Homoleptic Molybdenum Complexes of α,β-Unsaturated Amides and Esters: Preparation and Crystal Structures†

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Bis(η^6-toluene)molybdenum reacted with *N,N*-dimethylacrylamide and methyl methacrylate under mild conditions with exchange of both arene ligands to yield the new homoleptic tris(1-oxa-1,3-diene)molybdenum complexes [Mo{$H_2C{=}CHC(O)NMe_2$}$_3$] and [Mo{$H_2C{=}C(Me)C(O)OMe$}$_3$] in 84 and 50% yield, respectively. The yellow, crystalline compounds exhibit three-fold symmetry in solution (^1H and ^{13}C NMR spectra) and also in the solid state (crystal structure analyses). The ligand bonding is best described as intermediate between η^4 and κ^2,η^2 co-ordination. For the first time in the tris(oxadiene) complex series, a non-symmetrical isomer can be isolated in low yield from the crude product mixture of the ester complexation reaction and has been characterised spectroscopically.

In the course of our investigations directed towards the preparation and reactivity of 1-oxa-1,3-diene complexes, we have already demonstrated that homoleptic molybdenum and tungsten complexes of α,β-unsaturated ketones can be obtained from a variety of 1-oxadienes.[1] Thus the two homoleptic but-3-en-2-one complexes first prepared by King and Fronzaglia,[2] of which the molybdenum compound was obtained in only 1.9% yield, are not unique to this specific ligand. Recently, in order further to improve the preparation of homoleptic molybdenum oxadiene complexes, we developed a new synthesis based on ligand exchange.[1b] As ligand substitution was expected to become more facile when complexing agents with weakly bound ligands were used, we chose bis(arene)molybdenum complexes for this purpose. Such complexes had already been employed successfully as a source of (η^6-arene)molybdenum fragments.[3] Specifically bis(η^6-toluene)molybdenum **1** was found to be the appropriate choice for several reasons, *viz.* the ease of its preparation, its high reactivity and reasonable stability. The synthesis of bis(arene)metal complexes, initiated by Fischer and co-workers[4] on compounds containing various metals, *e.g.* bis(benzene)vanadium, has recently been improved in several instances, including the molybdenum compound, by Calderazzo *et al.*[5] employing a more simple secondary reduction procedure. As we have recently reported for the reaction of **1** with vinyl ketones,[1b] it is highly reactive even under mild conditions (room temperature and below). Therefore we decided to investigate its reactivity towards 1-oxadienes containing heteroatom substituents. Such substrates, *e.g.* acrylic amides or esters, are easily oligomerised at elevated temperatures in the presence of various transition-metal compounds, and hitherto, to our knowledge, no homoleptic complexes with ligands of these types have been reported. Recently we were also able to synthesise several carbonyl complexes containing unsaturated amides or ester ligands bound to molybdenum or tungsten *via* both the carbonyl and alkene fragments of the oxadiene.[6] These were prepared by ligand substitution using tri- or tetra-carbonyl starting complexes. However, we have so far been unable to remove the carbonyl ligands completely from the metal in such a reaction. Here we describe an alternative route to homoleptic molybdenum complexes of α,β-unsaturated amides and esters from bis(η^6-toluene)molybdenum by ligand substitution.

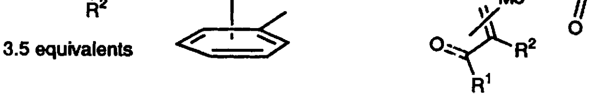
Results and Discussion

Preparation and Properties.—Simplification and modification of the procedure reported for the preparation of bis(η^6-toluene)molybdenum **1**,[5] *i.e.* of the secondary reduction and extraction steps (see Experimental section), allowed us to prepare **1** in up to 70% isolated yield, thus providing access to multigram quantities of this starting material from molybdenum pentachloride within a few days.

Addition of tetrahydrofuran (thf) solutions of *N,N*-dimethylacrylamide or methyl methacrylate to a green suspension of **1** in thf at room temperature results in an immediate change to yellow-brown (Scheme 1). After 12 h at room temperature the reaction was complete in the amide case. The reaction mixture obtained with methyl methacrylate was still slightly greenish and complete conversion of the starting complex could only be achieved by heating to 50 °C for 12 h.

The amide complex **2** is formed as a single isomer in high yield (80–90%). In its ^1H and ^{13}C NMR spectra distinct, sharp signals are observed for the methyl protons of the dimethylamino groups. This is in contrast to the uncomplexed *N,N*-dimethylacrylamide where two separate but broadened signals are observed for these protons at room temperature, indicating slow rotation around the amide bond. Obviously, the rotation barrier increases on complexation of the oxadiene moiety.

