

## Dimeric and trimeric molybdenum(II) complexes containing 2-substituted $\eta^3$ -bonded butadienyl bridging ligands

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### Abstract

Reaction of  $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2(\text{COCl})\text{C}=\text{CH}_2)\text{phen}]$  (phen = 1,10-phenanthroline) (**1**) with 1,2-ethanediol or *N,N'*-diethylethylenediamine in 2:1 mole ratio gave dimeric complexes  $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2(\text{COACH}_2)\text{C}=\text{CH}_2)\text{phen}]_2$  containing two molybdenum centres bridged by a pair of  $\eta^3$ -bonded butadienyl units linked by 2-substituted ester (A = O) or amide (A = NEt) groups. Analogous reactions involving hydroquinone or 1,4-phenylenediamine led to monomeric complexes of the type  $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2(\text{COA})\text{C}=\text{CH}_2)\text{phen}]$  (A =  $\text{OC}_6\text{H}_4\text{OH}$ ,  $\text{NHC}_6\text{H}_4\text{NH}_2$ ), however, dimeric complexes were isolated from reactions involving 4,4'-ethylenedianiline or *p*-xylylenediamine. Attempts to prepare a novel complex bridged by three linked amide substituted butadienyl groups using diethylenetriamine were unsuccessful, however, reaction of **1** and triethanolamine or tris(2-aminoethyl)amine in 3:1 mole ratio gave trimeric complexes  $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2(\text{COACH}_2\text{CH}_2)\text{C}=\text{CH}_2)\text{phen}]_3\text{N}$  (A = O, NH) in good yield. © 1997 Elsevier Science S.A.

### 1. Introduction

Transition metal complexes containing  $\eta^3$ -bonded butadienyl groups are important because of their relationship to metal-coordinated  $\eta^2$ -alkenes and  $\eta^4$ -dienes, their conversion to  $\eta^3$ -allyls and their relevance to organic synthesis. A recent review [1], containing several general reaction pathways to  $\eta^3$ -butadienyl complexes, illustrates the variety of substituents that may be found at C(1), C(2) or C(4) of the C(1)C(2)C(3)=C(4) unit and reveals the limited number of known dimeric complexes linked through this organic framework [2,3]. For example, while several synthetic methods have now been established for the formation of monomeric  $\eta^3$ -butadienyl complexes with H, alkyl, aryl, ester or amide groups at C(2) [1,4–7], dimeric complexes linked through this position were until recently unknown. In 1994, the author and others reported the reaction of  $\text{Ph}_4\text{P}[\text{MoCl}(\text{CO})_3\text{L}_2]$  with 1,4-dichlorobut-2-yne to give the butadienyl complex  $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2(\text{COCl})\text{C}=\text{CH}_2)\text{L}_2]$  ( $\text{L}_2 = 2,2'$ -bipyridyl or 1,10-phenanthroline) (**1**) containing a chlorocarbonyl substituent [8], and recently showed that reaction of **1** with bifunctional amines or thiols  $\text{HA}(\text{CH}_2)_2\text{AH}$  (A = NH,

NMe, S) in 2:1 mole ratio gave dimeric complexes containing two metal centres bridged by a pair of  $\eta^3$ -bonded butadienyl groups linked at C(2) by a 1,2-diamido or dithiolato unit [9]. However, dimers could not be isolated from analogous reactions involving **1** and 1,2-ethanediol, and mixed bifunctional reactants  $\text{HA}(\text{CH}_2)_2\text{BH}$  (A = N; B = O, S; A = O; B = S) afforded monomeric complexes only; the less electronegative atom of the donor pair remaining unreacted. In this publication, the conditions for formation of the dimeric diester complex are established, the boundaries of dimer formation are examined by use of bifunctional reagents linked by sterically hindered or rigid groups and the first trimeric complexes bridged by three linked  $\eta^3$ -butadienyl groups are reported.

