The promotion of air oxidation and carbonyl substitution reactions of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ by trimethylamine *N*-oxide or nitrosonium tetrafluoroborate: the synthesis of $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}RCCR')]$ (R = R′ = CO_2Me or Ph; R = H, R′ = Ph; or R = H, R′ = CO_2Me) and $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(NO)(\mu\text{-}RCCR')][BF_4]$ (R = R′ = CO_2Me, Me or H; or R = H, R′ = CO_2Me)

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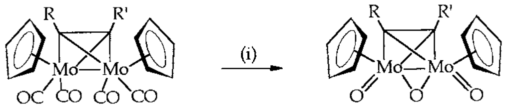
Trimethylamine *N*-oxide promotes the air oxidation of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ to afford the novel organometallic oxo complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}RCCR')]$ [R = R′ = CO_2Me or Ph; R = H, R′ = Ph; or R = H, R′ = CO_2Me). Trimethylamine *N*-oxide also promotes the near quantitative substitution of one of the carbonyl groups in $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}MeO_2CC_2CO_2Me)]$ by either Bu^tNC or $(MeO)_3P$ (L), giving $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(L)(\mu\text{-}MeO_2CC_2CO_2Me)]$ at room temperature. The addition of $[NO][BF_4]$, in place of Me_3NO, to solutions of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ under the same reaction conditions, does not promote air oxidation but leads instead to the new dimolybdenum nitrosyl complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(NO)(\mu\text{-}RCCR')][BF_4]$ (R = R′ = CO_2Me, Me or H; or R = H, R′ = CO_2Me). The structure of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(NO)(\mu\text{-}MeO_2CC_2CO_2Me)][BF_4]$ has been determined by X-ray crystallography.

Owing to their numerous catalytic applications, organometallic oxo complexes of molybdenum have received much attention.[1] Dinuclear organometallic oxo complexes of molybdenum have been prepared previously by oxidation of the corresponding organometallic carbonyl complexes,[2] but the synthesis of a dinuclear organometallic molybdenum oxo complex incorporating a transverse bridging alkyne has not been reported. As part of our investigations into the chemistry of alkyne bridged Group 6 metal complexes[3] we have now attempted the synthesis of such an oxo complex from the alkyne bridged dimolybdenum carbonyl complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ (R = R′ = CO_2Me or Ph; R = H, R′ = Ph; or R = H, R′ = CO_2Me).

The conventional method of preparing organometallic oxo complexes from carbonyl complexes involves a thermally or photochemically induced reaction in the presence of air or oxygen.[4] However, the complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ are stable under such reaction conditions and it was decided to use trimethylamine *N*-oxide in the presence of oxygen, in an attempt to labilise the carbonyl ligands and facilitate their replacement by oxo groups. The ability of amine *N*-oxides to act as decarbonylation agents for carbonyl substitution in transition-metal complexes is well documented.[5,6]

Results and Discussion

Herein we report the synthesis of the new complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}RCCR')]$ (R = R′ = CO_2Me **2** or Ph **3**; R = H, R′ = Ph **4**; or R = H, R′ = CO_2Me **5**), *via* the air oxidation of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$[7] in the presence of trimethylamine *N*-oxide. In the absence of air, oxidation does not take place but, if Bu^tNC or $(MeO)_3P$ is present, the trimethylamine *N*-oxide promotes monosubstitution of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ to form $[(\eta^5\text{-}C_5H_5)_2Mo_2(L)(CO)_3(\mu\text{-}RCCR')]$ [R = R′ = CO_2Me; L = Bu^tNC **7** or $(MeO)_3P$ **8**] in virtually quantitative yields at room temperature. A preliminary account of part of this work has been published.[8]



2 R = R′ = CO_2Me

3 R = R′ = Ph

4 R = H, R′ = Ph

5 R = H, R′ = CO_2Me

Scheme 1 (*i*) Excess Me_3NO, air, 1 : 1 MeCN : CH_2Cl_2, 298 K

Synthesis of $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}RCCR')]$ (R = R′ = CO_2Me 2 or Ph 3; R = H, R′ = Ph 4; or R = H, R′ = CO_2Me 5)

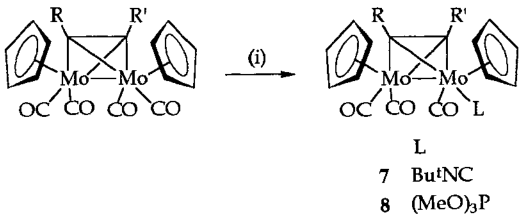
The complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}RCCR')]$ (R = R′ = CO_2Me **2** or Ph **3**; R = H, R′ = Ph **4** or R = H, R′ = CO_2Me **5**) were prepared by air oxidation of the parent alkyne bridged carbonyl complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$[7] in a 1 : 1 acetonitrile–dichloromethane solution containing an excess of freshly sublimed trimethylamine *N*-oxide (Scheme 1). Air oxidation of a similar solution in the absence of trimethylamine *N*-oxide resulted only in decomposition products and starting material after the same reaction time.

In our preliminary communication[8] we reported the molecular structure of **2**, $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}MeO_2CC_2CO_2Me)]$, which was determined by X-ray diffraction. The quasi-tetrahedral structure of the central Mo_2C_2 moiety in **2** corresponds to that of the related parent carbonyl complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ (R = R′ = H, Et or Ph).[7,9] Complex **2** has been fully characterised by IR, ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectroscopy, fast atom bombardment (FAB) mass spectrometry and microanalysis as described in the Experimental section.

The complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}RCCR')]$ (R = R′ = Ph **3**; R = H, R′ = Ph **4**; or R = H, R′ = CO_2Me **5**) were characterised by IR, ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectroscopy and FAB mass spectrometry, the data being closely comparable with those for **2**. Although a yield of 31% was obtained for complex **2** (R = R′ = CO_2Me), the yields of the analogous complexes **3**, **4** and **5** with less electron withdrawing alkyne substituents were poor, the highest being 17% for **5** (R = H, R′ = CO_2Me). It appears that the yield of [(η^5-C_5H_5)$_2$$Mo_2(O)_2$($\mu$-O)($\mu$-RCCR′)] is maximised by electron withdrawing substituents on the alkyne, perhaps because this reduces π-back bonding from the metal to the carbonyl ligands thus increasing their lability. This suggested that the yield might be improved further by the introduction of electron withdrawing substituents onto the cyclopentadienyl ligands in addition to those on the alkyne. To test this suggestion, the complexes [(η^5-$C_5H_4CO_2Me$)$_2$$Mo_2(CO)_4$($\mu$-RCCR′)][10] (R = R′ = CO_2Me and R = H, R′ = CO_2Me) were synthesised and oxidised in the presence of trimethylamine *N*-oxide. However, the complexes rapidly suffered total decomposition to give a mixture of intractable ‘isopolymolybdates’.[11] This decomposition is perhaps initiated by nucleophilic attack of the trimethylamine *N*-oxide on the carbomethoxy ring substituents, although the CO_2Me groups on the alkyne in [(η^5-C_5H_5)$_2$$Mo_2(CO)_4$($\mu$-RCCR′)] (R = R′ = CO_2Me or R = H, R′ = CO_2Me) are presumably not attacked in this way. An alternative explanation is that the oxidised products or reaction intermediates are destabilised by the presence of the ring substituents which may withdraw electron density from the metal centres to an extent which weakens the bonds between these centres and the alkyne ligand.

The oxo ligands in complexes **2**–**5** could originate from the oxygen released by decomposition of excess trimethylamine *N*-oxide or from the air bubbled through the solution. In order to investigate this, a ‘control’ reaction was carried out on [(η^5-C_5H_5)$_2$$Mo_2(CO)_4$($\mu$-$MeO_2CC_2CO_2Me$)] **1** using similar reaction conditions, but purging the solution of **1** with argon rather than air. After 18 h the colour of the solution had changed and the IR spectra, taken *in situ*, showed carbonyl vibrations not characteristic of the starting material. The new complex giving rise to these absorptions may result from substitution of one or more carbonyl ligands of **1** by acetonitrile and would then have the formula [(η^5-C_5H_5)$_2$$Mo_2(CO)_{(4-x)}$($CH_3CN$)$_x$($\mu$-$MeO_2CC_2CO_2Me$)] **6**. A complex, thought to be [(η^5-C_5H_5)Mo(CO)$_2$(CH_3CN)I], was similarly obtained by dissolution of [(η^5-C_5H_5)Mo(CO)$_3$I] in acetonitrile in the presence of $(CH_3)_3NO$.[12] Addition of Bu^{t}NC or $(MeO)_3P$ to **6** *in situ* gave almost quantitative yields of the monosubstituted complexes [(η^5-C_5H_5)$_2$$Mo_2(CO)_3$(L)($\mu$-RCCR′)] [L = Bu^{t}NC or $(MeO)_3P$], described in more detail below. This result suggests that $x = 1$ in the acetonitrile complex **6**, but unfortunately it could not be isolated. On exposure to air it formed mainly intractable decomposition products and a small quantity of the oxo complex **2**. The probable formation of an acetonitrile substituted complex, instead of direct formation of **2** in the above reaction, demonstrates that the air purge is necessary in order for the oxo species to form and hence that the oxo ligands are derived from this source.

Complex **2**, [(η^5-C_5H_5)$_2$$Mo_2(O)_2$($\mu$-O)($\mu$-$MeO_2CC_2CO_2Me$)], is stable towards substitution, thermolysis and photolysis. It was not possible to replace the oxo ligands with CO, even at high pressure and temperature [100 atm (1013250 Pa) CO, 150 °C]. Protonation with HCl and trifluoroacetic acid was investigated for comparative purposes with the corresponding known reactions of the parent carbonyl species[13] but treatment with either acid resulted in immediate decomposition. A well known route to the preparation of imido species is the treatment of an analogous oxo complex with an isocyanate.[14] No reaction was observed on treating complex **2** with phenyl isocyanate under reduced pressure at 120 °C for several days, conditions similar to those used by Green and co-workers[15] to prepare bis(cyclopentadienyl) dimolybdenum imido complexes from their corresponding dimolybdenum oxo analogues.



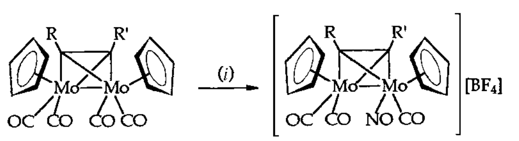
Scheme 2 R = R′ = CO_2Me. (*i*) Excess Me_3NO, Bu^{t}NC (**7**) or $(MeO)_3P$ (**8**), MeCN, 298 K

The use of trimethylamine *N*-oxide in the synthesis of [(η^5-C_5H_5)$_2$$Mo_2(CO)_3$(L)($\mu$-RCCR′)] [L = Bu^{t}NC or $(MeO)_3P$] under controlled, mild conditions

It was of interest to investigate the extent to which ligands other than oxygen might replace the carbonyl groups in [(η^5-C_5H_5)$_2$$Mo_2(CO)_4$($\mu$-$MeO_2CC_2CO_2Me$)] **1** in the presence of trimethylamine *N*-oxide. Acetonitrile solutions of **1** were treated separately with excess Bu^{t}NC or $(MeO)_3P$ in the presence of Me_3NO, under nitrogen. In both cases a single monosubstituted product [(η^5-C_5H_5)$_2$$Mo_2(CO)_3$(L)($\mu$-RCCR′)] [R = R′ = CO_2Me; L = Bu^{t}NC **7** or $(MeO)_3P$ **8**] was obtained in high yield at room temperature (Scheme 2). These complexes have been fully characterised by IR, ^1H and ^{13}C-{^1H} NMR spectroscopy, FAB mass spectrometry and microanalysis as described in the Experimental section. A thermolytic synthesis giving a 71% yield of [(η^5-C_5Me_5)$_2$$Mo_2(CO)_3$(Bu^{t}NC)($\mu$-$MeO_2CC_2CO_2Me$)], analogous to **7**, has previously been described.[16] However the milder conditions afforded here by the use of trimethylamine *N*-oxide enable near quantitative yields to be achieved. The complex [(η^5-C_5H_5)$_2$$Mo_2(CO)_3${P(OMe)$_3$}($\mu$-HCCH)], analogous to **8**, has previously been synthesised photolytically as part of a study on the cleavage of monophosphine ligands at a dimolybdenum centre, although the yield was not reported.[17]

