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Reactions of Tetracyclone Molybdenum Complexes with Electrophilic Alkynes: Cyclopentadienone−Alkyne Coupling and Alkyne Coordination

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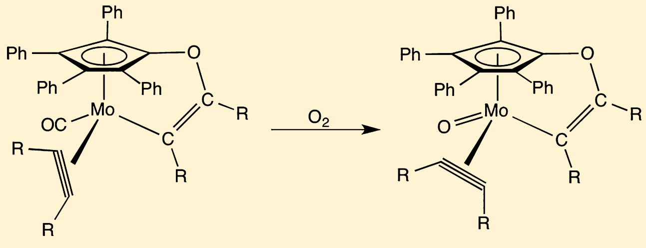
Supporting Information

ABSTRACT: The reactions of the complexes $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ and $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$ with the alkynes dimethyl acetylenedicarboxylate (DMAD; $RC{\equiv}CR$ where R = CO_2Me) and methyl propiolate ($RC{\equiv}CH$) have been studied. In the case of DMAD, the initial product is the green carbonyl complex $[Mo(CO)(RC{\equiv}CR)(\eta^5,\sigma\text{-}C_4Ph_4COCR{=}CR)]$ (**3**), in which two alkyne molecules have been incorporated: one is linked to the carbonyl group of the tetracyclone ligand, whereas the other is π-bound to the metal as a four-electron donor. Oxidation of this compound affords yellow $[Mo(O)(RC{\equiv}CR)(\eta^5,\sigma\text{-}C_4Ph_4COCR{=}CR)]$ (**8**). When the π-acceptor carbonyl ligand is replaced by the π-donor oxo group, the alkyne ligand changes orientation: it lies parallel to the Mo−CO bond in **3** but perpendicular to the Mo=O group in **8**. Analogous complexes (**9**, **10**) were isolated in the case of methyl propiolate; each exists as a mixture of two isomers depending on the orientation of the unsymmetrical alkyne ligand.



3 **8**

INTRODUCTION

Originally isolated as low-yield products from the reactions of metal carbonyls with alkynes,[1] complexes containing cyclopentadienone ligands have attracted a substantial amount of renewed interest in recent years. Among these, ruthenium complexes of tetraphenylcyclopentadienone (commonly referred to as tetracyclone) and in particular Shvo's catalyst, $[Ru_2(CO)_4(\mu\text{-}H)(\mu,\eta^5{:}\eta^5\text{-}C_4Ph_4COHOCC_4Ph_4)]$, have been demonstrated to be active catalysts for a number of important reactions, such as the transfer hydrogenation of aldehydes, ketones, and imines and the dehydrogenation of ammonia−borane.[2,3] The catalyst functions by reversible dissociation to the interrelated mononuclear fragments $[RuH(CO)_2(\eta^5\text{-}C_4Ph_4COH)]$ and $[Ru(CO)_2(\eta^4\text{-}C_4Ph_4CO)]$, which can act as hydrogenating and dehydrogenating agents, respectively (Scheme 1). It is therefore an example of a bifunctional system, in that one hydrogen is delivered from the metal and the other from the hydroxy group of the ligand.[4] More recently, attempts have been made to replace ruthenium with cheaper, more earth-abundant metals such as iron in catalysts developed by Casey, Beller, Wills, and others.[5]

Some time ago we reported efficient preparations of several molybdenum complexes containing tetracyclone ligands, including $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ (**1**) and $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$ (**2**) (Chart 1) and demonstrated that their reactions with phosphines afforded complexes of the type $[Mo(CO)_3L(\eta^4\text{-}C_4Ph_4CO)]$ (L = PPh_3, PPh_2Me, PPh_2H) or $[Mo(CO)_2(L_2)(\eta^4\text{-}C_4Ph_4CO)]$ (L_2 = dppm, dppe).[6] In these reactions one (and only one) of the tetracyclone ligands of **1** could be displaced by a phosphine. Although molybdenum is not traditionally associated with high catalytic activity in hydrogenation reactions, it is interesting to note that Waymouth and co-workers have recently reported that **2** also displays Shvo-type reactivity in transfer hydrogenation reactions.[7]

Recently we showed that the reaction of **1** with phenylacetylene resulted in an unusual cyclotrimerization process to give an η^6-fulvene ligand.[8] In this paper we report the reactions of **1** and **2** with the activated alkynes DMAD ($RC{\equiv}CR$; R = CO_2Me throughout this paper) and methyl propiolate ($RC{\equiv}CH$). Part of this work was included in a preliminary publication.[9]

RESULTS AND DISCUSSION

Reactions with DMAD. Heating a toluene solution of **1** with an excess of DMAD to reflux for 17 h led to the production of green $[Mo(CO)(RC{\equiv}CR)(\eta^5,\sigma\text{-}C_4Ph_4COCR{=}CR)]$ (**3**) in 70% yield as the only organometallic product after separation by column chromatography (Scheme 2). The organic byproducts included tetracyclone, hexamethyl mellitate from the cyclotrimerization of DMAD, and dimethyl tetraphenylphthalate formed by the Diels−Alder reaction of the liberated tetracyclone with DMAD. Curiously,

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Scheme 1. Formation of Catalytically Active Species by Dissociation of Shvo's Catalyst

