

Synthesis and reactivity of organochalogen ester substituted η^3 -butadienyl complexes of Mo(II): crystal structure of $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COSePh})\text{C}=\text{CH}_2)(1,10\text{-phenanthroline})] \cdot 0.5 \text{CH}_2\text{Cl}_2$

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Abstract

A series of organochalogen ester substituted η^3 -butadienyl complexes of the type $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COXR})\text{C}=\text{CH}_2)(\text{phen})]_n$ (phen = 1,10-phenanthroline, R = alkyl, aryl) were prepared from the acyl chloride precursor (**1**) and either thiols (X = S, $n = 1-4$), selenols (X = Se, $n = 1,2$) or bis(organochalogen) mercurials, $\text{Hg}[\text{XR}]_2$ (X = Se, Te, $n = 1,2$), and the structure of the first selenoester substituted η^3 -butadienyl complex (**4**) was determined by a single-crystal X-ray diffraction analysis. Reactions of various nucleophiles or electrophiles with **1**, **4** or the ester substituted complex, XR = OMe, were examined, and compared to those of related η^3 -allyl analogues and to their predicted behaviour based upon the structural evidence and molecular modelling calculations.

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1. Introduction

In view of the recent recognition that (1,2,3- η)-*trans*-butadienyl metal complexes may occur as key intermediates in certain synthetic procedures [1], there is a need to further understand the chemical behaviour of this type of ligand. We have been investigating the formation of complexes of general formula $[\text{MY}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COXR})\text{C}=\text{CH}_2)(\text{L}_2)]$ (M = Mo, W; $\text{L}_2 = 2,2'$ -bipyridyl, 1,10-phenanthroline; Y = Cl) from reactions of $\text{Ph}_4\text{P}[\text{MCl}(\text{CO})_3\text{L}_2]$ and 1,4-dichloro-2-butyne in chlorinated solvents (XR = Cl) or methanol (XR = OMe), and have prepared and characterised derivatives containing amide or thioester 2-butadienyl substituents [2–5]. Although the general reaction chemistry of these complexes has not yet been explored, the author and others have used the X-ray diffraction

data obtained for $[\text{Mo}(\text{O}_2\text{CC}_3\text{F}_7)(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{CONHMe})\text{C}=\text{CH}_2)(\text{bipy})]$ (bipy = 2,2'-bipyridine) to carry out calculations using the standard extended Hückel molecular orbital (EHMO) method, and to predict the probable sites of nucleophilic or electrophilic attack within the η^3 -butadienyl unit [6]. In principle, isomeric forms of these complexes are possible, involving either *E/Z*-conformations of the two-substituent and butadienyl double bond or rotation of bidentate L_2 and ligand Y at the metal relative to the carbonyl groups and butadienyl fragment. In view of the known synthetic utility of organochalogen esters of general type $\text{R}'\text{COXR}$ (X = O, S, Se, Te; R', R = alkyl, aryl) [7], and our wish to test these predictions experimentally, we herein report the formation of a series of new mono- and polymeric chalcogenoester substituted butadienyl complexes, using organomercurials as a new synthetic route, present the crystal structure of the first selenoester substituted η^3 -bonded butadienyl complex and describe the first reactivity study of acyl chloride, ester and selenoester substituted butadienyl complexes.

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2. Experimental

2.1. General

Except where indicated, all reactions were carried out under dinitrogen at room temperature (r.t.) using degassed solvents and liquid reagents previously dried over molecular sieves to prevent oxidation of the thiol- and selenium-containing products. The acyl chloride (**1**) and ester (**11**) substituted butadienyl complexes were freshly prepared from $\text{Ph}_4\text{P}[\text{MoCl}(\text{CO})_3(\text{phen})]$ according to the published methods [2], and were recrystallised from CH_2Cl_2 -petrol mixtures before use. Infrared spectra were recorded on a Perkin Elmer 781 spectrometer using samples prepared as nujol mulls on sodium chloride discs. The $^1\text{H-NMR}$ spectra were recorded at 300 MHz, with solutions in dichloromethane- d_2 or dimethylsulphoxide- d_6 and referenced to tetramethylsilane as internal standard. The trithiol $\text{MeC}(\text{CH}_2\text{SH})_3$ was synthesised from the commercially available triol via the tritosyl and trithiocyanate precursors [8]. The selenols $\text{PhC}(\text{H})\text{MeSeH}$ and $\text{HSe}(\text{CH}_2)_4\text{SeH}$ were obtained by reduction of the appropriate selenocyanates [9], and the bis(organochalcogenyl)mercury complexes $\text{Hg}[\text{XR}]_2$ were prepared [10] from reactions of mercury(II) chloride and the diorganodichalcogenides, $[\text{XR}]_2$. Phenyl trimethylsilyl selenide was prepared by the literature method [11]. Other chemicals were purchased from commercial sources and used without further purification.

2.2. Preparation of $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COSCH}_2\text{CO}_2\text{Me})\text{C}=\text{CH}_2)(\text{phen})]$ and $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COSCH}_2\text{Ph})\text{C}=\text{CH}_2)(\text{phen})]$

Excess triethylamine (0.2 cm^3) and complex **1** (0.483 g, 1.0 mmol) were stirred in dichloromethane (50 cm^3), and to this mixture methyl thioglycolate (0.2 cm^3 , 2.24 mmol) or benzyl mercaptan (0.12 cm^3 , 1.02 mmol) was added dropwise. The orange solution darkened on addition, and after stirring for two hours, the filtered solution was mixed with petrol (25 cm^3) and stored overnight at low temperature. The title compounds **2** and **3** were isolated as orange–red microcrystals that were recrystallised from CH_2Cl_2 -petrol mixtures. Yields = 55–65%.

2.3. Preparation of $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COSePh})\text{C}=\text{CH}_2)(\text{phen})]$ and $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COSeCMe}(\text{H})\text{Ph})\text{C}=\text{CH}_2)(\text{phen})]$

Method a: to a stirred mixture of **1** (0.483 g, 1.0 mmol) and excess triethylamine (0.5 cm^3) in CH_2Cl_2 (50 cm^3) was added benzeneselenol or 1-ethylbenzeneselenol

(1.09 mmol). After 4 h, petrol was added to the filtered solution, and storage at low temperature precipitated the yellow–orange products. Method b: the conditions adopted by Silveira et al. for reaction of $\text{Hg}[\text{SePh}]_2$ or $\text{Hg}[\text{SeCMe}(\text{H})\text{Ph}]_2$ with various acyl chlorides were adapted for use as follows. To a stirred suspension of the appropriate organochalcogen mercurial (1 mmol) and *n*-tetrabutylammonium bromide (0.0129 g, 0.04 mmol) in CH_2Cl_2 (5 cm^3) was added a solution of **1** (0.483 g, 1 mmol) in the same solvent (50 cm^3), and the mixture was stirred for 5 h. After filtration, the solvent was removed under high vacuum. For both a and b the crude solids were finally recrystallised from CH_2Cl_2 -petrol mixtures to give the title compounds **4** or **5**. Yields of each method were similar, and in the range 68–71%. The dark red tellurium analogue of **4** was prepared from $\text{Hg}[\text{TePh}]_2$ using method b and a reaction time of 2 h only.

