Polymerization of *tert*-butylacetylene by seven-coordinate heterobimetallic tungsten(II) and molybdenum(II) compounds

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Abstract

The reaction of *tert*-butylacetylene (*t*-BA) in the presence of seven-coordinate tungsten(II) and molybdenum(II) compounds [MCl(M′Cl$_3$)(CO)$_3$(NCR)$_2$] (M = Mo, W; M′ = Sn, Ge; R = Me, Et) leads to the catalytic coupling of *t*-BA molecules and the formation of high-molecular-weight ($\overline{M}_n > 10^5$) soluble polymers. The geometric structure of poly(*tert*-butylacetylene) (P-*t*-BA) was determined by means of ^{1}H- and ^{13}C-NMR spectroscopy. The monitoring of the reaction between *t*-BA and the metal complex by means of ^{1}H-NMR spectroscopy provided further insight into the initiation step of this polymerization process. The reaction of a heterobimetallic compound with a stoichiometric amount of *t*-BA yields compounds in which CO and/or nitrile ligands have been replaced by a *t*-BA ligand. The alkyne molybdenum(II) and tungsten(II) complexes formed were characterized structurally by means of IR and NMR spectroscopy. The possible mechanisms for the formation of very reactive intermediate compounds and their role in the catalytic process are discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Over the past several years we have been exploring the chemistry of seven-coordinate tungsten(II) and molybdenum(II) complexes. As [WCl$_2$(CO)$_3$L$_2$] (L = PPh$_3$, AsPh$_3$SbPh$_3$) compounds have been shown to be efficient catalysts in a number of important catalytic reactions [1–5], we have turned our attention towards the synthesis of more soluble and versatile derivatives containing nitrile ligands, which are often more labile than phosphines and may

result in enhanced activity. In particular, hetero-bimetallic compounds [MCl(M′Cl$_3$)(CO)$_3$-(NCR)$_2$] (M = Mo, W; M′ = Sn, Ge; R = Me, Et) with a metal−metal bond are intriguing because of the possibility that in reaction with an alkyne, the unsaturated carbon−carbon bond may be activated. We recently reported the synthesis and structure of such compounds [6–9]. The reactivity of these compounds with alkynes (PhC≡CPh, PhC≡CMe, PhC≡CH) has been studied [6–9], but reactions with *tert*-butyla-cetylene (*t*-BA) have not yet been investigated in a comparative fashion. The high catalytic activity of the heterobimetallic species in the polymerization of phenylacetylene led us to in-vestigate how these compounds behaved to-

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wards *t*-BA. Our goal was to obtain more information about the catalytically active species formed in the initiating step of alkyne polymerization.

2. Experimental

2.1. General data

The synthesis and manipulation of all chemicals was carried out under nitrogen using standard Schlenk techniques. Solvents and liquid reagents were dried and distilled from CaH_2 under nitrogen prior to use. *t*-BA (Aldrich) was used as supplied. Solution IR spectra were obtained using KBr or NaCl plates, while solid samples were recorded using KBr pellets on an FT-IR Model-400 Nicolet instrument. NMR spectra were run using a Bruker AMX-300 spectrometer. The analysis of the catalytic reaction products was performed on a Hewlett-Packard GC-MS system as well as by ^{1}H-NMR and IR spectroscopy. Molecular weights of the poly(*tert*-butylacetylene) (P-*t*-BA) were measured using $CHCl_3$ solutions, a refractive index detector and a Plgel 10 m MIXED-B column. The values recorded are the weight of polystyrene that would exhibit the chromatograms observed.

2.2. Synthesis

The compounds $[MCl(M'Cl_3)(CO)_3(NCR)_2]$ (M = Mo, W; M' = Sn, Ge; R = Me, Et) were prepared by reacting $[M(CO)_4(NCMe)_2]$ (M = Mo or W) with $SnCl_4$ or $GeCl_4$ in a solution of CH_2Cl_2 using the familiar procedures [6–9]. $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ was obtained in the photochemical reaction of $W(CO)_6$ and $SnCl_4$ as reported in the literature [10]. The alkyne complexes $[MoCl_2(NCMe)_2(RC\equiv CR')_2]$ (R = Ph, R' = Ph, H) were synthesized in a reaction of $[MoCl(MCl_3)(CO)_3(NCMe)_2]$ (M = Ge, Sn) and an appropriate alkyne [8,9]

2.3. Procedure for testing catalytic activity

In a typical experiment, the reaction mixture composed of CH_2Cl_2 (5 cm^3), cyclopentane (0.5 mol dm^{-3}) (the internal chromatographic standard), *t*-BA (1 mol dm^{-3}), and a metal complex M (*t*-BA /M = 100) was stirred at room temperature under nitrogen for 24 h in a 50 cm^3 glass reactor provided with a septum through which liquid reactants were introduced and removed by means of a syringe. The disappearance of *t*-BA was confirmed by GC. The P-*t*-BA was precipitated in methanol (20 cm^3) as white powder. Polymerization yield (%) was defined by comparing the polymer weight with the weight of the *t*-BA used. The polymer was analysed by ^{1}H- and ^{13}C-NMR spectroscopy in $CDCl_3$ and gel-permeation chromatography in $CHCl_3$. The geometric structure of the polymers was determined from the ^{1}H-NMR integrals of the signals at $\delta = 6.19$ (*cis*-P-*t*-BA) and at $\delta = 5.98$ (*trans*-P-*t*-BA) [11] and from the ^{13}C-NMR spectra by means of the Masuda equation: *cis*-P-*t*-BA (%) = $100 \times H_a/(H_a + H_b + H_c)$, where H_a, H_b, and H_c are the heights of the signals at δ 31.2, 32.4, and 30.2, respectively [12].

