# Reactions of Co-ordinated Ligands. Part 56.[1] Synthesis and Reactivity of $[Mo\{\eta^3,\eta^3\text{-}CH(Me)C(Me)CHCHC(Me)CH_2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ formed by Coupling of But-2-yne and Isoprene Ligands; Reactions of $[Mo(\eta^2\text{-}C_2H_4)(\eta^2\text{-}MeC_2Me)(CO)(\eta\text{-}C_5H_5)][BF_4]$ *

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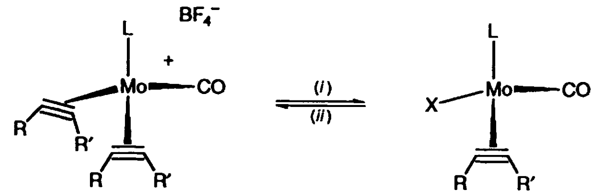
Reaction of Grignard reagents MgRX or alternatively $MgX_2$ with $[Mo(\eta^2\text{-}R'C_2R'')_2(CO)L][BF_4]$ ($R' = R'' = Me$; $R' = Me$, $R'' = Ph$; $R' = Bu^t$, $R'' = H$; $L = \eta\text{-}C_5H_5$ or $\eta^5\text{-}C_9H_7$) afforded the air-sensitive complexes $[MoBr(\eta^2\text{-}MeC_2Me)(CO)(\eta\text{-}C_5H_5)]$ **2**, $[MoCl(\eta^2\text{-}MeC_2Me)(CO)(\eta\text{-}C_5H_5)]$ **3**, $[MoI(\eta^2\text{-}MeC_2Me)(CO)(\eta\text{-}C_5H_5)]$ **4**, $[MoBr(\eta^2\text{-}MeC_2Me)(CO)(\eta^5\text{-}C_9H_7)]$ **5**, $[MoBr(\eta^2\text{-}Bu^tC_2H)(CO)(\eta\text{-}C_5H_5)]$ **6** and $[MoBr(\eta^2\text{-}PhC_2Me)(CO)(\eta\text{-}C_5H_5)]$ **7**. Reaction of **2** with isoprene and $AgBF_4$ leads to a novel carbon–carbon coupling reaction and the formation of $[Mo\{\eta^3,\eta^3\text{-}CH(Me)C(Me)CHCHC(Me)CH_2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ **8**, the single-crystal X-ray diffraction structure of which shows the presence of an unusual $\eta^3,\eta^3$-bonded hexatrienyl ligand which wraps itself around a $Mo(CO)(\eta\text{-}C_5H_5)^+$ fragment. Generalisation of the reaction established that buta-1,3-diene undergoes analogous reactions and that unsymmetrical alkynes couple with the 1,3-diene regioselectively. Reaction of **7** with $CD_2{=}CHCH{=}CD_2$ and $AgBF_4$ afforded $[Mo\{\eta^3,\eta^3\text{-}CD(Ph)C(Me)CDCHCHCD_2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ leading to definitive conclusions about the mechanism of the coupling reaction. The reaction of **8** with nucleophilic reagents has been examined, $Li[BHEt_3]$, LiMe and LiPh delivering '$H^-$', '$Me^-$' and '$Ph^-$' to the substituted end carbon of the $\eta^3,\eta^3\text{-}C_6$ ligand, whereas the sterically more demanding reagent $K[BHBu^s{}_3]$ delivers '$H^-$' to both 'inside' and 'outside' carbons. Reaction of **2**, $[MoCl(\eta^2\text{-}PhC_2Ph)(CO)(\eta\text{-}C_5H_5)]$ and **5** with $C_2H_4$ and $AgBF_4$ affords the alkene–alkyne complexes $[Mo(\eta^2\text{-}C_2H_4)(\eta^2\text{-}MeC_2Me)(CO)(\eta\text{-}C_5H_5)][BF_4]$, $[Mo(\eta^2\text{-}C_2H_4)(\eta^2\text{-}PhC_2Ph)(CO)(\eta\text{-}C_5H_5)][BF_4]$ and $[Mo(\eta^2\text{-}C_2H_4)(\eta^2\text{-}MeC_2Me)(CO)(\eta^5\text{-}C_9H_7)][BF_4]$. The reactions of the first of these products with nucleophilic reagents, $P(OMe)_3$, CO and isoprene, have been studied.

As described in the previous paper in this series,[1] there is a developing interest in a group of metal-mediated reactions which can lead to the formation of 1,3-dienes by the formal addition of an alkene carbon–hydrogen bond to an alkyne. We reasoned that one way of developing an understanding of this chemistry was to devise synthetic pathways to a relatively unexplored class of compound, that is species containing a co-ordinated alkene and an alkyne, the latter ligand functioning either as a four- or a three-electron donor. Development of this idea led to our discovery of a new class of complex carrying a $\eta^3,\eta^3$-bonded hexatrienyl ligand. This paper develops our initial observations[2] and explores the reactivity of some of the new complexes which have been obtained.



**2** $L = \eta\text{-}C_5H_5$, $R = R' = Me$, $X = Br$
**3** $L = \eta\text{-}C_5H_5$, $R = R' = Me$, $X = Cl$
**4** $L = \eta\text{-}C_5H_5$, $R = R' = Me$, $X = I$
**5** $L = \eta^5\text{-}C_9H_7$, $R = R' = Me$, $X = Br$
**6** $L = \eta\text{-}C_5H_5$, $R = H$, $R' = Bu^t$, $X = Br$
**7** $L = \eta\text{-}C_5H_5$, $R = Ph$, $R' = Me$, $X = Br$

**Scheme 1** (*i*) MgRX or $MgX_2$; (*ii*) $AgBF_4$, $RC_2R'$

## Results and Discussion

A new approach to cationic alkene/alkyne complexes was discovered serendipitously. We had previously[3] observed that lithium dimethylcuprate reacts with the readily available cation $[Mo(\eta^2\text{-}MeC_2Me)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ **1** to form $[Mo(\eta^2\text{-}MeC_2Me)(CO)\{(\sigma\text{-}CMe{=}CMe_2)(\eta\text{-}C_5H_5)]$, and in attempting to explore further this type of reaction the cation **1** was treated with MgEtBr in tetrahydrofuran (thf). This led somewhat surprisingly to the displacement of but-2-yne by bromide anion and the formation in good yield of an air-sensitive, green, crystalline neutral material, which was identified by elemental analysis, IR and NMR spectroscopy as the complex $[MoBr(\eta^2\text{-}MeC_2Me)(CO)(\eta\text{-}C_5H_5)]$ **2**. It was found that this reaction could be generalised, and in this way reasonable yields of the complexes $[MoCl(\eta^2\text{-}MeC_2Me)(CO)(\eta\text{-}C_5H_5)]$ **3**, $[MoI(\eta^2\text{-}MeC_2Me)(CO)(\eta\text{-}C_5H_5)]$ **4**, $[MoBr(\eta^2\text{-}MeC_2Me)(CO)(\eta^5\text{-}C_9\text{-}$

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

$H_7$)] **5**, [MoBr($\eta^2$-Bu$^t$$C_2$H)(CO)($\eta$-$C_5H_5$)] **6** and [MoBr($\eta^2$-Ph$C_2$Me)(CO)($\eta$-$C_5H_5$)] **7** (Scheme 1) were obtained as green air-sensitive crystals. Spectroscopic features of the complexes included a strong infrared carbonyl stretching band between 1930 and 1940 cm$^{-1}$. For **2** the $^1$H NMR spectrum displayed a six-proton singlet for the two methyl groups, at room temperature. The $^{13}$C NMR spectrum showed two signals for the acetylenic four-electron donor alkyne signals at δ 202.0 and 196.4 at room temperature.[4] This suggested that the alkyne ligand was close to being static on the NMR time-scale. Indeed, a low-temperature proton NMR study of a solution of **2** gave a coalescence temperature of 285 K, only just below ambient temperature, giving a calculated barrier to alkyne rotation of 61 ± 1 kJ mol$^{-1}$.

It is interesting to recall that complexes similar to **2**–**7** have previously[5–7] been prepared by the thermal reaction of [MCl(CO)$_3$($\eta$-$C_5H_5$)] (M = Mo or W) with diphenyl- or (phenyl)-methylacetylene, however this route does not provide a general, selective, high-yield synthesis, a variety of products being isolated depending on the conditions and the choice of alkyne. For example, reaction with but-2-yne[7] leads instead to the formation of either a duroquinone (2,3,5,6-tetramethyl-*p*-benzoquinone) complex or [MoCl($\eta^2$-Me$C_2$Me)$_2$($\eta$-$C_5H_5$)], whereas with hexafluorobut-2-yne[5] a cyclopentadienone complex or [MoCl($\eta^2$-$CF_3C_2CF_3$)$_2$($\eta$-$C_5H_5$)] is obtained depending on whether carbon monoxide was periodically removed from the reaction vessel.

Thus, this new route from the bis(alkyne) carbonyl cations involving non-forcing conditions and lack of excess of carbon monoxide has distinct advantages. It was subsequently demonstrated that the reaction also proceeded if magnesium halides $MgX_2$ (X = Cl or Br) were used, although paradoxically the purification procedures proved less straightforward and so Grignard reagents continued to be employed. Of the bis(alkyne) cations treated with a Grignard reagent, only [Mo($\eta^2$-Ph$C_2$Ph)$_2$(CO)($\eta$-$C_5H_5$)][$BF_4$] failed to give a tractable product, although as noted above the complex [MoCl($\eta^2$-Ph$C_2$Ph)(CO)($\eta$-$C_5H_5$)] can be obtained directly from [MoCl(CO)$_3$($\eta$-$C_5H_5$)] and diphenylacetylene.[6]

Having formed the halogeno complexes **2**–**7** attention was turned to halide-anion abstraction reactions with $AgBF_4$. Regeneration of parent cation **1** from **2** was facile. When **2** was stirred in dichloromethane solution with 1 equivalent of $AgBF_4$ and an excess of but-2-yne the complex **1** was obtained in high (84%) isolated yield. With this success attention was then focused on the possibility of accessing alkene/alkyne substituted cations. However, in our initial study, instead of using a simple alkene, a 1,3-diene was used to capture the cation [Mo($\eta^2$-Me$C_2$Me)(CO)($\eta$-$C_5H_5$)]$^+$ presumed to be formed on halide abstraction. A rapid reaction occurred on addition of $AgBF_4$ to a stirred solution of **2** and isoprene in dichloromethane, and work-up afforded a reasonable yield (49%) of a cationic yellow crystalline material **8**, which exhibited a single terminal carbonyl band in its IR spectrum. The $^1$H NMR spectrum showed that three inequivalent methyl groups were present in the product (one appearing as a doublet). There was also a complex pattern of five proton signals between δ 2.50 and 4.75, and a cyclopentadienyl singlet resonance at δ 5.69. These features, together with the appearance of only one carbon '$CH_2$' resonance in the $^{13}$C NMR spectrum, inferred that something more complex than simple $\eta^4$(4e) co-ordination of the diene had occurred. It was suspected that coupling of the isoprene and but-2-yne ligands had taken place, and this was confirmed by an X-ray crystallographic analysis of **8**.

