Reactions of Co-ordinated Ligands. Part 17.[1] The Synthesis and Reactions of Cationic η^5-Indenyl- and η-Cyclopentadienyl-molybdenum Complexes containing 1,3-Diene and Acetylene Ligands

By **Martin Bottrill** and **Michael Green**,* Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Reaction of $[\{Mo(CO)_3(\eta^5\text{-}C_9H_7)\}_2]$ with $Ag[BF_4]$ in MeCN affords $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$, which reacts with $L = P(OMe)_3$, $Ph_2PCH_2CH_2PPh_2$, buta-1,3-diene, isoprene, 2,3-dimethylbuta-1,3-diene, or *trans*-penta-1,3-diene to form $[Mo(CO)_2L_2(\eta^5\text{-}C_9H_7)][BF_4]$; alternatively, the 1,3-diene complexes, including those of cyclohexa-1,3-diene and cyclo-octatetraene, can be formed directly from $[\{Mo(CO)_3(\eta^5\text{-}C_9H_7)\}_2]$, $Ag[BF_4]$, and the 1,3-diene. Reaction of $Na[BH_4]$ or 1-morpholinocyclopent-1-ene with the 1,3-diene cations results in regioselective formation of the *anti*-substituted η^3-allyl complexes. Treatment of $[Mo(CO)_2(NCMe)_2(\eta^5\text{-}C_9H_7)][BF_4]$ with acetylenes or reaction of $[\{Mo(CO)_3(\eta^5\text{-}C_9H_7)\}_2]$ or $[\{Mo(CO)_3(\eta^5\text{-}C_5H_5)\}_2]$ with $Ag[BF_4]$ and the respective acetylene in CH_2Cl_2 affords the 16-electron cations $[Mo(CO)(\eta^2\text{-}RC_2R')_2L'][BF_4]$ ($R = R' = Me$ or Ph; $R = H$, $R' = Me$; $R = H$, $R' = Bu^t$; $L' = \eta^5\text{-}C_9H_7$ or $\eta\text{-}C_5H_5$). Reaction of these complexes with excess of $P(OMe)_3$ gives $[Mo(\eta^2\text{-}RC_2R')\{P(OMe)_3\}_2L'][BF_4]$. In contrast, with the bis(acetylene) cations the acetylene in the latter complexes readily undergoes propeller rotation.

ALTHOUGH significant progress has been made on the synthesis of cationic transition-metal complexes,[2] there has been little effort devoted, with one or two notable exceptions,[3] to exploring and understanding the chemistry of such species. It had been reported[4] that a redox reaction occurred when dicarbonyl(η-cyclopentadienyl)iron dimer was treated with silver(I) tetrafluoroborate in acetonitrile, resulting in the formation of silver metal and the cation $[Fe(NCMe)(CO)_2(\eta\text{-}C_5H_5)][BF_4]$. In connection with a study[5] of insertion reactions of molybdenum(II) complexes, we were prompted into exploring related reactions in molybdenum chemistry, and observed interesting differences in reactivity patterns depending on the nature of the ligands present. In this paper are described our initial investigations concerned with the synthesis of cationic 1,3-diene complexes, their reactions with nucleophiles, and the synthesis of 16-electron bis(acetylene)monocarbonyl complexes.†

RESULTS AND DISCUSSION

We had found that insertion reactions of η^5-indenyl complexes of the type $[MoR(CO)_3(\eta^5\text{-}C_9H_7)]$,[6] and displacement reactions of the rhodium(I) complex $[Rh(C_2H_4)_2(\eta^5\text{-}C_9H_7)]$,[7] occurred at significantly higher rates than the corresponding η-cyclopentadienyl complexes. This led us to explore the redox reactions of $[\{Mo(CO)_3(\eta^5\text{-}C_9H_7)\}_2]$[8] with silver(I) ions. Treatment of a solution of the dimer in acetonitrile with $Ag[BF_4]$ led to the rapid deposition of a silver mirror, cleavage of the molybdenum–molybdenum bond, and the formation in high yield of (1), bis(acetonitrile)dicarbonyl(η^5-indenyl)molybdenum tetrafluoroborate, characterised by the presence in the i.r. spectrum of two terminal carbonyl bands and bands corresponding to co-ordinated acetonitrile. Although the η-cyclopentadienyl analogue of (1) had been obtained[9] a number of years ago by a rather unattractive route involving $AlCl_3$, the chemistry had not been explored, and it was interesting that an attempt to extend the silver redox reaction to the $\eta\text{-}C_5H_5$ system was unsuccessful. A further point of interest was the contrast between the molybdenum and iron systems.

Reaction of (1) with trimethyl phosphite or 1,2-bis(diphenylphosphino)ethane (dppe) led to the displacement of both acetonitrile ligands and the formation of (2) and (3) as yellow crystalline complexes, showing the expected characteristic i.r. and ^1H n.m.r. spectra. More significant reactions occurred with the 1,3-dienes, buta-1,3-diene, isoprene, 2,3-dimethylbuta-1,3-diene, *trans*-penta-1,3-diene, cyclohexa-1,3-diene, and cyclo-octatetraene, to form respectively the crystalline complexes (4), (5), (6), (7), (8), and (9). These complexes can also be formed directly by reaction of the respective diene with $[\{Mo(CO)_3(\eta^5\text{-}C_9H_7)\}_2]$ and $Ag[BF_4]$ in methylene chloride, thus avoiding the intermediate (1).

The cyclo-octatetraene complex (9) tended to decompose in solution; however, the ^1H spectra of (6) and (8) showed the expected features, sharp resonances corresponding to the presence of only one conformational isomer, either (a) or (b), being observed. The spectra of the remaining 1,3-diene complexes showed sharp methyl resonances, but some broadness of the remaining resonances of the co-ordinated 1,3-diene was observed. The ^1H spectrum of, for example, (4) did not show any appreciable sharpening in the diene part of the spectrum on cooling [-90 °C, $(CD_3)_2CO$], suggesting that both

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† All the complexes described were characterised by elemental analysis and where applicable by mass spectroscopy.

[1] Part 16, M. Bottrill, R. Davies, M. Green, R. P. Hughes, R. Goddard, B. Lewis, and P. Woodward, *J.C.S. Dalton*, 1977, 1252.

[2] See, for example, E. W. Abel and S. P. Tyfield, *Adv. Organometallic Chem.*, 1969, **8**, 117.

[3] R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 1976, **98**, 2134 and refs. therein.

[4] W. E. Williams and F. J. Lalor, *J.C.S. Dalton*, 1973, 1329.

[5] J. L. Davidson, M. Green, J. Z. Nyathi, C. Scott, F. G. A. Stone, A. J. Welch, and P. Woodward, *J.C.S. Chem. Comm.*, 1976, 714.

[6] M. Bottrill and M. Green, unpublished work.

