

Synthesis of secondary allenylidene–molybdenum complexes with a ferrocenyl substituent from carbenium ions species stabilized by two organometallic moieties

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Abstract

The monoallenylidene complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\sigma\text{:}\eta^2\text{-C}=\text{C}=\text{C}(\text{Fc})(\text{H})\}]$ (5) and the diallenylidene complex $\{[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\sigma\text{:}\eta^2\text{-C}=\text{C}=\text{C}(\text{H})\}]_2\text{Fc}\}$ (6) have been obtained from the corresponding monocarbenium ion $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HC}\equiv\text{C}-\text{C}(\text{H})(\text{Fc})\}][\text{BF}_4]$ (3) and the dicarbenium ion $\{[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HC}\equiv\text{C}-\text{C}(\text{H})\}]_2\text{Fc}\}[\text{BF}_4]_2$ (4) respectively, and their spectroscopic data are determined.

Keywords: Iron; Ferrocene; Molybdenum; Carbenium ions; Allenylidene complexes

1. Introduction

In the cationic compounds $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HC}\equiv\text{C}-\text{C}(\text{R}_1)(\text{R}_2)\}][\text{BF}_4]$ the metal exerts a powerful stabilizing effect at the adjacent propargylic carbenium ion centre [1–12]. Various nucleophiles can alkylate these cations [1,6,13]. We have previously described the unexpected selective abstraction of the acetylenic proton in the carbenium ions by the acetylide reagent $\text{LiC}\equiv\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$ [14] (Scheme 1). The resulting compounds were $\mu\text{-}\sigma\text{:}\eta^2$ allenylidene species $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\sigma\text{:}\eta^2\text{-C}=\text{C}=\text{C}(\text{R}_1)(\text{R}_2)\}]$. The first example of such a compound was made by Green and co-workers by a different procedure [15].

Secondary (R_1 or $\text{R}_2 = \text{H}$) and primary ($\text{R}_1 = \text{R}_2 = \text{H}$) allenylidene complexes are thermally unstable (unlike the tertiary derivatives) and must be kept in solution below -35°C to prevent degradation. The secondary allenylidene complexes A ($\text{R}_1 = \text{Et}$, $\text{R}_2 = \text{H}$) and B ($\text{R}_1 = \text{Me}$, $\text{R}_2 = \text{H}$) (Scheme 2) exist as two diastereoisomers depending on the relative position of the substituents on the C_γ atom.

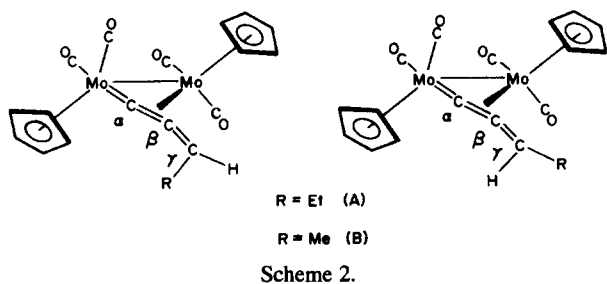
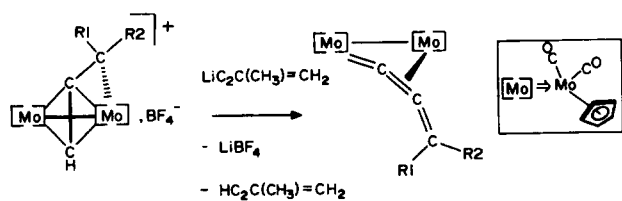
We describe herein further secondary allenylidene compounds with a ferrocenyl substituent ($\text{R} = \text{Fc}$, $\{(\text{C}_5\text{H}_4)\text{Fe}(\text{C}_5\text{H}_5)\}$). We hoped that the presence of a bulky substituent on the carbon chain could lead to the formation of only one diastereomer of a thermally stable allenylidene complex. Increasing demand for new materials, and particularly metallocene compounds, which might exhibit properties essential for second-order non-linear optical (NLO) behaviour [16,17], could make allenylidene complexes with a ferrocenyl substituent very attractive. We also report the synthesis of interesting starting materials and synthetic intermediates, which we have described elsewhere [18].

2. Results and discussion

The route to dimolybdenum allenylidene complexes involves the activation of 2-propyn-1-ol ($\text{HC}\equiv\text{C}-\text{C}(\text{OH})(\text{R}_1)(\text{R}_2)$) and comprises three steps (method A, Scheme 3):

