Metathesis *vs.* Polymerization of Terminal Acetylenes over $[W(CBu^t)(OBu^t)_3]$

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Terminal acetylenes $RC{\equiv}CH$ are transformed catalytically into metathesis products $RC{\equiv}CR$ and C_2H_2 on the carbyne complex $[W(CBu^t)(OBu^t)_3]$, a process which is rapidly followed by a polymerization of the alkyne; in the case of sterically hindered $Bu^tC{\equiv}CH$, a stoichiometric reaction is observed, by which a dinuclear compound $\mu\text{-}C_2H_2[W(OBu^t)_3]_2$ **1** and the deprotiotungstenacyclobutadiene $[WC_3(Bu^t)_2(OBu^t)_2]$ **2** are formed.

Homogeneous metathesis of disubstituted alkynes $2\ R^1C{\equiv}CR^2 \leftrightarrows R^1C{\equiv}C\text{–}R^1 + R^2C{\equiv}CR^2$ is a well-known reaction, which was originally described as using molybdenum–phenol-based catalytic combinations, such as $[Mo(CO)_6]$[1] or $[MoO_2(acac)_2]$ $-AlEt_3$[2] as catalyst precursors.

Well-defined tungsten and molybdenum carbyne complexes have also been shown to act as initiators for the same reaction;[3] these latter complexes allowed the isolation in some cases of stable metallacyclobutadienes, considered as the catalytic intermediate species.[4,3c]

Up to now, however, catalytic metathesis of terminal acetylenes has never been realized, although the reaction of $[Mo(CBu^t)(OBu^t)_3]$ with $RC{\equiv}CH$ gave the expected $Bu^tC{\equiv}CH$ metathesis product and the resulting $[Mo(CR)(OBu^t)_3]$ carbyne complex. Attempts in this field have given substoichiometric yields of oct-4-yne from $[Mo(CPr)(OBu^t)_3]$ and an excess of pent-1-yne.[5] This failure has been explained, at least with phenylacetylene as substrate, by the production of stable catalytically non-active deprotiometallacycles immediately after the formation of the symmetrical metallacyclobutadiene intermediate and this gave rise to a stoichiometric reaction.[6]

We now report that, depending on the reaction conditions and the substrate used, catalytic metathesis of terminal alkynes occurs to some extent on the tungsten carbyne complex $[W(CBu^t)(OBu^t)_3]$, but is rapidly masked by polymerization of the alkyne.

As indicated in Table 1, the reaction of $[W(CBu^t)(OBu^t)_3]$ conducted at ambient temperature with phenylacetylene does not give diphenylacetylene but only a quantitative amount of $Bu^tC{\equiv}CH$ and polymerization (runs 1 and 2).

However, small amounts (*ca.* 4%, 2 turnovers) of diphenylacetylene could be detected when the reaction was conducted at the higher temperature of 70 °C (run 3). In contrast, the reaction of linear, terminal acetylenes such as pent-1-yne and hept-1-yne give quite good conversion into metathesis products, especially at higher temperatures according to eqn. (1).

$$2RC{\equiv}CH \leftrightarrows HC{\equiv}CH + RC{\equiv}CR \qquad (1)$$

Together with this initial burst in metathetic properties (in the first minute) there is usually some polymerization observed but, there after the reaction course diverts and only the production of a coloured polymer of the alkyne is observed as the reaction goes to 100% conversion (runs 4–9).

The selectivity for metathesis products strongly depends on the bulk of the alkyl group, as well as on the solvent used (runs 6 and 7). With *tert*-butylacetylene, a maximum conversion into

Table 1 Metathesis and polymerization of terminal alkynes catalysed by $[W(CBu^t)(OBu^t)_3]^a$