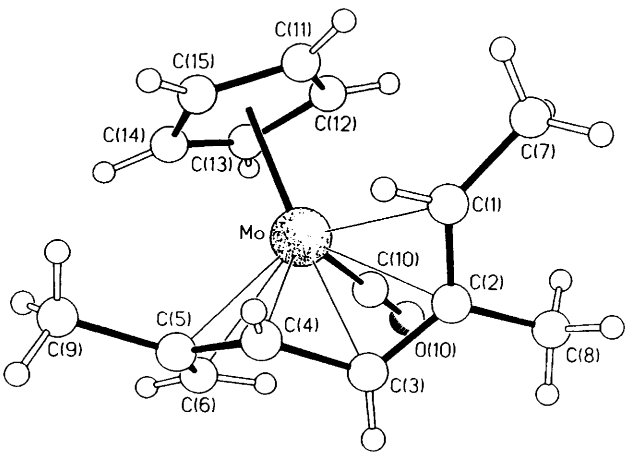


**Fig. 1** Molecular structure showing the labelling scheme of the cation contained within the complex **8**

**Table 1** Selected bond lengths (Å) and angles (°) for complex **8** with estimated standard deviations in parentheses

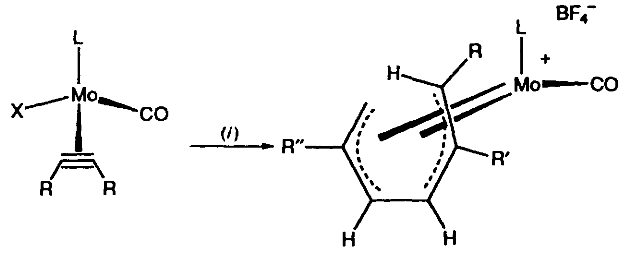
| | | | |
|---|---|---|---|
| Mo–C(1) | 2.491(8) | Mo–C(2) | 2.348(10) |
| Mo–C(3) | 2.232(8) | Mo–C(4) | 2.198(7) |
| Mo–C(5) | 2.317(8) | Mo–C(6) | 2.372(8) |
| Mo–C(10) | 2.984(8) | Mo–C(11) | 2.346(7) |
| Mo–C(12) | 2.289(7) | Mo–C(13) | 2.287(6) |
| Mo–C(14) | 2.342(6) | Mo–C(15) | 2.377(6) |
| C(1)–C(2) | 1.417(16) | C(1)–C(7) | 1.477(14) |
| C(2)–C(3) | 1.340(12) | C(2)–C(8) | 1.511(14) |
| C(3)–C(4) | 1.474(12) | C(4)–C(5) | 1.372(12) |
| C(5)–C(6) | 1.431(12) | C(5)–C(9) | 1.550(13) |
| C(10)–O(10) | 1.179(11) | | |
| C(2)–C(1)–C(7) | 127.7(7) | C(1)–C(2)–C(3) | 119.3(9) |
| C(1)–C(2)–C(8) | 114.7(8) | C(3)–C(2)–C(8) | 125.7(10) |
| C(2)–C(3)–C(4) | 120.8(9) | C(3)–C(4)–C(5) | 114.8(8) |
| C(4)–C(5)–C(6) | 119.7(7) | C(4)–C(5)–C(9) | 120.4(8) |
| C(6)–C(5)–C(9) | 119.0(7) | Mo–C(10)–O(10) | 178.2(7) |

The structure determination established the molecular geometry of the cation shown in Fig. 1, selected bond lengths and interbond angles being listed in Table 1. Thus, regioselective coupling of the co-ordinated but-2-yne with an isoprene molecule has occured followed by a 1,3-H-shift process accessing a $C_6$ ligand, which is $\eta^6$-bonded to a [Mo(CO)($\eta$-$C_5H_5$)]$^+$ fragment. The $C_6$ ligand is formally a trimethyl-substituted hexa-1,3,5-triene, however examination of the bond lengths C(1)–C(2) 1.417(16), C(2)–C(3) 1.340(12), C(3)–C(4) 1.474(12), C(4)–C(5) 1.372(12) and C(5)–C(6) 1.431(12) Å suggests[8] that the ligand can be more accurately described as two $\eta^3$-allyl systems linked by a carbon–carbon single bond, *i.e.* C(3)–C(4). The $\eta^3$,$\eta^3$-$C_6$ ligand wraps itself around the metal centre this being reflected in a 126.4° angle between the C(1)–C(2)–C(3) and C(4)–C(5)–C(6) planes. In addition to these features the cyclopentadienyl ligand is asymmetrically bonded with Mo–C(11) 2.346(7), Mo–C(12) 2.289(7), Mo–C(13) 2.287(6), Mo–C(14) 2.342(6) and Mo–C(15) 2.377(6) Å, which may be related to relief of steric interaction between the $C_5H_5$ and $\eta^3$,$\eta^3$-$C_6$ ligands.

It was found that this reaction could be generalised. Thus treatment of [MoBr($\eta^2$-Ph$C_2$Me)(CO)($\eta$-$C_5H_5$)] **7** or [MoCl($\eta^2$-Ph$C_2$Ph)(CO)($\eta$-$C_5H_5$)] with $AgBF_4$ and isoprene resulted in the formation in good yield of [Mo{$\eta^3$,$\eta^3$-CH(Ph)C(Me)CHCHC(Me)$CH_2$}(CO)($\eta$-$C_5H_5$)][$BF_4$] **9** and [Mo{$\eta^3$,$\eta^3$-CH(Ph)C(Ph)CHCHC(Me)$CH_2$}(CO)($\eta$-$C_5H_5$)][$BF_4$] **10** respectively (Scheme 2). These reactions are regiospecific both in the sense in which the unsymmetrical 1,3-diene isoprene couples with the alkyne, and also in the way the unsymmetrical alkyne Me$C_2$Ph links only one way round, *i.e.* the phenyl substituent is selectively placed in a terminal position on the $C_6$ chain. Buta-1,3-diene can also be used in the coupling reaction, and in this way the cations [Mo{$\eta^3$,$\eta^3$-CH(Me)C(Me)CHCHCH$CH_2$}(CO)($\eta$-$C_5H_5$)][$BF_4$] **11**, [Mo{$\eta^3$,$\eta^3$-CH(Ph)C(Me)CHCHCH$CH_2$}(CO)($\eta$-$C_5H_5$)][$BF_4$] **12** and [Mo{$\eta^3$,$\eta^3$-CH(Ph)C(Ph)CHCHCH$CH_2$}-

$(CO)(\eta\text{-}C_5H_5)[BF_4]$ **13** were formed. As was the case with **9** the coupling reaction with the unsymmetrical alkyne is regioselective.

The formation of a $\eta^3,\eta^3$-bonded hexatrienyl ligand by coupling of an alkyne and 1,3-diene is unprecedented (there are a number of examples of such ligands bonded to two metal centres)[9] and therefore a discussion of possible reaction pathways is justified. In the reaction of, for example complex **2**, with isoprene and $AgBF_4$ it might be expected that initially the cation **A** (Scheme 3) would be formed in which the but-2-yne maintains its role as a 4e donor ligand and the isoprene is $\eta^2$-bonded *via* the unsubstituted double bond. Since there are few examples[10] of carbon–carbon coupling reactions between alkenes and $\eta^2$(4e)-donor alkynes a possible next step is the reversible transformation of **A** into **B** where the isoprene is now $\eta^4$-bonded and the but-2-yne has switched its bonding mode to become a two-electron donor. There is ample precedent[11] for the coupling of a $\eta^2$(2e)-bonded alkyne with a $\eta^4$-1,3-diene, and thus it is then reasonable to postulate the step **B** ⟶ **C** in the assembly of the $C_6$ chain. Once **C** is formed then obviously the isomers **D** and **E** can also be accessed. There remains, however, the problem as to how a hydrogen-shift process can occur so as to transform **C**, **D** or **E** into the final product. Scheme 4 illustrates the most obvious ways this could be achieved. In principle a 1,3-H shift could transform **D** into **F**, however such a reaction would involve a forbidden suprafacial sigmatropic shift[12,*] and is therefore unlikely. Similarly, a β-H elimination reaction **D** ⟶ **G** again seems unlikely in view of the lack of conformational flexibility shown by models of **D**. There are, however, two other pathways from **D** to **8** which merit consideration. The first involves a α-hydrogen elimination reaction **D** ⟶ **H**, followed by reductive elimination **H** ⟶ **I**, and migration (1,2) of a β-hydrogen from the $CH_2$ group onto the carbene carbon, *i.e.* **I** ⟶ **8**. The second pathway requires an initial rearrangement of **D** into the more flexible isomer **E**. Examination of models of **E** shows that in the molybdenacyclohepta-2,5-diene ring the methylene δ-hydrogens can interact with the metal centre, and such an interaction could trigger the transformation **E** ⟶ **G** ⟶ **8**.

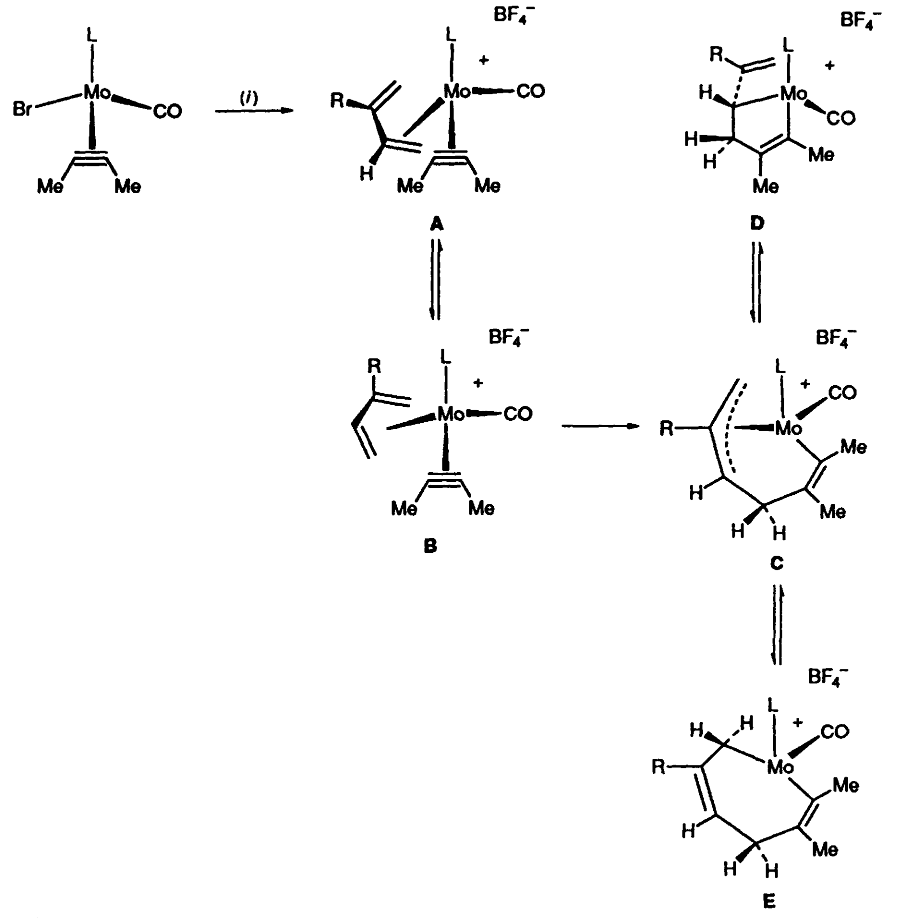


**2** X = Br, R = R′ = Me
**7** X = Br, R = Ph, R′ = Me
X = Cl, R = R′ = Ph

**8** R = R′ = R″ = Me
**9** R = Ph, R′ = R″ = Me
**10** R = R′ = Ph, R″ = Me
**11** R = R′ = Me, R″ = H
**12** R = Ph, R′ = Me, R″ = H
**13** R = R′ = Ph, R″ = H

**Scheme 2** L = $\eta\text{-}C_5H_5$. (*i*) Isoprene or buta-1,3-diene, $AgBF_4$, $CH_2Cl_2$

With the intention of distinguishing between these pathways the deuterium-labelling experiment depicted in Scheme 5 was carried out. Reaction of complex **7** with $CD_2{=}CHCH{=}CD_2$[14] and $AgBF_4$ in dichloromethane afforded $[^2H_4]$**12** in excellent yield. Examination of the $^1H$ and $^2H$ NMR spectra (see Experimental section) showed that the tetradeuterio-isomer of **12** illustrated was formed regioselectively. This important



