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Synthesis and characterisation of monomeric and dimeric 2-substituted η^3-bonded butadienyl complexes of molybdenum(II)

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Abstract

Addition of excess thiol RSH (R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu or ^{i}Bu) to solutions of $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C{=}CH_2)(phen)]$ (1) (phen = 1,10-phenanthroline) gave good yields of the complexes $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COSR)C{=}CH_2)(phen)]$, containing a 2-substituted butadienyl ligand. On reaction of 1 with 1,2-ethanedithiol in 2:1 molar ratio under basic conditions, dimeric complexes were obtained containing two metal centres bridged by a pair of 2-substituted butadienyl groups linked by the dithiol unit. Analogous dimeric complexes containing linked amido η^3-butadienyl groups were isolated from a similar 2:1 reaction of 1 and diamines $RHN(CH_2)_2NHR$ (R = H or Me). However, reactions involving 1 and mixed bifunctional reactants $HA(CH_2)_2BH$ (A = NH, B = O, S or A = O, B = S) under the same conditions gave monomeric complexes exclusively, the less electronegative atom of the donor pair remaining unreacted.

Keywords: Molybdenum; Butadienyl; Dimer; Bridging ligand

1. Introduction

The structure, bonding, reactivity and dynamic properties of transition metal η^3-allyl complexes have been widely studied, because of their relative ease of conversion to η^1-allyls and metal-coordinated alkenes and dienes and their relevance to organic synthesis. In contrast, the chemistry of related η^3-bonded butadienyl complexes has been relatively neglected. However, in the past decade several general reaction pathways to these complexes have been discovered, and the butadienyl moiety containing a variety of substituents at C_2 has been characterised crystallographically. A recent review [1] has been timely in summarising the general synthetic routes to η^3-butadienyl derivatives of transition metals, highlighting their importance to the future development of C_4 organometallic chemistry and identifying areas that require further study. Of particular relevance to this work is the current paucity of information concerning such complexes with sulphur substituents attached to the butadienyl or dinuclear transition metal species bridged by η^3-bonded butadienyl groups [2].

In an extension of previous investigations into the reactivity of $Ph_4P[MoCl(CO)_3L_2]$ (L_{2} = 2,2'-bipyridyl or 1,10-phenanthroline) with 1,4-dichlorobut-2-yne [3–5], the authors and others have recently described the formation of the complexes $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C{=}CH_2)L_2]$ in high yield [6]. Analogous reactions carried out in the presence of excess alcohols ROH or amines RR'NH resulted in formation of complexes of the type $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CO_2Me)C{=}CH_2)L_2]$ or $[MoCl(CO)_2(\eta^3\text{-}CH_2C(CONRR')C{=}CH_2)L_2]$ respectively. A single-crystal X-ray diffraction study of the complex $[Mo(CO)_2(\eta^3\text{-}CH_2C(CONHMe)C{=}CH_2)(2,2'\text{-bipyridyl})(O_2CC_3F_7)]$ [4,5] was used as a basis for an extended Hückel molecular orbital analysis of the bonding within the organic fragment, and confirmed that these complexes may best be regarded as η^3(3e)-buta-2,3-dienyl derivatives, in which the uncoordinated carbon–carbon double bond remains unconjugated with respect to the π-delocalisation within the η^3-allyl fragment. Whilst ester- and amide-substituted complexes were also accessible from direct reactions of $Ph_4P[MoCl(CO)_3L_2]$ with 1,4-dichlorobut-2-yne in aqueous or amine-containing methanolic solutions, attempts to prepare the analogous complexes $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COSR)C{=}CH_2)L_2]$ were unsuccessful, and gave highly insoluble products of variable elemental composition [7]. We now report the synthesis and characterisation of

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such complexes via the intermediacy of [$MoCl(CO)_2$-(η^3-$CH_2C(COCl)C{=}CH_2$)(1,10-phenanthroline)] (**1**), and describe reactions of this complex with a series of ligands containing two donor atoms, which might be expected to produce dimeric butadienyl complexes.

