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# Reaction of sodium amalgam with ($\mu$-enyne)bis(dicarbonyl-$\eta^5$-cyclopentadienylmolybdenum(I)) and ($\mu$-$\eta^2$,$\eta^3$-allenyl)bis(dicarbonyl-$\eta^5$-cyclopentadienylmolybdenum) tetrafluoroborate complexes. Crystal structure of $[[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2\{\mu\text{-}HC{\equiv}CCH(CH_2CH_3)\}]_2]$

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**Abstract**

The behaviour of $\mu$-enyne complexes $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}CR)]$ $[Cp_2Mo_2(CO)_4 = [Mo(\eta^5\text{-}C_5H_5)(CO)_2]_2$; R = $C(CH_3){=}CH_2$ (1); R = $CH{=}CHCH_3$ (2); R = $C_6H_9$ (3)] and of the corresponding $\mu$-$\eta^2$,$\eta^3$-allenyl $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CR')][BF_4]$ [R' = $C(CH_3)_2$ (4); R' = $CHCH_2CH_3$ (5); R' = $C_6H_{10}$ (6)] towards Na/Hg has been studied and compared with that of the vinylacetylene and protonated vinylacetylene species $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}CCH{=}CH_2)]$ (11) and $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCHCH_3)][BF_4]$ (14), respectively. It appears that when the $C_\gamma$ carbon atom of the $\mu$-enyne bears a hydrogen atom (complexes 2 and 11), dimerization occurs leading to tetrametallic species $[[\{Cp_2Mo_2(CO)_4\}(\mu\text{-}HC{\equiv}CCH_2CHCH_3)]_2]$ (8) and $[[\{Cp_2Mo_2(CO)_4\}(\mu\text{-}HC{\equiv}CCH_2CH_2)]_2]$ (12). In the other cases, $\mu$-$\sigma$,$\eta^3$ allylic species such as $[Cp_2Mo_2(CO)_4\{\mu\text{-}\sigma,\eta^3\text{-}HC{\cdots}CH{\cdots}C(CH_3)_2\}]$ (7) are formed. Reaction of Na/Hg with most of the $\mu$-$\eta^2$,$\eta^3$ allenyl complexes regenerates the parent $\mu$-enyne compounds. When the "$C^+$" carbon atom bears a hydrogen atom, carbon–carbon coupling leading to a dimerization is favoured. The crystal structure of tetrametallic $[[\{Cp_2Mo_2(CO)_4\}\{\mu\text{-}HC{\equiv}CCH(CH_2CH_3)\}]_2]$ (10) obtained from 5 has been determined.

*Key words:* Molybdenum; Sodium; Tetrafluoroborate; Crystal structure; Alkyne; Enyne

## 1. Introduction

In recent years, there has been a growing interest in the study of the reactivity of enynes towards transition metal complexes [1–12]. For instance, such species containing substituted $\eta^3$-but-1-en-ynes have been suggested as key intermediates in alkyne dimerization/oligomerization processes [12].

Transformation of conjugated enynes has also attracted interest, in particular but-1-en-3-yne ($HC{\equiv}C{-}CH{=}CH_2$, vinylacetylene), which is one of the constituents of the "$C_4$" out of hydrocarbons.

In a previous paper [11] (see Scheme 1), we described the reactivity of the adduct $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}C{-}CH{=}CH_2)]$ (11), ($Cp_2Mo_2(CO)_4 = [Mo(\eta^5\text{-}C_5H_5)(CO)_2]_2$). Reduction of that adduct with sodium amalgam Na/Hg gives rise to two compounds: a dimer, 12, equivalent to octa-1,7-diyne whose two acetylenic bonds are complexed with $Cp_2Mo_2(CO)_4$ entities, and a $\mu$-$\sigma$,$\eta^3$ allylic species $[Cp_2Mo_2(CO)_4(\mu\text{-}\sigma,\eta^3\text{-}HC{\cdots}CH{\cdots}CHCH_3)]$ (13). Reduction of the protonated species $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}C{-}CHCH_3]^+$ (14) with sodium amalgam in toluene results in dimerization to $[[\{Cp_2Mo_2(CO)_4\}(\mu\text{-}HC{\equiv}CCHCH_3)]_2]$ (15) which is formed as a mixture of stereoisomers (the meso $R^*S^*$ and a racemic mixture $SS$ and $RR$). When the reaction

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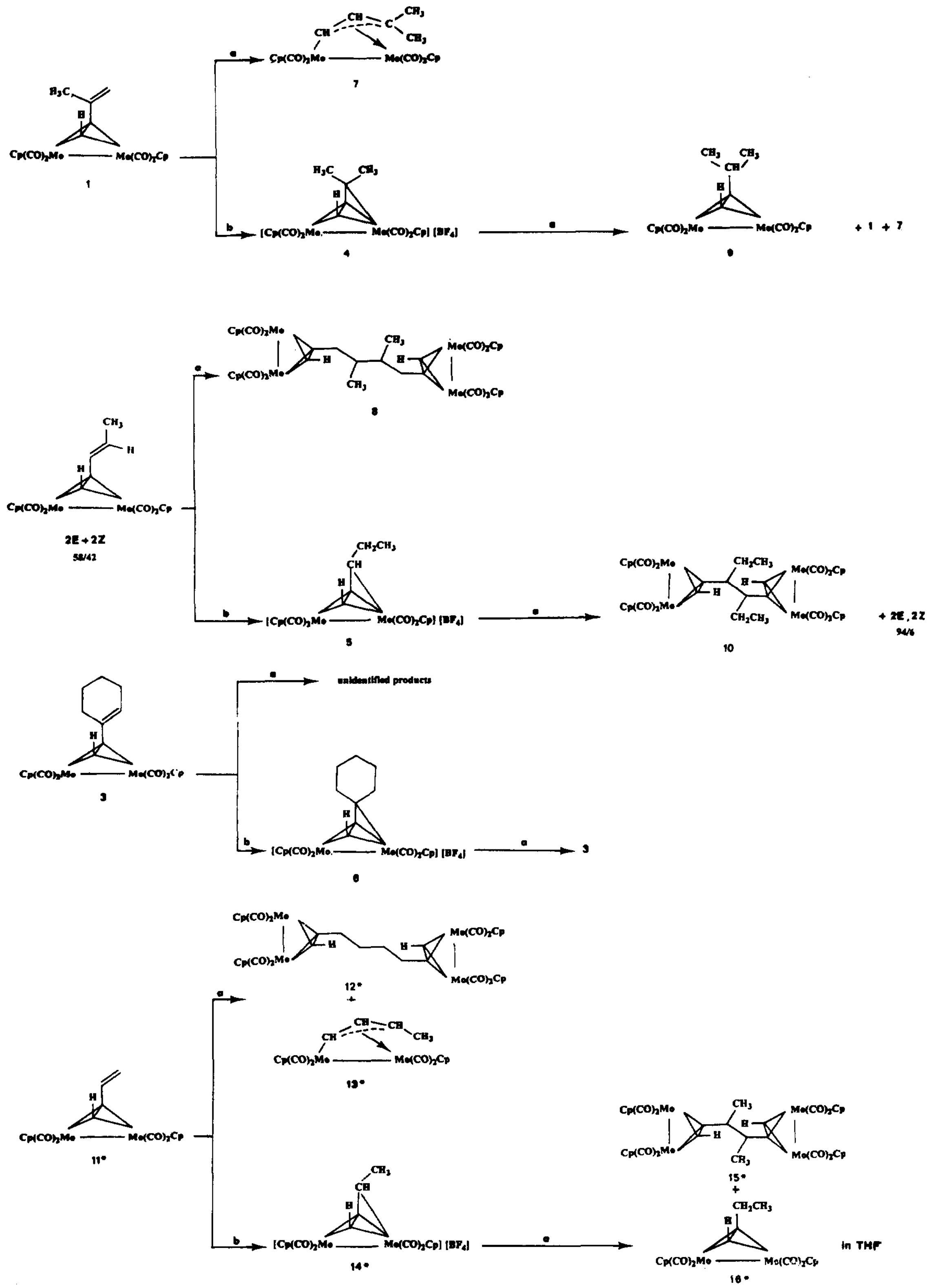