**Scheme 3** L = $\eta\text{-}C_5H_5$. (*i*) isoprene (R = Me) or buta-1,3-diene (R = H), $AgBF_4$, $CH_2Cl_2$

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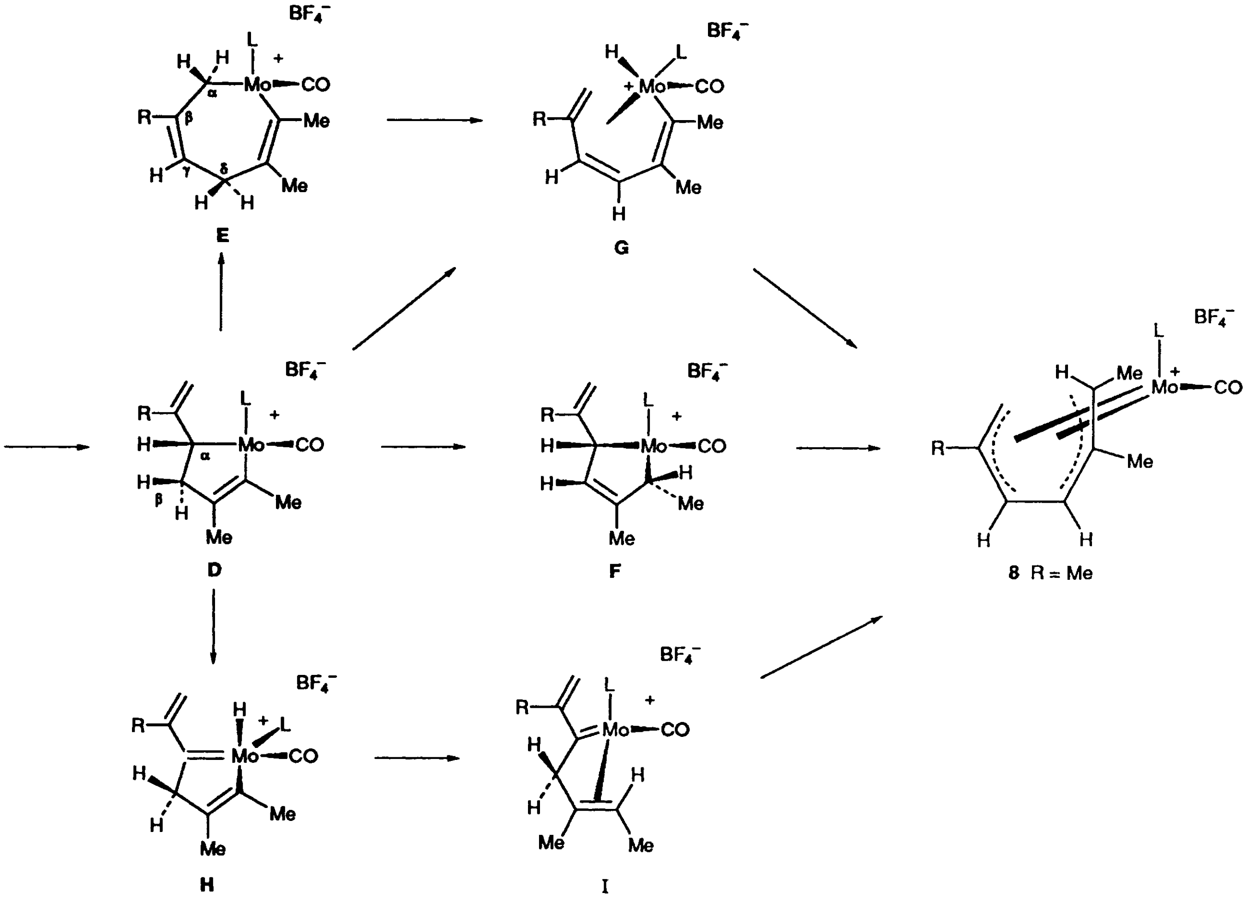
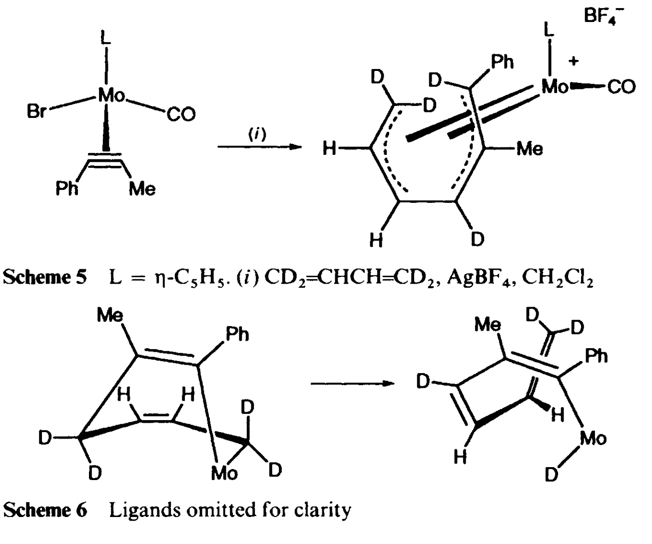
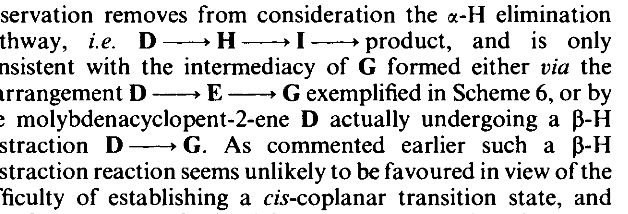
[*] The possibility of a rhenium-assisted, otherwise forbidden, suprafacial 1,3-H shift has been mentioned,[13] however, the nature of the metal assistance was not discussed.



Scheme 4 L = η-$C_5H_5$



Scheme 5 L = η-$C_5H_5$. (*i*) $CD_2{=}CHCH{=}CD_2$, $AgBF_4$, $CH_2Cl_2$

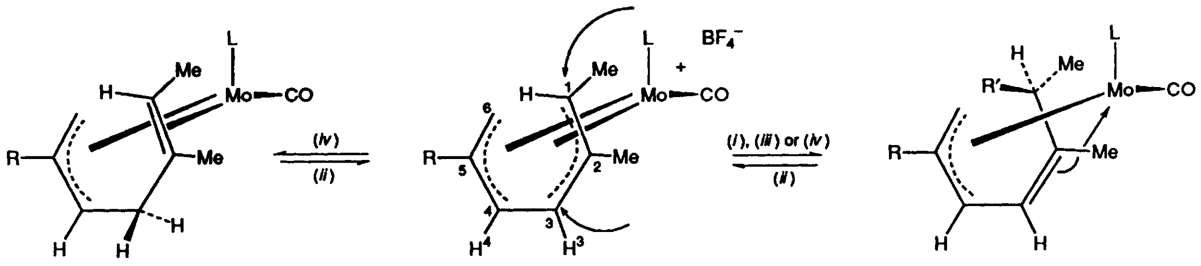


Scheme 6 Ligands omitted for clarity

observation removes from consideration the α-H elimination pathway, *i.e.* **D** $\longrightarrow$ **H** $\longrightarrow$ **I** $\longrightarrow$ product, and is only consistent with the intermediacy of **G** formed either *via* the rearrangement **D** $\longrightarrow$ **E** $\longrightarrow$ **G** exemplified in Scheme 6, or by the molybdenacyclopent-2-ene **D** actually undergoing a β-H abstraction **D** $\longrightarrow$ **G**. As commented earlier such a β-H abstraction reaction seems unlikely to be favoured in view of the difficulty of establishing a *cis*-coplanar transition state, and therefore because of this difficulty, and the availability of an alternative pathway, we favour the involvement of the process depicted in Scheme 6, *i.e.* **E** $\longrightarrow$ **G** $\longrightarrow$ **8**, which is fully consistent with the deuterium-labelling experiments.

The cations **8**–**13** are interesting not only from the standpoint of synthesis, mechanism of formation and structure, but also in terms of their potential reactivity toward nucleophilic reagents. The $\eta^3,\eta^3$-bonded hexatriene ligand is novel and important questions are which of the atoms of the $C_6$ chain are attacked by nucleophiles, and are the reactions regioselective? The Davies–Green–Mingos (DGM) rules predict[15] attack on one end of the open $C_6$ ligand.

Reaction of complex **8** with Li[$BHEt_3$] or Li[$BDEt_3$] in thf at low temperature afforded respectively on column chromatography of the reaction mixture the bright yellow low-melting solids **14** or **14D** (Scheme 7). Elemental analysis and mass spectra suggested the molecular formula [Mo{$CH_2C(Me)CHCHC(Me)CH(R')Me$}(CO)(η-$C_5H_5$)] (R′ = H or D) for the products, and in agreement the IR spectrum showed a single terminal carbonyl bond at 1905 $cm^{-1}$. Examination of the $^1H$ and $^{13}C-\{^1H\}$ NMR spectra showed that '$H^-$' or '$D^-$' had been delivered regioselectively to the substituted end ($C^1$) of the $\eta^3,\eta^3$-$C_6$ ligand with formation of a $\eta^2,\eta^3$-bonded pentadienyl ligand. The same regioselectivity was also observed on reaction of **8** with LiMe or LiPh in thf when the complexes **15** and **16** were formed in good yield. The reactions of the cation **12** were also briefly examined and it was observed that treatment with Li[$BHEt_3$] afforded a complex **17** analogous to **14**. Interestingly, when **8** was treated with the bulky substituted borohydride K[$BHBu^s{}_3$] a mixture (1 : 4) of **14** and an isomeric complex **18** was formed. This could not be separated by column chromatography, but examination of the $^1H$ and $^{13}C-\{^1H\}$ NMR spectra of the mixture showed that **18** was formed by competitive nucleophilic attack on the inside carbon atom $C^3$. In agreement with these structural assignments when **14**, or the mixture of **14** and **18**, was allowed to react with trityl tetrafluoroborate in dichloromethane the parent cation **8** was reformed in high yield. Thus, these observations serve to underline the inherent weakness[16] of the DGM rules, which not only assume that nucleophilic attack occurs under charge

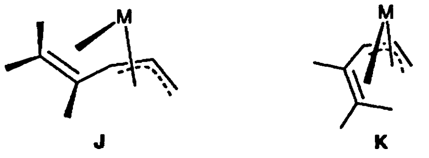


**18** R = Me

**8** R = Me

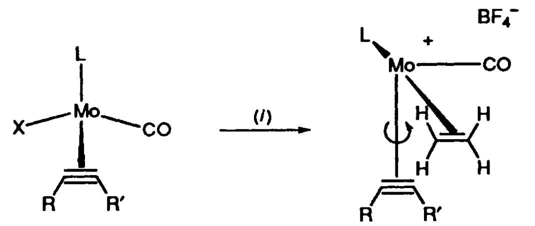
**14** R = Me, R' = H(D)
**15** R = R' = Me
**16** R = Me, R' = Ph

**Scheme 7** L = $\eta$-$C_5H_5$. (*i*) R' = H or D, Li[$BHEt_3$] or Li[$BDEt_3$], thf; (*ii*) [$CPh_3$][$BF_4$], $CH_2Cl_2$; (*iii*) R' = Me or Ph, LiMe or LiPh, thf; (*iv*) K[$BHBu^s{}_3$], thf



**J** **K**

**Scheme 8**



**19** L = $\eta$-$C_5H_5$, R = R' = Me
**20** L = $\eta$-$C_5H_5$, R = R' = Ph
**21** L = $\eta^5$-$C_9H_7$, R = R' = Me

**Scheme 9** (*i*) $AgBF_4$, $C_2H_4$, $CH_2Cl_2$

control, but also do not take the structure of the nucleophile into account.

One other aspect of the chemistry illustrated in Scheme 7 deserves comment, and that relates to the bonding mode of the $\eta^2,\eta^3$-pentadienyl ligand formed, for example, in the reaction **8** $\longrightarrow$ **14**. Reaction with a nucleophile would be expected to occur on $C^1$ *via* attack on that face of the $\eta^3$-allyl opposite to the molybdenum centre. Because of the geometry of the $\eta^3,\eta^3$-$C_6$ ligand this results in the formation of a $\eta^2,\eta^3$-pentadienyl ligand with the topology **J** rather than the familiar[17] planar **K** form shown in Scheme 8. These two forms differ as to which face of the alkene is co-ordinated to the metal, and it is interesting that prior to this work only the **K** bonding mode has been observed. Obviously interconversion of **J** and **K** would require disconnection of the alkene, *i.e.* an $\eta^5$ to $\eta^3$ change in the bonding mode of the pentadienyl ligand, and rotation about a C–C bond.

Attention was next turned to the synthesis of simple alkene/alkyne cationic complexes. Reaction of the green complex [MoBr($\eta^2$-$MeC_2Me$)(CO)($\eta$-$C_5H_5$)] **2** with $AgBF_4$ in $CH_2Cl_2$ in the presence of a stream of ethylene resulted in rapid precipitation of AgBr and the formation of a red material, which on recrystallisation (−30 °C) from $CH_2Cl_2$–$Et_2O$ in the presence of $C_2H_4$ afforded deep red crystals of **19**, which could be stored at −30 °C under an atmosphere of ethylene. Analogous reactions of [MoCl($\eta^2$-$PhC_2Ph$)(CO)($\eta$-$C_5H_5$)] and [MoBr($\eta^2$-$MeC_2Me$)(CO)($\eta^5$-$C_9H_7$)] with $C_2H_4$ and $AgBF_4$ afforded respectively the labile red crystalline cations **20** and **21** (Scheme 9). The IR spectra of these complexes showed a single terminal carbonyl stretch in the range 2020–1950 $cm^{-1}$.

