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Solvent-controlled formation of η^3-butadienyl or η^3-allyl group 6 transition metal complexes in water or alcohols

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Abstract

Preparation of acyl chloride, ester, amide or thioester-substituted η^3-butadienyl complexes of the type $[MCl(CO)_2(\eta^3\text{-}CH_2C(COXR)C{=}CH_2)(L_2)]$ (M = Mo,W; XR = Cl, OR, NHR, SR; L_2 = 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline) from 1,4-dichloro-2-butyne and $Ph_4P[MCl(CO)_3(L_2)]$ in water resulted in improved yields (M = Mo) and recycling of reagents. Whilst analogous reactions in anhydrous methanol to yield either substituted η^3-butadienyl (XR = OR) or η^3-allyl $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CO_2R)C(OR)Me)(phen)]$ were dependent upon the presence of organic bases or ethers, reactions in propanol or butanol gave the η^3-butadienyl complexes only. Possible mechanisms are discussed. Halide extraction from ester or amide butadienyl complexes in hydroxylic solvents gave highly reactive cations of the type $[Mo(CO)_2(\eta^3\text{-butadienyl})(phen)(solvent]^+$, and carboxylate products were obtained by displacement of metal-bound solvent by glucuronate or hydroxybutyrate ions.

Keywords: Molybdenum; Tungsten; Butadienyl; Allyl; Aqueous chemistry

1. Introduction

Transition metal complexes containing η^3-bonded butadienyl ligands 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 [1]. Following discovery of the first complex containing a (1,2,3-η^3)-*trans*-butadienyl ligand by Nesmeyanov over 20 years ago [2], several synthetic routes to this class of complex have been established. These include attack by metal carbonylate anions or salts on allenes or alkynes [3], deprotonation or desilylation of butadienes [4], ring opening of cycloalkenyl ligands [5] and vinylidine coupling reactions [6]. All of the published procedures involve metal reagents, intermediates or products that require exclusion of water from the reaction. Whilst many of these butadienyl complexes have been characterised spectroscopically and crystallographically [1], reactivity and mechanistic studies have received less attention. In 1996, the author and others carried out a theoretical study of the bonding between a molybdenum metal centre and the (1,2,3-η^3)-*trans*-butadienyl unit, and investigated the probable sites of nucleophilic or electrophilic attack on this organic fragment [7]. Preliminary reactivity studies have agreed with these predictions and have identified some similarities between the chemical behaviour of substituted η^3-butadienyl and η^3-allyl complexes [8]. During the course of this work, formation of 2-substituted η^3-butadienyl complexes by nucleophilic attack of $[MoCl(CO)_3(phen)]^-$ (**1**) on 1,4-dichloro-2-butyne was found to be solvent-dependent. Thus, whilst reaction carried in dichloromethane to give $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C{=}CH_2)(phen)]$ (**2**) was controlled by the presence of hydrogen ions, production of the related ester $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)C{=}CH_2)(phen)]$ in methanol occurred in the presence of an acid scavenger, such as pyridine [9]. Furthermore, addition of tetrahydrofuran (THF) to this reaction in dichloromethane or methanol resulted in complete inhibition of **2** or production of the related allyl $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)C(OMe)Me)(phen)]$,

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respectively [10]. Further work was therefore required to explain both the ability of THF to control production of η^3-allyl rather than η^3-butadienyl in methanol and an inability to isolate either butadienyl or allyl ester-substituted complexes from reactions of **1** and 1,4-dichloro-2-butyne under the same conditions in other alcohols. In this publication we report the first synthesis of an η^3-butadienyl complex in water in good yield, investigate some aqueous chemistry of this complex and describe the controlled production of either substituted η^3-butadienyl or η^3-allyl complexes from reactions carried out in various alcohols.

2. Experimental

2.1. General

Reactions were carried out under dinitrogen at room temperature unless otherwise specified. Organic solvents and non-aqueous liquid reagents were dried with molecular sieve, and all liquids were degassed with dinitrogen before use. The starting materials $Ph_4P[MCl(CO)_3(L_2)]$ were freshly prepared by the published method [9] and other chemicals were purchased from commercial sources and used without further purification. Infrared spectra of samples were recorded as nujol mulls on sodium chloride discs. The ^1H NMR spectra were obtained at 300 MHz and referenced to tetramethylsilane as internal standard.

2.2. Reactions in deionised water

2.2.1. Synthesis of $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C{=}CH_2)(phen)]$ (**2**)

A suspension of complex **1** (0.367 g, 0.5 mmol) contained in water (20 cm^3) was stirred with excess 1,4-dichloro-2-butyne (0.15 cm^3). After 0.5 h, the liquid was decanted from the orange-brown solid, and the residue was washed with minimum cold water and dried to constant weight at 50 °C. Yield 97.7%. The crude solid was recrystallised from dichloromethane–petrol (40–60 °C) mixtures and identified as complex **2** by comparison with the published spectroscopic data.

2.2.2. Synthesis of $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CONHR)C{=}CH_2)(phen)]$ ($R = CH_2CO_2Me$ **3**, CH_2CO_2Et **4**, CH_2CN **5**)

Potassium carbonate (0.56 g, 4 mmol) and the amine hydrochloride (4 mmol) were stirred in water (20 cm^3) for 0.5 h. To this was added complex **1** (0.550 g, 0.75 mmol), followed by an excess of 1,4-dichloro-2-butyne (0.20 cm^3). The orange products were filtered from solution after 0.5 h, washed with minimum cold water, dried at 50 °C to constant weight and finally recrystallised from CH_2Cl_2–petrol mixtures. Yields 65.3–70.6%.

