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THE REACTIONS OF $Mo_2Ru(CO)_7Cp_2(\mu_3\text{-}S)$ WITH PHENYLACETYLENE AND $Ru(CO)_5$

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Abstract—The reactivity of the heteronuclear cluster complex $Mo_2Ru(CO)_7Cp_2(\mu_3\text{-}S)$ (**1**) toward HC_2Ph was investigated and compared with the reactivity of the homonuclear complexes $Ru_3(CO)_{10}(\mu_3\text{-}S)$ (**2**) and $[Mo(CO)_2Cp]_2$ (**3**). The reaction of **1** with HC_2Ph yielded the new compound $Mo_2Ru(CO)_2Cp_2[\mu_3\text{-}\eta^6\text{-}HCC(Ph)CHC(Ph)CHC(Ph)](\mu_3\text{-}S)$ (**6**), 15%. The compound contains a 1,3,5-triphenyldimetallahexatrienyl ligand formed by the head-to-tail coupling of three HC_2Ph molecules. The C_6-chain bridges one face of the triangular cluster. Three of the carbon atoms of the chain are π-bonded to one molybdenum atom. The other three carbon atoms are π-bonded to the ruthenium atom. The two ends of the chain are σ-bonded to the second molybdenum atom. When treated with CO at 100°C/25 atm, **6** eliminates 1,3,5,triphenylbenzene and reforms **1**. At 125°C under nitrogen, the C_6-chain in **6** is split at the C(3)—C(4) bond to yield the two isomeric products $Mo_2Ru(CO)_2Cp_2[\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH][\mu\text{-}\eta^3\text{-}PhCC(H)CPh](\mu_3\text{-}S)$ (**7**) and $Mo_2Ru(CO)_2Cp_2[\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH][\mu\text{-}\eta^3\text{-}PhCC(Ph)CH](\mu_2\text{-}S)$ (**8**). Both products contain two dimetallaallyl ligands. One bridges the face of the cluster. The other bridges the Mo—Mo edge. Compound **7** is converted into **8** at 125°C. When **1** is treated with Me_3NO and HC_2Ph at 25°C, the compound $Mo_2Ru(CO)_5Cp_2[\mu\text{-}\eta^4\text{-}PhCC(H)CC(H)Ph](\mu_3\text{-}S)$ (**9**) is formed in 11% yield. Compound **9** consists of an open cluster with a PhCC(H)CC(H)Ph ligand that bridges the open edge of the cluster. The four-carbon chain is π-bonded to a molybdenum atom while one carbon serves as the bridging link by bonding to the ruthenium atom. Compound **9** does not appear to be an intermediate en route to **6**. When **1** is treated with $Ru(CO)_5$ at 80°C, two higher nuclearity cluster products $Mo_2Ru_4(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CO)Cp_2(\mu_4\text{-}S)$ (**10**) and $Mo_2Ru_5(CO)_{14}(\mu_4\text{-}\eta^2\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ (**11**) are formed. Compound **10** consists of a square pyramidal Mo_2Ru_4 cluster containing a quadruply bridging sulphido ligand on the square base. An $Ru(CO)_3$ group bridges an Ru—Ru edge of the square base. A dihapto quadruply bridging carbonyl ligand is bonded by its carbon atom to an $MoRu_2$ triangle of the square pyramid and is bonded by its oxygen atom to the $Ru(CO)_3$ group. Compound **11** is similar to **10** but has an additional $Ru(CO)_3$ group bridging the second Ru—Ru basal edge of the cluster and also has a second dihapto quadruply bridging carbonyl ligand. IR spectra show that the two quadruply bridging carbonyl ligands are vibrationally coupled by the appearance of two C—O stretching absorptions at 1419 and 1453 cm^{-1}. When **10** is heated to 80°C, it is converted to an isomer **12** by shifting the quadruply bridged carbonyl ligand to a terminal bonding mode. The cluster is transformed from an edge bridging form in **10** to a face capped form in **12**.

The most important question concerning the design and use of a multimetallic (heteronuclear) catalyst is, "Will it produce reactivity that is different from that of its components?" To answer this question, one must have a knowledge of the reactivity of each of the components to compare with that of the heteronuclear system. Molecular cluster complexes can provide a unique opportunity to make these comparisons, because the details of the reactivity can be established very precisely.