With methyl methacrylate the complexation reaction is less efficient, at present a 50% yield has been obtained. Apart from the major product **3**, which has a symmetrical structure in solution according to the NMR spectra [see Fig. 1(*a*) for the ^1H NMR spectrum], recrystallisation of the crude product yields a second molybdenum ester complex, which can be obtained from the mother-liquor in low yield (6%). The NMR and mass



	R¹	R²	
2	NMe₂	H	84%
3	OMe	Me	50%

Scheme 1

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

spectra indicate that this easily soluble compound **4** is an isomer of **3**. In contrast to the latter, a triple set of signals is observed for the ligands in the NMR spectra, suggesting that this compound has C_1 symmetry [see Fig. 1(*b*) for the ^{1}H NMR spectrum]. The ^{13}C NMR shift values and co-ordination shifts for compounds **2**–**4** are summarised in Table 1.

The remarkably small upfield (compound **4**) and even downfield (**2** and **3**) co-ordination shifts of the carbonyl carbon atom signals can be interpreted in terms of a pronounced bonding contribution of the carbonyl oxygens and not of the carbonyl π system as a whole. This results from a polarisation of the C=O fragment, possibly assisted by an additional electron-withdrawing effect from the ester oxygen or the amide nitrogen. Closely similar spectra have been obtained from an explicitly κ:η^2-bound, β,γ-unsaturated ketone in a molybdenum complex.[7] These results are in contrast to the spectra observed for homoleptic complexes of vinyl ketones, where upfield complexation shifts of 20–40 ppm are found for the carbonyl carbons.[1b] Co-ordination shifts of the vinyl carbon atoms C_α and C_β are in the range 54–82 ppm, which is slightly more than the usual 40–60 ppm observed for other oxadiene complexes with different bonding modes.[1b,6,8a,b]

In the case of unsymmetrically substituted diene ligands, related hydrocarbon complexes with a symmetry lower than C_3 in solution, *e.g.* in a tris(isoprene)molybdenum case, have already been reported.[9] The molecular structure of complex **4** is currently under investigation in order to clarify which bonding modes are responsible for the lack of symmetry in this compound. Inspection of the NMR spectra indicates that two of the ligands are very similarly co-ordinated, whereas one set of signals always lies markedly apart from the other two. From a topological point of view, several possibilities exist for an unsymmetrical isomer, *i.e.* either an antiparallel orientation of one of the oxadiene ligands with respect to the others (**A**), a parallel arrangement of all three ligands with one being co-ordinated from the other enantiotopic face of the prochiral oxadiene moieties (**B**) or even a combination of these.

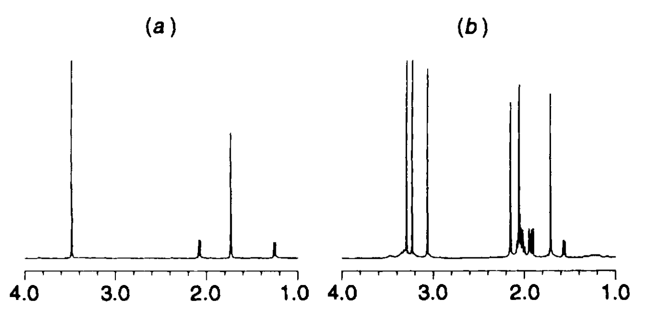
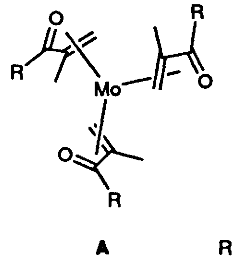
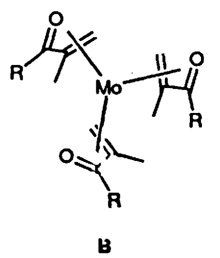


Fig. 1 Proton NMR spectra of the homoleptic methyl methacrylate complexes **3** (*a*) and **4** (*b*) (200 MHz, C_6D_6, 20 °C)



A

R = OMe



B

Our previous crystallographic investigations on bis- and tris-(oxadiene)complexes[8] suggest that an orientation of the oxadienes is especially favourable when the O–M–O* angle is about 90°. This leads us to prefer structure **B** for complex **4**. Structure **B** contrasts with the previous assignment of NMR data in the related case of tris(isoprene)-molybdenum and -tungsten,[10] where an 'in phase' arrangement of all three ligands (type **A**) was suggested on the basis of analogy with other structurally characterised homoleptic diene complexes, as well as by ^2J(WH) coupling-constant analysis. It could well be that dienes and oxadienes have different requirements with respect to the most stable ligand arrangement. It should also be mentioned that in contrast to the results on the tris(isoprene)-complexes, we have not been able to find any indication of an equilibrium between symmetrical and unsymmetrical tris(acrylic ester) complexes.