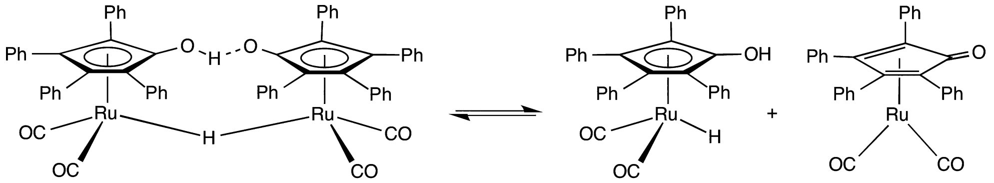
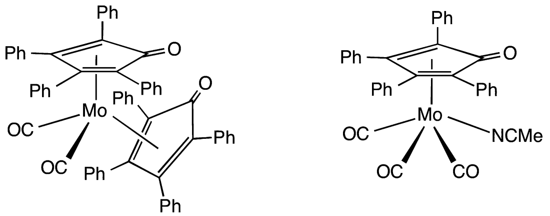
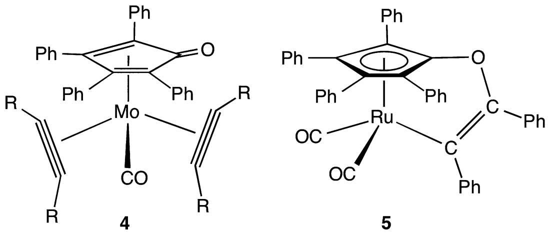


Chart 1

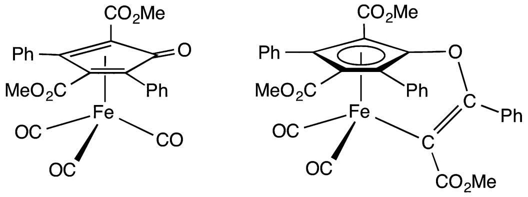


1 **2**

Chart 2



4 **5**



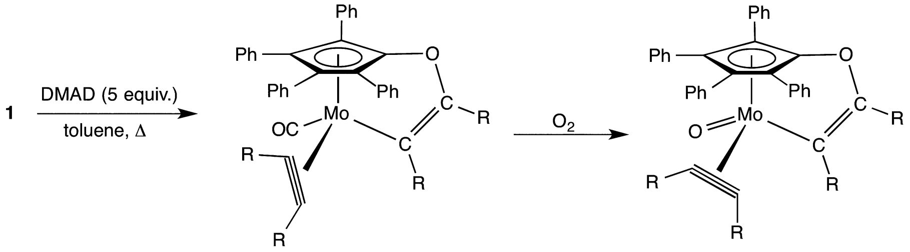
6 **7**

in the light of the results obtained below, complex **2** did not give any tractable products on treatment with DMAD.

Complex **3** was initially characterized by spectroscopic techniques. The mass spectrum and analytical data established the loss of one tetracyclone ligand and the incorporation of two alkyne molecules. The IR spectrum showed a terminal CO absorption at 2000 cm^{-1} together with weaker peaks at 1735 and 1720 cm^{-1} due to the ester groups. The ^1H NMR spectrum revealed the presence of four inequivalent methyl groups in addition to phenyl peaks due to one tetracyclone ligand. The main point of interest, however, proved to be the $^{13}C\{^1H\}$ NMR spectrum. Two different sets of peaks for the two alkyne moieties were observed: the C≡C carbons of the first resonate at 193.2 and 190.0 ppm and those of the second at 161.1 and 155.2 ppm. Assignment of the spectrum in the 140−200 ppm region was assisted by recording a ^1H-coupled version; the alkyne carbons and the carbonyl of the cyclopentadienone ring remain as singlets, whereas the ester carbonyl groups collapse to quartets due to coupling with the methyl protons. The carbon atoms of the cyclopentadienone ring also show coupling to the ortho hydrogens of their respective phenyl rings (see the Supporting Information).

In our original communication we proposed structure **4**, $[Mo(CO)(RC{\equiv}CR)_2(\eta^4\text{-}C_4Ph_4CO)]$, for the product (Chart 2).[9] However, we later realized that structure **3**, in which one alkyne is linked to the cyclopentadienone ring, is more consistent with the spectroscopic data. For example, it is well established that in Mo(II) complexes the ^{13}C chemical shifts of alkyne ligands can be correlated with the number of electrons donated to the metal; typical values are approximately 200 ppm for 4-electron-donor alkynes and 115 ppm for 2-electron donors.[10,11] In structure **4** the two alkyne ligands would be required to donate 6 electrons in total to the $Mo(CO)(\eta^4\text{-}C_4Ph_4CO)$ unit to achieve an 18-electron configuration, and even though it would be a Mo(0) complex as drawn, the two alkynes would probably be equivalent with an average shift of around 150−180 ppm. The alternative, that one alkyne donates 4 electrons and the other 2, is unlikely, and even then the shift of the latter would be rather high. In structure **3**, however, the peaks at lower field can be readily assigned to the 4-electron-donor alkyne, whereas the vinylic carbons would be expected to appear at the observed value of ca. 150−160 ppm. Second, previous work has shown that the Shvo complex $[Ru_2(CO)_4(\mu\text{-}H)(\mu,\eta^5{:}\eta^5\text{-}C_4Ph_4COHOCC_4Ph_4)]$ reacts with alkynes such as C_2Ph_2 to afford the related vinyl complex $[Ru(CO)_2(\eta^5,\sigma\text{-}C_4Ph_4COCPh{=}CPh)]$ (**5**), in which a similar linking of the alkyne to the cyclopentadienone has occurred; moreover, the ^{13}C chemical shift of the vinylic carbons in these compounds was also around 150 ppm.[12] Further literature precedent for such a structure can be found in the products of the reaction between $[Fe_2(CO)_9]$ and methyl phenylpropiolate: not only was cyclopentadienone complex **6** isolated, but so was **7**, its

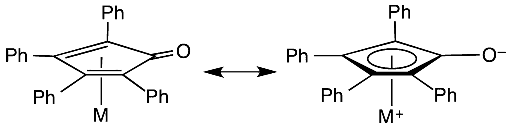
Scheme 2. Synthesis of the DMAD Complexes 3 and 8



3 **8**

addition product with further alkyne.[13] The nucleophilic nature of the carbonyl oxygen in cyclopentadienone complexes can be attributed to the canonical form shown in Chart 3, in which it bears a negative charge.