Scheme 1. (a) Na/Hg; (b) $HBF_4$, $Et_2O$. * Products previously described in ref. 11.

was performed in THF, a second compound, **16**, in which the carbon chain is the 1-butyne bridged between two molybdenum atoms was formed.

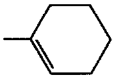
Other workers, using different methods, have synthesized ionic compounds of the same type: $[Cp_2Mo_2(CO)_4\{\mu\text{-}HC{\equiv}C\text{-}C(CH_3)_2\}][BF_4]$ [13], $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}C\text{-}CH_2)][BF_4]$ [14] and $[Cp'_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}C\text{-}CH_2)][BF_4]$ ($Cp' = C_5H_4CH_3$) [15]. This last product dimerizes in the presence of sodium amalgam.

In this paper, we describe the influence of different substituents on the reaction pathway; we compare the behaviour of various ($\mu$-enyne) complexes and of their protonated derivatives with that of $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}C\text{-}CH{=}CH_2)]$ and of $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}C\text{-}CHCH_3)][BF_4]$ towards sodium amalgam.

## 2. Results and discussion

The reactions described in this paper are represented in Scheme 1. The action of an excess of alkyne ($HC{\equiv}CC(CH_3){=}CH_2$, 2-methyl-but-1-en-yne; $HC{\equiv}C\text{-}CH{=}CHCH_3$, pent-2-en-4-yne and $HC{\equiv}C\text{-}C_6H_9$, 1-ethynylcyclohexene) with $[Cp_2Mo_2(CO)_4]$ in toluene solutions gives rise to the classical formation of a 1:1 adduct: $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}C\text{-}R)]$

[$R = C(CH_3){=}CH_2$ (**1**); $R = CH{=}CHCH_3$ (**2**);

R =  (**3**)]

containing the pseudotetrahedral core $Mo_2C_2$. In fact, complex **2** is obtained as a mixture of the ($2E$) and ($2Z$) isomers in a 58:42 ratio. ($E$) and ($Z$) isomers of the pure alkyne were also obtained in comparable amounts.

### 2.1. Reactivity of complexes 1, 2 and 3 towards $HBF_4$

In solution in diethyl ether, complexes **1**, **2** and **3** react with $HBF_4$ to give the orange ionic compounds $[Cp_2Mo_2(CO)_4\{\mu\text{-}HC{\equiv}CC(CH_3)_2\}][BF_4]$ (**4**), $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}CCHCH_2CH_3)][BF_4]$ (**5**) and $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}C\text{-}C_6H_{10})][BF_4]$ (**6**), respectively, corresponding to an electrophilic addition of proton following the Markovnikov rule. Compound **4** was obtained previously by reaction of $HBF_4 \cdot Et_2O$ with the $\sigma,\eta^2$(4e)-allenilydene complex $[Cp_2Mo_2(CO)_4(\sigma,\eta^2\text{-}C{=}C{=}C(CH_3)_2]$ [13].

A recent paper describing the crystal and molecular structures of the ($\mu$-$\eta^2$,$\eta^3$-propargyl)bis(dicarbonyl-$\eta^5$-cyclopentadienylmolybdenum) tetrafluoroborate $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH_2)][BF_4]$ and of the ($\mu$-$\eta^2$,$\eta^3$-1,1-dimethylpropargyl)bis(dicarbonyl-$\eta^5$-cyclopentadienyl-molybdenum) tetrafluoroborate $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CC(CH_3)_2\}][BF_4]$ shows different Mo–$C^+$ bond lengths which, according to the authors, accounts for different stability and fluxional behaviour of these compounds in solution [14]. At the same time, we described the structure of the derivative of vinylacetylene $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCH\text{-}CH_3)][BF_4]$ (**14**) [11]. Although no energy calculations have been performed with our complex, it shows the same fluxionality as the previous products. The $^1H$ NMR spectrum contains unresolved peaks at room temperature, but it is noticeable that at 213 K, there are two "Cp" resonances and that the signal of the proton borne by the "$C^+$" atom produces a well resolved quartet. The crystal structure of our product confirms that the number of alkyl groups at the carbocationic centre influences the molecular geometry and, in particular, the $C^+$–M distance. The Mo(1)–$C^+$ bond lengths (Mo(1) is the molybdenum atom to which three carbon atoms are bonded) are 2.439(6) Å with $C^+H_2$, 2.613(5) Å with $C^+H(CH_3)$ and 2.75(1) Å with $C^+(CH_3)_2$.

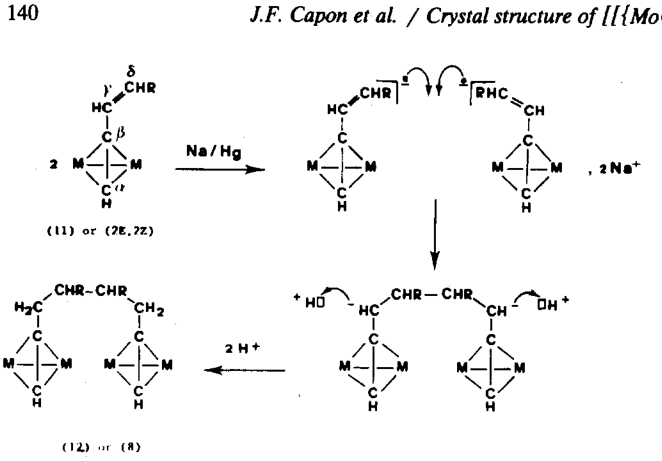
The Mo–Mo distances decrease slightly with the number of alkyl substituents: ($-CH_2$, 3.021(1) Å; $-CH(CH_3)$, 3.007 Å; $-C(CH_3)_2$, 2.982(2) Å). Among the molybdenum "acetylenic" carbon distances, only the Mo(1)–C(H)≡ bond length shows appreciable variations (2.216(5) Å with $-CH_2$, 2.16(1) Å with $-C(CH_3)_2$ but only 2.126(7) Å with $-CH(CH_3)$). In the three compounds, the carbon–carbon bond lengths suggest an important electronic delocalization over the bridging organic ligand.