### 2. Results and discussion

#### 2.1. Reactions with bifunctional reagents

Addition of 1,2-ethanediol or *N,N'*-diethylethylenediamine to a solution of **1** in dichloromethane in 1:2 mole ratio afforded dimeric complexes of general formula  $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2(\text{COACH}_2)\text{C}=\text{CH}_2)\text{phen}]_2$  (A = O (**2**), A = NEt (**3**)), containing a pair of bridging  $\eta^3$ -butadienyl units. Their elemental analyses and perti-

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nent IR spectroscopic data are presented in Table 1. Interestingly, the presence of triethylamine in these reactions (to facilitate removal of HCl) completely inhibited formation of **2** only. This may suggest that protonation of the diol must occur for reaction to occur, and may be related to the observation that while the chlorocarbonyl substituent of **1** is known to react with an extensive range of amines and thiols, only methanol and ethanol have been found to yield ester substituted butadienyl complexes. Propanol and larger alcohols undergo autoprotolysis to a lesser extent than methanol and ethanol, but this behaviour is enhanced and accelerated by the presence of a strong acid such as HCl. All subsequent reactions of **1** with diol or triol reagents were, therefore, carried out in the absence of the tertiary amine. Dimeric complex **3** readily formed from *N,N'*-diethylethylenediamine, however, no analogous reaction occurred between **1** and *N,N'*-diphenylethylenediamine (A = NPh). Many monomeric amides have been previously isolated (for example,  $H_2NR$ , R = Me, Et, Pr<sup>n</sup>, Bu<sup>n</sup>, Ph, CH<sub>2</sub>Ph and HNR<sub>2</sub>, R = Me, Et, Pr<sup>n</sup> all yield amide complexes), but steric and electronic factors may prevent certain amines from reacting with **1** ( $H_2NR$ , R = Pr<sup>i</sup>, Bu<sup>i</sup>, Bu<sup>t</sup> and HNR<sub>2</sub>, R = Ph, Pr<sup>i</sup>, Bu<sup>i</sup>, Bu<sup>t</sup> do not) [10]. A series of reactions of **1** with diamines containing sterically hindered or rigid links was therefore carried out (Scheme 1) in order to define the limitations of such reactions and to inform the selection of suitable reagents to access new trimeric butadienyl complexes.

Addition of one mole of 1,2-diaminopropane to a solution of two moles of **1** afforded an orange product (**4**), which was identified from its IR and <sup>1</sup>H NMR spectra and elemental analysis as the monomer  $[MoCl(CO)_2(\eta^3-CH_2C(CONHCH_2CH(Me)NH_2)C=$

$CH_2)(phen)]$ . Failure to isolate a dimeric species was not surprising in view of the fact that **1** is known to readily form amide complexes with primary *n*-alkyl amines, but not with primary iso-alkyl amines [10]. Analogous reactions of **1** and hydroquinone or 1,4-phenylenediamine (*p*-HAC<sub>6</sub>H<sub>4</sub>AH; A = O, NH) in a 2:1 mole ratio were then investigated. Spectroscopic evidence suggested that only one end of the diol or diamine had combined with **1**, to give monomeric complexes of general formula  $[MoCl(CO)_2(\eta^3-CH_2(COAC_6H_4AH)C=CH_2)phen]$  (**5** A = O and **6** A = NH). The related amine C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> has been found to readily form an amide substituted monomeric complex on reaction with **1**, suggesting that dimer formation for the aromatic diol or diamine is prevented not by the bulk of the aromatic group, but by unfavourable steric and spatial requirements for two connected metal-butadienyl units. It was therefore postulated that chain extension or flexibility between the donor pair of a primary diamine may be a requirement for dimer formation. Consequently, 2:1 mole ratio reactions were carried out between **1** and H<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH<sub>2</sub> (*p*-xylylenediamine) or NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (4,4'-diethylenedianiline), which possess greater distance between the donor pair and impart flexibility at amine or between phenyl groups, respectively. Both the resulting products (**7** and **8**) were identified as dimeric by IR and NMR spectroscopy and elemental analysis, and thus several criteria for dimer formation were established; (i) the diamine should be terminated by two identical NHR groups (R = H or *n*-alkyl only), (ii) the donor pair should be separated by a unit containing at least one CH<sub>2</sub> group, and (iii) aromatic linkages between the amine termini are not precluded, provided they are present in combination with methylene groups.