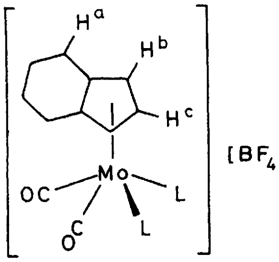
[7] P. Caddy, M. Green, E. O'Brien, L. E. Smart, and P. Woodward, *Agnew. Chem.*, 1977, **89**, 671.

[8] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1965, **5**, 475.

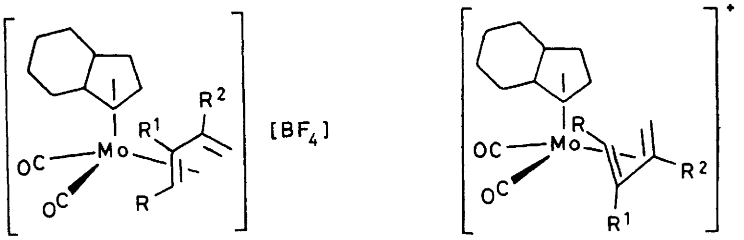
[9] K. W. Barnet, P. M. Treichel, and R. L. Shubkin, *J. Organometallic Chem.*, 1967, **7**, 449.

conformers are present in solution even at low temperature. Attempts to obtain spectra at lower temperatures were frustrated by solubility problems.*

It was shown[10] that the buta-1,3-diene and isoprene η-cyclopentadienyl analogues can be prepared less directly by a sequence of reactions involving hydride abstraction from the corresponding *anti*-but-2-enyl and 1,1-dimethylallyl complexes, which can be obtained by the reaction of the anion $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]^-$ with halogenoallyl compounds. Our observation of the formation of these 1,3-diene cations directly from the corresponding diene is particularly important from the standpoint of using such complexes to form derivatives of 1,3-dienes.

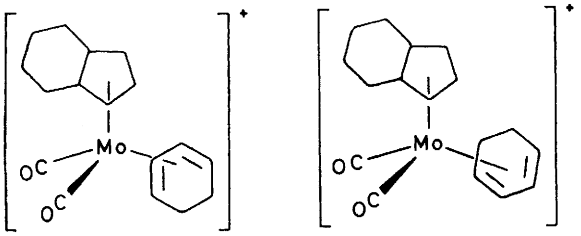


(1) L = MeCN
(2) L = P(OMe)$_3$
(3) L$_2$ = dppe



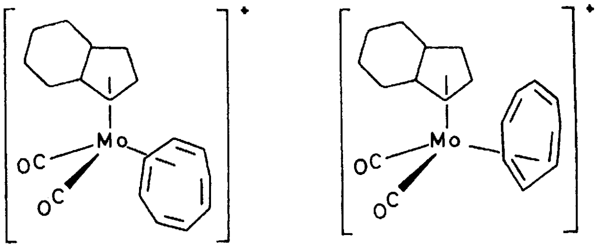
(a) (b)

(4) R = R^1 = R^2 = H
(5) R = R^2 = H, R^1 = Me
(6) R = H, R^1 = R^2 = Me
(7) R = Me, R^1 = R^2 = H



(a) (b)

(8)



(a) (b)

(9)

Reaction of (4) with sodium tetrahydroborate [tetrahydrofuran (thf), room temperature] leads to a regioselective reaction at C^1 affording the thermodynamically less stable *anti*-substituted η^3-but-2-enyl complex (11). Corresponding reactions with the isoprene, 2,3-dimethylbuta-1,3-diene, *trans*-penta-1,3-diene, and cyclohexa-1,3-diene cations proceeded in the same kinetically controlled manner affording selectively the η^3-allylic complexes (10), (12), (13), and (14) respectively. The assignment of the conformation (*exo* or *endo*) of these complexes was aided by the presence of η^5-indenyl ligands, the magnetic anisotropy of the benzene ring providing a definitive method of assigning resonances.[11] It has been shown that protons pointing in the direction of the benzene ring are shifted upfield. Thus in an *exo* conformer the central allylic proton occurs at *ca.* τ 10.5, whereas in the *endo* conformation shifts of the order of τ 6.5 are observed. Similarly, the *anti*-protons are shifted (δ −1.32 p.p.m.) upfield in the *endo* conformation. In this way the *exo* conformation could be assigned to all the η^3-allylic complexes as illustrated.

It was important to investigate whether the formation of the *anti*-substituted allyl species was related to the size of the reacting nucleophile. Therefore, the reaction of the bulky nucleophile 1-morpholinocyclopent-1-ene with the *trans*-penta-1,3-diene (7) and the isoprene cation (5) were examined. A rapid reaction occurred at room temperature, and chromatography of the reaction mixture on alumina gave directly the 2-substituted cyclopentan-1-one η^3-allyl complex (15). The stereochemistry of the crystalline products was established by ^{1}H n.m.r. spectroscopy. Thus, as illustrated, the kinetically controlled product was obtained selectively. These observations require that nucleophilic attack occurs directly on the sp^2-hybridised carbon atoms of the coordinated 1,3-dienes. As shown in the Scheme, reaction at the molybdenum centre would require that the diene becomes bonded in the 1—2-η^2 mode leading not only to the possible formation of isomers, but also to the formation of the incorrect product, since the least-

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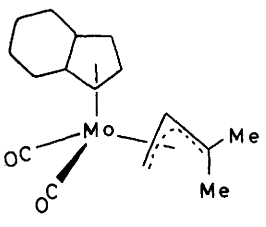
* *Note added in proof.* The low-temperature 270 MHz spectra of the corresponding η-C_5H_5 complexes have been resolved (J. W. Faller and A. M. Rosan, *J. Amer. Chem. Soc.*, 1977, **99**, 4858).

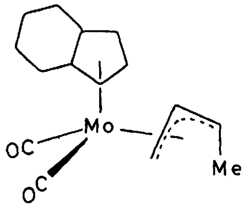
[10] J. W. Faller and A. M. Rosan, Lecture at the New York Academy of Sciences Conference on 'The Place of Transition Metals in Organic Synthesis,' New York, November 1976.

[11] J. W. Faller, C. C. Chen, M. J. Mattina, and A. Jakubowski, *J. Organometallic Chem.*, 1973, **52**, 361.

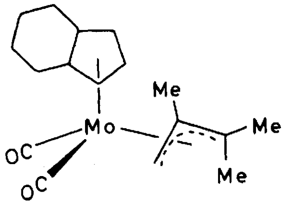
substituted olefin would be expected to remain bonded to the metal prior to insertion into the Mo–H bond. Earlier studies [12] on the reaction of nucleophiles such as $[BH_4]^-$ with $[M(CO)_3(C_7H_7)]^+$ (M = Cr or Mo) suggest that the reactions observed here involve attack on the face of the co-ordinated 1,3-diene opposite to the metal. The reasons for the observed direction of attack are not clear, but could be related to charge distribution.