An unexpected reaction occurs with the alkylating agent $CF_3SO_3CH_3$ in the presence of complex **1**. A compound analogous to **4** but containing the $CF_3SO_3^-$ anion was formed instead of the expected "$\mu\text{-}HC{\equiv}C(CH_3)CH_2CH_3^+$" cationic complex. It is possible that traces of moisture in the reaction media transform the sulfonic ester into the acid $CF_3SO_3H$ before it can react with the organic ligand. The same behaviour has been observed by us with $[Cp_2Mo_2(CO)_4(\mu\text{-vinylacetylene})]$ [16].

On the other hand, alkylation of the cationic compound **4** occurs classically in the presence of $LiCH_3$ leading to the t-butyl-substituted $\mu$-alkyne complex $[Cp_2Mo_2(CO)_4\{\mu\text{-}HC{\equiv}CC(CH_3)_3\}]$ (**17**).

### 2.2. Reaction of the $\mu$-enyne complexes 1, 2 and 3 with Na/Hg

Although no experiments relating to mechanistic questions could be performed, the results obtained here are consistent with the hypothesis proposed in a previous paper concerning the reactivity of complexed



Scheme 2. R = H **11** and **12**; R = $CH_3$ (**2***E*), (**2***Z*) and **8**.

vinylacetylene [11]. It seems obvious that the degree of substitution on the $C_\gamma$ carbon atom of the $\mu$-enyne ligands plays an important role in determining the pathway reaction. We note that when the $C_\gamma$ atom is substituted by a methyl group (complex **1**) or included in a cycle (complex **3**) dimerization does not occur, while complex **2**, in which the $C_\gamma$ atom bears a hydrogen atom, behaves similarly to complex **11** towards carbon–carbon coupling following a radical mechanism (Scheme 2).

Our previous proposition for producing the $\mu$-$\sigma$,$\eta^3$ allylic species **13**, one- or two-electron reduction, may also be proposed for the formation of **7**. It seems that in this case the degree of substitution on the $C_\gamma$ atom should not influence the reaction pathway because these mechanisms do not involve changes on that carbon atom [11]. Unfortunately, even if compound **7** is obtained by reduction of **1**, the low yields of the products do not allow us to characterize $\mu$-$\sigma$,$\eta^3$ allylic species derived from **2** and **3**. Thus it is difficult to confirm the validity of these last mechanisms.

### *2.3. Reaction of $\mu$-$\eta^2$,$\eta^3$-allenyl complexes 4, 5 and 6 with Na / Hg*

Similarly, the environment of the "$C^+$" carbon atom must be considered. Reactions of $\mu$-$\eta^2$,$\eta^3$ allenyl complexes with sodium amalgam suggest that carbon–carbon coupling leading to a dimerization (complexes **10** and **15**) is also favoured when that "$C^+$" atom bears a hydrogen atom, while complex **4**, for instance, in which two geminal methyl groups exist and complex **6** in which the "$C^+$" atom is contained in a cycle do not give rise to such a coupling reaction. Dimerization has been observed also previously with $[Cp'_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC\equiv CCH_2)][BF_4]$ ($Cp' = C_5H_4CH_3$) under the same experimental conditions [15].

Whereas in the case of complex **15**, three configurations were envisaged because of the presence of two sets of signals in the NMR spectra (a *meso* compound $R^*S^*$ which gave one NMR spectrum and a racemic mixture *SS* and *RR* providing the second spectrum) [11], only one set of signals is observed with complex **10**. It was therefore decided to determine the structure of **10** by X-ray diffraction. The result is shown in Fig. 1.

The structure confirms the presence of the 3,4-diethyl-hexa-1,5-diyne ligand in which the two acetylenic bonds are complexed by two $[Cp_2Mo_2(CO)_4]$ groups. The molecule is symmetrical and possesses two centres of chirality joined by the C(33)–C(34) bond. However,

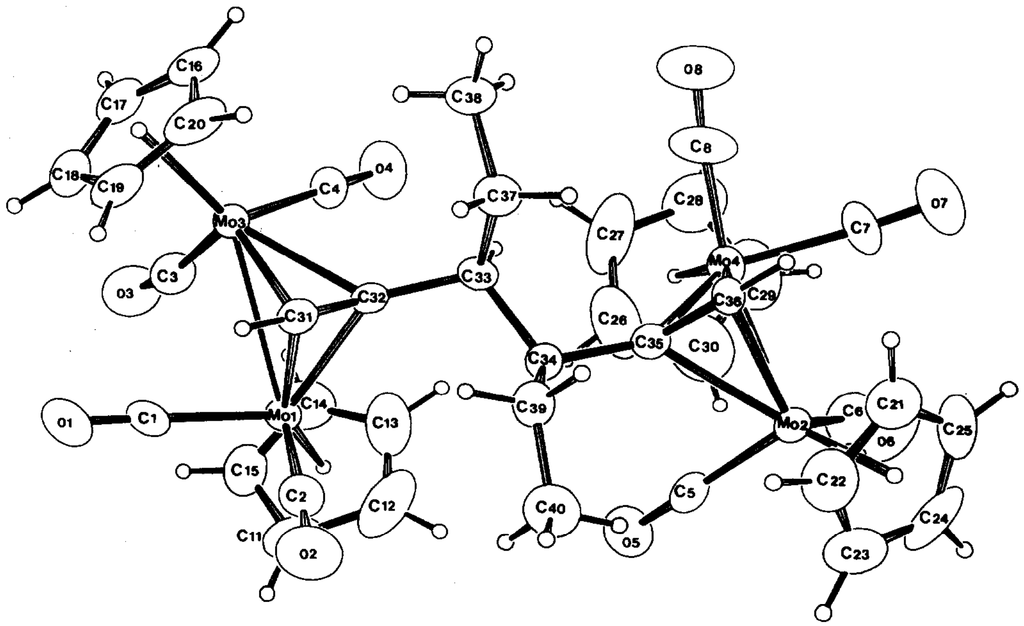


Fig. 1. ORTEP drawing of $[[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2\{\mu\text{-}HC\equiv CCH(CH_2CH_3)\}]_2]$ (**10**).

TABLE 1. Selected bond lengths (Å) and bond angles (°) for **10** [a]

