

## REACTIONS OF THE METAL-METAL TRIPLE BOND IN $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ AND RELATED COMPLEXES

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**Abstract**—The reactions of the  $\text{M}\equiv\text{M}$  triple bonds in compounds of type  $\text{Cp}_2\text{M}_2(\text{CO})_4$  ( $\text{M} = \text{Cr}, \text{Mo}$  or  $\text{W}$ ) are reviewed. These reactions are grouped under the headings of synthesis and structures of  $\text{Cp}_2\text{M}_2(\text{CO})_4$ -type compounds, nucleophilic additions to the  $\text{M}\equiv\text{M}$  bonds, reactions with 1,3-dipoles, oxidative reactions with nonmetals, and cluster-building reactions. Literature coverage is until the end of 1985 with 102 references.

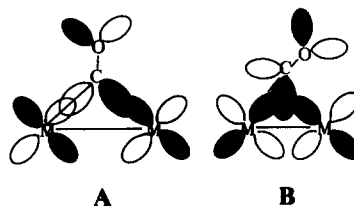
Our discovery of a simple, high-yield synthesis of the triply-bonded compound  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$  (**1**) and our subsequent demonstration of the diverse chemistry associated with the  $\text{Mo}\equiv\text{Mo}$  triple bond has stimulated the use of this and related compounds in many new areas. In the 5 years since we first reviewed<sup>1</sup> the chemistry of **1**, the molecule has continued to attract interest and is now a standard, more reactive alternative to  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  as a starting material in CpMo chemistry.

Most of the new chemistry has been reported for (**1**) or  $\text{Cp}^*_2\text{Mo}_2(\text{CO})_4$  (**2**) ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ).  $\text{Cp}_2\text{Cr}_2(\text{CO})_4$  shows a disappointing lack of reactivity associated with the  $\text{Cr}\equiv\text{Cr}$  triple bond, per se, and  $\text{Cp}_2\text{W}_2(\text{CO})_4$  seems to parallel its Mo congener in much of its chemistry. This article reviews work which has been published since the last review<sup>1</sup> as well as unpublished work from the author's laboratory. In order to present a comprehensive picture, some overlap with the previous article occurs here. The literature coverage extends to the end of 1985.

### SYNTHESIS AND STRUCTURES OF $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ -TYPE COMPOUNDS

The structure of **1** was shown to have a linear Cp-Mo-Mo-Cp skeleton and four semi-bridging carbonyls.<sup>2</sup> The semi-bridging carbonyls are linear, as opposed to the nonlinear M-CO structure usually associated with semi-bridging carbonyls. It was proposed that these two classes of semi-bridging carbonyls represented donor (linear) and acceptor (nonlinear) interactions.<sup>3,4</sup>

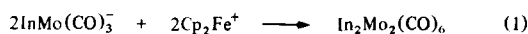
An EHMO calculation for **1** indicated the linear, semi-bridging COs were electron acceptors, although no rationale for the bent vs linear classification was proposed.<sup>5</sup> Hall and coworkers<sup>6</sup> have recently reported a PES study of  $\text{Cp}_2\text{M}_2(\text{CO})_4$  ( $\text{M} = \text{Cr}, \text{Mo}$  or  $\text{W}$ ) and also have addressed the question of linear vs bent semi-bridging carbonyl groups with Fenske-Hall MO calculations.<sup>6</sup> They find that the geometry of the bridging CO is determined by the nature of the HOMO associated with the metal-metal interaction. If the HOMO is a  $\pi^*$ -orbital (as is usually the case for M-M single bonds between late transition metals), the M-C-O group is bent (**A**), whereas if the HOMO is an M-M  $\pi$ -bond, the M-C-O group is nearly linear (**B**). The calculations show a nest of tightly spaced M-M orbitals of  $\sigma$ -,  $\delta$ -,  $\delta^*$ -,  $\pi_{xz}$ - and  $\pi_{yz}$ -symmetry, and are consistent with the observed PES.



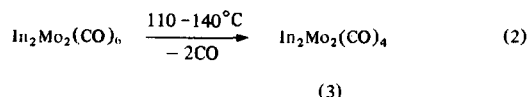
The mechanism of the formation of **1** from the thermolysis of a solution of  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  has been shown<sup>7</sup> to involve loss of CO *without* M-M bond homolysis as originally proposed.<sup>8</sup> The presumed intermediate,  $\text{Cp}_2\text{Mo}_2(\text{CO})_5$ , has been observed in a matrix.<sup>9</sup>

The structure of **2** has been determined and shown to have a bent  $\text{Cp}^*\text{--Mo--Mo--Cp}^*$  axis ( $\omega = 168^\circ$ ).<sup>10</sup> The  $\text{Mo}\equiv\text{Mo}$  bond length [2.488(3) Å] is somewhat longer than the 2.448(1) Å observed for **1**.<sup>2</sup>

The compound originally reported<sup>11</sup> as  $(\text{indenyl})_2\text{Mo}_2(\text{CO})_6$  has been shown by X-ray crystallography to be the triply-bonded tetracarbonyl  $\text{In}_2\text{Mo}_2(\text{CO})_4$  (**3**).<sup>12</sup> The overall structure closely resembles that of **2** in that only two of the four COs are semi-bridging and the  $\text{InMoMoIn}$  axis is nonlinear (Fig. 1). The  $\text{Mo}\equiv\text{Mo}$  distance is 2.500(1) Å. The triply-bonded tetracarbonyl reacts readily with CO at room temperature to give authentic  $\text{In}_2\text{Mo}_2(\text{CO})_6$ .<sup>12</sup> The latter is also obtained from ferricenium ion oxidation of  $\text{InMo}(\text{CO})_3^-$  [eqn (1)].<sup>12(b),(c)</sup> Thermolysis of the purified hexacarbonyl dimer gives the highest yields of triply-bonded **3** [eqn (2)]:



$\text{In} = \eta^5\text{-indenyl}$



To date, no "indenyl effect" on the reactivity of **3** *vis-à-vis* **1** has been observed, probably because the unsaturation inherent in the  $\text{Mo}\equiv\text{Mo}$  triple bond overrides any such effect.<sup>12(c)</sup>

Oxidation of the  $\text{TpMo}(\text{CO})_3^-$  anion with  $\text{Cp}_2\text{Fe}^+$  gives the mononuclear, 17e radical  $\text{TpMo}(\text{CO})_3$  (**4**) (Tp = hydridotrispyrazolylborato) [eqn (3)].<sup>13</sup> Refluxing acetonitrile solutions of (**4**) gives the triply-bonded dimer **5** [eqn (4)]:

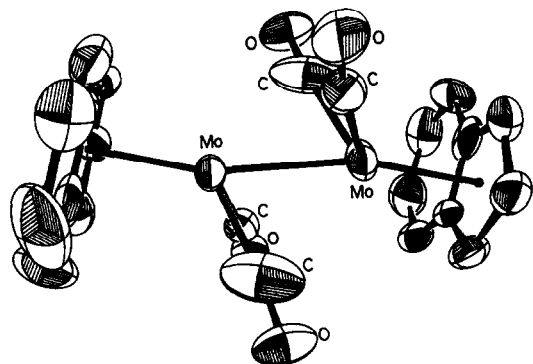
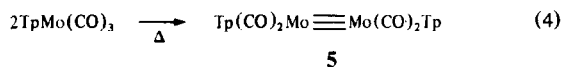
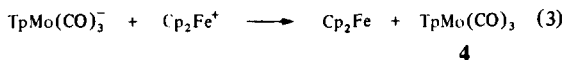
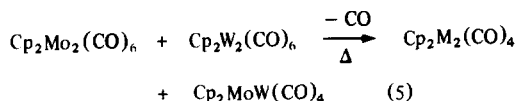


Fig. 1. ORTEP plot of  $(\text{indenyl})_2\text{Mo}_2(\text{CO})_4(\text{Mo}\equiv\text{Mo})$ .

The  $\text{Tp--Mo--Mo--Tp}$  axis in **5** is also nonlinear and only two of the four carbonyl groups are semi-bridging. The  $\text{Mo}\equiv\text{Mo}$  distance is 2.507(1) Å. The coordination about each Mo is quasi-octahedral if the metal-metal bond is considered to occupy one coordination site.

The chemistry associated with the  $\text{Mo}\equiv\text{Mo}$  bond in **5** is rather disappointing. No reaction was observed with acetylenes,  $\text{Ph}_2\text{CN}_2$ ,  $\text{CH}_2\text{N}_2$ ,  $\text{S}_8$ , propylene sulfide,  $\text{P}(\text{OMe})_3$  or  $\text{H}_2$ . Even CO does not react with **5** at atmospheric pressure. Prolonged reaction of **5** with CO (172 atm,  $35^\circ\text{C}$ ) gave  $\text{Mo}(\text{CO})_6$  as the only carbonyl-containing product. In its reactions with  $\text{Br}_2$  or  $\text{I}_2$ , **5** resembles **2** in that CO transfer occurs and  $\text{RMo}(\text{CO})_3\text{X}$  ( $\text{R} = \text{Tp}$  or  $\text{Cp}^*$ ) are the only carbonyl products isolated.

A mixed  $\text{Mo}\equiv\text{W}$  triply-bonded compound may be prepared by refluxing a diglyme solution of  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  and  $\text{Cp}_2\text{W}_2(\text{CO})_6$  according to eqn (5).<sup>14</sup> The use of diglyme as solvent also gives an improved synthesis of compound **1**.<sup>14</sup> A mixed  $\text{Tp--Cp}$  dimer could not be prepared either by heating a solution of  $\text{TpMo}(\text{CO})_3$  and  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  or by mixing  $\text{TpMo}(\text{CO})_3^-$  with  $\text{CpMo}(\text{CO})_3\text{BF}_4$ .<sup>13(b)</sup> In the former case, only **1** and unreacted  $\text{TpMo}(\text{CO})_3$  were recovered, while the latter reaction gave  $\text{TpMo}(\text{CO})_3$  and  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  by an electron-transfer process.



$\text{M} = \text{Mo or W}$

The  $\text{R}_2\text{M}_2(\text{CO})_4$  compounds described in this section all display the same basic structure. However, the details of their reactivity seem to be influenced enormously by subtle changes in the steric and electronic properties of the groups R. We turn now to a survey of the chemistry associated with the metal-metal multiple bonds. Where warranted, the chemistry of some of the more interesting compounds prepared from **1** and its homologs will also be described.

## NUCLEOPHILIC ADDITIONS TO THE $\text{M}\equiv\text{M}$ BONDS

### Molecular-orbital basis for reactivity

In molecular-orbital parlance, a molecule interacting with a nucleophile must possess a relatively low energy acceptor orbital. Both the Fenske-Hall<sup>6</sup> and EHMO<sup>5,15</sup> calculations on  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$  show the  $\pi_{yz}^*$  MO to be the LUMO when the Cp rings are centered on the  $\text{Mo--Mo}$  axis. The  $\pi_{xz}^*$

orbital lies at slightly higher energy. When the rings are tilted off the Mo-Mo axis as shown in Fig. 2, the energy of the  $\pi_{xz}^*$  orbital drops and it becomes the LUMO.

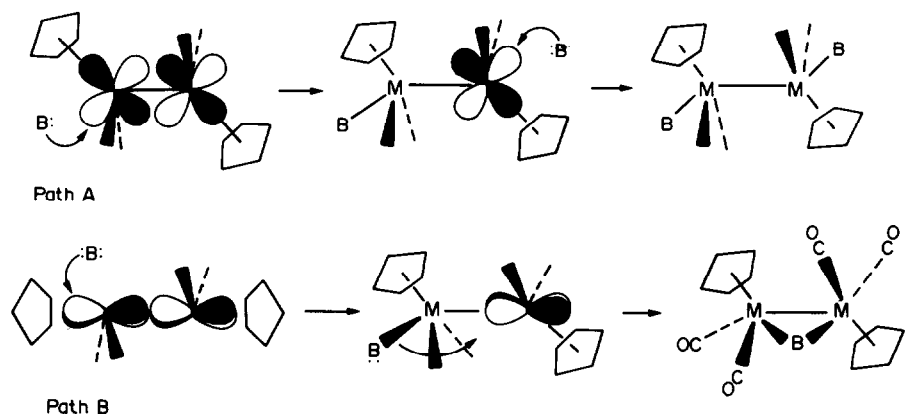
An inspection of the structures of the products of a variety of nucleophilic additions suggests that the regioselectivity of nucleophilic addition may be controlled by either  $\pi_{xz}^*$  or  $\pi_{yz}^*$ . The energy barrier to bending the  $\text{CpMoMoCp}$  axis is apparently quite low,<sup>5</sup> so that either path A or path B (Scheme 1) may be followed, depending on subtle electronic and steric requirements of the reactants. Path A seems to be followed by bulkier nucleophiles, e.g. phosphines and phosphites,<sup>8,14</sup> whereas bridging ligands, e.g. cyanide ion,<sup>3</sup> alkynes and diazoalkanes, seem to prefer path B (see below). Isomerization of the products has been noted in

some instances (see below), so that the observed geometries of the isolated products may not correspond to those of initial, kinetic products, however.

In any event, simple electron counting suggests that an  $\text{M}=\text{M}$  double bond should result if the *net* result of a reaction is the addition of two electrons to the dimetal unit, an  $\text{M}-\text{M}$  single bond results from adding 4 electrons net, while donation of six electrons disrupts the metal-metal bonding.

#### Reactions with sulfur-containing reagents

Molybdenum is the chief constituent of many hydrotreating catalysts, especially those used for hydrosulfurization (HDS).<sup>16</sup> The reactions of the  $\text{Mo}\equiv\text{Mo}$  bond with sulfur-containing molecules has therefore been of interest. Alper and coworkers



Scheme 1.