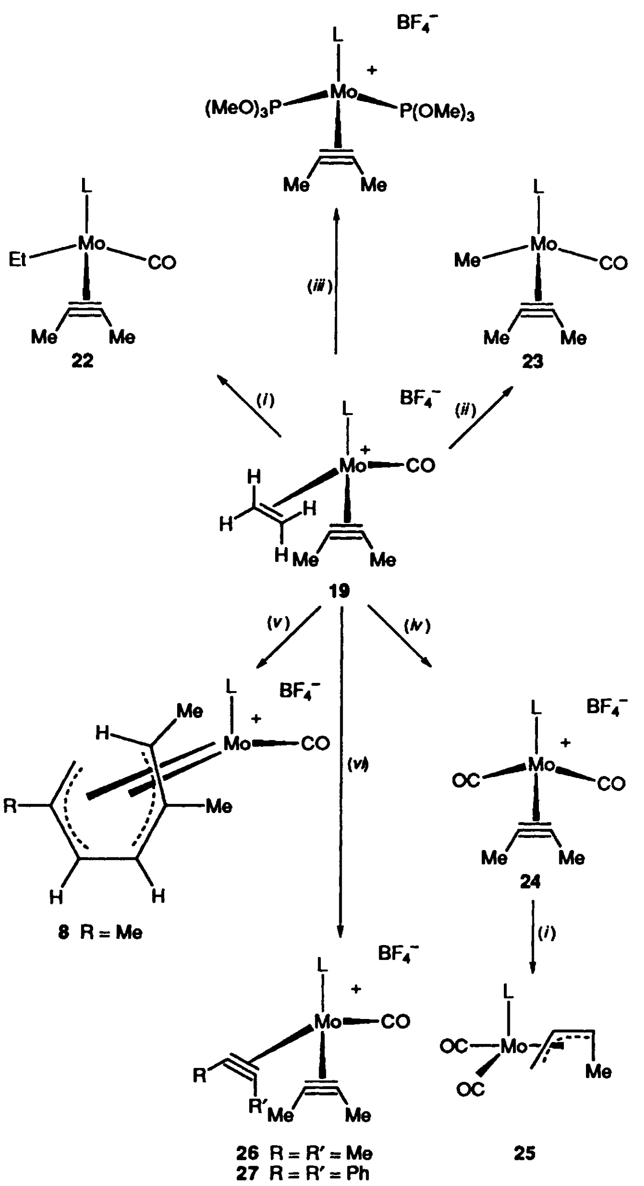
Examination of the $^1H$ and $^{13}C$-{$^1H$} NMR spectra of the but-2-yne substituted cations **19** and **21** showed that at ambient temperature only the alkyne was rotating ($\Delta G^*_{T_c}$ 53 ± 1 kJ $mol^{-1}$, $T_c$ 260 ± 3 K for **19**). Although there was some broadening of the co-ordinated ethylene signals for **19** and **20** there was no evidence for rotation, and in the case of the indenyl-substituted cation **21** the *J*(HH) splitting pattern of the $C_2H_4$ was well resolved at ambient temperature allowing the establishment of the *J* values listed in the Experimental section. These values are typical for ethylene $\eta^2$-bonded to a transition metal.

There are only a few reported examples of $\eta^2$(2e)-alkene/$\eta^2$(4e)-alkyne complexes, the first example being the X-ray crystallographically identified complex [Mo(dpps)($\eta^2$-$MeC_2Me$)($\eta$-$C_5H_5$)][$BF_4$] (dpps = *o*-diphenylphosphinostyrene).[18] In addition to this compound there is also a group of tungsten complexes of general formula [W($\eta^2$-alkyne)($\eta^2$-alkene)($S_2CNEt_2$)] (alkyne = $PhC_2H$, alkene = maleic anhydride or tetracyanoethylene), the stability of which depends on the presence of electronegatively substituted alkenes.[19] Interestingly, in a theoretical analysis of these species based on extended-Hückel molecular orbital (EHMO) calculations a rationale was provided for the higher barrier to rotation of alkenes compared with alkynes, and this analysis can be extended to explain the non-rotation of co-ordinated ethylene in the cations **19**–**21**.

With regards to the reactivity of $\eta^2$(2e)-alkene/$\eta^2$(4e)-alkyne complexes, Templeton and co-workers[19] have reported that reaction of [W($\eta^2$-$PhC_2H$)($\eta^2$-OCCH=$CHCO_2$)($S_2CNEt_2$)] with $PMe_3$ leads to apparent nucleophilic attack on the unsubstituted alkyne carbon, affording the $\eta^2$(3e)-vinyl complex [W{=C(Ph)CH($PMe_3$)($\eta^2$-OCCH=$CHCO_2$)($S_2CNEt_2$)]. We have also reported[18] that [Mo(dpps)($\eta^2$-$MeC_2Me$)($\eta$-$C_5H_5$)][$BF_4$] reacts with acetonitrile to give the carbon–carbon coupled product [Mo(NCMe){$\eta^4$-MeCH=C(Me)CH=$CHC_6H_4PPh_2$-*o*}($\eta$-$C_5H_5$)][$BF_4$]. It was therefore important to examine the reactivity of cations like **19**–**21**. For this initial study the cation **19** was chosen.

Reaction of complex **19** with the hydride anion source K[$BHBu^s{}_3$] in thf afforded purple crystals of the σ-ethyl complex **22** (Scheme 10) arising either from direct attack on $C_2H_4$ or from initial nucleophilic attack at the molybdenum centre with a concomitant switch (4e $\longrightarrow$ 2e) in the bonding mode of the but-2-yne followed by 'insertion' of the co-ordinated ethylene into the resulting Mo–H bond. In contrast, treatment of **19** with LiMe in thf gave the σ-methyl complex **23** suggesting direct delivery of '$Me^-$' to the metal followed by loss of $C_2H_4$ had occurred rather than 'insertion' of ethylene into the Mo–Me bond. In both of these reactions the but-2-yne functions as an 'interested' spectator, there being no evidence for products arising from either direct attack on the alkyne or 'insertion' into Mo–H or Mo–Me bonds.

Trimethyl phosphite reacts with complex **19** to give the known [Mo($\eta^2$-$MeC_2Me$){P$(OMe)_3$}$_2$($\eta$-$C_5H_5$)][$BF_4$] presumably *via* initial displacement of $C_2H_4$ followed by



**Scheme 10** L = η-$C_5H_5$. (*i*) K[$BHBu^s_3$], thf; (*ii*) LiMe, thf; (*iii*) $P(OMe)_3$, $CH_2Cl_2$; (*iv*) CO, $CH_2Cl_2$; (*v*) isoprene, $CH_2Cl_2$; (*vi*) $RC_2R'$, $CH_2Cl_2$

displacement of CO. Similarly, bubbling carbon monoxide through a dichloromethane solution of **19** affords the purple crystalline air-sensitive cationic dicarbonyl complex **24**. The IR spectrum of **24** exhibited two terminal carbonyl bands at 2080m and 1980s $cm^{-1}$, and the $^1H$ NMR spectrum showed a cyclopentadienyl resonance and a singlet methyl signal integrating for six protons, indicating alkyne rotation. This was confirmed by variable-temperature studies leading to a calculated barrier to rotation of 41 ± 1 kJ $mol^{-1}$ ($T_c$ 213 K). Dicarbonyl complexes of a similar nature have received little attention, being cited either as reactive intermediates or as by-products. Unlike their neutral counterparts in Group 5, for example [V($\eta^2$-$MeC_2Me$)$(CO)_2$(η-$C_5H_5$)], these complexes are not very stable. However, **24** shows a similar reactivity pattern to that exhibited by the more stable [Mo($\eta^2$-$MeC_2Me$){$P(OMe)_3$}$_2$(η-$C_5H_5$)][$BF_4$], reacting with K[$BHBu^s_3$] in thf to form the $\eta^3$-allylic complex **25** presumably *via* a similar reaction pathway to that established for the bis(phosphite)-substituted counterpart.

The co-ordinated ethylene in complex **19** can also be displaced by a 1,3-diene or by alkynes. Treatment of **19** with an excess of isoprene led to a change in colour of the reaction mixture from red to deep yellow and the formation (72% yield) of **8**. Addition of but-2-yne to **19** resulted in the formation in essentially quantitative yield of [Mo($\eta^2$-$MeC_2Me$)$_2$(CO)(η-$C_5H_5$)][$BF_4$] suggesting that it might be possible to synthesise mixed bis(alkyne) complexes. Reaction of **19** with 1 molar equivalent of diphenylacetylene in dichloromethane as solvent resulted in an immediate change in colour from red to yellow, and addition of diethyl ether gave yellow crystals of **27** in good yield (72%). Examination of the NMR spectra of this material showed that it was essentially pure [Mo($\eta^2$-$MeC_2Me$)($\eta^2$-$PhC_2Ph$)(CO)(η-$C_5H_5$)][$BF_4$] with a trace of [Mo($\eta^2$-$PhC_2Ph$)$_2$(CO)(η-$C_5H_5$)][$BF_4$], which could be removed by recrystallisation. A similar reaction between **19** and $PhC_2Me$ again afforded a mixed bis(alkyne) complex **28**, however in this case a higher proportion (6:1) of the cation [Mo($\eta^2$-$PhC_2Me$)$_2$(CO)(η-$C_5H_5$)][$BF_4$][20] was also formed by an alkyne–alkyne exchange reaction.

## Experimental

All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen, using standard Schlenk techniques. Solvents were freshly distilled over an appropriate drying agent and further degassed before use where necessary. Column chromatography was performed using BDH alumina, Brockman activity II as the solid support. Reagents were obtained from commercial sources unless otherwise indicated. The $^1H$ and $^{13}C$-{$^1H$} NMR spectra were recorded on a Brucker AM360 spectrometer. Chemical shifts are quoted as positive to high frequency of tetramethylsilane, with coupling constants in Hz. Data given are for room-temperature measurements unless otherwise stated. Infrared spectra were measured using a Perkin Elmer 983G spectrometer. Mass spectra and analytical data were obtained courtesy of the University of London Service.

*Preparations.*—[MoBr($\eta^2$-$MeC_2Me$)(CO)(η-$C_5H_5$)] **2**. The cation [Mo($\eta^2$-$MeC_2Me$)$_2$(CO)(η-$C_5H_5$)][$BF_4$] **1**[20] (0.7 g, 1.8 mmol) was suspended in tetrahydrofuran (thf) (20 $cm^3$). Ethylmagnesium bromide (1.8 mmol, 1 mol $dm^{-3}$ solution in thf) was added at room temperature, and the solution immediately turned green. It was stirred for 10 min and then the volume was reduced *in vacuo* to *ca.* 5 $cm^3$ and diethyl ether (30 $cm^3$) was added. The resulting precipitate was filtered off through Celite and all volatiles removed *in vacuo*. The resulting green oil was washed with hexane (2 × 10 $cm^3$) and the product extracted with diethyl ether (4 × 15 $cm^3$). The volume was reduced to *ca.* 5 $cm^3$ and hexane (25 $cm^3$) was added to precipitate a green solid. Crystallisation from diethyl ether–hexane (−30 °C) gave green, air-sensitive *crystals* of complex **2** (0.38 g, 65%) (Found: C, 37.2; H, 3.5. $C_{10}H_{11}BrMoO$ requires C, 37.2; H, 3.5%), $\nu_{CO}$($CH_2Cl_2$) 1935 $cm^{-1}$. NMR: $^1H$($CDCl_3$), δ 5.55 (s, 5 H, $C_5H_5$), 3.15 (s, 6 H, *Me*$C_2$*Me*); $^{13}C$-{$^1H$} ($CD_2Cl_2$), δ 232.2 (CO), 202.0 (Me*C*≡CMe), 196.4 (MeC≡*C*Me), 97.9 ($C_5H_5$), 22.5 (*Me*C≡CMe) and 19.2 (MeC≡C*Me*). Mass spectrum: *m/z* = 323, $[M]^+$; 294, $[M - CO]^+$. The rotation of the alkyne was frozen out at low temperatures, the singlet at δ 3.15 separating into two peaks (Δν 16 Hz). The coalescence temperature was approximately 285 K giving a calculated barrier to rotation, $\Delta G^*_{T_c}$ 61 ± 1 kJ $mol^{-1}$.

