Reaction of sodium amalgam with carbenium ions species stabilised by two adjacent organometallic moieties

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Abstract

The ionic complexes $[Cp_2Mo_2(CO)_4\{\mu-\eta^2:\eta^3-HC\equiv C-C(H)(Fc)\}][BF_4]$ (1) and $[\{Cp_2Mo_2(CO)_4(\mu-\eta^2:\eta^3-HC\equiv C-C(H)\}_2Fc][\{BF_4\}_2]$ (5) react with Na–Hg in toluene solution. The results are interpreted in terms of a radical mechanism involving intramolecular and intermolecular coupling reactions.

Keywords: Carbenium ions; Molybdenum clusters; Ferrocenyl; Ferrocenophane

1. Introduction

Recently we have been interested in the reactivity of carbon-centred organometallic radicals formed from the carbenium ions $[Cp_2Mo_2(CO)_4\{\mu-\eta^2:\eta^3-HC\equiv C-C(R_1)(R_2)\}]^+$ [1,2]. Free radical intermediates are assumed to be present during the reductive dimerization of such compounds (Scheme 1) [1–3]. The structures of the dimers $[Mo_2Cp_2(CO)_4(\mu-\eta^2:\eta^2-HC\equiv CCH_2-)]_2$ [3] and $[Mo_2Cp_2(CO)_4(\mu-\eta^2:\eta^2-HC\equiv CC(H)(Et)-]_2$ [2] were established by X-ray diffraction. The work also shows that for the best results in the coupling reactions the R_1 and R_2 groups should be free from acidic protons: for example, if $R_1 = R_2 =$ Methyl or Cyclohexyl, the formation of μ-enyne complexes $[Cp_2Mo_2(CO)_4\{\mu-\eta^2:\eta^2-HC\equiv C-C(R) = C(R')(R'')\}]$ is favoured (Scheme 1 (b)).

Similar reactions of ferricinium ions involving a carbonium-ion-centre C^+ stabilised by an organometallic fragment have been known for many years [4]. They are interpreted as proceeding through the reduction of the ferricinium ion by electron transfer from the reducing agent with the formation of a radical, followed by a coupling reaction to produce a dimer. More recently, photolysis of ferrocenyl ethers has been shown to give

ferricinium ion radicals that can dimerise or abstract a proton from the solvent [5].

Here, we describe coupling reactions involving free radical intermediates of the carbenium ions $[Cp_2Mo_2(CO)_4\{\mu-\eta^2:\eta^3-HC\equiv C-C(R_1)(R_2)\}]^+$ with a ferrocenyl group ($R_1 = Fc:(C_5H_4)Fe(C_5H_5)$). The carbon atom bearing the positive charge is adjacent both to a ferrocenyl group and an acetylenic cluster. Such compounds, lacking any acidic protons ($R_1 = Fc$ and $R_2 = H$), cannot give μ-enyne complexes. The nature of the stabilisation of the C^+ atom has already been discussed for the complex $[Cp_2Mo_2(CO)_4\{\mu-\eta^2:\eta^3-CH_3(CH_2)_4-C\equiv C-C(H)(Fc)\}][BF_4]$ [6].

2. Results and discussion

2.1. Reduction of $[Cp_2Mo_2(CO)_4\{\mu-\eta^2:\eta^3-HC\equiv C-C(H)(Fc)\}][BF_4]$ (1)

Treatment of $[Cp_2Mo_2(CO)_4\{\mu-\eta^2:\eta^3-HC\equiv C-C(H)(Fc)\}][BF_4]$ (1) (Scheme 2) with Na–Hg (in toluene 18°C, 18 h) gives a mixture of $[Cp_2Mo_2(CO)_4\{\mu-\eta^2:\eta^2-HC\equiv C-C(H)_2(Fc)\}]$ (2) (yield 23%), $[\{Cp_2Mo_2(CO)_4\}_2(\mu-\eta^2:\eta^2-HC\equiv C-C(H)(Fc)-C(H)(Fc)-C\equiv CH)]$ (4) (yield 7%) and $[Cp_2Mo_2(CO)_4\{\mu-\sigma:\eta^3-HC:CH:C(H)(Fc)\}]$ (3) (yield 10%), which can easily be separated (SiO_2, CH_2Cl_2–hexane). The compounds (2) and (4) result from a typical radical mechanism; com-

pound (4) comes from a coupling reaction between two free radicals (an intermolecular coupling reaction) and compound (2) is formed by abstraction of protons from the solvent or traces of moisture. Complex (4) contains two asymmetric centres, and the dl/meso diastereomers obtained in equal amount cannot be separated. Product (3) probably comes from fragmentation or rearrangement reaction of the μ-alkyne complex (2) which may react with the excess Na. Such processes were discussed previously for the reduction of μ-enyne [1,2] or μ-alkyne complexes [7].