(10)



(11)



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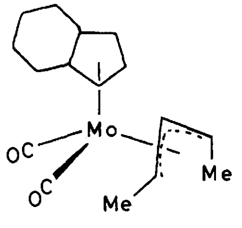

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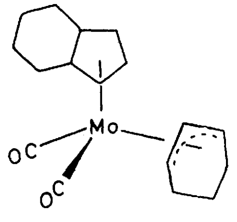

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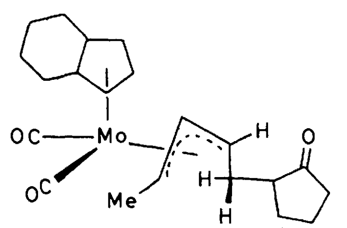

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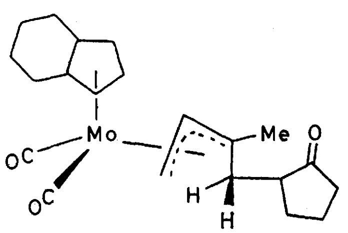

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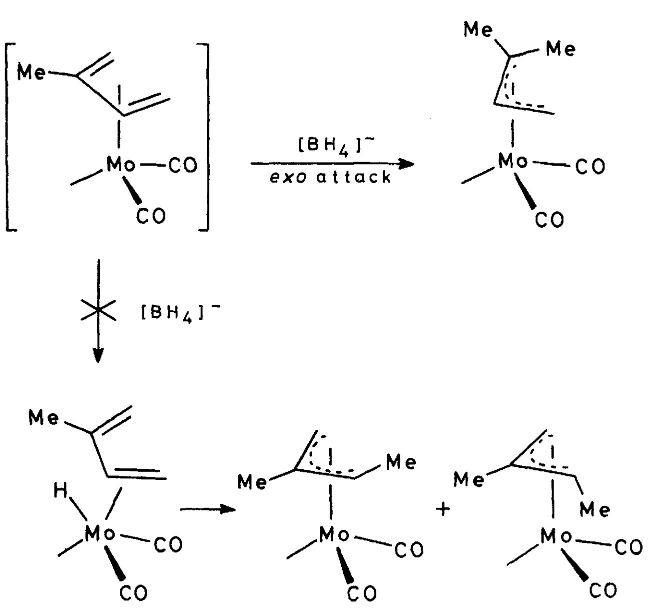

SCHEME η^5-C_9H_7 ligand omitted for clarity

The bis(acetonitrile) cation (1) also provides an important entry to a range of acetylene cationic complexes. Reaction (room temperature) of (1) with an excess of 3,3-dimethylbut-1-yne, but-2-yne, diphenylacetylene, acetylene, or prop-1-yne led to the loss of carbon monoxide and the formation of the bis(acetylene)monocarbonyl cations (17), (18), (19), (20) and (21). Alternatively, these cations can be obtained directly from the reaction of the metal–metal-bonded dimer $[\{Mo(CO)_3(\eta^5\text{-}C_9H_7)\}_2]$ with $Ag[BF_4]$ and the respective acetylene in methylene chloride as solvent. As pointed out above, the η-C_5H_5 analogue of (1) is not readily available; however, the direct reaction of $Bu^tC{\equiv}CH$, $MeC{\equiv}CMe$, $PhC{\equiv}CPh$, or $MeC{\equiv}CH$ with $Ag[BF_4]$ and $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ afforded in good yield the cations (22), (23), (24), and (25) as yellow crystalline complexes.

It has been previously [13,14] found that acetylenes ($CF_3C_2CF_3$, PhC_2Ph, or PhC_2Me) react with $[MX(CO)_3(\eta\text{-}C_5H_5)]$ (M = Mo or W; X = Cl, Br, or I) to form neutral 16-electron species $[MX(\eta^2\text{-}RC_2R)_2(\eta\text{-}C_5H_5)]$, and a single-crystal X-ray diffraction study [14] established the structure of $[WCl(\eta^2\text{-}CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)]$, where the tungsten is in an essentially octahedral environment and the acetylenes and halogen each occupy adjacent sites. However, our previous attempts to convert these halogeno complexes into cationic species were unsuccessful. It is clear that this has now been achieved by a different approach, and it is suggested that the bis(acetylene)monocarbonyl cations are isostructural with the neutral species. In agreement, the ^1H n.m.r. spectra of the but-2-yne complexes (18) and (23) show two methyl environments, and the bis(acetylene) complex (21) two $HC{\equiv}C$ environments. Moreover, the bis(prop-1-yne) cations (21) and (25) show resonances corresponding to the presence of the three illustrated isomers, whereas the ^1H spectra of the sterically more demanding bis(3,3-dimethylbut-1-yne) cations show resonances consistent with the presence of only one isomer, presumably the *trans* isomer, in solution. In

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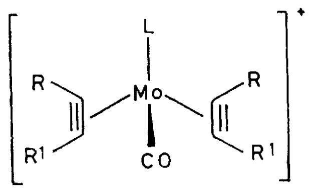
[12] P. L. Pauson, G. H. Smith, and J. H. Valentine, *J. Chem. Soc.* (*C*), 1967, 1057.

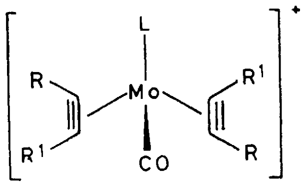
[13] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 2531.

[14] J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1976, 738.

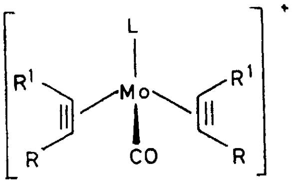
contrast to the bis(hexafluorobut-2-yne) complexes [$MCl(\eta^2\text{-}CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)$],[14] the acetylenes in the cationic complexes do not rotate, the ^1H spectra being temperature invariant.



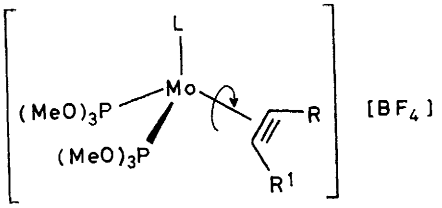
(18) L = $\eta^5\text{-}C_9H_7$, R = R^1 = Me
(23) L = $\eta\text{-}C_5H_5$, R = R^1 = Me
(19) L = $\eta^5\text{-}C_9H_7$, R = R^1 = Ph
(24) L = $\eta\text{-}C_5H_5$, R = R^1 = Ph
(20) L = $\eta^5\text{-}C_9H_7$, R = R^1 = H
(21) L = $\eta^5\text{-}C_9H_7$, R = H, R^1 = Me



(17) L = $\eta^5\text{-}C_9H_7$, R = H, R^1 = Bu^t
(22) L = $\eta\text{-}C_5H_5$, R = H, R^1 = Bu^t
(25a) L = $\eta\text{-}C_5H_5$, R = H, R^1 = Me



(25b) L = $\eta\text{-}C_5H_5$, R = H, R^1 = Me



(26) L = $\eta^5\text{-}C_9H_7$, R = R^1 = Me
(27) L = $\eta^5\text{-}C_9H_7$, R = R^1 = Ph
(28) L = $\eta^5\text{-}C_9H_7$, R = H, R^1 = Me
(29) L = $\eta\text{-}C_5H_5$, R = H, R^1 = Bu^t
(30) L = $\eta\text{-}C_5H_5$, R = R^1 = Me
(31) L = $\eta\text{-}C_5H_5$, R = R^1 = Ph