[MoCl($\eta^2$-$MeC_2Me$)(CO)(η-$C_5H_5$)] **3**. Similarly, reaction of complex **1** (0.7 g, 1.8 mmol) with Mg($CH_2SiMe_3$)Cl or $MgCl_2$ (1.8 mmol) gave green *crystals* of **3** (65%) (Found: C, 43.1; H, 4.0. $C_{10}H_{11}ClMoO$ requires C, 43.1, H, 4.0%), $\nu_{CO}$($CH_2Cl_2$) 1930 $cm^{-1}$. NMR: $^1H$ ($CDCl_3$), δ 5.55 (s, 5 H, $C_5H_5$) and 3.2 (s, 6 H, *Me*$C_2$*Me*); $^{13}C$-{$^1H$} ($CD_2Cl_2$), δ 233.0 (CO), 98.5 ($C_5H_5$), 25.7 (*Me*C≡CMe) and 17.6 (MeC≡C*Me*). Mass spectrum: *m/z* = 280 $[M]^+$, 252, $[M - CO]^+$.

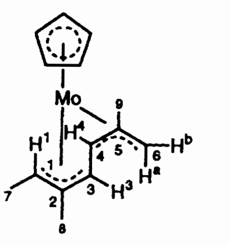
[MoI($\eta^2$-$MeC_2Me$)(CO)(η-$C_5H_5$)] **4**. In a similar way, reaction of complex **1** (0.7 g, 1.8 mmol) with MgMeI (1.8 mmol) afforded **4** (55%) (Found: C, 32.6; H, 2.9. $C_{10}H_{11}IMoO$ requires C, 32.3; H, 2.9%), $\nu_{CO}(CH_2Cl_2)$ 1935 $cm^{-1}$. NMR: $^1H$ ($CDCl_3$), $\delta$ 5.55 (s, 5 H, $C_5H_5$) and 3.05 (s, 6 H, $\mathit{Me}C_2\mathit{Me}$); $^{13}C$-{$^1H$}($CD_2Cl_2$), $\delta$ 234.9 (CO), 205.2 ($\mathrm{Me}\mathit{C}{\equiv}\mathrm{CMe}$), 200.5 ($\mathrm{MeC}{\equiv}\mathit{C}\mathrm{Me}$), 97.2 ($C_5H_5$), 23.1 ($\mathit{Me}C_2\mathrm{Me}$) and 19.6 ($\mathrm{Me}C_2\mathit{Me}$). Mass spectrum: $m/z$ = 370, $[M]^+$, 342 $[M - CO]^+$.

$[MoBr(\eta^2\text{-}MeC_2Me)(CO)(\eta^5\text{-}C_9H_7)]$ **5**. Reaction of $[Mo(\eta^2\text{-}MeC_2Me)_2(CO)(\eta^5\text{-}C_9H_7)][BF_4]$ (1.5 mmol) with MgEtBr (1.5 mmol) gave green *crystals* of complex **5** (75%) (Found: C, 44.9; H, 3.5. $C_{14}H_{13}BrMoO$ requires C, 45.0; H, 3.5%), $\nu_{CO}(CH_2Cl_2)$ 1935 $cm^{-1}$. NMR: $^1H(CDCl_3)$, $\delta$ 7.9–7.2 (m, 4 H, $C_9H_7$), 5.41 (m, 1 H, $C_9H_7$), 4.94 (m, 1 H, $C_9H_7$) and 3.07 (s, 6 H, $\mathit{Me}C_2\mathit{Me}$); $^{13}C$-{$^1H$}($CDCl_3$), $\delta$ 233.4 (CO), 197.0 ($\mathrm{Me}\mathit{C}{\equiv}\mathrm{CMe}$), 128.7, 127.0, 126.4, 124.7 ($C_9H_7$), 123.5, 117.9 ($C_9H_7$), 90.8, 85.4, 80.9 ($C_9H_7$) and 19.9 ($\mathit{Me}C_2\mathit{Me}$). Mass spectrum: $m/z$ = 371, $[M]^+$; 346, $[M - CO]^+$.

$[MoBr(\eta^2\text{-}Bu^tC_2H)(CO)(\eta\text{-}C_5H_5)]$ **6**. Similarly, reaction of $[Mo(\eta^2\text{-}Bu^tC_2H)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ (1.5 mmol) with MgEtBr (1.5 mmol) gave green crystals of **6** (75%) (Found: C, 41.0; H, 4.2. $C_{12}H_{15}BrMoO$ requires C, 41.0; H, 4.3%), $\nu_{CO}(Et_2O)$ 1945 $cm^{-1}$. NMR ($CDCl_3$): $^1H$, $\delta$ 11.82 (s, 1 H, $HC{\equiv}C$), 5.69 (s, 5 H, $C_5H_5$) and 1.51 (s, 9 H, $Bu^tC{\equiv}C$); $^{13}C$-{$^1H$}, $\delta$ 233.5 (CO), 187.9 ($H\mathit{C}{\equiv}CBu^t$), 183.0 ($Bu^t\mathit{C}{\equiv}C$), 97.3 ($C_5H_5$), 41.5 ($\mathit{C}Me_3$) and 31.2 ($C\mathit{Me}_3$).

$[MoBr(\eta^2\text{-}PhC_2Me)(CO)(\eta\text{-}C_5H_5)]$ **7**. Reaction of $[Mo(\eta^2\text{-}PhC_2Me)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ (1.5 mmol) with MgEtBr (1.5 mmol) afforded green *crystals* of complex **7** (72%) (Found: C, 46.1; H, 3.2. $C_{15}H_{13}BrMoO$ requires C, 46.8; H, 3.4%), $\nu_{CO}(CH_2Cl_2)$ 1940 $cm^{-1}$. NMR ($CD_2Cl_2$): $^1H$, $\delta$ 7.8–7.2 (s, 5 H, Ph), 5.6 (s, 5 H, $C_5H_5$) and 3.4 (s, 3 H, $MeC{\equiv}C$); $^{13}C$-{$^1H$}, $\delta$ 232.9 (CO), 202.5 ($Ph\mathit{C}{\equiv}CMe$), 198.5 ($PhC{\equiv}\mathit{C}Me$), 136.6, 130.7, 130.5, 129.5 (Ph), 98.4 ($C_5H_5$) and 21.2 ($\mathit{Me}C{\equiv}CPh$).

*Reaction of* $[MoBr(\eta^2\text{-}MeC_2Me)(CO)(\eta\text{-}C_5H_5)]$ *with* $AgBF_4$ *and* $MeC_2Me$. To complex **2** (0.1 g, 0.31 mmol) in $CH_2Cl_2$ (10 $cm^3$) was added but-2-yne (0.07 g, 0.1 $cm^3$, 1.3 mmol) and $AgBF_4$ (0.06 g, 0.31 mmol). The reaction mixture was stirred for 10 min at room temperature as the solution changed from green to yellow. It was filtered through Celite and the volume of the solvent was then reduced to 3 $cm^3$. Diethyl ether (15 $cm^3$) was added, precipitating a yellow solid which was dried *in vacuo*. Crystallisation from diethyl ether–dichloromethane gave yellow crystals of $[Mo(\eta^2\text{-}MeC_2Me)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ (0.1 g, 84%), identical (IR and NMR spectra) with an authentic sample.



$[Mo\{\eta^3,\eta^3\text{-}CH(Me)C(Me)CHCHC(Me)CH_2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ **8**. To complex **2** (0.3 g, 0.93 mmol) in $CH_2Cl_2$ (15 $cm^3$) was added 2-methylbuta-1,3-diene (isoprene) (3 mmol, 0.3 $cm^3$) and $AgBF_4$ (0.18 g, 0.93 mmol) and the mixture was stirred at room temperature for 15 min, changing from green to deep yellow. The reaction mixture was filtered through Celite and the volume of the solvent was reduced *in vacuo* to 5 $cm^3$. Addition of diethyl ether (20 $cm^3$) afforded a yellow solid, which was collected and recrystallised (−30 °C) from diethyl ether–dichloromethane, affording dark yellow *crystals* of complex **8** (0.18 g, 49%) (Found: C, 45.2; H, 4.8. $C_{15}H_{19}BF_4MoO$ requires C, 45.2; H, 4.7%), $\nu_{CO}(CH_2Cl_2)$ 2000 $cm^{-1}$. NMR $[(CD_3)_2CO]$: $^1H$, $\delta$ 5.69 (s, 5 H, $C_5H_5$), 4.75 [q, 1 H, $H^1$, $^3J(MeH^1)$ 5.85], 3.64 [br d, 1 H, $H^4$, $^3J(H^3H^4)$ 4.58], 3.35 [d, 1 H, $H^3$, $^3J(H^3H^4)$ 4.58], 2.75 [dd, 1 H, $H^{6b}$, $^4J(H^4H^{6b})$ 0.91, $^2J(H^{6a}H^{6b})$ 3.38], 2.55 [dd, 1 H, $H^{6a}$, $^4J(H^4H^{6a})$ 1.47, $^2J(H^{6a}H^{6b})$ 3.30], 2.31 (s, 3 H, $C^9H_3$), 2.15 (s, 3 H, $C^8H_3$) and 1.78 [d, 3 H, $C^7H_3$, $^3J(MeH)$ 6.05 Hz]; $^{13}C$-{$^1H$}, $\delta$ 228.0 (CO), 118.6 ($C^5$), 114.5 ($C^2$), 101.3 ($C^1$), 95.6 ($C_5H_5$), 85.0 ($C^4$), 76.4 ($C^3$), 38.4 ($C^6$), 22.3 ($C^9$), 17.9 ($C^8$) and 16.1 ($C^7$).

Complexes **9**–**13** were prepared in a similar manner and on the same scale.

$[Mo\{\eta^3,\eta^3\text{-}CH(Ph)C(Me)CHCHC(Me)CH_2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ **9**. Reaction of complex **7** with isoprene and $AgBF_4$ in $CH_2Cl_2$ gave dark yellow *crystals* of **9** (63%) (Found: C, 52.0; H, 4.4. $C_{20}H_{21}BF_4MoO$ requires C, 52.2; H, 4.6%), $\nu_{CO}(CH_2Cl_2)$ 1990 $cm^{-1}$. NMR ($CD_3NO_2$): $^1H$, $\delta$ 7.55–7.25 (m, 5 H, Ph), 5.29 (s, 5 H, $C_5H_5$), 5.23 (s, 1 H, $H^1$), 3.83 [br d, 1 H, $H^4$, $^3J(H^4H^3)$ 4.43], 3.14 [d, 1 H, $H^3$, $^3J(H^3H^4)$ 4.56], 2.78 [dd, 1 H, $H^{6b}$, $^2J(H^{6a}H^{6b})$ 3.7, $^4J(H^4H^{6b})$ 3.7], 2.56 (s, 3 H, $C^9H_3$), 2.50 [dd, 1 H, $H^{6a}$, $^2J(H^{6a}H^{6b})$ 3.85, $^4J(H^{6a}H^{6b})$ 1.6 Hz] and 2.19 (s, 3 H, $C^8H_3$); $^{13}C$-{$^1H$}, $\delta$ 223.3 (CO), 137.6 (*ipso*-C), 131.1, 130.2, 130.0 (Ph), 119.4 ($C^2Me$), 117.0 ($C^5Me$), 98.1 ($C_5H_5$), 86.6 ($\mathit{C}^1HPh$), 79.8 ($C^3H$), 78.0 ($C^4H$), 40.4 ($C^6H_2$), 23.7 ($CH_3$) and 19.0 ($CH_3$).