2.4. Structure determination of $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COSePh})\text{C}=\text{CH}_2)(\text{phen})] \cdot 0.5 \text{CH}_2\text{Cl}_2$

Crystals of complex **4** were grown from a CH_2Cl_2 -petrol mixture. Data were collected on a Siemens P4 diffractometer and experimental details from the structure determination are given in Table 4. Data were corrected for Lorentz and polarisation effects, and for absorption using *R*-scans. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXTL-PLUS) [12]. Hydrogen atoms of the η^3 -butadienyl group were directly located and all other hydrogen atoms except those on the disordered dichloromethane solvate molecule were included at calculated positions. Anisotropic displacement parameters were assigned to all full occupancy non-hydrogen atoms.

2.5. Preparation of $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COSCH}_2\text{CO}_2\text{CH}_2)\text{C}=\text{CH}_2)(\text{phen})]_2$, $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COSCH}_2\text{C}_3\text{H}_7)\text{C}=\text{CH}_2)(\text{phen})]_2$ and $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COSe}(\text{CH}_2)_2)\text{C}=\text{CH}_2)(\text{phen})]_2$

A solution of complex **1** (0.483 g, 1.00 mmol) in dichloromethane (50 cm^3) was stirred with excess triethylamine (0.5 cm^3). To this was added dropwise a solution of the appropriate dithiol or diselenol (0.5 mmol) in dichloromethane (5 cm^3), and the reaction mixture was stirred for 2 h. After storage at low temperature, the products were filtered from solution, recrystallised from CH_2Cl_2 -petrol mixtures and dried under vacuum to give complexes **6–8**. Yields = 47–64%.

2.6. Preparation of [$\{MoCl(CO)_2(\eta^3-CH_2C(COSCH_2)C=CH_2)(phen)\}_3CMe$] and of [$\{MoCl(CO)_2(\eta^3-CH_2C(COSCH_2CO_2CH_2)C=CH_2)(phen)\}_4C$]

Excess triethylamine (0.21 cm³, 1.5 mmol) was added to a stirred solution of **1** (0.386 g, 0.8 mmol) in dichloromethane (80 cm³) at r.t., and to this was added either 1,1,1-tris(mercaptomethyl)ethane (0.042 g, 0.25 mmol) in dichloromethane (80 cm³) or 1.0 cm³ of a solution of pentaerythritol tetrakis(2-mercaptoacetate) (2.5 mmol) in CH₂Cl₂ (10 cm³). The mixture was stirred for 3 h. The filtered, orange product was washed first with minimum, cold CH₂Cl₂ to remove any unreacted **1**, and then recrystallised as given in 2.5 to give complexes **9** or **10**. Yields = 56 and 46%.

2.7. Preparation of [$\{Mo(CO)_2(\eta^3-CH_2C(CO_2Me)C=CH_2)(phen)\}_2(\mu-Cl)^+$]

Silver tetrafluoroborate (0.049 g, 0.25 mmol) was added to a stirred, saturated solution of complex **11** (0.239 g, 0.5 mmol) in dichloromethane (20 cm³). After 20 min the mixture was filtered, petrol was added, and the mixture was stored for 48 h at low temperature to give the product **12** as a red microcrystalline solid. Yield = 51%.

2.8. Preparation of [$\{Mo(NCMe)(CO)_2(\eta^3-CH_2C(CO_2Me)C=CH_2)(phen)\}^+$] and [$\{Mo(acetone)(CO)_2(\eta^3-CH_2C(CO_2Me)C=CH_2)(phen)\}^+$]

A suspension of **11** (0.359 g, 0.75 mmol) in acetonitrile or acetone (80 cm³) was stirred with silver tetrafluoroborate (0.156 g, 0.8 mmol) for 30 min. After filtration of the mixture, the solvent was removed under vacuum and an orange–red solid (**13**, **14**) was isolated in quantitative yield.

2.9. Preparation of [$Mo(O_2CC_3F_7)(CO)_2(\eta^3-CH_2C(CO_2Me)C=CH_2)(phen)$]

Method a: a freshly prepared sample of **14** in acetone was filtered into a stirred solution of excess sodium heptafluorobutyrate (0.709 g, 3.0 mmol) in acetone (75 cm³) and the mixture was stirred for 1 h. The solvent was removed under vacuum, and the residue was recrystallised from acetone–petrol to yield **15** as orange–red crystals. Method b: to a stirred suspension of **11** (0.479 g, 1.0 mmol) and NaO₂CC₃F₇ (0.400 g, 1.69 mmol) in acetone (100 cm³) was added dropwise a solution of AgBF₄ (0.200 g, 1.03 mmol) in acetone (10 cm³). 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 tempera-

ture. Samples of **15** produced by methods a and b gave identical IR and NMR spectra and yields in the range 43–58%.

2.10. Preparation of [$\{Mo(pyridine)(CO)_2(\eta^3-CH_2C(CO_2Me)C=CH_2)(phen)\}^+$]

Method a: excess pyridine (2.5 mmol, 0.1 cm³) was added to a suspension of freshly prepared **11** (0.239 g, 0.5 mmol) in acetone (75 cm³), and to this a solution of AgBF₄ (0.100 g, 0.5 mmol) in acetone (15 cm³) was added dropwise. The mixture was stirred for 6 h, filtered and the liquor stored with petrol. Orange–red crystals of the product precipitated at low temperature, and were recrystallised from CH₂Cl₂–petrol mixtures. Method b: a solution of **12** (0.504 g, 0.5 mmol) in acetone (100 cm³) was stirred with excess pyridine for 2 h. The volume was reduced under vacuum, and addition of petrol to the filtered solution and cooling gave the title complex. Samples of **16** produced by methods a and b gave identical IR and NMR spectra and yields in the range 32–55%.

2.11. Preparation of [$MoCl(CO)_2(\eta^3-CH_2C(CO_2Me)C(SePh)Me)(phen)$] or [$MoCl(CO)_2(\eta^3-CH_2C(COSePh)C(SePh)Me)(phen)$]

To complex **1** or **4** (0.5 mmol) in a mix of dichloromethane (25 cm³) and methanol (5 cm³) was added PhSeSiMe₃ (0.227 g, 1.0 mmol), and the mixture was stirred at r.t. for 2 h. Chromatography on silica gel using the same solvent mix gave the products **18** and **19**, respectively.

2.12. Reactions of **4** and methanol in the presence of CuCl₂ or HgCl₂

A solution of **4** (0.182 g, 0.3 mmol) in acetone (50 cm³) and methanol (10 cm³) was stirred with excess triethylamine (0.07 cm³, 0.5 mmol) and cooled over ice. To this mixture, a solution of copper(II) chloride or mercury(II) chloride (0.3 mmol) in acetone (70 cm³) was added dropwise over 0.5 h. After a further 1.5 h at ambient temperature, excess solvent was removed under vacuum, and the filtered solution gave the ester substituted complex **11** in 83 and 58% yield, respectively.

2.13. Reaction of **4** with CuCl₂ and *n*-propylamine

Excess *n*-propylamine (0.1 cm³) was stirred with a solution of complex **4** (0.0385 g, 0.06 mmol) in acetone (20 cm³), and the mixture was cooled over ice. To this, copper(II) chloride (0.008 g, 0.06 mmol) in acetone (30 cm³) was added over 0.5 h. After stirring at r.t. for a further 1.5 h, excess solvent was removed under reduced

pressure to give the amide substituted butadienyl complex in 70% yield.

