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One pot synthesis of η<sup>3</sup>-butadienyl complexes of Mo(II) or W(II): Crystal structure of [MoCl(CO)<sub>2</sub>(η<sup>3</sup>-CH<sub>2</sub>C(CONHCH<sub>2</sub>C=CH)C=CH<sub>2</sub>)(2,2'-bipyridine)]

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#### Abstract

A one pot reaction of  $[M(CO)_4L_2]$  (M = Mo,  $L_2 = 2,2'$ -bipyridine, 1,10-phenanthroline; M = W,  $L_2 = 2,9$ -dimethyl-1,10-phenanthroline) with 1,4-dichloro-2-butyne and Ph<sub>4</sub>PCl was examined in chlorinated solvents over the range 40–129 °C. Production of either  $[MCl(CO)_2(\eta^3-CH_2C(COCl)C=CH_2)L_2]$  (4) or  $[MCl_2(CO)(\eta^2-ClCH_2C=CCH_2Cl)L_2]$  was found to be dependent upon the solvent temperature, and these reactions were found to be insensitive to the presence of water. Under controlled conditions, one pot reactions carried out in the presence of alcohols, amines or thiols gave related ester, amide or thioester substituted  $\eta^3$ -butadienyl complexes in good yield. The structure of the propargyl amide complex was confirmed by X-ray analysis. © 2006 Elsevier Ltd. All rights reserved.

Keywords: One pot; Molybdenum; Tungsten; Butadienyl; Alkyne; Water

# 1. Introduction

Transition metal complexes containing  $\eta^3$ -dienyl ligands are important, because of their relationships to  $\eta^2$ -diynes,  $\eta^3$ -allyls and  $\eta^4$ -dienes, and for their roles as key intermediates in certain catalytic processes [1–3]. Synthesis of these complexes typically requires exclusion of moisture due to the sensitivity of reactants, intermediates and products to water, and many are carried out in dried ethers or chlorinated solvents. For example, substituted complexes of the type [Mo(CO)<sub>2</sub>( $\eta^3$ -CH<sub>2</sub>CHC=CR<sup>1</sup>R<sup>2</sup>)L<sub>3</sub>] (R<sup>1</sup>,R<sup>2</sup> = H, Me) have been obtained by reaction of electrophilic allenes TsOCH<sub>2</sub>CH=C=CR<sup>1</sup>R<sup>2</sup> with [Mo(CO)<sub>3</sub>L<sub>3</sub>]<sup>-</sup> (L<sub>3</sub> = Cp or Tp) in Na dried THF [4,5]. However in a previous publication, the author with others reported the formation of  $[MoCl(CO)_2(\eta^3-CH_2C(COCl)C=CH_2)(phen)]$  in good yield from reactions of 1,4-dichloro-2-butyne and  $Ph_4P[MoCl(CO)_3(phen)]$  in either  $CH_2Cl_2$  or water [6]. This acyl chloride complex was found to be stable when suspended in water for several hours, and could be handled in air for short periods with minimal oxidation. Whilst the tungsten analogue could be isolated in chlorinated solvents, the reaction proved more sensitive to water and yielded the alternative product [WCl<sub>2</sub>(CO)<sub>3</sub>(phen)]. Production of the precursor complex  $Ph_4P[MCl(CO)_3(phen)]$ occurred in a two step process, involving refluxing the metal hexacarbonyl and L<sub>2</sub> in toluene (Mo) or xylene (W), followed by heating the product  $[M(CO)_4L_2]$  with Ph<sub>4</sub>PCl in the same solvent and acetonitrile. In an attempt to improve yields, and to reduce the overall reaction time for the three stage conversion of  $[M(CO)_6]$  to the butadienyl (Mo 5 h, W 20 h), one pot reactions of these reagents have been investigated in chlorinated solvents or in water over the temperature range 40-129 °C.

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# 2. Experimental

#### 2.1. Materials and physical methods

The complexes  $[M(CO)_4L_2]$  and  $Ph_4P[MCl(CO)_3L_2]$ were freshly prepared by the published method [7], and all other chemicals were purchased from commercial sources and used without further purification. Experiments were carried out under an N<sub>2</sub> atmosphere. Infrared spectra were recorded on a Perkin–Elmer 781 spectrometer using samples prepared as nujol mulls on sodium chloride discs. The <sup>1</sup>H NMR spectra were obtained for solutions in dimethylsulfoxide- $d_6$  and were referenced to the solvent as internal standard.

2.2. Synthesis of  $[MoCl(CO)_2(\eta^3-CH_2C(COCl)-C=CH_2)L_2]$  ( $L_2 = bipy$  4a,  $L_2 = phen$  4b)

A mixture of  $[Mo(CO)_4L_2]$  (2.0 mmol), Ph<sub>4</sub>PCl (824 mg, 2.2 mmol) and excess 1,4-dichloro-2-butyne (3) (0.2 ml) was refluxed in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) for 6 h, cooled to room temperature and then stored at 5 °C for 3 days. The orange product was filtered from solution and dried *in vacuo*. Yields = 69% 4a, 73% 4b.

