ELSEVIER

Journal of Organometallic Chemistry 487 (1995) 201–208

Journal of Organometallic Chemistry

# New synthesis of μ-allenylidene complexes from dimolybdenum carbenium ions crystal structure of $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu,\eta^2\text{-}C{=}C{=}C_6H_{10})]$

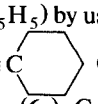
J.F. Capon [a], N. Le Berre-Cosquer [a], S. Bernier [a], R. Pichon [a], R. Kergoat [a,*], P. L'Haridon [b]

[a] *URA CNRS No. 322, Chimie, Electrochimie Moléculaires et Chimie Analytique, Equipe de Chimie Inorganique Moléculaire, Université de Bretagne Occidentale, 6 Avenue Le Gorgeu, BP 809, 29285 Brest Cédex, France*

[b] *URA CNRS No. 1496, Verres et Céramiques, Laboratoire de Chimie des Matériaux, Université de Rennes-Beaulieu, 35042 Rennes Cédex, France*

Received 13 June 1994

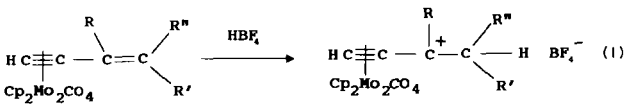
**Abstract**

A selective abstraction of the acetylenic proton of cationic allenyl complexes $[\{MoCp(CO)_2\}_2(\mu\text{-}\eta^2,\eta^3\text{-}HC{\equiv}CCR^1R^2)][BF_4]$ ($Cp{\equiv}\eta^5\text{-}C_5H_5$) by using the acetylide $LiC{\equiv}CC(CH_3){=}CH_2$ gives rise to allenylidene complexes $[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}C{=}C{=}CR^1R^2)]$ (($CR^1R^2{\equiv}C$  (**1b**); $R^1 = R^2 = CH_3$, (**2b**); $R^1 = H$, $R^2 = C_2H_5$ (**3b**); $R^1 = H$, $R^2 = CH_3$ (**4b**); $R^1 = R^2 = H$ (**5b**); $R^1 = CH_3$, $R^2 = C_6H_5$ (**6c**). Compounds **3b** and **4b** exist as two isomers while for **6c** the formation reaction is stereoselective. The crystal structure of $[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}C{=}C{=}C_6H_{10})]$ (**1b**) has been determined.

*Keywords:* Molybdenum; Allenylidene cpxs; Acetylide; X-ray structure; Cyclopentadienyl

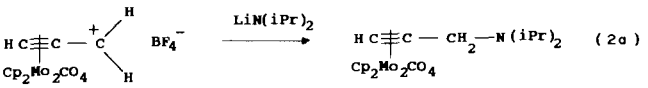
## 1. Introduction

In previous papers [1–3] it has been shown that $\mu\text{-}\eta^2,\eta^3$ allenyl cationic compounds, in which the carbon atom bearing the positive charge is variously substituted, could be obtained from (μ-enyne) [bis(dicarbonyl($\eta^5$-cyclopentadienyl)molybdenum(I)]] complexes:

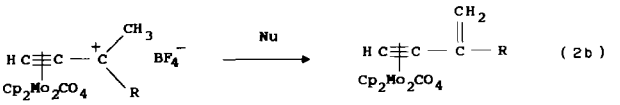



These cationic species are intermediates in the synthesis of tetrametallic complexes containing a relatively unreactive saturated bridging carbon chain [1,2,4].

However, the $C^+$ carbon atom behaves as a site in the allenyl entity of enhanced reactivity, in particular for nucleophilic attack [4,5], as exemplified below:



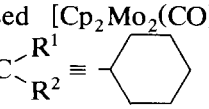

Moreover, it confers a labile or acidic character on the hydrogen atom in the α position to $C^+$ [6]:



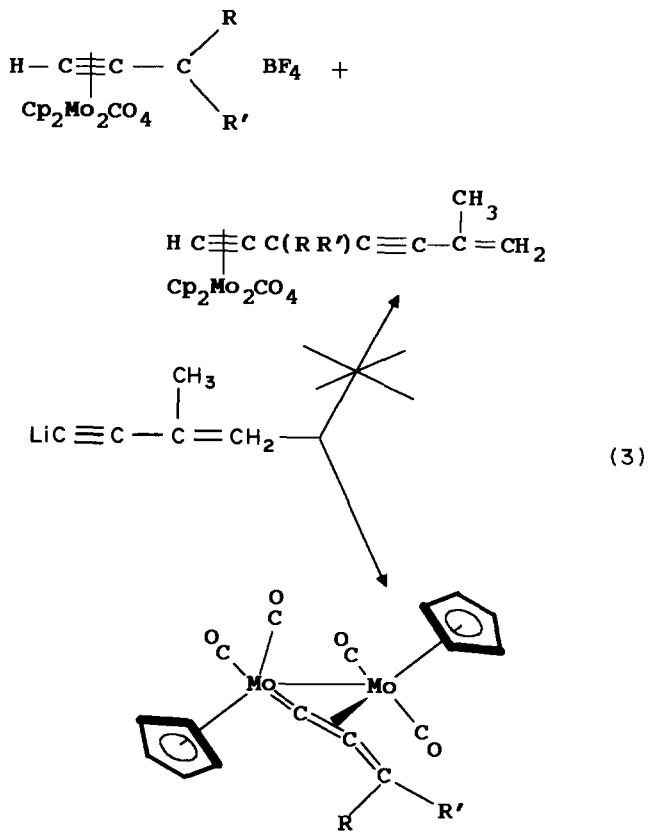

In order to extend the study of the reactivity of carbenium ions towards other nucleophiles, the acetylide $LiC{\equiv}CC(CH_3){=}CH_2$ has been used. An unprecedented selective abstraction of the acetylenic proton occurred, whereas carbon–carbon coupling reactions by fixation of anionic unsaturated entities at the $C^+$ atom had been expected (Eq. (3)).

The synthesis and the spectroscopic data of such dimolybdenum $\mu,\eta^2$ allenylidene complexes are described in this paper.

## 2. Results and discussion

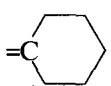
The cationic complexes used $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2,\eta^3\text{-}HC_\alpha{\equiv}C_\beta C{<}^{R^1}_{R^2})][BF_4]$ ($-C{<}^{R^1}_{R^2} \equiv$  (**1a**);

0022-328X/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
*SSDI* 0022-328X(94)05117-8

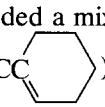


(3)

$R^1 = R^2 = CH_3$ (**2a**); $R^1 = H$, $R^2 = C_2H_5$ (**3a**); $R^1 = H$, $R^2 = CH_3$ (**4a**); $R^1 = R^2 = H$ (**5a**); $R^1 = CH_3$, $R^2 = C_6H_5$ (**6b**)) (Table 1) result from an electrophilic attack of $HBF_4$ on the corresponding molecular μ-enyne derivatives (**1a**, **2a**, **3a**, **4a**) or on the corresponding μ-acetylenic alcohol (**5a**, **6b**) (see experimental details).