Complexes **2**–**5** are the first complexes reported in which more than one CO group in [(η^5-C_5H_5)$_2$$Mo_2(CO)_4$($\mu$-RCCR′)] has been replaced by other ligands, without transformation of the alkyne bridge. To determine whether ligands other than oxo groups could multiply substitute the CO groups in [(η^5-C_5H_5)$_2$$Mo_2(CO)_4$($\mu$-RCCR′)], the monosubstituted complexes **7** and **8** were treated with respectively an excess of either Bu^{t}NC or $(MeO)_3P$ under more forcing conditions. In each case the complexes were (*i*) refluxed in acetonitrile in the presence of excess $(CH_3)_3NO$ or (*ii*) refluxed in toluene. No evidence for further substitution was obtained in any of the experiments. It is possible that steric factors may hinder multiple substitution of [(η^5-C_5H_5)$_2$$Mo_2(CO)_4$($\mu$-RCCR′)] by such ligands as Bu^{t}NC or $(MeO)_3P$. A crystallographic determination of the molecular structure of the unsubstituted complexes [(η^5-C_5H_5)$_2$$Mo_2(CO)_4$($\mu$-RCCR′)] (R = R′ = H, Et or Ph) showed that one of the carbonyl ligands adopts a semi-bridging site close to the metal–metal bond.[7,9] This was taken as evidence of a high degree of internal crowding in the molecule due to the large solid angle required by the η^5-C_5H_5 ligands. Multiple substitution of [(η^5-C_5H_5)$_2$$Mo_2(CO)_4$($\mu$-RCCR′)] by Bu^{t}NC or $(MeO)_3P$ may also be unfavourable due to additional π-back bonding to the remaining three carbonyl ligands on monosubstitution of [(η^5-C_5H_5)$_2$$Mo_2(CO)_4$($\mu$-RCCR′)] by Bu^{t}NC or $(MeO)_3P$. This additional π-back bonding will reduce the lability of the CO groups towards further substitution.

The reason oxo ligands can multiply substitute CO groups in [(η^5-C_5H_5)$_2$$Mo_2(CO)_4$($\mu$-RCCR′)] may be that substitution of a CO ligand by O, which increases the formal oxidation state of the metal, thereby reduces the electron density around the metal centre. In turn, this will reduce the π-back bonding to the remaining CO ligands, facilitating further substitution. There is no evidence for the formation of any mixed carbonyl–oxo species during the course of the oxidation reactions. It follows that once one



9 R = R' = CO_2Me
10 R = R' = Me
11 R = R' = H
12 R = H, R' = CO_2Me

Scheme 3 (*i*) Excess [NO][BF_4], CH_2Cl_2, 298 K

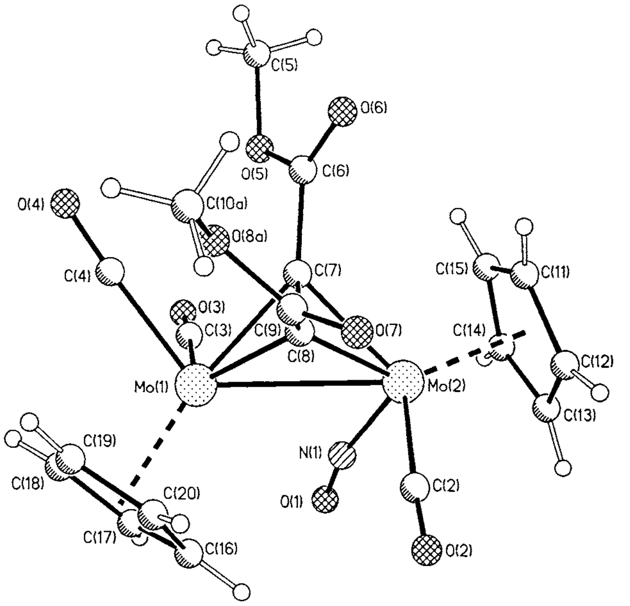


Fig. 1 Molecular structure of the cation $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(NO)(\mu\text{-}RCCR')]^+$ in complex **9**. Only one component of the disordered OMe group is shown for clarity

CO is replaced by O any mixed carbonyl oxo intermediates are unstable with respect to formation of the final product.

The attempted oxidation of $[(\eta^5\text{-}C_5H_5)_2MoW(CO)_4(\mu\text{-}RCCR')]$

The mixed-metal transverse alkyne bridged complex $[(\eta^5\text{-}C_5H_5)_2MoW(CO)_4(\mu\text{-}RCCR')]$ has been prepared previously and its reactivity investigated.[13,18] It was of interest to investigate the susceptibility of this complex towards air oxidation in the presence of trimethylamine *N*-oxide since if the integrity of the complex were to be maintained during the oxidation, a single heterobimetallic oxo product $[(\eta^5\text{-}C_5H_5)MoW(O)_2(\mu\text{-}O)(\mu\text{-}RCCR')]$ would result. In fact, air oxidation of $[(\eta^5\text{-}C_5H_5)_2MoW(CO)_4(\mu\text{-}MeO_2CC_2CO_2Me)]$ in the presence of trimethylamine *N*-oxide led only to the formation of decomposition products and $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}RCCR')]$ **2**. It follows that metal–metal bond cleavage and dissociation into monometallic fragments must have occurred under the reaction conditions. Even so, the mixed-metal oxo complex might have been expected as one product, and the fact that it was not obtained indicates that it may not be stable.

