DALTON

Synthesis and reactivity of η^3-γ-lactonyl complexes of molybdenum; crystal structures of $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCH}\}(CO)_2(\eta\text{-}C_5Me_5)]$, $[Mo\{\eta^2\text{-}PhCH_2NHCHCH{=}CH(CO_2H)\}(CO)_2(\eta^5\text{-}C_9H_7)]$ and $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCHCO}\}(NCMe)(CO)(\eta\text{-}C_5H_5)]$†

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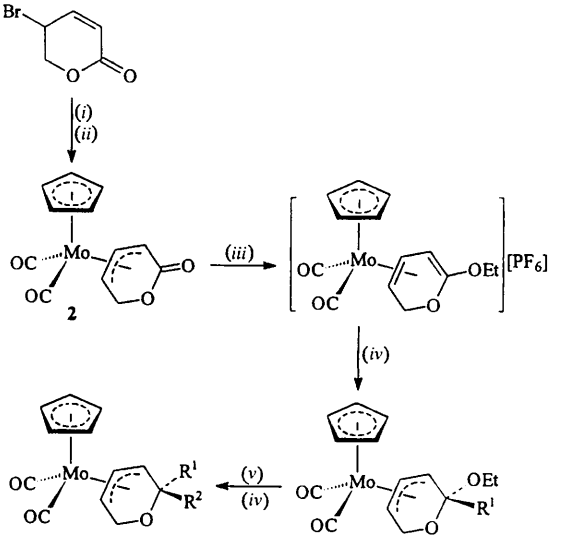
Reaction of 2-(trimethylsilyloxy)furan with the compounds *cis*-$[Mo(NCMe)_2(CO)_2L][BF_4]$ (L = η-C_5H_5, η-C_5Me_5 or η^5-C_9H_7) afforded the η^3-γ-lactonyl complexes $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCH}\}(CO)_2L]$. The structure of one of these species, $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCH}\}(CO)_2(\eta\text{-}C_5Me_5)]$, has been established by a single-crystal X-ray diffraction study, which confirmed that the γ-lactonyl moiety is bound to the molybdenum *via* three carbon atoms as an η^3-allyl. Treatment of these lactonyl complexes with nucleophilic reagents (amines, methoxide) resulted in lactone ring opening and overall addition of the nucleophile to the γ-carbon of the lactone ring, rather than at the lactonyl carbonyl carbon atom as might have been expected. The product of the reaction between $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCH}\}(CO)_2(\eta^5\text{-}C_9H_7)]$ and $PhCH_2NH_2$ has been structurally characterised by an X-ray diffraction study as the zwitterionic, η^2-alkene complex $[Mo\{\eta^2\text{-}PhCH_2NHCH\text{-}CH{=}CH(CO_2H)\}(CO)_2(\eta^5\text{-}C_9H_7)]$. Similarly, $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCH}\}(CO)_2(\eta\text{-}C_5H_5)]$ and methoxide anion gives, after acidification, $[Mo\{anti\text{-}\eta^3\text{-}(MeO)CHCHCH(CO_2H)\}(CO)_2(\eta\text{-}C_5H_5)]$, in which the lactone ring has been cleaved to give an η^3-allyl moiety ligating the metal centre. An extended Hückel molecular orbital calculation on $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCH}\}(CO)_2(\eta\text{-}C_5Me_5)]$ suggests that these reactions proceed *via* initial attack at the metal centre, followed by a rearrangement which effectively transfers the nucleophilic moiety to the γ-carbon of the lactone ring. Reaction of the η^3-lactonyl complex $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCH}\}(CO)_2(\eta\text{-}C_5H_5)]$ with $HBF_4{\cdot}Et_2O$ resulted in a remarkable ring-enlargement reaction, in which a co-ordinated carbon monoxide formally inserts into the lactone carbon–oxygen bond to form the crystallographically characterised complex $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCHCO}\}(NCMe)(CO)(\eta\text{-}C_5H_5)]$.

During the course of investigations into metal–acetylene chemistry, we have previously established the formation of several interesting η^3-bonded (allyl-substituted) lactonyl complexes.[2,3] For example, $[Mo(COCF_3)(CO)_3(\eta\text{-}C_5H_5)]$ was found to react thermally with an excess of but-2-yne (hexane, 60 °C) to afford the red crystalline σ-bonded vinyl ketone complex $[Mo(CO)_2\{C(Me)C(Me)C(CF_3)O\}(\eta\text{-}C_5H_5)]$, which readily undergoes a reaction with CO to form the η^3-γ-lactonyl complex $[Mo(CO)_2\{\eta^3\text{-}C(CF_3)C(Me)C(Me)C(O)O\}(\eta\text{-}C_5H_5)]$ **1**. The subsequent reactivity of complex **1** has not been investigated. Indeed, there have been surprisingly few studies of the synthetic potential of isolated transition-metal π complexes of unsaturated heterocycles.[4–8] Recently, however, Liebeskind and co-workers[9,10] have reported the preparation of several pyranyl-derived π complexes of molybdenum and demonstrated their potential in organic synthesis. One such complex is the η^3-δ-lactonyl species **2** (Scheme 1) which is prepared *via* the allylic bromide derived from the reaction of dihydropyrone with *N*-bromosuccinimide. A simple strategy for the stereocontrolled introduction of substituents into the lactonyl fragment in these complexes has also been developed (Scheme 1) based on the precedented *exo*-facial addition of nucleophiles to cationic complexes of the type $[Mo(CO)_2(\eta^4\text{-diene})(\eta\text{-}C_5H_5)]^+$, and results in the overall replacement of the lactonyl carbonyl group. This methodology has also been extended to an optically active system allowing the enantiospecific synthesis of several substituted dihydro- and tetrahydro-pyrans.[9,10]

† Reactions of Co-ordinated Ligands. Part 61.[1]



Scheme 1 (*i*) $[Mo(NCMe)_3(CO)_3]$; (*ii*) $Li(C_5H_5)$; (*iii*) $[Et_3O][PF_6]$; (*iv*) LiR^1 or LiR^2; (*v*) $[Ph_3C][PF_6]$

We envisaged an alternative approach to substituted heterocyclic compounds involving the displacement of the labile acetonitrile ligands present in complexes of the type $[Mo(NCMe)_2(CO)_2(\eta\text{-}C_5H_5)][BF_4]$, and this paper describes our initial study of furanyl-derived π complexes of molybdenum.

Results and Discussion

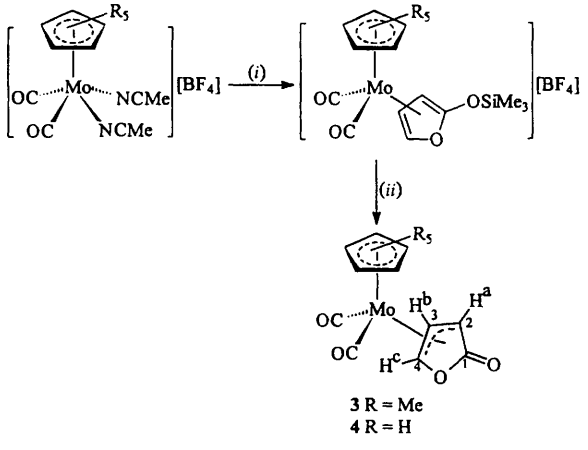
Our initial efforts in this area were concerned with the direct complexation of furan to a '$[Mo(CO)_2(\eta\text{-}C_5H_5)]^+$' fragment by means of a ligand-substitution reaction. However, all attempts to carry out such a procedure proved to be unsuccessful. An excess of furan was added to a dichloromethane solution of *cis*-$[Mo(NCMe)_2(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ and the resultant mixture was left to stir at ambient temperature for 7 d. Monitoring by IR spectroscopy showed that no reaction had taken place. Heating the reaction mixture to reflux similarly did not lead to the formation of the desired η^4-furan complex. Attempts to prepare the furan-substituted complex by protonation of the η^3-allyl complex $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(\eta\text{-}C_5H_5)]$ in the presence of furan were also unsuccessful.

In view of these observations the direct complexation of a substituted furan to a molybdenum centre was examined. It was found that room-temperature addition of an excess of 2-(trimethylsilyloxy)furan to a dichloromethane solution of *cis*-$[Mo(NCMe)_2(CO)_2(\eta\text{-}C_5Me_5)][BF_4]$ led to facile ligand substitution and formation of the novel η^3-γ-lactonyl complex $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCH}\}(CO)_2(\eta\text{-}C_5Me_5)]$ **3** (Scheme 2), obtained as a bright yellow powder in 62% yield. Presumably, as is illustrated, this reaction proceeds *via* a fluoride-anion-induced desilylation mechanism.

The solution IR spectrum of compound **3** displayed a major set of carbonyl bands at 1968, 1892 (metal carbonyls) and 1748 cm^{-1} (γ-lactone carbonyl), along with a corresponding minor set of carbonyl bands at 1985, 1917 and 1721 cm^{-1}. The two sets of bands were in the ratio 3:1 (in CH_2Cl_2) suggesting the presence of *exo* and *endo* conformers of **3**. This was confirmed by examination of the NMR spectral data. The room-temperature ^1H NMR spectrum showed a single set of broadened resonances (due to *exo–endo* fluxional interconversion) at δ 6.38 (H^c), 4.99 (H^b), 3.02 (H^a) and 1.92 (C_5Me_5). On lowering the temperature of the NMR probe to −80 °C conformational exchange was slowed, and the ^1H spectrum displayed two sets of well resolved resonances in the ratio 7:1. An examination of the respective chemical shift values indicated that the *exo* conformation was predominant in solution, at least at low temperature.

In order to establish the nature of the bonding and orientation within complex **3** a single-crystal X-ray diffraction experiment was carried out. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are given in Table 1.

