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Nucleophilic reactions of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_6H_7)$

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Abstract

In the presence of a Lewis acid, $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_6H_7)$ (complex **1**) reacted with aldehydes to form adducts. Proton removal by a base led to reversal of the reaction with regeneration of **1**. The use of a Lewis acid such as Me_3Al, which also acted as a proton scavenger, led to a smooth reaction to give **6**, **7** or **8**. Complex **1** also reacted with NBS to yield a complex, **9**, which incorporates a succinimide group. Solid state structures of **8b** and **9** were characterized by single crystal X-ray analyses.

Keywords: Molybdenum; Aluminium; Metal carbonyl cation; Allyls; Cyclopentadienyl

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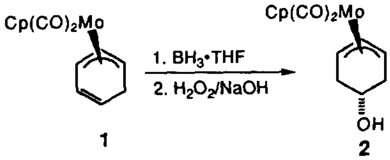
1. Introduction

The cationic molybdenum η^4-cyclohexadienyl complex **4** has been shown to react with a variety of nucleophiles, allowing the stereocontrolled synthesis of cyclohexene derivatives [1]. However, the nucleophilic reactions of the neutral species the η^3-cyclohexadienyl complex **1**, leading to cyclohexene derivatives have been relatively unexplored [2]. Recently, it has been shown that **1** reacted with borane (see Scheme 1), giving rise, after hydrogen peroxide treatment, to a regio- and stereo-selective hydroxyl compound [3]. The nucleophilic property of **1** is of considerable interest, because it may provide an alternative approach to the functionalization of cyclohexenes. Following our interest in promoting the use of organometallic complexes in synthesis, we reacted **1** with aldehydes and with some other electrophiles. Reactions and the crystal structures of **8b** and **9** are discussed.



Scheme 1.

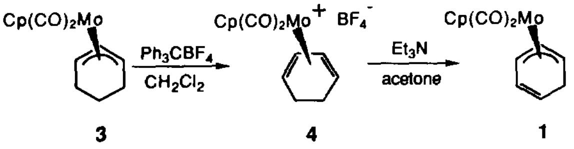
2. Results and discussion

2.1. Preparation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_6H_7)$ (1)

Complex **1** was prepared from $(\eta^5\text{-}C_5H_5)Mo(CO)_2$-$(\eta^3\text{-}C_6H_9)$ (**3**) in two steps. Hydride abstraction of **3** (Ph_3CBF_4, CH_2Cl_2, 0°C) [4], gave the cationic dienyl complex **4** which was then deprotonated (Et_3N, CH_2Cl_2, 25°C), providing **1** in 90% yield (see Scheme 2).

2.2. Reaction of 1 with aldehydes: activation by Lewis acids

Treatment of an ethereal solution of **1** and benzaldehyde with one equivalent of zinc chloride gave a yellow precipitate of complex **5** (see Scheme 3). The IR spectrum showed carbonyl stretchings characteristic of an η^4-cationic compound at 2018 and 1961 cm^{-1}. The ^1H NMR spectrum revealed two bands of equal intensity of cyclopentadienyl protons as singlets at δ 6.05 and 6.06, suggesting an approximately 1:1 ratio of



Scheme 2.

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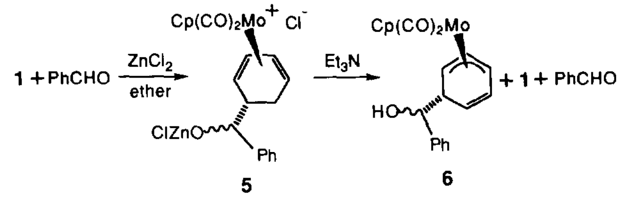


Scheme 3.

diastereomeric isomers. That substrates may come from opposite sides of the metal has been well documented [4,5]. Therefore, the hypothesis was proposed of a diastereomeric mixture arising from the differentiation of two carbonyl faces, leading to a mixture of alkoxyl groups. When a bulkier aldehyde such as pivaldehyde was used, the ratio rose to 1:3. Deprotonation of **5** with Et_3N in CH_2Cl_2 provided 20% of the desired compound **6** and 80% of reversed compound **1**. Similar reversal of reaction was reported by Pearson in the reaction of η^3-cyclohexenone with benzaldehyde [3]. Use of BF_3 as activator in CH_2Cl_2 and/or in Et_2O gave similar results.