Table 1  
Yields, selected infrared and analytical data for complexes **2–11b**

No.	A	Complex <sup>a</sup> R	Yield %	Infrared data <sup>b</sup> , cm <sup>-1</sup>			Analysis, found (calculated <sup>f</sup> ) %		
				$\nu(C\equiv O)$	$\nu(C=O)$	$\nu(N-H)$	C	H	N
<b>2</b>	O	(CH <sub>2</sub> ) <sub>2</sub>	57	1933, 1859	1653		46.82(47.30)	3.21(2.88)	5.76(5.38)
<b>3</b>	NEt	(CH <sub>2</sub> ) <sub>2</sub>	63	1975, 1894	1620		50.28(49.36)	3.88(3.65)	7.97(7.67)
<b>4</b>	NH	CH <sub>2</sub> CH(Me)	65	1961, 1883	1640	3410br, 3240w	45.76(45.58)	4.12(3.80)	8.79(9.24)
<b>5<sup>c</sup></b>	O	C <sub>6</sub> H <sub>4</sub>	58	1932, 1855	1656		48.16(48.63)	2.74(2.96)	4.08(4.36)
<b>6</b>	NH	C <sub>6</sub> H <sub>4</sub>	64	1971, 1898	1655	3584br, 3372w	49.59(50.04)	3.01(3.36)	8.73(8.98)
<b>7</b>	NH	CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	59	1968, 1893	1646	3430w	50.16(50.62)	3.16(3.23)	7.72(7.54)
<b>8</b>	NH	C <sub>6</sub> H <sub>4</sub> (CH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	62	1977, 1905	1650	3386w	54.32(53.44)	3.77(3.36)	7.13(7.05)
<b>9</b>	NH	(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>2</sub>	71	1970, 1892	1642	3350–3450br	47.46(47.73)	3.58(3.42)	7.46(7.83)
<b>10</b>	O		65	1932, 1855	1656		47.08(47.60)	3.15(3.25)	5.98(6.37)
<b>11a</b>	NH		63	1971, 1892	1640	3374brw	48.10(48.90)	3.47(3.37)	8.59(8.91)
<b>11b</b>	NH <sup>g</sup>		68	1975, 1893	1671 <sup>d</sup> 1693 <sup>e</sup>	3400brw	46.22(46.58)	2.84(2.93)	7.61(7.76)

<sup>a</sup>From reactant HARAH or  $[HA(CH_2)_2]_3N$  (**10**, **11**); <sup>b</sup>As nujol mulls. All bands strong unless otherwise indicated; <sup>c</sup> $\nu(OH)$  3364w; <sup>d</sup> $\nu(CONH)$ ; <sup>e</sup> $\nu(CO_2)$ ; <sup>f</sup>CH<sub>2</sub>Cl<sub>2</sub> calculated; <sup>g</sup>Trifluoroacetate complex.