The filtrate obtained after the precipitation of the polymers was evaporated to dryness and the CH_2Cl_2 solution of the residue was investigated by GC-MS. Analysis showed mainly 1,3,5-tri-*t*-butylbenzene (TBB) (retention time (r.t.) = 11.84; $m/z = 246$). Small amounts of *t*-BA dimer (r.t. = 8.24, $m/z = 164$), four isomers of di-*t*-butylbutadiene (r.t. = 8.45, 8.88, 8.95 and 9.19; $m/z = 166$), di-*t*-butylchlorobutadiene (r.t. = 10.70, $m/z = 200$) and di-*t*-butyl-dichlorobutadiene (r.t. = 12.76, $m/z = 235$) were identified with different percentages depending upon the reaction conditions.

Oligomerization yield was calculated as the difference between the conversion and the yield of the polymerization reaction.

The influence of the solvent on the polymerization reaction was investigated using, besides CH_2Cl_2, such solvents as toluene,

CH$_3$CN, THF and heptane. In toluene solution, a gummy solid of P-*t*-BA was formed, so heptane (5 cm^3) was added to the reaction mixture and then removed, until the solid lost its gummy appearance (two to three cycles).

2.4. Stoichiometric reactions of metal compounds with t-BA

2.4.1. Reaction of [WCl(SnCl$_3$)(CO)$_3$(NCMe)$_2$] 1 with t-BA

To a solution of **1** (0.13 g, 0.23 mmol) in 10 cm^3 of CH$_2$Cl$_2$ was added *t*-BA (0.05 cm^3, 0.43 mmol). The mixture was stirred and the progress of the reaction was monitored by the disappearance of ν(CO) bands due to **1**. At the beginning of the reaction (2–4 h), one new ν(CO) band appears and increases at about 2080 cm^{-1} which subsequently decays after prolonged reaction time. The dark orange colour of **1** gave way to a light green colour as the reaction proceeded. The solution was filtered off to remove an insoluble white solid containing SnCl$_2$ and P-*t*-BA. Evaporation of the solvent in vacuo produced a pale green residue which was washed several times with heptane and dried. The product was identified by IR and NMR studies as a mixture of *t*-BA compounds containing the major product (ca. 63% by ^{1}H-NMR): IR (KBr) ν(CO) band at 2069 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 11.27 and 11.07 ($^2J_{\text{WH}}$ = 9.3 Hz, $\equiv$CH); ^{13}C-NMR (CDCl$_3$) δ 205.33 (CO), 179.89 ($\equiv C^t$Bu), 170.11 ($^1J_{\text{CH}}$ = 231 Hz, $\equiv C$H), 152.67 ($^1J_{\text{CH}}$ = 220 Hz, $\equiv C$H), 143.59 ($\equiv C^t$Bu), 125.40 (NCMe), 41.58 and 39.89 (CMe$_3$), 29.78 and 29.54 (CMe_3). On the basis of these spectroscopic data, the compound was formulated as [WCl(SnCl$_3$)(CO)(NCMe)(HC$\equiv$C^{t}Bu)$_2$].

2.4.2. Reaction of [MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$] 2 with t-BA

t-BA (0.09 cm^3, 0.74 mmol) was added to a solution of complex **2** (0.18 g, 0.37 mmol) in

CH$_2$Cl$_2$ (22 cm^3) at room temperature. The procedure was the same as in Section 2.4.1. The product was identified by ^{1}H-NMR studies as a mixture of compounds with several different-intensity signals of acetylenic protons ($\equiv$CH) in the region of 11.0–10.3 ppm. The major product (ca. 50% by ^{1}H-NMR) is characterized by one signal of acetylenic protons ($\equiv$CH) at δ 10.76 and acetylenic carbon signals at δ 197.96 ($\equiv C^t$Bu) and 178.24 ($^1J_{\text{CH}}$ = 223 Hz, $\equiv C$H). On the basis of these spectroscopic data, this compound can be formulated as [MoCl$_2$(NCMe)$_2$(HC$\equiv$C^{t}Bu)$_2$].

2.5. NMR tube reactions

These reactions were all carried out using a similar procedure. Approximately 50 mg of a Mo or W compound dissolved in ca. 0.7 cm^3 of CDCl$_3$ or CD$_2$Cl$_2$ was placed in an NMR tube and *t*-BA (2–10 equiv) was added using a microlitre syringe. The tube was closed with a glass cap. The ^{1}H-NMR spectrum was recorded and the reaction followed with time at room temperature. Solid P-*t*-BA was deposited along the sides of the tube, but this did not cause any serious loss of ^{1}H-NMR sensitivity. From integral comparisons with the internal standard (hydrogen signals due to solvent), the conversion of *t*-BA was calculated. Complete transformation of the metal complex was detected by the decay of the signal due to nitrile ligand protons. At the same time, new signals of free and coordinated nitrile appeared and the signal of free *t*-BA ($\equiv$CH) at δ 2.03 had decayed but new signals appeared and increased in the region characteristic for *t*-BA coordinated to metal at δ 12–10 ppm.

2.6. Hydrolysis of t-BA adducts formed in reaction of 1

To a solution of **1** (0.06 g, 0.1 mmol) in 17 cm^3 of CH$_2$Cl$_2$ was added *t*-BA (0.025 cm^3, 0.2 mmol). The mixture was stirred for 24 h.

The solution was filtered off to remove an insoluble white solid. The residue obtained after evaporation of the solvent in vacuo was dissolved in diethyl ether (5 cm^3) and treated with a water/acetone solution (0.04 cm^3, 10% v/v). After the mixture had been stirred for 30 min, the sample was dried by allowing it to stand over MgSO$_4$ for 2 days. The resulting mixture was filtered, and the solvent was removed in vacuo yielding a colourless oil. The hydrolysis product was identified by NMR [13,14] and GC–MS studies as 1,3,5-TBB and di-t-butyldichlorobutadiene.