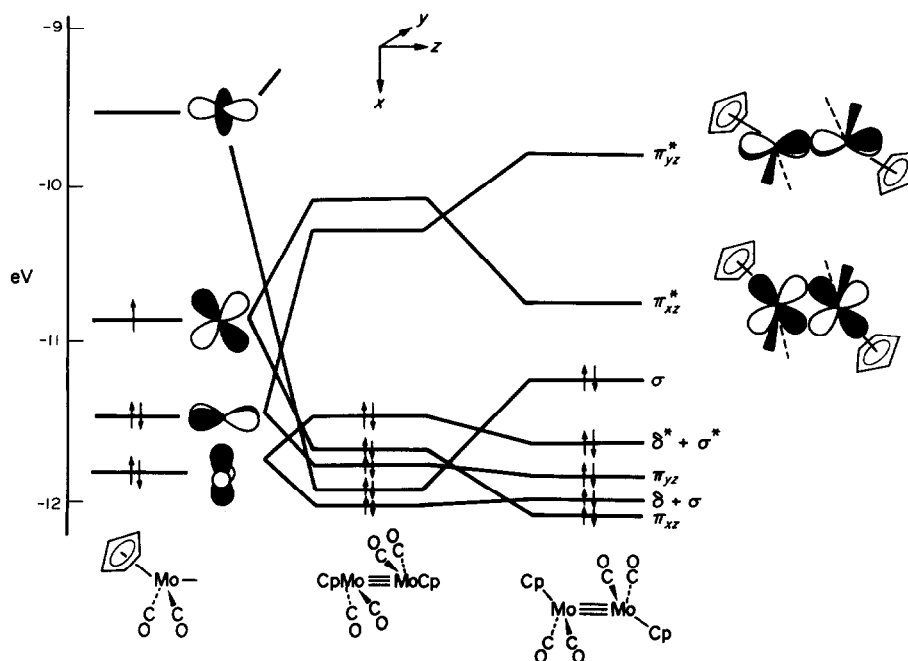
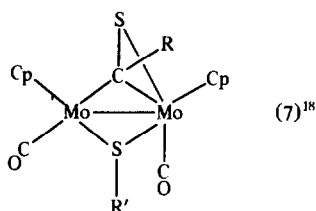
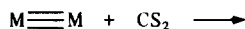
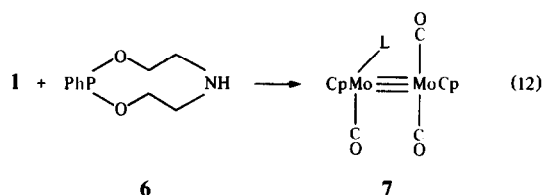


Fig. 2. MO energy levels of  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$  as a function of the  $\text{Cp}-\text{Mo}-\text{Mo}$  angle ( $\omega$ ).

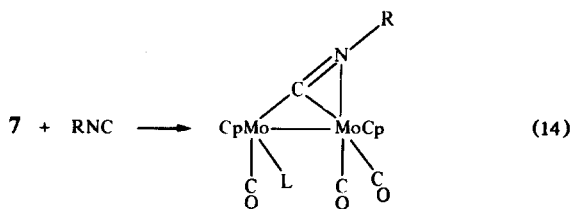
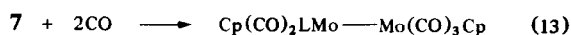
Refluxing a CS<sub>2</sub> solution of **1** gave the CS<sub>2</sub> adduct in ca 20% yield [eqn(11)]:<sup>22</sup>



Most simple phosphines or phosphites react with **1** to give the disubstituted dimers corresponding to path A of Scheme 1. The cyclic phosphite (**6**) reacts with **1** with CO *substitution* and retention of the Mo≡Mo triple bond [Mo–Mo distance in **7** = 2.506(1) Å] [eqn (12), L = **6**].<sup>23</sup>

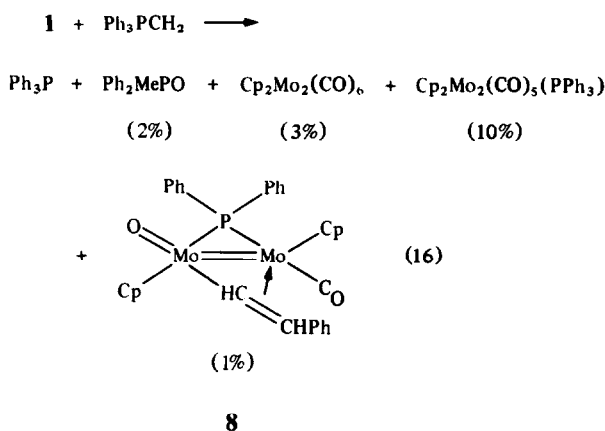


Compound **7** reacts with CO and isonitriles in the same manner that the parent **1** reacts [eqns (13) and (14)], but with  $\text{P(OMe)}_3$ , the ligand **6** is displaced [eqn (15)].<sup>23</sup> There is no ready explanation for the unusual behavior of phosphite **6**.

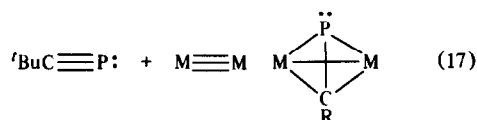

$$M^* = Mo(CO)_2Cp^*$$

\* Reactions of 1 with  $\text{Me}_3\text{PCH}_2$  or  $\text{Me}_2\text{P}(\text{CH}_2)_2^-$  gave very complex mixtures.<sup>24</sup>

The products, **8** and  $\text{Ph}_3\text{P}$ , show that extensive fragmentation of the ligand occurs.<sup>25</sup> The Mo=Mo distance in **8** is 2.885(1) Å.

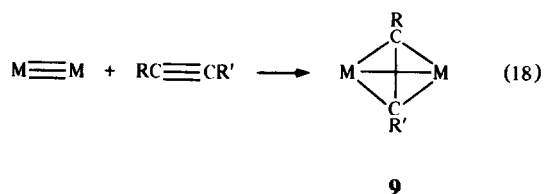


The phosphalkyne  $\text{'BuC}\equiv\text{P}$  reacts with **1** to give an adduct with the same tetrahedrane type structure obtained from **1** and alkynes.<sup>26</sup>



#### Reactions with alkynes and alkenes

At room temperature, **1** reacts rapidly with all but the most hindered alkynes to give tetrahedrane-type adducts [eqn (18)].<sup>8,27-29</sup> These adducts typically have the following bond lengths (Å): Mo-Mo, 2.98; Mo-C, 2.18; and C-C, 1.33. The  $^{13}\text{C}$  chemical shifts of the acetylenic carbons of a variety of adducts of type **9** are collected in Table 1. The values range from  $\delta$  29 for a silyl-substituted carbon to *ca* 140 for stannyl substitution. Large differences between two differently substituted carbons in the same coordinated acetylene are evident, viz. 100.7 and 29.3 for  $\text{HCCSiMe}_3$ , and 117 and 40 for  $\text{MeCCSiMe}_3$ . The usual range for C- or H-substitution is 60–90 ppm.



These alkyne adducts show interesting reactivity. At higher temperatures ( $>100^\circ\text{C}$ ), they lose CO and react with additional alkynes to form new

Table 1.  $^{13}\text{C}$  NMR chemical shifts of acetylene and acetylide dimolybdenum complexes

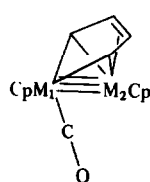
R <sup>a</sup>	R'	$\delta$ C	$\delta$ C'	Reference
H	H <sup>b</sup>	61.9	—	27
Me	Me <sup>b</sup>	82.6	—	27
Co <sub>2</sub> Me	Co <sub>2</sub> Me	62.0	—	27
H	CH <sub>2</sub> CH <sub>2</sub> OH	87.2	?	27
H	Et	86.0	60.9	29
Me	SiMe <sub>3</sub>	117.4	40.4	28
Ph <sub>3</sub> Sn	Ph <sub>3</sub> Sn	140.4	—	29
H	SiMe <sub>2</sub> Ph	100.7	29.3	28
— <sup>c</sup>	Ph	185.8	101.8	40

<sup>a</sup> R and R' are acetylenic substituents in structure **9**.

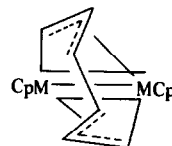
<sup>b</sup> Free acetylenes resonate at 71.6 and 73.9, respectively.

<sup>c</sup> Acetylide structure **23**.

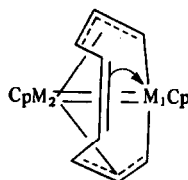
ligands derived from sequential coupling of two-four alkyne ligands.<sup>28,30-33</sup> The structural types so produced are indicated by **10**–**13** shown below:



**10**



**11**



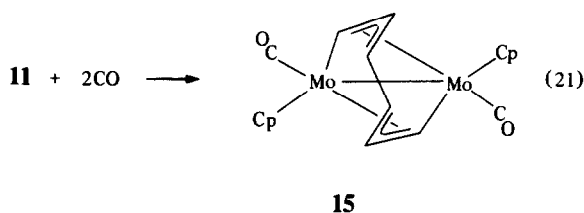
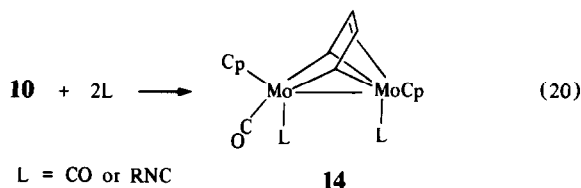
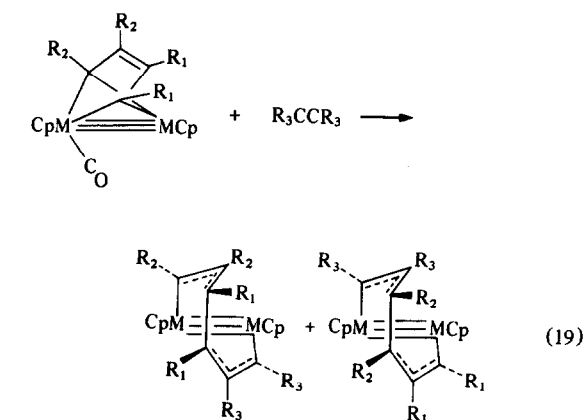
**12**



**13**

When terminal alkynes ( $\text{RCCH}$ ) are employed, the  $\text{C}_4$ -ring in **10** shows predominate head-to-tail coupling of the two alkynes. The isomers of **11**–**13** which are formed by the reaction of alkynes with **10** show that the new alkynes which are incorporated may enter at either Mo–C bond in the  $\text{MoC}_4$  ring [eqn (19)]. Structures of type **12** are also formed by one electron reduction of the mononuclear,  $\text{CpMo(RCCR)}_2(\text{NCMe})^+$  complexes.<sup>34</sup>

In addition to the main products shown above, smaller quantities of compounds of type **14** and **15** may be isolated from the reaction mixtures. These compounds are probably formed by the reaction of the triply-bonded precursors **10** and **11** with CO as has been demonstrated in one instance [eqns (20) and (21)].<sup>32</sup>



The details of the structures of these alkyne adducts show some interesting features. The terminal carbons of the C<sub>4</sub>-fragment in **10** are symmetrically bonded to both metals [ $d(\text{Cr}-\text{C}) = 2.025(7) \text{ \AA}$  avg.] and thus appear to be bridging alkylidene carbons. Their <sup>13</sup>C NMR resonance ( $\delta \sim 210 \text{ ppm}$ ) is consistent with this description.<sup>35</sup> The middle carbons of the M<sub>1</sub>C<sub>4</sub> fragment are  $\eta^2$ -bonded to the M<sub>2</sub> metal [ $d(\text{M}_2-\text{C}) = 2.23 \text{ \AA}$ ]. The M<sub>1</sub>C<sub>4</sub> ring system itself appears to be delocalized<sup>36</sup> with equal C—C bond lengths ( $\approx 1.42 \text{ \AA}$  avg.).

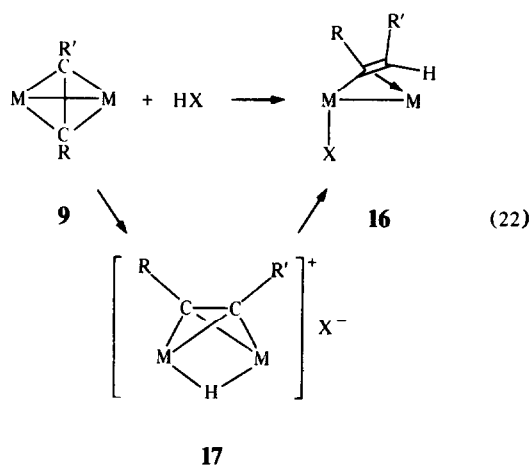
Structure types **12** and **13** are isomeric. In **12**, both termini (C<sub>1</sub>) of the C<sub>8</sub>-ligand are very tightly bonded to one metal [ $d(\text{M}_1-\text{C}_1) = 2.08 \text{ \AA}$ ,  $d(\text{M}_2-\text{C}_1) = 2.23 \text{ \AA}$ ]. The M<sub>1</sub>—C<sub>1</sub> distance approaches that expected for Mo=C double bonds,<sup>37</sup> while the M<sub>2</sub>—C<sub>1</sub> distance is in the range found for Mo—C single bonds. M<sub>2</sub> is  $\eta^3$ -bonded to opposite ends of the C<sub>8</sub>-fragment while M<sub>1</sub> is also  $\eta^2$ -bonded to the two central carbons.

In **13**, the two terminal carbons bridge the two metals in a nearly symmetrical manner (the M<sub>2</sub>C<sub>2</sub> rhombus has essentially C<sub>2</sub>-symmetry with two opposite M—C bonds of length 2.18  $\text{\AA}$  and another opposite set of two M—C bonds of length 2.14  $\text{\AA}$ ) (cf. structure **10**). The next three carbons from each

end of the C<sub>8</sub>-chain are  $\eta^3$ -bonded to one metal each and the two halves are joined by a C—C single bond. This description of the bonding differs from that originally proposed.<sup>30,31</sup>

In both isomers, **12** and **13**, the electron count demands a Mo=Mo double bond to achieve an 18-electron count at each Mo.<sup>1</sup> The Mo=Mo distances<sup>31,34</sup> range from 2.595(1) to 2.635(1)  $\text{\AA}$ . This distance compares with *ca* 3.0  $\text{\AA}$  for bridged M—M single bonds and 2.448(1)  $\text{\AA}$  for the Mo≡Mo bond in **1**.

