

Effect of substituents on the molybdenum mediated carbonylation and methoxycarbonylation of dihaloalkynes

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Abstract

Dihaloalkynes of the type $\text{YCH(R)C}\equiv\text{CCH(R)Y}$ ($\text{Y} = \text{Cl, Br, I}$; $\text{R} = \text{H}$ or Me) or $\text{YCM}_2\text{C}\equiv\text{CCMe}_2\text{Y}$ were prepared from their diol precursors and reacted with $[\text{Mo}(\text{CO})_3(\text{phen})\text{Y}]^-$ ($\text{phen} = 1,10\text{-phenanthroline}$) in chlorinated solvent, methanol or water. Formation and stability of substituted products of the type $[\text{Mo}(\text{CO})_2(\eta^3\text{-CH(R)C(COX)C}=\text{CH(R)})(\text{phen})\text{Y}]$ ($\text{X} = \text{Y}$ or $\text{X} = \text{OMe}$) were found to be dependent upon the nature of the halogen and degree of alkyl substitution of the alkyne. Reactions carried out in mixtures of methanol and ethers gave an alternative double addition product of the type $[\text{Mo}(\text{CO})_2(\eta^3\text{-CH(R)C(CO}_2\text{Me)C}=\text{C(OMe)(CH}_2\text{R)})(\text{phen})\text{Y}]$ for $\text{R} = \text{H}$, $\text{Y} = \text{Cl}$ only.

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1. Introduction

Transition metal carbonyl complexes are efficient catalysts for carbonylation or methoxycarbonylation of alkynes, since they can be modified to alter the coordination sphere and potential reaction site and provide a source of molecular CO for reaction. Anhydrous conditions and inert atmospheres are often essential however, because sensitivity of reactants or organometallic intermediates to moisture and air can limit the purity and yield of products [1]. In a previous publication, the author with others reported the first clean synthesis in good yield of an η^3 -butadienyl complex by reaction of $[\text{Mo}(\text{CO})_3(\text{phen})\text{Cl}]^-$ and 1,4-dichloro-2-butyne in water [2]. The acyl chloride substituent in $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C(COCl)C}=\text{CH}_2)(\text{phen})]$ was considered to have arisen by insertion of molecular CO into a metal-allenyl intermediate, followed by chloride attack and rearrangement to form the product. Complexes containing the η^3 -butadienyl ligand are important, because of their relationship to metal-coordinated η^2 -alkenes and η^4 -

dienes, their relative ease of conversion to η^3 -allyls and their relevance to organic synthesis [3]. Reports that η^3 -butadienyl complexes of palladium and iridium containing terminal substituents are key intermediates in certain catalytic processes has provided an additional incentive to explore the scope of our carbonylation reactions more widely [4,5], in particular to investigate the influence of alkyne substituents upon successful carbonylation in different solvents. Dihaloalkynes of the type $\text{YCH(R)C}\equiv\text{CCH(R)Y}$ or $\text{YCR}_2\text{C}\equiv\text{CCR}_2\text{Y}$ were therefore synthesized using variations of literature methods, and reactions with nucleophilic anions $[\text{Mo}(\text{CO})_3(\text{phen})\text{Y}]^-$ were investigated in organic solvents and water. This publication describes the influences of halogen and degree of alkyne substitution on the type and stability of product formed.

2. Experimental

2.1. Materials and physical methods

Reactions were carried out under N_2 at room temperature unless otherwise specified. Solvents and liquid reagents were dried with molecular sieve and degassed with N_2

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before use. The starting materials $R_4Z[Mo(CO)_3(phen)Y]$ ($R_4Z = Ph_4P$, $Y = Cl$ **1a**, $Y = Br$ **1b**; $R_4Z = Et_4N$, $Y = I$ **1c**) and 1,4-dihalo-2-butyne, $YCH_2C\equiv CCH_2Y$ **a-c**, were freshly prepared by the published methods [6,7]. Synthesis of 2,5-dihalo-3-hexyne ($Y = Cl$ **a'**, Br **b'**) or 2,5-dihalo-2,5-dimethyl-3-hexyne ($Y = Cl$ **a''**, Br **b''**) was achieved by conversion of the commercially available alkyne diol, as described below. All other chemicals were purchased from commercial sources and used without further purification. Deionized water was used where appropriate. Infrared spectra of samples were recorded as nujol mulls on sodium chloride discs. The 1H or ^{13}C NMR spectra were recorded at 300 or 75 MHz, respectively, and referenced to the deuterated solvent.