The bis(acetylene) cations are, however, highly reactive towards ligand substitution. Treatment with an excess of $P(OMe)_3$ *at room* temperature leads to the displacement of carbon monoxide and one acetylene to give the highly coloured crystalline 16-electron monoacetylenebis(trimethyl phosphite) complexes (26)—(31), characterised by analysis and n.m.r. spectroscopy. Recently, in a preliminary communication,[15] a synthesis of the related complex [$Mo(\eta^2\text{-}MeC_2Me)(dppe)(\eta\text{-}C_5H_5)$][$PF_6$] was described involving a sequence of reactions starting with a bis(arene)molybdenum(0) complex. The approach detailed in this paper represents a somewhat simpler method of synthesis of these unusual complexes, for which the illustrated structure is suggested. Interestingly, it was reported that propeller rotation of the co-ordinated but-2-yne occurs in the dppe-substituted cation, but the coalescence to *one Me*C≡C resonance in the ^1H spectrum only occurs in the region of 110 °C. This observation is unexpected in view of our findings.

The ^1H spectrum of complex (26) at room temperature showed resonances corresponding to an $\eta^5\text{-}C_9H_7$ ligand, co-ordinated $P(OMe)_3$, and a sharp triplet [^4J(HP) 1.0 Hz] centred at τ 7.7, which is assigned to *Me*C≡C. On cooling this signal collapsed to give *two Me*C≡C resonances at τ 7.0 and 8.4, a coalescence temperature of −40 °C being observed. This is clearly consistent with a propeller rotation of the but-2-yne, about an axis through the molybdenum and perpendicular to the C≡C bond. The observation of ^{31}P–^1H coupling at room temperature between the ^{31}P nuclei of the identical trimethyl phosphite ligands and the ^1H nuclei of the acetylenic methyl groups demonstrates the absence of acetylene dissociation. In addition it was observed that the ^1H spectrum of the $\eta\text{-}C_5H_5$ analogue (30) showed *Me*C≡C coalescence at < -90 °C. These observations suggest that either there is a pronounced ligand effect on the barrier to rotation of acetylenes in these complexes or that acetylene dissociation intervenes in the case of the dppe-substituted system.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 MHz with $SiMe_4$ (τ 10.00) as internal reference. Carbon-13 n.m.r. spectra were obtained on a JEOL PFT-100 spectrometer at 25.15 MHz; chemical shifts are relative to $SiMe_4$ as external reference. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer, mass spectra on an A.E.I.

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[15] J. A. Segal, M. L. H. Green, J. C. Daren, and K. Prout, *J.C.S. Chem. Comm.*, 1976, 766.

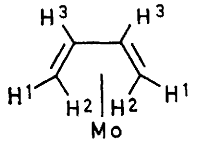
MS 902 spectrometer operating at 70 eV.* Reactions were conducted in a dry oxygen-free nitrogen atmosphere.

Preparations.— *Bis(acetonitrile)dicarbonyl(η^5-indenyl)molybdenum tetrafluoroborate* (1). A solution of $[\{Mo(CO)_3(\eta^5\text{-}C_9H_7)\}_2]$ (2.0 g, 3.4 mmol) and silver(I) tetrafluoroborate (1.33 g, 6.8 mmol) in acetonitrile (20 cm^3) was stirred [room temperature (r.t.)] After 0.5 h a silver mirror had formed. The reaction mixture was filtered and the solvent removed *in vacuo*. The residue was dissolved in methylene chloride, and addition of diethyl ether gave orange crystals of (1) (2.09 g, 71%) (Found: C, 40.9; H, 3.1; N, 6.2. $C_{15}H_{13}BF_4MoN_2O_2$ requires C, 41.3; H, 3.0; N, 6.4%), $\nu_{max.}$ (Nujol) at 2295m (CN), 1970s (CO), and 1880s cm^{-1} (CO). The ^{1}H n.m.r. spectrum in CD_3NO_2 showed resonances at τ 2.1—2.5(m, 4 H, indenyl H^a), 3.60[d, 2 H, H^b, J(H^{b}H^c) 3.0], 4.1[t, 1 H, H^c, J(H^{c}H^b) 3.0 Hz], and 8.00(s, 6 H, CH_3CN).

Dicarbonyl(η^5-indenyl)bis(trimethyl phosphite)molybdenum tetrafluoroborate (2). Trimethyl phosphite (0.4 g, 3 mmol) was added to a stirred (r.t.) solution of (1) (0.2 g, 0.45 mmol) in methylene chloride (10 cm^3). After 0.5 h the reaction mixture was filtered and diethyl ether added (70 cm^3) to give dark yellow crystals of (2) (0.14 g, 51%) (Found: C, 33.6; H, 4.3. $C_{15}H_{25}BF_4MoO_8P_2$ requires C, 33.9; H, 4.2%), $\nu_{max.}$ (Nujol) at 1980s (CO) and 1900s cm^{-1} (CO). The ^{1}H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 2.5—2.9(m, 4 H, indenyl H^a), 4.00[d, 2 H, H^b, J(H^{b}H^c) 3.0], 4.50[t, 1 H, H^c, J(H^{c}H^b) 3.0], and 6.20[d, 18 H, $POCH_3$, $|J(POCH)|$ 12.0 Hz].

[1,2-Bis(diphenylphosphino)ethane]dicarbonyl(η^5-indenyl)molybdenum tetrafluoroborate (3). Similarly, reaction of (1) (0.4 g, 0.92 mmol) and dppe (0.37 g, 0.92 mmol) in CH_2Cl_2 (20 cm^3) gave dark yellow *crystals* of (3) (0.38 g, 54%) (Found: C, 58.6; H, 4.2. $C_{37}H_{31}BF_4MoO_2P_2$ requires C, 59.0; H, 4.1%), $\nu_{max.}$ (MeCN) at 1 981s (CO) and 1913s cm^{-1} (CO). The ^{1}H n.m.r. spectrum in CD_3NO_2 gave resonances at τ 2.3—2.9(m, 24 H, indenyl H^a + C_6H_5P), 3.90(m, 2 H, indenyl), 4.60(m, 1 H, indenyl), and 7.90(s, 4 H, PCH_2).

