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Selective Terminal Alkyne Metathesis: Synthesis and Use of a Unique Triple Bonded Dinuclear Tungsten Alkoxy Complex Containing a Hemilabile Ligand

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Abstract: The *in situ* synthesis of new alkyne metathesis catalysts is described, with particular emphasis on the search for tris-alkoxytungsten-based terminal alkyne metathesis. In that context, hemilabile, ether-containing alkoxy ligands have proved to be suitable and have led to the design and use of a sterically hindered hemilable ligand for the synthesis of a well-defined binuclear, triple-bonded W≡W complex. This complex is shown to be a highly active and selective catalyst precursor for terminal alkyne metathesis, and allows the unprecedented metathesis of phenylacetylene.

Keywords: alkynes; catalysis; metathesis; terminal alkynes; tungsten

Metathesis, in particular alkene metathesis, has received intense interest in recent years and has now become a powerful tool in organic and polymer synthesis.[1] Extensive searches for new active carbene complexes have resulted in the discovery of well-defined catalysts which now have application in diverse fields of chemistry such as total organic synthesis and polymerization.[2]

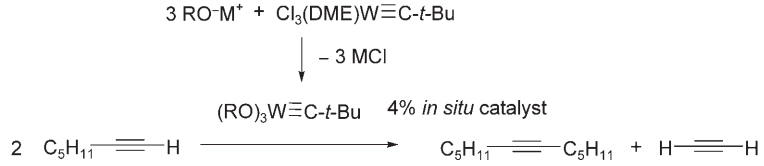
The related area of alkyne metathesis has been known for more than three decades[3] and has received renewed interest during the last decade.[4] In organic syntheses, this reaction has been used mostly for the controlled synthesis of *E*- or *Z*-olefinic disubstituted compounds *via* a two-step procedure involving first a triple bond metathesis reaction then a stereoselective hydrogenation. At the same time the synthesis of aromatic polyynes has been realized by the polymerization of α,ω-aromatic disubstituted diynes.[5,6]

However, the extension of this chemistry to terminal alkynes has been far less studied: early work by Schrock using his well-defined, highly active, (*t*-BuO)$_3$W≡C-*t*-Bu catalyst **1** has shown that phenylacetylene only polymerized.[7] Using the same catalyst we have demonstrated some promising results on alkyl-monosubstituted alkynes using diethyl ether as solvent.[8]

More recent results in our group have shown that the addition of an external ligand such as quinuclidine to complex **1** could improve the selectivity: an 80% metathesis selectivity was attained using hept-1-yne as substrate.[9]

Based on the idea that coordination at the metal centre was responsible for this improvement in selectivity, we decided to look at the synthesis of new catalysts where ligand modification would give rise to variable coordination within the first coordination sphere of the metal by using a hemilabile ligand.

First experiments were made using a procedure by which ligand variation has been screened *via* the *in situ* synthesis of tungstenacarbyne species, followed by catalytic reactions using hept-1-yne as substrate: the metathetic reaction of 3 equivalents of alcoholates with Cl$_3$(DME)W≡C-*t*-Bu (Scheme 1) was used for these screening experiments (Table 1).



Scheme 1. *In situ* synthesis of tungsten carbyne for hept-1-yne metathesis.

Table 1. Screening of alcoholates as ligands for hept-1-yne metathesis.[a]

Entry	Alcoholate	Metathesis Yield [%] of **4**[b]	Polymerization Yield [%]
1	*t*-BuONa	40	56
2	$MeO(CH_2)_2ONa$	12	44
3[c]	$MeOCH_2CH(Me)ONa$	24	71

[a] Reactions were carried out using hept-1-yne (190 μL, 1,45 mmol), decane (100 μL), solvent toluene (5 mL), 3.5 mol% catalyst, *T* 80 °C, reaction time 1 min.
[b] Determined by GC using *n*-decane as internal standard.
[c] Reaction time 5 min.

The best selectivity was obtained with the *tert*-butoxy ligand corresponding to the *in situ* synthesis of complex **1** (entry 1).

However, whereas sterically unhindered alkoxy-substituted tungstenacarbyne complexes are unknown as alkyne metathesis catalysts, a metathetic reaction is observed upon using β-methoxy-substituted alcoholate ligands: the hemilability of the ether function is undoubtedly one of the major factors governing this selectivity improvement.