2.2. Synthesis of dihalohexynes, $YCH(R)CCCH(R)Y$ or $YCMe_2CCCMe_2Y$

2.2.1. Synthesis of 2,5-dichloro-3-hexyne (**a'**)

A mixture of 3-hexyne-2,5-diol (5.70 g, 5.65 cm³, 49.94 mmol) and pyridine (1.17 g, 1.2 cm³, 14.84 mmol) in diethyl ether (25 cm³) was placed in a 100 cm³ three-neck flask fitted with dropping funnel, thermometer and CaCl₂ guard tube. The contents were cooled to $-10^\circ C$ using an ice/salt bath, and thionyl chloride (14.27 g, 8.75 cm³, 119.95 mmol) was added dropwise over 2 h. The temperature was maintained between 0 and $-10^\circ C$ during addition and for a further 65 h. The reaction mixture was then added with stirring to aqueous 0.2 M hydrochloric acid (80 cm³) cooled over ice, and then extracted three times with petroleum ether (40–60 °C, 15 cm³ portions). Solvent was removed from the combined extracts under reduced pressure, and the residue was cautiously added to a solution of NaHCO₃ (21.41 g) in de-ionized water (350 cm³). After vigorous shaking, the mixture was extracted three times with diethyl ether (45 cm³ total). The combined ethereal extracts were dried over magnesium sulfate, and finally concentrated under vacuum to give the crude product as a light brown oil. Yield = 3.95 g. 1H NMR (300 MHz, CDCl₃): 1.61 (d, 6.88, 6H), 4.58 (q, 6.62, 2H). ^{13}C NMR (75 MHz, CDCl₃): 26.26 (s, Me), 45.35 (s, CH(Cl)), 84.46 (s, C≡C).

2.2.2. Synthesis of 2,5-dibromo-3-hexyne (**b'**)

A solution of finely ground 3-hexyne-2,5-diol (2.7048 g, 23.7 mmol) in diethyl ether (70 cm³) was stirred over ice in a two neck flask fitted with a dinitrogen inlet tube and a pressure equalizing dropping funnel, equipped with a CaCl₂ drying tube. Phosphorus(III) bromide (4.72 g, 1.64 cm³, 17.3 mmol) in diethyl ether (70 cm³) was added dropwise over 0.75 h. The cooling bath was removed and stirring continued for a further 2 h. Ice cooled water (70 cm³) was added, the mixture separated and the aqueous layer extracted three times with diethyl ether (15 cm³). The combined ethereal solutions were dried over MgSO₄, and removal of solvent under reduced pressure gave the crude product as a pale yellow oil. Yield = 4.21 g. 1H NMR (300 MHz, CDCl₃): 1.88 (d, 6.88, 6H), 4.62 (m, 2H). ^{13}C

NMR (75 MHz, CDCl₃): 27.08 (s, Me), 63.04 (s, CH(Br)), 86.62 (s, C≡C).

2.2.3. Synthesis of 2,5-dichloro-2,5-dimethyl-3-hexyne (**a''**)

A mixture of finely ground 2,5-dimethyl-3-hexyne-2,5-diol (7.10 g, 49.94 mmol) and pyridine (1.17 g, 1.2 cm³, 14.84 mmol) in diethyl ether (100 cm³) was reacted with thionyl chloride (14.27 g, 8.75 cm³, 119.95 mmol) as described in Section 2.2.1. Yield = 4.97 g. 1H NMR (300 MHz, CDCl₃): 1.47 (m, 12H). ^{13}C NMR (75 MHz, CDCl₃): 31.30 (s, Me), 65.51 (s, C(Cl)), 92.89 (s, C≡C). Unsuccessful attempts to improve the percentage of **a''** in the crude product included, addition of SOCl₂ at -40 or $-84^\circ C$, and reaction times of 20 or 69 h.

2.2.4. Synthesis of 2,5-dibromo-2,5-dimethyl-3-hexyne (**b''**)

A solution of excess PBr₃ (4.72 g, 1.64 cm³, 17.3 mmol) in diethyl ether (20 cm³) was added dropwise to an ice cooled solution of 2,5-dimethyl-3-hexyne-2,5-diol (3.39 g, 23.8 mmol) in the same solvent (60 cm³), as described in Section 2.2.2. Yield = 5.5 g. 1H NMR (300 MHz, CDCl₃): 1.99 (s, 12H). ^{13}C NMR (75 MHz, CDCl₃): 36.14 (s, Me), 47.90 (s, CBr), 88.38 (s, C≡C). Unsuccessful attempts to improve the percentage of **b''** in the crude product included, addition of PBr₃ at -20 or $-40^\circ C$, and reaction times of 6 or 18 h.