2.2.3. Synthesis of $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CONHR)C{=}CH_2)(phen)]$ ($R = (CH_2)_2PPh_2$ **6**, $(CH_2)_2OH$ **8**, $(CH_2)_2SH$ **9**)

Excess 2-(diphenylphosphine)ethylamine, aminoethanol or aminoethanethiol (0.5 cm^3) in water (20 cm^3) was stirred with complex **1** (0.367 g, 0.5 mmol), and 1,4-dichloro-2-butyne (0.15 cm^3) was added. The products were isolated as given in Section 2.2.2 and gave yields in the range 62.0–73.4%.

2.2.4. Synthesis of $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CO_2(CH_2)_2SH))C{=}CH_2)(phen)]$ (**7**)

This complex was prepared from mercaptoethanol according to Section 2.2.3. Yield 54.3%.

2.2.5. Synthesis of $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COSEt)C{=}CH_2)(phen)]$ (**10**)

Excess triethylamine (1.0 cm^3) and ethanethiol (1.0 cm^3) were mixed together in water (40 cm^3). To this were added successively complex **1** (0.734 g, 1.0 mmol) and excess 1,4-dichloro-2-butyne (0.3 cm^3), and the mixture was stirred for 0.75 h. The purified product was obtained as described in Section 2.2.2 with 65.4% yield.

2.3. Reactions in methanol

2.3.1. Reactions in the presence of added organic compounds to give η^3-butadienyl **11** or η^3-allyl **12**

A stirred mixture of methanol (5 cm^3) and the added compound (5 cm^3) were cooled over ice, and to this was added successively complex **1** (0.367 g, 0.5 mmol) and excess 1,4-dichloro-2-butyne (0.15 cm^3). The cooling bath was removed after 0.5 h and the red precipitate that had formed after a further 1.0 h was filtered from solution. Yields 73–95%. The products were identified from their published IR and ^1H NMR data. Compounds giving predominantly **11**: pyridine, triethylamine, imidazole, pyrrolidine, piperazine, collidine, oxetane, 3-chloropropanol, tetrahydrothiophene and 1,4-dithiane. Compounds giving predominantly **12**: tetrahydrofuran, tetrahydropyran, furan and thioxane. Compounds giving mixtures of **11** and **12**: diethylether, 1,2-dimethoxyethane and bis-2-methoxyethyl ether.

2.3.2. Synthesis of $[Mo(O_2CC_3F_7)(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)C{=}CH_2)(phen)]$ (**14**)

To a stirred suspension of **11** (0.478 g, 1.0 mmol) and excess $NaO_2CC_3F_7$ (0.400 g, 1.69 mmol) in methanol (100 cm^3) was added dropwise a solution of $AgBF_4$ (0.200 g, 1.03 mmol) in the same solvent (10 cm^3). After 2 h, the mixture was filtered, the liquor reduced to dryness in vacuo, and the crude product was recrystallised from acetone and petrol at low temperature. Yield 52.0%.

*2.3.3. Synthesis of [MoY(CO)$_2$(η^3- CH$_2$C(CONHCH$_2$-CO$_2$R′)C=CH$_2$)(phen)] (Y = glucuronate, R′ = Me **15**, Y = 3-hydroxybutyrate, R′ = Et **16**)*

A suspension of **3** or **4** (0.38 mmol) in methanol (50 cm^3), respectively, was stirred with excess sodium D-glucuronate or DL-3-hydroxybutyrate (1.19 mmol), and to this was added dropwise a solution of silver tetrafluoroborate (0.0973 g, 0.50 mmol) in the same solvent (5.0 cm^3). After a period of 2 h, the reaction mixture was filtered and the volume reduced under vacuum to ca. 50 cm^3. Addition of petrol and storage at low temperature yielded orange microcrystals of the product. Yields: **15** 52.3% and **16** 45.9%.