In this study, we have investigated the reactivity of the molybdenum–ruthenium mixed-metal cluster complex $Mo_2Ru(CO)_7Cp_2(\mu_3\text{-}S)$ (**1**) towards phenylacetylene, HC_2Ph. This complex was originally made by Vahrenkamp by a sequence of molyb-

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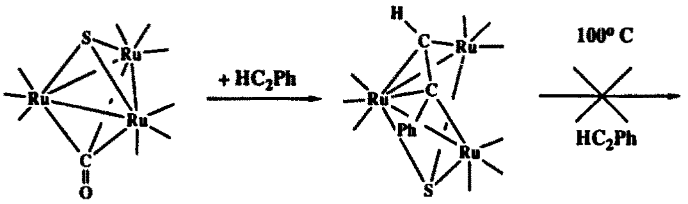
$$\mathrm{RuCo_2(CO)_9(\mu_3\text{-}S)} \xrightarrow{+\,\mathrm{CpMo(CO)_3AsMe_2}} \underset{42\%}{\mathrm{RuCoMo(CO)_8Cp(\mu_3\text{-}S)}} \xrightarrow{+\,\mathrm{[CpMo(CO)_3]_2}} \underset{48\%}{\mathrm{RuMo_2(CO)_7Cp_2(\mu_3\text{-}S)}} \qquad (1)$$

$$\mathrm{Ru_3(CO)_{10}(\mu_3\text{-}S)} + \mathrm{[CpMo(CO)_2]_2} \xrightarrow{-2\,\mathrm{CO}} \mathrm{Ru_3Mo_2(CO)_{12}Cp_2(\mu_4\text{-}S)} \xrightarrow{-2\,\mathrm{Ru}} \underset{49\%\ \text{overall}}{\mathrm{RuMo_2(CO)_7Cp_2(\mu_3\text{-}S)}} \qquad (2)$$

denum atom substitutions on the complex $RuCo_2(CO)_{11}(\mu_3\text{-}S)$, eq. (1),[1] and more recently by us through the one step reaction of $Ru_3(CO)_9(\mu_3\text{-}S)$ (**2**) with $[Mo(CO)_2Cp]_2$ (**3**), eq. (2).[2] Compound **1** has been characterized by crystallographic methods and was shown to consist of a triangular cluster of two molybdenum and one ruthenium atoms with a triply bridging sulphido ligand (see Fig. 1).

The reactivity of **2**[3] and **3**[4–8] toward HC_2Ph at 100°C has been reported. Compound **2** forms the substitution product $Ru_3(CO)_9(\mu_3\text{-}HC_2Ph)(\mu_3\text{-}S)$ (**4**) at 100°C when the $HC_2Ph/\mathbf{2}$ ratio is less than 10. Under these conditions, **4** exhibits no further tendency to add HC_2Ph, eq. (3). Compound **3** is well-known to add one equivalent of alkyne to form the compound $Mo_2(CO)_4Cp_2(\mu\text{-}HC_2Ph)$ (**5**) at 25°C and, at 100°C, **5** will react with a variety of alkynes to yield dimolybdenum products containing alkyne oligomers.



(3)

For several years, we have also been investigating the ability of sulphur-containing cluster complexes to undergo enlargement by the addition of small metal carbonyl fragments.[9] $Ru(CO)_5$ is known to lose a CO ligand upon mild heating and the $Ru(CO)_4$ fragments will combine to form clusters (e.g. $Ru_3(CO)_{12}$). We have used $Ru(CO)_5$ recently to assist in the preparation of a variety of new high nuclearity sulphido ruthenium carbonyl cluster complexes.[10,11] Thus, we have also investigated the potential of **1** to undergo cluster enlargement by reactions with $Ru(CO)_5$. Several new higher nuclearity molybdenum–ruthenium cluster complexes have been prepared. Two of these have been found to possess quadruply bridging carbonyl ligands and one of these provides the first example of a molecular complex to contain two quadruply bridging carbonyl ligands.[12] In the second part of this report the structures and properties of these higher nuclearity clusters is described.

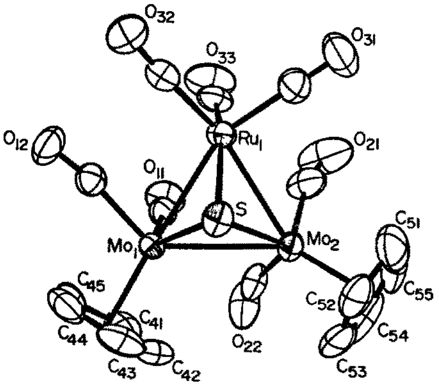


Fig. 1. An ORTEP diagram of $Mo_2Ru(CO)_7Cp_2(\mu_3\text{-}S)$ (**1**).