Chart 3



After many years we succeeded in growing crystals of **3** suitable for X-ray diffraction; the structure is shown in Figure 1 with important bond lengths given in its caption. There are two independent molecules in the unit cell, one of which exhibits disorder of the carbonyl oxygen of one of the CO_2Me groups; the molecule depicted here (B) is the nondisordered one. The structure determination confirms the linking of the tetracyclone carbonyl oxygen to one of the alkyne molecules, creating a cyclopentadienyl ligand tethered through the vinyl group. The five-membered ring is bonded to the metal in a slightly tilted η^5 manner: the Mo−C bond lengths lie between 2.302(4) and 2.392(4) Å, with those to C(4) and C(5) being the shortest. In complex **5**, the ligand was significantly tilted the opposite way, with the oxygen-bearing carbon being closest to the Ru. The bond lengths in the vinylic portion of the ligand are the same, within experimental error, as those in complex **5**.[12,14]

The second alkyne is bound to the molybdenum as an η^2 ligand; the compound therefore belongs to the well-established $CpM(RC{\equiv}CR)LX$ class.[15,16] Both the C≡C bond length of 1.312(6) Å and the Mo−C bond lengths (2.031(4) and 2.059(4) Å) are commensurate with this ligand acting as a 4-electron donor, as required by electron-counting considerations.[11] It is also noteworthy that the alkyne lies parallel to the CO ligand, a point discussed further below.

Although complex **3** is relatively air stable in the solid state, exposure of a dichloromethane solution to air overnight resulted in a color change from green to yellow accompanied by the disappearance of the carbonyl peak in the IR spectrum. The same transformation can be brought about instantaneously by dissolving the compound in THF that has been deliberately exposed to air and sunlight (the active agent presumably being a peroxide). From the yellow solutions, the corresponding oxo complex $[Mo(O)(RC{\equiv}CR)(\eta^5,\sigma\text{-}C_4Ph_4COCR{=}CR)]$ (**8**) can be isolated in excellent yield (Scheme 2). The presence of the Mo═O group was confirmed by observation of a peak at 937 cm^{-1} in the solid-state IR spectrum. The ^1H NMR spectrum of **8** is very similar to that of **3**, with four inequivalent methyl groups, but distinct differences are apparent in the ^{13}C NMR spectrum, where all four alkyne carbons now appear in the region between 167.2 and 149.7 ppm: i.e., there is an upfield shift of approximately 40 ppm in the metal-bonded alkyne. We attribute this to the replacement of the π-acceptor carbonyl by the π-donor oxo ligand which can compete with the alkyne ligand for available metal orbitals, as discussed extensively by Templeton and others.[17−20] For example, the

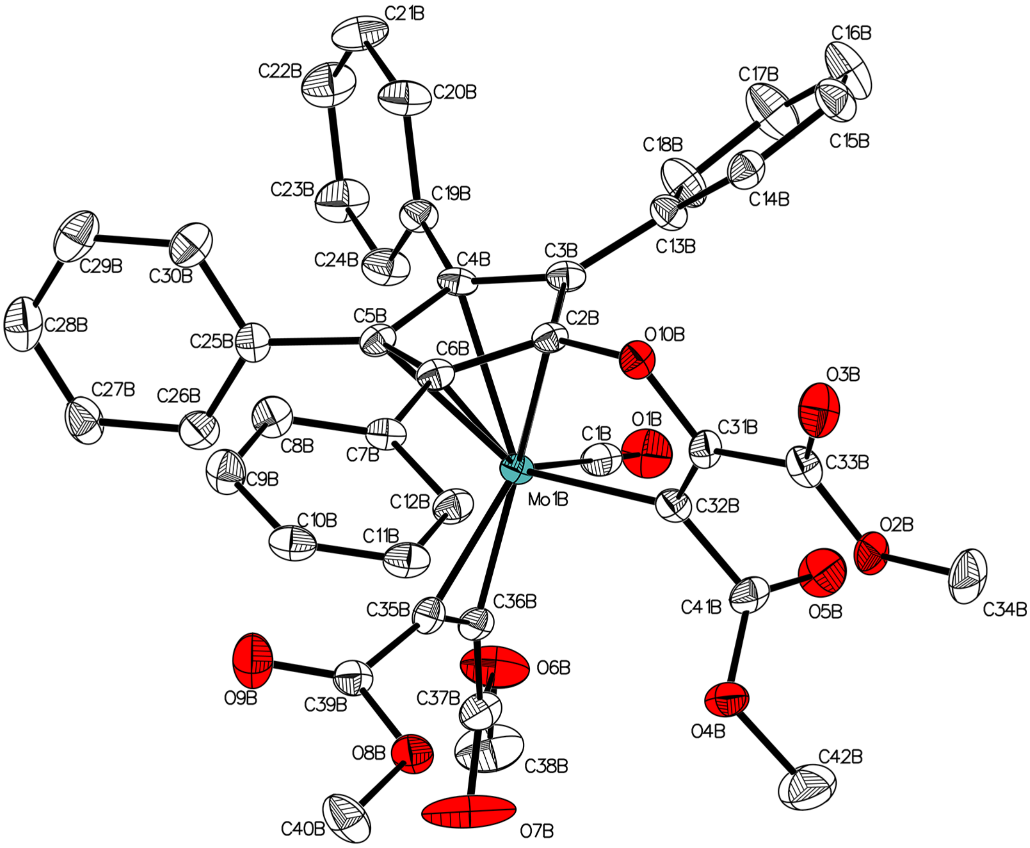


Figure 1. Single-crystal X-ray structure of $[Mo(CO)(RC{\equiv}CR)(\eta^5,\sigma\text{-}C_4Ph_4COCR{=}CR)]$ (**3**). Selected bond lengths (Å): Mo(1B)−C(1B), 2.014(5); Mo(1B)−C(32B), 2.151(4); Mo(1B)−C(35B), 2.031(4); Mo(1B)−C(36B), 2.059(4); C(31B)−C(32B), 1.345(6); C(35B)−C(36B), 1.312(6); O(10B)−C(2B), 1.374(5); O(10B)−C(31B), 1.396(5).

