Reactions of Co-ordinated Ligands. Part 19.[1] Insertion Reactions of Acetylenes, Methylenecyclopropane, and Buta-1,3-diene with Tricarbonyl(η^5-indenyl)methylmolybdenum and Dicarbonyl(η^5-indenyl)methyliron

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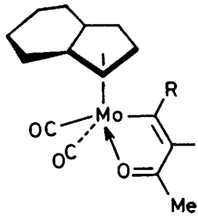
Reaction of [MoMe(CO)(η^5-C_9H_7)] with but-2-yne affords the vinyl ketone complex [Mo{C(Me)=C(Me)C(Me)O}(CO)$_2$(η^5-C_9H_7)]. In contrast, 3,3-dimethylbut-1-yne reacts under similar conditions to give consecutively [Mo{CH=C(Bu^t)C(Me)O}(CO)$_2$(η^5-C_9H_7)] and the η^3-pyranyl complex [Mo{η^3-C(Me)C(Bu^t)CHCH=C(Bu^t)O}(CO)$_2$(η^5-C_9H_7)]. But-2-yne and 3,3-dimethylbut-1-yne react with [FeMe(CO)$_2$(η^5-C_9H_7)] to give the corresponding vinyl ketone complexes. Methylenecyclopropane reacts slowly with [MoMe(CO)$_3$(η^5-C_9H_7)] to give the 1,2-ring-opened complex [Mo{η^3-*anti*-CH(Me)C(COMe)CH$_2$}(CO)$_2$(η^5-C_9H_7)] and with buta-1,3-diene to afford [Mo{η^3-CH$_2$CHCHCH$_2$(COMe)}(CO)$_2$(η^5-C_9H_7)]. The mechanism of formation of these products is discussed.

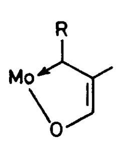
FOLLOWING the kinetic observations[2-4] that the η^5-indenyl complexes [MoX(CO)$_3$(η^5-C_9H_7)] (X = Me, Cl, Br, or I) are more reactive towards phosphines than the corresponding η^5-cyclopentadienyl complexes, we observed[5] a related enhanced reactivity of [Rh(C_2H_4)$_2$(η^5-C_9H_7)], compared with the η^5-cyclopentadienyl analogue, which we have shown has important synthetic consequences. In this paper are reported studies of the reactions of [MoMe(CO)$_3$(η^5-C_9H_7)] and [FeMe(CO)$_2$(η^5-C_9H_7)] with acetylenes, methylenecyclopropane, and buta-1,3-diene; the higher reactivity of the η^5-C_9H_7 system enables a more detailed understanding to be obtained of insertion reactions with Mo–Me and Fe–Me σ bonds.

RESULTS AND DISCUSSION

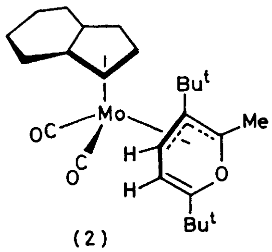
Whereas [MoMe(CO)$_3$(η-C_5H_5)] reacted[6] with but-2-yne only on heating, the corresponding η^5-indenyl complex[7] [MoMe(CO)$_3$(η^5-C_9H_7)] reacts at room temperature with but-2-yne (using an excess of the acetylene as solvent) to form the red crystalline 1 : 1 adduct (1). The i.r. spectrum showed the presence of two terminal carbonyl bands at 1 970 and 1 892 cm^{-1} together with a weak band at 1 530 cm^{-1} corresponding[6,8] to an end-bonded ketonic carbonyl group, suggesting the formation of a σ-bonded vinyl ketone complex analogous to that observed with the η-C_5H_5 system. In agreement, the ^{1}H n.m.r. spectrum showed typical resonances of an η^5-indenyl system with a complex multiplet centred at τ 3.3 for the indenyl H^a proton, a doublet for the indenyl H^b protons [τ 4.8, J(H^{b}H^c) 3 Hz], and a triplet at τ 5.3 for indenyl H^c; three methyl singlets at τ 7.2, 8.2, and 8.45 completed the spectrum. An alternative bonding mode (1b) for this complex involving a Mo–O σ bond and a co-ordinated carbene was eliminated by examination of the ^{13}C spectrum, which showed resonances consistent with a vinyl ketone complex.



(1a) R = R′ = Me
(3) R = H, R′ = Bu^t



(1b)