The mono-alkyne adducts (**9**) are readily protonated by strong acids to produce the  $\mu, \eta^1, \eta^2$ -vinyl complexes **16**.<sup>29,38</sup> The stereochemistry of the protonated product suggested that the proton was delivered to the alkyne moiety via the metal in an intermediate, e.g. **17**. The tungsten analogue of **17** was subsequently observed as a product of the protonation of the carbyne complex Cp(CO)<sub>2</sub>W≡CR.<sup>39</sup>



Excess acid protonates the trifluoroacetate group ("X" in **16**) giving coordinatively unsaturated intermediate **18** which is fluxional on the NMR scale. The coordination unsaturation of **18** allows for the oxidative addition of H<sub>2</sub> and subsequent stoichiometric hydrogenation of the alkyne. Under catalytic conditions with a large excess of alkyne, the excess alkyne inhibits the oxidative addition of hydrogen and the alkyne is polymerized instead [eqn (23b)].<sup>29</sup>

Methoxyallene reacts with **1** to give the adduct **19** [eqn (24)]. Fluoroboric acid reacts with **19** to give MeOH and the cation **20**. Cation **20** is also obtained from the reaction of the adduct of methyl propargyl ether (9: R = H, R' = CH<sub>2</sub>OMe) with HBF<sub>4</sub> [eqn (25)].<sup>40</sup> Figure 3 is a PLUTO drawing of **20**. This perspective shows that **20** may be regarded as a cationic  $\mu-\eta^1, \eta^1, \eta^3$ -allenyl complex in which the C<sub>3</sub>-fragment is  $\pi$ -bonded to Mo1 and

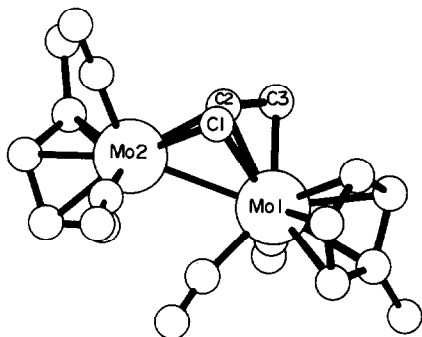
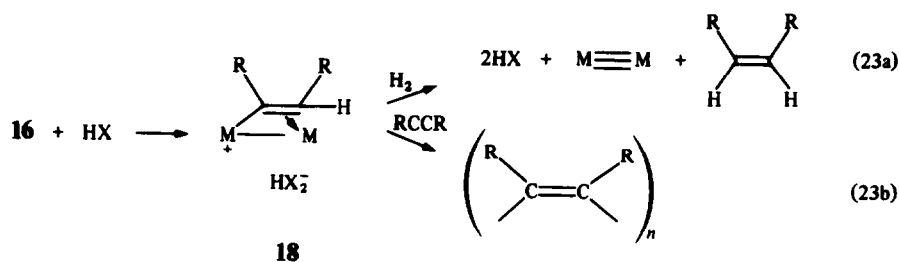
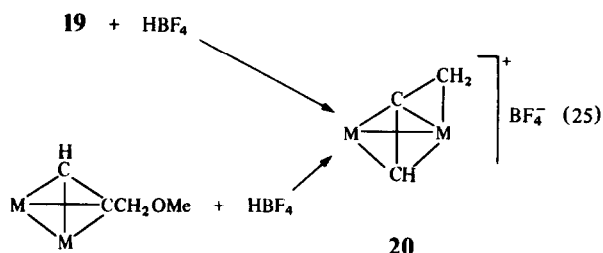
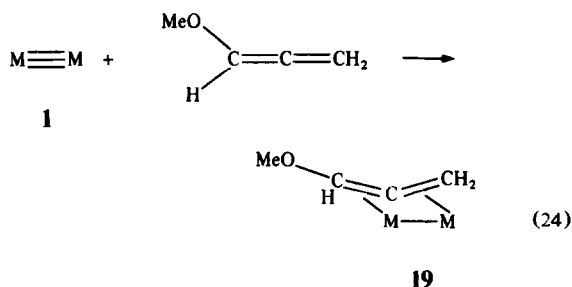


Fig. 3. PLUTO drawing of the cation,  $\text{Cp}_2\text{Mo}_2(\text{CO})_4-(\mu\text{-C}_3\text{H}_3)^+$  (**20**).

two C—H bonds of the  $\pi$ -allyl group have been replaced with two Mo2—C  $\sigma$ -bonds.



**9** ( $\text{R} = \text{H}$ ,  $\text{R}' = \text{CH}_2\text{OMe}$ )

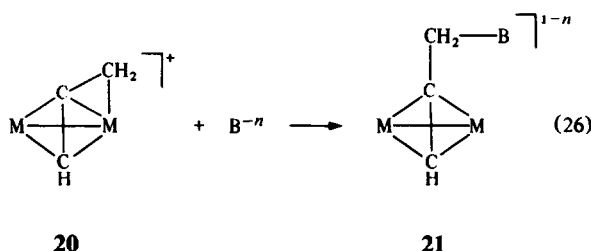
Complex **20** is fluxional on the  $^1\text{H}$  NMR time scale ( $\Delta G^\ddagger = 16.9 \text{ kcal mol}^{-1}$  at 338 K). At  $-60^\circ\text{C}$ , the spectrum is consistent with the solid-state structure (two types of Cp groups):  $\delta 6.76$  (d,  $J = 1.7 \text{ Hz}$ ,  $=\text{CH}$ ),  $5.33$  (d,  $J = 1.7$ ,  $-\text{CH}_2$ ),  $5.05$  (s,  $-\text{CH}_2$ ). At  $75^\circ\text{C}$ , the Cp groups are equivalent

but the signals due to the  $\text{C}_3\text{H}_3$  fragment do not vary with temperature. The dynamic process shown in Scheme 2 interconverts enantiomers of **20** via the symmetrically bridged intermediate in which the plane of the  $\text{C}_3\text{H}_3$  fragment is perpendicular to the Mo—Mo bond. This process resembles the higher energy fluxional processes<sup>27,28</sup> in the acetylene adducts (**9**) and  $\mu$ -vinyl complexes (**16**).<sup>29,38</sup>

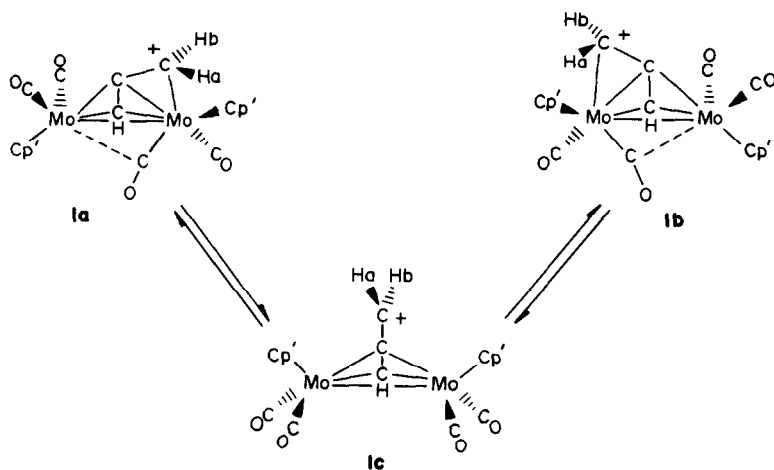
The  $^{13}\text{C}$  NMR shifts of the  $\text{C}_3$ -fragments in **20** and its precursor complexes **19** and **9** ( $\text{R} = \text{H}$ ,  $\text{R}' = \text{CH}_2\text{OMe}$ ) show interesting trends. We label the MeO-bearing carbon  $\text{C}\alpha$  in the precursors. Upon loss of  $\text{MeO}^-$  to form **20**,  $\text{C}\alpha$  of **19** but  $\text{C}\gamma$  of **9** become  $\text{C1}$  of **20**. These relationships and the chemical shifts of corresponding carbons are shown below (see Fig. 3 for numbering scheme of **20**):

<b>19</b>	<b>20</b>	<b>9</b> ( $\text{R} = \text{H}$ , $\text{R}' = \text{CH}_2\text{OMe}$ )
38 ( $\text{C}\gamma$ )	$\rightarrow$ 76 ( $\text{C3}$ )	$\leftarrow$ 76 ( $\text{C}\alpha$ )
176 ( $\text{C}\beta$ )	$\rightarrow$ 118 ( $\text{C2}$ )	$\leftarrow$ 56 ( $\text{C}\beta$ )
101 ( $\text{C}\alpha$ )	$\rightarrow$ 81 ( $\text{C1}$ )	$\leftarrow$ 86 ( $\text{C}\gamma$ )

Insofar as these chemical-shift changes reflect charge redistribution, it is seen that the electronic structure of the  $\text{C}_3$ -fragment in **20** resembles more closely that of the acetylene adduct **9** than the allene adduct **19**. In particular, the deshielding of  $\text{C}\gamma$  in **19** suggests that positive charge is transferred from  $\text{C}\alpha$  to  $\text{C}\gamma$  in the transformation **19**  $\rightarrow$  **20**. This conclusion is borne out by the reactivity of **20** toward nucleophiles [eqn (26)].<sup>40</sup> Even hindered bases, e.g.  $^i\text{Pr}_2\text{NLi}$ , attack the terminal carbon,  $\text{C3}$ , to yield alkyne complexes **21**. We have been unsuccessful in attempts to remove a proton from **20**.

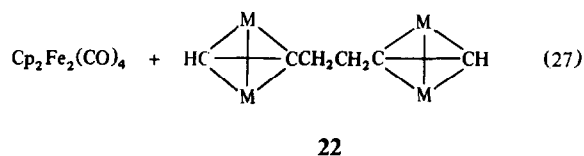
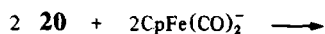


$\text{B} = \text{Py}$ ,  $^i\text{Pr}_2\text{N}^-$ ,  $\text{MeO}^-$ ,  $\text{CN}^-$  or  $\text{R}_3\text{P}$

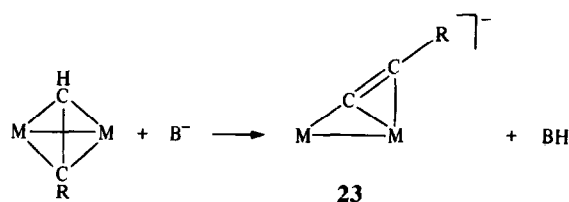


Scheme 2.

Metal carbonyl anions react [eqn (27)] with **20** in a redox manner to give the bis-adduct (**22**)<sup>40</sup> of 1,5-hexadiyne, previously prepared from **1** and the free diyne.<sup>30</sup> The reduction of **20** to give **22** is also accomplished with Na amalgam. Figure 4 is a PLUTO drawing of the structure of **22**.



Complexes (**9**) of terminal alkynes react with strong bases, preferably <sup>i</sup>Pr<sub>2</sub>NLi or NaNH<sub>2</sub>, to produce  $\mu\text{-}\eta^1, \eta^2\text{-acetylide}$  complexes (**23**) [eqn (28)].<sup>41</sup> The molecular structure of **23** (R = CH<sub>2</sub>-



R = Ph or CH<sub>2</sub>OMe

OMe) is shown in Fig. 5. The counter ion in this crystal is Na(15-crown-5)<sup>+</sup>. The Na<sup>+</sup> ion is also chelated by the methoxy oxygen and to one carbonyl oxygen in the solid state. Similar coordination of alkali cations to carbonyl groups has been observed previously.<sup>42</sup> These  $\mu\text{-}\eta^1, \eta^2\text{-acetylide}$  complexes exhibit the same "windshield wiper" fluxional motion previously established for the

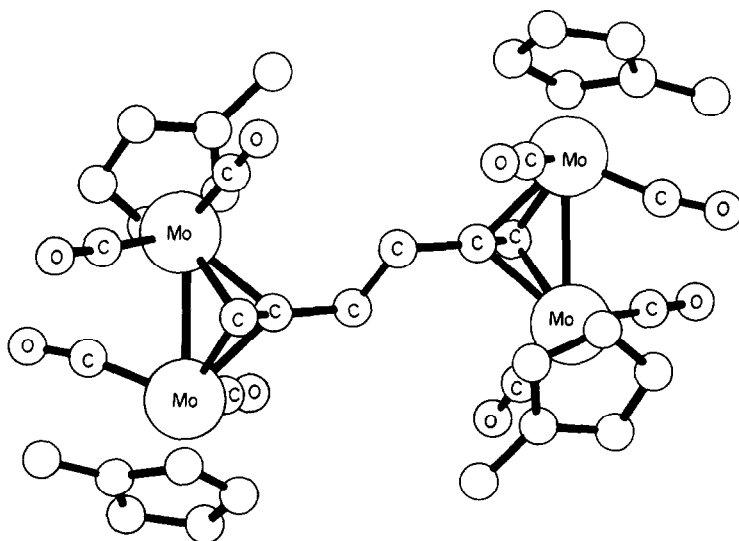
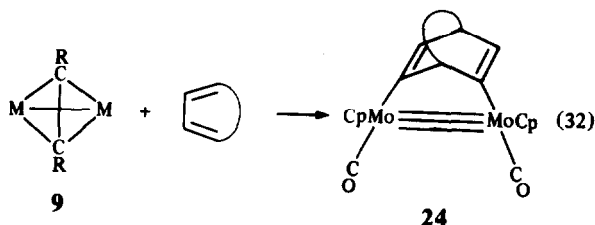


Fig. 4. PLUTO drawing of the 1,5-hexadiyne adduct (**22**) of Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>4</sub>.





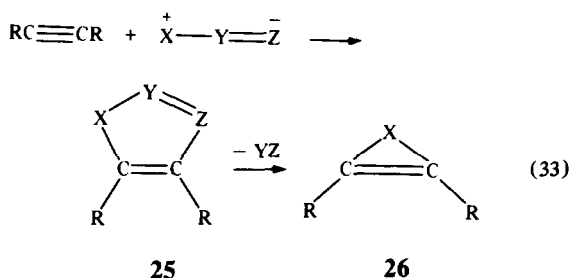
The alkyne adducts (**9**) react with cyclic, conjugated dienes to give products with ligands derived from formal Diels–Adler condensation of the diene with the coordinated alkyne [eqn (32)].<sup>47</sup> The Mo≡Mo bond length in **24** is 2.504(1) Å. All of these rather complex reactions involving alkenes undoubtedly occur with prior loss of CO from **1** or **9**.<sup>32</sup>



The reactions described in the section amply demonstrate that the easily prepared alkyne adducts of the Mo≡Mo triple bond form the basis for an extensive chemistry of hydrocarbon conversions on a bimetallic center. Even in those reactions which require higher temperatures and proceed with loss of CO, the strength of the Mo≡Mo triple bond serves to maintain the integrity of the dinuclear unit and suppress the formation of mononuclear products.

### REACTIONS WITH 1,3-DIPOLES

The reactions of carbon–carbon multiple bonds with 1,3-dipolar reagents have been studied extensively.<sup>48</sup> For example, alkynes normally react with the 1,3-dipole to give the cycloadduct **25**. This adduct may expel the small molecule Y=Z to give a three-membered ring (**26**) [eqn (33)].

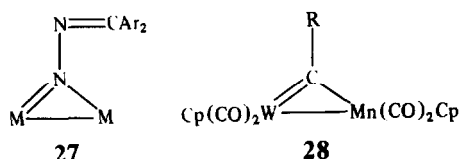


It is therefore of interest to determine how metal–metal multiple bonds interact with 1,3-dipolar reagents. What are the similarities and differences in behavior of metal–metal multiple bonds *vis-à-vis* their well-studied organic counterparts? The answers to such questions lead to increased understanding of factors governing chemical reactivity and, at the same time, provide the synthetic chemist with new routes to molecules of interest in related areas.

