Molybdenum-mediated Methoxycarbonylation of Propargyl Halides: Molecular and Crystal Structure of the Vinylmolybdenum(II) Complex $[Mo(bipy)(CO)_2(C_5H_7O_2)(py)]BF_4$*

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Treatment of a methanolic suspension of $[PPh_4][Mo(bipy)(CO)_3X]$ (bipy = 2,2′-bipyridine, X = Cl or Br) held at −17 °C with propargyl (prop-2-ynyl) chloride or bromide yields the *cis*-dicarbonylmolybdenum complexes $[Mo(bipy)(CO)_2(C_5H_7O_2)X]$ [X = Cl (**1**) or Br (**2**)], which are believed to contain an η^3-oxacyclobutenyl ligand formed by methoxycarbonylation of the propargyl moiety. Reaction of complex (**1**) or (**2**) with $Na(O_2CC_2F_5)$, or with $AgBF_4$ in acetone followed by pyridine, yields $[Mo(bipy)(CO)_2(C_5H_7O_2)(O_2CC_2F_5)]$ (**3**) and $[Mo(bipy)(CO)_2(C_5H_7O_2)(py)]BF_4$ (**4**) (py = pyridine) respectively, in which the mode of bonding of the $C_5H_7O_2$ ligand has changed from η^3-allyl to σ-vinyl. Crystal structure analysis shows that in the molecule (**4**) the molybdenum atom is seven-co-ordinate being bonded to bipy [2.241(7), 2.164(7) Å], pyridine [2.275(8) Å], two carbonyl groups [1.936(10), 1.983(11) Å], and the bidentate $C_5H_7O_2$ ligand [Mo–O 2.164(6) and Mo–C 2.155(10) Å].

There has been considerable recent interest in developing synthetically useful organic reaction sequences using inexpensive metal templates as alternatives to palladium-based systems.[1] In one such study, $[Mo(bipy)(CO)_4]$ (bipy = 2,2′-bipyridine) and other simple substituted molybdenum carbonyl derivatives were shown to be effective catalysts for highly chemo- and regio-selective allylic alkylation reactions.[2] These reactions are thought to proceed *via* η^3-allylmolybdenum intermediates in view of the known oxidative-addition reactions of allyl halides and allyl acetate with $[Mo(bipy)(CO)_4]$ and its analogues to yield $[Mo(\eta^3\text{-allyl})(CO)_2(L\text{–}L)X]$ (L–L = bidentate ligand, X = anion), [3] and the observation that some of these products will undergo nucleophilic attack at the allyl group.[2,4] We have shown that, under similar experimental conditions, $[Mo(bipy)(CO)_4]$ in the presence of certain resonance-stabilised carbanions catalyses allylic coupling rather than alkylation reactions.[5] As a consequence we are currently investigating the nature and role of metallo intermediates in these processes and determining whether new molybdenum-mediated C–C bond formations can be achieved with other unsaturated organics capable of oxidative addition to molybdenum(0) carbonyl complexes. In this paper we report our studies on the propargyl (prop-2-ynyl) moiety.

Results and Discussion

Attempts to induce clean propargyl coupling or alkylation reactions using catalytic or stoicheiometric quantities of either $[Mo(bipy)(CO)_4]$ or a mixture of $[Mo(bipy)(CO)_4]$ and a resonance-stabilised anion under reaction conditions which were satisfactory for allyl substrates[5] were unsuccessful for propargyl halides. However, in some reactions spectroscopic evidence for a thermally unstable dicarbonylmolybdenum species was obtained, so an attempt was made to reduce the severity of the reaction conditions by increasing the nucleophilicity of the metal centre. This was achieved by replacing a CO group in $[Mo(bipy)(CO)_4]$ by a halide ion, and the $[Mo(bipy)(CO)_3X]^-$ anions (X = Cl or Br) so formed were found to react cleanly with methanolic solutions of the corresponding propargyl halide to yield the *cis*-dicarbonylmolybdenum complexes $[Mo(bipy)(CO)_2(C_5H_7O_2)X]$ [X = Cl (**1**) or Br (**2**)]. The co-ordinated $C_5H_7O_2$ ligand, which exhibits a moderately strong i.r. absorption at *ca.* 1 080 cm^{-1} characteristic of an O-alkyl linkage, is evidently formed from a combination of the propargyl moiety with MeOH and a CO group [equation (1)].

$$[PPh_4][Mo(bipy)(CO)_3X] + CH{\equiv}CCH_2X + MeOH \longrightarrow [Mo(bipy)(CO)_2(C_5H_7O_2)X] + PPh_4X \quad (1)$$