Crystal Structures of Complexes **2** *and* **3**.—The molecular structures of complexes **2** and **3** in the crystal are given in Figs. 2

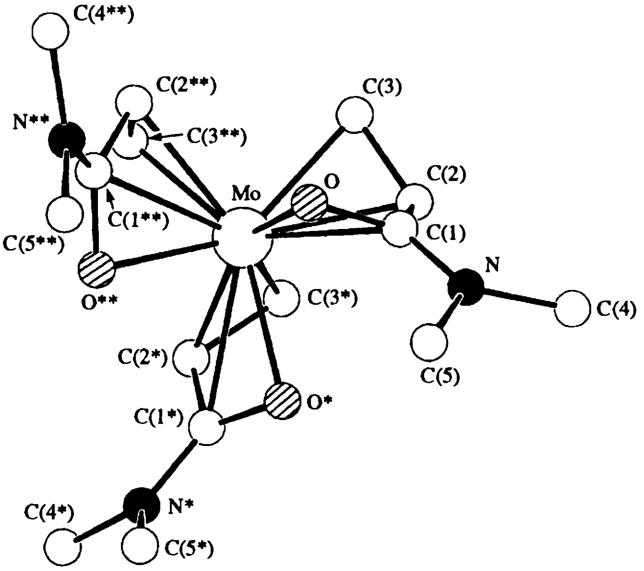


Fig. 2 Molecular structure of $[\mathrm{Mo\{H_2C{=}CHC(O)NMe_2\}_3}]$ **2**

Table 1 Carbon-13 NMR chemical shifts (δ) (solvent C_6D_6) and co-ordination shifts Δδ for the metal-co-ordinated carbon atoms in homoleptic molybdenum complexes **2**–**4** and the corresponding atoms in the free oxadienes (in parentheses)

	δ(^{13}C)			Δδ(^{13}C)[a]		
	C=O	C_α	C_β	C=O	C_α	C_β
2	171.56	57.10	55.87	−6.01	+71.38	+70.71
	(165.55)	(128.48)	(126.58)	—	—	—
3	167.40	68.24	63.06	−0.14	+68.49	+61.91
4[b]	154.89	82.55	57.17	+12.37	+54.18	+67.80
	155.28	81.32	55.41	+11.98	+55.41	+69.56
	167.06	70.60	43.35	+0.20	+66.13	+81.62
	(167.26)	(136.73)	(124.97)	—	—	—

[a] Definition: Δδ = δ(oxadiene) − δ(complex). [b] The connectivities of the atoms within ligands corresponding to the three sets of signals have not yet been assigned.

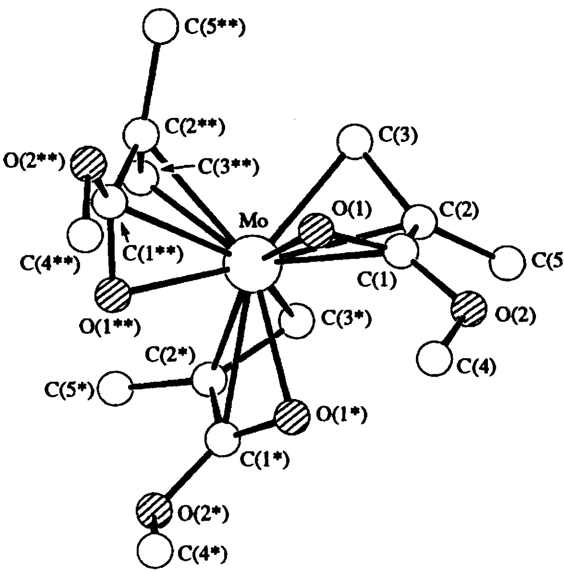
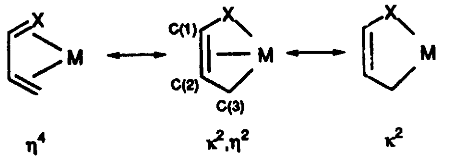


Fig. 3 Molecular structure of [Mo{H_2C=C(Me)C(O)OMe}$_3$] **3**

Table 2 Selected interatomic distances (Å) and angles (°) for [Mo{H_2C=CHC(O)NMe_2}$_3$] **2** and [Mo{H_2C=C(Me)C(O)-OMe}$_3$]·0.5Et_2O **3**