It is clear that **3** crystallises in the *exo* conformation, thus confirming the predominance of the *exo* conformer as this compound approaches the solid state. The central molybdenum atom can be formally described as seven-co-ordinate, being bonded to two terminal carbonyl ligands, an η^3-γ-lactonyl fragment and a pentamethylcyclopentadienyl ligand. Both metal carbonyl groups are essentially linear, within experimental error, with Mo–C–O angles of 175.6(3) and 177.1(3)°, the Mo–C and C–O bond lengths being typical.[11] These two carbonyl ligands lie at an angle of 83.7° to one another. The C_5Me_5 ligand is essentially planar and is bound at a mean distance of 2.346(5) Å from the metal atom. The γ-lactonyl fragment is bound to the metal *via* three carbon atoms as an η^3-allyl. This C(14)–C(15)–C(16) moiety adopts an *exo* orientation with respect to the η^5-C_5Me_5 ring, with a bond angle of 103.6(4)° due to the constrained nature of the five-membered heterocyclic ring. As with the majority of molybdenum(II) *exo*-η^3-allyls, the inner carbon atom of the allyl moiety is closer to



Scheme 2 (*i*) 2-(Trimethylsilyloxy)furan, CH_2Cl_2, 25 °C; (*ii*) $-Me_3SiF$

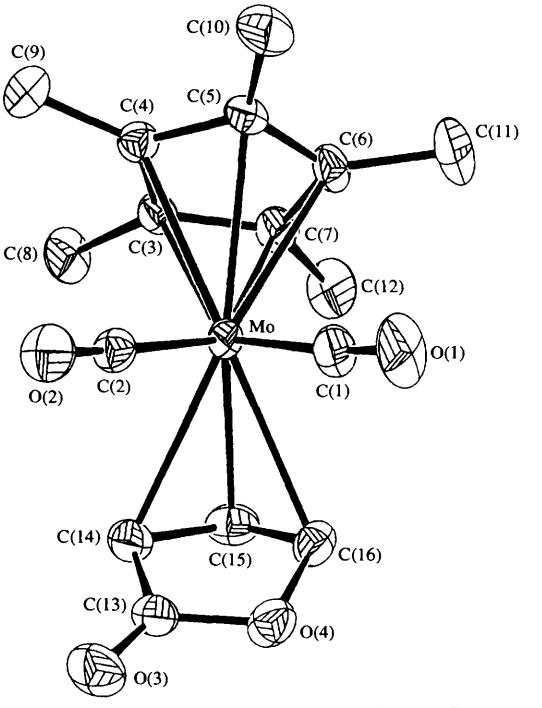


Fig. 1 Molecular structure of $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCH}\}(CO)_2(\eta\text{-}C_5Me_5)]$ **3**; thermal ellipsoids are shown at the 40% probability level

Table 1 Selected bond lengths (Å) and angles (°) for $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCH}\}(CO)_2(\eta\text{-}C_5Me_5)]$ **3** with estimated standard deviations (e.s.d.s) in parentheses

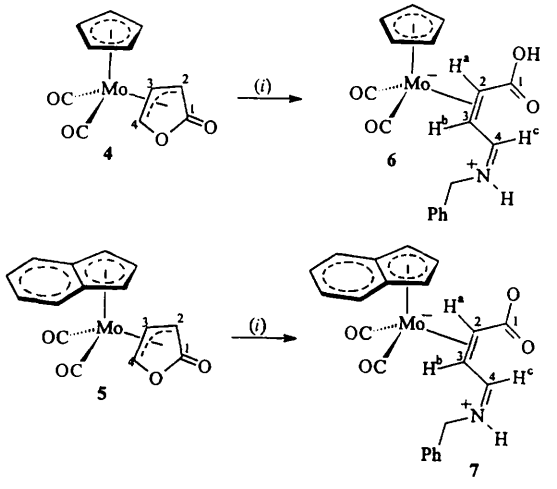
Mo–C(1)	1.942(6)	Mo–C(2)	1.969(6)	Mo–C(3)	2.391(5)	
Mo–C(4)	2.352(5)	Mo–C(5)	2.296(5)	Mo–C(6)	2.318(5)	
Mo–C(7)	2.374(5)	Mo–C(14)	2.369(6)	Mo–C(15)	2.189(5)	
Mo–C(16)	2.358(6)	C(1)–O(1)	1.151(5)	C(2)–O(2)	1.139(6)	
C(13)–O(3)	1.205(5)	C(13)–O(4)	1.388(5)	C(16)–O(4)	1.431(5)	
C(13)–C(14)	1.439(6)	C(14)–C(15)	1.415(7)	C(15)–C(16)	1.390(7)	

C(1)–Mo–C(2)	83.7(3)	Mo–C(1)–O(1)	175.6(3)	C(13)–C(14)–C(15)	107.5(4)	C(14)–C(15)–C(16)	103.6(4)
Mo(1)–C(2)–O(2)	177.1(3)	C(14)–Mo–C(15)	35.9(1)	C(15)–C(16)–O(4)	110.3(4)	C(16)–O(4)–C(13)	104.6(4)
C(14)–Mo–C(16)	55.6(2)	C(15)–Mo–C(16)	35.4(2)	O(4)–C(13)–O(3)	118.7(5)	O(4)–C(13)–C(14)	108.4(4)

the metal [Mo–C(15) 2.189(5) Å] than both the outer carbons [Mo–C(14) 2.369(6) and Mo–C(16) 2.358(6) Å].[12,13] The lactonyl fragment can be seen to exist in an envelope-type conformation with the lactone moiety bent away from the metal out of the plane of the allyl carbon atoms. Finally, it should be noted that the carbon–carbon interatomic distances within the metal-bound part of this ligand are somewhat unsymmetrical [C(14)–C(15) 1.415(7) and C(15)–C(16) 1.390(7) Å]. This, together with the bond distances C(13)–C(14) 1.439(6) and C(13)–O(3) 1.205(5) Å, implies some degree of π conjugation between the η^3-allyl and the lactone carbonyl group.[14]

The analogous η^5-cyclopentadienyl system was also examined. Addition of an excess of 2-(trimethylsilyloxy)furan to a dichloromethane solution of *cis*-[Mo(NCMe)$_2$(CO)$_2$(η-C$_5$H$_5$)][BF$_4$] led to the formation of the desired η^3-γ-lactonyl complex [Mo{η^3-OC(O)CHCHCH}(CO)$_2$(η-C$_5$H$_5$)] **4** in 55% yield, obtained as a bright yellow powder (Scheme 2). Complex **4** could also be prepared by protonation of the η^3-allyl complex [Mo(η^3-C$_3$H$_5$)(CO)$_2$(η-C$_5$H$_5$)] followed by addition of 2-(trimethylsilyloxy)furan, albeit in much lower yield (37%). As in the case of complex **3**, the IR and NMR spectral data for **4** indicated the presence of *exo* and *endo* conformers in solution. The IR spectrum displayed two distinct sets of carbonyl bands in the ratio 2 : 1. The room-temperature NMR spectrum showed a set of time-averaged broadened resonances and thus low-temperature experiments were again necessary to distinguish between the conformers and to determine the coupling constants. On lowering the temperature of the NMR probe to −60 °C exchange between the conformations was slowed, and the spectrum displayed two sets of well resolved resonances in the ratio 7 : 1. As before, an examination of the chemical shift values for the η^3-lactonyl protons indicated that the *exo* conformer was the major isomer present in solution.

The corresponding reaction between 2-(trimethylsilyloxy)-furan and the η^5-indenyl complex *cis*-[Mo(NCMe)$_2$(CO)$_2$(η^5-C$_9$H$_7$)][BF$_4$] proceeded in a similar fashion, to afford the anticipated η^3-γ-lactonyl complex [Mo{η^3-OC(O)CHCHCH}-(CO)$_2$(η^5-C$_9$H$_7$)] **5** in 57% yield, as a bright yellow solid. Complex **5** was found to exhibit only one set of carbonyl bands in its solution IR spectrum (at 1979, 1904 and 1752 cm^{-1}). The room-temperature ^{1}H NMR spectrum displayed one set of slightly broadened resonances indicating the possibility of a conformational equilibrium. However, on lowering the temperature of the NMR probe to −45 °C the spectrum showed only one set of well resolved resonances, with peaks for the η^3-lactonyl protons at δ 6.62 (H^c), 3.14 (H^a) and 1.26 (H^b). Such chemical shift values were unequivocally assigned to the singular presence of an *exo* conformer. In particular, the relatively high upfield shift observed for the central allyl proton (H^b) is typical[15] of [Mo(*exo*-η^3-allyl)(CO)$_2$(η^5-indenyl)] complexes, being caused by the anisotropic shielding effect of the indenyl ring. The absence of an *endo* conformer (*cf.* complexes **3** and **4**) can be attributed to the unfavourable steric interactions that would occur between the η^5-indenyl ligand and the lactone moiety in an *endo* configuration.



Scheme 3 (*i*) 2 equivalents benzylamine, CH_2Cl_2, 25 °C

Having established the ready availability of the η^3-γ-lactonyl molybdenum complexes **3**–**5** their reactivity towards nucleophilic addition was examined. The addition of nucleophiles to the corresponding η^3-δ-lactonyl complexes prepared by Liebeskind and co-workers[9] has not been reported. It was anticipated that such additions would occur at the lactone carbonyl functionality present in these complexes, possibly resulting in cleavage of the lactonyl ring. The reaction between the complex **4** or **5** and benzylamine was our initial area of study. When 2 molar equivalents of benzylamine were added at room temperature to a dichloromethane solution of the lactone complexes a smooth reaction ensued over 17 h and work-up afforded good yields (85%) of the bright yellow complexes **6** and **7** (Scheme 3). Significantly, when these reactions were repeated using only 1 molar equivalent of benzylamine much lower yields (*ca.* 8%) were obtained. Interestingly, however, both elemental analysis and the NMR spectra for these complexes indicated they were 1 : 1 adducts of benzylamine and **4** or **5**, respectively. In order to establish the structural identities of these adducts a single-crystal X-ray diffraction study of the η^5-indenyl complex **7** was carried out.