The reaction of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ with [NO][BF_4] to form the monosubstituted products $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(NO)(\mu\text{-}RCCR')][BF_4]$ (R = R' = CO_2Me 9, Me 10 or H 11; or R = H, R' = CO_2Me 12)

In an attempt to find a carbonyl labilising agent which might be more efficient than trimethylamine *N*-oxide in converting $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ into $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}RCCR')]$, the use of [NO][$BF_4$] was explored. This reagent was considered because of its potential ability to bring about chemical oxidation of one or both of the metal centres of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ and thereby to reduce the degree of metal π-back donation to the carbonyl ligands. It had previously been found that chemical oxidation of $[(\eta^5\text{-}C_5Me_5)_2Mo_2(CO)_3(Bu^tNC)(\mu\text{-}MeO_2CC_2CO_2Me)]$ with $[(\eta^5\text{-}C_5H_5)_2Fe][PF_6]$ gave a sensitive violet product, shown by *in situ* IR and ESR spectroscopy to be the monocation $[(\eta^5\text{-}C_5Me_5)_2Mo_2(CO)_3(Bu^tNC)(\mu\text{-}MeO_2CC_2CO_2Me)]^+$.[16] It is known that the compound [NO][BF_4] may act either as a chemical oxidising agent or as the source of the nitrosyl ligand NO^+, a two-electron donor ligand, isoelectronic with CO.[19]

Treatment of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ with [NO][BF_4] in the presence of air, did not lead to the formation of oxo products analogous to those obtained in the corresponding reaction of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ with Me_3NO. Instead, the sole products obtained were the monosubstituted nitrosyl species $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(NO)(\mu\text{-}RCCR')][BF_4]$ (R = R' = CO_2Me **9**, Me **10** or H **11**; or R = H, R' = CO_2Me **12**) (Scheme 3). It was not established in these reactions whether one-electron chemical oxidation of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ by [NO][BF_4] takes place and is then followed by reaction of the oxidised product with NO generated as part of the redox process, or whether the carbonyl ligands are directly substituted by NO^+.

The molecular structure of **9** has been determined by X-ray crystallography and is shown in Fig. 1 with selected bond lengths and angles listed in Table 1. To our knowledge, this is the first example of an alkyne bridged bis(cyclopentadienyl) dimolybdenum complex containing a nitrosyl ligand. Indeed there are relatively few known examples of dimolybdenum nitrosyl complexes,[20] the only other dimolybdenum nitrosyls to have been prepared by the use of [NO][BF_4] being the recently reported complexes $[Mo_2(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_7(NO)]$ (n = 1–4).[21]

Complex **9** displays the same quasi-tetrahedral central Mo_2C_2 moiety as is present in **2**, while the Mo–Mo bond length [2.9762(9) Å] is comparable with those reported for the parent carbonyl complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ [R = R' = H 2.984(1); Et 2.977(1); Ph 2.956(1) Å].[7,9] In the parent complexes the most noteworthy structural aspect is the lack of any symmetry in the arrangement of the ligands around the Mo_2C_2 core with each of the four CO groups lying in a different environment, one of them in a semi-bridging position. The unsymmetrical arrangement is believed to result from internal crowding in the molecule due to the large solid angle required by the $\eta^5\text{-}C_5H_5$ ligands. Because of the crowding, one CO group is forced into the region close to the Mo–Mo bond, opposite the bridging alkyne, and in consequence the rest of the CO ligands are arranged in an unsymmetrical fashion. As an example, in the complex $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}HCCH)]$ the metal to carbonyl bond lengths were found to be 1.993(4), 1.989(3), 1.951(4) and 1.953(4) Å, the shortest distance being that for the metal to semi-bridging carbonyl.[7] The angles Mo–C–O for the four carbonyls were found to be 178.5(3), 179.3(4), 178.9(5) and 168.5(3)°, the most acute angle being that for the semi-bridging carbonyl. In complex **9** the unsymmetrical arrangement of ligands is still apparent, the substituted nitrosyl ligand having taken the semi-bridging site; this is not unexpected since the nitrosyl ligand is a better π acceptor than the CO ligands. The metal to carbonyl bond lengths in complex **9** were found to be 2.051(9), 2.046(9) and 2.019(9) Å with a molybdenum to semi-bridging nitrosyl distance of 1.824(6) Å. The Mo–C–O angles in complex **9** were observed to be 176.3(9), 176.4(7) and 177.2(8)°, while the metal–semi-bridging nitrosyl angle was found to be considerably more acute [162.9(6)°].

Complex **9** was also characterised by IR, ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectroscopy, FAB mass spectrometry and microanalysis. The IR spectrum in dichloromethane solution was compatible with substitution of the semi-bridging carbonyl by a nitrosyl. In the parent species $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}MeO_2CC_2CO_2Me)]$ **1** carbonyl absorptions are observed at

Table 1 Selected bond lengths (Å) and angles (°) for $[(\eta^5\text{-}C_5H_5)_2\text{-}Mo_2(CO)_3(NO)(\mu\text{-}MeO_2CC_2CO_2Me)][BF_4]$ **9**