2		**3**	
Mo–O	2.177(2)	Mo–O(1)	2.173(3)
Mo–C(1)	2.482(2)	Mo–C(1)	2.428(4)
Mo–C(2)	2.241(2)	Mo–C(2)	2.284(4)
Mo–C(3)	2.170(2)	Mo–C(3)	2.170(4)
O–C(1)	1.295(3)	O(1)–C(1)	1.276(5)
C(1)–C(2)	1.439(3)	C(1)–C(2)	1.414(5)
C(2)–C(3)	1.453(4)	C(2)–C(3)	1.454(6)
N–C(1)	1.337(3)	O(2)–C(1)	1.336(5)
N–C(4)	1.451(3)	O(2)–C(4)	1.438(6)
N–C(5)	1.453(3)	C(2)–C(5)	1.497(6)
C(3)–Mo–C(2)	38.4(1)	C(3)–Mo–C(2)	38.0(2)
C(3)–Mo–C(1)	63.7(1)	C(3)–Mo–C(1)	63.1(1)
C(3)–Mo–O	77.1(1)	C(3)–Mo–O(1)	76.7(1)
C(2)–Mo–C(1)	35.0(1)	C(2)–Mo–C(1)	34.8(1)
C(2)–Mo–O	62.9(1)	C(2)–Mo–O(1)	62.8(1)
C(1)–Mo–O	31.4(1)	C(1)–Mo–O(1)	31.6(1)
C(1)–O–Mo	87.5(1)	C(1)–O(1)–Mo	85.3(2)
C(5)–N–C(4)	117.0(2)		
C(5)–N–C(1)	120.3(2)		
C(4)–N–C(1)	122.3(2)	C(4)–O(2)–C(1)	115.9(3)
C(2)–C(1)–N	124.6(2)	C(2)–C(1)–O(2)	118.5(4)
C(2)–C(1)–O	114.9(2)	C(2)–C(1)–O(1)	119.6(3)
C(2)–C(1)–Mo	63.3(1)	C(2)–C(1)–Mo	67.0(2)
N–C(1)–O	120.1(2)	O(2)–C(1)–O(1)	121.5(3)
N–C(1)–Mo	143.2(2)	O(2)–C(1)–Mo	140.0(3)
O–C(1)–Mo	61.2(1)	O(1)–C(1)–Mo	63.1(2)
C(3)–C(2)–C(1)	117.3(2)	C(3)–C(2)–C(1)	114.7(4)
C(3)–C(2)–Mo	68.2(1)	C(3)–C(2)–Mo	66.8(2)
C(1)–C(2)–Mo	81.7(1)	C(1)–C(2)–Mo	78.2(2)
C(2)–C(3)–Mo	73.4(1)	C(2)–C(3)–Mo	75.2(2)
		C(5)–C(2)–Mo	130.2(3)
		C(5)–C(2)–C(1)	120.7(4)
		C(5)–C(2)–C(3)	124.1(4)
Interligand angles			
O*–Mo–O	86.0(1)	O(1*)–Mo–O(1)	85.9(1)
C(1*)–Mo–C(1)	106.2(1)	C(1*)–Mo–C(1)	107.5(1)
C(2*)–Mo–C(2)	116.5(1)	C(2*)–Mo–C(2)	115.6(2)
C(3*)–Mo–C(3)	85.6(1)	C(3*)–Mo–C(3)	85.8(1)
O*–Mo–C(3)	124.9(1)	O(1*)–Mo–C(3)	127.1(1)
O**–Mo–C(3)	142.7(1)	O(1**)–Mo–C(3)	140.4(1)



Scheme 2

and 3, respectively. Owing to the thermal sensitivity of both complexes, data collection was performed at low temperature. The crystal of 3 contained diethyl ether, which was found to be in the space between the molecules. Attempts to remove this solvent after the crystallisation prior to the structure determination resulted in destruction of the crystal. To overcome this problem, data were collected from a crystal in an atmosphere saturated with diethyl ether. Both the amide and the ester complex, in contrast to complexes of α,β-unsaturated ketones we have also investigated,[1b] exhibit crystallographic three-fold symmetry in the solid state. In this regard, they parallel the structure reported for the tris(but-3-en-2-one) tungsten complex by Bau and co-workers.[11]