2.3. Reaction of 1 with aldehydes: activation by trimethylaluminium (Me_3Al)

In order to eliminate the reverse reaction described above, Me_3Al was tested. In addition to being a Lewis acid, Me_3Al is also known as an acidic proton scavenger [6]. We were anticipating that Me_3Al will first react as a Lewis acid to promote the addition of **1** with carbonyl groups, and will then scavenge a proton from the η^4-cationic intermediate, resulting in a neutral complex of the type of **6**. Indeed, treatment of an ethereal solution of **1** and benzaldehyde with Me_3Al gave complex **6** in 3:2 diastereomeric mixture. A significant amount of α-methylbenzyl alcohol was also isolated. In the case of pivaldehyde and crotonaldehyde, the intermediate aluminium alkoxides **7a** and **7b** reacted further with excess aldehyde to give the Oppenauer oxidation [7] compounds **8a** and **8b** respectively (see Scheme 4). In both keto compounds, the olefinic double bond is in the deconjugated position, attested by the absence of evidence of CH_2 carbons in DEPT experiments. The structure of **8b** was unequivocally characterized by a single crystal X-ray analysis (see Fig. 1). No disubstituted complex was obtained. Attempts to isomerize the double bond to the conjugated position by using bases (Et_3N or $NaN(SiMe_3)_2$; H_2O) or acid (CF_3COOH) were not successful.

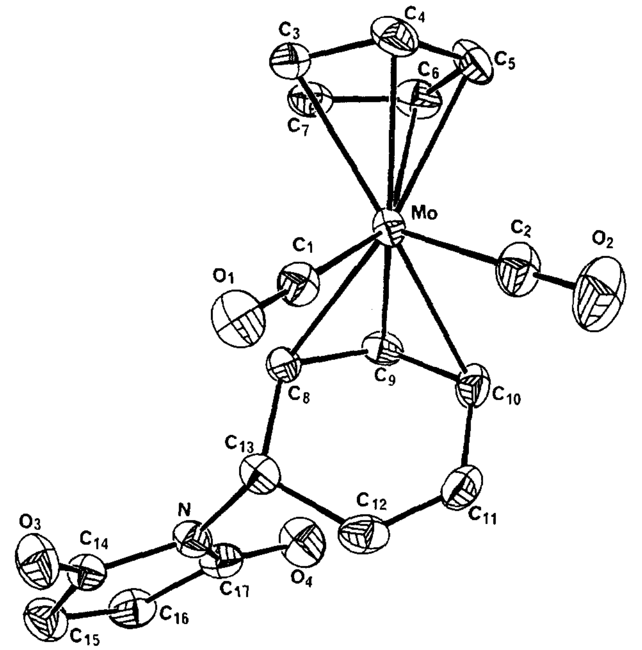
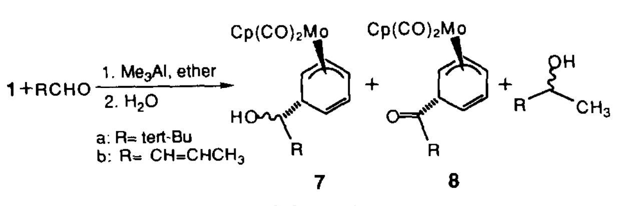


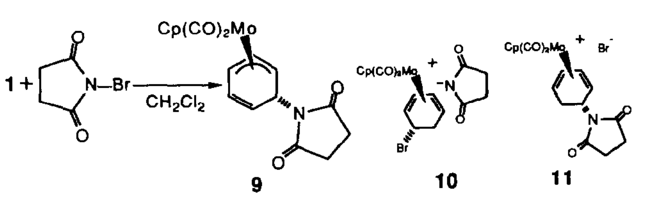
Fig. 1. ORTEP drawing of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_6H_6COC_3H_5)$ (**8b**).



Scheme 4.

2.4. Reaction of 1 with N-bromosuccinimide (NBS)

Treatment of **1** in CH_2Cl_2 with NBS gave the expected cationic dienyl intermediate (IR: 2056m, 2021s, 1965s cm^{-1}). Further treatment with Et_3N provided complex **9** incorporating a succinimide group (see Scheme 5), instead of the anticipated bromo-compound. This was indicated by the characteristic succinimide group absorptions which appeared in the infrared (1701 cm^{-1}) and ^1H NMR (δ 2.66, s) spectra. Formation of **9** could have proceeded through the bromodienyl cationic intermediate **10** followed by succinimide anion addition and fast bromide expulsion to give intermediate **11**. Finally, basic deprotonation would give compound **9**. Single crystal X-ray analysis suggested that the succinimide group and the metal were at the *trans* position of the six-membered ring (see Fig. 2). Therefore, direct substitution of bromine with succinimide anion was unlikely, as if the reaction



Scheme 5.

