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ARYLOXY COMPLEXES AND CYCLOMETALLATED ARYLOXY ALKYLIDENE COMPLEXES OF TUNGSTEN (VI). APPLICATION TO THE METATHESIS OF FUNCTIONALIZED OLEFINS*

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Abstract—In this review article, the synthesis of aryloxy complexes of tungsten with the general formula $W(OAr)_xCl_{6-x}$ is described together with that of aryloxy (chloro)neopentylidene-tungsten complexes. The properties of these compounds in the metathesis of non-functionalized and functionalized olefins are reviewed. The aryloxy complexes of tungsten are good air-stable precursor catalysts when combined with organotin or -lead cocatalysts. In particular, depending on the cocatalyst and substituents on the aryloxide ligands, one can achieve either linear or cross-linked polydicyclopentadienes. One can also govern the induction period for the obtention of cross-linked polydicyclopentadiene, a phenomenon compatible with the requirements of the RIM processing. The cyclometallated neopentylidene tungsten complex **1** can be synthesized by two different routes, either from the $W(OAr)_2Cl_4$ (OAr = $\text{-O-2,6-}C_6H_3Cl_2$ or $\text{-O-2,6-}C_6H_3Ph_2$) precursor or from the Schrock carbyne $W(CCMe_3)(Cl_3)(dme)$. In both cases, when OAr = $\text{O-2,6-}C_6H_3Ph_2$, a metallation occurs by cleavage of the C—H bond in one substituting phenyl group. Complex **1** is probably one of the most active and stereoselective catalysts for metathesis of *cis*- and *trans*-2-pentene (total retention of the configuration of the starting olefin). Similarly, it selectively transforms 1-methyl-norbornene to 100% *cis*, 100% head-tail syndiotactic poly-1-methyl-norbornene. Complex **1** is also one of the most active catalysts for metathesis of functionalized olefins: with ethyl oleate **1** converts approximatively 250 equivalents of ethyl oleate into 9-octadecene and diethyl-9-octadecenedioate at 25°C. Compound **1** converts approximatively 100 equivalents of unsubstituted diallyl ether into the corresponding 2,5-dihydrofurane, and it (as well as the bicomponent catalysts) is able to realize metathesis of ω-unsaturated glucosides into the corresponding di-glucosides. It is also able to convert cyclic and acyclic double bonds with thio-ether functionalities to the corresponding polymer or cyclic products. For example, **1** converts diallyl sulphide or related compounds to the corresponding 2,5-dihydrothiophene derivatives. Similarly, phosphorus, silicon and tin diallyl derivatives can be transformed into the corresponding cyclic compound $\overline{\text{E—CH}_2\text{—CH=CH—CH}_2}$, E = P, Si, Sn.

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*This manuscript is dedicated to the memory of Michel Leconte.

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Since the discovery of the olefin metathesis reaction,[1] the interest of industrial and academic researchers in such catalytic reactions has never declined. The metathesis reaction has constituted and still constitutes both industrial and academic challenges. In the field of functionalized olefins, the number of examples is still limited. This is probably related to the lack of suitable homogeneous or heterogeneous catalysts. Nevertheless, some preliminary results obtained by us and others on the $W(OAr)_xCl_{6-x}$ complexes showed that the nature of substituents on the aromatic group had a pronounced effect on both the activity and the stereoselectivity for non-functionalized and functionalized olefins.[2,3] As a consequence, we prepared many complexes displaying the $W(OAr)_x Cl_{6-x}$ formula and used them in the metathesis of acyclic and cyclic olefins. The synthesis of these complexes was motivated by the objective of obtaining stereoselective ligand effects for a better control of the stereoselectivity of the metathesis reaction (e.g. with *cis*- and *trans*-2-pentene). This allowed us to obtain highly active bi-component systems. Indeed, it appeared that, depending on the aryloxide ligand, these complexes, when associated with alkylating agents (organo-aluminium, organotin or -lead compounds), showed various types of activities and/or stereoselectivities.[4–6]

The study of the interaction between the precursor complexes $W(OAr)_2Cl_4$ and $SnMe_4$ was suspected to generate *in situ* the active metallocarbene by the following reaction:

$$W(OAr)_2Cl_4 + 2\,SnMe_4 \rightarrow [W(OAr)_2({=}CH_2)Cl_2] + SnMeCl_3.$$

Although the metallocarbene complex $[W(OAr)_2({=}CH_2)Cl_2]$ was detected as a very reactive intermediate by ^1H NMR, it could not be isolated as a pure compound. Only its lifetime could be increased by introduction of diethylether during the preparation of the catalytically active solution. The extremely high activity encountered by these two-component catalytic systems, especially for *o,o'*-dichloro aryloxide ligands, led us to undertake the preparation of the corresponding metallocarbene with variously substituted aryloxide ligands. This resulted in the preparation and characterization of aryloxy(chloro)neopentylidene-tungsten complexes, which are, to our knowledge, some of the most active catalysts for the metathesis of functional olefins. This review describes the synthesis and characterization of all these catalysts (mono- and bi-component) and their use in the metathesis of functional olefins.