3. Results and discussion

3.1. Preparation and spectroscopic characterisation of η^3 -butadienyl complexes

Addition of excess methyl thioglycolate, benzyl mercaptan, benzeneselenol or 1-ethylbenzeneselenol (RXH) to a basic solution of the complex $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COCl})\text{C}=\text{CH}_2)(\text{phen})]$ (**1**) in chlorinated solvents gave rise to a series of orange–red products **2–5**. These were identified from their elemental analyses and infrared and NMR spectra (Tables 1 and 2) as thioester or selenoester two-substituted butadienyl complexes of the type $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COXR})\text{C}=\text{CH}_2)(\text{phen})]$ (Scheme 1). The selenoester complexes **4** and **5** were also obtained by a second method. Silveira and co-workers have shown that organic acyl chlorides $\text{R}'\text{COCl}$ can be converted to the corresponding thioester, selenoester or telluroester $\text{R}'\text{COXR}$ by reaction with bis(organochalcogenyl)mercury complexes $\text{Hg}[\text{XR}]_2$ in the presence of catalytic amounts of tetraalkylammonium salts [10]. Following their general methodology, $\text{Hg}[\text{SePh}]_2$ and $\text{Hg}[\text{SeMe}(\text{H})\text{Ph}]_2$ were prepared by reaction of either diphenyldiselenide and elemental mercury or the appropriate selenol and mercury(II) chloride. On reaction with complex **1** in the presence of $n\text{-Bu}_4\text{NBr}$, these mercurials gave rise to the butadienyl complexes **4** and **5** in good yield. (The tellurium

analogue of complex **4** could be prepared in a similar manner from $\text{Hg}[\text{TePh}]_2$, but proved highly unstable in air.) Addition of a solution of ethylene glycol bithioglycolate, 1,4-benzenedimethanethiol or 1,4-propanedimethanethiol to a solution of **1** in exactly 1:2 mole ratio under basic reaction conditions afforded dimeric complexes **6–8**, respectively, having general formula $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COXR})\text{C}=\text{CH}_2)(\text{phen})]_2$. The trimeric complex **9** and tetrameric **10** were prepared and characterised in a similar manner by a combination of appropriate ratios of complex **1** and either 1,1,1-tris(2-mercaptopmethyl)ethane (3:1) or pentaerythritol tetrakis(2-mercaptoacetate) (4:1). Solid samples of the thioester and selenoester complexes were stable in air for several days. However prolonged storage of the latter in moist air or oxygenated solvents led to the production of non-carbonyl-containing metal species and the corresponding diselenides.

The infrared spectra of all the complexes showed a pair of strong IR absorptions between 1893 and 1981 cm^{-1} which were typical of a metal-*cis*-dicarbonyl unit, and a band of medium intensity near 1930 or 1950 cm^{-1} arose from the carbonyl of the thioester or selenoester respectively. The influence of chalcogen, X, on the position of this latter band for various compounds of the type $\text{R}'\text{COXR}$ (R' , R = alkyl, aryl) has been investigated by Renson and Draguet [13], and these results conform to their findings. An additional peak near 1740 cm^{-1} was also observed for complexes **2**, **6** and **10**, and this arose from the C=O stretching mode of the ester butadienyl substituent. Weak absorptions at about 1675 cm^{-1} due to the vinylic double bond could

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

No.	Butadienyl substituent, COXR	Y	Infrared data ^a			Analysis, found (calculated) (%)		
			$\nu(\text{C}\equiv\text{O})$	$\nu(\text{CO}_2)$	$\nu(\text{C}=\text{O})$	C	H	N
2	$\text{COSCH}_2\text{CO}_2\text{Me}$	Cl	1893, 1970	1735	1637	47.70 (47.78)	2.90 (3.07)	4.93 (5.06)
3	COSCH_2Ph	Cl	1899, 1971	–	1630	54.26 (54.68)	3.31 (3.33)	4.88 (4.90)
4	COSePh	Cl	1897, 1975	–	1650	47.21 (47.37)	2.72 (2.78)	4.37 (4.33) ^c
5	$\text{COSeCMe}(\text{H})\text{Ph}$	Cl	1889, 1969	–	1623	48.59 (48.96)	2.98 (3.26)	3.97 (4.15) ^c
6	$[\text{COSCH}_2\text{CO}_2\text{CH}_2]_2$	Cl	1901, 1977	1752	1631	45.36 (45.45)	3.16 (2.86)	4.93 (4.71) ^b
7	$[\text{COSCH}_2\text{C}_3\text{H}_7]_2$	Cl	1893, 1966	–	1627	46.84 (46.71)	2.62 (2.91)	4.50 (4.54)
8	$[\text{COSe}(\text{CH}_2)_2]_2$	Cl	1884, 1966	–	1625	43.01 (43.22)	2.63 (2.85)	4.58 (4.69) ^b
9	$[\text{COSCH}_2]_3\text{CMe}$	Cl	1906, 1981	–	1628	47.26 (47.47)	2.98 (2.95)	5.02 (5.27) ^b
10	$[\text{COSCH}_2\text{CO}_2\text{CH}_2]_4\text{C}$	Cl	1904, 1979	1741	1640	46.40 (46.89)	2.97 (2.86)	4.62 (4.86) ^b
11	CO_2Me	Cl	1894, 1972	1690	–	49.90 (50.10)	3.20 (3.13)	5.60 (5.85)
12	CO_2Me	Cl ^d	1905, 1984	1698	–	47.27 (47.59)	2.77 (2.97)	5.07 (5.55)
13	CO_2Me	MeCN	1869, 1951	1681	–	–	– ^e	–
14	CO_2Me	Acetone	1885, 1960	1690	–	–	– ^e	–
15	CO_2Me	$\text{O}_2\text{CC}_3\text{F}_7$	1860, 1964	1699	1642	44.15 (43.90)	1.89 (2.28)	4.47 (4.26)
16	CO_2Me	Pyridine	1867, 1949	1692	–	47.18 (47.04)	3.60 (3.07)	6.95 (6.45) ^c

^a As nujol mulls, cm^{-1} .

^b CH_2Cl_2 calculated.

^c 0.5 CH_2Cl_2 calculated.

^d Bridging atom.

^e Highly unstable.

