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Activation of propargylic alcohols by dimolybdenum tris(μ-thiolate) complexes: Influence of the substituents R in HC≡CCR$_2$(OH)-vinylidene/allenylidene transformation. Reactivity of allenylidene complexes

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Abstract

Reaction of the bis(nitrile) complex [Mo$_2$Cp$_2$(μ-SMe)$_3$(NCMe)$_2$](BF$_4$) (**1**) with dimethylpropargylic alcohol, HC≡CCMe$_2$(OH), at room temperature in dichloromethane produced good yields of the μ-alkynol species [Mo$_2$Cp$_2$(μ-SMe)$_3${μ-CHCCMe$_2$(OH)}](BF$_4$) (**2a**) through replacement of the two acetonitrile ligands in **1** by the alkynol. The NMR spectra of **2a** indicate a μ-η^1:η^1 coordination mode for the alkyne which is thereby incorporated into a dimetallacyclobutene ring like that found here by X-ray diffraction (XRD) analysis of the related complex [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-η^1:η^1-CHCCO$_2$Me)](BPh$_4$) (**2b**). When **2a** was stirred with Et$_3$N at room temperature in dichloromethane, deprotonation gave high yields of the μ-3-hydroxyalkynyl derivative [Mo$_2$Cp$_2$(μ-SMe)$_3${μ-η^1:η^2-CCCMe$_2$(OH)}] (**3**), together with small amounts of the already-known vinylacetylide [Mo$_2$Cp$_2$(μ-SMe)$_3${μ-η^1:η^2-CCC(Me)CH$_2$}] (**4**) resulting from dehydration of **3**. Treatment of **3** with 1 equiv. of HBF$_4$ · OEt$_2$ in diethyl ether at room temperature gave the 3-hydroxyvinylidene derivative [Mo$_2$Cp$_2$(μ-SMe)$_3${μ-η^1:η^2-CCHCMe$_2$(OH)}](BF$_4$) (**5**) as the major product, together with other minor products [Mo$_2$Cp$_2$(μ-SMe)$_3${μ-η^1:η^2-CCHC(Me)CH$_2$}](BF$_4$) (**6**), [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-η^1:η^2-CCCMe$_2$)](BF$_4$) (**7**), [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-η^1:η^2-CCH$_2$)](BF$_4$) (**8**), [Mo$_2$Cp$_2$(μ-SMe)$_3${μ-η^1:η^2-CCH(CHMe$_2$)}](BF$_4$) (**9**) and [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-O)](BF$_4$) (**10**). The vinylidene (**6**) and allenylidene (**7**) species resulted from dehydration of the 3-hydroxyvinylidene complex **5** whereas the vinylidene derivative **8** was formed by deketonisation of **5**. When **3** reacted with a large excess of HBF$_4$ · OEt$_2$ in dichloromethane, the 3-isopropylvinylidene complex **9** was obtained nearly quantatively *via* a H$^\cdot$ radical process. When left for several days CD$_2$Cl$_2$ solutions of **5** afforded mainly the vinylidene species **8** by deketonisation and the side-oxoproduct [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-O)](BF$_4$) (**10**) by hydrolysis or reaction with oxygen. Addition of nucleophiles (H$^-$, OMe$^-$, OH$^-$, SMe$^-$) to the allenylidene complex [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-η^1:η^2-CCCPh$_2$)](BF$_4$) (**11**) resulted in the formation of the corresponding μ-acetylide derivatives [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-η^1:η^2-CCCRPh$_2$)] [R = H (**12**), OMe (**16a**), OH (**17**), SMe (**16b**)], which by further reaction with tetrafluoroboric acid afforded either the vinylidene species [Mo$_2$Cp$_2$(μ-SMe)$_3${μ-η^1:η^2-CCH(CRPh$_2$)}](BF$_4$) when R = H (**13**), or the starting complex **11** when R is a leaving group (OMe). Reaction of **13** with Na(BH$_4$) gave the μ-alkylidyne complex [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-η^1-CCH$_2$CPh$_2$H)] (**14**) by nucleophilic attack of H$^-$ at the C$_\beta$ carbon atom of the vinylidene chain. Proton addition at C$_\alpha$ in **14** led to the formation of a μ-vinylidene compound **15** containing an agostic C–H bond. New complexes have been characterised by elemental analyses and spectroscopic methods, supplemented for **2b** and **3** by X-ray diffraction studies.

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1. Introduction

The activation of propargylic alcohols by transition metal complexes generally leads, either directly or *via* the resulting hydroxyvinylidene compounds, to the formation of allenylidene complexes. These may in turn undergo further reactions [1]. The facile dehydration of the hydroxyvinylidene derivatives often prevents their isolation and characterisation [2]; exceptions to this rule include those which cannot be dehydrated to give an allenylidene [3] and those which are particularly resistant to dehydration [4]. It is well established that for aliphatic alkyn-1-ols, as opposed to their aromatic analogues, dehydration of the corresponding hydroxyvinylidene cations, $\{[M]{=}C_\alpha{=}C_\beta HC_\gamma RR'(OH)\}^+$, can proceed in two distinct ways: (i) across the C_β–C_γ bond to give an allenylidene derivative, or (ii) across a C_γ–C_δ bond to afford alkenylvinylidene species. The precise factors which govern the mode of dehydration of hydroxyvinylidene derivatives [5] are still unclear. Moreover, it should be noted that dehydration, which most of the time is spontaneous, is the characteristic reaction of hydroxyvinylidene complexes; in contrast, elimination of ketones, which requires harsh conditions, has rarely been observed [6].

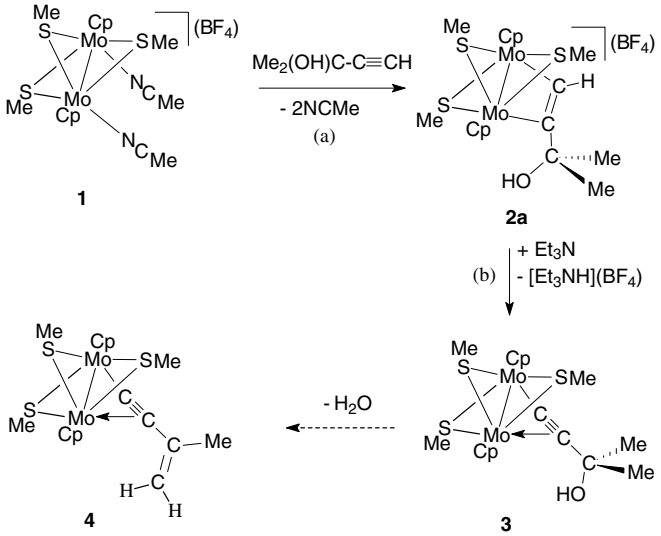
Though the synthesis and properties of hydroxy- and alkenyl-vinylidene derivatives [5,7] have attracted much attention, even more has been focused on the formation and reactivity of allenylidene complexes [8]. The rapid development of the chemistry of allenylidene derivatives is mainly the result of the presence in the carbon chain of both electrophilic and nucleophilic sites. Many types of reaction are thereby made feasible. Thus, since transition metal allenylidene species are delocalised systems, one may expect that their properties will critically depend on the electronic and steric characteristics of both the substituents of the C_γ carbon atom and of the ancillary ligands at the metal atoms. Indeed, it has been shown in theoretical and experimental studies [1b,8c,9] that the reactivity of these derivatives is mainly governed by the electron-deficient character of the C_α and C_γ carbon atoms which are potential sites for nucleophilic attack. Moreover, it has been calculated that the respective charges on C_α, C_β and C_γ are −0.48, −0.02 and −0.19 in a typical μ-η^2-allenylidene dimolybdenum species [10]; this suggests that in similar complexes nucleophilic attack on C_α and C_γ is expected to be orbital-controlled, whereas electrophilic attack on C_α would be charge-controlled.

The activation of propargylic alcohols by transition metal complexes to give allenylidene derivatives *via* 3-hydroxyalkynyl and 3-hydroxyvinylidene intermediates is predominantly a reaction of mononuclear [1,11] or trinuclear [12] derivatives of Fe, Ru and Os. Examples involving binuclear compounds of other transition metals have until now been scarce [13]. We recently [2d] reported the activation of the propargylic alcohol $HC{\equiv}CCPh_2(OH)$ by the bis(nitrile) complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(NCCH_3)_2](BF_4)$ (**1**) to give the allenylidene compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}C{=}CPh_2)](BF_4)$ (**11**) *via* a μ-alkynyl derivative, implying a four step process. However, though two of the three postulated intermediates were isolated, the third, a hydroxyvinylidene species, proved elusive. It is reasonable to expect that the activation of propargylic alcohols $HC{\equiv}CCRR'(OH)$ will change if the R and R′ substituents are electron-releasing alkyl groups rather than π-acceptors such as phenyl. Accordingly, we now describe the activation of $HC{\equiv}CCMe_2(OH)$ by the tris(thiolate) dimolybdenum derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3(NCMe)_2](BF_4)$ (**1**) and compare the results with those previously obtained with $HC{\equiv}CCPh_2(OH)$ and **1** [2d]. We have also considered the effect of the R/R′ groups of the alkynol on the reactivity of the corresponding allenylidene complexes with various nucleophiles.

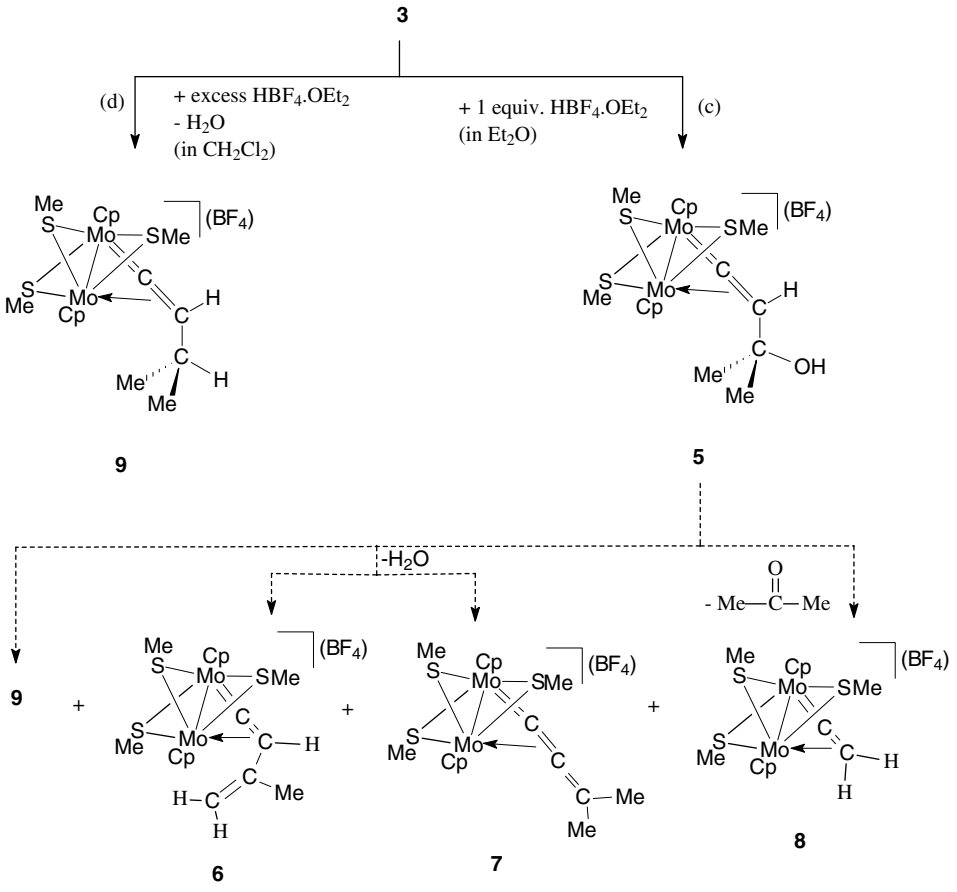
2. Results and discussion

2.1. Activation of $HC{\equiv}CCMe_2(OH)$ by the dimolybdenum tris(thiolate) complex 1: multi-step syntheses of vinylidene and allenylidene derivatives

Schemes 1 and 2 summarise the activation reactions of dimethylpropargylic alcohol discussed here. The first step of the synthesis of vinylidene and allenylidene derivatives



Scheme 1.