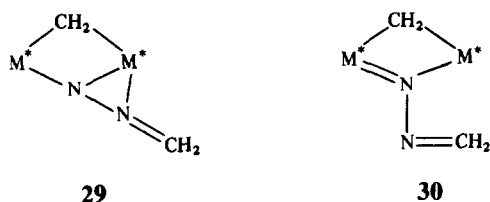
### Reactions with diazoalkanes

Diazoalkanes ( $R_2C=N_2$ ) are prototypal 1,3-dipoles. In addition to the interest attached to the bonding of the diazoalkane ligand itself to a dimetal fragment, loss of  $N_2$  from the adduct may give metal alkylidene complexes. The latter compounds are still of interest in connection with CO reduction chemistry.<sup>35</sup>

The coordination chemistry of diazoalkanes with  $M\equiv M$  (**1**) and related complexes has been both rewarding and frustrating in its complexity. No less than *seven* different reaction paths of diazoalkanes with  $M\equiv M$  have been well characterized. These are summarized in Scheme 3. The reaction of **1** with diaryldiazomethanes was the first reaction of this type to be reported and the product was shown to have the unusual bonding mode depicted in **27** ( $M = Mo(CO)_2Cp$ ).<sup>49,50</sup> This structure is isolobal and isoelectronic with the bridging alkylidyne (**28**).<sup>51</sup>

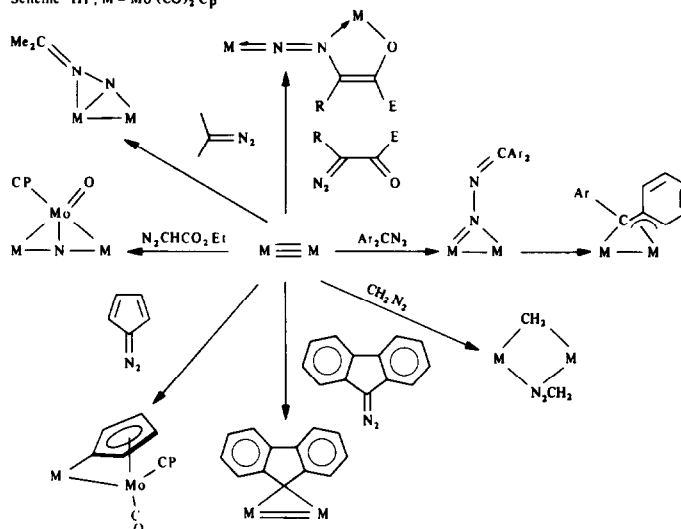


The parent diazomethane ( $CH_2=N_2$ ) reacts with **1**, but no stable complex could be isolated— $N_2$  is evolved and polymethylene is formed.<sup>1</sup> However,  $CH_2N_2$  reacts with the pentamethylcyclopentadienyl analog of **1**, hereinafter denoted by  $M^*\equiv M^*$  [ $M^* = Mo(CO)_2(C_5Me_5)$ ], with loss of  $N_2$  to give an adduct with either structure **29** or **30**.<sup>52,53</sup>

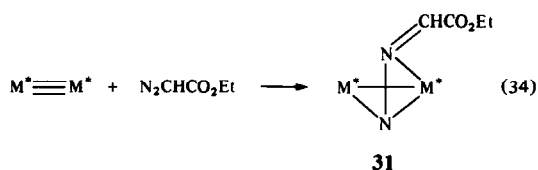


Diazopropane ( $Me_2C=N_2$ ) reacts with either  $M\equiv M$  or  $M^*\equiv M^*$  to give an adduct in which the terminal nitrogen is bonded to both Mo atoms, and the central nitrogen also bonded to one of the Mo atoms.<sup>54,55</sup> In solution, a second isomer of  $M_2(N_2CMe_2)$  is present as shown by the NMR spectrum.<sup>50,54</sup>

Ethyl diazoacetate reacts cleanly with  $M^*\equiv M^*$  to give adduct **31** which has the same coordination mode as the  $Me_2CN_2$  adducts [eqn (34)].<sup>50</sup> An ORTEP plot of the structure of **31** is shown in Fig. 6. The major difference between the structure types **31** and **27** is that in **27** the terminal N donates a

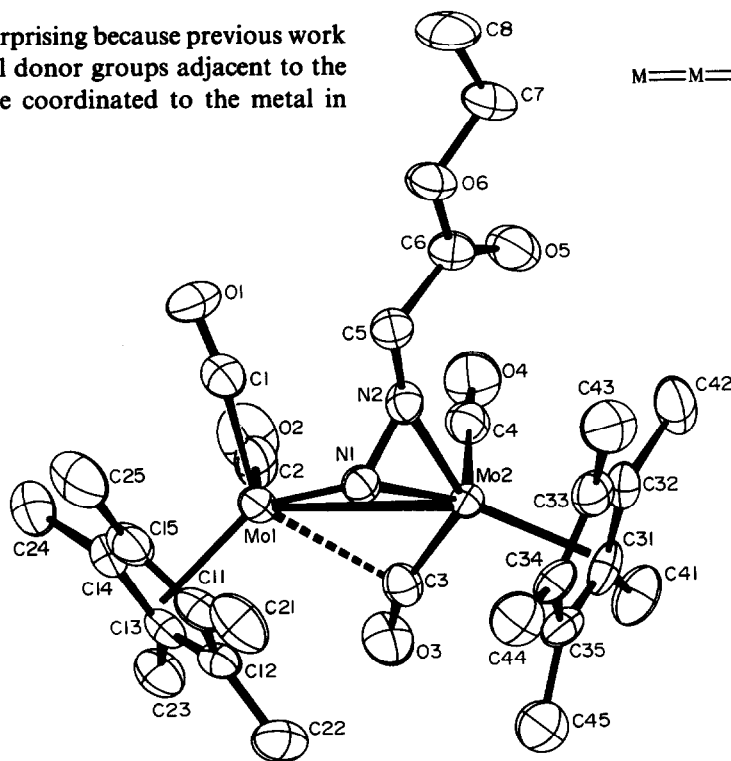
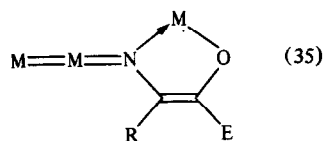
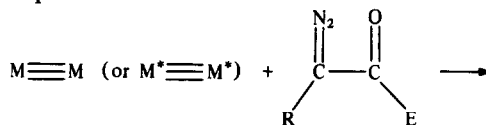
Scheme III,  $\text{M} = \text{Mo}(\text{CO})_2\text{Cp}$ 

total of four electrons to the dimetal fragment, whereas in **31** the terminal N donates two electrons and the central N donates two also. In spite of their seemingly disparate structures, the bond distances and angles in the  $\text{N}_2\text{C}$  portion of the molecules **27** and **31** are virtually identical.

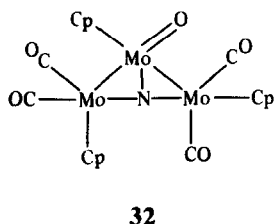


Reaction (34) is surprising because previous work had shown potential donor groups adjacent to the diazo group become coordinated to the metal in

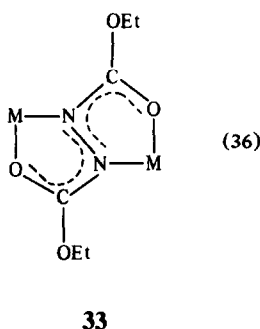
these diazoalkane adducts. Thus  $\alpha$ -ketodiazalkanes<sup>56</sup> and diethyl diazomalonate<sup>50,54</sup> react with  $\text{M}\equiv\text{M}$  or  $\text{M}^*\equiv\text{M}^*$  to give products containing a chelate ring which incorporates the keto or carboxyl oxygen [eqn(35)]. In these adducts, the  $\alpha$ -keto or  $\alpha$ -carboxyl diazoalkane reacts as a six-electron donor so the  $\text{M}\equiv\text{M}$  bond is completely disrupted.

Fig. 6. ORTEP plot of  $\text{Cp}_2^*\text{Mo}_2(\text{CO})_4(\text{N}_2\text{CHCO}_2\text{Et})$  (**31**).

Ethyl diazoacetate reacts with  $M\equiv M$  (**1**) at temperatures from  $-78^\circ\text{C}$  to  $+110^\circ\text{C}$  to give extremely complex mixtures.<sup>54,57</sup> Feasey *et al.* isolated cluster **32** in 5% yield from such a mixture.<sup>57</sup>



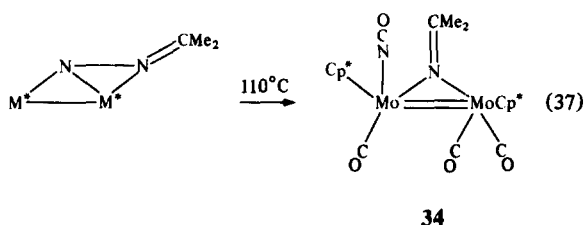
The reaction of **1** with the dienophile, diethyl azidodicarboxylate, gives a product (**33**) with a structure related to those depicted in eqn (35).<sup>58</sup> The molecular structure of **33** is shown in Fig. 7.



### Reactions of diazoalkane adducts

By analogy with the organic chemistry of 1,3-dipolar cycloadducts depicted in eqn (33), it was of interest to investigate the tendency of the diazoalkane adducts of **1** and related compounds to lose  $\text{N}_2$  and form dimetallacyclopropenes, i.e.  $\mu$ -alkylidene complexes.

Herrmann *et al.* found that the adduct of 2-diazopropane and  $M^*\equiv M^*$  underwent a rearrangement in which the N-N bond was broken, one nitrogen then inserting into an Mo-CO bond to form an isocyanate, and the  $\text{Me}_2\text{CN}$  fragment forming a  $\mu$ -imido group [eqn (37)].<sup>53</sup>



$\text{Me}_2\text{CN}_2$  or  $\text{C}_5\text{H}_4\text{N}_2$  react with the triply-bonded tungsten complex,  $\text{Cp}^*_2\text{W}_2(\text{CO})_4$ , at *ca*  $-20^\circ\text{C}$  to give the  $\mu$ -imido isocyanate W complexes analogous to **34**.<sup>59</sup>

The doubly-bonded complex **34**, and its W analog, add one equivalent of CO to form singly-bonded **35**.<sup>53,59</sup> In order for each metal to maintain the 18-electron count during this transformation,

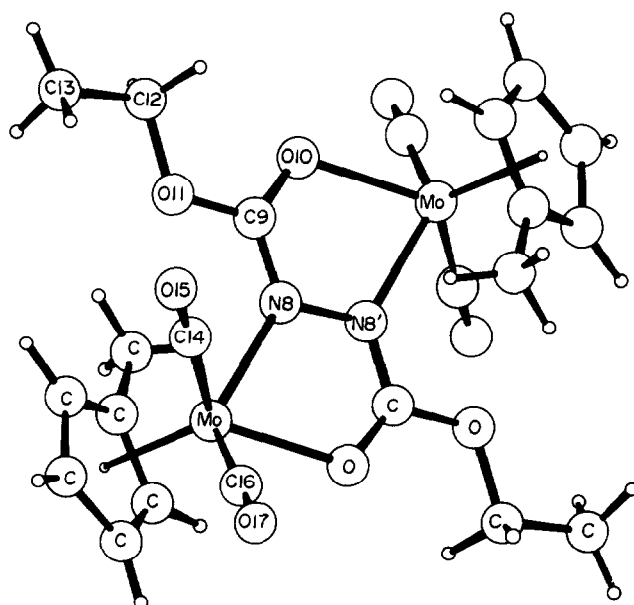
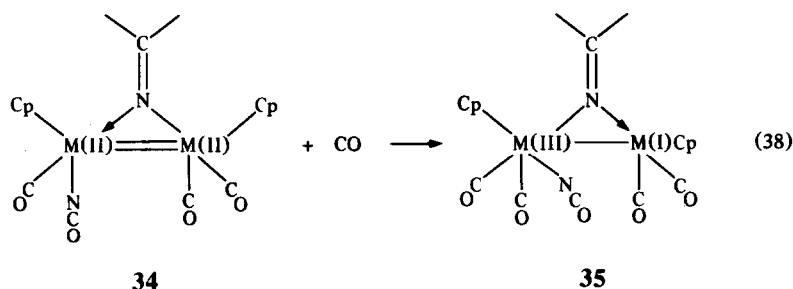
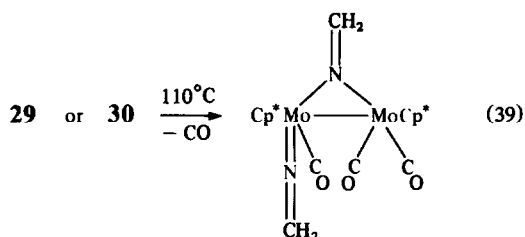


Fig. 7. ORTEP drawing of adduct (**33**) of diethyl azidodicarboxylate and  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ .

an internal redox disproportionation must occur as illustrated in eqn (38).

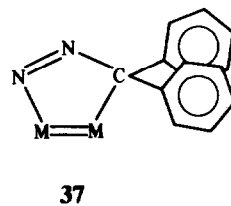
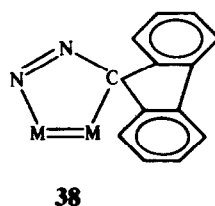
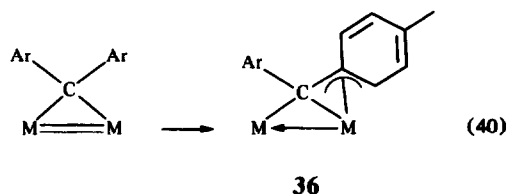
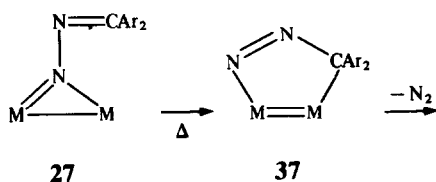
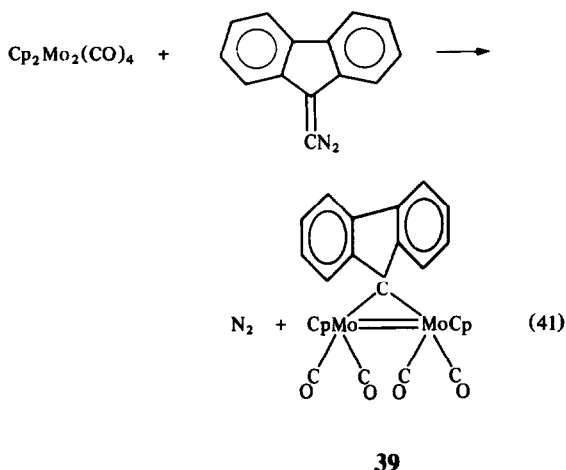


The adduct with structure **29** or **30** also undergoes an isomerization upon heating, but in this case the nitrogen inserts into the methylene bridge and two methyleneimido ligands are formed [eqn (39)].<sup>53</sup>

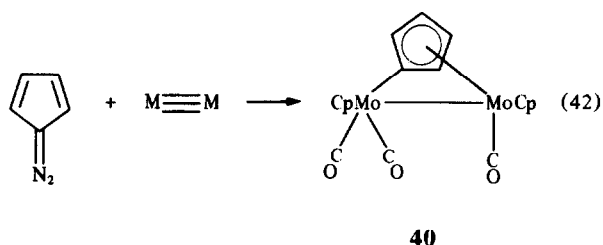


To date, the only diazoalkane adducts which cleanly lose  $\text{N}_2$  and form  $\mu$ -alkylidene complexes were the first to be discovered, viz. the diaryl-diazomethane adducts (**27**).<sup>49,50</sup> Heating **27** ( $\text{Ar}$  = phenyl or *p*-tolyl) to  $60^\circ\text{C}$  causes an intramolecular loss of dinitrogen. The resulting  $\mu$ -diaryl-alkylidenes were shown to have the structure depicted in **36** in which one aryl group has become coordinated to one Mo.<sup>49,50</sup> The intramolecular loss of  $\text{N}_2$  from **27** is believed to occur through the 1,3-dipolar cycloadduct (**37**). This view is supported by the fact that the complexes  $\text{M}_2^*(\mu\text{-N}_2\text{CAR}_2)$  do not lose  $\text{N}_2$  cleanly, presumably because attainment of the transition state **37** is blocked by steric

interactions between the bulky  $\text{Cp}^*$  groups and the aryl groups.<sup>50</sup> Conversely, 9-diazo fluorene reacts with **1** with loss of  $\text{N}_2$  even below room temperature, presumably because the steric congestion in intermediate **38** is less than that in **37** as shown below. The product is the  $\mu$ -fluorenylidene complex **39** which now has a  $\text{Mo}=\text{Mo}$  bond [ $2.798(1)\text{ \AA}$ ] since the aryl groups are tied together and cannot bend over and coordinate to a metal as does the aryl group in **36**. The reactions of the  $\mu$ -alkylidenes **36** and **39** with small molecules, e.g.  $\text{CO}$ ,  $\text{H}_2$ , isocyanides and alkynes, are the subject of several reports.<sup>60-62</sup>