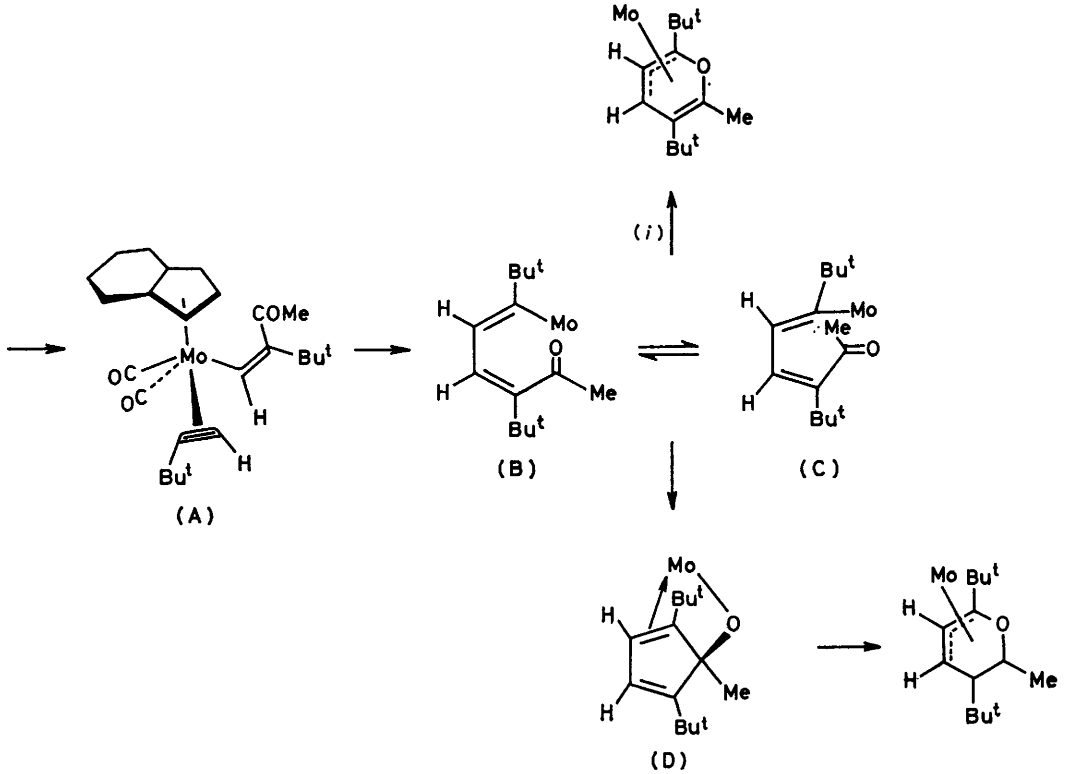
(2)

In contrast, the corresponding reaction of [MoMe(CO)$_3$(η^5-C_9H_7)] with 3,3-dimethylbut-1-yne afforded complexes (2) and (3), which were separated by column chromatography. The second complex (3) eluted from the column was shown on examination (analysis, m.s., and n.m.r. spectroscopy) to be a vinyl ketone complex analogous to (1). The ^{1}H n.m.r. spectrum showed, apart from resonances due to a η^5-indenyl system, singlets at τ 3.6 (H^1), 8.2 (Me^3), and 8.6 (Bu^t). Comparison of the chemical shift of the H^1 proton with those reported[9,10] for other σ-bonded metal vinyl complexes suggested the illustrated structure, in which the hydrogen is attached to a carbon adjacent to the molybdenum. Further support for the structure of (3) was provided by the reaction with carbon monoxide to form a η^3-lactone complex (8), a type of reaction which had been previously[6] demonstrated with the η-C_5H_5 system [equation (1)].

$$\text{[Mo\{C(Me)=C(Me)C(Me)O\}(}\eta\text{-}C_5H_5\text{)]} \xrightarrow{CO} \text{[Mo\{}\eta^3\text{-C(Me)C(Me)C(Me)(O)O\}(}\eta\text{-}C_5H_5\text{)]} \quad (1)$$

It is likely that, because of the bulk of the t-butyl substituent, the η^3-allylic system adopts the normally[11] less-stable illustrated *endo* configuration.

The other complex (2) isolated from the reaction analysed as a 2 : 1 adduct of 3,3-dimethylbut-1-yne and [MoMe(CO)$_3$(η^5-C_9H_7)]. This conclusion was supported by the mass spectrum, which showed a parent ion and peaks corresponding to the consecutive loss of two CO groups, and an organic fragment comprised of two acetylene molecules and an acetyl group. The i.r. spectrum of (2) showed two terminal carbonyl bands at 1 945 and 1 875 cm^{-1} together with a peak at 1 635 cm^{-1} assignable to an unco-ordinated double bond. This



SCHEME 1 Ligands attached to metal are omitted for clarity. (*i*) Disrotatory ring closure

evidence indicated that (2) was an η^3-pyranyl complex,[8] a suggestion which was supported by the ^{1}H n.m.r. spectrum which showed coupled [$J(H^1H^2)$ 2.0 Hz] resonances for the olefinic proton H^1, and the adjacent η^3-allylic proton H^2 at τ 4.4 and 8.6 respectively.

It was confirmed that (3) was a precursor of (2) by reaction (7 d) of 3,3-dimethylbut-1-yne with (3) in a sealed tube giving the pyranyl complex (2) in 20% yield. This reaction provided further support for the geometry of the vinyl complex (3), and also demonstrated that in the formation of (2) the two $Bu^tC{\equiv}CH$ molecules had linked tail to tail, resulting in the hydrogen substituents being on adjacent carbon atoms. It is interesting that in the reaction of phenylacetylene with [$MnR(CO)_5$] (R = Me or Ph) the conversion of a vinyl ketone complex into a η^5-pyranyl complex was assumed, but could not be demonstrated.[8] A further point of contrast is that in the η^5-pyranyl complex obtained from the manganese system a formal head-to-tail linking of the acetylene was observed.[8] The most plausible explanation for the difference would be to invoke a dominant steric effect for the Bu^t substituent.