| | | | |
|---|---|---|---|
| Mo(1)–Cp(1) | 2.008 | Mo(2)–Cp(2) | 2.033 |
| Mo(3)–Cp(3) | 2.034 | Mo(4)–Cp(4) | 2.000 |
| Mo(1)–Mo(3) | 2.9512(7) | Mo(2)–Mo(4) | 2.9482(7) |
| Mo(1)–C(1) | 1.971(7) | Mo(2)–C(5) | 1.927(7) |
| Mo(1)–C(2) | 1.936(7) | Mo(2)–C(6) | 1.949(8) |
| Mo(3)–C(3) | 1.942(7) | Mo(4)–C(7) | 1.977(8) |
| Mo(3)–C(4) | 1.937(7) | Mo(4)–C(8) | 1.969(9) |
| C(1)–O(1) | 1.150(9) | C(5)–O(5) | 1.167(9) |
| C(2)–O(2) | 1.179(9) | C(6)–O(6) | 1.153(9) |
| C(3)–O(3) | 1.16(1) | C(7)–O(7) | 1.15(1) |
| C(4)–O(4) | 1.141(9) | C(8)–O(8) | 1.14(1) |
| Mo(1)–C(31) | 2.193(6) | Mo(2)–C(36) | 2.127(6) |
| Mo(1)–C(32) | 2.239(6) | Mo(2)–C(35) | 2.269(6) |
| Mo(3)–C(31) | 2.143(6) | Mo(4)–C(36) | 2.189(6) |
| Mo(3)–C(32) | 2.267(6) | Mo(4)–C(35) | 2.224(6) |
| C(31)–C(32) | 1.336(8) | C(36)–C(35) | 1.337(9) |
| C(32)–C(33) | 1.531(9) | C(35)–C(34) | 1.518(9) |
| C(33)–C(37) | 1.542(9) | C(34)–C(39) | 1.547(8) |
| C(37)–C(38) | 1.52(1) | C(39)–C(40) | 1.51(1) |
| C(33)–C(34) | 1.558(9) | | |
| Mo(1)–C(1)–O(1) | 178.0(7) | C(31)–C(32)–C(33) | 135.1(5) |
| Mo(1)–C(2)–O(2) | 175.6(7) | C(32)–C(33)–C(37) | 110.7(5) |
| Mo(3)–C(3)–O(3) | 169.1(6) | C(33)–C(37)–C(38) | 114.9(6) |
| Mo(3)–C(4)–O(4) | 179.0(6) | C(32)–C(33)–C(34) | 112.1(4) |
| Mo(2)–C(5)–O(5) | 178.7(6) | C(33)–C(34)–C(39) | 111.5(5) |
| Mo(2)–C(6)–O(6) | 168.9(6) | C(34)–C(39)–C(40) | 114.6(6) |
| Mo(4)–C(7)–O(7) | 176.4(7) | C(33)–C(34)–C(35) | 112.2(4) |
| Mo(4)–C(8)–O(8) | 173.5(8) | C(34)–C(35)–C(36) | 136.8(5) |

[a] Cp denotes the centroids of the $C_5$ rings. Numbers in parentheses are estimated standard deviations.

in the solid state, the symmetry is not perfect. There is only a "pseudo" twofold axis passing through the middle of the C(33)–C(34) bond, nearly perpendicular to the plane of the drawing. The molecule shown in Fig. 1 corresponds to the *SS* chirality and because of the centrosymmetric nature of the space group, a racemic *RR* and *SS* mixture is obtained.

The C(3)O(3) and C(6)O(6) ligands are semi-bridging (Mo(1)–C(3) = 2.930 Å and Mo(4)–C(6) = 2.870 Å). A consequence of this interaction is the angles 169.1° and 168.9° of the Mo(3)–C(3)–O(3) and Mo(2)–C(6)–O(6), respectively. The other Mo...C "interactions" are longer than 3.12 Å, and the non-linearity of some Mo–C–O fragments (i.e. Mo(1)–C(2)–O(2) = 175.6(7)° and Mo(4)–C(8)–O(8) = 173.5(8)°) seems due to the lattice or to steric hindrances. The distances Mo(3)...C(2) and Mo(2)...C(8) are nearly 4.3 Å. The values for the C(31)–C(32) and C(35)–C(36) bond lengths and the C(31)–C(32)–C(33) and C(34)–C(35)–C(36) angles correspond to those found usually in $[Cp_2Mo_2(CO)_4(\mu\text{-}RC{\equiv}CR')]$ entities [17]. The other bond lengths and angles values for the carbon chain are as expected for saturated carbon atoms.

Selected bond lengths and angles are given in Table 1, and final fractional coordinates in Table 2.

If we except complex **14**, the reaction of the $\mu$-$\eta^2,\eta^3$ allenyl cationic compounds with Na/Hg leads exclusively or partially to the initial $\mu$-enyne complexes **1**, $(2E)+(2Z)$ in the ratio 96:4, and **3**.

Complex **7** which was also obtained directly by action of Na/Hg on **1** is formed here from the cationic **4**, but in this case the proposed mechanism, although also including radical species is slightly different from that suggested for the formation of that same compound **7** from **1** (Scheme 3).

## 3. Experimental details

All the reactions and purifications were performed under dinitrogen using Schlenk techniques. The solvents were freshly distilled under dinitrogen from drying agents as follows: sodium/benzophenone for THF and toluene; $CaH_2$ for dichloromethane, hexane and diethyl ether. The deuterated solvents were dried over activated molecular sieves prior to use.

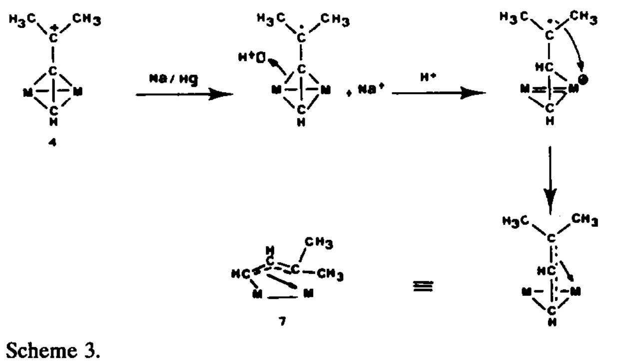
Infrared spectra were obtained with a Perkin-Elmer 1430 spectrometer, using solutions in $CH_2Cl_2$ or KBr pellets. Infrared frequencies are reported in wavenumber units ($cm^{-1}$). Intensities were given as: vs, very strong; s, strong; w, weak; vw, very weak.

$^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AC 300 ($^1H$, 300.13 MHz; $^{13}C$, 75.47 MHz) instrument. Chemical shifts are reported as $\delta$ in units of parts per million (ppm) relative to an internal reference of tetramethylsilane (TMS). Coupling constants are reported in hertz (Hz). The following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; h, heptet; m, multiplet.

Mass spectra were obtained from a HP 5695C GC/MS apparatus. The $m/e$ values were based on the $^{96}Mo$ isotope.

Analyses were performed at the Service Central d'Analyses of the CNRS.

$[Cp_2Mo_2(CO)_4]$ was obtained by a published method [18]. The alkynes, pent-2-en-4-yne ($HC{\equiv}CCH{=}CHCH_3$),




Scheme 3.