Table 1
Selected bond lengths (Å), bond angles (°) and torsion angles (°) in complex **8b**

Mo–C(1)	1.931(10)	C(8)–C(9)	1.393(12)
Mo–C(2)	1.926(9)	C(8)–C(13)	1.504(10)
Mo–C(8)	2.368(7)	C(9)–C(10)	1.375(13)
Mo–C(9)	2.189(7)	C(10)–C(11)	1.446(16)
Mo–C(10)	2.350(8)	C(11)–C(12)	1.344(17)
O(1)–C(1)	1.164(12)	C(12)–C(13)	1.511(13)
O(2)–C(2)	1.162(10)	C(13)–C(14)	1.534(11)
O(3)–C(14)	1.206(10)	C(14)–C(15)	1.469(11)
C(3)–C(4)	1.411(13)	C(15)–C(16)	1.341(11)
C(4)–C(5)	1.416(15)	C(16)–C(17)	1.482(12)
C(1)–Mo–C(2)	80.5(4)	C(10)–C(11)–C(12)	122.8(8)
C(5)–C(6)–C(7)	108.2(9)	C(11)–C(12)–C(13)	120.8(8)
C(8)–C(9)–C(10)	117.1(7)	O(3)–C(14)–C(13)	121.0(7)
Mo–C(1)–O(1)	177.1(8)	O(3)–C(14)–C(15)	122.1(7)
Mo–C(2)–O(2)	178.7(7)	C(14)–C(15)–C(16)	123.3(8)
C(7)–C(3)–C(4)–C(5)	−0.1(5)	C(11)–C(12)–C(13)–C(8)	−4.2(4)
C(10)–C(11)–C(12)–C(13)	−2.8(4)	O(3)–C(14)–C(15)–C(16)	9.1(4)
C(4)–C(5)–C(6)–C(7)	1.0(5)	C(14)–C(15)–C(16)–C(17)	179.1(8)

had proceeded through S_N2, a *cis* relationship of the succinimide group and the metal might be expected.

*2.5. Solid state structure of **8b** and **9***

Single crystal X-ray diffractometric analyses showed that both **8b** and **9** were η^3 coordinated cyclohexadienyl molybdenum complexes (Figs. 1 and 2). The substituent and molybdenum were on different faces of the six-membered ring. The features of the $(\eta^5$-$C_5H_5)Mo(CO)_2$(allyl) fragment are similar to those of the analogous $(\eta^5$-$C_5H_5)Mo(CO)_2(\eta^3$-$C_6H_9)$ (**3**) [4] and $(\eta^5$-$C_5H_5)Mo(CO)_2(\eta^3$-$C_3H_5)$ [8]. The bond length of central carbon (C9) to molybdenum was about 0.16 Å shorter than that of terminal carbons (C8 and C10) in the allyl portion (see Tables 1 and 2) compared to 0.17 Å shorter for **3** and 0.12 Å shorter for η^3-C_3H_5. Molybdenum–carbonyl was in a linear geometry with C(1)–Mo–C(2) bond angles of 80.5° for **8b** and 81.6° for **9** compared to 82.7° for **3** and 82.5° for η^3-C_3H_5. The bond length data revealed that C(11)–C(12) was a double bond in both compounds (1.344 Å for **8b**, 1.308 Å for **9**). This confirmed that the keto-group of compound **8b** was deconjugated with the ring double bond.

3. Experimental section

All reactions were performed under an argon atmosphere with use of Schlenk techniques. Diethyl ether (Et_2O) and n-hexane were distilled from sodium benzophenone ketyls; methylene chloride (CH_2Cl_2) was

Table 2
Selected bond lengths (Å), bond angles (°) and torsion angles (°) in complex **9**

Mo–C(1)	1.932(4)	O(3)–C(14)	1.200(5)
Mo–C(2)	1.954(4)	O(4)–C(17)	1.199(5)
Mo–C(8)	2.345(3)	C(3)–C(4)	1.395(5)
Mo–C(9)	2.209(3)	C(4)–C(5)	1.409(5)
Mo–C(10)	2.397(3)	C(8)–C(9)	1.409(5)
N–C(13)	1.490(4)	C(8)–C(13)	1.510(5)
N–C(14)	1.393(4)	C(9)–C(10)	1.400(5)
N–C(17)	1.396(4)	C(10)–C(11)	1.459(5)
O(1)–C(1)	1.156(5)	C(11)–C(12)	1.308(6)
O(2)–C(2)	1.147(5)	C(12)–C(13)	1.498(5)
C(1)–Mo–C(2)	81.65(15)	C(10)–C(11)–C(12)	122.8(4)
C(5)–C(6)–C(7)	108.5(3)	C(11)–C(12)–C(13)	121.4(3)
C(8)–C(9)–C(10)	115.3(3)	C(14)–C(15)–(16)	106.0(3)
Mo–C(1)–O(1)	178.2(3)	N–C(14)–C(15)	107.6(3)
Mo–C(2)–O(2)	177.9(3)	N–C(14)–O(3)	124.2(3)
C(17)–N–C(14)–O(3)	−179.8(4)	C(15)–C(16)–C(17)–N	−1.8(2)
C(3)–C(4)–C(5)–C(6)	0.0(2)	C(2)–Mo–C(9)–C(10)	−2.4(2)
C(5)–C(6)–C(7)–C(3)	0.7(2)	C(13)–N–C(14)–C(15)	173.9(4)
C(10)–C(11)–C(12)–C(13)	−7.2(2)	C(13)–N–C(17)–C(16)	−172.7(4)
C(11)–C(12)–C(13)–C(8)	0.9(2)	N–C(14)–C(15)–C(16)	−0.7(2)
O(3)–C(14)–C(15)–C(16)	178.6(5)	C(14)–C(15)–C(16)–C(17)	1.5(2)