2. Results and discussion

Reaction of **1** with excess thiol RSH (R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu or ^{t}Bu) in the presence of base yielded complexes **2–6**, which were characterised by IR and ^{1}H NMR spectroscopy and elemental analysis as complexes of general formula [$MoCl(CO)_2(\eta^3$-$CH_2C(COSR)$-$C{=}CH_2$)(phen)] (phen = 1,10-phenanthroline), containing a 2-substituted η^3-bonded butadienyl ligand. Pertinent data for these complexes are presented in Tables 1 and 2. The only related complex in the literature is the 2-substituted η^3-allyl [$cpM(CO)_2L(\eta^3$-1-$RCHC$-$(COSR)CH_2$)], which was isolated from reaction of a highly reactive σ-propargyl metal carbonyl [$cpM(CO)_2L(\eta^1$-$CH_2C{\equiv}CR$)] (M = Mo, W; L = CO, PPh_3; R = alkyl, aryl; cp = η^5-C_5H_5) with thiols R'SH (R' = Me, Et) [8,9]. No crystallographic characterisation of either system has yet been achieved, however conversion of **3** to the more soluble trifluoroacetate complex by established methods [5] has produced crystals suitable for X-ray analysis and these are currently under investigation.

Addition of 0.5 mmol dithiol $HS(CH_2)_2SH$ to 1 mmol **1** in dichloromethane solution under the same conditions gave a single metal-containing complex **7**. This was identified from spectroscopic evidence as a dimeric species, in which two metal centres were bridged by a pair of 2-substituted butadienyl groups linked through the dithiol unit (illustrated in Scheme 1). There was no evidence for formation of a monomeric complex in which only one end of the dithiol was attached to a butadienyl unit. Similarly, dropwise addition of 0.5 mmol of the bifunctional amines $HRN(CH_2)_2NRH$ (R = H or Me) to basic solutions containing 1.0 mmol **1** gave orange microcrystalline complexes, that were shown by elemental analysis, IR and ^{1}H NMR spectroscopy to be dimeric and of general formula [{$MoCl(CO)_2(\eta^3$-$CH_2C(CON(R)CH_2)C{=}CH_2$)(phen)}$_2$] (R = H **8**, R = Me **9**). However, attempts to prepare analogous dimeric complexes by combination of **1** and 1,2-ethanediol led to decomposition products only, suggesting that the role of alcohols in the formation of substituted butadienyls may differ from that of amines or thiols.

On addition of **1** to solutions of either ethanolamine, 2-aminoethanethiol or 2-mercaptoethanol in 2:1 molar ratio, monomeric complexes of general type [$MoCl(CO)_2(\eta^3$-$CH_2C(COA(CH_2)_2BH)C{=}CH_2$)(phen)] (A = NH, B = O (**10**), A = NH, B = S (**11**) or A = O, B = S (**12**) respectively) were isolated, and there was no evidence for the formation of dimeric species. Spectroscopic evidence was used to identify which end of the ligand was attached to the organic fragment. The monomeric complexes **10–12** were of low solubility in common solvents, and this may preclude further reaction with **1** to give dimeric products. Dimeric complexes **7–9** were precipitated from reactions of 2:1 molar quantities of **1** with $HA(CH_2)_2AH$ (A = S, NH, NMe respectively) in these solvents, indicating that for these reactants both ends of the molecule react with **1** at the same rate, and insoluble monomeric complexes are not therefore isolated.

