

Molybdenum(III) chloride–tetrahydrothiophene (tht) complexes in the catalytic polymerization and cyclotrimerization of alkynes: structures and reactivities of the possible intermediates $[\text{MoCl}_3(\text{tht})_2(\text{PhC}\equiv\text{CR})]$ ($\text{R} = \text{Me}$ or Et)[†]

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The binuclear complexes $[\text{Mo}_2\text{Cl}_6(\text{tht})_3]$ (both the C_{2v} and C_s isomers, tht = tetrahydrothiophene) have been found to be active catalysts for the selective polymerization and cyclotrimerization of a variety of alkynes. The mononuclear complex $[\text{MoCl}_3(\text{tht})_3]$ shows similar behaviour, leading to the postulate that the active species in all cases is mononuclear. Two unique molybdenum(III) alkyne complexes, $[\text{MoCl}_3(\text{tht})_2\text{L}]$ ($\text{L} = \text{PhC}\equiv\text{CMe}$ or $\text{PhC}\equiv\text{CEt}$) have been isolated and structurally characterized. The structural parameters for these complexes suggest that the alkynes behave as four-electron donors. These complexes are also catalytically active, and the alkyne L is incorporated into the product cyclotrimers and polymers suggesting they are the first intermediates in the formation of active catalysts from the original thioether complexes.

There is an extensive literature on the catalytic reactions of molybdenum and tungsten complexes with substituted alkynes. Several general classes of compound have been identified^{1–3} that are capable of polymerizing alkynes. These include: (i) metal halides in high oxidation states e.g. MoCl_5 and WCl_6 ; (ii) high-oxidation-state metal halides activated by a co-catalyst e.g. $\text{MoCl}_5 + \text{SnBu}^n$; (iii) UV-irradiated solutions of a metal carbonyl in a halogenated solvent e.g. $[\text{Mo}(\text{CO})_6]-\text{CCl}_4$; (iv) alkylidyne and alkylidene complexes of Mo or W in which the metal is formally in the oxidation state vi. It is notable that in the first three cases the likelihood is that in the active catalytic species the metal is in an intermediate oxidation state, formed by either the reduction [(i) and (ii)] or the oxidation [(iii)] of the initial metal complex. Conversely, however, the alkylidyne complexes can be prepared from the metathesis of M^{III}_2 complexes containing $\text{M}\equiv\text{M}$ bonds, and an alkyne's $\text{C}\equiv\text{C}$ bond.² Otherwise, relatively little information has been published on the direct application of compounds of M^{III} and M^{IV} as catalysts for alkyne polymerization. The synthesis in our laboratories⁴ of a series of complexes of general formula $\text{Mo}_2\text{Cl}_6(\text{thioether})_3$ prompted our interest in reactions of molybdenum(III) complexes with alkynes. Earlier work by Cotton *et al.*⁵ on analogous niobium and tantalum complexes had demonstrated that they were capable of selectively polymerizing and/or cyclotrimerizing terminal and internal alkynes. In addition, a number of alkyne complexes were generated during that study.^{6,7} The known structures of binuclear complexes of general formula $\text{M}_2\text{X}_6\text{L}_3$ ($\text{M} = \text{Mo}$ or W ; $\text{L} = \text{thioether}$) are shown in Fig. 1. The complexes of niobium and tantalum studied by Cotton *et al.*⁵ possessed the C_{2v} structure. In addition to having available the molybdenum complex with this structure, namely **1**,⁴ we had also prepared the isomer with the C_s structure, **2**.⁴ Of particular interest was the fact that whereas the C_{2v} isomer is diamagnetic, with a short $\text{Mo}-\text{Mo}$ bond (2.470 Å), the C_s isomer has a significantly weaker interaction between the two Mo atoms (2.689 Å) and it is antiferromagnetic. The likelihood that this difference in electronic structure might be reflected in their catalytic properties was the main reason for studying

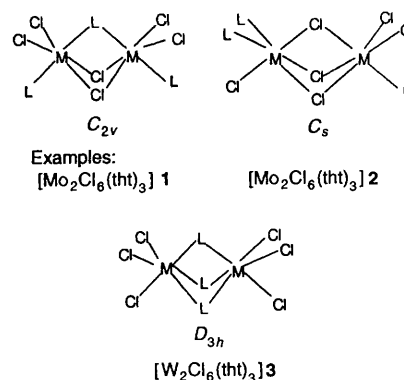


Fig. 1 Known structures for $[\text{M}_2\text{Cl}_6(\text{tht})_3]$ complexes ($\text{M} = \text{Mo}$ or W , tht = tetrahydrothiophene)

their reactions with alkynes. In addition, we had characterized two complexes of W^{III} with D_{3h} symmetry, namely $[\text{W}_2\text{Cl}_6(\text{tht})_3]$ **3** and $[\text{W}_2\text{Cl}_6(\text{Et}_2\text{S})_3]$, which contain very tightly coupled W_2 moieties.⁸ Reports by Green and co-workers⁹ of interesting alkyne interactions with both bridged and unbridged ditungsten(III) complexes prompted us to include **3** in our initial catalytic study.

There is one further complication in this kind of system, however, and that is the possibility that the binuclear structure might not be preserved in the active catalytic species, and that in fact a mononuclear species could be generated in the presence of an excess of ligands, such as the alkynes we wished to polymerize. Such equilibria have been studied extensively for molybdenum halides and phosphine ligands by Poli and co-workers.^{10,11} We therefore prepared and characterized the complex $[\text{MoCl}_3(\text{tht})_3]$ **4** and studied its behaviour, since it could possibly generate the same species in solutions with alkynes as would the dissociated binuclear complexes. In this paper we describe the range of catalytic behaviour observed for **1**, **2** and **4** and the lack of any catalytic activity for the tungsten complex **3**. Complexes have been isolated in which one tht from the mononuclear complex **4** has been replaced by an alkyne ligand. The possible intermediacy of complexes of this sort in the catalytic process is discussed.

[†] Non-SI unit employed: $\mu_{\text{B}} = 9.27 \times 10^{-24} \text{ J T}^{-1}$.

Table 1 Products identified from reactions of selected alkynes with the molybdenum(III) complexes **1**, **2** and **4**

Alkyne	Catalyst		
	1	2	4
HC≡CH	ip	ip	ip
MeC≡CEt	ip	ip	ip
EtC≡CEt	ip	ip	ip
MeC≡CPh	c (6.7:1)	c (4.3:1)	c (4.1:1)
EtC≡CPh	c (8.9:1)	c (5.2:1)	c (8:1)
HC≡CPh	c (3.7:1)	c (1:1.7)	c (5.3:1)
HC≡CBu ⁿ	c (1:1.8)	c (1.5:1)	c (1:1.3)
HC≡CPr ⁿ	c (1.9:1)	n.a.	c (1:1.3)
HC≡CBu ^t	sp, c (2.1:1), o	sp, c (1:1.2), o	sp, c (1.3:1), o
ClCH ₂ C≡CH	ip, c	ip, trace c	ip, c

ip = Insoluble polymer, sp = soluble polymer, c = cyclotrimer, o = oligomer. The number after c (in parentheses) is the ratio of 1,3,5-substituted benzene to the 1,2,4 isomer. Conditions: usually 22 °C, 50 mg catalyst in toluene (50 cm³); turnover: 50–120 g polymer per g catalyst per hour. Reactions with complex **4** were at 0 °C. Under the same conditions, the following species were unreactive: PrⁿC≡CPh, BuⁿC≡CPh, PhC≡CPh, Me₃SiC≡CSiMe₃, dec-1-ene and buta-1,3-diene.

