# Alkyne Ligands as Three-electron Donors: Crystal Structures of $[Mo(CO)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ and $[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ *

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The cations $[Mo(CO)(MeC_2Me)_2(\eta\text{-}C_5H_5)]^+$ and $[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)]^+$ crystallise with 'three-legged piano stool' geometry, the three legs comprising the two bonds between Mo and the centre of the alkyne together with the bond to either CO or MeCN. For both species, and in accordance with theoretical considerations (which are discussed), the alkyne bonds lie parallel to the Mo–CO or Mo–NCMe directions, and the alkyne ligands function formally as three-electron donors. For the carbonyl species the bonding of the alkyne to the metal is slightly asymmetric [Mo–C 2.072(4) and 2.130(4) Å, as compared with 2.060(4) and 2.068(4) in the acetonitrile complex] and these bond distances also reflect the expected tighter binding in the acetonitrile complex. Crystals of $[Mo(CO)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ (1) are monoclinic, space group $P2_1/c$ (no. 14) with $Z = 4$ in a unit cell of dimensions $a = 8.994(4)$, $b = 14.059(8)$, $c = 13.255(5)$ Å, $\beta = 116.23(3)°$. The structure has been refined to $R$ 0.048 ($R'$ 0.052) for 2 144 reflections at 220 K. Crystals of the complex $[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ (2) are orthorhombic, space group $P2_12_12_1$ (no. 19), with $Z = 4$ in a unit cell of dimensions $a = 8.780(4)$, $b = 11.656(4)$, $c = 16.225(6)$ Å, $R$ 0.032 ($R'$ 0.032) for 2 466 reflections at 200 K.

The complex $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ undergoes redox cleavage of the metal–metal bond by silver tetrafluoroborate in the presence of but-2-yne to form $[Mo(CO)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ (1).[1] Treatment of (1) with refluxing acetonitrile in the presence of but-2-yne affords the closely related complex $[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ (2);[2] very closely related complexes have also been made by alternative routes.[3] We report herein the results of structural studies by *X*-ray diffraction on complexes (1) and (2), which were carried out in order to ascertain the nature of the acetylene bonding in this class of complex.

## Results and Discussion

The molecular geometry and crystallographic numbering schemes for the cations of (1) and (2) are shown in Figures 1 and 2. Selected bond lengths and angles are in Tables 1 and 2. In both complexes the molybdenum atom is pseudo-octahedrally co-ordinated, three facial sites being occupied by the $\eta^5$-cyclopentadienyl ligand, two by the but-2-yne moieties, and one by a carbonyl ligand, in (1), or an acetonitrile ligand, in (2). In the crystal, the cations and the tetrafluoroborate counter ions are well separated, the only contacts <2.5 Å being, in (1): F(2) · · · H(12) 2.34, F(1) · · · H(9C) 2.38; and in (2): F(2) · · · H(12) 2.14, F(1) · · · H(O1B) 2.47, F(4) · · · H(14) 2.31, F(4) · · · H(9A) 2.43, F(1) · · · H(151) 2.36, F(1) · · · H(6A) 2.45, and F(4) · · · H(O1C) 2.48 Å.

In both structures the axes of the two acetylenic bonds are parallel to one another and to the carbonyl or acetonitrile ligand. The vectors $C(3) \longrightarrow C(4)$, $C(7) \longrightarrow C(8)$, and $Mo \longrightarrow C(1)$ in (1) and $Mo \longrightarrow N$ in (2) are all aligned within 12° of one another. A space-filling diagram of (2) (Figure 3) neatly shows this parallel configuration. In the carbonyl complex (1) the bonding of the alkyne to the metal is significantly asymmetric. If we denote the carbon atom nearer to the σ-bonded ligand as $C^\alpha$ and the other as $C^\beta$, the mean Mo–$C^\alpha$ separation is 2.130(4) while the mean Mo–$C^\beta$ is 2.072(4) Å. It is tempting to ascribe the longer Mo–$C^\alpha$ distance to the steric influence of the CO ligand, but in (2), where the steric influence might be expected to be greater, the difference is smaller [indeed, not significant on the e.s.d.s given: Mo–$C^\alpha$ 2.068(4), Mo–$C^\beta$ 2.060(4) Å]. The overall molybdenum–alkyne bond lengths are, however, significantly shorter for (2) than for (1), indicating tighter binding in (2). This observation is in accord with the i.r. spectrum of complex (2), which shows an asymmetric doublet at 2 315 and 2 295 cm$^{-1}$, ascribed to a coupling of the C–N and N–Mo stretching vibrations and to an increased C–N force constant. The acetonitrile is by implication[4] acting as a simple σ-donor ligand. If the acetonitrile does indeed act principally as a σ-donor, more electron density is available on the metal atom for π