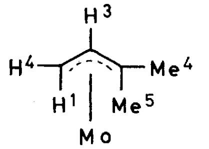
(Buta-1,3-diene)dicarbonyl(η^5-indenyl)molybdenum tetrafluoroborate (4). An excess of buta-1,3-diene (13 mmol) was condensed into a tube (100 cm^3, fitted with a Westof Stopcock) containing a solution of (1) (0.20 g, 0.46 mmol) in methylene chloride (20 cm^3). After 24 h at room temperature the reaction mixture was filtered, and diethyl ether added affording yellow *crystals* of (4) (0.12 g, 62%) (Found: C, 43.5; H, 3.2. $C_{15}H_{13}BF_4MoO_2$ requires C, 43.9; H, 3.2%), $\nu_{max.}$ (Nujol) at 2070s (CO) and 2020s cm^{-1} (CO). The ^{1}H n.m.r. spectrum in CD_3NO_2 at 32 °C showed resonances at τ 2.4—2.9(m, 4 H, indenyl H^a), 3.70[d, 2 H, H^b, J(H^{b}H^c) 3.0], 4.1[t, 1 H, H^c, J(H^{c}H^b) 3.0 Hz], 4.50(br s, 2 H, H^3), 6.60(br s, 2 H, H^1), and 9.30(br s, 2 H, H^2).



Dicarbonyl(η^5-indenyl)isoprenemolybdenum tetrafluoroborate (5). Silver(I) tetrafluoroborate (0.66 g, 3.4 mmol) was added to a stirred (r.t.) solution of $[\{Mo(CO)_3(\eta^5\text{-}C_9H_7)\}_2]$ (1.0 g, 1.70 mmol) and isoprene (1 cm^3, 15 mmol) in methylene chloride (20 cm^3). Silver metal was deposited and after 24 h the reaction mixture was filtered and diethyl ether added to give yellow *crystals* of (5) (0.71 g, 50%) (Found: C, 45.4; H, 3.6. $C_{16}H_{15}BF_4MoO_3$ requires C, 45.6; H, 3.6%), $\nu_{max.}$ (Nujol) at 2 070s (CO) and 2010s cm^{-1} (CO). The ^{1}H n.m.r. spectrum in CD_3NO_2 at 32 °C showed resonances at τ 2.5(s, 4 H, indenyl H^a), 3.8[d, 2 H, H^b, J(H^{b}H^c)], 4.2[t, 1 H, H^c, J(H^{c}H^b) 3.0 Hz], 5.5(br m, 1 H, H^3), 6.6(br m, 2 H, H^1), 7.7(s, 3 H, CH_3^3), and 10.0 (br m, 2 H, H^2).

The following complexes were similarly prepared by the first method. *Dicarbonyl(2,3-dimethylbuta-1,3-diene)(η^5-indenyl)molybdenum tetrafluoroborate* (6), yellow crystals (60%) (Found: C, 46.8; H, 3.9. $C_{17}H_{17}BF_4MoO_2$ requires C, 46.6; H, 3.9%), $\nu_{max.}$ (Nujol) at 2060s (CO) and 2000s cm^{-1} (CO); ^{1}H n.m.r. resonances in CD_3NO_2 at 32 °C at τ 2.5—2.9(m, 4 H, indenyl H^a), 3.81[d, 2 H, H^b, J(H^{b}H^c) 3.0], 4.30[t, 1 H, H^c, J(H^{c}H^b) 3.0 Hz], 6.40(s, 2 H, H^1), 7.61(s, 6 H, Me), and 10.62(s, 2 H, H^2). *Dicarbonyl(η^5-indenyl)(*trans*-penta-1,3-diene)molybdenum tetrafluoroborate* (7), yellow crystals (50%) (Found: C, 45.1; H, 3.6. $C_{16}H_{15}BF_4MoO_2$ requires C, 45.6; H, 3.6%), $\nu_{max.}$ (Nujol) at 2070s (CO) and 2010s cm^{-1} (CO); ^{1}H n.m.r. resonances in CD_3NO_2 at 32 °C at τ 2.3—2.7(m, 4 H, indenyl H^a), 3.7—4.4(br m, 3 H, indenyl H^a and H^b), 5.5(br m, 2 H, H^3), 6.6(br s, 1 H, H^1), 8.2(br m, 3 H, CH_3^1), 8.8(br m, 1 H, H^2), and 10.4(br m, 1 H, H^2). *Dicarbonyl(cyclohexa-1,3-diene)(η^5-indenyl)molybdenum tetrafluoroborate* (8), yellow crystals (50%) (Found: C, 47.5; H, 4.0. $C_{17}H_{15}BF_4MoO_2$ requires C, 47.0; H, 3.46%), $\nu_{max.}$ (Nujol) at 2060s (CO) and 2000s cm^{-1} (CO); ^{1}H n.m.r. resonances in CD_3NO_2, at 32 °C at τ 2.3—2.6(m, 4 H, indenyl H^a), 3.71[d, 2 H, H^b, J(H^{b}H^c) 3.0], 3.90 [t, 1 H, H^c, J(H^{c}H^b) 3.0 Hz], 5.30 (s, 4 H, CH=CH), and 7.8—8.2(m, 4 H, CH_2). *Dicarbonyl(1—4-η-cyclo-octatetrene)(η^5-indenyl)molybdenum tetrafluoroborate.* (9), red crystals (31%) (Found: C, 49.5; H, 3.5. $C_{19}H_{15}BF_4MoO_2$ requires C, 49.8; H, 3.3%), $\nu_{max.}$ (Nujol) at 2040s (CO) and 1965 cm^{-1} (CO).

Reactions of Sodium Tetrahydroborate.—(*a*) *With dicarbonyl(η^5-indenyl)isoprenemolybdenum tetrafluoroborate.* Sodium tetrahydroborate (0.10 g, 2.6 mmol) was added (r.t.) to a stirred solution of (5) (0.30 g, 0.9 mmol) in dry tetrahydrofuran (thf) (20 cm^3). After 1 h the solvent was removed *in vacuo*, and the residue was extracted with diethyl ether and chromatographed on an Alumina-packed column. Elution with diethyl ether, removal of the solvent, and sublimation (80 °C, 0.1 mmHg) on to a water-cooled probe afforded yellow crystals of *dicarbonyl(*exo*-1—3-η-3,3-dimethylallyl)(η^5-indenyl)molybdenum* (10) (0.19 g, 77%) (Found: C, 57.1; H, 4.9. $C_{16}H_{16}MoO_2$ requires C, 57.2; H, 4.8%), $\nu_{max.}$ (hexane) at 1945s (CO) and 1873s cm^{-1} (CO).



The ^{1}H n.m.r. spectrum on $CDCl_3$ at 32 °C showed resonances at τ 2.6—3.2(m, 4 H, indenyl H^a), 4.10(m, 1 H, indenyl), 4.31(m, 1 H, indenyl), 4.40(m, 1 H, indenyl), 8.20[dd, 1 H, H^2, J(H^{2}H^1) 3.0, J(H^{2}H^3) 8.0], 8.50(s, 3 H, Me^4), 8.7[dd, 1 H, H^1, J(H^{1}H^3) 10.0], 9.2(s, 3 H, Me^5), and 9.7[m, 1 H, H^3, J(H^{3}H^1) 10.0, J(H^{3}H^2) 8.0 Hz]. The mass spectrum

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* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J; 1 mmHg ≈ 13.6 × 9.8 Pa.

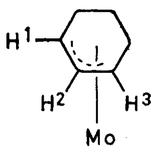
showed peaks at *m/e* 338 (*P*), 310 (*P* — CO), and 282 (*P* — 2CO).