2.2. Reduction of [{Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^3-HC$\equiv$C–C(H)}$_2$Fc][{BF$_4$}$_2$] (5)

The reaction of Na–Hg with the dication [{Cp$_2$-Mo$_2$(CO)$_4$(μ-η^2:η^3-HC$\equiv$C–C(H)}$_2$Fc][{BF$_4$}$_2$] (5) (Scheme 3) yields a mixture of products which can be separated by column-chromatography on silica. Use of the above conditions in the case of dication (5) again gives both coupling and H-atom abstraction, to form compounds (6) and (7). The two main features are that (a) complex (6) is obtained by an intramolecular radical
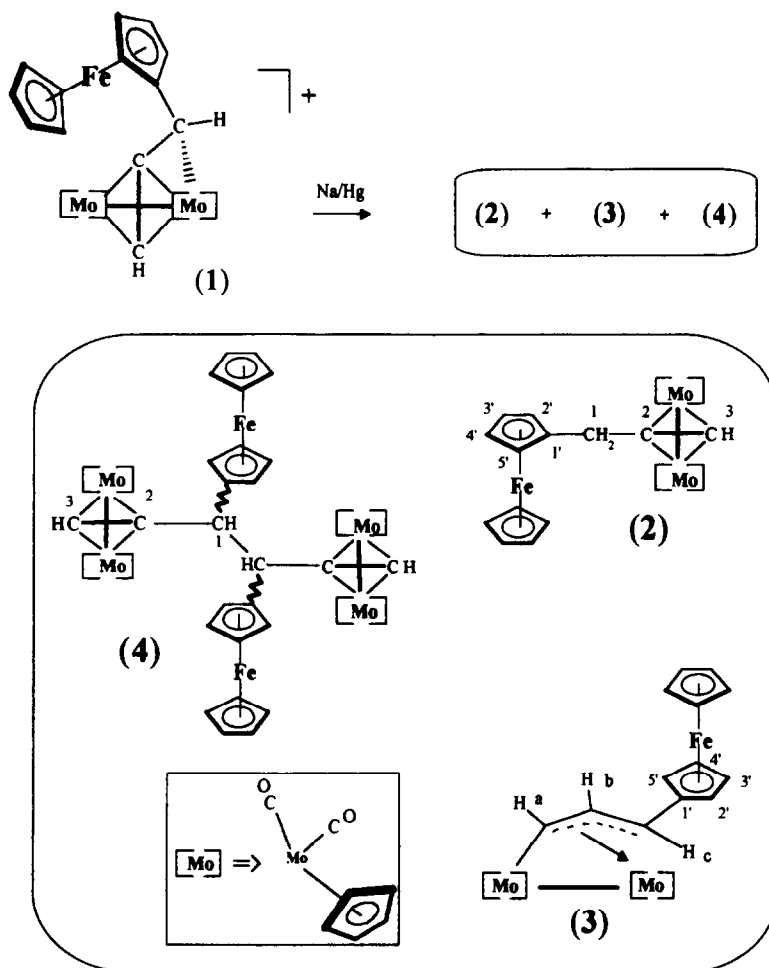