1,3,5-TBB: ^{1}H-NMR (CDCl$_3$), δ 7.3 (CH) and 1.3 (CMe_3); ^{13}C-NMR (CDCl$_3$), δ 149.8 (C^{t}Bu), 119.4 ($^1J_{CH} = 153$ Hz, CH), 34.9 (CMe$_3$), and 31.5 (CMe_3); GC–MS, r.t. = 11.84; $m/z = 246$).

di-t-Butyldichlorobutadiene: ^{1}H-NMR (CDCl$_3$), δ 6.96 d and 5.83 d ($^3J_{HH} = 16.3$ Hz, = CH); GC–MS, (r.t. = 12.76, $m/z = 235$).

3. Results and discussion

3.1. Catalytic conversion of t-BA

Polymerization of t-BA occurs very smoothly at room temperature in CH$_2$Cl$_2$ containing a catalytic amount of Mo or W compounds.

Treatment of the reaction mixture with a large amount of methanol produced quantitatively P-t-BA as a fine white powder which had a weight-average molecular weight ($\overline{M}_w$) of from 0.8 to 8×10^5, determined by GPC (Table 1). All the polymers produced were soluble in CH$_2$Cl$_2$, CHCl$_3$ and toluene. ^{1}H- and ^{13}C-NMR spectroscopy was used to establish the configuration of P-t-BA [11,12]. Both ^{1}H- and ^{13}C-NMR techniques allow the measurement of the cis isomer content. The ^{1}H-NMR spectra of P-t-BA in CDCl$_3$ displayed a sharp signal due to the olefinic protons at δ 6.19, which was correlated to the cis structure of P-t-BA [11], in addition to a broad signal at δ 5.98 characteristic for the trans isomer. In ^{13}C-NMR spectra, a signal at δ 31.2 is characteristic for the three equivalent methyl groups of cis-P-t-BA and signals at δ 32.4 and 30.2 of its trans isomer [11,12] (Fig. 1). The olefinic carbon resonances of P-t-BA were observed at δ 144.57 and 128.09 (Fig. 1). For the reactions investigated here, cis isomer contents between 20 and 70% were observed, depending upon the catalyst and solvent used (Table 1). As was mentioned earlier [11,12], the trans configuration of P-t-BA is more stable than the cis configuration and cis-P-t-BA very readily isomerizes to yield the trans isomer. This process can be observed in a reaction followed in an NMR tube (Fig. 2). After the

Table 1
Polymer characterization

Catalyst	Solvent	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	cis-P-t-BA (%)[a]
[WCl(SnCl$_3$)(CO)$_3$(NCMe)$_2$]	CH$_2$Cl$_2$	1.14	0.56	2.06	50
[MoCl(SnCl$_3$)(CO)$_3$(NCMe)$_2$]	CH$_2$Cl$_2$	7.94	4.00	1.96	47
	toluene	8.21	1.68	4.88	38
	THF	4.42	2.01	2.14	20
[WCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$]	CH$_2$Cl$_2$	2.82	1.27	2.21	44
[MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$]	CH$_2$Cl$_2$	2.64	0.93	2.83	35
	MeCN	_[b]	_[b]	_[b]	49
[MoCl$_2$(NCMe)$_2$(HC≡CPh)$_2$]	CH$_2$Cl$_2$	2.73	1.25	2.18	26
[MoCl$_2$(NCMe)$_2$(PhC≡CPh)$_2$]	CH$_2$Cl$_2$	8.37	4.04	2.07	69
[(CO)$_4$W(μ-Cl)$_3$W(SnCl$_3$)(CO)$_3$]	CH$_2$Cl$_2$	0.77	0.43	1.77	35

[a]The cis-P-t-BA content was determined by ^{13}C-NMR [12].
[b]Was not measured.
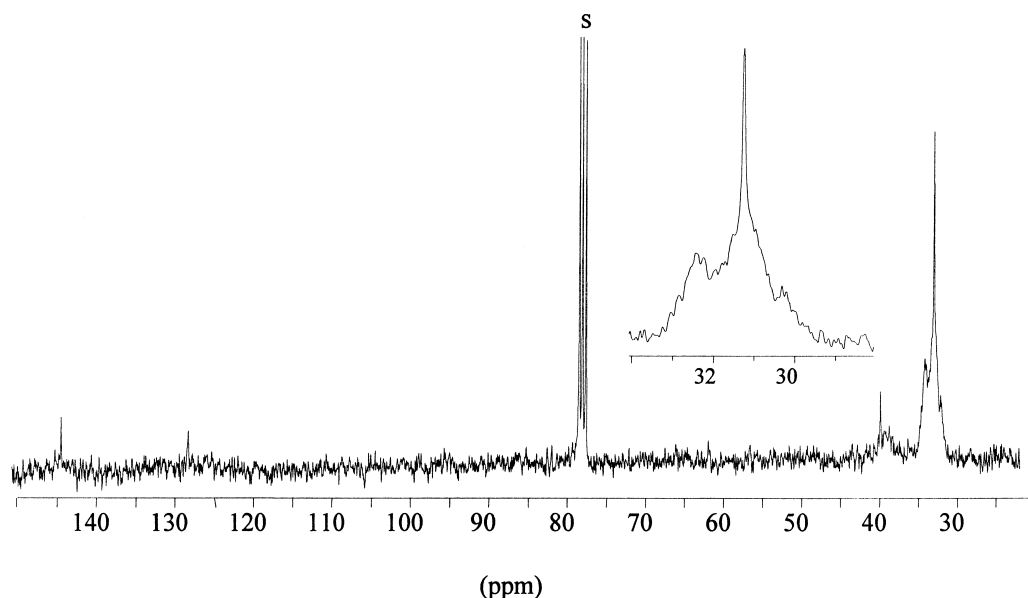
Fig. 1. The ^{13}C-NMR spectrum (75 MHz) in CDCl$_3$ of P-*t*-BA (69% *cis* isomer) produced with [MoCl$_2$(NCMe)$_2$(PhC≡CPh)$_2$] as catalyst. The carbon signals of the methyl groups are shown at scale expansion in the inset.

addition of *t*-BA to the solution of [WCl-(SnCl$_3$)(CO)(NCMe)(HC≡C^{t}Bu)$_2$] in CDCl$_3$, predominantly *cis*-P-*t*-BA is formed with a signal at δ 6.19 (Fig. 2). However, after prolonged reaction time, the broad signal due to the *trans* isomer at δ 5.98 increased and covered the signal at δ 6.19. This suggests that the propagation step can be stereospecific but the geometric structure of the isolated polymer depends on the relative rates of polymerization and isomerization.