Neither complex was very soluble in normal n.m.r. solvents, but the ^1H n.m.r. spectrum of (**1**) in CD_2Cl_2 showed $C_5H_7O_2$ absorbances at δ 3.65 (doublet), 3.60 (singlet), and 3.05 p.p.m. (quartet) in the intensity ratio 3:3:1, which can be ascribed to C–Me, O–Me, and methine proton signals respectively. No analogous products could be obtained when the reaction was carried out under similar conditions in other alcohols ROH (R = Et or $PhCH_2$) or in methanethiol, nor could any organometallic intermediate be isolated when the reaction was carried out in the non-hydroxylic solvents $CHCl_3$, CH_2Cl_2, or tetrahydrofuran (thf).

It has been shown previously[6] that the propargylic complexes $[M(\eta^5\text{-}C_5H_5)(CO)_3(\sigma\text{-}CH_2C{\equiv}CH)]$ (M = Mo or W) are alkoxycarbonylated in methanol to yield organometallics containing either the η^3-2-$MeO_2CC_3H_4$ ligand (**A**) or the σ-vinyl ligand (**B**). Both complexes (**1**) and (**2**) exhibit ν(CO) [and (**1**) a ν(MoCl)] stretching modes in their i.r. spectra which are typical of $[Mo(\eta^3\text{-allyl})(bipy)(CO)_2X]$ complexes,[3,4,7] but the ^1H n.m.r. data for the $C_5H_7O_2$ ligand in these complexes are not compatible with either structural type (**A**), which requires an entirely different proton intensity pattern from that observed, or type (**B**) which requires a vinylic proton signal in the range 5.5—8.0 p.p.m.[6,8] Alternative modes of bonding of this ligand which preserve the 18-electron configuration of the

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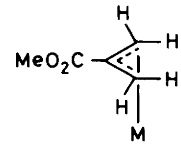
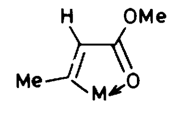
* 2,2′-Bipyridinedicarbonyl(4-methoxy-4-oxobut-2-en-2-yl-C^2O)-pyridinemolybdenum(II) tetrafluoroborate.

Supplementary data available (No. SUP 56626, 5 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.



(A)



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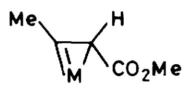
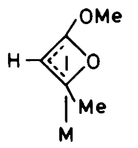


(C)

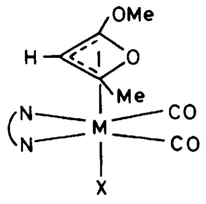


(D)

molybdenum atom in (**1**) or (**2**) and are in keeping with the ^1H n.m.r. data are illustrated in (**C**) and (**D**).

The low solubilities of both complexes (**1**) and (**2**) precluded ^{13}C n.m.r. measurements which would readily differentiate between a three-electron η^2-bonded alkylidene species[9] such as (**C**), and the η^3-oxacyclobutenyl ligand (**D**). However, there was no i.r. evidence for an unco-ordinated $-CO_2Me$ group,[6,10] and consequently, based on the limited spectroscopic data available, we believe complexes (**1**) and (**2**) contain the η^3-2-methoxy-4-methyl-1-oxacyclobutenyl ligand (**D**). In previous studies, a σ-oxacyclobutenyl product has been isolated from the reaction of $[Fe(CO)_2(C{\equiv}CPh)(\eta^5\text{-}C_5H_5)]$ with hexafluoroacetone,[11] and a possible mechanism for metal carbonyl-mediated formation of an η^3-oxacyclobutenyl ring system from an alkyne precursor has also been described. The intermediacy of vinyl ketone (see below) and 4-oxabutadiene metal species which subsequently form the oxacyclobutenyl ring system *via* a conrotatory ring closure was postulated.[12]

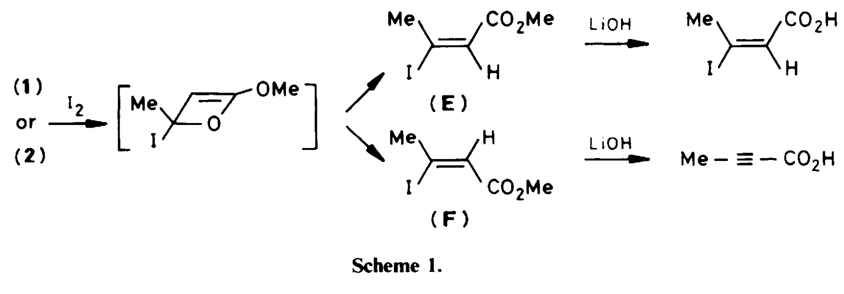
The normal structure adopted by hindered allyl complexes of the type $[Mo(\eta^3\text{-allyl})(bipy)(CO)_2X]$ (X = anion) is pseudo-octahedral with the allyl group *trans* to the anion X.[13] In this configuration the hydrogen atom on the central carbon of the allyl moiety lies above the plane of the bipy ligand and consequently suffers a high-field shift.[14] The proton signal of intensity 1 at 2.95 ± 0.1 p.p.m. for both (**1**) and (**2**) has the expected chemical shift for the η^3-2-methoxy-4-methyl-1-oxacyclobutenyl ligand in such a complex with the stereochemistry shown below.