Table 2
¹H-NMR data for selected complexes 2–10^a

No.	H _{anti} ['] , H _{syn} [']	H _{anti} ^{''} , H _{syn} ^{''}	Aliphatic	Aromatic
2 ^b	1.95 (s, H), 3.75 (s, H)	5.83 (d, 2.38, H), 6.38 (d, 2.38, H)	2.28 (m, 2H), 3.46 (s, 3H)	7.97 (m, 2H), 8.04 (s, 2H), 8.65 (m, 2H), 9.14 (d, 5.13, H), 9.20 (m, 5.13, H)
3	1.97 (s, H), 3.76 (s, H)	5.80 (d, 2.38, H), 6.35 (d, 2.38, H)	2.56 (d, 3.55, H), 2.96 (d, 3.55, H)	6.59 (m, 2H), 7.11 (m, 3H), 7.87 (m, 4H), 8.36 (d, 8.24, H), 8.51 (d, 8.24, H), 9.10 (d, 4.94, H), 9.17 (d, 5.13, H)
4	1.97 (s, H), 3.76 (s, H)	5.92 (d, 2.55, H), 6.44 (d, 2.55, H)		6.97 (m, 2H), 7.14 (m, 3H), 8.05 (m, H), 8.17 (m, H), 8.25 (m, 2H), 8.87 (m, 2H), 9.27 (d, 4.78, H), 9.32 (d, 4.78, H)
5	1.88 (s, H), 1.91 (s, H), 3.82 (s, H), 3.85 (s, H)	5.78 (d, 2.19, H), 5.80 (d, 2.22, H), 6.28 (d, 2.22, H), 6.33 (d, 2.19, H)	0.46 (d, 7.15, 6H), 3.24 (m, 2H)	6.58 (m, 2H), 6.86 (m, 2H), 7.10 (m, 2H), 7.12 (m, 2H), 7.18 (m, H), 7.73 (m, H), 7.85 (m, 2H), 8.00 (m, H), 8.13 (m, 4H), 8.23 (s, H), 8.25 (s, H), 8.45 (m, H), 8.85 (m, 2H), 9.12 (m, H), 9.27 (d, 5.22, H), 9.38 (d, 4.95, H)
6	1.98 (s, 2H), 3.72 (s, 2H)	5.86 (d, 2.00, 2H), 6.41 (d, 2.00, 2H)	0.85 (m, 4H), 2.16 (m, 2H), 2.35 (m, 2H)	7.91 (m, 8H), 8.48 (m, 4H), 9.14 (m, 4H)
7 (1, 4)	1.97 (s, 2H), 3.83 (s, 2H)	5.78 (d, 2.38, 2H), 6.28 (d, 2.38, 2H)	2.48 (m, 2H), 2.88 (m, 2H)	6.34 (m, 2H), 6.76 (m, 2H), 7.98 (m, 8H), 8.56 (d, 8.20, 2H), 8.78 (d, 8.20, 2H), 9.08 (d, 5.07, 2H), 9.29 (d, 5.13, 2H)
7a (1, 2)	1.95 (s, 2H), 3.80 (s, 2H)	5.83 (d, 2.38, 2H), 6.29 (d, 2.38, 2H)	2.07 (d, 13.55, 2H), 2.41 (d, 13.57, 2H)	6.29 (m, 2H), 6.94 (m, 2H), 8.00 (m, 4H), 8.05 (s, 4H), 8.64 (d, 8.24, 2H), 8.77 (d, 8.24, 2H), 9.13 (d, 5.13, 2H), 9.30 (d, 4.95, 2H)
8	1.99 (s, 2H), 3.67 (s, 2H)	5.39 (d, 2.49, 2H), 5.90 (d, 2.19, 2H)	1.88 (m, 4H), 3.42 (m, 4H)	7.50 (m, 4H), 7.68 (s, 4H), 8.13 (d, 1.65, 2H), 8.16 (d, 1.92, 2H), 9.03 (d, 1.92, 2H), 9.04 (d, 1.65, 2H)
10	1.96 (s, 4H), 3.63 (s, 4H)	5.83 (m, 4H), 6.36 (m, 4H)	2.06 (m, 8H), 3.54 (m, 8H)	7.85 (m, 16H), 8.39 (m, 8H), 9.10 (m, 8H)

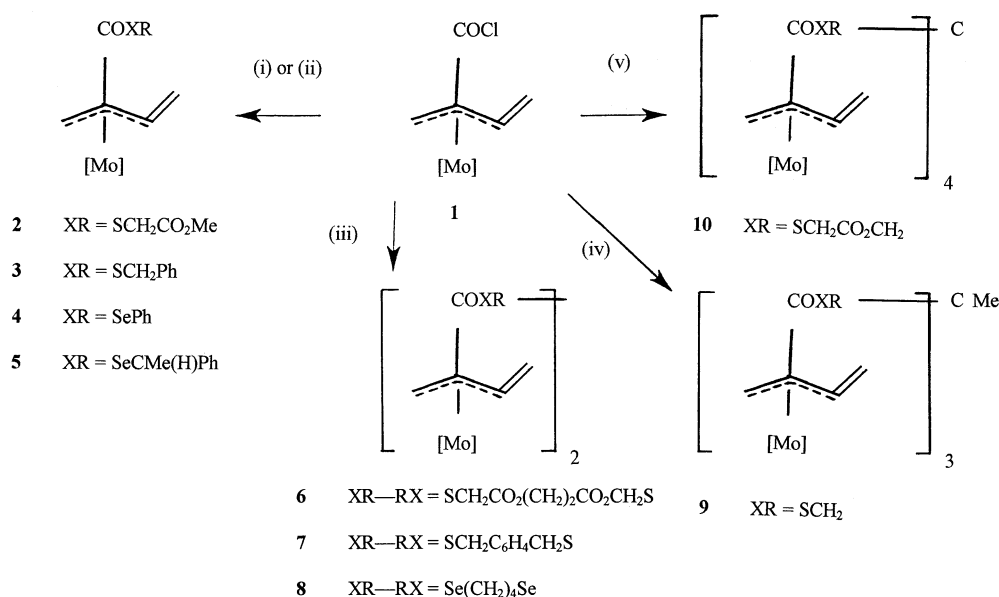
^a Spectra recorded as solutions in dimethylsulphoxide-*d*₆ unless otherwise stated. Data reported in ppm, multiplicity, coupling constant (Hz), number of protons.

^b Run in dichloromethane-*d*₂.

be identified for some complexes. For the polymeric complexes 6–10, absorptions for $\nu(\text{SH})$ and $\nu(\text{SeH})$ near 2100 and 2500 cm^{-1} , respectively were absent, and there was no evidence to support the presence of monomeric complexes containing pendant chalcogenol substituents.

The low solubilities of the new complexes in common organic solvents precluded measurement of good quality

¹³C-NMR spectra, however detailed ¹H-NMR spectra were obtained for complexes 2–8 and 10. For the monomeric complexes 2–4, the terminal methylene protons of the butadienyl gave rise to two doublets between 5.78 and 6.44 ppm, with coupling constants of 2.38 or 2.55 Hz, and the allylic protons of the butadienyl produced two singlets near 1.97 and 3.76 ppm. Only the



Scheme 1. Conditions: [Mo] = MoCl(CO)₂(phen) (i) excess RXH; (ii) Hg[XR]₂/Bu₄NCl; (iii) HXR₂XH and **1** in 1:2 mole ratio; (iv) [HXR]₃CMe and **1** in 1:3 mole ratio; (v) [HXR]₄C and **1** in 1:4 mole ratio.

spectrum of complex **5** exhibited two sets of NMR signals of approximately equal intensity across the range 0–10 ppm. Reactions of achiral thiols and selenols with the enantiomeric pair of compound **1** yielded products in which the butadienyl substituents existed in similar magnetic environments, and isomeric forms of **2–4** could not therefore be readily differentiated from their $^1\text{H-NMR}$ spectra. However, a racemic mixture of either PhC(H)MeSeH or $[\text{PhC(H)MeSe}]_2\text{Hg}$ in the synthesis of complex **5** led to the production of four isomers, and since enantiomeric relationships existed between two sets of pairs, two sets of NMR signals were observed within the spectrum.