Scheme 2.

consists in reacting the bis(nitrile) complex **1** with $HC{\equiv}CCMe_2(OH)$ in dichloromethane at room temperature to give compound **2a** in 60% yield after work-up. Crystals of **2a** suitable for X-ray analysis could not be obtained. Nevertheless, **2a** has been formulated as the electron-deficient Mo^{III}-Mo^{III} species $[Mo_2Cp_2(\mu\text{-}SMe)_3\{HCCCMe_2(OH)\}](BF_4)$ by spectroscopy and elemental analysis (see Section 4) though these methods did not allow the mode of coordination of the alkyne to be reliably established. In an attempt to address this problem, we have examined by X-ray analysis the structure of the related complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(HCCCO_2Me)](BPh_4)$ (**2b**) which we previously synthesised [14]. The structural results for **2b** are complicated by the disorder of the cation and only brief discussion is appropriate.

Each atom of the **2b** cation is distributed 2:1 over two sites, A and B. The more populated A sites define the structure shown in Fig. 1 in which the well-known $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ unit is bridged by a bidentate, doubly bent $HC{\equiv}C\text{–}CO_2Me$ group σ-bonded to the Mo_2 unit through both carbon atoms [Mo–C 2.03(2) and 2.08(2) Å]. The alkyne lies parallel to the metal–metal bond with a Mo1–C4–C5–Mo2 torsion angle of 2°. The bending

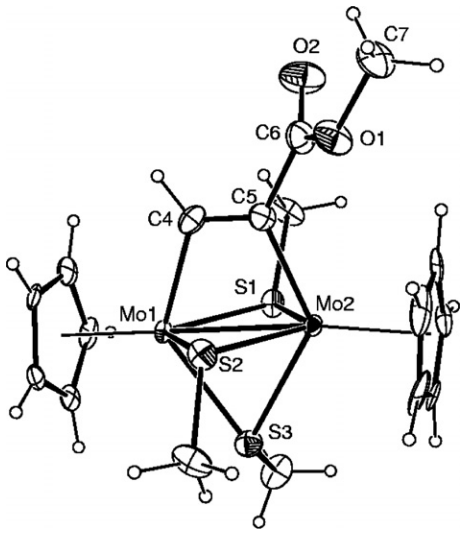


Fig. 1. View of the $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}HCCCO_2Me)]^+$ cation in crystals of **2b**. Each atom of the cation is disordered over two sites; only the major sites with occupancy 0.67 are shown here. Ellipsoids at the 20% probability level are shown, except for hydrogen atoms. Selected distances (Å) and angles (°): Mo1–Mo2 2.705(7); Mo1–C4 2.08(2); Mo2–C5 2.03(2); C4–C5 1.26(2); C5–C6 1.55(2); Mo–S 2.40(1)–2.48(1); C5–C4–Mo1, 111(1); C4–C5–C6, 122(1); C4–C5–Mo2, 110(1); C6–C5–Mo2, 129(1).

back angle of the carboxy substituent C4–C5–C6 [122(1)°] is typical of alkynes bound in this fashion [15]. The μ-η^1,η^1 bridge is unusual for molybdenum and only one similar complex has been the subject of a diffraction study, namely *syn*-[Mo_2Cp_2(μ-S)(μ-SPr^i)$_2$(μ-η^1,η^1-C_2Ph_2)] [16]. Its Mo1–Mo2 distance of 2.684 Å is similar to that of 2.705(7) Å in **2b**; both are typical for quadruply bridged $Mo(III)_2Cp_2(\mu\text{-}SMe)_3$ moieties and indicate bonds of unit order [17]. It is apparent from Fig. 1 that the methyl groups of the thiolate bridges have an *anti*-orientation in **2b**. The B sites define an equivalent cation with the alternative *anti* tris(thiolate) arrangement (see Supplementary material). We consider that the X-ray study establishes **2b** as a μ-η^1,η^1-complex and therefore formulate **2a** as [$Mo_2Cp_2(\mu\text{-}SMe)_3$(μ-$\eta^1$:$\eta^1$-$HCCCMe_2(OH)$)]($BF_4$), with a parallel orientation of the C–C axis of the alkyne relative to that of the Mo–Mo bond, on the basis of the similarity of the spectroscopic data of **2a** and **2b**.

Treatment of the isolated complex **2a** with triethylamine in dichloromethane at room temperature produced deprotonation of the η^1:η^1-alkyne ligand to give the alkynyl derivative **3** as the major product (~76.5% yield), together with small amount of the vinylacetylide species **4**. The latter complex resulted from slow dehydration of **3**, possible for a $C(CH_3)_2C(OH)$ system with deprotonable methyl groups (Scheme 1). Compounds **3** and **4** were inseparable by chromatography. However, they have been characterised by NMR spectroscopy and the molecular structure of **3** was established by X-ray analysis of dark green crystals which separated from a cold diethylether solution of a mixture of **3** and **4** in 5:1 ratio. Complex **4** was identified as the vinylacetylide [{$Mo_2Cp_2(\mu\text{-}SMe)_3$(μ-$\eta^1$-CCC(Me)-$CH_2$}] by comparison of its ^{1}H NMR data with those of an authentic sample which we had made previously by a different route [14]. The ^{13}C–{^{1}H} NMR spectra in solution for **3** were highly informative about the structure: they showed the low-field resonance for the α-carbon at 131.1 ppm and the β-carbon at higher field (δ 120.1 ppm), as expected for acetylenic carbon atoms [18], as well as a singlet at δ 66.2 ppm attributable to the *C*Me_2(OH) carbon atom [2d].

The X-ray analysis of **3** confirms the unsymmetrical *side-on* coordination of the bridging acetylide ligand (Fig. 2). The Mo–Mo separation [2.622(2) Å] is typical for quadruply bridged $Mo_2^{III}Cp_2(\mu\text{-}SMe)_3$ systems with single metal–metal bonds [17]. The structure of **3** strongly resembles that of the related *p*-tolylacetylide derivative [Mo_2Cp_2(μ-$SMe)_3$(μ-η^1:η^2-C≡C–C_6H_4Me)] which we have described previously [14]. Thus, the three-electron-donor acetylide in **3** σ-bonds terminally to Mo1 and π-bonds unsymmetrically *via* its C4–C5 triple bond to Mo2. Valuable back-donation from Mo1 is responsible for the shortening of the Mo1–C4 bond to 2.066(4) Å and the lengthening of the C4–C5 bond to 1.212(6) Å. For comparison, in the *p*-tolylacetylide species the corresponding distances are 2.068(3) and 1.238(4) Å [14]. In **3**, the coordination of the *sp*-hybridised C4 carbon atom deviates slightly from

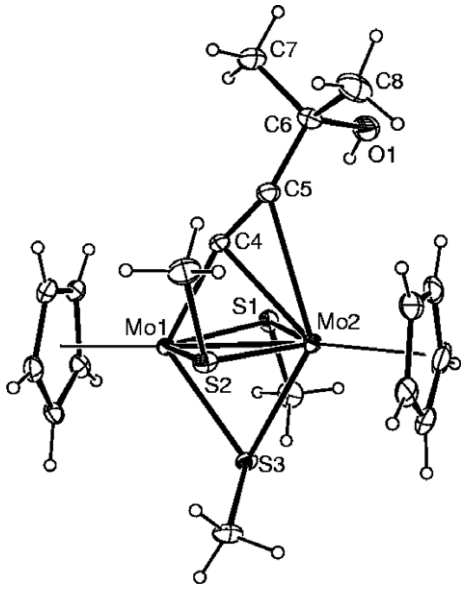
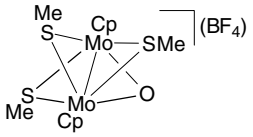


Fig. 2. View of a molecule of complex **3** showing 20% probability ellipsoids for non-hydrogen atoms. Selected distances (Å), angles (°) and torsion angles (°): Mo1–Mo2 2.622(2); Mo1–C4 2.066(4); Mo2–C4 2.365(4); Mo2–C5 2.701(4); C4–C5 1.212(6); C5–C6 1.481(5); Mo–S 2.440(2)–2.486(2); C4–C5–C6 161.2(4); C5–C4–Mo1 163.2(3); C5–C4–Mo2 92.4(3); C4–C5–Mo2 61.0(2); C6–C5–Mo2 135.0(3); S3–Mo1–Mo2–C4 175.3(1); S1–Mo1–Mo2–S2 176.1(1); C4–Mo1–Mo2–C5 −3.2(2).

linearity but the Mo1–C4–C5 angle [163.2(3)°] is within the range expected for M_2(μ-η^1:η^2-CCR) groups [18]. The C4–C5–C6 and Mo2–C5–C6 angles in **3** are 161.2(4)° and 135.0(3)°, respectively. They differ slightly from the corresponding values for the related *p*-tolylacetylide species of 168.5(3)° and 125.2(2)°, respectively [14]. Lastly, the *S*-methyl groups again show the *anti*-arrangement also found in **2b**.