2.3. Synthesis of $[Mo(CO)_2(\eta^3-CH_2C(COY)C=CH_2)-(phen)Y]$ ($Y = Cl$ **2a**, Br **2b**)

A suspension of complex **1** (0.36 g **1a**, 0.39 g **1b**, 0.5 mmol) contained in CH₂Cl₂ (5 cm³) or water (20 cm³) was stirred with excess 1,4-dihalo-2-butyne **a** or **b** (0.15 cm³), respectively. For the former solvent, the liquid was filtered after 2 h, and the dark orange-red solution further stored at $-5^\circ C$ for 10 days to increase the yield. Complex **2a** precipitated from water over 0.5 h. Products were filtered from solution, washed with minimum cold CH₂Cl₂ and dried under reduced pressure to constant weight.

2.4. Synthesis of $[Mo(O_2CCF_3)(CO)_2(\eta^3-CH_2C(CO_2COCF_3)C=CH_2)(phen)]$ (**2d**)

To a stirred suspension of **2** (0.24 g **2a**, 0.29 g **2b**, 0.5 mmol) and excess NaO₂CCF₃ (0.23 g, 1.69 mmol) in acetone (100 cm³) was added dropwise a solution of AgBF₄ (0.200 g, 1.03 mmol) in the same solvent (10 cm³). After 2 h, the mixture was filtered, the liquor reduced to dryness in vacuo, and the crude product was recrystallized from acetone and petrol at low temperature.

2.5. Synthesis of $[Mo(CO)_2(\eta^3-CH(Me)C(COY)C=CH(Me))(phen)Y]$ ($Y = Cl$ **3a**, $Y = Br$ **3b**)

The reaction was carried out as described in Section 2.3, using an excess of **a'** or **b'** (0.15 cm³).

2.6. Synthesis of $[Mo(CO)_2(\eta^3-CH_2C(CO_2Me)-C=CH_2)(phen)Y]$ ($Y = Cl$ **4a**, Br **4b**)

Method a: A sample of **2** (0.48 g **2a**, 0.57 g **2b**, 1.0 mmol) was stirred in methanol (10 cm³) with triethylamine (0.5 cm³) for 2 h. After reducing the volume to 10 cm³ in vacuo, the solid was filtered from solution, washed with minimum ice cold MeOH and dried under vacuum. *Method b:* Reaction of **1a** or **1b** with **a** or **b**, respectively, was carried out as described in Section 2.3, in a mixture of methanol (5 cm³) and water (0.5 cm³). Yields from methods *a* and *b* were similar.

2.7. Synthesis of $[Mo(CO)_2(\eta^3-CH(Me)C(CO_2Me)-C=CH(Me))(phen)Y]$ ($Y = Cl$ **5a**, Br **5b**)

The reaction was carried out as described in Section 2.6 *method b*, using **1a** or **1b** and **a'** or **b'**, respectively. Contamination of **5b** by $[Mo(CO)_3(phen)Br_2]$ was removed by washing with CH₂Cl₂.

2.8. Synthesis of $[Mo(CO)_2(\eta^3-CH(R)C(CO_2Me)-C=C(CH_2R)(OMe))(phen)Y]$

The reaction was carried out using **a**, **a'**, **b** or **b'** as described in Section 2.6 *method b*, but replacing water by furan, THF or tetrahydropyran. The product was obtained for R = H, Y = Cl (**6**), yield 73%.

2.9. Formation of $[MoCl(CO)_2(\eta^3-CH_2C(CO_2H)-C=CH_2)(phen)]$ (**7**)

Method a: A suspension of **2a** (0.3035 g, 0.624 mmol) in an equivolume mixture of water and DMF (10 cm³) was stirred for 1 h, and on filtration a dark red solid was obtained. This was washed successively with water and acetone, and then dried in vacuo. *Method b:* Excess 1,4-dichloro-2-butyne (0.15 cm³) was added to a stirred solution of **1a** (0.365 g, 0.5 mmol) in an equivolume mixture of water and DMF (10 cm³). The product was isolated as *method a* after 2 h. Yields from methods *a* and *b* were similar, 41%.

