Synthesis, characterisation and reactivity of the first heptamethylindenyl–molybdenum complexes: crystal structures of [Mo(CO)(η²-MeC≡CMe)₂(η⁵-C₉Me₇)]BF₄ and [Mo(CO)₂(η³-C₃H₅)(η⁵-C₉Me₇)]

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Abstract

The synthesis and characterisation of the first (η⁵-heptamethylindenyl)molybdenum complexes are reported. Reaction of Li[C₉Me₇] with Mo(CO)₆ in refluxing THF readily forms Li[Mo(CO)₃(η⁵-C₉Me₇)], which is shown to be a useful precursor in the formation of (carbonyl)(η⁵-heptamethylindenyl)molybdenum complexes. The compounds [MoI(CO)₃(η⁵-C₉Me₇)] 3, [Mo(Me)(CO)₃(η⁵-C₉Me₇)] 4 and [Mo(CO)₂(η³-C₃H₅)(η⁵-C₉Me₇)] 5 have been prepared from this intermediate and characterised. Treatment of 3 with AgBF₄ and MeC≡CMe affords [Mo(CO)(MeC≡CMe)₂(η⁵-C₉Me₇)]BF₄ 6a; for this and the indenyl analogue, a new route to carbonyl-bis(alkyne)–molybdenum derivatives is demonstrated. Reaction of 3 with TlPF₆ in MeCN forms the complex [Mo(MeCN)₂(CO)₂(η⁵-C₉Me₇)]PF₆ 7. Protonation of 5 in the presence of MeC≡CMe, or reaction of 7 with the same acetylene, also yields 6 with appropriate counter anions. Single crystal X-ray diffraction studies of compounds 5 and 6a are reported.

Keywords: Molybdenum; Indenyl; Heptamethylindenyl; Permethylindenyl; Alkyne; Carbonyl; Crystal structure

1. Introduction

Transition metal alkyne complexes have for some time been of considerable theoretical and synthetic interest [1–4]; the former arising from the ligand's electronic flexibility and the development of appropriate bonding principles [5], and the latter from their utility both as synthetic intermediates [2,4,6] and as precursors to species in which carbon–carbon coupling takes place within the coordination sphere [7,8]. We and others have studied extensively the chemistry of alkynes at metal centres of the type {(η⁵-C₅H₅)Mo}, and have found that much of this chemistry is paralleled in analogues where the cyclopentadienyl group is replaced by other η⁵-ligands such as pentamethylcyclopentadienyl or indenyl. However, this has been complemented

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by many examples of complexes in which the differing steric and/or electronic properties of the η⁵-bound moiety have produced notable variations in behaviour, and often entirely different products [9].

The recent publication [10] of a straightforward synthesis of heptamethylindene, from which there is ready access to the (η⁵-)heptamethylindenyl (Ind*) ligand, has been followed by reports of various heptamethylindenyl complexes, including metallocene analogues [11] and compounds containing {(η⁵-C₉Me₇)M} fragments (M = Zr, Ti [12]; M = Rh [13]). As part of our continuing programme to expand the alkyne chemistry of compounds related to the above {(η⁵-C₅H₅)Mo}-containing parents, we have initiated a study of {(η⁵-C₉Me₇)Mo} species, in anticipation that the (now considerable) electronic and steric differences associated with the heptamethylindenyl ligand will result in unusual structure and chemistry. This paper describes the first (η⁵-heptamethylindenyl)molybdenum complexes, in which these enhanced effects are already evident. In the course of these preliminary studies, we have developed a new

route by which complexes of the type $[(L)Mo(\eta^2$-alkyne)$_2(CO)]^+$ (L = η^5-C$_9$H$_7$, η^5-C$_9$Me$_7$, etc.) may be prepared.

2. Discussion

A central aim at the outset of this work was the synthesis of cationic molybdenum–alkyne complexes of the type $[Mo(CO)(\eta^2$-alkyne)$_2(\eta^5$-C$_9$Me$_7)]^+$, prior to (future) conversion of these to other (η^5-heptamethylindenyl)molybdenum species. We generally prepare these bis(alkyne)carbonyl complexes by protonation (HBF$_4 \cdot$OEt$_2$) of species such as [Mo(Me)(CO)$_3$(η^5-C$_5$H$_5$)], followed by addition of the alkyne [14], or by the action of AgBF$_4$ upon dimeric precursors such as [Mo(CO)$_3$(η^5-C$_9$H$_7$)]$_2$ in the presence of the appropriate alkyne [15]; indeed, the intermediate [Mo(MeCN)$_2$(CO)$_2$(η^5-C$_9$H$_7$)]BF$_4$ can be isolated by reaction of this dimer with AgBF$_4$ in MeCN, and subsequently treated with the alkyne [15].

However, our preliminary studies indicated that in the present system the molybdenum dimer "[Mo(CO)$_3$(η^5-C$_9$Me$_7$)]$_2$" (compound **8**, see Section 4) could not readily be obtained in good yield or purity; and that, moreover, the alternative precursor [Mo(Me)(CO)$_3$(η^5-C$_9$Me$_7$)] was rather unstable in comparison with its cyclopentadienyl or indenyl relatives. Although these difficulties are far from insurmountable (and, indeed, we see no reason why these two should not ultimately become viable synthetic intermediates), we sought an alternative route to the above target bis(alkyne) complexes.

An appealing alternative was treatment of a halide derivative of {Mo(CO)$_3$(η^5-C$_9$Me$_7$)} with (for example) AgBF$_4$ in the presence of the appropriate alkyne. Accordingly, we have prepared the known [16–18] compound [MoI(CO)$_3$(η^5-C$_9$H$_7$)] **1**, and confirmed that it can be converted to the 'desired' product [Mo(CO)(η²-MeC≡CMe)$_2$(η^5-C$_9$H$_7$)]BF$_4$ **2** [15] as proposed.