# 2.3. Synthesis of $[WCl(CO)_2(\eta^3 - CH_2C(COCl)C = CH_2) - (2,9-Me_2phen)]$ (4c)

A mixture of  $[W(CO)_4(2,9-Me_2phen)]$  (504 mg, 1.0 mmol) and Ph<sub>4</sub>PCl (400 mg, 1.07 mmol) in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (25 ml) was refluxed for 6 h with an excess of **3** (0.1 ml). Reduction of the solvent volume under reduced pressure followed by storage at 5 °C for 3 days gave the orange title product. This was filtered from solution and dried *in vacuo*. Yield = 76%.

#### 2.4. Attempted preparation of 4a

 $Mo(CO)_6$  (264 mg, 1.0 mmol), phen (180 mg, 1.0 mmol), Ph<sub>4</sub>PCl (400 mg, 1.1 mmol) and **3** (0.1 ml) were refluxed in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> or CH<sub>2</sub>Br<sub>2</sub> (25 ml) and monitored by IR spectroscopy for 3–72 h.

# 2.5. Thermal study of 4a

*Method a*: Mixtures of  $[Mo(CO)_4(phen)]$  (1a) (50 mg, 0.13 mmol) and Ph<sub>4</sub>PCl (60 mg, 0.16 mmol) were refluxed with 3 (0.1 ml) in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, 1,1,1-C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>, 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, CH<sub>2</sub>Br<sub>2</sub> or C<sub>6</sub>H<sub>5</sub>Cl (25 ml) for 3–6 h. *Method b:* The reaction was carried out as *a*, but 1a and Ph<sub>4</sub>PCl were replaced by 4a (60 mg, 0.12 mmol). For both methods, the complex  $[MoCl_2(CO)(\eta^2$ -ClCH<sub>2</sub>C $\equiv$ CCH<sub>2</sub>Cl)(phen)] (5) was obtained from those solvents boiling in the range 61–96 °C. For 5: <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>, 5.41 (brs, 4H), 8.05–9.35 (m, 8H); IR (Nujol) 1956 cm<sup>-1</sup>; elemental *Anal.* Calc. for ( $\cdot$ 0.5CH<sub>2</sub>Cl<sub>2</sub>): C, 38.85; H, 2.40; N 5.18. Found: C, 39.70; H, 2.34; N 5.43.

2.6. Synthesis of  $[MoCl(CO)_2(\eta^3-CH_2C(COBr)-C=CH_2)(phen)]$ 

A suspension of 4a (365 mg, 0.5 mmol) and potassium bromide (595 mg, 5.0 mmol) in refluxing acetone (50 ml) was stirred for 18 h. The resulting mixture was poured into water (20 ml), and then extracted twice with dichloromethane (25 ml). The separated organic layer was dried over MgSO<sub>4</sub>, and removal of solvent in vacuo gave the orange-red product. Yield = 45%.

2.7. Synthesis of  $[MoCl(CO)_2(\eta^3-CH_2C(COX)C=CH_2)-L_2]$  (X = NHCH<sub>2</sub>CH=CH<sub>2</sub>, L<sub>2</sub>=bipy 6 or phen 7; X = NC<sub>5</sub>H<sub>10</sub>, L<sub>2</sub> = bipy 8; X = NHCH<sub>2</sub>C=CH, L<sub>2</sub> = bipy 9)

Method a: A mixture of  $[Mo(CO)_4L_2]$  (1.0 mmol) and Ph<sub>4</sub>PCl (393 mg, 1.05 mmol) was stirred in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) with an excess of allyl amine, piperidine or propargyl amine (0.25 ml), and to this was added 3 (0.1 ml). The mixture darkened on addition, and after refluxing for 7 h, the volume was reduced by half using a flow of N<sub>2</sub>. Storage overnight at low temperature gave the product as orangered microcrystals. These were filtered from solution, and recrystallized from methanol or CH<sub>2</sub>Cl<sub>2</sub>-petrol mixtures. Method b: The acyl chloride complex was prepared as given in Section 2.2, and to this was added the amine. After a further 1 h reaction under reflux, the product was isolated as described above. Method c: The reaction was carried out as described in a, but  $[Mo(CO)_4L_2]$  and Ph<sub>4</sub>PCl were replaced by  $Ph_4P[MoCl(CO)_3L_2]$  (1.0 mmol). Yields of each complex obtained by methods a-c were similar, and in the range 42-68%.