Table 2 Physical properties of (Bu^tCCH)_n, as a function of the catalyst employed

Catalyst	Polymer yield (%)	$\bar{M}_w/g \text{ mol}^{-1}$	Radius of gyration/nm	UV $\lambda_{\text{max}}/\text{nm}$
1	61	1.1×10^5	18.5 ± 0.4	272
2	45	8.6×10^4	18.1 ± 0.4	270
4	60	5.6×10^4	10 ± 1	269

Results

General description of catalytic behaviour

The catalytic coupling of alkynes can yield at least three types of product, namely linear polymers with conjugated polyenic structures, cross-linked polymeric structures (ladder polymers) and cyclic oligomers (especially the aromatic cyclotrimers).^{1,3} Minor amounts of other oligomers can arise, both cyclic and linear, that may contain, for example, Cl derived from the catalyst. It has been pointed out⁵ that since cyclotrimerization yields more thermodynamically stable products than does linear polymerization, it would be expected that more potential catalysts would exist for the former process. However, the catalytic pathways are dependent on a multitude of factors, especially the nature of the alkyne monomer.

A summary of the comparative catalytic activity of complexes **1**, **2** and **4** towards selected alkynes is given in Table 1. The binuclear tungsten complex **3** is inactive under the conditions employed and hence has not been included in the table. The replacement of tht in **4** by a phosphine, or even by tetrahydrofuran (thf), destroys catalytic activity under the conditions of our experiments. It is clear that the lability of the thioether plays a key role in the catalytic processes.

The relative amounts of polymeric products obtained from different reactions are given in the Experimental section. Generally, polymeric products were produced from internal alkynes, and cyclotrimers from terminal alkynes, but some notable exceptions are discussed below. The selectivity towards polymerization of alkynes, as opposed to alkenes, is high. Even buta-1,3-diene does not polymerize with these catalysts under the conditions used. Since **4** tends to dimerize to **1** or **2** at room temperature, a low-temperature reaction (<0 °C) was normally carried out. Hence the data for **4** are not strictly comparable with those from the other two complexes. Nevertheless, the following general observations can be made. Most obviously, there is a strong similarity between the behaviour of the C₂, C₃ dimers **1** and **2** and the mononuclear complex **4**. There are subtle differences in the ratios of the 1,2,4:1,3,5-substituted isomers of the cyclotrimeric products. The symmetric 1,3,5 isomer is the dominant product for alkynes with bulky substituents. Although terminal alkynes usually give predominantly cyclotrimers, while internal alkynes generally yield oligomers or

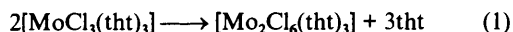
polymers, an important exception is the phenylalkyne class, PhCCR, which cyclotrimerize. Indeed, in all of the reactions we studied, the presence of a phenyl substituent on the alkyne correlated with the exclusive production of cyclic products. The one alkyne that yielded a soluble, linear polyene is Bu^tC≡CH, and even in this case there is also some cyclotrimer produced. The properties of this polymer as produced by the three catalyst precursors are shown in Table 2.

The \bar{M}_w obtained from a static light-scattering spectrometer is $1.1 \times 10^5 \text{ g mol}^{-1}$. The large radius of gyration is attributed to a rigid rod structure, a factor that also interfered with experiments aimed at getting \bar{M}_n data from a GPC study. The relatively low molecular weight and radius of gyration of the polymers from complex **4** is likely due to the lower temperature of reaction (0 °C). The poly(Bu^tCCH) produced with the three different catalysts gave almost the same information from IR and ¹H NMR spectra. The three values of maximum UV absorption are very close and represent higher-energy transitions than comparable literature values,¹ indicative of highly conjugated polymer chains in our products. Carbon-13 NMR spectroscopy has been used to establish the stereochemistry in (Bu^tCCH)_n. For catalyst **1** the chemical shift for the tertiary carbon of the Bu^t group clearly shows that only one isomer is produced, which we assign as *cis*, based on literature data.¹ From **2** the polymer appeared to possess both *cis* and *trans* linkages, while the third product, from **4**, has an additional resonance for the quaternary carbon, suggesting a more complex mixture of isomers. All the other polymers produced were insoluble, thermally robust materials that displayed no evidence of C=C bonds in their IR spectra. Their C,H analyses are compatible with their formulation as (RCCR')_n, and we therefore believe they are completely cross-linked, 'ladder' structures. Similar products have been described by previous workers.^{5,12}

Attempts to isolate possible intermediates

In most cases where reactions were observed they were rapid and consumed the alkyne completely to give, without the addition of any chain-terminating reagent, the products described in Table 1. The molybdenum complex that could be isolated after this process was usually the C₂, binuclear complex **1** regardless of the identity of the original molybdenum complex used. This, coupled with the similarity of product distribution

from the three compounds, suggests that **1**, **2** and **4** are all precursors to a common catalytic species. In the absence of excess of tht, **4** dimerizes in a solvent such as toluene, yielding predominantly **1** [equation (1)]. Hence if the active catalytic



species is a co-ordinatively unsaturated molybdenum(III) centre it might be possible to detect it directly by studying the equilibria between the mononuclear complex **4** and various alkynes. The paramagnetic nature of **4** makes it difficult to follow these reactions using ^1H NMR spectroscopy, but qualitatively we were able to detect the replacement of tht by alkyne. Numerous attempts to isolate such species failed to produce crystalline products, but after one catalytic cyclotrimerization reaction of $\text{PhC}\equiv\text{CMe}$ in toluene solution the monoalkyne complex $[\text{MoCl}_3(\text{tht})_2(\text{PhC}\equiv\text{CMe})]$ **5** was isolated and its crystal structure determined. A procedure was then found for preparing **5** in quantitative yield. Interestingly, it was observed that whereas $\text{PhC}\equiv\text{CMe}$ and $\text{PhC}\equiv\text{CEt}$ react to give cyclotrimers, $\text{PhC}\equiv\text{CPr}^n$ is inactive under the same conditions. This suggested that perhaps the steric crowding imparted by the longer chain disrupted the transition state. Hence we attempted to isolate the $\text{PhC}\equiv\text{CEt}$ analogue of **5**, namely $[\text{MoCl}_3(\text{tht})_2(\text{PhC}\equiv\text{CEt})]$ **6**. This proved successful and its structure was also determined, together with that of **4** for comparison. These are the first examples of molybdenum(III) alkyne complexes to be reported. A detailed structural analysis of **5** and **6** is given later.

Reactions of alkynes with $[\text{MoCl}_3(\text{tht})_2(\text{PhCCMe})]$ **5**

The alkyne complexes **5** and **6** were both shown to be active catalysts for the polymerization and/or cyclotrimerization of selected alkynes. Since in toluene solution at room temperature **5** and **6** will gradually dimerize to **1** and **2** with the loss of alkyne ligand, the catalytic reactions were carried out in acetone at 0°C (as used for **4**) rather than under the conditions used for **1** and **2**. The results are summarized in Table 3. In order to detect the participation of **5**, especially the co-ordinated $\text{MeC}\equiv\text{CPh}$, in the polymerization process, a higher than usual concentration of catalyst was employed. Showing parallel behaviour to **5**, **6** polymerized $\text{EtC}\equiv\text{CMe}$ and cyclotrimerized $\text{PhC}\equiv\text{CH}$ and $\text{PhC}\equiv\text{CMe}$. The insoluble polymers produced in the reactions with EtCCMe were similar in their physical properties to those produced using **1**, **2** and **4**, suggesting a cross-linked structure. They differed, however, in one important respect. The broad IR band centred at *ca.* 1620 cm^{-1} was considerably more intense, suggesting that MeCCPh had been incorporated into the structure. Although there is ambiguity in this assignment since either $-(\text{C}=\text{C})_n-$ or phenyl rings could be responsible for this band, the insolubility of this material would suggest that it does not contain extensive conjugated 'C=C' segments. More definite evidence for the incorporation of MeCCPh from **5** into the polymerization products was obtained from the cyclotrimerization of $\text{PhC}\equiv\text{CH}$. Analysis of the products from this reac-

Table 3 Products (%) from catalytic reactions of complex **5** and selected alkynes*

Product	Alkyne		
	$\text{EtC}\equiv\text{CMe}$	$\text{PhC}\equiv\text{CH}$	$\text{PhC}\equiv\text{CMe}$
Cyclotrimer	—	72	90
Polymer	90	—	—
Oligomers	<5	≈ 24	<2

* The concentrations of catalysts were *ca.* 100 mg in solvent (20 cm^3) and the ratio of alkyne to catalyst >50:1.

tion showed that the cyclotrimers contained a small fraction of a methyl/phenyl-substituted benzene, which clearly indicated the involvement of $\text{MeC}\equiv\text{CPh}$. In the reaction of $\text{PhC}\equiv\text{CMe}$ no chlorinated products were produced, whereas in that of $\text{PhC}\equiv\text{CH}$ chlorinated species were the key by-products.