Reaction (refluxing THF, 18 h) of Li[C$_9$Me$_7$] with Mo(CO)$_6$ affords Li[Mo(CO)$_3$(η^5-C$_9$Me$_7$)]; the progress of the reaction may be monitored by the disappearance of ν[Mo(CO)$_6$] in the CO stretching region. The latter lithium salt is very readily converted (at ambient temperature) to a variety of Mo complexes: with I$_2$, [MoI(CO)$_3$(η^5-C$_9$H$_7$)] **3** is formed in good yield (66%); whilst with MeI or CH$_2$=CHCH$_2$Cl, [Mo(Me)(CO)$_3$(η^5-C$_9$Me$_7$)] **4** or [Mo(CO)$_2$(η^3-C$_3$H$_5$)(η^5-C$_9$Me$_7$)] **5** (74%) respectively are obtained. Compound **3** is a brick-red solid, stable in air for several days, which may be stored under N$_2$ at $-30\,°$C for many months. We note that the routes to the compounds **1** and **3** here are rather more straightforward [from Mo(CO)$_6$] than that originally reported for **1**,

namely the oxidative addition of I$_2$ to [Mo(CO)$_3$(η^5-C$_9$H$_7$)]$_2$ [16,17].
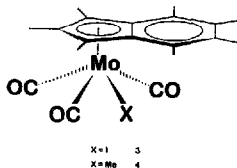
The Mo–methyl compound **4** is an orange–yellow solid. To date we have not fully characterised this species, as it decomposes rather significantly over just a few h at room temperature; solutions of **4** are particularly susceptible. In contrast, compound **5** is a bright-yellow solid, which is moderately air stable and, like **3**, may be stored unchanged for some time at $-30\,°$C under N$_2$. (Crystals of **5** survive at room temperature in air for several days.) In solution, **5** is perhaps rather less robust than **3**.
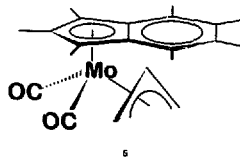
We have observed that **5** is formed via an η^1-C$_3$H$_5$ intermediate: this has been seen only by infrared spectroscopy; we have not attempted to isolate any such species. Although such a stepwise coordination of the elements of the allyl moiety is well-precedented [19], we note that in the present system the smoothness and facility with which the increase in allyl hapticity occurs is at least as great as that [16] for the indenyl analogue: the displacement of CO by the alkene residue proceeds to completion at room temperature over just a few h, accompanied by lightening of the reaction mixture and gentle effervescence. It is likely that the Ind* moiety undergoes an $\eta^5 \rightarrow \eta^3$ 'slip', which affords a coordination site for the pendant alkene residue; a subsequent $\eta^3 \rightarrow \eta^5$ movement causes CO loss. This may additionally be aided by the electronic influence of the Ind* ligand: since this causes the Mo centre to become relatively electron-rich, the Mo $\leftarrow$ (CO) σ (bonding) donation must decrease, weakening this attachment and

rendering the CO ligand more susceptible to displacement. [A similar effect presumably weakens the Mo ← Me bonding, destabilising compound 4; the latter, moreover, has no possibility (cf. 'η¹-allyl' precursor to 5) of gaining stability via internal reorganisation.]

In solution, 5 exists as a mixture of *exo*- and *endo*-isomers in an approximate ratio of 5:1 (by ¹H NMR spectroscopy), typical [20] for such a system. A single crystal X-ray diffraction study (see below) of 5 has confirmed the anticipated gross structure; in this determination, it is the *exo*-isomer that is also observed in the crystalline state.

When a CH_2Cl_2 solution of 3 is treated (25 °C) with AgBF₄ in the presence of excess but-2-yne, the iodo compound is converted to $[Mo(CO)(\eta^2\text{-}MeC\equiv CMe)_2(\eta^5\text{-}C_9Me_7)]BF_4$ 6a in very good yield (> 84%); in our experience this reaction appears to occur more cleanly than does that between $[Mo(Me)(CO)_3(\eta^5\text{-ligand})]$ and $HBF_4 \cdot OEt_2 / MeC\equiv CMe$, and the product also appears more easily purified. The salt 6a is also formed, in similar yields, by protonation (−78 °C, $HBF_4 \cdot OEt_2$) of 5, followed by addition of excess but-2-yne. [We assume that this proceeds via $[Mo(CO)_2(\eta^2\text{-}CH_2=CHCH_3)(\eta^5\text{-}C_9Me_7)]BF_4$, stabilised by Mo ⋯ H interactions at the propene methyl group.] Here, again, the crude product obtained on evaporation of the reaction mixture is purified by simple pentane washing. We are not aware of any previous use of this last route to obtain (bis-alkyne) complexes of this type.

Z = BF₄ 6a
Z = PF₆ 6b
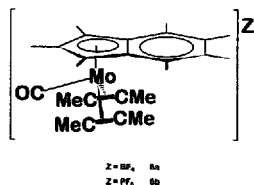
The blood-red microcrystalline solid 6 is similar in air and temperature stability to 3 and 5. Compound 6a has been fully characterised spectroscopically, and by a single crystal X-ray diffraction study (see later). As was expected, the ¹³C chemical shifts of the alkyne contact carbon atoms (mean 159 ppm) confirm the two but-2-yne ligands both to be (on average) 3-electron donors [3,21]; likewise, other spectroscopic features are not unusual.

The bis-acetonitrile compound *cis*-$[Mo(MeCN)_2(CO)_2(\eta^5\text{-}C_9Me_7)]PF_6$ 7 was obtained in very good yield (ca. 85%) by treatment of 3 with TlPF₆ in MeCN. Compound 7 is a dark orange solid, similar

in stability to 3, 5 and 6, and to analogues such as the {η⁵-C₅Me₅} and {η⁵-C₉H₇} derivatives. To our knowledge, this ready route to such bis(acetonitrile)–dicarbonyl complexes of molybdenum has not previously been exploited. We have shown that 7 may be converted to the PF₆ salt of 6 (i.e. 6b) by reaction with MeC≡CMe. However, we note that, in contrast to the indenyl analogue of 7, which readily forms 2 [15], the 7 → 6b transformation appears to be accompanied by some decomposition. (At present we are unable fully to account for this.)

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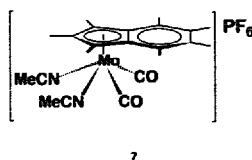
As a complement to our synthetic studies, we have also determined the solid state structures of 5 and 6a by single crystal X-ray diffraction methods with a view to examining any effects arising from the presence of the heptamethylindenyl ligand. Perspective views of 5 and of the cation in 6a are shown in Figs. 1 and 2 respectively. In Tables 1 and 2 are listed selected interatomic
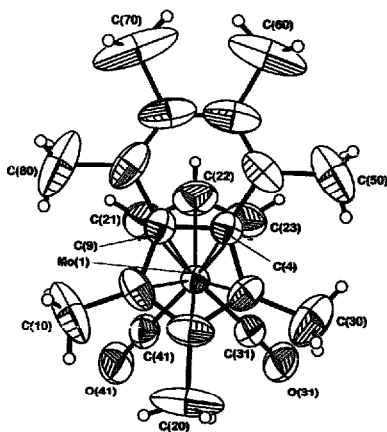

Fig. 1. Perspective view of 5, drawn with 50% probability thermal ellipsoids, except for H atoms which have artificial radii for clarity. The atomic numbering is such that the methyl carbon atom C(nO) is bound to the ring carbon atom C(n). Note the 'slip' of the Mo atom (cf. Fig. 3).
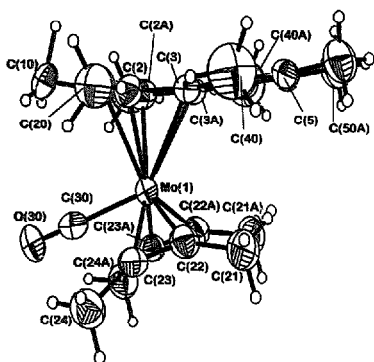
Fig. 2. Perspective view of a whole cation of 6a (drawn with the same conventions as in Fig. 1). Atoms labelled with a terminal 'A' are generated by x, $1 - y$, z; heptamethylindenyl carbon atoms are numbered $C(n)/C(nO)$ or $C(nA)/C(nOA)$ as in Fig. 1.

distances and interbond angles for 5 and 6a respectively.