While mononuclear transition metal complexes containing both 3-hydroxyalkynyl and hydrido ligands rearrange spontaneously to their 3-hydroxyvinylidene isomers [1m], such a transformation needs to begin with addition of protons to the acetylide ligand in the case of **3**. Thus, treatment of **3** with 1 equiv. of $HBF_4 \cdot OEt_2$ in diethylether at room temperature gave the 3-hydroxyvinylidene derivative **5** as the major product, together with minor products **6**–**10** [Scheme 2 – reaction (c) and Section 4]. Unfortunately, we have not been able to separate these complexes by chromatography and all attempts to isolate them as crystalline solids from the reaction mixture failed. Despite this, the characterisation of these compounds can be carried out on the basis of the NMR [^{1}H and ^{13}C–{^{1}H}] and 2D NMR data recorded on the reaction mixtures. Comparison of these data with those of authentic samples allows us to identify safely the minor products **6**, **8** and **10** as [$Mo_2Cp_2(\mu\text{-}SMe)_3$(μ-$\eta^1$:$\eta^2$-C=CH($CMe=CH_2$)}]($BF_4$) [14], [$Mo_2Cp_2(\mu\text{-}SMe)_3$(μ-$\eta^1$:$\eta^2$-C=$CH_2$)]($BF_4$) [14], and [$Mo_2Cp_2$(μ-O)(μ-$SMe)_3$]($BF_4$), respectively. It has been assumed that **6** is mainly formed by dehydration of the vinylidene product **5** (Scheme 2). However, it should be noted that the hydroxyl-alkynyl compound **3** cannot be



10

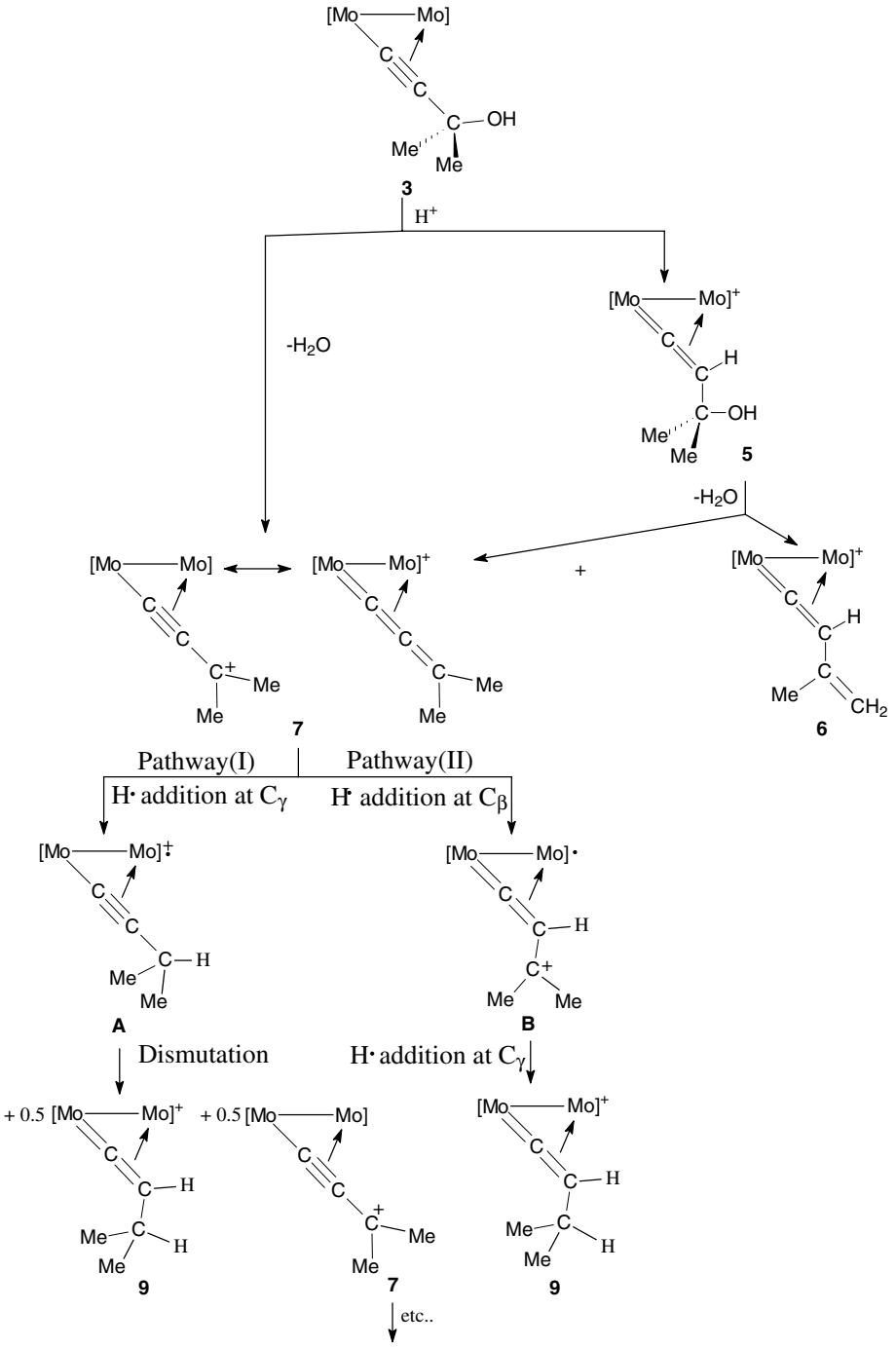
Chart 1.

obtained in pure form (see Section 4), being contamined with traces of the enynyl derivative **4**, therefore part amounts of complex **6** could also result from direct protonation of **4**. Complex **10** is identified with an oxo-derivative, that was previously obtained by another route and characterised by elemental analyses and ^{1}H NMR spectroscopy [19] (Chart 1). This side product probably results from the reaction of either **3** or **5** with traces of either dioxygen or water in the solvent. A more clear way to give **10** would involve a vinylidene π-alkyne tautomerization and subsequent displacement of the coordinated alkyne by oxygen; however, such a mechanism is not firmly confirmed, because no terminal alkyne was detected in the reaction media by ^{1}H NMR spectroscopy. The minor product **9** was identified on the basis of ^{1}Hand ^{13}C NMR data as $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}CH(CHMe_2)\}](BF_4)$; it will be discussed below. It should be noted that a separate experiment showed that compound **7** is formed in higher yields through the reaction of **3** with $HBF_4 \cdot OEt_2$ in dichloromethane instead of diethyl ether (see Section 4). The new vinylidene (**5**) and allenylidene (**7**) compounds were identified by NMR spectroscopy. The vinylidene bridge $\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_\alpha{=}C_\beta HR$ ($R = C(OH)Me_2$) was characterised by the observation of a ^{1}H resonance of 7.01 ppm, which was assigned to the $=C_\beta HR$ group, and of two resonances in the ^{13}C NMR spectrum at low field in the typical carbene (360.9 ppm) and vinyl (125.7 ppm) ranges: these were assigned to C_α and C_β, respectively. The 2D experiments revealed for **5** the expected correlation ($^1J_{C-H} = 167.5$ Hz) of the vinylidene group at δ 7.01 with C_β at δ 125.7, confirming the proposed structure. The $^{13}C\text{–}\{^1H\}$ NMR spectra of **7** contain three resonances at low or very low field, δ 307.6, 170.0 and 139.2, in the typical allenylidene chain range, which were assigned to C_α, C_β and C_γ, respectively. The very low field chemical shift (δ 307.6), attributed to the carbenoid carbon atom (C_α) of **7**, is indicative of an asymmetric side-on coordination mode of the allenylidene group bridging a bimetallic core ([M]-[M]) for which a $^{13}C_\alpha$ chemical shift is usually observed in the range 310-282 ppm [13a,18b,20], and it contrasts with the values of 206.5–173 ppm reported for related end-on species [13b,21]. Finally, a single resonance was observed for the two cyclopentadienyl groups in the vinylidene and allenylidene compounds **5** and **7**, suggesting that windshield wiper fluxionality occurs in solution at room temperature [18b].

The evolution over time of solutions containing the mixture of products from reaction (c) (Scheme 2) was examined six times under the same conditions and gave similar results. In a typical reaction the thermal transformation of a mixture containing **5** (65%), **6** (8.5%), **7** (7.0%), **8** (2.0%), **9** (7.0%), **10** (7.0%) and **2a** (3.5%) was undertaken in CD_2Cl_2 and was monitored by the changes in the room temperature ^{1}H NMR spectra with time. The most striking feature was the dramatic decrease in the relative amount of **5** from 65.0 to 19.0%, balanced by sharp increases in the amounts of **8** (2.0 → 27.0%) and acetone present. Evidently vinylidene **5** is transformed into vinylidene **8** by loss of a molecule of acetone, as indicated in Scheme 2. However, another important feature of the results was the noticeable increase in the amount of oxo-compound **10** (7.0 → 26%). This could be explained if the vinylidene derivatives reacted with oxygen or water present in the CD_2Cl_2 solution. Otherwise, the small amounts of complexes **6**, **7** and **9** also present in the starting mixture did not change much with time (see Section 4), suggesting that these three vinylidene and allenylidene species are rather stable in solution at room temperature. Finally, it should be noted that very small amounts of the μ-alkyne derivative **2a** and an uncharacterised cyclopentadienyl compound were formed in some experiments; the latter was detected only by its ^{1}H–Cp signal at δ 6.57. The most notable feature of the chemistry of 2-methyl-3-butyn-2-ol coordinated to two molybdenum atoms evident from these reactions was its transformation in solution in a few hours at room temperature into acetone and a vinylidene ligand. The latter species is a tautomer of the η^2-acetylene ligand. Elimination of acetone involves a highly reactive hydroxyvinylidene complex **5**, which simultaneously undergoes a $C_\beta\text{–}C_\gamma$ bond cleavage and an internal proton addition to the nucleophilic C_β atom of the unsaturated chain. Elimination of a ketone in this way is rare, and we know of only one similar example which involves the reaction of $Fe_3(CO)_{12}$ with internal propargylic alcohols to give uncharacterised products [6]. Interestingly, the reaction observed here is the reverse of the synthetic route to propargylic alcohols based on the condensation of an alkyne with a ketone [22]. However, it is worth noting that reactions giving rise to ketones from C–C bond scissions in vinylidene or allenylidene ligands are already known, though they involve $C_\alpha\text{–}C_\beta$ rather than $C_\beta\text{–}C_\gamma$ cleavages. For example, Cadierno and Gimeno have demonstrated that 1,1-diphenyl-2-propyn-1-ol can be isomerised into 3,3-diphenyl-2-propenal by hydrolysis of the $C_\alpha\text{–}C_\beta$ double bond of the allenylidene ligand of a mononuclear cationic ruthenium complex, acting in this case as an active catalyst [1i]. It has also been shown that hydrolysis of coordinated terminal alkynes leads to alkyl-carbonyl ruthenium or iridium complexes according to a mechanism which involves a metal-assisted $C_\alpha\text{–}C_\beta$ bond cleavage, postulated to occur *via* vinylidene intermediates [23].

Unexpectedly, the 3-hydroxyvinylidene derivative **5** was not obtained when the protonation of the μ-acetylide **3** was performed with a large excess of $HBF_4 \cdot OEt_2$. Instead, a new complex was formed. Thus, **3** reacted with about 10 equiv. of tetrafluoroboric acid in dichloromethane to give,

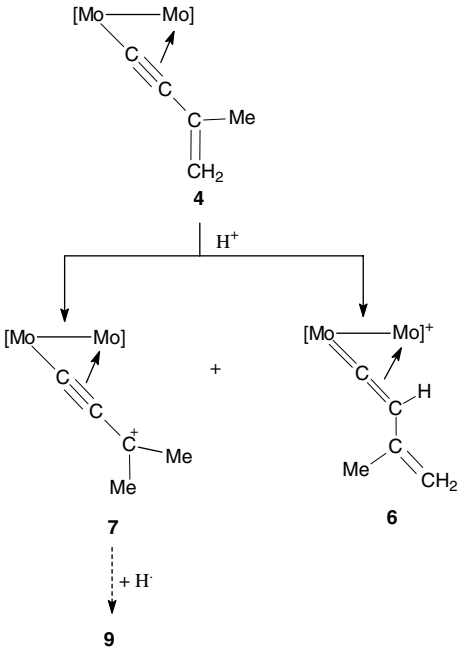
after work up, substantial amounts of a red powder [see Section 4; Scheme 2 – reaction (d)]. Solutions of this powder in dichloromethane-d solution contained only one product **9** detectable by ^{1}H NMR. Its structure is based on elemental analysis, 1D ^{1}H, ^{13}C–{^{1}H}, and 2D NMR experiments. ^{1}H–^{13}C HMBC experiments reveal the expected correlations ($^{2}J_{C-H}$) of the protons of the methyl groups at δ 1.05 with Cγ (δ 31.25) and those of the proton at δ 2.42 with signals for the C$_\beta$ [at δ 123.4 ($^{2}J_{C-H}$)] and C$_\alpha$ [at δ 365.05 ($^{3}J_{C-H}$)] carbon atoms of a vinylidene ligand. Additional correlations of the proton of the vinylidene group at δ 6.68 with signals for the Cγ [at 31.25 ($^{2}J_{C-H}$)] and C$_{methyl}$ [at δ 25.3 ($^{3}J_{C-H}$)] carbon atoms confirm the presence of an isopropyl group in **9**. In parallel, the observation of a septuplet at δ 2.42 in the ^{1}H NMR spectrum indicates coupling of a proton with two methyls, as expected for a CH(CH$_3$)$_2$ group. In addition, with the aim of verifying further the selective formation of an isopropyl moiety, a ^{1}H–^{1}H COSY showed a correlation of the proton at δ 6.67 with that at 2.42 *via* a $^{3}J_{H-H}$



Scheme 3. Proposed routes for the formation of **9** from the acetylide **3**. [Mo–Mo] = CpMo(μ-SMe)$_3$MoCp.