In some cases, the catalytic *t*-BA polymerization reaction is quite rapid and virtually the only reaction observed (Table 2). More often, however, other reactions compete or dominate, most commonly cyclotrimerization of the *t*-BA producing 1,3,5-TBB. The formation of TBB was observed by means of the GC-MS chromatography of the residue obtained after the separation of P-*t*-BA with methanol. During the reaction followed by ^{1}H-NMR, the signal due to three equivalent protons of the aromatic ring of TBB was detected at δ ca. 7.3 [13] (Figs. 2–4). Minor amounts of other oligomers arise, mainly linear di-*t*-butylbutadienes (DBBD), which con-

tain, for example, hydrogen derived from the solvent or moisture. Trace amounts of chloro- and dichloro-di-*t*-butylbutadiene, which contain chlorine derived from the catalyst, were also detected by GC-MS and ^{1}H-NMR.

The tungsten(II) or molybdenum(II) complexes [MCl(M′Cl$_3$)(CO)$_3$(NCR)$_2$] (M = Mo, W; M′ = Sn, Ge; R = Me) showed similar high catalytic activity (Table 2). However, the selectivity of the polymerization reaction catalysed by complexes containing germanium in CH$_2$Cl$_2$ as the solvent is lower than the selectivity of reactions catalysed by tin compounds. At this point, it can be explained by the influence of the solvent on the stability of the metal−metal bond. It was observed previously [7,9] that in CH$_2$Cl$_2$ solution W−Ge and Mo−Ge compounds release the GeCl$_2$ moiety very easily, easier than in toluene or heptane. W−Sn and Mo−Sn compounds are much more stable in these conditions.

Alkyne adducts of the type [MoCl$_2$(NCMe)$_2$-(RC≡CR′)$_2$] (R = Ph, ^{t}Bu, R′ = Ph, H) are very active in polymerization reactions. In the case of [MoCl$_2$(NCMe)$_2$(PhC≡CPh)$_2$] as catalyst,
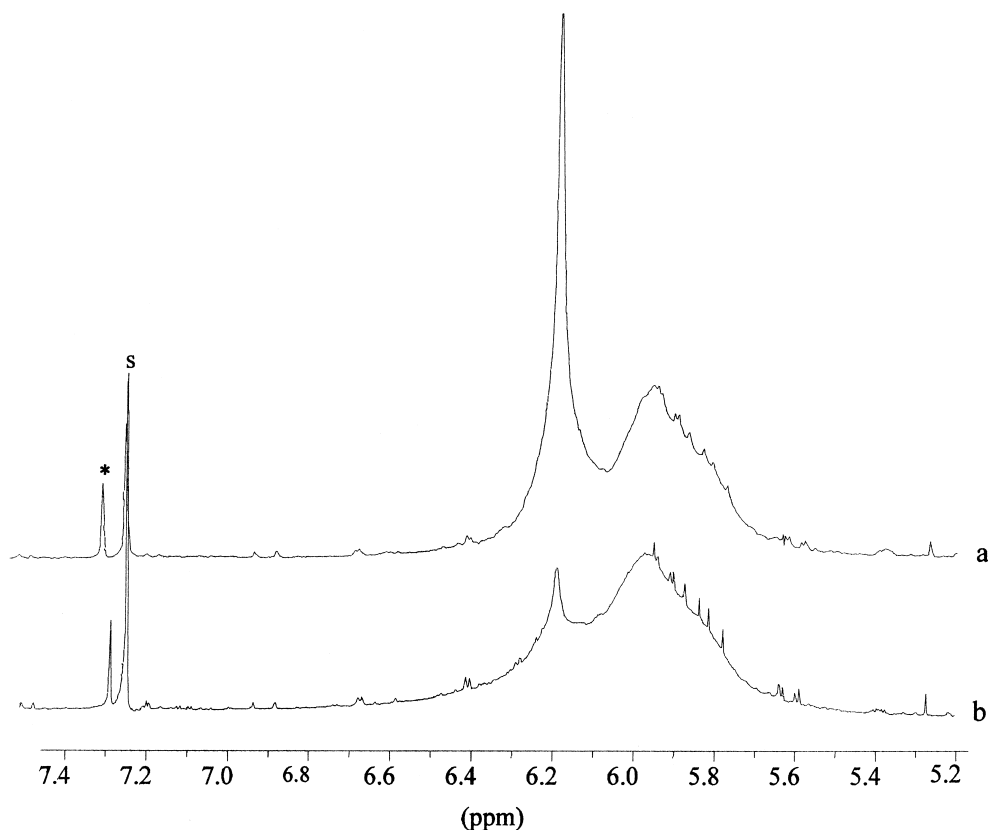
Fig. 2. ^{1}H-NMR spectra (300 MHz) showing the *cis* and *trans*-P-*t*-BA formation in the NMR tube reaction of *t*-BA catalysed by [WCl(SnCl$_3$)(CO)(NCMe)(HC≡C^{t}Bu)$_2$]: (a) after 1 day, (b) after 5 days. The resonance at δ 7.24 denoted by **s** arises from protio impurities in the solvent CDCl$_3$. The TBB resonance is denoted by an asterisk at δ 7.3.

the P-*t*-BA with the highest molecular weight ($\overline{M}_w = 8.4 \times 10^5$) and the highest *cis* isomer content (69%) was obtained. If, as was observed by Masuda et al. [12], the *cis–trans* isomerization and also degradation of P-*t*-BA is induced by acids, the latter catalyst has the lowest possibility to initiate these processes. The dinuclear compound [(CO)$_4$W(μ-Cl)$_3$W(SnCl$_3$)(CO)$_3$] polymerizes *t*-BA with a yield comparable to a mononuclear compound, but the polydispersity of the P-*t*-BA is lower ($\overline{M}_w/\overline{M}_n = 1.77$, Table 1).