The reaction of the previous $\mu$-$\eta^2$,$\eta^3$ allenyl complexes with an equivalent of $LiC{\equiv}CC(CH_3){=}CH_2$ in dichloromethane leads to the $\mu$,$\eta^2$ allenylidene compounds $[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}C_\alpha{=}C_\beta{=}C_\gamma{<}^{R^1}_{R^2})]$ ($=C{<}^{R^1}_{R^2}$: $=C$  (**1b**); $R^1 = R^2 = CH_3$ (**2b**); $R^1 = H$, $R^2 = C_2H_5$ (**3b**); $R^1 = H$, $R^2 = CH_3$ (**4b**); $R^1 = R^2 = H$ (**5b**); $R^1 = CH_3$, $R^2 = C_6H_5$ (**6c**)) (Table 1) with good yields by a selective abstraction of the acetylenic proton. All these complexes were obtained as green powders, except **6c**, which is yellow–brown.

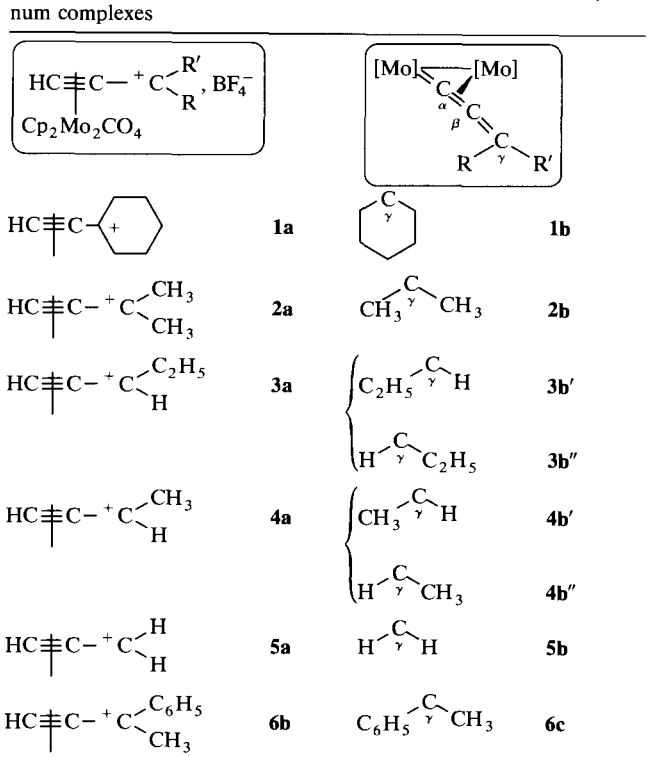
Compound **2b** has been reported previously, but its synthesis consisted of the protonation of the anion of $Li[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^2\text{-}C_2C(CH_3){=}CH_2\}]$ on an alumina column. The μ-enyne $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}CC(CH_3){=}CH_2)]$ was also obtained in the same reaction [7,8].

The use of $LiC{\equiv}CC(CH_3){=}CH_2$ is determinant. Moreover the low boiling point (32°C) of the alkyne $HC{\equiv}CC(CH_3){=}CH_2$ formed makes its elimination very easy. Therefore we have examined the reactivity of the cationic species towards a series of other nucleophilic molecules to understand the factors which control the abstraction of the acetylenic proton. Such an abstraction occurs also with other acetylides such as $LiC{\equiv}CPh$, but in this case the reactions are not selective. Attempts with **2a** for instance produce also 20% of $[Cp_2Mo_2(CO)_4\{\mu\text{-}HC{\equiv}CC(CH_3){=}CH_2\}]$ by elimination of a proton on a carbon atom adjacent to the $C^+$ atom. With $Li^nBu$, the major species is the μ-enyne complex. For instance, its reaction with **1a** afforded a mixture of **1b** (30%) with $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}CC$  $)]$ (70%) [2].

With $LiCH_3$, only nucleophilic additions of $CH_3^-$ to the $C^+$ atom were observed. Such a reaction gave $[Cp_2Mo_2(CO)_4\{\mu\text{-}HC{\equiv}CCH(CH_3)_2\}]$ and $[Cp_2Mo_2(CO)_4\{\mu\text{-}HC{\equiv}CC(CH_3)_3\}]$ that have been previously described [1,2]. Finally uncharacterized products were formed by other bases such as 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) or pyridine.

The temperature and the nature of the solvent also played an important role in the formation of $\mu$,$\eta^2$ (**4e**) allenylidene complexes. Dichloromethane solutions of

Table 1
$\mu$-$\eta^2$,$\eta^3$-allenyl and the corresponding $\mu$,$\eta^2$-allenylidene molybdenum complexes



| | | | |
|---|---|---|---|
| $HC{\equiv}C{-}^+C{<}^{R'}_{R}$, $BF_4^-$ ($Cp_2Mo_2CO_4$) | | [Mo]–[Mo] $C_\alpha$–$C_\beta$–$C_\gamma$ (R, R′) | |
| $HC{\equiv}C{-}$ | **1a** |  | **1b** |
| $HC{\equiv}C{-}^+C{<}^{CH_3}_{CH_3}$ | **2a** | $CH_3{-}C_\gamma{-}CH_3$ | **2b** |
| $HC{\equiv}C{-}^+C{<}^{C_2H_5}_{H}$ | **3a** | $C_2H_5{-}C_\gamma{-}H$ | **3b′** |
| | | $H{-}C_\gamma{-}C_2H_5$ | **3b″** |
| $HC{\equiv}C{-}^+C{<}^{CH_3}_{H}$ | **4a** | $CH_3{-}C_\gamma{-}H$ | **4b′** |
| | | $H{-}C_\gamma{-}CH_3$ | **4b″** |
| $HC{\equiv}C{-}^+C{<}^{H}_{H}$ | **5a** | $H{-}C_\gamma{-}H$ | **5b** |
| $HC{\equiv}C{-}^+C{<}^{C_6H_5}_{CH_3}$ | **6b** | $C_6H_5{-}C_\gamma{-}CH_3$ | **6c** |

[Mo] = $CpMo(CO)_2$.

**3b**, **4b** and **5b** for which the $C_\gamma$ atom bears a hydrogen atom must be kept at low temperatures during the synthesis; **5b**, the most unstable, could not be fully characterized. When tetrahydrofuran (THF) was used as solvent, the solutions did not turn green but became red, and a mixture of uncharacterized products was formed under the same conditions, while in pentane no reaction occurred.

### *2.1. Spectroscopic and crystallographic data for μ-allenylidene complexes*

The $^{13}C$ NMR spectra show around 290 ppm a signal characteristic of the $C_\alpha$ carbenoid atom. Because of the asymmetry of the molecules, four peaks assignable to the carbonyl ligands are observed in the 225–240 ppm range and the resonances of the two cyclopentadienyl groups are also separate.