(8.0 Hz) coupling. These data confirm the 3-isopropylvinylidene structure proposed for **9** in Scheme 2.

We have shown above that the addition of 1 equiv. of $HBF_4 \cdot OEt_2$ to a diethyl ether solution of the μ-acetylide complex **3** led mainly to the 3-hydroxyvinylidene derivative **5** by protonation of the C_β carbon atom of the acetylide ligand, together with **6**, **7**, **8** and **9** as minor products [Scheme 2 – reaction (c)]. It is obvious that **5** was the initial product of this reaction, partially evolving during the taking of the ^1H NMR spectrum at room temperature in dichloromethane-d into **6, 7, 8** and **9**. Substitution of dichloromethane for diethyl ether (see Section 4) favoured production of the allenylidene **7** at the expense of **5** but the yield of **9** barely changed. In contrast, **9** was the only product detected by ^1H NMR when **3** reacted with a large excess of tetrafluoroboric acid in dichloromethane [Scheme 2 – reaction (d)]. Evidently, both the amount of acid added and the solvating properties of CH_2Cl_2 and Et_2O help to determine whether **5** or **9** is the major product of these reactions. While the route to the μ-3-hydroxyvinylidene complex **5** from the μ-acetylide **3** is well established, the processes which produce the μ-3-isopropylvinylidene derivative **9** are less clear. We therefore decided to monitor reactions (c) and (d) (Scheme 2) by cyclic voltammetry. This revealed that for both reactions several steps are probably involved. Separate experiments showed that the μ-acetylide compound **3** was readily consumed in these reactions. Thus, the main feature of the CV was the presence in the solution of two products whose potentials, $E_{1/2}^{red} = -0.60$ and −0.90 V, are consistent with those of μ-acetylide and μ-vinylidene derivatives [24], respectively. Several attempts to get X-ray grade crystals of the new μ-acetylide compound ($E_{1/2}^{red} = -0.60$ V) from the reaction mixture were unsuccessful. Despite this, it is possible (see Scheme 3) to propose two reaction paths from **3** to **9** consistent with both the CV observations and the known structures though some of the elementary steps involved remain conjectural. The initial step, common to both pathways, is dehydration of the μ-acetylide complex **3** promoted by proton addition, to give directly or *via* the μ-3-hydroxyvinylidene **5** the intermediate **7**, shown in Scheme 3 in both its propargyl carbocation and cationic allenylidene forms. In solution, **7** is weakly stable and, like other mononuclear acetylides [25], readily adds H· radicals, either at the C_γ carbon atom to give either intermediate **A** (pathway (I)) or at the C_β carbon atom to give intermediate **B** (pathway (II)). Intermediate **A** is probably the μ-acetylide species detected in cyclic voltammetry experiments. It finally dismutates into the μ-3-isopropylvinylidene product **9** and the propargyl carbocation form of **7** (pathway (I)). Alternatively, the radical species **B** adds a second H· radical at the C_γ carbon atom, finally giving **9** (pathway (II)). This mechanism is also supported by the characterisation of the side-product **6** in reaction (c). Low yields of **9** in reaction (c) may be attributed both to the high stability of **5** in solution and the competition between the dehydration and deketonisation processes.



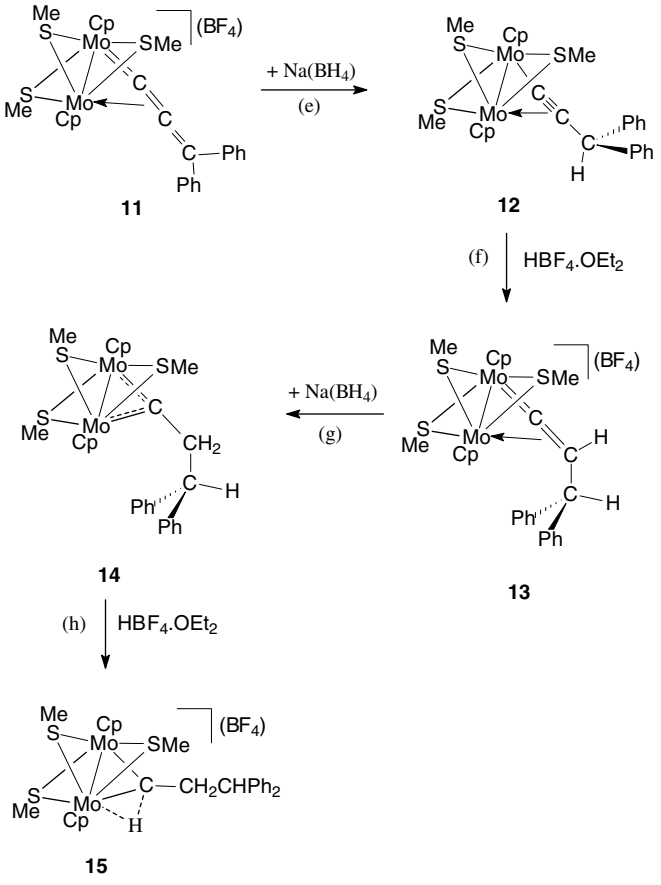
Scheme 4. Proposed route for the formation of **9** from the acetylide **4**. [Mo–Mo] = $CpMo(\mu\text{-}SMe)_3MoCp$.

To examine further the role of **7** as an intermediate we reacted the μ-vinylacetylide compound **4** [14] with an excess of $HBF_4 \cdot OEt_2$ in dichloromethane. As hoped, the μ-isopropylvinylidene species **9** was obtained as the major product, together with moderate yields of the μ-vinylidene compound **6** (see Section 4). The first step of this reaction (Scheme 4) reasonably involves the formation of **7** (in its propargyl carbocation form) by direct protonation at C_δ. Its subsequent reaction with H· radicals leads to **9** *via* the route proposed in pathways (I) and (II) of Scheme 3. Compound **9** was not obtained quantitatively, presumably because of competition with the proton addition at C_γ in **4** to afford the minor product **6**. These results are consistent with our hypothesis that the route to **9** is through **7**, as suggested in Scheme 3.

2.2. Reactivity of the diphenylallenylidene compound *11*

One of the aims of the present work was to see how different substituents affect reactions of allenylidenes with electrophiles and nucleophiles. The low stability of solutions of the dimethylallenylidene derivative **7** has unhappily precluded a complete study. Therefore, we mainly consider here the reactivity of the diphenylallenylidene complex **11**, previously isolated as a pure derivative in the reaction of the propargylic alcohol, $HC{\equiv}CCPh_2(OH)$, with the bis(nitrile) complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(NCCH_3)_2](BF_4)$ (**1**) [2d].

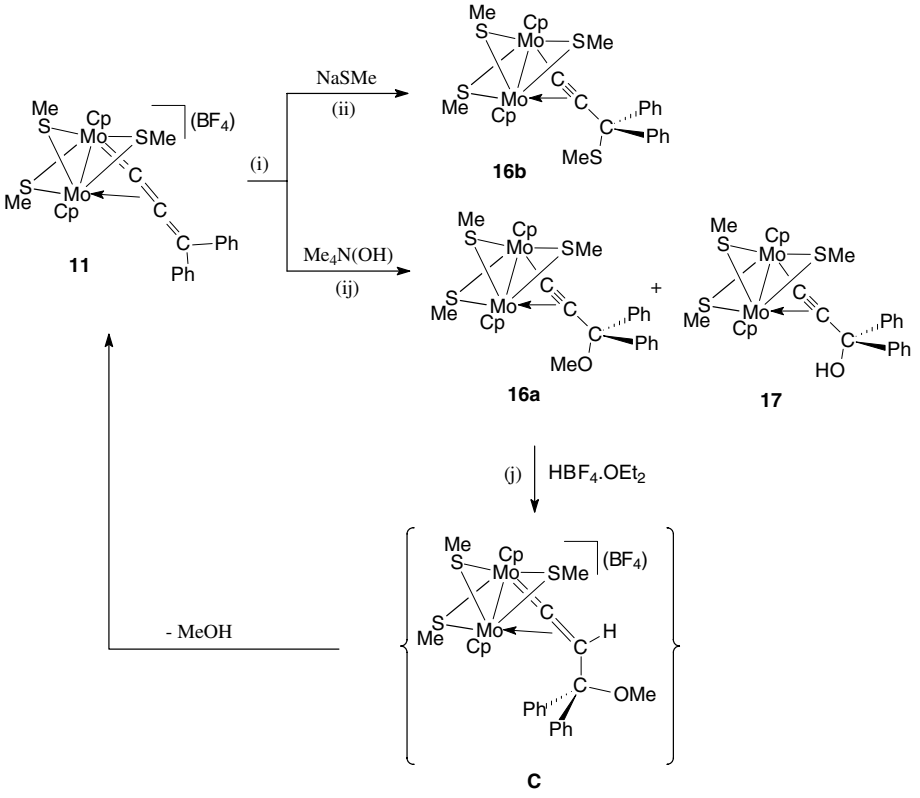
In an attempt to exploit the electron-deficient character of the C_α and C_γ carbon atoms of the unsaturated allenylidene chain we added methanol to the μ-diphenylallenylidene compound **11**, but no reaction was observed. Evidently, nucleophilic attack of methanol on the electrophilic C_α



Scheme 5.

carbon atom did not occur, perhaps inhibited by the two phenyl substituents which tend to delocalise the positive charge and thus to stabilise the allenylidene ligand see Ref. [1o]. However, when **11** was treated with a strong nucleophile such as sodium borohydride in acetonitrile, good yields of the μ-acetylide compound **12** were obtained by selective addition of hydride at the electrophilic C_γ carbon atom [Reaction (e) in Scheme 5]. Similarly, **11** in dichloromethane reacted with 1.5 equiv of $Me_4N(OH)$ in MeOH to give μ-acetylide derivatives **16a** (yield: 68.5%) and **17** (yield: 9%), together with low amounts of an oxochloro by-product [Reaction (ij) in Scheme 6]. Formation of **16a** and **17** illustrates the ability of $Me_4N(OH)$ in MeOH to act as both a strong (OMe^-) and moderately strong (OH^-) nucleophile, adding selectively to the electrophilic C_γ allenylidene carbon atom. When sodium thiomethoxide was added to a dichloromethane solution of **11**, a mixture of products inseparable by chromatography was obtained. Despite this, the characterisation of a μ-thioacetylide species **16b**, obtained in low yields (~27%), is possible from ^{1}H NMR data recorded on the reaction mixture [Reaction (ii) in Scheme 6]. This result may suggest that the thiomethoxide anion is a weaker nucleophile than H^-, OMe^- or OH^-.