RESULTS AND DISCUSSION

1. *Reactions of* $Mo_2Ru(CO)_7Cp_2(\mu_3\text{-}S)$ (**1**) *with* HC_2Ph

Two products were isolated from the reaction of **1** with HC_2Ph at 98°C.[13] Both products were formed by the loss of five carbonyl ligands from **1** and the addition of three equivalents of HC_2Ph; thus, they are isomers, but they have significantly different structures as was determined from crystallographic studies. One has the molecular formula $Mo_2Ru(Co)_2Cp_2[\mu_3\text{-}\eta^6\text{-}HCC(Ph)C(H)C(Ph)C(H)C(Ph)](\mu_3\text{-}S)$ (**6**) and was obtained in 15% yield. An ORTEP drawing of its molecular structure is shown in Fig. 2. The molecule consists of a triangular cluster of metal atoms with a triply bridging sulphido ligand. The three alkyne molecules have been joined in a head-to-tail fashion by the formation of carbon–carbon bonds. This resulted in the formation of a 1,3,5-triphenyl-

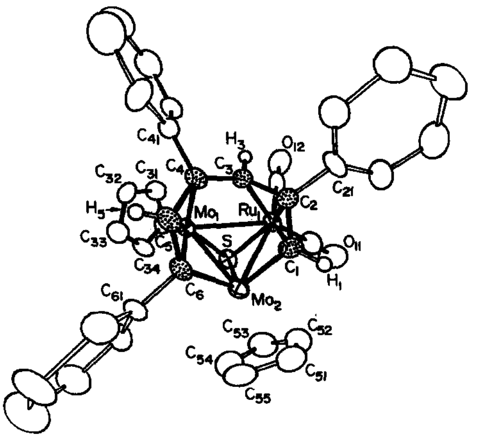


Fig. 2. An ORTEP diagram of $Mo_2Ru(CO)_2Cp_2[\mu_3\text{-}\eta^6\text{-}HCC(Ph)CHC(Ph)CHC(Ph)](\mu_3\text{-}S)$ (**6**).

dimetallahexatrienyl ligand that is coordinated across the face of the cluster that is opposite that of the sulphido ligand. Three of the carbon atoms are π-bonded to the ruthenium atom. The remaining three are π-bonded to one of the molybdenum atoms. The termini of the C_6-chain are σ-bonded to the second molybdenum atom. The C—C bond distances in the C_6-chain all lie in the range 1.42(1)–1.46(1) Å. This indicates that the C—C π-bonding is distributed fairly uniformly across the entire chain. The electron count about the metal atoms is 46, two less than that required by the Effective Atomic Number (EAN) rule. Interestingly, the Mo—Mo metal–metal bond is unusually short, 2.663(1) Å, and is similar to that of the Mo—Mo double bond found in the complex $Mo_2Cp_2[(MeO_2)C_2(CO_2Me)(HC_2H)\{(MeO_2C)C_2(CO_2Me)\}_2]$, 2.618(1) Å.[14] Thus, the shortness of the Mo—Mo bond in **6** could be due to a localization of the unsaturation. The Mo(1)—Ru and Mo(2)—Ru distances are significantly different, 3.031(1) vs 2.775(1) Å. The former is similar to the Mo—Ru distances found in **1**. The shortness of the Mo(2)—Ru bond could be due to bond contraction effects caused by the presence of the bridging carbon atom, C(1). Likewise, the shortness of the Mo—Mo bond in **6** could also be attributed in part to the bridging carbon atom C(6). It seemed reasonable to think that the formation of a carbon–carbon bond between the atoms C(1) and C(6) could be induced and would lead to 1,3,5-triphenylbenzene. This was successfully accomplished by the treatment of **6** with CO (at 100°C/25 atm). A 74% yield of triphenylbenzene was accompanied by the formation of an equivalent amount of **1**. Although this **1** could be converted back into **6** by reaction with HC_2Ph, the process is not catalytic because **6** is not formed from **1** and HC_2Ph under the conditions required for the triphenylbenzene elimination reaction.