2.1. Spectroscopic data

The IR spectra of all the complexes showed two strong absorption bands between 1979 and 1892 cm^{-1}, typical of *cis*-dicarbonyl species, and a weak band near 1670 cm^{-1} which could be assigned to the uncoordi-

Table 1
Yields, selected infrared and analytical data for monomeric complexes **2–6** and **10–12** and dimeric **7–9** [a]

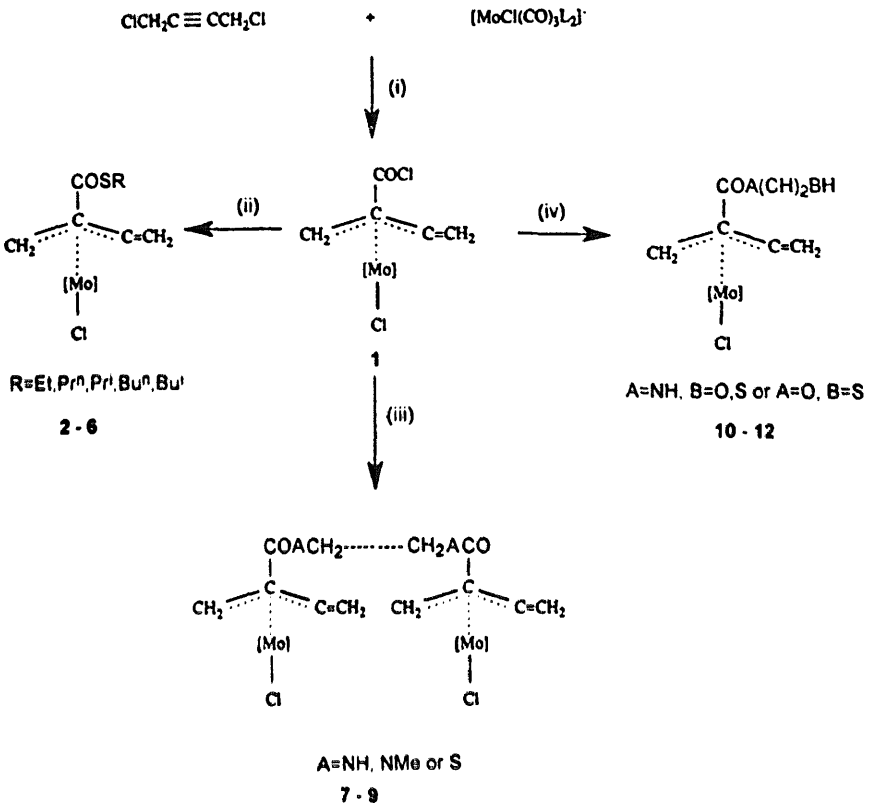
No.	Complex [b]		Yield (%)	Infrared data [c] (cm^{-1})				Anal. Found (Calc.) (%)			
	A	B		ν(C≡O)	ν(C=O)	ν(C=C)	ν(X–H)	C	H	N	S
2	EtS		76	1905, 1979	1628	1673w		49.28 (49.55)	3.20 (3.34)	5.72 (5.50)	6.03 (6.29)
3	^{n}PrS		69	1904, 1979	1630	1678w		49.99 (50.52)	3.71 (3.63)	5.30 (5.35)	5.99 (6.12)
4	^{i}PrS		63	1906, 1981	1621	1675w		50.12 (50.52)	3.68 (3.63)	5.14 (5.35)	6.19 (6.12)
5	^{n}BuS		70	1892, 1981	1636	1679w		51.23 (51.44)	3.90 (3.91)	5.22 (5.21)	5.54 (5.96)
6	^{t}BuS		64	1900, 1982	1633	1675w		51.38 (51.44)	4.15 (3.91)	5.22 (5.21)	5.67 (5.96)
7	S		59	1894, 1969	1634	1680w		44.28 (45.89)	2.78 (2.79)	5.12 (5.22)	
8	NH		62	1894, 1947	1647	1671sh	3394w [d]	47.43 (47.39)	3.30 (3.08)	8.15 (8.09)	
9	NMe		68	1890, 1967	1626	1679w		48.93 (48.40)	3.48 (3.37)	8.15 (7.87)	
10	NH	O	61	1896, 1971	1651	1678w	3412 [d], 3478 [e]	45.94 (44.55)	3.78 (3.37)	7.47 (7.08)	
11	NH	S	69	1895, 1965	1645	1660sh	2598w [f], 3385w [d]	47.92 (48.13)	3.69 (3.43)	8.02 (8.02)	
12	O	S	70	1905, 1978	1638	1684w	2600w [f]	43.68 (43.31)	3.09 (3.11)	4.97 (4.59)	