Products **12**, **16a**, **16b** and **17** were characterised analytically and from multinuclear (^{1}H and ^{13}C) NMR spectroscopic data given in Section 3. Complex **17** and the oxochloro by-product obtained in reaction (ij) (Scheme 6) were identified by comparing their ^{1}H NMR spectra with



Scheme 6.

those of authentic samples of $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CCPh_2(OH)\}]$ [2d] and $[Mo_2Cp_2(O)(Cl)(\mu\text{-}SMe)_3]$ [26]. The presence of the alkynyl ligand in **12** was established from the $^{13}C\text{–}\{^1H\}$ spectrum which has only one resonance corresponding to the acetylenic carbon atoms [18a,2d] at 113.45 ppm and a singlet at 49.0 ppm due to the CPh_2H. The close similarity of the ^1H NMR of **12** with those of **16a** and **16b** suggests that these three compounds have similar geometries and that **16a** and **16b** also contain alkynyl fragments. The ^1H NMR spectra of compounds **12**, **16a** and **16b** differ obviously by the resonances attributable to the alkynyl substituents: 4.53 ppm to $CPh_2\mathit{H}$ in **12**, 2.98 ppm to $CPh_2(O\mathit{Me})$ in (**16a**) and 1.62 ppm to $CPh_2(S\mathit{Me})$ in **16b**. The ^1H NMR spectra of **12**, **16a** and **16b** display only one Cp signal, indicating that these complexes are fluxional at room temperature.

Turning to allenylidene complexes with electron-releasing substituents in their unsaturated chains, we have shown [Section 2.1: Scheme 2 – reaction (d), and Scheme 3] that a dichloromethane solution of the μ-allenylidene complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}C{=}CMe_2)](BF_4)$ (**7**) undergoes $H^{\cdot}$ radical reaction in presence of an excess of $HBF_4\cdot OEt_2$. This involves hydrogen abstraction from the solvent to give the μ-isopropylvinylidene species **9**. This contrasts with the stabilisation of $\mu\text{-}\eta^1{:}\eta^2$-(4e)(side-on) allenylidene ligands by carbonyl groups in related dimolybdenum and -tungsten complexes which add protons to give propargylium cations $[\{M_2(CO)_4Cp_2\}(\mu\text{-}\eta^2\text{-}HC_2CMe_2)]^+$ (M = Mo, W) [10,18b] rather than the isopropylvinylidene cations obtained here. These propargylium cations are thought to be stabilised by the presence of electron-donating substituents on the unsaturated chain and by ancillary carbonyl ligands. In fine, it should be noted that two types of allenylidene complex are here compared: the three μ-thiolate donor ligands of **7** contrast with the four π-acceptor carbonyl groups of the $[\{M_2(CO)_4Cp_2\}(\mu\text{-}\eta^2\text{-}HC_2CMe_2)]^+$ (M = Mo, W) complexes [10,18b].

Further reactions of the μ-diphenylalkynyl derivative **12** with tetrafluoroboric acid allowed the isolation in high yield of the stable μ-vinylidene compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}CHCPh_2H)](BF_4)$ (**13**) [Reaction (f) in Scheme 5 and Section 4]. Compound **13** was formed by proton attack at the nucleophilic C_β carbon atom of the acetylide ligand. It should be noted that the corresponding hydroxyvinylidene derivative, $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}CHCPh_2(OH)\}](BF_4)$, was an elusive species which readily dehydrated into allenylidene **11** [2d]. Compound **13** was identified by analytical data and NMR spectroscopy. The ^1H NMR spectrum exhibited the two sets of resonances expected for the $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ core and for the $\mu\text{-}\eta^1{:}\eta^2\text{-}C_\alpha{=}C_\beta HCPh_2H$ vinylidene bridge. The latter gives rise to a multiplet between 7.45 and 7.33 ppm and two doublets at 7.37 and 4.66 ($J_{H\text{–}H}$ = 14.4 Hz) ppm; these were, respectively, assigned to the two phenyl groups, the $C_\beta\mathit{H}R$ group (R = CPh_2H) and the $CPh_2\mathit{H}$ alkyl group. The ^{13}C NMR spectra showed two resonances at low field in the carbene (365.55 ppm) [27] and vinyl (118.3 ppm) ranges; they were assigned to C_α and C_β, respectively, thus confirming the structure ascribed to this complex in Scheme 5. When $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}CCCPh_2(OMe)\}]$ (**16a**), where the alkynyl ligand contains a good leaving group, reacted with 1 equiv. of tetrafluoroboric acid in diethyl ether at room temperature, **11** was quantitatively obtained [Reaction (j) in Scheme 6] instead of a vinylidene species. Compound **11** may be formed by spontaneous loss of methanol from the uncharacterised $\mu\text{-}\eta^1{:}\eta^2$-methoxyvinylidene intermediate **C** (Scheme 6).

Reaction of **13** with an excess of $Na(BH_4)$ in acetonitrile at room temperature readily afforded deep blue solutions from which $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CCH_2CPh_2H)]$ (**14**) was isolated in good yield as a blue powder [Scheme 5 – reaction (g) and Section 4]. The dinuclear complex **14** was formed by a classical addition [28] of H^- to the electrophilic C_β atom of the vinylidene $C_\alpha{=}C_\beta HCPh_2H$ bridge in **13**. It was characterised by elemental analysis and NMR spectroscopy. Its ^1H NMR (C_6D_6) spectrum was typical for derivatives with a $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ core; it exhibited a single resonance at 5.22 ppm for the two cyclopentadienyl ligands and three peaks for the three SMe bridges [17]. Instead of the characteristic ^1H NMR resonance of the C_β HR group in **13** at δ 7.37, two protons were detected as a doublet ($J_{H\text{–}H}$ = 8.0 Hz) between 4 and 5 ppm, confirming that the hydride anion had added to the outer carbon atom (C_β) of the vinylidene group to give a new hydrocarbyl bridging compound. The ^{13}C NMR spectra of **14** displayed a typical μ-alkylidyne signal at extreme low field (445.4 ppm) [29]. The equivalence of the Cp groups suggests that the alkylidyne bridge is symmetrically bonded to the two molybdenum atoms and that the π-Mo–C overlap required by electron-counting rules, is delocalised through the Mo–C–Mo bridge. A poor-quality X-ray analysis of a single crystal of **14**, obtained at room temperature from a CH_2Cl_2 solution layered with diethyl ether, is consistent with these conclusions (see Supplementary material). It shows a $\mu\text{-}CCH_2CPh_2H$ group symmetrically bridging the two molybdenum atoms of a $[Mo_2Cp_2\{\mu\text{-}SMe)_3\}]$ core through a single carbon atom. The Mo–C distances [2.02(2) and 2.03(2) Å] in **14** lie between the values of 1.894(5) Å for the formally double Mo=C bond in the vinylidene compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}CHTol)](BF_4)$ and 2.068(3) Å for the single Mo–C bond in the acetylide derivative $[Mo_2Cp_2(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CPh)]$ [14]. They indicate a symmetrical coordination of the alkylidene group through Mo–C bonds of order 1.5. Several other μ-alkylidyne-molybdenum species, such as $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CCH_2\mathit{n}\text{-}Pr)]$, $[Mo_2Cp(\mu\text{-}SMe)_3\{\mu\text{-}(\eta^5\text{-}C_5H_4)(\mathit{t}\text{-}BuN)CN(\mathit{t}\text{-}Bu)C\}]$ and $[Mo_2Cp(\mu\text{-}SMe)_2\{\mu\text{-}(\eta^5\text{-}C_5H_4)(xylN)CN(xyl)C\}\{\mu\text{-}OCNRR'\}]$ complexes, have been structurally characterised [28,30]. The coordination of the bridging carbon atom in **14** resembles those of the corresponding atoms in other μ-alkylidyne bimetallic complexes, for example $[(C_5Me_5)WMe(\mu_2\text{-}CCH_3)]_2$ [31]

and $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CCH_2n\text{-}Pr)]$ [28] and the length of the Mo–Mo single bond [2.578(2) Å] is typical of the values reported for other $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}X)]$ complexes [17]. The methyl groups of the thiolate bridges again adopt the *anti*-orientation.

We have previously shown that μ-alkylidyne derivatives $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CCH_2R)]$ were readily protonated, forming μ-alkylidene species $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCH_2R)](BF_4)$ (R = Tol, *n*-Pr), which, according to NMR evidence, exhibit α-agostic interactions [28]. A computed structure of the μ-alkylidene model $[Mo_2Cp_2(\mu\text{-}SH)_3(\mu\text{-}CHCH_2\ Tol)](BF_4)$ confirmed the presence of an α-agostic interaction [32]. Since this is yet to be confirmed by XRD analysis, we reacted **14** with 1 equiv. of tetrafluoroboric acid in diethyl ether at room temperature, obtaining good yields of the desired μ-alkylidene derivative **15** [Reaction (h) in Scheme 5 and Section 4]. Analytical data and NMR spectroscopy clearly indicated that **15** arose from a *face-addition* [33] of a proton to a Mo–C bond in **14**. Thus, the ^{1}H NMR spectrum displayed the resonances expected for the phenyl groups, the $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ core and the methylene group (at 4.20 ppm), as well as a broad (unresolved triplet) high-field resonance at −4.78 ppm ascribed to a single hydrogen atom. This high-field shift strongly suggests the presence of a $\{Ph_2CH_2C(\mu\text{-}H)Mo\}$ backbone featuring an α-agostic interaction [33,34]. Comparison of the ^{1}H and ^{13}C NMR data of **15** (see Section 4) with those of the closely related compounds $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}CHCH_2R)](BF_4)$ (R = Tol, *n*-Pr) [28] supports this suggestion. Unfortunately, several attempts to perform an X-ray analysis on different samples of crystals of **15**, formed at room temperature from a CH_2Cl_2 solution layered with diethylether, cannot be considered satisfactory (see Supplementary material). The most that can be said is that the X-ray results are consistent with the chemical and spectroscopic evidence which indicates the formation of a $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CHCH_2CPh_2H)]^+$ cation containing an asymmetrically bridging μ-C carbon atom [Mo–C 2.02(2) and 2.29(2) Å], in agreement with an agostic interaction. It should be noted that the more common β-agostic structure [35] is not adopted by **15**, perhaps for steric reasons.

2.3. Electrochemistry of the allenylidene complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}CCCPh_2)](BF_4)$ (**11**)

The cyclic voltammetry of **11** in CH_2Cl_2-$[NBu_4][PF_6]$ showed that the complex underwent two one-electron reductions steps with $E_{1/2}{}^{red1} = -0.93$ V and $E_{1/2}{}^{red2} = -1.32$ V (Fig. 3a, Scheme 7), as well as two irreversible oxidation peaks at $E_p{}^{ox1} = 0.39$ V and $E_p{}^{ox2} = 0.99$ V. Both

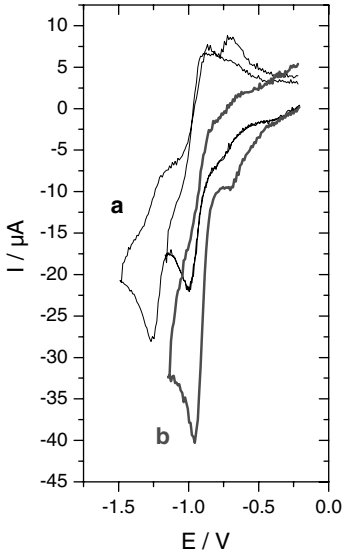


Fig. 3. Cyclic voltammetry of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}CCCPh_2)](BF_4)$ (**11**) (ca. 0.6 mM) (a) in the absence of acid, and (b) after addition of 3 equiv. of CF_3CO_2H in CH_2Cl_2-$[NBu_4][PF_6]$ (vitreous carbon electrode).