Scheme 1.
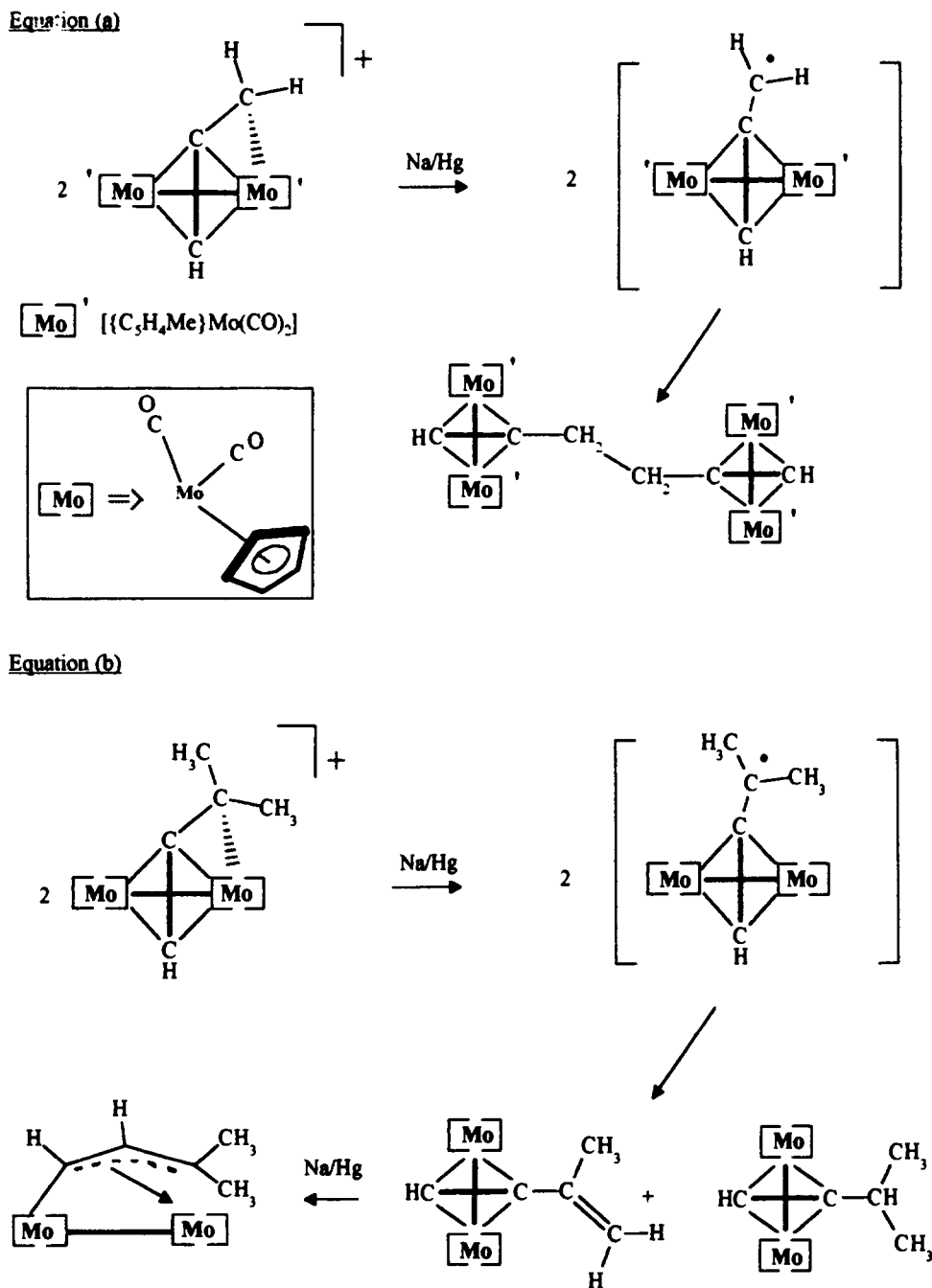
process (unlike the formation of (4) which involved an intermolecular radical process), and (b) only one diastereomer is obtained (diastereoselectivity 100%).

This reaction generates chiral carbon atoms α to the organometallic moieties, and as a consequence the ^{1}H NMR spectrum of (6) displays two signals for cyclopentadienyl ligands linked to molybdenum atoms; the C_5H_5–Mo groups are diastereotopic [8]. Moreover, all the protons of the C_5H_4–Fe ring display different chemical shifts (ABCD spin system) as expected for molecules with a stereogenic carbon atom [9]. Compound (6) is an ansa-ferrocene with two carbon atoms as bridging substituents; it belongs to the [2] (1,1') ferrocenophane class of compounds which attract much attention because of their ability to give access to polyferrocenylethylenes by ring-opening polymerization [10]. These results have to be compared with those for reductive cyclization of $Co_2(CO)_6$-complexed propargyl cations which provided a new route to cycloalkadiynes by a radical intramolecular process [11].