[a] CH_2Cl_2 calculated. [b] From reactant AH, $HA(CH_2)_2AH$ or $HA(CH_2)_2BH$. [c] As Nujol mulls. All bands strong unless otherwise indicated. [d] X = N; [e] X = O; [f] X = S.

Table 2
^{1}H NMR data for complexes **2–12** [a]

Complex	H'_{anti}	H''_{anti}	Aliphatic			Aromatic
	H'_{syn}	H''_{syn}	CH_2	CH_3	XH	
2	1.90 (s, H)	5.82 (d, 2.38, H)	1.60 (m, 2H)	−0.5 (t, 7.33, 3H)		8.08 (m, 2H), 8.19 (s, 2H), 8.84 (m, 2H)
	3.80 (s, H)	6.28 (d, 2.38, H)				9.18 (d, H), 9.31 (d, H)
3	1.94 (s, H)	5.81 (d, 2.32, H)	1.54 (m, H)	0.42 (t, 3H)		7.88 (m, 2H), 7.91 (s, 2H), 8.48 (m, 2H)
	3.76 (s, H)	6.35 (d, 2.32, H)	1.63 (m, H)			9.15 (m, 2H)
4 [b]	1.88 (s, H)	5.82 (d, 2.20, H)		0.03 (d, 6.78, 3H)	1.20 (m, H)	7.89 (m, 2H), 7.91 (s, 2H), 8.45 (m, 2H)
	3.80 (s, H)	6.27 (d, 2.20, H)		0.56 (d, 6.78, 3H)		9.16 (m, 2H)
5	1.94 (s,H)	5.81 (d, 2.35, H)	0.35 (m, 2H), 0.80 (m, 2H)	0.62 (t, 3H)		7.87 (m, 2H), 7.91 (s, 2H), 8.48 (m, 2H)
	3.76 (s, H)	6.34 (d, 2.20, H)	1.56 (m, H), 1.65 (m, H)			9.15 (m, 2H)
6 [b]	1.94 (s, H)	5.81 (d, 2.20, H)	1.35 (m, H)	0.39 (d, 6.23, 3H)	1.26 (m, H)	7.87 (m, 2H), 7.91 (s, 2H), 8.48 (m, 2H)
	3.75 (s, H)	6.35 (d, 2.20, H)	1.58 (m, H)	0.44 (d, 6.23, 3H)		9.15 (m, 2H)
7 [c]	1.93 (s, 2H)	5.99 (d, 2.44, 2H)	0.11 (m, H), 0.86 (m, H)			8.09–8.48 (m, 8H), 8.46 (m, 4H)
	3.85 (s, 2H)	6.51 (d, 2.44, 2H)	1.09 (m, H), 1.20 (m, H)			9.36 (m, 4H)
8 [d]	1.81 (s, 2H)	5.65 (d, 2.13, 2H)	0.60 (m, 2H)		5.84 (brs, 2H)	7.96 (m, 4H), 8.07 (d, 4H), 8.70 (m, 4H)
	3.78 (s, 2H)	6.18 (d, 2.13, 2H)	0.84 (m, 2H)			8.97 (d, 2H), 9.17 (d, 2H)
10 [d]	1.87 (s, H)	5.74 (d, 2.34, H)	0.54 (m, 2H), 1.51 (m, H)		6.16 (t, H)	8.01 (m, 2H), 8.37 (s, 2H), 8.78 (m, 2H)
	3.86 (s, H)	6.27 (d, 2.34, H)	2.00 (m, H)			9.13 (d, H), 9.25 (d, H)
12	1.91 (s, H)	5.84 (d, 2.38, H)	1.69 (m, 2H)			8.07 (m, 2H), 8.18 (s, 2H), 8.80 (m, 2H)
	3.80 (s, H)	6.30 (d, 2.38, H)	2.16 (m, 2H)			8.97 (d, 2H), 9.17 (d, 2H)

[a] Spectra recorded as solutions in DMSO-d_6 unless otherwise stated. Data reported in ppm, multiplicity, coupling constant (Hz), number of protons.
[b] X = C.
[c] Run in dimethylformamide-d_7.
[d] X = N.