The mechanism suggested[6] for the formation of a vinyl ketone complex in the system [$MoMe(CO)_3(\eta\text{-}C_5H_5)$] + $C_2Me_2 \longrightarrow$ [$Mo\{\overline{C(Me)=C(Me)C(Me)O}\}(CO)_2(\eta\text{-}C_5H_5)$] can be extended to the η^5-indenyl system. In the absence of kinetic observations it is reasonable to assume competing dissociative and associative processes,* as demonstrated for the reaction of [$MoMe(CO)_3(\eta^5\text{-}C_9H_7)$] with phosphorus ligands in hexane as solvent, where the enhanced reactivity $\eta^5\text{-}C_9H_7 > \eta^5\text{-}C_5H_5$ was attributed[2] to a sideways ($\eta^5 \longrightarrow \eta^3$) slippage of the indenyl ligand in the case of the associative process.

In the conversion of the vinyl ketone complex into a η^3-pyranyl complex it is reasonable to propose that the first step involves an associative process between a second molecule of 3,3-dimethylbut-1-yne and the vinyl ketone complex (3) to form the intermediate (A) (Scheme 1). It is interesting that in this intermediate the σ-bonded vinyl ketone group could migrate either on to a co-ordinated carbonyl group or on to the co-ordinated acetylene; however, the latter process is clearly preferred. In this way, access is gained to a σ-oxahexatrienyl complex, which is likely to be the immediate precursor of the η^3-pyranyl system.† In discussing the formation of a η^5-pyranyl complex in the manganese system it was suggested[8] that ring closure occurred *via* nucleophilic attack by the ketonic oxygen on the vinylic carbon σ-bonded to the metal. However, we suspect that mechanistically the problem is more complex, and suggest a parallel situation to that discussed[12] for the insertion reactions of but-2-yne into the palladium–chlorine bond. As illustrated (Scheme 1), the σ-bonded oxahexatrienyl system can adopt two conformations (B) and (C), which

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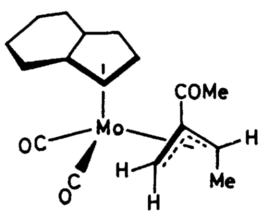
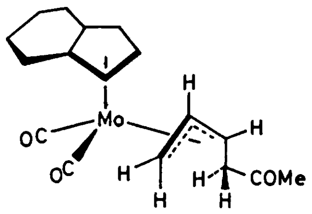
* In neat acetylene as solvent the associative process is likely to be dominant.

† It is important to note that migration of $CH{=}C(Bu^t)COMe$ on to co-ordinated 3,3-dimethylbut-1-yne occurs in the opposite direction to that observed where COMe migrates on to co-ordinated $Bu^tC{\equiv}CH$. This serves to underline the delicate balance of the factors involved in directing such reactions of unsymmetrical acetylenes.

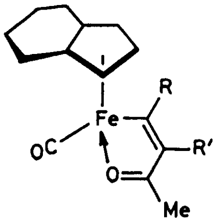
could, either *via* a thermally allowed disrotatory ring-closure reaction or by an insertion reaction to form a C_5 ring system (D), form a pyranyl ring system. At present there is no way of distinguishing between these two alternative reaction paths.



(4)

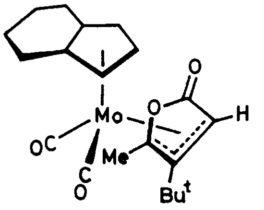


(5)



(6) R = R' = Me

(7) R = H, R' = Bu^t



(8)

With a view to extending the insertion reactions of alkylated acetylenes to the iron triad, reactions of $[FeMe(CO)_2(\eta^5\text{-}C_9H_7)]$ [7] were undertaken. Both but-2-yne and 3,3-dimethylbut-1-yne were found to react to give green crystals of the corresponding vinyl ketone complexes (6) and (7). Analytical and mass-spectral data confirmed that these complexes were 1 : 1 adducts and in the i.r. spectrum one terminal carbonyl band at 1 946 and 1 935 cm^{-1} was observed respectively. The ^{1}H n.m.r. spectra showed the resonances expected for the illustrated structures, and in particular a vinylic hydrogen resonance at τ 3.6 (H^1) was observed in the spectrum of the 3,3-dimethylbut-1-yne product, indicating that insertion had occurred in the same direction as for the molybdenum system.