## 2.2. Reactions with trifunctional reagents

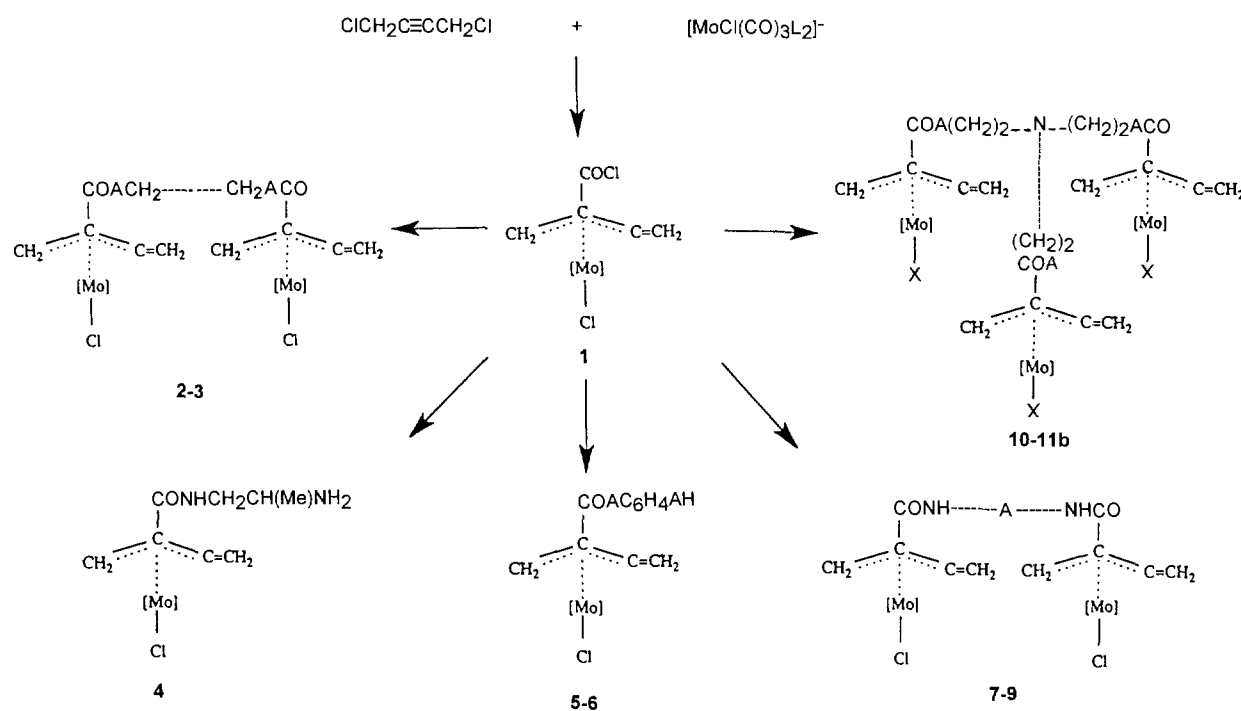
The successful formation of dimeric complexes from reactions of **1** and diamines containing the CH<sub>2</sub>CH<sub>2</sub> unit, suggested that reaction of **1** and diethylenetriamine in 3:1 mole ratio should provide a route to novel trimeric butadienyl complexes. However, the elemental analysis of the orange product (**9**) and absence of an absorption peak for NH<sub>2</sub> in its IR spectrum indicated a dimeric species had formed, with a central unreacted imino nitrogen. (The complex was too insoluble for the proton NMR spectrum to be recorded.) The reactivity of such internal NH groups was also explored by use of 3,3'-iminobis(*N,N*-dimethylpropylamine), in which an imino group separates a pair of three flexible methylene units linked to terminal NMe<sub>2</sub> groups. On reaction of this amine with **1**, the chlorocarbonyl complex was recovered unchanged, and there was no evidence for the formation of an amide complex.

Triethanolamine and tris(2-aminoethylamine) both have the potential to form trimeric complexes on reaction with **1**, since each contains three reactive groups linked by a flexible CH<sub>2</sub>CH<sub>2</sub> chain to a central tertiary nitrogen and possesses no steric or electronic competition between the three donors groups. On addition of one mole of triethanolamine or tris(2-aminoethylamine) to a stirred solution of three moles of **1** in

dichloromethane complexes **10** and **11a**, respectively, were afforded, whose elemental analyses and IR spectra supported a trimeric formula. However the low solubility of both these chloro complexes in common organic solvents prevented the recording of <sup>1</sup>H NMR spectra, and attempts were, therefore, made to convert these chloro complexes into their more soluble trifluoroacetate derivatives using a published method [10]. Complex **10** gave decomposition products only, however, **11a** yielded an orange, crystalline product (**11b**) which was identified by elemental analysis and IR and <sup>1</sup>H NMR spectroscopy as the trimer [Mo(O<sub>2</sub>CCF<sub>3</sub>)(CO)<sub>2</sub>(η<sup>3</sup>-CH<sub>2</sub>(CONHCH<sub>2</sub>CH<sub>2</sub>)C=CH<sub>2</sub>)phen]<sub>3</sub>N.

## 2.3. Spectroscopic data

The IR spectra of all the complexes were dominated by a pair of strong absorption bands between 1977 and 1855 cm<sup>-1</sup>, which are typical of *cis*-dicarbonyl species. Only one IR absorption band due to the C=O stretching mode was observed for each complex, at significantly lower wavenumber than for the parent complex **1** (ν(C=O) 1708 cm<sup>-1</sup>). Carbonyl stretching peaks for amide complexes **3**, **4**, **6–9** and **11a** occurred at ca. 1640–1655 cm<sup>-1</sup> and for ester complexes **2**, **5** and **10** at ca. 1656 cm<sup>-1</sup>, typical of values observed elsewhere [10]. The higher wavenumber for the carbonyl stretch



Key: [Mo] = Mo(CO)<sub>2</sub>phen; **2** A=O; **3** A=NEt; **5** A=O; **6** A=NH; **7** A=CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>; **8** A=C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>;

**9** A=(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>; **10** A=O, X=Cl; **11a** A=NH, X=Cl; **11b** A=NH, X=O<sub>2</sub>CCF<sub>3</sub>

Scheme 1.

for trimeric complex **11b** ( $1671\text{ cm}^{-1}$ ) reflects the differing electronegativity of the chloro and trifluoroacetate groups at the metal centre.