Scheme 1. Conditions: CH_2Cl_2; 20°C; (i) excess 1,4-dichlorobut-2-yne; (ii) RSH in five-fold excess; (iii) 1.0 mmol **1** and 0.5 mmol $HA(CH)_2AH$; (iv) 1 mmol **1** and 0.5 mmol $HA(CH_2)_2BH$; [Mo] = $Mo(CO)_2(phen)$.

nated double bond of the butadienyl group. The absence of weak IR stretching modes near 2590 cm^{-1} due to unreacted SH groups in the IR spectrum of **7** indicated that a dimeric complex had been formed. Spectra of complexes **8**, **10** and **11**, formed from reactions of **1** with ethylenediamine, ethanolamine and 2-aminoethanethiol respectively, all showed a single, weak absorption for NH at ca. 3400 cm^{-1} and peaks due to NH_2 stretching frequencies were absent. Complex **9**, prepared from N,N'-dimethylethylenediamine, exhibited no peaks attributable to an NH stretching mode in the IR spectrum, and this, combined with the absence of a resonance peak for this group in the ^1H NMR spectrum, indicated that a dimeric complex had been formed. A monomeric formulation for complexes **10**, **11** and **12** was supported by the presence of a weak IR absorption at 3478 cm^{-1} due to the uncomplexed hydroxy group of amido butadienyl complex **10** and the weak IR absorptions near 2590 cm^{-1} assigned to stretching modes of the unreacted SH groups of amido complex **10** and ester complex **12**. The complexes were further identified as monomeric (**10–12**) or dimeric (**7–9**) by a comparison of integrals for resonance peaks due to phenanthroline, the butadienyl and methylene groups that were observed in their ^1H NMR spectra (Table 2).

All complexes gave only one band due to the C=O stretching mode, and these occurred at significantly lower wavenumber than for acyl chloride **1** (ν(C=O) 1708 cm^{-1}). Thus the IR spectra of monomeric complexes **2** to **6** and dimeric **7** each showed a peak of medium intensity near 1630 cm^{-1} which could be assigned to the C=O of the thiolato group. The amido dimers **8**, **9** and monomers **10**, **11** exhibited peaks arising from these C=O stretching modes near 1650 cm^{-1}, whilst the ester group of complex **12** gave a peak due to C=O stretching at 1638 cm^{-1}. The position of this band reflects the differing electronegativities of the atom attached to the carbonyl, and can thus be used as a diagnostic tool in determining whether both ends of $HA(CH_2)_2AH$ (A = S or A = NH or NMe) and which end of $HA(CH_2)_2BH$ (A = NH, B = O, S or A = O, B = S) have reacted with complex **1**.

All the complexes were relatively insoluble in common polar and chlorinated solvents, however ^1H NMR spectra of most of these complexes were obtained on solutions recorded in dimethylsulphoxide-d_6, and pertinent data are reported in Table 2. No variations in these spectra were observed within the temperature range +25 to −70°C, and no evidence was found for double addition of thiols to **1** leading to an η^3-($CH_2C(COSR)$-$CMe(SR)$) ligand-containing complex. All spectra were consistent with the presence of *trans*-butadienyl ligands, with the terminal methylene protons of the η^3-bonded species giving rise to singlets near 1.9 ppm (H_{anti}) and 3.8 ppm (H_{syn}) and those of the double bond occurring as doublets near 5.8 ppm (H_{anti}) and