A comparison of the integrations for $^1\text{H-NMR}$ signals arising from the bridging methylene and aromatic groups of the butadienyl substituent with those due to phen and terminal butadienyl protons within the complexes **6–8** supported a dimeric formula. For example, the spectrum of **7** contained two multiplets arising from the bridging methylene protons of the $\text{SCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{S}$ unit at 2.48 and 2.88 ppm and two multiplets at 6.34 and 6.76 ppm due to this aromatic group. Each of these signals, and the allylic singlets at 1.97 and 3.83 ppm, integrated for two protons, in keeping with two butadienyl groups per bridging unit. To assess whether the structure of the dithioester bridge could control monomer or dimer formation, reactions of complex **1** with 1,2- or 1,4-benzenedimethanethiol in 2:1 mole ratio were compared. The IR spectra and elemental data for these products (complexes **7a** and **7**, respectively) were similar, and only the latter is therefore given in Table 1. The proton NMR data for both **7a** and **7** are presented in Table 2. The spectra were consistent with dimeric species in each case, and therefore the proximity of two thiol functionalities in the 1,2-dithiol did not appear to impose undue steric restriction on linkage of two substituted butadienyl units. It is possible that flexibility, conferred by the methylene groups of the dithiol, had permitted the aromatic linkage to orientate away from the two approaching metal–butadienyl units. Complex **9** proved too insoluble to characterise by NMR spectroscopy, however the IR and microanalytical data are in accord with a trimeric formula. Integration of NMR signals arising from the phenanthroline and butadienyl ligands in complex **10** showed four metal–butadienyl centres were associated with the tetrathioester unit, and elemental microanalysis supported a tetrameric formula. Repeated attempts to grow crystals of the polymeric complexes **6–10** suitable for an X-ray diffraction analysis were unsuccessful. However, a solid-state crystal structure determination of the monomeric, selenoester complex **4** was carried out, both to determine the stereochemistry of the unusual η^3 -butadienyl ligand and to assist in predicting the reactivity of this organic fragment.

3.2. Crystal structure determination of **4**

A view of the molecule and the atomic labelling scheme used are shown in Fig. 1. Crystal data for complex **4** are given in Table 3, and important interatomic parameters are given in Table 4. In accord with the microanalytical data, each pair of molecules of **4** was associated with one molecule of dichloromethane. The central molybdenum atom can be described as hepta-coordinate, being bonded to two carbonyl groups [Mo–C(21) 1.957(10) Å; Mo–C(22) 1.978(10) Å], two nitrogens of 1,10-phenanthroline [Mo–N(1) 2.230(7) Å; Mo–N(2) 2.216(7) Å], a chlorine atom [Mo–Cl 2.479(2) Å] and a bidentate, two-substituted butadienyl unit $\text{C}_{11}\text{H}_9\text{OSe}$. The metal–carbon and C–O carbonyl bond lengths [C(21)–O(21) 1.161(11) Å; C(22)–O(22) 1.133(11) Å] and angles [Mo–C(21)–O(21) 179.4(10)°; Mo–C(22)–O(22) 174.9(10)°; C(21)–Mo–C(22) 80.5(4)°] are typical of a pair of mutually cis carbonyl groups. The rings of the phenanthroline unit are approximately planar within experimental error, and the bond lengths and angles are unexceptional. The metal–butadienyl unit contains C(1)–C(2)–C(3) separations of 1.431(12) and 1.418(12) Å, a C(1)–C(2)–C(3) angle of 112.5(7)° and Mo–C(1) and Mo–C(2) distances of 2.300(9) and 2.228(8) Å, respectively. Whilst these results are typical of parameters found in related two-substituted η^3 -allyl complexes of molybdenum [14], the Mo–C(3) distance of 2.208(9) Å is noticeably shorter than that normally observed between molybdenum and the terminus of an allyl system. (The fourth carbon atom C(4) of the butadienyl system is considered non-bonded to the metal centre.) A short bond between the metal and quaternary carbon C(3) has been observed before in substituted (1,2,3- η)-*trans*-butadienyl complexes [15], and this carbon typically resonates at an unusually low field in the $^{13}\text{C-NMR}$ spectrum. The observed range for this signal extends from 240 ppm, for complexes

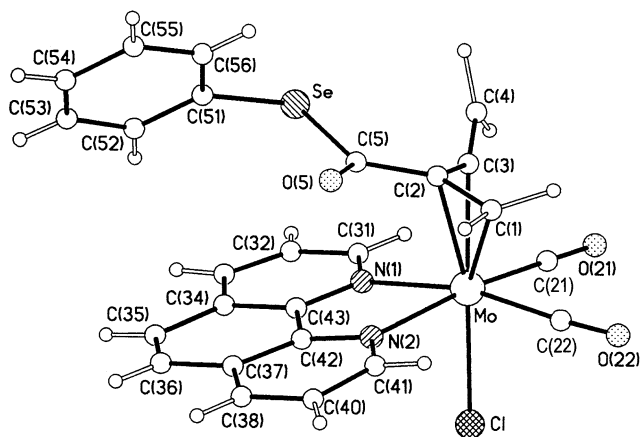


Fig. 1. Structure of $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COSePh})\text{C}=\text{CH}_2)(\text{phen})]$ (**4**) with atom labelling scheme.

Table 3
Crystal data for complex **4**·0.5 CH₂Cl₂

Formula	C _{25.5} H ₁₈ Cl ₂ MoN ₂ O ₃ Se
<i>f</i> _w	646.22
Space group	<i>P</i> 2 ₁ / <i>n</i>
Crystal system	Monoclinic
Unit cell dimensions	
<i>a</i> (Å)	11.0611(14)
<i>b</i> (Å)	7.7220(16)
<i>c</i> (Å)	30.422(4)
α (°)	–
β (°)	97.081(8)
γ (°)	–
Crystal size (mm ³)	0.50 × 0.20 × 0.12
<i>V</i> (Å ³)	2578.6(7)
μ (Mo–K α) (mm ⁻¹)	2.157
λ (Mo–K α) (Å)	0.71073
ρ _{calc} (g cm ⁻³)	1.665
<i>Z</i>	4
No. of reflections collected	4887
No. of independent reflections	3567 [<i>R</i> _{int} = 0.0548]
Limiting indices	–12 ≤ <i>h</i> ≤ 1, –8 ≤ <i>k</i> ≤ 1, –33 ≤ <i>l</i> ≤ 33
2 θ (°)	1.89–23.00
<i>F</i> (000)	1276
<i>T</i> (K)	198(2)
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0699
<i>R</i>	0.0699
<i>R</i> _w	0.1905
<i>TR</i> ₂ (all data)	0.2183
Largest difference peak and hole (e Å ⁻³)	1.494, –1.306

Table 4
Bond lengths (Å) and bond angles (°) with standard deviations in parentheses for [MoCl(CO)₂(η^3 -CH₂C(COSePh)C=CH₂)(phen)]·0.5 CH₂Cl₂

<i>Bond lengths</i>			
Mo–C(21)	1.957(10)	Mo–C(1)	2.300(9)
Mo–C(22)	1.978(10)	Mo–C(2)	2.228(8)
Mo–N(1)	2.230(7)	Mo–C(3)	2.208(9)
Mo–N(2)	2.216(7)	C(1)–C(2)	1.431(12)
Mo–Cl	2.479(2)	C(2)–C(3)	1.418(12)
C(2)–C(5)	1.473(12)	C(3)–C(4)	1.242(13)
C(5)–O(5)	1.192(10)	C(21)–O(21)	1.161(11)
C(5)–Se	1.960(8)	C(22)–O(22)	1.133(11)
<i>Bond angles</i>			
C(21)–Mo–C(22)	80.5(4)	C(1)–C(2)–C(3)	112.5(7)
N(1)–Mo–N(2)	74.3(2)	C(2)–C(3)–C(4)	141.3(9)
O(21)–C(21)–Mo	179.4(10)	O(22)–C(22)–Mo	174.9(10)
C(2)–C(5)–O(5)	124.0(8)	O(5)–C(5)–Se	122.0(6)
C(5)–Se–C(51)	97.0(4)		

carrying electron-withdrawing substituents, to about 160 ppm for unsubstituted systems. It has been suggested that for the former, a zwitterionic form contributes a degree of carbenoid character to the M–C(3) bond, and this further deshields the quaternary carbon [16]. In many other cases, the short metal–C(3) bond and inequivalence of carbon–carbon bond lengths within the metal–bound butadienyl moiety has been

attributed to contributions from structures with either η^1 -bonding at C(3) and a coordinating double bond C(1)–C(2) or with η^1 -bonding at C(1) and double bond coordination at C(2)–C(3). The ¹³C-NMR spectrum for complex **4** was recorded [17], and resonances for the butadienyl appeared at 31.2, 63.9, 173.0 and 108.9 ppm for C(1) to C(4), respectively. However the spectroscopic and crystallographic data do not strongly support any one of these three structures.