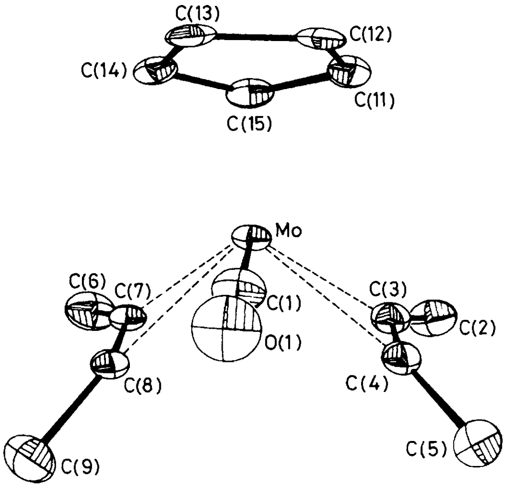

**Figure 1.** The molecular structure of the cation $[Mo(CO)(MeC_2Me)_2(\eta\text{-}C_5H_5)]^+$ of (1) showing the crystallographic numbering scheme

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* Bis(but-2-yne)carbonyl(η-cyclopentadienyl)molybdenum tetrafluoroborate and acetonitrilebis(but-2-yne)(η-cyclopentadienyl)molybdenum tetrafluoroborate.

*Supplementary data available* (No. SUP 23482, 44 pp.): structure factors, thermal parameters, H-atom co-ordinates, and complete bond lengths and angles for complexes (1) and (2). See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

**Table 1.** Selected bond lengths and angles with estimated standard deviations in parentheses for $[Mo(CO)(MeC{\equiv}CMe)_2(\eta\text{-}C_5H_5)][BF_4]$ (1)

(*i*) Distances (Å)

| | | | |
|---|---|---|---|
| Mo–C(11) | 2.409(4) | Mo–C(12) | 2.338(4) |
| Mo–C(13) | 2.340(5) | Mo–C(14) | 2.379(4) |
| Mo–C(15) | 2.396(4) | Mo–C(1) | 2.001(4) |
| Mo–C(3) | 2.082(5) | Mo–C(4) | 2.136(4) |
| Mo–C(7) | 2.061(4) | Mo–C(8) | 2.124(4) |
| C(11)–C(12) | 1.403(8) | C(11)–C(15) | 1.421(6) |
| C(12)–C(13) | 1.438(7) | C(13)–C(14) | 1.409(7) |
| C(14)–C(15) | 1.419(7) | C(1)–O(1) | 1.125(5) |
| C(3)–C(2) | 1.491(7) | C(3)–C(4) | 1.267(6) |
| C(4)–C(5) | 1.488(5) | C(7)–C(6) | 1.492(6) |
| C(7)–C(8) | 1.277(5) | C(8)–C(9) | 1.480(5) |
| B–F(1) | 1.389(5) | B–F(2) | 1.382(6) |
| B–F(3) | 1.384(7) | B–F(4) | 1.385(6) |

(*ii*) Angles (°)

| | | | |
|---|---|---|---|
| C(2)–C(3)–C(4) | 147.5(4) | C(6)–C(7)–C(8) | 145.9(4) |
| C(3)–C(4)–C(5) | 147.6(5) | C(7)–C(8)–C(9) | 144.9(4) |
| C(3)–Mo–C(4) | 34.9(2) | C(7)–Mo–C(8) | 35.4(2) |
| C(3)–Mo–C(7) | 98.3(2) | C(4)–Mo–C(8) | 99.4(1) |
| C(3)–Mo–C(8) | 108.4(2) | C(4)–Mo–C(7) | 110.9(2) |
| C(3)–Mo–C(1) | 109.5(2) | C(7)–Mo–C(1) | 109.4(2) |
| C(4)–Mo–C(1) | 74.6(2) | C(8)–Mo–C(1) | 74.0(8) |
| Mo–C(3)–C(2) | 137.6(3) | Mo–C(7)–C(6) | 139.0(2) |
| Mo–C(4)–C(5) | 142.1(4) | Mo–C(8)–C(9) | 145.5(3) |
| Mo–C(1)–O(1) | 177.9(3) | | |

