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Terminal alkyne metathesis has been improved upon addition of quinuclidine as an external ligand to the $(tBuO)_3W{\equiv}CtBu$ carbyne complex, giving yield of 80% during hept-1-yne metathesis. Extension of this system to terminal/ disubstituted alkynes co-metathesis affords the expected cross reaction products.

Dedicated to Yves Chauvin, Richard R. Schrock and Robert H. Grubbs, our 2005 Nobel's

Introduction

Homogeneous internal alkyne metathesis was first reported to be catalysed by molybdenum/phenols-based catalyst systems, either starting from molybdenum hexacarbonyl as the metal source and thermal or photochemical activation,[1] or from higher oxidation state complexes such as $MoO_2(acac)_2$/aluminium alkyls based precursors,[2] the latter giving rise to much more active catalysts, allowing the reaction to be applied to functionalized alkynes and to occur at room temperature, eqn.(1).[3]

((equation 1))

On the other hand well-defined tungsten[4] and molybdenum[5] catalysts were synthesized and also proved to be very efficient catalysts for this reaction.
All those catalysts, as well as others based on molybdenum tris-arylamido carbynes[6] are presently used in metathesis reactions, ring closing alkyne metathesis[7] (RCAM) and metathesis polymerisation,[8] using disubstituted alkynes as substrates.
In contrast, there are only few publications dealing with the metathesis reaction of terminal alkynes using metallacarbynes as catalysts, eqn. (2).

((equation 2))

First attempts described by Schrock using phenylacetylene as substrate and the well-defined $(tBuO)_3W{\equiv}CPh$ complex only led to polymer formation, via a process where the initial metallacyclobutadiene intermediates are shown to readily deprotonate, giving rise to the production of deprotiometallacycles, which are very efficient terminal alkynes polymerisation species, eqn. (3).[9]

((equation 3))

Another possible reason for the failure of this approach is the fact that acetylene formed during the first turnover reacts readily with the metallacarbyne to produce the dimeric compound $[W_2(OtBu)_6](\mu C_2H_2)$:[10] both processes leading to these metathesis inactive species may occur , as exemplified in eqn. (4).

((equation 4))

On the other hand, we have shown that under specific conditions, and using *alkyl*-substituted terminal alkynes such as hept-1-yne[11] this reaction could be catalytic leading to the expected metathesis products acetylene and dodec-6-yne, eqn. (2). However, after several turnovers, the initial very fast metathesis reaction was irreversibly followed by polymerisation and the metathesis turnover number remained quite low. One interesting feature was the fact that the best results were obtained using diethylether as the solvent, suggesting that the coordinating properties of an external ligand may give rise to a stabilization of the catalytic species *vs* their tendency for irreversible deprotonation.

Another point which was at the origin of our renewed interest in this reaction comes from other data reported in the mid eighties related to the fact that upon addition of pyridine to the dimeric complex $[W_2(OtBu)_6](\mu\text{-}C_2H_2)$, $[W_2(OtBu)_6](\mu\text{-}C_2H_2)(py)$ was formed and shown to be in equilibrium with the monomeric tunsgstacarbyne methylidyne species $(tBuO)_3W{\equiv}CH$;[10] furthermore, the use of quinuclidine as ligand has proved to be very useful to stabilize tris-alkoxy carbyne complexes via formation of stable, isolable $(tBuO)_3W{\equiv}CR(Quin)$ 1/1 adducts, including the methylidyne $(tBuO)_3W{\equiv}CH$ (Quin) eqn. (5).[12]

((equation 5))

We anticipated therefore that the use of coordinating ligands, and particularly these two amines, would provide a useful way for controlling the reaction course, due to some stabilization of the methylidyne intermediates.

Results and Discussion

In Table 1 are reported selected results related to the metathesis reaction of hept-1-yne using 4 mol % carbyne catalyst $(tBuO)_3W{\equiv}CtBu$ and equimolar amounts of potentially coordinating ligands as modifiers at different temperatures.