This result can be related to others obtained in alkene metathesis, where the introduction of ether functions in the coordination sphere of the ligand in well-defined ruthenacarbene species has resulted in improved activity and stability of the catalyst.[10]

All attempts to isolate pure tungsten complexes using the above salt metathesis procedure failed: therefore we next decided to change the *in situ* procedure for catalyst synthesis. Using the tungsten complex $W_2(NMe_2)_6$ as starting material, dinuclear complexes $(RO)_3W{\equiv}W(OR)_3$ can be synthesized *via* direct protonolysis using an excess of alcohol.[11] The interest in this reaction relies on the fact that not only does the synthesis yield volatile dimethylamine as by-product, but also that such $W{\equiv}W$ complexes are known to react with disubstituted alkynes, readily giving the mononuclear carbyne propagating species.[12]

Reacting $W_2(NMe_2)_6$ in toluene with an excess of the sterically hindered 1-methoxy-2-methylpropan-2-ol (MMPOH) leads to the formation of the bimetallic complex $W_2(MMPO)_6$ **2** virtually quantitatively (Scheme 2).

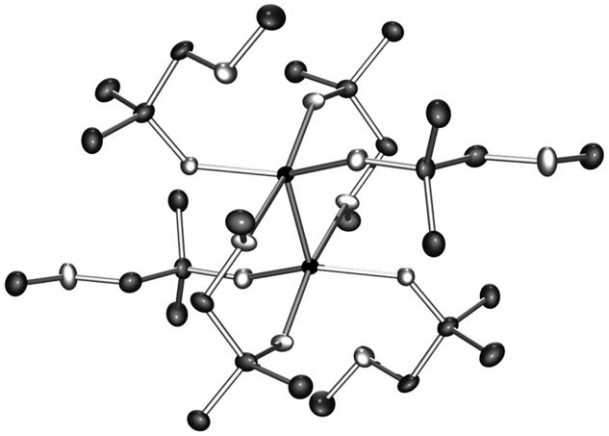


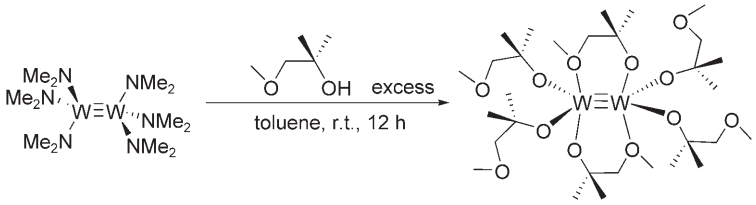
Figure 1. ORTEP view of the structure of complex **2**, ellipsoids at 30% probability, hydrogens are omitted for clarity (tungsten in black, oxygen in white, carbon in grey).

Crystallization of the product by slow evaporation of a concentrated toluene solution gives analytically pure black crystals, suitable for X-ray diffraction analysis (Figure 1).[13]

The length of the $W{\equiv}W$ triple bond, 2.430(8) Å, is comparable to that in similar complexes in the literature.[14] The ether function of one of the ligands coordinates the other tungsten atom with a W–O length of 2.257(3) Å, *vs.* 1.957(3) Å, 1.897(3) Å, and 1.920(3) Å for the three W–O bonds to non-bridging ligands. Each tungsten atom adopts a square pyramidal geometry imposed by the topology of the ligand, which differs from the classic tetrahedral geometry usually observed in $X_3W{\equiv}WX_3$ species.

Complex **2** catalyzes internal alkyne metathesis, since non-4-yne is readily transformed at 25 °C into metathesis compounds at equilibrium (Table 2). 1-Phenyl-1-propyne requires a higher temperature to be metathesized and a benzylidyne carbyne could be characterized by ^{13}C NMR spectroscopy with a chemical shift at 273.89 ppm ($J_{C,W}=277.17$ Hz) for the carbyne and 148.53 ppm ($J_{C,W}=49.25$ Hz) for the *ipso* carbon of the phenyl ring.

This catalyst was then further used for hept-1-yne metathesis and compared with the well-defined metallacarbyne **1** and the dinuclear complex **3** generated *in*



Scheme 2. Reaction scheme for the preparation of the bimetallic complex **2**.