**Table 2.** Selected bond lengths and angles with estimated standard deviations in parentheses for $[Mo(NCMe)(MeC{\equiv}CMe)_2(\eta\text{-}C_5H_5)][BF_4]$ (2)

(*i*) Distances (Å)

| | | | |
|---|---|---|---|
| Mean Mo–C in $C_5H_5$ ligand * | 2.384(6) | | |
| Mean C–C in $C_5H_5$ ligand * | 1.420 | | |
| Mo–C(3) | 2.055(4) | Mo–C(8) | 2.064(4) |
| Mo–C(4) | 2.070(4) | Mo–C(7) | 2.066(5) |
| C(2)–C(3) | 1.491(6) | C(6)–C(7) | 1.492(7) |
| C(3)–C(4) | 1.278(6) | C(7)–C(8) | 1.268(6) |
| C(4)–C(5) | 1.490(6) | C(8)–C(9) | 1.485(6) |
| Mo–N | 2.144(4) | N–C(1) | 1.137(6) |
| C(1)–C(01) | 1.456(7) | | |
| B–F(1) | 1.383(7) | B–F(2) | 1.379(7) |
| B–F(3) | 1.370(7) | B–F(4) | 1.350(7) |

(*ii*) Angles (°)

| | | | |
|---|---|---|---|
| C(2)–C(3)–C(4) | 146.7(4) | C(9)–C(8)–C(7) | 146.3(4) |
| C(3)–C(4)–C(5) | 144.2(4) | C(8)–C(7)–C(6) | 144.4(4) |
| C(3)–Mo–C(4) | 36.1(2) | C(7)–Mo–C(8) | 35.7(2) |
| C(3)–Mo–C(8) | 88.5(2) | C(4)–Mo–C(7) | 109.5(2) |
| C(3)–Mo–C(7) | 110.1(2) | C(4)–Mo–C(8) | 108.4(2) |
| C(3)–Mo–N | 117.7(1) | C(8)–Mo–N | 117.5(1) |
| C(4)–Mo–N | 81.7(1) | C(7)–Mo–N | 82.0(2) |
| Mo–C(3)–C(2) | 140.6(3) | Mo–C(8)–C(9) | 141.4(3) |
| Mo–C(4)–C(5) | 144.4(3) | Mo–C(7)–C(6) | 143.5(3) |
| Mo–N–C(1) | 176.8(3) | N–C(1)–C(01) | 178.9(5) |

* The cyclopentadienyl ligand was positionally disordered in the ratio 6 : 4, and was constrained as two regular pentagonal components in the refinement process.

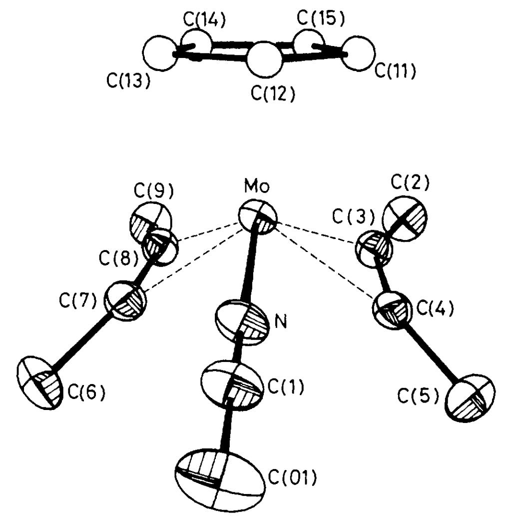

**Figure 2.** The molecular structure of the cation $[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)]^+$ of (2) showing the crystallographic numbering scheme [note differences from (1)]

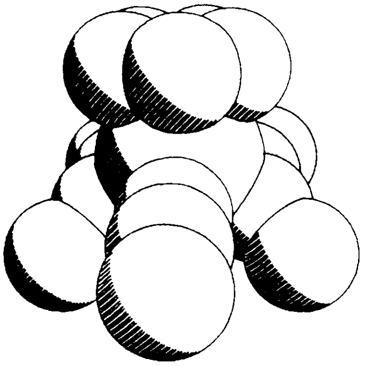

**Figure 3.** A space-filling diagram of the cation $[Mo(NCMe)(MeC_2Me)_2(\eta\text{-}C_5H_5)]^+$ of (2)

back-donation to the alkyne ligands. Unfortunately the errors in the C–C distances are too large to enable detection of small differences. For all the alkyne ligands the Mo atom lies very close to the planes defined by the two alkyne ligands.