TABLE 2. Positional parameters and their estimated standard deviations

| Atom | x | y | z | B (Å²) |
|---|---|---|---|---|
| Mo(1) | 0.11499(5) | 0.31573(3) | 0.34767(2) | 2.22(1) |
| Mo(2) | 0.32310(5) | 0.30850(4) | 0.08320(2) | 2.26(1) |
| Mo(3) | −0.12392(5) | 0.42791(3) | 0.32337(2) | 2.06(1) |
| Mo(4) | 0.03960(5) | 0.28370(4) | 0.06310(3) | 2.73(1) |
| O(1) | 0.1033(6) | 0.4044(5) | 0.4661(3) | 5.8(2) |
| O(2) | 0.3878(5) | 0.4078(5) | 0.3736(3) | 5.6(2) |
| O(3) | −0.1854(6) | 0.2620(4) | 0.3958(3) | 5.6(1) |
| O(4) | −0.2408(5) | 0.3069(4) | 0.2198(3) | 4.9(1) |
| O(5) | 0.3453(6) | 0.1839(4) | 0.1903(3) | 4.9(1) |
| O(6) | 0.2566(7) | 0.1332(4) | 0.0090(3) | 6.9(2) |
| O(7) | 0.0588(7) | 0.3294(6) | −0.0632(3) | 7.2(2) |
| O(8) | −0.1534(7) | 0.4478(5) | 0.0371(4) | 8.2(2) |
| C(1) | 0.1069(7) | 0.3732(5) | 0.4219(3) | 3.4(1) |
| C(2) | 0.2834(7) | 0.3749(5) | 0.3617(3) | 3.5(2) |
| C(3) | −0.1511(7) | 0.3197(5) | 0.3680(3) | 3.4(2) |
| C(4) | −0.1975(6) | 0.3525(5) | 0.2579(3) | 2.9(1) |
| C(5) | 0.3381(6) | 0.2304(5) | 0.1497(3) | 3.3(1) |
| C(6) | 0.2683(8) | 0.1988(5) | 0.0371(4) | 4.2(2) |
| C(7) | 0.0561(8) | 0.3132(6) | −0.0163(3) | 4.4(2) |
| C(8) | −0.0792(8) | 0.3903(7) | 0.0496(4) | 5.5(2) |
| C(11) | 0.2187(8) | 0.1778(5) | 0.3756(4) | 4.6(2) |
| C(12) | 0.2109(9) | 0.1878(5) | 0.3137(4) | 6.2(2) |
| C(13) | 0.084(1) | 0.1843(5) | 0.2886(4) | 5.4(2) |
| C(14) | 0.0075(9) | 0.1704(5) | 0.3296(4) | 4.8(2) |
| C(15) | 0.0890(8) | 0.1689(5) | 0.3827(3) | 4.0(2) |
| C(16) | −0.2769(7) | 0.5468(5) | 0.3048(4) | 3.6(2) |
| C(17) | −0.3011(7) | 0.4966(5) | 0.3514(4) | 3.7(2) |
| C(18) | −0.1941(7) | 0.5121(5) | 0.3979(3) | 3.7(2) |
| C(19) | −0.1073(7) | 0.5679(5) | 0.3770(4) | 3.7(2) |
| C(20) | −0.1548(7) | 0.5905(5) | 0.3202(4) | 4.2(2) |
| C(21) | 0.4079(7) | 0.4394(5) | 0.0435(4) | 4.2(2) |
| C(22) | 0.4842(7) | 0.4246(6) | 0.0961(4) | 4.5(2) |
| C(23) | 0.5433(7) | 0.3402(7) | 0.0949(4) | 5.4(2) |
| C(24) | 0.5063(7) | 0.3020(6) | 0.0409(4) | 5.5(2) |
| C(25) | 0.4203(8) | 0.3651(7) | 0.0091(4) | 5.1(2) |
| C(26) | 0.0037(9) | 0.1692(6) | 0.1279(4) | 6.1(2) |
| C(27) | −0.1127(8) | 0.2103(7) | 0.1063(4) | 6.8(2) |
| C(28) | −0.1416(8) | 0.1924(7) | 0.0470(5) | 6.0(2) |
| C(29) | −0.038(1) | 0.1382(6) | 0.0325(4) | 6.2(2) |
| C(30) | 0.048(1) | 0.1242(6) | 0.0847(5) | 6.5(3) |
| C(31) | 0.0723(6) | 0.4574(4) | 0.3165(3) | 2.3(1) |
| C(32) | 0.0321(5) | 0.4023(4) | 0.2714(3) | 2.0(1) |
| C(33) | 0.0398(6) | 0.4052(4) | 0.2079(3) | 2.2(1) |
| C(34) | 0.1748(5) | 0.3737(4) | 0.1972(3) | 2.1(1) |
| C(35) | 0.1728(5) | 0.3533(4) | 0.1345(3) | 2.1(1) |
| C(36) | 0.1687(6) | 0.4023(4) | 0.0865(3) | 2.3(1) |
| C(37) | 0.0035(7) | 0.5022(5) | 0.1826(3) | 3.5(1) |
| C(38) | −0.1412(8) | 0.5222(6) | 0.1684(4) | 5.3(2) |
| C(39) | 0.2815(6) | 0.4451(5) | 0.2207(3) | 2.9(1) |
| C(40) | 0.4156(7) | 0.4042(7) | 0.2394(4) | 5.0(2) |
| H(1) | 0.2939 | 0.1792 | 0.4055 | 5.7 * |
| H(2) | 0.2771 | 0.1934 | 0.2930 | 6.9 * |
| H(3) | 0.0479 | 0.1886 | 0.2476 | 6.7 * |
| H(4) | −0.0857 | 0.1638 | 0.3230 | 5.4 * |
| H(5) | 0.0609 | 0.1627 | 0.4187 | 5.0 * |
| H(6) | −0.3357 | 0.5490 | 0.2688 | 4.4 * |
| H(7) | −0.3762 | 0.4585 | 0.3527 | 4.7 * |
| H(8) | −0.1873 | 0.4889 | 0.4363 | 4.6 * |
| H(9) | −0.0257 | 0.5894 | 0.3990 | 4.8 * |
| H(10) | −0.1123 | 0.6282 | 0.2953 | 4.9 * |

TABLE 2. (continued)

| Atom | x | y | z | B (Å²) |
|---|---|---|---|---|
| H(11) | 0.3516 | 0.4920 | 0.0331 | 5.2 * |
| H(12) | 0.4915 | 0.4661 | 0.1288 | 5.2 * |
| H(13) | 0.6016 | 0.3125 | 0.1260 | 6.6 * |
| H(14) | 0.5310 | 0.2439 | 0.0274 | 6.3 * |
| H(15) | 0.3799 | 0.3581 | −0.0301 | 6.2 * |
| H(16) | 0.0426 | 0.1704 | 0.1679 | 7.3 * |
| H(17) | −0.1665 | 0.2445 | 0.1278 | 7.7 * |
| H(18) | −0.2180 | 0.2173 | 0.0203 | 6.6 * |
| H(19) | −0.0318 | 0.1177 | −0.0055 | 6.6 * |
| H(20) | 0.1273 | 0.0892 | 0.0898 | 7.7 * |
| H(21) | 0.0989 | 0.4972 | 0.3491 | 3.0 * |
| H(22) | −0.0239 | 0.3625 | 0.1882 | 2.7 * |
| H(23) | 0.1933 | 0.3167 | 0.2181 | 2.7 * |
| H(24) | 0.1649 | 0.4367 | 0.0514 | 3.2 * |
| H(25) | 0.0366 | 0.5078 | 0.1479 | 4.4 * |
| H(26) | 0.0450 | 0.5470 | 0.2091 | 4.4 * |
| H(30) | 0.2586 | 0.4774 | 0.2528 | 3.7 * |
| H(31) | 0.2848 | 0.4909 | 0.1914 | 3.7 * |
| H(32) | 0.4788 | 0.4499 | 0.2530 | 6.4 * |
| H(33) | 0.4153 | 0.3591 | 0.2690 | 6.4 * |
| H(34) | 0.4415 | 0.3727 | 0.2076 | 6.4 * |
| H(27) | −0.1570 | 0.5826 | 0.1536 | 6.0 * |
| H(28) | −0.1842 | 0.4781 | 0.1419 | 6.0 * |
| H(29) | −0.1759 | 0.5174 | 0.2031 | 6.0 * |

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

1-ethynylcyclohexene ($HC{\equiv}C{-}C_6H_9$) were prepared from (±)4-pentyn-2-ol and 1-ethynylcyclohexanol, respectively, by published procedures [19]; 2-methylbut-1-en-3-yne ($HC{\equiv}CC(CH_3){=}CH_2$) was a commercial product from Aldrich.