3. Results and discussion

3.1. Preparation of dihaloalkynes

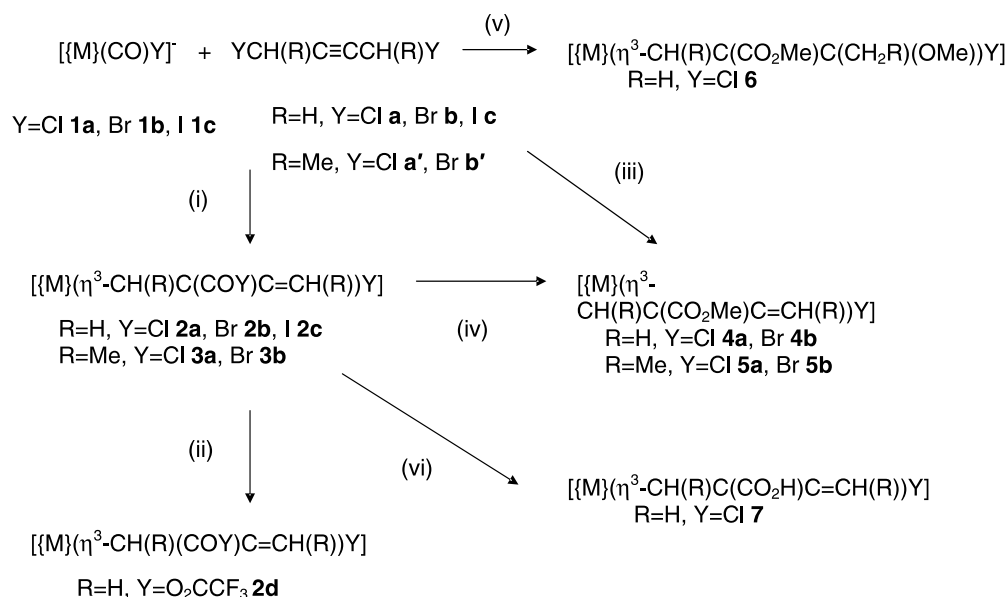
The butynes, YCH₂C≡CCH₂Y (Y = Cl **a**, Y = Br **b**, Y = I **c**), and hexynes, YCH(Me)C≡CCH(Me)Y (Y = Cl **a'**, Y = Br **b'**), were satisfactorily prepared by reaction of the diol with either thionyl chloride and pyridine or PBr₃. Rearrangement of **a** or **a'** to give either 2,3-dihalo-1,3-diene or 3,4-dihalo-2,4-diene did not occur on storage at room temperature, and was slow over 6 months for dibromoalkynes, **b** and **b'**. Although **a** was largely unchanged on heating overnight, isomerization products predominated on attempting to purify **b**, **a'** or **b'** by distillation under

reduced pressure and warming. As judged by NMR methods, the freshly prepared dihalobutyne and dihalohexyne constituted over 70% and 50% respectively, of the crude product, and subsequent reactions were carried out using an excess of these unpurified products to ensure sufficient reagent was present. The diiodobutyne, **c**, proved most susceptible to rearrangement, and storage at room temperature or purification by heating under dinitrogen precipitated a cream, highly insoluble solid of unknown composition. Freshly prepared, crude samples of **a–c** were therefore used for reactions. On synthesizing dimethylhexynes YCMe₂C≡CCMe₂Y (Y = Cl **a''**, Br **b''**) from the diol, complex mixtures of alkyne, dihaloallene and dihalodiene were obtained. Rearrangement of dihaloalkynes can be expected to increase across a series from diprimary to ditertiary, since the additional inductive effect of alkyl groups facilitates elimination of halide ions, a situation exacerbated by the less electronegative halogens. Control of equilibration between these compounds was attempted by reduction of reaction temperature, and by variation of reaction time. Of the preparative conditions examined, the greatest proportion of dihaloalkyne in the crude product (about 35%) was judged to be 18 h at –40 °C for **a''** and 3 h at –5 °C for **b''**. Attempted distillation of **a''** or **b''** led to increased rearrangement, and therefore the freshly prepared, crude oils were used for subsequent reactions with metal carbonyl anions. Report of a successful conversion of the related acetylenic carbinol, HC≡CC(Me)₂OH, to the corresponding chloroalkyne prompted investigation of an alternative route to convert the alkyne diol to **a''** [8]. This involved passing gaseous HCl through a suspension of NH₄Cl, CuCl and copper bronze in a solution of 2,3-dimethyl-3-hexyne-2,5-diol in ether. However the proportion of **a''** in the crude product was not increased compared to use of thionyl chloride and pyridine; indeed copper(I) chloride would appear to promote isomerization to the allene.