6.3 ppm (H_{syn}) (coupling constants of ca. 2.3 Hz). In general, peaks assigned to the remaining methylene groups of the butadienyl were shifted upfield due to the anisotropic effect of the phenanthroline ring system, and each CH_2 unit produced a complex overlapping multiplet or two single multiplets due to the slightly differing magnetic environments of the two protons. Triplet resonances assigned to the methyl groups in the n-alkyl thiol complexes **2** to **4** were significantly upfield, occurring at −0.5, 0.42 and 0.62 ppm respectively, and multiplets near 1.26 ppm were attributed to the methine protons in the iso-alkyl thiol complexes **4** and **6**. The latter complexes also gave rise to a pair of doublets due to methyl groups, and in **4** one of these occurs upfield, reflecting the proximity of the phenanthroline ring system.

A comparison of the integrals for peaks assigned to phenanthroline, η^3-butadienyl and methylene groups of $A(CH_2)_2A$ or $A(CH_2)_2B$ permitted identification of the complexes **7–12** as monomeric or dimeric (Table 2, Scheme 1). For example, **8** gave rise to two singlets for H_{anti} and H_{syn} of the double bond at 1.81 and 3.78 ppm, which integrated for two protons each, and two multiplets due to bridging methylene groups, which integrated for two protons each. Thus two η^3-substituted butadienyl groups per CH_2CH_2 unit were identified, supporting a dimeric formulation for this complex. In contrast the spectrum of **10** exhibited multiplets integrating for a total of four methylene protons and analogous resonances for H_{anti} and H_{syn} of the double bond at 1.87 and 3.76 ppm, each integrating for one proton only. Thus only one butadienyl unit was attached to $A(CH_2)_2B$ in a monomeric complex. Spectra of monomers **10**, **12** and dimer **8** additionally exhibited broad triplets near 6 ppm due to NH protons. Complexes **9** and **11** were too insoluble in common solvents for ^1H NMR spectra to be recorded, and attempts to prepare more soluble analogous perfluorocarboxylate complexes by halide extraction [4] were unsuccessful, leading to decomposition products only.

2.2. Competition reactions

Reaction of **1** with ^{t}BuSH failed to produce a thiol-substituted butadienyl complex, and addition of an excess of an equimolar mixture of the thiols ^{i}PrSH and ^{t}BuSH to a solution of **1** gave **6** as the major metal-containing product, suggesting that steric factors are important in determining the reaction product. Competition reactions in which equimolar amounts of any two of the mixed bifunctional reactants $HA(CH_2)_2BH$ and **1** were combined in 1:2 molar ratio gave one product only, in which the molecule with the more basic terminal functional group had reacted preferentially. Similarly, competition reactions involving **1** and a mixture of ethylenediamine and N,N′-dimethylethylenediamine (pK_a of conjugate acids 10.71 and 10.40 respectively) gave **8** as the only product, confirming the importance of basicity in controlling the type of complex formed.

3. Conclusions

The η^3-$CH_2C(COCl)C{=}CH_2$ moiety has proved a versatile ligand, giving access to a variety of 2-substituted monomeric and dimeric complexes of molybdenum(II). Spectroscopic methods have proved effective in identifying the presence of dimeric butadienyl species and of unreacted functional groups in the monomers. However, both the orientation of the carbon–carbon double bond relative to the metal dicarbonyl fragment and the relative position of the C=O group remain unknown, and await X-ray diffraction studies. Extended Hückel molecular orbital analysis of the bonding within the organic fragment [5] has indicated that nucleophiles should attack C_1 of the butadienyl fragment $C_1C_2C_3{=}C_4$. Preliminary studies of the reactions of η^3-substituted butadienyl complexes [$MoCl(CO)_2(\eta^3$-$CH_2C(COB)C{=}CH_2$)(phen)] (B = NRR′ and SR′) with a series of nucleophiles follow this prediction in general, and their reactivity shows a strong dependence on the nature of B. These results will be reported in detail elsewhere. In view of the importance of reaction conditions and the nature of the butadienyl substituent in controlling the products formed in these reactions, and the known synthetic utility of other allyl and butadienyl molybdenum complexes [10], we are currently investigating the potential of these complexes to serve as organic synthons.