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average chemical shift of the alkyne carbons in $[W(CO)(HC{\equiv}CH)(S_2CNEt_2)_2]$ is 206 ppm, typical for a 4-electron-donor alkyne, whereas in the analogous oxo complex $[W(O)(HC{\equiv}CH)(S_2CNEt_2)_2]$ it is 150 ppm: i.e., the alkyne is a much less effective π donor in the latter.

The X-ray crystal structure of **8** is shown in Figure 2, with important bond lengths detailed in the caption. The Mo═O distance of the terminal oxo ligand is 1.693(5) Å, which is typical for Mo(IV) oxo complexes of this type.[21] Whereas the bonds between Mo and the four former diene carbons C(8)−C(11) are equal within experimental error, that to the oxygen-bearing carbon C(7) is now significantly shorter than in complex **3**. The remaining distances within the vinylic portion of the complex are unchanged, however.

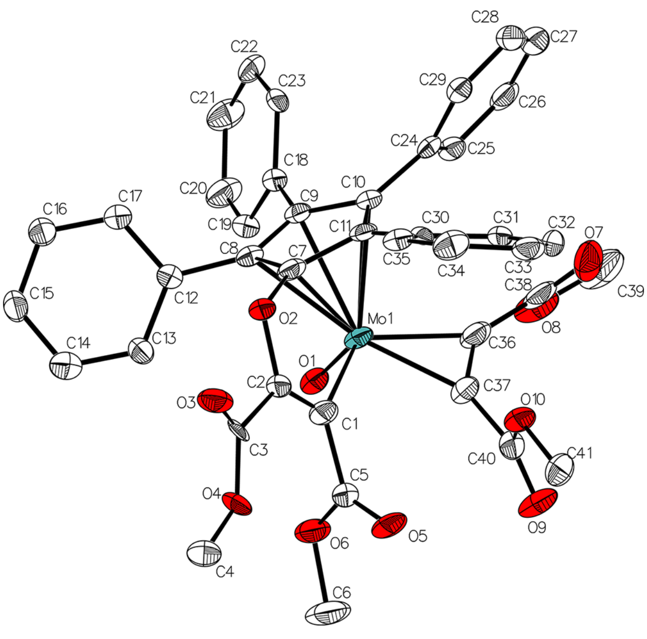


Figure 2. Single-crystal X-ray structure of $[Mo(O)(RC{\equiv}CR)(\eta^5,\sigma\text{-}C_4Ph_4COCR{=}CR)]$ (**8**). Selected bond lengths (Å): Mo(1)−O(1), 1.693(5); Mo(1)−C(1), 2.173(8); Mo(1)−C(36), 2.100(8); Mo(1)−C(37), 2.101(7); C(1)−C(2), 1.333(11); C(36)−C(37), 1.293(11); C(2)−O(2), 1.378(8); C(7)−O(2), 1.363(9).

The main structural change concerns the alkyne ligand. The Mo−C distances have increased significantly, in accordance with the idea that the alkyne is less strongly bound in the oxo complex. Although the C≡C bond length might have been expected to decrease, this does not appear to be the case within experimental error (1.312(6) Å in **3** in comparison to 1.293(11) Å in **8**). A more obvious difference is the reorientation of the alkyne ligand so that it is now perpendicular to the Mo═O bond: i.e., it has rotated by 90° in comparison to its position in the carbonyl complex **3**, due to competition for the available metal d orbitals with the strong π-donor oxo ligand. The same reorientation of the alkyne ligand was shown to have taken place in the X-ray crystal structures of two related complexes, $[Mo(CO)(SC_6F_5)(F_3CC{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$ and $[Mo(O)(SC_6F_5)(F_3CC{\equiv}CCF_3)(\eta\text{-}C_5H_5)]$,[21] and the alkyne in $[W(O)(Ph)(PhC{\equiv}CPh)(\eta\text{-}C_5H_5)]$ also adopts the same geometry.[22]

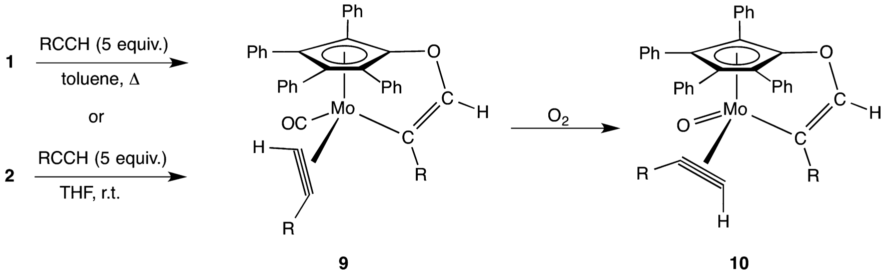
Reactions with Methyl Propiolate. Our initial problems in obtaining crystals for structural characterization from the complexes derived from DMAD prompted us to explore the reactions of **1** and **2** with methyl propiolate, because of the additional information that the CH groups of the alkyne might provide in the ^{1}H and ^{13}C NMR spectra, especially since the CH and CR carbons can be readily distinguished in the latter by use of an attached proton test. This indeed proved to be the case, though the results were complicated by the presence of two isomers.

The reaction of complex **1** with an excess of methyl propiolate in refluxing toluene proceeded in a way similar to the DMAD reaction above; a green zone could be separated by chromatography which was shown to contain two isomers of $[Mo(CO)(RC{\equiv}CH)(\eta^5,\sigma\text{-}C_4Ph_4COCH{=}CR)]$ (**9a**,**b**) together with a small amount of the corresponding oxo species $[Mo(O)(RC{\equiv}CH)(\eta^5,\sigma\text{-}C_4Ph_4COCH{=}CR)]$ (**10a**,**b**), which also exists as two isomers (Scheme 3). Also present in the crude material was methyl tetraphenylbenzoate derived from Diels−Alder addition of tetracyclone with methyl propiolate.