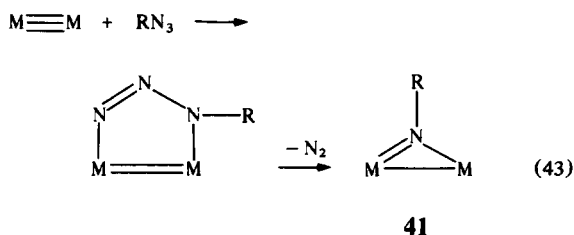


An uncrowded transition state similar to **38** also explains the facile loss of  $\text{N}_2$  and subsequent formation of **40** when diazocyclopentadiene reacts with **1** [eqn (42)].<sup>63</sup>

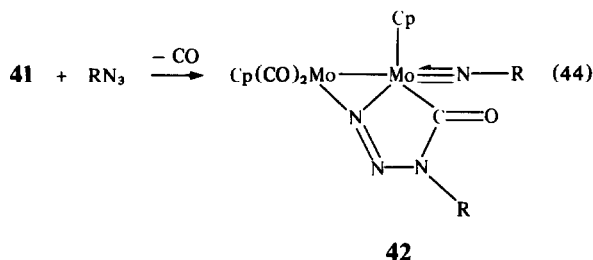


### Reactions with other 1,3-dipoles

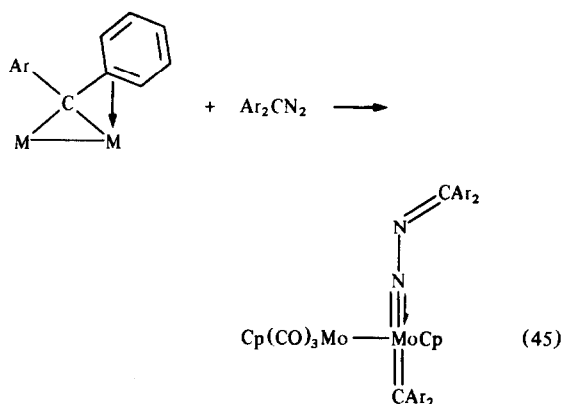
Organoazides are isoelectronic with diazoalkanes. Hence, the interaction of an organoazide with the  $\text{M}\equiv\text{M}$  triple bond could lead to a dimetallatriazene (the cyclic 1,3-adduct) which would be expected to lose  $\text{N}_2$  and form a nitrene complex [eqn (43)].



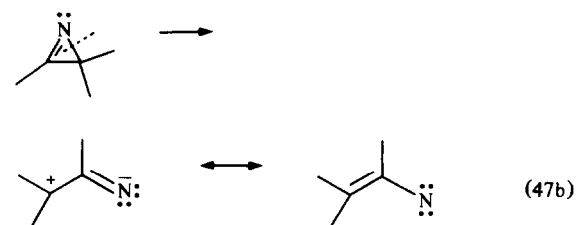
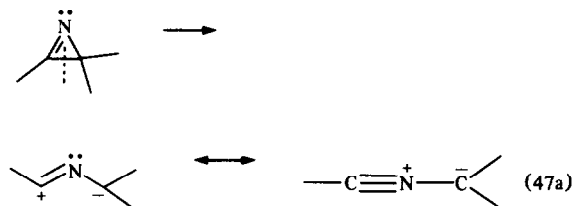
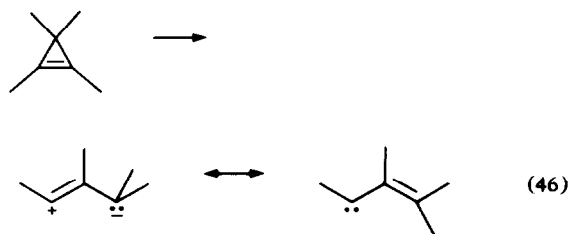
In fact, the reaction of aryl or alkyl azides with **1** follows a different course.<sup>54,64</sup> The initial product is probably the nitrene adduct (**41**). However, this initial product reacts with additional azide nearly as fast as it is formed to give the final complex (**42**).



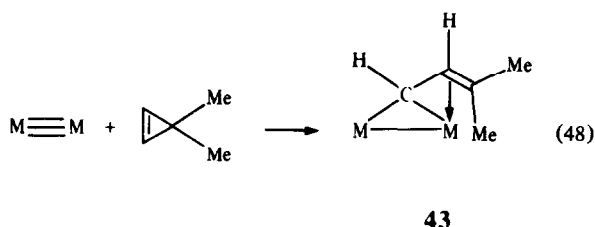
The final product contains a terminal nitrene triply bonded to Mo [ $\text{Mo}\equiv\text{N} = 1.75(1) \text{ \AA}$ ] and a bridging chelate ring formed by attack of the second azide on a coordinated carbonyl. The transformation of a bridging nitrene to a terminal nitrene upon reaction with excess azide has its exact parallel in the transformation of an alkylidene from bridging to terminal upon reaction with excess diazoalkene [eqn (45)].<sup>61</sup> The major difference is that the carbon of the diazoalkane is not sufficiently nucleophilic to attack a coordinated carbonyl as does the N in eqn (44).



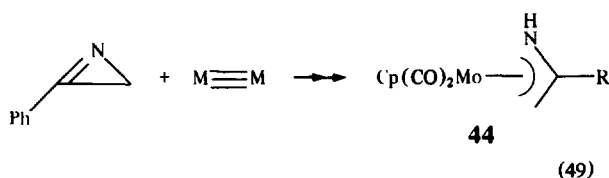
Cyclopropenes and azirines may be regarded as "masked" 1,3-dipoles.<sup>48</sup> The cyclopropene is a masked vinylcarbene [eqn (46)] and the azirine a masked nitrile ylide [eqn (47a)] or a masked vinyl nitrene [eqn (47b)].



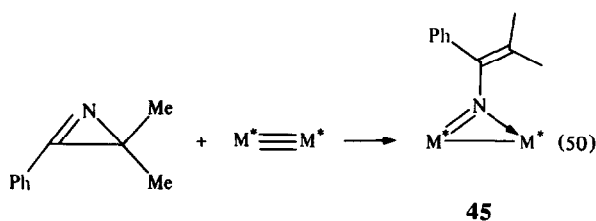
In fact, **1** reacts with 1,1-dimethylcyclopropene to give the bridged, vinyl alkylidene (**43**).<sup>65</sup> The pattern of Mo-C (bridge) distances in **43** are very similar to those in **36** as might be expected. Thus, cyclopropene adds to the  $\text{Mo}\equiv\text{Mo}$  triple bond as if it were a vinyl carbene [cf. eqn (46)].



We have found that the  $\text{Mo}\equiv\text{Mo}$  triple bond is *very reactive towards azirines*. Compound **1** reacts with 2-phenyl-1-azirine to form a red, thermally labile complex which decomposes above  $0^\circ\text{C}$  to a green mixture of products.<sup>66</sup> Green and coworkers have isolated the azaallyl complex **44** by column chromatography from this mixture.<sup>67</sup> The extra proton on the azaallyl ligand presumably comes from the column packing.

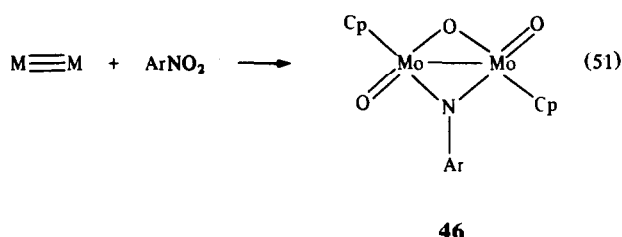


The phenylazirine also reacts with  $\text{M}^*\equiv\text{M}^*$  to give a labile adduct. However, 2-phenyl-3,3-dimethyl-1-azirine with  $\text{M}^*\equiv\text{M}^*$  gives a thermally stable product believed to have structure **45** on the basis of its NMR spectra (an X-ray structure determination is planned).<sup>66</sup> It thus appears that the azirine ring is behaving as a masked vinyl nitrene in reactions with  $\text{Mo}\equiv\text{Mo}$  triple bonds.



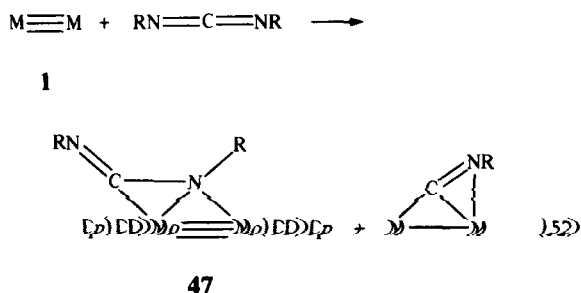
Alper *et al.*<sup>68</sup> have found that nitro arenes ( $\text{ArNO}_2$ ) react with **1** or the W-analog to give the complex shown in eqn (51). Although  $\text{ArNO}_2$  may be classified as a 1,3-dipole,<sup>48</sup> it is doubtful that this property is required for reaction (51) since aryl nitroso compounds ( $\text{ArNO}$ ) react with **1** to give the same products.<sup>68</sup>

The Mo-Mo single bond distance in **46** is only 2.65 Å, a distance which is shorter than the formal  $\text{Mo}=\text{Mo}$  double bonds in compounds **34** and **39** discussed above. In compounds in which the Mo is in a high formal oxidation state, e.g. in **46**,

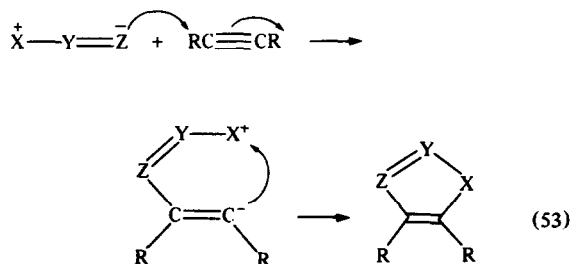


extensive  $\pi$ -bonding with the bridging ligands undoubtedly serves to contract the Mo-Mo bond distance.

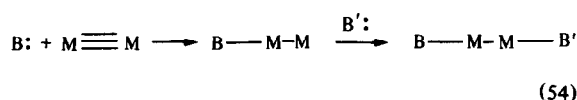
Compound **1** reacts slowly with excess carbodiimides in refluxing toluene to give the products shown in eqn (52).<sup>69</sup> The high temperature and slow rate of reaction again suggest that the reaction is proceeding by prior loss of CO from **1** followed by coordination of the carbodiimide. The  $\text{Mo}\equiv\text{Mo}$  triple bond in **47** reacts with CO to give a saturated derivative  $[\text{Cp}_2\text{Mo}_2(\text{CO})_5(\text{RNCNR})]$ .<sup>69</sup>



Although many interesting structures are formed by the interaction of 1,3-dipolar reagents with the  $\text{M}\equiv\text{M}$  triple bonds in **1** and related compounds, only in the decomposition of the adducts of  $\text{Ar}_2\text{CN}_2$  with **1** [eqn (40)] is there any persuasive evidence that 1,3-dipolar cycloadducts are formed. The lack of cycloadduct formation is in keeping with the different behavior of these  $\text{M}\equiv\text{M}$  triple bonds *vis-à-vis*  $\text{C}\equiv\text{C}$  triple bonds. Attack of the nucleophilic end of the 1,3-dipole on a  $\text{C}\equiv\text{C}$  bond generates a nucleophilic site on the contiguous carbon. Ring closure then occurs when this nucleophilic carbon reacts with the electrophilic end of the dipolar reagent [eqn (53)].

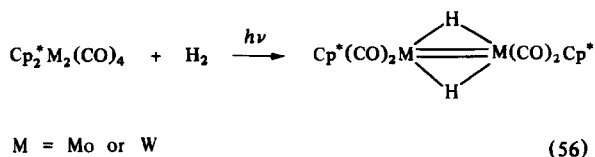
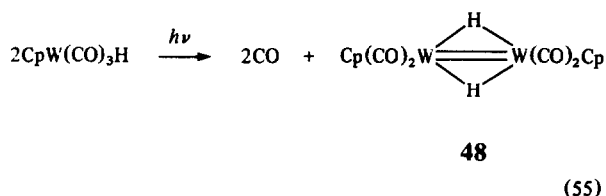


In contrast, attack by a nucleophile on one end of the  $M\equiv M$  triple bond in **1** generates a 16-electron, *electrophilic* site on the remote metal [eqn(54)] due to collapse of electrons into non-bonding levels which are not available to carbon (see electron-counting arguments in Ref. 1). Thus, there is no charge development which directs ring closure to a 1,3-dipolar cycloadduct. Instead, the preferred reaction path seems to be first coordination of the most nucleophilic portion of the dipolar reagent, followed by rearrangements and/or coordination of other donor functions on the dipolar reagent to eventually "saturate" the  $M\equiv M$  triple bond according to the scheme in eqn (54) ( $B'$  represents any second donor function, i.e.  $B$  and  $B'$  may be in the same molecule or on different molecules).

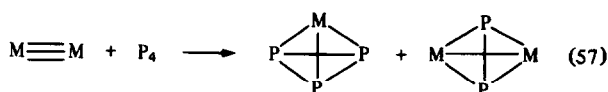


### OXIDATIVE REACTIONS WITH NON-METALS

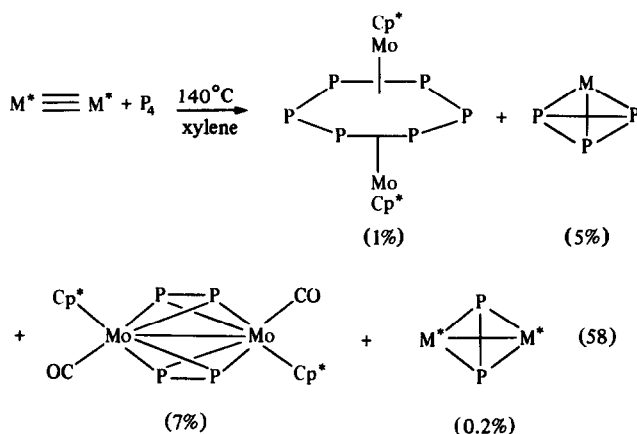
In our initial explorations of the chemical behavior of compound **1**, we were disappointed in its lack of reactivity toward molecular  $H_2$ . However, it was demonstrated recently that photolysis of  $CpW(CO)_3H$  gives the  $\mu$ -dihydride [eqn(55)].<sup>70</sup> Compound **48** is unstable in solution, presumably dissociating to  $H_2$  and  $Cp_2W_2(CO)_4$ . The  $C_5Me_5$  derivatives are stable, however, and may be prepared by the direct reaction of the  $M^*\equiv M^*$  bonded compounds with  $H_2$  under UV photolysis.