The second product obtained from the reaction of **1** and HC_2Ph has the formula $Mo_2Ru(CO)_2Cp_2[\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH][\mu\text{-}\eta^3\text{-}PhCC(H)CPh](\mu_3\text{-}S)$ (**7**) 11%.[13] An ORTEP drawing of its structure is shown in Fig. 3. Compound **7** consists of a triangular cluster of metal atoms with a triply bridging sulphido ligand and two dimetallaallyl ligands. One of these, HCC(Ph)CH, serves as a triply bridging ligand that is π-bonded to the ruthenium atom and each end σ-bonded to a different molybdenum atom. The second dimetallaallyl ligand, PhCC(H)CPh, bridges the Mo—Mo edge of the cluster and is π-bonded to Mo(2) and σ-bonded to Mo(1). It appears that **7** could be formed from **6** simply by a cleavage of the C(3)—C(4) bond in the C_6-chain followed by minor reorganization of the coordination to the metal atoms. Interestingly, the C(3)—C(4) bond was the location of the C—C triple bond of one of the original HC_2Ph molecules. Indeed, when compound **6** was heated to 125°C for 3 h, it was converted to **7** in 57% yield, but in addition another isomer $Mo_2Ru(CO)_2Cp_2[\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH][\mu\text{-}\eta^3\text{-}PhCC(Ph)CH](\mu_3\text{-}S)$ (**8**) was also formed in 38% yield. The structure of **8** is described below. Compound **7** contains 48 valence electrons and is thus saturated according to the EAN rule. However, the Mo(1)—Mo(2) is nearly as short as that in **6**. In this case, the shortness must be due to bond contraction effects caused by the bridging atoms C(4) and C(6). It is believed that the removal of the electronic unsaturation about the Mo—Mo bond in **6** may be the driving force for cleavage of the carbon–carbon bond in the C_6-chain.

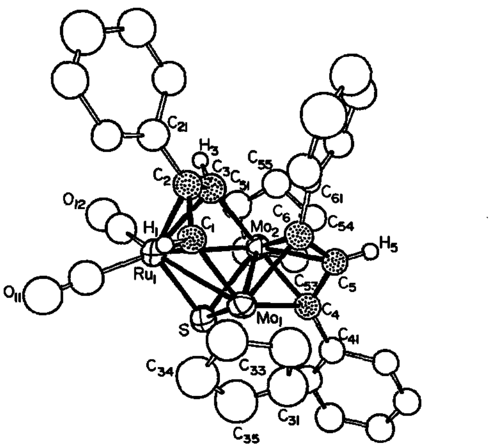


Fig. 3. An ORTEP diagram of $Mo_2Ru(CO)_2Cp_2[\mu\text{-}\eta^3\text{-}PhCC(H)C(Ph)][\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH](\mu_3\text{-}S)$ (**7**).

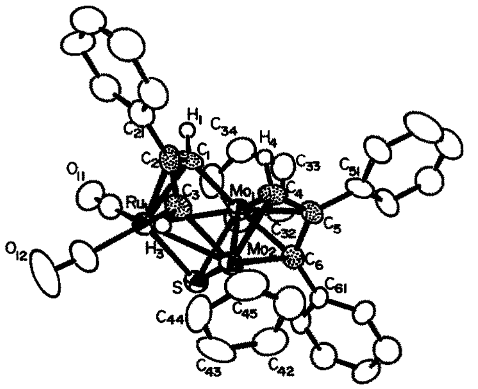


Fig. 4. An ORTEP diagram of $Mo_2Ru(CO)_2Cp_2[\mu\text{-}\eta^3\text{-}HCC(Ph)CPh][\mu_3\text{-}\eta^3\text{-}HCC(Ph)CH](\mu_3\text{-}S)$ (**8**).