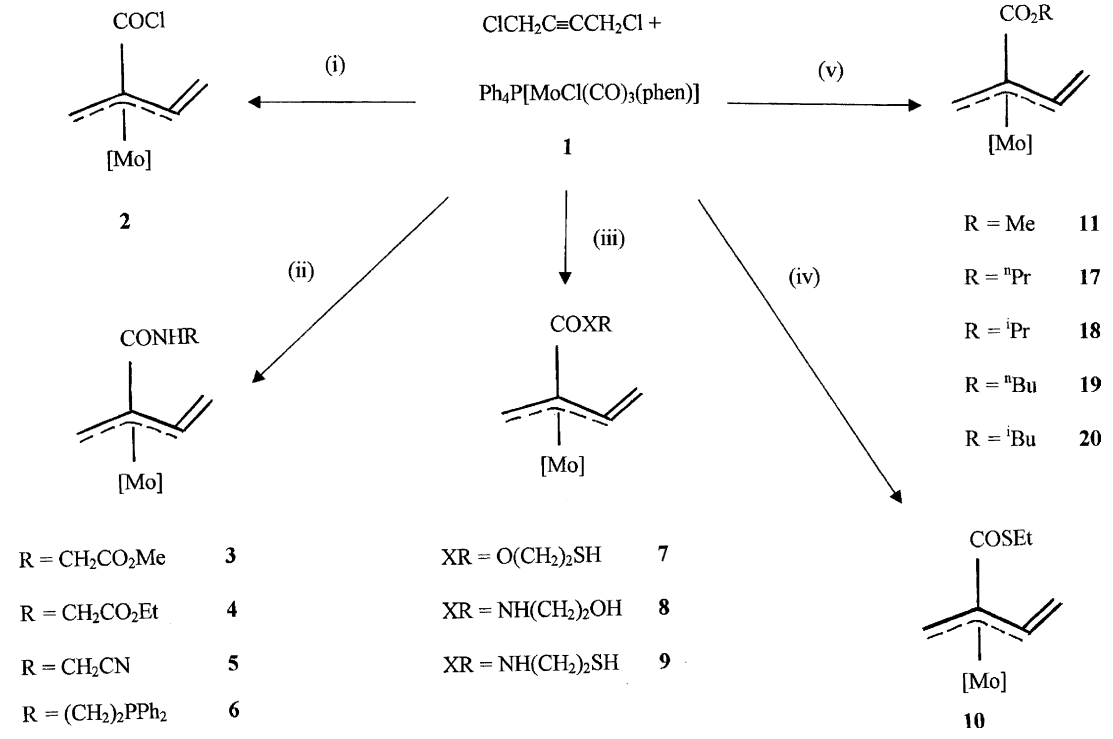
2.4. Reactions in propanol or butanol

Excess 1,4-dichloro-2-butyne (0.15 cm^3) was added to a suspension of complex **1** (0.365 g, 0.5 mmol) in the alcohol (5 cm^3). After stirring for 1–18 h, the mixture was filtered, washed with minimum ice-cold alcohol and dried at 50 °C to constant weight. Yields of **17**–**20** were in the range 57–66%.

3. Results and discussion

3.1. Reactions in water

A suspension of Ph$_4$P[MoCl(CO)$_3$(phen)] (**1**) in water was stirred at room temperature with 1,4-dichloro-2-butyne. After several minutes the purple mixture darkened and an orange-brown oily solid precipitated after 30 min. The liquid was decanted from the vessel and recrystallisation of the reaction residue from CH$_2$Cl$_2$–petrol mixtures yielded the known complex [MoCl(CO)$_2$(η^3-CH$_2$C(COCl)C=CH$_2$)(phen)] (**2**) in almost quantitative yield. Extraction of the decanted liquid into dichloromethane and chromatography on silica gel led to recovery of Ph$_4$PCl in 63–74% yield. No reaction occurred between **1** and the alkyne in aqueous pyridine. However, replacement of pyridine by glycine alkyl ester, aminoacetonitrile or 2-(diphenylphosphino)ethylamine yielded orange-red products of the type [MoCl(CO)$_2$(η^3-CH$_2$C(CONHR)C=CH$_2$)(phen)] (R = CH$_2$CO$_2$Me **3**, CH$_2$CO$_2$Et **4**, CH$_2$CN **5**, (CH$_2$)$_2$PPh$_2$ **6**) and known ester (**7**) or amide (**8**, **9**) complexes were obtained on substitution of these amines by reagents of the type HA(CH$_2$)$_2$BH (A = O, B = S or A = NH, B = O, S). Isolation of **7** from reaction of alkyne and anion in water and ethylene sulphide indicated that acid-catalysed ring opening had occurred in solution to give mercaptoethanol [11]. Scheme 1 summarises these reactions. Thioester complex **10** was obtained from reactions involving aqueous ethanethiol and was identified from the published data. This pattern of reactivity of anion **1** and 1,4-dichloro-2-butyne in water paralleled that previously observed in chlorinated solvents, however, improved product yields were obtained from the aqueous systems. For example, formation of **2** in dichloromethane and reaction in situ with glycine alkyl esters gave amides **3** and **4** in decreased yields of 45 and



Scheme 1. Key [Mo] = Mocl(CO)$_2$(phen); (i) = water, 25 °C, (ii) water, H$_2$NR, (iii) water, RXH, (iv) water, EtSH, (v) ROH.

53% respectively. The new complexes **3**–**6** were characterised by their elemental microanalyses and IR and ^{1}H NMR spectra (Tables 1 and 2).

Reactions of $Ph_4P[WCl(CO)_3(L_2)]$ ($L_2 = 2,9$-dimethyl-1,10-phenanthroline) and 1,4-dichloro-2-butyne in water were investigated for comparison [12]. Infra-red analysis of the crude reaction mixture obtained using method in Section 2.2.1 showed the formation of $[WCl(CO)_2(\eta^3\text{-}CH_2C(COCl))C{=}CH_2)(L_2)]$ (1987, 1907 cm^{-1} ν(C≡O), 1729 cm^{-1} ν(C=O)) and $[WCl_2(CO)_3(L_2)]$ (2054, 1954, 1864 cm^{-1} ν(C≡O). Unfortunately this mixture proved unstable in solution, and consequently separation and further characterisation could not be achieved. However, reactions of this acyl chloride in situ with (R)-phenylglycine methyl ester using method in Section 2.2.2 led to precipitation of the more stable complex $[WCl(CO)_2(\eta^3\text{-}CH_2C(CONHCPh(H)CO_2Me))C{=}CH_2)(L_2)]$ in 42% yield [13]. Similarly both $[WCl_2(CO)_3(phen)]$ and the known complex $[WCl(CO)_2(\eta^3\text{-}CH_2C(CONEt_2))C{=}CH_2)(phen)]$ were produced on reaction of the tungsten analogue of **1** and the alkyne in aqueous diethylamine [9]. Thus in general, replacing chlorinated solvents by water as reaction medium for complexes of the type $Ph_4P[MCl(CO)_3(L_2)]$ with 1,4-dichloro-2-butyne led to improved yields of η^3-butadienyl complexes for M = Mo, but decreased yields for M = W. In view of this finding, further reactivity studies in alcohols were confined to those of complex **1** only.

3.2. Reactions in methanol

Formation of **2** or $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)C{=}CH_2)(phen)]$ (**11**) by addition of anion **1** to 1,4-dichloro-2-butyne in methanol was strongly influenced by the presence of water. Monitoring by NMR spectroscopy showed that a methanol/water volume ratio of 1:5 resulted in formation of complex **2** only. Addition of further methanol to the reaction mixture gave increasing quantities of the ester **11** and signals due to **2** disappeared at solvent ratios above 20:1. None of these spectra showed evidence of the ester-substituted allyl $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)C(OMe)Me)(phen)]$ (**12**). However, replacing water by THF gave **12** in good yield, and therefore a series of organic compounds were examined for their ability to influence the production of **11** or **12** from reaction of $Ph_4P[MoCl(CO)_3(phen)]$ and 1,4-dichloro-2-butyne in methanol.