Mo(1)–Mo(2)	2.9762(9)	Mo(2)–C(7)	2.160(7)
Mo(1)–C(3)	2.046(9)	Mo(2)–C(8)	2.167(7)
Mo(1)–C(4)	2.019(9)	Mo(2)–C(11)	2.305(9)
Mo(1)–C(7)	2.147(7)	Mo(2)–C(12)	2.323(9)
Mo(1)–C(8)	2.150(7)	Mo(2)–C(13)	2.313(8)
Mo(1)–C(16)	2.350(8)	Mo(2)–C(14)	2.341(9)
Mo(1)–C(17)	2.302(8)	Mo(2)–C(15)	2.328(8)
Mo(1)–C(18)	2.279(7)	O(1)–N(1)	1.195(8)
Mo(1)–C(19)	2.296(8)	O(2)–C(2)	1.111(10)
Mo(1)–C(20)	2.354(8)	O(3)–C(3)	1.122(10)
Mo(2)–N(1)	1.824(6)	O(4)–C(4)	1.135(9)
Mo(2)–C(2)	2.051(9)	C(7)–C(8)	1.381(10)
C(4)–Mo(1)–C(3)	83.1(4)	C(11)–Mo(2)–Mo(1)	138.7(3)
C(4)–Mo(1)–C(7)	79.0(3)	C(13)–Mo(2)–Mo(1)	158.1(3)
C(4)–Mo(1)–C(8)	90.0(3)	C(12)–No(2)–Mo(1)	167.1(3)
C(3)–Mo(1)–C(7)	85.5(3)	C(15)–Mo(2)–Mo(1)	124.9(3)
C(3)–Mo(1)–C(8)	122.5(3)	C(14)–Mo(2)–Mo(1)	133.0(3)
C(7)–Mo(1)–C(8)	37.5(3)	O(1)–N(1)–Mo(2)	162.9(6)
C(3)–Mo(1)–Mo(2)	94.0(2)	O(2)–C(2)–Mo(2)	176.3(9)
C(4)–Mo(1)–Mo(2)	125.3(2)	O(3)–C(3)–Mo(1)	177.2(8)
C(7)–Mo(1)–Mo(2)	46.5(2)	O(4)–C(4)–Mo(1)	176.4(7)
C(8)–Mo(1)–Mo(2)	46.7(2)	C(8)–C(7)–C(6)	132.4(6)
C(16)–Mo(1)–Mo(2)	93.2(2)	C(8)–C(7)–Mo(1)	71.4(4)
C(17)–Mo(1)–Mo(2)	115.5(2)	C(6)–C(7)–Mo(1)	137.9(5)
C(18)–Mo(1)–Mo(2)	150.3(2)	C(8)–C(7)–Mo(2)	71.7(4)
C(19)–Mo(1)–Mo(2)	137.8(3)	C(6)–C(7)–Mo(2)	129.8(5)
C(20)–Mo(1)–Mo(2)	103.9(2)	Mo(1)–C(7)–Mo(2)	87.4(2)
N(1)–Mo(2)–C(2)	95.6(3)	C(7)–C(8)–C(9)	133.2(7)
N(1)–Mo(2)–C(7)	100.0(3)	C(7)–C(8)–Mo(1)	71.1(4)
N(1)–Mo(2)–C(8)	107.1(3)	C(9)–C(8)–Mo(1)	129.7(5)
C(2)–Mo(2)–C(7)	113.7(3)	C(7)–C(8)–Mo(2)	71.4(4)
C(2)–Mo(2)–C(8)	76.5(3)	C(9)–C(8)–Mo(2)	138.0(5)
C(7)–Mo(2)–C(8)	37.2(3)	Mo(1)–C(8)–Mo(2)	87.2(3)
N(1)–Mo(2)–Mo(1)	62.0(2)	C(12)–C(11)–Mo(2)	73.3(6)
C(2)–Mo(2)–Mo(1)	91.1(3)	C(15)–C(11)–Mo(2)	73.2(5)
C(7)–Mo(2)–Mo(1)	46.1(2)	C(11)–C(12)–Mo(2)	71.9(5)
C(8)–Mo(2)–Mo(1)	46.2(2)	C(13)–C(12)–Mo(2)	72.2(5)
C(14)–C(13)–Mo(2)	74.0(5)	C(11)–C(15)–Mo(2)	71.5(5)
C(12)–C(13)–Mo(2)	73.0(5)	C(17)–C(16)–Mo(1)	70.7(5)
C(13)–C(14)–Mo(2)	71.8(5)	C(20)–C(16)–Mo(1)	72.7(5)
C(15)–C(14)–Mo(2)	72.4(5)	C(16)–C(17)–Mo(1)	74.4(5)
C(14)–C(15)–Mo(2)	73.5(5)	C(18)–C(17)–Mo(1)	71.3(4)
C(17)–C(18)–Mo(1)	73.1(4)	C(18)–C(19)–Mo(1)	71.4(5)
C(19)–C(18)–Mo(1)	72.7(4)	C(19)–C(20)–Mo(1)	70.3(5)
C(20)–C(19)–Mo(1)	74.9(5)	C(16)–C(20)–Mo(1)	72.5(5)

2022, 1969 and 1849 cm^{-1}, the lowest frequency absorption being attributed to the semi-bridging carbonyl. The IR spectrum of complex **9** possessed two terminal carbonyl absorptions, shifted to higher frequencies at 2071 and 2032 cm^{-1} due to the positive charge on the complex, but the semi-bridging carbonyl absorption observed in **1** was no longer present. The nitrosyl absorption[22] was observed at 1636 cm^{-1}.

The analogous complexes $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(NO)\text{-}(\mu\text{-}RCCR')][BF_4]$ ($R = R' = Me$ **10** or H **11**; or $R = H$, $R' = CO_2Me$ **12**) were characterised by IR and ^1H NMR spectroscopy, FAB mass spectrometry and microanalysis. By comparison with the data for complex **9** it was determined that the nitrosyl ligand occupies the semi-bridging site in each case. In no case was there any evidence for multiple substitution of the carbonyl ligands by the nitrosyl group or for the formation of oxo products.

To determine whether the remaining carbonyl ligands in $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(NO)(\mu\text{-}MeO_2CC_2CO_2Me)][BF_4]$ **9** were labile towards substitution by (*i*) oxo or (*ii*) phosphine ligands, an acetonitrile solution of **9** was purged with air for 18 h. After this time it was found that no reaction had occurred other than some decomposition. Separate acetonitrile solutions of **9** were treated with $(MeO)_3P$ or Ph_3P and stirred under nitrogen. No substitution products were obtained, even after the temperature of the solutions was elevated and the reaction mixtures refluxed for several hours. The experiments were repeated in the presence of trimethylamine *N*-oxide to determine whether the presence of Me_3NO would labilise the carbonyl ligands. However, in each case, complete decomposition had taken place after several hours and no new products could be isolated after shorter reaction periods.

Experimental

Except where stated, all reactions were carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled under nitrogen, from appropriate drying agents, and degassed prior to use. The starting materials $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RCCR')]$ ($R = R' = CO_2Me$ or Ph; $R = H$, $R' = Ph$; or $R = H$, $R' = CO_2Me$) were prepared by literature methods.[7] Trimethylamine *N*-oxide was purchased from Aldrich and sublimed under vacuum prior to use. All other chemicals were purchased from commercial suppliers and used without further purification. Column chromatography was performed on Kieselgel 60 (70–230 or 230–400 mesh). Products are given in order of decreasing R_f values.