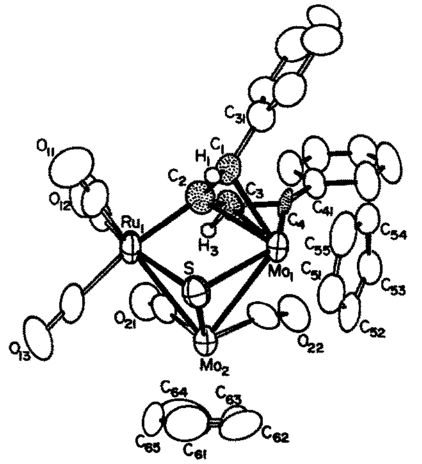
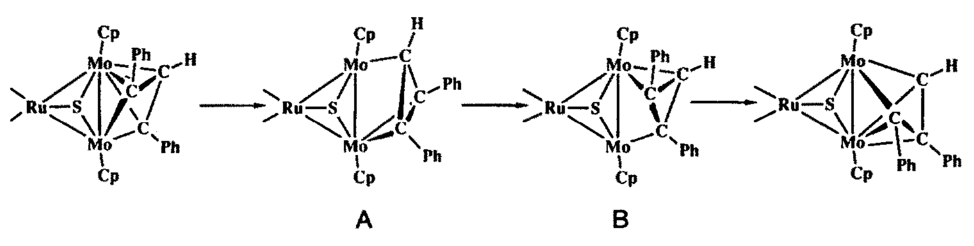


Fig. 5. An ORTEP diagram of $Mo_2Ru(CO)_5Cp_2[\mu\text{-}\eta^4\text{-}PhCC(H)CC(H)Ph](\mu_3\text{-}S)$ (**9**).

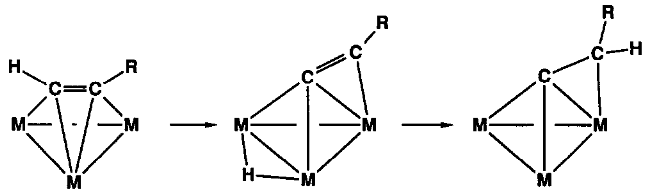
The molecular structure of **8** is shown in Fig. 4. The structure is analogous to that of **7** except that the phenyl groups of the edge bridging dimetallaallyl group are located on adjacent carbon atoms, HCC(Ph)C(Ph). It was found that **8** could be obtained in 24% yield by heating **7** to 125°C for 3 h. This remarkable isomerization is believed to occur by a 1,2 interchange of the C(5)—H(5) and C(6)—Ph groups of the edge bridging dimetallaallyl ligand in **7**. The mechanism is believed to involve the formation of a cyclopropenyl ligand by the formation of a carbon–carbon bond between the atoms C(4) and C(6) (see intermediate **A** in Scheme 1). This step links the two phenyl-substituted carbon atoms. After a 60° rotation of the cyclopropenyl ligand to **B**, a cleavage of the carbon–carbon bond between the CH and one CPh group will give **8**. A similar process was proposed by Chisholm to explain an interchange of carbon atoms in a dimetallaallyl ligand on a ditungsten centre.[15] In that case, the interchange was rapid on the NMR timescale. We have no evidence for the existence of 1,2-interchange processes involving the triply bridging HCC(Ph)CH, dimetallaallyl ligand. If the reason for this is due to a higher activation barrier, this could imply an important difference between the basic reactivity of the trinuclear metal site and the dinuclear metal site. Site-sensitivity such as this could have an analogy to the structure–function reactivity relationships that are believed to play an important role in the chemistry of small molecule transformations on metal surfaces.[16]

We have not been able to isolate any products from the reaction of **1** with HC_2Ph at 98°C that contain only one or two equivalents of HC_2Ph. Certainly, such species must have been traversed in the formation of **6**. In an effort to obtain such species, the reaction of **1** with HC_2Ph was performed at 25°C with an initiation by Me_3NO.[17] Under these conditions, a species formed by the addition of two HC_2Ph equivalents was obtained in 11% yield. Its formula $Mo_2Ru(CO)_5Cp_2[\mu\text{-}\eta^4\text{-}PhCC(H)CC(H)Ph](\mu_3\text{-}S)$ (**9**) was established by a crystallographic analysis and an ORTEP drawing of its molecular structure is shown in Fig. 5. This compound consists of an open cluster of three metal atoms. There are only two metal–metal bonds, Mo(1)—Mo(2) = 3.024(2) and Mo(2)—Ru = 3.015(2) Å. There is a PhCC(H)CC(H)Ph ligand that bridges the non-bonded pair of metal atoms Mo(1)···Ru. The four-carbon chain is π-bonded to Mo(1). Carbon C(2) is also bonded



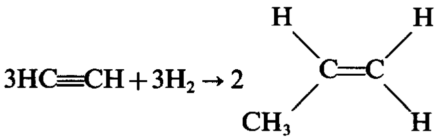
Scheme 1.

to Ru and serves as the bridge. The presence of the two substituents H and Ph on the carbon C(1) requires the occurrence of a substituent shift in the original HC_2Ph molecule. Most likely, this was a hydrogen shift since it has been shown previously that metal clusters can isomerize coordinated terminal alkynes to vinylidene ligands, eq. (4).[18] A coupling of the vinylidene carbon atom to the hydrogen-substituted end of an HC_2Ph molecule should lead directly to the ligand found in **9**. As one might expect, the reaction of **9** with additional HC_2Ph does not lead to **6**, **7** or **8**. Thus, **9** is believed not to be an intermediate in their formation.