Structural results

The ORTEP¹³ diagrams of complexes **4–6** are shown in Figs. 2–4 respectively. Selected bond lengths and angles are given in Table 4. For **5** there are two independent molecules in the asymmetric unit, for both of which the parameters are given. The first feature of note is that the structures all retain the *mer* geometry of **4**, and in both **5** and **6** the η^2 -bonded alkynes replace the middle tht, *i.e.* that *trans* to a Cl. Similar behaviour was reported by Poli and Gordon¹¹ who showed that in the displacement of thf by phosphine in *mer*- $[\text{MoCl}_3(\text{thf})_3]$ the first thf to be replaced was that *trans* to Cl. This geometry was referred to as *mer,trans*, a terminology that we will retain here. These authors ascribed the stereochemistry of the substituted product to the *trans*-labilizing influence of chloride on the thf ligand, and showed that it is always the first to be displaced. In Table 5 we compare a number of related structures of Mo^{III} , W^{III} and Nb^{III} , including those of **4–6**. The normal pattern is that the halides *trans* to each other display longer bond lengths than that *trans* to a neutral ligand, while the neutral ligands show the opposite trend. This pattern is only partially followed by **4**; although the *trans* Mo–Cl bond lengths are slightly longer than that *trans* to a tht, the reciprocal effect is not shown by the Mo–S bond lengths. The relative orientations of the tht rings as a result of the crystal packing may be responsible for the small deviation observed here. Nevertheless, in the replacement reaction it is the tht *trans* to a Cl which is replaced by an alkyne ligand. The geometry of both **5** and **6** is therefore *mer,trans*. An exception to the *mer,trans* geometry is $[\text{NbCl}_3(\text{thf})_2(\text{PhCCMe})]$ reported by Cotton and Shang.⁷ It was prepared directly from $[\text{NbCl}_4(\text{thf})_2]$ by Na/Hg reduction in the presence of the alkyne, and has *mer,cis* geometry. The *trans* influence of the alkyne is a dominating feature of all the $\text{MX}_3\text{L}_2(\text{alkyne})$ structures.

The structural parameters involving the alkynes in complexes **5** and **6** are compatible with the four-electron alkyne-donor model described by Templeton.¹⁷ The M–C bond lengths are in the ranges 2.03–2.05 (**5**) and 1.97–2.01 Å (**6**); the alkyne C–C bond lengths are 1.27(1) and 1.31(1) (**5**), and 1.32(3) Å (**6**). The complexes are thus formally 17-electron systems, as compared with the formal 15-electron status of **4**. The bonding in com-

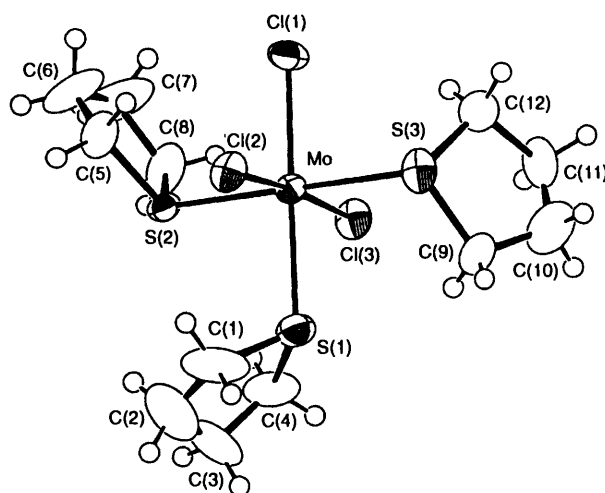


Fig. 2 Molecular structure of complex **4**. The thermal ellipsoids of the non-hydrogen atoms enclose 50% of the electron density

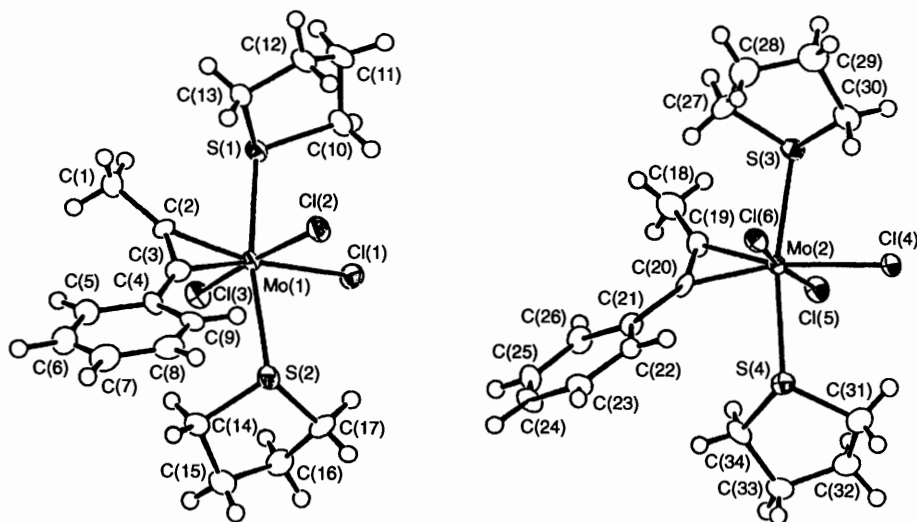


Fig. 3 Molecular structure of the two crystallographically independent molecules of complex 5, showing the atom labelling scheme. Details as in Fig. 2

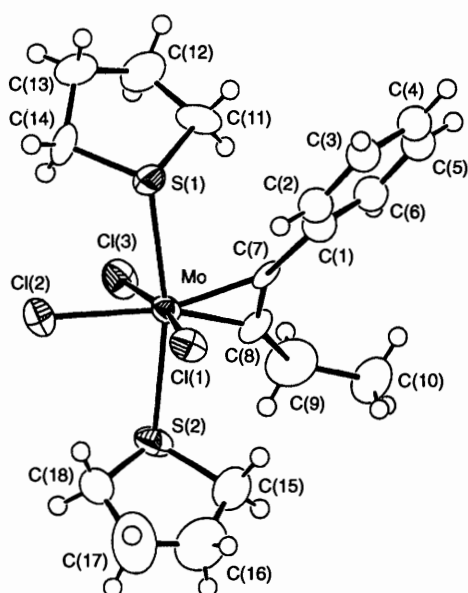


Fig. 4 Molecular structure of complex 6. Details as in Fig. 2

plexes with structural parameters in this range was discussed by Cotton and Hall,⁶ and by Cotton and Shang.⁷ It was argued that formally the alkyne might be considered to represent a dinegative ligand, with a concomitant increase in the oxidation state of the metal by two units. More recently, Nielson *et al.*^{16,18} have reported the syntheses and structures of a number of tungsten complexes with diphenylacetylene, and also presented evidence for considering the metal to have transferred sufficient electron density to the alkyne that the resulting oxidation state of the metal has been increased by two units *e.g.* in $[\text{WCl}_3(\text{PhC}_2\text{Ph})(\text{PMe}_2)_2]$ they would consider the oxidation state of W to be formally +5, a d^1 system. This complex has the same *mer,trans* geometry as that of 5 and 6. From the structural parameters of this, and related compounds, the authors considered the alkyne to be a four-electron donor, but point out that the omission of the metal-to-ligand back bonding in this description may give misleading implications of the electron distribution.