### 3.1. *Synthesis of $[Cp_2Mo_2(CO)_4\{\mu\text{-}HC{\equiv}CC(CH_3){=}CH_2\}]$ (1)*

2-Methylbut-1-en-3-yne (3 ml, 31.2 mmol) was added dropwise to a cold solution (−40°C) of $[Cp_2Mo_2(CO)_4]$ (6 g, 13.8 mmol) in toluene (200 ml). The mixture was allowed to reach room temperature and stirred for 18 h. The solution turned from brown to deep red. The solvent was evaporated *in vacuo*, and complex **1** was extracted with 150-ml portions of hexane. Removal of solvent from the combined hexane solutions yielded dark red crystals (yield 70%).

This product had been obtained previously by Green *et al.* from $[Cp_2Mo_2(CO)_4\{\sigma,\eta^2\text{-}C{=}C{=}C(CH_3)_2\}]$ [13], and also in small amounts in the reaction of protonation of the product from $LiC{\equiv}CC(CH_3){=}CH_2$ and $[Cp_2Mo_2(CO)_4]$ [20]. $^1H$ NMR data ($CDCl_3$ solution) were indicated in these papers.

$^1H$ NMR data ($C_6D_6$ solution): 5.29 (s, ≡CH); 5.01 (qd, 1H of $=CH_2$); 4.88 (qd, 1H of $=CH_2$); 4.86 (s, $C_5H_5$); 1.76 (dd, $CH_3$). $^{13}C\{^1H\}$ NMR ($C_6D_6$ solution):

232.3 (s, CO); 229.4 (s, CO); 148.3 (s, $=C(CH_3)$); 113.8 (tq, $=CH_2$, $^1J$(C–H) = 145.4, $^3J$(C–H) = 5.4); 91.5 ($C_5H_5$); 82.2 (d, ≡CH, $^1J$(C–H) = 208.9); 64.5 (s, ≡C); 26.2 (qdd, $-CH_3$, $^1J$(C–H) = 131.2). Infrared (KBr): $\nu$(C≡O) 1970 s, 1910s, 1820s.

*3.2. Synthesis of $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}CCH{=}CH\text{-}CH_3)]$ (2E) + (2Z)*

An excess of pent-2-en-4-yne (1.8 g, 27.2 mmol) diluted in a cold solution (−60°C) in toluene (50 ml) was transferred to a cold solution (−60°C) in toluene (150 ml) of $[Cp_2Mo_2(CO)_4]$ (3 g, 6.3 mmol). The mixture was allowed to reach room temperature and stirred for 12 h. The solution turned from brown to deep red. The solvent was evaporated *in vacuo*, and complex **2** was extracted with 100-ml portions of pentane. Removal of solvent from the combined pentane solutions yielded 2.83 g of complex **2** (yield 82%). A mixture of the (2*E*) and (2*Z*) isomers was formed in the ratio 58:42.

An alternative to purify complex **2** consisted of chromatography (silica gel column, elution with dichloromethane/hexane (2:1 by vol.)) of the crude solid obtained after evaporation of toluene. Comparable results were obtained when THF was used as solvent.

Complex **2**. Anal. Found: C, 45.47; H, 2.92. $C_{19}H_{16}Mo_2O_4$ calcd.: C, 45.62; H, 3.12%. Infrared ($CH_2Cl_2$ solution): $\nu$(C≡O) 2000s, 1930vs, 1850s.

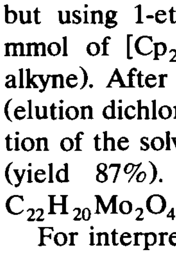
*Labelling of the protons in the organic ligand, $H_cC{\equiv}CCH_b{=}CH_aCH_3$.* Complex (2*E*): $^1$H NMR data ($C_6D_6$ solution): 6.35 (m, H*b*, $^3J(H_a\text{–}H_b)$ = 14.7); 5.66 (dq, H*a*, $^3J(H_a\text{–}CH_3)$) = 6.6, $^3J(H_a\text{–}H_b)$ = 14.7); 5.21 (d, H*c*, $^4J(H_c\text{–}H_b)$ = 0.6); 4.86 (s, $C_5H_5$); 1.71 (dd, $CH_3$, $^3J(H_a\text{–}CH_3)$ = 6.6, $^4J(H_b\text{–}CH_3)$ = 1.6). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$ solution): 231.8 (CO), 229.8 (CO); 133.5 (H*C*=CH($CH_3$), $^1J$(C–H) = 155.8); 126.1 (HC=*C*H($CH_3$), $^1J$(C–H) = 152); 91.8 ($C_5H_5$); 73.9 (H–C≡, $^1J$(C–H) = 209.5, $^3J$(C–H) = 3.6); 65.1 (–C≡); 18.1 (=CH(*C*H3), $^1J$(C–H) = 125.9, $^2J$(C–H) = 6.3, $^3J$(C–H) = 4.9).

Complex (2*Z*): $^1$H NMR data ($C_6D_6$ solution): 6.44 (m, H*b*); 5.29 (dq, H*a*, $^3J(H_a\text{–}CH_3)$ = 7.0, $^3J(H_a\text{–}H_b)$ = 10.3); 5.13 (d, H*c*, $^4J(H_c\text{–}H_b)$ = 0.6); 4.85 (s, $C_5H_5$); 1.69 (dd, $CH_3$, $^3J(H_a\text{–}CH_3)$ = 7.1, $^4J(H_b\text{–}CH_3)$ = 1.75. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$ solution): 230.9 (CO), 230.4 (CO); 132.0 (H*C*=CH($CH_3$), $^1J$(C–H) = 160.6); 123.9 (HC=*C*H($CH_3$), $^1J$(C–H) = 154.9); 92.0 ($C_5H_5$); 70.0 (–C≡); 65.2 (H–C≡, $^1J$(C–H) = 213.3; $^3J$(C–H) = 6.0); 14.9 (=CH(*C*$H_3$), $^1J$(C–H) = 126.1, $^2J$(C–H) = 9.6, $^3J$(C–H) = 4.0). MS (*m/e*): 500: $[M]^+$; 444: $[M-2CO]^+$; 416 $[M-3CO]^+$; 388 $[M-4CO]^+$.

*3.3. Synthesis of $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}CC_6H_9)]$ (3)*

Complex **3** was prepared as described for complex **2**, but using 1-ethynylcyclohexene (amounts 0.9 g, 2.07 mmol of $[Cp_2Mo_2(CO)_4]$ and 0.55 g, 5.2 mmol of alkyne). After chromatography on a silica gel column (elution dichloromethane/hexane 50:50) and evaporation of the solvent, 0.97 g of complex **3** was recovered (yield 87%). Anal. Found: C, 48.72; H, 3.93. $C_{22}H_{20}Mo_2O_4$ calcd.: C, 48.91; H, 3.73%.

