Reactions of Acyl- and Alkyl-(tricarbonyl)(η^5-cyclopentadienyl)-molybdenum and -tungsten Complexes with But-2-yne; Molecular Structures of [Mo(CO)(Bu^{t}NC)(η^3-{O·C(O)·CMe·CMe·CMe})(η^5-C$_5$H$_5$)] and [Mo·C(O)·C(Me){C(Me)}$_2$C(Me)·C(CF$_3$)·O(CO)(η^5-C$_5$H$_5$)]

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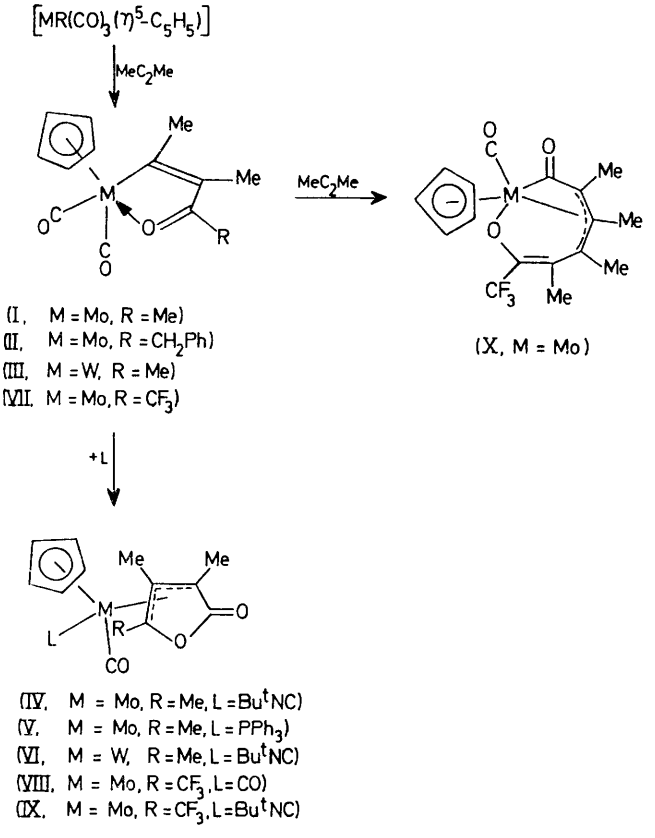
Summary Reaction of [MR(CO)$_3$(η^5-C$_5$H$_5$)] (M = Mo, W; R = Me, CH$_2$Ph, COCF$_3$) with but-2-yne affords either the vinylketone complexes [M·C(Me) : C(Me)·C(O)R(CO)$_2$-(η^5-C$_5$H$_5$)], which on treatment with ligands L form lactone complexes [M(CO)L(η^3-{O·C(O)·CMe·CMe·CMe})-(η^5-C$_5$H$_5$)], or the eight-membered ring complex [Mo·C(O)·C(Me){C(Me)}$_2$C(Me)·C(CF$_3$)·O(CO)(η^5-C$_5$H$_5$)]; the identity of the products is established by *X*-ray crystallography.

In the tetracarbonylnickel-catalysed reaction of acetylenes and carbon monoxide with alkyl, allyl, or arylhalides to form lactones, unstable acylnickel carbonyl intermediates have been implicated.[1,2] Moreover, η^3-(penteno-4-lactonyl)tricarbonylcobalt complexes are obtained from reactions of acetyl(tetracarbonyl)cobalt and di-substituted acetylenes, and it is believed that vinyl ketone(tricarbonyl)-cobalt intermediates undergo a further insertion reaction with CO before undergoing a cyclisation reaction.[3] We report synthetic and structural studies with η^5-cyclopentadienyl-molybdenum and -tungsten complexes which provide an insight into the mechanisms of these reactions.