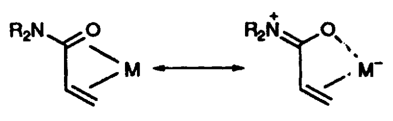
The short and almost identical distances (Table 2) between the metal and terminal oxadiene atoms [Mo–O 2.177(2), Mo–C(3) 2.170(2) Å in **2** and Mo–O(1) 2.173(3), Mo–C(3) 2.170(4) Å in **3**] as well as the long C=C and C=O distances within the ligands [O–C(1) 1.295(3), C(2)–C(3) 1.453(4) Å in **2** and O(1)–C(1) 1.276(5), C(2)–C(3) 1.454(6) Å in **3**] are remarkable. Both these characteristic values indicate a bonding situation between an η^4 [long M–X and M–C(3) distances] and a κ^2,η^2 co-ordination mode [short M–X and M–C(3), X–C(1) and C(2)–C(3) distances significantly longer than C(1)–C(2)] (Scheme 2). The former is observed in dicarbonylbis(oxadiene)-metal complexes,[8a,b] the latter in the case of homoleptic complexes of α,β-unsaturated ketones.[1b] The tendency for intermediacy between the above bonding modes is also reflected in the distance difference Δ*d*, defined in equation (1) (−0.188 Å

$$\Delta d = 0.5\{d(\text{M–X}) + d[\text{M–C(3)}]\} - 0.5\{d[\text{M–C(1)}] + d[\text{M–C(2)}]\} \quad (1)$$

for **2** and −0.185 Å for **3**). These values are larger than those typically calculated for dicarbonylbis(1-oxadiene)metal complexes (−0.08 Å) but considerably smaller than those of tris(vinyl ketone) complexes (typically −0.30 Å).

Interestingly, since the angles M–X–C(1) and M–C(3)–C(2) are smaller than 90° [87.5(1) and 73.4(1) for **2**, 85.3(2) and 75.2(2)° for **3**], rehybridisation seems to be a relatively insensitive indication of the bond character. Ideally, these angles should be 109° in the case of sp^3 hybridisation (metal–alkyl and -alkoxide bonding) or 120° for a lone-pair co-ordination at oxygen.

The N–C(1) distance of 1.337(3) Å in the acrylamide ligands of complex **2** is slightly shorter than the tabulated 1.346 Å,[12] expected for an uncomplexed acrylamide with a *planar* substituent geometry around nitrogen. It is significantly shorter than that expected for an enamine structure with *pyramidal* nitrogen (1.416 Å), which is a much more appropriate model for a nitrogen with non-delocalised lone-pair electrons. This reasoning tends to support the concept of donor stabilisation of the co-ordinated oxadiene fragment by the nitrogen lone pair and is in accordance with the increased rotational barrier found in the NMR spectroscopic investigation (see above). Analogous spectroscopic and structural characteristics of a dialkylamino group have been reported for a 2-diethylamino(η^3-1-oxallyl) ligand on a dicarbonyl(η^5-cyclopentadienyl)tungsten fragment [N–C 1.333(4) Å].[13] A dipolar resonance structure **II** should therefore not be ruled out for the ligands in **2**. In the case of the ester complex **3**, on the other hand, where a comparable resonance structure is very unfavourable, the O(2)–C(1) distance [1.336(5) Å] is almost identical to the expected value of 1.332 Å for an unsaturated carboxylic ester.[12]



I II

Whereas the acrylamide ligands in complex **2** are clearly non-planar [torsion angle O–C(1)–C(2)–C(3) 26°], this is less so for the methyl methacrylate ligands in **3** [torsion angle O(1)–C(1)–C(2)–C(3) 21°]. The observed deviations from planarity indicate some reduction of conjugative interaction between carbonyl and alkene fragments of the oxadienes in both cases.

Experimental

Preparation and handling of all the organometallic compounds was performed under an inert atmosphere of dried and purified argon using standard Schlenk techniques. All solvents were purified prior to use by standard procedures, usually employing $Na[AlEt_4]$ as drying agent, and subsequently saturated with argon. Melting points were determined in capillary tubes sealed under argon using a Kofler microscope and are uncorrected.

The NMR spectra were recorded on Bruker spectrometers AM 200 [200.1 (^1H), 50.3 MHz (^{13}C)] or AMX 400 [400.134 (^1H), 100.614 MHz (^{13}C)], with solvent signals being used as internal standards. Signal multiplicities obtained from distortionless enhancements of polarisation transfer (DEPT) experiments are given in parentheses after the shift values. Mass spectra were obtained using a Varian 311A spectrometer (for metal-containing ions, signals corresponding to the major isotope ^{98}Mo are reported), IR spectra from a Nicolet 7199 FT-IR instrument. Microanalyses were performed by Dornis and Kolbe, Microanalytical Laboratory, Mülheim an der Ruhr.