Two signals are observed in the $^1H$ and $^{13}C$ NMR spectra of **1b**, **2b** and **6c** for the Cp groups while, for **3b** and **4b**, four peaks are observed, indicating that these last two compounds exist as two diasteroisomers depending on the relative position of the substituents on the $C_\gamma$ atom (see below).

The crystal structure of $[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}C{=}C{=}C_6H_{10})]$ (**1b**) (Fig. 1) reveals a geometry close to that of $[Cp_2Mo_2(CO)_4\{\mu,\eta^2\text{-}C{=}C{=}C(CH_3)_2\}]$ [8]. Carbonyl ligands and $\eta^5$-cyclopentadienyl rings are arranged in an approximately mutually *trans* orientation.

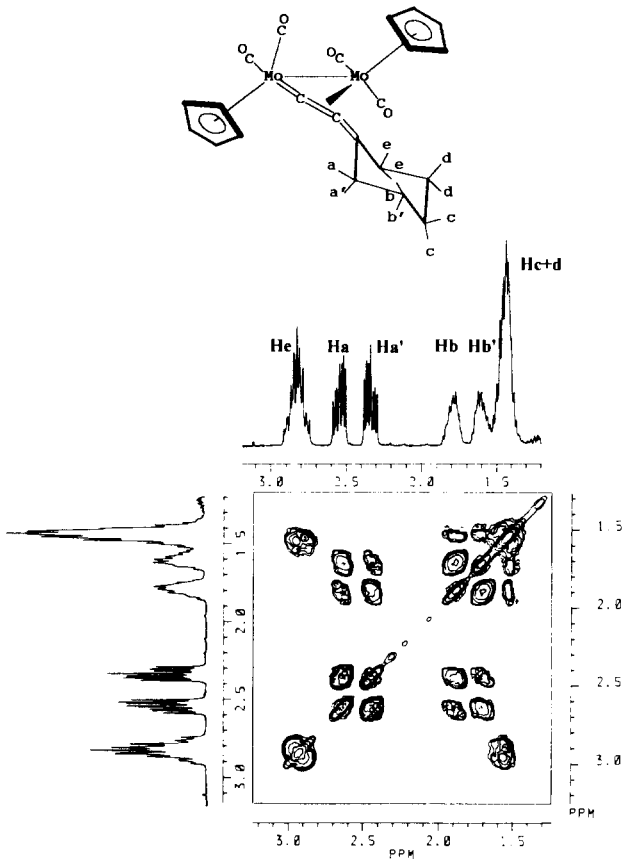



Fig. 2. 2D $^1H$ NMR spectrum of **1b**.

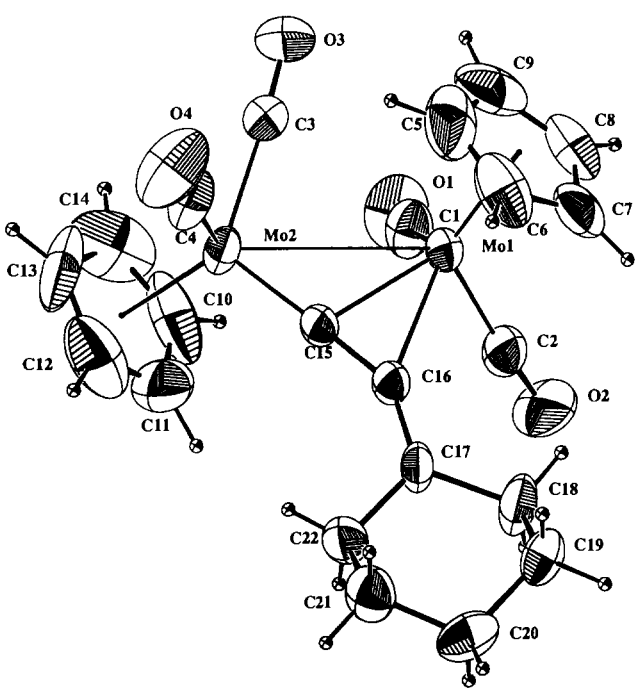


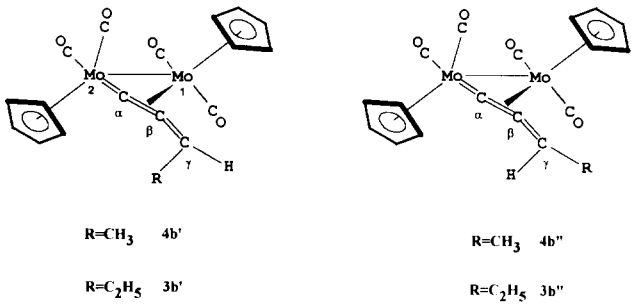

Fig. 1. ORTEP drawing of $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2(\mu,\eta^2\text{-}C{=}C{=}C_6H_{10})]$.

The Mo(1)–Mo(2) distance of 3.163(2) Å corresponds to a single bond. The short Mo(2)–C(15) separation of 1.90(1) Å is appropriate to a Mo=C double bond. The asymmetrically bridged allenylidene ligand acts as a four-electron donor by means of the Mo=C(15) double bond and the C(15)=C(16) double bond (1.35(1) Å). A consequence of that donation is the C(15)–C(16)–C(17) angle value of 146(1)° whereas, in μ-σ,σ(2e) allenylidenes, the C=C=C< fragment is linear [9–12]. Inside the C(17)–C(22) cycle, the $CH_2$–$CH_2$ bond length and $CH_2$–$CH_2$–$CH_2$ angle values are as expected for saturated carbon atoms.

A 2D H–H COSY spectrum was required for complete interpretation of the $^1H$ NMR spectrum of **1b** (Fig. 2). Each of the protons Ha′ and Ha″ appear as a multiplet (ddd) at 2.55 ppm ($J_{Ha'a''}$ = 13.5 Hz; $J_{Ha'b'}$ = 4.5 Hz and $J_{Ha'b''}$ = 7 Hz for Ha′; $J_{Ha''a'}$ = 13.5 Hz $J_{Ha''b'}$ = 4.3 Hz and $J_{Ha''b''}$ = 8 Hz for Ha″). Selective irradiation of the multiplet at 1.43 ppm (protons c + d) transforms the multiplet at 2.82 ppm (protons e) to an AB spectrum ($\delta_A$ = 2.86 ppm; $\delta_B$ = 2.78 ppm; $J_{AB}$ = 13 Hz).