Within the substituted butadienyl system, the carbonyl and aromatic ring of the COSePh unit are orientated away from the terminal C=CH₂ moiety, and the phenyl group is located well above the phen plane. At the terminus of the butadienyl, the torsion angle between the C(3)=C(4) vector and the three metal-bonded atoms of the butadienyl was found to be 119.4°. Although the C(3)–C(4) bond length [1.242(13)Å] is considerably shorter than the C–C(terminal) separation of 1.344 ± 0.001 Å in free butadiene [18] and found in related structures, the value is within the range found for the uncoordinated C=CH₂ of a ligated allene [19] and for unsubstituted η^3 -butadienyl complexes [20]. The angle between the two planes defined by C(4) and its hydrogen atoms, H(4A) and H(4B), and by C(4), C(3) and C(2) was 164°, whilst at the opposite end of the ligand, the torsion angle between the C(1)–C(2) vector and the plane containing C(1) and its hydrogen atoms, H(1A) and H(1B), was found to be 118°. If the C₁₁H₉OSe ligand is viewed as a two-substituted η^3 -allyl system, with an additional double bond substituted at one end, then the uncoordinated double bond can be considered to be between the limits of being unconjugated or conjugated with the allyl unit, depending upon the positions of the hydrogen atoms on the terminal carbon atoms C(1) and C(4). With the C(1) hydrogen atoms and the allyl unit non-planar, the double bond is conjugated if the H atoms on C(4) are orthogonal to the plane of the allyl system (Fig. 2, I), and unconjugated with these H atoms co-planar with the allyl system (Fig. 2, II). The orthogonality of the terminal CH₂ units was shown by an improper torsion angle between the plane C(4), H(4A), H(4B) and the plane C(1), H(1A), H(1B) of 95°, and thus the double bond is not considered conjugated to the allyl system.

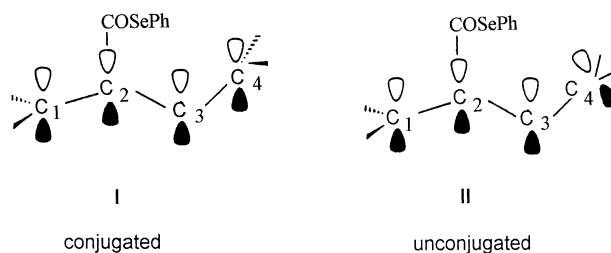


Fig. 2. Extreme orientations of the C(3) and C(4) p π orbitals in the η^3 -butadienyl fragment.

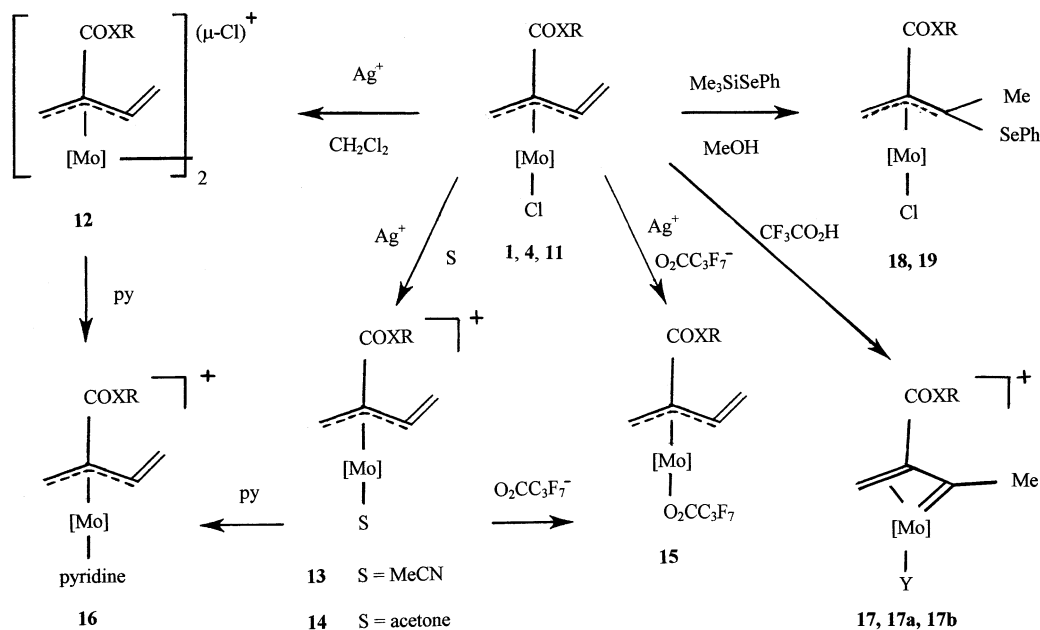
Thus whilst asymmetry at the metal centre due to rotation of L_2Y against the $(\eta^3)\text{M}(\text{CO})_2$ unit is known [21–23], and the putative mechanism for formation of η^3 -butadienyl complex **1** from $\text{Ph}_4\text{P}[\text{MCl}(\text{CO})_3L_2]$ and 1,4-dichloro-2-butyne does not preclude the formation of isomers of this type [2], to date no evidence has been found for this form of isomerism occurring in solid or solution states for analogous η^3 -butadienyl complexes.

3.3. Reactivity studies

Reactions of representative complexes **1**, **4** and methyl ester **11** with various nucleophiles or electrophiles were examined. Whilst addition of silver tetrafluoroborate to a solution of complex **1** in chlorinated solvents in 1:2 mole ratio gave oxidation products only, a similar reaction with **11** gave a red, crystalline product **12** (Scheme 2). Tables 1 and 2 give selected spectroscopic data and elemental analyses of the new complexes. Comparison of the $^1\text{H-NMR}$ spectra of **11** and **12** showed that the peak positions for the terminal protons of the butadienyl and phen ligand were little changed. However, the singlet arising from the methyl ester substituent had moved significantly downfield from 2.12 to 3.34 ppm. Curtis and Fotinos reported that a similar reaction between silver ions and the complex $[\text{MoCl}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{bipy})]$ gave rise to a dimeric cation containing a bridging chlorine atom [24]. This precedent, together with the elemental analyses and IR spectra for **12**, suggested that halide extraction from **11** had initially produced the coordinately unsaturated cation $[\text{Mo}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{CO}_2\text{Me})\text{C}=\text{CH}_2)(\text{phen})]^+$ and that this 16-electron intermediate, being a suffi-