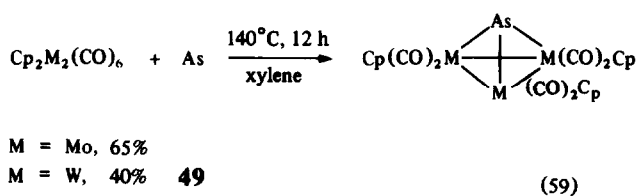
The multiply-bonded Mo dimers show high reactivity toward other non-metals, e.g. P, As, S, Se etc. With white phosphorus, **1** forms tetrahedrane clusters [eqn(57)].<sup>71</sup>



Under more forcing conditions, the derivatives react to give a mixture of structurally novel complexes in low yield [eqn(58)].<sup>72</sup> Included in the products is a triple-decker complex with a  $P_6$ -ring sandwiched between two  $Cp^*Mo$  moieties. The Mo-Mo distance in this complex is 2.647(1) Å and the Mo-P avg. distance is *ca* 2.54 Å. There is some evidence for a ring current associated with the  $P_6$ -ring: the Me groups of the  $Cp^*$  ligands resonate at  $\delta$  0.47 instead of their more usual value of *ca* 2.



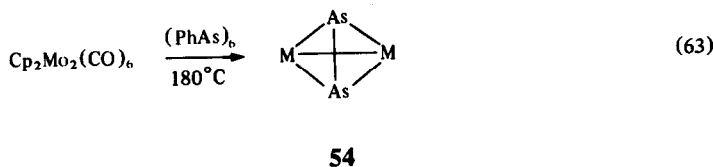
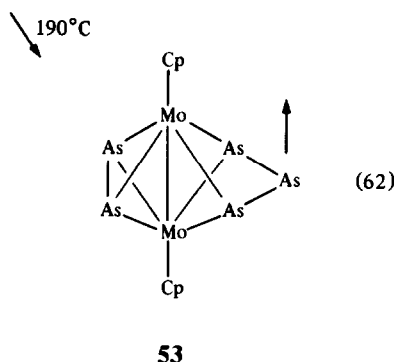
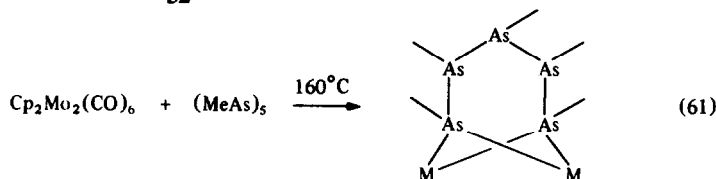
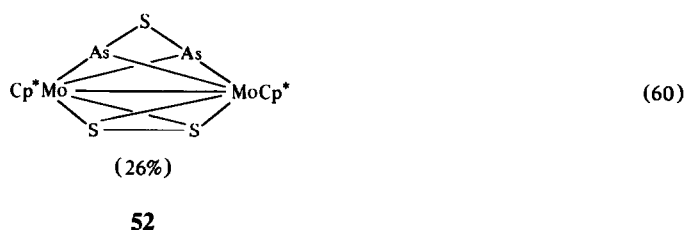
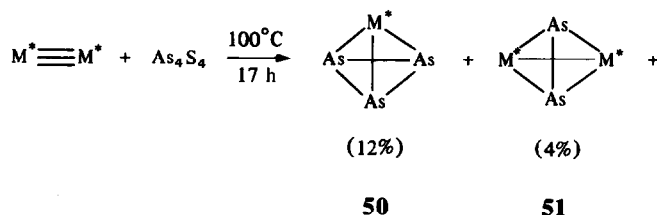
Arsenic and its derivatives also react with **1** [or its precursors,  $Cp_2Mo_2(CO)_6$  or  $CpMo(CO)_3H$ ] at elevated temperatures to give novel Mo-As clusters [eqns (59),<sup>73</sup> (60),<sup>74</sup> (61),<sup>75</sup> (62)<sup>76</sup> and (63)<sup>77</sup>].



The structure of **49** is similar to that of the isoelectronic cation,  $Cp_3Mo_3(CO)_6S^+$  (see below) except that in **49** the  $CpMo(CO)_2$  units are twisted relative to one another in such a way that the cluster has no symmetry, whereas the sulfur cation cluster has approximate  $C_3$ -symmetry in the solid state.<sup>78</sup>

Reactions (61)–(63) do not use the triply-bonded dimers as starting material, but the reactions are conducted under conditions where **1** (or **2**) forms rapidly. In any event, the products are so closely





related to those obtained from **1** or **2** that they are included here for completeness.

Compound **53** was described originally by the authors as having a  $\text{Mo}=\text{Mo}$  double bond. However, if the ligands are considered to be  $\mu\text{-As}_2^{4-}$  and  $\mu\text{-As}_3^{4-}$ , then the formal oxidation state of Mo is  $+5(d^1)$  so the maximum Mo-Mo bond order is one. The Mo-Mo distance [ $2.75 \text{ \AA}$ ] is consistent with an Mo-Mo single bond bridged by three or four groups.\* Complex **53** is quite unusual

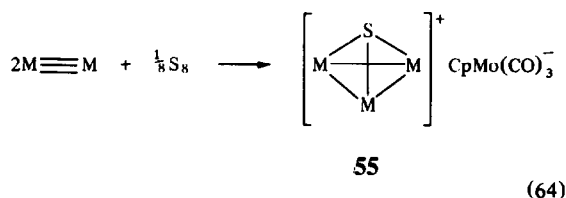
nevertheless. The five As atoms are essentially coplanar and the Mo-Mo bond is perpendicular to the As plane. The As atoms are segregated into two groups,  $\text{As}_2$  and  $\text{As}_3$ , and an odd electron is apparently localized on the central As of the  $\mu, \eta^2\text{-As}_3$  ligand.<sup>76</sup> Reaction 61 is very similar to the reaction of  $\text{M}\equiv\text{M}$  with disulfides ( $\text{RSSR}$ ).<sup>8</sup>

The series,  $\text{M}_n\text{As}_{4-n}$  ( $n = 1-3$ ), is represented by compounds **50**, **51** or **54**, and **49**. The  $n = 0$  ( $\text{As}_4$ ) is known in the gas phase, but there is no convincing evidence for the existence of the  $n = 4$  member, i.e.  $\text{M}_4$ .<sup>8,14</sup> The As-As distance in **54** is  $2.31 \text{ \AA}$ , commensurate with an  $\text{As}=\text{As}$  double bond. Complexes **51** and **54** may then be regarded as adducts of

\* Mo-Mo distances in a variety of Mo-S dimers and clusters show a strong correlation with the number of sulfide bridges:  $\mu\text{-S}$ ,  $\text{Mo-Mo} \approx 2.9\text{--}3.0 \text{ \AA}$ ;  $2\mu\text{-S}$ ,  $\text{Mo-Mo} = 2.75\text{--}2.8 \text{ \AA}$ ; 3 or  $4\mu\text{-S}$ ,  $\text{Mo-Mo} = 2.65\text{--}2.7 \text{ \AA}$ .<sup>79</sup>

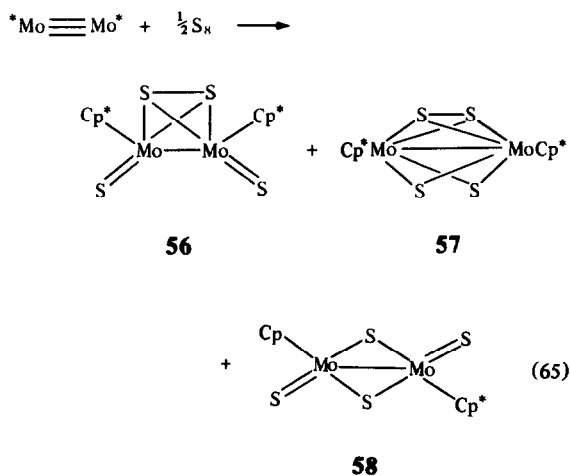
$M\equiv M$  with the alkyne analogue  $As\equiv As$ . Synergic bonding reduces the  $As-As$  bond order from 3 to 2 in the same manner that the  $C-C$  bond order is reduced in the alkyne adducts.

The  $M\equiv M$  triple bond is also quite reactive with the chalcogens. The reaction of **1** with excess sulfur produces red, insoluble polysulfides<sup>78</sup>  $[CpMoS_x]_n$  identical to those obtained from the reaction of  $Cp_2Mo_2(CO)_6$  with excess sulfur. However, if the stoichiometry is carefully controlled and  $\frac{1}{8}S_8$  (solution in  $CH_2Cl_2$ ,  $CS_2$  or toluene) is added to the solution of **1** a surprising disproportionation of two dimers into a trimer and a monomer is observed [eqn (64)].

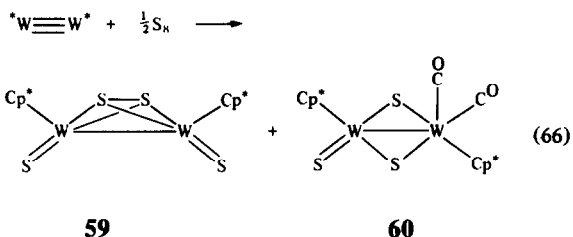


Yields of the cation **55** of 50–70% have been realized. The  $CpMo(CO)_3^-$  anion is easily replaced with halide either by adding  $RX$  and washing the  $CpMo(CO)_3R$  ( $R = H$  or  $Me$ ) away from the salt (**55**· $X$ ) with petroleum ether.

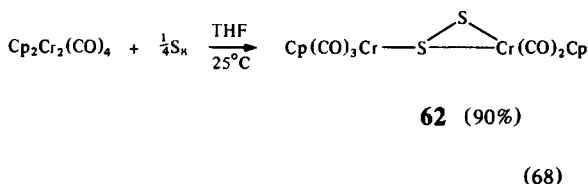
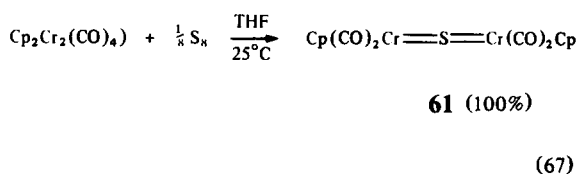
The more soluble (and more hindered)  $Cp^*$  complexes of  $Cr$ ,  $Mo$  and  $W$  react with excess sulfur to give discrete tetrasulfide complexes which display an interesting series of isomeric forms.<sup>80</sup> These isomers may have different formal oxidation states due to the formation of  $S-S$  bonds in the ligands [eqn (65)]. Prolonged refluxing of the reaction mixture converts **57** into **56**. Under UV photolysis, **58** is converted into **57** which in turn is converted to **56**. Photolysis of **56** regenerates **58** so that a photo-steady-state mixture of all three isomers results.<sup>81</sup>



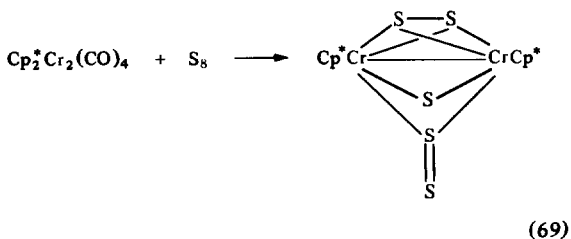
The reaction of  $Cp^*_2W_2(CO)_4$  with sulfur proceeds as in eqn (66). Compound **60** reacts with excess sulfur to form **59**.<sup>80</sup> Similar sulfur compounds to those shown in eqns (65) and (66) may be obtained from either the single-bonded dimers,  $Cp_2M_2(CO)_6$ , or the hydrides,  $CpM(CO)_3H$ .<sup>82</sup>



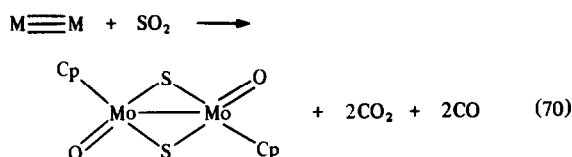
The  $Cr\equiv Cr$  triple bond in  $Cp_2Cr_2(CO)_4$  is reported to react with sulfur as shown in eqns (67) and (68).<sup>83</sup> In our laboratory, we have been unable to obtain the disulfide **62** according to eqn (68); only **61** was isolated.



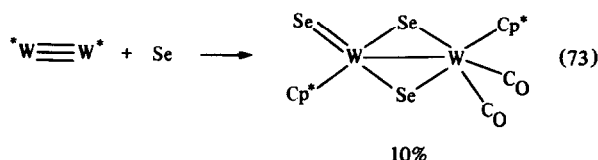
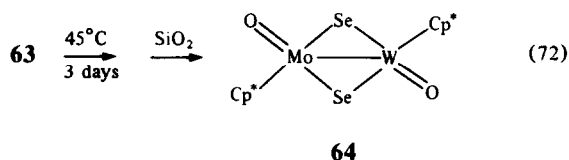
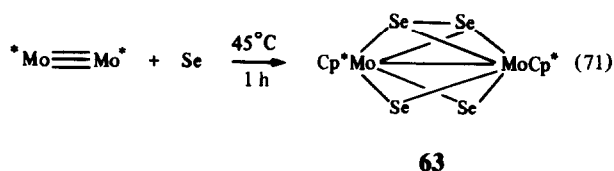
The more hindered  $Cp^*$  complex reacts with excess sulfur to give a 22% yield of the pentasulfide shown in eqn (69).<sup>84(a)</sup> The  $Cr-Cr$  distance is 2.489(2) Å, and the  $Cr-S$  distances range from 2.24 to 2.35 Å. The  $S-S$  and  $S=S$  distances are 2.15 and 2.10 Å, respectively.



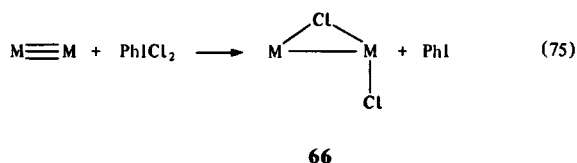
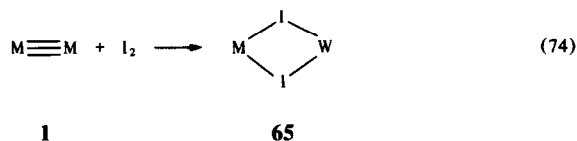
Compound **1** reacts with  $SO_2$  according to eqn (70).<sup>85</sup>



Results for the heavier chalcogens is limited to the reaction of **2** with Se.<sup>84(b)</sup> A short reaction time gives a 10% conversion to the tetraselenide (**63**); most of the Mo is recovered as unchanged starting material. When a toluene solution of **63** was stirred at 45°C for 3 days, a 45% yield of **64** was obtained following chromatography on silica gel. The source of the oxygen is unknown. The tungsten compound gave the Se analog of **60** [eqn (73)].