Owing to the relatively large estimated standard deviations (e.s.d.s) in the structural parameters for complex 6, no valid, detailed comparison can be made between the two alkyne complexes.

¹H NMR spectra

The reports of the spectra of $[\text{MoCl}_3(\text{thf})_3]$ and a variety of phosphine derivatives of this complex^{10,11} provided an important stimulus for using NMR spectroscopy for studying the solution behaviour of 4–6. The appearance of two resonances at low field ($\delta +35$ and 29) in the spectrum of 4 is compatible with the assignment to the α -protons of the tht rings in the 1 : 2 ratio expected for this *mer* complex. The assignment of resonances due to the β protons is less certain, since solutions of 4 begin to liberate tht as dimerization occurs. Resonances in the δ 2–4 range may therefore be due to either the β -protons of 1, or dimeric products. In addition there is overlap with free tht resonances to complicate the interpretation. The solution magnetic moment for compound 4 ($3.7 \mu_B$) suggests a $S = \frac{3}{2}$ ground state, which is reduced to $S = \frac{1}{2}$ after complexation of an alkyne (5, $1.9 \mu_B$; 6, $1.6 \mu_B$). The NMR spectra of these complexes are broadened, but do not display the huge chemical shift effects of 4, its thf analogue, and the phosphine derivatives of this complex. In this regard the explanation of Nielson *et al.*,^{16,18} namely that the alkyne complexes should be considered to have been oxidized to Mo^V , would be a plausible explanation. That the spin state is merely reduced by the lowering in symmetry as a tht is replaced is less plausible in that a similar substitution of thf by phosphine still leaves a highly paramagnetic complex ($S = \frac{3}{2}$).¹¹

Discussion

The difficulty in establishing the mechanisms of rapid catalytic reactions is well documented. The intermediates formed in mechanisms most frequently suggested^{1,3} for the catalytic polymerization and cyclotrimerization of alkynes are: (i) metal-lacyclic species (for cyclization); (ii) alkylidene or alkylidyne complexes; (iii) σ -vinyl complexes; (iv) metal acetylides. A collection of three pathways to account for the major products observed in this study is shown in Scheme 1. The key observation is that chlorinated species are usually only very minor products, and that in most reactions a large percentage of the molybdenum in the original catalyst is recovered as 1. The formation of ladder polymers and cyclotrimers as the major products in many reactions can be accommodated in this scheme. In the former case this would involve a series of 2+2 cycloadditions as suggested by Simionescu and Percec.¹² For the latter case, oxidative coupling and the formation of a series of metal-lacyclic species would occur. We have in some instances observed small amounts of cyclotetramer as well as cyclotrimer,

Table 4 Selected bond lengths (Å) and angles (°) for [MoCl₃(tht)₃] **4**, [MoCl₃(tht)₂(PhCCMe)] **5**, and [MoCl₃(tht)₂(PhCCEt)] **6**

Complex 4			
Mo–Cl(1)	2.401(3)	Mo–S(1)	2.539(4)
Mo–Cl(2)	2.407(3)	Mo–S(2)	2.519(4)
Mo–Cl(3)	2.410(3)	Mo–S(3)	2.541(4)
Cl(1)–Mo–Cl(2)	91.2(1)	Cl(2)–Mo–S(3)	89.2(1)
Cl(1)–Mo–Cl(3)	94.4(1)	Cl(3)–Mo–S(1)	86.4(1)
Cl(1)–Mo–S(1)	177.9(1)	Cl(3)–Mo–S(2)	90.3(1)
Cl(1)–Mo–S(2)	91.8(1)	Cl(3)–Mo–S(3)	91.0(1)
Cl(1)–Mo–S(3)	88.7(1)	S(1)–Mo–S(2)	90.1(1)
Cl(2)–Mo–Cl(3)	174.4(1)	S(1)–Mo–S(3)	89.4(1)
Cl(2)–Mo–S(1)	88.0(1)	S(2)–Mo–S(3)	178.6(1)
Cl(2)–Mo–S(2)	89.4(1)		
Complex 5			
Molecule 1		Molecule 2	
Mo(1)–Cl(1)	2.462(3)	Mo(2)–Cl(4)	2.474(3)
Mo(1)–Cl(2)	2.377(3)	Mo(2)–Cl(5)	2.415(3)
Mo(1)–Cl(3)	2.428(3)	Mo(2)–Cl(6)	2.389(3)
Mo(1)–S(1)	2.540(3)	Mo(2)–S(3)	2.540(3)
Mo(1)–S(2)	2.550(3)	Mo(2)–S(4)	2.533(3)
Mo(1)–C(2)	2.030(9)	Mo(2)–C(19)	2.029(9)
Mo(1)–C(3)	2.048(9)	Mo(2)–C(20)	2.039(9)
C(1)–C(2)	1.49(1)	C(18)–C(19)	1.48(1)
C(2)–C(3)	1.27(1)	C(19)–C(20)	1.31(1)
C(3)–C(4)	1.47(1)	C(20)–C(21)	1.47(1)
Cl(1)–Mo(1)–Cl(2)	86.6(1)	Cl(4)–Mo(2)–Cl(5)	84.42(9)
Cl(1)–Mo(1)–Cl(3)	83.98(9)	Cl(4)–Mo(2)–Cl(6)	85.49(9)
Cl(1)–Mo(1)–S(1)	83.95(9)	Cl(4)–Mo(2)–S(3)	84.12(9)
Cl(1)–Mo(1)–S(2)	85.98(9)	Cl(4)–Mo(2)–S(4)	84.32(9)
Cl(1)–Mo(1)–C(2)	159.3(3)	Cl(4)–Mo(2)–C(19)	159.5(3)
Cl(1)–Mo(1)–C(3)	163.9(3)	Cl(4)–Mo(2)–C(20)	162.8(3)
Cl(2)–Mo(1)–Cl(3)	170.55(9)	Cl(5)–Mo(2)–Cl(6)	169.90(9)
Cl(2)–Mo(1)–S(1)	87.99(9)	Cl(5)–Mo(2)–S(3)	92.26(9)
Cl(2)–Mo(1)–S(2)	88.04(9)	Cl(5)–Mo(2)–S(4)	88.4(4)
Cl(2)–Mo(1)–C(2)	84.5(3)	Cl(5)–Mo(2)–C(19)	83.2(3)
Cl(2)–Mo(1)–C(3)	88.8(2)	Cl(5)–Mo(2)–C(20)	103.7(3)
Cl(3)–Mo(1)–S(1)	90.14(9)	Cl(6)–Mo(2)–S(3)	86.81(9)
Cl(3)–Mo(1)–S(2)	92.17(9)	Cl(6)–Mo(2)–S(4)	90.47(9)
Cl(3)–Mo(1)–C(2)	84.5(3)	Cl(6)–Mo(2)–C(19)	106.6(3)
Cl(3)–Mo(1)–C(3)	100.5(2)	Cl(6)–Mo(2)–C(20)	86.0(3)
S(1)–Mo(1)–S(2)	169.37(9)	S(3)–Mo(2)–S(4)	168.29(9)
S(1)–Mo(1)–C(2)	79.0(3)	S(3)–Mo(2)–C(19)	80.2(3)
S(1)–Mo(1)–C(3)	111.3(3)	S(3)–Mo(2)–C(20)	110.3(3)
S(2)–Mo(1)–C(2)	111.5(3)	S(4)–Mo(2)–C(19)	111.5(3)
S(2)–Mo(1)–C(3)	78.4(3)	S(4)–Mo(2)–C(20)	80.9(3)
C(2)–Mo(1)–C(3)	36.4(4)	C(19)–Mo(2)–C(20)	37.6(4)
C(3)–C(2)–Mo(1)	72.6(6)	C(20)–C(19)–Mo(2)	71.6(6)
C(2)–C(3)–Mo(1)	71.0(6)	C(19)–C(20)–Mo(2)	70.8(8)
C(1)–C(2)–C(3)	141.6(9)	C(18)–C(19)–C(20)	144(1)
C(4)–C(3)–C(2)	141.09(9)	C(21)–C(20)–C(19)	142.1(9)
Complex 6			
Mo–Cl(1)	2.402(1)	Mo–C(7)	2.01(2)
Mo–Cl(2)	2.479(6)	Mo–C(8)	1.97(2)
Mo–Cl(3)	2.411(6)	C(7)–C(8)	1.32(3)
Mo–S(1)	2.539(6)	C(7)–C(1)	1.47(1)
Mo–S(2)	2.534(6)	C(8)–C(9)	1.53(3)
Cl(1)–Mo–Cl(2)	84.5(2)	Cl(2)–Mo–Cl(3)	84.7(2)
Cl(1)–Mo–C(3)	169.1(2)	Cl(2)–Mo–S(1)	82.1(2)
Cl(1)–Mo–S(1)	91.0(2)	Cl(2)–Mo–S(2)	85.2(3)
Cl(1)–Mo–S(2)	87.4(2)	Cl(2)–Mo–C(7)	160.0(5)
Cl(1)–Mo–C(7)	87.5(5)	Cl(2)–Mo–C(8)	161.2(6)
Cl(1)–Mo–C(8)	105.0(6)	Cl(3)–Mo–C(7)	79.7(5)