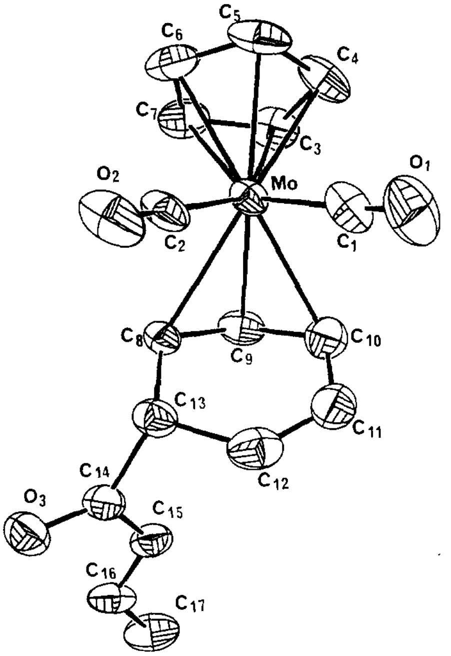


Fig. 2. ORTEP drawing of $(\eta^5\text{-}C_5H_5)Mo(CO)_2[\eta^3\text{-}C_6H_6N(COCH_2)_2]$ (9).

distilled from CaH_2. Infrared solution spectra were recorded on a Perkin-Elmer 882 infrered spectrophotometer using 0.1 mm cells with CaF_2 windows. Melting points were determined by using a Yanaco model MP micro melting point apparatus and were uncorrected. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) were obtained with a Bruker AC-200 FT spectrophotometer. ^1H NMR spectra (500 MHz) were obtained with a Bruker AMX-500 spectrophotometer. All chemical shifts are reported in parts per million (ppm) relative to Me_4Si. Elemental analyses were obtained on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra were recorded on a VG 70-250S mass spectrophotometer.

3.1. Preparation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_6H_7)$ (1)

To a stirred yellow solution of $(\eta^5\text{-}C_5H_5)Mo(CO)_2\text{-}(\eta^3\text{-}C_6H_9)$ (3) (10.9 g, 36.6 mmol) in CH_2Cl_2 at 0°C was added triphenylcarbenium tetrafluoroborate as an orange powder (12.1 g, 36.6 mmol) in one portion. Precipitation was observed. After stirring for 30 min, the ice-water bath was removed and Et_2O (100 ml) was added. Solvents were decanted. Solids were washed twice with Et_2O (50 ml × 2), giving $[(\eta^5\text{-}C_5H_5)Mo\text{-}(CO)_2(\eta^4\text{-}C_6H_8)]^+[BF_4]^-$ (4) as a yellow powder.

4, a yellow powder, was suspended in CH_2Cl_2 (70 ml) at room temperature. Et_3N (20 ml) was then added and stirred until all solids had disappeared (15–20 min). After the solution became homogeneous, CH_2Cl_2 and excess Et_3N were evaporated. The desired compound was then taken up with Et_2O extraction (three times 120 + 60 + 60 ml), providing 9.8 g (90%) of **1** as an orange crystalline compound after removal of Et_2O. The purity was excellent and the sample was used directly without further purification. An analytically pure sample was obtained by recrystallization from a solution of CH_2Cl_2 + hexanes. IR (CH_2Cl_2): 1934s, 1852s cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.14–6.06 (1H, m), 5.24 (5H, s), 4.65–4.56 (1H, m), 4.14–4.11 (2H, m), 3.99–3.92 (1H, m), 2.60–2.31 (2H, m). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 239.6(CO), 235.3 (CO), 130.8(CH), 115.9(CH), 91.7(5 × CH), 57.8(CH), 53.8(CH), 50.3(CH), 27.4(CH_2). Mass spec (EI, 20 eV, ^{98}Mo): 270 (35, $M^+ - CO$), 242 (92, $M^+ - 2CO$). Anal. Found: C, 52.86; H, 3.80. $C_{13}H_{12}O_2Mo$ calc.: C, 52.72; H, 4.08%.