2.8. Synthesis of  $[WCl(CO)_2(\eta^3-CH_2C(COX))C=CH_2-(2,9-Me_2phen)]$  (X = N(CH\_2CH=CH\_2)\_2 10 or NHCH(Ph)CO\_2Me 11)

The synthesis was carried out as described in Section 2.7 method *a*, but using  $1,2-C_2H_4Cl_2$  and the appropriate amine. Yields = 49% 10, 54% 11.

2.9. Synthesis of  $MoCl(CO)_2(\eta^3-CH_2C(CO_2CH_2C\equiv CH)-C=CH_2)(phen)]$  (12) and  $[MoCl(CO)_2(\eta^3-CH_2C-(COS(CH_2)_2SH)C=CH_2)(phen)]$  (13)

The reaction was carried out as described in Section 2.7 method *a*, with the amine replaced by propargyl alcohol or 1,2-ethanedithiol (0.5 ml) and triethylamine (0.1 ml). Yields = 54% **12**, 47% **13**.

## 2.10. X-ray crystallography

A single orange crystal of **9**  $(0.50 \times 0.20 \times 0.12 \text{ mm})$  was grown from a CH<sub>2</sub>Cl<sub>2</sub>-petrol mixture and mounted on a glass fibre in paratone oil. Data were collected at 120 K on an Nonius KappaCCD area detector diffractometer located at the window of a Nonius FR591 rotating anode X-ray generator, equipped with a molybdenum target ( $\lambda$  Mo K $\alpha$  = 0.71073 Å). The structure was solved and refined using the sHELX-97 suite of programs and data were corrected for absorption effects by means of comparison of equivalent reflections using the program sADABS [8,9]. Non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were fixed in idealised positions with their thermal parameters riding on the values of their parent atoms. Positional disorder (180° rotation) was found to be present in the propargyl chain (C18–C20) with an occupancy ratio of 66:34, and only one orientation of this chain is shown in Fig. 1 for clarity. C<sub>20</sub>H<sub>16</sub>ClMoN<sub>3</sub>O<sub>3</sub>, monoclinic, P2<sub>1</sub>/c, a = 7.4910(1), b = 16.9292(3), c = 15.2343 (2) Å,  $\beta$  = 93.9620(10)°, volume = 1927.35(5) Å<sup>3</sup>, Z = 4,



Fig. 1. The crystal structure of  $[MoCl(CO)_2(\eta^3-CH_2C(CONHCH_2 C \equiv CH)C = CH_2)(2,2'-bipyridine)]$  (9), with the second component of the disordered propargyl chain (C18'-C20') omitted for clarity.

 $D_{\rm c} = 1.646 \text{ Mg/m}^3$ ,  $\mu = 0.846 \text{ mm}^{-1}$ , 29518 measured, 4422 unique ( $R_{\rm int} = 0.0358$ ) and 3827 ( $F_{\rm o} > 4\sigma(F_{\rm o})$ ) reflections,  $R_1$  (obs) = 0.0287 and  $wR_2$  (all data) = 0.0732  $\rho_{\rm max}/\rho_{\rm min} = 0.650/-0.933$  e Å<sup>-3</sup>.

## 3. Results and discussion

#### 3.1. Synthesis of substituted butadienyl complexes

A mixture of  $[Mo(CO)_4L_2]$  (L<sub>2</sub> = phen, **1a**, bipy **1b**), Ph<sub>4</sub>PCl and 1,4-dichloro-2-butyne (3) was refluxed in CH<sub>2</sub>Cl<sub>2</sub>, and the product was monitored by IR and NMR spectroscopy over time. After 3 h approximately equal quantities of unreacted 1 and [MoCl(CO)2- $(\eta^3$ -CH<sub>2</sub>C(COCl)C=CH<sub>2</sub>)L<sub>2</sub>] (4a,4b) were obtained, and complete conversion of 1 to 4 was achieved after a further 3 h (Eq. (1), Scheme 1). During this period the orange reaction mixture showed no signs of darkening due to formation of purple  $Ph_4P[MoCl(CO)_3L_2]$  (2a,2b), nor was there evidence of this compound in the spectra. This was not unexpected, since 2 reacted rapidly with 3 at 20 °C, and at elevated temperatures would be consumed on formation. Whilst yields of 4 were similar to the previous two stage process (Eqs. (2) and (3)), the new reaction time exceeds the latter by 3 h. A mixture of  $[W(CO)_4(2,9-Me_2phen)]$ (1c), Ph<sub>4</sub>PCl and 3 heated in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> or 1,1,1-C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub> (40-72 °C) over the same 6 h period showed no spectroscopic change. However increasing the temperature to 81 °C (1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>) afforded the acyl chloride (4c) in good yield, and this new reaction time compares favourably with the previous two stage total of 18 h (Eqs. (2) and (3)). The practical and environmental advantages of transferring to the one pot method are therefore, (i) isolation of products in good yield using minimum glassware and cleaning solvents, (ii) complete elimination of MeCN (Eq. (2)), (iii) reduction of solvent temperatures by 60-70 °C (previously 110 °C Mo and 140 °C W, Eq. (2))