The rate of the disappearance of *t*-BA (conversion) was followed by gas chromatography at room temperature. Plots of $\ln[t\text{-BA}]_0/[t\text{-BA}]_t$ vs. time in the presence of 0.01 equiv of a metal

complex were found to be linear through more than three half-lives and the obtained value of the initial disappearance of *t*-BA (k_{obs}) was in the range $0.1–13 \times 10^{-4}$ s^{-1}.

The polymerization of *t*-BA by tungsten(II) and molybdenum(II) catalysts occurs in different solvents (Table 2); however, the best solvent is CH$_2$Cl$_2$. The influence of this solvent can be explained by its good dissolubility of metal compounds and its very low coordination ability, enabling the creation of very reactive coordinatively unsaturated species. In contrast, THF and CH$_3$CN can coordinate to metal and block coordination sites for the alkyne. Toluene does not disturb coordination of the alkyne to metal and the reaction of *t*-BA is even faster than in

Table 2
Polymerization of *t*-BA by tungsten(II) and molybdenum(II) compounds

Catalyst	Solvent	Conversion (%)		Yield (%)	Selectivity (%)
		after 2 h	24 h	after 24 h	
[WCl(SnCl$_3$)(CO)$_3$(NCMe)$_2$]	CH$_2$Cl$_2$	10	92	92	100
[MoCl(SnCl$_3$)(CO)$_3$(NCMe)$_2$]	CH$_2$Cl$_2$	39	92	92	100
	toluene	99[a]	–[b]	79	80
	THF	–[b]	–[b]	61	–[b]
[WCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$]	CH$_2$Cl$_2$	48	98	40	40
	toluene	30	79	77	96
	THF	–[b]	–[b]	14	–[b]
	heptane	–[b]	38	38	100
[MoCl(GeCl$_3$)(CO)$_3$(NCMe)$_2$]	CH$_2$Cl$_2$	91	100	63	63
	toluene	96	97	97	96
	THF	16	73	73	100
	MeCN	–[b]	–[b]	28	–[b]
[MoCl$_2$(NCMe)$_2$(HC≡CPh)$_2$]	CH$_2$Cl$_2$	–[b]	–[b]	56	–[b]
[MoCl$_2$(NCMe)$_2$(PhC≡CPh)$_2$]	CH$_2$Cl$_2$	89	100	92	92
[(CO)$_4$W(μ-Cl)$_3$W(SnCl$_3$)(CO)$_3$]	CH$_2$Cl$_2$	–[b]	–[b]	56	–[b]

[a]After 1 h reaction.
[b]Was not measured.

CH$_2$Cl$_2$, but in toluene solution a jelly-like polymer of *t*-BA is formed and the reaction is stopped. The polymerization of *t*-BA occurs even in heptane, although in that solvent the
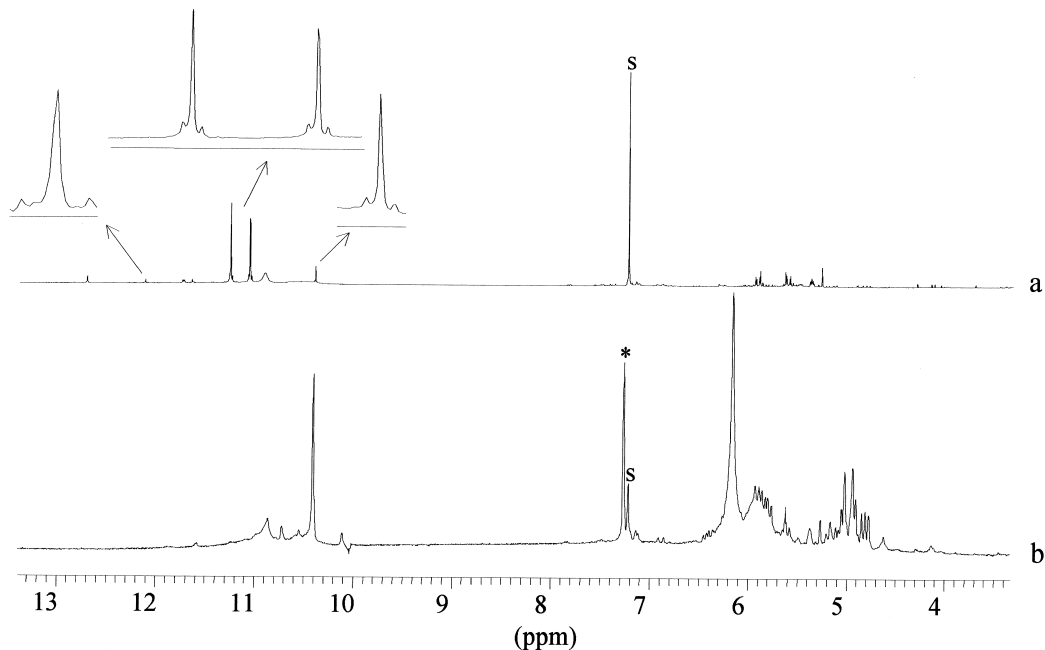