The presence of bases, such as pyridine, triethylamine, imidazole, pyrrolidine or piperazine, in methanolic reactions of **1** and the alkyne gave butadienyl **11** only, implying that acid was not a requirement for this product to form. A similar result from reactions in methanol and sterically hindered 2,4,6-trimethylpyridine indicated that coordination of this base to the metal was not part of the mechanism. Competition reactions carried out in mixtures of methanol and 3-chloropropanol or oxetane both gave the methyl ester **11** only, suggesting that ring opening of this highly strained ring had occurred in the presence of acid to produce 3-chloropropanol and that the more basic alcohol had reacted preferentially. Mixtures of methanol and diethylether, 1,2-dimethoxyethane or bis-2-methoxyethyl ether in these reactions gave both **11** and **12** in varying ratios, however, substitution by THF, tetrahydropyran or furan afforded complex **12** only. On reaction of **1** and the alkyne in the presence of methanol and 1,4-dioxane, only non-carbonyl containing decomposition products were obtained. In contrast, replacement of THF or dioxane by their sulphur analogues tetrahydrothiophene or 1,4-dithiane gave predominently butadienyl **11**, whilst thioxane led to allyl **12**.

Table 1
Selected infrared and analytical data for complexes $[Mo(CO)_2(\eta^3\text{-}CH_2C(COXR)C{=}CH_2)(phen)Y]$

No.	COXR	Y	Infrared data[a]		Analysis, found (calculated) %		
			ν(C≡O)	ν(C=O), ν(CO_2)	C	H	N
3	$CONHCH_2CO_2Me$	Cl	1885, 1966	1644, 1742	48.62 (49.29)	3.30 (3.36)	7.56 (7.84)
4	$CONHCH_2CO_2Et$	Cl	1902, 1978	1640, 1732	50.24 (50.22)	3.67 (3.63)	7.41 (7.64)
5	$CONHCH_2CN$	Cl	1905, 1980	1646	47.58 (47.33)	2.88 (2.93)	10.05 (10.27)[b]
6	$CONH(CH_2)_2PPh_2$	Cl	1900, 1970	1648	53.13 (53.13)	4.13 (3.81)	5.56 (5.52)[c]
13	CO_2Me	MeOH	1873, 1954	1691		–[d]	
15	$CONHCH_2CO_2Me$	Glucuronate	1904, 1990	1642, 1742	48.95 (48.48)	3.60 (3.89)	5.86 (6.06)
16	$CONHCH_2CO_2Et$	3-Hydroxybutyrate	1893, 1984	1638, 1739	50.72 (50.04)	4.56 (4.24)	5.92 (6.36)[c]
17	CO_2Pr^n	Cl	1896, 1969	1690		–[d]	
18	CO_2Pr^i	Cl	1900, 1964	1682		–[d]	
19	CO_2Bu^n	Cl	1893, 1969	1689		–[d]	
20	CO_2Bu^i	Cl	1896, 1970	1692		–[d]	

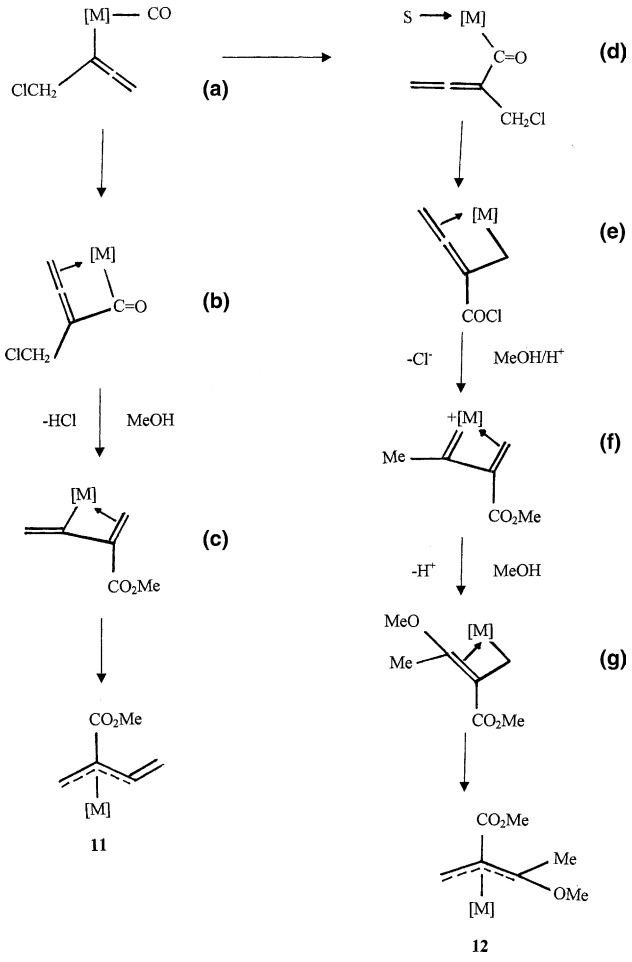
[a] As nujol mulls, cm^{-1}. All bands strong.
[b] $0.5 \cdot CH_2Cl_2$ calculated.
[c] CH_2Cl_2 calculated.
[d] Non-reproducible results, highly unstable.