The molecular structure and atomic numbering scheme used are shown in Fig. 2. Selected bond lengths and angles are given in Table 2. Complex **7**, which exists as a racemate, displays a typical 'piano-stool' type arrangement, in which the central molybdenum atom is bonded to two terminal carbonyl ligands, an organic fragment and an η^5-indenyl ring. The organic fragment is bonded to molybdenum in an η^2 fashion, *via* a *cis*-disubstituted olefin (the substituents being an iminium moiety and a carboxylic acid group), and orientated such that the hydrogen atoms H(141) and H(131) lie underneath the indenyl ligand. The iminium moiety (PhCH$_2$N$^+$HCH) is positioned away from the metal such that the N–C(15) and C(13)–C(14) double bonds are effectively *trans* to each other. The carboxylic acid moiety lies underneath the two metal–carbonyl ligands. The η^2-olefin is bound to the metal asymmetrically with Mo–C bond distances of 2.237(8) and 2.272(9) Å, which are both considerably shorter than typical[11] molybdenum–olefin bond distances (*ca.* 2.369 Å). Such values are consistent with a significantly increased degree of back bonding from the metal. This is also reflected in the C(13)–C(14) bond distance [1.45(1) Å] which is closer to the length of a standard carbon–carbon single bond (1.530 Å) than that of a standard *cis*-disubstituted carbon–carbon double bond (1.317 Å).[14] Thus, the C(13) and C(14)

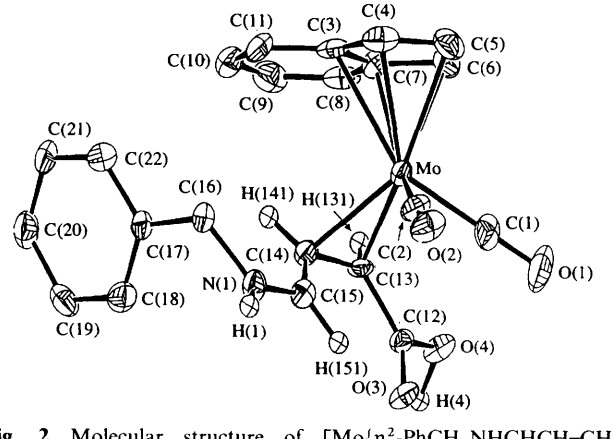


Fig. 2 Molecular structure of [Mo{η^2-PhCH$_2$NHCHCH=CH-(CO$_2$H)}(CO)$_2$(η^5-C$_9$H$_7$)] **7**; thermal ellipsoids are shown at the 40% probability level

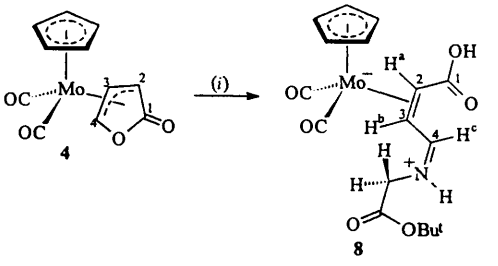
carbon atoms can be considered to have a small degree of sp^3 character. The bond angles about these atoms provide further evidence of this. The C(12)–C(13)–H(131) bond angle of 113(4)° is lower than the 120° expected for an sp^2-hybridised moiety (sp^3 hybridisation corresponds to a bond angle of 109.5°). Finally, of interest are the shortened carbon–carbon bond lengths C(12)–C(13) [1.45(1) Å] and particularly C(14)–C(15) [1.38(1) Å]. This, coupled with the observed bond distances C(12)–O(3) [1.259(9) Å] and N–C(15) [1.333(9) Å], implies a degree of π delocalisation around the six atom moiety from N to O(3).

The metal carbonyl groups lie at an angle of 79.9(4)° to one another and are both essentially linear, within experimental error, with Mo–C–O angles of 178.6(6) and 175.7(7)°. The Mo–C and C–O bond lengths show some deviation from typical values,[11] suggesting increased back bonding from the metal (as expected for a metal anion). Notably, a ring-slippage pattern was observed in the metal–indenyl bonding. The carbon atoms C(4)–C(6) lie closer to the molybdenum centre at distances of 2.320(9), 2.30(1) and 2.328(9) Å, compared with the distances Mo–C(3) 2.445(9) and Mo–C(7) 2.431(8) Å. This allyl–ene metal–ligand pattern is a common feature in metal–indenyl bonding.[16]

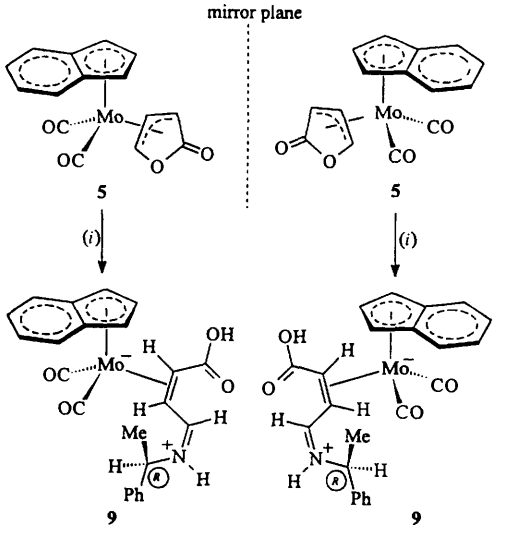
The solution IR and NMR spectroscopic data for compound **7** are in good agreement with the solid-state X-ray structural observations. Thus, the IR spectrum displayed strong metal carbonyl bands at 1933 and 1842 cm^{-1} along with a weaker band at 1653 cm^{-1} (carboxylic acid carbonyl group). Such relatively low-frequency bands can be explained in terms of the back-bonding and π-delocalisation effects described above. In addition to resonances assigned to the indenyl and benzyl groups, the ^1H NMR spectrum showed two broadened peaks at δ 9.72 and 6.61 due to the CO_2H and NH groups, respectively, along with three further resonances at δ 6.79 (H^c), 1.70 (H^a) and 1.13 (H^b). Of interest are the relatively high-field chemical shift values observed for H^a and H^b, which can be attributed to the increased amount of sp^3 character associated with the olefinic carbons to which these protons are attached. The magnitude of the vicinal ^3J(HH) coupling constants between H^a, H^b and H^c confirmed the geometry of the η^2-olefinic ligand. Thus, $J(H^aH^b)$ = 7.4 Hz, implying that H^a is *cis* to H^b, whereas $J(H^bH^c)$ = 11.2 Hz, indicative of a transoid relationship between H^b and H^c. The corresponding resonances were also exhibited in the ^{13}C-$\{^1H\}$ NMR spectrum which, in particular, displayed peaks at δ 177.7 (C^1), 133.9 (C^4), 55.2 (C^3) and 41.9 (C^2).

The potential generality of the lactone ring-opening reactions involved in the transformations **4** ⟶ **6** and **5** ⟶ **7** was briefly explored. Thus, reaction of compound **4** with glycine *tert*-butyl ester hydrochloride in the presence of triethylamine afforded a good yield (71%) of yellow crystals of the complex **8** (Scheme 4) characterised by elemental analysis, IR and NMR spectroscopy. Also, as mentioned earlier the lactone complexes **3**–**5** are chiral at the metal centre, and so reactions with an enantiomerically pure amine should give a pair of diastereoisomers, distinguishable by NMR spectroscopy. This was confirmed by examining the corresponding reaction of **5** with (*R*)-α-methylbenzylamine. The reaction carried out under standard conditions afforded a 1:1 mixture of the (*R*,*R*/*S*) and (*R*,*S*/*R*) diastereoisomers **9** (Scheme 5).

The requirement in the formation of the lactone ring-opened products **6**–**9** of more than 1 molar equivalent of amine, and the fact that the products clearly do not arise from simple nucleophilic attack on the lactone carbonyl carbon atom, as initially expected, posed a mechanistic problem. An insight into a possible reaction pathway was provided by an extended Hückel molecular orbital (EHMO) calculation using the bond parameters established by X-ray crystallography for complex **3**. Representations of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) are shown in Fig. 3 and the relative charge distribution is illustrated in Fig. 4. The calculations clearly show a high degree of localised positive charge (+1.180) at C^1 (the carbonyl carbon, Fig. 4), as expected. The γ-carbon atom, C^4 (corresponding to the overall site of addition to **5**), also displays a small positive charge (+0.404). However, the molybdenum centre is significantly more electropositive, having a localised charge of +1.106. This



Scheme 4 (*i*) Glycine *tert*-butyl ester hydrochloride, NEt_3, CH_2Cl_2, 25 °C

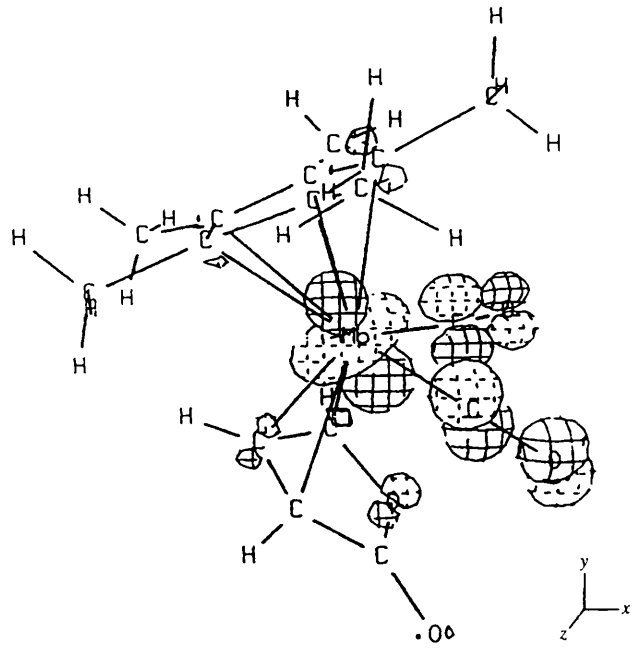


Scheme 5 (*i*) (*R*)-α-Methylbenzylamine, CH_2Cl_2, 25 °C

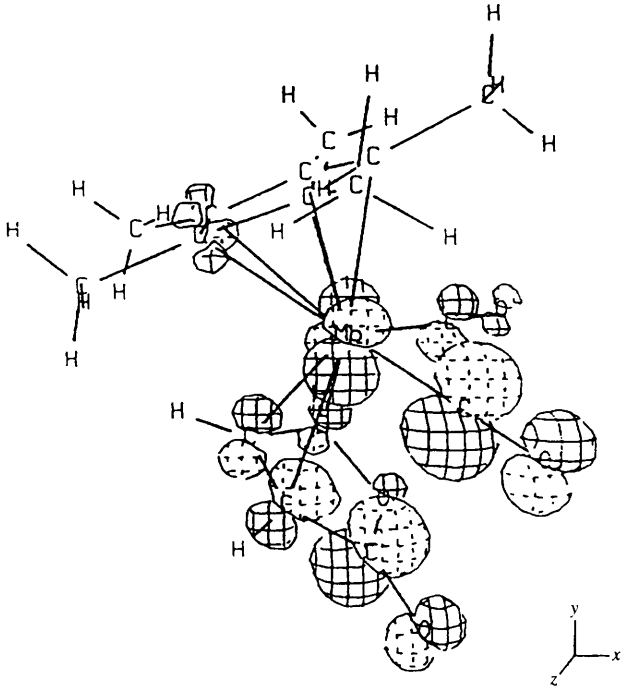
Table 2 Selected bond lengths (Å) and angles (°) for [Mo{η^2-PhCH$_2$NHCHCH=CH(CO$_2$H)}(CO)$_2$(η^5-C$_9$H$_7$)] **7**, with e.s.d.s in parentheses