Bis(η^6-*toluene*)*molybdenum* $[Mo(C_6H_5Me)_2]$ **1**.[5]—A two-necked round-bottom flask (500 cm^3) was charged with molybdenum pentachloride (10.6 g, 39 mmol), sublimed, anhydrous aluminium chloride (6.0 g, 45 mmol) and aluminium dust (4.2 g, 155 mmol) in this order. Toluene (120 cm^3) was added and the mixture vigorously stirred and heated to reflux in a heating bath at about 135 °C. After 40 h the mixture was cooled to 40 °C and thf (100 cm^3) was added slowly (exothermal reaction!). It was then again heated to reflux in an oil-bath (100 °C) for 18 h, cooled to ambient temperature and filtered through a sintered glass frit to remove the excess of aluminium powder. The latter was washed once with pentane and the combined green-brown filtrates were evaporated to dryness *in vacuo* (0.1 Pa). The brown, solid residue was then extracted with boiling pentane (10 × 60 cm^3). The resulting green extracts were filtered through a sintered D4-glass frit and then concentrated to a total volume of 200 cm^3. On cooling to −78 °C a green, crystalline precipitate of complex **1** was obtained. After siphoning off the mother-liquor at low temperature, the remaining crystals were dried *in vacuo* and stored in a freezer. Yield 7.8 g, 28 mmol, 71.8%, m.p. 79–81 °C (lit.,[2] 80 °C). $\delta_H(C_6D_6)$ 4.88–4.80 (8 H, m), 4.80–4.77 (2 H, m) and 2.01 (6 H, s, CH_3); $\delta_C(C_6D_6)$ 94.95 (2 C, s, C–CH_3), 78.70 (4 C, d), 76.03 (2 C_p, d), 75.08 (4 C, d) and 21.62 (2 C, q, CH_3).

Tris(N,N-*dimethylacrylamide*)*molybdenum* $[Mo\{H_2C{=}CH{-}C(O)NMe_2\}_3]$ **2**.—To a green suspension of bis(toluene)molybdenum **1** (560 mg, 2.0 mmol) in thf (10 cm^3), *N*,*N*-dimethylacrylamide (990 mg, 10 mmol) was added *via* a syringe. Within a few minutes a yellow-brown colour developed and formation of a cloudy yellowish precipitate was observed. After being stirred at room temperature for 24 h, a yellow-brown, almost clear reaction mixture had formed. It was evaporated *in vacuo*, the residue was extracted with diethyl ether (3 × 15 cm^3), the extracts filtered through a sintered glass frit (D4), concentrated *in vacuo* again and remaining volatile components were removed under high vacuum (10^{-2} Pa). The brown, partly crystalline product was then redissolved in diethyl ether (25 cm^3) and slowly cooled to −40 °C. Large, clear, yellow crystals of complex **2** were obtained. They were dried under high vacuum. Yield: 660 mg, 1.68 mmol, (84%). Decomposition began at 100 °C under Ar, sublimation on rapid heating to 200 °C (Found: C, 45.8; H, 6.9; Mo, 24.4, N, 10.7. $C_{15}H_{27}MoN_3O_3$ requires C, 45.9; H, 7.1; Mo, 24.4; N, 10.6%); $\tilde{\nu}_{max}$/cm^{-1} 3042s, 3020w, 2955vs, 2920w, 2870w, 1557vs, 1412vs, 1400 (sh), 1170s and 729vs (KBr); $\delta_H(C_6D_6$, 200.1 MHz) 2.46 (3 × 3 H, s, NCH_3), 2.31–2.18 [3 × 1 H, dd, *J*(HH) 6.0, 7.2], 2.17 (3 × 3 H, s, NCH_3), 2.16–2.10 [3 × 1 H, dd, *J*(HH) 2.7, 7.2] and 1.82–1.78 [3 × 1 H, dd, *J*(HH) 2.7, 6.0 Hz]; $\delta_C(C_6D_6$, 50.3 MHz, all signals arising from three symmetry-equivalent carbons) 171.56 (s, C=O), 57.10 (d, =CH), 55.87 (t, $=CH_2$), 36.56 (q, NCH_3) and 34.58 (q, NCH_3); *m*/*z* [electron impact (EI), relative intensity in %]. 395 (M^+, 57), 294 ($M^+ - C_5H_9NO$, 41%), 84 ($C_4H_6NO^+$, 71) and 68 (100%).

Tris(*methyl methacrylate*)*molybdenum* $[Mo\{H_2C{=}C(Me){-}C(O)OMe\}_3]$ **3**.—To a stirred suspension of complex **1** (840 mg, 3.0 mmol) in thf (10 cm^3), methyl methacrylate (5.0 g, 50 mmol) was added *via* a syringe at room temperature. A spontaneous change to yellow-brown was observed. After stirring at ambient temperature for 12 h the reaction mixture was heated to 50 °C for 12 h to insure complete reaction of the arenemolybdenum complex. Afterwards, the volatile components (mostly solvent and excess of methyl methacrylate) were removed under reduced pressure. A brown, oily residue was obtained, which according to NMR analysis mainly consisted of the homoleptic complex **3**. The crude product was purified by recrystallisation from a small amount of diethyl ether (about 5 cm^3) between 20 and −78 °C. After drying under high vacuum (10^{-2} Pa), pale yellow crystals of analytically pure **3** were obtained. From the mother-liquor, after further reduction of the volume to about 2 cm^3, a small amount of an orange, crystalline material was obtained upon cooling to −78 °C. This compound **4** was identified as an isomer of **3** with a lower, *i.e.* C_1 symmetry.