Table 2
^{1}H NMR data for selected complexes **3**–**6**, **13**, **15**, **16**, **17**–**20**[a]

No.	H'_{anti}, H'_{syn}	H''_{anti}, H''_{syn}	NH	Aliphatic	Aromatic
3	1.89(s,H), 3.77(s,H)	5.75(d,2.19,H), 6.26(d,2.22,H)	6.40(t,5.77,H)	2.14(m,2H), 3.37(s,3H)	7.99(m,2H), 8.17(s,2H), 8.80(m,2H), 9.11(d,4.42,H), 9.23(d,4.39,H)
4	2.04(s,H), 3.84(s,H)	5.80(d,2.02,H), 6.31(d,2.20,H)	5.52(t,5.60,H)	1.14(t,7.14,3H), 1.92(m,H), 2.95(m,H), 3.97(q,6.96,2H)	7.90(m,4H), 8.43(d,8.24,H), 8.52(d, 8.25,H), 9.12(d,5.13,H), 9.19(d,4.95,H)
5[b]	1.89(s,H), 3.82(s,H)	5.75(d,2.02,H), 6.30(d,2.01,H)	6.81(t,5.50,H)	2.71(m,2H)	7.99(m,2H), 8.11(m,2H), 8.77(m,2H), 9.09(d,4.03,H), 9.24(d,4.95,H)
6[b]	1.83(s,H), 3.86(s,H)	5.73(d,2.20,H), 6.23(d,2.20,H)	6.37(t,5.40,H)	0.66(m,H), 0.83(m,H), 1.95(m,2H)	7.06(m,2H), 7.37(s,4H), 7.56(m,3H), 7.74(m,2H), 7.89(m,H), 8.00(m,2H), 8.57(d,7.15,H), 8.74(d,8.24,H), 9.11(d,4.95,H), 9.24(d,4.95,H)
13[c]	2.06(s,H), 3.82(s,H)	6.10(d,2.20,H), 6.49(d,2.20,H)		3.47(s,3H), 4.78(s,3H)	8.05(m,2H), 8.22(m,2H), 8.86(m,2H), 9.32(d,5.13,H), 9.38(d,4.40,H)
15[b]	1.96(s,H), 2.10(s,H), 4.01(s,H), 4.07(s,H)	5.99(d,3.12,H), 6.02(d,3. 11,H), 6.40(d,3.12,H), 6.43(d,3.12,H)	6.63(t,5.58,H), 6.70(t,5.58,H)	2.11(s,6H), 2.15(m,4H), 3.38(s,5H), 3.39(s,5H)	8.08(m,4H), 8.19(s,4H), 8.85(m,4H), 9.27(m,H), 9.34(m,H), 9.37(m,H), 9.42(m,H)
16[b]	1.80(s,H), 3.90(s,H)	5.77(d,1.92,H), 6.29(d,1.92,H)	6.35(brm,H)	0. 23(d,6.23,2H), 1.01(t,7.14,3H), 1.69(m,2H), 2.09(s,3H), 2.31(m,H), 2.81(m,2H), 3.30(s,H)	7.99(m,2H), 8.16(s,2H), 8.79(m,2H), 9.14(d,4.95,H), 9.25(d,4.95,H)
17	2.07(s,H), 3.72(s,H)	5.74(d,2.19,H), 6.29(d,2.19,H)		0.46(t,7.15,3H), 0.71(m,2H), 2.20(m,H), 2.55(m,H)	7.83(m,2H), 7.91(s,2H), 8.47(m,2H), 9.17(d,5.13,H), 9.22(m,H)
18	2.06(s,H), 3.76(s,H)	5.74(d,1.92,H), 6.31(d,1.92,H)		0.17(d,6.34,3H), 0.30(d,6.07,3H), 3.54(m,H)	7.81(m,2H), 7.90(s,2H), 8.46(m,2H), 9.18(m,H), 9.22(m,H)
19	2.05(s,H), 3.72(s,H)	5.74(d,2.22,H), 6.28(d,2.22.H)		0.62(m,H), 0.65(t,7.15,3H), 0.84(m,3H), 2.26(m,H), 2.60(m,H)	7.62(m,2H), 7.91(s,2H), 8.45(m,2H), 9.17(m,H), 9.23(m,H)
20	2.06(s,H), 3.73(s,H)	5.73(d,2.19,H), 6.29(d,2.19,H)		0.45(d,6.61,3H), 0.91(d,6.88,3H), 1.92(m,H), 2.43(m,H), 3.40(m,H)	7.81(m,2H, 7.91(s,2H), 8.44(m,2H), 9.17(m,H), 9.23(m,H)

[a] Spectra recorded as solutions in chloroform-d_3 unless otherwise stated. Data reported in ppm, multiplicity, coupling constant (Hz), number of protons.
[b] Run in dimethylsulphoxide-d_6.
[c] Run in methanol-d_4.

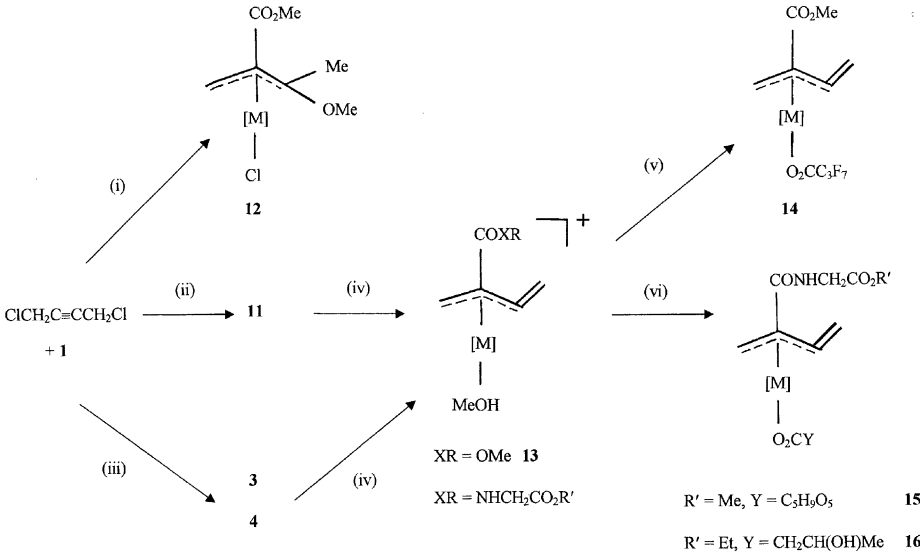
A mechanism was proposed (Scheme 2) to account for the control of product type exerted by these organic compounds. In common with the proposed mechanism for production of acyl chloride **2** in dichloromethane [9], σ-allenyl intermediate (a) was formed by nucleophilic attack of $[MoCl(CO)_3L_2]^-$ on 1,4-dichloro-2-butyne. In methanol only the reaction could then take one of two pathways depending upon the type of organic compound added. Insertion of CO into the metal–carbon bond of allenyl intermediate (a) might be accompanied by coordination to the metal centre of either the allenyl, as shown by (b), or by the added organic compound (S), as given by (d). Organic bases promoted further conversion of (b) to intermediate (c) and final rearrangement to butadienyl **11**. Alternatively, very weak bases or non-basic reagents (S) in intermediate (d) might be displaced on rearrangement to give the π-allenyl (e). Protonation and reaction with methanol to give the ester-substituted η^3-vinyl carbene (f) could then be followed by reaction with methanol to finally yield η^3-allyl **12**. Thus, those solvents capable of coordinating to the metal in (d), but which remove H^+ from the reaction mixture, could inhibit conversion of π-allenyl (e) to allyl (g), and thus serve to promote production of **11** through