Mo–C(1)	1.929(9)	Mo–C(2)	1.94(1)	Mo–C(3)	2.445(9)	
Mo–C(4)	2.230(9)	Mo–C(5)	2.30(1)	Mo–C(6)	2.328(9)	
Mo–C(7)	2.431(8)	Mo–C(13)	2.237(8)	Mo–C(14)	2.272(9)	
C(1)–O(1)	1.177(9)	C(2)–O(2)	1.158(9)	C(12)–O(3)	1.259(9)	
C(12)–O(4)	1.319(8)	C(12)–C(13)	1.45(1)	C(13)–C(14)	1.45(1)	
C(14)–C(15)	1.38(1)	N–C(15)	1.333(9)	N–C(16)	1.467(9)	

C(1)–Mo–C(2)	79.9(4)	Mo–C(1)–O(1)	178.6(6)	C(12)–C(13)–C(14)	124.3(7)	C(13)–C(14)–C(15)	123.6(7)
Mo–C(2)–O(2)	175.7(7)	C(13)–Mo–C(14)	37.5(2)	C(14)–C(15)–N	127.1(7)	C(15)–N–C(16)	123.9(7)
C(13)–C(12)–O(3)	125.6(7)	C(13)–C(12)–O(4)	114.5(7)	N–C(16)–C(17)	115.2(6)		

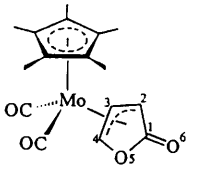


HOMO



LUMO

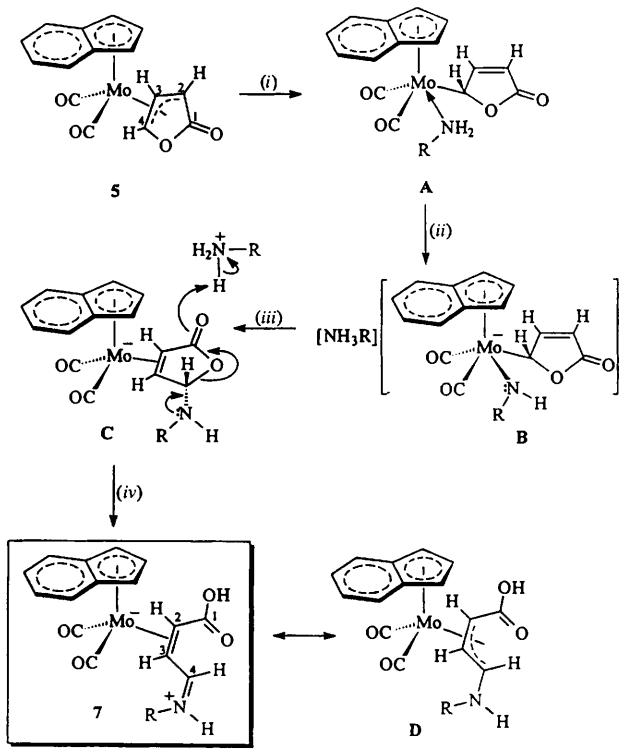
Fig. 3 Representations of the HOMO and LUMO orbitals for $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCH}\}(CO)_2(\eta\text{-}C_5Me_5)]$ **3**



C^1	+1.180	O^5	-0.753
C^2	-0.107	O^6	-1.131
C^3	-0.078	Mo	+1.106
C^4	+0.404		

Fig. 4 Relative charge distribution for compound **3**

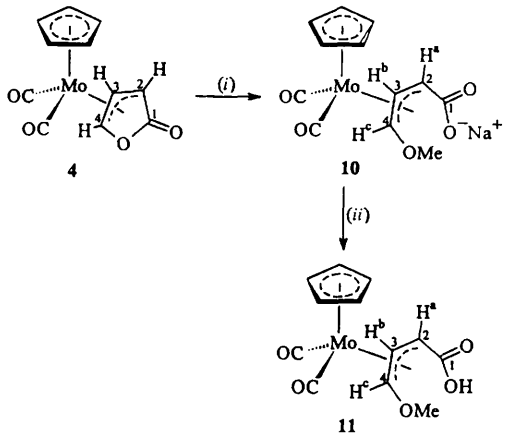
suggests that the formation of the adducts **6–9** involves initial attack by the primary amine NH_2R at the molybdenum centre assisted by the positive charge and by the availability of a



Scheme 6 (*i*) $+NH_2R$; (*ii*) $+NH_2R$, $-[NH_3R]^+$; (*iii*) reductive elimination; (*iv*) $+[NH_3R]^+$, $-NH_2R$

suitable LUMO. Thus, as is illustrated in Scheme 6, direct co-ordination of NH_2R *via* N to the metal centre of complex **5**, facilitated by an η^3 to η^1 slippage of the bonding mode of the lactone ligand, leads to the formation of **A**. A second molecule of RNH_2 can then effect deprotonation of the co-ordinated amine to form the amido-substituted anionic species **B**. This then undergoes a reductive elimination reaction in which the amido moiety is transferred to C^4 affording the anionic η^2-alkene-substituted intermediate **C**, subsequent electron redistribution *via* the nitrogen lone pair resulting in ring opening of the lactone and proton transfer from NH_3R^+ to the carbonyl oxygen, thus providing a pathway to the zwitterionic η^2-alkene complex **7**. It is interesting that **6–9** prefer to exist as zwitterions rather than neutral η^3-allylic complexes **D**.

The reactivity of these η^3-γ-lactonyl complexes towards an oxygen nucleophile was next examined. Treatment of $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCH}\}(CO)_2(\eta\text{-}C_5H_5)]$ **4** with sodium methoxide [tetrahydrofuran (thf), 20 °C] gave rise to a rapid reaction (0.5 h), and following work-up a yellow powder was obtained in 80% yield. This was identified by mass and NMR spectroscopy as the methoxy- and carboxylate-substituted acyclic *anti*-η^3-allyl complex **10** (Scheme 7). Acidification of **10** with HCl afforded the corresponding carboxylic acid-substituted complex **11** (Scheme 7). Complex **10** was found to be rather unstable and only soluble in the more polar common organic solvents, as expected for such a charged species. The solution IR spectrum showed a broadened band at 1572 cm^{-1} attributed to the presence of the carboxylate anion. Two sets of metal carbonyl bands were also observed (1946, 1871 and 1936, 1852 cm^{-1}) indicating the presence of *exo* and *endo* conformers. This was confirmed from an examination of the ^1H NMR spectrum, which displayed two sets of well resolved allylic resonances in the ratio 11:9. The relative chemical shift values for the allylic protons suggested that the *exo* conformer was the major isomer. In addition, the vicinal $^3J(HH)$ couplings of the allylic protons $[J(H^aH^b) = J(H^bH^c) = 8.4\ Hz]$ implied that both the methoxy and carboxylate substituents were orientated in an *anti* configuration relative to the backbone of the allyl ligand. Similarly, the solution IR and NMR data for the carboxylic

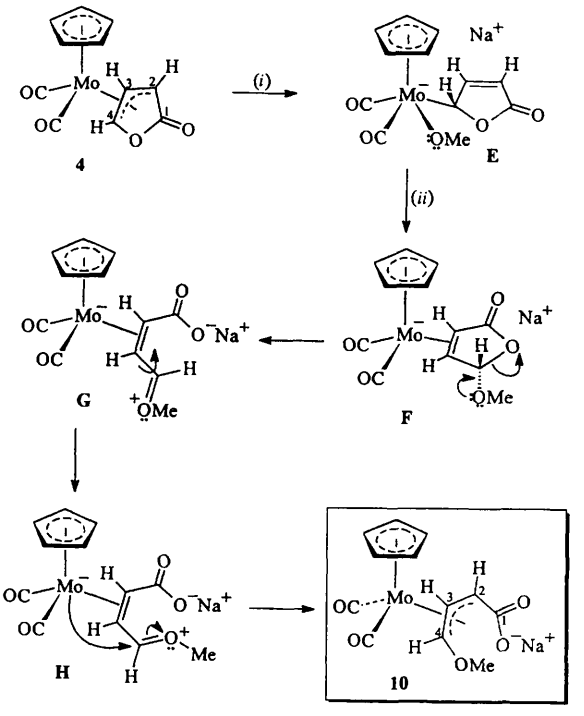


Scheme 7 (*i*) NaOMe, thf; (*ii*) HCl, thf

acid complex **11** showed the presence of *exo* and *endo* conformers in the ratio 5:1.

Evidently, complex **10** is formed by means of an overall addition of methoxide at C^4 in **4**, resulting in cleavage of the lactone ring. Presumably this process occurs in a similar manner to the amine reactions, in which initial attack by the nucleophile takes place at the metal. A suggested mechanism is illustrated in Scheme 8. The first stage in this sequence involves direct attack of methoxide anion at the molybdenum centre in **4** with concomitant η^3 to η^1 slippage of the lactone ligand to form **E** (Scheme 8). A reductive elimination followed by a ring-opening reaction *via* the lone pair at the methoxy-oxygen atom in **E** would then give the zwitterionic intermediate **G** containing a carboxylate anion. Interestingly, this species was not isolated, the actual product **10** being an *anti*-η^3-allyl complex. Conversion from **G** into **10** could occur *via* rotation about the C–C single bond in **G** to give the cisoid intermediate **H**, in which the positive charge at the methoxy-oxygen atom is stabilised by its close proximity to the carboxylate moiety. Subsequent nucleophilic attack at the molybdenum centre then leads to the formation of complex **10**.