As mentioned above, **3b** ($R^1$ = H, $R^2 = C_2H_5$) and

**4b** ($R^1 = H$, $R^2 = CH_3$) exist in solution as two diastereoisomers:




Integration of the proton spectra suggests a relative ratio of 3 : 1 when $R = CH_3$ (**4b**), while the two isomers of **3b** ($R = C_2H_5$) are present in the final product in almost equivalent amounts. On this basis it is difficult to conclude which isomer is favoured. However, with more bulky substituents ($R^1 = CH_3$, $R^2 = C_6H_5$) (**6c**), only one form is present. It may be assumed that in this case the methyl group is close to Mo(1). With vinylidene complexes that stereoselectivity was observed systematically even with a terminal proton [8]. The deshielding of the terminal protons in **3b** and **4b** compared with the hydrogen atoms of free allenes ($H_2C{=}C{=}CH_2$, $CH_3(H)C{=}C{=}CH_2$ and $CH_3(H)C{=}C{=}C(H)CH_3$) ($\delta_H$ (terminal in allenes) 5.08–4.55 ppm) [13] is also noteworthy.

In contrast, a large difference of the chemical shifts of the terminal proton of the two isomers ($R = CH_3$, 7.74 and 5.99 ppm; $R = C_2H_5$, 7.62 and 6.06 ppm) is observed, while the signals of the alkyl groups are much less separated. To our knowledge, very few allenylidene complexes with terminal protons have been reported, but such an important difference of chemical shifts (1–1.9 ppm) has also been noticed in heteronuclear metal-μ-alkenyl compounds $[(CO)_3Fe(\mu\text{-}\eta^2,\eta^3\text{-}RC{=}C{=}CH_2)MCp(CO)_2]$ (M = Mo or W) [14]. In this case the chemical shifts of the protons are greatly influenced by the nature of the metal.

Obviously the chemical environment of the terminal proton ($C_\gamma H$) is different in the two series of isomers (**3b'**, **4b'** and **3b"**, **4b"**). By using a similar skeleton as that determined by X-ray diffraction for **1b** (this work) and **2b** [8], the distance between this proton and the oxygen atom of the nearest C≡O ligand in **3b'** and **4b'** was calculated to be about 3.3. Å ($C_\gamma$–H was taken as 0.95 Å). An analogous separation (about 3.2 Å) between the terminal proton and the oxygen atom of the C=O group was calculated for (*E*)-2-methylbutenoate $CH_3(H)C{=}C(CH_3)C(=O)OCH_3$. Deshielding of the terminal proton in the (*E*) isomer ($\delta_H = 6.73$ ppm) relative to that in the (*Z*) form ($\delta_H = 5.98$ ppm) is considered to be a consequence of a field effect of the C=O group [15]. However, the natures of the two CO groups (the carbonyl ligand in **3b** and **4b** and the CO ester group in the organic molecule) are different. Similar behaviours were noted for the terminal protons of methyl methacrylate ($CH_2{=}C(CH_3)C(O)OCH_3$) ($\delta_H$ = 5.49 and 6.04 ppm) [16]. Therefore with some reservations we consider that the most deshielded proton belongs to the **3b'** or **4b'** diastereoisomers. However, the electronic effects of the Mo(1) atom *cis* (**3b'**, **4b'**) or *trans* position (**3b"**, **4b"**) to the terminal proton must also be evaluated.

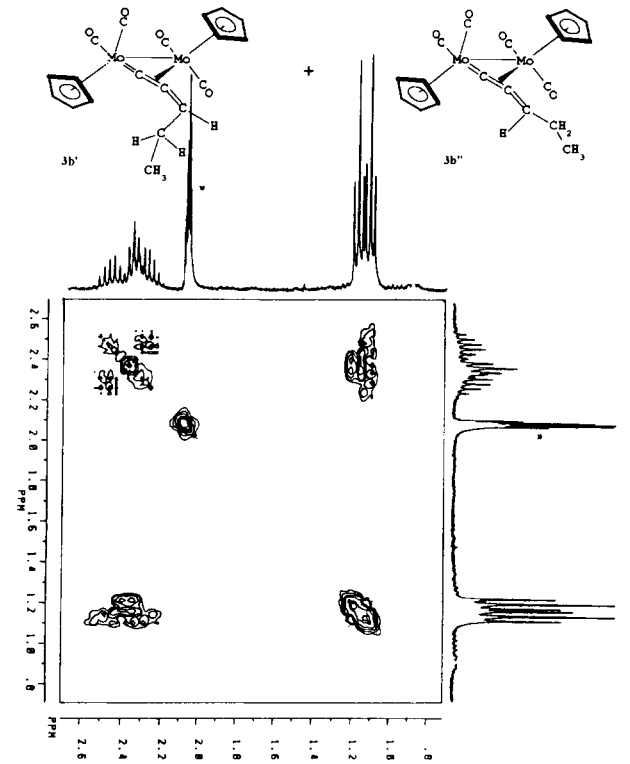
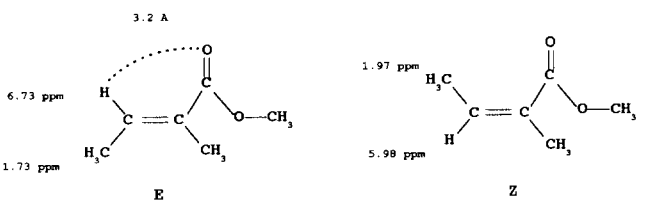



Fig. 3. 2D $^1$H NMR spectrum of **3b**.




Multipulse NMR ($^1$H–$^1$H COSY (Fig. 3) and *J* modulation) and selective irradiation were required to assign fully the peaks of both isomers of **3b**. For one isomer, the two protons of the $CH_2$ group are diastereotopic. Indeed, the two-dimensional homonuclear *J*-resolved $^1$H NMR spectrum shows a multiplet at 2.45 ppm for one proton and another multiplet at 2.25 ppm for the second hydrogen. For **3b"**, only one multiplet appears at 2.31 ppm, indicating the equivalence of the two protons of the $CH_2$ group. This was confirmed by selective irradiation of the $CH_3$ protons which produced a doublet assignable to $CH_2$ ($^3J = 6.1$ Hz).

## 3. Conclusion

While metal complexes containing allenylidene ligands are an important and rapidly growing class of compounds [12,17–19], the synthetic methods used to prepare them have not been well developed. We have therefore investigated carbenium ions as reagents for synthesis of various types of allenylidene complex. The crux of our synthetic strategy is the use of $LiC{\equiv}CC(CH_3){=}CH_2$ as a soft base. The present study suggests that such reactions may provide a useful general synthetic approach to a much wider variety of allenylidene complexes and allow studies of their reactivity. Subsequent work in our laboratory should furnish additional support for these claims.

## 4. Experimental details

All the reactions and purifications were performed under dinitrogen using Schlenk techniques. The solvents were freshly distilled 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.

IR spectra were obtained with a Perkin–Elmer 1430 spectrometer, using solutions in $CH_2Cl_2$ or KBr pellets. IR frequencies are reported in wavenumber units ($cm^{-1}$). Intensities were given as follows: vs, very strong; s, strong; m, middle; 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 $\delta$ (ppm) relative to internal tetramethylsilane (TMS). Coupling constants are reported in hertz (Hz). The following abbreviations were used: s; singlet; d, doublet; t, triplet; q, quartet; qn, quintet.

Mass spectra were obtained from a HP 5695 gas chromatography–mass spectroscopy apparatus. The $m/e$ values were based on the $^{96}Mo$ isotope.