Scheme 1. Conditions: Eq. (1)  $\Delta$  CH<sub>2</sub>Cl<sub>2</sub> (Mo, 6 h) or 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (W, 6 h), Eq. (2)  $\Delta$  toluene (Mo, 1 h) or xylene (W, 16 h) and MeCN, Eq. (3) RT CH<sub>2</sub>Cl<sub>2</sub>2 h, Eqs. 94) and (5)  $\Delta$  CHCl<sub>3</sub>6 h, Eq. (6)  $\Delta$  CH<sub>2</sub>Cl<sub>2</sub> (Mo, 7 h) or 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (W, 7 h).

and (iv) reaction time for tungsten complexes reduced by 12 h.

In an effort to decrease the time required to convert  $[Mo(CO)_4L_2]$  to 4, reactions of 1a, Ph<sub>4</sub>PCl and 3 were carried out in higher boiling point solvents. Coordinating solvents were avoided in view of their potential reaction with 1 to form solvated compounds of the type  $[M(CO)_3(L_2)(S)]$ [10], and chlorinated solvents were selected for their ability to dissolve reactants and products. After 4 h in CHCl<sub>3</sub> (61 °C), peaks due to carbonyl stretching in **1a** had been replaced by those of 4a and an additional peak of almost equal intensity at  $1956 \text{ cm}^{-1}$ . The latter predominated on raising the temperature to 96 °C (CH<sub>2</sub>Br<sub>2</sub>), and the complex  $[MoCl_2(CO)(\eta^2-ClCH_2C)=CCH_2Cl)(phen)]$  (5) was isolated from solution. This product was also obtained on refluxing a mixture of 4a and excess 1,4-dichloro-2butyne in this solvent (Eqs. (4) and (5), Scheme 1), and one pot production of 5 occurred in solvents of higher boiling point until onset of decomposition of intermediate 2 occurred at 129 °C ( $C_6H_5Cl$ ). Dichloroalkyne 3 is not expected to undergo rearrangement within this temperature range [11], and therefore the additional chlorine in 5 originates from decomposition of 4a. On refluxing 4a in acetone containing bromide ions, the derivative [MoCl- $(CO)_2(\eta^3-CH_2C(COBr)C=CH_2)(phen)]$  was obtained,<sup>1</sup> and thus both 4a and its acyl bromide analogue were stable at 56 °C. Isolation of 5 from one pot reactions of 1a,  $Ph_4PCl$  and 3 in solvents boiling within the range 61– 129 °C was therefore attributable to destabilization at these higher temperatures.

Attempts to prepare 4a or 4b by a one pot method using  $[Mo(CO)_6]$ , L<sub>2</sub>, Ph<sub>4</sub>PCl and **3** in refluxing CH<sub>2</sub>Cl<sub>2</sub> over several days were less successful. Loss of CO from the hexacarbonyl was found to be slow at this temperature, and 12 h were required to form uncontaminated 1. The diimine ligands bipy and phen, being weaker pi acceptors than CO, labilize  $[M(CO)_4L_2]$  complexes towards dissociative ligand loss from the position cis to them. This cis labilization results in reaction substitution rates several orders of magnitude larger for these chelate complexes than for Mo(CO)<sub>6</sub>. After 24 h the IR solution spectrum showed carbonyl stretching absorptions due to 1 and acyl chloride complex 4 of approximately equal intensity. However continued reaction times resulted in decreasing strength of these bands, suggesting the acyl chloride was thermally unstable over extended periods. A good yield of 4 could not be obtained via this method after 48 h (21%), and little remained in solution after refluxing for 72 h. Increasing the reaction temperature by use of CHCl<sub>3</sub> or CH<sub>2</sub>Br<sub>2</sub> was found to accelerate formation of 1 and 4, but also resulted in more rapid decomposition of the latter.