As Fig. 1 shows, molecules of 5 have approximate mirror symmetry, with the two carbonyl ligands lying *trans* to the ring junction of the C_9Me_7 group; the overall arrangement is broadly similar to that in

$[Mo(CO)_2(\eta^3-1'-Me-C_3H_4)(\eta^5-C_9H_7)]$ A [22]. In detail, the structure determined for 5 differs little from that of A: the C–O distances in 5 are numerically shorter than the corresponding distances in the above indenyl analogue, but not significantly so; and the Mo–CO separations are essentially identical to those in A. The Mo–C–O angles deviate slightly more from linearity than previously, but again this is not to any significant extent. The internal geometry of the $(\eta^3-C_3H_5)$ ligand, and the distances and angles from this to Mo(1), similarly do not differ significantly from those in A, with the possible exception of the C(21)–C(22) and C(22)–C(23) separations, at 1.359(10) and 1.337(11) Å respectively, which are perhaps slightly shorter than the corresponding distances [1.373(8) and 1.359(8) Å] in the indenyl relative. Finally, the dihedral angle between the plane of the allyl carbon atoms and that of the C_5 residue of $\eta^5-C_9H_7$ in 5 is 30.3° (cf. 31.9° in A), perhaps as a consequence of the spatial demands of the Ind* ligand.

As has been noted [22] in a variety of indenyl, and indeed heptamethylindenyl, complexes, the formally *penta-hapto* residue of the Ind* ligand in 5 departs from a locally symmetrical Mo–$\{C_5\}$ arrangement. This generally occurs such that the Mo atom 'slips' away from the two carbon atoms at the ring junction (cf. Figs. 1 and 3), resulting in a Δ value [22] of 0.129 Å similar to that (0.144 Å) in A, and is accompanied by a 'fold-

Table 1
Selected bond lengths (Å) and interbond angles (°) for compound 5

Mo(1)–C(1)	2.338(5)	C(2)–C(3)	1.408(9)
Mo(1)–C(2)	2.307(6)	C(3)–C(4)	1.438(7)
Mo(1)–C(3)	2.334(6)	C(4)–C(5)	1.432(8)
Mo(1)–C(4)	2.414(5)	C(4)–C(9)	1.421(7)
Mo(1)–C(9)	2.429(5)	C(5)–C(6)	1.354(11)
Mo(1)–C(21)	2.337(6)	C(6)–C(7)	1.379(12)
Mo(1)–C(22)	2.209(6)	C(7)–C(8)	1.373(11)
Mo(1)–C(23)	2.322(6)	C(8)–C(9)	1.455(8)
Mo(1)–C(31)	1.947(6)	C(21)–C(22)	1.359(10)
Mo(1)–C(41)	1.938(6)	C(22)–C(23)	1.337(11)
C(1)–C(2)	1.427(9)	C(31)–O(31)	1.154(7)
C(1)–C(9)	1.427(8)	C(41)–O(41)	1.152(7)
C(22)–Mo(1)–C(21)	34.6(3)	C(9)–C(4)–C(5)	120.6(5)
C(22)–Mo(1)–C(23)	34.2(3)	C(6)–C(5)–C(4)	118.5(7)
C(23)–Mo(1)–C(21)	62.7(3)	C(5)–C(6)–C(7)	121.9(7)
C(41)–Mo(1)–C(31)	78.5(2)	C(8)–C(7)–C(6)	122.9(6)
C(31)–Mo(1)–C(21)	116.1(3)	C(7)–C(8)–C(9)	117.7(6)
C(41)–Mo(1)–C(21)	75.2(3)	C(4)–C(9)–C(1)	108.2(5)
C(31)–Mo(1)–C(22)	107.9(3)	C(1)–C(9)–C(8)	133.4(6)
C(41)–Mo(1)–C(22)	106.2(3)	C(4)–C(9)–C(8)	118.3(5)
C(31)–Mo(1)–C(23)	76.3(3)	C(21)–C(22)–C(23)	127.9(9)
C(41)–Mo(1)–C(23)	112.6(3)	C(21)–C(22)–Mo(1)	77.9(4)
C(9)–C(1)–C(2)	107.0(5)	C(22)–C(23)–Mo(1)	68.3(4)
C(3)–C(2)–C(1)	109.6(5)	C(22)–C(21)–Mo(1)	67.5(4)
C(2)–C(3)–C(4)	107.0(5)	C(23)–C(22)–Mo(1)	77.5(4)
C(5)–C(4)–C(3)	131.2(6)	O(31)–C(31)–Mo(1)	177.7(6)
C(9)–C(4)–C(3)	108.2(5)	O(41)–C(41)–Mo(1)	176.9(6)

Table 2
Selected bond lengths (Å) and interbond angles (°) for compound 6a [a]

Mo(1)–C(1)	2.366(11)	C(3)–C(2)	1.444(10)
Mo(1)–C(2)	2.356(8)	C(3)–C(3A)	1.43(2)
Mo(1)–C(3)	2.457(7)	C(3)–C(4)	1.438(11)
Mo(1)–C(22)	2.081(8)	C(4)–C(5)	1.361(13)
Mo(1)–C(23)	2.129(8)	C(5)–C(5A)	1.44(2)
Mo(1)–C(30)	2.005(12)	C(21)–C(22)	1.491(11)
O(30)–C(30)	1.113(13)	C(23)–C(22)	1.274(11)
C(1)–C(2)	1.412(10)	C(24)–C(23)	1.497(11)
C(30)–Mo(1)–C(22)	109.9(3)	C(3A)–C(3)–C(4)	120.0(5)
C(22)–Mo(1)–C(22A)	91.5(5)	C(5)–C(4)–C(3)	118.5(8)
C(30)–Mo(1)–C(23)	75.1(3)	C(4)–C(5)–C(5A)	121.6(6)
C(22)–Mo(1)–C(23)	35.2(3)	C(21)–C(22)–Mo(1)	139.0(7)
C(22)–Mo(1)–C(23A)	108.1(3)	C(23)–C(22)–Mo(1)	74.4(5)
C(23)–Mo(1)–C(23A)	103.8(4)	C(23)–C(22)–C(21)	146.5(9)
C(2)–C(1)–C(2A)	109.9(9)	C(22)–C(23)–Mo(1)	70.4(5)
C(1)–C(2)–C(3)	107.1(7)	C(24)–C(23)–Mo(1)	143.5(6)
C(4)–C(3)–C(2)	132.1(8)	C(22)–C(23)–C(24)	146.1(8)
C(3A)–C(3)–C(2)	107.7(5)	O(30)–C(30)–Mo(1)	178.8(9)