((Table 1))

As reported in previous papers in this field,[11]one main feature during this reaction is the fact that the metathesis reaction rapidly stops and that the transformation rapidly moves

towards polymerization. This observation was confirmed in almost all runs conducted with the phosphorus and nitrogen based ligands (Runs 1-5, Table 1), leading to poor yields and selectivities into metathesis at room temperature.

In contrast, the use of quinuclidine (runs 6-7), although reducing the reaction rate, gave increased amounts of metathesis products: a 73% metathesis selectivity was even maintained after 1 hour. The same observation was confirmed using diethylether as solvent (entry 8), but the metathesis only occurs during 15 minutes to reach a 41 % maximum conversion, and no further transformation of the alkyne was observed (run 8).

Knowing that a temperature increase benefits to metathesis vs polymerization,[11] further experiments were conducted at 80°C (runs 10-12). Although pyridine itself gave rise to a slight increase, the use of quinuclidine as modifier gave the best yield ever reported for this reaction, as expected: a 80% yield at 91% conversion (87% selectivity) was attained under these conditions.

Due to the relative stability of the $(tBuO)_3W{\equiv}CtBu$/quinuclidine catalyts, we next untertained to follow the reaction using ^1H NMR spectroscopy. The in situ ^1H NMR study of the catalytic reaction recorded after 5 min at room temperature, using a 10/1 hept-1-yne/catalyst ratio (Fig 1), revealed several species in solution.

((figure 1))

The most characteristic signal is a singlet at 5.15 ppm, wheree WH satellites are observed (J_{HW}= 90 Hz) corresponding to the $(tBuO)_3W{\equiv}C$-H(Quin) methylidyne complex, already described by Schrock.[12]

Several signals are detected in the 3.8-4.2 range, among which three of those may be assigned to a triplet corresponding to the methylene group of the alkylidyne propagating species $(tBuO)_3W{\equiv}CC\mathit{H}_2CH_2Pr$(Quin) ($J_{HH}$= 8 Hz): the ^1H nmr analysis of a metathesis reaction conducted with non-4-yne under those conditions using the same catalyst gave the multiplet pattern (**b)** corresponding to the α methylene protons in the mixture of the $[W]{\equiv}CC\mathit{H}_2CH_2CH_3$ and $[W]{\equiv}CC\mathit{H}_2Pr$ propagating species.

At last, the singlet at 10.71 ppm with an unusual 30 Hz J_{WH} coupling(the J_{WH} values of the β hydrogen in metallacyclobutadienes are usually in the range 11.6-15.3 Hz-see ref 9) can be ascribed to the two α protons in a monosubstituted metallacyclobutadiene, which could only give rise to degenerate metathesis and may well be considered as a dormant species. This assumption is in agreement with the fact that this species is the most stable *vs* time: this downfield signal only decreases when the two signals corresponding to the

propagating metallacarbynes have disappeared. Accordingly, new carbene signals arising from the deprotonation process (eqn 3) appear progressively in the 8.4-13 ppm range, together with those corresponding the production of polymer, only after the disappearance of these former three species.

The identification of stable methylidyne species during catalysis could explain the increasing amounts of metathesis products, but the presence of the singlet at 10.71 ppm may also lead to the conclusion that quinuclidine also stabilizes metallacyclobutadiene intermediates via complexation. This avoïds or inhibits at least in part the deprotonation process, and probably also contributes to some extent to the metathesis productivity enhancement.

Due to its propensity to metathesize both terminal and disubstituted alkynes, we next attempted a cross metathesis reaction using equimolar amounts of hept-1-yne and dec-5-yne, using the quinuclidine modified catalyst (3.5 mol%) in toluene for 1 hour at room temperature (eqn 6).

((Equation 6))

GC analyses using n-decane as internal standard showed that all the expected products coming from homo and *cross* metathesis were obtained (mol%): *hex-1-yne* (10.6), hept-1-yne (6.8), dec-5-yne (22.9), *undec-5-yne* (25.5), dodec-6-yne (7.3).