Table 2. Metathesis of internal and terminal alkynes using different catalyst precursors.[a]

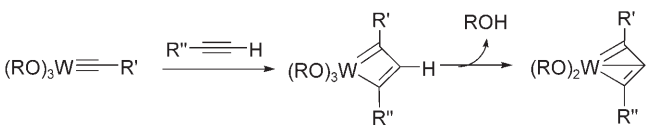
Entry	Catalyst	Alkyne	*T* [°C]	Conversion [%]	Metathesis [%]
1[b]	**2**	non-4-yne	25	50	50
2	**2**	1-phenyl-1-propyne	80	70	70
3[c]	**1**	hept-1-yne	80	89	33
4	**1**	hept-1-yne	25	93	23
5[c]	**3**	hept-1-yne	80	78	33
6	**2**	hept-1-yne	25	25	25
7	**2**	hept-1-yne	80	87	65
8[d]	**2**	hept-1-yne	80	86	77
9	**2**+quinuclidine	hept-1-yne	80	50	47
10	**1**	phenylacetylene	80	100	0
11	**2**	phenylacetylene	80	22	10

[a] [Alkyne]/[W] = 28.5; solvent toluene; temperature 80 °C; reaction time 1 hour; the difference between conversion and metathesis is assumed to correspond to polymerization.
[b] Same conditions but at 25 °C.
[c] Same conditions but reaction time 1 min.
[d] Same conditions but under static vacuum.

situ from $W_2(NMe_2)_6$ and *tert*-butyl alcohol. Remarkably, a strong enhancement of the metathesis selectivity was found: at 25 °C, no polymerization was observed (100 % selectivity, run 6), but the conversion was reduced to 25 %. Increasing the temperature to 80° with complex **2** improved the activity, and conducting the reaction under a static vacuum (to allow the acetylene to be rapidly removed from the reaction mixture) led to a further increase in the metathesis yield, up to 77 %. The combination of catalyst **2** and one equivalent of quinuclidine was even more selective (94 % selectivity, run 9), but resulted in a drop in conversion.

Phenylacetylene, which previously has never been metathesized, still gave a low, but definite, catalytic metathetic reaction using **2**, and, in contrast to complex **1**, did not give further polymerisation. (run 11).

As far as selectivity is concerned, mechanistic investigations have already established that the major reason why the reaction did not follow a metathetic course derives from the fact that the metallacyclobutadiene intermediate is prone to an irreversible deprotonation process, leading to a deprotiometallacyclobutadiene responsible for polymerization (Scheme 3).[7] Accordingly,such species synthesized from complex **1** and *tert*-butylacetylene have been found to be extremely reactive towards phenylacetylene polymerization at room temperature.[8]



Scheme 3. General scheme for deprotonation of metallacyclobutadiene.

In our case, using hemilabile alkoxy ligands, the presence of the extra coordinating moiety in the coordination sphere undoubtedly plays a major role in the selectivity enhancement: DFT calculations on these metallacyclic intermediates and transition states are currently underway to determine the precise role of these ligands in the deprotonation process.

The activity and selectivity obtained with this new catalyst allow this reaction to be applied to alkyl-substituted terminal alkynes for applications in organic synthesis. Although some interesting results have been obtained using phenylacetylene,[17] progress needs to be made in that context to improve the yield of metathesis compound for this substrate. Using the hemilability concept with other ligands would help in that context: further work is in progress in that direction in our laboratory.

Experimental Section

General Remarks

All experiments were carried out under argon in a glove box or using Schlenk techniques. Solvents were purchased from SDS or the Scharlau Company. Toluene and decane (Aldrich) were dried over sodium and distilled under argon. Triethylamine and pyridine were dried over KOH and distilled under argon. Alkynes (Aldrich or GFS Chemicals) were dried over CaH_2 and distilled under argon. Benzene-d_6 (Eurisotop) was dried over sodium and distilled under argon. All solvents were degassed by three freeze-pump-thaw cycles prior to use. $Cl_3(DME)W{\equiv}C$-*t*-Bu,[15] and $(t\text{-}BuO)_3W{\equiv}C$-*t*-Bu[16] were synthesized as described in the literature. Alcohols were obtained from commercial sources, dried over CaH_2, and distilled under argon. Alcoholates were obtained from commercial sources and used without further purification or synthezised by mixing the corre-

sponding alcohol in excess with sodium in diethyl ether until all sodium has disappeared, and then dried overnight under vacuum.