3.2. Reactions of dihaloalkynes

3.2.1. In chlorinated solvents

Addition of dihalobutyne **a** or **b** to a cooled suspension of **1a** or **1b** respectively, resulted in conversion of the purple mixture to a red-orange precipitate. This was filtered from solution and identified as the η^3 -dienyl complex $[Mo(CO)_2(\eta^3-CH_2C(COY)C=CH_2)(phen)Y]$ (Y = Cl **2a**, Br **2b**, Scheme 1) on the basis of the spectroscopic data (Tables 1 and 2). The acyl bromide was obtained in lower yield, possibly because of the reduced susceptibility of the bromoalkyne to nucleophilic attack. Whilst **2a** was readily recrystallized from CH₂Cl₂, **2b** proved poorly soluble in organic solvents, and ease of oxidation to $[Mo_2Br_2O_4(phen)_2]$ in DMSO or DMF resulted in non-reproducible elemental analysis [9]. Reaction of **1c** and diiodobutyne **c** gave non-carbonyl containing products only, however monitoring the reaction by IR spectroscopy suggested butadienyl complex **2c** was initially formed ($\nu(C=O)$



Key: {M} = Mo(CO)₂(phen). Conditions: (i) CH₂Cl₂, (ii) Ag⁺/O₂CCF₃⁻, (iii) MeOH/H₂O, (iv) MeOH/NEt₃, (v) MeOH/THF, (vi) H₂O/DMSO.

Scheme 1.

Table 1
Yields, selected infrared and analytical data for complexes [Mo(CO)₂(η³-CH(R)C(COX)C=CH(R))(phen)Y]

No.	COX	R	Y	Yield (%)	Infrared data ^a		Analysis, found (calculated)%		
					ν(C≡O)	ν(C=O)	C	H	N
2a	COCl	H	Cl	74	1982, 1917	1711	46.8 (47.2)	2.48 (2.48)	5.80 (5.79)
2b	COBr	H	Br	65	1980, 1915	1657		^c	
2d	CO ₂ COCF ₃ ^b	H	O ₂ CCF ₃	56	1981, 1896	1699, 1672	44.6 (44.8)	2.44 (2.58)	4.85 (4.82)
3a'	COCl	Me	Cl	59	1977, 1915	1645		^c	
3b'	COBr	Me	Br	47	1981, 1917	1644		^c	
4a	CO ₂ Me	H	Cl	81	1972, 1894	1690	50.1 (49.9)	3.13 (3.20)	5.85 (5.60)
4b	CO ₂ Me	H	Br	69	1975, 1899	1693		^c	
5a	CO ₂ Me	Me	Cl	68	1962, 1880	1690		^c	
5b	CO ₂ Me	Me	Br	43	1960, 1879	1693		^c	

^a As nujol mulls, cm⁻¹.

^b Calc. acetone.

^c Highly insoluble, non-reproducible results.

1972, 1910, ν(C=O) 1627 cm⁻¹). Both **2a** and **2b** were further identified by their reaction with Ag⁺ and trifluoroacetate ions to form the carboxylate derivative (Y = O₂CCF₃, **2d**). All the complexes gave rise to a pair of IR peaks between 1982 and 1896 cm⁻¹, typical of a *cis*-dicarbonyl group, and decreasing electronegativity of halogen Y resulted in the peak due to the acyl group moving to lower wavenumber. For **2d**, peaks at 1699 and 1672 cm⁻¹ could be ascribed to the metal-trifluoroacetate and butadienyl substituent, respectively. The ¹H NMR spectra of complexes **2a**, **2b** and **2d** were similar, with two singlets near 2.35 and 4.33 ppm attributable to the allylic protons and a pair of doublets or broad singlets due to the terminal protons of the double bond near 5.75 and 6.37 ppm. Attempts to prepare and characterize mixed acyl halide/metal halide complexes, for example by reactions such as **1a** with **b**, gave

products that were highly insoluble, exhibited complex IR spectra (probably as a result of halide exchange), and were not investigated further.