Attempts to confirm these predictions by *X*-ray crystallography were thwarted by the low stabilities and solubilities of both complexes (**1**) and (**2**) in suitable solvents for recrystallisations. Consequently, confirmatory chemical evidence for the skeletal structure of the $C_5H_7O_2$ ligand was obtained from chemical studies while new metallo derivatives with more tractable physical properties were sought.

Both (**1**) and (**2**) suspended in acetonitrile reacted cleanly under mild conditions with an excess of iodine to give two isomeric alkenes which were readily separated by column chromatography. Each isomer gave an elemental analysis corresponding to $C_5H_7IO_2$ and this formula was confirmed by mass spectrometry when a molecular ion peak at *m/z* 226 was observed together with fragments at *m/z* 195 and 167, due to consecutive losses of MeO and CO, and at *m/z* 99 (base peak) due to loss of an iodine atom from the molecular ion. The presence of the carbomethoxy group was again evident from the fragment *m/z* 59. This mass spectral evidence suggested that the two isomers were iodo-derivatives of methyl crotonate or of methyl methacrylate. The ^{13}C n.m.r. spectra of isomers (**E**) and (**F**) were found to correspond closely with the data published for (*E*)- and (*Z*)-methyl 3-iodocrotonate respectively,[15] but since neither the source nor the physical constants of the model compounds were given, these assignments were checked as follows. Both isomers reacted completely with LiOH in aqueous tetrahydrofuran within 4 h. Isomer (**F**) was rapidly converted into tetrolic acid (but-2-ynoic acid) and isomer (**E**) into (*E*)-3-iodocrotonic acid, with no trace of tetrolic acid being detected. Differential nuclear Overhauser effect (n.O.e.) measurements made at 400 MHz indicated that the C-methyl group and the vinylic proton were close to each other in (**F**) and distant in (**E**) (full spectral data are provided in the Experimental section). Both these observations place the methyl group and the vinylic proton in a *syn* relationship in (**F**) which is therefore the (*Z*) isomer. The foregoing confirms the published assignments of the two iodo-esters and further supports the skeletal carbon arrangement indicated by ^1H n.m.r. measurements. Mechanistically, the overall formation of the two esters from the oxacyclobutenyl ligand can be regarded as an oxidative cleavage by iodine of the Mo–C bond giving an iodo-oxacyclobutene, each of the two possible conrotatory opening modes of which then yields a different geometrical isomer of 3-iodocrotonic ester (Scheme 1).

It has been established that the halogeno complexes $[Mo(\eta^3\text{-allyl})(bipy)(CO)_2X]$ (X = Cl or Br) may readily be converted into more soluble derivatives by anion exchange with $Na(O_2CR')$ (R′ = CF_3, C_2F_5, or C_3F_7),[14] or by conversion into cationic species[16] (Scheme 2). Both these procedures were applied to complexes (**1**) and (**2**) in an attempt to obtain soluble derivatives for ^{13}C n.m.r. and *X*-ray crystallographic studies, but although the stoicheiometry of the $C_5H_7O_2$ ligand remained the same in $[Mo(bipy)(CO)_2(C_5H_7O_2)(O_2CC_2F_5)]$ (**3**) and in $[Mo(bipy)(CO)_2(C_5H_7O_2)(py)]BF_4$ (**4**) (py = pyridine) its mode of bonding had changed from that in (**1**) and (**2**) as evidenced by both i.r. and ^1H n.m.r. spectral observations. Of particular significance was the appearance of a CO_2Me absorption at *ca.* 1 570 cm^{-1} in the i.r. spectrum of the co-



Scheme 1.

$$\begin{tikzcd}
{[Mo(\eta^3\text{-allyl})(bipy)(CO)_2X]} \arrow[r, "(i)"] \arrow[d, "(ii)"] & {[Mo(Me_2CO)(\eta^3\text{-allyl})(bipy)(CO)_2]BF_4} \arrow[dl, "(ii)"'] \arrow[d, "L"] \\
{[Mo(\eta^3\text{-allyl})(bipy)(CO)_2(O_2CR')]} & {[Mo(\eta^3\text{-allyl})(bipy)(CO)_2L]BF_4}
\end{tikzcd}$$