The cyclopentadienyl ligands show no deviation from planarity or from pentagonal geometry, but in (2) this ligand is positionally disordered (60 : 40%). In Figure 2 only the 60% component is shown. The carbonyl and acetonitrile ligands have the expected linear geometry; the discrete tetrafluoroborate anions are tetrahedral.

A formal electron count for complexes (1) and (2) suggests that the but-2-yne ligands must each donate effectively three electrons to the molybdenum atom. There is considerable precedent for the involvement of both sets of $\pi$ orbitals in certain types of acetylenic bonding to metals;[2,3,5–12] theoretical studies also support this idea.[13–15] Furthermore, it has been shown[14] that the number of electrons donated by an acetylenic bond can be correlated with the $^{13}C$ chemical shifts of the bonded C atoms. For complex (1) these shifts are 146.2 and 165.1 p.p.m., and for (2) are 161.9 and 181.7 p.p.m.;[16] this is consistent with a system in which each acetylene donates three electrons to the molybdenum atom,

**Table 3.** Structural comparisons of some molybdenum alkyne complexes; distances in Å, angles in degrees

| Complex | Ref. | Mean Mo–C (alkyne) | Mean C–C–C (alkyne) |
|---|---|---|---|
| $[Mo(CO)(PEt_3)(MeC_2Me)(\eta^5\text{-}C_9H_7)][BF_4]$ | 2 | 2.046(4) | 140.7(5) |
| $[Mo(PMe_3)_2(MeC_2Me)(\eta^5\text{-}C_9H_7)][BF_4]$ | 2 | 2.013(8) | 136.3(9) |
| $[Mo(CO)(SC_6F_5)(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)]$ | 7 | 2.034(5) | 137.2(5) |
| $[Mo(PhC_2Ph)(\eta^5\text{-}C_5H_5)_2]$ | * | 2.143(6) | — |
| $[Mo(CO)(MeC_2Me)_2(\eta^5\text{-}C_5H_5)][BF_4]$ (1) | This work | 2.100(4) | 146.4(4) |
| $[Mo(NCMe)(MeC_2Me)_2(\eta^5\text{-}C_5H_5)][BF_4]$ (2) | This work | 2.064(4) | 145.4(4) |

* See A. De Cian, J. Colin, M. Schappacher, L. Ricard, and R. Weiss, *J. Am. Chem. Soc.*, 1981, **103**, 1850.

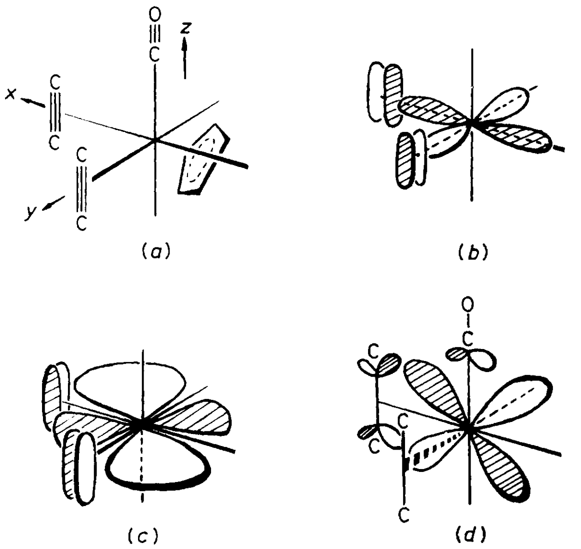

**Figure 4.** Molecular orbital interactions in bis-alkyne molybdenum complexes. (*a*) Axis labelling and orientation of ligands in (1); (*b*) overlap of alkyne $\pi_{\parallel}$ with Mo $d_{x^2-y^2}$; (*c*) overlap of alkyne $\pi_{\perp}$ with Mo $d_{xy}$; and (*d*) overlap of alkyne $\pi^*_{\parallel}$ with Mo $d_{xz}$ in (1)

the more downfield shift of (2) again emphasising the tighter alkyne bonding in the acetonitrile complex.