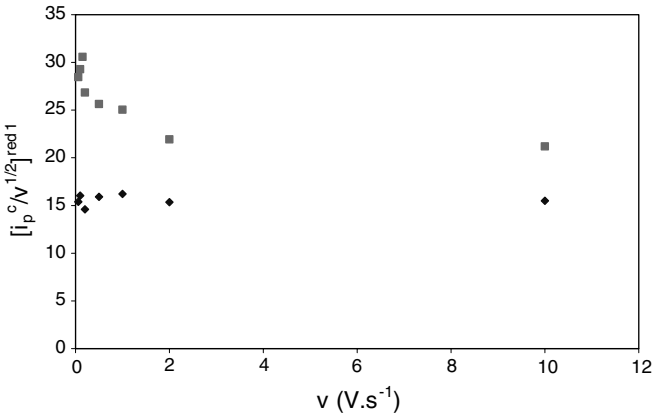
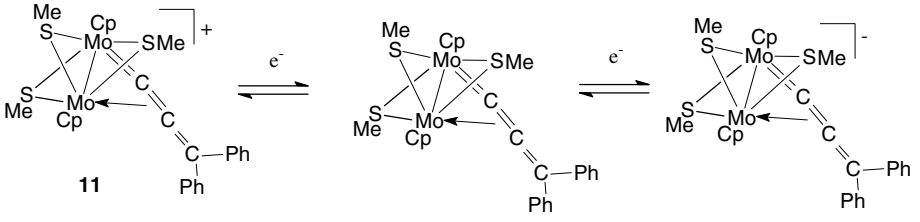
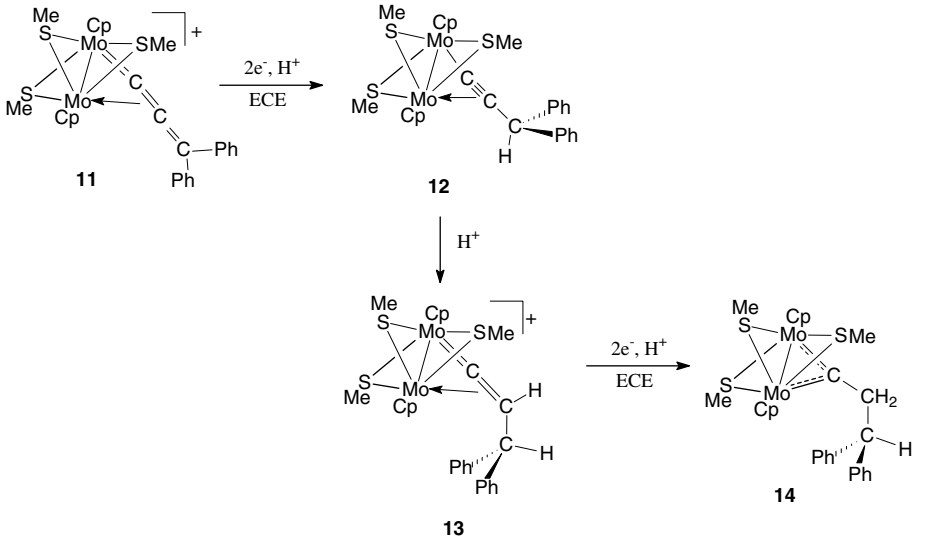


Fig. 4. Scan rate dependence of the current function $[i_p{}^c/v^{1/2}]^{red}$ for a CH_2Cl_2-$[NBu_4][PF_6]$ solution of **11** (ca. 0.3 mM) (a) (♦) in the absence and (b) (■) in the presence of 1 equiv. of $HBF_4 \cdot OEt_2$.



$E_{1/2}{}^{red1}$ = -0.93 V $E_{1/2}{}^{red2}$ = -1.32 V

Scheme 7.



Scheme 8.

reduction steps are essentially electrochemically reversible, with $\Delta E_p = 100$ mV at $v = 0.2$ V s^{-1}. However, measurements of the peak current ratio $[(i_p^a/i_p^c)^{red} < 1$, $(i_p^a/i_p^c)^{red}$ increased with increasing scan rate] indicated that the electron transfers were followed by chemical reactions (EC process) whose products were detected by the appearance of an oxidation peak around −0.6 V on the reverse scan.

Controlled-potential reduction of **11**, carried out at a potential of 100 mV negative relative to that of the first reduction process, was complete after the passage of ca. 1 F mol^{-1}. Cyclic voltammetry and ^{1}H NMR of the catolyte confirmed the instability of the reduced form of **11** and the presence of an EC process. Unfortunately, attempts to determine the nature of the products formed upon electrochemical reduction of **11** failed.

Upon addition of acid ($HBF_4 \cdot OEt_2$ or CF_3CO_2H) to a CH_2Cl_2-[NBu_4][PF_6] solution of **11**, CV showed that the current of the first reduction increases while that of the second decreases, consistent with the occurrence of an ECE process (Fig. 3b). Furthermore, the variations of the current function $i_p^{red}/v^{1/2}$ against v deviate markedly from linearity at slow scan rates (Fig. 4b), again confirming that the reduction of **11** in the presence of acid occurred according to an ECE process (Scheme 8).

Controlled-potential reduction of **11** in the presence of 3 equiv. of CF_3CO_2H (3.3 F mol^{-1} **11**) led to the formation of [Mo_2Cp_2(μ-SMe)$_3$(μ-η^1:η^2-CCCPh$_2$H)] (**12**) and [Mo_2Cp_2(μ-SMe)$_3$(μ-CCH$_2$CPh$_2$H)] (**14**) as the major products (45% and 55%, respectively), as shown by the ^{1}H NMR spectrum of the solid residue separated from the supporting electrolyte. During the electrolysis the dark purple solution turned blue. Electrolysis performed in the presence of 1 equiv. of $HBF_4 \cdot OEt_2$ produced (**14**) (ca. 30%) and unidentified product (ca. 70%) after transfer of ca. 3 F mol^{-1} **11**.

The formation of [Mo_2Cp_2(μ-SMe)$_3$(μ-η^1:η^2-CCCPh$_2$H)] (**12**) could be expected by both electrochemical reduction of **11** and protonation at Cγ. This is confirmed by the fact that **12** was the product of the chemical reaction of hydride with **11** (see above). However, the amount of **12** formed during the reaction showed that a consecutive protonation, occurring at the C_β atom of **12**, must be significantly fast and would produce the vinylidene species [Mo_2Cp_2(μ-SMe)$_3${μ-η^1:η^2-CC(H)CPh$_2$H}][BF_4] (**13**). Previously, we demonstrated that the electrochemical reduction in the presence of acid of the [Mo_2Cp_2(μ-SMe)$_3$(μ-η^1:η^2-CCPhH]$^+$ cation (at $E_p = -1.1$ V) gave quantitatively the corresponding alkylidyne derivative [Mo_2Cp_2(μ-SMe)$_3$(μ-CCH$_2$Ph)] by a two-electron ECE process [24]. Therefore, the rapid reaction of the μ-acetylide complex **12** with acid accounted for the formation of **13**, which was reduced at the potential of the cathode ($E_q = 1.1$ V) to give the μ-alkylidyne species [Mo_2Cp_2(μ-SMe)$_3$(μ-CCH$_2$CPh$_2$H)] (**14**) by reaction with acid (Scheme 8). Theoretically, 3 equiv. of acid and 4 F mol^{-1} **13** are needed to form **14** quantitatively, but this was not experimentally observed. Some acid might be lost during the electrolysis (3 h) by either oxidation or slow reaction involving solvents. The electrolysis performed with larger excesses of acid gave the μ-alkylidyne complex as the major product.

3. Conclusion

In summary, the activation of aromatic alkyn-1-ols by mononuclear transition metal complexes has generally resulted in the selective formation of allenylidene compounds by dehydration of 3-hydroxyvinylidene intermediates *via* successively the proposed η^2-alkynol and hydroxyalkynyl derivatives [1m]. Here, in contrast, the activation of aliphatic alkyn-1-ols (e.g. HC≡CCMe$_2$(OH)) with the bis(nitrile) dimolybdenum compound [Mo_2Cp_2(μ-SMe)$_3$(NCCH$_3$)$_2$][BF_4] (**1**) afforded either the μ-3-hydroxyvinylidene (**5**) or the μ-3-isopropylvinylidene (**9**) derivatives depending on experimental conditions. In these reactions,

the formation of **9** would imply an unprecedented radical process. The route to the two vinylidene species **5** and **9** has implicated the μ-η^1:η^1-alkynol-bridged complex **2a** and the μ-hydroxyalkynyl **3** as successive intermediates; both were isolated and fully characterised by NMR spectroscopy and X-ray analysis. Further evolution of solutions of the μ-3-hydroxyvinylidene complex **5** involved either dehydration across the C_β–C_γ or C_γ–C_δ bonds to give the dimethylallenylidene (**7**) and alkenylvinylidene (**6**) derivatives, respectively, or deketonisation affording the vinylidene **8**.

The properties of allenylidene complexes are mainly based on both the electron-deficient and electron-rich characters of the C_γ or C_β carbon atoms of the unsaturated chain of the allenylidene ligand [1b,8c–10].We have now demonstrated that both the substituents of the allenylidene chain and the ancillary ligands in our complexes help to direct the reaction. For example, protonation of allenylidene complexes with electron-donating substituents in the unsaturated chain involved either $H^\bullet$ radical reaction in the case of compound **7**, or formation of propargylium cations when the dialkylallenylidene derivative is stabilised by ancillary carbonyl ligands [10,18b]. When the allenylidene complexes contain electron-withdrawing substituents in their unsaturated chain, e.g. **11**, they display typical reactivity with nucleophiles: thus, addition of H^-, OMe^-, OH^- or SMe^- to **11** gave the expected hydroxyalkynyl derivatives **12**, **16a**, **17** or **16b**. Further addition to these isolated acetylide complexes of H^+, H^- and again H^+ successively afforded the new μ-diphenylvinylidene (**13**), μ-alkylidyne (**14**) and α-agostic μ-alkylidene (**15**) derivatives. Finally, it should be noted that the instability of solutions of the μ-dimethylallenylidene **7** makes it difficult to compare its reactivity with the μ–diphenylallenylidene analogue **11**.

4. Experimental

4.1. General procedures

All reactions were carried out using standard Schlenk techniques under an inert atmosphere. Solvents were deoxygenated and dried according to standard procedures. The starting materials $[Mo_2Cp_2(\mu\text{-}SMe)_3(NCCH_3)_2](BF_4)$ (**1**) [36] and $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}C{=}CPh_2)](BF_4)$ (**11**) [2d] were prepared as described previously. All other reagents were purchased commercially. Elemental analyses were obtained from the Service de Microanalyse I.C.S.N., Gif sur Yvette (France). The NMR spectra (^1H, ^{13}C) were recorded at room temperature in CD_2Cl_2, C_6D_6, $CDCl_3$, or $(CD_3)_2CO$ solution on either a Bruker AC 300 or AMX3 400 and DRX 500 spectrometers and were referenced to $SiMe_4$. ^1H–$^1H$and ^1H–^{13}C experiments were performed on a Bruker DRX 500 spectrometer. Column chromatography was carried out with silica gel.