Scheme 2. (*i*) $AgBF_4$, acetone; (*ii*) $Na(O_2CR')$

Table 1. Atomic co-ordinates (× 10^4) for complex (**4**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	1 195.4(6)	1 494.2(6)	3 250(1)	C(1)	407(6)	1 036(7)	1 810(10)
N(11)	2 530(4)	1 243(4)	2 755(7)	C(2)	49(7)	1 850(7)	3 698(10)
C(12)	2 798(5)	1 625(5)	1 649(9)	O(2)	−615(4)	2 045(5)	3 934(9)
C(13)	3 602(6)	1 465(7)	1 194(12)	O(41)	1 254(4)	1 198(4)	5 427(6)
C(14)	4 147(6)	917(8)	1 933(13)	C(42)	1 207(5)	436(7)	5 734(9)
C(15)	3 884(7)	536(8)	3 091(13)	C(43)	1 202(6)	−154(7)	4 687(11)
C(16)	3 073(6)	724(7)	3 461(10)	O(44)	1 178(5)	221(5)	7 048(7)
C(17)	2 198(5)	2 202(6)	950(9)	C(45)	1 217(5)	151(6)	3 419(10)
C(18)	2 389(7)	2 721(7)	−130(11)	C(46)	1 345(8)	−461(8)	2 241(12)
C(19)	1 793(8)	3 299(8)	−652(13)	C(48)	1 233(7)	855(9)	8 043(11)
C(20)	1 017(8)	3 340(7)	−135(12)	B	8 952(7)	4 208(8)	2 255(12)
C(21)	844(6)	2 794(7)	903(10)	F(1)	9 081(10)	3 552(11)	1 384(16)
N(22)	1 420(4)	2 242(5)	1 464(7)	F(2)	9 427(8)	4 331(8)	3 486(13)
N(31)	1 762(4)	2 655(5)	4 323(8)	F(3)	8 852(10)	4 987(10)	1 716(14)
C(32)	1 349(8)	3 381(6)	4 300(11)	F(4)	8 205(9)	4 016(10)	2 746(16)
C(33)	1 646(10)	4 050(8)	5 073(14)	F(11)	9 385(18)	4 678(19)	1 273(28)
C(34)	2 395(10)	3 991(9)	5 884(14)	F(12)	8 177(16)	4 608(17)	1 976(26)
C(35)	2 799(8)	3 271(9)	5 909(13)	F(13)	8 886(23)	3 374(24)	2 063(43)
C(36)	2 490(6)	2 596(8)	5 122(11)	F(21)	9 357(21)	3 955(25)	1 184(31)
O(1)	−119(5)	834(5)	959(8)	F(22)	9 652(20)	4 114(21)	3 175(33)

Table 2. Molecular dimensions in the co-ordination sphere (distances in Å, angles in °)

Mo–N(11)	2.241(7)	N(11)–Mo–N(22)	72.71(25)	N(22)–Mo–C(2)	103.57(34)	C(2)–Mo–O(41)	79.05(32)
Mo–N(22)	2.164(7)	N(11)–Mo–N(31)	84.49(26)	N(31)–Mo–C(2)	89.74(35)	N(11)–Mo–C(45)	80.11(30)
Mo–N(31)	2.275(8)	N(22)–Mo–N(31)	80.33(27)	C(1)–Mo–C(2)	74.05(42)	N(22)–Mo–C(45)	127.52(33)
Mo–C(1)	1.936(10)	N(11)–Mo–C(1)	109.59(35)	N(11)–Mo–O(41)	102.13(24)	N(31)–Mo–C(45)	140.85(30)
Mo–C(2)	1.983(11)	N(22)–Mo–C(1)	76.57(36)	N(22)–Mo–O(41)	155.61(25)	C(1)–Mo–C(45)	71.54(40)
Mo–O(41)	2.164(6)	N(31)–Mo–C(1)	147.52(37)	N(31)–Mo–O(41)	75.41(26)	C(2)–Mo–C(45)	106.21(39)
Mo–C(45)	2.155(10)	N(11)–Mo–C(2)	173.58(36)	C(1)–Mo–O(41)	126.56(35)	O(41)–Mo–C(45)	73.04(31)