The reaction of methylenecyclopropane with $[MoMe(CO)_3(\eta^5\text{-}C_9H_7)]$ was next investigated, it being surmised that the enhanced reactivity of the η^5-indenyl system combined with the co-ordinating ability of the double bond *exo*-cyclic to a three-membered ring would lead to an insertion reaction of the type we had previously observed with the palladium–chlorine system.[13] In methylenecyclopropane as solvent a slow (14 d, room temperature) reaction occurred with $[MoMe(CO)_3(\eta^5\text{-}C_9H_7)]$ to give in moderate yield, after separation from polymeric material and sublimation, a yellow crystalline complex (4), which from the mass spectrum and elemental analysis could be formulated as a 1 : 1 adduct. Examination of the i.r. spectrum showed the presence of two terminal carbonyl bands at 1 964 and 1 897 cm^{-1} together with an absorption at 1 660 cm^{-1} typical of an $\alpha\beta$-unsaturated ketone. The ^{1}H n.m.r. spectrum showed resonances expected [6,11] for an η^3-allyl system indicating that opening of the three-membered ring had occurred. Indenyl protons H^a resonated as a multiplet between τ 2.5 and 2.9 while the three protons comprising H^b and H^c were all inequivalent multiplets between τ 4.3 and 4.6. The absence of a resonance assignable to a central η^3-allylic proton suggested that an acetyl group (COMe at τ 7.75) occupied the central position. In agreement with the illustrated *exo* structure,* an *anti*-methyl resonance occurred as a doublet [J(H^{1}H^2) 7.0 Hz] at τ 9.1, whilst the *syn* proton H^1 appeared as a doublet of quartets centred at τ 6.05 [J(H^{1}H^2) 7.0, J(H^{1}H^4) 2.0 Hz], the other *syn* proton H^4 (τ 7.1) being coupled to the *anti* proton H^5 [τ 8.75, J(H^{4}H^5) 2.0 Hz].

It is suggested that the initial step in the reaction sequence (Scheme 2) leading to the formation of (4) involves co-ordination of methylenecyclopropane in the η^2-bonding mode,[14] the reaction paralleling that observed with phosphines and acetylenes. Either directly or under subsequent thermodynamic control, the generated acetyl group and the co-ordinated methylenecyclopropane achieve a relative *cis* configuration prior to migration of the COMe ligand on to the olefin. It is important to note that the acetyl group becomes attached to the central carbon atom of the methylenecyclopropane, the same regiospecificity being observed [13] for the chlorine ligand in the *cis*-chloropalladation reaction. Rotation about a C–C bond in intermediate (A) would then allow interaction of the molybdenum with the cyclopropane ring and ring cleavage of the 1,2 bond, as has been observed in the reaction of substituted methylenecyclopropanes with $[Pd(NCMe)_2Cl_2]$, $[Fe_2(CO)_9]$,[15] and Ni^0.[16,17] Dissociation of the co-ordinated olefin in the butenyl intermediate (B) would then allow a β-elimination reaction affording a *cis* (η^2-1,3-diene) hydride species (C), which after olefin rotation and insertion into the Mo–H bond affords under kinetic control the *anti*-methyl-substituted η^3-allylic system (4). Since only the thermodynamically less-stable *anti*-methyl isomer was formed, the *cis* olefin-insertion reaction must occur faster than single carbon–carbon bond rotation to give the *trans* (η^2-1,3-diene) hydride, which on insertion would give the *syn*-methyl isomer of (4).

It had previously been shown [18,19] that buta-1,3-diene and *trans*-penta-1,3-diene react with $[MnR(CO)_5]$ (R = Me or Ph) to afford acyl-substituted η^3-allylic complexes. In order to try and obtain further support for the mechanisms suggested for these reactions, the reaction of buta-1,3-diene with $[MoMe(CO)_3(\eta^5\text{-}C_9H_7)]$ was examined. In buta-1,3-diene as solvent, reaction occurred (6 d, room temperature) to form (36% yield) a yellow crystalline complex (5), which was isolated by column chromatography and sublimation and identified by analysis and mass spectroscopy as a 1 : 1 adduct. This was supported by the i.r. spectrum which exhibited absorptions due to