Addition of primary or secondary amines XH to the one pot reaction mixture of 1, Ph<sub>4</sub>PCl and 3 in CH<sub>2</sub>Cl<sub>2</sub> afforded substituted complexes of the type [MCl(CO)<sub>2</sub>- $(\eta^3$ -CH<sub>2</sub>C(COX)C=CH<sub>2</sub>)L<sub>2</sub>](6–11), and in the presence of triethylamine and alcohol or thiol, the corresponding ester and thioester complexes could also be achieved (X =OCH<sub>2</sub>C=CH 12, S(CH<sub>2</sub>)<sub>2</sub>SH 13). These were characterized by their IR and NMR spectra (Tables 1 and 2), and the stereochemistry of 9 was investigated by a single crystal X-ray analysis. In some cases, where complexes were only soluble in DMSO, reproducible elemental analyses could not be obtained since oxidation to  $[Mo_2Cl_2O_4(L_2)_2]$ occurred readily on recrystallization [12]. Complete replacement of CH<sub>2</sub>Cl<sub>2</sub> by water in this one pot method was not possible due to insolubility of 1. However 4 and 6-9 could be achieved from a two phase CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O system, and where small volumes of the former were used, water assisted mixing and filtration. For example, similar yields of 4a and 6 were obtained when 10 ml CH<sub>2</sub>Cl<sub>2</sub> was replaced by 10 ml water and 0.5 ml CH<sub>2</sub>Cl<sub>2</sub> in Sections 2.2 and 2.7, respectively. The tungsten complexes however proved more sensitive to water, and on heating 1c, Ph<sub>4</sub>PCl and 3 to 80 °C in an equivolume mixture of 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> and water (2.3), a mixture of 4c and the known complex [WCl<sub>2</sub>(CO)<sub>3</sub>(2,9-Me<sub>2</sub>phen)] was obtained.

# 3.2. Characterization of complexes

# 3.2.1. Spectroscopic data

All the  $\eta^3$ -butadienvl complexes exhibited a pair of strong absorptions in their IR spectra between 1982 and  $1894 \text{ cm}^{-1}$  due to the metal *cis*-dicarbonyl fragment. A band of medium intensity near 1710 cm<sup>-1</sup> arising from v(C=O) of the acyl chloride 4 was shifted to lower wavenumber in 6–13, and weak peaks near 3400 or  $3250 \text{ cm}^{-1}$ were assigned to v(NH) or  $v(C \equiv CH)$ , respectively. The <sup>1</sup>H NMR spectra showed two singlets near 1.8 and 3.7 ppm due to the methylene terminus of the  $\eta^3$ -bonded butadienyl, and a pair of doublets arising from the double bond of this unit appeared near 5.7 and 6.2 ppm, with coupling constants of 2.2 Hz. Amide complexes containing NH gave rise to a triplet between 6.1 and 6.6 ppm, and a further triplet at 2.84 ppm was attributable to the terminal propargyl proton of 9. Other signals due to aliphatic substituents of the butadienyl and aromatic protons of the L<sub>2</sub> ligand were unexceptional. As a result of their low solubilities, the <sup>13</sup>C NMR spectra of 6–13 were not recorded.

## 3.2.2. Crystal structure determination of 9

A solid-state crystal structure determination of [MoCl-(CO)<sub>2</sub>( $\eta^3$ -CH<sub>2</sub>C(CONHCH<sub>2</sub>C $\equiv$ CH)C $\equiv$ CH<sub>2</sub>)(2,2'-bipyridine)] was carried out to determine the stereochemistry of the substituted  $\eta^3$ -butadienyl fragment. Fig. 1 shows a view of the molecule and the atomic labeling scheme used, and selected bond lengths and angles for **9** are given in Table 3. The coordination geometry about the Mo centre may be considered to be that of a slightly distorted octahedron

<sup>&</sup>lt;sup>1</sup> For [MoCl(CO)<sub>2</sub>(η<sup>3</sup>-CH<sub>2</sub>C(COBr)C=CH<sub>2</sub>)phen]: <sup>1</sup>H NMR in DMSO- $d_6$  1.91 (s, H), 3.79 (s, H), 5.67 (d, 1.38H), 6.19 (d, 1.38H), 7.99 (m, 2H), 8.18 (s, 2H), 8.82 (m, 2H), 9.13 (d, 4.42H), 9.29 (d, 4.66H); IR (Nujol), cm<sup>-1</sup>. 1989, 1912, 1650.

Table 1			
Selected infrared and	analytical data for	or [MCl(CO) <sub>2</sub> (n <sup>3</sup> -CH	$_{2}C(COX)C=CH_{2}L_{2}^{B}$

No.	Х	L <sub>2</sub>	Infrared data <sup>a</sup>			Analysis, found (calculated) %		
			ν(C≡O)	v(C=O)	v(NH)	С	Н	Ν
6	NHCH <sub>2</sub> CH=CH <sub>2</sub>	bipy	1958, 1881	1639	3402	50.10 (50.05)	3.47 (3.75)	8.65 (8.75)
7	NHCH <sub>2</sub> CH=CH <sub>2</sub>	phen	1964, 1888	1647	3429		e	
8	$NC_5H_{10}$	bipy	1960, 1890	1609		51.38 (51.15)	4.64 (4.81)	7.63 (7.78) <sup>f</sup>
9 <sup>b</sup>	NHCH <sub>2</sub> C=CH	bipy	1958, 1882	1654	3412	50.20 (50.26)	3.31 (3.35)	8.47 (8.79)
10	$N(CH_2CH=CH_2)_2$	Me <sub>2</sub> phen	1980, 1896	1628			e	
11	NHCH(Ph)CO <sub>2</sub> Me	Me <sub>2</sub> phen	1970, 1890	1644, 1745	3408	47.81 (47.51)	3.54 (3.76)	5.46 (5.45)
12 <sup>c</sup>	$OCH_2C \equiv CH$	phen	1973, 1897	1701			e	
13 <sup>d</sup>	SCH <sub>2</sub> CH <sub>2</sub> SH	phen	1968, 1891	1637		46.37 (46.62)	2.84 (3.14)	5.55 (5.18)

<sup>a</sup> As nujol mulls, cm<sup>-1</sup>.