Preliminary electrochemical studies on (6) show that the presence of a C–C bond has a marked influence on the mechanism of oxidation, making it a quasi-reversi-

ble process ($Ep_{ox} = -0.08$ V versus ferrocene) leading to the dication (5). In contrast, two reversible oxidations were observed in the case of 1,1,12,12-tetramethyl-[1.1]silaferrocenophane [12] and its carbon or tin analogue [13]. More complete electrochemical studies of the behaviour of the various carbenium ions, including the nature of the radical intermediate, are in progress in our laboratory.

Recent examination by McClain et al. [14] of the reduction of the dicarbenium complex (A) [$Cp_2Mo_2(CO)_4(CH_2CCCH_2)$][$BF_4$]$_2$ with Na–Hg in the hope of making a polymer was unsuccessful, whereas reduction of the monocarbenium complex (B) [($C_5H_4Me)_2Mo_2(CO)_4(\mu-\eta^2:\eta^3$-HC≡C–CH$_2$)][$BF_4$] [3] gave a C–C coupled product. Unlike that in (B), the LUMO of the dicarbenium complex (A) places no electron density on the ligand upon reduction, so avoiding C–C coupling reactions. Complex (A) is a binuclear compound with a 'C_4H_4' ligand, whereas the dication (5) [{$Cp_2Mo_2(CO)_4(\mu-\eta^2:\eta^3$-HC≡C–C(H)}$_2$Fc][{$BF_4$}$_2$] is a tetranuclear compound that can be considered as two independent carbenium complexes linked by a ferrocenyl substituent. Therefore the behaviour of (5) in one elec-

Scheme 2.

tron reduction is expected to be closer to compound (**B**) than to (**A**). A C–C coupling reaction occurs fortunately by an intramolecular process; in the case of an inter-molecular process, the reaction would probably have been uncontrollable.

In conclusion the results described above show how carbenium ions stabilized by $[Cp_2Mo_2(CO)_4]$ can be used as precursors of dimers $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^2:\eta^2\text{-}HC\equiv CC(R_1)(R_2)-)]_2$ by inter- or intramolecular C–C coupling.

3. Experimental details

3.1. General

All reactions and purifications were performed under dinitrogen using Schlenk techniques. The solvents were freshly distilled under dinitrogen from sodium–benzo-phenone for toluene and from CaH_2 for dichloromethane and hexane.

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 as δ in units of parts per million (ppm) relative to a tetramethylsilane internal reference. Coupling constants are reported in hertz.

The starting materials (**1**) and (**5**) were prepared by treating the alcohol precursors $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^2:\eta^2\text{-}HC\equiv C\text{-}C(H)(OH)(Fc)\}]$ and $[\{Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2:\eta^2\text{-}HC\equiv C\text{-}C(H)(OH)\}_2Fc]$ [15] with an excess of HBF_4 by the standard procedure used for the carbenium ions stabilized by $[Cp_2Mo_2(CO)_4]$ [6,16].

3.2. Reduction of compound $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^2:\eta^3\text{-}HC\equiv C\text{-}C(H)(Fc)\}][BF_4]$ (1)

To a 2% Na–Hg amalgam prepared from 0.3 g of Na and 14.7 g of Hg was added a suspension of $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^2:\eta^3\text{-}HC\equiv C\text{-}C(H)(Fc)\}][BF_4]$ (**1**) (2 g, 2.7 mmol) in 60 ml of toluene. The mixture was stirred at room temperature for 18 h. After filtration, the solvent was removed from the filtrate in vacuo and the residue was chromatographed on silica gel using mixtures of hexane–dichloromethane as eluent.