The instrumentation used to obtain spectroscopic data has been described previously.[23] Proton and $^{13}C\text{-}\{^1H\}$ NMR spectra were recorded in $CDCl_3$ at 293 K. Chemical shifts are given in ppm on the δ scale relative to $SiMe_4$ (δ 0.0); the solvent resonance was used as an internal standard. In all ^{31}P spectra, chemical shifts are given relative to $P(OMe)_3$ with upfield shifts negative. The ^{13}C and ^{31}P spectra were ^1H gated decoupled.

Preparations

$[(\eta^5\text{-}C_5H_5)_2(O)_2(\mu\text{-}O)(\mu\text{-}MeO_2CC_2CO_2Me)]$ 2. To $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}MeO_2CC_2CO_2Me)]$ **1** (1.0 g, 1.74 mmol), dissolved in 1:1 acetonitrile–dichloromethane (150 cm^3), was added an excess of freshly sublimed trimethylamine *N*-oxide (0.39 g, 5.22 mmol, 3 equivalents). The orange-red solution was stirred at room temperature whilst being purged gently with air for 24 h, more solvent being added as necessary. At the end of this time a slight change in the colour of the solution to orange-yellow could be detected. The solvent was removed *in vacuo*, the residue redissolved in dichloromethane and purified by column chromatography. Elution with dichloromethane gave a red–orange band due to $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4\text{-}(\mu\text{-}MeO_2CC_2CO_2Me)]$ **1** (0.21 g, 14%). Further elution with ethyl acetate–acetone (1:1) gave an orange-yellow band which, on removal of solvent, gave a powdery orange solid $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}MeO_2CC_2CO_2Me)]$ **2** (0.41 g, 31%). Analytically pure samples of **2** were prepared by recrystallisation from dichloromethane at −4 °C (Found: C, 37.34; H, 3.10. $C_{16}H_{16}Mo_2O_7$ requires C, 37.52; H, 3.15%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1692 (COOMe); (Mo=O) and (Mo–O–Mo) 894, 799, 645; δ_H(400 MHz, $CDCl_3$) 3.79 (6 H, s, CO_2CH_3), 6.14 (10 H, s, C_5H_5); δ_C(400 MHz, $CDCl_3$) 52.5 (2 C, s, CO_2CH_3), 89.7 (10 C, s, C_5H_5), 212.6 (2 C, s, CO_2CH_3) [Mo–$C_2(CO_2Me)_2$ were not observed]; *m/z* 513 [(M^+) + H].

The reaction was repeated using separate solutions of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}RC_2R')]$ ($R = R' = Ph$, 1.06 g, 1.74 mmol; $R = H$, $R' = Ph$, 0.94 g, 1.74 mmol; $R = H$, $R' = CO_2Me$, 0.90 g, 1.74 mmol) in 1:1 acetonitrile–dichloromethane (150 cm^3). The solutions were treated with an excess of freshly sublimed trimethylamine *N*-oxide (0.39 g, 5.22 mmol, 3 equivalents) and stirred at room temperature for 24 h whilst being purged gently with air, more solvent being added as required. In each reaction the orange-yellow product was isolated from unreacted starting materials and decomposition products by column chromatography, using ethyl acetate–acetone (1:1) as the eluent. The products were obtained as yellow-orange solids, $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}RC_2R')]$ [$R = R' = Ph$ **3** (0.104 g, 11%); $R = H$, $R' = Ph$ **4** (0.114 g, 14%); $R = H$, $R' = CO_2Me$ **5** (0.132 g, 17%)].

Complex 3. $\nu_{max}(CH_2Cl_2)/cm^{-1}$ (Mo=O) and (Mo–O–Mo) 899, 805, 640; δ_H(400 MHz, $CDCl_3$) 6.07 (10 H, s, C_5H_5), 7.28–7.51 (10 H, m, C_6H_5); δ_C(400 MHz, $CDCl_3$) 92.2 (10 C, s, C_5H_5), 127.0–136.7 (12 C, m, C_6H_5), [Mo–*C*$_2$Ph$_2$ were not observed]; *m/z* 549 [(M^+) + H].

Complex 4. $\nu_{max}(CH_2Cl_2)/cm^{-1}$ (Mo=O) and (Mo–O–Mo) 894, 810, 636, 628; δ_H(400 MHz, $CDCl_3$) 6.34 (1 H, s, *H*CCPh), 6.89 (10 H, s, C_5H_5), 7.34–7.58 (5 H, m, C_6H_5); δ_C(400 MHz, $CDCl_3$) 89.7 (5 C, s, C_5H_5), 91.3 (5 C, s, C_5H_5), 125.5–134.2 (6 C, m, C_6H_5) [Mo–*C*$_2$(Ph)(H) were not observed]; *m/z* 473 [(M^+) + H].

Complex 5. $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1690 (C*O*OMe); (Mo=O) and (Mo–O–Mo) 899, 787, 659, 643; δ_H(400 MHz, $CDCl_3$) 3.84 (3 H, s, CO_2CH_3), 6.25 (1 H, s, *H*C$_2$CO$_2$Me), 6.43 (10 H, s, C_5H_5); δ_C(400 MHz, $CDCl_3$) 52.2 (1 C, s, CO$_2$*C*H$_3$), 88.9 (10 C, s, C_5H_5), 225.2 (1 C, s, *C*O$_2$CH$_3$) [Mo–*C*$_2$(CO$_2$Me)(H) were not observed]; *m/z* 455 [(M^+) + H].