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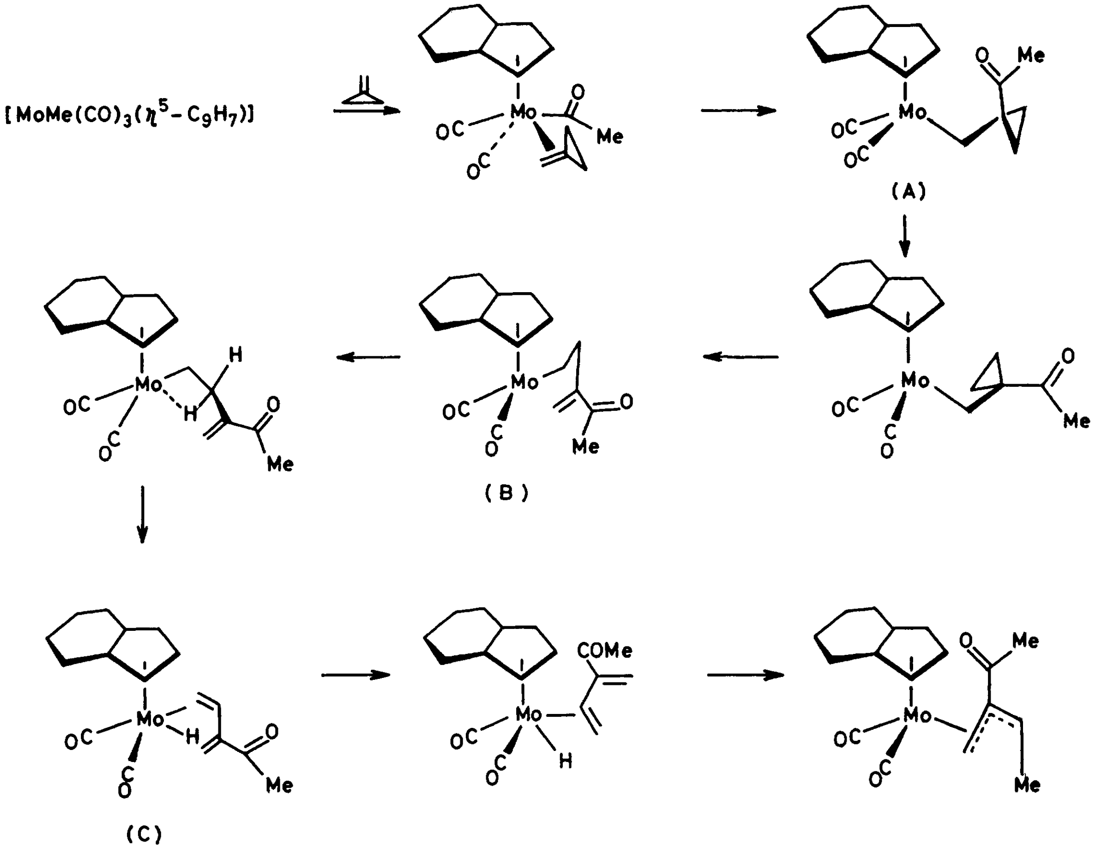
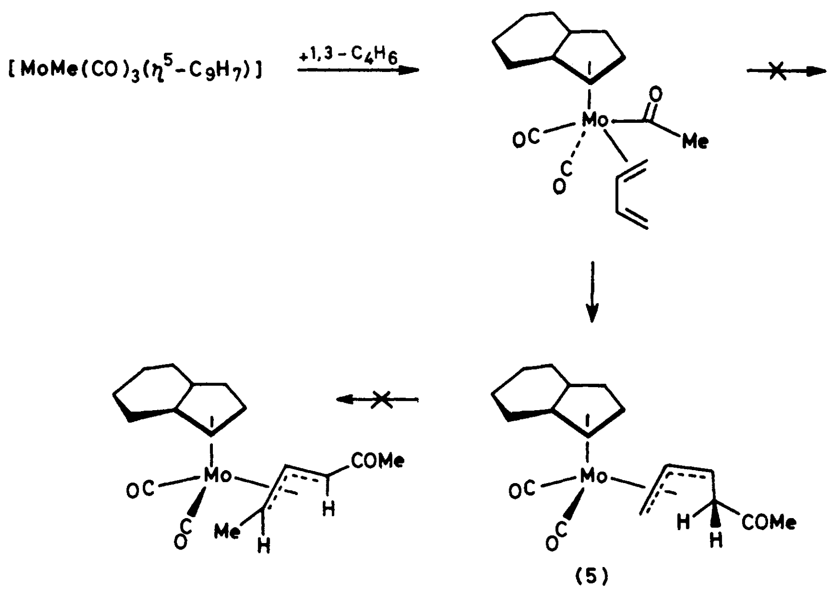
* The *exo* configuration would normally be preferred, although it is possible that the central acetyl substituent could have a destabilising influence.

terminal carbonyl ligands at 1 954 and 1 879 cm^{-1} together with a ketonic carbonyl group at 1 723 cm^{-1}.

Examination of the ^{1}H n.m.r. spectrum revealed the presence of a characteristic multiplet resonance at τ 10.2 of a central η^3-allylic proton H^3 of a [Mo(CO)$_2$(η^3-allyl)-(η^5-C$_9$H$_7$)] complex in an *exo* conformation.[11] The remainder of the spectrum was complex, and was elucidated in terms of the illustrated structure by ^{1}H-decoupling experiments. The proton H^3 showed typical η^3-allylic coupling to the *anti* proton H^1 [J(H^{1}H^3) 12.0 Hz] and the *syn* protons H^2 and H^4 [J(H^{2}H^3) 8.0, J(H^{3}H^4) 9.0 Hz], whilst H^1 exhibited a small coupling to H^2 [J(H^{1}H^2) 2.0



SCHEME 2



SCHEME 3

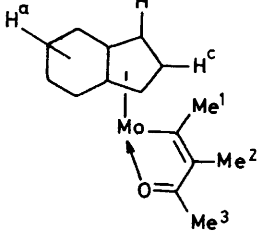
Hz] with H^2 being coupled to H^4 [$J(H^2H^4)$ 2.0 Hz]. The ketonic protons H^5 and H^6 exhibited different chemical shifts at τ 8.95 and 7.3 respectively [$J(H^5H^6)$ 17.0 Hz]. Molecular models indicated that rotation about the C–C bond on which H^4, H^5, and H^6 are sited would be hindered by the acyl group. This lack of rotation was confirmed by the temperature invariance of the coupling constants between the *syn* η^3-allylic proton H^4 and protons H^5 and H^6 [$J(H^4H^5)$ 11.0, $J(H^4H^6)$ 4.0 Hz]. The magnitude of $J(H^4H^5)$ suggests a dihedral angle between H^4 and H^5 of *ca.* 180°, implying that H^5 is directed towards the molybdenum, thus providing a possible explanation for the high chemical shift of this proton.