Run	Alkyne	T/°C	Conversion[b] (mol %)	Metathesis TN[b,c]	Polymerization TN[b]	Time for 100% conv./h	Polymer/M_w
1	PhC≡CH	20	14.2	—	8.2	2	11000
2	PhC≡CH[d]	20	60.0	—	30.0	1.5	20000
3	PhC≡CH	70	64.3	3.8	28.4	1.0	—
4	PrC≡CH	20	24.5	5.8	5.2	2	18000
5	BuC≡CH	20	57.3	3.2	25.4	2	1000
6	$C_5H_{11}C≡CH$	20	32.0	4.8	11.2	1.5	25000
7	$C_5H_{11}C≡CH$[d]	20	15.4	7.3	0.4	3.0	—
8	$C_5H_{11}C≡CH$	50	32.6	6.8	9.5	1.0	—
9	$C_5H_{11}C≡CH$[e]	100	60.4	12.7	17.5	1.0	—
10	Bu^tC-C≡CH	20	2.3	0.6	—	—	—

[a] Conditions: solvent = n-hexane, except runs 2, 7 and 9 (9 ml); $[W(CBu^t)(OBu^t)_3]$ = 0.057 mmol; RC≡CH/W = 50. [b] After 1 min reaction time. [c] TN = moles of terminal alkyne transformed into metathesis product or polymerization per mole of tungsten. [d] Solvent = diethyl ether. [e] Solvent = toluene.

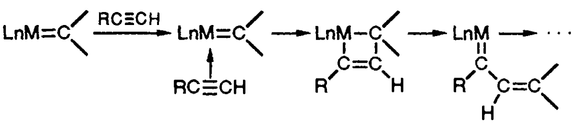
1 mol of di-*tert*-butylacetylene was observed and less than 3 mol of $Me_3CC≡CH$ were converted per mol of tungsten after 24 h. This observation led us to look at the residue obtained after evaporation of the solvent from this reaction mixture. ^1H and ^{13}C NMR spectroscopic studies† showed the presence of two compounds whose data are in good agreement with the formation of a new alkyne-bridged ditungsten compound μ-$C_2H_2[W(OBu^t)_3]_2$ **1**, and deprotiotungstenacyclobutadiene $[WC_3(Bu^t)_2(OBu^t)_2]$ **2**.

The production of these complexes is consistent with the formation of quantitative amounts of *tert*-butyl alcohol according to eqn. (2).

$$3[W(CBu^t)(OBu^t)_3] + 3Bu^tC≡CH \rightarrow \mu\text{-}C_2H_2[W(OBu^t)_3]_2 + [WC_3(Bu^t)_2(OBu^t)_2] + Bu^tC≡CBu^t + Bu^tOH \quad (2)$$

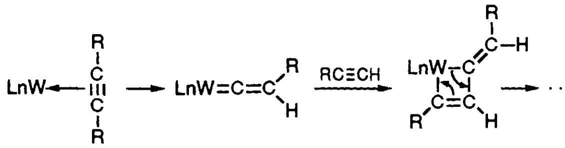
The formation of these products may be explained by an initial stoichiometric metathesis reaction between the carbyne and *tert*-butylacetylene, and formation of two different metallacyclobutadiene species. Symmetrical tungstenacyclobutadienyl complex can be deprotonated to form deprotiometallacyclobutadiene **2** as already described by Schrock *et al.*,[6b] the reaction of the asymmetric species forms tungstenamethylidyne complexes, which can easily dimerize, especially at lower temperature,[7] to produce the ethyne-bridged ditungsten compounds **1** (Scheme 1).

During reactions of the less-hindered alkynes, the conversion into metathesis products rapidly declines and the reaction course changes into polymerization. The polymers are tractable, dissolve easily in halogenated and aromatic hydrocarbons, and the molecular masses are high. The structure of polyphenylacetylene was determined according to the method of Simionescu *et al.* by IR and ^1H NMR spectroscopies.[8] They are identified as *cis*-transoidal polymers with a 97.5% *cis* content, which is comparable to polymers obtained in reaction where carbene or carbyne complexes are used as initiators. The mechanism for polymerization of terminal acetylenes has been proposed to occur *via* metallaalkylidene and metallacyclobutene intermediates[9] [eqn. (3)].