As mentioned earlier, the charge distribution within the lactone complex **3** can be derived from an EHMO calculation. Examination of Fig. 4, where these calculations are summarised, shows that the lactonyl carbonyl oxygen atom O(6) carries a substantial negative charge. This suggested to us that protonation of these lactone complexes should result in the formation of a 2-hydroxyfuran-substituted cationic complex. In the event a most unusual reaction occurred. Addition (room temperature) of HBF_4·Et_2O to a dichloromethane solution of the η^5-cyclopentadienyl-substituted complex **4** resulted in the formation in high yield of an orange solid **12**, which showed in its IR spectrum bands corresponding to the presence of *exo* and *endo* isomers carrying a terminal carbonyl and an organic carbonyl group. The proton NMR spectrum confirmed the presence of such isomers and indicated the presence of an *anti*-1,3-disubstituted η^3-allyl ligand. Unfortunately the instability of the complex prevented an accurate elemental analysis or a ^{13}C-$\{^1H\}$ NMR spectrum being obtained. However, when **12** was dissolved in acetonitrile a reaction occurred resulting in the formation of a stable complex **13**, which analysed well for a neutral species with the molecular formula $[Mo(C_5H_3O_3)(NCMe)(CO)(\eta\text{-}C_5H_5)]$. The ^1H NMR spectrum of **13** is similar to that observed for **12**. The above-mentioned structural features were confirmed in the ^{13}C-$\{^1H\}$ spectrum, but interestingly this also showed resonances at δ 173.6 and 173.0 consistent with the presence in **13** of *two* organic carbonyl environments. This latter observation taken together with the fact that the product of this protonation reaction was not a cationic complex indicated that an unusual reaction had occurred. The structural identity of **13** was



Scheme 8 (*i*) NaOMe, thf; (*ii*) reductive elimination

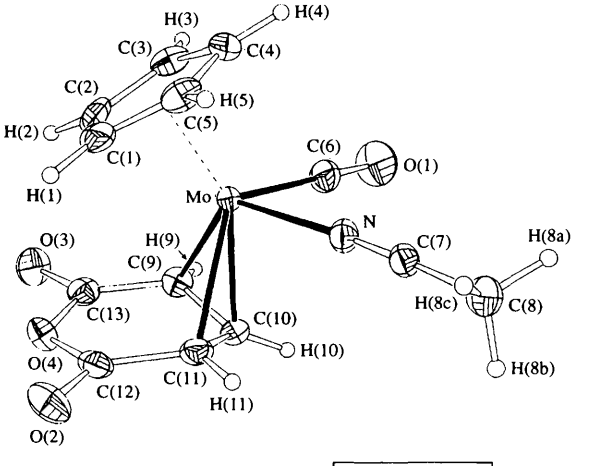


Fig. 5 Molecular structure of $[Mo\{\eta^3\text{-}\overline{OC(O)CHCHCHCO}\}(NCMe)(CO)(\eta\text{-}C_5H_5)]$ **13**; thermal ellipsoids are shown at the 40% probability level

established by a single-crystal X-ray crystallographic study with a suitable crystal obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the complex. The resulting structure is shown in Fig. 5; selected bond lengths and angles are given in Table 3.

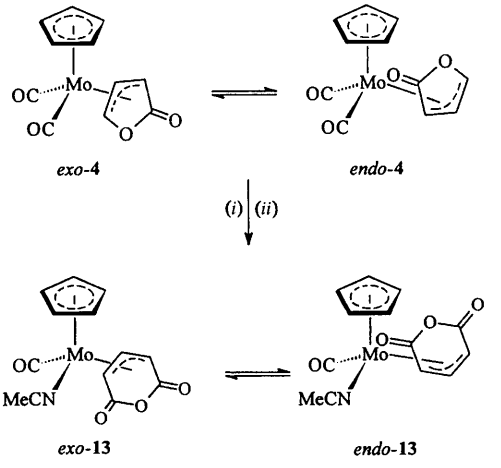
It is evident from Fig. 5 that compound **13** crystallises in the *endo* conformation, but what is very interesting is that it contains an $(\eta\text{-}C_5H_5)Mo(CO)(NCMe)$ fragment with predictable bond parameters, co-ordinated to a conventionally bonded η^3-allylic system, in which the *anti*-1,3 positions are spanned by a C(O)OC(O) anhydride. As is summarised in Scheme 9, the reaction of **4** with HBF_4·Et_2O leads to an unprecedented formal 'insertion' of a co-ordinated carbon monoxide into a lactone carbon–oxygen bond.

A possible explanation for this remarkable reaction is shown in Scheme 10, where for simplicity only the *exo* isomers are depicted. The reaction of compound **4** with HBF_4·Et_2O occurs as predicted by the EHMO calculations (Fig. 4) on the lactone carbonyl oxygen to give a cationic species, which can be depicted in terms of the two canonical forms **I** and **J**. Slippage of the $(\eta\text{-}C_5H_5)Mo(CO)_2$ fragment, which can be best understood in terms of a change ($\eta^3 \longrightarrow \eta^1$) in the bonding mode

Table 3 Selected bond lengths (Å) and angles (°) for [Mo{η^3-OC(O)CHCHCHCO}(NCMe)(CO)(η-C_5H_5)] **13**, with e.s.d.s in parentheses

Mo–C(9)	2.271(4)	Mo–C(10)	2.171(4)	Mo–C(11)	2.288(4)
Mo–C(6)	1.961(4)	Mo–N	2.143(4)	Mo–C(1)	2.350(4)
Mo–C(2)	2.305(4)	Mo–C(3)	2.269(4)	Mo–C(4)	2.280(4)
Mo–C(5)	2.321(4)	C(9)–C(10)	1.422(6)	C(11)–C(12)	1.434(6)
C(12)–O(2)	1.202(5)	C(12)–O(4)	1.397(5)	O(4)–C(13)	1.395(5)
C(13)–O(3)	1.210(5)	C(9)–C(13)	1.435(6)	C(6)–O(1)	1.145(5)
N–C(7)	1.133(5)	C(7)–C(8)	1.445(6)	C(10)–C(11)	1.417(6)

Mo–C(6)–O(1)	179.4(4)	Mo–N–C(7)	174.6(3)	C(11)–C(12)–O(2)	127.1(4)	C(11)–C(12)–O(4)	117.7(4)
C(6)–Mo–N	85.1(2)	C(9)–Mo–C(10)	37.3(2)	C(12)–O(4)–C(13)	121.0(3)	O(4)–C(13)–O(3)	114.4(4)
C(9)–Mo–C(11)	62.5(2)	C(10)–Mo–C(11)	36.9(2)	O(4)–C(13)–C(9)	118.6(4)		
C(9)–C(10)–C(11)	112.8(4)	C(10)–C(11)–C(12)	121.1(4)				



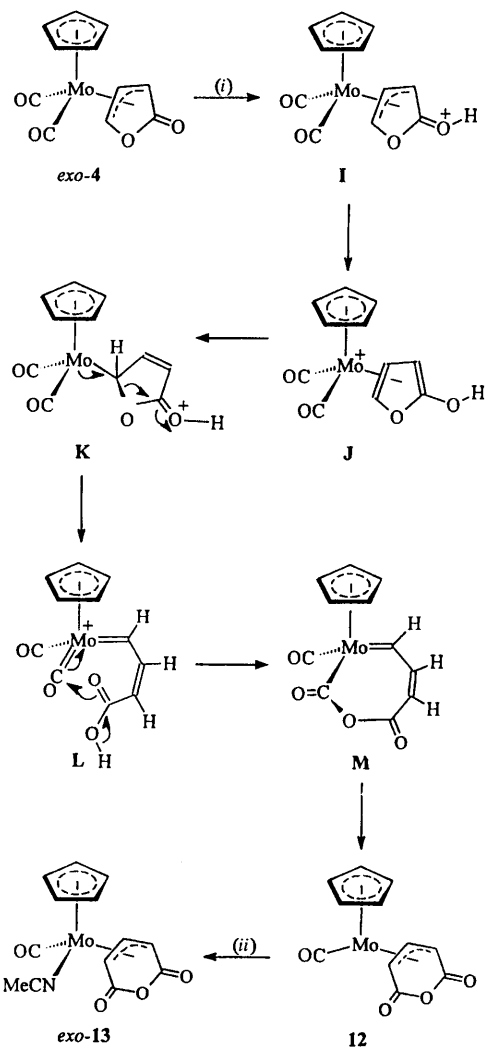
Scheme 9 (*i*) HBF_4·Et_2O, CH_2Cl_2, 25 °C; (*ii*) MeCN

of the allylic fragment in canonical form **I**, then allows a ring-opening reaction (**K** ⟶ **L**) to occur, which is assisted by the formation of a molybdenum to carbon double bond. Proton loss from the cation **L** with concomitant nucleophilic attack by the carboxylate carbonyl group on a co-ordinated carbon monoxide then affords the intermediate **M**, which on migration of the acyl group from the metal onto the carbene carbon provides access to the unstable 16-electron complex **12**. Stabilisation of this species by acetonitrile then gives the complex **13** isolated as a mixture of *exo* and *endo* isomers. Importantly, this reaction sequence is catalytic in protons as confirmed by preliminary experiments.

In summary, this paper describes a new pathway to η^3-bonded lactonyl complexes which show unusual reactivity towards both nucleophiles and protons. Both of these types of reaction could have importance in synthetic organic chemistry.

Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk techniques. Solvents were freshly distilled over an appropriate drying agent prior to use. Column chromatography was performed using Aldrich alumina (Brockmann Activity II) as the solid support. Reagents were obtained from commercial sources unless otherwise indicated. The NMR spectra were recorded on JEOL JNM GX270 and EX400 spectrometers at the temperatures indicated. The ^1H and ^{13}C-{^1H} chemical shifts are quoted as positive to high frequency of tetramethylsilane. Infrared spectra were measured on a Nicolet 510P FT-IR spectrometer. The compounds [Mo(NCMe)$_2$(CO)$_2$(η-C_5H_5)][BF_4],[17] [Mo(NCMe)$_2$(CO)$_2$(η-C_5Me_5)][BF_4],[17] [Mo(NCMe)$_2$(CO)$_2$(η^5-C_9H_7)][BF_4],[18] and [Mo(η^3-C_3H_5)(CO)$_2$(η-C_5H_5)][19] were prepared according to the published literature procedures.