Scheme 2. Key: [M] = $MoCl(CO)_2(phen)$.

intermediates (b) and (c). In accord with this mechanism, basic amines were found to generate η^3-butadienyl **11**, whilst coordinating, non-basic reagents, such as cyclic ethers, afforded η^3-allyl **12**. Linear ethers gave mixtures of these two complexes, possibly because the lone-pair electrons of the ether donor atom are less accessible for metal coordination due to steric restrictions of the alkyl groups. Cyclic 1,4-dioxane produced neither product, possibly because both oxygen donors were involved in coordination to a pair of metal centres and this inhibited further reaction. Whilst the weaker sulphur analogues of THF and dioxane may have failed to coordinate to metal centres (favouring pathways (a)–(c)), the weakly basic heterocycle thioxane may undergo coordination to metal intermediate (d) via the oxygen atom, resulting in formation of allyl **12**.

Addition of a solution of Ag(I) ions in methanol to a suspension of complex **11** in the same solvent over ice resulted in precipitation of silver chloride and darkening of the mixture. The IR spectrum of the filtered solution showed two broad absorptions between 1873 and 1954 cm^{-1} due to a metal *cis*-dicarbonyl unit, and similar solutions derived from this reaction in methanol-d_4 gave ^1H NMR spectra in which the butadienyl and its ester substituent were still present (Table 2). The cationic species $[Mo(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)C{=}CH_2)(phen)(MeOH)]^+$ (**13**) may have been formed, however attempts to isolate the highly reactive species were unsuccessful. Addition of sodium heptafluorobutyrate to this solution led to production of the known complex $[Mo(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)C{=}CH_2)(phen)(O_2CC_3F_7)]$ (Scheme 3, **14**), presumably by displacement of coordinated solvent from the cation metal centre [8]. Attempts to isolate species of the type $[Mo(CO)_2(\eta^3\text{-}CH_2C(CONHR)C{=}CH_2)(phen)(R'OH)]^+$ by addition of Ag(I) ions to a suspension of **3** in methanol or water (R′OH) were also unsuccessful, giving non-carbonyl containing products only. However, halide extraction from **3** in the presence



Scheme 3. Key: [M] = $Mo(CO)_2(phen)$; (i) = THF, methanol, (ii) = water, methanol, (iii) = water, amine, (iv) = Ag^+, methanol, (v) = water, $NaO_2CC_3F_7$, (vi) = water, NaY.

of sodium D-glucuronate or from **4** and sodium DL-3-hydroxybutyrate in methanol gave carboxylate (Y) complexes of general formula $[Mo(CO)_2(\eta^3\text{-}CH_2C(CONHR)C{=}CH_2)(phen)Y]$ (R = CH_2CO_2Me **15**, CH_2CO_2Et **16**), possibly via the highly reactive cationic intermediate. The structures of **15** and **16** can be predicted with some confidence, based upon the known X-ray analysis of $[Mo(CO)_2(\eta^3\text{-}CH_2C(CONHMe)C{=}CH_2)(2,2,'\text{-bipyridyl})(O_2CC_3F_7)]$ [7] and the spectroscopic evidence [vide infra]. The highly symmetrical nature of the $(phen)Mo(CO)_2$ unit in either **3** or **4** placed both the butadienyl and its substituent in magnetically equivalent environments for each isomer (Fig. 1(a) and (b)). Following reaction with a chiral carboxylate, a total of four isomers of **15** or **16** were produced. Pairs C/F and D/E shown in Fig. 2 represent the pairs of diastereomers arising from L- and D-3-hydroxybutyrate respectively. The symmetrical nature of the $(CO)_2Mo(phen)$ unit results in similar magnetic environments for the carboxylate in the pair C/D, and thus this enantiomeric pair gives rise to one set of resonances. Similarly, the magnetic environments of these groups in the pair E/F are equivalent, and this pair also produces a single set of resonances. Thus, the spectra of L-, D- and DL-**16** would all be expected to show two sets of very similar signals. Whilst this was true of **15**, only one set was observed for **16**, possibly because the stereogenic centre in 3-hydroxybutyrate was more distant from the influence of the anisotropic ring system.