In the hope of obtaining a product free from organic contaminants, the reaction of the alkyne with **2**, which contains a labile MeCN ligand, was explored under milder conditions. Stirring a THF solution of **2** with methyl propiolate (5 equiv) at room temperature for 1 h caused a change from orange to green. Column chromatography gave some free tetracyclone due to decomposition, a small amount of an organometallic byproduct, $[Mo_2(H_2O)(CO)_5(\mu\text{-}C_4Ph_4CO)(\eta\text{-}C_4Ph_4CO)]$, which is presumably formed by the presence of adventitious water[23,24] and a green zone consisting of **9**. It is not necessary to isolate pure **2** as a starting material; a one-pot synthesis directly from $[Mo(CO)_6]$ gave **9** in an improved yield of 76%.

There are four possible isomers of complex **9**, depending on the orientation of the alkyne ligand and the regiochemistry of the alkyne−cyclopentadienone linkage, but only two of these are observed, in a ratio of 1.3:1. The ^{1}H NMR spectrum of the mixture of isomers shows peaks for the CH of the π-bound alkyne ligand at δ 10.86 for the major isomer **9a** and at δ 11.49

Scheme 3. Synthesis of the Methyl Propiolate Complexes 9 and 10[a]



[a]The major isomer **9a** is depicted; in the minor isomer **9b** the η^2-methyl propiolate ligand is rotated by 180°.

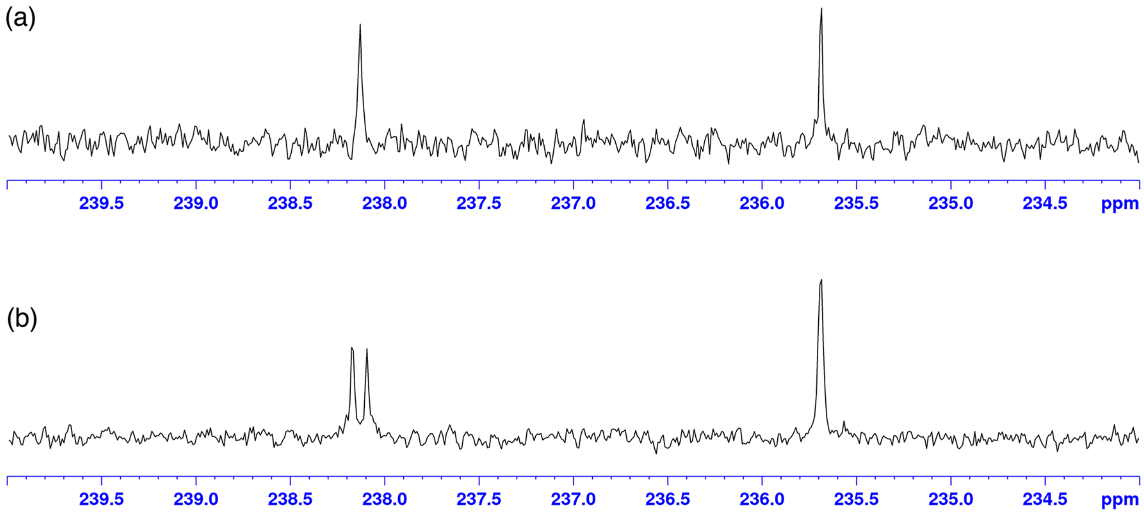


Figure 3. (a) Expansion of $^{13}C\{^1H\}$ spectrum of **9** in the carbonyl region. (b) ^1H-coupled spectrum showing $J(CH)$ = 10 Hz in isomer **9b**.

for the minor isomer **9b**.[23] The corresponding peaks for the vinylic CH groups appear at δ 7.58 and 7.64, respectively. In the reaction of Shvo's complex with PhC≡CH to give $[Ru(CO)_2(\eta^5,\sigma\text{-}C_4Ph_4COCPh{=}CH)]$ (the analogue of **5**), the ^1H NMR signal for the vinylic proton was observed at 5.81 ppm, on which basis the coupling of the cyclopentadienone oxygen was proposed to occur exclusively to the CPh terminus of the alkyne; only one isomer was present.[12] This shift is far removed from those in **9**, implying the opposite regiochemistry in our case, a deduction confirmed crystallographically.[25] Given that the linkage with the tetracyclone ligand is likely to be regiospecific, attacking the CH terminus of the alkyne, we attribute the presence of two isomers to the two possible orientations of the unsymmetrical alkyne ligand. This is clearly confirmed by the ^1H-coupled ^{13}C NMR spectrum: as shown in Figure 3, the signal due to the CO ligand of the minor isomer exhibits a coupling of 10 Hz to the proton of the alkyne ligand. By analogy with the structure of **3**, we assume that this isomer has the CH terminus located closer to the CO ligand. Interconversion of the two isomers (e.g., by alkyne rotation) was not observed even at elevated temperatures (^1H NMR, 353 K in d_8-toluene).

A combination of attached proton test, ^1H-coupled spectra, and 2D-NMR techniques allowed the complete assignment of the ^{13}C NMR spectra of both isomers of **9** (see the Supporting Information for full details). The alkyne carbons appear at approximately 190 ppm, with the vinylic carbons at about 170 ppm (CH) and 151 ppm (CCO_2Me), respectively (see Table 1 below), consistent again with the alkyne acting as a 4-electron donor.