Reaction of 2,5-dichloro-3-hexyne (**a'**) with **1a** or 2,5-dibromo-3-hexyne (**b'**) with **1b** yielded the complexes [Mo(CO)₂(η³-CH(Me)C(COY)C=CH(Me))(phen)Y] (Y = Cl **3a**, Br **3b**) as red solids. A lower yield of the bromo complex was again obtained, the positive inductive effect of two alkyl substituents and lower halogen electronegativity serving to reduce susceptibility of the alkyne to nucleophilic attack. Successful elemental microanalysis of **3a** or **3b** was prevented by their poor solubility in common organic solvents, and by their tendency to decompose in solution over time. However both IR and NMR data were in accord with the given formula. Thus pairs of peaks in the IR spectra at 1977 and 1915 cm⁻¹ (**3a**) or 1981 and

Table 2
¹H NMR data for selected complexes **2–5**^a

No.	C–Me	C–H	COX	Phen
2a ^c		2.15 (s, H), 3.73 (s, H), 5.81 (d, 1.38, H), 6.40 (d, 1.38, H)		7.99 (m, 2H), 8.19 (s, 2H), 8.81 (m, 2H), 9.12 (d, 4.42, H), 9.30 (d, 4.66, H)
2b		2.35 (s, H), 4.33 (s, H), 5.75 (brs, H), 6.37 (brs, H)		7.81 (m, 2H), 7.96 (s, 2H), 8.29 (m, H), 8.39 (m, H), 9.12 (brs, H), 9.33 (brs, H)
2d		1.95 (s, H), 4.06 (s, H), 5.84 (d, 2.2, H), 6.35 (d, 2.2, H)		8.06 (m, 2H), 8.18 (s, 2H), 8.52 (m, 2H), 9.36 (d, 4.40, H), 9.48 (d, 4.45, H)
3a ^b	1.33 (d, 6.32, 3H), 1.34 (d, 6.32, 3H), 1.67 (d, 6.89, 3H), 1.71 (d, 6.89, 3H), 1.96 (d, 6.62, 3H), 2.18 (d, 6.89, 3H), 2.36 (d, 6.89, 3H), 2.37 (d, 6.89, 3H)	4.46 (q, 6.86, H), 4.52 (q, 6.86, H), 4.52 (q, 6.86, H), 5.03 (q, 6.86, H), 5.04 (q, 6.86, H), 5.11 (q, 6.88, H), 5.12 (q, 6.86, H), 6.05 (q, 6.32, H)		8.01–8.06 (m, 8H), 8.21 (brs, 8H), 8.80–8.88 (m, 8H), 9.25 (d, 5.23, 4H), 9.37 (d, 4.96, 4H)
3b	1.23 (d, 6.07, 6H), 1.81 (d, 6.61, 3H), 1.91 (d, 6.61, 3H), 2.00 (d, 6.61, 3H), 2.12 (d, 6.61, 3H), 2.17 (d, 6.88, 3H), 2.36 (d, 6.88, 3H)	4.33 (q, 6.07, 2H), 5.10 (q, 6.61, H), 5.94 (q, 6.61, 2H), 5.70 (obs, H), 6.74 (q, 6.88, H), 6.93 (q, 6.65, H)		8.01 (m, 8H), 8.17 (s, 8H), 8.78 (m, 8H), 9.03 (m, 2H), 9.10 (m, 2H), 9.18 (d, 5.50, H), 9.23 (d, 4.96, H), 9.28 (obs, H), 9.31 (d, 4.61, H)
4a ^c		2.01 (s, H), 3.70 (s, H), 5.72 (brs, H), 6.26 (brs, H)	2.12 (s, 3H)	7.89 (m, 2H), 7.96 (s, 2H), 8.53 (m, 2H), 9.14 (d, 4.42, H), 9.19 (d, 4.12, H)
4b		1.96 (s, H), 3.70 (s, H), 5.64 (brs, H), 6.12 (brs, H)	2.01 (s, 3H)	8.05 (m, 2H), 8.21 (s, 2H), 8.86 (m, 2H), 9.13 (d, 4.42, H), 9.31 (d, 4.12, H)
5a	1.26 (d, 6.07, 6H), 1.86 (d, 6.62, 3H), 1.88 (d, 6.62, 3H), 2.07 (d, 6.88, 3H), 2.10 (d, 6.88, 3H), 2.22 (m, 3H), 2.30 (m, 3H)	4.35 (q, 6.07, 2H), 5.75 (q, 6.58, H), 6.01 (q, 6.58, H), 6.26 (m, H), 6.53 (q, 7.70, H), 6.71 (q, 6.88, H), 6.84 (q, 6.88, H)	1.97 (s, 3H), 1.99 (s, 3H), 2.13 (s, 6H)	7.99–8.65 (m, 8H), 8.20 (brs, 8H), 8.81–8.89 (m, 8H), 9.03 (d, 5.23, H), 9.06 (d, 4.96, H), 9.11 (d, 4.96, H), 9.14 (d, 5.23, H), 9.16 (d, 5.23, H), 9.21 (d, 5.23, H), 9.26 (d, 5.23, H), 9.37 (d, 5.23, H)
5b	1.25 (d, 6.07, 3H), 1.46 (d, 6.88, 3H), 1.60 (m, 3H), 1.82 (d, 6.88, 3H), 2.24 (d, 7.15, 3H), 2.30 (d, 7.15, 3H), 2.36 (d, 6.85, 3H), 2.40 (d, 7.18, 3H)	4.33 (q, 6.04, H), 4.38 (q, 6.34, H), 5.07 (m, 2H), 5.71 (q, 6.61, H), 5.97 (q, 6.61, H), 6.65 (m, H), 6.76 (q, 6.61, H)	1.88 (s, 3H), 2.00 (s, 3H), 2.14 (s, 6H)	8.01 (m, 8H), 8.21 (s, 8H), 8.82 (m, 8H), 9.03 (d, 5.23, 2H), 9.05 (d, 4.96, H), 9.11 (d, 4.88, H), 9.18 (d, 5.23, H), 9.23 (d, 5.23, 2H), 9.27 (d, 5.23, H)