ciently strong Lewis acid, had competed against Ag^+ for chloride in a second molecule of **11** to yield the dimeric species $[\{\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{CO}_2\text{Me})\text{C}=\text{CH}_2)(\text{phen})\}_2(\mu\text{-Cl})]^+$. In contrast, chloride extraction from **11** in the presence of acetonitrile or acetone (S) yielded highly reactive, solvent-coordinated cations of the type $[\text{Mo}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{CO}_2\text{Me})\text{C}=\text{CH}_2)(\text{phen})\text{S}]^+$. Proton NMR spectra for these complexes (**13** and **14**, respectively) were rather broad due to decomposition of the samples, however peaks could be assigned for the butadienyl and phen units, and a broad singlet near 2.00 ppm arose from exchange of free and coordinated solvent. On addition of excess sodium heptafluorobutyrate to either a solution of **11** and AgBF_4 or to cationic **14** in acetone, the carboxylate derivative $[\text{Mo}(\text{O}_2\text{CC}_3\text{F}_7)(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{CO}_2\text{Me})\text{C}=\text{CH}_2)(\text{phen})]$ (**15**) was isolated. Thus, in the presence of coordinating solvents or reagents, the 16-electron intermediate attains greater stability by formation of an appropriate 18-electron complex. In support of this observation, addition of pyridine to a mixture of **11** and $\text{Ag}(\text{I})$ ions in acetone, or to a solution of **14**, resulted in the formation of the cationic species $[\text{Mo}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{CO}_2\text{Me})\text{C}=\text{CH}_2)(\text{phen})(\text{pyridine})]^+$ (**16**). This behaviour shows parallels to that observed by Powell, who similarly prepared the related cation $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{bipy})(\text{pyridine})]^+$ from the chloro precursor [25]. Complex **16** could also be obtained from mixtures of dimeric **12** and pyridine, showing the halogen bridge to be susceptible to cleavage by bases.

Electrophilic attack on the η^3 -butadienyl ligand was examined by addition of trifluoroacetic acid to a cooled (-78°C) solution of **4** in CH_2Cl_2 . An immediate



Scheme 2. Key: $[\text{Mo}] = \text{Mo}(\text{CO})_2(\text{phen})$; **1** XR = Cl; **4** XR = SePh; **11–16** XR = OMe; **17** XR = SePh, Y = Cl; **17a** XR = CO_2CF_3 , Y = Cl; **17b** XR = CO_2CF_3 , Y = CO_2CF_3 ; **18** XR = OMe; **19** XR = SePh.

reaction was apparent, as shown by the appearance of several new peaks in the IR spectrum due to metal–carbonyl absorptions between 1890 and 2000 cm^{-1} and by a significant weakening of the selenoester signal at 1650 cm^{-1} . However after warming to room temperature and chromatography on silica gel, the mixture gave $[\text{Mo}(\text{CO})_2(\text{phen})(\text{O}_2\text{CCF}_3)_2]$ as the only isolable metal-containing species. Monitoring the reaction by $^1\text{H-NMR}$ spectroscopy immediately after mixing was more informative. A sample of complex **4** (30 mg) was shaken rapidly with a solution of $\text{CF}_3\text{CO}_2\text{H}$ (ca. two equivalents) in CDCl_3 (0.5 cm^3), and the mixture was filtered into a 5 mm NMR tube. The $^1\text{H-NMR}$ spectrum was recorded immediately. After protonation, the two doublets arising from terminal protons of the butadienyl double bond in **4** were absent, and three sets of signals of a similar pattern were present between 0.8 and 4.4 ppm. Each set consisted of two doublets integrating for one proton each and a singlet due to a methyl proton. The coupling constants for the pairs of doublets were 2.73 Hz (2.97 and 3.70 ppm), 1.92 Hz (2.99 and 3.80 ppm) and 1.08 Hz (3.02 and 4.20 ppm), and these signals were consistent with three pairs of allylic methylene protons. The three methyl singlets were observed at 0.87, 2.42 and 2.49 ppm. Although the spectrum in the region 8–10 ppm was complex due to overlapping sets of peaks, signals attributable to aromatic protons of the selenoester substituent were clearly observed at 6.30 ppm (d, 7.2 Hz, 2H), 7.02 ppm (t, 7.5 Hz, 2H) and 7.12 ppm (d, 7.1 Hz, H), and new peaks had appeared at 7.90 (m, 6H) and 7.96 (m, 4H) due to diphenyldiselenide. The total integration across the whole spectrum was consistent with the presence of three η^3 -vinylcarbene complexes; one containing a COSePh two-substituent and two with non-proton containing two-substituents arising from loss of diphenyldiselenide and formation of the $\text{CO}_2\text{-COCF}_3$ group. Whilst Slugovc and co-workers have demonstrated that protonation of the highly substituted η^3 -butadienyl ligand in $[\text{Ru}(\text{hydrido}(\text{trispyrazolyl})\text{borato})\{5,6-\eta^3\}\text{-}2\text{-[2-phenyl-1-ethenylidene]-5-cyclooctenyl}]$ gave rise to the corresponding η^2 -butadiene complex via attack of H^+ at C(3) of the $\text{C}(1)\text{C}(2)\text{C}(3)=\text{C}(4)$ unit [26], the NMR data for protonation of selenoester **4** were not consistent with attack at this carbon atom. In contrast extended Hückel molecular orbital calculations on the complex $[\text{Mo}(\text{CO})_2(\eta^3\text{-CH}_2\text{CHC}=\text{CH}_2)(\eta\text{-C}_5\text{Me}_5)]$ predicted that for both charge control and frontier-orbital control, electrophilic attack should occur at the terminal carbon of the double bond to yield an η^3 -vinylcarbene fragment [20]. These results concurred with our calculations based on the X-ray data of the (methylamido)butadienyl complex, and predicted that electrophilic attack would occur at C(4) of the selenoester complex **4**. The pattern of NMR signals observed for protonation of this complex was consistent with this, and thought to arise

from the following series of reactions. Initial protonation at C(4) of the η^3 -butadienyl ligand in complex **4** led to an unstable η^3 -vinylcarbene (**17**), and, since the selenium–carbon bond of the butadienyl substituent was susceptible to nucleophilic attack by trifluoroacetate anion, cleavage to give Ph_2Se_2 was accompanied by conversion of the selenoester to COCO_2CF_3 (**17a**). Following exchange of the metal-bound chlorine atom for trifluoroacetate (**17b**), loss of the organic fragment and capture of the resultant electron deficient species by CF_3CO_2^- finally yielded $[\text{Mo}(\text{CO})_2(\text{phen})(\text{O}_2\text{CCF}_3)_2]$. Low temperature NMR studies of these processes did not yield further information.

The susceptibilities of the η^3 -butadienyl moiety in **1** and **4** to nucleophilic attack were investigated by reaction of methanolic phenyl trimethylsilylselenide. This reagent was selected both for its known potential to deliver the anion PhSe^- to transition metal centres [27,28] and its synthetic utility for the benzeneselenylation of unsaturated organic compounds [11,29]. Our molecular modelling studies on amide substituted η^3 -butadienyl complexes [6] (and related work by Curtis and Eisenstein on η^3 -allyls [30]) predicted that under frontier molecular orbital (FMO) control, nucleophilic attack on these three-carbon units should be directed towards the termini of the allyl function, i.e. at C(1) or C(3) of the $\text{C}(1)\text{C}(2)\text{C}(3)=\text{C}(4)$ system. However, under charge control, nucleophilic attack should be directed toward C(3) of the butadienyl, since this carbon atom possessed the most positive net charge. The product of stirring **1** with excess methanolic Me_3SiSePh (**18**) gave rise to an IR stretching absorption at 1705 cm^{-1} and a singlet in the $^1\text{H-NMR}$ spectrum at 2.37 ppm (3H) suggesting preferential reaction of the acyl chloride substituent with methanol rather than benzeneselenol. However, other features of the IR and $^1\text{H-NMR}$ spectra of **18** were inconsistent with the presence of **11**. Thus, the pair of strong IR absorptions at 1871 and 1952 cm^{-1} attributed to the *cis* metal–dicarbonyl unit of **18** were observed at significantly lower wavenumber than for **11** (1894 and 1972 cm^{-1}), and the $^1\text{H-NMR}$ spectrum of **18** showed no doublets arising from methylene protons of a butadienyl double bond and the appearance of a new singlet, integrating for three protons, at 3.16 ppm. These results were consistent with nucleophilic attack having occurred at C(3) as predicted, and with addition of PhSeH across the double bond to form the η^3 -allylic complex $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{CO}_2\text{Me})\text{C}(\text{Me})\text{SePh})(\text{phen})]$. Reaction of complex **4** with methanolic Me_3SiSePh under the same conditions gave **19**, which was identified from its IR and $^1\text{H-NMR}$ data as the selenoester two-substituted analogue to **18** [31]. There was no spectroscopic evidence for the presence of the η^3 -allylic complexes of the type $[\text{MoCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COXR})\text{C}(\text{Me})\text{OMe})(\text{phen})]$ (XR = OMe or SePh) formed by addition of methanol across