Fig. 3. ^{1}H-NMR spectra (300 MHz) of [WCl(SnCl$_3$)(CO)(NCMe)(HC≡C^{t}Bu)$_2$] at 293 K in CDCl$_3$: (a) before and (b) after the addition of 10 equiv of *t*-BA. The η^2-*H*C≡C^{t}Bu proton signals at δ 11.27, 11.07 and 10.41 and alkylidene proton signals at δ 12.13 are shown at scale expansion to present the coupling between [183]W and [1]H. The resonance at δ 7.24 denoted by **s** arises from protio impurities in the solvent CDCl$_3$. The TBB resonance is denoted by an asterisk at δ 7.3.
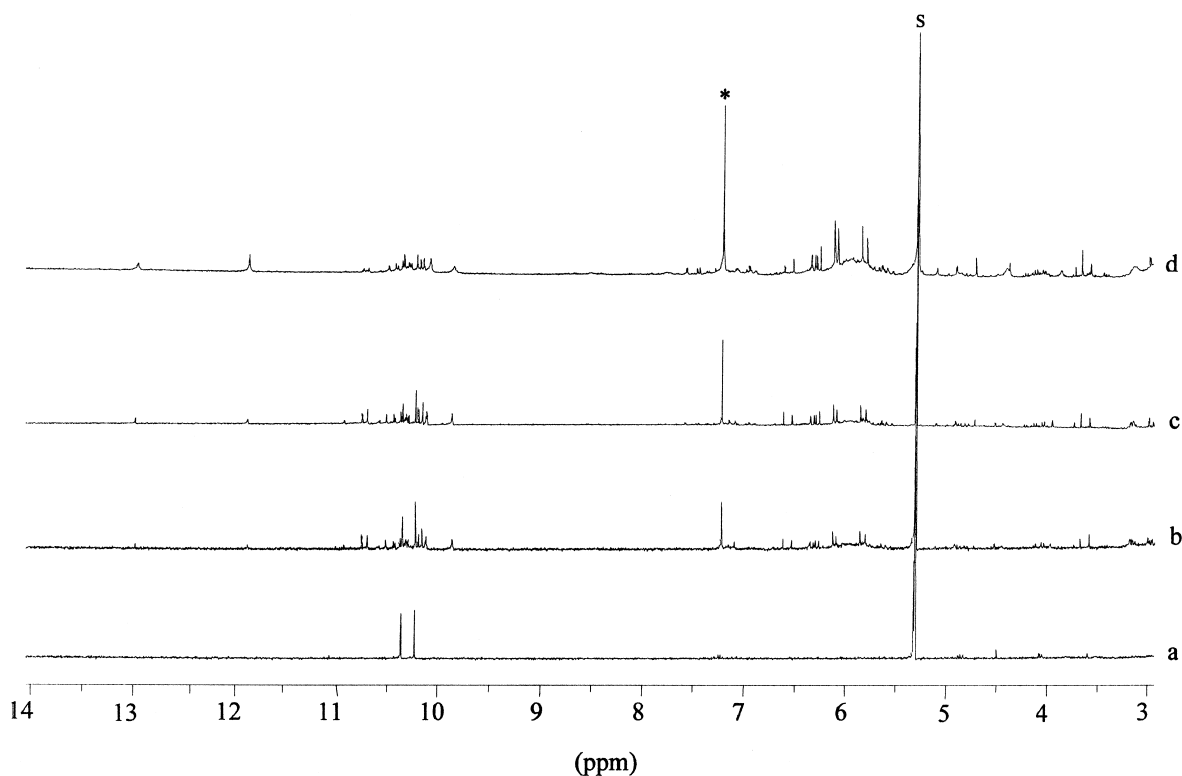
Fig. 4. ^{1}H-NMR spectra recorded at 300 MHz during the reaction of $[MoCl(SnCl_3)(CO)_3(NCEt)_2]$ and *t*-BA at 293 K in CD_2Cl_2, showing the formation of compounds with *t*-BA as an η^2 ligand, alkylidene ligand and free 1,3,5-TBB: (a) after 4 h, (b) 2 days, (c) 3 days and (d) 2 months. The resonance denoted by **s** at δ 5.31 arises from protio impurities in the solvent CD_2Cl_2. The TBB resonance is denoted by an asterisk at δ 7.3.

solubility of the metal complex is very low. In heptane solution the reaction is slower but occurs with 100% selectivity (Table 2).

3.2. Attempts to detect possible intermediates

Previously, we reported reactions between $[MCl(M'Cl_3)(CO)_3(NCR)_2]$ (M = Mo, W; M' = Sn, Ge; R = Me, Et) and alkynes (PhC≡CPh, PhC≡CMe, PhC≡CH) and the isolation of a mixture of alkyne compounds containing such products as $[MCl_2(CO)(NCMe)(RC≡CR')_2]$ and $[MCl_2(NCMe)_2(RC≡CR')_2]$ [6–9], existing in equilibrium with dinuclear compounds. Similar bis(alkyne) compounds were detected in the reaction of bimetallic compounds and *t*-BA. However, in the reaction of $[WCl(SnCl_3)(CO)_3(NCMe)_2]$ and *t*-BA we were enable to

observe (ca. 63% by ^{1}H-NMR) the bis(alkyne) complex containing a W−Sn bond, viz. $[WCl(SnCl_3)(CO)(NCMe)(HC≡C^tBu)_2]$. The latter compound was detected due to two equal-intensity signals of acetylenic protons (≡CH) at δ 11.27 and 11.07 ($^2J_{WH}$ = 9.3 Hz) in ^{1}H-NMR (Fig. 3a) and a ν(CO) band at 2069 cm^{-1} in IR (KBr). The signals of carbon atoms were observed in ^{13}C-NMR at δ 205.33 (CO), 179.89 and 143.59 (≡C^tBu), 170.11 ($^1J_{CH}$ = 231 Hz) and 152.67 ($^1J_{CH}$ = 220 Hz, ≡CH), 125.40 (NCMe), 41.58 and 39.89 (CMe$_3$), 29.78 and 29.54 (CMe_3). An important point is that this compound arises only when ca. 2 equiv of *t*-BA is added. Another η^2-alkyne complex detected (ca. 6% by ^{1}H-NMR) has a signal for an acetylenic proton (≡CH) at δ 10.41 ($^2J_{WH}$ = 6.6 Hz) (Fig. 3a). The latter η^2-alkyne species

was observed alone after the addition of an excess of *t*-BA to the CDCl$_3$ solution of [WCl(SnCl$_3$)(CO)(NCMe)(HC≡C^{t}Bu)$_2$] in an NMR tube reaction (Fig. 3b).