For interpretation of the spectroscopic data, hydrogen atoms are labelled as follows:




$^1$H NMR data ($C_6D_6$ solution) (assignments from selective irradiations) 5.86–5.55 (7 peaks, $H_c$, $^3J(H_c\text{–}H_{d,e})$ = 4.0, $^4J(H_c\text{–}H_{a,b})$ = 1.5); 5.36 (s, H–C≡); 5.29 (s, $C_5H_5$); 2.18–2.13 (m, $H_{d,e}$); 1.95–1.90 (m, $H_{a,b}$); 1.68–1.55 (m, $CH_2$). $^{13}C\{^1H\}$ NMR ($C_6D_6$ solution): 232.2 (s, CO); 230.2 (s, CO); 140.3 (s, >*C*=CH); 126.3 (dm, >C=*C*H, $^1J$(C–H) = 162.0); 91.6 ($C_5H_5$); 76.5 (d, H*C*≡C, $^1J$(C–H) = 208.9); 71.7 (s, HC≡*C*); 32.5 (t, $^1J$(C–H) = 124.7); 26.4 (t, $^1J$(C–H) = 126.5); 23.9 (tm, $^1J$(C–H) = 127.1); 22.9 (tm, $^1J$(C–H) = 129.9) ($CH_2$). Infrared ($CH_2Cl_2$ solution): $\nu$(C≡O) 1995s, 1920s, 1840s. MS: (*m/e*) 540: $[M]^+$; 484: $[M-2CO]^+$; 456: $[M-3CO]^+$, 428: $[M-4CO]^+$.

*3.4. Synthesis of $[Cp_2Mo_2(CO)_4\{\mu\text{-}HC{\equiv}C\text{-}C(CH_3)_2\}][BF_4]$ (4)*

This product, previously obtained by Green *et al.* from $[Cp_2Mo_2(CO)_4\{\sigma,\eta^2\text{-}C{=}C{=}C(CH_3)_2\}]$ [13] was prepared here from **1** by addition of $HBF_4$ in diethyl ether following the same procedure as that used for synthesis of **5** and **6**.

*3.5. Synthesis of $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}C\text{-}CH\text{-}CH_2CH_3)][BF_4]$ (5)*

To a stirred solution of 1.2 g (2.4 mmol) of **2** in 50 ml of diethyl ether was added dropwise an equimolecular amount (0.35 ml, 2.4 mmol) of a solution of $HBF_4$ in diethyl ether. The orange precipitate formed was separated off, washed with diethyl ether (2 × 5 ml) and then purified through a short Celite column ($CH_2Cl_2$ as eluent). The solvent was removed *in vacuo* and an orange solid precipitated (yield 95%). Anal. Found: C, 37.48; H, 2.73; F, 12.45; $C_{19}H_{17}BF_4Mo_2O_4$ calcd.: C, 38.81; H, 2.91; F, 12.92%. Infrared (KBr): $\nu$(C≡O) 2050s, 1990s, 1900s; $\nu$(B–F) 1100 broad.

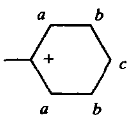
NMR spectra were unresolved at room temperature. $^1$H NMR data ($CD_2Cl_2$ solution, 210 K): 6.12 (t, *H*C–$CH_2CH_3$, $^3J$(H–H) = 6.5, 6.04 (s, HC≡); 5.62, 5.58 (s,

$C_5H_5$); 1.96 (m, $CH_2$); 1.12 (t, $CH_3$, $^3J$(H–H) = 7.3). $^{13}C$ NMR ($CD_2Cl_2$ solution, 210 K): 227.6, 227.2, 217.8, 217.0 (CO); 110.3 ("$C^+$"); 103.6 (C≡); 92.7, 92.2 ($C_5H_5$); 77.0 (H–C≡); 28.6 ($CH_2$); 15.8 ($CH_3$). MS: ($m/e$) 501: $[M - BF_4]^+$; 445; $[M - BF_4 - 2CO]^+$; 417: $[M - BF_4 - 3CO]^+$; 389: $[M - BF_4 - 4CO]^+$.

### 3.6. Synthesis of $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}CC_6H_{10})][BF_4]$ (6)

Complex **6** was prepared from **3** following the procedure used for **5** (amounts complex **3**, 660 mg, 1.22 mmol; $HBF_4 \cdot Et_2O$, 0.17 ml, 1.22 mmol; yield, 90%). Anal. Found: C, 43.71; H, 3.78. $C_{22}H_{21}BF_4Mo_2O_4$ calcd.: C, 42.07; H, 3.37%. Infrared (KBr): $\nu$(C≡O) 1995s, 1910s, 1830s; $\nu$(B–F) 1050 (broad).

The protons of the cycle are labelled as follows for NMR data.




$^1H$ NMR data ($CDCl_3$) solution): 6.50 (H–C≡); 5.64 ($C_5H_5$); 2.21–2.16 (broad m, $CH_{2a}$); 1.76–1.71 (broad m, $CH_{2b}$); 1.69 (m, $CH_{2c}$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$ solution): 222.7, 222.4 (CO); 151.6 ("$C^+$"); 104.4 (–C≡); 93.8 ($C_5H_5$); 73.5 (HC≡, $^1J$(C–H) = 222.8); 32.9 (t, $CH_{2a}$, $^1J$(C–H) = 125.0); 30.9 (t, $CH_{2c}$, $^1J$(C–H) = 128.0); 26.2 (t, $CH_{2b}$, $^1J$(C–H) = 126.1). MS: ($m/e$) 541: $[M - BF_4]^+$; 485: $[M - BF_4 - 2CO]^+$; 457: $[M - BF_4 - 3CO]^+$; 429: $[M - BF_4 - 4CO]^+$.

### 3.7. Reaction of 1 with Na / Hg

Complex **1** (500 mg, 1.0 mmol) was dissolved in 50 ml of THF or toluene. The resulting solution was transferred onto 15 g of 2% sodium amalgam. The mixture was stirred for 18 h at room temperature, the solution was filtered, and the solvent was removed *in vacuo*. The crude solid was chromatographed on silica gel. A red-orange band was eluted with a dichloromethane/hexane mixture (1:1 by vol.). Concentration of the solution gave small red-orange crystals of the complex **7** $[Cp_2Mo_2(CO)_4\{\mu\text{-}\sigma,\eta^3\text{-}HC{\cdots}CH{\cdots}C(CH_3)_2\}]$ (yield, 20%). This compound had been obtained previously by Green *et al.* from the reaction between $[Cp_2Mo_2(CO)_4]$ and the 3,3-dimethylcyclopropene [21].

### 3.8. Reaction of 2 with Na / Hg

The same procedure was used. The crude solid obtained by evaporation of THF was chromatographed on silica gel. A red band was eluted with a dichloromethane/hexane (15:85 by vol.) giving the starting complex **2** (yield 50%). A second red band containing very small amounts (yield ≈ 3%) of complex **8** $[[\{Cp_2Mo_2(CO)_4\}\{\mu\text{-}HC{\equiv}CCH_2\text{-}CH(CH_3)\}]_2]$ was eluted with 50:50 hexane/dichloromethane. Because of the very low yield of **8** only the $^1H$ NMR spectrum could be recorded. It consisted of two sets of peaks with the relative intensities (3:1). One set corresponded to **8A** ($R^*S^*$) and the other one to a mixture of **8B** ($SS$) and **8C** ($RR$), but it was impossible to assign the sets.

