclopropane ring is opened when the compound (23) is heated and compound (24) is formed, equation 5.



(5)

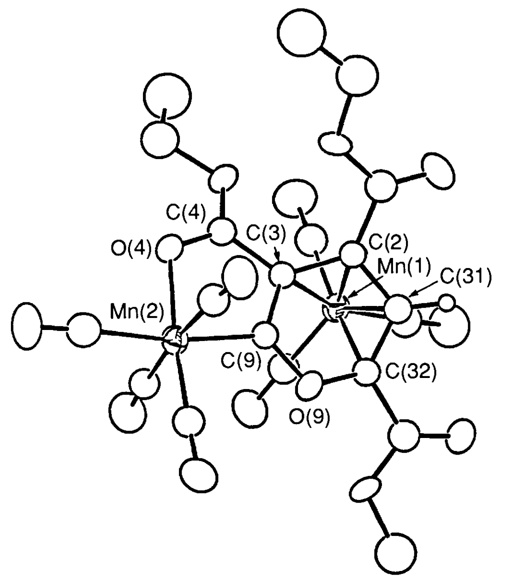


Figure 3 An ORTEP diagram of the molecular structure of the metallated pyran complex Mn$_2$(CO)$_7$[μ-η^4-OCC(CO$_2$Et)C(CO$_2$Et)C(H)C(CO$_2$Me)] (25a)
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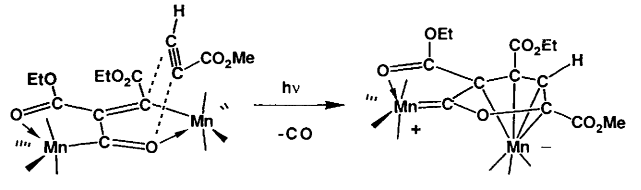
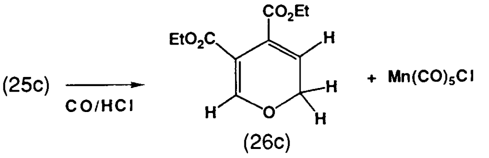
Recently, we have found that the CO-coupled alkyne ligand in the complex (12) engages in a novel coupling reaction with additional alkyne in the presence of UV/VIS irradiation. The products Mn$_2$(CO)$_7$[μ-η^4-OCC(CO$_2$Et)C(CO$_2$Et)C(H)C(CO$_2$Me)] (25a) and Mn$_2$(CO)$_7$[μ-η^4-OCC(CO$_2$Et)C(CO$_2$Et)C(CO$_2$Et)C(CO$_2$Et)] (25b) and Mn$_2$(CO)$_7$[μ-η^4-OCC(CO$_2$Et)C(CO$_2$Et)CHCH] (25c) were formed by that addition of the alkynes HC≡CCO$_2$Me, EtO$_2$CC≡CCO$_2$Et, and HC≡CH to (12).[23] Compound (25a) was characterized crystallographically and a drawing of its structure is shown in Figure 3. This compound contains a six-membered pyran ring that is metallated at the carbon C(9) by the metal atom Mn(2). Carbon C(9) is formally a carbene centre. The second metal atom Mn(1) is π-bonded to four of the carbon atoms of the pyran ring. One carboxylate group is coordinated to the metal Mn(2) by its carbonyl oxygen atom. The formation of the pyran ring is equivalent to a hetero Diels–Alder reaction between the enone grouping of (12) with the incoming alkyne molecule, see Scheme 4.[24a] The role of the irradiation has not been established, but may be required to induce the loss of CO from (12) to clear a pathway for the addition of the alkyne to the enone grouping. It is also possible that the alkyne may add to the decarbonylated metal atom prior to its coupling to the enone grouping. Treatment of the compounds (25) with a mixture of CO and HCl gases results in removal of the metal atoms and formation of the free pyran molecules which possess the α-structure as established for the pyran (26c) obtained from (25c), equation 6.



Scheme 4



(6)

The coupling of alkynes to CO generally leads to the formation of cyclopentadieneone rings[1] The formation of pyrans in this manganese system appears to be a novel result and may be related to the fact that the oxygen atom of the enone grouping is coordinated to one of the metal atoms which enforces a *cis*-geometry at the C(2)–C(9) bond (Figure 3) that is required for the hetero Diels–Alder coupling Pyran rings are important functional groupings that are found in a wide variety of natural products[24]

4 Conclusions

These studies demonstrate the ability of alkynes to insert into metal–metal bonds in dinuclear metal complexes These insertions may have similarities to the insertions of alkynes into metal–hydrogen and metal–carbon bonds[25] In reactions described in this review all of the alkynes have contained carboxylate or ethoxy groupings It is clear that these substituents stabilize the products Coordination of the carboxylate grouping is one important way Compounds (3) and (4) do react with alkyl- and aryl-substituted alkynes, but complex mixtures of products are obtained probably due to the lack of stabilization provided by these substituents Analysis of these reactions has not proved feasible to date Nevertheless, the insertion of alkynes into metal–metal bonds appears to be an important reaction pathway for dinuclear metal complexes of the Group VII Dimetallated olefin products are formed, in general, in the first step, and these complexes can engage in reactions with a variety of reagents to functionalize the alkyne These products can lead to the formation of new organic compounds by the subsequent removal of the metal atoms

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