(*b*) *With (buta-*1,3-*diene)dicarbonyl(*η^5*-indenyl)molybdenum tetrafluoroborate.* A similar reaction and work-up procedure gave yellow crystals of (exo-1—3-η-*but-2-enyl)-dicarbonyl(*η^5*-indenyl)molybdenum* (11) (40%) (Found: C, 56.0; H, 4.5. $C_{15}H_{14}MoO_2$ requires C, 55.9; H, 4.4%), $\nu_{max.}$ (hexane) at 1951s (CO) and 1875s cm^{-1} (CO). The ^{1}H n.m.r. spectrum in $CDCl_3$ at 32 °C showed resonances at τ 3.0(s, 4 H, indenyl H^a), 4.1(m, 2 H, H^b), 4.4[t, 1 H, H^c, *J*(H^{c}H^b) 3.0], 6.81[qd, 1 H, H^4, ^3J(H^{4}H^5) 7.0, ^3J(H^{3}H^4) 7.0, *J*(H^{1}H^4) 2.0], 7.80[dt, 1 H, H^2, ^3J(H^{2}H^3) 8.0, ^2J(H^{1}H^2)], 8.60[dd, 1 H, H^1, *J*(H^{1}H^3) 12.0], 9.2[d, 3 H, Me, *J*(H^{4}H^5) 7.0 Hz], and 10.3(m, 1 H, H^3). The mass spectrum showed peaks at *m/e* 324 (*P*), 296 (*P* — CO), and 268 (*P* — 2CO).

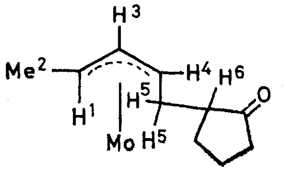
(*c*) *With dicarbonyl(*2,3-*dimethylbuta-*1,3-*diene)(*η^5*-indenyl)molybdenum tetrafluoroborate.* In a similar manner reaction of (6) with Na[BH$_4$] gave yellow crystals of *dicarbonyl(*η^5*-indenyl)(*1—3-η-2,3,3-*trimethylallyl)molybdenum* (12) (80%) (Found: C, 58.7; H, 5.4. $C_{17}H_{18}MoO_2$ requires C, 58.3; H, 5.2%), $\nu_{max.}$ (hexane) at 1946s (CO) and 1873s cm^{-1} (CO). The ^{1}H n.m.r. spectrum in $CDCl_3$ at 32 °C showed resonances at τ 2.5—3.1(m, 4 H, indenyl H^a), 4.2[t, 1 H, H^c, *J*(H^{c}H^b) 3.0], 4.61(m, 2 H, H^b), 7.90(s, 3 H, Me^3), 8.71[d, 1 H, H^4, *J*(H^{4}H^5) 2.0], 8.8(s, 3 H, Me^2), 8.9[d, 1 H, H^5, *J*(H^{5}H^4) 2.0 Hz], and 9.3(s, 3 H, Me^1). The mass spectrum showed peaks at *m/e* 352 (*P*), 324 (*P* — CO), and 296 (*P* — 2CO).

(*d*) *With dicarbonyl(*η^5*-indenyl)(*trans-*penta-*1,3-*diene)-molybdenum tetrafluoroborate.* Similarly, reaction of (7) with Na[BH$_4$] afforded yellow crystals of *dicarbonyl(*exo-1—3-η-1,3-*dimethylallyl)(*η^5*-indenyl)molybdenum* (13) (67%) (Found: C, 57.2; H, 4.8. $C_{16}H_{16}MoO_2$ requires C, 57.2; H, 4.8%), $\nu_{max.}$ (hexane) at 1947s (CO) and 1872s cm^{-1} (CO). The ^{1}H n.m.r. spectrum in $CDCl_3$ at 32 °C showed resonances at τ 2.9—3.1(m, 4 H, indenyl H^a), 4.1(m, 1 H, indenyl H^c), 4.4(m, 2 H, indenyl H^b), 7.5[q, 1 H, H^4, ^3J(H^{4}H^5) 7.0, ^3J(H^{4}H^3) 7.0], 7.9[m, 1 H, H^1, ^3J(H^{1}H^2) 7.0, ^3J(H^{1}H^3) 10.0], 8.40[d, 3 H, Me^2, *J*(H^{2}H^1) 7.0], 9.1[d, 3 H, Me^5, *J*(H^{5}H^4) 7.0], and 9.9[dd, 1 H, H^3, *J*(H^{1}H^3) 10.0, *J*(H^{3}H^4) 7.0 Hz]. The mass spectrum showed peaks at *m/e* 338 (*P*), 310 (*P* — CO), and 282 (*P* — 2CO).

(*e*) *With dicarbonyl(cyclohexa-*1,3-*diene)(*η^5*-indenyl)-molybdenum tetrafluoroborate.* In the same manner, reaction of (8) with Na[BH$_4$] gave yellow crystals of (1—3-η-*cyclohexenyl)(*η^5*-indenyl)molybdenum* (14) (42%) (Found: C, 58.9; H, 4.7. $C_{17}H_{16}MoO_2$ requires C, 58.6; H, 4.6%), $\nu_{max.}$ (hexane) at 1948s (CO) and 1875 cm^{-1} (CO). The ^{1}H n.m.r. spectrum in $CDCl_3$, at 32 °C showed resonances at τ 3.0(m, 4 H, indenyl H^a), 4.1[d, 2 H, H^b, *J*(H^{b}H^c), 3.0], 4.4[t, 1 H, H^c, *J*(H^{c}H^b) 3.0], 6.9[br d, 2 H, H^1 and H^3, ^3J(H^{2}H^3) 8.0], 8.4(m, 4 H, CH$_2$), 9.2(m, 1 H, CH$_2$), 9.8(m, 1 H, CH$_2$), and 10.6[t, 1 H, H^2, *J*(H^{2}H^3) 8.0 Hz].



Reactions of 1-*Morpholinocyclopent-*1-*ene.*—(*a*) *With complex* (7). 1-Morpholinocyclopent-1-ene (0.2 cm^3, 1.3 mmol) was added (r.t.) to a stirred solution of (7) (0.20 g, 0.47 mmol) in dry methylene chloride (20 cm^3). Reaction occurred immediately. The solvent was removed *in vacuo*, and the residue extracted with diethyl ether. Chromatography on an alumina column and elution with diethyl ether followed by recrystallisation (−78 °C) from diethyl ether–hexane gave yellow crystals of *dicarbonyl(*η^5*-indenyl)-*{1—3-η-1-*methyl-*3-[(2-*oxocyclopentyl)methyl*]*allyl*}*molybdenum* (15) (0.13 g, 66%) (Found: C, 59.9; H, 5.7. $C_{21}H_{22}MoO_3$ requires C, 60.3; H, 5.3%), $\nu_{max.}$ at 1944s (CO), 1871s (CO), and 1746s cm^{-1} (CO). The ^{1}H n.m.r. spectrum in $CDCl_3$ at 32 °C showed resonances at τ 2.9(m, 4 H, indenyl H^a), 4.0(m, 1 H, indenyl), 4.3(m, 1 H, indenyl), 4.4(m, 1 H, indenyl), 7.4—8.5(m, 1 H, H^1, H^4, H^5, H^6, and CH$_2$), 8.4[d, 3 H, Me^2, *J*(H^{2}H^1) 7.0 Hz], and 10.0(m, 1 H, H^3). The mass spectrum showed peaks at *m/e* 420 (*P*), 392 (*P* — CO), and 364 (*P* — 2CO).