Three-electron donation by each of the two alkynes can be rationalised in terms of the known molecular configurations of (1) and (2) as follows. The principal bond directions between the Mo atom and the two acetylene ligands and the carbonyl are approximately orthogonal and may be designated, respectively, as *x*, *y*, and *z* [Figure 4(*a*)]. The but-2-yne $C\equiv C$ bonds are themselves aligned parallel to *z*. The $\sigma$ bond from CO to Mo is thus along *z*, and that from the two acetylenes, involving $\sigma$ donation from the orbital commonly designated $\pi_{\parallel}$, along *x* and *y*. Back-donation from Mo to CO will, therefore, involve $d_{xz}$ and $d_{yz}$, and the extent to which electrons in these orbitals are used to enhance the M–CO bond will imply correspondingly less interaction with the but-2-yne ligands. Now, although the principal bonding between each but-2-yne and the metal will involve $\sigma$ donation from the $\pi_{\parallel}$ ligand orbital to the metal [Figure 4(*b*)], two other important interactions are possible. These are (*i*) $\pi$ donation from the $\pi_{\perp}$ ligand orbital into the $d_{xy}$ orbital on the metal, and (*ii*) back-donation from the filled $d_{xz}$ and $d_{yz}$ orbitals on the metal into the antibonding ($\pi^*_{\parallel}$) orbital of each ligand. Each of these is estimated[14] to contribute *ca.* 10% of the total overlap, and is therefore by no means negligible. Two considerations immediately arise, however. First, in (*i*) both $\pi_{\perp}$ ligand orbitals are competing for the same metal orbital [Figure 4(*c*)] giving a three-centre four-electron interaction, but of these four electrons two are non-bonding. [The *cis*-$Mo(MeC_2Me)_2$ moiety has local $C_{2v}$ symmetry and produces $\pi_{\perp}$ orbital combinations of $a_1$ and $b_2$ symmetry. The $a_1$ combination overlaps effectively with $d_{xy}$, but the $b_2$ combination is non-bonding as there is no suitable metal orbital of $b_2$ symmetry.] The total electron donation is thus three electrons per but-2-yne ligand, comprising effectively 2 $\pi_{\parallel}$ and 1 $\pi_{\perp}$. Secondly, in (*ii*) the situation [Figure 4(*d*)] is very different for the carbonyl complex (1) as compared with the acetonitrile complex (2). Because there is virtually no $\pi$ back-donation to the acetonitrile in (2), evidence for which has already been given, there is effectively more electron density available in (2) to enhance the metal–acetylene bonding than in (1). The above discussion helps to interpret the observed geometries of other complexes[17–20] $[ML(RC_2R)_2(\eta\text{-}C_5H_5)]$ (M = Nb or W; L = CO or Cl; R = H, Ph, or $GePh_3$), which all have the alkyne ligands oriented parallel to the M–L axis.

Finally, the geometry of acetylene co-ordination, specifically the Mo–C bond lengths and C–C–C bend-back angles, lend support to our argument that the alkynes are acting as three-electron donors in the title complexes. Table 3 shows the Mo–C lengths and bend-back angles for a small selection of molybdenum complexes. The first three complexes are examples of four-electron donation, and the fourth is constrained by the effective atomic number rule to have two-electron donation.

Although there are variations caused by changing either the other ligands present or the acetylene substituents, it can be clearly seen that the values for complexes (1) and (2) are consistent with three-electron donation.

## Experimental

(*a*) $[Mo(CO)(MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ (1).—Crystals of (1) grow as tabular yellow prisms. Intensity data were collected at 220 K from a crystal of dimensions 0.60 × 0.30 × 0.50 mm in the range $2.9 \leqslant 2\theta \leqslant 50°$. Of the 2 665 independent intensities measured on a Nicolet $P2_1m$ four-circle diffractometer, only those 2 144 which satisfied the condition $I \geqslant 2.5\,\sigma(I)$ were used in subsequent solution and refinement of the structure. Check reflections $\bar{1}\bar{1}6$ and $0\bar{3}\bar{3}$ were remeasured every 50 reflections and showed no evidence of decay during the 63 h of exposure. Corrections were applied for Lorentz and polarisation effects, but not for the effects of *X*-ray absorption ($\mu = 8.9$ cm$^{-1}$).