Compound **3**: yield 594 mg, 1.50 mmol (50%); pale yellow crystals; m.p. 104–105 °C (Found: C, 45.5; H, 6.1; Mo, 24.2. $C_{15}H_{24}MoO_6$ requires C, 45.6; H, 6.1; Mo, 24.3%); $\tilde{\nu}_{max}$/cm^{-1} 3038w, 2978s, 2952s, 2908s, 2880s, 1500vs, 1475vs, 1364vs, 1211s, 1199s, 1171s, 1021s and 732s (KBr); $\delta_H(C_6D_6$, 200.1 MHz) 3.42 (3 × 3 H, s, OCH_3), 2.04 [3 × 1 H, d, $=CH_2$, ^2J(HH) 3.3 Hz], 1.81 (3 × 3 H, s, CCH_3) and 1.27 (3 × 1 H, d, $=CH_2$); $\delta_C(C_6D_6$, 50.3 MHz, all signals arising from three equivalent carbons) 167.40 (s, C=O), 68.24 (s, $=CCH_3$), 63.06 (t, $=CH_2$), 52.33 (q, OCH_3) and 15.46 (q, CCH_3); *m*/*z* (EI) 398 (M^+, 12), 298 ($M^+ - C_5H_8O_2$, 10), 270 (20), 200 (61), 69 ($C_4H_5O^+$, 50) and 41 ($C_3H_5^+$, 100%).

Compound **4**: yield 71 mg, 0.18 mmol (6%); orange crystals; m.p. 102–103 °C; $\tilde{\nu}_{max}$/cm^{-1} 3050w, 3031w, 2980s, 2952vs, 2908s, 2868s, 1502s, 1470vs, 1375 (sh), 1360vs, 1192vs, 1174s, 1018s, 796m and 721m (KBr); $\delta_H(C_6D_6$, 200.1 MHz) 3.29 (3 H, s, OCH_3), 3.23 (3 H, s, OCH_3), 3.06 (3 H, s, OCH_3), 2.15 (3 H, s, CCH_3), 2.06 (3 H, s, CCH_3), 2.07–2.00 (3 H, m, $=CH_2$), 1.96 [1 H, d, $=CH_2$, *J*(HH) 3.4 Hz], 1.95 [1 H, d, $=CH_2$, *J*(HH) 3.5], 1.78 (3 H, s, CCH_3) and 1.57 [1 H, d, $=CH_2$, *J*(HH) 3.4 Hz]; $\delta_C(C_6D_6$, 50.3 MHz) 167.06 (s, C=O), 155.28 (s, C=O), 154.89 (s, C=O), 82.55 (s, $=CCH_3$), 81.32 (s, $=CCH_3$), 70.60 (s, $=CCH_3$), 57.17 (t, $=CH_2$), 55.41 (t, $=CH_2$), 52.40 (q, OCH_3), 52.23 (q, $=OCH_3$), 51.68 (q, OCH_3), 43.35 (t, $=CH_2$), 16.62 (q, CCH_3), 14.85 (q, CCH_3) and 12.53 (q, CCH_3); *m*/*z* (EI) 398 (M^+, 12), 298 ($M^+ - C_5H_8O_2$, 10), 200 (39), 69 ($C_4H_5O^+$, 40) and 41 ($C_3H_5^+$ 100%); high-resolution mass spectrum *m*/*z* 398.062 729 (required for $C_{15}H_{24}MoO_6$ 398.062 798).