(*b*) *With complex* (5). A similar reaction gave yellow crystals of (η^5*-indenyl)*{1—3-η-3-*methyl-*3-[(2-*oxocyclopentyl)methyl*]*allyl*}*molybdenum* (16) (43%) (Found: C, 60.5; H, 5.7. $C_{21}H_{22}MoO_3$ requires C, 60.3; H, 5.3%), $\nu_{max.}$ (hexane) at 1953s (CO), 1881s (CO), and 1739 cm^{-1} (CO). The ^{1}H n.m.r. spectrum in $CDCl_3$ at 32 °C showed resonances at τ 2.6—3.1(m, 4 H, indenyl H^a), 4.0—4.6(m, 3 H, H^b and H^c), 6.50(m, 1 H, H^6), 7.9—9.1(br m, 11 H, H^1, H^2, H^3, H^5, and CH$_2$), 8.70(s, 3 H, Me^4), and 9.7(m, 1 H, H^3). The mass spectrum showed peaks at *m/e* 420 (*P*), 392 (*P* — CO), and 364 (*P* — 2CO).

Reaction of Complex (1) *with t-Butylacetylene.*—An excess of t-butylacetylene (13 mmol) was condensed (−196 °C) into a tube (100 cm^3, Westef stopcock) containing (1) (0.30 g, 0.7 mmol) in methylene chloride (20 cm^3). After 4 h at room temperature the reaction mixture had changed from orange to yellow. The solution was filtered and diethyl ether added to give yellow crystals of *carbonyl-(*η^5*-indenyl)bis(t-butylacetylene)molybdenum tetrafluoroborate* (17) (0.23 g, 69%) (Found: C, 53.8; H, 5.8. $C_{22}H_{27}BF_4MoO$ requires C, 53.9; H, 5.5%), $\nu_{max.}$ (Nujol) at 2080s cm^{-1} (CO). The ^{1}H n.m.r. spectrum in $CDCl_3$, at 32 °C showed resonances at τ 0.20 (two separated by 2 Hz, each corresponding to 1 H, HC≡C), 1.9(br s, 1 H, indenyl), 2.3—2.9(m, 4 H, indenyl), 3.9(br s, 1 H, indenyl), 4.1(t, 1 H, indenyl), 8.6(s, 9 H, Bu^t), and 9.1(s, 9 H, Bu^t adjacent to indenyl).

The same method was used to obtain the following complexes. *Bis(but-*2-*yne)carbonyl(*η^5*-indenyl)molybdenum tetrafluoroborate* (18), yellow crystals (75%) (Found: C, 49.7; H, 4.5. $C_{18}H_{19}BF_4MoO$ requires C, 49.8; H, 4.4%), $\nu_{max.}$ (Nujol) at 2075s cm^{-1} (CO); ^{1}H n.m.r. resonances in $CDCl_3$ at 32 °C at τ 2.5—2.9(m, 4 H, indenyl H^a), 3.2[d, 2 H, H^b, *J*(H^{b}H^c) 3.0], 4.0[t, 1 H, H^c, *J*(H^{c}H^b) 3.0 Hz], 6.9(s, 6 H, Me^2), and 7.5(s, 6 H, Me^1). *Carbonylbis(diphenylacetylene)(*η^5*-indenyl)molybdenum tetrafluoroborate* (19), yellow crystals (68%) (Found: C, 66.4; H, 4.0. $C_{37}H_{27}BF_4MoO$ requires C, 66.9; H, 4.0%), $\nu_{max.}$ (Nujol) at 2070s cm^{-1} (CO); ^{1}H n.m.r. resonances in $CDCl_3$ at 32 °C at τ 2.2—2.8(m, 24 H, C_6H_5 and indenyl), 3.0(m, 2 H, indenyl), and 3.6(m, 1 H, indenyl). *Bis(acetylene)carbonyl(*η^5*-indenyl)molybdenum tetrafluoroborate* (20), dark yellow crystals (74%) (Found: C, 44.2; H, 3.0. $C_{14}H_{11}BF_4MoO$ requires

C, 44.3; H, 2.9%), $\nu_{max.}$ (Nujol) at 2070s cm^{-1} (CO); ^{1}H n.m.r. resonances in CD_3NO_2 at 32 °C at τ 0.5 (two separated by 2 Hz, each corresponding to 1 H, HC≡C), 2.2—2.6(m, 4 H, indenyl H^a), 3.2[d, 2 H, H^b, J(H^{b}H^c) 3.0], and 4.4 [t, 1 H, H^c, J(H^{c}H^b) 3.0 Hz]. *Carbonyl*(η^5-*indenyl*)*bis*(*prop*-1-*yne*)*molybdenum tetrafluoroborate* (21), pale yellow crystals (60%) (Found: C, 47.3; H, 3.9. $C_{16}H_{15}BF_4MoO$ requires C, 47.3; H, 3.7%), $\nu_{max.}$ (Nujol) at 2080s cm^{-1} (CO); ^{1}H n.m.r. resonances in CD_3NO_2 at 32 °C at τ 0.8—1.3 [four separate quartets (ratio 1 : 1 : 1 : 1), 2 H, HC≡C, ^3J(HMe) 2.0], 2.0—2.7(m, 4 H, indenyl), 3.0—3.5[four separate multiplets (1 : 1 : 1 : 1), indenyl], 4.0—4.4(three separate triplets, 1 H, indenyl), and 6.7—7.3 [four separate doublets, 6 H, $CH_3C≡C$, ^3J(MeH) 2.0 Hz].

Preparation of Carbonyl(η-*cyclopentadienyl*)*bis*(*t-butylacetylene*)*molybdenum tetrafluoroborate* (22).—Silver tetrafluoroborate (1.60 g, 8.2 mmol) was added to a stirred solution of [{Mo(CO)$_3$(η-C_5H_5)}$_2$] (2.0 g, 4.1 mmol) and t-butylacetylene (30 mmol) in methylene chloride (20 cm^3). After 12 h at room temperature the reaction mixture was filtered to remove precipitated silver metal. Addition of diethyl ether to the filtrate gave yellow crystals of (22) (2.1 g, 59%) (Found: C, 49.0; H, 5.6. $C_{18}H_{25}BF_4MoO$ requires 49.1; H, 5.7%), $\nu_{max.}$ (Nujol) at 2070s cm^{-1} (CO). The ^{1}H n.m.r. spectrum in $CDCl_3$ at 32 °C showed resonances at τ 1.0(s, 2 H, HC≡C), 4.0(s, 5 H, C_5H_5), 8.6(s, 9 H, Bu^t), and 8.7(s, 9 H, Bu^t, adjacent to cyclopentadienyl).