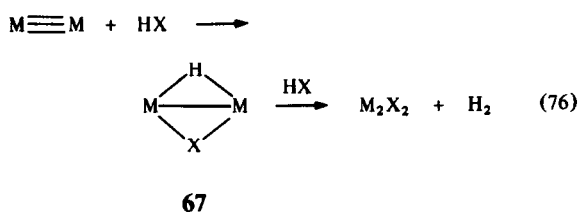


The  $\text{M}\equiv\text{M}$  triple bond in **1** reacts readily with halogens to give dinuclear adducts.<sup>86</sup> With  $\text{I}_2$ , the structure is the  $\mu$ -diiodide (**65**) but the dichloride is suggested to have the unsymmetrical structure (**66**) on the basis of Cl-XPS and NMR data.



Hydrogen halides, HCl and HI, react with **1** to give the oxidative addition products **67** ( $\text{X} = \text{Cl}$  or  $\text{I}$ ). These hydrohalide adducts react with excess HX

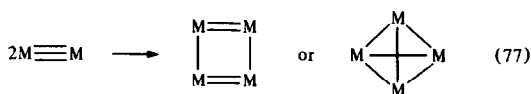
to give their respective dihalides (**65** or **66**) and  $\text{H}_2$ .<sup>86</sup>



In the oxidative reactions of the type discussed above it makes little difference if the starting complex is saturated  $\text{Cp}_2\text{M}_2(\text{CO})_6$  or  $\text{CpM}(\text{CO})_3\text{H}$ , or the unsaturated, multiply-bonded derivatives  $\text{Cp}_2\text{M}_2(\text{CO})_4$ , if: (a) elevated temperatures, or (b) a large excess of the non-metal is used in the reaction. The utility of the unsaturation in the  $\text{M}\equiv\text{M}$  bond is best realized when the reactions are carried out under mild conditions with stoichiometric quantities of reagents. Then the enhanced reactivity of the metal-metal multiple bond is advantageous and allows for the isolation of thermally labile or kinetically controlled products, e.g. **55**, **67** etc.

## CLUSTER-BUILDING REACTIONS

One of the most useful properties of carbon-carbon multiple bonds is their ability to polymerize and oligomerize into larger structures which maintain the basic skeleton of the monomers. An analogous oligomerization of metal-metal multiply bonded complexes gives metal clusters. To date, the simple oligomerization of  $\text{M}\equiv\text{M}$  bonds as depicted in eqn (77) has not been observed.<sup>14,\*</sup> Nevertheless, the  $\text{M}\equiv\text{M}$  triple bond in **1** has served as a convenient synthon in the construction of trinuclear and tetranuclear clusters containing the  $\text{M}_2$  unit.

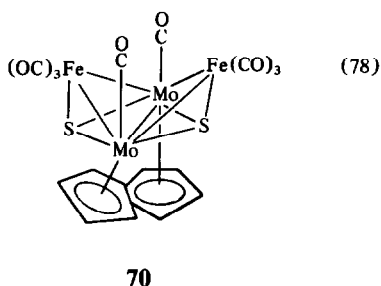
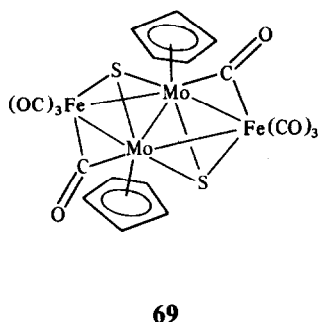
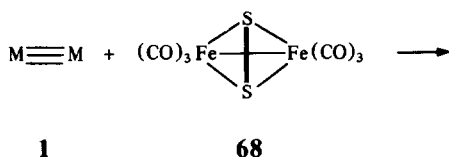


In our first paper on the reactivity of **1**, we noted that  $(\text{R}_3\text{P})_2\text{Pt}^{(0)}$  could be added to the  $\text{M}\equiv\text{M}$  bond to give  $\text{M}_2\text{Pt}$  triangulo clusters.<sup>8</sup> Unfortunately, the instability of these clusters has precluded an X-ray structure determination. Several clusters of types  $\text{MX}_3$ ,  $\text{M}_2\text{X}_2$  and  $\text{M}_3\text{X}$  are produced in the oxidative reactions of  $\text{M}\equiv\text{M}$  with non-metals (see above). However, the most useful cluster-building

\* Oligomerization of metal-metal multiply bonded species upon loss of ligand<sup>87(a)</sup> or through the formation of ligand bridges<sup>87(b),(c)</sup> has been realized.

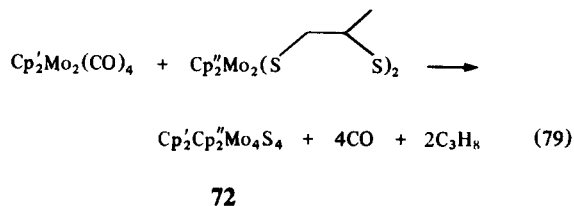
reactions of  $M\equiv M$  are those which give ligand-bridged, bimetallic clusters.

Thus, **1** reacts with the disulfide linkage in **68** to give the isomeric clusters **69** and **70**.<sup>88,89</sup> Both **69** and **70** are 62-electron clusters and have five metal-metal bonds in accordance with various electron-counting schemes.<sup>90</sup> They differ primarily in the disposition of the sulfide ligands—in the planar isomer (**69**), the sulfide ligands are on opposite sides of the  $Mo_2Fe_2$  plane (the molecule is centrosymmetric) whereas in **70** the sulfurs are cisoid and the metals are in the more common butterfly geometry. The chromium derivative,  $Cp_2Cr_2(CO)_4$ , reacts with **68** to give the Cr butterfly analogous to **70**.<sup>91</sup> These  $Mo_2Fe_2S_2$  clusters and related  $Mo_2Co_2S_3$  clusters<sup>92</sup> are effective catalysts for CO methanation and thiophene HDS when supported on  $Al_2O_3$ .<sup>93</sup>

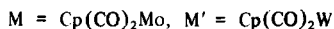


The triple bond in **1** also displaces propene from  $Cp_2Mo_2(SCH_2CH(Me)S)_2$  [eqn. (79)] or  $H_2$  from  $Cp_2Mo_2(\mu-SH)_2(\mu-S)_2$  (**71**) to give the  $Mo_4S_4$  cubane, **72**.<sup>88</sup> This route to these cubanes is the most convenient and allows one to control the substitution on the Cp rings almost at will. The reaction of **71** with  $Cp_2W_2(CO)_4$  failed to give the  $Cp_4Mo_2W_2S_4$  cubane.<sup>94</sup> The  $Cp_4Mo_4S_4$  cubanes

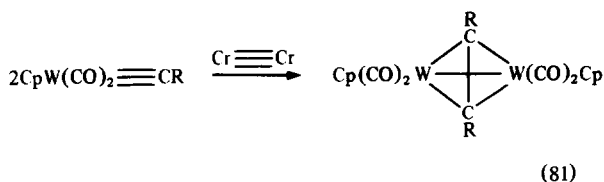
are very readily oxidized to mono- or dications, the structures of which have been determined.<sup>95</sup> The PES of the  $Mo_4S_4$  cubanes,<sup>95</sup> their cyclic voltammetry, their structural parameters, and an EHMO calculation<sup>94</sup> are all consonant with an electron configuration of  $a_1^2e^4t_2^6$  for the six cluster framework electron pairs as originally suggested by Trinh-Toan *et al.*<sup>96</sup>



A beautiful illustration of the utility of the isolobal principle is the addition of a metal carbyne to the  $M\equiv M$  bond to give trimetalla-tetrahedrane structures as shown in eqn (80) [cf. eqn (18)].<sup>97</sup>



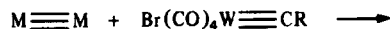
Cluster **73** is obtained in quantitative yield when  $M = Mo$  and  $M' = W$ . The reaction of the W carbyne with  $Cp_2Cr_2(CO)_4$  led to the dimerization of the carbyne [eqn(81)]. It was found that the  $Cr\equiv Cr$  complex *catalyzes* the dimerization of the carbyne.<sup>97</sup>



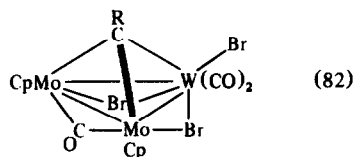
Green *et al.*<sup>97</sup> found that a complex mixture resulted when **1** was allowed to react with  $Br(CO)_4W\equiv CR$  in ether. A 22% yield of the trimetallic cluster **73** [ $M = M' = Mo(CO)_2Cp$ ], was obtained by chromatography of the mixture over Florisil. Cotton and Schwotzer isolated a 20% yield of cluster **74** from the nearly identical reaction (THF solvent, followed by chromatography over silica gel).<sup>98</sup> Either the solvent exerts a strong influence on the course of this reaction, or the reaction mixture reacts further on the chromato-

graphy column to give products which depend on the column packing.

Ti(II) to Ti(III). Lewis bases (B) cleave the dimeric structure to give  $\text{Cp}_2\text{Ti}(\text{B})\text{OC}(\text{CO})_2\text{MoCp}$ .<sup>101</sup>

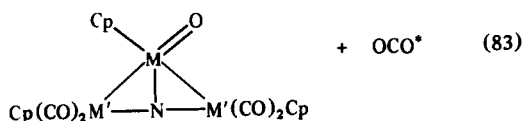


1



74

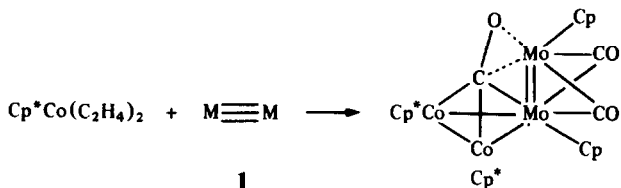
The nitrosyl complexes,  $\text{Cp}(\text{CO})_2\text{M}\equiv\text{NO}$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) react with  $\text{Cp}_2\text{M}'_2(\text{CO})_6$  ( $\text{M}' = \text{Mo}$  or  $\text{W}$ ) to give trimetallic nitrido clusters (75) in a reaction that is superficially related to the reactions of the carbynes above.<sup>99</sup> However, the conditions (200°C, sealed tube, 1 h), low yields, and the demonstrated cleavage of the N–O bond suggest the mechanism of formation of the clusters 75 is not a straightforward addition of the  $\text{M}\equiv\text{NO}$  bond to the  $\text{M}\equiv\text{M}$  bond.



75

$\text{M}$  and  $\text{M}' = \text{Mo}$  or  $\text{W}$

Attempts to insert the  $\text{M}\equiv\text{M}$  unit into preformed clusters by thermal reactions have been largely unsuccessful.<sup>1</sup> However, 1 does react with  $\text{Cp}^*\text{Co}(\text{C}_2\text{H}_4)_2$  under UV photolysis to give the novel cluster 76 in 20% yield.<sup>100</sup>

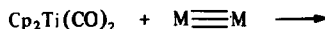


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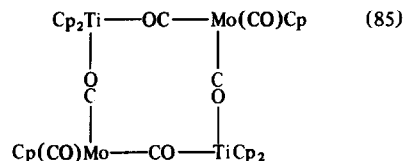
76

(84)

Finally,  $\text{Cp}_2\text{Ti}(\text{CO})_2$  reacts with 1 as shown in eqn (85). The carbonyl groups are transferred from Ti to Mo and the Ti is formally oxidized from



1



(85)

## CONCLUSION

The compounds  $\text{Cp}_2\text{M}_2(\text{CO})_4$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) and related substituted-Cp derivatives have proven to be extremely versatile reagents for the elaboration of more complex molecules containing the  $\text{Cp}_2\text{M}_2$  units. The  $\text{M}\equiv\text{M}$  units may be thought of as dimetal fragments which have been stripped of two ligands (four electrons) and are thus extremely electrophilic. Consequently, reactions with nucleophiles often occur under very mild conditions so that thermally labile products may be isolated and new bonding modes revealed.

At higher temperatures ( $>100^\circ\text{C}$ ), or under UV photolysis, CO is lost from the  $\text{M}\equiv\text{M}$  unit and more complex modes of reactivity are often observed. Even here, however, the presence of the metal-metal triple bond may be instrumental in directing the reaction to give dinuclear products. It is well known,<sup>7,8</sup> that the Mo–Mo or W–W single bonds in  $\text{Cp}_2\text{M}_2(\text{CO})_6$  complexes are extensively dissociated at elevated temperatures, and these single-bonded dimers often form mononuclear products as a result. In contrast, there is no evidence at all that the triply-bonded dimers dissociate into mononuclear fragments either thermally or under UV photolysis.<sup>102</sup>

The  $\text{Cr}\equiv\text{Cr}$  triple bond in  $\text{Cp}_2\text{Cr}_2(\text{CO})_4$  and related complexes has not been as useful a starting material as its Mo and W congeners. Intractable mixtures are often produced.

Finally, a word about the concept of an “inorganic functional group” is appropriate. The term “functional group”, as derived from organic chemistry, connotes more than a reactive grouping of atoms in a larger molecule. The term also suggests that a particular grouping of atoms will react in certain specified ways when exposed to certain conditions and/or reagents.

Are the  $\text{Mo}\equiv\text{Mo}$  and  $\text{W}\equiv\text{W}$  triple bonds in  $\text{Cp}_2\text{M}_2(\text{CO})_4$  “inorganic functional groups”? They are certainly reactive and some generalizations

concerning their reactivity can be made. However, as the reactions of  $M\equiv M$  with diazoalkanes so amply demonstrate, the course of the reactions of  $M\equiv M$  may be greatly altered by subtle changes in the reagents, the substitution on the Cp ring etc. Under such circumstances, the utility of the functional group *concept* is clearly limited.

The utility of the  $M\equiv M$  compounds is not restricted by our limited ability to predict the exact course of the reactions, however. The rational syntheses of the clusters 69–73, or the metallacyclopentene (39) clearly show that the reactivity of the  $M\equiv M$  unit can be extrapolated successfully to new areas. In any event, it is clear that the availability of compounds with metal–metal multiple bonding opens a new dimension to the synthetic chemist, and that the exploration of metal–metal multiple bond reactivity will continue to be an exciting area of research.