[(η^5-C_5H_5)$_2$Mo$_2$(CO)$_{(4-x)}$(MeCN)$_x$(μ-MeO$_2$CC$_2$CO$_2$Me)] 6. A solution of [(η^5-C_5H_5)$_2$Mo$_2$(CO)$_4$(μ-MeO$_2$CC$_2$CO$_2$Me)] **1** (0.5 g, 0.87 mmol) in acetonitrile (100 cm^3) was treated with an excess of freshly sublimed trimethylamine *N*-oxide (0.33 g, 4.35 mmol, 5 equivalents). The solution was stirred at room temperature for 18 h whilst purging gently with argon. The orange-brown product, thought to be [(η^5-C_5H_5)$_2$Mo$_2$(CO)$_{(4-x)}$(MeCN)$_x$(μ-MeO$_2$CC$_2$CO$_2$Me)] could not be isolated from unreacted starting materials and decomposition products without itself decomposing, forming small quantities of [(η^5-C_5H_5)$_2$Mo$_2$(O)$_2$(μ-O)(μ-MeO$_2$CC$_2$CO$_2$Me)] **2** as a side product. $\nu_{max}(CH_3CN)/cm^{-1}$ 1922, 1815, 1684 (CO).

[(η^5-C_5H_5)$_2$Mo$_2$(CO)$_3$(Bu^{t}NC)(μ-MeO$_2$CC$_2$CO$_2$Me)] 7. A solution of [(η^5-C_5H_5)$_2$Mo$_2$(CO)$_4$(μ-MeO$_2$CC$_2$CO$_2$Me)] **1** (1 g, 1.74 mmol) in acetonitrile (150 cm^3) was treated with an excess of freshly sublimed trimethylamine *N*-oxide (0.39 g, 5.22 mmol, 3 equivalents). An excess of Bu^{t}NC was added (0.46 cm^3, 4.35 mmol, 2.5 equivalents) and the orange-red solution then stirred at room temperature for 2 h. The solvent was removed *in vacuo*, the residue redissolved in dichloromethane and purified by column chromatography. Elution with 1:1 hexane–ethyl acetate gave an orange-red band which was evaporated *in vacuo* to give a crystalline orange solid [(η^5-C_5H_5)$_2$Mo$_2$(CO)$_3$(Bu^{t}NC)(μ-MeO$_2$CC$_2$CO$_2$Me)] **7** (1.1 g, 96%) (Found: C, 45.86; H, 4.13; N, 2.33. $C_{24}H_{25}Mo_2NO_7$ requires C, 45.66; H, 3.99; N, 2.22%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1937, 1824, 1684 (CO); 2154 (CN); δ_H(400 MHz, $CDCl_3$) 1.42 [9 H, s, C(CH$_3$)$_3$], 3.70 (3 H, s, CO_2CH_3), 3.74 (3 H, s, CO_2CH_3), 5.18 (5 H, s, C_5H_5), 5.26 (5 H, s, C_5H_5); δ_C(400 MHz, $CDCl_3$) 30.45 [3 C, s, C(*C*H$_3$)$_3$, 51.7 (1 C, s, CO$_2$*C*H$_3$), 52.5 (1 C, s, CO$_2$*C*H$_3$), 87.7 (5 C, s, C_5H_5), 88.4 (5 C, s, C_5H_5), 210.2 (2 C, s, *C*O$_2$CH$_3$) [Mo–*C*$_2$(CO$_2$Me)$_2$, Mo–CO and Mo–*C*(CH$_3$)$_3$ were not observed]; *m/z* 632 [(M^+) + H], [(M^+) − *n*CO] (*n* = 1–3).

[(η^5-C_5H_5)$_2$Mo$_2$(CO)$_3${P(OMe)$_3$}(μ-MeO$_2$CC$_2$CO$_2$Me)] 8. A solution of [(η^5-C_5H_5)$_2$Mo$_2$(CO)$_4$(μ-MeO$_2$CC$_2$CO$_2$Me)] **1** (1 g, 1.74 mmol) in acetonitrile (150 cm^3) was treated with an excess of freshly sublimed trimethylamine *N*-oxide (0.39 g, 5.22 mmol, 3 equivalents). An excess of P(OMe)$_3$ was added (0.49 cm^3, 4.35 mmol, 2.5 equivalents) and the orange-red solution then stirred at room temperature for 6 h. The solvent was removed *in vacuo*, the residue redissolved in dichloromethane and purified by column chromatography. Elution with 1:1 hexane–ethyl acetate gave an orange-red band which was evaporated *in vacuo* to give a crystalline orange solid [(η^5-C_5H_5)$_2$Mo$_2$(CO)$_3${P(OMe)$_3$}(μ-MeO$_2$CC$_2$CO$_2$Me)] **8** (1.1 g, 95%) (Found: C, 39.16; H, 3.59; P, 4.79. $C_{22}H_{25}Mo_2O_{10}P$ requires C, 39.31; H, 3.75; P, 4.61%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1930, 1826, 1686 (CO); δ_H(400 MHz, $CDCl_3$) 3.54 (3 H, s, CO_2CH_3), 3.79 (3 H, s, CO_2CH_3), 3.92 [9 H, s, P(OCH$_3$)$_3$], 5.12 (5 H, s, C_5H_5), 5.30 (5 H, s, C_5H_5); δ_C(400 MHz, $CDCl_3$) 51.8 (1 C, s, CO$_2$*C*H$_3$), 52.0 (1 C, s, CO$_2$*C*H$_3$), 52.9 [3 C, s, P(OCH$_3$)$_3$], 91.1 (5 C, s, C_5H_5), 93.1 (5 C, s, C_5H_5) [Mo–*C*$_2$(CO$_2$Me)$_2$ and Mo–CO were not observed]; δ_P(250 MHz, $CDCl_3$) 21.2 [P(OMe)$_3$]; *m/z* 673 [(M^+) + H], [(M^+) − *n*CO] (*n* = 1–3).