4. Experimental details

Solvents and liquid reactants were dried over 4 Å molecular sieves and thoroughly degassed by dinitrogen prior to use. All reactions were carried out under an atmosphere of dinitrogen. The starting material [$MoCl(CO)_2(\eta^3$-$CH_2C(COCl)C{=}CH_2$)(phen)] (**1**) was freshly prepared according to the literature method [6], and recrystallised from dichloromethane–petrol mixtures prior to use. A solution of 2-aminoethanethiol was prepared by stirring a suspension of 2-aminoethanethiol hydrochloride (0.056 g, 0.5 mmol) in dichloromethane (20 cm^3) with triethylamine (0.21 cm^3, 1.5 mmol) at room temperature for 0.5 hours. All other chemicals were purchased from Aldrich and used without further purification. Infrared spectra were recorded on a Perkin–Elmer 599B spectrometer as paraffin mulls, and NMR spectra were obtained using a JEOL GX 270 MHz FT instrument, with samples dissolved in dimethylsulphoxide-d_6 and tetramethylsilane used as internal standard.

4.1. Preparation of thiol complexes 2–6

A solution of 1 (0.48 g, 1.0 mmol) in dichloromethane (50 cm^3) was stirred with excess triethylamine (0.21 cm^3, 1.5 mmol). To this mixture was added dropwise a solution of the thiol RSH (R = Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{i}Bu, 1.0 mmol) in dichloromethane (10 cm^3), and the resulting suspension was stirred for 2 h at room temperature. The ethanethiol product (2) precipitated as an orange powder, that was filtered from solution, washed with petrol (40–60 °C) and dried in vacuo. The remaining reaction mixtures produced no solids on filtration, but on addition of petrol (60 cm^3) to the solutions and storage at low temperature (−5 °C) gave the products as orange microcrystalline solids. All products were finally recrystallised from dichloromethane–petrol mixtures.

4.2. Preparation of dimeric complexes 7, 8 and 9

Triethylamine (0.21 cm^3, 1.5 mmol) was added to a stirred solution of 1 (0.48 g, 1.0 mmol) in dichloromethane (50 cm^3) at ambient temperature, and a solution of 1,2-ethanedithiol, ethylenediamine or N,N′-dimethylethylenediamine (0.5 mmol) in dichloromethane (10 cm^3) was added dropwise to the mixture. After a period of 3 h, the crude product was filtered off as a red (thiol) or orange (amine) powder, that was recrystallised from dichloromethane–petrol mixtures, washed with petrol and finally dried in vacuo.

4.3. Preparation of complexes 10, 11 and 12

A solution of ethanolamine, 2-aminoethanethiol or 2-mercaptoethanol (0.5 mmol) in dichloromethane (10 cm^3) was added dropwise to a stirred solution of 1 (0.48 g, 1.0 mmol) in dichloromethane (50 cm^3) containing excess triethylamine (1.8 mmol), and the mixture stirred at room temperature for 2 h. The products precipitated from solution as orange powders, that were filtered from solution and recrystallised from large volumes of dichloromethane.

4.4. Competition reactions

Reactions of 1 (1.0 mmol) were carried out in a dichloromethane solution of excess triethylamine, with (i) a mixture of 0.25 mmol each of two bifunctional reactants of the type $HA(CH_2)_2BH$ (A = NH, B = O, S and A = O, B = S), (ii) a mixture of ethylenediamine (0.25 mmol) and N,N′-dimethylethylenediamine (0.25 mmol), or (iii) a mixture of 2.5 mmol each of ^{i}PrSH and ^{i}BuSH. Only one major product was isolated from each reaction, as discussed above.

Acknowledgements

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