[a] Symmetry transformation used to generate equivalent atoms: A $x, -y + 1, z$.

ing' of the ligating C_5 ring with $\Omega = 3.0°$ [22], identical to that in the analogue A. The C_5 and C_6 rings of the C_9Me_7 ligand are almost coplanar, having an interplanar angle of only 2.1°.

The influence of intramolecular crowding due to the Ind* ligand is somewhat more pronounced in the structure determined for the cation 6 in the BF_4 salt 6a. The cation has crystallographically imposed C_s symmetry and, as may be seen in Fig. 2, the two acetylenic moieties lie nearly parallel to each other and to the carbonyl ligand. This mirrors the situation in the η^5-C_5H_5 analogue B [23], and in other related species $[Mo(X)(\eta^2-RC\equiv CR)_2(\eta^5-C_5H_5)]^{n+}$ (R = Me, X = NCMe, $n = 1$ C [23]; R = Me, X = I, $n = 0$ D [8]; R = Ph, X = CO, $n = 1$ E [24]). Likewise, the Mo(1)–C(30)–O(30) angle is not far from 180°; and the Mo(1)–C(30) and C(30)–O(30) distances are not far from those in the cyclopentadienyl relative B. As was noted above for 5, the Mo atom suffers 'slippage' away from the C_5/C_6 ring junction, having $\Delta = 0.115$ Å.

The most serious distortion in 6a, which is almost certainly a consequence of the presence of the bulky Ind* ligand, is a depression in the 'tilt angle' of the

Fig. 3. The 'slipping' and 'folding' parameters Δ and Ω.

acetylenes. Generally, the dihedral angle between the C_5 plane of the η^5-ligand and the plane defined by the four acetylenic carbon atoms is ca. 25°: for the four analogues of 6 listed above it is, respectively, 29.7 (B), 22.7 (C), 26.6 (D) and 26.4° (E). In 6, this interplane angle is only 17.3°, some 12° less than in B, the most comparable analogue. In addition, the C_5 and C_6 planes of the C_9Me_7 ligand are inclined at 6° to each other. There is, moreover, a larger folding of the coordinating C_5 ring in 6a ($\Omega = 6.6°$) than in 5. Perhaps somewhat surprisingly, these effects are not accompanied by any significant compression in the C–C–Me angles, nor by any change in the Mo–C_{alkyne} or acetylenic C–C distances, although the above noted changes in interplanar angles may be sufficient to accommodate the enhanced congestion.

3. Conclusion

We have described the synthesis and characterisation of a variety of new molybdenum complexes, the first to be reported containing the η^5-C_9Me_7 ligand, and have demonstrated facile interconversions between these species; a number of these routes may find wider application as synthetic approaches in organomolybdenum chemistry. In future studies, we intend to investigate more fully the reaction chemistry of 6, and of other heptamethylindenyl–molybdenum species reported herein, with some emphasis on electronic effects and the anisotropic steric requirements of the Ind* ligand. The present work, and other preliminary studies [25], suggest this area to have considerable potential.
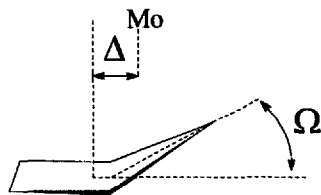
4. Experimental details

4.1. Synthesis and characterisation

All manipulations were performed under an atmosphere of dry, oxygen-free N_2 using standard Schlenk line techniques. C_9Me_7H was prepared by literature methods [10]; all other reagents were used as received.

4.1.1. Preparation of $[MoI(CO)_3(\eta^5\text{-}C_9H_7)]$ (1)

A solution of freshly-distilled indene (1.0 cm³, 1.0 g, 8.62 mmol) in THF (50 cm³) was cooled to 0 °C and ⁿBuLi (5.5 cm³ of 1.6 M solution in hexane, 8.8 mmol) added; the stirred (0 → 25 °C) solution rapidly became yellow. After 30 min, $Mo(CO)_6$ (1.90 g, 7.20 mmol) was added and the mixture heated to reflux temperature for 18 h. The resulting dark red–brown solution of $Li[Mo(CO)_3(\eta^5\text{-}C_9H_7)]$ was cooled and a solution of I_2 (2.0 g, 7.87 mmol) in THF (10 cm³) added, producing a very dark red solution which was stirred for a further 2 h. Removal of volatiles in vacuo afforded a dark, viscous oil which was subjected to column chromatography (Florisil®, $Et_2O:CH_2Cl_2$ 3:2); a broad red band was collected, evaporated in vacuo, and washed with pentane (3 × 25 cm³, 0 °C) to afford essentially pure 1 as a brick-red solid. Yield 2.16 g, 5.11 mmol, 71.0%.

Anal. Found: C, 34.7; H, 1.86. $C_{12}H_7IMoO_3$ Calc: C, 34.2; H, 1.67%. IR (CH_2Cl_2): ν(CO) 2041 and 1972 cm⁻¹. ¹H NMR (CD_2Cl_2): δ 7.53 (dd, 2H, benzenoid H on C_9H_7; $^3J_{HH}$ 6.3, $^4J_{HH}$ 3.0 Hz), 7.31 (dd, 2H, benzenoid H on C_9H_7), 6.03 (d, 2H, H on C_5 ring of C_9H_7; $^3J_{HH}$ 2.9 Hz), 5.45 (t, 1H, unique H on C_5 ring of C_9H_7) ppm. ¹³C{¹H} NMR (CD_2Cl_2): δ 238.1 (CO), 220.2 (2CO), 128.7 (benzenoid CH on C_9H_7), 127.2 (benzenoid CH on C_9H_7), 114.7 (C, ring junction of C_9H_7), 91.3 (unique CH on C_5 ring of C_9H_7), 82.4 (2CH on C_5 ring of C_9H_7) ppm. FAB MS: m/z^+ 424 (M⁺, $^{12}C_{12}^{1}H_7^{127}I^{98}Mo^{16}O_3$), 396 (M − CO)⁺, 340 (M − 2CO)⁺, 115 ($^{12}C_9^{1}H_7^+$; m/z^- 127 ($^{127}I^-$).