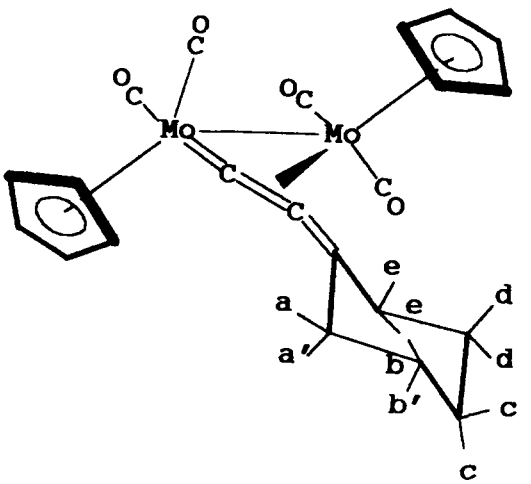
Analyses were performed at the Service Central d'Analyses of the CNRS. However, some complexes were stable only at low temperature and elemental analyses could not be performed.

$[Cp_2Mo_2(CO)_4]$ was obtained by a published method [20]. 2-methylbut-1-en-3-yne ($HC{\equiv}CC(CH_3){=}CH_2$), D-L-2-phenyl-3-butyn-2-ol ($HC{\equiv}CC(CH_3)(C_6H_5)OH$) and propargylic alcohol ($HC{\equiv}CCH_2OH$) were commercial products. $LiC{\equiv}CC(CH_3){=}CH_2$ was prepared from $Li^nBu$ (2.5 M in hexane) and $HC{\equiv}CC(CH_3){=}CH_2$.

### 4.1. Synthesis of $[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}C{=}C{=}C_6H_{10})]$ (1b)

A cold solution (−70°C) of $[Cp_2Mo_2(CO)_4(\mu\text{-}HC{\equiv}CC_6H_{10})][BF_4]$ (**1a**) [2] (0.52 g, 0.83 mmol) in $CH_2Cl_2$ (70 ml) was added to a stirred suspension of $LiC{\equiv}CC(CH_3){=}CH_2$ (0.83 mmol) ($HC{=}CC(CH_3){=}CH_2$, 0.1 ml; $Li^nBu$, 0.33 ml) in cold diethyl ether (−70°C, 5 ml), causing a rapid colour change from brown to green. The mixture was allowed to warm to room temperature and was stirred for about 1 h. The solution was filtered through a Celite pad (3 × 10 cm) to remove $LiBH_4$. Removal of the solvent in vacuo gave the analytically pure green complex **1b** (yield, 0.36 g (86%)).

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




$^1H$ NMR ($C_6D_6$ solution); $\delta$ 4.98 (s, 5H, $C_5H_5$); 4.97 (s, 5H, $C_5H_5$); 2.82 (m, 2H, He); 2.58–2.29 (m, 2H, Ha–a'); 1.84–1.59 (m, 2H, Hb–b'); 1.43 (m, 4H, Hc, Hd). $^{13}C$ NMR ($C_6D_6$ solution): $\delta$ 289.5 (Mo=C); 237.7, 233.5, 231.2, 230.7 (CO); 155.9 ($C{=}C^{\prime}$); 147.5 ($C{=}C^{\prime}$); 94.9, 93.5 ($C_5H_5$); 44.9, 36.4, 29.2, 29.0, 26.5 ($CH_2$). IR (KBr pellet): $\nu$ (C≡O) 1965 m, 1910 s, 1875 s, 1850 m; $\nu$(C=C=C) 1675 s $cm^{-1}$ MS: $m/e$ 540 $[M]^+$; 484 $[M-2CO]^+$; 456 $[M-3CO]^+$; 428 $[M-4CO]^+$. Anal. Found: C, 49.60; H, 3.78. $C_{22}H_{20}Mo_2O_4$ Calc.: C, 48.91; H, 3.73%.

### 4.2. Synthesis of $[Cp_2Mo_2(CO)_4\{\mu,\eta^2\text{-}C{=}C{=}C(CH_3)_2\}]$ (2b)

This complex has been obtained previously in a different way [7,8]. In this work, the procedure described for **1b** was used. The amounts were as follows: $[Cp_2Mo_2(CO)_4\{\mu\text{-}HC{\equiv}CC(CH_3)_2\}][BF_4]$ (**2a**) [2] (1 g, 1.7 mmol); $LiC{\equiv}CC(CH_3){=}CH_2$ (1.7 mmol) ($HC{\equiv}CC(CH_3){=}CH_2$, 0.2 ml; $Li^nBu$, 0.68 ml), (yield, 0.74 g (87%)).

Spectroscopic and analytical data were the same as those given in [7,8].

### 4.3. Synthesis of $[Cp_2Mo_2(CO)_4\{\mu,\eta^2\text{-}C{=}C{=}C(H)\text{-}C_2H_5\}]$ (3b)

$[Cp_2Mo_2(CO)_4\{\mu\text{-}HC{\equiv}CC(H)C_2H_5\}][BF_4]$ **3a** [2] (0.56 g, 0.96 mmol) in suspension in cold pentane (50

ml; −50°C) was added to a suspension of LiC≡CC($CH_3$)=$CH_2$ in diethyl ether (50 ml; −50°C) (HC≡CC($CH_3$)=$CH_2$, 0.1 ml; Li$^n$Bu, 0.385 ml). Addition of cold dichloromethane (−50°C) allowed the reaction to start. The colour of the solution turned immediately from brown to green and was stirred at −50°C for 30 min. The mixture was transferred rapidly into a separatory funnel at about −45°C. Removal of the solvent in vacuo very slowly for 3–4 h at that temperature gave a green residue. The crude solid was extracted twice with 30 ml portions of cold pentane (−30°C). The resulting green solution was concentrated in vacuo to 5 ml and kept at −55°C for 3 h, leading to a green precipitate (yield, 0.3 g (65%)). Complex **3b** was obtained as two isomers in a 1:1 ratio (see discussion).

$^1$H NMR (toluene-$d_8$ solution, 250 K) (assignments to the different isomers from selective irradiations): isomer **3b′** 7.62 (t, pseudo dd, 1H, C($H$)$C_2H_5$, $^3J$(H–H) = 7.7 Hz; 2.45 (m, 1H, $CH_2$); 2.25 (m, 1H, $CH_2$); 1.09 (t, 3H, $CH_3$, $^3J$(H–H) = 7.5 Hz); isomer **3b″** 6.06 (t, 1H, C($H$)$C_2H_5$, $^3J$(H–H) = 6.3 Hz); 2.31 (m, pseudo qn, 2H, $CH_2$); 1.17 (t, 3H, $CH_3$, $^3J$(H–H) = 7.3 Hz); 4.88, 4.87, 4.83, 4.78 (4 $C_5H_5$, isomers **3b′** and **3b″**). $^{13}$C NMR (toluene-$d_8$ solution, 250 K); 292.3, 291.8 (2 Mo=C); 238.1, 237.3, 237.1, 234.8, 233.5, 231.4, 228.2, 227.7 (8 CO); 156.7, 153.7 ($C$=C< and C=$C$<); 141.3, 140,0 ($C$=C< and C=$C$<); 95.9, 95.5, 94.1, 93.0 (4 $C_5H_5$); 34.9, 34.8 (2 $CH_2$); 28.7, 23.3 (2 $CH_3$). IR (toluene solution): $\nu$(C≡O) 1970 m, 1910 s, 1850 m; $\nu$(C=C=C) 1680 m cm$^{-1}$ MS: $m/e$ 500 [$M$]$^+$; 444 [$M$ − 2CO]$^+$; 416 [$M$ − 3CO]$^+$; 388 [$M$ − 4CO]$^+$.