The first red band eluted with hexane–dichloromethane (70:30 in volume) was shown to contain compound (**2**) (0.41 g, yield 23%).
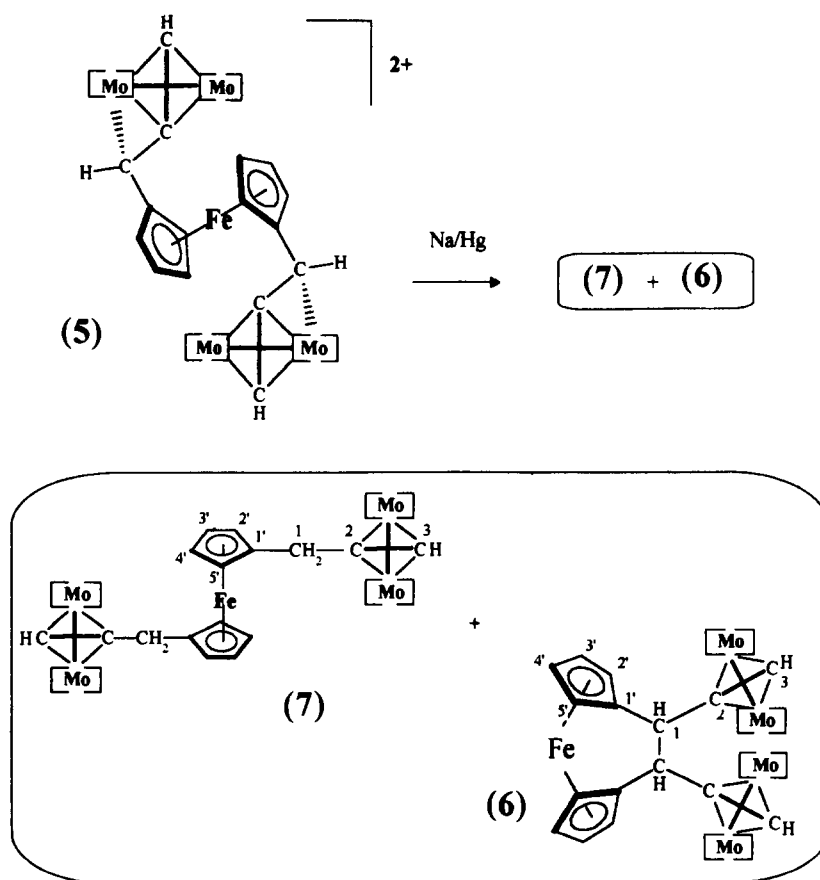
Scheme 3.

The second band containing the red complex (4) (0.12 g, yield 7%) was eluted with hexane–dichloromethane (30:70).

The third orange band, eluted with dichloromethane, gave complex (3) (0.18 g, yield 10%).

Spectroscopic data for $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^2:\eta^2\text{-}HC\equiv C\text{-}C(H)_2(Fc)\}]$ (2):

^{1}H NMR (CD_2Cl_2): 5.81 (s, 1H, HC3); 5.13 (s, 10H, 2 C_5H_5–Mo); 4.08 (s, 5H, C_5H_5–Fe); 3.94 (t, 2H, (H2'–5'), ^3J(H–H) = 1.85); 3.88 (t, 2H, (H3'–4'), ^3J(H–H) = 1.85); 3.53 (s, 2H, CH_2). ^{13}C NMR (CD_2Cl_2): 233.5 (CO); 91.5 (C_5H_5–Mo); 90.2 (C1'); 88.7 (C3); 88.3 (C2); 68.8 (C_5H_5–Fe); 67.7 and 67.6 (C_5H_4, C2', C3', C4', C5'); 36.4 (CH_2). IR (CH_2Cl_2): ν(CO): 1995, 1900, 1825. Anal. Found: C, 48.76; H, 3.27. $C_{27}H_{22}FeMo_2O_4$. Calc.: C, 49.27; H, 3.37%.

Spectroscopic data for $[Cp_2Mo_2(CO)_4\{\mu\text{-}\sigma:\eta^3\text{-}HC\overset{\cdot}{=}CH\overset{\cdot}{=}C(H)(Fc)\}]$ (3):

^{1}H NMR (acetone d_6): 10.15 (dd, 1H, Ha, ^3J(Ha–Hb) = 8.8; ^4J(Ha–Hc) = 1.0); 6.5 (dd, 1H, Hb, ^3J(Hb–Ha) = 8.8; ^3J(Hb–Hc) = 10.6); 5.4 (s, 5H, C_5H_5–Mo); 5.3 (s, 5H, C_5H_5–Mo); 2.5 (d, 1H, Hc, ^3J(Hb–Hc) = 11.0); 4.1 (m, 4H, C_5H_4); 4.16 (s, 5H, C_5H_5–Fe). ^{13}C NMR (acetone d_6): 250.2, 246.8, 242.0 and 241.3 (4 CO); 168.1 (Ca, d, ^1J(C–Ha) = 144.3); 131.8 (Cc, d, ^1J(C–Hc) = 164.4); 129.4 (Cb, d, ^1J(C–Hb) = 162.9); 95.8 (C_5H_5–Mo, d, ^1J(C–H) = 176.0); 92.9 (C_5H_5–Mo, d, ^1J(C–H) = 178.6); 84.0 (C1'); 70.1 (C_5H_5–Fe, d, ^1J(C–H) = 175.6); 69.9, 69.3, 68.1 and 65.9 (C_5H_4, C2', C3', C4', C5', d, ^1J(C–H) = 174.8). IR (CH_2Cl_2) ν(CO): 1940, 1900, 1835. Ca, Cb and Cc represent the carbon atom bearing the Ha, Hb and Hc protons respectively (Scheme 2). Anal. Found: C, 49.71; H, 2.96. $C_{27}H_{22}FeMo_2O_4$. Calc.: C, 49.27; H, 3.37%.