The preparation and the purification of the $[NBu_4][PF_6]$ supporting electrolyte were as described previously [37]. Cyclic voltammetric experiments were performed with a PGSTAT 12 driven by an AUTOLAB software. Controlled-potential electrolyses were performed using Tacussel/Radiometer 6CU potentiostat and IG5-N integrator. The cell and electrodes were as described previously [37]. All the potentials (text, Table 1, figures) are quoted against the ferrocene-ferrocenium couple; ferrocene was added as an internal standard at the end of the experiments.

4.2. Synthesis of the μ-alkyne *2a*

A solution of complex **1** (200 mg, 0.316 mmol) in CH_2Cl_2 (20 mL) was stirred in the presence of 1 equiv. of $HC{\equiv}CCMe_2(OH)$ (30 μL) for 50 min at room temperature. The solution turned from red to green. The solvent was then concentrated, and diethyl ether (30 mL) was added. A green solid precipitated, was collected by filtration, was washed with pentane (2 × 15 mL) and then was dried under vacuum. Compound **2a** was obtained as a green powder (120 mg) in 60% isolated yield. ^1H NMR [$(CD_3)_2CO$]: δ 13.30 (s, 1H, *H*C═C), 6.74 (s, 10H, C_5H_5), 4.37 (s, 1H, O*H*), 2.26, 2.07 and 1.91 (s, 3H, SCH_3), 0.96 (s, 6H, CH_3). Anal. Calc. for $C_{18}H_{27}BF_4Mo_2OS_3$: C, 34.1; H, 4.2. Found: C, 33.8; H, 3.8%.

4.3. Synthesis of the μ-acetylide *3*

A solution of **2a** (140 mg, 0.22 mmol) in dichloromethane (10 mL) was stirred in the presence of 2 equiv. of Et_3N (62 μL) for 15 min at room temperature. The colour of the solution turned from pale green to dark green. The

Table 1
Crystallographic data for complexes **2b** and **3**

Compound	**2b**	**3**
Empirical formula	$C_{41}H_{43}BMo_2O_2S_3$	$C_{18}H_{26}Mo_2OS_3$
Formula weight	866.62	546.45
Temperature (K)	170	295
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	11.1944 (16)	7.854 (3)
b (Å)	9.9876(6)	8.416(6)
c (Å)	34.0784(14)	16.0643(12)
α (°)		93.08(2)
β (°)	97.669(5)	98.02(2)
γ (°)		104.10(5))
V (Å^3)	3776.1(3)	1015.6(8)
Z	4	2
ρ_{calc} (Mg mm^{-3})	1.524	1.787
μ (mm^{-1})	0.865	1.546
Crystal size (mm)	0.55 × 0.40 × 0.02	0.16 × 0.12 × 0.08
Range of θ (°)	2.9–25.2	2.8–26.3
Reflections measured	23460	4983
R_{int}	0.040	0.019
Unique data/parameters	5867/535	4110/223
R_1 [$I > 2\sigma(I)$]	0.081	0.0363
R_1 (all data)	0.089	0.0460
wR_2 (all data)	0.164	0.104
Goodness-of-fit on F^2	1.096	1.038
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.41, −1.34	1.02, −1.12

solvent was then removed under vacuum and organometallic products were extracted with diethyl ether (2 × 15 mL). The diethyl ether was removed and the crude products (120 mg) were analysed in C_6D_6 by ^1H NMR spectroscopy. Compounds **3** and **4**, and two uncharacterised by-products were, respectively, formed in about the 10:2:1 ratio. On the basis of ^1H NMR spectra of the mixture the yields of **3** and **4** were estimated at 76.5% and 15.5%, respectively. Attempts to separate cleanly the complexes by chromatography failed, only the by-products were eliminated from the mixture of products. For this reason, no elemental analysis is available for **3**. However, the major product **3** has been fully characterised by X-ray analysis of dark green crystals of this complex, which were picked from a cold (−20 °C) diethyl ether solution of a mixture of **3** and **4** in a 5:1 ratio. Compound **4** has been characterised by comparison of its ^1H NMR data with those of an authentic sample [14]. Compound **3**: ^1H NMR (C_6D_6): δ 5.32 (s, 10H, C_5H_5), 1.66, 1.61 and 1.51 (s, 3H, SCH_3), 1.37 (s, 6H, CH_3); O*H* is not observed. ^{13}C–{^1H} NMR (C_6D_6): δ 131.1 (Mo–*C*≡C), 120.1 (Mo–C≡*C*), 91.0 (C_5H_5), 66.2 (C(OH)Me_2), 25.1 (C(OH)(CH_3)$_2$), 17.0, 12.8 and 11.8 (SCH_3).

4.4. Reaction of 3 with $HBF_4 \cdot OEt_2$ (1 equiv.) in diethyl ether

In a typical experiment, 1 equiv. of $HBF_4 \cdot OEt_2$ (27 μL) in diethyl ether (20 mL) was added with stirring to a solution of **3** (110 mg, 0.2 mmol) in diethyl ether (5 mL) at room temperature. A brick-red solid readily precipitated from the solution and was collected by filtration and washed with diethyl ether (3 × 15 mL). The ^1H NMR spectrum of the resultant powder (129 mg) indicated the presence mainly of six products **5**, **6**, **7**, **9, 10** and **8**, in a molar ratio of 9.5:1.25:1:1:1 and 0.25. Attempts to separate cleanly the complexes by either chromatography or crystallisation failed, and therefore no analytical data are available for the main new products **5** and **7**. However, all the new compounds have been properly characterised by ^1H and ^{13}C NMR spectroscopy and by 2D NMR experiments (^1H, ^{13}C HMQC and HMBC). The other complexes in CD_2Cl_2 [**6** and **8** [14], **9** (see below), and **10** [19]] have been identified by comparison of their NMR data with those of pure samples. The above experiment was performed six times and was shown to be reproducible, except for moderate to notable changes in the amounts of products **5**, **6**, **7**, **8**, **9** and **10** (+ small trace of the starting compound **2a**), which were formed in 56.0–74.0%, 5.0–9.0%, 6.5–24.0%, 0.0–9.0%, 2.0–9.0% and 0.0–6.5% (%: relative to all diamagnetic products) yields, respectively. *Caution:* the tetrafluoroboric acid-diethyl ether complex used for the experimental should be rigorously anhydrous. ^{13}C–{^1H} NMR and ^2D NMR experiments were undertaken on a sample containing **5** and **7** as major products, i.e. 60% and 24%, respectively. Full ^{13}C NMR assignments of compounds **5** and **7** were based on ^1H–^{13}C HMQC and HMBC experiments. Compound **5**: ^1H NMR (CD_2Cl_2): δ 7.01 (s, 1H, =C*H*), 6.21 (s, 10H, C_5H_5), 2.72 (s.br, 1H, O*H*), 1.86, 1.56 and 1.49 (s, 3H, SCH_3), 1.29 (s, 6H, CH_3). NMR ^{13}C–{^1H} ($CDCl_3$): δ 360.9 (Mo=*C*=C), 125.7 (=*C*H), 97.4 (C_5H_5), 76.4 (C(OH)Me_2), 33.0 (C(OH)Me_2), 18.6, 10.5 and 6.7 (SCH_3).

Compound 7: ^1H NMR (CD_2Cl_2): δ 6.16 (s, 10H, C_5H_5), 2.36 (s, 6H, CH_3), 1.92, 1.61 and 1.42 (s, 3H, SCH_3). ^{13}C–{^1H} NMR (CD_2Cl_2): δ 307.6 (Mo=*C*=C=C), 170.0 (Mo=C=*C*=C), 139.2 (Mo=C=C=*C*), 96.8 (C_5H_5), 29.6 (=CMe_2), 22.2, 11.7 and 8.9 (SCH_3).

4.5. Reaction of 3 with $HBF_4 \cdot OEt_2$ (1 equiv.) in dichloromethane

In a similar manner, 1 equiv. of $HBF_4 \cdot OEt_2$ (14 μL) was added to a solution of **3** (58 mg, 0.10 mmol) in dichloromethane (5 mL) instead of diethyl ether. The mixture was then stirred for 5 min, at room temperature. A greenish solid was precipitated by addition of diethyl ether (20 mL) and was collected by filtration and washed with diethyl ether (3 × 15 mL). The ^1H NMR spectrum of acetone-d solution of the resultant powder (36 mg) indicated the presence of four products **5**, **6**, **7**,and **9**, in a molar ratio of 5.5:1:3:1.

4.6. Thermal evolution of solutions containing a mixture of the products obtained in reaction (d)

In a typical experiment (see Section 4.4), a NMR tube was charged with a mixture of **5** (65.0%), **6** (8.5%), **7** (7.0%), **8** (2.0%), **9** (7.0%), **10** (7.0%) and **2a** (3.5%) (15 mg) in CD_2Cl_2 (0.5 mL). The evolution of the compounds with time was monitored by ^1H NMR spectroscopy at room temperature. Formation of acetone was observed by means of ^1H NMR spectroscopy in a few hours (18 h), with concomitant severe decrease of **5** (19.0%) and noticeable increase of **8** (27.0%) and **10** (26.0%). On the basis of the ^1H NMR spectrum measured at this time, the yields of the other compounds **6**, **7**, **9** and **2a** were estimated at 7.5%, 8.0%, 8.5% and 4.0%, respectively. All these compounds were identified by comparison of their ^1H NMR data with those of pure samples.

4.7. Reaction of 3 with an excess of $HBF_4 \cdot OEt_2$ in dichloromethane: synthesis of 9

Complex **3** (51 mg, 0.093 mmol) and a large excess of $HBF_4 \cdot OEt_2$ (10 drops) were stirred in dichloromethane (5 mL) at room temperature for 5 min. After filtration, diethyl ether (15 mL) was added to the solution to precipitate a red brown powder (56 mg), that was washed twice with cold pentane (2 × 15 mL) and analysed by ^1H NMR spectroscopy, which indicated the presence of only one NMR detectable product **9** in dichloromethane-d solution. Elemental analysis of this powder gave satisfactory data, consistent with **9**. However, by monitoring the above

reaction by electrochemistry, C.V. of the catholyte showed the formation of two products in these experiments, consistent with those of the vinylidene complex **9** and of an acetylide derivative, undetected by NMR. For this reason, the analytical results for **9** are not enclosed here, because we cannot exclude with assurance the presence in the powder of some amounts of a paramagnetic derivative (**A**) of formula differing from that of **9** by only one hydrogen unit.**9:** ^{1}H NMR (CD_2Cl_2): δ 6.67 (d, $J_{H-H} = 8.0$ Hz, 1H, C=C*H*), 6.12 (s, 10H, C_5H_5), 2.41 (spt, 1H, C*H*Me$_2$), 1.90, 1.55 and 1.48 (s, 3H, SCH_3), 1.05 (d. br, $J_{H-H} = 8.0$ Hz, 6H, CH_3). ^{13}C–{^{1}H} NMR (CD_2Cl_2): 365.05 (Mo=*C*=C), 123.6 (=*C*H), 97.1 (C_5H_5), 31.25 (*C*HMe$_2$), 25.3 (CH_3), 21.9, 10.35 and 6.35 (S*C*H$_3$).