as might be expected *via* this route. Linear, conjugated polyenic polymers from Bu^tC≡CH would have to form *via* a different process, in which the initial formation of a σ-alkynyl complex *via* oxidative addition of the C–H bond to molybdenum is proposed. Termination could occur *via* elimination of either a Cl ligand (this would preclude reformation of **1**) or of the hydride (this would allow the regeneration of **1**). For terminal alkynes

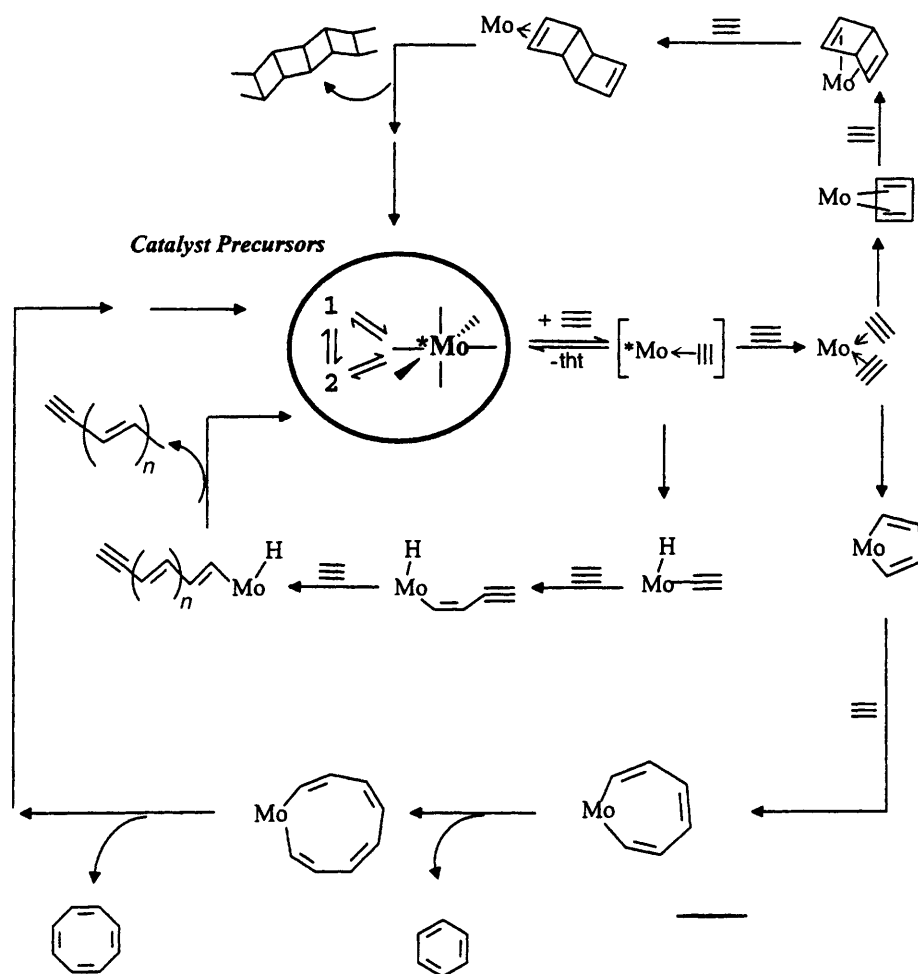
the formation of a vinylidene intermediate is also possible, but for this to operate for internal alkynes it would require the breaking of a C–C bond in the substrate alkyne, which is generally considered to be energetically unfavourable.

Our results contribute information directly only to the first step, and strongly suggest that loss of a labile ligand to form a co-ordinatively unsaturated mononuclear centre is common to

Table 5 Comparison of structural parameters for several *mer*-MX₃L₃, *mer,trans*-MX₃L₂(alkyne) and *mer,cis*-MX₃L₂(alkyne) complexes

Compound	M-X ^a /Å	M-L ^b /Å
[MoCl ₃ (thf) ₃] ¹⁴	Cl _t 2.411(2), 2.411(2) Cl _c 2.387(2)	O _t 2.136(4), 2.120(4) O _c 2.189(4)
[MoI ₃ (thf) ₃] ¹⁵	I _t 2.790(1), 2.790(1) I _c 2.746(2)	O _t 2.193(8), 2.193(8) O _c 2.212(12)
[MoCl ₃ (tht) ₃] (this work)	Cl _t 2.407(3), 2.410(3) Cl _c 2.401(3)	S _t 2.519(4), 2.541(4) S _c 2.539(4)
[MoCl ₃ (tht) ₂ (PhCCMe)] (This work, two independent molecules)	Cl _t 2.415(3), 2.389(3) Cl _c 2.474(3) Cl _t 2.377(3), 2.428(3) Cl _c 2.462(3)	S _t 2.540(3), 2.533(3) S _t 2.540(4), 2.550(3)
[MoCl ₃ (tht) ₂ (PhCCEt)] (This work)	Cl _t 2.402(5), 2.411(6) Cl _c 2.479(6)	S _t 2.539(6), 2.534(6)
[WCl ₃ (PhCCPh)(PMe ₃) ₂] ¹⁶	Cl _t 2.393(3), 2.413(6) Cl _c 2.479(6)	P _t 2.549(3), 2.552(3)
[NbCl ₃ (PhCCMe)(thf) ₂] ⁷	Cl _t 2.374(2), 2.407(2) Cl _c 2.377(2)	O (trans to alkyne) 2.354(4) O (trans to Cl) 2.203(4)

^a X = halide. ^b L = O of thf, S of tht or P of PMe₃.



Scheme 1

all the reactions we have studied. The resulting *Mo centre (Scheme 1) is conceivably capable of providing up to three sites for co-ordination of alkynes or their coupled derivatives. The stereochemistry at this site might vary depending on the precursor, and this could explain the differences in the isomer distributions in the alkyne products. We have been unable to isolate any intermediate beyond the first monoalkyne complex. To replace a second tht requires such a large excess of alkyne that at this stage the catalytic reaction proceeds rapidly. Our results cannot rigorously exclude the possibility of other pathways occurring which involve loss of halide from the catalyst centre, since

minor amounts of products containing halide have been observed, and in no reaction has all the molybdenum been recovered as **1**. One such mechanism that has been demonstrated is the insertion of an alkyne into a vinylmetal complex.^{1,3} This would require, as the first step, the insertion of the alkyne into a M-X bond. This mechanism is entirely possible for the Bu^cCCH polymerization reactions. However, the net result will be incorporation of Cl into the product, and will preclude the regeneration of the dimer **1**.