Conclusion

The activity/selectivity observed in these reactions using this simple Schrock carbyne/quinuclidine modified catalyst are of interest from a synthetic point of view: the metathesis yield could be enhanced to 80% using a simply modified catalyst in 4 mol % catalytic amounts. Accordingly, this catalyst may be used for either cross metathesis reactions or ring closer metathesis involving either mixed terminal/disubstituted α-ω diynes or terminal α-ω diynes. Further studies are in due course using this concept, via the synthesis of other modified tunsgtenacarbyne complexes, as these results pave the way for a new synthetic tool in organic chemistry.

Experimental

All experiments were carried out under argon in glove box or using Schlenk technique. Solvents were purchased from SDS or Scharlau Company.
Toluene and decane (Aldrich) were dried over sodium and distilled under nitrogen. Triethylamine and pyridine were dry over KOH and distilled under argon . Alkynes (Aldrich or GFS Chemicals) were dried over CaH_2 and distilled under argon. Quinuclidine (Aldrich) was purified by sublimation prior to use. [D_6] benzene (Eurisotop) was dried over sodium and distilled under argon. All solvents were degassed by three freeze-pump-thaws prior to use.
$(tBuO)_3W{\equiv}CtBu$ was synthesize as describe in the literature.
GC analyses are performed on a CHROMPACK CP-9002 equipped with a CPSil-8CB column.
^1H NMR were measured on a Brucker AVANCE 300.13 MHz spectrometer equipped with a QNP Probe. Chemical shifts of ^1H are expressed in parts per million downfield from tetramethylsilane (δ=0 ppm). Residual ^1H signal of [D_6] benzene 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: $\%metathesis=(2n_{dodec\text{-}6\text{-}yne}/ni_{hept\text{-}1\text{-}yne})*100$, where $n_{dodec\text{-}6\text{-}yne}$ refers to the amount of dodec-6-yne produced(in mol) and $ni_{hept\text{-}1\text{-}yne}$ refers to the initial amount of hept-1-yne used for the reaction (in mol).

General procedure for alkyne metathesis

A round bottom flask was charged with hept-1-yne (0.19 mL, 1.48 mmol), toluene (5 mL), n-decane (0.1 mL) and a magnetic stirring bar. The solution was stirred at 80°C.
A Schlenk flask was charged with $(tBuO)_3W{\equiv}CtBu$ (0.024g, 0.05 mmol), quinuclidine (0.005 g, 0.05 mmol), toluene (1 mL) and a magnetic stir bar. The solution was stirred at room temperature for 15 minutes and then added to the previous solution with a syringe. Aliquots were withdrawn during the reaction, quenched with methanol to precipitate the undesired polymer, and then analysed by GC.
The same procedure was used for alkyne cross metathesis, except an equimolar amount of dec-5-yne(0.27ml, 1.48 mmol) was added together with hept-1-yne

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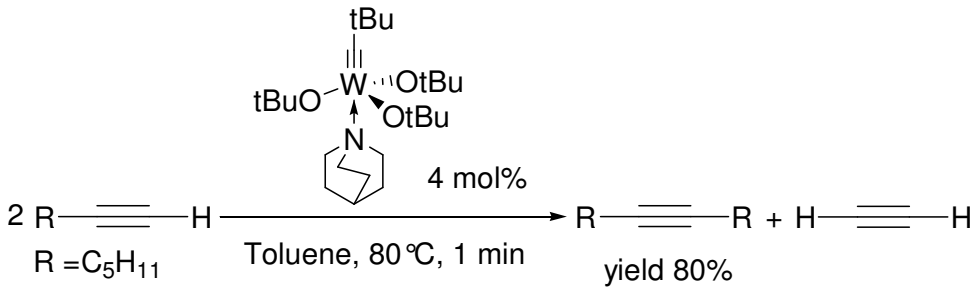
Graphical Abstract