4.8. Reaction of the vinyl-acetylide **4** with $HBF_4 \cdot OEt_2$ (excess): formation of **6** and **9**

A solution of a pure sample of **4** [14] (105 mg, 0.20 mmol) in dichloromethane (10 mL) was stirred in the presence of an excess of $HBF_4 \cdot OEt_2$ (10 drops) for 10 min at room temperature. The solvent was then partially removed under vacuum, the products were precipitated by addition of diethyl ether (20 mL) from the solution and then were collected by filtration and washed with cold pentane (2×15 mL). The crude products were analysed in (CD_2Cl_2) by ^{1}H NMR spectroscopy which showed that **4** wholly disappeared, and **9** and **6** were formed in the 2.5:1 ratio.

4.9. Reaction of the allenylidene **11** with hydride: synthesis of **12**

A solution of compound **11** $\cdot$ CH_2Cl_2 (162 mg, 0.196 mmol) in acetonitrile (15 mL) was stirred in the presence of 2 equiv. of Na(BH_4) (44 mg) for 20 min at room temperature. The colour of the solution turned from violet to green. The solvent was then removed under vacuum and the organometallic products were extracted with diethyl ether (3×15 mL). Evaporation of the volatiles afforded complex **12** as an analytically pure, green solid (90 mg, 70% yield). However, it should be noted that in some experiments small amounts of the μ-carbyne complex **14** were formed together with the main product **12**. Compound **12**: ^{1}H NMR (C_6D_6): δ 7.43–6.94 (m 10H, C_6H_5), 5.08 (s, 10H, C_5H_5), 4.53 (s, 1H, C*H*Ph$_2$), 1.65, 1.56 and 1.53 (s, 3H,SCH_3). ^{13}C–{^{1}H} NMR ($CDCl_3$): δ 142.9 (*C ipso* Ph), 128.2 (*C ortho* Ph), 127.8 (*C meta* Ph), 126.5 (*C para* Ph), 113.45 (C_β), 90.3 (C_5H_5), 49.0 (C_γ), 16.5, 11.2 and 8.6 (S*C*H$_3$). Anal. Calc. for $C_{28}H_{30}Mo_2S_3$: C, 51.4; H, 4.6. Found: C, 51.9; H, 5.1%.

4.10. Synthesis of the μ-vinylidene **13**

To a green solution of **12** (85 mg, 0.13 mmol) in diethyl ether (5 mL) was added a drop of $HBF_4 \cdot OEt_2$ diluted in diethyl ether (20 mL), at room temperature. A greenish powder readily precipitated. After filtration, the solid was washed with cold pentane (3×15 mL), affording **13** in high yields (81 mg, 84%). Compound **13**: ^{1}H NMR ($CDCl_2$): δ 7.45–7.33 (m, 10H, C_6H_5), 7.37 (d, $J_{H-H} = 14.4$ Hz, 1H, =C*H*), 5.94 (s, 10H, C_5H_5), 4.66 (d, $J_{H-H} = 14.4$ Hz, 1H, C*H*CPh$_2$), 1.93, 1.63 and 1.56 (s, 3H, SCH_3). ^{13}C–{^{1}H} NMR (CD_2Cl_2): δ 365.55 (C_α), 143.3 (*C ipso* Ph), 129.3 (*C ortho* Ph), 128.1(*C meta* Ph), 127.9 (*C para* Ph), 118.3 (C_β), 97.5 (C_5H_5), 47.4 (C_γ), 15.3, 10.5 and 6.6 (S*C*H$_3$). Anal. Calc. for $C_{28}H_{31}BF_4Mo_2S_3$: C, 45.3; H, 4.2. Found: C, 45.4; H, 4.8%.

4.11. Synthesis of the μ-alkylidyne **14**

A solution of complex **13** (138 mg, 0.185 mmol) in acetonitrile (20 mL) was stirred in the presence of 2 equiv. of Na(BH_4) (28 mg) for 30 min, at room temperature. The colour of the solution turned from green to blue. The solvent was then removed and the residue was chromatographed on silica gel. Elution with a mixture of CH_2Cl_2/hexane (1:1.5) removed a blue band. Evaporation of the volatiles afforded compound **14** as an analytically pure blue powder (75 mg, 61.5% yield). Crystals of **14**, suitable for X-ray analysis, were formed by crystallisation at room temperature from a CH_2Cl_2 solution layered with diethyl ether. Compound **14**: ^{1}H NMR (C_6D_6): δ 7.34–6.99 (m, 10H, C_6H_5), 5.22 (s, 10H, C_5H_5), 4.82 (d, $J_{H-H} = 8.0$ Hz, 2H, CH_2), 4.32 (t, $J_{H-H} = 8.0$ Hz, 1H, C*H*Ph$_2$), 1.94, 1.60 and 1.43 (s, 3H, SCH_3). NMR ^{13}C–{^{1}H} ($CDCl_3$): δ 445.4 (Mo$_2$*C*), 146.1 (*C ipso* Ph), 128.4 (*C ortho* Ph), 127.9 (*C meta* Ph), 126.0 (*C para* Ph), 67.0 (*C*H$_2$), 50.4 (*C*HPh$_2$), 30.5, 8.1 and 6.9 (S*C*H$_3$). Anal. Calc. for $C_{28}H_{32}Mo_2S_3$: C, 51.2; H, 4.9. Found: C, 51.6; H, 5.1%.

4.12. Synthesis of the μ-alkylidene **15**

To a blue solution of **14** (57.6 mg, 0.088 mmol) in diethyl ether (5 mL) was added a drop of $HBF_4 \cdot OEt_2$ diluted in diethyl ether (20 mL), at room temperature. A greyish solid precipitated immediately. After filtration, the powder was washed with diethyl ether (3×15 mL) and then with cold pentane (2×15 mL), affording **15** in moderate yields (41 mg, 63%). Compound **15**: ^{1}H NMR (CD_2Cl_2): δ 7.37–7.18 (m, 10H, C_6H_5), 5.98 (s, 10H, C_5H_5), 4.20 (m, 2H, CH_2), 3.72 (t, $J_{H-H} = 8.0$ Hz, C*H*Ph$_2$), 1.99, 1.75 and 1.51 (s, 3H, SCH_3), −4.78 (s. br, 1H, MoC$_\alpha$*H*). ^{13}C–{^{1}H} NMR (CD_2Cl_2): δ μ*C*H not observed, 142.4 (*C ipso* Ph), 129.6 (*C ortho* Ph), 128.1 (*C meta* Ph), 127.8 (*C para* Ph), 99.3 (C_5H_5), 61.0 ($C_\beta H_2$), 51.5 (C_γHPh$_2$), 37.1, 13.3 and 10.7 (S*C*H$_3$). Anal. Calc. for $C_{28}H_{33}BF_4Mo_2S_3$: C, 45.2; H, 4.5. Found: C, 45.2; H, 4.9%.

4.13. Reaction of the allenylidene **11** with $Me_4N(OH)$: formation of the acetylide **16a**

To a solution of compound **11** (100 mg, 0.13 mmol) in dichloromethane (20 mL) was added 83 μL of tetrameth-

ylammonium hydroxide (1.5 equiv.) in methanol. The mixture was stirred for 1 h at room temperature. The solvent was then removed and products were extracted twice with diethyl ether (2 × 15 mL) as a green powder (73 mg), and were analysed in $CDCl_3$ by ^1H NMR spectroscopy. Compounds **16a**, $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CC(OH)Ph_2\}]$ (**17**) and $[Mo_2Cp_2(O)(Cl)(\mu\text{-}SMe)_3]$ were, respectively, formed in the ratio 9.5:1.25:1. On the basis of ^1H NMR spectra of the mixture and assuming that no paramagnetic compound was formed, the isolated yields of **16a** and **17** were estimated at 68.5% and 9.0%, respectively. Unfortunately, compounds **16a**, **17** and the other oxochloro by-product cannot be separated by chromatography, because these derivatives decomposed on the column (silica gel). In fine, **16a** was separated from the other complexes by crystallisation in cold dichloromethane-hexane. Compounds **17** [2d] and $[Mo_2Cp_2(O)(Cl)(\mu\text{-}SMe)_3]$ [26] were identified by comparison of their ^1H NMR spectra with those of authentic samples. Compound **16a**: ^1H NMR ($CDCl_3$) δ 7.81–6.20 (m, 10H, C_6H_5), 5.28 (s, 10H, C_5H_5), 2.98 (s, 3H, OCH_3), 1.60, 1.45 and 1.39 (s, 3H, SCH_3). Anal. Calc. for $C_{29}H_{32}Mo_2OS_3$: C, 50.9; H, 4.7. Found: C, 51.3; H, 5.1%.

4.14. Reaction of the acetylide *16a* with proton

One equivalent of $HBF_4 \cdot OEt_2$ (10 μL) in diethyl ether (5 mL) was added with stirring to a green solution of **16a** (48 mg 0.07 mmol) in diethyl ether (10 mL) at room temperature. A purple solid readily precipitated from the solution and was collected by filtration and washed with cold pentane. The allenylidene complex **11** was thus obtained quantitatively as a purple powder and was characterised by comparison of its ^1H NMR spectrum with that of an authentic sample [2d].

4.15. Reaction of the allenylidene *11* with sodium thiomethoxide: formation of the acetylide *16b*

To a purple solution of compound **11** (83 mg, 0.10 mmol) in dichloromethane (20 mL) was added an excess of Na(SMe) (12 mg, 0.17 mmol). The mixture was stirred for 1 h at room temperature, after which time the solution became greenish. The solvent was then removed under vacuum and the organometallic products were extracted from the residue with diethyl ether (3 × 15 mL). Evaporation of the volatiles afforded greenish solids which were washed with cold pentane (2 × 10 mL) and shown by ^1H NMR analyses to be a mixture of inseparable products (41.2 mg) by chromatography. However, the major compound was clearly identified as the μ-acetylide complex **16b**. On the basis of the ^1H NMR spectrum of the mixture, the yield of **16b** was estimated at 27%. Compound **16b**: ^1H NMR ($CDCl_3$): δ 7.43–7.13 (m 10H, C_6H_5), 5.24 (s, 10H, C_5H_5), 5.24 (s, 10H, C_5H_5), 1.84 (s, 3H, $C(SCH_3)Ph_2$), 1.62, 1.55 and 1.48 (s, 3H, SCH_3).

4.16. X-ray structural determinations

Measurements for compounds **2b**, **14** and **15** were made in Brest on a Oxford Diffraction X-Calibur-2 CCD diffractometer equipped with a jet cooler device. Those for **3** were made in Glasgow on a Nonius CAD4 diffractometer. Graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$) was used in all experiments. The structures were solved and refined by standard procedures [38]. H atoms were positioned using stereochemical considerations.

The crystal specimens for **14** and **15** were of poor quality and gave only weak, low-resolution diffraction patterns. Despite the efforts made to obtain them, the results of the diffraction analyses for **14** and **15** do not, in our view, provide *independent* proof of the proposed structures, though they are consistent with our chemical and spectroscopic experiments. They are available as Supplementary material.

For **2a** and **3** selected bond lengths and angles are given in the captions to Figs. 1 and 2 and crystal data in Table 1.

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Appendix A. Supplementary material

CCDC 652779 and 652780 contain the supplementary crystallographic data for **2b** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Also deposited as supplementary data are molecular drawings and tables of crystallographic data, atomic parameters and bond lengths and angles for **2b**, **3**, **14** and **15**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.023.

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