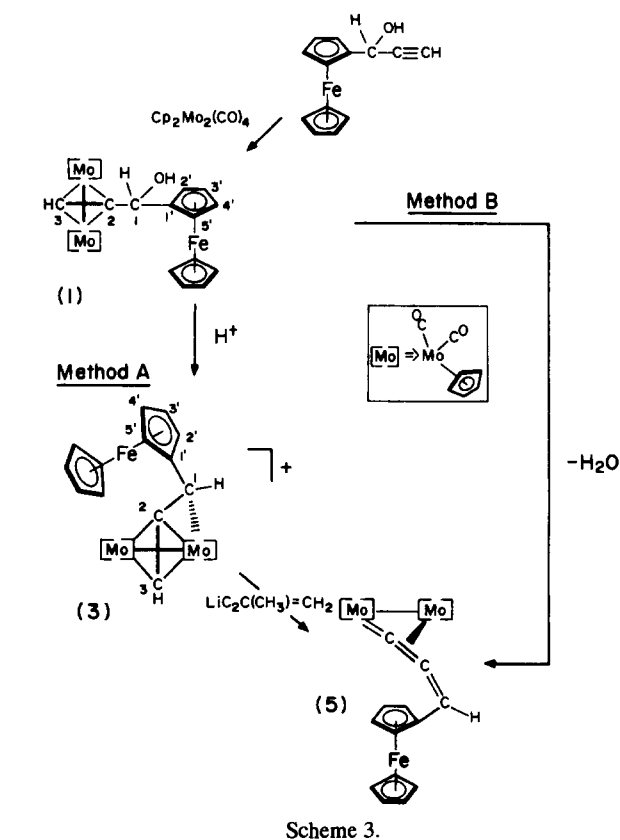
- (1) formation of the alkyne adduct with a tetrahedral C_2Mo_2 by treatment of the triply metal–metal bonded species $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ with the appropriate alkyne;

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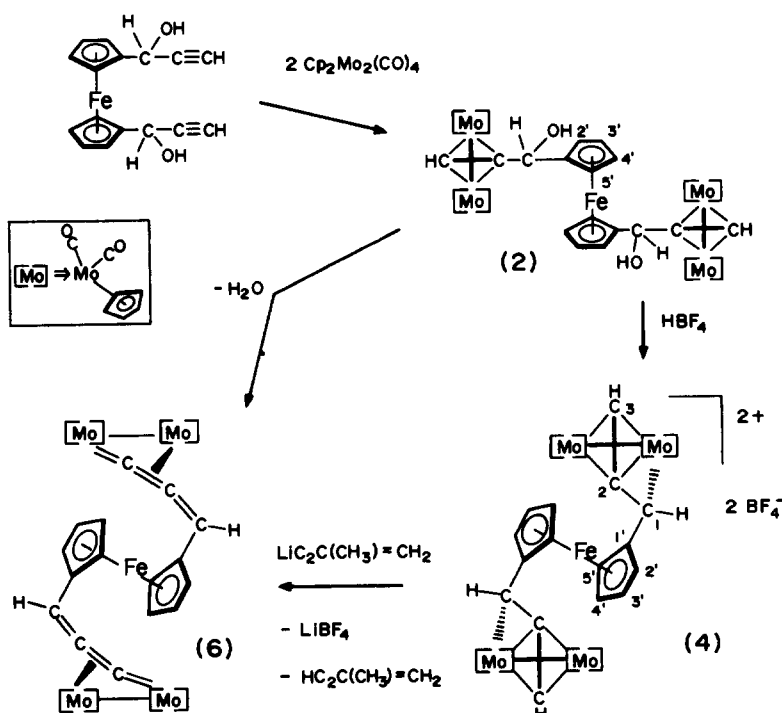


- (2) protonation of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-RC}\equiv\text{C-C(OH)(R}_1\text{)(R}_2\text{)}\}]$ followed by elimination of water gives the carbenium ion;
- (3) addition of $\text{LiC}\equiv\text{C-C(CH}_3\text{)=CH}_2$ to the carbenium ion in $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HC}\equiv\text{C-C(R}_1\text{)(R}_2\text{)}\}][\text{BF}_4^-]$ leads to the allenylidene complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\sigma\text{:}\eta^2\text{-C=C=C(R}_1\text{)(R}_2\text{)}\}]$.

An important feature of method B (Scheme 3) is that treatment of the μ -alkyne compound $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-(HC}\equiv\text{C-C(OH)(H)(Fc))}\}]$ (1) with Al_2O_3 or SiO_2



(chromatography) causes direct elimination of H_2O to yield an allenylidene complex. These various features are described separately below.



2.1. Coordination by $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$

The classical procedure for the synthesis of μ -alkyne compounds is used [19], involving addition of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ to a solution of the alkyne ($\text{HC}\equiv\text{C}-\text{C}(\text{OH})(\text{H})(\text{Fc})$) followed by stirring for 18 h at room temperature yields the compound $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu-\eta^2:\eta^2-(\text{HC}\equiv\text{C}-\text{C}(\text{OH})(\text{H})(\text{Fc}))\}]$ (1) (80%). In contrast, heating of the solution is necessary in the case of bulky alkynes [20].

For (1) the shift of the acetylenic proton resonance ($\text{H}-\text{C}\equiv$) is, as expected, upfield from that of the free alkyne, i.e. 5.50 ppm for complex (1) compared with 2.60 ppm for $\text{HC}\equiv\text{C}-\text{C}(\text{OH})(\text{H})(\text{Fc})$. The $^1J(\text{C}\equiv\text{H})$ coupling constant is also changed, being 212 Hz for compound (1) and 250 Hz for $\text{HC}\equiv\text{C}-\text{C}(\text{OH})(\text{H})(\text{Fc})$.

