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Metathetical cyclization of dienes: tolerance and behavior of a cyclometallated aryloxycarbene complex of tungsten towards diallylic compounds

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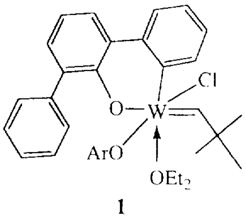
Summary – Intramolecular metathesis of various diallylic compounds containing the O, S, Si or P hetero-elements was achieved in good yields by using the cyclometallated carbene complex W(OAr)(OAr)($CHCMe_3$)Cl(OEt_2). Unsubstituted diallyl ether is converted into 2,5-dihydrofuran; diallyl sulfide is converted into 2,5-dihydrothiophen; diallylphenyl phosphine is converted into 1-phenyl-2,5-dihydro-1*H*-phosphole; and diallyldimethyl- or diphenylsilanes are converted into the corresponding silacyclopentenes. The metathesis reaction of methyl-substituted diallyl sulfides shows that steric effects are very important. Depending on the position of the methyl groups, the reaction can proceed normally or be completely inhibited.

metathesis / tungsten / cyclization / steric hindrance / heteroatom

Introduction

The olefin metathesis reaction represents a powerful tool in carbon-carbon bond formation reactions [1]. The metathesis of diene compounds (ADMET) is now widely used in applied organic synthesis for preparation of functionalized polymers or unsaturated cyclic products. Up to very recently, only a few examples of the metathesis of dialkenyl ethers [2], amines [3], carbonates [4], ketones [5] and sulfides [6] had been described in the literature, opening novel fields of application. In most cases the catalyst was Schrock molybdenum carbene Mo(=NAr)(=$CHCMe_2Ph$)$(OR)_2$ [7]. We have recently reported the synthesis of the cyclometallated *o*,*o*′-diphenylaryloxo(chloro)neopentylidene tungsten complex W(OAr)(OAr)($CHCMe_3$)Cl(OEt_2) **1** (scheme 1) [8, 9].



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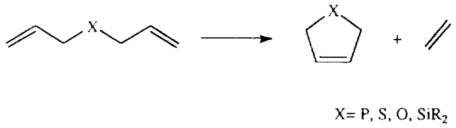
Scheme 1

The complex **1** is probably one of the most active (and sometimes the most stereoselective) systems for the metathesis of *cis*-2-pentene [10], but it also catalyzes the metathesis of olefinic esters [9], olefinic sulfides [11, 12], and olefinic carbohydrates [13–15]. We would like to report here that **1** is also a selective catalyst for the cyclization of heterosubstituted diallylic compounds where the hetero-element is O, S, P or Si (scheme 2).



Scheme 2

Results and discussion

Under our experimental conditions, **1** is highly selective for such metathetical cyclization, because polymeric materials were never detected.

Diallyl ether leads to dihydrofuran, which is the first example of *unsubstituted* diallyl ether homogeneous metathesis (table I, entry 7) [16]. We were pleasantly surprised that diallyl(phenyl)phosphine led to the desired phospholene derivative (table I, entry 10). This is to our knowledge the first example of metathesis of an olefin with a not very bulky phosphine derivative, which

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† This paper is dedicated to the memory of Michel Leconte, deceased on August 10, 1993.

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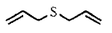
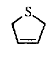
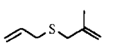
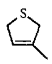
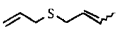
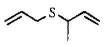
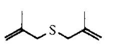
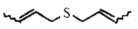
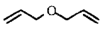
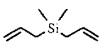
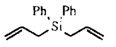
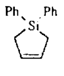
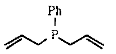
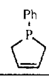
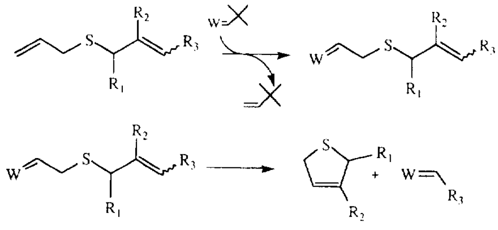
is expected to coordinate strongly to tungsten derivatives. Diallyldimethyl or diallyldiphenylsilyl compounds led to the corresponding unsaturated cyclic compounds (table I, entries 8 and 9). Diallyl sulfides led in some cases to the expected cyclization products but in other cases no reaction occurred. Steric factors become important depending on the position of the methyl group on the two chains; the metathesis reaction proceeds normally (entries 2 and 3) or is inhibited (entry 4). Two symmetrical methyl groups result in an inhibition (entries 5 and 6). These results suggest that the first propagating carbene species can only be generated by coordination of the unsubstituted allyl group (in this step the corresponding tungstacyclobutane has only two substituents in the 1-3 position) [17].