3.2. Reaction of 1 with benzaldehyde activated by zinc chloride

To a stirred yellow solution of **1** (200 mg, 0.67 mmol) and benzaldehyde (97 mg, 0.91 mmol) in Et_2O (10 ml) cooled in iced water was added over 3 min an ethereal solution of zinc chloride (0.8 ml × 1M). The resulting suspension was stirred for 30 min. The yellow precipitate was collected by centrifugation and washed once with Et_2O. A mixture of alkoxides **5** was obtained in a pale yellow powder in 85% yield (310 mg) to show infrared and ^1H NMR spectra as follows. IR (CH_3CN): 2055m, 2018s, 1961s cm^{-1}. ^1H NMR (C_3D_6O, 200 MHz): δ 7.40–7.21 (5H, m, phenyl-H's), 6.35–6.18 (2H, m), 6.06 (5H, s, Cp–H's; isomer a), 6.05 (5H, s, Cp–H's, isomer b), 4.85–4.64 (3H, m), 2.77–2.68 (1H, m), 2.12–1.88 (2H, m). ^{13}C NMR (C_3D_6O, 50 MHz): δ 223.3 (CO), 223.1 (CO), 143.1 (C, phenyl), 130.4, 128.5, 127.6, 126.9 and 126.4 (CH, phenyl-C's), 94.5 (CH × 5, Cp-C's), 85.4–84.0 (CH, broad), 78.1 (CH), 76.0 (CH), 46.4 (CH), 45.6 (CH), 25.9 (CH_2).

The above alkoxides were suspended in CH_2Cl_2 (5 ml) and Et_3N (1 ml) was added. After stirring at room temperature for 10 min, the resulting homogeneous solution was concentrated. Residues were dissolved with CH_2Cl_2 (2 ml). The resulting brown solution was added to a stirred ether solution (20 ml). Brown precipitates were discarded and the yellow solution was filtered through Celite to give a yellow liquid after removal of solvents. Examination by ^1H NMR showed that it contained 80% of **1** and 20% of a 1 : 1 mixture of **6**.

3.3. Preparation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_6H_6CH\text{-}OHPh)$ (6)

To a stirred yellow solution of **1** (0.605 g, 2.04 mmol) and benzaldehyde (0.6 ml, 5.4 mmol) in Et_2O (30 ml) at room temperature was added over 5 min an ethereal solution of Me_3Al (4 ml × 2M, 8 mmol). Gentle heat and evolution of gas was observed. After stirring for 1 h, H_2O (2 ml) was added slowly with caution. The ether layer was concentrated. The yellow oil residue was then flash chromatographed on silica gel [9], using 20% EtOAc in hexanes solution as an eluent. A yellow band was collected and concentrated to give a mixture of **6** and α-methylbenzyl alcohol. The α-methylbenzyl alcohol was then removed under vacuum at 60°C. The residue was flash chromatographed again on silica gel and 15% EtOAc in hexanes as an eluent, providing 0.668 g (81%) of **6** as yellow liquid. TLC (silica gel): $R_f = 0.13$ (15% EtOAc in hexanes). IR (CH_2Cl_2): 1938s, 1857s cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.42–7.26 (5H, m, phenyl–H's), 6.22 (1H, dd, J = 9.6, 5.2 Hz), 5.25 (s) and 5.22 (s) (5H, Cp–H's), 4.82 (0.5H, dd, J = 5.2, 5.0 Hz, benzylic–H, isomer a), 4.69 (0.5H, dd, J = 5.2, 2.2 Hz, benzylic–H, isomer b), 4.40–4.25 (2H, m), 4.03–3.96 (2H, m), 2.77–2.70 (1H, m), 2.15 (0.5H, d, J = 5.2 Hz, –OH, isomer a), 2.11 (0.5H, d, J = 2.2 Hz, –OH isomer b). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 240.0 and 239.7 (CO), 235.3 and 235.1 (CO), 142.3 (C, phenyl), 134.2 and 133.6 (CH, olefin), 128.0 and 127.8 (CH × 2, phenyl), 127.1 and 127.0 (CH, phenyl), 126.2 and 125.9 (CH × 2, phenyl), 116.2 and 113.8 (CH, olefin), 91.7 (CH × 5, Cp-C's), 77.6 and 77.3 (CH, hydroxyl-C), 58.5 (CH, η^3-allyl), 50.8 (CH, η^3-allyl), 50.5 (CH, η^3-allyl), 45.5 and 45.4 (CH). Anal. Found: C, 59.76; H, 4.14. $C_{20}H_{18}O_3Mo$ calc.: C, 59.71; H, 4.51%.

3.4. Preparation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_6H_6CHOH^tBu)$ (7a) and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_6H_6CO^tBu)$ (8a)

To a stirred yellow solution of **1** (3.27 g, 11 mmol) and pivaldehyde (6 ml, 55 mmol) in Et_2O (110 ml) at room temperature was added a hexane solution of Me_3Al (17 ml × 2M) slowly over 30 min. A cloudiness was observed which disappeared immediately. The resulting orange solution was stirred for 20 h. Water (10 ml) was added slowly with caution. The orange ethereal layer was concentrated and then flash chromatographed on silica gel, using 5% EtOAc followed by 15% EtOAc in hexanes as eluents. Two fractions were obtained:

1). First fraction providing 2.30 g (55%) of **8a** as an orange solid. TLC (silica gel): $R_f = 0.60$ (25% EtOAc in hexanes). An analytically pure sample was obtained by recrystallization from a CH_2Cl_2/hexanes (1/5), solution at –20°C. m.p. 130–131°C. IR (CH_2Cl_2): 1937s, 1858s, 1691m cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 6.24–6.20 (1H, m), 5.27 (5H, s), 4.40–4.38 (2H, m), 4.03–4.00 (1H, m), 3.85–3.83 (1H, m), 3.81–3.79 (1H, m), 1.21 (9H, s). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 239.0 (CO), 235.4 (CO), 214.8 (C=O), 133.4 (CH), 113.0 (CH), 91.9 (5 × CH, Cp), 58.8 (CH), 52.1 (CH), 50.0 (CH), 45.4 (CH), 45.0 (C), 25.9 (CH_3). Mass spec (EI, 20 eV, Mo – 190): 354 (100, $M^+ - CO$), 269 (43, $M^+ - CO - C_5H_9O$), 241 (82, $M^+ - 2CO - C_5H_9O$). Anal. Found: C, 56.79; H, 5.29. $C_{18}H_{20}O_3Mo$ calc.: C, 56.85; H, 5.30%.

2). Second fraction providing 0.320 g (7.6%) of a 3 : 1 mixture of **7a** as orange liquid. TLC (silica gel): R_f = 0.39 (25% EtOAc in hexanes). ^1H NMR ($CDCl_3$, 200 MHz): δ 6.36–6.28 (0.75H, m), 6.23–6.15 (0.25H, m), 5.27 (5H, s, Cp–H's), 4.53–4.17 (2H, m), 4.02–3.88 (2H, m), 3.37 (0.75H, dd, J = 8.0, 1.2 Hz), 3.30–3.28 (0.25H, m), 2.76–2.72 (0.75H, m), 2.70–2.64 (0.25H, m), 1.75 (0.25H, d, J = 3.8 Hz, –OH), 1.70 (0.75H, d, J = 8.0 Hz, –OH), 1.07 (0.25 × 9H, t-Bu), 0.95 (0.75 × 9H, s, t-Bu).

3.5. Preparation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_6H_6COC_3H_5)$ (8b)

To a stirred yellow solution of **1** (3.950 g, 13.34 mmol) and crotonaldehyde (5.5 ml, 66 mmol) in Et_2O (130 ml) cooled in iced water was added a hexane solution of Me_3Al (20 ml × 2M) slowly over 30 min. The ice-water bath was removed and allowed to stir at room temperature for 20 h. Gas evolution was observed during the warm-up period. Water (10 ml) was added to the resulting orange solution with caution. The orange ethereal layer was concentrated. The orange liquid residues were flash chromatographed on silica gel, using 10% EtOAc followed by 20% EtOAc in hexanes as eluents. An orange band at $R_f = 0.14$ (10% EtOAc in hexanes) was collected and concentrated to give 1.85 g (38%) of complex **8b** as orange solids. An analytically pure sample was obtained by recrystallization from a CH_2Cl_2/hexanes (1/10) solution at –20°C. Mp. 132–133.5°C. IR (CH_2Cl_2): 1941s, 1862s, 1679m, 1664m, 1625m cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.98 (1H, dq, J = 15.4, 6.9 Hz, H_9), 6.38 (1H, dq, J = 15.4, 1.7 Hz, H_8), 6.30–6.21 (1H, m, H_4), 5.28 (5H, s, Cp–H's), 4.61–4.52 (1H, m, H_5), 4.37 (1H, t, J = 6.6 Hz, H_2), 4.09–3.87 (2H, m, H_1 and H_3), 3.39–3.36 (1H, m, H_6), 1.92 (3H, dd, J = 6.9, 1.7 Hz, H'_{10}s). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 239.3 (CO), 234.6 (CO), 198.8 (CO), 143.4 (C_9), 134.1 (C_4), 128.7 (C_8), 112.7 (C_5), 92.0 (Cp-C's), 58.6, 51.0, 50.7, 50.3, 18.3 (C_{10}). Anal. Found: C, 55.85; H, 4.35, $C_{17}H_{16}O_3Mo$ calc.: C, 56.06; H, 4.43%.

3.6. Preparation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2[\eta^3\text{-}C_6H_6N(COCH_2)_2]$ (9)

To a stirred yellow solution of **1** (2.96 g, 10 mmol) in CH_2Cl_2 (50 ml), kept cool in a dry ice-acetone bath, was added powdered N-bromosuccinimide (1.97 g, 11 mmol) in portions over 10 min. After stirring for an additional 10 min, the dry ice-acetone bath was re-