4.1.2. Reaction of 1 with $AgBF_4$ in the presence of $MeC\equiv CMe$: formation of $[Mo(CO)(MeC\equiv CMe)_2(\eta^5\text{-}C_9H_7)]BF_4$ (2)

A solution of 1 (0.10 g, 0.24 mmol) in CH_2Cl_2 (20 cm³) was cooled to −78 °C. Solid $AgBF_4$ (0.046 g, 0.24 mmol) and MeC≡CMe (74 μl, 51 mg, 0.9 mmol) were added; the mixture was allowed to warm and was stirred for 18 h. The resultant was filtered (Celite®) and evaporated in vacuo to give a yellow solid, which was washed with pentane (3 × 15 cm³). The product was confirmed to be 2 by comparison of IR and ¹H NMR spectra with those published [15].

IR (CH_2Cl_2): ν(CO) 2053 cm⁻¹. ¹H NMR (CD_2Cl_2): δ 7.49 (dd, 2H, H on C_6 ring of C_9H_7; $^3J_{HH}$ 6.5, $^4J_{HH}$ 3.1 Hz), 7.21 (dd, 2H, H on C_6 ring of C_9H_7), 6.62 (d, 2H, H on C_5 ring of C_9H_7; $^3J_{HH}$

3.2 Hz), 5.89 (t, 1H, unique H on C_5 ring of C_9H_7), 3.04 (br, 6H, ≡CCH_3), 2.50 (br, 6H, ≡CCH_3) ppm.

4.1.3. Preparation of $[MoI(CO)_3(\eta^5\text{-}C_9Me_7)]$ (3)

In a manner analogous to that by which 1 was obtained, an intense red solution of $Li[C_9Me_7]$ in THF (50 cm³) was formed from C_9Me_7H (1.30 g, 6.06 mmol) and ⁿBuLi (3.8 cm³ of 1.6 M solution, 6.08 mmol). $Mo(CO)_6$ (1.601 g, 6.06 mmol) was added, the mixture refluxed for 18 h, and I_2 (1.55 g, 6.11 mmol in 10 cm³ THF) added dropwise at room temperature to the dark red–brown $Li[Mo(CO)_3(\eta^5\text{-}C_9Me_7)]$ solution. Evaporation, then column chromatography (Florisil®, $Et_2O:CH_2Cl_2$ 1:1) and evaporation of the resulting (collected) deep red band afforded crude 3 as a brick-red solid. A second, carbonyl-containing contaminant (unidentified) was removed from the product by washing with pentane (3 × 20 cm³, 0 °C), to give essentially pure 3. Yield 1.98 g, 4.02 mmol, 66.4%.

Anal. Found: C, 44.8; H, 4.27. $C_{19}H_{21}IMoO_3$ Calc: C, 43.9; H, 4.07%. IR (CH_2Cl_2): ν(CO) 2027 and 1954 cm⁻¹. ¹H NMR (CD_2Cl_2): δ 2.62 (6H, C_9Me_7), 2.49 (6H, C_9Me_7), 2.28 (6H, C_9Me_7), 2.02 (3H, C_9Me_7) ppm. ¹³C{¹H} NMR (CD_2Cl_2): δ 241.5 (CO), 222.7 (CO), 137.4 (C_9Me_7), 130.8 (C_9Me_7), 113.8 (C_9Me_7), 111.5 (C_9Me_7), 95.7 (C_9Me_7), 17.4 (C_9Me_7), 16.9 (C_9Me_7), 14.5 (C_9Me_7), 11.5 (C_9Me_7) ppm. FAB MS: m/z^+ 494 [(M − CO)⁺, $^{12}C_{18}^{1}H_{21}^{127}I^{98}Mo^{16}O_2$], 438 (M − 3CO)⁺, 213 ($^{12}C_{16}^{1}H_{21}$); m/z^- 127 ($^{127}I^-$).

4.1.4. Preparation of $[Mo(Me)(CO)_3(\eta^5\text{-}C_9Me_7)]$ (4)

A solution of $Li[Mo(CO)_3(\eta^5\text{-}C_9Me_7)]$ in THF (25 cm³) was prepared as before (3) from C_9Me_7H (0.5 g, 2.33 mmol), ⁿBuLi (1.5 cm³ of 1.6 M solution, 2.40 mmol) and $Mo(CO)_6$ (0.61 g, 2.31 mmol). To this was added dropwise (0 °C) a solution of MeI (0.15 cm³, 0.355 g, 2.36 mmol) in THF (10 cm³). After 3 h, the solution was evaporated in vacuo, and the resulting yellow–brown solid applied to a chromatographic column (alumina, CH_2Cl_2). A single mobile orange–yellow band was collected, evaporated in vacuo, and crystallised from pentane at −30 °C to give 4 as an orange–yellow powder. Yield 0.38 g, 0.93 mmol, 40.2%.

The product appeared rather unstable and no satisfactory microanalysis could be obtained. IR (CH_2Cl_2): ν(CO) 2004, 1921 cm⁻¹. ¹H NMR (CD_2Cl_2): δ 2.65 (6H, C_9Me_7), 2.37 (6H, C_9Me_7), 2.32 (3H, C_9Me_7 or Mo*Me*), 2.20 (6H, C_9Me_7), 2.14 (3H, C_9Me_7 or Mo*Me*) ppm. FAB MS: m/z^+ 410 (M⁺, $^{12}C_{20}^{1}H_{24}^{98}Mo^{16}O_3$), 382 (M − CO)⁺, 326 (M − 3CO)⁺, 213 ($^{12}C_{16}^{1}H_{21}$)⁺.