The dipropargyl alcohol derivative complex $\{[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu-\eta^2:\eta^2-\text{H}-\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{H}))\}_2(\text{Fc})\}$ (2), was obtained from the diyne compound $\{\text{H}-\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{H})\}_2(\text{Fc})$, by a procedure very similar to that used for complex (1) (Scheme 4).

A mixture of monocoordinated and dicoordinated compounds is usually formed in the reaction of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ with diynes, as for example in the case of octa-1,7 diyne [21] or hexa-1,5 diyne [22]. The mixture obtained from the diol $\{[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu-\eta^2:\eta^2-\text{H}-\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{H}))\}_2(\text{Fc})\}$ (2) is expected to be difficult to separate chromatographically because compound (2) decomposes on silica or alumina columns. In order to avoid this complication the formation of the monocoordinated compound was prepared by stirring the solution of the diyne compound $\{\text{H}-\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{H})\}_2(\text{Fc})$ in the presence of an excess of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ for 36 h.

A very important feature of ferrocene compound (2) is the presence of two stereogenic functionalized side chains, which means that theoretically both racemic ($\text{RR} + \text{SS}$) and meso ($\text{RS}=\text{SR}$) forms are possible. The ^1H NMR spectrum for the crude product mixture displays a complex profile of ($\text{C}_5\text{H}_5-\text{Mo}$) and ($\text{C}_5\text{H}_4-\text{Fe}$) resonances due to the presence of the two stereoisomers. Repeated extractions with cold pentane gave a single isomer, but analysis of its spectroscopic data does not allow us to conclude whether it is the RS or the ($\text{RR} + \text{SS}$) diastereoisomer. As alcohol (2) contains stereogenic carbon atoms, two resonances are observed for the ($\text{C}_5\text{H}_5-\text{Mo}$) groups, as in the case of other diynes complexes $[\text{Mo}_2\text{Cp}_2(\text{CO})_4(\mu-\eta^2:\eta^2-\text{HC}\equiv\text{C}(\text{R}_1)(\text{R}_2)-)]_2$ ($\text{R}_1 = \text{H}$, $\text{R}_2 = \text{Me}$ [6]; $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{Et}$ [7]).

2.2. Synthesis of the carbenium ions

Addition of HBF_4 to compounds (1) and (2) leads to formation of the corresponding carbenium ion salts $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu-\eta^2:\eta^3-\text{HC}\equiv\text{C}-\text{C}(\text{H})(\text{Fc})\}][\text{BF}_4]$ (3)

and $\{[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu-\eta^2:\eta^3-\text{HC}\equiv\text{C}-\text{C}(\text{H}))\}_2(\text{Fc})\}[\text{BF}_4]_2$ (4) by elimination of H_2O . The carbon atom bearing the positive charge in compounds (3) and (4) is adjacent both to a ferrocenyl substituent and to an acetylenic cluster. It has been demonstrated that the dimolybdenum cluster is mainly responsible for the stabilization of the C^+ centre in the salt $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu-\eta^2:\eta^3-\text{CH}_3(\text{CH}_2)_4-\text{C}\equiv\text{C}-\text{C}(\text{H})(\text{Fc})\}][\text{BF}_4]$ [23,24]. The cation in the latter compound and that in the complex (3) both contain secondary carbenium ions; the signals from the (C^+-H) protons in acetone d_6 , 8.16 ppm and 7.88 ppm respectively, both lie upfield, as expected for a proton on a positively charged centre. Examination of the non-decoupled ^{13}C NMR spectrum of compound (3) and comparisons with NMR data for various carbenium ions previously reported allowed us to assign the various signals.

Although less extensively studied, several dicarbenium ions (essentially dimetallic complexes) have been described [25]. The dication (4) is a tetrametallic dicarbenium ion whereas that in the compound $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{CH}_2\text{C}\equiv\text{CCH}_2)][\text{BF}_4]_2$ [26] is a bimetallic dication with a $(\text{C}_4\text{H}_4)^{2+}$ ligand. Compound (4) behaves as if it were two independent carbenium ions, like the $\text{Co}_2(\text{CO})_6$ complexed propargyl dication described by Nicholas and co-workers [27]. The dicarbenium complex (4) and the monocarbenium compound (3) display quite similar ^1H NMR spectra between 4.3 and 8 ppm. The very low solubility of compound (4) has so far prevented us obtaining suitable crystals for an X-ray study.

As expected for secondary carbenium ions [23,24,28], the ^1H and ^{13}C NMR spectra of compounds (3) and (4) recorded in acetone d_6 solution at room temperature indicate that these molecules show no chiral features: the ($\text{C}_5\text{H}_5-\text{Mo}$) groups display only one signal and two pseudotriplets appear for the ($\text{C}_5\text{H}_4-\text{Fe}$) protons with a $\text{AA}'\text{BB}'$ spin system with $J_{\text{AB}} \approx 2$ Hz.