Scheme 10 Counter anion BF_4^-. (*i*) HBF_4·Et_2O; (*ii*) MeCN

Preparations

[Mo{η^3-OC(O)CHCHCH}(CO)$_2$(η-C_5Me_5)] 3. An excess of 2-(trimethylsilyloxy)furan (1.84 cm^3, 10.96 mmol) was added to a suspension of the blood-red complex *cis*-[Mo(NCMe)$_2$(CO)$_2$(η-C_5Me_5)][BF_4] (1.00 g, 2.19 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 4 d at room temperature the resulting dark yellow solution was filtered through a small pad of alumina. The yellow filtrate was collected and concentrated to a small volume before being chromatographed on alumina. Elution with CH_2Cl_2 afforded a single yellow fraction which on recrystallisation from CH_2Cl_2–pentane gave bright yellow crystals of compound **3** (0.503 g, 62%). X-Ray-quality *crystals* of the *exo* isomer were obtained by CH_2Cl_2–toluene–pentane

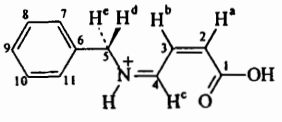
layer diffusion at room temperature (Found: C, 51.9; H, 4.9. $C_{16}H_{18}MoO_4$ requires C, 51.9; H, 4.9%). $\nu_{CO}(CH_2Cl_2)$ 1968vs, 1892s, 1748ms (*exo*) and 1985m, 1917m, 1721w cm^{-1} (*endo*). NMR (CD_2Cl_2): ^1H (−80 °C), *exo* isomer, δ 6.46 [dd, 1 H, H^c, $J(H^cH^b)$ 2.7, $J(H^cH^a)$ 2.5], 5.00 [dd, 1 H, H^b, $J(H^bH^a)$ = $J(H^bH^c)$ 2.7], 2.97 [dd, 1 H, H^a, $J(H^aH^b)$ 2.7, $J(H^aH^c)$ 2.5] and 1.85 (s, 15 H, C_5Me_5); *endo* isomer, δ 5.84 [dd, 1 H, H^c, $J(H^cH^b)$ 2.7, $J(H^cH^a)$ 2.5], 5.78 [dd, 1 H, H^b, $J(H^bH^a)$ = $J(H^bH^c)$ 2.7], 3.06 [dd, 1 H, H^a, $J(H^aH^b)$ 2.7, $J(H^aH^c)$ 2.5 Hz] and 1.81 (s, 15 H, C_5Me_5); ^{13}C-{^1H} (−50 °C), *exo* isomer, δ 240.2 (MoCO), 236.1 (MoCO), 175.9 (C^1), 105.4 (C_5Me_5), 95.4 (C^4), 75.4 (C^3), 37.9 (C^2) and 10.2 (C_5Me_5); *endo* isomer, δ 235.7 (MoCO), 233.9 (MoCO), 174.6 (C^1), 104.6 (C_5Me_5), 90.4 (C^4), 80.2 (C^3), 37.0 (C^2) and 9.8 (C_5Me_5).

[Mo{η³-$\overline{OC(O)CHCHCH}$}$(CO)_2$(η-C_5H_5)] 4. *Method A.* An excess of 2-(trimethylsilyloxy)furan (3.27 cm^3, 19.43 mmol) was added to a suspension of the blood-red complex *cis*-[Mo$(NCMe)_2(CO)_2$(η-C_5H_5)][BF_4] (1.50 g, 3.89 mmol) in CH_2Cl_2 (40 cm^3). After stirring for 3 d at room temperature the resulting dark yellow solution was filtered through a small pad of alumina. The yellow filtrate was concentrated to a small volume and chromatographed on alumina. Elution with CH_2Cl_2 afforded a single yellow fraction which gave, after removal of solvent and recrystallisation from CH_2Cl_2–pentane, [Mo{η³-$\overline{OC(O)CHCHCH}$}$(CO)_2$(η-C_5H_5)] **4** as a bright yellow powder (0.645 g, 55%).

Method B. A solution of the yellow complex [Mo(η³-C_3H_5)$(CO)_2$(η-C_5H_5)] (0.324 g, 1.26 mmol) in CH_2Cl_2 (30 cm^3) was cooled to −78 °C. To this was added dropwise HBF_4·Et_2O (220 μl, 1.27 mmol) causing an immediate change to deep reddish violet. After stirring for 0.5 h at −78 °C the mixture was treated with an excess of 2-(trimethylsilyloxy)furan (1.06 cm^3, 6.28 mmol) and then allowed to warm to ambient temperature. The reaction mixture was stirred for 2 h and then filtered through Celite to give a reddish yellow solution. This was concentrated to a small volume under reduced pressure and chromatographed on alumina. Elution with CH_2Cl_2 afforded a single yellow fraction which gave, after removal of solvent and recrystallisation from CH_2Cl_2–pentane, [Mo{η³-$\overline{OC(O)CHCHCH}$}$(CO)_2$(η-C_5H_5)] **4** as a bright yellow powder (0.139 g, 37%) (Found: C, 43.8; H, 2.7. $C_{11}H_8MoO_4$ requires C, 44.0; H, 2.7%). $\nu_{CO}(CH_2Cl_2)$ at 2000vs, 1935s, 1750ms (*exo*) and 1986ms, 1912m, 1721m cm^{-1} (*endo*). NMR (CD_2Cl_2): ^1H (−60 °C), *exo* isomer, δ 6.43 [dd, 1 H, H^c, $J(H^cH^b)$ 2.5, $J(H^cH^a)$ 2.4], 5.86 [dd, 1 H, H^b, $J(H^bH^a)$ = $J(H^bH^c)$ 2.5], 5.37 (s, 5 H, C_5H_5) and 3.54 [dd, 1 H, H^a, $J(H^aH^b)$ 2.5, $J(H^aH^c)$ 2.4]; *endo* isomer, δ 6.62 [dd, 1 H, H^c, $J(H^cH^b)$ 2.7, $J(H^cH^a)$ 2.5], 6.08 [dd, 1 H, H^b, $J(H^bH^a)$ = $J(H^bH^c)$ 2.7], 5.45 (s, 5 H, C_5H_5) and 3.43 [dd, 1 H, H^a, $J(H^aH^b)$ 2.7, $J(H^aH^c)$ 2.5 Hz]; ^{13}C-{^1H} (−50 °C), *exo* isomer, δ 233.1 (MoCO), 232.3 (MoCO), 177.2 (C^1), 94.1 (C_5H_5), 91.2 (C^4), 81.0 (C^3) and 37.9 (C^2); *endo* isomer, δ 236.6 (MoCO), 232.8 (MoCO), 175.9 (C^1), 94.8 (C^4), 92.8 (C_5H_5), 67.4 (C^3) and 33.9 (C^2).

[Mo{η³-$\overline{OC(O)CHCHCH}$}$(CO)_2$(η⁵-C_9H_7)] 5. An excess of 2-(trimethylsilyloxy)furan (2.47 cm^3, 14.71 mmol) was added to a suspension of the blood-red complex *cis*-[Mo$(NCMe)_2(CO)_2$(η⁵-C_9H_7)][BF_4] (1.20 g, 2.94 mmol) in CH_2Cl_2 (35 cm^3). After stirring for 3 d at room temperature the resulting dark yellow solution was filtered through a small pad of alumina. The yellow filtrate was collected and concentrated to a small volume before being chromatographed on alumina. Elution with CH_2Cl_2 afforded a single yellow fraction which gave, after removal of solvent and recrystallisation from CH_2Cl_2–pentane, [Mo{η³-$\overline{OC(O)CHCHCH}$}$(CO)_2$(η⁵-C_9H_7)] **5** as a bright yellow powder (0.590 g, 57%) (Found: C, 51.4; H, 2.8. $C_{15}H_{10}MoO_4$ requires: C, 51.5; H, 2.9%). $\nu_{CO}(CH_2Cl_2)$ 1979vs, 1904s and 1752ms cm^{-1}. NMR (CD_2Cl_2): ^1H (−45 °C), δ 7.32–7.11 (m, 4 H, indenyl), 6.62 [dd, 1 H, H^c, $J(H^cH^b)$ 2.7, $J(H^cH^a)$ 2.4], 6.22 (m, 1 H, indenyl), 5.98 (m, 1 H, indenyl), 5.60 (dd, 1 H, indenyl), 3.14 [dd, 1 H, H^a, $J(H^aH^b)$ 2.7, $J(H^aH^c)$ 2.4] and 1.26 [dd, 1 H, H^b, $J(H^bH^a)$ 2.7, $J(H^bH^c)$ 2.7 Hz]; ^{13}C-{^1H} (−45 °C), δ 237.7 (MoCO), 232.6 (MoCO), 173.1 (C^1), 126.9, 125.7 (indenyl), 124.5, 123.1 (indenyl), 112.5, 110.8 (indenyl), 99.9 (C^4), 88.2 (indenyl), 85.7 (C^3), 81.0, 80.8 (indenyl) and 45.1 (C^2).

Reaction of benzylamine. *With complex* **4**. To a solution of [Mo{η³-$\overline{OC(O)CHCHCH}$}$(CO)_2$(η-C_5H_5)] **4** (0.13 g, 0.43 mmol) in CH_2Cl_2 (15 cm^3) was added benzylamine (95 μl, 0.87 mmol) and the resultant mixture was stirred for 17 h. The volume of solvent was then reduced *in vacuo* to *ca.* 5 cm^3 and pentane was added to precipitate an orange powder. This was recrystallised from thf–Et_2O to give orange *microcrystals* of [Mo(η²-$C_{11}H_{12}NO_2$)$(CO)_2$(η-C_5H_5)] **6** (0.15 g, 85%) (Found: C, 53.1; H, 4.3; N, 3.5. $C_{18}H_{17}MoNO_4$ requires C, 53.1; H, 4.2; N, 3.4%). ν_{CO}(thf) 1927vs, 1840s and 1694mw cm^{-1}. NMR (C_4D_8O, 20 °C): ^1H, δ 7.60–7.40 (5 H, Ph), 6.99 (br, 1 H, H^c), 6.96 (br, 1 H, NH), 5.42 (s, 5 H, C_5H_5), 4.22 (br, 2 H, H^d, H^e), 3.63 [dd, 1 H, H^b, $J(H^bH^a)$ 7.1, $J(H^bH^c)$ 8.2] and 3.22 [d, 1 H, H^a, $J(H^aH^b)$ 7.1 Hz]; ^{13}C-{^1H}, δ 248.9 (MoCO), 241.7 (MoCO), 180.0 (C^1), 139.3 (C^6), 133.2 (C^4), 129.9, 129.0, 128.7 (Ph), 91.7 (C_5H_5), 49.7 (C^3), 43.5 (C^5) and 30.1 (C^2).