^a Solution spectra in DMSO-*d*₆ unless otherwise stated. Data in ppm, multiplicity, coupling constant (Hz), number of protons.

^b Run in DMF-*d*₇.

^c Run in CD₂Cl₂.

1917 cm⁻¹ (**3b**), and a broad singlet near 1644 cm⁻¹, were typical of a *cis*-Mo(CO)₂ fragment and acyl halide respectively. For both acyl chloride and bromide, different orientations of the two methyl groups at the termini of the η³-fragment gave rise to four diastereomers, and this resulted in complex spectra. The (*syn, syn*), (*syn, anti*), (*anti, syn*) and (*anti, anti*) arrangements of the two methyl substituents in each molecule of the complex gave rise to eight doublets (**3a** 1.33–2.37 ppm; **3b** 1.23–2.36 ppm) due to methyl groups, and eight quartets appeared (**3a** 4.46–6.05 ppm; **3b** 4.33–6.74 ppm) due to methine protons. Multiplet resonances due to the phen ligand were in the expected range 8.01–9.37 ppm. Attempts to prepare complexes of the type [Mo(CO)₂(η³-Me₂CC(COY)C=CMe₂)-(phen)Y] from either **a'** or **b'** were unsuccessful, leading to [Mo(CO)₃(phen)Y₂] only.

3.2.2. Reactions in other solvent mixtures

In contrast to the clean, efficient synthesis and stability of **2a** in water, reactions of **1b** and **b** in this medium gave mixtures of **2b** and [MoBr₂(CO)₃(phen)], and these complexes decomposed over time to non-carbonyl containing

products. Synthesis of **3a** or **3b** from **a'** or **b'** proved similarly sensitive to water, and yields were commensurably low compared to their production in CH₂Cl₂. Whilst uncontaminated ester substituted complexes of the type [Mo(CO)₂(η³-CH(R)C(CO₂Me)C=CH(R))(phen)Y] (R = H, Y = Cl **4a**, Br **4b**, R = Me, Y = Cl **5a**) could be obtained in good yield from mixtures of **1a** or **1b** and the appropriate dihaloalkyne in methanol containing small volumes of water, formation of **5b** (R = Me, Y = Br) was frequently accompanied by [MoBr₂(CO)₃(phen)]. Both **4b** and **5b** proved poorly soluble in organic solvents, and this, together with their ease of oxidation to [Mo₂Br₂O₄(phen)₂], resulted in non-reproducible elemental analyses. Conversion of **2** to ester **4** could also be achieved in methanol in the presence of base, however the poor solubility of **3** prevented conversion to **5** by this method. Esters **4** or **5** were not considered to have been formed via intermediacy of acyl halide **2** or **3**. Whilst production of **2a** or **2b** in CH₂Cl₂ was completely inhibited by the presence of pyridine, formation of the esters in methanol was not prevented by this tertiary amine, and an alternative mechanism to that proposed in chlorinated solvents may pertain in alcohols.