2.3. Synthesis of the allenylidene complexes

Addition of $\text{LiC}\equiv\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$ to a cooled suspension of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu-\eta^2:\eta^3-\text{HC}\equiv\text{C}-\text{C}(\text{H})(\text{Fc})\}][\text{BF}_4]$ (3) caused an immediate colour change from violet to green (Scheme 3). Elemental analysis, IR and NMR spectral data are consistent with the formation of a $\mu-\sigma:\eta^2(4e^-)$ allenylidene complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu-\sigma:\eta^2-\text{C}=\text{C}=\text{C}(\text{Fc})(\text{H})\}]$ (5).

When solutions of the secondary allenylidene compounds previously described are warmed to room temperature fast decomposition occurs, the green solution turning to red and an intractable mixture being formed. In contrast, compound (5) is thermally stable for a short time in solution even at room temperature. Electron release by the ferrocenyl group should stabilize the

allenylidene moiety as in allenylidene compounds without H-substituents on the C γ atom.

The ^{13}C NMR spectrum of (5) recorded at -10°C exhibits one signal for the C α atom, at 282 ppm, four signals for the carbonyl ligands, between 239 and 230 ppm, and two peaks in the (C $_5\text{H}_5$ -Mo) region. Compound (5) exists as only one diastereomer. We assume that for these reasons the most favoured isomer is that

shown in Fig. 1, in which the H-substituent is closer to the CpMo(1)(CO) $_2$ group; the ferrocenyl ligand and the CpMo(1)(CO) $_2$ group are probably in a trans disposition. It is noteworthy that only one isomer (the thermodynamically preferred diastereomer) is also observed in the case of vinylidene compounds [$\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\sigma\text{:}\eta^2\text{-C=C(R)(R')}\}$] containing two different substituents R and R' [15].