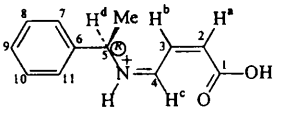
With complex **5**. Benzylamine (0.686 cm^3, 0.628 mmol) was added to a solution of the yellow complex [Mo{η³-$\overline{OC(O)CHCHCH}$}$(CO)_2$(η⁵-C_9H_7)] **5** (0.110 g, 0.314 mmol) in CH_2Cl_2 (15 cm^3). The mixture was left to stir overnight at room temperature resulting in a bright orange solution. Analysis by TLC and infrared spectroscopy showed the complete consumption of starting material and the formation of a new product. The mixture was concentrated to a small volume *in vacuo*, following which slow addition of pentane precipitated a bright yellow solid. This was washed with pentane and recrystallised from CH_2Cl_2–pentane to afford [Mo(η²-$C_{11}H_{12}NO_2$)$(CO)_2$(η⁵-C_9H_7)] **7** as a bright yellow powder (0.122 g, 85%). X-Ray-quality *crystals* of **7** were obtained by CH_2Cl_2–Et_2O–pentane layer diffusion at room temperature (Found: C, 51.4; H, 3.9; N, 2.7. $C_{22}H_{19}MoNO_4$·CH_2Cl_2 requires C, 50.9; H, 3.9; N, 2.6%). $\nu_{CO}(CH_2Cl_2)$ 1933vs, 1842s and 1653mw cm^{-1}. NMR [$(CD_3)_2CO$, 20 °C]: ^1H, δ 9.72 (br s, 1 H, OH), 7.52–7.49 (m, 4 H, indenyl), 7.48–7.38 (m, 3 H, phenyl), 7.21–7.12 (m, 2 H, phenyl), 6.79 [dm, 1 H, H^c, $J(H^cH^b)$ 11.2], 6.61 (br m, 1 H, NH), 6.20 (m, 1 H, indenyl), 6.11 (m, 1 H, indenyl), 5.65 (dd, 1 H, indenyl), 4.17 [dm, 2 H, H^d and H^e, $J(H^dH^e)$ 5.1], 1.70 [d, 1 H, H^a, $J(H^aH^b)$ 7.4] and 1.13 [dd, 1 H, H^b, $J(H^bH^c)$ 11.2, $J(H^bH^a)$ 7.4 Hz]; ^{13}C-{^1H}, δ 247.2 (MoCO), 240.9 (MoCO), 177.7 (C^1), 137.7 (C^6), 133.9 (C^4), 128.8, 128.0, 127.7 (C^7–C^{11}), 125.0, 124.4, 124.2 (indenyl), 112.9, 112.5 (indenyl), 89.7 (indenyl), 80.2 (indenyl), 55.2 (C^3), 48.6 (C^5), and 41.9 (C^2).

Reaction of complex 4 with glycine *tert*-butyl ester hydrochloride. A solution of [Mo{η³-$\overline{OC(O)CHCHCH}$}$(CO)_2$(η-C_5H_5)] (0.100 g, 0.335 mmol) in CH_2Cl_2 (30 cm^3) was treated with glycine *tert*-butyl ester hydrochloride (0.112 g, 0.669 mmol) followed by triethylamine (93 μl, 0.670 mmol) and the resulting mixture was stirred for 2 d. The volume of solvent was then reduced *in vacuo* to *ca.* 5 cm^3 and hexane (20 cm^3) was added to give a yellow precipitate of [Mo(η²-$C_{10}H_{16}NO_4$)$(CO)_2$(η-C_5H_5)] **8** (0.102 g, 71%) (Found: C, 47.5; H, 5.2; N, 3.1. $C_{14}H_{21}MoNO_6$ requires C, 47.3; H, 4.9;

N, 3.3%). ν_{CO}(thf) 1929vs, 1844vs, 1743m and 1693m cm^{-1}. NMR (C_4D_8O, 20 °C): ^1H, δ 6.71 [dd, 1 H, H^c, $J(H^cH^b)$ 11.0, $J(H^cH^a)$ 5.8], 6.12 (br, 1 H, NH), 5.43 (s, 5 H, C_5H_5), 3.67 [dd, 1 H, H^b, $J(H^bH^c)$ 11.0, $J(H^cH^a)$ 7.1 Hz], 3.82, 3.57 [(ABC), 2 H, CH_2, J(AB) 16.0, $J(HH^{NH})$ 5.3], 3.21 [d, 1 H, H^a, $J(H^aH^b)$ 7.1 Hz] and 1.61 (s, 9 H, CMe_3); ^{13}C-{^1H}, δ 247.8 (MoCO), 241.3 (MoCO), 179.9 (C^1), 169.8 (C=O), 128.0 (C^4), 92.0 (C_5H_5), 82.7 (CH_2), 48.0 (C^3), 45.4 (C^2), 30.7 (CMe_3) and 28.7 (CMe_3).

Reaction of complex 5 with (*R*)-(+)-α-methylbenzylamine. (*R*)-(+)-α-Methylbenzylamine (0.132 cm^3, 1.00 mmol) was added to a solution of the yellow complex [Mo{η³-OC(O)CHCHCH}(CO)$_2$(η⁵-C_9H_7)] **5** (0.175 g, 0.500 mmol) in CH_2Cl_2 (30 cm^3). The mixture was left to stir overnight at room temperature resulting in the precipitation of a bright yellow solid. Analysis by TLC and infrared spectroscopy showed the complete consumption of the starting material and the formation of a new product. The solvent volume was reduced *in vacuo*, following which slow addition of pentane precipitated more of the bright yellow solid. This was washed with pentane and dried *in vacuo* to afford [Mo(η²-$C_{12}H_{14}NO_2$)(CO)$_2$(η⁵-C_9H_7)] **9** (0.205 g, 87%) as a bright yellow powder (Found: C, 58.8; H, 4.5; N, 3.0. $C_{23}H_{21}MoNO_4$ requires C, 58.6; H, 4.5; N, 3.0%). $\nu_{CO}(CH_2Cl_2)$ 1933vs, 1844s and 1653mw cm^{-1}. According to NMR spectroscopy **9** exists as a 1:1 mixture of the (*R*,*R S*) and (*R*,*S*/*R*) diastereoisomers. NMR [$(CD_3)_2CO$, 20 °C]: (*R*,*R*/*S*) ^1H, δ 9.73 (br s, 1 H, OH), 7.60–7.52 (m, 4 H, indenyl), 7.47–7.36 (m, 3 H, phenyl), 7.25–7.08 (m, 2 H, phenyl), 6.72 [dm, 1 H, H^c, $J(H^cH^b)$ 11.2], 6.48 (br m, 1 H, NH), 6.16 (m, 1 H, indenyl), 6.08 (m, 1 H, indenyl), 5.64 (dd, 1 H, indenyl), 4.58 [q, 1 H, H^d, $J(H^dMe)$ 6.8], 1.64 [d, 1 H, H^a, $J(H^aH^b)$ 7.3], 1.63 [d, 3 H, Me, $J(MeH^d)$ 6.8] and 1.11 [dd, 1 H, H^b, $J(H^bH^c)$ 11.2, $J(H^bH^a)$ 7.3 Hz]; ^{13}C-{^1H}, δ 247.6 (MoCO), 241.4 (MoCO), 178.0 (C^1), 143.6 (C^6), 133.3 (C^4), 128.9, 127.6, 126.5 (C^7–C^{11}), 125.1, 124.4, 124.2 (indenyl), 112.9, 112.5 (indenyl), 90.5, 81.2, 79.8 (indenyl), 55.8 (C^3), 54.6 (C^5), 42.6 (C^2) and 23.2 (Me); (*R*,*S*/*R*) ^1H, δ 9.73 (br s, 1 H, OH), 7.60–7.52 (m, 4 H, indenyl), 7.47–7.36 (m, 3 H, phenyl), 7.25–7.08 (m, 2 H, phenyl), 6.67 [dm, 1 H, H^c, $J(H^cH^b)$ 11.2], 6.48 (br m, 1 H, NH), 6.16 (m, 1 H, indenyl), 6.08 (m, 1 H, indenyl), 5.60 (dd, 1 H, indenyl), 4.14 [q, 1 H, H^d, $J(H^dMe)$ 6.8], 1.66 [d, 1 H, H^a, $J(H^aH^b)$ 7.3], 1.60 [d, 3 H, Me, $J(MeH^d)$ 6.8] and 1.38 [dd, 1 H, H^b, $J(H^bH^c)$ 11.2, $J(H^bH^a)$ 7.3 Hz]; ^{13}C-{^1H}, δ 247.3 (MoCO), 240.9 (MoCO), 177.6 (C^1), 143.2 (C^6), 131.8 (C^4), 128.9, 127.4, 126.2 (C^7–C^{11}), 124.7, 124.3, 124.0 (indenyl), 112.8, 111.8 (indenyl), 89.9, 80.2, 79.8 (indenyl), 54.6 (C^3), 54.0 (C^5), 41.6 (C^2) and 22.9 (Me).

[Mo{η³-*anti*-(MeO)CHCHCH(CO_2Na)}(CO)$_2$(η-C_5H_5)] 10. Sodium methoxide (2.80 cm^3 of a 0.23 mol dm^{-3} solution in thf, 0.64 mmol) was added to a solution of the yellow complex [Mo{η³-OC(O)CHCHCH}(CO)$_2$(η-C_5H_5)] **4** (0.19 g, 0.63 mmol) in thf (25 cm^3). The mixture was allowed to stir at ambient temperature for 0.5 h, after which the volatiles were removed under reduced pressure and the resultant yellow residue was briefly dried *in vacuo* before being extracted with thf (2 × 10 cm^3). The extracts were combined and filtered through Celite and the filtrate was reduced to a small volume (*ca.* 5 cm^3) *in vacuo*. Slow addition of Et_2O (30 cm^3) afforded **10** as a yellow powder (0.18 g, 80%). The unstable nature of this complex prevented a satisfactory elemental analysis being obtained. Positive-ion FAB mass spectrum in 3-nitrobenzyl alcohol: *m*/*z* 355, $[M]^+$ and 327, $[M - CO]^+$. ν_{CO}(thf) 1946vs, 1871s, 1572m (br) (*exo*) and 1936vs, 1852s, 1572m (br) cm^{-1} (*endo*).



NMR [$(CD_3)_2CO$, 20 °C]: ^1H, *exo* isomer, δ 5.98 [d, 1 H, H^c, $J(H^cH^b)$ 8.4], 5.42 (s, 5 H, C_5H_5), 4.41 [dd, 1 H, H^b, $J(H^bH^a)$ 8.4, $J(H^bH^c)$ 8.4], 3.60 (s, 3 H, OMe), and 3.57 [d, 1 H, H^a, $J(H^aH^b)$ 8.4]; *endo* isomer, δ 7.01 [d, 1 H, H^c, $J(H^cH^b)$ 8.4], 5.31 (s, 5 H, C_5H_5), 3.90 [dd, 1 H, H^b, $J(H^bH^a)$ 8.4, $J(H^bH^c)$ 8.4], 3.63 [d, 1 H, H^a, $J(H^aH^b)$ 8.4 Hz] and 3.54 (s, 3 H, OMe); ^{13}C-{^1H}, *exo* isomer, δ 243.4 (MoCO), 241.8 (MoCO), 181.6 (C^1), 109.3 (C^4), 92.7 (C_5H_5), 75.4 (C^3), 58.8 (C^2) and 44.1 (OMe); *endo* isomer, δ 242.8 (MoCO), 239.5 (MoCO), 181.8 (C^1), 115.8 (C^4), 93.1 (C_5H_5), 59.6 (C^3), 58.4 (C^2) and 41.3 (OMe).