Dimensions in the $C_5H_7O_2$ ligand

O(41)–C(42)	1.258(12)	Mo–O(41)–C(42)	116.5(5)	C(42)–O(44)–C(48)	118.2(8)
C(42)–C(43)	1.388(14)	O(41)–C(42)–C(43)	118.7(8)	Mo–C(45)–C(43)	115.7(7)
C(42)–O(44)	1.329(12)	O(41)–C(42)–O(44)	119.1(8)	Mo–C(45)–C(46)	125.5(7)
C(43)–C(45)	1.329(14)	C(43)–C(42)–O(44)	122.1(9)	C(43)–C(45)–C(46)	118.4(9)
O(44)–C(48)	1.399(14)	C(42)–C(43)–C(45)	115.7(9)		
C(45)–C(46)	1.533(16)				

ordinated $C_5H_7O_2$ ligand, and the change in the ^1H n.m.r. chemical shift of the CH resonance of this ligand from *ca.* 3.0 p.p.m. in (**1**) and (**2**) to *ca.* 6.4 p.p.m. in both (**3**) and (**4**). These latter values are very similar to data reported on other σ-vinyl ketone complexes of molybdenum and tungsten,[6,8] and indicate that a structural rearrangement has occurred on halide abstraction from (**1**) and (**2**). In order to confirm this important structural feature a single-crystal *X*-ray diffraction study of complex (**4**) was undertaken.

Discussion of the Structure.—Atomic co-ordinates and molecular dimensions in the metal co-ordination sphere and in the $C_5H_7O_2$ ligand are summarised in Tables 1 and 2 respectively. The cation is shown in Figure 1 together with the atomic numbering scheme. The molybdenum atom is seven-co-ordinate being bonded to bipyridyl [Mo–N(11) 2.241(7), Mo–N(22) 2.164(7) Å], pyridine [Mo–N(31) 2.275(8) Å], two carbonyl groups [Mo–C(1) 1.936(10), Mo–C(2) 1.983(11) Å], and the bidentate $C_5H_7O_2$ ligand. The metal is bonded to O(41) and C(45) from this ligand [Mo–O(41) 2.164(6), Mo–C(45) 2.155(10) Å]. As is apparent from Figure 1, this ligand is approximately planar. Least-squares calculations show that atoms O(41), C(42), C(43), and C(45) are planar within experimental error. Other atoms are close to this plane [*viz.*, Mo 0.14, O(44) −0.02, C(46) 0.22, and C(48) 0.03 Å]. It would appear from the bond lengths that C(43)–C(45) [at 1.329(14) Å] has more double-bond character than C(42)–C(43) [1.388(14) Å]. Similarly O(41)–C(42) at 1.258(12) Å is shorter than C(42)–O(44) [1.329(12) Å] and the pattern of bonding is therefore comparable to that of (**B**) with limited delocalisation in the ring. Although we can find no reference to a crystal structure determination on a complex with the same $C_5H_7O_2$ ligand, two structural reports on analogues have appeared,[17,18] in which dimensions in the C=C–C=O skeleton are in general similar to those reported in Table 2.

The geometry of the seven-co-ordinate polyhedron around

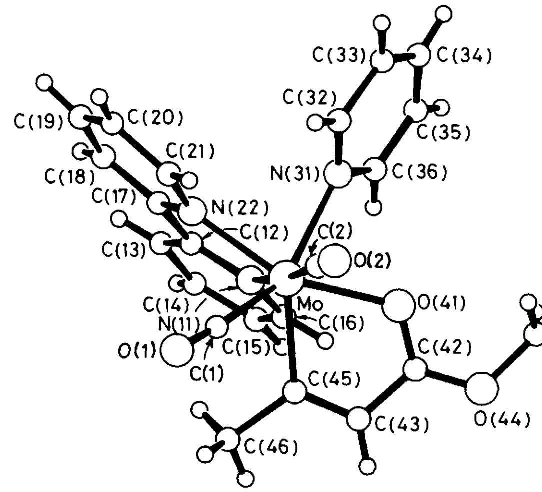


Figure 1. The structure of complex (**4**)

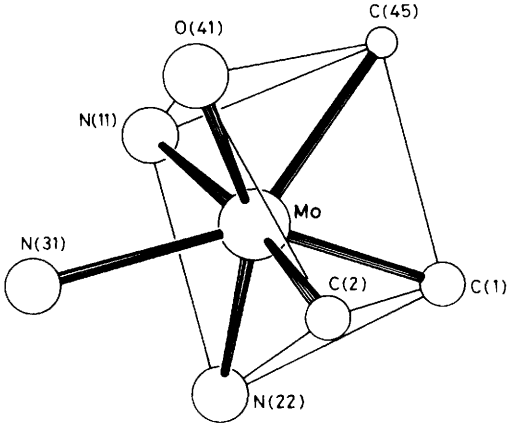


Figure 2. The co-ordination sphere of the molybdenum atom in complex (**4**) showing the distorted capped trigonal prismatic geometry