Table 3
Crystal data and details of the structure determination of complex **8b** and **9**

formula	$C_{17}H_{20}O_3Mo$	$C_{17}H_{15}NO_4Mo$
mol wt	368.28	393.25
cryst syst	triclinic	monoclinic
space group	$P-1$	$P2_1/c$
a (Å)	8.1040(18)	6.4414(8)
b (Å)	9.2405(12)	22.525(3)
c (Å)	11.2224(7)	10.5893(12)
α (deg)	104.723(8)	90
β (deg)	95.080(11)	94.962(16)
γ (deg)	105.316(14)	90
cell vol (Å^3)	773(1)	1530.7(3)
Z; D_{calc} (g cm^{-3})	2; 1.582	4; 1.706
F(000)	376	792
cryst size (mm)	0.13 × 0.13 × 0.44	0.28 × 0.41 × 0.41
scan range (deg)	0.70 + 0.35 tan(θ)	0.60 + 0.35 tan(θ)
2θ range (deg)	4-45	4-45
h, k, l range	(−8; 8), (0; 9), (−12; 11)	(−6; 6), (0; 24), (0; 11)
μ (cm^{-1})	8.34	8.542
no. of collcd reflns	2189	2197
no. of unique reflns	2015	1993
no. of reflns with $I > 2\sigma$ (I)	1520	1752
no. of refined params	190	268
weighting scheme	$1/\sigma^2$ (F)	$1/\sigma^2$ (F)
final R, R_w	0.040, 0.047	0.022, 0.028
GOF	1.58	1.77
maximum shift/σ ratio	0.004	0.034
min, max diff map (e Å^{-3})	−0.410, 0.430	−0.340, 0.280

placed with an ice-water bath. Stirring was continued for 30 min. Et_3N (5 ml) was then added to the resulting dark orange solution and stirred for 10 min. Solvents were evaporated. The resulting brown solids were flash chromatographed on silica gel, using 40% EtOAc followed by 80% EtOAc in hexanes as eluents. A yellow band at $R_f = 0.77$ (100% EtOAc) was collected

Table 4
Atomic coordinates and B_{iso} of **8b**

Atom	x	y	z	B_{iso}
Mo	0.29289(9)	0.29790(8)	0.19750(6)	3.84(3)
O(1)	0.2887(10)	0.3330(10)	−0.0696(6)	9.2(6)
O(2)	−0.1005(8)	0.1728(8)	0.0964(7)	8.5(4)
O(3)	−0.1528(7)	0.6324(7)	0.3968(5)	5.7(3)
C(1)	0.2933(11)	0.3238(11)	0.0321(9)	6.1(5)
C(2)	0.0471(11)	0.2207(9)	0.1358(8)	5.2(4)
C(3)	0.5356(12)	0.2711(10)	0.3140(8)	5.9(5)
C(4)	0.5269(12)	0.1961(13)	0.1863(9)	6.8(6)
C(5)	0.3708(14)	0.0706(11)	0.1494(9)	6.9(6)
C(6)	0.2875(13)	0.0681(10)	0.2517(10)	6.7(6)
C(7)	0.3866(13)	0.1917(11)	0.3529(8)	6.0(5)
C(8)	0.1630(10)	0.4661(8)	0.3263(6)	4.0(4)
C(9)	0.3408(11)	0.5285(9)	0.3320(7)	4.6(4)
C(10)	0.3946(11)	0.5698(10)	0.2292(9)	5.9(5)
C(11)	0.2806(17)	0.6265(10)	0.1588(9)	7.0(6)
C(12)	0.1168(14)	0.6162(10)	0.1772(8)	6.0(5)
C(13)	0.0398(10)	0.5368(8)	0.2703(7)	4.6(4)
C(14)	−0.0060(11)	0.6534(9)	0.3763(7)	4.4(4)
C(15)	0.1374(10)	0.7892(9)	0.4520(7)	4.6(4)
C(16)	0.1220(12)	0.8878(9)	0.5581(8)	5.4(5)
C(17)	0.2612(13)	1.0254(10)	0.6397(8)	6.7(5)

Table 5
Atomic coordinates and B_{iso} of **9**

Atom	x	y	z	B_{iso}
Mo	0.27152(4)	0.0708(1)	0.22585(2)	2.54(1)
N	0.1140(4)	0.1625(1)	−0.1737(2)	3.02(12)
O(1)	0.6183(4)	0.0600(1)	0.0456(2)	4.34(13)
O(2)	0.6178(5)	0.1535(1)	0.3704(3)	6.93(17)
O(3)	0.3151(4)	0.1131(1)	−0.3082(2)	4.47(12)
O(4)	−0.1416(4)	0.2168(1)	−0.0892(3)	5.06(13)
C(1)	0.4877(6)	0.0677(1)	0.1122(3)	3.13(15)
C(2)	0.4872(6)	0.1265(2)	0.3168(4)	4.26(17)
C(3)	0.2160(6)	−0.0241(2)	0.2401(3)	3.56(17)
C(4)	0.3261(7)	−0.0046(2)	0.3516(3)	3.88(17)
C(5)	0.1959(6)	0.0334(2)	0.4151(3)	4.03(18)
C(6)	0.0064(6)	0.0368(2)	0.3416(4)	3.90(18)
C(7)	0.0190(6)	0.0019(2)	0.2337(4)	3.64(17)
C(8)	0.1168(5)	0.1127(1)	0.0312(3)	2.70(14)
C(9)	0.0403(5)	0.1410(1)	0.1364(3)	2.90(14)
C(10)	0.1782(6)	0.1807(2)	0.2015(3)	3.45(16)
C(11)	0.3211(6)	0.2135(2)	0.1277(4)	3.85(17)
C(12)	0.3454(6)	0.2013(2)	0.0091(4)	3.78(17)
C(13)	0.2455(5)	0.1479(2)	−0.0550(3)	3.04(15)
C(14)	0.1611(6)	0.1409(1)	−0.2912(3)	3.24(15)
C(15)	−0.0141(7)	0.1582(2)	−0.3868(4)	4.33(20)
C(16)	−0.1687(6)	0.1912(2)	−0.3143(4)	4.12(18)
C(17)	−0.0746(6)	0.1933(2)	−0.1787(3)	3.58(17)