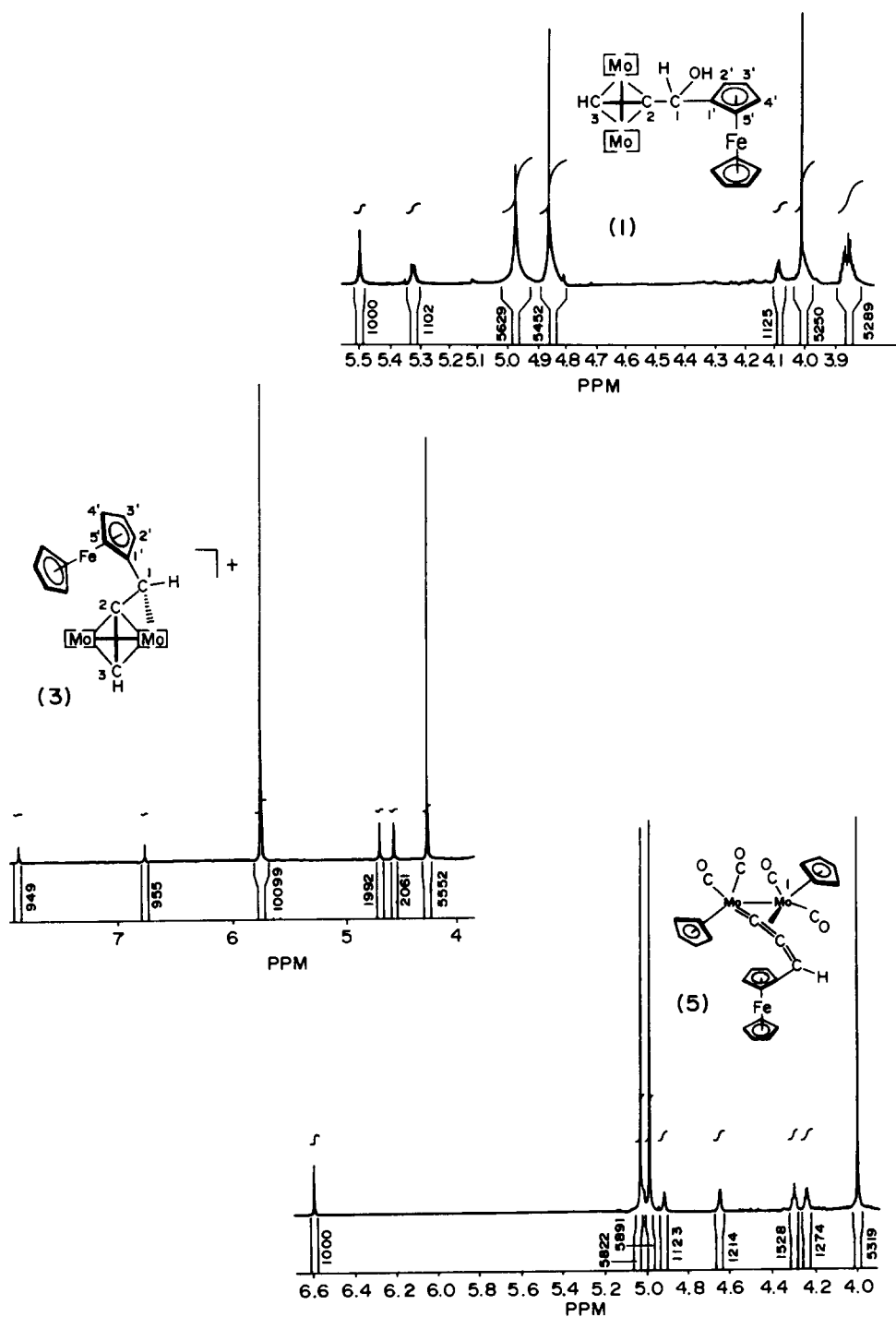


Fig. 1. ^1H NMR spectra of compounds [$\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HC=C(OH)(H)(Fc)}\}$] (1), [$\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\eta^2\text{:}\eta^3\text{-HC=C(OH)(H)(Fc)}\}$][BF $_4$] (3) and [$\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\sigma\text{:}\eta^2\text{-C=C(Fc)(H)}\}$] (5).

Owing to the presence of asymmetrically bridged allenylidene ligand, the effective symmetry for compound (5) is C_1 at room temperature: the two cyclopentadienyl ligands linked to a molybdenum centre are in a different environment [15] and so two signals are observed in the ^1H and ^{13}C NMR spectra. The four protons of the ($\text{C}_5\text{H}_4\text{-Fe}$) group are all magnetically inequivalent and form an ABCD spin system, as in the case of ferrocenyl compounds containing a stereogenic centre.

The diallenylidene compound $[(\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\sigma\text{:}\eta^2\text{-C=C=C(H)}))_2\text{Fc}]$ (6) is obtained by the same procedure as that used for complex (5) but using an excess of $\text{LiC}\equiv\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$. The thermal instability of compound (6) prevents satisfactory elemental analysis (see Section 3). This instability is like that of the diacetylenic compound $\text{Fc}-(\text{C}\equiv\text{C}-\text{H})_2$, whereas the characterisation of the monoacetylenic compound $\text{Fc}-\text{C}\equiv\text{C}-\text{H}$ is easier [29]. Except for the ($\text{C}_5\text{H}_5\text{-Fe}$) signal, the ^1H NMR spectrum of compound (6) has twice as many peaks as the monoallenylidene complex (5): there are two singlets, at 6.60 and 6.65 ppm, corresponding to the ($\text{C}\gamma\text{H}$) protons, four inequivalent cyclopentadienyl resonances and eight multiplets (not always well resolved) from the ($\text{C}_5\text{H}_4\text{-Fe}$) protons. Compound (6) exists in solution as a mixture of two diastereomers, the meso and racemic forms. This is also the case for the diol $\text{Fc}-\{\text{C}(\text{OH})(\text{H})(\text{Ph})\}_2$ which possesses two stereogenic centres [30]. However, in the case of the diallenylidene complex (6) the chirality arises from the presence of the asymmetrically bridged allenylidene ligands. Attempts to separate the two isomers by fractional crystallization have been unsuccessful due to decomposition.

2.4. One step synthesis of allenylidene compounds

An alternative way of preparing complex (5) involves chromatography of compound $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HC}\equiv\text{C}-\text{C}(\text{OH})(\text{H})(\text{Fc})\}]$ (1) on a silica column. Small amounts of $[\text{Cp}_2\text{Mo}_2(\text{CO})_6]$ were first eluted with a hexane–dichloromethane mixture. A second band containing traces of the starting material (1) was eluted with pure dichloromethane. When diethyl ether was added to the column it turned green and the complex (5) formed was eluted in moderate yields (17%).

By using the same procedure, but starting from the diol $[(\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2\text{:}\eta^2\text{-HC}\equiv\text{C}-\text{C}(\text{OH})(\text{H})))_2\text{Fc}]$ (2), only very low yields of diallenylidene complex (6) were isolated because of its instability.

This type of reaction has only been observed previously for the μ -alkyne complexes with a ferrocenyl substituent. Probably the mild acidity of the silica gel suffices to produce the ferrocenyl carbocation [31], which rearranges to the allenylidene compound.

In conclusion, a convenient method for the preparation of monoallenylidene and diallenylidene compounds of ferrocene is outlined in this paper. The diallenylidene compound $[(\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\sigma\text{:}\eta^2\text{-C=C=C(H)}))_2\text{Fc}]$ (6) is unstable. Incorporation of metals into NLO systems has much potential in this field of study [15,16], and so we are seeking methods of obtaining more stable allenylidene complexes of ferrocene.

3. Experimental details

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

The infrared spectra were obtained with a Perkin–Elmer 1430 spectrometer, using solutions in CH_2Cl_2 or KBr pellets. Infrared frequencies are reported in wavenumbers (cm^{-1}).