### 4.4. Synthesis of [$Cp_2Mo_2(CO)_4\{\mu,\eta^2$-C=C=C(H)-$CH_3\}$] (4b)

[$Cp_2Mo_2(CO)_4\{\mu$-HC≡CC(H)$CH_3\}$][$BF_4$] (**4a**) [1] (0.51 g, 0.88 mmol) in suspension in cold pentane (50 ml; −50°C) was added to a suspension of an equimolar amount of LiC≡CC($CH_3$)=$CH_2$ (HC≡CC($CH_3$)=$CH_2$, 0.1 ml; Li$^n$Bu, 0.355 ml) in cold diethyl ether (50 ml, −50°C). The reaction started on addition of cold dichloromethane (20 ml; −50°C). The resulting solution was stirred for 30 min at −50°C, filtered in vacuo through Celite and concentrated to 10 ml while the temperature was kept at −50°C. The addition of cold pentane (3 ml) precipitated **4b**. The solid was washed with pentane (3 × 15 ml) (yield, 0.25 g (56%)). Complex **4b** was obtained as two isomers in a 3:1 ratio.

$^1$H NMR (toluene-$d_8$ solution, 230 K): $\delta$ major isomer (**4b′**) 7.74 (q, 1H, C($H$)$CH_3$, $^3J$(H–H) = 7.2 Hz); 4.85 (s, 5H, $C_5H_5$); 4.81 (s, 5H, $C_5H_5$); 1.90 (d, 3H, C(H)C$H_3$, $^3J$(H–H) = 7.2 Hz); minor isomer (**4b″**) 5.99 (q, 1H, C($H$)$CH_3$, $^3J$(H–H) = 7.3 Hz); 4.88 (s, 5H, $C_5H_5$); 4.77 (s, 5H, $C_5H_5$); 2.15 (d, 3H, C(H)C$H_3$, $^3J$(H–H) = 7.3 Hz). $^{13}$C NMR (toluene-$d_8$ solution, 220 K): $\delta$ 292,0 (Mo=C, minor); 291.7 (Mo=C, major); 237.2, 236.3; 235.0, 233.7, 231.4, 228.2, 227.8, 227.0 (8 CO); 158.2, 156.7 (C=$C$< and $C$=C<, major); 137.1, 135.2 (C=$C$< and $C$=C<, minor); 95.5, 94.1 ($C_5H_5$, major); 95.0, 93.8 ($C_5H_5$, minor); 29.8, 23.2 (2 $CH_3$). IR (cold $CH_2Cl_2$ solution): $\nu$(C≡O) 1975 m, 1910 s, 1855 m; $\nu$(C=C=C) 1685 m cm$^{-1}$ MS: $m/e$ 430 [$M$ − 2CO]$^+$; 402 [$M$ − 3CO]$^+$; 374 [$M$ − 4CO]$^+$.

### 4.5. Synthesis of [$Cp_2Mo_2(CO)_4(\mu,\eta^2$-C=C=$CH_2$)] (5b)

Compound **5b** is the most unstable of the series; so it could not be fully characterized. Dichloromethane solutions must be always kept below −60°C.

Following a classical procedure, [$Cp_2Mo_2(CO)_4(\mu$-$\eta^2,\eta^3$-HC≡C$CH_2$)][$BF_4$] (**5a**) was obtained by addition of $HBF_4$ on [$Cp_2Mo_2(CO)_4(\mu$-HC≡C$CH_2$OH)]. Then **5a** (0.772 g, 1.38 mmol) was added to a suspension of an equimolar amount of LiC≡CC($CH_3$)=$CH_2$ (HC≡CC($CH_3$)=$CH_2$, 0.15 ml; Li$^n$Bu, 0.55 ml) in diethyl ether frozen in liquid nitrogen. Cold dichloromethane (30 ml) was added to the mixture which was placed in a cold alcohol bath (−80°C). The solution which was stirred for 30 min, quickly turned to green. It was filtered in vacuo and concentrated to 2 ml. Addition of cold pentane afforded a green precipitate which was washed with cold pentane.

$^1$H NMR (THF-$d_8$ solution, 235 K): $\delta$ 5.72 (s, 5H, $C_5H_5$); 5.68 (s, 5H, $C_5H_5$). IR (KBr pellet): $\nu$(C≡O) 1950 m, 1900 s, 1830 m cm$^{-1}$.

### 4.6. Synthesis of [$Cp_2Mo_2(CO)_4\{\mu$-HC≡CC($CH_3$)-($C_6H_5$)OH}] (6a)

D-L-2-phenyl-3-butyn-2-ol (HC≡CC($CH_3$)($C_6H_5$)OH) (0.67 g, 4.6 mmol) was added to a solution of [$Cp_2Mo_2(CO)_4$] (2 g, 4.6 mmol) in toluene. The mixture was stirred at room temperature for 18 h. The solvent was removed in vacuo and the residue was chromatographed on a neutral alumina column. A small amount of [$Cp_2Mo_2(CO)_6$] was eluted with a hexane–dichloromethane mixture (9:1 in volume). A second band (elution $CH_2Cl_2$) afforded complex **6a** (yield, 1.13 g (42%)).

$^1$H NMR (acetone-$d_6$ solution, room temperature): $\delta$ 7.20 (m, 5H, $C_6H_5$); 6.40 (s, 1H, H–C≡); 5.26 (s, 10H, 2 $C_5H_5$); 2.80 (s, 3H, $CH_3$); 2.70 (s, 1H, OH). IR (KBr pellet): $\nu$(C≡O) 1995 m, 1915 s, 1830 s cm$^{-1}$ MS: $m/e$ 562 [$M$ − $H_2O$]$^+$; 534 [$M$ − $H_2O$ − CO]$^+$; 506 [$M$ − $H_2O$ − 2CO]$^+$; 478 [$M$ − $H_2O$ − 3CO]$^+$; 450 [$M$ − $H_2O$ − 4CO]$^+$. Anal. Found: C, 50.11; H, 3.45. $C_{24}H_{20}Mo_2O_5$ Calc.: C, 49.67; H, 3.47%.