$[Mo\{\eta^3,\eta^3\text{-}CH(Ph)C(Ph)CHCHC(Me)CH_2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ **10**. Similarly, reaction of $[MoCl(\eta^2\text{-}PhC_2Ph)(CO)(\eta\text{-}C_5H_5)]$ with isoprene and $AgBF_4$ in $CH_2Cl_2$ gave dark yellow *crystals* of complex **10** (69%) (Found: C, 57.5; H, 4.4. $C_{25}H_{23}BF_4MoO$ requires C, 57.5; H, 4.4%), $\nu_{CO}(CH_2Cl_2)$ 1980 $cm^{-1}$. NMR ($CD_3NO_2$): $^1H$, $\delta$ 7.7–7.0 (m, 10, Ph), 5.39 (s, 1 H, $H^1$), 5.30 (s, 5 H, $C_5H_5$), 3.99 [br d, 1 H, $H^4$, $^3J(H^3H^4)$ 4.15], 3.40 [d, 1 H, $H^3$, $^3J(H^3H^4)$ 4.22], 3.00 [dd, 1 H, $H^{6b}$, $^2J(H^{6a}H^{6b})$ 3.98, $^4J(H^{6b}H^4)$ 1.2], 2.61 [dd, 1 H, $H^{6a}$, $^2J(H^{6a}H^{6b})$ 4.05, $^4J(H^{6a}H^4)$ 1.5] and 2.28 (s, 3 H, $C^9H_3$); $^{13}C$-{$^1H$}, $\delta$ 224.3 (CO), 138.4, 134.8 (*ipso*-C), 132.0, 131.5, 131.4, 129.8, 129.7 (Ph), 125.5 ($\mathit{C}Me$), 117.3 ($\mathit{C}Ph$), 99.0 ($C_5H_5$), 87.5 (CH), 77.0 (CH), 75.6 (CH), 41.1 ($CH_2$) and 23.8 ($CH_3$).

$[Mo\{\eta^3,\eta^3\text{-}CH(Me)C(Me)CHCHCHCH_2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ **11**. Reaction of complex **2** with buta-1,3-diene and $AgBF_4$ in $CH_2Cl_2$ gave yellow *crystals* of **11** (40%) (Found: C, 42.5; H, 4.2. $C_{14}H_{17}BF_4MoO$ requires C, 42.8; H, 4.2%), $\nu_{CO}(CH_2Cl_2)$ 1990 $cm^{-1}$. NMR: $^1H(CD_3NO_2)$, $\delta$ 5.60 (s, 5 H, $C_5H_5$), 5.37 [dddd, 1 H, $H^5$, $^3J(H^5H^{6b})$ 9.9, $^3J(H^5H^{6a})$ 8.2, $^3J(H^5H^4)$ 5.1, $^4J(H^5H^3)$ 0.78], 4.55 [q, 1 H, $H^1$, $^3J(H^1Me)$ 6.05], 3.56 [br t, 1 H, $H^4$, $^3J(H^4H^3) \approx {}^3J(H^4H^5)$ 4.91], 3.13 [br d, 1 H, $H^3$, $^3J(H^3H^4)$ 4.91], 2.71 [ddd, 1 H, $H^{6b}$, $^3J(H^{6b}H^5)$ 9.75, $^2J(H^{6a}H^{6b})$ 3.21, $^4J(H^6H^4)$ 0.72], 2.55 [ddd, 1 H, $H^{6a}$ $^3J(H^{6a}H^5)$ 8.03, $^2J(J^{6a}H^{6b})$ 3.37, $^4J(H^{6a}H^4)$ 1.1], 2.33 (s, 3 H, $C^8H_3$) and 1.80 [d, 3 H, $C^7H_3$, $^3J(MeH^1)$ 6.04 Hz]; $^{13}C$-{$^1H$} ($CD_2Cl_2$), $\delta$ 222.3 (CO), 121.5 ($\mathit{C}Me$), 95.8 ($C_5H_5$), 94.0 ($\mathit{C}HMe$), 87.0 (CH), 77.3 (CH), 75.6 (CH), 39.7 ($CH_2$), 18.9 (Me) and 17.2 (Me).

$[Mo\{\eta^3,\eta^3\text{-}CH(Ph)C(Me)CHCHCHCH_2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ **12**. Reaction of complex **7** with buta-1,3-diene and $AgBF_4$ in $CH_2Cl_2$ gave yellow *crystals* of **12** (85%) (Found: 50.6; H, 4.0. $C_{19}H_{19}BF_4MoO$ requires C, 51.1; H, 4.3%), $\nu_{CO}(CH_2Cl_2)$ 1995 $cm^{-1}$. NMR: $^1H$ ($CD_3NO_2$), $\delta$ 7.75–7.25 (m, 5 H, Ph), 5.5 [dddd, 1 H, $H^5$, $^3J(H^5H^{6b})$ 10.0, $^3J(H^5H^{6a})$ 8.0, $^3J(H^5H^4)$ 4.9, $^4J(H^5H^3)$ 0.9], 5.37 (s, 5 H, $C_5H_5$), 5.25 (br s, 1 H, $H^1$), 3.93 [br dd, 1 H, $H^4$, $^3J(H^4H^3)$ 4.9, $^3J(H^4H^5)$ 4.8], 3.21 [br d, 1 H, $H^3$, $^3J(H^4H^3)$ 5.0], 2.85 [ddd, 1 H, $H^{6b}$, $^3J(H^{6b}H^5)$ 10.4, $^2J(H^{6a}H^{6b})$ 3.4, $^4J(H^{6b}H^4)$ 1.0], 2.62 [ddd, 1 H, $H^{6a}$, $^3J(H^{6a}H^5)$ 7.9, $^2J(H^{6a}H^{6b})$ 3.5, $^4J(H^{6a}H^4)$ 1.2 Hz] and 2.57 (s, 3 H, Me); $^{13}C$-{$^1H$} ($CD_2Cl_2$), $\delta$ 221.8 (CO), 137.7, 131.1, 130.3, 130.1 (Ph), 120.6 ($\mathit{C}Me$), 97.1 ($C_5H_5$), 94.5 (CH), 87.6 (CH), 79.6 ($C^3$), 75.9 ($C^4$), 40.8 ($CH_2$) and 19.1 (Me).

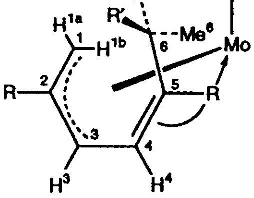
$[Mo\{\eta^3,\eta^3\text{-}CD(Ph)C(Me)CDCHCHCD_2\}(CO)(\eta\text{-}C_5H_5)][BF_4]$ $[^2H_4]$**12**. Similarly, reaction of complex **7** with $CD_2{=}CHCH{=}CD_2$ and $AgBF_4$ in $CH_2Cl_2$ gave yellow *crystals* of $[^2H_4]$**12** (85%), $\nu_{CO}(CH_2Cl_2)$ 1995 $cm^{-1}$. NMR ($CD_3NO_2$): $^1H$, $\delta$ 7.5–7.3 (m, 5 H, Ph), 5.47 [d, 1 H, $H^5$, $^3J(H^5H^4)$ 4.95], 5.36 (s, 5 H, $C_5H_5$), 3.91 [d, 1 H, $H^4$, $^3J(H^4H^5)$ 4.95 Hz] and 2.56 (s, 3 H, Me); $^2H$, $\delta$ 5.06 (br s, $D^1$), 2.9 (br s, $D^3$), 2.6 (br s, $D^6$) and 2.5 (br s, $D^6$).

$[Mo\{\eta^3,\eta^3\text{-}CH(Ph)C(Ph)CHCHCHCH_2\}(CO)(\eta\text{-}C_5H_5)]$-

[BF$_4$] **13**. Similarly, reaction of [MoCl(η$^2$-PhC$_2$Ph)(CO)(η-C$_5$H$_5$)] with buta-1,3-diene and AgBF$_4$ in CH$_2$Cl$_2$ gave yellow *crystals* of complex **13** (74%) (Found: C, 56.5; H, 4.5. C$_{24}$H$_{21}$BF$_4$MoO requires C, 56.7; H, 4.2%), ν$_{CO}$(CH$_2$Cl$_2$) 1995 cm$^{-1}$. NMR (CD$_3$NO$_2$): $^1$H, δ 7.5–7.1 (m, 10 H, Ph), 5.6 [dddd, 1 H, H$^5$, $^3J$(H$^5$H$^{6b}$) 10.0, $^3J$(H$^5$H$^{6a}$) 7.95, $^3J$(H$^5$H$^4$) 4.8, $^4J$(H$^5$H$^3$) 0.90], 5.38 (s, 1 H, H$^1$), 5.37 (s, 5 H, C$_5$H$_5$), 5.25 [dd, 1 H, H$^4$, $^3J$(H$^4$H$^3$) 4.80, $^3J$(H$^4$H$^5$) 4.8], 4.10 [br d, 1 H, H$^3$, $^3J$(H$^3$H$^4$) 4.83], 3.10 [ddd, 1 H, H$^{6b}$, $^3J$(H$^{6b}$H$^5$) 9.9, $^2J$(H$^{6a}$H$^{6b}$) 3.3, $^4J$(H$^{6b}$H$^4$) 0.8] and 2.75 [ddd, 1 H, H$^{6a}$, $^3J$(H$^{6a}$H$^5$) 7.9, $^2J$(H$^{6a}$H$^{6b}$) 3.3, $^4J$(H$^{6a}$H$^4$) 1.25 Hz]; $^{13}$C-{$^1$H}, δ 222.9 (CO), 138.6, 134.8, 131.9, 131.6, 131.5, 129.8, 129.6 (Ph), 126.3 (*ipso*-Ph), 97.9 (C$_5$H$_5$) and 94.5 (CH$_2$).

[Mo{η$^5$-CH$_2$C(Me)CHCHC(Me)CH$_2$Me}(CO)(η-C$_5$H$_5$)] **14**. A suspension of complex **8** (0.1 g, 0.25 mmol) in thf (10 cm$^3$) was cooled to −78 °C. A solution of Li[BHEt$_3$] (0.25 mmol, 1 mol dm$^{-3}$ solution in thf) was then added dropwise with stirring and the reaction mixture allowed to warm to room temperature. The resulting yellow solution was filtered through an alumina plug (5 × 2.5 cm) and all volatiles were removed *in vacuo*. The crude product was redissolved in hexane and chromatographed (alumina, 15 × 2.5 cm) eluting with hexane. One major band was collected and removal of the solvent *in vacuo* gave a bright yellow oil **14** (0.52 g, 66%) (Found: C, 57.5; H, 6.2. C$_{15}$H$_{20}$MoO requires C, 57.7; H, 6.4%), ν$_{CO}$(hexane) 1905 cm$^{-1}$. NMR (CD$_2$Cl$_2$): $^1$H, δ 4.89 (s, 5 H, C$_5$H$_5$), 3.44 [br d, 1 H, H$^3$, $^3J$(H$^3$H$^4$) 5.98], 2.56 [dd, 1 H, H$^{1b}$, $J$(H$^{1a}$H$^{1b}$) 2.53, $^4J$(H$^{1a}$H$^3$) 1.02], 1.94 (s, 3 H, Me$^5$), 1.71 [q, 2 H, H$^{6a}$, H$^{6b}$, $^3J$(HMe) 7.34], 1.68 (s, 3 H, Me$^2$), 1.18 [d, 1 H, H$^4$, $^3J$(H$^3$H$^4$) 6.0], 0.95 (m, 1 H, H$^{1a}$), and 0.93 [t, 3 H, Me$^6$, $^3J$(HMe) 7.3 Hz]; $^{13}$C-{$^1$H}, δ 234.8, 101.9 (C$^5$), 91.4 (C$_5$H$_5$), 76.6 (C$^4$), 75.5 (C$^2$), 69.3, 42.7 (C$^6$), 33.7 (*C*H$_2$Me), 28.6 (Me), 24.7 (Me), and 18.1 (Me). Mass spectrum: *m*/*z* = 314, [*M*$^+$]$^+$; 242, [*M* − CO − CMeCH$_2$Me]$^+$.

Complexes **14D**–**17** were prepared in a similar manner, and on the same scale.