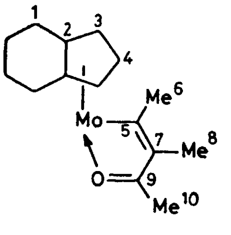
As shown in Scheme 3 the formation of (5) is consistent with the co-ordination of a η^2-bonded buta-1,3-diene in a cisoid configuration, the acyl group migrating on to the co-ordinated 1,3-diene faster than single C–C bond rotation. It is interesting that attempts to affect the thermal isomerisation of (5) to a η^3-allylic complex with a stereochemistry the same as observed with the manganese system were unsuccessful. It is also noteworthy that in the buta-1,3-diene reaction the acyl group migrates on to the least-substituted carbon of the diene, in contrast with the methylenecyclopropane system. This might reflect some steric control over the direction of formal insertion.

EXPERIMENTAL

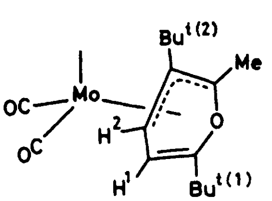
N.m.r. studies were made with JEOL PFT and PS 100 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer. Experiments were carried out under a dry oxygen-free nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use. Starting materials were synthesised by published methods.

Reactions of Tricarbonyl(η^5-indenyl)methylmolybdenum.—(*a*) *With but-2-yne.* An excess of but-2-yne (40 mmol) was condensed (−196 °C) into a tube fitted with a Westef high-pressure stopcock containing $[MoMe(CO)_3(\eta^5\text{-}C_9H_7)]$ (0.5 g, 1.6 mmol). After 2 d at room temperature the volatile material was removed *in vacuo* from the red solution, and the residue chromatographed on an alumina-packed column. Elution with hexane–diethyl ether (4 : 1) gave first the starting material followed by an orange band, which on crystallisation (−78 °C) from hexane gave red *crystals* of (1) (0.26 g, 44%) (Found: C, 56.2; H, 4.3. $C_{17}H_{16}MoO_3$ requires C, 56.0; H, 4.4%), ν(CO) in hexane at 1 970s and 1 892s cm^{-1}, ν in Nujol at 1 530w cm^{-1} (co-ordinated C=O). N.m.r. spectra in C_6D_6: ^1H, τ 3.1—3.5 (m, 4 H, indenyl H^a), 4.8 [d, 2 H, H^b, $J(H^bH^c)$ 3.0], 5.3 [t, 1 H, H^c, $J(H^bH^c)$ 3.0 Hz], 7.2 (s, 3 H, Me^1), 8.2 (s, 3 H, Me^3), and 8.45 (s, 3 H, Me^2); ^{13}C, −261.1 p.p.m. (s, C^9), −134.1 (s, C^5), −128.9 (s, C^7), −125.7 (s, C^1), −125.1 (s, C^1), −115.1 (s, C^2), −88.9 (s, C^4), −79.2 (s, C^3), −33.3 (s, Me^6), −25.0 (s, Me^{10}), and −13.7 (s, Me^8). The mass spectrum showed peaks at *m/e* 366 (*P*), 338 (*P* − CO), 310 (*P* − 3CO), and 115 (C_9H_7).

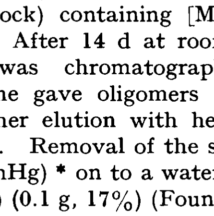




(*b*) *With* 3,3-*dimethylbut*-1-*yne*. A similar reaction (4 d) between $[MoMe(CO)_3(\eta^5\text{-}C_9H_7)]$ (0.5 g, 1.6 mmol) and 3,3-dimethylbut-1-yne (40 mmol) gave a red-orange solution. Chromatography on alumina and elution with hexane gave first starting material, followed by an orange band which on recrystallisation (−78 °C) from hexane gave orange *crystals* of (2) (0.1 g, 13%) (Found: C, 63.3; H, 6.5. $C_{25}H_{30}MoO_3$ requires C, 63.4; H, 6.4%), ν(CO) in hexane at 1 945s and 1 875s cm^{-1}, ν(C=C) in Nujol at 1 635w cm^{-1}. Hydrogen-1 n.m.r. spectrum in C_6D_6: τ 2.9 (m, 1 H, indenyl H^a), 3.3 (m, 3 H, indenyl H^a), 4.4 [d, 1 H, H^1, $J(H^1H^2)$ 2.0], 4.5 [t, 1 H, indenyl H^b, $J(H^bH^c)$ 3.0 Hz], 4.7 [m, 1 H, indenyl H^b, $J(H^bH^c)$ 3.0, $J(H^bH^b)$ 2.0 Hz], 4.8 [m, 1 H, indenyl H^b, $J(H^{b'}H^c)$ 3.0, $J(H^bH^b)$ 2.0], 8.4 (s, 3 H, Me), 8.6 [d, 1 H, H^2, $J(H^1H^2)$ 2.0 Hz], 8.8 (s, 9 H, Bu^1), and 8.95 (s, 9 H, Bu^2). The mass spectrum showed peaks at *m/e* 476 (*P*), 448 (*P* − CO), 420 (*P* − 2CO), and 207 ($C_{14}H_{23}O$).