4.1.5. Preparation of $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_9Me_7)]$ (5)

A THF solution of $Li[Mo(CO)_3(\eta^5\text{-}C_9Me_7)]$ was prepared as for 3 above from C_9Me_7H (0.5 g,

2.33 mmol), ^{n}BuLi (1.5 cm^3 of 1.6 M solution, 2.40 mmol) and Mo(CO)$_6$ (0.61 g, 2.31 mmol). To this was added dropwise (0 °C) a solution of CH$_2$=CHCH$_2$Cl (0.19 cm^3, 0.182 g, 2.38 mmol) in THF (10 cm^3), during which the colour of the reaction mixture lightened slightly. IR spectroscopy of the solution showed two peaks, at 2002 and 1923 cm^{-1}. The molybdenum complex formed initially in solution is almost certainly [Mo(η^1-C$_3$H$_5$)(CO)$_3$(η^5-C$_9$Me$_7$)]. As stirring of the reaction mixture continued, the colour lightened further and a gas (CO?) was evolved. Monitoring of reaction progress during this time by IR spectroscopy confirmed the loss of a carbonyl ligand and the presumed $\eta^1 \rightarrow \eta^3$ conversion of the allyl ligand. After 3 h, the solution was evaporated in vacuo, and the resulting yellow–brown solid applied to a chromatographic column (alumina/pentane). The column was first eluted with 3:1 pentane/Et$_2$O to remove organic residues. Upon switching to CH$_2$Cl$_2$ as eluant, a single, mobile, bright yellow band was collected; this was evaporated in vacuo, and crystallised from pentane at −30 °C to give yellow crystals of pure 5. Yield 0.70 g, 1.72 mmol, 74.5%.

Anal. Found: C, 61.7; H, 6.45. C$_{21}$H$_{26}$MoO$_2$ Calc: C, 62.1; H, 6.45%. IR (CH$_2$Cl$_2$): ν(CO) 1933 and 1846 cm^{-1}.

exo   *endo*
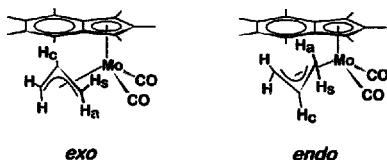
^{1}H NMR (CD$_2$Cl$_2$): δ [*exo*-isomer] 2.64 (6H, C$_9$Me$_7$), 2.36 (6H, C$_9$Me$_7$), 2.19 (6H, C$_9$Me$_7$), ca. 2.17 (2H, H$_s$, partly obscured), 2.13 (3H, C$_9$Me$_7$), 1.80 (2H, H$_a$, $^3J_{ac} \approx$ 11.1 Hz), 0.29 (1H, H$_c$) [$^2J_{sa}$ and $^3J_{sc} <$ 0.4 Hz, not resolved]; [*endo*-isomer] 3.34 (2H, H$_a$), 2.67 (6H, C$_9$Me$_7$), ca. 2.6 (1H, H$_c$), 2.37 (6H, C$_9$Me$_7$), 2.32 (6H, C$_9$Me$_7$), 2.22 (3H, C$_9$Me$_7$), −0.94 (2H, H$_s$, $^3J_{ac} \approx$ 10.6 Hz) [$^2J_{sa}$ and $^3J_{sc} <$ 0.4 Hz, not resolved] ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ [*exo*-isomer] 240.7 (CO), 132.1 (C$_9$Me$_7$), 127.5 (C$_9$Me$_7$), 109.4 (C$_9$Me$_7$), 107.9 (C$_9$Me$_7$), 90.5 (C$_9$Me$_7$), 83.7 (CH$_2$CHCH$_2$), 46.9 (CH$_2$CHCH$_2$), 16.7 (C$_9$Me$_7$), 16.4 (C$_9$Me$_7$), 14.8 (C$_9$Me$_7$), 12.5 (C$_9$Me$_7$) ppm. [Resonances due to the *endo*-isomer could not be resolved.] FAB MS: m/z^+ 408 (M$^+$, ^{12}C$_{21}$^{1}H$_{26}$^{98}Mo^{16}O$_2$), 380 (M − CO)$^+$, 365 (M − C$_3$H$_5$)$^+$, 352 (M − 2CO)$^+$, 324 (M − 3CO)$^+$, 322 (M − CO–C$_3$H$_5$)$^+$, 213 (^{12}C$^1_{16}$H$_{21}$).

A single crystal of 5 suitable for X-ray diffraction analysis was obtained by cooling a pentane solution to −30 °C for several days.

4.1.6. Reaction of 3 with AgBF$_4$ in the presence of MeC≡CMe: formation of [Mo(CO)(MeC≡CMe)$_2$(η^5-C$_9$Me$_7$)]BF$_4$ (6a)

By a route analogous to that by which 2 was formed above, reaction between 3 (1.00 g, 1.92 mmol), AgBF$_4$ (0.38 g, 1.95 mmol) and MeC≡CMe (10 cm^3, 6.91 g, 128 mmol) in CH$_2$Cl$_2$ (20 cm^3), and similar work-up, afforded 6a as a blood-red solid. Yield 0.86 g, 1.62 mmol, 84.4%.

Anal. Found: C, 56.4; H, 6.12. C$_{25}$H$_{33}$BF$_4$MoO Calc: C, 56.4; H, 6.25%. IR (CH$_2$Cl$_2$): ν(CO) 2033 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.61 (6H, Me), 2.55 (12H, Me), 2.54 (6H, Me), 2.26 (6H, Me), 1.87 (3H, C$_9$Me$_7$) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 224.3 (CO), 168.7 (≡CC), 149.1 (≡CC), 137.9 (C$_9$Me$_7$), 126.9 (C$_9$Me$_7$), 118.8 (C$_9$Me$_7$), 116.6 (C$_9$Me$_7$), 100.0 (C$_9$Me$_7$), 36.3 (≡CC), 17.2 (≡CC or C$_9$Me$_7$), 16.8 (≡CC or C$_9$Me$_7$), 15.0 (≡CC or C$_9$Me$_7$), 14.2 (≡CC or C$_9$Me$_7$), 11.2 (≡CC or C$_9$Me$_7$) ppm. FAB MS (M$^+$BF$_4^-$): m/z^+ 447 (M$^+$, ^{12}C$_{25}$H$_{33}^{98}$Mo^{16}O), 419 (M − CO)$^+$; m/z^- 87 (^{11}B^{19}F$_4$)$^-$.

Crystals of 6a suitable for an X-ray diffraction study were obtained by slow diffusion of hexane into a concentrated CH$_2$Cl$_2$ solution at −30 °C.