the molybdenum atom is highly distorted, no doubt by the steric constraints of the ligands. Using our method for polyhedron analysis,[19] we found that the geometry is intermediate between a capped trigonal prism [root-mean-square (r.m.s.) deviation 0.11 Å] and a capped octahedron (r.m.s. deviation 0.15 Å). In the capped trigonal prism, N(31) is in the unique capping position, C(2), O(41), N(11), and N(22) occupy the capped face, and C(45) and C(1) the remaining edge. This polyhedron is distorted towards a capped octahedron with C(1) in the capping position, N(22), C(45), and C(2) in the capped face, and O(41), N(31), and N(11) in the uncapped face. The r.m.s. deviation from a pentagonal bipyramid with N(11) and C(2) in axial positions is 0.20 Å.

This is an unusual geometry for molecules of formula M(bidentate ligand)$_2$(unidentate ligand)$_3$ as in nearly all structures of this type the two bidentate ligands occupy similar sites in a polyhedron,[19,20] *i.e.* two edges in the equatorial girdle of a pentagonal bipyramid or two edges in the capped face of a capped trigonal prism. However, in this case the bipy ligand of bite (distance ratio L $\cdots$ L/M–L, where L = donor ligand) 1.29 occupies an edge in the capped face, and the $C_5H_7O_2$ ligand (bite 1.19) an edge between a site in the capped face and a site in the uncapped edge (Figure 2). The two bidentate ligands intersect each other at an angle of 58.7°. These bites, particularly that of the bipy ligand, are rather large for a seven-co-ordinate molecule and it may well be that this is a cause of the unusual geometry. An additional factor may be the bulk of the two chelate rings as both have planar groups bonded to the chelate ring which add to the general congestion in the co-ordination sphere. The two rings in the bipy ring are themselves planar within experimental error but they intersect at an angle of 8.1°. The pyridine ring takes up an orientation so as to maximise contacts with atoms in the quadrilateral face [deviations from the pyridine ring plane N(11) −1.18, N(22) −1.67, C(2) 1.40, and O(41) 1.97 Å]. There are no intramolecular contacts less than the sum of the van der Waals radii.

Although crystallographic data are not available for complex (**3**), the similarities in the i.r. and ^{1}H n.m.r. spectra of the $C_5H_7O_2$ ligands in (**3**) and (**4**), together with the ^{13}C n.m.r. spectrum of (**3**) which exhibits a Mo–CH= signal at 243.0 p.p.m., indicate that this ligand is bonded in a similar way in both complexes. The asymmetric and symmetric CO_2 stretching modes occur as single strong bands at 1 660 and 1 435 cm^{-1} in the solid-state spectrum of (**3**), and the separation [$\nu_{asym}(CO_2) - \nu_{sym}(CO_2)$] of 225 cm^{-1} shows the carboxylate ligand to be monodentate[21] as expected for an 18-electron metal atom configuration. Attempts to convert the chelating $C_5H_7O_2$ ligand into a monodentate vinyl group, or to reform complex (**1**) or (**2**) containing the η^3-oxacyclobutenyl ligand, by treating (**3**) or (**4**) with an excess of halide ions, were unsuccessful and resulted instead in loss of the $C_5H_7O_2$ group and formation of 2,2′-bipyridinemetal carbonyl species.

Experimental

All preparations involving metal carbonyl derivatives were performed in an atmosphere of dry N_2 gas using solvents and liquid reagents freed from moisture and oxygen by standard procedures. The starting materials [Mo(bipy)(CO)$_4$] and [PPh$_4$][Mo(bipy)(CO)$_3$X][22] (X = Cl or Br) were prepared by literature methods.

Infrared spectra were obtained in the region 4 000—200 cm^{-1} using a Perkin-Elmer 597 spectrophotometer. Hydrogen-1 and ^{13}C n.m.r. spectra were measured in $CDCl_3$ or CD_2Cl_2 unless otherwise stated using JEOL PS 100 and FX 90Q FT instruments respectively, and δ values are quoted as shifts in p.p.m. downfield from $SiMe_4$ as internal standard.