(4)

Our studies have shown that **1** clearly exhibits a greater tendency to oligomerize HC_2Ph than **2**, but is probably less effective than **3**. We believe that the enhanced alkyne oligomerization reactivity of **1** can be attributed to the presence of the dimolybdenum centre in this cluster. However, as shown by the structure of **6**, all the metal atoms participate in the oligomerization process. To our knowledge, there have been no reports that **3** is capable of producing the splitting of alkyne trimers into C_3-groupings. Thus, the reactivity of **1** does have one feature that distinguishes it from **3**. It also seems reasonable to attribute this, at least in part, to the presence of the ruthenium atom since the ruthenium atom is bonded both to the C_6-chain in **6** and to one of the C_3-fragments in **7**. We have not yet obtained products derived from **7** or **8**, but the implications of the trimerization/splitting reaction are very intriguing. If one could incorporate it into a catalytic process, such as hydrogenation, it could provide the basis for the expansion of C_2 functionality to C_3 functionality, e.g. eq. (5).



$$3HC{\equiv}CH + 3H_2 \rightarrow 2\ (H)(CH_3)C{=}C(H)(H) \qquad (5)$$

2. *Reactions of* **1** *with* $Ru(CO)_5$

Two higher nuclearity clusters were obtained from the reaction of **1** with $Ru(CO)_5$, 80°C/1 h. These have been identified as $Mo_2Ru_4(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CO)Cp_2(\mu_4\text{-}S)$ (**10**), 23% yield and $Mo_2Ru_5(CO)_{14}(\mu_4\text{-}\eta^2\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ (**11**), 15% yield. These products are also obtained in very low yields from the synthesis of **1**.[12] Both products were characterized by crystallographic methods. An ORTEP diagram of **10** is shown in Fig. 6.[12] The molecule consists of a square pyramidal cluster of three ruthenium plus two molybdenum atoms. A molybdenum atom occupies the apical position of the pyramid and a quadruply bridging sulphido ligand spans the Ru_3Mo square base. An $Ru(CO)_3$ group bridges an Ru—Ru edge of the pyramid and there is a quadruply bridging CO ligand that lies in the Ru_3Mo fold. The carbon atom is bonded to an $MoRu_2$ triangular face of the pyramid and the oxygen atom is coordinated solely to the edge bridging $Ru(CO)_3$ group. Quadruply bridging carbonyl ligands generally exhibit elongated C—O bonds and reduced C—O stretching frequencies.[19] This is true for this ligand also, C—O = 1.262(8) Å, and $\nu(CO) = 1457\ cm^{-1}$.

An ORTEP drawing of **11** is shown in Fig. 7.[12] The structure of **11** is very similar to **10** except that it contains an additional $Ru(CO)_3$ group that bridges the second Ru—Ru basal edge of the square pyramidal cluster. Most interestingly, there is a quadruply bridging carbonyl ligand lying in this Ru_3Mo fold also. This molecule is the first one ever

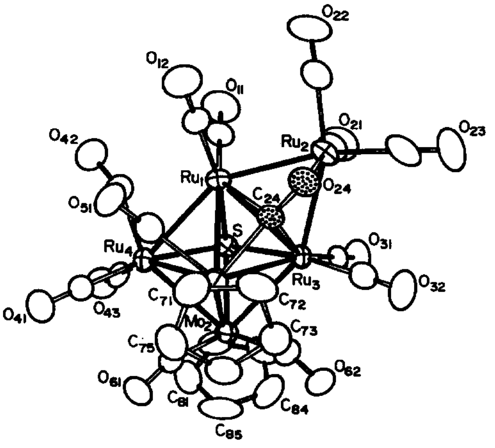


Fig. 6. An ORTEP diagram of $Mo_2Ru_4(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CO)Cp_2(\mu_4\text{-}S)$ (**10**).