Further elution with hexane–diethyl ether (4 : 1) gave a red band, which on recrystallisation (−78 °C) from hexane afforded red *crystals* of (3) (0.1 g, 16%) (Found: C, 59.6; H, 5.6. $C_{17}H_{20}MoO_3$ requires C, 59.5; H, 5.8%), ν(CO) in hexane at 1 970s and 1 888s cm^{-1}, ν(C=O) (co-ordinated) in Nujol at 1 530mw cm^{-1}. Hydrogen-1 n.m.r. spectrum in C_6D_6: τ 2.9—3.4 (m, 4 H, indenyl H^a), 3.6 (s, 1 H, H^1), 4.55 (br m, 2 H, indenyl H^b), 5.4 [t, 1 H, indenyl H^b, $J(H^bH^c)$ 3 Hz], 8.2 (s, 3 H, Me), and 8.6 (s, 9 H, Bu^2). The mass spectrum showed peaks at *m/e* 394 (*P*), 366 (*P* − CO), and 338 (*P* − 2CO).



(*c*) *With methylenecyclopropane.* An excess of methylenecyclopropane (40 mmol) was condensed (−196 °C) into a tube (Westef stopcock) containing $[MoMe(CO)_3(\eta^5\text{-}C_9H_7)]$ (0.5 g, 1.6 mmol). After 14 d at room temperature the reaction mixture was chromatographed on alumina. Elution with hexane gave oligomers of methylenecyclopropane, then further elution with hexane–diethyl ether gave a yellow band. Removal of the solvent and sublimation (80 °C, 0.1 mmHg) * on to a water-cooled probe gave yellow *crystals* of (4) (0.1 g, 17%) (Found: C, 56.3; H, 4.5. $C_{17}H_{16}MoO_3$ requires C, 56.0; H, 4.4%), ν(CO) in hexane at 1 964s and 1 897s cm^{-1}, ν in Nujol at 1 660s (CO), 1 372m, 1 354w, 1 340w, 1 261m, 810m, and 742m cm^{-1}. Hydrogen-1 n.m.r. spectrum in $CDCl_3$: τ 2.5—2.9 (m, 4 H, indenyl H^a),

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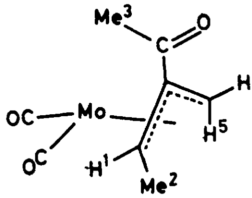
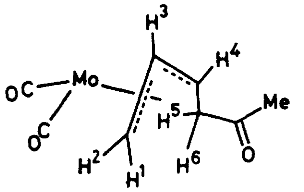
* Throughout this paper: 1 mmHg ≈ 13·6 × 9.8 Pa; 1 atm = 101 325 Pa.

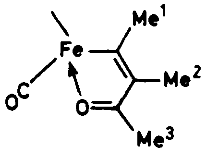
4.3 [t, 1 H, indenyl H^{c}, J(H^{b}H^{c}) 3.0], 4.5 (m, 1 H, indenyl H^{b}), 4.6 (m, 1 H, indenyl H^{b}), 6.05 [dq, 1 H, H^{1}, J(H^{1}H^{2}) 7.0, J(H^{1}H^{4}) 2.0], 7.1 [t, 1 H, H^{4}, J(H^{4}H^{5}) = J(H^{2}H^{4}) 2.0], 7.75 (s, 3 H, Me^{3}), 8.75 [d, 1 H, H^{5}, J(H^{4}H^{5}) 2.0], and 9.1 [d, 3 H, Me^{2}, J(H^{1}H^{2}) 7.0 Hz]. The mass spectrum showed peaks at *m/e* 366 (*P*), 338 (*P* – CO), and 310 (*P* – 2CO).