to give 1.32 g (36%) of complex **9** as a yellow foam after removal of solvents. An analytically pure orange crystal was obtained by slow diffusion of a CH_2Cl_2 solution into hexane (CH_2Cl_2/hexane = 1/10) at 25°C. Mp. 110°C (dec.). IR (CH_2Cl_2): 1948s, 1866s, 1701s cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.40–6.32 (1H, m), 5.25 (5H, s, Cp–H's), 4.72–4.60 (2H, m), 4.41–4.33 (1H, m), 4.20–4.14 (1H, m), 3.68–3.61 (1H, m), 2.66 (4H, s). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 239.8 (CO), 234.5 (CO), 176.6 (CO × 2), 135.6 (CH), 111.5 (CH), 92.1 (CH × 5), 61.2 (CH), 51.0 (CH × 2), 47.8 (CH), 28.1 ($CH_2 \times 2$). Anal. Found: C, 51.52; H, 3.54; N, 3.55. $C_{17}H_{15}NO_4Mo$ calc.: C, 51.92; H, 3.84; N, 3.56%.

3.7. *Crystal structure of* $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_6H_6\text{-}COC_3H_5)$ *(8b) and* $(\eta^5\text{-}C_5H_5)Mo(CO)_2[\eta^3\text{-}C_6H_6N\text{-}(COCH_2)_2]$ *(9)*

A single crystal of **8b** was grown in a 1:10 solution of dichloromethane and n-hexane at −20°C. The single crystal of **9** was grown by slow diffusion of a CH_2Cl_2 solution of **9** into hexane (CH_2Cl_2/hexane = 1/10) at 25°C. Diffraction measurements of both compounds were made on an Enraf-Nonius CAD-4 diffractometer by use of graphite-monochromated Mo Kα radiation (λ = 0.7093 Å) in the θ-2θ scan mode. Unit cell dimensions were obtained by least-squares refinement with use of 22 centred reflections for which $15.63° < 2\theta < 31.99°$ for **8b** and $16.43° < 2\theta < 36.49°$ for **9**. Other crystal data and refinement details are listed in Table 3. Atomic coordinates and B_{iso} of **8b** and **9** are listed in Tables 4 and 5 respectively.

4. Supplementary material available

Lists of crystal data and refinement details, atomic coordinates and B_{iso} bond lengths and angles and torsion angles of **8b** and **9** are available from T.-F.W.

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References

[1] A.J. Pearson and R. Mortezaei, *Tetrahedron Lett.*, *30* (1989) 5049; A.J. Pearson, V.D. Khetani and B.A. Roden, *J. Org. Chem.*, *54* (1989) 5141; S. Hansson, J.F. Miller and L.S. Liebeskind, *J. Am. Chem. Soc.*, *112* (1990) 9660; W.J. Vong, S.M. Peng, S.H. Lin, W.J. Lin and R.S. Liu, *J. Am. Chem. Soc.*, *113* (1991) 573.

[2] M. Green, S. Greenfield and M. Kersting, *J. Chem. Soc., Chem. Commun.* (1985) 18; J. Feldman and J.C. Calabrese, *J. Chem. Soc., Chem. Commun.* (1991) 134; T.F. Wang and Y.S. Wen, *J. Organomet. Chem.*, *439* (1992) 155.

[3] A.J. Pearson and M.W.D. Perry, *J. Chem. Soc., Chem. Commun.*, (1989) 389.

[4] J.W. Faller, H.H. Murray, D.L. White and K.H. Chao, *Organometallics*, *2* (1983) 400.

[5] J.W. Faller, J.A. John and M.R. Mazzieri, *Tetrahedron Lett.*, *30* (1989) 1769.

[6] B.B. Snider, D.J. Rodini, M. Karras, T.C. Kirk, E.A. Deutsch, R. Cordova and R.T. Price, *Tetrahedron*, *37* (1981) 3927.

[7] C. Djerassi in *Organic Reactions*, *6* (1951) 207.

[8] J.W. Faller, D.F. Chodosh and D. Katahira, *J. Organomet. Chem.*, *187* (1980) 227.

[9] W.C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, *43* (1978) 2923.