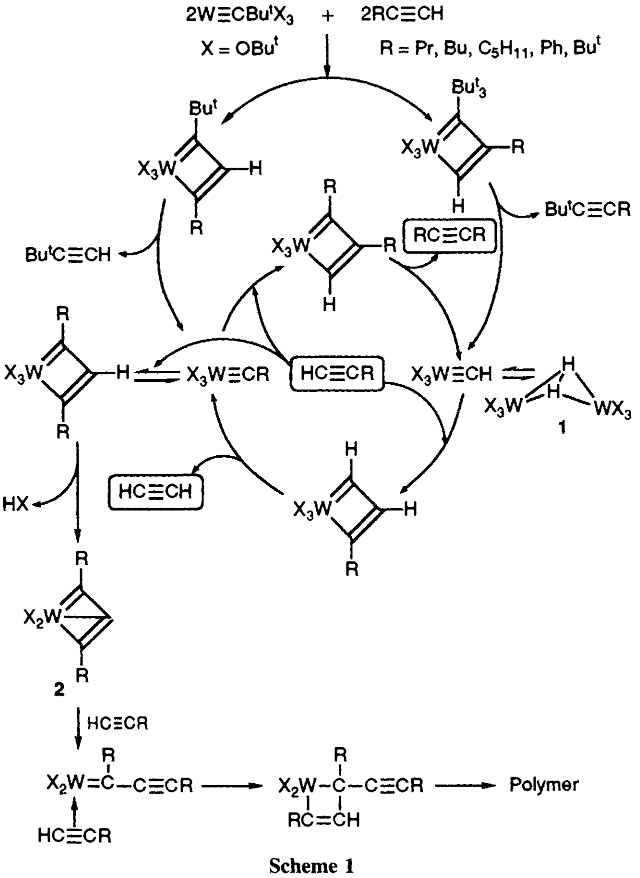
(3)

Our results suggest that the alkylidyne complex $[W(CBu^t)(OBu^t)_3]$ only acts as a metathesis catalytic species for metathesis at the early stage of the reaction and is very rapidly deactivated by deprotonation of the metallacyclobutadiene intermediates and formation of ethyne-bridged complex. The polymerization process probably occurs on vinylidene complexes which could be formed from the coordinatively unsaturated $[W(CBu^t)(OBu^t)_3]$ according to eqn. (4).



(4)

This rearrangement has recently been proposed by Geoffroy *et al.*[10] in photoassisted polymerization of terminal alkynes by $[W(CO)_6]$. The large differences in metathesis



Scheme 1

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† ^1H NMR (400 MHz, CD_2Cl_2) δ 1.06 9-H, 1.53 27-H and 1.85 9-H (*tert*-butoxy and *tert*-butyl groups); the resonance of the two ethyne protons is found as a singlet at δ 7.53. ^{13}C NMR ([$^2H_8$]toluene) δ 215.5 ($2C_\alpha$) and 170.8 (C_β). Both appear with tungsten satellites with $^1J_{CW}$ 139.5 Hz (C_α) and $^1J_{CW}$ 25.8 Hz (C_β). The equivalent carbon atoms of the ethyne group appear at δ 120.5 as a doublet of doublets ($^1J_{CH}$ 152.6 and $^2J_{CH}$ 6.6 Hz) with tungsten satellites (J_{CW} 58.7 Hz).

yields observed with different solvents (Table 1) are in accordance with this: a solvent like diethyl ether is much better than hexane for metathesis (*cf.* runs 6 and 7) and this can be explained by a better coordination of the former, competing with the alkyne during the process described in eqn. (4). Another alternative for initiation of the polymerization reaction is the isomerization of the deprotiotungstenacyclobutadiene complex into intermediate carbene species in the presence of an excess of terminal alkyne (Scheme 1). Indeed the complex $[WC_3(Bu^t)_2(OBu^t)_2]$ obtained in a separate reaction initiates a very fast polymerization of phenylacetylene showing that at least in part, this polymerization uses complex **2** as initiator.

Although these results show clearly that the metathesis of terminal acetylenes is really catalytic, a good choice of the metal environment (*i.e.* the use of less electrophilic alkoxy ligands) would be necessary to improve the metathesis yield (*vs.* polymerization) by stabilization of the required carbyne propagating species and by limiting the production of deprotiometallacycles.

We thank Mrs Sylvie Bages, Mr Patrick Pennequin and Dr Bernard Mouchel for their assistance in this work. We are grateful to the CNRS and the MRT for financial support to A. B. and T. S. B.

Received, 22nd July 1992; Com. 2/03935D

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