3.3. Reactions in other alcohols

Reactions between **1** and 1,4-dichloro-2-butyne were carried out in different alcohols, and the products were examined over time by NMR spectroscopy. Of those examined, *sec*-butyl, *tert*-butyl and benzyl alcohols all failed to give either butadienyl or allyl complexes. However *n*-propyl and *n*-butyl ester η^3-butadienyl complexes (**17** and **19**) were formed over a period of 3 h, and were identified from their IR and NMR spectra (Tables 1 and 2). Similar reactions in either *iso*-propyl or

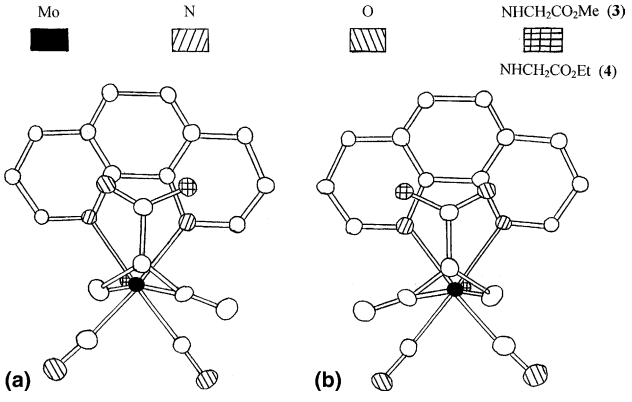


Fig. 1. Enantiomeric forms of complexes **3** and **4**.

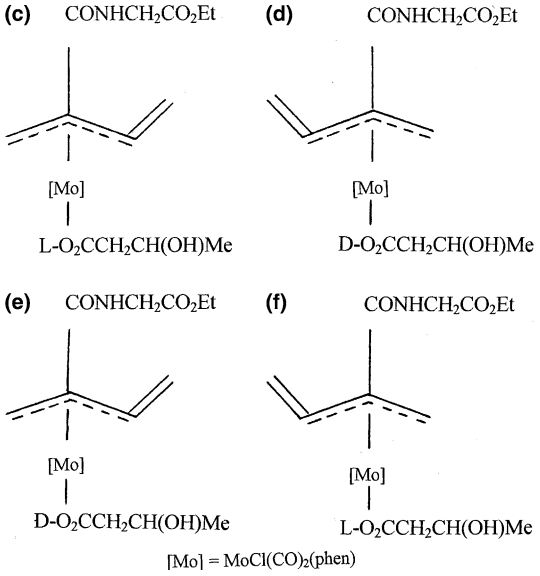


Fig. 2. Isomers of complexes L-**16** and D-**16**.

iso-butyl alcohols gave mixtures of ester butadienyl (**18** or **20**) and acyl chloride complex **2** in about 5:1 mole ratio. Monitoring all successful reactions over time showed that whilst the proportion of ester increased after 6 h, decomposition products also started to form, and over 18 h the latter became increasingly dominant. Similarly, solutions of **17**–**20** in organic solvents became darker over time, and purification by recrystallisation was therefore prevented by the presence of varying amounts of the resultant impurities. Production of **17**–**20** was completely inhibited by the presence of pyridine or THF, and allyl complexes of the type $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CO_2R)C(OR)(Me))(phen)]$ were not isolated. These results differed from those carried out in methanol and were consistent with the initial formation of **2**, followed by conversion to the less stable propyl or butyl esters. Increased proportions of **2** isolated from reactions in *iso*-alkyl alcohols may be attributable to the differing p*K*a of primary and secondary alcohols, since a competition reaction of anion **1** and alkyne in equal volumes of Pr^nOH and Pr^iOH gave complex **17** only from the more basic alcohol. For Bu^sOH, Bu^tOH or PhOH, neither ester-substituted η^3-butadienyl nor η^3-allyl complexes were formed, in accord with the lower basicity of tertiary and aromatic alcohols and their reduced capacity to react with **2** formed in situ.

3.4. Infrared and NMR spectra

The infrared spectra of all the complexes exhibited two strong absorptions between 1885 and 1990 cm^{-1}, typical of metal *cis*-dicarbonyl units. Butadienyl substituents of the new amide (**3**–**6**, **15** and **16**) and ester (**13** and **17**–**20**) complexes gave rise to ν(C=O) absorptions

near 1646 and 1690 cm^{-1}, respectively, and complexes **15** and **16** gave additional broad peaks for both ester and carboxylate groups near 1740 cm^{-1}. A weak peak near 1675 cm^{-1} due to ν(C=C) of the η^3-butadienyl fragment could be identified for some complexes, and weak singlets near 3375–3428 cm^{-1} were assigned to NH groups in **3**–**6**, **15** and **16**.

The ^{1}H NMR spectra of amides **3**–**6** showed two singlets near 1.9 and 3.8 ppm due to the methylene terminus of the butadienyl and pairs of doublets near 5.7 and 6.2 ppm (average coupling constants 2.2 Hz) arising from the butadienyl double bond. The NH groups gave rise to triplets within the range 5.52–6.81 ppm (average coupling constants 5.5 Hz), and signals for the phenanthroline ligand were similar to those reported for the acyl chloride **2**. The glycine methyl ester **3** gave rise to two overlapping multiplets for the methylene protons at 2.14 ppm, and a singlet at 3.37 ppm was assigned to the methyl ester group. For the ethyl ester **4**, the methyl triplet had moved upfield to 1.14 ppm and the methylene protons gave three multiplets at 1.92, 2.95 and 3.97 ppm due to the differing anisoptropic effect of the phen ring system. A chiral centre in [$WCl(CO)_2(\eta^3$-$CH_2C(CONHCPh(H)CO_2Me))C{=}CH_2)(L_2)$] resulted in two sets of ^{1}H NMR resonances being observed across the spectrum, the asymmetry of the molecule additionally leading to four different magnetic environments for the methyl groups of L_2 [14]. Coupling constants for signals due to terminal protons of this butadienyl double bond were lower (1.47 Hz) than typically observed for related molybdenum complexes (1.9–3.1 Hz).