*Crystal data for* (1). $C_{14}H_{17}BF_4MoO$, $M = 384.0$, Monoclinic, $a = 8.994(4)$, $b = 14.059(8)$, $c = 13.255(5)$ Å, $\beta = 116.23(3)°$, $U = 1\,503(1)$ Å$^3$, $D_m$ not measured, $Z = 4$, $D_c = 1.70$ g cm$^{-3}$, $F(000) = 768$, space group $P2_1/c$ (no. 14), Mo-$K_\alpha$ *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu$(Mo-$K_\alpha$) = 8.9 cm$^{-1}$.

The structure was solved by conventional heavy-atom

**Table 4**. Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for [Mo(CO)-(MeC$\equiv$CMe)$_2$($\eta$-C$_5$H$_5$)][BF$_4$] (1)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Mo | 0.825 45(4) | 0.747 44(2) | 0.189 29(2) |
| C(11) | 1.045 5(6) | 0.714 9(4) | 0.373 2(4) |
| C(12) | 0.891 3(6) | 0.698 7(4) | 0.372 9(4) |
| C(13) | 0.805 9(6) | 0.788 2(4) | 0.354 2(4) |
| C(14) | 0.908 7(6) | 0.857 6(3) | 0.340 7(4) |
| C(15) | 1.055 2(6) | 0.812 6(3) | 0.349 5(4) |
| C(1) | 0.598 0(5) | 0.690 8(3) | 0.125 5(4) |
| O(1) | 0.468 4(4) | 0.661 2(3) | 0.087 4(3) |
| C(2) | 1.152 7(6) | 0.665 4(4) | 0.160 4(4) |
| C(3) | 0.977 6(5) | 0.664 3(3) | 0.143 7(4) |
| C(4) | 0.838 2(5) | 0.622 7(3) | 0.101 3(4) |
| C(5) | 0.737 7(6) | 0.540 3(3) | 0.036 3(4) |
| C(6) | 0.933 8(6) | 0.949 0(4) | 0.106 8(4) |
| C(7) | 0.821 8(5) | 0.868 5(3) | 0.100 5(3) |
| C(8) | 0.675 7(5) | 0.834 2(3) | 0.050 0(3) |
| C(9) | 0.508 6(6) | 0.848 1(4) | −0.043 8(4) |
| B | 0.598 1(6) | 0.431 3(4) | 0.283 4(4) |
| F(1) | 0.688 0(4) | 0.388 8(3) | 0.387 6(3) |
| F(2) | 0.677 5(4) | 0.514 0(3) | 0.278 3(3) |
| F(3) | 0.591 4(4) | 0.369 7(3) | 0.200 1(3) |
| F(4) | 0.439 2(4) | 0.453 6(3) | 0.267 6(3) |

techniques and was refined by blocked-cascade least-squares methods. All non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms were incorporated at calculated positions in a ' riding ' mode,[21] and those of the methyl groups were constrained to tetrahedral geometry. Chemically equivalent hydrogen atoms were given a common isotropic thermal parameter which was allowed to refine. The data were weighted according to the scheme $w = [\sigma^2(F_o) + 0.002|F_o|^2]^{-1}$; refinement converged at *R* 0.048 (*R'* 0.052). The final electron-density difference synthesis showed no residual density $>1.53$ or $< -1.85$ e Å$^{-3}$, the largest peaks lying in close proximity to the molybdenum atom. Scattering factors, which included corrections for the effects of anomalous dispersion, were taken from ref. 22. All computations were carried out within the laboratory on a Data General ' Eclipse ' minicomputer using the SHELXTL system of programs.[23] The atomic co-ordinates for (1) are shown in Table 4.