Spectroscopic data for $[\{Cp_2Mo_2(CO)_4\}(\mu\text{-}\eta^2:\eta^2\text{-}HC\equiv C\text{-}C(H)(Fc)\text{-}C(H)(Fc)\text{-}C\equiv CH)]$ (4):

^{1}H NMR spectrum consists of two sets of peaks of about equal intensity, one set corresponding to the R*S* compound and the other to the SS–RR compound. Attempts to obtain a high quality ^{13}C NMR spectrum of (4) were unsuccessful owing to its very poor solubility in a range of deuterated solvents. ^{1}H NMR (THF d_8): 7.57 (s, 4H, HC3); 5.64 (s, 10H, 2 C_5H_5–Mo); 5.47 (s, 10H, 2 C_5H_5–Mo); 5.29 (s, 10H, 2 C_5H_5–Mo); 4.90 (s, 10H, 2 C_5H_5–Mo); 4.42 (s, 10H, 2 C_5H_5–Fe); 4.26 (s, 10H, 2 C_5H_5–Fe); 5.68, 5.10, 4.87, 4.66, 4.63, 4.26, 4.25, 4.13, 3.99, 3.95 (m, C_5H_4 and HC1). IR (THF): ν(CO): 1985, 1900, 1890, 1830. Anal. Found: C, 48.90; H, 3.33. $C_{54}H_{42}Fe_2Mo_4O_8$. Calc.: C, 49.35; H, 3.22%.

3.3. Reduction of compound $[\{Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2:\eta^3\text{-}HC\equiv C\text{-}C(H)\}_2(Fc)][BF_4]_2$ (5)

The procedure described for compound (1) was used: a suspension of $[\{Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2:\eta^3\text{-}HC\equiv C\text{-}$

$C(H)\}_2(Fc)][BF_4]_2$ (5) (1.5 g, 1.15 mmol) in 50 ml of toluene was added to 15 g of 2% Na–Hg amalgam. After stirring 18 h and filtration, the solution was filtered and solvent removed in vacuo to leave a residue which was chromatographed on silica gel with using mixtures of hexane and dichloromethane as eluent.

The first red band was eluted with hexane–dichloromethane (60:40) and gave compound (7) (0.27 g, yield 21%).

The second band eluted with hexane–dichloromethane (40:60) yielded compound (6) (0.23 g, 18%). Owing to the rather similar chromatographic properties of the products, elutions had to be developed very slowly.

Spectroscopic data for $[\{Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2:\eta^2\text{-}HC\equiv C\text{-}C(H)\text{-}\}_2(Fc)]$ (6):

^{1}H NMR (acetone d_6): 6.11 (s, 2H, 2 HC3); 5.40 (s, 10H, 2 C_5H_5–Mo); 5.30 (s, 10H, 2 C_5H_5–Mo); 4.72 (s, 2H, 2 HC1); 4.92 (m, 2H), 4.56 (m, 2H), 4.05 (m, 2H) and 3.82 (m, 2H): 2 (H2'–3'–4'–5'). IR (CH_2Cl_2) ν(CO): 1995, 1910, 1830. Anal. Found: C, 46.72; H, 3.37. $C_{44}H_{32}FeMo_4O_8$. Calc.: C, 46.84; H, 2.86%.

Spectroscopic data for $[\{Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2:\eta^2\text{-}HC\equiv C\text{-}CH_2)_2(Fc)]$ (7):

^{1}H NMR (acetone d_6): 6.06 (s, 2H, 2 HC3); 5.22 (s, 20H, 2 C_5H_5–Mo); 3.99 (t, 4H, 2 (H2'–5'), ^3J(H–H) = 1.8); 3.96 (t, 4H, 2 (H3'–4'), ^3J(H–H) = 1.8); 3.62 (s, 4H, 2 CH_2). ^{13}C NMR (acetone d_6): 233.6 (CO); 230.1 (CO); 93.5 (C1'); 92.0 (C_5H_5–Mo); 90.5 (C3); 89.1 (C2); 69.8 and 68.6 (C_5H_4, C2', C3', C4', C5'); 36.5 (CH_2). IR (CH_2Cl_2) ν(CO): 1995, 1900, 1825. Anal. Found: C, 45.97; H, 3.12. $C_{44}H_{34}FeMo_4O_8$. Calc.: C, 46.75; H, 3.03%.