A monomeric formulation for complexes **4** and **6** formed from 1,2-propanediamine and 1,4-phenylenediamine, respectively, was supported by the presence of a weak IR absorption for  $\text{NH}_2$  near  $3450\text{ cm}^{-1}$ , and by a comparison of integrals for peaks due to phenanthroline, the butadienyl and bridging aromatic or aliphatic groups that were observed in their  $^1\text{H}$  NMR spectra. In addition, these complexes and **7–9** formed from reactions of **1** and *p*-xylylenediamine, 4,4'-ethylenediamine and diethylenetriamine, respectively, all showed a single, weak absorption for NH at ca.  $3400\text{ cm}^{-1}$ . Peaks due to  $\text{NH}_2$  stretching frequencies were absent for these complexes, and this, combined with the relative integrals for NH and butadienyl in the  $^1\text{H}$  NMR spectra, indicated that dimeric complexes had been formed. The spectrum of **3** formed from *N,N'*-diethylenediamine exhibited no peaks for NH, and can also be identified as dimeric.

IR spectra of complexes **2** and **10** formed from reactions of **1** and 1,2-ethanediol and triethanolamine, respectively, exhibited no peaks in the region  $2500\text{--}3600\text{ cm}^{-1}$  due to uncomplexed hydroxyl groups, supporting dimeric and trimeric formulae, respectively. However, the hydroquinone product **5**, gave rise to a broad absorption at  $3364\text{ cm}^{-1}$  due to the unreacted OH group of this monomeric complex. The chloro (**11a**) and trifluoroacetate (**11b**) complexes derived from tris(2-aminoethyl)amine each gave rise to a single weak IR

absorption near  $3400\text{ cm}^{-1}$  which was assigned to stretching modes of the NH groups, and a peak of medium intensity at  $1693\text{ cm}^{-1}$  due to the trifluoroacetate ligand was also observed for **11b**. The absence of peaks due to  $\text{NH}_2$  groups in the IR spectra of **10** and **11**, together with the  $^1\text{H}$  NMR evidence for **11b** supported the presence of trimeric complexes.

Most of the complexes were of low solubility in common polar and chlorinated solvents, however,  $^1\text{H}$  NMR spectra of representative complexes were obtained for solutions recorded in dimethylsulphoxide- $d_6$ , and pertinent data are reported in Table 2. With the exception of complex **11b**, all spectra exhibited a pair of singlets near 1.90 ppm ( $\text{H}_{\text{anti}}$ ) and 3.85 ppm ( $\text{H}_{\text{syn}}$ ) attributable to the terminal methylene protons of the  $\eta^3$ -bonded species and two doublets near 5.85 ppm ( $\text{H}_{\text{anti}}$ ) and 6.30 ppm ( $\text{H}_{\text{syn}}$ ) for the double bond. The peak positions for the phenanthroline ring system were unexceptional, however, the methylene and aromatic groups of the C(2)-substituents in the butadienyl were shifted upfield due to the anisotropic effect of this ring system. Coupling constants for the four protons of the aromatic diamine complexes **6** and **8** were typical for values for  $^3J$  in *para*-substituted ring systems. It has been shown previously in conformational studies of alanine dipeptides of general formula  $\text{R}'\text{CONHCH}(\text{Me})\text{CONR}''\text{CH}(\text{Me})\text{CO}_2\text{Me}$  [11] that the vicinal proton coupling constants  $^3J(\text{NH}-\text{CH})$  can be correlated with the dihedral values  $\omega$  between planes H-N-C and N-C-H. Thus, for complex **7** containing the  $\text{NHCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}$  unit, coupling of two methy-