4.1.7. Reaction of 5 with HBF$_4$ · OEt$_2$ and subsequent addition of MeC≡CMe: alternative route to 6a

A CH$_2$Cl$_2$ (25 cm^3) solution of 5 (0.350 g, 0.87 mmol) was cooled to −78 °C and HBF$_4$ · OEt$_2$ (182 μl of 85% solution, 155 mg, 0.95 mmol) added, producing a rapid yellow → burgundy colour change. After 15 min, but-2-yne (0.25 cm^3, 0.173 g, 3.2 mmol) was added and the mixture allowed to warm slowly to room temperature. After 2 h, infrared spectroscopy confirmed the reaction to be complete. Volatiles were removed in vacuo to yield a sticky red solid. Washing with pentane (3 × 20 cm^3) afforded essentially pure 6a, identified by infrared and ^{1}H NMR spectroscopy and microanalysis. Yield 386 mg, 0.73 mmol, 83.4%

4.1.8. Preparation of [Mo(MeCN)$_2$(CO)$_2$(η^5-C$_9$Me$_7$)]PF$_6$ (7)

Compound 3 (1.00 g, 1.92 mmol) and TlPF$_6$ (0.70 g, 2.00 mmol) were suspended in MeCN (30 cm^3) and stirred at room temperature. A yellow precipitate (TlI) rapidly formed; monitoring of the reaction by IR spectroscopy revealed gradual formation of the bis(MeCN) product, with no evidence of a mono-(MeCN)-substituted species. When the reaction was deemed complete (16 h), volatiles were removed in vacuo and the orange residue extracted with CH$_2$Cl$_2$ (2 × 30 cm^3); the

resulting suspension was filtered (Celite[8]) and the filtrate concentrated by evaporation in vacuo to $10 \, cm^3$. Slow addition of pentane ($100 \, cm^3$) and cooling ($-30 \, °C$) afforded the product as dark red–orange crystals. Yield 0.97 g, 1.63 mmol, 84.9%.

Anal. Found: C, 44.0; H, 4.59; N, 4.54. $C_{22}H_{27}F_6MoN_2O_2P$ Calc: C, 44.6; H, 4.59; N, 4.73%. IR (CH_2Cl_2): ν(CO) 1973 and $1890 \, cm^{-1}$. ^1H NMR (CD_2Cl_2): δ 2.55 (6H, C_9Me_7), 2.50 (6H, C_9Me_7), 2.37 (6H, $MeCN^*$), 2.30 (6H, C_9Me_7), 1.84 (3H, C_9Me_7) [* resonance disappears on addition of trace CD_3CN] ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 251.4 (CO), 140.0 (MeCN or C_9Me_7), 138.5 (C_9Me_7 or MeCN), 131.1 (C_9Me_7), 117.2 (C_9Me_7), 108.7 (C_9Me_7), 92.6 (C_9Me_7), 17.2 (C_9Me_7), 17.1 (C_9Me_7), 14.5 (C_9Me_7), 11.7 (C_9Me_7), 3.9 (MeCN) ppm. FAB MS ($M^+BF_4^-$): m/z^+ 408 [(M − NCMe)$^+$, $^{12}C_{20}^1H_{24}^{98}Mo^{14}N^{16}O_2$], 213 ($^{12}C_{16}^1H_{21}$)$^+$; m/z^- 145 ($^{31}P^{19}F_6$)$^-$.

4.1.9. Reaction of 7 with MeC≡CMe: formation of [Mo(CO)(MeC≡CMe)$_2$(η^5-C_9Me_7)]PF$_6$ (6b)

Reaction between 7 and MeC≡CMe (4 equiv.) in CH_2Cl_2 solution (monitored by IR spectroscopy) readily formed the bis-alkyne product. In addition, IR spectroscopic monitoring suggested the presence of [Mo(CO)$_2$(MeC≡CMe)(η^5-C_9Me_7)]PF$_6$ as an intermediate [IR approx. ν(CO) 2055 and $1990 \, cm^{-1}$] in this reaction. After ca. 15 h, the reaction mixture had become very dark, and the IR spectrum (CO stretching region) of an aliquot suggested exclusive formation of the bis-alkyne product. However, the colouration of the reaction mixture perhaps suggests that eliminated MeCN may interfere with the reaction, and some decomposition was suspected.

4.1.10. Attempted preparation of [Mo(CO)$_3$(η^5-C_9Me_7)]$_2$ (8)

A THF solution ($150 \, cm^3$) of Li[Mo(η^5-C_9Me_7)(CO)$_3$] was prepared as above from C_9Me_7H (1.65 g, 7.7 mmol), ^nBuLi ($5 \, cm^3$ of 1.6 M solution, 8.0 mmol) and Mo(CO)$_6$ (2.0 g, 7.6 mmol), and cooled to 0 °C. A solution of Ph$_3$CCl (2.147 g, 7.7 mmol) in CH_2Cl_2 ($20 \, cm^3$) was added dropwise over ca. 30 min. The reaction mixture gradually became an intense dark red colour; after a further 30 min, volatiles were removed in vacuo and the dark residue subjected to column chromatography (alumina). Initial elution with hexane afforded a very broad dark red band (trityl dimers). After this, CH_2Cl_2 as eluant produced a very slow-moving red–purple band, collected and tentatively identified (IR and ^1H NMR spectroscopy) as 8. The very poorly soluble crude product so obtained was in only very poor yield (< 100 mg), and apparently contaminated with both a second carbonyl-containing species and trityl dimers.

IR (CH_2Cl_2): ν(CO) 1904 (s, br) and 1931 (m). ^1H

NMR (CD_2Cl_2): δ 2.48 (6H, C_9Me_7), 2.30 (6H, C_9Me_7), 2.04 (6H, C_9Me_7), 2.03 (3H, C_9Me_7) ppm.

4.2. Crystallographic studies

Crystal data and details of data collection and structure refinement for compounds 5 and 6a are listed in Table 3. Reflection data were measured at 293(2) K on a Siemens P4 automatic four-circle diffractometer operating in the ω-scan mode using graphite monochromated Mo Kα X-radiation ($\bar{\lambda} = 0.71073 \, Å$). Cell parameters and the orientation matrix were determined from 26 accurately measured reflections. For both data sets a semi-empirical absorption correction (psi scans) was performed. In the latter stages of refinement, data were weighted according to $w^{-1} = [\sigma^2(F_o^2) + g_1^2P^2 + g_2P]$ where $P = (F_o^2 + 2F_c^2)/3$. Figs. 1 and 2 show perspective views of 5 and of the cation in 6a respectively. Tables 1 and 2 list selected interatomic distances and interbond angles for 5 and 6a respectively. Fractional atomic coordinates for compounds 5 and 6a are listed in Tables 4 and 5 respectively. Full lists of bond

Table 3

Crystallographic data and details of data collection and structure refinement for compounds 5 and 6a