[(η_5-C_5H_5)$_2$Mo$_2$(CO)$_3$(NO)(μ-RCCR′)][BF$_4$] (R = R′ = CO$_2$Me 9, Me 10 or H 11; or R = H, R′ = CO$_2$Me 12). Separate solutions of [(η^5-C_5H_5)$_2$Mo$_2$(CO)$_4$(μ-RCCR′)] **1** [R = R′ = CO$_2$Me (0.50 g, 0.87 mmol), R = R′ = Me (0.42 g, 0.87 mmol), R = R′ = H (0.40 g, 0.87 mmol) or R = H, R′ = CO$_2$Me (0.45 g, 0.87 mmol)] in dichloromethane (75 cm^3) were each treated with an excess of [NO][BF$_4$] (0.15 g, 1.28 mmol, 1.5 equivalents). Each of the solutions was stirred at room temperature for 30 min. After this time, diethyl ether (30 cm^3) was added to precipitate the product. The product was collected by filtration and recrystallised from the minimum of 1:1 diethyl ether–dichloromethane to afford yellow-brown crystals of [(η^5-C_5H_5)$_2$Mo$_2$(CO)$_3$(NO)(μ-RCCR′)][BF$_4$] [R = R′ = CO$_2$Me **9** (0.52 g, 90%), R = R′ = Me **10** (0.44 g, 87%), R = R′ = H **11** (0.43 g, 91%) or R = H, R′ = CO$_2$Me **12** (0.46 g, 87%)].

Complex **9** (Found: C, 34.56; H, 2.39; N, 1.89. $C_{19}H_{16}BF_4Mo_2NO_8$ requires C, 34.32; H, 2.42; N, 2.10%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2071, 2032, 1710 (CO); 1636 (NO); δ_H(400 MHz, $CDCl_3$) 3.86 (3 H, s, CO_2CH_3), 3.98 (3 H, s, CO_2CH_3), 5.88 (5 H, s, C_5H_5), 6.02 (5 H, s, C_5H_5); δ_C(400 MHz, $CDCl_3$) 52.57 (1 C, s, CO$_2$*C*H$_3$), 52.89 (1 C, s, CO$_2$*C*H$_3$), 92.61 (5 C, s, C_5H_5), 93.35 (5 C, s, C_5H_5) [Mo–*C*$_2$(CO$_2$Me)$_2$ and 3 Mo–CO were not observed]; *m/z* 579 [(M^+) + H], [(M^+) − *n*CO] (*n* = 1–3).

Complex **10** (Found: C, 35.60; H, 3.00; N, 2.27. $C_{17}H_{16}BF_4Mo_2NO_4$ requires C, 35.39; H, 2.79; N, 2.43%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2044, 1995, 1970 (CO); 1697 (NO); δ_H(400 MHz, $CDCl_3$) 2.21 (3 H, s, H$_3$CC$_2$C*H*$_3$), 2.33 (3 H, s, *H*$_3$CC$_2$CH$_3$), 5.94 (5 H, s, C_5H_5), 6.40 (5 H, s, C_5H_5); *m/z* 490 [(M^+)], [(M^+) − *n*CO] (*n* = 1–3).

Complex **11** (Found: C, 33.00; H, 2.43; N, 2.36. $C_{15}H_{12}BF_4Mo_2NO_4$ requires C, 32.82; H, 2.20; N, 2.55%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2058, 2040, 2006 (CO); 1624 (NO); δ_H(400 MHz, $CDCl_3$) 3.56 (2 H, s, br, HCCH), 3.98 (3 H, s, CO_2CH_3), 5.88 (5 H, s, C_5H_5), 6.02 (5 H, s, C_5H_5); *m/z* 462 [(M^+)], [(M^+) − *n*CO] (*n* = 1–3).

Complex **12** (Found: C, 33.80; H, 2.85; N, 2.20. $C_{17}H_{16}BF_4Mo_2NO_4$ requires C, 33.64; H, 2.66; N, 2.31%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2066, 2025, 1987, 1723 (CO); 1652 (NO); δ_H(400 MHz, $CDCl_3$) 3.96 (3 H, s, CO_2CH_3), 5.88 (5 H, s, C_5H_5), 5.93 (1 H, s, *H*C$_2$CO$_2$Me), 6.12 (5 H, s, C_5H_5); *m/z* 521 [(M^+) + H], [(M^+) − *n*CO] (*n* = 1–3).

Crystallography

Crystal data and data collection parameters for complex 9. $C_{19}H_{16}BF_4Mo_2NO_8$, $M_r = 665.02$, monoclinic, space group $P2_1/n$ (no. 14), $a = 13.382(2)$, $b = 13.655(2)$, $c = 14.770(2)$ Å, $\beta = 116.074(7)$, $U = 2424.3(5)$ Å^{-3} (by least-squares refinement on diffractometer angles from 25 centred reflections, $15 < \theta < 20°$), $Z = 4$, $D_c = 1.822$ Mg m^{-3}, μ(Mo-Kα) = 1.109 mm^{-1}, semiempirical absorption correction based on ψ scans, relative transmission factors 0.92–1.00, $F(000) = 1304$, orange–brown block with dimensions 0.40 × 0.40 × 0.20 mm. Data were collected by the ω–2θ scan method on a Rigaku AFC5R four-circle diffractometer at room temperature using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) in the range $7.40 < 2\theta < 55.1°$, $+h$, $+k$, $\pm l$; 3 standard reflections showed no significant variation in intensity; 4466 reflections of which 4263 were independent ($R_{int} = 0.042$) and used in all calculations.

Structure solution and refinement. The structure was solved using direct methods[24] and subsequent Fourier-difference syntheses, and refined by full-matrix least squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[25] The nitrosyl ligand was identified by comparison of thermal displacement parameters. Hydrogen atoms were placed in geometrically idealised positions and refined using a riding model or as rigid methyl groups. In the final cycles of refinement a weighting scheme of the form $w^{-1} = [\sigma^2(F_o^2) + (0.0371P)^2 + 8.56P]$, where $P = (F_o^2 + 2F_c^2)/3$, was employed, which produced a flat analysis of variance. Final $R(F) = 0.0465$, $wR(F^2) = 0.1053$ for 2833 observed reflections $[I > 2\sigma(I)]$, $R(F) = 0.1036$, $wR(F^2) = 0.1278$ for all data; 311 parameters, 28 restraints (to thermal and positional parameters of BF_4^- anion and disordered OMe group); $S = 1.038$, maximum $\Delta/\sigma = 0.001$. Maximum peak and hole in final Fourier-difference map 0.86 and −0.66 e Å^{-3} respectively.

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.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/516.

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