A similar picture was obtained by following the reaction of [MoCl(SnCl$_3$)(CO)$_3$(NCEt)$_2$] with *t*-BA by means of ^{1}H-NMR (Fig. 4). At the beginning of this reaction the intermediate alkyne compound is formed with two equal-intensity signals of acetylenic protons (≡C*H*) at δ 10.37 and 10.24 which then transforms to a mixture of several alkyne compounds as evidenced by the increase in the number of signals in the region 11.0–9.8 ppm.

In CH$_2$Cl$_2$ solution, bimetallic alkyne compounds very easily release Lewis acid (SnCl$_2$ or GeCl$_2$) and a CO ligand and dimerize yielding a product less soluble in CH$_2$Cl$_2$ and CHCl$_3$, most probably [M(μ-Cl)Cl(NCMe)(HC≡C^{t}Bu)$_2$]$_2$. Crystallization of that greenish-yellow solid from acetonitrile restores the mononuclear bis(acetonitrile) compound [MCl$_2$(NCMe)$_2$(HC≡C^{t}Bu)$_2$]. A full NMR characterization of these complexes is difficult owing to the fact that they are in equilibrium with the corresponding dinuclear complexes in solution. Although the NMR characterization of *t*-BA

adducts leaves little doubt concerning their formulation, we were unable to separate these compounds and to obtain a crystalline sample.

During a reaction of *t*-BA and a metal complex, besides signals due to coordinated *t*-BA, other signals appear in the low field region of the ^{1}H-NMR spectrum (δ 12.98 and 11.89, Fig. 4), which can be attributed to alkylidene ligands of the type M = C*H*-C^{t}Bu = C^{t}BuR (II) (Scheme 1). In a similar region of the ^{1}H-NMR spectrum, Wengrovius and Schrock detected proton signals due to the alkylidene ligands of several tungsten compounds, e.g. at δ 11.89 for [W(O)(C*H*^{t}Bu)Cl$_2$(PMe$_3$)$_2$] and at δ 10.68 ($^2J_{WH}$ = 12 Hz) for [W(O)(C*H*^{t}Bu)(O^{t}Bu)$_2$]$_2$ [15]. In the reaction of compound **1** and *t*-BA, such signals appear at δ 12.71 and 12.13 ($^2J_{WH}$ = 12 Hz) (Fig. 3a). The intensity of these proton signals increased slightly over the reaction time but never achieved a high level (Figs. 3 and 4). However, owing to the lack of ^{13}C-NMR data as a consequence of the concentration of the species being too low, the attribution of these signals is not very certain.

In the olefinic protons region (7–4 ppm) of the ^{1}H-NMR spectrum of the reaction mixture containing a metal complex and *t*-BA, several

Scheme 1.
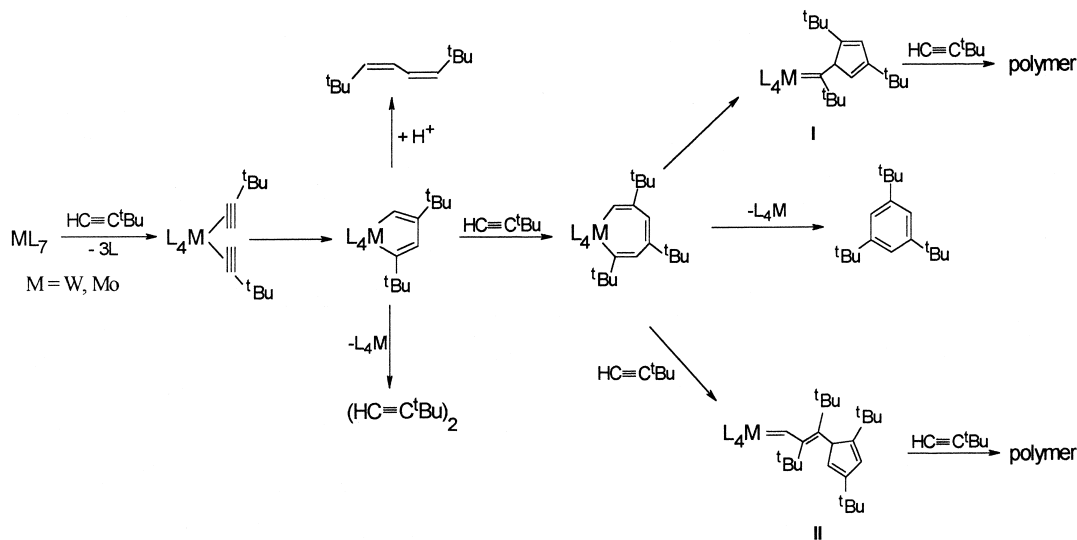
signals arise and grow, e.g. singlets at δ 6.62 and 6.53, doublets with $^3J_{HH}$ = 9.8 Hz at δ 6.35, 6.30 and 6.11, doublets with $^3J_{HH}$ = 15.6 Hz at δ 5.83 and singlets at δ 4.73 and 4.53, in the reaction of $[MoCl(SnCl_3)(CO)_3(NCEt)_2]$ (Fig. 4). These signals can be due to olefinic protons of the alkylidene ligands formed after the addition of a *t*-BA molecule to the previously formed alkylidene compound I and II (Scheme 1). The first and subsequent additions of *t*-BA molecules to alkylidene compound II can lead to the appearance of a first and subsequent sets of olefinic proton doublets in ^{1}H-NMR spectra with the proton-proton coupling constant equal to ca. 10 Hz (*cis* configuration) or ca. 16 Hz (*trans* configuration), just as can be observed in Fig. 4. A similar observation was made by Schrock et al. during living polymerization of alkynes by a molybdenum alkylidene complex [16]. They detected a second set of olefinic proton doublets of the alkylidene ligand at 6.11 and 5.27 ppm ($^3J_{HH}$ = 15.6 Hz) [16]. The addition of a *t*-BA molecule to the metal-carbon double bond of alkylidene species I (Scheme 1) leads to the appearing of singlets in the olefinic proton region (Figs. 3 and 4). In other reactions, two doublets at δ 6.97 and 5.73 with a coupling constant ($^3J_{HH}$ = 16 Hz) characteristic of *trans* hydrogen on a carbon=carbon double bond were additionally observed (Figs. 2 and 3). The latter two signals can be due to two *trans* olefinic protons of the alkylidene ligand of the type $M = C^tBu$-$CH = CH$-$C^tBu = C^tBuR$, arising from the addition of *t*-BA to the previously formed alkylidene compound II (Scheme 1). For the olefinic protons in the compound $[CpCl_3W = C^tBu$-$CH = CH^tBu]$ formed after the prior addition of *t*-BA to the metal=carbon double bond, McCullough et al. observed two doublets at δ 8.38 and 7.14 ($^3J_{HH}$ = 15.4 Hz) [17].