Whereas [MoCF$_3$(CO)$_3$(η^5-C$_5$H$_5$)] reacts with but-2-yne under u.v. irradiation to form a 16-electron[4] species [MoCF$_3$-(CO)(MeC$_2$Me)(η^5-C$_5$H$_5$)], the methyl and benzyl complexes [MoR(CO)$_3$(η^5-C$_5$H$_5$)] react thermally (hexane, 60 °C) with MeC$_2$Me to give the red-orange crystalline products (I) [ν_{CO}(hexane) 1 970s and 1 878s cm^{-1}] and (II), characterised as σ-bonded vinyl ketone complexes in which the keto-group is co-ordinated to the molybdenum. The analogous tungsten complex (III) was only obtained on u.v. irradiation of but-2-yne and [WMe(CO)$_3$(η^5-C$_5$H$_5$)].



(I, M = Mo, R = Me)
(II, M = Mo, R = CH$_2$Ph)
(III, M = W, R = Me)
(VII, M = Mo, R = CF$_3$)

(X, M = Mo)

(IV, M = Mo, R = Me, L = Bu^{t}NC)
(V, M = Mo, R = Me, L = PPh$_3$)
(VI, M = W, R = Me, L = Bu^{t}NC)
(VIII, M = Mo, R = CF$_3$, L = CO)
(IX, M = Mo, R = CF$_3$, L = Bu^{t}NC)

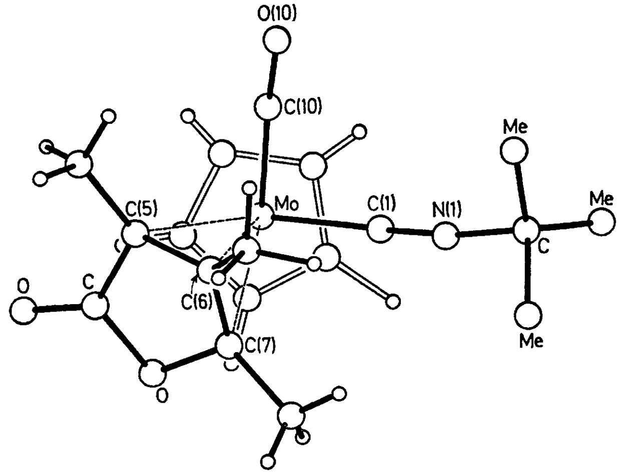


Figure 1. Molecular structure of [Mo(CO)(Bu^{t}NC)(η^3-{OC(O)CMeCMeCMe})(η^5-C$_5$H$_5$)] (IV). Bond lengths to molybdenum: C(10) 1·955(8), C(1) 2·053(5), C(5) 2·353(7), C(6) 2·243(6), C(7) 2·284(6), cyclopentadiene C (mean) 2·334 Å. Other lengths: C(5)–C(6) 1·434(9), C(6)–C(7) 1·409(9), C(10)–O(10) 1·153(10), C(1)–N(1) 1·153(7) Å.

Related *cis*-insertion reactions have been previously reported[5] between substituted acetylenes and methyl-, acetyl-, or phenyl-pentacarbonylmanganese; however, these 1 : 1 adducts did not undergo the expected further reaction with carbon monoxide. In contrast, the molybdenum and tungsten complexes react with isocyanides (room temperature, Bu^{t}NC) or triphenylphosphine to form, for example, the complexes (IV), (V) and (VI), all of which showed a strong band in the i.r. spectrum in the 1 725 cm^{-1} region. A similar reaction (60 °C) occurred between [MoCOCF$_3$(CO)$_3$(η^5-C$_5$H$_5$)] and but-2-yne to form both (VII) and (VIII). The complex (VII) reacted with CO (10 atm, 60 °C) to form (VIII) and with Bu^{t}NC to give (IX). A single-crystal *X*-ray diffraction study on (IV) established the structure shown in Figure 1. *Crystal data:* C$_{18}$H$_{23}$MoNO$_3$, M = 397·33, monoclinic, space group $P2_1/a$, a = 9·301(1), b = 22·161(6), c = 9·353(3) Å, β = 102·76(2)°, U = 1881·8(9) Å^3, Z = 4, μ(Mo-$K_{\bar{\alpha}}$) = 7·0 cm^{-1}. Least-squares refinement (Mo, N, O, C, anisotropic; H, isotropic) using 3412 reflections ($I \geqslant 1{\cdot}0\,\sigma$, Syntex $P2_1$ diffractometer) has converged to R 0·058. These observations clearly establish the stepwise nature of the lactone ring-forming reactions with acetylenes.