<sup>b</sup>  $v(C \equiv CH)$  3256 cm<sup>-1</sup>.

<sup>c</sup>  $v(C \equiv CH)$  3249 cm<sup>-1</sup>.

<sup>d</sup> v(SH) 2593 cm<sup>-1</sup>.

<sup>e</sup> Non-reproducible results, highly insoluble or unstable.

<sup>f</sup> Calc. MeOH.

 $^{\rm g}\,$  M = Mo for all complexes, except 10, 11 where M = W.

Table 2					
<sup>1</sup> H NMR	data	for	complexes	6-13	a

No.	$H'_{anti}$	$\mathbf{H}''_{anti}$	NH	Aliphatic	Aromatic
	H <sub>syn</sub>	H <sub>syn</sub>			
6	1.79 (s, H),	5.63 (d, 2.2, H),	6.30 (t, 5.5, H)	2.79 (m, H), 3.02 (m, H),	7.96 (m, 2H), 8.17 (m, 2H), 8.50 (m, 2H),
	3.70 (s, H)	6.27 (d, 1.9, H)		4.77 (m, 2H), 5.13 (m, H)	8.69 (d, 4.4, H), 8.81 (d, 4.9, H)
7	1.86 (s, H),	5.74 (d, 2.2, H),	6.15 (t, 5.8, H)	2.24 (m, H), 2.43 (m, H),	8.00 (m, 2H), 8.17 (s, 2H), 8.80 (m, 2H),
	3.84 (s, H)	6.29 (d, 2.2, H)		4.47 (m, 2H), 4.54 (m, H)	9.11 (d, 4.9, H), 9.24 (d, 4.9, H)
8	1.94 (s, H),	5.54 (d, 2.3, H),		1.77 (m, 6H), 2.12 (m, H),	7.83 (m, 2H), 8.08 (m, 2H), 8.42 (m, 2H),
	3.91 (s, H)	6.09 (d, 2.4, H)		3.18 (m, H), 3.53 (m, 2H)	8.66 (m, H), 8.81 (m, H)
9	1.78 (s, H),	5.63 (d, 2.2, H),	6.58 (t, 5.5, H)	2.84 (t, 2.22H), 3.07 (m, 2H),	7.64 (m, 2H), 8.16 (m, 2H), 8.5 (m, 2H),
	3.68 (s, H)	6.25 (d, 2.5, H)			8.68 (d, 4.4, H), 8.81 (d, 4.7, H)
10	1.91 (s, H),	5.62 (d, 2.2, H),		3.30 (s, 3H), 3.35 (s, 3H),	7.78 (m, 2H), 7.90 (s, 2H), 8.40 (m, 2H)
	3.69 (s, H)	6.16 (d, 2.2, H)		3.75 (d, 5.502H), 4.05 (d,	
	() )			5.50,2H), 5.14 (m, 4H),	
				5.71 (m, 2H)	
11	1.88 (s, H),	5.43 (d, 1.3, H),	5.79 (d, 7.5, H),	3.20 (s, 3H), 3.32 (s, 3H),	6.85–7.15 (m, 10H), 7.65–7.89 (m, 10H),
	1.95 (s, H),	5.49 (d, 1.5, H),	6.37 (d, 6.4, H)	3.33 (s, 3H), 3.35 (s, 3H),	8.33 (d, 2.4, H), 8.36 (d, 2.4, H)
	3.46 (s, H),	6.34 (d, 1.5, H),		3.43 (s, 3H), 3.62 (s, H),	
	3.70 (s, H)	6.48 (d, 1.5, H)		3.66 (s, 3H), 3.86 (brs, H)	
12	1.97 (s, H),	5.71 (d, 2.2, H),		2.96 (m, H), 3.13 (m, 2H)	8.04 (m, 2H), 8.20 (s, 2H), 8.84 (m, 2H),
	3.74 (s, H)	6.23 (d, 2.2, H)			9.14 (m, H), 9.33 (m, H)
13	1.93 (s. H).	5.78 (d. 2.2, H).		2.16 (m. 2H), 2.34 (m. 2H)	8.09 (m. 2H), 8.19 (s. 2H), 8.82 (m. 2H),
-	3.85 (s, H)	6.31 (d, 2.2, H)		(,), (,)	9.12 (d, 4.9, H), 9.28 (d, 4.9, H)