**14** R = Me, R′ = H(D)
**15** R = R′ = Me
**16** R = Me, R′ = Ph

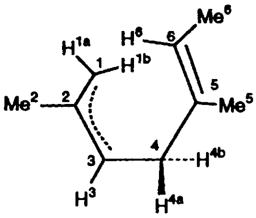
[Mo{η$^5$-CH$_2$C(Me)CHCHC(Me)CHDMe}(CO)(η-C$_5$H$_5$)] **14D**. Reaction of complex **8** with Li[BDEt$_3$] gave a yellow oil **14D** (63%), ν$_{CO}$(hexane) 1905 cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$): δ 4.89 (s, 5 H, C$_5$H$_5$), 3.44 [br d, 1 H, H$^3$, $^3J$(H$^3$H$^4$) 6.0], 2.56 [dd, 1 H, H$^{1b}$, $^2J$(H$^{1a}$H$^{1b}$) 2.53, $J$(H$^{1a}$H$^3$) 1.02], 1.94 (s, 3 H, Me$^5$), 1.68 (s, 3 H, Me$^2$), 1.65 (br s, 1 H, H$^6$), 1.18 [d, 1 H, H$^4$, $^3J$(H$^3$H$^4$) 6.0 Hz], 0.96 (m, 1 H, H$^{1a}$) and 0.94 (br s, 3 H, Me$^6$).

[Mo{η$^5$-CH$_2$C(Me)CHCHC(Me)CHMe$_2$}(CO)(η-C$_5$H$_5$)] **15**. Reaction of complex **8** with LiMe gave a yellow oil **15** (70%) (Found: C, 58.6; H, 6.5. C$_{16}$H$_{22}$MoO requires C, 58.9; H, 6.7%), ν$_{CO}$(hexane) 1890 cm$^{-1}$. NMR (CD$_2$Cl$_2$): $^1$H, δ 5.0 (s, 5 H, C$_5$H$_5$), 3.65 [d, 1 H, H$^3$, $^3J$(H$^3$H$^4$) 6.05], 2.60 [dd, 1 H, H$^{1b}$, $^2J$(H$^{1b}$H$^{1a}$) 2.74, $^4J$(H$^{1b}$H$^3$) 0.92], 2.10 [spt, 1 H, H$^6$, $^3J$(H$^6$Me) 6.78], 1.94 (s, 3 H, Me$^5$), 1.57 (s, 3 H, Me$^2$), 1.08 [d, 1 H, H$^4$, $^3J$(H$^3$H$^4$) 6.22], 1.02 [d, 3 H, Me$^6$, $^3J$(H$^6$Me) 6.78], 1.00 [d, 3 H, Me, $^3J$(H$^6$Me) 6.78] and 0.84 [br d, 1 H, H$^{1a}$, $^2J$(H$^{1a}$H$^{1b}$) 2.74 Hz]; $^{13}$C-{$^1$H} δ 242.8 (CO), 101.0 (C$^5$), 90.5 (C$_5$H$_5$), 80.3 (C$^2$), 78.5 (C$^4$), 68.7 (C$^3$), 41.5 (CH$_2$), 36.1 (*C*HMe), 27.3 (Me), 24.7 (Me), 24.5 (Me) and 20.6 (Me). Mass spectrum: *m*/*z* = 328 [*M*]$^+$.

[Mo{η$^5$-CH$_2$C(Me)CHCHC(Me)CH(Me)Ph}(CO)(η-C$_5$H$_5$)] **16**. Reaction of complex **8** with LiPh gave a yellow oil **16** (65%), ν$_{CO}$(hexane) 1910 cm$^{-1}$. NMR (CD$_2$Cl$_2$): $^1$H, δ 7.6–7.1 (m, 5 H, Ph), 5.08 (s, 5 H, C$_5$H$_5$), 3.78 [br d, 1 H, H$^3$, $^3J$(H$^3$H$^4$) 6.05], 3.28 [q, 1 H, H$^6$, $^3J$(H$^6$Me) 7.2], 2.52 [br d, 1 H, H$^{1b}$, $^2J$(H$^{1b}$H$^{1a}$) 2.76], 1.93 (s, 3 H, Me$^5$), 1.72 (s, 3 H, Me$^2$), 1.43 [d, CH*Me*, $^3J$(H$^6$Me) 7.23], 1.16 [d, 1 H, H$^4$, $^3J$(H$^3$H$^4$) 6.08], and 0.90 [br d, 1 H, H$^{1a}$, $^3J$(H$^{1a}$H$^{1b}$) 2.74 Hz]; $^{13}$C-{$^1$H}, δ 132.3, 130.6, 130.2 (Ph), 91.2 (C$_5$H$_5$), 79.8 (C$^3$), 69.3 (C$^4$), 42.7 (*C*HPhMe), 41.5 (CH$_2$), 26.0 (Me), 24.9 (Me), and 18.9 (Me). Mass spectrum: *m*/*z* = 390, [*M*]$^+$.

[Mo{η$^5$-CH$_2$CHCHCHC(Me)CH$_2$Ph}(CO)(η-C$_5$H$_5$)] **17**. Reaction of complex **12** with Li[BHEt$_3$] afforded the yellow oil **17** (58%) (Found: C, 63.5; H, 6.8. C$_{19}$H$_{20}$MoO requires C, 63.3; H, 6.7%), ν$_{CO}$(diethyl ether) 1905 cm$^{-1}$. NMR (CD$_2$Cl$_2$): $^1$H, δ 7.35–7.15 (m, 5 H, Ph), 5.11 (s, 5 H, C$_5$H$_5$), 4.88 [ddd, 1 H, H$^2$, $^3J$(H$^2$H$^{1b}$) 9.6, $^3J$(H$^2$H$^{1a}$) 7.6, $^3J$(H$^2$H$^3$) 5.0], 3.74 [br dd, 1 H, H$^3$, $^3J$(H$^2$H$^3$) 5.1, $^3J$(H$^3$H$^4$) 5.8], 2.98 [AB system, 2 H, C*H*$_2$Ph, *J* 14.0], 2.70 [ddd, 1 H, H$^{1b}$, $^3J$(H$^2$H$^{1b}$) 8.1, $^2J$(H$^{1b}$H$^{1a}$) 2.9, $^4J$(H$^{1b}$H$^3$) 0.6], 1.60 (s, 3 H, Me$^5$), 1.39 [d, 1 H, H$^4$, $^3J$(H$^3$H$^4$) 6.1] and 1.20 [ddd, 1 H, H$^{1a}$, $^3J$(H$^{1a}$H$^2$) 7.2, $^2J$(H$^{1a}$H$^{1b}$) 2.5, $^4J$(H$^{1a}$H$^3$) 0.6 Hz]; $^{13}$C-{$^1$H}, δ 241.5 (CO), 143.8, 128.7, 128.4, 126.0 (Ph), 90.3 (C$_5$H$_5$), 84.6 (C$^5$), 76.6 (C$^4$), 73.5 (*C*Me), 67.8 (C$^3$), 45.9 (CH$_2$), 40.8 (*C*H$_2$Ph) and 28.8 (Me).

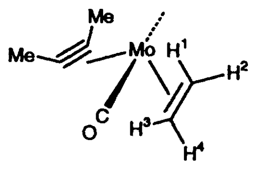
*Reactions of complex* **8** *with* K[BHBu$^s_3$]. The reaction was carried out in the same way as described for the formation of complex **14** except that K[BHBu$^s_3$] (0.25 mmol) was used instead of Li[BHEt$_3$]. One yellow band was collected by column chromatography which on solvent removal afforded a mixture of the yellow oils **14** and **18** (4 : 1) (62%) (Found: C, 57.5; H, 6.2. C$_{15}$H$_{20}$MoO requires C, 57.7; H, 6.4%), ν$_{CO}$(hexane) 1905 and 1895 cm$^{-1}$. NMR (CD$_2$Cl$_2$) for **18**: $^1$H, δ 4.81 (s, 5 H, C$_5$H$_5$), 3.21 [q, 1 H, H$^6$, $^3J$(H$^6$Me) 5.7], 3.14 [dd, 1 H, H$^{1b}$, $^2J$(H$^{1b}$H$^{1a}$) 2.0, $^4J$(H$^{1b}$H$^3$) 2.0], 2.68 [dd, 1 H, H$^{4a}$, $^3J$(H$^{4a}$H$^{4b}$) 14.59, $^3J$(H$^3$H$^{4a}$) 7.7], 2.19 [d, 1 H, H$^{1a}$, $^2J$(H$^{1a}$H$^{1b}$) 1.7], 1.98 [ddd, 1 H, H$^3$, $^2J$(H$^3$H$^{4b}$) 4.7, $^3J$(H$^{4a}$H$^3$) 7.32, $^4J$(H$^3$H$^{1b}$) 1.9], 1.61 (s, 3 H, Me$^2$), 1.45 [dd, 1 H, H$^{4b}$, $^3J$(H$^{4b}$H$^{4a}$) 14.6, $^2J$(H$^{4b}$H$^3$) 4.54], 1.38 [d, 3 H, Me$^6$, $^3J$(H$^6$Me) 6.0 Hz] and 1.20 (s, 3 H, Me$^5$); $^{13}$C-{$^1$H}, δ 249.6 (CO), 99.4 (C$^5$), 92.3 (C$^2$), 90.5 (C$_5$H$_5$), 44.6 (C$^3$), 41.8 (CH$_2$), 36.8 (C$^1$), 33.3 (C$^4$), 32.3 (C$^6$), 27.3 (Me), 21.4 (Me) and 19.1 (Me).



[Mo(η$^2$-C$_2$H$_4$)(η$^2$-MeC$_2$Me)(CO)(η-C$_5$H$_5$)][BF$_4$] **19**. The complex [MoBr(η$^2$-MeC$_2$Me)(CO)(η-C$_5$H$_5$)] **2** (0.5 g, 1.55 mmol) was stirred in CH$_2$Cl$_2$ (20 cm$^3$) whilst a stream of ethylene was bubbled through the solution for 15 min. Addition of AgBF$_4$ (0.3 g, 1.55 mmol) resulted in the precipitation of a white solid (AgBr). After 15 min the reaction mixture was filtered through Celite and the volume of solvent reduced to *ca.* 10 cm$^3$ by evaporation under a stream of C$_2$H$_4$. Diethyl ether (25 cm$^3$) was added, precipitating an orange solid. Crystallisation from dichloromethane–diethyl ether (saturated with C$_2$H$_4$) afforded red *crystals* of **19** (0.35 g, 63%) (Found: C, 40.7; H, 4.3. C$_{12}$H$_{15}$BF$_4$MoO requires C, 40.2; H, 4.2%), ν$_{CO}$(CH$_2$Cl$_2$) 2020 cm$^{-1}$. $^1$H NMR (CD$_2$Cl$_2$): δ 5.97 (s, 5 H, C$_5$H$_5$), 3.19 (s, 6 H, *Me*C≡C*Me*), 2.8 (m, 1 H, CH), 2.61 (m, 1 H, CH), 2.46 (br dd, 1 H, CH) and 1.22 (m, 1 H, CH) (all the C$_2$H$_4$ signals appeared as broad multiplets with one coupling of between 10 and 12 Hz discernible). The alkyne rotation may be frozen out at low temperature, the singlet at δ 3.19 separating into two peaks (Δν 58.0 Hz). The coalescence temperature was 260 K, giving a calculated barrier to rotation $\Delta G^{*}_{T_c}$ 53 ± 1 kJ mol$^{-1}$. $^{13}$C-{$^1$H} NMR (CD$_2$Cl$_2$): δ 223.2 (CO), 100.7 (C$_5$H$_5$), 63.0 (CH$_2$=*C*), 46.0 (*C*H$_2$=C) and 22.1 (*Me*C$_2$*Me*).

The following complexes were prepared in a similar manner and on a similar scale to **19**.

$[Mo(\eta^2\text{-}C_2H_4)(\eta^2\text{-}PhC_2Ph)(CO)(\eta\text{-}C_5H_5)][BF_4]$ **20**. Reaction of $[MoCl(\eta^2\text{-}PhC_2Ph)(CO)(\eta\text{-}C_5H_5)]$ with $C_2H_4$ and $AgBF_4$ gave red *crystals* of complex **20** (69%) (Found: C, 55.1; H, 4.0. $C_{22}H_{19}BF_4MoO$ requires C, 54.8; H, 3.9%), $\nu_{CO}(CH_2Cl_2)$ 1950 cm$^{-1}$. NMR ($CD_2Cl_2$): $^1$H, δ 7.8–7.6 (m, 10 H, Ph), 6.06 (s, 5 H, $C_5H_5$), 3.42, 2.7, 2.5, 1.65 (all broad multiplets integrating for 1 H, ethylene signals); $^{13}$C-{$^1$H}, δ 224.3 (CO), 135.7 (C, Ph), 133.1, 130.0, 129.4 (CH, Ph), 101.2 ($C_5H_5$), 46.7 ($CH_2$=C) and 45.5 ($CH_2$=C).