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 instrument (^1H , 300.13 MHz; ^{13}C , 75.47 MHz). Chemical shifts are reported in units of parts per million (ppm) relative to a tetramethylsilane internal reference. Coupling constants are reported in hertz.

Mass spectra were obtained with an 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.

The complex $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ was obtained by a published method [32]. The starting compounds $\text{H}-\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{H})(\text{Fc})$ and $\{\text{H}-\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{H})\}_2(\text{Fc})$ were readily made from ferrocene aldehyde and 1,1'-ferrocene dialdehyde [33,34] by standard procedures [35]. $\text{LiC}\equiv\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$ was prepared from Li^nBu (2.5 M in hexane) and $\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$ in THF [36].

3.1. Synthesis of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-HC}\equiv\text{C}-\text{C}(\text{OH})(\text{H})(\text{Fc})\}]$ (1)

$\text{H}-\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{H})(\text{Fc})$ (0.44 g, 1.84 mmol) was added to a solution of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ (0.8 g, 1.84 mmol) in toluene (60 ml). The mixture was stirred at room temperature for 18 h. The solvent was removed in vacuo and the residue was chromatographed on a Florisil column. Elution with a hexane–dichloromethane mixture (70:30 in volume) afforded complex (1) (yield, 1 g; 80%).

Spectroscopic data for (1):

^1H NMR (toluene d_8 solution): 5.50 (d, 1H, $\text{HC}\equiv$,

$^4J(\text{H}-\text{H}) = 0.5$ Hz); 5.32 (d, 1H, HC, $^3J(\text{H}-\text{H}) = 2.25$ Hz); 4.97 (s, 5H, $\text{C}_5\text{H}_5-\text{Mo}$); 4.86 (s, 5H, $\text{C}_5\text{H}_5-\text{Mo}$); 4.09 (m, 1H, C_5H_4); 3.85 (m, 3H, C_5H_4); 4.01 (s, 5H, $\text{C}_5\text{H}_5-\text{Fe}$). ^{13}C NMR (C_6D_6 solution): 233.3, 233.1, 229.1 (CO); 96.8 (C1'); 91.2 ($\text{C}_5\text{H}_5-\text{Mo}$); 91.1 ($\text{C}_5\text{H}_5-\text{Mo}$); 75.2 (C1, d $^1J(\text{C}-\text{H}) = 147$ Hz); 87.9 (C3, d, $^1J(\text{C}-\text{H}) = 212$ Hz); 59.5 (C2); 68.8 ($\text{C}_5\text{H}_5-\text{Fe}$); 69.5 (C_5H_4 , d, $^1J(\text{C}-\text{H}) = 176$ Hz); 64.2 (C_5H_4 , d, $^1J(\text{C}-\text{H}) = 176$ Hz); 67.6 (C_5H_4 , d, $^1J(\text{C}-\text{H}) = 176$ Hz); 67.4 (C_5H_4 , d, $^1J(\text{C}-\text{H}) = 175$ Hz). IR (KBr pellet): $\nu(\text{CO})$: 1995, 1910, 1830. MS: (m/e) 656: $[\text{M}-\text{H}_2\text{O}]^+$; 600: $[\text{M}-\text{H}_2\text{O}-2\text{CO}]^+$; 544: $[\text{M}-\text{H}_2\text{O}-4\text{CO}]^+$. Anal. Found: C, 47.13; H, 3.78. $\text{C}_{27}\text{H}_{22}\text{FeMo}_2\text{O}_5$. Calc.: C, 48.10; H, 3.22%.

3.2. Synthesis of $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu-\eta^2:\eta^2-\text{H}-\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{H}))\}_2(\text{Fc})] (2)$

$[\text{Cp}_2\text{Mo}_2(\text{CO})_4]$ (4.7 g, 10.9 mmol) was added to a freshly prepared solution of $\{\text{H}-\text{C}\equiv\text{C}-\text{C}(\text{OH})(\text{H})\}_2(\text{Fc})$ (1.28 g, 4.4 mmol) in toluene (40 ml) and the mixture stirred for 36 h. Work-up as for compound (1) gave 3.3 g (yield 65%) of (2).

Spectroscopic data for (2):

^1H NMR (CDCl_3 solution). After extraction with pentane, only one diastereoisomer was recovered: 5.89 (s, 2H, 2 HC \equiv); 5.09 (s, 10H, 2 $\text{C}_5\text{H}_5-\text{Mo}$); 4.93 (s, 10H, 2 $\text{C}_5\text{H}_5-\text{Mo}$); 4.13 (s, 2H, 2 HO or 2 HC); 4.01 (t, 4H, C_5H_4 , (H2'-5'), $^3J(\text{H}-\text{H}) = 2.1$ Hz); 3.89 (t, 4H, C_5H_4 , (H3'-4'), $^3J(\text{H}-\text{H}) = 2.0$ Hz); 3.84 (s, 2H, 2 HO or 2 HC). ^{13}H NMR (CD_2Cl_2 solution, 272 K) (below 272 K coalescence occurred; at higher temperatures compound (2) decomposed in the solution before the spectrum could be fully recorded): 233.1, 232.6, 229.0 (CO); 97.1 (C1'); 92.3 (C3, d, $^1J(\text{C}-\text{H}) = 185$ Hz); 91.3, 91.2 ($\text{C}_5\text{H}_5-\text{Mo}$); 74.7 (C1, d, $^1J(\text{C}-\text{H}) = 141$ Hz); 74.5–67.7 ($\text{C}_5\text{H}_4-\text{Fe}$); 60.3 (C2). IR (KBr pellet): $\nu(\text{CO})$: 1995, 1910, 1830. Anal. Found: C, 45.91; H, 3.22. $\text{C}_{44}\text{H}_{34}\text{FeMo}_4\text{O}_{10}$. Calc.: C, 45.47; H, 2.95%.