The complexes were identified from their IR and NMR spectra (Tables 1 and 2). For reactions of **1** and dihaloalkynes in methanol, replacing water by cyclic ethers resulted in an allylic complex of the type $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}(\text{H})\text{RC}(\text{CO}_2\text{-Me})\text{C}(\text{OMe})(\text{CH}_2\text{R}))(\text{phen})\text{Y}]$ (**6**) for $\text{R} = \text{H}$, $\text{Y} = \text{Cl}$ only [10], and mixtures of this complex and **4a** were formed in methanol in the absence of water. The stability of **2a** in water was also examined by its formation in an equivolume mixture of DMF or DMSO and water. This afforded a dark red complex which, unlike the acyl chloride, proved completely insoluble in chlorinated solvents. The same product (**7**) was achieved when pre-formed **2a** was added to this solvent mixture, and dissolution of the acyl chloride followed by hydrolysis to yield $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{CO}_2\text{H})\text{C}=\text{CH}_2)(\text{phen})]$ was inferred from the IR and NMR data [11]. Sensitivity of **2b** to water prevented isolation of the bromo analogue. Reactions of **1a** or **1b** with **a''** or **b''** under any of these conditions gave $[\text{Mo}(\text{CO})_3(\text{phen})\text{Y}_2]$ exclusively.

4. Summary

Both 1,4-dihalo-2-butyne and 2,5-dihalo-3-hexyne undergo nucleophilic attack by halocarbonyl anions $[\text{Mo}(\text{CO})_3(\text{phen})\text{Y}]^-$ to form acyl halide or ester substituted η^3 -dienyl metal complexes of the type $[\text{Mo}(\text{CO})_2(\eta^3\text{-CH}(\text{R})\text{C}(\text{COX})\text{C}=\text{CH}(\text{R}))(\text{phen})\text{Y}]$ in CH_2Cl_2 or aqueous methanol, respectively. Decreasing the electronegativity of the halogen, Y, resulted in reduced yields and lower stability and solubility in organic solvents or water. Isolation of the η^3 -hexadienyl products in lower yields than their η^3 -butadienyl analogues, and lack of related product from 2,5-dihalo-2,5-dimethyl-3-hexyne, reflects decreasing electrophilicity of the dihaloalkyne with increasing numbers of substituents having a positive inductive effect. Differences were also observed for these reactions carried out in anhydrous methanol, with the ester being found to be contaminated with an η^3 -allyl product $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}(\text{H})\text{RC}(\text{CO}_2\text{Me})\text{C}(\text{OMe})(\text{CH}_2\text{R}))(\text{phen})\text{Y}]$ for $\text{R} = \text{H}$, $\text{Y} = \text{Cl}$, but not $\text{R} = \text{H}$, $\text{Y} = \text{Br}$, and by $[\text{Mo}(\text{CO})_3(\text{phen})\text{Y}]$ for $\text{R} = \text{Me}$, $\text{Y} = \text{Br}$, but not $\text{R} = \text{Me}$, $\text{Y} = \text{Cl}$. Thus the susceptibility of dihaloalkynes to undergo nucleophilic attack by these metal carbonyl anions is dependent upon both the degree of alkyl substitution and the nature of the halogen. The acyl chloride complexes proved least

sensitive to the presence of water, and dissolution in aqueous DMSO formed the hydrolysis product ($\text{X} = \text{OH}$). Oxidation of the acyl bromide to form $[\text{Mo}_2\text{Br}_2\text{O}_4(\text{phen})_2]$ occurred more readily in this solvent. Thus dichloroalkynes containing substituents with negative inductive effects can be expected to form stable dienyl complexes in good yield in organic solvents, and these complexes should be isolable in the presence of water. The reactivity of these complexes in water is being investigated further.

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- [10] For **6**, selected IR data (nujol mulls/cm⁻¹): $\nu(\text{C}=\text{O})$ 1951, 1868, $\nu(\text{C}=\text{O})$ 1685. ¹H NMR data (CDCl₃): 1.24 (s, H), 2.22 (s, 3H), 2.37 (brs, 3H), 3.23 (brs, 3H), 3.47 (s, H), 7.91–9.14 (m, 8H). Elemental microanalysis, found (calc.)%: 49.00 (49.36) C, 3.72 (3.72) H, 5.31 (5.48) N.
- [11] For **7**, selected IR data (nujol mulls/cm⁻¹): $\nu(\text{OH})$ 3154, $\nu(\text{C}=\text{O})$ 1977, 1896, $\nu(\text{C}=\text{O})$ 1696. ¹H NMR data (DMSO-*d*₆): 1.92 (s, H), 3.75 (s, H), 5.68 (brs, H), 6.20 (brs, H), 8.02 (m, 2H), 8.17 (s, 2H), 8.80 (m, 2H), 9.14 (m, H), 9.30 (brs, H), 11.00 (brs, H). ¹³C NMR data (DMSO-*d*₆) for C¹C²(CO₂H)C³=C⁴ unit: 50.54 C¹, 55.11 C², 105.89 C⁴, 170.39 C³, 173.32 CO₂H; for C=O 219.48, 221.10.