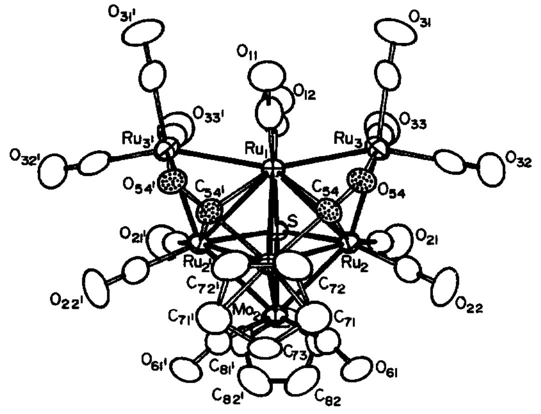


Fig. 7. An ORTEP diagram of $Mo_2Ru_5(CO)_{14}(\mu_4\text{-}\eta^2\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ (**11**).

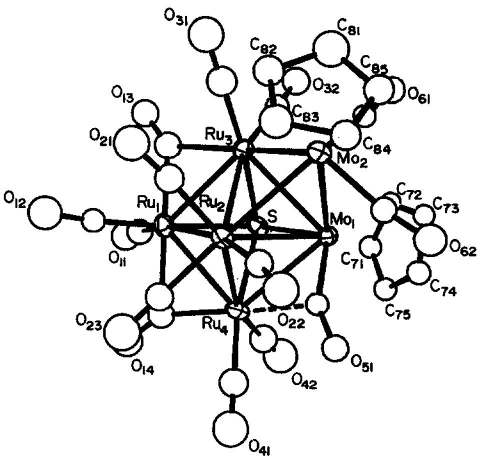
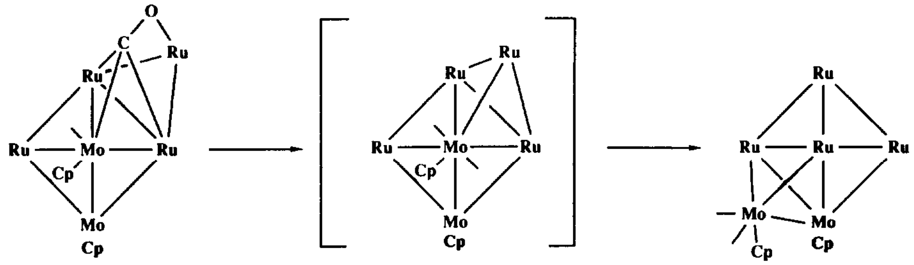


Fig. 8. An ORTEP diagram of $Mo_2Ru_4(CO)_{14}Cp_2(\mu_4\text{-}S)$ (**12**).

prepared that contains two quadruply bridging carbonyl ligands. These ligands are related by a molecular plane of symmetry that passes through the two molybdenum atoms, ruthenium Ru(1), and the sulphido ligand. The CO distance 1.25(1) Å is long, as expected. Most interestingly, however, the CO stretching vibration appears as two absorptions, 1419 and 1453 cm^{-1}, even though the ligands are equivalent. The splitting of the band can be attributed to vibrational coupling that yields symmetric and antisymmetric modes. In accord with the coupling theories that have been applied to CO ligands in mono- and dinuclear metal complexes, the higher frequency absorption should be assigned to the symmetrically coupled mode and the lower frequency to the antisymmetrically coupled mode.[20] The magnitude of the coupling, 34 cm^{-1}, indicates that the coupling is surprisingly large.

The mechanism of formation of **10** has not been established, but we have shown that **11** can be made from **10** in 47% yield by reaction with $Ru(CO)_5$, 80°C/3 h. A plausible mechanism for the formation of **11** would involve the interaction of an $Ru(CO)_4$ fragment with the oxygen atom of the terminally coordinated carbonyl ligand on Mo(1). Metal–oxygen interactions of this type have been structurally characterized for cases where the metal belongs to one of the early groups of the transition series.[18] CO elimination accompanied by metal–metal bond formation is a well-established process. A series of these should lead to **11** directly.