<sup>a</sup> Spectra recorded in DMSO-d<sub>6</sub>. Data reported in ppm, multiplicity, coupling constant (Hz), number of protons.

if the central atom of the butadienyl based ligand (C14) is considered to be the point of attachment. The central molybdenum atom is bonded to two carbonyl groups [Mo1–C1 1.980(2) Å; Mo1–C2 1.976(2) Å], two nitrogens of 2,2'-bipyridine [Mo1–N1 2.2309(17) Å; Mo1–N2 2.2246(16) Å], a chlorine atom [Mo1–Cl1 2.4997(5) Å] and a 2-substituted butadienyl unit, C<sub>8</sub>H<sub>8</sub>NO. The metal– CO and carbonyl bond lengths [C1–O1 1.150(3) Å; C2– O2 1.147(3) Å] and angles [Mo1–C1–O1 179.3(2)°; Mo1– C2–O2 178.5(2)°], and the C1–Mo1–C2 bond angle [82.22(9)°], are all typical of a pair of mutually *cis* carbonyl groups. The rings of the bipyridine unit are approximately planar within experimental error, and their bond lengths and angles are similar to values found for related molybde-num  $\eta^3$ -allyl and  $\eta^3$ -pentadienyl bipyridyl complexes [13–15].

Within the butadienyl moiety, the C13–C14–C15 angle of  $113.27(19)^\circ$ , the C13–C14 and C14–C15 bond lengths

Table 3 Selected bond lengths (Å) and angles (°) for  $[MoCl(CO)_2(\eta^3-CH_2C-(CONHCH_2C=CH)C=CH_2)(bipy)]$  (9)

(continenze=		(2)	
Mo1–C1	1.980(2)	Mo1–C13	2.300(9)
Mo1–C2	1.976(2)	Mo1–C14	2.228(8)
Mo1–N1	2.2309(17)	Mo1-C15	2.208(9)
Mo1-N2	2.2246(16)	C13-C14	1.423(3)
Mo1–Cl1	2.4997(5)	C14-C15	1.414(3)
C14–C17	1.495(3)	C15-C16	1.317(3)
C17–O3	1.226(3)	C101	1.150(3)
C17–N3	1.346(3)	C2–O2	1.147(3)
N3-C18	1.456(4)	C18-C19	1.458(6)
		C19–C20	1.180(4)
C1-Mo1-C2	82.22(9)	C13-C14-C15	113.27(19)
N1-Mo1-N2	73.37(6)	C14-C15-C16	141.6(2)
O1-C1-Mo1	179.3(2)	O2-C2-Mo1	178.5(2)
C14-C17-O3	121.2(2)	O3-C17-N3	122.9(2)
C17-N3-C18	117.9(2)	N3-C18-C19	110.8(4)
C14-Mo1-N1	87.25(7)	C18-C19-C20	178.9(4)
C2-Mo1-C15	69.71(8)	C1-Mo1-C15	109.90(8)
C2-Mo1-N2	165.93(8)	C1-Mo1-N2	99.56(8)
C15-Mo1-N2	121.85(7)	C2-Mo1-C14	104.34(8)
C1-Mo1-C14	102.18(8)	C15-Mo1-C14	37.26(7)
N2-Mo1-C14	88.99(7)	C2-Mo1-N1	102.37(8)
C1-Mo1-N1	168.27(7)	C15-Mo1-N1	81.83(7)
C2-Mo1-C13	107.51(9)	C1-Mo1-C13	66.94(9)
C15-Mo1-C13	63.39(8)	N2-Mo1-C13	85.84(7)
C14-Mo1-C13	36.52(8)	N1-Mo1-C13	120.77(7)
C2-Mo1-Cl1	85.62(6)	C1-Mo1-C11	86.67(6)
C15-Mo1-C11	147.29(5)	N2-Mo1-C11	80.58(4)
C14-Mo1-C11	167.36(5)	N1-Mo1-C11	82.96(4)
C13-Mo1-C11	147.83(6)		

of 1.423(3) and 1.414(3) Å respectively, and the Mo1-C13 and Mo1-C14 separations of 2.300(9) and 2.228(8) Å are all similar to 1- and 2-substituted  $\eta^3$ -allyl complexes of molybdenum [16-18]. However the shorter Mo1-C15 distance of 2.208(9) Å may reflect an intermediate bond order between 1 and 2 that is not expected within an  $\eta^3$ -allyl system. (Compare  $[Mo(CO)_2(\eta^3-1-RC_3H_4)(phen)(O_2CCF_3)]$ R = H 2.316(5) Å, R = Me 2.411(13) Å. Although the C15–C16 bond length of 1.317(3) Å is slightly longer than that observed for the related selenoester 2-substituted complex [1.242(13) Å], this value is consistent with related dienyl complexes of the type  $[Mo(CO)_2(\eta^3-CH_2CHC=$  $CR^{1}R^{2}L_{3}$ ] (L<sub>3</sub> = Cp, Tp; R<sup>1</sup>, R<sup>2</sup> = H, Me) [4,5,19]. A non-planar arrangement of hydrogen atoms at terminal atoms C13 and C16 suggests the double bond C15-C16 is not conjugated with respect to the C13-C14-C15 unit, and this should be reflected in the chemical reactivity. The amide group of the butadienyl fragment is approximately planar, with the carbonyl orientated away from the C= $CH_2$  terminus, and the propargyl substituent extends over the bipy ring system. The C18-C19-C20 angle of  $178.9(4)^{\circ}$  and the C19–C20 bond length of 1.180(6) Å are both in accord with this linear chain.