The same method was used to obtain the following complexes. *Bis*(*but*-2-*yne*)*carbonyl*(η-*cyclopentadienyl*)-*molybdenum tetrafluoroborate* (23), yellow crystals (64%) (Found: C, 43.7; H, 4.7. $C_{14}H_{17}BF_4MoO$ requires C, 43.8; H, 4.4%), $\nu_{max.}$ (Nujol) at 2040s cm^{-1} (CO); ^{1}H n.m.r. resonances in CD_3NO_2 at 32 °C at τ 4.0(s, 5 H, C_5H_5), 6.9(s, 6 H, Me^1), and 7.2(s, 6 H, Me^2). *Carbonyl*(η-*cyclopentadienyl*)*bis*(*diphenylacetylene*)*molybdenum tetrafluoroborate* (24), yellow crystals (49%) (Found: C, 64.5; H, 4.0. $C_{34}H_{25}BF_4MoO$ requires C, 64.5; H, 4.0%), $\nu_{max.}$ (Nujol) at 2070s cm^{-1} (CO); ^{1}H n.m.r. resonances in CD_3NO_2 at 32 °C at τ 2.1—2.6(m, 20 H, $C_6H_5C≡C$) and 3.7(s, 5 H, C_5H_5). *Carbonyl*(η-*cyclopentadienyl*)*bis*(*prop*-1-*yne*)*molybdenum tetrafluoroborate* (25), yellow crystals (55%) (Found: C, 40.6; H, 3.6. $C_{13}H_{15}BF_4MoO$ requires C, 40.5; H, 3.7%), $\nu_{max.}$ (Nujol) at 2075s cm^{-1} (CO); ^{1}H n.m.r. resonances in CD_3NO_2 at 32 °C at τ 0.2—1.1 [four separate quartets, 2 H, HC≡C, ^3J(HMe)2.0], 4.0—4.1 (four separate singlets, 5 H, C_5H_5), 6.8—7.0 [four separate triplets, 6 H, $CH_3C≡C$, ^3J(MeH) 2 Hz].

Reaction of Trimethyl Phosphite with Complex (18).—An excess of P(OMe)$_3$ (0.5 g, 4.0 mmol) was added to a stirred (r.t.) solution of (18) (0.4 g, 0.9 mmol) in methylene chloride (15 cm^3). Gas was evolved and the reaction mixture changed from yellow to purple. The resulting solution was filtered, and diethyl ether (15 cm^3) added giving dark purple crystals of *but*-2-*yne*(η^5-*indenyl*)*bis*(*trimethyl phosphite*)*molybdenum tetrafluoroborate* (26) (0.44 g, 80%) (Found: C, 37.5; H, 5.2. $C_{19}H_{31}BF_4MoO_6P_2$ requires C, 38.0; H, 5.2%). The ^{1}H n.m.r. spectrum in CD_3NO_2 at 32 °C showed resonances at τ 2.4—2.6(m, 4 H, indenyl), 3.9[m, 2 H, H^b, J(HH) = J(HP) 3.0], 4.8(m, 1 H, H^c), 6.41(m, 18 H, POMe), and 7.70[t, 6 H, Me^1 and Me^2, ^4J(HP) 1.0 Hz]; on cooling (coalescence at −40 °C), resonances at τ 7.0(br s, 3 H, Me) and 8.4(br s, 3 H, Me nearest to indenyl) were observed [$(CD_3)_2CO$ as solvent].

The following complexes were prepared in the same manner. *Diphenylacetylene*(η^5-*indenyl*)*bis*(*trimethyl phosphite*)*molybdenum tetrafluoroborate* (27), blue-green crystals (67%) (Found: C, 48.2; H, 5.2. $C_{29}H_{35}BF_4MoO_6P_2$ requires C, 48.1; H, 4.9%); ^{1}H n.m.r. resonances in $CDCl_3$ at 32 °C at τ 2.7—3.2(m, 14 H, $C_6H_5≡C$ and indenyl), 3.8[m, 2 H, H^b, J(HH) = J(HP) 3.0 Hz], 4.60(m, 1 H, H^c), and 6.41(m, 18 H, POMe). (η^5-*Indenyl*)(*prop*-1-*yne*)*bis*(*trimethyl phosphite*)*molybdenum tetrafluoroborate* (28), purple crystals (88%) (Found: C, 37.0; H, 5.1. $C_{18}H_{29}BF_4$-MoO_6P_2 requires C, 36.8; H, 5.2%); ^{1}H n.m.r. resonances in $CDCl_3$ at 32 °C at τ −0.6[t, 1 H, HC≡C, J(HP) 12.0], 2.4(m, 4 H, indenyl), 3.8[m, 2 H, H^b, J(HH) = J(HP) 4.0 Hz], 4.8(m, 1 H, H^c), 6.4(m, 18 H, POMe), and 7.9(br s, 3 H, Me). (*t-Butylacetylene*)(η^5-*cyclopentadienyl*)*bis*(*trimethyl phosphite*)*molybdenum tetrafluoroborate* (29), purple crystals (84%) * (Found: C, 35.2; H, 5.5. $C_{24}H_{23}BF_4MoO_6P_2$ requires C, 35.3; H, 5.7%); ^{1}H n.m.r. resonances in $CDCl_3$ at 32 °C at τ −1.6[t, 1 H, HC≡C, J(HP) 16.0], 4.2[t, 5 H, C_5H_5, J(HP) 2.0 Hz], 6.4(m, 18 H, POMe), and 8.6(s, 9 H, Bu^{t}C). (*But*-2-*yne*)(η-*cyclopentadienyl*)*bis*(*trimethyl phosphite*)*molybdenum tetrafluoroborate* (30), violet crystals (89%) (Found: C, 32.5; H, 5.4. $C_{15}H_{19}BF_4MoO_6P_2$ requires C, 32.7; H, 5.3%); ^{1}H n.m.r. resonances in CD_3NO_2 at 32 °C at τ 4.4 [t, 5 H, C_5H_5, J(HP) 2.0], 6.4(m, 18 H, POMe), and 6.9[t, 6 H, Me, J(HP) 1.0 Hz]. (η-*Cyclopentadienyl*)(*diphenylacetylene*)*bis*(*trimethyl phosphite*)-*molybdenum tetrafluoroborate* (31), dark blue crystals (90%) (Found: C, 44.5; H, 5.0. $C_{25}H_{23}BF_4MoO_6P_2$ requires C, 44.6; H, 4.9%); ^{1}H n.m.r. resonances in CD_3NO_2 at 32 °C at τ 2.5(br s, 10 H, $C_6H_5C≡C$), 4.2[t, 5 H, C_5H_5, J(HP) 2.0 Hz], and 6.4(m, 18 H, POMe).

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* This complex was prepared at −78 °C in CH_2Cl_2 as solvent.