The proton NMR spectrum of carboxylate derivative **15** also exhibited two sets of signals, and their relative intensities varied with fractional crystallisation of the diastereomers present. Peaks due to phenanthroline and terminal butadienyl protons of propyl and butyl complexes **17**–**20** were similar to those of the methyl ester, and signals arising from methyl, methylene and methine protons of the substituent were found upfield from their free alcohol positions due to the anisotropic phen system. There was no ^{1}H NMR evidence for asymmetry within either the $Mo(CO)_2$(phen)Cl or $W(CO)_2(L_2)$Cl units of the complexes produced, temperature invariance over the range −70 to 20 °C indicated dynamic behaviour was not occurring. Low solubility of these complexes in common organic solvents prevented good quality ^{13}C NMR spectra from being recorded.

4. Summary

Successful preparation of the η^3-$CH_2C(COCl)C{=}CH_2$ moiety from reactions of $Ph_4P[MoCl(CO)_3(phen)]$ and $ClCH_2C{\equiv}CCH_2Cl$ in water has been achieved. This has eliminated the need for a less environmentally acceptable organic solvent as reaction medium and facilitated recovery of Ph_4PCl in good yield for re-use. Formation of this acyl chloride in situ permitted ester-, amide- or thioester-substituted complexes to be isolated from aqueous alcohol, amine or thiol, and improved yields were obtained because of the insolubility of these complexes in water. Access to amide-substituted tungsten butadienyl complexes was also achieved, however formation of [$WCl_2(CO)_3(L_2)$] as a by-product reduced final yields. For molybdenum, reactions of **1** in aqueous methanol led to increasing contamination of **11** by **2** as the proportion of water to methanol was raised. The complex [$MoCl_2(CO)_3(L_2)$] was not isolated from reactions of **1** in any solvent studied, however production of the tungsten tricarbonyl complex dominated reactions of anion and alkyne in aqueous methanol. Uncontaminated ester butadienyl complex was isolated from these reactions in dry *n*-propanol or *n*-butanol, however the lower basicity of *iso*-alcohols resulted in mixtures of acyl chloride and the ester complexes. Unlike the methyl ester **11**, which was stable in alcohols and chlorinated solvents over time, the propyl and butyl ester analogues decomposed to give non-carbonyl containing products. Reactions carried out in dry methanol were found to be influenced by the presence of added organic compounds. Reagents which could undergo protonation, such as bases, served to promote the production of butadienyl **11**, whilst weak bases, or non-basic reagents which could undergo coordination to the metal centre, led to formation of the allyl **12**. The proposed mechanism for these processes was also in accord with the failure to isolate analogous complexes of the type [$MoCl(CO)_2$-(η^3-$CH_2C(CONHR)C(NHR)(Me)$)(phen)] from mixtures of amine and THF in methanol. Spectroscopic evidence suggested that halide extraction from the ester or amide complexes and coordination of solvent R′OH to the metal centre in a highly reactive 16 electron metal cation gave species of the type [$MoCl(CO)_2(\eta^3$-$CH_2C(COXR)C{=}CH_2)$(phen)(R′OH)]$^+$. Although these cations proved too unstable for isolation, displacement of coordinated solvent by nucleophilic glucuronate or hydroxybutyrate ions occurred readily to give the carboxylate complexes.

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[12] $W(CO)_4(L_2)$] and $Ph_4P[WCl(CO)_3(L_2)]$ (L_2 = 2,9-dimethyl-1,10-phenanthroline were prepared as given for the phen complexes in Ref. [9]. For $[W(CO)_4(L_2)]$, ^1H NMR in CD_2Cl_2 ppm, 3.31[s,6H], 7.72–8.31[m,6H], IR spectrum, cm^{-1}. 2006, 1875, 1854, 1808; elemental analysis (%) Calc. for $WC_{18}H_{12}N_2O_4$: C, 42.85; H, 2.38; N, 5.55. Found: C, 42.66; H, 2.29; N, 5.34%. For $Ph_4P[WCl(CO)_3(L_2)]\cdot CH_2Cl_2$, ^1H NMR in CD_2Cl_2 ppm, 2.87[s,6H], 7.51–8.15[m,26H], IR spectrum, cm^{-1}. 1874, 1752, 1722; elemental analysis (%) Calc. for $WC_{42}H_{34}N_2O_3PCl_3$: C, 53.85; H, 3.63; N, 2.99. Found C, 54.09; H, 3.63; N, 2.99%.

[13] For $[WCl(CO)_2(\eta^3\text{-}CH_2C(CONHCPh(H)CO_2Me))C{=}CH_2)(L_2)]\cdot 0.5CH_2Cl_2$, ^1H NMR in CD_2Cl_2 ppm, 1.88[s,H'_{anti}], 1.95[s,H'_{anti}], 3.46[s,H'_{syn}], 3.70[s,H'_{syn}], 3.20[s,3H,L_2], 3.32[s,3H,L_2], 3.33[s,3H,L_2], 3.35[s,3H,L_2], 3.43[s,CO_2Me], 3.62[brs,NCH], 3.66[s,3H,CO_2Me], 3.86[brs,NCH], 5.43[d,1.28,H''_{anti}], 5.49[d,1.47, H''_{anti}], 5.79[d,7.51,H,Ph], 6.37[d,6.41,H,Ph], 6.43[d,1.47,H''_{syn}], 6.48[d, 1.47,H''_{syn}], 6.85–7.15[m,8H,Ph], 7.65–7.89[m,10H,L_2], 8.33[d,2.39, H,L_2], 8.36[d,2.38,H,L_2]; IR spectrum, cm^{-1}. 3408 ν(NH), 1970, 1890ν(C≡O), 1745ν(CO_2Me), 1644ν(C=O); elemental analysis (%) Calc. for $WC_{30.5}H_{29}N_3O_5Cl_3$: C, 47.51; H, 3.76; N, 5.45. Found: C, 47.81; H, 3.54; N, 5.46%.