### 4.7. Synthesis of [$Cp_2Mo_2(CO)_4\{\mu$-$\eta^2,\eta^3$HC≡CC-($CH_3$)$C_6H_5$}][$BF_4$] (6b)

Complex **6a** was dissolved in diethyl ether (50 ml). To the stirred solution was added dropwise 1 ml of a

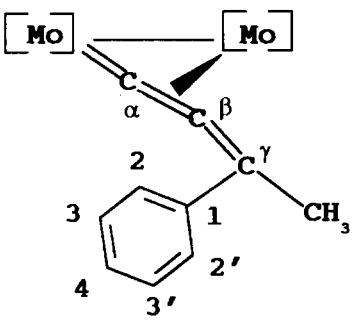
solution of $HBF_4$ in diethyl ether. The brown precipitate was filtered off and washed with diethyl ether (2 × 5 ml) (yield, 97%).

$^1$H NMR (acetone-$d_6$ solution, room temperature: δ 7.6 (m, 2H, $C_6H_5$); 7.4 (m, 3H, $C_6H_5$); 7.2 (s, 1H, H–C≡); 5.7 (s, 10H, 2 $C_5H_5$); 2,5 (s, 3H, $CH_3$). $^{13}$C NMR (acetone-$d_6$ solution, room temperature): δ 224.4, 223.0 (CO); 145.3, 130.3, 129.4, 126.8 ($C_6H_5$); 107.0 ("$C^+$"); 95.4 ($C_5H_5$); 77.7 (H*C*≡C); 69.0 (HC≡*C*); ≈ 29.6 ($CH_3$, superimposed upon solvent signals). IR (KBr pellet): ν(C≡O) 2040 m, 2020 s, 1990 m, 1950 s; ν(B–F) 1050 broad cm$^{-1}$. Anal. Found: C, 43.65; H, 2.97. $C_{24}H_{19}BF_4Mo_2O_4$ Calc.: C, 44.34; H, 2.94%.

### 4.8. Synthesis of $[Cp_2Mo_2(CO)_4\{\mu,\eta^2\text{-}C{=}C{=}C(CH_3)\text{-}C_6H_5\}]$ (6c)

The procedure described for **1b** was used. The amounts were as follows: **6b**, 0.75 g, 1.2 mmol; HC≡CC($CH_3$)=$CH_2$, 0.2 ml; Li$^n$Bu, 0.46 ml, compound **6c** precipitated as a yellow–brown powder (yield, 0.42 g (62%)).

For assignment of the spectroscopic data, the carbon atoms were labelled as follows:




$^1$H NMR (acetone-$d_6$ solution, room temperature): δ {8.10 (dd, 2H), 7.40 (dt, 3H), 7.30 (t, 1H)} ($C_6H_5$); 5.7 (s, 5H, $C_5H_5$); 5.5 (s, 5H, $C_5H_5$); 2.61 (s, 3H, $CH_3$). $^{13}$C NMR ($C_6D_6$ solution, room temperature: δ 287.2 ($C_\alpha$); 237.4, 233.9, 229.8, 229.1 (CO); 155.2 ($C_1$); 143.4 ($C_\beta$); 95.3, 94.2 ($C_5H_5$); 142.3 ($C_\gamma$); 128.6 ($C_2$, $C_{2'}$); 126.0 ($C_3$, $C_{3'}$); 128.2 ($C_4$); 23.0 ($CH_3$). IR ($CH_2Cl_2$ solution); ν(C≡O) 1966 m, 1902 s, 1848 m; ν(C=C=C) 1653 m cm$^{-1}$ MS: *m/e* 562 [M]$^+$; 534 [M − CO]$^+$; 506 [M − 2CO]$^+$; 478 [M − 3CO]$^+$; 450 [M − 400]$^+$.

### 4.9. X-ray structure analysis of 1b

A single crystal of $[Cp_2Mo_2(CO)_4(\mu\text{-}C{=}C{=}C_6H_{10})]$ grown from a dichloromethane–pentane mixture was mounted on a Enraf–Nonius CAD-4 four-circle automatic diffractometer. The unit cell was determined and refined from 25 randomly selected reflections observed by the use of the CAD-4 automatic routines.

Crystal data: formula, $C_{22}H_{20}Mo_2O_4$; molecular weight, 540.282; triclinic $P\bar{1}$ (No 2); $a$ = 9.295(4), $b$ = 10.765(4), $c$ = 11.801(6) Å; $\alpha$ = 75.05(4), $\beta$ = 69.49(5), $\gamma$ = 70.46(4)°; $V$ = 1028.93 Å$^3$, λ(Mo Kα) = 0.71069 Å; μ(Mo Kα) = 12.135 cm$^{-1}$, $Z$ = 2; $d_{calcd}$ = 1.744 g cm$^{-3}$.

The intensities of 1778 independent reflections mea-

Table 2
Selected bond lengths (Å) and bond angles (°) for **1b**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Mo(1)–Mo(2) | 3.163(2) | C(15)–C(16) | 1.35(1) |
| Mo(1)–C(1) | 1.94(1) | C(16)–C(17) | 1.33(1) |
| Mo(1)–C(2) | 1.93(1) | C(17)–C(18) | 1.52(2) |
| Mo(2)–C(3) | 1.99(1) | C(17)–C(22) | 1.50(2) |
| Mo(2)–C(4) | 1.96(1) | C(18)–C(19) | 1.54(2) |
| Mo(1)–C(15) | 2.20(1) | C(19)–C(20) | 1.56(2) |
| Mo(2)–C(15) | 1.90(1) | C(20)–C(21) | 1.51(2) |
| Mo(1)–C(16) | 2.26(1) | C(21)–C(22) | 1.52(2) |
| *Bond angles* | | | |
| Mo(1)–C(1)–O(1) | 174.(1) | Mo(1)–C(16)–C(15) | 69.9(7) |
| Mo(1)–C(2)–O(2) | 177.(1) | C(15)–C(16)–C(17) | 146.(1) |
| Mo(2)–C(3)–O(3) | 176.(1) | C(16)–C(17)–C(18) | 125.(1) |
| Mo(2)–C(4)–O(4) | 179.(1) | C(16)–C(17)–C(22) | 121.(1) |
| Mo(1)–C(15)–Mo(2) | 100.6(4) | C(17)–C(18)–C(19) | 111.(1) |
| C(15)–Mo(1)–C(16) | 35.2(4) | C(18)–C(19)–C(20) | 110.(1) |
| Mo(1)–C(15)–C(16) | 74.9(8) | C(19)–C(20)–C(21) | 109.(1) |
| Mo(2)–C(15)–C(16) | 168.5(8) | C(20)–C(21)–C(22) | 111.(1) |

Numbers in parentheses are estimated standard deviations.