Table 2  
TNMR data for representative complexes **4–11b**<sup>a</sup>

	$\text{H}'_{\text{anti}}$	$\text{H}'_{\text{syn}}$	$\text{H}''_{\text{anti}}$	$\text{H}''_{\text{syn}}$	Aliphatic			Aromatic
					$\text{CH}_3$	$\text{CH}_2$	XH	
<b>4</b>	1.89 (s, H)	5.82 (d, 2.20, H)	3.76 (s, H)	6.29 (d, 2.20, H)	0.39 (d, 6.20, 3H)	2.28 (m, H), 2.66 (m, H)	1.23 (m, H) <sup>b</sup> 5.39 (br, H) <sup>c</sup> 5.87 (m, 2H) <sup>c</sup>	7.89 (m, 2H), 7.91 (s, 2H), 8.48 (m, 2H), 9.16 (m, 2H)
<b>6</b>	1.91 (s, H)	5.82 (d, 2.40, H)	3.80 (s, H)	6.30 (d, 2.40, H)				7.87 (m, 2H), 7.92 (s, 2H), 8.45 (m, 2H), 9.18 (m, 2H), 6.08 (d, 8.1, 2H), 6.61 (d, 8.1, 2H)
<b>7</b>	1.87 (s, 2H)	5.72 (d, 1.83, 2H)	3.83 (s, 2H)	6.28 (d, 1.83, 2H)		2.78 (m, 6.23, 2H)	6.42 (t, 5.87, 2H) <sup>c</sup>	7.93 (m, 8H), 8.65 (d, 2H), 8.78 (d, 2H) 9.08 (d, 2H), 9.24 (d, 2H) 5.76 (s, 2H), 6.34 (s, H)
<b>8</b>	1.95 (s, 2H)	5.85 (s, 2H)	3.97 (s, 2H)	6.51 (s, 2H)		1.14 (m, 2H)	5.76 (brs, 2H) <sup>c</sup>	7.83 (m, 8H), 8.42 (d, 2H), 8.67 (d, 2H), 9.17 (d, 2H), 9.28 (d, 2H), 6.04 (d, 8.06, 2H), 6.60 (d, 8.06, 2H)
<b>11b</b>	1.90 (s, 2H)	5.80 (s, 2H)	1.92 (s, 2H)	5.83 (s, H)		0.28 (m, 4H), 0.48 (m, H)	5.99 (t, 4.95, 2H) <sup>c</sup>	7.78–8.17 (m, 12H), 8.66 (d, 8.06, 2H), 8.78 (d, 8.06, H), 8.84 (d, 8.06, H), 8.95 (d, 8.06, 2H), 9.10 (d, 4.40, 2H), 9.17 (d, 4.76, H), 9.37 (d, 4.75, H), 9.42 (d, 4.48, 2H)
	4.14 (brs, 3H)	6.22 (s, 2H)	6.24 (s, H)			0.85 (m, H), 1.40 (m, 3H)	6.12 (t, 4.95, H) <sup>c</sup>	

<sup>a</sup>Spectra recorded as solutions in  $d_6$ -DMSO. Data reported in ppm, multiplicity, coupling constant (Hz), number of protons; <sup>b</sup>X = C; <sup>c</sup>X = N.

lene protons to NH gave constants of 5.8–6.9 Hz, in agreement with  $\omega$  values of 30–40°, the other coupling constants for 80–90° being very small or not observed.

A comparison of the integrals for peaks assigned to phenanthroline, terminal  $\eta^3$ -butadienyl protons and C(2)-substituents permitted identification of complexes as monomeric, dimeric or trimeric. For example, complex **7** formed from **1** and *p*-xylylenediamine gave rise to two doublets for  $H_{\text{anti}}$  and  $H_{\text{syn}}$  of the double bond at 5.72 and 6.28 ppm, which integrated for two protons each, three multiplets due to bridging methylene groups which integrated for a total of four protons, and two peaks at 6.34 and 5.76 ppm for the four protons of the bridging aromatic ring. Thus, two  $\eta^3$ -butadienyl groups per  $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$  unit were identified, supporting a dimeric formulation. In contrast, the spectrum of **6** exhibited doublets for the aromatic protons of the diamine which integrated for a total of four protons and doublets at 5.83 and 6.30 ppm for the double bond integrating for one proton each. Thus, only one butadienyl ligand was attached to the phenylenediamine unit in a monomeric complex. Peaks occurring between 5.3 and 6.4 ppm were assigned to NH protons by consideration of their multiplicity and integration, and supported the dimeric and monomeric formulae, respectively.