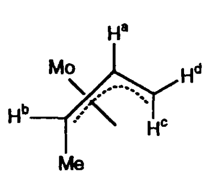
$[Mo(\eta^2\text{-}C_2H_4)(\eta^2\text{-}MeC_2Me)(CO)(\eta^5\text{-}C_9H_7)][BF_4]$ **21**. Treatment of $[MoBr(\eta^2\text{-}MeC_2Me)(CO)(\eta^5\text{-}C_9H_7)]$ **5** with $AgBF_4$–$C_2H_4$ in $CH_2Cl_2$ afforded deep red *crystals* of complex **21** (52%), $\nu_{CO}(CH_2Cl_2)$ 2000 cm$^{-1}$. NMR ($CD_2Cl_2$): $^1$H, δ 7.55–7.15 (m, 4 H, $C_9H_7$), 6.05 [t, 1 H, $C_9H_7$, $^3J$(HH) 3.1], 5.85 (br s, 1 H, $C_9H_7$), 5.35 (br s, 1 H, $C_9H_7$), 3.21 (s, 6 H, $MeC_2Me$), 2.32 [ddd, 1 H, $H^2$, $^3J(H^2H^3)$ 14.3, $^3J(H^2H^4)$ 11.5, $^2J(H^2H^1)$ 2.9], 1.46 [ddd, 1 H, $H^3$, $^3J(H^3H^2)$ 14.5, $^3J(H^3H^1)$ 10.6, $^2J(H^3H^4)$ 2.1], 1.3 [ddd, 1 H, $H^4$, $^3J(H^4H^1)$ 17.0, $^3J(H^4H^2)$ 11.8, $^2J(H^4H^3)$ 2.0] and 0.03 [ddd, 1 H, $H^1$, $^3J(H^1H^4)$ 17.0, $^3J(H^1H^3)$ 10.7, $^2J(H^1H^2)$ 2.9 Hz]; $^{13}$C-{$^1$H}, δ 224.2 (CO), 169.4 (Me*C*≡C), 131.1, 129.6, 125.3, 122.3 (CH, $C_9H_7$), 114.8 (C, $C_9H_7$), 102.7, 91.3, 79.7 (CH, $C_9H_7$), 53.7 ($CH_2$=C), 51.8 ($CH_2$=C) and 22.1 (*Me*C≡C).

*Reactions of* $[Mo(\eta^2\text{-}C_2H_4)(\eta^2\text{-}MeC_2Me)(CO)(\eta\text{-}C_5H_5)][BF_4]$ **19**. (*a*) *With* $K[BHBu^s_3]$. Complex **19** (0.1 g, 0.25 mmol) was suspended in thf (10 cm$^3$) and cooled to −78 °C. The salt $K[BHBu^s_3]$ (0.3 mmol, 1 mol dm$^{-3}$ solution in thf) was added and the reaction mixture allowed to warm to room temperature. It gradually turned purple. The solution was filtered through alumina (4 × 2.5 cm) and the volatile material removed *in vacuo*. The purple oil was dissolved in hexane and chromatographed on an alumina-packed column (8 × 2.5 cm). Elution with hexane–diethyl ether (50:1) gave a purple oil. Recrystallisation (−78 °C) from hexane afforded low-melting purple *crystals* of $[MoEt(\eta^2\text{-}MeC_2Me)(CO)(\eta\text{-}C_5H_5)]$ **22** (0.03 g, 39%) (Found: C, 52.8; H, 5.9. $C_{12}H_{16}MoO$ requires C, 52.9; H, 5.9%), $\nu_{CO}$(hexane) 1910 cm$^{-1}$. NMR ($CD_2Cl_2$): $^1$H, δ 5.25 (s, 5 H, $C_5H_5$), 2.95 (s, 3 H, *Me*C≡C), 2.87 (s, 3 H, *Me*C≡C), 1.05 [t, 3 H, C*H*$_3$CH$_2$, $^3J$(HH) 7.5], 0.8 [dq, 1 H, $CH_3C\mathit{H}H^1$, $^3J(H^1Me)$ 11.7, $^2J(HH^1)$ 7.3] and 0.25 [dq, 1 H, $CH_3CH\mathit{H}^1$, $^3J(H^1Me)$ 11.8, $^2J(HH^1)$ 7.4 Hz]; $^{13}$C-{$^1$H}, δ 245.6 (CO), 191.9 (Me*C*≡C), 189.6 (Me*C*≡C), 94.0 ($C_5H_5$), 24.1 (*C*H$_3$CH$_2$), 20.1 (*Me*C≡C), 17.5 (*Me*C≡C) and 11.0 (CH$_3$*C*H$_2$).

(*b*) *With* LiMe. This reaction was carried out in a similar way affording the purple, air-sensitive low-melting solid $[MoMe(\eta^2\text{-}MeC_2Me)(CO)(\eta\text{-}C_5H_5)]$ **23** (69%) (Found: C, 51.0; H, 5.5. $C_{11}H_{14}MoO$ requires C, 51.2; H, 5.4%), $\nu_{CO}$(diethyl ether) 1910 cm$^{-1}$. NMR ($CD_2Cl_2$): $^1$H, δ 5.28 (s, 5 H, $C_5H_5$), 2.98 (s, 3 H, *Me*C≡C), 2.88 (s, 3 H, *Me*C≡C) and −0.46 (s, 3 H, Me); $^{13}$C-{$^1$H}, δ 243.4 (CO), 193.2 (Me*C*≡C), 190.9 (Me*C*≡C), 94.3 ($C_5H_5$), 20.6 (*Me*C≡C), 15.1 (*Me*C≡C) and −7.9 (Me).

$[Mo(\eta^2\text{-}MeC_2Me)(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **24**. Complex **19** (0.2 g, 0.56 mmol) was dissolved in $CH_2Cl_2$ (15 cm$^3$). Carbon monoxide was bubbled through the solution for 10 min, which changed from red to purple. The volume of solvent was reduced *in vacuo* to *ca.* 5 cm$^3$ and diethyl ether (20 cm$^3$) added, precipitating a purple solid. This was washed with diethyl ether (3 × 15 cm$^3$) and recrystallised from dichloromethane–diethyl ether to give air-sensitive, purple *crystals* of **24** (0.14 g, 70%) (Found: C, 36.8, H, 3.2. $C_{11}H_{11}BF_4MoO_2$ requires C, 36.4; H, 3.6%), $\nu_{CO}(CH_2Cl_2)$ 2080m and 1980s cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): δ 6.26 (s, 5 H, $C_5H_5$) and 3.38 (s, 6 H, *Me*C≡C*Me*). Alkyne rotation may be frozen out at low temperatures, with the signal at δ 3.38 collapsing into two peaks (Δν 22.8 Hz); the coalescence temperature of 213 K leads to a calculated barrier to rotation $\Delta G^*_{T_c}$ 41 kJ mol$^{-1}$. $^{13}$C-{$^1$H} NMR ($CD_2Cl_2$): δ 221.1 (CO), 217.9 (CO), 100.7 ($C_5H_5$) and 23.3 (*Me*C≡C*Me*).

*Reaction of complex* **24** *with* $Li[BHBu^s_3]$. Complex **24** (0.06 g, 0.17 mmol) was suspended in thf (10 cm$^3$) and cooled to −78 °C. The salt $K[BHBu^s_3]$ (0.17 mmol, 1 mol dm$^{-3}$ solution in thf) was added dropwise with stirring. On warming to room temperature the solution became orange, and was then filtered through alumina (3 × 2.5 cm) and all volatiles removed *in vacuo*. The orange solid was redissolved in hexane (3 cm$^3$) and chromatographed. Elution with hexane–diethyl ether (50:1) gave one yellow band which was collected and recrystallised (−30 °C) from hexane to give deep yellow *crystals* of $[Mo(\eta^3\text{-}CH_2CHCHMe)(CO)_2(\eta\text{-}C_5H_5)]$ **25** (0.03 g, 67%) (Found: C, 48.8; H, 4.3. $C_{11}H_{12}MoO_2$ requires C, 48.5; H, 4.4%), $\nu_{CO}$(hexane) 1955s and 1880s cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): δ 5.26 (s, 5 H, $C_5H_5$), 4.05 [br dd, 1 H, $H^a$, $^3J(H^aH^c)$ 10.8, $^3J(H^aH^b)$ 7.7], 3.90 [ddq, 1 H, $H^d$, $^3J(H^dMe)$ 6.6, $^4J(H^dH^b)$ 1.4, $^3J(H^dH^a)$ 7.6], 2.85 [ddd, 1 H, $H^b$, $^3J(H^aH^b)$ 7.1, $^2J(H^bH^c)$ 2.4, $^4J(H^dH^b)$ 1.7], 1.35 [dd, 1 H, $H^c$, $^3J(H^aH^c)$ 10.8, $^2J(H^bH^c)$ 2.2] and 0.94 [d, 3 H, Me, $^3J(H^dMe)$ 6.4 Hz].



*Reactions of complex* **19**. (*a*) *With isoprene*. Isoprene (0.1 g, 1.47 mmol) was added at room temperature to a stirred solution of complex **19** (0.15 g, 0.42 mmol) in $CH_2Cl_2$ (10 cm$^3$). After 10 min the colour changed from red to deep yellow. The reaction mixture was filtered through Celite (3 × 2.5 m) and the solvent volume reduced *in vacuo* to *ca.* 3 cm$^3$. Diethyl ether (20 cm$^3$) was added and the resulting precipitate collected and recrystallised from dichloromethane–diethyl ether to give yellow *crystals* of **8** (0.12 g, 72%).

(*b*) *With diphenylacetylene*. One equivalent of $PhC_2Ph$ (0.025 g, 0.14 mmol) was added to a stirred solution of complex **19** (0.05 g, 0.14 mmol) in $CH_2Cl_2$ (10 cm$^3$). The solution immediately turned from red to yellow. After 10 min the reaction mixture was filtered through Celite. The solvent volume was reduced to *ca.* 5 cm$^3$ and diethyl ether (20 cm$^3$) added. A yellow solid precipitated which was worked up with $Et_2O$ (2 × 20 cm$^3$) and crystallised from $CH_2Cl_2$–$Et_2O$ to give yellow *crystals* of $[Mo(\eta^2\text{-}MeC_2Me)(\eta^2\text{-}PhC_2Ph)(CO)(\eta\text{-}C_5H_5)][BF_4]$ **27** (78%) (Found: C, 56.7; H, 4.0. $C_{24}H_{21}BF_4MoO$ requires C, 56.7; H, 4.1%), $\nu_{CO}(CH_2Cl_2)$ 2060 cm$^{-1}$. NMR ($CD_2Cl_2$): $^1$H, δ 7.9–7.3 (m, 10 H, Ph), 6.00 (s, 5 H, $C_5H_5$), 3.29 (s, 3 H, Me), and 2.86 (s, 3 H, Me); $^{13}$C-{$^1$H}, δ 219.6 (CO), 169.0 (Ph*C*≡), 165.6 (Me*C*≡), 152.4 (Ph*C*≡), 149.6 (Me*C*≡), 133.8, 132.8 (Ph), 132.6, 132.5, 131.2, 130.1, 129.6, 128.0 (Ph), 101.6 ($C_5H_5$), 21.6 (*Me*C), and 16.7 (*Me*C).

(*c*) *With Methyl(phenyl)acetylene*. Similarly, reaction of complex **19** (0.14 mmol) with $PhC_2Me$ (0.14 mmol) gave yellow *crystals* of $[Mo(\eta^2\text{-}MeC_2Me)(\eta^2\text{-}PhC_2Me)(CO)(\eta\text{-}C_5H_5)][BF_4]$ **28** (60%), $\nu_{CO}(CH_2Cl_2)$ 2050 cm$^{-1}$. $^1$H NMR ($CDCl_3$): δ 7.8–7.4 (m, 5 H, Ph), 5.93 (s, 5 H, $C_5H_5$), 3.18 (s, 3 H, MeC≡), 3.08 (s, 3 H, $PhC_2Me$) and 2.85 (s, 3 H, MeC≡). The spectrum also showed (6:1) signals due to the known cation $[Mo(\eta^2\text{-}PhC_2Me)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$.

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