Table 3 Crystal data and details of data collection for [Mo{H_2C=CHC(O)NMe_2}$_3$] **2** and [Mo{H_2C=C(Me)C(O)OMe}$_3$]·0.5Et_2O **3**[a]

Compound	**2**	**3**
Formula	$C_{15}H_{27}MoN_3O_3$	$C_{15}H_{24}MoO_6 \cdot 0.5Et_2O$
M	393.3	433.4
Crystal size/mm	0.35 × 0.35 × 0.39	0.42 × 0.42 × 0.32
Space group	$R\bar{3}$	$R\bar{3}c$
a/Å	9.603(1)	16.248(4)
α/°	88.50(2)	41.91(3)
U/Å^3	884.6(2)	1731(1)
Z	2	4
D_c/g cm^{-3}	1.48	1.66
μ/cm^{-1}	7.37	7.71
F(000)	408	816
h k l ranges	−13 to 13, −13 to 13, 0–13	−16 to 16, −16 to 16, 0–22
No. of measured reflections	4548	8146
No. used in refinement	1356	1318
No. of variables	67	72
R_{int}	0.02	0.06
S	1.15	1.16
Final difference electron density/e Å^{-3}	0.60	1.57
Maximum shift/error	0.001	0.22
*R*1	0.028	0.038
*wR*2[b]	0.086	0.102
Weighting parameters *A*, *B*[c]	0.0449, 1.0678	0.0511, 1.7632

[a] Details in common: yellow prism; trigonal; 100 K; $[(\sin\theta)/\lambda]_{max}$ 0.65 Å^{-1}. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$. [c] Weighting scheme used $w = [\sigma^2(F_o^2) + (AP)^2 + (BP)]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 4 Atomic fractional coordinates for [Mo{H_2C=CHC(O)NMe_2}$_3$] **2** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Mo	0.2299(1)	0.2299(1)	0.2299(1)
O	0.3419(2)	0.4163(2)	0.1671(2)
N	0.5628(2)	0.3558(2)	0.0951(2)
C(1)	0.4254(2)	0.3366(2)	0.0950(2)
C(2)	0.3607(3)	0.2204(3)	0.0336(2)
C(3)	0.2132(3)	0.2349(3)	0.0049(3)
C(4)	0.6596(3)	0.2806(3)	0.0041(3)
C(5)	0.6224(3)	0.4422(3)	0.1991(3)

Table 5 Atomic fractional coordinates for [Mo{H_2C=C(Me)C(O)OMe}$_3$]·0.5 Et_2O, **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo	0.1003(1)	0.1003(1)	0.1003(1)
O(1)	0.1761(2)	−0.0978(2)	0.1321(2)
O(2)	0.3705(2)	−0.1246(2)	−0.0594(2)
O(3)	0.75	−0.25	−0.25
O(4)	0.783(2)	−0.217(2)	−0.217(2)
O(5)	0.730(2)	−0.270(2)	−0.270(2)
O(6)	0.7580(5)	−0.2420(5)	−0.2420(5)
O(7)	0.781(2)	−0.219(2)	−0.219(2)
O(8)	0.769(2)	−0.231(2)	−0.231(2)
C(1)	0.2912(2)	−0.0922(2)	0.0423(2)
C(2)	0.3287(2)	−0.0347(3)	0.0397(2)
C(3)	0.2556(2)	−0.0310(2)	0.1670(2)
C(4)	0.3101(3)	−0.1459(3)	−0.0728(3)
C(5)	0.4470(3)	0.0014(3)	−0.0806(3)

Crystal Structure Determinations of Complexes **2** *and* **3**.—*Crystal growth*. Crystals of complex **2** were obtained by slowly cooling a concentrated solution in hexane to −30 °C. Crystals of **3** were obtained from solutions in diethyl ether upon slow (about 5° h^{-1}) cooling to −40 °C. The crystals isolated by removal of the supernatant solution at that temperature had to be kept in an ether-saturated atmosphere at low temperature for X-ray analysis. Material kept at room temperature or dried *in vacuo* does not immediately decompose but its crystallinity is significantly reduced (diffraction pictures), presumably because of loss of diethyl ether.

Data collection and refinement. X-Ray intensity data were collected on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Crystal data and data collection parameters are given in Table 3. Lattice parameters were determined by least-squares refinement from 25 centred reflections. Intensities were measured in the ω–2θ scan mode and were corrected for decay of three control reflections (less than 5%), monitored every 30 min, and for Lorentz and polarisation factors. Spherical absorption corrections were applied in both cases. The metal atoms were located by Patterson methods and the remaining heavy atoms by successive Fourier difference syntheses. Refinement was by least squares, where the quantity minimised was $\Sigma w(F_o^2 - F_c^2)^2$. The positions of the H atoms were calculated and allowed to refine (riding model). In the case of complex **3** a region of electron density (≈2–3 e Å^{-3}) was found at ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$) extending along the three-fold axis of symmetry. Solvent of crystallisation (presumably diethyl ether) was modelled by a disordered O atom [O(3)–O(8)] on the three-fold axis (U_O = 0.025 Å^2).

Atomic coordinates for complexes **2** and **3** are given in Tables, 4 and 5, respectively. Details of the computer programs used on a VAX 4000–300 computer are given in ref. 14.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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