The complexes **10** and **11a** were too insoluble for  $^1\text{H}$  NMR spectra to be recorded. However, the latter was successfully converted to the more soluble trifluorocarboxylate derivative **11b** using Ag(I) ions, and data are given for this complex in Table 2. At ambient temperature, the proton NMR of **11b** showed two sets of resonances in intensity ratio 2:1 for both the aromatic rings and the butadienyl framework, indicating two identical and one unique magnetic environment for each group. This pattern was invariant up to 70°C, suggesting

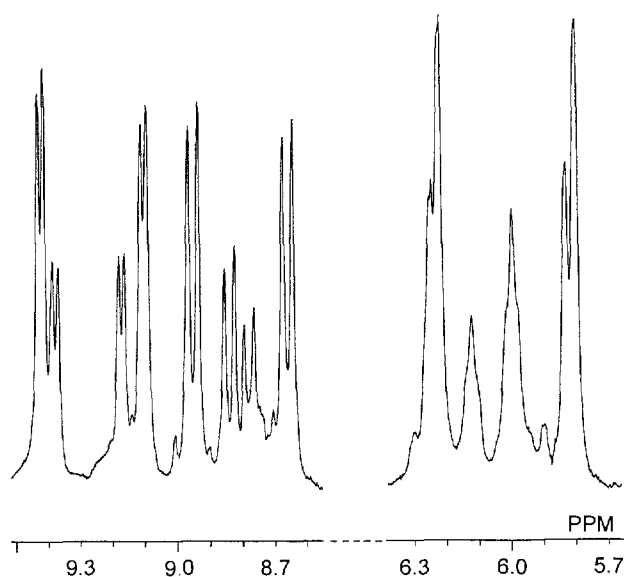


Fig. 1. Part of the  $^1\text{H}$  NMR spectrum of trimeric complex **11b**.

that the molecule was not dynamic. Signals for the bridging methylene protons were broad and could not be clearly resolved into two sets of signals, however phenanthroline, NH and terminal butadienyl protons all gave rise to the same 2:1 intensity pattern (Fig. 1). For example, four signals could be assigned to the double bonds of the butadienyl groups, with two singlets at 5.80 and 6.22 ppm (integrating for two protons each) and two singlets at 5.83 and 6.24 ppm, (integrating for one proton each) indicating three metal bound butadienyl ligands were present in two different magnetic environments. A series of multiplets with total integration for twelve protons and two broad triplets at 5.99 and 6.12 ppm of relative intensity 2:1 confirmed that the  $\text{N}(\text{CH}_2\text{CH}_2\text{NH})_3$  unit was present. Attempts to obtain crystals of this novel trimeric complex for X-ray analysis have proved unsuccessful to date.

### 3. Conclusion

The  $\eta^3\text{-CH}_2(\text{COCl})\text{C}=\text{CH}_2$  moiety has provided access to a variety of dimeric and trimeric complexes of molybdenum(II) containing 2-substituted butadienyl bridging ligands, and the required skeletal elements which permit formation of these complexes or monomeric species have been defined. Spectroscopic methods have proved useful in identifying the presence of unreacted amine groups in monomeric and dimeric complexes, and have indicated that there are two different magnetic environments for the three metal coordinated  $\eta^3$ -butadienyl units in the novel trimer. The relative orientations of the three metal species and pairs of C=O and carbon-carbon double bonds in **11b** await an X-ray diffraction study. Molecular modelling studies based on the crystal structure of  $[\text{Mo}(\text{Co})_2(\eta^3\text{-CH}_2(\text{CONHMe})\text{C}-\text{CH}_2)(\text{bipy})(\text{O}_2\text{CC}_3\text{F}_7)]$  [10] suggest that complex **1** has significant potential to form more extensive polymeric forms, and the synthetic versatility of the chlorocarbonyl butadienyl ligand is currently under further investigation.

### 4. Experimental details

The starting material  $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2(\text{COCl})\text{C}=\text{CH}_2)\text{phen}]$  (phen = 1,10-phenanthroline) (**1**) was freshly prepared according to the literature procedure [8] and recrystallised from dichloromethane-petrol mixtures prior to use. All other chemicals were purchased from Aldrich Chemical and used without further purification. Solvents and liquid reagents were dried over molecular sieve 4A and thoroughly degassed by dinitrogen prior to use. All reactions were carried out at ambient temperature under an atmosphere of dinitrogen. Infrared spectra were recorded

on a Perkin-Elmer 781 spectrometer as paraffin mulls, and  $^1\text{H}$  NMR spectra were obtained using a JEOL GX 270 MHz FT instrument, with samples dissolved in  $d_6$ -dimethylsulphoxide and tetramethylsilane used as an internal standard.