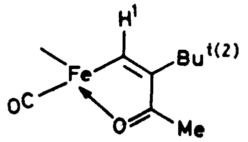
(*d*) *With buta*-1,3-*diene*. An excess of buta-1,3-diene (40 mmol) and [MoMe(CO)$_3$(η^5-C$_9$H$_7$)] (0.5 g, 1.6 mmol) was allowed to react (6 d) at room temperature in a sealed tube. Chromatography of the involatile products gave starting material followed [hexane–diethyl ether (1 : 1)] by a yellow band. Removal of the solvent and sublimation (80 °C, 0.1 mmHg) on to a water-cooled probe gave yellow *crystals* of (5) (0.21 g, 36%) (Found: C, 56.3; H, 4.7. C$_{17}$H$_{16}$MoO$_3$ requires C, 56.0; H, 4.4%), ν(CO) in hexane at 1 954s, 1 879s, and 1 723m cm^{-1}, ν in Nujol at 1 380w, 1 342w, 1 171w, 1 144w, 900w, 825m, and 768m cm^{-1}. Hydrogen-1 n.m.r. spectrum CDCl$_3$: τ 2.95 (s, 4 H, indenyl H^{a}), 4.00 [d, 2 H, indenyl H^{b}, J(H^{b}H^{c}) 3.0], 4.4 [t, 1 H, indenyl H^{c}, J(H^{b}H^{c}) 3.0], 6.8 [m, 1 H, H^{4}, J(H^{2}H^{4}) 2.0, J(H^{3}H^{4}) 9.0, J(H^{4}H^{5}) 11.0, J(H^{4}H^{6}) 4.0], 7.3 [dd, 1 H, H^{6}, J(H^{5}H^{6}) 17.0, J(H^{4}H^{6}) 4.0], 7.7 [dt, 1 H, H^{2}, J(H^{1}H^{2}) 2.0], J(H^{2}H^{3}) 8.0, J(H^{2}H^{4}) 2.0], 8.0 (s, 3 H, Me), 8.7 [dd, 1 H, H^{1}, J(H^{1}H^{2}) 2.0, J(H^{1}H^{3}) 12.0], 8.95 [dd, 1 H, H^{5}, J(H^{4}H^{5}) 11.0, J(H^{5}H^{6}) 17.0], and 10.2 [m, 1 H, H^{3}, J(H^{1}H^{3}) 12.0, J(H^{2}H^{3}) 8.0, J(H^{3}H^{4}) 9.0 Hz].



Reactions of Dicarbonyl(η^5-*indenyl*)*methyliron*.—(*a*) *With but*-2-*yne*. In a similar manner but-2-yne (40 mmol) and [FeMe(CO)$_2$(η^5-C$_9$H$_7$)] (0.3 g, 1.25 mmol) were allowed to react at room temperature for 4 d in a sealed tube. Chromatography on alumina gave [hexane–diethyl ether (4 : 1)] a green band, which on crystallisation (–78 °C) from hexane gave green *crystals* of (6) (0.14 g, 37%) (Found: C, 64.4; H, 5.8. C$_{16}$H$_{16}$FeO$_2$ requires C, 64.8; H, 5.4%), ν(CO) in hexane at 1 946s cm^{-1}. Hydrogen-1 n.m.r. spectrum in C$_6$D$_6$: τ 2.5—3.2 (m, 4 H, indenyl H^{a}), 4.9 (br m, 1 H, indenyl), 5.3 (br m, 1 H, indenyl), 7.5 (br m, 1 H, indenyl), 7.5 (s, 3 H, Me^{1}), 8.35 (s, 3 H, Me^{3}), and 8.4 (s, 3 H, Me^{2}). The mass spectrum showed peaks at *m/e* 296 (*P*) and 268 (*P* – CO).



(*b*) *With* 3,3-*dimethylbut*-1-*yne*. A similar reaction (10 d, room temperature) between [FeMe(CO)$_2$(η^5-C$_9$H$_7$)] (0.9 g, 3.7 mmol) and 3,3-dimethylbut-1-yne (20 mmol) in hexane (20 cm^3) gave on chromatography (elution with hexane) a green band, which on crystallisation (–78 °C) from hexane gave green *crystals* of (7) (0.15 g, 13%) (Found: C, 66.9; H, 6.3. C$_{18}$H$_{20}$FeO$_2$ requires C, 66.6; H, 6.2%), ν(CO) in hexane at 1 935s cm^{-1}. Hydrogen-1 n.m.r. spectrum C$_6$D$_6$: τ 2.4—3.1 (m, 4 H, indenyl H^{a}), 3.6 (s, 1 H, H^{1}), 4.6 (m, 1 H, indenyl), 4.8 (m, 1 H, indenyl), 6.7 (m, 1 H, indenyl), 8.3 (s, 3 H, Me), and 8.7 (s, 9 H, Bu^{2}). The mass spectrum showed peaks at *m/e* 324 (*P*) and 296 (*P* – CO).



Reaction of Carbon Monoxide with Complex (3).—A solution of (3) (0.23 g, 0.6 mmol) in hexane (20 cm^3) was placed in a glass-lined autoclave (100 cm^3) and pressurised to 80 atm with carbon monoxide. After 6 h at room temperature the solvent was removed *in vacuo* and the residue crystallised (–78 °C) from hexane to give yellow *crystals* of (8) (0.2 g, 81%) (Found: C, 57.2; H, 4.8. C$_{18}$H$_{20}$MoO$_4$ requires C, 57.2; H, 4.8%), ν(CO) in hexane at 1 949s and 1 819 cm^{-1}, ν in Nujol at 1 709s cm^{-1}. Hydrogen-1 n.m.r. spectrum in CDCl$_3$: τ 2.8 (m, 4 H, indenyl H^{a}), 4.08 [d, 1 H, indenyl H^{b}, J(H^{b}H^{c}) 3.0], 4.14 [d, 1 H, indenyl H^{b}, J(H^{b}H^{c}) 3.0], 4.34 [dd, 1 H, indenyl H^{c}, J(H^{b}H^{c}) = J(H$^{b'}$H^{c}) 3.0 Hz], 6.92 (s, 1 H, H), 8.40 (s, 3 H, Me), and 8.78 (s, 9 H, Bu^{t}).

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