3.3. Synthesis of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu-\eta^2:\eta^3-\text{HC}\equiv\text{C}-\text{C}(\text{H})(\text{Fc})\}][\text{BF}_4] (3)$

To a stirred solution of (1) (1 g, 1.84 mmol) in diethyl ether (80 ml) was added dropwise a solution of 0.5 ml of HBF_4 in diethyl ether. The violet precipitate was filtered off and washed with diethyl ether (3 \times 7 ml) to leave 1.33 g (yield 97%) of (3).

Spectroscopic data for (3):

^1H NMR (acetone d_6 solution): 7.88 (s, 1H, HC1); 6.76 (s, 1H, HC3); 5.76 (s, 10H, 2 $\text{C}_5\text{H}_5-\text{Mo}$); 4.69 (t, 2H, C_5H_4 , (H2'-5'), $^3J(\text{H}-\text{H}) = 1.85$ Hz); 4.56 (t, 2H, C_5H_4 , (H3'-4'), $^3J(\text{H}-\text{H}) = 1.85$ Hz); 4.26 (s, 5H, $\text{C}_5\text{H}_5-\text{Fe}$). ^{13}C NMR (acetone d_6): 223.0 (CO); 120.8 (C1, d, $^1J(\text{C}-\text{H}) = 168.4$ Hz); 102.3 (C1'); 94.1 ($\text{C}_5\text{H}_5-\text{Mo}$, d, $^1J(\text{C}-\text{H}) = 183.0$ Hz); 86.2 (C2); 76.9

(C3, d, $^1J(\text{C}-\text{H}) = 224.3$ Hz; $^3J(\text{C}-\text{H}) = 5.6$ Hz); 71.0 ($\text{C}_5\text{H}_5-\text{Fe}$, d, $^1J(\text{C}-\text{H}) = 176.9$ Hz); 72.5 (C3'-C4', d, $^1J(\text{C}-\text{H}) = 177.5$ Hz); 65.8 (C5'-C2', d, $^1J(\text{C}-\text{H}) = 180.1$ Hz). IR (KBr pellet) $\nu(\text{CO})$: 2015, 2000, 1875; $\nu(\text{BF})$: 1100. Anal. Found: C, 43.80; H, 2.93; F, 10.72. $\text{C}_{27}\text{H}_{21}\text{BF}_4\text{FeMo}_2\text{O}_4$. Calc.: C, 43.59; H, 2.85; F, 10.21%.

3.4. Synthesis of $[\{\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu-\eta^2:\eta^3-\text{HC}\equiv\text{C}-\text{C}(\text{H}))\}_2(\text{Fc})][\{\text{BF}_4\}_2] (4)$

To a solution of (2) (2 g, 1.7 mmol) in 30 ml of dichloromethane (complex (2) is less soluble than (1)), was added 0.3 ml of a solution of HBF_4 in diethyl ether. An immediate change of colour from red to violet occurred. Addition of 60 ml of diethyl ether and cooling to -15°C yielded a violet precipitate of compound (4) (1.9 g, 88%).

Spectroscopic data for (4):

^1H NMR (acetone d_6): 7.7 (s, 2H, 2 HC1); 6.73 (s, 2H, 2 HC3); 5.72 (s, 20H, 4 $\text{C}_5\text{H}_5-\text{Mo}$); 4.75 (t, 4H, C_5H_4 , 2 (H2'-5'), $^3J(\text{H}-\text{H}) = 1.87$ Hz); 4.56 (t, 4H, C_5H_4 , 2 (H3'-4')). ^{13}C NMR (acetone d_6): 116.3 (C1); 105.5 (C1'); 94.3 ($\text{C}_5\text{H}_5-\text{Mo}$); 88.0 (C2); 77.6 (C3); 74.1 and 74.0 (C_5H_4 , C2', C3', C4', C5'); CO not observed. IR (CH_2Cl_2): $\nu(\text{CO})$: 2040, 1995, 1875; $\nu(\text{BF})$: 1050. Anal. Found: C, 40.07; H, 3.01; F, 9.98. $\text{C}_{44}\text{H}_{32}\text{B}_2\text{F}_8\text{FeMo}_4\text{O}_8$. Calc.: C, 40.59; H, 2.47; F, 11.67%.