General Instrumentation

GC analyses were performed on a CHROMPACK CP-9002 equipped with a CPSil-8CB column. ^{1}H NMR spectra were measured on a Brucker AVANCE 300.13 MHz spectrometer. ^{1}H chemical shifts are expressed in parts per million downfield from tetramethylsilane ($\delta = 0$ ppm). The residual ^{1}H signal of benzene-d_6 was used as reference. The amount of dodec-6-yne was calculated on the basis of a calibration curve made with pure dodec-6-yne and *n*-decane.

Metathesis yields were calculated on the basis of dodec-6-yne formed as follows: % metathesis $= (2n_{\text{dodec-6-yne}}/ni_{\text{hept-1-yne}}) \times 100$, where $n_{\text{dodec-6-yne}}$ refers to the amount of dodec-6-yne produced (in mol) and $ni_{\text{hept-1-yne}}$ refers to the initial amount of hept-1-yne used for the reaction (in mol). The amount of dodec-6-yne is calculated using *n*-decane as internal standard. The same method was used to determine the amount of tolane.

Synthesis of $W_2(MMPO)_6$

In a glove box, a Schlenk flask was charged with 0.1 g (0.16 mmol) of $W_2(NMe_2)_6$, 10 mL of toluene and a magnetic stir bar. A solution of methoxy-methylpropan-2-ol (1 g, 9.6 mmol) in 5 mL of toluene was then added and the reaction mixture is stirred at room temperature for 12 h. After evaporation of the solvent and excess alcohol under vacuum, the product was obtained quantitatively as an orange-yellow solid that can be used without further purification.

Crystallization of the compound from a highly concentrated solution in toluene at room temperature afforded black crystals suitable for X-ray diffraction analysis and elemental analysis (yield after crystallization: 50%). ^{1}H NMR (C_6D_6): $\delta = 1.71$ [s, 6H, OC(*Me*)$_2$CH$_2$], 3.22 (s, 3H, CH$_2$O*Me*), 3.59 (s, 2H, C*H*$_2$OMe); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 29.09$ [s, OC(*C*H$_3$)$_2$CH$_2$], 59.80 (s, CH$_2$O*C*H$_3$), 79.04 [s, O*C*(CH$_3$)$_2$CH$_2$], 83.20 (s, *C*H$_2$OCH$_3$); anal. calcd.: C 36.52%, H 6.74%; found: C 36.62%, H 6.82%.

General Procedure for the Screening in Alcoholate

In a glove box, a round-bottom flask was charged with the alkyne (1.45 mmol), toluene (5 mL), *n*-decane (0.1 mL) and a magnetic stirring bar. The flask was then connected to an argon/vacuum line, placed under argon and stirred at 80 °C. In a glove box, the catalytic solution was prepared in a Schlenk flask by mixing $Cl_3(DME)W \equiv C$-*t*-Bu (0.45 g, 0.101 mmol) and the alcoholate (0.303) mmol in toluene (2 mL) with a magnetic stirring bar at room temperature. The flask containing the solution was then connected to an argon/vacuum line, placed under argon and stirred at room temperature for 15 min. Stirring was stopped and 1 mL of the supernatant was withdrawn with a syringe and injected into the alkyne solution. After 1 min, the reaction was quenched with methanol and the products analyzed by GC.

General Procedure for Alkyne Metathesis Reaction

In a glove box, a round-bottom flask was charged with the alkyne (1.45 mmol), toluene (5 mL), *n*-decane (0.1 mL) and a magnetic stirring bar. The round-bottom flask was then connected to an argon/vacuum line, placed under argon and stirred at 80 °C. In a glove box, the catalytic solution was prepared in a Schlenk flask with $W_2(MMPO)_6$ (0.0254 mmol), toluene (1 mL) and a magnetic stir bar. The flask containing the solution was then connected to an argon/vacuum line, placed under argon and stirred at room temperature for 15 min, following which the catalytic solution was injected by syringe into the alkyne solution. After 1 hour, the reaction was quenched with methanol and the products analyzed by GC.

Note: For the reaction under reduced pressure, the alkyne solution in the round-bottom flask was *cooled at 0 °C and then put under static vacuum (2 mm Hg)*. The catalytic solution was then added *via* an addition funnel at normal pressure already connected to the round-bottom flask in the glove box. The internal standard (*n*-decane) was added after quenching the reaction with methanol and opening to air.

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[17] Disubstituted aromatic alkynes are much less prone to metathesis than their dialkyl homologues (see Table 2, entries 1 and 2). This might explain why such a low selectivity is obtained with phenylacetylene. Other details concerning the analysis of the polymers are available in the Supporting Information.