Exposure of the isomeric mixture of **9** to air results in complete conversion to the corresponding oxo complex **10**, which again exists as two isomers, again in a ratio of 1.3:1.[26] The ^1H NMR spectrum of **10** contains peaks at δ 9.00 and 8.22 due to the CH protons of **10a** and at δ 8.80 and 8.20 for its isomer **10b**. The alkyne protons have shifted significantly to higher field in comparison to those in the carbonyl analogue, consistent with the reduced π-donor capability of the alkyne ligand in the oxo complex, whereas the vinylic protons have moved slightly in the opposite direction, presumably as a consequence of the higher oxidation state of the Mo atom. Detailed examination of the ^{13}C NMR spectrum revealed that the vinylic carbon atoms remain relatively unchanged by the oxidation process, whereas the chemical shifts of the alkyne carbons are reduced by over 40 ppm (Table 1).

Table 1. ^{13}C Chemical Shifts and C−H Coupling Constants for the Alkyne-Derived Carbon Atoms in Complexes 9 and 10

compound	δ of alkyne CH (^1J(CH) in Hz)	δ of alkyne CCO_2Me (^2J(CH) in Hz)	δ of vinylic CH (^1J(CH) in Hz)	δ of vinylic CCO_2Me (^2J(CH) in Hz)
9a	189.9 (213)	190.2 (9)	170.7 (194)	151.5 (8)
9b	191.2 (224)	190.15 (8)	171.1 (193)	151.6 (8)
10a	143.9 (217)	147.0 (9)	178.6 (192)	155.8 (9)
10b	151.5 (223)	140.0 (12)	177.6 (192)	156.4 (9)

Confirmation that the cyclopentadienone oxygen is linked to the CH terminus of the alkyne was obtained from an X-ray crystal structure determination of one isomer of **10** (see the Supporting Information).[25] The gross features of the structure are similar to those of complex **8**, with the π-bound methyl propiolate ligand oriented perpendicular to the metal−oxo bond.

■ CONCLUSIONS

In this paper we have shown that the reaction of $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ with electrophilic alkynes results in the incorporation of two alkyne molecules: one of these becomes linked to the oxygen of the cyclopentadienone ligand, whereas the other is coordinated to the metal as a 4-electron π-bound ligand. In the case of methyl propiolate the same complex can be prepared from $[Mo(CO)_6]$ in a one-pot reaction via the acetonitrile complex $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$. Clearly the coupling of cyclopentadienone ligand and alkyne parallels the reaction of Shvo's complex with alkynes. However, the ability of the molybdenum complexes to lose additional ligands (tetracyclone ring and CO in **1**, acetonitrile and CO in **2**) allows the coordination of a second alkyne molecule. Oxidation of the complex leads to the replacement of the Mo−CO group by a Mo=O unit and provides a further example of the reorientation of an alkyne ligand depending on the π-acceptor/π-donor properties of the coligand in two analogous complexes that have both been crystallographically characterized.

EXPERIMENTAL SECTION

General experimental techniques were as detailed in other papers from this laboratory.[6,8,27] Infrared spectra were recorded in CH_2Cl_2 solution (0.5 mm NaCl cells) over the range 2200−1550 cm^{-1}, as KBr disks or neat with a diamond ATR device over the range 4000−400 cm^{-1}, on a PerkinElmer Spectrum Two instrument. The ^1H (400 or 500 MHz) and ^{13}C (100 or 125.8 MHz) NMR spectra were obtained in $CDCl_3$ solution (unless otherwise stated) on Bruker Avance AV400 and AV500 machines, the first of these having an automated sample changer. Chemical shifts are given on the δ scale relative to $SiMe_4$ at 0.0 ppm. The $^{13}C\{^1H\}$ NMR spectra were routinely recorded using an attached proton test technique (DEPT pulse sequence). Mass spectra were recorded on a Kratos MS 80 instrument operating in fast atom bombardment mode with 3-nitrobenzyl alcohol as matrix or on a VG AutoSpec instrument operating in electron impact mode and are given for the most abundant isotope (^{98}Mo). Elemental analyses were carried out by the Microanalytical Service of the Department of Chemistry.

Tetracyclone and the complexes $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ and $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$ were prepared by literature procedures.[6,28] Alkynes were obtained from Aldrich and used as received. Light petroleum refers to the fraction boiling in the range 40−60 °C. THF for oxidation reactions was prepared by allowing a stoppered clear glass flask of the solvent to stand on a sunny windowsill for several weeks. *Warning!* All peroxides should be treated as potentially explosive, and under no circumstances should THF treated in this way be subsequently distilled.

Synthesis of $[Mo(CO)(RC\equiv CR)(\eta^5,\sigma\text{-}C_4Ph_4COCR{=}CR)]$ (3). Five equivalents of DMAD (1.0 cm^3, 8.15 mmol) was added to a solution of $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ (1.528 g, 1.59 mmol) in toluene (175 cm^3). The yellow solution was heated to reflux for 17 h, changing first to purple then to green-brown. Monitoring by TLC showed that the purple color was due to released tetracyclone. The reaction mixture was cooled to room temperature, a small amount of silica was added, and the toluene was removed on the vacuum line. The resulting solid was loaded onto a chromatography column. Elution with a mixture of light petroleum and dichloromethane (1/1) produced a faint yellow band that was not collected, followed by the recovered tetracyclone. Elution with dichloromethane afforded a yellow band of organic material (IR 1741 cm^{-1}), identified as a mixture of dimethyl tetraphenylphthalate (by comparison with an authentic sample prepared from DMAD and tetracyclone in refluxing toluene)[29] and hexamethyl mellitate.[30] Elution with a mixture of CH_2Cl_2 and acetone (99/1) separated a small yellow-brown band, and changing to a 95/5 ratio of the same solvents produced the dark green zone due to $[Mo(CO)(RC\equiv CR)(\eta^5,\sigma\text{-}C_4Ph_4COCR{=}CR)]$. Yield: 922.3 mg, 70%. On some occasions an unidentified dark red band could subsequently be eluted with acetone: IR (KBr) 1736 cm^{-1}.