The unusual aspect of these catalytic systems is that they are potentially capable of displaying radical character, since the

molybdenum(III) centres are paramagnetic, but there is no evidence that this plays a role in the catalytic processes.

Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon, or in a nitrogen-atmosphere glove-box. The most convenient starting material for molybdenum(III) chemistry, $[\text{MoCl}_3(\text{thf})_3]$, was prepared by a literature method.¹⁹ Complexes **1** and **2** were prepared as described previously.⁸ Tetrahydrothiophene was dried and distilled over CaH_2 and stored over 4 Å molecular sieves. Tetrahydrofuran, diethyl ether and toluene were dried over sodium-benzophenone. Alkynes were dried over MgSO_4 and distilled over 4 Å molecular sieves. All solvents and reagents were degassed prior to use. Infrared spectra (polyethylene pellets or Nujol mulls, KBr plates) were run on a Mattson 4030 Galaxy Series Fourier-transform spectrometer, ^1H NMR spectra by using a Bruker ACE-200 or AM-400 spectrometer. Magnetic susceptibility measurements were made using the Evans method,²⁰ in CD_2Cl_2 solution. Elemental analyses were performed by the Microanalytical and Spectroscopy Laboratory, Department of Chemistry, University of Calgary. Cyclotrimers and oligomers were identified by using a Hewlett-Packard 5890 Series II GC-MS system and also by ^1H NMR spectroscopy.

Procedures for testing catalytic activity and characterization of organic products

The procedures used to work up the catalytic test reactions were standardized to the general method now described. Minor differences were sometimes necessary. After a reaction was complete the low-boiling point organic products were removed by vacuum distillation, collected in a cold trap (liquid N_2), and kept for gas chromatography-mass spectrometry (GC-MS) analysis. When a solid polymeric product was formed the reaction mixture was normally gel-like, but could be filtered on a very fine sintered-glass filter. The polymers were then kept on the sintered glass, washed and dried under vacuum. The clear mother-liquor was reduced almost to dryness, Et_2O or hexane was introduced to extract any cyclotrimers or oligomers which were then characterized by GC-MS and/or ^1H NMR spectroscopy. In some instances an elemental analysis was carried out for further confirmation. The mass spectra were compared with those in a data bank. The reaction residue, after this extraction, was redissolved in CDCl_3 or $(\text{CD}_3)_2\text{CO}$, and checked by ^1H NMR spectroscopy, which invariably showed resonances belonging to the complex **1**. No other metal-containing residue was ever identified. The following selected catalytic testing reactions will illustrate the experimental procedures, the results of which have been documented in the tables.

Reaction of pent-2-yne ($\text{MeC}\equiv\text{CEt}$) with complex **4.** Complex **4** (50 mg, 0.107 mmol) was dissolved in toluene (50 cm^3) at 0 °C. Pent-2-yne (0.5 cm^3 , 0.0052 mol) was added to the solution dropwise. The reaction mixture was then stirred for *ca.* 6 h. A light red gelatinous solution resulted which was degassed prior to vacuum distillation. The colourless, clear distillate, which contained the most volatile products, was collected in a liquid-nitrogen trap. The distillation was stopped when ≈ 5 cm^3 of liquid had accumulated in the trap. The rest of this solution was concentrated to ≈ 5 cm^3 and then filtered through a filter-stick. The gel-like material on the sintered glass was then washed with toluene (2×10 cm^3) and CH_2Cl_2 (2×10 cm^3) and dried under vacuum. Polymer yield: 0.30 g, 85% based on the alkyne used. The solvent of the catalyst solution was removed under vacuum, the residual solid was washed with Et_2O (3×5 cm^3) using an ultrasonic bath, and dried under vacuum. The Et_2O was kept for GC-MS analysis. This dark red residue was identified as complex **1** (23 mg) by ^1H NMR spectroscopy. The GC-MS analysis of the Et_2O extract showed some oligomers, and a trace

amount of chlorinated species. Only solvent and free tht were detected by GC-MS analysis of the distillate [Found: C, 87.1; H, 11.2. Calc. for polymers $(\text{C}_5\text{H}_8)_n$: C, 88.15; H, 11.85%]. IR (KBr pellet, cm^{-1}) 2978s, 2930s, 2874s, 1628w, 1615w, 1462s, 1371m, 1315s, 1103m, 999m, 936m and 798m. The polymer formed a gel in benzene, carbon tetrachloride, toluene and chlorobenzene, but was insoluble in all other common organic solvents that were tested. An attempted melting-point determination showed that the product is very refractory, and only begins to decompose at >300 °C.

The same procedures were used for the reactions of pent-2-yne with complexes **1** and **2**. Yields of polymer: for **1**, 51%; *ca.* 70% of the original amount of **1** was recovered after the reaction; for **2**, 92%; 46% of the original catalyst was recovered as **1**.

Hex-3-yne ($\text{EtC}\equiv\text{CEt}$). The same procedures were used as for the $\text{MeC}\equiv\text{CEt}$ reactions. Polymer yields were 62, 30 and 60% using complexes **4**, **2** and **1** as catalyst respectively. The major by-product was hexaethylbenzene, which was detected by GC-MS ($m/z = 246$). In the case of **1**, $\text{Et}(\text{Cl})\text{C}=\text{C}(\text{Cl})\text{Et}$ was detected as well. The insoluble polymeric products did not soften in the temperature range 0–460 °C, but darkened.

Hex-1-yne ($\text{Bu}^n\text{C}\equiv\text{CH}$). The compound $\text{Bu}^n\text{C}\equiv\text{CH}$ (1.3 cm^3 , 0.0114 mol) was added to a solution of complex **2** (0.165 g, 0.247 mmol) in toluene (50 cm^3) at room temperature. The solution underwent a change from deep purple to dark red, but no solid polymers were observed. After 36 h the standard work-up procedure was carried out. The GC-MS analysis showed that the light fraction contained only solvent. The hexane extract contained cyclotrimers (m/z 246), 51% 1,3,5-tributylbenzene, 35% 1,2,4-tributylbenzene; 4% hydrochlorinated dimers (m/z 200); 2% hydrochlorinated linear trimers (m/z 282); 2% linear trimers (m/z 248); 1% cyclotetramers (m/z 328); 2% monochlorinated cyclotetramers (m/z 363); 1% cyclopentamers and others. The dark red residue, after separating the organic products, was confirmed to be **1** (56 mg). Similar reactions were carried out with hex-1-yne and **1** and **4**, and pent-1-yne with **1**, **2** and **4**. In each case, cyclic trimers were the major products, and **1** was identified as the residual molybdenum-containing complex.

Phenylethyne ($\text{PhC}\equiv\text{CH}$). The procedures were basically the same as those described for the $\text{Bu}^n\text{C}\equiv\text{CH}$ and $\text{Pr}^n\text{C}\equiv\text{CH}$ reactions. The reactions of this terminal alkyne with complexes **1**, **2** and **4** yielded, in all cases, mainly cyclotrimers. Similar results were obtained for $\text{MeC}\equiv\text{CPh}$ and $\text{EtC}\equiv\text{CPh}$, but $\text{Pr}^n\text{C}\equiv\text{CPh}$ did not react. The major products were 1,3,5- and 1,2,4-trisubstituted benzenes formed in different ratios.

1-Phenylprop-1-yne ($\text{PhC}\equiv\text{CMe}$). The alkyne (0.30 cm^3 , 0.002 42 mol) was added to a solution of complex **4** (50 mg, 0.112 mmol) in toluene (50 cm^3) at 0 °C. The procedure was the same as for the $\text{PhC}\equiv\text{CH}$ reaction. No gel-like materials were observed and the reaction was terminated after 8 h. The products based on GC-MS characterization were mainly cyclotrimers (Found: 80% 1,3,5-trimethyltriphenylbenzene; 20% 1,2,4-trimethyltriphenylbenzene). In an analogous way, the alkyne (0.30 cm^3 , 0.002 42 mol) was treated with **1** or **2** (50 mg, 0.0747 mmol) toluene solution (50 cm^3). After 36 h the products were identified as: for **2**, 80% 1,3,5-trimethyltriphenylbenzene (m/z 348), 19% 1,2,4-trimethyltriphenylbenzene; for **1**, 85% 1,3,5-trimethyltriphenylbenzene, 13% 1,2,4-trimethyltriphenylbenzene.