$^1H$ NMR data ($CDCl_3$ solution): 6.34, 6.07 (2s, H–C≡); 5.32, 5.31–5.26, 5.25 (4s, $C_5H_5$), 2.6–1.2 (different multiplets, the other protons). Infrared ($CH_2Cl_2$ solution): $\nu$(C≡O) 1990s, 1910s, 1830s.

### 3.9. Reaction of 4 with Na / Hg

Complex **4** (500 mg, 0.85 mmol) was placed in toluene (50 ml) and then transferred on to 15 g of 2% sodium amalgam. The mixture was stirred for 18 h. The solution was filtered and the solvent was removed *in vacuo*. The crude solid was chromatographed on silica gel. A red band was eluted with a dichloromethane/hexane mixture (1:5 by vol.). Evaporation of the solution gave red crystals (yield 15%) of $[Cp_2Mo_2(CO)_4\{\mu\text{-}HC{\equiv}C\text{-}CH(CH_3)_2\}]$ (**9**) previously obtained by nucleophilic addition of $CH_3^-$ from $LiCH_3$ to $[Cp_2Mo_2(CO)_4\{\mu\text{-}HC{\equiv}C\text{-}CH(CH_3)\}][BF_4]$ [11]. A second red band (elution dichloromethane/hexane 1:2) allowed the recovery of the complex **1** (yield 20%) and a third band (elution dichloromethane/hexane 1:1) gave the red-orange $\mu$-$\sigma,\eta^3$ complex **7** (yield 20%).

When the reaction of **4** with Na/Hg was performed in THF, only the complex **7** was recovered (yield 20%).

### 3.10. Reaction of 5 with Na / Hg

The same procedure as that described for **4** was used. The crude solid obtained after evaporation of the solvent (toluene) was chromatographed on silica gel. A first band containing the mixture (**2**$E$) + (**2**$Z$) (ratio 94:6) (yield 40%) was eluted with a dichloromethane/hexane mixture (5:95). A second red band (elution dichloromethane/hexane 1:1) yielded the tetranuclear species $[[\{Cp_2Mo_2(CO)_4\}\{\mu\text{-}HC{\equiv}CCH(CH_2\text{-}CH_3)\}]_2]$ (**10**) (yield 6%). Anal. Found: C, 46.03; H, 3.63. $C_{38}H_{34}Mo_4O_8$ calcd.: C, 45.53; H, 3.41%. Infrared ($CH_2Cl_2$ solution): $\nu$(C≡O) 1990s, 1910vs, 1840s. $^1H$ NMR data ($CDCl_3$ solution): 6.02 (s, H–C≡); 5.32, 5.31 (2s, $C_5H_5$); 2.52 (t, –C$H$-Et, $^3J$(H–H) = 7.9); 1.15 (m, $CH_2$); 0.89 (t, $CH_3$, $^3J$(H–H) = 7.3). $^{13}C$ NMR ($CD_2Cl_2$ solution): 234.1 (CO); 92.4–92.0 ($C_5H_5$); 86.5 (H–C≡); 59.5 (–C≡); 34.4 ($C$H–Et); 22.7 ($CH_2$); 14.2 ($CH_3$).

### *3.11. Reaction of 6 with Na / Hg*

An analogous procedure to that used for **4** or **5** gave rise to the formation of complex **3** (yield 60%).

### *3.12. Synthesis of $[Cp_2Mo_2(CO)_4\{\mu-HC\equiv CC(CH_3)_3\}]$ (17)*

$LiCH_3$ (1.6 M in diethyl ether) (0.4 ml) was added dropwise to a cold solution (−60°C) of 350 mg (0.6 mmol) of **1** in 100 ml of dichloromethane. The mixture was stirred for 2 h while it was allowed to reach room temperature. The solution was filtered, and the solvent was removed *in vacuo*. The residue was chromatographed on silica gel using a mixture of hexane and dichloromethane (5:1 by vol.) as eluent. After removal of solvent, complex **17** was obtained as a red powder (yield 30%). Anal. Found: C, 46.33; H, 4.16. $C_{20}H_{20}Mo_2O_4$ calcd.: C, 46.53; H, 3.90%. Infrared (KBr): $\nu(C\equiv O)$ 1990s, 1910s, 1840s. $^1H$ NMR data ($C_6D_6$ solution): 5.72 (s, HC≡); 4.93 (s, $C_5H_5$); 1.03 (s, $CH_3$). $^{13}C\{^1H\}$ NMR ($C_6D_6$ solution): 235.8, 235.6, 234.2, 227.1 (CO); 94.7 (d, ≡CH, $^1J(C-H) = 206.7$); 90.9 ($C_5H_5$); 66.3 (s, C≡); 37.5 (s, $-C(CH_3)_3$); 34.2 (qh, $CH_3$, $^1J(C-H) = 125.5$, $^3J(C-H) = 4.7$).

### *3.13. X-Ray structure analysis of 10*

A single crystal of $[[\{Cp_2Mo_2(CO)_4\}\{\mu-HC\equiv CCH(CH_2CH_3)\}]_2]$ (**10**) grown from dichloromethane/hexane was mounted on an Enraf-Nonius CAD-4 four circle automatic diffractometer. The unit cell was determined and refined from 25 randomly selected reflections observed by use of the CAD-4 automatic routines.

Crystal data: formula $C_{38}H_{34}Mo_4O_8$, molecular weight 1002.45, monoclinic, $P2_1/n$, $a = 10.513(5)$, $b = 14.441(4)$, $c = 23.812(5)$ Å, $\beta = 101.09(2)°$, $V = 3547.8$ Å$^3$, $\lambda$(Mo K$\alpha$) 0.71069 Å, $\mu$(Mo K$\alpha$) 13.95 cm$^{-1}$, $Z = 4$, $d_{calcd}$ 1.877 g cm$^{-3}$.

The intensities of 5062 independent reflections, measured in an $\omega-2\theta$ scan ($\theta_{min}$ 1°, $\theta_{max}$ 27°), with $I > 3\sigma(I)$ among 8468 data collected, were used in the solution and refinement of the structure. All calculations were carried out by use of the Enraf-Nonius SDP package [22]. The structure was solved and refined (452 variables) by conventional direct methods, difference Fourier and full-matrix least-squares programs. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated by the "hydro" program of SDP and included in the final calculations with $B_{iso}(H) = B_{iso}(C)$ (C is the carbon atom bearing the hydrogen atom). The final residuals were $R = 0.045$ and $R_w = 0.065$, GOF = 1.54. The weighting scheme employed was $w^{-1} = 1/4[\sigma(I)/I + 0.07(I)^2]$. Secondary extinction coefficient was included in the last cycle with a final value of $0.8 \times 10^{-7}$. A list of observed and calculated structure factors is available from the authors, and full lists of other parameters have been deposited with the Cambridge Crystallographic Data Centre.

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