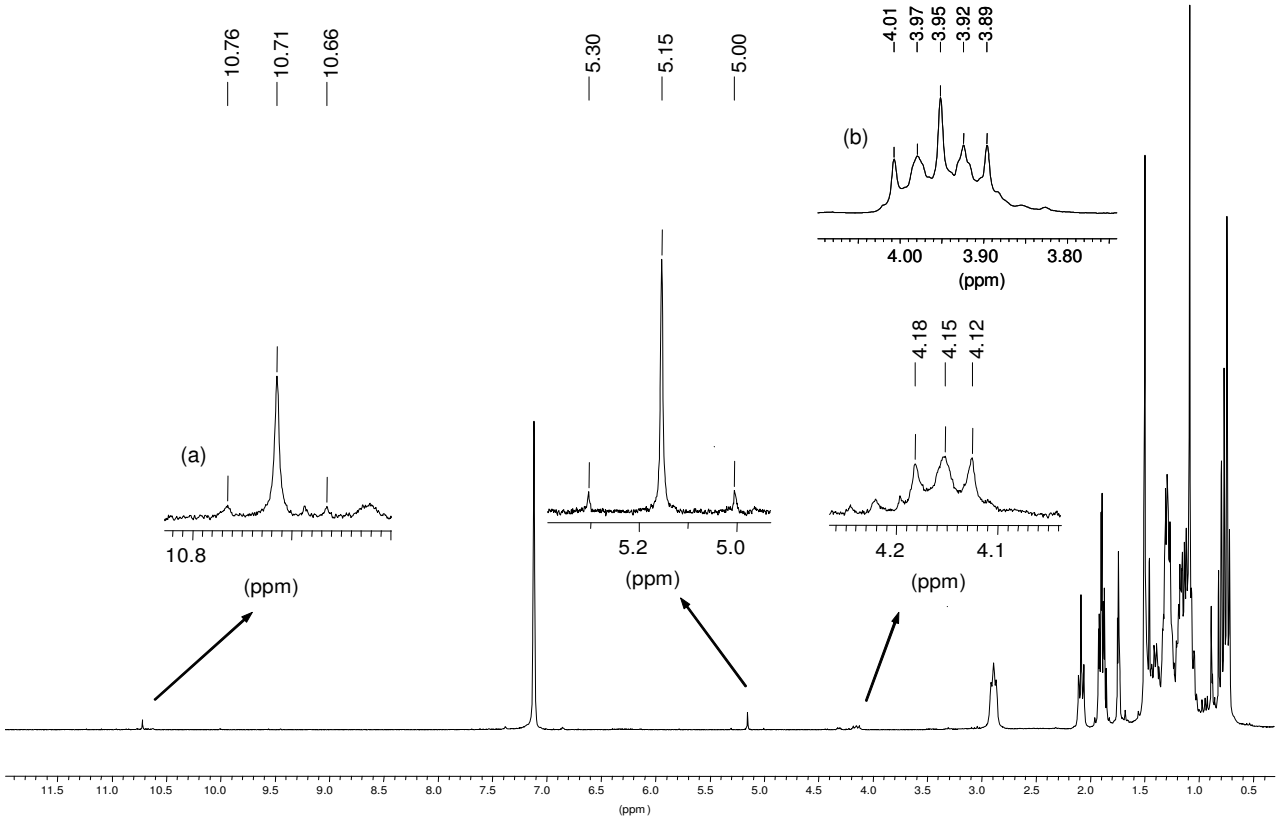
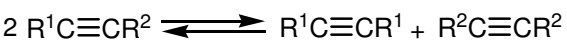
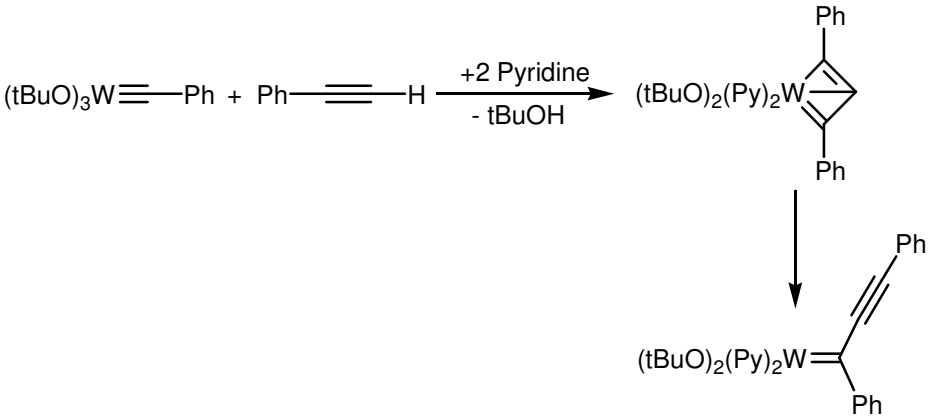