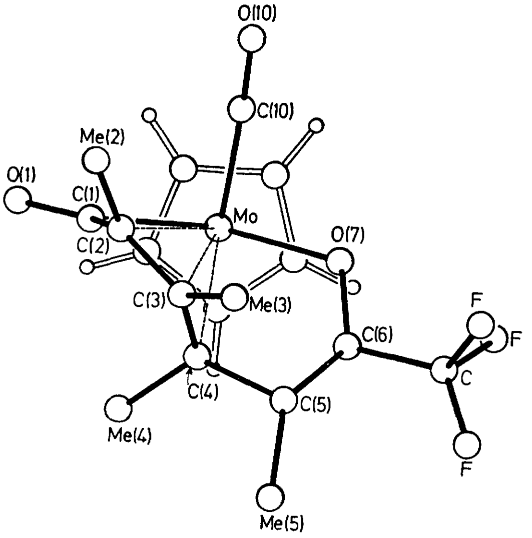


FIGURE 2. Molecular structure of [Mo·C(O)·C(Me){C(Me)}$_2$C(Me)·C(CF$_3$)·O(CO)(η^5-C$_5$H$_5$)] (X). Bond lengths[a] to molybdenum: C(10) 2·010, C(1) 2·073, C(2) 2·438, C(3) 2·436, C(4) 2·300, O(7) 2·115, cyclopentadiene C (mean) 2·310 Å. Other lengths[a]: C(2)–C(3) 1·390, C(3)–C(4) 1·470, C(10)–O(10) 1·153 Å.

[a] Averaged over two independent molecules per asymmetric unit.

A third product (X), obtained in low yield (10%) as a purple-red crystalline material (m.p. 148—150 °C) from the reaction (hexane, 24 h, 60 °C) of [MoCOCF$_3$(CO)$_3$(η^5-C$_5$H$_5$)] with but-2-yne, did not show a lactone band in the i.r. spectrum but showed an acyl band at 1 675 cm^{-1}. Since n.m.r. data did not establish the structure, a single-crystal diffraction study was undertaken. *Crystal data:* C$_{17}$H$_{17}$F$_3$MoO$_3$, M = 424·26, monoclinic, space group $P2_1/n$, a = 18·389(4), b = 11·137(3), c = 16·686(5) Å, β = 92·55(2)°, U = 3413(1) Å^3, Z = 8, μ(Mo-$K_{\bar{\alpha}}$) = 8·9 cm^{-1}. R is currently 0·086 for 5411 reflections ($I \geqslant 1{\cdot}0\,\sigma$) measured to $\theta_{\max}$ = 30° (Mo-K_α radiation).

The molecular structure (Figure 2) involves an unusual eight-membered ring metallocycle. The molybdenum atom is bonded within the ring *via* two σ bonds [to C(1) and O(7)], and one η^3-allyl linkage which shows a marked distortion towards π [C(2)=C(3)]-σ [C(4)] localisation.

The formation of a complex of this type is without precedent, and presumably involves insertion of a second molecule of but-2-yne into (VII) followed by a carbonyl insertion. However, in contrast with the lactone-forming reaction, which could be envisaged[6] as involving nucleophilic attack by the –C(O)CF$_3$ carbonyl lone pair on the Mo·C(O)·CMe acyl group, an unusual oxidative [Mo$^{\mathrm{II}} \rightarrow$ Mo$^{\mathrm{IV}}$] reaction occurs where the C(O)CF$_3$ oxygen becomes σ-bonded to the molybdenum.

The possibility that (X) might undergo a reductive-elimination reaction to form a seven-membered lactone ring co-ordinated to the metal *via* a η^3- or η^5-system is being investigated. An extension of this idea suggests an alternative mechanism for formation of the lactone complexes [*e.g.* (IV)], involving an analogous oxidative-reduction sequence.

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