the butadienyl double bond in **1** or **4**, respectively. The former complex was previously obtained by reaction of $\text{Ph}_4\text{P}[\text{MoCl}(\text{CO})_3(\text{phen})]$ and 1,4-dichloro-2-butyne in methanolic tetrahydrofuran, and the structure of the bipyridine complex has been determined [32]. However simple replacement of methanol by amine, thiol or selenol in these reactions does not yield the analogous compounds $[\text{MCl}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}(\text{COXR})\text{C}(\text{Me})\text{XR})(\text{L}_2)]$ ($\text{X} = \text{NR}, \text{S}, \text{Se}$). The reaction of **1** or **4** with methanolic Me_3SiSePh thus provides a new route to this class of 2,3,3-trisubstituted, η^3 -allylic complexes.

The ability of selenoester substituted complex **4** to perform as an acyl transfer agent was investigated. On stirring a solution of the complex in a mixture of acetone and either basic methanol or excess *n*-propylamine no reaction occurred. However, addition of copper or mercury(II) chlorides to these reaction mixtures gave rise to the production of the methylester and *n*-propylamide substituted complexes, respectively, in good yield. These were identified by comparison with the published spectroscopic data [6]. The general mechanism of these reactions can be expected to proceed via initial attack of alcohol or amine on the acyl carbon of the selenoester substituent to give a conventional tetrahedral intermediate, the copper or mercury ion associating with the selenium atom. Departure of the metal selenolate then yields the ester or amide product. Comparison of the methanolysis reaction for complex **4** with that of the thioester complex **3** showed a longer reaction time (8 h) was required for the latter, in accord with the greater carbon–sulphur bond strength in the thioester butadienyl substituent. These results are in accord with published observations that organochalcogen esters of the type $\text{R}'\text{COER}$ ($\text{R}' = \text{Me}, \text{Ph}, \text{Bz}$, $\text{R} = \text{SeBu}, \text{TeBu}$ [33], $\text{R}' = \text{octyl}$, $\text{ER} = \text{SeMe}$ [7]) react with metal halides in methanol or diethylamine to give the corresponding ester and amide. Thus complex **4** shows promise as an effective acyl transfer agent.

A solution of complex **4** (0.5 mmol) in dichloromethane (50 cm^3) was brominated (0.5 mmol in 5 cm^3 acetone) at low temperature (-5°C), and the mixture was monitored at different time intervals by infrared spectroscopy. After 0.5 h a reduction in the intensity of the $\nu(\text{COSe})$ stretching frequency at 1650 cm^{-1} was observed, and a new broad absorption near 1700 cm^{-1} was assigned to formation the acyl bromide. This was in accord with the known reaction of aryl selenoesters with halogens to give the corresponding areneselenenyl trihalide and acyl halide [34]. However, extended reaction times, or on warming the mixture to room temperature, the pair of strong absorptions at 1897 and 1975 cm^{-1} due to a *cis* metal–dicarbonyl unit decreased in intensity. Increasing amounts of diphenyldiselenide and $\text{MoBr}_4(\text{phen})$ were isolated from the reaction, and it was apparent that the metal fragment

had detached from the butadienyl ligand. No bromination products of the butadienyl could be isolated.

4. Conclusions

Thioester, selenoester or telluroester substituted η^3 -butadienyl complexes were formed by reaction of the η^3 - $\text{CH}_2\text{C}(\text{COCl})\text{C}=\text{CH}_2$ moiety with either chalcogenols (S, Se) or bisorganochalogen mercurials (Se, Te). The introduction of the latter synthetic method did not lead to significant improvement in yields, however, it provided a route to previously inaccessible tellurium derivatives. Use of polythiols or polyselenols ($n = 2-4$) gave rise to polymeric complexes, in which substituted η^3 -butadienyl units served as bridging ligands between several metal centres. Substituted η^3 -butadienyl metal complexes derived from achiral chalcogenols or bisorganochalogen mercurials showed no spectroscopic evidence for the presence of isomers in solution, and NMR spectra were invariant over the range -80 to $+25^\circ\text{C}$. In the solid state, selenoester complex **4** contained a *Z*-substituted, *trans*-butadienyl moiety, with the uncoordinated double bond $\text{C}(3)=\text{C}(4)$ being unconjugated with respect to π -delocalisation within the metal bound $\text{C}(1)\text{C}(2)\text{C}(3)$ unit. This organic fragment was therefore expected to undergo many reactions expected for related metal η^3 -allyl complexes. In agreement with this prediction, halide extraction from the ester substituted butadienyl complex gave a highly reactive 16-electron cation, whose reactions with Lewis bases, anions and labile solvent molecules, closely parallels those previously described for $[\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{bipy})]^+$. The sites of electrophilic or nucleophilic attack within the substituted butadienyl fragment (protonation at C(4) to give a vinylcarbene moiety or attack by the phenylselenide anion at C(3) to give a 2,3-disubstituted η^3 -allyl unit) were in accord with predictions based on molecular modelling techniques. The phenylselenoester two-substituted butadienyl complex **4** proved unstable to oxidation by bromine, but readily acted as an acyl transfer agent for methanol and propylamine in the presence of soft, selenophilic metal cations. The potential for these complexes to serve as organic synthons is being investigated.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 188645 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-

mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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- [31] ^1H -NMR data (DMSO- d_6) for η^3 -allyl complex **18**: 2.19 (s, H), 2.37 (s, 3H), 3.16 (s, 3H), 3.73 (s, H), 7.83 (m, H), 8.07 (s, H), 8.27 (m, 2H), 8.39 (s, H), 8.42 (s, H), 8.68 (d, 7.15, H), 8.92 (m, 2H), 9.10 (m, 2H), 9.32 (d, 6.07, H), 9.77 (d, 4.96, H); for complex **19**: 2.07 (s, H), 3.29 (s, 3H), 3.70 (s, H), 6.98 (m, 2H), 7.19 (m, 3H), 7.85–8.03 (m, 5H), 8.15 (m, 2H), 8.29 (m, 2H), 8.77 (m, 2H), 9.14 (m, H), 9.32 (m, H). Selected IR data (nujol mulls) for **18**: $\nu(\text{C}=\text{O})$ 1852, 1940 cm^{-1} , $\nu(\text{C}=\text{O})$ 1705 cm^{-1} ; for **19**: $\nu(\text{C}=\text{O})$ 1871, 1952 cm^{-1} , $\nu(\text{C}=\text{O})$ 1651 cm^{-1} .
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