Upon reacting a metal complex and *t*-BA at room temperature and examining the entire reaction mixture by NMR, we found 1,3,5-TBB present in every reaction (Figs. 2–4). Although arene formation by alkyne cycloaddition chem-

istry is well-known [18–20], this reaction represents a rare example of the direct conversion of an η^2-alkyne complex to a free arene, a key step in [2 + 2 + 2} cycloaddition chemistry.

3.3. Plausible mechanism of the initiation of t-BA polymerization by tungsten(II) and molybdenum(II) based catalysts

Since the first idea of Masuda et al. [21] concerning the metathesis mechanism for the polymerization of acetylenes, it has been very well documented that acetylenes are polymerized by carbene complexes [17,22–26]. The question then arises: "How can the catalytically active carbene species be formed from the catalysts used here?" To gain knowledge about the mechanism of the initiation of alkynes polymerization by seven-coordinate Mo and W compounds, we monitored, by means of ^{1}H-NMR, the catalytic and stoichiometric reactions of these metal compounds with *t*-BA and observed the intermediate species (see Section 3.2). A reasonable mechanism of the formation of the alkylidene species initiating *t*-BA polymerization is shown in Scheme 1. Our results provide direct information on several steps of this mechanism. The first step, viz. the coordination of two *t*-BA molecules to a metal centre, was very well evidenced by NMR spectroscopy (Section 3.2). In the reactions of tungsten(II) or molybdenum(II) complexes with alkynes that were investigated, the alkyne complexes that could be isolated usually contained a *cis* arrangement of the two alkyne ligands [6–9,27–30]. The two *cis* η^2-alkyne ligands can very easily rearrange producing a metallacyclopentadiene moiety, as was observed previously for titanium [31] and tantalum compounds [14,32–35]. Although in our studies we could not directly observe the formation of the metallacyclopentadiene, the hydrolysis product of this species (di-*t*-butylbutadiene, di-*t*-butylchlorobutadiene and di-*t*-butyldichlorobutadiene) was detected by GC-MS analysis of the reaction mixture (Sections 2.3 and 2.6).

The insertion of an alkyne into the metal−carbon bond of the metallacyclopentadiene species leads to the formation of metallacycloheptatriene (Scheme 1). The latter species was not observed directly but its decomposition product 1,3,5-TBB was detected by GC-MS and NMR studies (Sections 2.3 and 2.6) in most of the reactions investigated. A reasonable mechanism for the formation of cyclotrimers from *t*-BA involves the initial coordination of two alkynes to the metal, rearrangement to a metallacyclopentadiene, insertion of a third alkyne into the M−C bond and reductive cyclization to the cyclotrimers [18–20] (Scheme 1).

Thus, the formation of linear polyenic polymers involves most probably oxidative coupling and the formation of a series of metallacyclic species. The metallacycle formed with three or four molecules of alkyne can then rearrange to an alkylidene ligand (I or II) initiating the increase of the polymer chain (Scheme 1). It is worth pointing out that such a transformation was observed for the first time by Yeh et al. in a reaction of $[W(CO)(PhC{\equiv}CPh)_3]$ with an excess of diphenylacetylene [36].

There is competition between cyclotrimer and alkylidene ligand formation. Depending upon the metallacycle stability, we could observe the initiation of polymerization or the formation of an aromatic compound (TBB).

4. Concluding remarks

The $[MCl(M'Cl_3)(CO)_3(NCR)_2]$ (M = Mo, W; M' = Sn, Ge; R = Me, Et) compounds provide coordinatively unsaturated centres to which alkynes may readily coordinate. We observed a mixture of NMR-detectable compounds with *t*-BA as the ligand. The resulting alkyne complexes are catalysts for the polymerization of *t*-BA.

The compounds described above are a new example of one-component tungsten(II) and molybdenum(II) catalyst initiating the poly-

merization of *t*-BA without an additional organometallic cocatalyst.

The ability of bimetallic seven-coordinate compounds to initiate the polymerization of alkynes signifies their ability to generate metal alkylidene. In the process of studying reactions between seven-coordinate complexes and *t*-BA, we discovered what we believed might be the initiating step in a polymerization process consisting of the formation of larger and larger unsaturated MC_x ring systems ($x = 4$–6). The MC_4 or MC_6 ring system can rearrange to metal alkylidene. Monitoring the polymerization of *t*-BA directly in the NMR tube provided evidence for such a course of reaction.

The fact that tungsten(II) and molybdenum(II) compounds are active in the cyclotrimerization of *t*-BA indicates that addition and elimination from the metal centre can occur readily.

Future studies will be aimed towards elucidating the nature of the other alkyne adducts formed in reactions between $[MCl(M'Cl_3)(CO)_3(NCR)_2]$ (M = Mo, W; M' = Sn, Ge; R = Me, Et) compounds and alkynes, as well as the identification of catalytically active species. The present work, and previous studies [6–9], suggest these compounds have considerable potential.

Acknowledgements

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