References

[1] N. Le Berre-Cosquer, R. Kergoat and P. L'Haridon, *Organometallics, 11* (1992) 721.

[2] J.-F. Capon, S. Cornen, N. Le Berre-Cosquer, R. Kergoat, R. Pichon and P. L'Haridon, *J. Organomet. Chem., 470* (1994) 137.

[3] A. Meyer, D. McCabe, M.D. Curtis, *Organometallics, 6* (1987) 1491.

[4] T.G. Taylor and J.C. Ware, *J. Am. Chem. Soc., 89* (1967) 2304; M. Cais and A. Eisenstadt, *J. Am. Chem. Soc., 86* (1964) 1148; K.L. Rinehart, Jr., C.J. Michejda and P.A. Kittle, *J. Am. Chem. Soc., 81* (1959) 3162; V. Weinmayr, *J. Am. Chem. Soc., 77* (1955) 309; P.L. Pauson and W.E. Watts, *J. Chem. Soc.* (1962) 3880.

[5] C. Baker and W.M. Horspool, *J. Chem. Soc. Perkin Trans., 1* (1979) 2294; C. Imrie, T.A. Modro and C.C.P. Wagner, *J. Chem. Soc. Perkin Trans., 2* (1994) 1379; R.A. Jackson, M. Scarmoutsos and A.K. Zarkadis, *J. Chem. Soc. Perkin Trans., 2* (1991) 809.

[6] L.L. Troitskaya, V.I. Sokolov, V.I. Bakhmutov, O.A. Reutov, M. Gruselle, C. Cordier and G. Jaouen, *J. Organomet. Chem., 364* (1989) 195; C. Cordier, M. Gruselle, J. Vaissermann, L.L. Troitskaya, V.I. Bakhmutov, V.I. Sokolov and G. Jaouen, *Organometallics, 11* (1992) 3825.

[7] S.F.T. Froom, M. Green, K.R. Nagle and D.J. Williams, *J. Chem. Soc. Chem.Commun.,* (1987) 1305.

[8] M. Savignac, G. Jaouen, C.A. Roger, R.E. Perrier, B.G. Sayer and M.J. McGlinchey, *J. Org. Chem., 51* (1986) 2328; M. Gruselle, H. El Hafa, M. Nikolski and G. Jaouen, J. Vaisserman, L. Li and M.J.McGlinchey, *Organometallics, 12,* (1993), 4917.

[9] P. Braunstein, T.G. Carnciro, D. Matt, F. Balegroune and D.

Grandjean, *J. Organomet. Chem., 367* (1989) 117; G. Doisneau, G. Balavoine, T. Fellebeen-Khan, J.-C. Cliret, J. Delaire, I. Ledoux, R. Loucif and G. Puccetti, *J. Organomet. Chem., 421* (1991) 299.

[10] J.M. Nelson, H. Rengel and I. Manners, *J. Am. Chem. Soc., 115* (1993) 7035.

[11] G.G. Melikyan, R.C. Combs, J. Lamirand, M. Khan and K.M. Nicholas, *Tetrahedron Lett., 35* (1994) 363.

[12] J. Park, Y. Seo, S. Cho, D. Whang, K. Kim and T. Chang, *J. Organomet. Chem., 489* (1995) 23.

[13] T.Y. Dong, M.Y. Hwang and Y.S. Wen, *J. Organomet. Chem., 391* (1990) 377.

[14] M.D. McClain, M.S. Hay, M.D. Curtis and J.W. Kampf, *Organometallics, 13* (1994) 4377.

[15] J.-F. Capon, N. Le Berre-Cosquer, B. Leblanc and R. Kergoat, *J. Organomet. Chem.,* in press.

[16] V.I. Sokolov, I.V. Barinov, O.A. Reutov, *Isv. Akad. Nauk SSSR, Ser. Khim.,* (1982) 1992.