Table 3
Positional parameters and their estimated standard deviations

| Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Mo(1) | 0.4017(1) | 0.41319(9) | 0.31454(8) | 2.83(2) |
| Mo(2) | 0.3405(1) | 0.16609(9) | 0.25903(8) | 3.18(2) |
| O(1) | 0.364(1) | 0.225(1) | 0.5660(8) | 6.5(3) |
| O(2) | 0.131(1) | 0.582(1) | 0.4965(8) | 6.8(3) |
| O(3) | 0.675(1) | 0.062(1) | 0.311(1) | 7.3(3) |
| O(4) | 0.538(1) | 0.156(1) | −0.0144(9) | 7.7(4) |
| C(1) | 0.373(1) | 0.292(1) | 0.470(1) | 4.3(3) |
| C(2) | 0.228(1) | 0.518(8) | 0.428(1) | 4.4(3) |
| C(3) | 0.552(1) | 0.105(1) | 0.291(1) | 4.2(3) |
| C(4) | 0.463(2) | 0.161(1) | 0.086(1) | 4.9(4) |
| C(5) | 0.650(2) | 0.386(1) | 0.162(2) | 7.3(5) |
| C(6) | 0.572(2) | 0.512(2) | 0.135(1) | 6.3(4) |
| C(7) | 0.535(1) | 0.578(1) | 0.235(1) | 5.3(4) |
| C(8) | 0.604(1) | 0.486(1) | 0.323(1) | 5.6(4) |
| C(9) | 0.680(2) | 0.363(2) | 0.277(2) | 7.0(5) |
| C(10) | 0.162(2) | 0.089(2) | 0.436(1) | 8.4(4) |
| C(11) | 0.074(2) | 0.156(2) | 0.363(2) | 7.2(5) |
| C(12) | 0.129(2) | 0.098(2) | 0.263(1) | 8.1(5) |
| C(13) | 0.251(2) | −0.016(1) | 0.278(1) | 8.2(5) |
| C(14) | 0.267(2) | −0.022(2) | 0.391(2) | 10.2(6) |
| C(15) | 0.268(1) | 0.356(1) | 0.2251(9) | 3.2(3) |
| C(16) | 0.202(1) | 0.488(1) | 0.2256(9) | 3.0(3) |
| C(17) | 0.088(1) | 0.594(1) | 0.2001(9) | 3.4(3) |
| C(18) | 0.055(2) | 0.731(1) | 0.232(1) | 5.1(3) |
| C(19) | 0.014(2) | 0.843(1) | 0.128(1) | 5.0(4) |
| C(20) | −0.128(2) | 0.828(1) | 0.096(1) | 5.1(4) |
| C(21) | −0.082(1) | 0.694(1) | 0.056(1) | 4.9(3) |
| C(22) | −0.038(1) | 0.580(1) | 0.157(1) | 4.8(3) |

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

sured in a $\omega$–$2\theta$ scan ($\theta_{min} = 1°$, $\theta_{max} = 25°$), with $I > 3\sigma(I)$ among 3609 data collected were used in the solution and refinement of the structure (253 variables).

The structure was solved by the direct methods program MULTAN [21]. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated by the "hydro" program of SDP and were not refined. All these atoms were included in the final calculations with $B_{iso}$ (H) = 1.3 $B_{iso}$ (C) (C is the carbon atom bearing the hydrogen atom).

Because of the small size of the crystal, no correction for absorption was carried out. The weighting scheme employed was $w = 4F_o^2/[\sigma^2(F_o)^2 + 0.08F_o^2]^2$. The final residuals were $R = 0.046$ and $R_w = 0.063$, goodness of fit = 1.18, $\Delta\rho(max) = 0.9$ e Å$^{-3}$. Selected bond distances and selected bond angles and the final atomic coordinates are listed in Tables 2 and 3. A list of observed and calculated structure factors is available from the authors. Full lists of bond lengths and angles, atomic coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

## Acknowledgement

We thank Dr. J. Talarmin (University of Brest) for helpful discussions.

## References

[1] N. Le Berre-Cosquer, R. Kergoat and P. L'Haridon, *Organometallics, 11* (1992) 721.
[2] J.F. Capon, S. Cornen, N. Le Berre-Cosquer, R. Pichon, R. Kergoat and P. L'Haridon, *J. Organomet. Chem., 470* (1994) 137.
[3] S.F.T. Froom, M. Green, K.R. Nagle and D.J. Williams, *J. Chem. Soc., Chem. Commun.*, (1987) 1305.
[4] A. Meyer, D.J. McCabe and M.D. Curtis, *Organometallics, 6* (1987) 1491.
[5] M. Gruselle, V. Philomin, F. Chaminant, G. Jaouen and K.M. Nicholas, *J. Organomet. Chem., 399* (1990) 317.
[6] M. Gruselle, C. Cordier, M. Salmain, H. El Amouri, C. Guérin, J. Vaissermann and G. Jaouen, *Organometallics, 9* (1990) 2993.
[7] S.F.T. Froom, M. Green, R.J. Mercer, K.R. Nagle, A.G. Orpen and S. Schwiegk, *J. Chem. Soc., Chem. Commun.*, (1986) 1666.
[8] S.F.T. Froom, M. Green, R.J. Mercer, K.R. Nagle, A.G. Orpen and R.A. Rodrigues, *J. Chem. Soc., Dalton Trans.*, (1991) 3171.
[9] H. Berke, P. Härter, G. Huttner and L. Zsolnai, *Chem. Ber., 115* (1982) 695.
[10] H. Berke, U. Grössmann, G. Huttner and L. Zsolnai, *Chem. Ber., 117* (1984) 3423.
[11] M. Etienne and L. Toupet, *J. Chem. Soc., Chem. Commun.*, (1989) 1110.
[12] M.I. Bruce, *Chem. Rev., 91* (1991) 197.
[13] W.I. Bailey Jr., M.H. Chisholm, F.A. Cotton, C.A. Murillo and L.A. Rankel, *J. Am. Chem. Soc., 100* (1978) 802.
[14] G.H. Young, M.V. Raphael, A. Wojcicki, M. Calligaris, G. Nardin and N. Bresciani-Pahor, *Organometallics, 10* (1991) 1934.
[15] R.M. Silverstein, G.C. Bassler and T.C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 4th edn., 1981, p. 229.
[16] L.M. Jackman and R.H. Wiley, *J. Chem. Soc.*, (1960) 2881.
[17] D. Pilette, K. Ouzzine, H. Le Bozec, P.H. Dixneuf, C.E.F. Rickard and W.R. Roper, *Organometallics, 11* (1992) 809.
[18] N. Pirio, D. Touchard and P.H. Dixneuf, *J. Organomet. Chem., 462* (1993) C18.
[19] D. Touchard, C. Morice, V. Cadierro, P. Haquette, L. Toupet and P.H. Dixneuf, *J. Chem. Soc., Chem., Commun.*, (1994) 859.
[20] M.D. Curtis, N.A. Fotinos, L. Messerle and A.P. Sattelberger, *Inorg. Chem., 22* (1983) 1559.
[21] P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.P. Declercq and M.M. Woolfson, MULTAN. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. University of York, York; University of Louvain, Louvain, 1982.