Asymmetry at the metal centre may occur in related complexes of the type  $[Mo(CO)_2(\eta^3-allyl)L_2Y]$  due to a non-dissociative trigonal twist rearrangement of  $L_2Y$ against the  $M(CO)_2(allyl)$  unit, and this may give rise to dynamic NMR spectra. For example, an asymmetric

arrangement of L<sub>2</sub>Y at the metal has been found in solution and solid states for bipy and phen complexes  $[Mo(CO)_2(\eta^3 - RC_3H_4)L_2Y]$  (R = H, 1-Me) [13,16]. In contrast, solid state structures of 9 and its phen thioester (M = W, X = SBu) and selenoester (M = Mo, X = SePh)analogues all exhibit a symmetrical arrangement of the M(CO)<sub>2</sub>L<sub>2</sub>Cl unit [20,21] and their NMR solution spectra are non-complex and invariant over the temperature range -50 to 20 °C. Whilst allyl complexes [W(CO)<sub>2</sub>- $(\eta^3$ -CH<sub>2</sub>CRCH<sub>2</sub>)L<sub>3</sub>]<sup>+</sup> (L<sub>3</sub> = bis(2-methylpyridyl)amine) exhibit dynamic behaviour in solution at room temperature for both R = H and Me, and an asymmetric arrangement of the tridentate ligand has been shown in the solid state [22], fluxionality has not been reported for either  $[Mo(CO)_2(\eta^3-CH_2CHC=CH_2)Cp]$  or  $[Mo(CO)_2(\eta^3-CH_2-$ CMeC=CH<sub>2</sub>)Tp] [4,5]. A more detailed molecular orbital description of bonding in metal  $\eta^3$ -butadienyl complexes is required to explain these differences.

#### 4. Conclusions

Complexes containing the  $\eta^3$ -CH<sub>2</sub>C(COCl)C=CH<sub>2</sub> moiety can be synthesized from 1,4-dichloro-2-butyne by a one pot reaction with  $[M(CO)_4L_2]$  and Ph<sub>4</sub>PCl. Chlorinated solvents with boiling points in the range 40-60 °C (M = Mo) or 83–96 °C (M = W) are required for this conversion, and at elevated temperatures destabilization of the butadienyl complex can occur to afford [MCl<sub>2</sub>(CO)- $(\eta^2$ -ClCH<sub>2</sub>C $\equiv$ CCH<sub>2</sub>Cl)L<sub>2</sub>]. Preparation of the  $\eta^3$ -dienyl complex from one pot reactions involving  $[M(CO)_6]$  are hindered by this temperature requirement. Loss of CO below 60 °C (Mo) or 96 °C (W) is relatively slow and rate determining, and over the necessarily extended periods, increasing decomposition of dienyl product occurs. In contrast, conversion of the tetracarbonyl to  $[MCl(CO)_3L_2]^{-1}$ occurs more rapidly, and reaction in situ with the dichloroalkyne is fast. Thus under conditions for successful one pot production of the acyl chloride, addition of alcohols, amines or thiols generates the analogous ester, amide and thioester complexes, and in general these are found to have greater thermal stability below 120 °C. Both Mo and W complexes can also be obtained in the presence of water, however for the latter, formation of  $[WCl_2(CO)_3L_2]$  as a co-product reduces final yields. Comparison of the structure of propargyl amide 9 with related selenoester and thioester reveals a common arrangement of the acyl substituent and non-coordinated double bond. Isomers of these forms have not been observed in solution or solid states, and a combination of steric and electrostatic factors may explain the preferred orientation. Crystallographic data of all three complexes suggest pi-delocalization within the metal bound C1C2C3 unit is unconjugated with respect to C3=C4, and whilst these complexes may undergo similar reactions to substituted  $\eta^3$ -allyl analogues, the unusually short M-C3 bond length suggests direct parallels can't be assumed. Their behaviour with nucleophilic and electrophilic reagents is under investigation.

#### Appendix A. Supplementary material

CCDC 612555 contains the supplementary crystallographic data for the crystal structure reported in this paper. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.10.040.

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