3.5. Synthesis of $[\text{Cp}_2\text{Mo}_2(\text{CO})_4\{\mu-\sigma:\eta^2-\text{C}=\text{C}=\text{C}(\text{Fc})(\text{H})\}] (5)$

Method A: compound (3) (1 g, 1.34 mmol) was added to a suspension of $\text{LiC}\equiv\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$ generated from $\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$ (0.15 ml, 1.6 mmol) and Li^nBu (0.54 ml, 1.34 mmol) in THF frozen in liquid nitrogen. The excess of $\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$ was used to prevent oligomerisation [35]. Dichloromethane (50 ml) was added, causing a rapid colour change from violet to green. The solution was allowed to warm to room temperature and was then filtered quickly through a Celite pad (3 \times 5 cm) to remove LiBF_4 . After removal of the solvent in vacuo the crude solid was extracted with diethyl ether and yielded 0.38 g (43%) of (5).

Method B: a solution of complex (1) (0.5 g, 0.74 mmol) in dichloromethane was rapidly eluted through a silica gel column made up with hexane. Small amounts of $[\text{Cp}_2\text{Mo}_2(\text{CO})_6]$ (elution hexane-dichloromethane, 4:1 in volume) and traces of unchanged compound (1) (elution dichloromethane) were first collected. Elution with diethyl ether then afforded the green allenylidene complex (5) (0.08 g, yield 17%).

Spectroscopic data for (5):

^1H NMR (C_6D_6): 6.59 (s, 1H, $=\text{C}(\text{H})-\text{Fc}$); 5.02 (s, 5H, $\text{C}_5\text{H}_5-\text{Mo}$); 4.98 (s, 5H, $\text{C}_5\text{H}_5-\text{Mo}$); 4.91 (m, 1H,

C_5H_4); 4.64 (m, 1H, C_5H_4); 4.29 (m, 1H, C_5H_4); 4.23 (m, 1H, C_5H_4); 3.99 (s, 5H, C_5H_5-Fe). ^{13}C NMR (acetone d_6) $-10^\circ C$: 281.9 (Mo=C); 239.0, 235.8, 232.8 and 230.8 (4 CO); 149.2 (Mo=C=C); 137.6 (Mo=C=C=C(H), d, $^1J(C-H) = 165$ Hz); 98.5 (C, (C_5H_4) quaternary carbon atom); 96.2 (C_5H_5-Mo , d, $^1J(C-H) = 177.7$ Hz); 94.5 (C_5H_5-Mo , d, $^1J(C-H) = 177.1$ Hz); 70.6 (C_5H_5-Fe , d, $^1J(C-H) = 175.8$ Hz); 71.9, 69.1, 69.9 and 69.2 (C_5H_4 , d, $^1J(C-H) = 176$ Hz). IR (KBr pellet) $\nu(CO)$: 1960, 1910, 1850; $\nu(C=C=C)$: 1650. MS: (m/e) 656: $[M]^+$; 600: $[M-2CO]^+$; 544: $[M-4CO]^+$. Anal. Found: C, 50.22; H, 3.10. $C_{27}H_{20}FeMo_2O_4$. Calc.: C, 49.42; H, 3.07%.

3.6. Synthesis of $[Cp_2Mo_2(CO)_4(\mu-\sigma:\eta^2-C=C=C(H))_2Fc]$ (6)

Compound (4) (0.53 g, 0.41 mmol) was added to a suspension of an excess of $LiC\equiv C-C(CH_3)=CH_2$ generated from $HC\equiv C-C(CH_3)=CH_2$ (0.2 ml, 2.1 mmol) and Li^iBu (0.75 ml, 1.9 mmol) in THF frozen in liquid nitrogen. Addition of dichloromethane initiated the reaction and the solution turned green. The mixture was filtered at $-30^\circ C$ and removal of the solvent from the filtrate in vacuo left a crude solid which was extracted with cold dichloromethane. The extract was concentrated in vacuo to 15 ml and diethyl ether was added to give a green precipitate (0.18 g, yield 38%).

The procedure used for (5), but starting from (2) gave $[Cp_2Mo_2(CO)_6]$ and small amounts of (6).

Spectroscopic data for (6):

1H NMR (toluene d_8): 6.60 (s, 2H, 2 =C(H)); 6.65 (s, 2H, 2 =C(H)); 5.08 and 5.05 (2s, 20H, 4 C_5H_5-Mo); 5.01 and 4.98 (2s, 20H, 4 C_5H_5-Mo); between 4.9 and 4.2 ppm eight multiplets (16H, 4 C_5H_4). ^{13}C NMR data (because of the poor stability of compound (6) only some peaks could be assigned): 297.6, 296.4 (Mo=C); 95.9, 94.1, 92.2, 91.5 (C_5H_5-Mo). IR (CH_2Cl_2): $\nu(CO)$: 1965, 1905, 1850; $\nu(C=C=C)$: 1650.

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