1-Phenylbut-1-yne ($\text{PhC}\equiv\text{CEt}$). The alkyne (0.12 cm^3 , 0.0015 mol) was added to a toluene solution of the catalyst (20 mg in 20 cm^3). The Et_2O extract still contained a significant amount of free alkyne after 4 d of reaction at room tem-

perature. Only 50% alkyne had been converted. The major products from GC-MS results were: for **4**, 88% 1,3,5-trimethyltriphenylbenzene, 12% 1,2,4-triethyltriphenylbenzene; for **2**, 84% 1,3,5-triethyltriphenylbenzene, 16% 1,2,4-triethyltriphenylbenzene; for **1**, 90% 1,3,5-triethyltriphenylbenzene, 10% 1,2,4-triethyltriphenylbenzene.

1-Phenylpent-1-yne (PhC≡CPrⁿ) and 1-phenylhex-1-yne (PhC≡CBuⁿ). The mole ratio of alkyne to catalyst was 50:1, using a solution of catalyst (30 mg) in toluene (30 cm³). The same conditions were used for each of the catalysts **1**, **2** and **4**. The reaction times were 4 and 6 d for PhC≡CPrⁿ and PhC≡CBuⁿ respectively. No reaction was detected after work-up. The temperature of the solution of **1** and PhC≡CPrⁿ was raised to 50 °C, but still no reaction was observed.

Ethyne (HC≡CH). The compound HC≡CH was bubbled through freshly distilled toluene (containing MgSO₄ drying agent) to give a saturated solution (-78 °C, atmospheric pressure). The saturated solution was then distilled to another flask, which was cooled in a liquid-nitrogen bath, and stored over 4 Å molecular sieves. The estimated concentration of the toluene solution, at room temperature, was ca. 6 mol% according to a ¹H NMR analysis in C₆D₃CD₃. This acetylene solution (20 cm³) was then introduced into a solution of complex **1** (50 mg) in CH₂Cl₂ (30 cm³) at 22 °C. A black precipitate was produced immediately. After 2 h the solution was filtered and the light red supernatant yielded a dark red solid, later characterized as **1**, but most of the original catalyst was trapped in the polymer. The black precipitate was washed with acetone (3 × 5 cm³) and dried *in vacuo*. Yield: 0.21 g, 70% based on the estimated 6 mol% ethyne. The GC-MS was done on a sample of the acetone washing and trace amounts of benzene, ClHC=CHCH=CH₂ and H₂C=CHCH=CH₂ were detected. The black material remained undissolved, however.

3,3'-Dimethylbut-1-yne (Bu^tC≡CH). The compound Bu^tC≡CH (0.40 cm³, 0.0032 mol) was syringed into a solution of complex **1** (50 mg, 0.149 mmol) in acetone (30 cm³) at 22 °C. (Acetone was found to be a more effective solvent than toluene for this system.) After 8 h the solution became viscous, and on filtering yielded a white gel-like precipitate. After washing with CH₂Cl₂ the yield of polymer was 0.146 g, 61%. The red filtrate was pumped to dryness and the ¹H NMR spectrum of this residue in CDCl₃ indicated that it was mainly **1**. The Et₂O washings were found from GC-MS to contain cyclotrimers and oligomers [Found: C, 87.8; H, 12.3. Calc. for polymers (C₆H₁₀)_n: C, 87.75; H, 12.25%]. IR (KBr, cm⁻¹) 2960s, 2870m, 1668m, 1628w, 1470s, 1375s, 1230, 1103, 910 and 870. UV/VIS (toluene, λ_{max}/nm) 272. NMR (CCl₄-CDCl₃): ¹H, δ 6.3 (HC=) and 1.2 [(CH₃)₃CC=]; ¹³C, δ 145 (=CBu^t), 128 (HC=), 38.7 (Me₃CC=) and 31.8 (H₃C). The melting range of the polymer was ca. 250–266 °C and continued heating resulted in carbonization.

The same procedure was used for the reaction of complex **2** (50 mg, 0.149 mmol) with Bu^tC≡CH (0.5 cm³, 0.004 07 mol). Polymer yield: 0.151 g, 45%. The properties of the polymer were slightly different from those of the polymers from **1**. UV/VIS (toluene, λ_{max}/nm) 270. IR (KBr, cm⁻¹) 2960s, 2870m, 1668m, 1628w, 1470s, 1375s, 1230m, 1103m, 910s and 870s. NMR (CCl₄-CDCl₃): ¹H, δ 6.3 (HC=) and 1.2 (CH₃); ¹³C, 145 (=CBu^t), 128 (HC=), 38.7 (Me₃CC=) and 31.8 (H₃C). Softening point ≈260 °C.

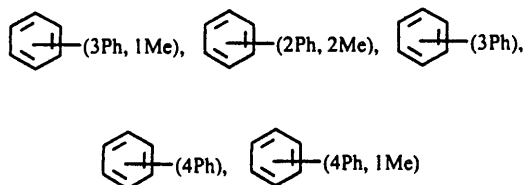
Similarly, complex **4** (50 mg, 0.112 mmol) was treated with Bu^tC≡CH (0.5 cm³, 0.004 07 mol) in acetone (50 cm³) at 0 °C for 8 h. Yield of polymer: 0.20 g (60%).

Reactions of [MoCl₃(tht)₂(PhCCMe)] **5**

(a) **With pent-2-yne.** The compound EtC≡CMe (1 cm³, 0.0104 mol) was syringed into acetone (60 cm³) with complex **5**

(130 mg, 0.263 mmol) at 0 °C, and after 2 h insoluble polymer was filtered off, washed and dried (0.32 g, 45%). The clear distillate was collected for GC-MS, and showed a trace amount of free MeC≡CPh, plus free EtC≡CMe. In the IR spectrum of the polymer (KBr) the bands at 2840 and 1628 cm⁻¹ (ν_{C-C}) were enhanced in comparison with those of polymers from **4**, suggesting incorporation of MeC≡CPh into the polymeric products.

(b) **With 1-phenylethyne.** The compound PhC≡CH (1.0 cm³, 0.009 08 mol) was added to a solution of complex **5** (0.111 g, 0.224 mmol) in acetone (50 cm³) at 0 °C. The reaction mixture was stirred for 36 h. The acetone distillate showed traces of free PhC≡CH and PhC≡CMe; the hexane washings contained several different cyclotrimers. The triphenylbenzenes represented >90% of the total.



(c) **With 1-phenylprop-1-yne.** The compound PhC≡CMe (0.30 cm³, 0.002 42 mol) was syringed into a solution of complex **5** (0.100 g, 0.220 mmol) in acetone (30 cm³) at ambient temperature. After 16 h the red reaction mixture had darkened, and upon work-up the product pattern was similar to that obtained in the reactions of **4** with PhC≡CMe.

Preparation of [MoCl₃(tht)₃] **4**

A solution of [MoCl₃(thf)₃] (4.00 g, 9.55 mmol) in tht (50 cm³) was stirred for 3 h at room temperature. The solution was then concentrated under vacuum until orange-yellow crystals formed. The crystals were filtered off, washed with diethyl ether and dried under vacuum. Yield: 4.1 g, 92% (Found: C, 34.4; H, 5.80. Calc. for C₁₂H₂₄Cl₃S₃Mo: C, 34.45; H, 5.80%). ¹H NMR (paramagnetic, CDCl₃); δ 35.4, 28.7 and 3.5–1.9 (br). IR (Nujol, cm⁻¹): 2935vs, 2858s, 1433s, 1305m, 1255s, 1076m, 885m, 808s, 665m, 575w and 327s.