#### 4.1. Preparation of dimeric complexes **2**, **3**, **7** and **8**

For complexes **3**, **7** and **8**, excess triethylamine (0.21  $\text{cm}^3$ , 1.5 mmol) was added to a stirred solution of **1** (0.48 g, 1.0 mmol) in dichloromethane (50  $\text{cm}^3$ ) at ambient temperature, and a solution of *N,N'*-diethylethylenediamine, *p*-xylylenediamine or 4,4'-ethylenediamine (0.5 mmol), respectively, in dichloromethane (10  $\text{cm}^3$ ) was added dropwise to the mixture. After a period of 2.5 h, the crude product was filtered off as an orange powder, recrystallised from dichloromethane–petrol mixtures, washed with petrol and finally dried in vacuo. Complex **2** was prepared by a similar method using 1,2-ethanediol, but omitting triethylamine from the reaction mixture.

#### 4.2. Preparation of monomeric complexes **4**, **5** and **6**

Dropwise addition of a solution of 1,2-propanediamine, anthroquinone or phenylenediamine (0.5 mmol) in dichloromethane to a stirred solution of **1** (0.48 g, 1.0 mmol) in dichloromethane (50  $\text{cm}^3$ ) gave the products as red (ester) or orange (amide) powders. For reactions of **1** with diamines only, an excess of triethylamine (0.21  $\text{cm}^3$ , 1.5 mmol) was present prior to amine addition. The products were washed with cold dichloromethane, petrol and dried in vacuo.

#### 4.3. Preparation of complex **9** from diethylenetriamine

A solution of **1** (1.0 mmol) in dichloromethane (50  $\text{cm}^3$ ) was stirred with excess triethylamine (0.5  $\text{cm}^3$ ). To this was added dropwise diethylenetriamine (0.33 mmol), and the mixture stirred for 2 h. The product was formed as an insoluble orange precipitate which was filtered from solution, washed with minimum cold dichloromethane, petrol and finally dried in vacuo. The yield was improved by addition of petrol to the liquor and cooling to  $-5^\circ\text{C}$  overnight.

#### 4.4. Preparation of trimeric complex **10**

Triethanolamine (0.0746 g, 0.5 mmol) in dichloromethane (1.0  $\text{cm}^3$ ) was added dropwise to a solution of **1** (0.749 g, 1.55 mmol) in dichloromethane (75  $\text{cm}^3$ ), and the mixture stirred for 3 h. After filtering, addition of petrol to the orange-brown liquor and storage at  $-5^\circ\text{C}$  gave the orange product. This was washed first with minimum dichloromethane to remove any unreacted **1**, then with petrol and finally dried in vacuo.

#### 4.5. Preparation of trimeric chloro complex **11a** and its trifluoroacetate derivative **11b**

Triethylamine (0.21  $\text{cm}^3$ , 1.5 mmol) was added to a stirred solution of **1** (0.749 g, 1.55 mmol) in dichloromethane (75  $\text{cm}^3$ ). To this was added dropwise tris(2-aminoethyl)amine (0.5 mmol, 0.076  $\text{cm}^3$ ) in dichloromethane (1.0  $\text{cm}^3$ ), and the reaction mixture stirred for 2.5 h. A dark red solution was produced, containing no solids on filtration. Petrol was added to the solution, and on storage at low temperature, **11a** precipitated as dark red microcrystals. These were filtered from solution, washed with minimum cold dichloromethane, petrol and finally recrystallised from dichloromethane–petrol mixtures. The trifluoroacetate complex was prepared by stirring **11a** (0.393 g, 0.25 mmol) in acetone (150  $\text{cm}^3$ ) with excess sodium trifluoroacetate (0.15 g, 1.1 mmol), and adding dropwise a solution of silver tetrafluoroborate in acetone (0.146 g, 0.75 mmol in 10  $\text{cm}^3$  prepared under dinitrogen in a dry glove box). After 3 h, insoluble silver chloride was filtered from the mixture, and the solvent was removed in vacuo. The residue was extracted with dichloromethane ( $4 \times 5 \text{ cm}^3$ ), and the orange solution filtered and dropped into excess petrol with stirring. The crude trifluoroacetate product **11b** was recrystallised from dichloromethane–petrol mixtures at low temperature.

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