Data for **3**: mp 135−138 °C; IR (CH_2Cl_2) 2000, 1735, 1720 cm^{-1}; ^1H NMR δ 7.79−6.49 (m, 20H, Ph), 3.98, 3.62, 3.58, 3.50 (all s, 3H, Me); $^{13}C\{^1H\}$ NMR δ 230.4 (CO), 193.2, 190.0 (both CCO_2Me), 170.6, 168.7, 166.6, (all CO_2Me), 161.1 (CCO_2Me) 156.2 (CO_2Me), 155.2 (CCO_2Me), 146.0 (ring CO), 132.6−127.6 (m, Ph), 114.4, 102.8, 101.9, 100.6 (all CPh), 53.3, 52.8, 52.1, 51.7 (all Me); mass spectrum m/z 766 $(M - CO)^+$. Anal. Found: C, 61.02; H, 4.36. Calcd for $C_{42}H_{32}O_{10}Mo\cdot 0.5CH_2Cl_2$: C, 61.11; H, 3.95.

Synthesis of $[Mo(O)(RC\equiv CR)(\eta^5,\sigma\text{-}C_4Ph_4COCR{=}CR)]$ (8). Complex **3** (519.4 mg) was dissolved in 50 cm^3 of THF containing peroxides and stirred under argon for 1 h. The solution rapidly changed color from green to yellow. The solvent was removed at room temperature on a rotary evaporator and the residue triturated with light petroleum to remove a small amount of tetracyclone. The yield was virtually quantitative.

Alternatively, dichloromethane (175 cm^3) was slowly added to $[Mo(CO)(RC\equiv CR)(\eta^5,\sigma\text{-}C_4Ph_4COCR{=}CR)]$ (352.9 mg, 425 mmol) with stirring in air. The solution was then placed under an argon atmosphere and stirred for 18 h. The products were separated by column chromatography. Elution with a mixture of light petroleum and CH_2Cl_2 (1/1) afforded a small amount of tetracyclone. Elution with a dichloromethane/acetone mixture (99/1) produced a yellow band which yielded $[Mo(O)(RC\equiv CR)(\eta^5,\sigma\text{-}C_4Ph_4COCR{=}CR)]$ (213.5 mg, 273.7 mmol, 78%) after removal of the solvent.

Data for **8**: mp darkens above 68 °C, melts at 110−114 °C; IR (CH_2Cl_2) 1772, 1719 cm^{-1}; IR (KBr) 937 cm^{-1} (Mo=O); ^1H NMR δ 7.73−6.91 (m, 20H, Ph), 3.77, 3.75, 3.65, 3.58 (all s, 3H, Me); $^{13}C\{^1H\}$ NMR δ 170.3, 167.9 (both CO_2Me), 167.2 (CCO_2Me), 165.4, 158.4 (both CO_2Me), 153.5, 150.1, 149.7 (all CCO_2Me) 142.4 (ring CO), 131.9−126.6 (m, Ph), 120.3, 116.0, 114.8, 109.9 (all CPh), 53.0, 52.8, 52.5, 52.2 (all Me); mass spectrum m/z 783 $(M + H)^+$. Anal. Found: C, 63.07; H, 4.34. Calcd for $C_{41}H_{32}O_{10}Mo$: C, 63.08; H, 4.10..

Synthesis of $[Mo(CO)(RC\equiv CH)(\eta^5,\sigma\text{-}C_4Ph_4COCH{=}CR)]$ (9) from $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$. Five equivalents of methyl propiolate (0.7 cm^3, 8.25 mmol) was added to a solution of $[Mo(CO)_3(NCMe)(\eta^4\text{-}C_4Ph_4CO)]$ (1.0102 g, 1.65 mmol) in THF (175 cm^3). The resulting mixture was stirred at room temperature with periodic TLC monitoring. After 1 h the product mixture was absorbed onto silica and chromatographed. Tetracyclone (0.1568 g) was eluted with a mixture of light petroleum and CH_2Cl_2 (1/1). Use of a 1/3 mixture of the same solvents caused the elution of a small orange band identified as $[Mo_2(H_2O)(CO)_5(\mu\text{-}\eta^5,\sigma\text{-}C_4Ph_4CO)(\eta^4\text{-}C_4Ph_4CO)]$ (48.4 mg, 0.043 mmol, 5.2%). The green band of $[Mo(CO)(RC\equiv CH)(\eta^5,\sigma\text{-}C_4Ph_4COCH{=}CR)]$ (402 mg, 36%) was eluted with CH_2Cl_2 and recrystallized by diffusion from toluene and diethyl ether. The product consists of an inseparable mixture of the two isomers of **9**.

In a separate experiment the synthesis was conducted as a one-pot procedure. Distilled acetonitrile (200 cm^3) was added to $[Mo(CO)_6]$ (5.0 g, 18.9 mmol). The solution was stirred and heated to reflux for 4.75 h. The solvent was removed in vacuo, and the resulting yellow-green $[Me(CO)_3(MeCN)_3]$ was redissolved in THF. Tetracyclone (7.5 g, 19.5 mmol) was added and the reaction mixture was stirred overnight. Methyl propiolate (8.6 cm^3, 94.5 mmol) was then added, and stirring was continued for a further 3 h. Column chromatography as above afforded orange $[Mo_2(H_2O)(CO)_5((\mu\text{-}\eta^5,\sigma\text{-}C_4Ph_4CO)(\eta^4\text{-}C_4Ph_4CO)]$ (430 mg, 0.385 mmol, 4%) and a green band (9.7 g). Crystallization by diffusion of light petroleum into a chloroform solution produced a blue solid which consists of a 1.3/1 mixture of isomers **9a**,**b** and which dissolves to give a blue-green solution.

Mp: 190−192 °C. IR (CH_2Cl_2): 1963, 1728, 1716, 1688, 1602 cm^{-1}. Mass spectrum: m/z 689 (M^+). Anal. Found: C, 67.27; H, 4.18. Calcd for $C_{38}H_{28}O_6Mo$: C, 67.46; H, 4.14.