Preparation of [MoCl₃(tht)₂(PhCCMe)] **5**

At 0 °C, PhCCMe (2.1 cm³, 16.8 mmol) was added to [MoCl₃(tht)₃] (0.771 g, 1.65 mmol) and sufficient toluene (≈10 cm³) was introduced to dissolve all the solid. After stirring for 2 h the solution changed from orange-yellow to dark red. The temperature was then raised to 22 °C and the solution was stirred for another hour after which it was concentrated to 5 cm³ and stored at -20 °C. After 8 h red crystals had formed, which were filtered off, washed with a small amount of toluene, then ether, and dried under vacuum. Yield: 0.42 g, 51.4%. A second crop can be obtained by precipitation with ether, but this tends to be contaminated by an oily by-product. With care the system can be manipulated to give an almost quantitative yield. Interestingly, the cyclotrimerization reaction is always ongoing while the product is being isolated (Found: C, 41.5; H, 4.80. Calc. for C₁₇H₂₄Cl₃MoS₂: C, 41.25; H, 4.90%). ¹H NMR (paramagnetic, CDCl₃); δ 8.0–7.4 (m, C₆H₅), 3.5–2.0 (br, unresolved m; H in tht) and 2.42 (s, CH₃). IR (cm⁻¹): 1732 [ν(C≡C)].

Preparation of [MoCl₃(tht)₂(PhCCEt)] **6**

A similar procedure to that for complex **5** above was followed, except that the reaction temperature was kept at 0 °C for 8 h. The reaction product was precipitated with ether (slightly soluble) and hexane. The solid filtered from this mixture was

slowly recrystallized at -20°C from toluene containing an excess of PhCCEt. Yields of $\approx 30\%$ of crystalline product could be obtained (Found: C, 42.5; H, 5.15. Calc. for $\text{C}_{18}\text{H}_{26}\text{Cl}_3\text{MoS}_2$: C, 42.55; H, 5.00%). ^1H NMR (paramagnetic; CDCl_3): δ 8.0–7.4 (m, H in Ph), 3.5–2.0 (br, H in tht), 2.42 (q, CH_2 in Et) and 1.89 (t, CH_3). IR (cm^{-1}): 1730 ($\text{C}\equiv\text{C}$ stretch).

Crystallography

Compound 4. *Crystal data.* $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{MoS}_3$, $M = 466.80$, monoclinic, space group $P2_1/n$ (alt. $P2_1/c$, no. 14), $a = 10.702(5)$, $b = 15.129(6)$, $c = 11.702(3)$ Å, $\beta = 99.21(2)^{\circ}$, $U = 1870(1)$ Å³, $Z = 4$, $D_c = 1.66$ g cm⁻³, $F(000) = 948$, $\mu(\text{Mo-K}\alpha) = 1.45$ mm⁻¹.

A yellow crystal of approximate dimensions $0.12 \times 0.10 \times 0.08$ mm was mounted on a glass fibre. All measurements were made on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) at -123°C . Accurate cell dimensions and a crystal orientation matrix were determined by least-squares refinement of the setting angles of 22 carefully centred reflections in the range $18.81 < 2\theta < 27.02^{\circ}$. Intensity data were collected in the ω - 2θ scan mode, to a maximum 2θ value of 45.1° . Scans of $(0.173 + 0.30 \tan \theta)^{\circ}$ were made at $4^{\circ} \text{min}^{-1}$ in ω . Weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of three scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflections and the ratio of the peak counting time to background time was 2:1. Of the 2744 reflections collected, 2585 were unique ($R_{\text{int}} = 0.060$). Three representative reflections were recorded after every 200. Over the course of the data collection the standards decreased by 1.2%. The intensities were corrected for this decay, and also for Lorentz-polarization effects. An empirical absorption was applied using the program DIFABS²¹ which resulted in transmission factors of between 0.79 and 1.16. The data were also corrected for secondary extinction. The structure was solved by the heavy-atom method,²² and expanded using Fourier techniques.²³ The non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in the model, but not refined. The final cycle of full-matrix least-squares refinement was based on 1303 observed reflections [$I > 3\sigma(I)$] and 172 variables. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, and $\sigma(F)$ was derived from counting statistics. The refinement converged with $R = 0.044$ and $R' = 0.043$. The standard deviation of an observation of unit weight was 1.53. There were no unexpected features in the final difference map. All calculations were performed using the TEXSAN package.²⁴ Neutral atom scattering factors were taken from Cromer and Weber.²⁵ Anomalous dispersion effects were included in F_{calc} ;²⁶ the values of $\Delta f'$ and $\Delta f''$ were those Creagh and McAuley.²⁷

Compound 5. *Crystal data.* $\text{C}_{17}\text{H}_{24}\text{Cl}_3\text{MoS}_2$, $M = 494.80$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.754(3)$, $b = 14.147(3)$, $c = 26.640(3)$ Å, $\beta = 99.61(2)^{\circ}$, $U = 3996(1)$ Å³, $Z = 8$, $D_c = 1.64$ g cm⁻³, $F(000) = 948$, $\mu(\text{Mo-K}\alpha) = 12.6$ cm⁻¹.

The procedures and equipment used were essentially the same as those described above for complex 4. The specific information pertinent to 5 is given in truncated form. The crystal was dark orange, irregular block-shaped, of approximate dimensions $0.45 \times 0.35 \times 0.55$ mm, mounted on a glass fibre and cooled to -123°C . Least-squares refinement of the setting angles of 22 carefully centred reflections in the range $46.25 < 2\theta < 49.59^{\circ}$. Scans of $(0.79 + 0.35 \tan \theta)^{\circ}$ were made at $8^{\circ} \text{min}^{-1}$ in ω . Of the 7758 reflections collected, 7342 were unique ($R_{\text{int}} = 0.131$). Over the course of the data collection the standards decreased by 4.8%. An empirical absorption correction resulted in transmission factors ranging from 0.81 to 1.00. The structure was solved by direct methods, and expanded using Fourier techniques. The final cycle of full-matrix least-

squares refinement was based on 5158 observed reflections [$I > 3\sigma(I)$] and 415 variables. The refinement converged with $R = 0.054$ and $R' = 0.070$. The standard deviation of an observation of unit weight was 2.24.

Compound 6. *Crystal data.* $\text{C}_{18}\text{H}_{26}\text{Cl}_3\text{MoS}_2$, $M = 508.82$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 13.609(3)$, $b = 14.701(3)$, $c = 10.720(3)$ Å, $U = 2144.7(8)$ Å³, $Z = 4$, $D_c = 1.58$ g cm⁻³, $F(000) = 1036$, $\mu(\text{Mo-K}\alpha) = 11.8$ cm⁻¹.

The procedures and equipment used were essentially the same as those described for complex 4. The crystal was a dark orange needle of approximate dimensions $0.67 \times 0.17 \times 0.15$ mm mounted on a glass fibre; data were collected at 23°C . Least-squares refinement of the setting angles of 22 carefully centred reflections in the range $20 < 2\theta < 30^{\circ}$. Intensity data were collected to a maximum 2θ value of 50.1° . Scans of $(1.42 + 0.34 \tan \theta)^{\circ}$ were made at $4^{\circ} \text{min}^{-1}$ in ω . A total of 2182 reflections were collected. Over the course of the data collection the standards decreased by 1.7%. An empirical absorption correction resulted in transmission factors ranging from 0.61 to 0.98. The structure was solved by direct methods, and expanded using Fourier techniques. All non-hydrogen atoms except the phenyl carbons were refined anisotropically; the phenyl carbon atoms were constrained as regular hexagons with an overall isotropic thermal parameter. Hydrogen atoms were included at geometrically idealized positions. The final cycle of full-matrix least-squares refinement was based on 1067 observed reflections [$I > 3\sigma(I)$] and 170 variables. The refinement converged with $R = 0.055$ and $R' = 0.056$. The standard deviation of an observation of unit weight was 1.89.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/257.

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