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## REFERENCES

1. M. D. Curtis, L. Messerle, N. A. Fotinos and R. F. Gerlach, *ACS Symp. Ser.* 1981, **155**, 221.
2. R. J. Klingler, W. M. Butler and M. D. Curtis, *J. Am. Chem. Soc.* 1978, **100**, 5024.
3. M. D. Curtis, K. R. Han and W. M. Butler, *Inorg. Chem.* 1980, **19**, 2096.
4. C. P. Horowitz and D. F. Shriver, *Adv. Organomet. Chem.* 1984, **23**, 219.
5. E. D. Jemmis, A. R. Pinhas and R. Hoffmann, *J. Am. Chem. Soc.* 1980, **102**, 2576.
6. B. J. Morris-Sherwood, C. B. Powell and M. B. Hall, *J. Am. Chem. Soc.* 1984, **106**, 5079.
7. N. N. Turaki and J. M. Huggins, *Organometallics* 1985, **4**, 1766.
8. M. D. Curtis and R. J. Klingler, *J. Organomet. Chem.* 1978, **17**, 2324.
9. R. H. Hooker, K. A. Mahmoud and A. J. Rest, *J. Organomet. Chem.* 1983, **254**, C25.
10. J.-S. Huang and L. F. Dahl, *J. Organomet. Chem.* 1983, **243**, 57.
11. R. B. King and M. B. Bisnette, *Inorg. Chem.* 1965, **4**, 475.
12. (a) M. A. Greaney, J. S. Merola and T. R. Halbert, *Organometallics* 1985, **4**, 2059; (b) I. Bakkar and M. D. Curtis, Abstracts, 19th ACS National Meeting, Chicago, II 1985, INOR 377; (c) I. Bakkar and M. D. Curtis, to be published.
13. (a) K.-B. Shiu, M. D. Curtis and J. C. Huffman, *Organometallics* 1983, **2**, 936; (b) M. D. Curtis, K.-B. Shiu, W. M. Butler and J. C. Huffman, *J. Am. Chem. Soc.* 1986, **108**, 3335.
14. M. D. Curtis, N. A. Fotinos, L. Messerle and A. P. Sattelberger, *Inorg. Chem.* 1983, **22**, 1559.
15. M. D. Curtis, to be submitted for publication.
16. F. E. Massoth, *Adv. Catal.* 1978, **27**, 265.
17. (a) H. Alper, N. D. Silavwe, G. I. Birnbaum and F. R. Akmed, *J. Am. Chem. Soc.* 1978, **101**, 6582; (b) H. Alper, F. W. B. Einstein, R. Nagai, J.-F. Petrignani and A. C. Willis, *Organometallics* 1983, **2**, 1291; (c) *ibid.* 1983, **2**, 1422.
18. (a) H. Alper, F. W. B. Einstein, F. W. Hartstock and A. C. Willis, *J. Am. Chem. Soc.* 1985, **107**, 173; *Organometallics* 1986, **5**, 9.
19. H. Alper and J. Hartgerink, *J. Organomet. Chem.* 1980, **190**, C25.
20. H. Brunner, H. Buchner, J. Wachter, I. Bernal and W. H. Ries, *J. Organomet. Chem.* 1983, **244**, 247.
21. R. D. Adams, D. A. Katahira and L.-W. Yang, *Organometallics* 1982, **1**, 231.
22. H. Brunner, W. Meier and J. Wachter, *J. Organomet. Chem.* 1981, **210**, C23.
23. J. Wachter, J. G. Riess and A. Mitschler, *Organometallics* 1984, **3**, 714.
24. J. Krause and M. D. Curtis, unpublished results.
25. K. Endrich, R. Korswagen, T. Zahn and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.* 1982, **21**, 919.
26. (a) J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto and J. F. Nixon, *J. Organomet. Chem.* 1982, **238**, C82; (b) G. Becker, W. A. Herrmann, W. Kalcher, G. W. Kriechbaum, C. Pahl, C. T. Wagner and M. L. Ziegler, *Angew. Chem.* 1983, **95**, 417; *Angew. Chem. Suppl.* 1983, 501.
27. W. I. Bailey, Jr, M. H. Chisholm, F. A. Cotton and L. A. Rankel, *J. Am. Chem. Soc.* 1978, **100**, 5764.
28. J. A. Beck, S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter and P. Woodward, *J. Chem. Soc., Dalton Trans.* 1982, 195.
29. R. F. Gerlach, D. N. Duffy and M. D. Curtis, *Organometallics* 1983, **2**, 1172.
30. S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter and P. Woodward, *J. Chem. Soc., Dalton Trans.* 1982, 173.
31. A. M. Boileau, A. G. Orpen, R. F. D. Stansfield and P. Woodward, *J. Chem. Soc., Dalton Trans.* 1982, 187.
32. S. Slater and E. L. Muetterties, *Inorg. Chem.* 1981, **20**, 946.
33. J. S. Bradley, *J. Organomet. Chem.* 1978, **150**, C1.
34. M. Green, N. C. Norman and A. G. Orpen, *J. Am. Chem. Soc.* 1981, **103**, 1269.
35. W. A. Herrmann, *Adv. Organomet. Chem.* 1982, **20**, 160.
36. D. L. Thorn and R. Hoffmann, *Nouv. J. Chim.* 1979, **3**, 39.
37. M. D. Curtis, K.-B. Shiu and W. M. Butler, *J. Am. Chem. Soc.* 1986, **108**, 1550.
38. J. A. Beck, S. A. R. Knox, G. H. Riding, G. E. Taylor and M. J. Winter, *J. Organomet. Chem.* 1980, **202**, C49.

39. J. C. Jeffery, J. C. V. Laurie, I. Moore and F. G. A. Stone, *J. Organomet. Chem.* 1983, **258**, C37.
40. A. Meyer and M. D. Curtis, submitted to *Organometallics*, 1987.
41. M. D. Curtis and A. Meyer, to be published.
42. D. J. Wink, J. R. Fox and N. J. Cooper, *J. Am. Chem. Soc.* 1985, **107**, 5012.
43. K.-W. Lee and T. L. Brown, *Organometallics* 1985, **4**, 1025.
44. J.-C. Daran, Y. Jeanin and O. Kristianson, *Organometallics* 1985, **4**, 1882.
45. R. Goddard, S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter and P. Woodward, *J. Chem. Soc., Dalton Trans.* 1982, 147.
46. M. Griffiths, S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter and P. Woodward, *J. Chem. Soc., Dalton Trans.* 1982, 159.
47. S. A. R. Knox, R. F. D. Stansfield, R. G. A. Stone, M. J. Winter and P. Woodward, *J. Chem. Soc., Dalton Trans.* 1982, 167.
48. (a) A. Padwa, Ed., *1,3-Dipolar Cycloaddition Chemistry*, Vols 1 and 2. Wiley Interscience, New York (1984); (b) R. Huisgen, *Angew. Chem., Int. Ed. Engl.* 1963, **2**, 565.
49. L. Messerle and M. D. Curtis, *J. Am. Chem. Soc.* 1980, **102**, 7789.
50. M. D. Curtis, L. Messerle, J. J. D'Errico, W. M. Butler and M. S. Hay, *Organometallics*, 1986, **5**, 2283.
51. J. A. Abad, L. W. Bateman, J. C. Jefferey, K. A. Mead, H. Razay, F. G. A. Stone and P. Woodward, *J. Chem. Soc., Dalton Trans.* 1983, 2075.
52. W. A. Herrmann and L. K. Bell, *J. Organomet. Chem.* 1982, **239**, C4.
53. W. A. Herrmann, L. K. Bell, M. L. Ziegler, K. Pfisterer and C. Dahl, *J. Organomet. Chem.* 1983, **247**, 39.
54. J. J. D'Errico, L. Messerle and M. D. Curtis, *Inorg. Chem.* 1983, **22**, 849 [note: the labelling of isomers 7a and 7b (eqn 2) in this reference are inadvertently interchanged].
55. L. K. Bell, W. A. Herrmann, G. W. Kriechbaum, H. Pfisterer and M. L. Ziegler, *J. Organomet. Chem.* 1982, **240**, 381.
56. (a) L. K. Bell, W. A. Herrmann, M. L. Ziegler and H. Pfisterer, *Organometallics* 1982, **1**, 1673; (b) W. A. Herrmann, G. W. Kriechbaum, M. L. Ziegler and H. Pfisterer, *Angew. Chem., Int. Ed. Engl.* 1982, **21**, 707.
57. N. D. Feasey, S. A. R. Knox and A. G. Orpen, *J. Chem. Soc., Chem. Commun.* 1982, 75.
58. M. D. Curtis and J. J. D'Errico, submitted to *Organometallics*, 1987.
59. W. A. Herrmann and G. Ihl, *J. Organomet. Chem.* 1983, **251**, C1.
60. J. J. D'Errico and M. D. Curtis, *J. Am. Chem. Soc.* 1983, **105**, 4478.
61. L. Messerle and M. D. Curtis, *J. Am. Chem. Soc.* 1982, **104**, 889.
62. M. D. Curtis, L. Messerle, J. J. D'Errico, H. E. Solis and I. D. Barcelo, *J. Can. Chem. Soc.* 1987, **109**, in press.
63. W. A. Herrmann, G. Kriechbaum, C. Bauer, E. Guggolz and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.* 1981, **20**, 815.
64. W. A. Herrmann, G. W. Kriechbaum, R. Dammel and H. Bock, *J. Organomet. Chem.* 1983, **254**, 219.
65. G. K. Barker, W. E. Carroll, M. Green and A. J. Welch, *J. Chem. Soc., Chem. Commun.* 1980, 1071.
66. M. Hay and M. D. Curtis, to be submitted for publication.
67. M. Green, R. J. Mercer, C. E. Morton and A. G. Orpen, *Angew. Chem., Int. Ed. Engl.* 1985, **24**, 422.
68. (a) H. Alper, J.-F. Petrignani, F. W. B. Einstein and A. C. Willis, *J. Am. Chem. Soc.* 1983, **101**, 1701; (b) J.-F. Petrignani and H. Alper, *Inorg. Chim. Acta* 1983, **77**, 1243.
69. H. Brunner, B. Hoffmann and J. Wachter, *J. Organomet. Chem.* 1983, **252**, C35.
70. H. G. Alt, K. A. Mahmoud and A. J. Rest, *Angew. Chem., Int. Ed. Engl.* 1983, **22**, 544.
71. O. J. Scherer, H. Sitzmann and G. Wolmershäuser, *J. Organomet. Chem.* 1984, **268**, C9.
72. O. J. Scherer, H. Sitzmann and G. Wolmershäuser, *Angew. Chem., Int. Ed. Engl.* 1985, **24**, 351.
73. K. Blechschmitt, H. Pfisterer, T. Zahn and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.* 1985, **24**, 66.
74. I. Bernal, H. Brunner, W. Meier, H. Pfisterer, J. Wachter and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.* 1984, **23**, 438.
75. A. L. Rheingold and M. R. Churchill, *J. Organomet. Chem.* 1983, **243**, 165.
76. A. L. Rheingold, M. J. Foley and P. J. Sullivan, *J. Am. Chem. Soc.* 1982, **104**, 4727.
77. P. J. Sullivan and A. L. Rheingold, *Organometallics* 1982, **1**, 1547.
78. M. D. Curtis and W. M. Butler, *J. Chem. Soc., Chem. Commun.* 1980, 998.
79. P. D. Williams and M. D. Curtis, to be published.
80. H. Brunner, W. Meier, J. Wachter, E. Guggolz, T. Zahn and M. L. Ziegler, *Organometallics* 1982, **1**, 1107.
81. A. E. Bruce and D. R. Tyler, *Inorg. Chem.* 1984, **23**, 3433.
82. (a) O. A. Rajan, M. McKenna, J. Noodlik, R. C. Haltiwanger and M. Rakowski-Dubois, *Organometallics* 1984, **3**, 831; (b) M. Rakowski-Dubois, D. L. Dubois, M. C. Van Derveer and R. C. Haltiwanger, *Inorg. Chem.* 1981, **20**, 3064; (c) D. L. Dubois, W. K. Miller and M. Rakowski-Dubois, *J. Am. Chem. Soc.* 1981, **103**, 3429.
83. L. Y. Goh, T. W. Hambley and G. B. Robertson, *J. Chem. Soc., Chem. Commun.* 1983, 1458.
84. (a) H. Brunner, J. Wachter, E. Guggolz and M. L. Ziegler, *J. Am. Chem. Soc.* 1982, **104**, 1765; (b) H. Brunner, J. Wachter and H. Wintergerst, *J. Organomet. Chem.* 1982, **235**, 77.
85. C. A. Poffenberger, N. H. Tennent and A. Wojcicki,

- J. Organomet. Chem.* 1980, **191**, 107.
86. M. D. Curtis, N. A. Fotinos, K. R. Han and W. M. Butler, *J. Am. Chem. Soc.* 1983, **105**, 2686.
87. (a) T. R. Ryan and R. E. McCarley, *Inorg. Chem.* 1982, **21**, 2072; (b) M. H. Chisholm, R. J. Errington, K. Folting and J. C. Huffman, *J. Am. Chem. Soc.* 1982, **104**, 2025; (c) M. J. Chetcuti, M. H. Chisholm, J. C. Huffman and J. Lionelli, *ibid.* 1983, **105**, 292.
88. P. D. Williams, M. D. Curtis, D. N. Duffy and W. M. Butler, *Organometallics* 1983, **2**, 165.
89. P. Braunstein, J.-M. Jud, A. Tiripicchio, M. Tiripicchio-Camellini and E. Sappa, *Angew. Chem., Int. Ed. Engl.* 1982, **21**, 307.
90. (a) J. W. Lauher, *J. Am. Chem. Soc.* 1978, **100**, 5305; (b) K. Wade, In *Transition Metal Clusters* (Edited by D. F. G. Johnson) p. 193. Wiley, New York (1980).
91. P. Braunstein, A. Tiripicchio, M. T. Camellini and E. Sappa, *Inorg. Chem.* 1981, **20**, 3586.
92. M. D. Curtis and P. D. Williams, *Inorg. Chem.* 1983, **22**, 2661.
93. M. D. Curtis, J. Schwank, L. Thompson, P. D. Williams, and O. Baralt, Preprint, Fuels Division, American Chemical Society National Meeting, Anaheim CA, September 1986.
94. P. D. Williams and M. D. Curtis, *Inorg. Chem.* 1986, **25**, 4562.
95. J. A. Bandy, C. E. Davies, J. C. Green, M. L. H. Green, K. Prout and D. P. S. Rogers, *J. Chem., Soc. Chem. Commun.* 1983, 1395.
96. Trinh-Toan, B. K. Teo, J. A. Ferguson, T. J. Meyer and L. F. Dahl, *J. Am. Chem. Soc.* 1977, **99**, 408.
97. M. Green, S. J. Porter and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.* 1983, 513.
98. F. A. Cotton and W. Schwotzer, *Angew. Chem., Int. Ed. Engl.* 1982, **31**, 629.
99. N. D. Feasey and S. A. R. Knox, *J. Chem. Soc., Chem. Commun.* 1982, 1062.
100. P. Brun, G. M. Dawkins, M. Green, A. D. Miles, A. G. Orpen and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.* 1982, 926.
101. J. S. Merola, K. S. Campo, R. A. Gentile, M. A. Modrick and S. Zentry, *Organometallics* 1984, **3**, 334.
102. J. L. Robbins and M. S. Wrighton, *Inorg. Chem.* 1981, **20**, 1133.