Table I. Metathesis of diene compounds **1–10**.

Entry	Substrate	Olefin/W	Product	Time (min)	Yield (%)
1		1000 500 250		60 60 60	30 75 100
2		100		60	100
3		100		60	90
4		100	-	60	0
5		100	-	60	0
6		100	-	60	0
7		200 100 40		120 120 120	50 70 100
8		200 100 50		20 20 20	50 70 90
9		100		60	8
10		20		300	95



R₁=R₃=H, R₂=Me (entry 2)

R₁=R₂=H, R₃=Me (entry 3)

R₁=Me, R₂=R₃=H (no reaction)(entry 4)

Scheme 3

These results explain the absence of reaction with the symmetrically substituted sulfides (the corresponding metallacyclobutane has three substituents in 1-2-3 positions) [17]. The next reaction step is an intramolecular coordination of the remaining unsaturated fragment to complete the cyclization with elimination of ethylene. This step is also probably driven by steric interactions (restricted number of substituents in the metallocycle). By building molecular models it is clear that the intramolecular coordination of the double bond is possible without any steric interaction with the bulky *o,o'*-diphenylaryloxo ligands for the crotyl and methallyl groups, whereas it is prevented when the methyl group is adjacent to the sulfur atom. These remarks are characteristic of this cyclometallated aryloxocarbene complex of tungsten, which has a 'cavity-shaped' structure [17-20].

Conclusion

In conclusion, although in most cases the heteroatom is not 'hindered', and thus could easily coordinate to **1**, it does not deactivate the alkylidene species. These results contrast with previous reports and are a supplementary proof of the *atypical behavior* of **1** in metathesis of functionalized olefins: inhibition by the heteroatom (O, S, P) is prevented but steric hindrance on the double bond seems to be a crucial parameter.

Experimental section

All experiments were carried out using classical Schlenk techniques working under dried and deoxygenated argon. The solvent (chlorobenzene) was distilled over phosphorus pentoxide under nitrogen purge. Diallyl sulfide, diallyl ether, diallylsilanes and diallylphenylphosphane were purchased from Aldrich. Mono- or disubstituted diallyl sulfides were prepared as described in references 19 and 20. All diallyl compounds (except phosphanes) were treated over activated alumina (12 h, 150°C, 1 Torr) immediately before use. Allylic phosphanes were used without further purification.

Diallyl sulfides

In a typical experiment (entry 2) 4 mL chlorobenzene, 0.1 mL *n*-octane (internal standard) and 0.33 mL sulfide (2.35×10^{-3} mol) were introduced into a 50 mL Schlenk reactor previously purged with argon. Whilst stirring and heating at 80°C, a solution of 20 mg (2.35×10^{-5} mol) of **1** in 1 mL of chlorobenzene was added. Conversion of the substrate was measured by chromatographic monotoring and no polymeric materials were detected. The same procedure was followed for diallylsilanes and diallyl ether.

Diallylphenylphosphane

The conversion rate was determined by measuring the evolution of ethylene with propane as an internal standard. In a typical experiment a solution of 89 mg (4.68×10^{-4} mol) of diallylphosphane in 1 mL chlorobenzene and 1 mL propane was introduced into a 50 mL Schlenk tube previously purged with argon. Whilst stirring and heating at 80°C, a solution of 20 mg (2.35×10^{-5} mol) of **1** in 1 mL chlorobenzene was added. After 12 h of reaction, the solvent was removed by evaporation at room temperature under 1 Torr pressure. The residue was then distilled at 100°C and condensed at liquid nitrogen (−196°C).

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