Figure 1. NMR spectrum (a) of hept-1-yne metathesis over the $(tBuO)_3W{\equiv}CtBu$ /quinuclidine system, and part of the spectrum (b) obtained using non-4-yne on the same catalyst.

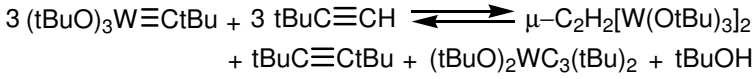


((**Equation1**))

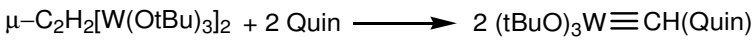
((**Equation 2**))



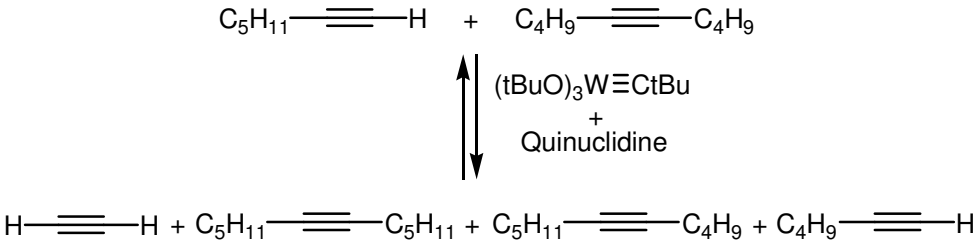
((Equation 3))



((**Equation 4**))



((**Equation 5**))



((Equation 6))

Table 1. Metathesis of 1-heptyne by Schrock carbyne with different ligands[a]

Entry	Ligand	Rtion time min.	T(℃)	Solvent	Conversion[b] %	Metathesis[c] Yield %	Metathesis selectivity %
1	-	60	RT	Toluene	93	23	25
2	Triphenyl phosphine	60	RT	Toluene	99	12	12
3	Tris-*o*-tolylphosphine	60	RT	Toluene	97	16	16.5
4	Pyridine	60	RT	Toluene	77	24	31
5	triethylamine	60	RT	Toluene	56	22	39
6	Quinuclidine	60	RT	Toluene	51	37	73
7	Quinuclidine	1	RT	Toluene	28	22	78
8	Quinuclidine	15	RT	Diethyl ether	41	30	73
9	-	1 (60)	RT	Diethyl ether	91 (>99)	25,7 (23)	28 (23)
10	-	1 (60)	80	Toluene	78 (>99)	33 (26)	42 (26)
11	Pyridine	1 (60)	80	Toluene	53 (>99)	44 (37)	83 (37)
12	Quinuclidine	1 (60)	80	Toluene	91 (>99)	80 (70)	88 (70)

[a] Reactions were carried out using hept-1-yne (190 µL, 1,45 micromoles), decane (100 µL), solvent (5 mL), 4 mol% catalyst and equimolar amounts of extra ligand.

[b] Conversions were determined by GC using n-decane as internal standard..

[c] Determined by GC, using the amount of dodec-6-yne as reference-no other internal alkyne was detected in the liquid phase.

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