Preparations of [Mo(bipy)(CO)$_2$(η^3-$C_5H_7O_2$)X] [X = Cl(**1**) *or* Br(**2**)].—Propargyl halide (34.0 mmol) was added dropwise to a stirred suspension of [PPh$_4$][Mo(bipy)(CO)$_3$X] (17.0 mmol) in dry deoxygenated methanol (200 cm^3) held at −17 °C. The mixture was stirred for 0.5 h at this temperature and for a further 0.5 h at ambient temperature. The product was isolated as a light brown powder, and was analytically pure after washing with cold MeOH and drying *in vacuo*. Yield: 60% for (**1**) or (**2**) [Found for (**1**): C, 45.7; H, 3.5; N, 6.5. Calc. for $C_{17}H_{15}ClMoN_2O_4$: C, 46.1; H, 3.4; N, 6.6%; i.r. (Nujol) 1 995 and 1 930 (CO), and 263 cm^{-1} (MoCl); ^{1}H n.m.r. (CD_2Cl_2) δ 3.05 [1 H, q, *J*(HH) 2, CH], 3.60 (3 H, s, OMe), 3.65 [3 H, d, *J*(HH) 2 Hz, CMe], and 7.9—9.1 (8 H, m, aromatics). Found for (**2**): C, 41.8; H, 3.15; N, 5.9. Calc. for $C_{17}H_{15}BrMoN_2O_4$: C, 41.9; H, 3.1; N, 5.8%; i.r. (Nujol) 1 998 and 1 930 cm^{-1} (CO); ^{1}H n.m.r. (CD_2Cl_2) δ 2.85 [1 H, q, *J*(HH) 2, CH], 3.55 [3 H, d, *J*(HH) 2 Hz, CMe], 3.60 (3 H, s, OMe), and 7.9—9.0 (8 H, m, aromatics)].

Reaction of [Mo(bipy)(CO)$_2$($C_5H_7O_2$)X] (X = Cl *or* Br) *with Iodine*.—A stirred suspension of complex (**1**) or (**2**) (0.04 mol) in dry, oxygen-free MeCN (500 cm^3) was treated at room temperature under a N_2 atmosphere with powdered iodine (41 g, 0.16 mol). After 40 min the volume of the solvent was reduced to *ca.* 50 cm^3. Silica gel (60PF-254) was added to the residue and the remainder of the solvent evaporated. The residual mixture was chromatographed using the grade of silica described above and hexane–ethyl acetate (6:1) as eluant, yielding a mixture of the two isomers (6.0 g, 66%). This mixture was fractionated using the same grade of silica and light petroleum (b.p. 60—80 °C)–ethyl acetate (6:1) as eluant. The first component (**E**) was (*E*)-methyl 3-iodocrotonate (1.2 g, 14%). I.r. (liquid film): 1 720, 1 615, 1 175, and 1 195 cm^{-1}. Mass spectrum: *m/z* 226 (M^+, 5), 195(20), 167(15), 99(100), and 59(30%); chemical ionisation (c.i.) mode (isobutane) 227(100) and 99(35). ^{1}H N.m.r. ($CDCl_3$), 400 MHz: δ 2.97 [3 H, d, *J*(HH) 1.5, CMe], 3.68 (3 H, s, OMe), and 6.62 [1 H, q, *J*(HH) 1.5 Hz, CH]. Irradiation at 6.62 or 2.97 p.p.m. in the n.O.e. experiment produced no enhancement. ^{13}C N.m.r. ($CDCl_3$): δ 164.2, 131.0, 120.5, 51.3, and 30.9.

An intermediate fraction consisted of a mixture of (*E*) and (*Z*) isomers (0.6 g) followed by the second component (**F**), (*Z*)-methyl 3-iodocrotonate (1.8 g, 21%). I.r. (liquid film): 1 725, 1 625, 1 170, and 1 190 cm^{-1}. Mass spectrum: *m/z* 226 (M^+, 90), 195(35), 167(30), 99(100), and 59(65%); c.i. mode (isobutane) 227(100) and 99(10). N.m.r. ($CDCl_3$), 400 MHz: ^{1}H, δ 2.73 [3 H, d, *J*(HH) 1.45, CMe], 3.73 (3 H, s, OMe), and 6.28 [1 H, q, *J*(HH) 1.45 Hz, CH]; ^{13}C, δ 164.2, 125.0, 113.3, 51.2, and 36.3.

Competitive Elimination Reactions of the (E) *and* (Z) *Isomers*.—Each isomer (1.2 g, 5.3 mmol) was dissolved in water–tetrahydrofuran (1:3, 30 cm^3) and to each solution under N_2 gas was added $LiOH{\cdot}H_2O$ (0.55 g, 13.0 mmol). The solutions were stirred at ambient temperature for 4 h and then poured into 2 mol dm^{-3} aqueous HCl (50 cm^3) and extracted once with dichloromethane (50 cm^3). The dried extracts were evaporated giving white crystalline solids in each case. These were identified as (*E*)-3-iodocrotonic acid (0.8 g, 71%) from isomer (**E**) and tetrolic acid (0.32 g, 71%) from isomer (**F**).