[Mo{η³-*anti*-(MeO)CHCHCH(CO_2H)}(CO)$_2$(η-C_5H_5)] 11. Complex **10** (0.20 g, 0.56 mmol) was dissolved in thf (30 cm^3) and dilute aqueous HCl was added dropwise until the infrared spectrum of the solution showed that all of the starting compound had been consumed. The resulting solution/suspension was evaporated to dryness *in vacuo* and the residue extracted with Et_2O (2 × 30 cm^3). Filtration of the combined extracts through a Celite plug gave a yellow solution which was reduced in volume *in vacuo* to *ca.* 5 cm^3. Hexane (20 cm^3) was added and the solution was cooled (−20 °C) overnight to give **11** as a yellow powder (0.14 g, 75%) (Found: C, 44.0; H, 3.6. $C_{12}H_{12}MoO_5$ requires C, 43.4; H, 3.6%). $\nu_{CO}(CH_2Cl_2)$ 1956vs, 1871vs, 1661m (*exo*) and 1972vs, 1894vs, 1661 m cm^{-1} (*endo*). NMR [$(CD_3)_2CO$, 20 °C]: ^1H, *exo* isomer, δ 5.97 [d, 1 H, H^c, $J(H^cH^b)$ 8.4], 5.52 (s, 5 H, C_5H_5), 4.61 [dd, 1 H, H^b, $J(H^bH^c)$ 8.4, $J(H^bH^a)$ 8.4], 3.63 (s, 3 H, OMe) and 3.39 [d, 1 H, H^a, $J(H^aH^b)$ 8.4]; *endo* isomer, δ 6.91 [d, 1 H, H^c, $J(H^cH^b)$ 8.4], 5.34 (s, 5 H, C_5H_5), 4.26 [dd, 1 H, H^b, $J(H^bH^c)$ 8.4, $J(H^bH^a)$ 8.4], 3.55 (s, 3 H, OMe) and 3.47 [d, 1 H, H^a, $J(H^aH^b)$ 8.4 Hz]. ^{13}C-{^1H}, *exo* isomer, δ 241.3 (MoCO), 235.7 (MoCO), 175.5 (C^1), 114.9 (C^4), 91.5 (C_5H_5), 57.4 (C^3), 56.6 (C^2) and 30.8 (OMe); *endo* isomer, δ 238.8 (MoCO), 238.0 (MoCO), 176.2 (C^1), 107.3 (C^4), 91.4 (C_5H_5), 72.5 (C^3), 56.6 (C^2) and 32.9 (OMe).

Protonation of complex 4. To a solution of complex **4** (0.30 g, 1.00 mmol) in CH_2Cl_2 (20 cm^3) at *ca.* 25 °C was added HBF_4·Et_2O (180 μl, 1.04 mmol). The resulting dark red solution was rapidly stirred for 1 h. The solvent volume was then reduced to *ca.* 5 cm^3 *in vacuo* and hexane (20 cm^3) was added to precipitate an orange powder. This was washed with Et_2O (2 × 20 cm^3) and dried *in vacuo* to yield **12** (0.35 g, 90%). The instability of the compound prevented an accurate elemental analysis being obtained. ν_{CO}(thf) 1927vs, 1914 (sh), 1744vs and 1700vs cm^{-1}. ^1H NMR [$(CD_3)_2CO$, 20 °C]: *exo* isomer, δ 5.85 [dd, 1 H, H^b, $J(H^bH^a)$ 5.1, $J(H^bH^c)$ 4.6], 5.21 (s, 5 H, C_5H_5), 3.42 [dd, 1 H, H^c, $J(H^cH^b)$ 4.6, $J(H^cH^a)$ 1.8] and 2.83 [dd, 1 H, H^a, $J(H^aH^b)$ 5.1, $J(H^aH^c)$ 1.8]; *endo* isomer, δ 5.63 [dd, 1 H, H^b, $J(H^bH^a)$ 5.0, $J(H^bH^c)$ 4.6], 5.12 (s, 5 H, C_5H_5), 3.33 [dd, 1 H, H^c, $J(H^cH^b)$ 4.6, $J(H^cH^a)$ 1.6] and 2.71 [dd, 1 H, H^a, $J(H^aH^b)$ 5.0, $J(H^aH^c)$ 1.6 Hz]. Low solubility and instability of the compound prevented measurement of a ^{13}C NMR spectrum.

[Mo{η³-OC(O)CHCHCHCO}(NCMe)(CO)(η-C_5H_5)] 13. Complex **12** (0.30 g, 1.00 mmol) was dissolved in MeCN (10 cm^3) and the resulting red solution was stirred for 0.5 h. Volatile material was removed *in vacuo*, the residue was extracted with CH_2Cl_2 (8 cm^3) and transferred to the top of an alumina chromatography column. The column was washed with CH_2Cl_2 (40 cm^3) then eluted with CH_2Cl_2–thf (4:1) to remove a yellow fraction. Solvent was removed *in vacuo* from this fraction and the resulting oil was crystallised from CH_2Cl_2–hexane (1:2) to give **13** as an orange powder (0.28 g, 82%). X-Ray quality *crystals* were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the complex (Found: C, 42.3; H, 3.2; N, 3.7. $C_{13}H_{11}MoNO_4$ requires C, 42.3; H, 3.2; N, 3.7%). $\nu_{CO}(CH_2Cl_2)$ 1939s, 1730s and 1692s cm^{-1}. NMR [$(CD_3)_2CO$, 20 °C]: ^1H, *exo* isomer, δ 5.364 [dd, 1 H, H^{10}, $J(H^{10}H^9)$ 4.9, $J(H^{10}H^{11})$ 4.9], 5.07 (s, 5 H, C_5H_5), 3.321 [dd, 1 H, H^9,

Table 4 Crystallographic data for compounds **3**, **7** and **13**[a]

Complex	**3**	**7**	**13**[b]
Empirical formula	$C_{16}H_{18}MoO_4$	$C_{22}H_{19}MoNO_4{\cdot}CH_2Cl_2$	$C_{13}H_{11}MoNO_4{\cdot}0.5CH_2Cl_2$
M	370.2	542.3	383.63
Crystal dimensions/mm	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.15	0.20 × 0.20 × 0.25
Space group	$C2/c$	$P2_1/n$	$C2/c$
a/Å	28.077(4)	13.809(5)	23.971(4)
b/Å	8.895(2)	8.598(2)	8.638(2)
c/Å	12.767(2)	18.908(5)	13.944(3)
β/°	104.49(1)	95.57(4)	97.32(2)
U/Å^3	3087.1	2234.3	2864(1)
Z	8	4	8
D_c/g cm^{-3}	1.59	1.61	1.78
F(000)	1504	1096	1528
μ(Mo-Kα)/cm^{-1}	8.4	8.6	11.2
2θ range/°	4–48	4–48	5–48
No. data collected	2649	3943	2351
No. unique data with $I \geqslant 2\sigma(I)$	2018	2354	2242
R	0.0262	0.0458	0.0285
R'	0.0273	0.0417	0.0665
Maximum, minimum residual electron density/e Å^{-3}	0.31, −0.13	0.34, −0.44	0.91, −0.44

[a] Details in common: λ(Mo-Kα) 0.710 69 Å; monoclinic; $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$, $\Delta = F_o - F_c$. $w = 2.9285[\sigma^2(F) + 0.000\,292(F)^2]^{-1}$ for **3**, 2.4318 $[\sigma^2(F) + 0.000\,402(F)^2]^{-1}$ for **7** and $[\sigma^2(F)^2 + (0.0425P)^2 + 3.7368P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ for **13**. [b] R, R' are actually $R1$ and $wR2$ for this structure which was refined using SHELXL 93.[20]

$J(H^9H^{10})$ 4.9, $J(H^9H^{11})$ 1.6], 2.949 [dd, 1 H, H^{11}, $J(H^{11}H^{10})$ 4.9, $J(H^{11}H^9)$ 1.6] and 2.47 (s, 3 H, NCMe); *endo* isomer, δ 5.359 [dd, 1 H, H^{10}, $J(H^{10}H^9)$ 4.9, $J(H^{10}H^{11})$ 4.9], 5.07 (s, 5 H, C_5H_5), 3.316 [dd, 1 H, H^9, $J(H^9H^{10})$ 4.9, $J(H^9H^{11})$ 1.8], 2.945 [dd, 1 H, H^{11}, $J(H^{11}H^{10})$ 4.9, $J(H^{11}H^9)$ 1.8 Hz] and 2.47 (s, 3 H, NCMe); ^{13}C-{^1H}, *exo* and *endo* isomers, δ 247.5 (MoCO), 173.6 (C=O), 173.0 (C=O), 139.3 (NCMe), 96.9 (C_5H_5), 79.1 (C^{10}), 45.4 (C^9), 38.6 (C^{11}) and 4.9 (NC*Me*). See Fig. 5 for atom labelling scheme.

Crystallography

Many of the details of the crystal structure analyses carried out on compounds **3**, **7** and **13** are in Table 4. Data were collected on a CAD4 automatic four-circle diffractometer at 293 K. Corrections for Lorentz-polarisation and X-ray absorption effects were applied, the latter by an empirical method using DIFABS.[21] The structures were solved by Patterson methods and refined using the SHELX suite of programs.[22,23] All non-hydrogen atoms were allowed to refine anisotropically during the final least-squares cycles. Unless stated below, all hydrogen atoms were included at geometrically calculated positions at a fixed distance of 0.96 Å from their parent atom. For complex **3** the hydrogen atoms H(141), H(151) and H(161) [attached to C(14), C(15) and C(16), respectively] were located in an advanced Fourier-difference map and allowed to refine at a distance of 0.96 Å from the relevant parent carbon atom, with a fixed isotropic thermal parameter (0.063 Å^2). Similarly, for **7** the atoms H(1), H(4), H(131), H(141) and H(151) [attached to N(1), O(4), C(13), C(14) and C(15), respectively] were located and refined, with a fixed isotropic thermal parameter (0.031 Å^2), at a distance of 0.96 Å from the relevant parent atom. For **13** the atoms H(9), H(10), H(11) and H(14) were located in the penultimate Fourier-difference synthesis and allowed to refine freely.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for such material should quote the full literature citation and the reference number 186/47.

Extended Hückel molecular orbital calculations

The EHMO calculation for $[Mo(\eta^3\text{-}C_4H_3O_2)(CO)_2(\eta\text{-}C_5Me_5)]$ **3** employed the CACAO2 program package developed by Mealli and Proserpio.[24]

Acknowledgements

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