Isomer **9a** (major): ^1H NMR δ 10.83 (s, 1H, CH), 7.57 (s, 1H, CH), 7.80−6.30 (m, 20H, Ph), 4.05, 3.40 (both s, 3H, CO_2Me); $^{13}C\{^1H\}$ NMR: δ 235.7 (CO), 190.2 (CCO_2Me), 189.9 (CH), 170.7 (CH), 170.2 (CO_2Me), 169.7 (CO_2Me), 151.5 (CCO_2Me), 139.0 (ring CO), 133.1−127.7 (m, Ph), 112.4, 102.9, 98.9, 96.5 (all CPh), 52.9, 51.5 (both Me).

Isomer **9b** (minor): ^1H NMR δ 11.48 (s, 1H, CH), 7.63 (s, 1H, CH), 7.80−6.30 (m, 20H, Ph), 3.57, 3.42 (both s, 3H, CO_2Me); $^{13}C\{^1H\}$ NMR: δ 238.1 (CO), 191.2 (CH), 190.15 (CCO_2Me), 171.4 (CO_2Me), 171.1 (CH), 169.55 (CO_2Me), 151.6 (CCO_2Me), 136.7 (ring CO), 133.1−127.7 (m, Ph), 112.9, 101.2, 100.9, 99.7 (all CPh), 52.3, 51.5 (both Me).

Synthesis of $[Mo(CO)(RC\equiv CH)(\eta^5,\sigma\text{-}C_4Ph_4COCH{=}CR)]$ (9) from $[Mo(CO)_2(\eta\text{-}C_4Ph_4CO)_2]$. Five equivalents of methyl propiolate (1.5 cm^3, 16.4 mmol) was added to a solution of $[Mo(CO)_2(\eta^4\text{-}C_4Ph_4CO)_2]$ (3.02 g, 3.28 mmol) in toluene (175 cm^3), and the reaction mixture was refluxed for 17 h with TLC monitoring. The solution was then absorbed onto a small amount of silica and chromatographed. A mixture of light petroleum and CH_2Cl_2 (1/1) eluted tetracyclone followed by two narrow yellow bands consisting of organic byproducts, which were not collected. A green band (1.47 g) was then eluted with CH_2Cl_2. The ^1H NMR spectrum showed it to consist of a mixture of the complexes **9a**,**b**, with small amounts of

10a,b and methyl 2,3,4,5-tetraphenylbenzoate (^{1}H NMR δ 7.95 (s, 1H, CH), 7.34−6.75 (m, 20H, Ph), 3.62 (s, 3H, CO_2Me)).

Synthesis of $[Mo(O)(RC\equiv CH)(\eta^5,\sigma\text{-}C_4Ph_4COCH{=}CR)]$ (10). An isomeric mixture of **9a** and **9b** from the above experiments (103.9 mg, 0.154 mmol) was dissolved in toluene (175 cm^3). The solution was briefly exposed to air by removing the stopper from the flask and then reconnected to the argon supply and stirred for 18 h with TLC monitoring. Column chromatography gave tetracyclone, eluted with a mixture of light petroleum and CH_2Cl_2 (2/5), followed by the yellow product $[Mo(O)(HC\equiv CR)(\eta^5,\sigma\text{-}C_4Ph_4COCH{=}CR)]$, which was eluted with CH_2Cl_2 and recrystallized from ethyl acetate and diethyl ether. Yield: 73.2 mg, 0.110 mmol, 73%.

Alternatively, **9** (303.6 mg, 0.44 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and THF containing peroxides (5 cm^3) was added.[31] The solution was stirred for 15 min, during which it changed from green to yellow. After addition of silica (5 g) the solvent was removed and the residue chromatographed. A mixture of light petroleum and CH_2Cl_2 (1/1) eluted a small amount of tetracyclone, and elution with CH_2Cl_2 and acetone (19/1) gave a yellow band of product. The solvent was rotary evaporated to leave an oil, which was dissolved in diethyl ether. Addition of light petroleum precipitated the product as a yellow solid.

IR (CH_2Cl_2): 1772, 1730, 1603 cm^{-1}. IR (KBr): 936 cm^{-1} (Mo═O). Mass spectrum: *m*/*z* 665 (M$^+$). Anal. Found: C, 63.71; H, 4.39. Calcd for $C_{37}H_{28}O_6Mo\cdot 0.5CH_2Cl_2$: C, 63.69; H, 4.10.

Isomer **10a** (major): ^{1}H NMR δ 9.02 (s, 1H, CH), 8.23 (s, 1H, CH); 7.80−6.60 (m, 20H, Ph), 3.64, 3.62 (both s, 3H, Me); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 178.6 (CH), 170.05, 169.7 (CO_2Me), 155.8 (CCO_2Me), 147.0 (CCO_2Me), 143.9 (CH), 139.9 (ring CO), 132.1−126.7 (m, Ph), 119.3, 114.0, 112.1, 108.8 (all CPh), 51.9, 51.6 (both Me).

Isomer **10b** (minor): ^{1}H NMR δ 8.83 (s, 1H, CH), 8.22 (s, 1H, CH), 7.80−6.30 (m, 20H, Ph), 3.70, 3.65 (both s, 3H, Me). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 177.6 (CH), 170.1, 170.0 (CO_2Me), 156.4 (CCO_2Me), 151.5 (CH), 140.0 (CCO_2Me), 139.4 (ring CO), 132.1−126.7 (m, Ph), 121.2, 113.2, 112.4, 110.1 (all CPh), 52.7, 51.7 (both Me).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00300.

> ^{1}H and ^{13}C NMR spectra of all compounds and full assignment of ^{13}C spectra with comparison between decoupled and coupled spectra and crystal data for complexes **3**, **8**, and **10** (PDF)

Accession Codes

CCDC 1544956−1544957 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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