Preparation of $[Mo(bipy)(CO)_2(C_5H_7O_2)(O_2CC_2F_5)]$ (**3**).—A stirred suspension of complex (**2**) (0.97 g, 2.0 mmol) in dry, oxygen-free acetone (15 cm^3) was treated with solid $Na(O_2CC_2F_5)$ (0.74 g, 4.0 mmol). After 24 h the mixture was filtered, and the filtrate evaporated under reduced pressure leaving a red oil which was recrystallised from water–acetone (5:2 v/v) to give a red solid (0.50 g, 44%). Application of the same procedure to complex (**1**) afforded (**3**) in 22% yield (Found: C, 42.1; H, 2.45; N, 5.1. $C_{20}H_{15}F_5MoN_2O_6$ requires C, 42.1; H, 2.65; N, 4.9%). I.r. (Nujol): 1 942 and 1 842 (CO), 1 660 (CO_2, asym), 1 560 (CO_2Me), and 1 435 cm^{-1} (CO_2, sym). N.m.r. (CD_3COCD_3): ^{1}H, δ 2.58 (3 H, s, CMe), 3.96 (3 H, s, OMe), 6.40 (1 H, s, CH), and 7.5—9.0 (8 H, m, aromatics); ^{13}C, δ 248.8 (CO), 243.0 (CMo), 173.0 (CO_2Me), 155.3, 153.6, 140.0, 126.5, 123.8 (aromatics), 116.5 (CH), 53.9 (CO_2*Me*), and 34.2 (C*Me*).

Preparation of $[Mo(bipy)(CO)_2(C_5H_7O_2)(py)]BF_4$ (**4**).—A stirred suspension of (**1**) or (**2**) (2.0 mmol) in dry, oxygen-free acetone (40 cm^3) was treated at ambient temperature with $AgBF_4$ (0.4 g, 2.0 mmol). After 0.75 h the resulting red solution was filtered and the filtrate treated dropwise with pyridine (1.0 cm^3). The mixture was stirred for a further 0.25 h, and then the solvent was evaporated to low bulk under reduced pressure. Red crystals of the product formed on refrigeration, and were collected by filtration, washed with Et_2O, and dried *in vacuo*. More product was formed by evaporating the filtrate to dryness and recrystallising the residue from acetone (1.0 g, 87%) (Found: C, 46.3; H, 3.6; N, 7.65. $C_{22}H_{20}BF_4MoN_3O_4$ requires C, 46.1; H, 3.5; N, 7.35%). I.r. (Nujol): 1 955 and 1 860 (CO), and 1 575 cm^{-1} (CO_2Me). ^{1}H N.m.r. (CD_3NO_2): δ 2.74 (3 H, s, CMe), 4.00 (3 H, s, OMe), 6.46 (1 H, s, CH), and 7.4—9.0 (13 H, m, aromatics).

X-Ray Crystallography.—Crystals of complex (**4**) were prepared as described above.

Crystal data. $C_{22}H_{20}BF_4MoN_3O_4$, M = 574.9, monoclinic, space group $P2_1/n$, a = 15.825(11), b = 15.991(11), c = 9.728(8) Å, β = 95.0(1)°, U = 2 449.3 Å^3, D_m = 1.53(3) g cm^{-3}, Z = 4, D_c = 1.55 g cm^{-3}, F(000) = 1 160, Mo-K_α radiation λ = 0.7107 Å, μ = 5.97 cm^{-1}.

A crystal of approximate size 0.03 × 0.30 × 0.20 mm was mounted on a Stoe Stadi-2 diffractometer and data collected *via* variable-width ω scan. Background counts were 20 s and the scan rate of 0.033° s^{-1} was applied to a width of (2.0 + sin μ/tan θ). 4 170 Independent reflections with 2θ < 50° of which 2 623 with $I > 3\sigma(I)$ were used in subsequent refinement. Neither an absorption nor an extinction correction was applied. The structure was determined by heavy-atom methods. The BF_4^- ion was disordered and three tetrahedra were observed. These tetrahedra were refined with respective occupancies of 0.5, 0.25, and 0.25. All atoms except for these disordered fluorines and the hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometric positions and only their thermal parameters were refined.

Calculations were performed using full-matrix least squares with a weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$. Scattering factors were taken from ref. 23. Calculations were performed using SHELX 76[24] on the Amdahl V7A computer at the University of Reading. The final R value was 0.058 (R' = 0.060). Final atomic co-ordinates are given in Table 1 and bond lengths and angles in the metal co-ordination sphere are given in Table 2.

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