When **10** was refluxed in cyclohexane for 4 h, it was converted to the new compound $Mo_2Ru_4(CO)_{14}Cp_2(\mu_4\text{-}S)$ (**12**) in 46% yield. The molecular structure of **12** is shown in Fig. 8. According to its formula, **12** is an isomer of **10**, but it has a significantly different structure. First, it does not contain a quadruply bridging carbonyl ligand. Second, the cluster consists of a square pyramidal arrangement of four ruthenium and one molybdenum atoms. The sulphido ligand remains as a quadruple bridge across the base of the pyramid. Unlike **10**, a ruthenium atom occupies the apical position of the pyramid and one of the molybdenum atoms has been squeezed out of the main body of the cluster into a capping position on the Mo(1), Ru(2), Ru(3)



10

90 cluster valence electrons

88 cluster valence electrons

12

88 cluster valence electrons

Scheme 2. Isomerization process. All structures obey skeletal electron pair theory.

face. Compound **12** contains 88 electrons and thus obeys the SEP theory.[21] Compound **10**, which has 90 valence electrons, also obeys the SEP theory. The two-electron difference between the electron counts in **10** and **12** is due to the conversion of the four-electron donating quadruply bridging CO ligand in **10** to a two-electron donating ligand in**12**. As a consequence, the cluster must condense, when the quadruply bridging CO ligand is shifted to a terminal position and it does so by converting from an edge bridged cluster, **10**, to a face capped cluster **12**. It is noteworthy, however, that a shift of the edge bridging ruthenium group to the capping site does not yield **12** (see Scheme 2). This ruthenium capped species is a logical intermediate which evidently isomerizes to **12** by interchanging the sites of the capping ruthenium atom with the apical molybdenum atom in the pyramid. It seems premature to propose details for this rearrangement at this time.

Our studies of the reactivity of **1** toward HC_2Ph have revealed some unusual details of a trimerization and ligand splitting process that appears to distinguish it from the reactivity properties of either of the homonuclear metal components. It is believed that unique features of the reactivity of **1** can be attributed to its heteronuclear metal content.

The higher nuclearity clusters have provided at least one interesting ligand ensemble that could have implications for surface phenomena; namely, the existence of quadruply bridging carbonyl ligands that have their carbon atoms coordinated on adjacent trinuclear metal sites. Studies of these systems are continuing.

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REFERENCES

1. F. Richter, E. Roland and H. Vahrenkamp, *Chem. Ber.* 1984, **117**, 2429.
2. R. D. Adams, J. E. Babin and M. Tasi, *Organometallics* 1988, **7**, 219.
3. R. D. Adams, J. E. Babin, M. Tasi and T. Wolfe, *Organometallics* 1987, **6**, 2228.
4. 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.
5. 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.
6. A. M. Boileau, A. G. Orpen, R. F. D. Stansfield and P. Woodward, *J. Chem. Soc., Dalton Trans.* 1982, 187.
7. S. Slater and E. L. Muetterties, *Inorg. Chem.* 1981, **20**, 946.
8. J. S. Bradley, *J. Organomet. Chem.* 1978, **150**, C1.
9. R. D. Adams, *Polyhedron* 1985, **4**, 2003, and references therein.
10. R. D. Adams, J. E. Babin and M. Tasi, *Inorg. Chem.* 1987, **26**, 2807.
11. R. D. Adams, J. E. Babin and M. Tasi, *Organometallics* 1988, **7**, 503.
12. R. D. Adams, J. E. Babin and M. Tasi, *Angew. Chem., Int. Ed. Engl.* 1987, **26**, 685.
13. R. D. Adams, J. E. Babin and M. Tasi, *Organometallics* 1987, **6**, 2247.
14. S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter and P. Woodward, *J. Chem. Soc., Chem. Commun.* 1978, 221.
15. M. H. Chisholm, J. A. Heppert and J. C. Huffman, *J. Am. Chem. Soc.* 1984, **106**, 1151.
16. G. A. Somorjai, *Adv. Catal.* 1977, **26**, 1.
17. R. D. Adams, J. E. Babin and M. Tasi, *Organometallics* 1988, **7**, 755.
18. E. Roland and H. Vahrenkamp, *J. Molec. Catal.* 1983, **21**, 233.
19. C. P. Horwitz and D. F. Shriver, *Adv. Organomet. Chem.* 1984, **23**, 219.
20. F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.* 1962, **48**, 4432.
21. (a) D. M. P. Mingos, *Accts Chem. Res.* 1984, **17**, 311; (b) K. Wade, in *Transition Metal Clusters* (Edited by B. F. G. Johnson). John Wiley, New York (1980); (c) B. F. G. Johnson and R. E. Benfield, in *Topics in Stereochemistry* (Edited by G. L. Geoffroy), Vol. 12. John Wiley, New York (1981).