Compound	5	6a
Formula	$C_{21}H_{26}MoO_2$	$C_{25}H_{33}BF_4MoO$
M_r	406.36	532.26
System	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/m$
a (Å)	12.3952(13)	19.4658(19)
b (Å)	9.5466(9)	17.636(3)
c (Å)	16.6038(13)	7.5932(7)
β (°)	104.746(5)	111.292(7)
U (Å^3)	1900.0(3)	2428.9(5)
Z	4	4 (four ion pairs)
D_c (Mg m^{-3})	1.625	1.456
μ (mm^{-1})	0.700	0.585
$F(000)$	840	1096
$\theta_{orientation}$ (°)	5–13	5–12
$\theta_{data collection}$ (°)	1.84–25.00	1.61–25.00
h_{min}, h_{max}	−1, 14	−1, 23
k_{min}, k_{max}	−1, 11	−1, 20
l_{min}, l_{max}	−19, 19	−9, 8
Data measured	4348	2566
Unique data	3345	2196
T_{min}, T_{max}	0.3012, 0.3436	0.3539, 0.4093
R_{int}	0.0289	0.0581
Observed data [$F_o > 4\sigma(F_o)$]	1891	1499
R_1 [observed data]	0.0437	0.0620
R_1 [all data]	0.0707	0.1073
wR_2 [all data]	0.1142	0.1710
S	1.013	1.058
g_1	0.0570	0.0697
g_2	0.7081	4.1730
Variables	217	160
Max. min residue (e Å^{-1})	0.69, −0.37	0.47 (in BF$_4$), −0.53

Table 4
Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3 \text{Å}^{-2}$) for compound 5

Atom	x	y	z	U_{eq}
Mo(1)	2421(1)	7987(1)	489(1)	42(1)
C(1)	4281(4)	7261(6)	924(4)	61(2)
C(2)	3684(5)	6732(7)	1489(3)	65(2)
C(3)	2869(5)	5772(6)	1074(3)	57(1)
C(4)	2989(4)	5643(5)	238(3)	46(1)
C(5)	2383(5)	4826(7)	−453(5)	72(2)
C(6)	2689(8)	4898(9)	−1179(4)	87(2)
C(7)	3569(8)	5719(9)	−1264(4)	85(2)
C(8)	4166(6)	6564(7)	−638(5)	73(2)
C(9)	3862(4)	6548(5)	152(3)	47(1)
C(10)	5263(6)	8226(9)	1175(7)	115(3)
C(20)	3959(8)	7064(11)	2414(4)	123(4)
C(30)	2184(8)	4879(9)	1505(5)	101(3)
C(50)	1441(7)	3905(11)	−362(7)	130(4)
C(60)	2036(10)	4108(12)	−1952(6)	161(6)
C(70)	3914(11)	5685(13)	−2078(5)	169(6)
C(80)	5105(8)	7495(10)	−706(7)	134(4)
C(21)	2285(7)	9502(8)	−638(4)	83(2)
C(22)	1629(7)	8349(10)	−844(4)	92(3)
C(23)	765(6)	7963(9)	−551(4)	80(2)
C(31)	1277(5)	8189(6)	1096(4)	59(1)
O(31)	625(4)	8290(6)	1480(3)	87(2)
C(41)	2768(5)	9822(6)	987(4)	60(2)
O(41)	2986(5)	10883(5)	1318(4)	97(2)

distances and interbond angles, hydrogen atom coordinates, anisotropic thermal parameters, and tables of observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Centre. In addition to the programs noted below, some additional geometric calculations were performed using

Table 5
Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3 \text{Å}^{-2}$) for compound 6a

Atom	x	y	z	U_{eq}
Mo(1)	7064(1)	1/2	5300(1)	41(1)
C(1)	6975(6)	1/2	2108(15)	57(3)
C(2)	7369(4)	5655(5)	2979(10)	48(2)
C(3)	8075(4)	5406(4)	4300(9)	41(2)
C(4)	8732(5)	5813(5)	5387(11)	55(2)
C(5)	9341(4)	5409(6)	6418(10)	66(3)
C(10)	6246(8)	1/2	−402(17)	84(6)
C(20)	7101(6)	6456(6)	2377(16)	80(3)
C(21)	8116(5)	6090(8)	8880(14)	93(4)
C(22)	7424(4)	5845(5)	7344(11)	53(2)
C(23)	6732(4)	5950(5)	6528(10)	44(2)
C(24)	6082(5)	6426(6)	6424(14)	66(2)
C(30)	5960(6)	1/2	−4152(15)	48(3)
O(30)	5348(4)	1/2	3483(12)	58(2)
C(40)	8748(8)	6663(6)	5309(19)	97(4)
C(50)	10035(6)	5813(10)	7505(15)	113(5)
B	1/2	7093(9)	0	60(4)
F(1)	5235(5)	6644(6)	1561(12)	144(4)
F(2)	5574(4)	7516(4)	−27(13)	110(2)

CALC [26] and molecular geometry figures were drawn using SHELXTL-PC [27].

4.2.1. $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_9Me_7)]$ (5)

An irregular yellow block of approximate dimensions $0.4 \times 0.4 \times 0.2 \text{ mm}^3$ was chosen for data collection. The structure was solved (Mo, O and most C atoms) without difficulty by direct methods (SHELXS-86 [28]) and refined (SHELXL-93 [29]) on F^2 by full-matrix least-squares methods; the remaining C atoms were readily located in the first difference Fourier synthesis. Although some of the H atoms could be found in subsequent difference Fourier maps, all were set riding in calculated positions [C–H = 0.98 Å (CH of allyl), 0.97 Å (CH$_2$ of allyl), 0.96 Å (CH$_3$)] with isotropic thermal parameters calculated as 1.2 (C_3H_5) or 1.5 (CH$_3$) times the corresponding (equivalent) isotropic thermal parameter for the parent C atom. Following isotropic convergence, all non-H atoms were successfully allowed anisotropic thermal motion. The model readily converged and no major residual electron density peaks occur in the final difference map.

4.2.2. $[Mo(CO)(MeC\equiv CMe)_2(\eta^5\text{-}C_9Me_7)]BF_4$ (6a)

A dark brick-red plate of approximate dimensions $0.5 \times 0.25 \times 0.15 \text{ mm}^3$ was chosen for data collection. The position of the Mo atom was determined by inspection of the Patterson function (SHELXS-86 [28]); the remaining non-H atoms were readily located in the first difference Fourier map. The structure was refined on F^2 by full-matrix least-squares using SHELXL-93 [29]. In subsequent difference Fourier maps, the position of most of the H atoms was apparent; however, all H atoms in methyl groups lying off the crystallographic mirror plane were treated as for those in 5 above; H(10A) and H(10B) [bound to C(10)] were allowed positional and isotropic thermal refinement. All non-H atoms were refined with anisotropic thermal parameters in the latter stages of refinement. Both the molybdenum-containing cation and the BF$_4$ counter anion lie across crystallographic mirror planes. In the former case, the atoms Mo(1), C(30), O(30), C(1) and C(10) lie in the plane, and the mirror image half of the ion is generated by x, $1 − y$, z. The B atom lies on another mirror plane, through which the remaining two F atoms are generated by $1 − x$, y, z.

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