**Table 5**. Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for [Mo(NCMe)-(MeC$\equiv$CMe)$_2$($\eta$-C$_5$H$_5$)][BF$_4$] (2)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| C(11) | 0.443 5(6) | 0.177 9(5) | 0.884 9(3) |
| C(12) | 0.565 0(6) | 0.242 7(5) | 0.919 1(3) |
| C(13) | 0.610 8(6) | 0.188 6(5) | 0.993 5(3) |
| C(14) | 0.517 6(6) | 0.090 4(5) | 1.005 3(3) |
| C(15) | 0.414 2(6) | 0.083 8(5) | 0.938 2(3) |
| C(111) | 0.523 4(8) | 0.230 7(5) | 0.900 5(4) |
| C(121) | 0.609 5(8) | 0.213 4(5) | 0.973 5(4) |
| C(131) | 0.552 2(8) | 0.113 9(5) | 1.013 5(4) |
| C(141) | 0.430 7(8) | 0.069 9(5) | 0.965 2(4) |
| C(151) | 0.412 9(8) | 0.142 1(5) | 0.895 4(4) |
| C(1) | 0.917 2(5) | 0.222 6(4) | 0.796 6(3) |
| C(01) | 1.025 1(6) | 0.300 5(4) | 0.757 8(4) |
| C(2) | 0.429 6(6) | −0.150 6(4) | 0.818 4(3) |
| C(3) | 0.546 9(5) | −0.058 5(4) | 0.812 0(3) |
| C(4) | 0.633 5(5) | −0.000 1(4) | 0.764 6(3) |
| C(5) | 0.679 5(6) | 0.018 4(5) | 0.677 2(3) |
| C(6) | 1.021 3(6) | −0.009 9(5) | 0.941 9(4) |
| C(7) | 0.852 2(6) | −0.018 7(4) | 0.935 4(3) |
| C(8) | 0.737 0(5) | −0.077 9(4) | 0.955 6(3) |
| C(9) | 0.680 6(6) | −0.182 0(4) | 0.998 7(3) |
| N | 0.831 0(5) | 0.162 5(3) | 0.826 2(3) |
| B | 0.784 6(6) | 0.563 1(5) | 0.827 7(4) |
| F(1) | 0.825 9(6) | 0.549 2(4) | 0.746 1(3) |
| F(2) | 0.733 7(5) | 0.459 3(4) | 0.857 8(3) |
| F(3) | 0.672 2(5) | 0.644 5(4) | 0.825 7(3) |
| F(4) | 0.905 3(6) | 0.602 0(4) | 0.871 1(4) |
| Mo | 0.661 84(4) | 0.057 49(2) | 0.884 33(2) |

(*b*) [Mo(NCMe)(MeC$_2$Me)$_2$($\eta$-C$_5$H$_5$)][BF$_4$] (2).—Crystals of (2) grow as yellow prisms. Data were collected in the range $2.9 \leqslant 2\theta \leqslant 60°$ at 200 K using a crystal of dimensions $0.45 \times 0.35 \times 0.40$ mm. Of the 2 719 independent intensities measured on a Nicolet *P*3*m* four-circle diffractometer, only those 2 466 with $I \geqslant 2.5\,\sigma(I)$ were used in structure solution and refinement. Check reflections $1\bar{5}\,\bar{5}$and 442 were remeasured every 50 reflections and showed no evidence of crystal decay during the 49 h of crystal exposure to *X*-radiation. Otherwise the procedure was as for (1).

*Crystal data for* (2). C$_{15}$H$_{20}$BF$_4$MoN, $M = 397.1$, Orthorhombic, $a = 8.780(4)$, $b = 11.656(4)$, $c = 16.225(6)$ Å, $U = 1\,660.4(10)$ Å$^3$, $D_m = 1.54$, $Z = 4$, $D_c = 1.59$ g cm$^{-3}$, $F(000) = 800$, space group $P2_12_12_1$ (no. 19), Mo-$K_\alpha$ *X*-radiation (graphite monochromator), $\lambda = 0.701\,69$ Å, $\mu$(Mo-$K_\alpha$) = 8.0 cm$^{-1}$.

The structure was solved by heavy-atom methods and was refined using blocked-cascade least-squares refinement. All non-hydrogen atoms were allowed anisotropic thermal parameters except for the carbon atoms of the cyclopentadienyl ligand which was positionally disordered. Hydrogen atoms were included at calculated positions and were refined in the same manner as those in the carbonyl derivative (1). The data were weighted according to the scheme $w = [\sigma^2(F_o) + 0.0002|F_o|^2]^{-1}$, and refinement converged at *R* 0.032 (*R'* 0.032). The final electron-density difference synthesis showed no features $>0.81$ or $< -0.66$ e Å$^{-3}$. A test to confirm that the correct enantiomer of the molecule had been located was carried out using $\eta$-refinement.[24] The parameter $\eta$ (coefficient of $f''$) refined to a value of 1.4(2) indicating a correct assignment of configuration. The atomic co-ordinates for (2) are shown in Table 5.

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