SYNTHESIS AND CHARACTERIZATION OF $W(OAr)_xCl_{6-x}$ COMPLEXES AS AIR-STABLE PRECURSORS FOR METATHESIS REACTION

Two-component systems containing a tungsten alkoxide and a tin or lead organometallic complex were found to be highly active catalysts for metathesis of olefins.[7,8] However, the catalytic activity was found to be greatly dependent on the nature and the number of ligands in the alkoxide complexes. It had been proposed that these ligands governed both activity and stereoselectivity by their electronic effects rather than their steric ones.[8] As a consequence, we carried out the synthesis of variously substituted aryloxide complexes of tungsten (VI) that can be used as precursor complexes in two-component catalytic systems.[7] The general advantage of such ligands, compared to the alkoxide ones, is that their electron-withdrawing properties can be easily varied by changing the substituents on the ring. Similarly, their steric effect in close proximity to tungsten can also be modified by changing the bulkiness of the substituents in *ortho* and *ortho'* positions on the ring.

The procedure used for these syntheses was adapted from that described by Funk and Baumann for the synthesis of $W(OPh)_4Cl_2$.[9] Typically, a solution of the desired phenol in toluene or carbon tetrachloride was added to a suspension of WCl_6 in the same solvent. The reaction mixture was stirred under reflux for 2–12 h. The solvent was then removed by evaporation and the products were purified by classical procedures. An extensive series of substituted phenols was used, and it was found that the number of chlorine atoms that may be substituted in WCl_6 was strongly dependent on the nature, the number and the position of the substituents on the aromatic ring of the phenol. Depending on the nature of the substituted phenol, three series of chloro aryloxides of tungsten were synthesized: $W(OAr)_4Cl_2$, $W(OAr)_3Cl_3$ and $W(OAr)_2Cl_4$.

Table 1 gives the list of compounds which were prepared and characterized by various analytical methods. In most cases, only one compound can be obtained by use of a given phenol, avoiding the presence of mixtures and allowing then an easy synthesis of these compounds. Clearly, steric effects are of importance for *ortho-ortho'* derivatives, preventing the formation of tetrasubstituted complexes. A similar effect can also explain the formation of the disubstituted complex only when HOAr is the 2,6-diphenyl phenol. However, electronic effects more probably explain the low reactivity and the obtention of only the disubstituted

Table 1. List of aryloxide complexes $W(OAr)_xCl_{6-x}$ as a function of the starting phenols

$W(OAr)_2Cl_4$	$W(OAr)_3Cl_3$	$W(OAr)_4Cl_2$
2,6-$Me_2C_6H_3OH$	2,6-$Me_2C_6H_3OH$	C_6H_5OH
2,4,6-$Me_3C_6H_3OH$	2,4,6-$Me_2C_6H_3OH$	3-MeC_6H_4OH
	2,6-*i*-$Pr_2C_6H_3OH$	4-MeC_6H_4OH
2,6-$Ph_2C_6H_3OH$		3,5-$Me_2C_6H_3OH$
2,6-$Br_2C_6H_3OH$		4-*t*-BuC_6H_4OH
2,6-$Cl_2C_6H_3OH$		4-$MeOC_6H_4OH$
2,6-$F_2C_6H_3OH$		4-PhC_6H_4OH
		2-ClC_6H_4OH
		4-ClC_6H_4OH

complexes with the 2,6-dihalogenated phenols, compared to what is observed with the 2,6-alkyl phenols.

The X-ray structures of two typical derivatives, W(O-2,6-C_6H_3-*i*-$Pr_2)_3Cl_3$ and W(O-2,6-$C_6H_3Ph_2)_2Cl_4$ were obtained. Figure 1 gives the corresponding ORTEP drawings.

In W(O-2,6-C_6H_3-*i*-$Pr_2)_3Cl_3$, the tungsten is in a slightly distorted octahedral geometry, the chlorine atoms occupying meridional positions. Largest deviations from ideal geometry occur for the coordination geometry of the chlorine atoms around the tungsten atom. On the other hand, the coordination geometry around the tungsten atom is more regular for the oxygen atoms, showing little deviation from a regular octahedral arrangement. The *trans* aryloxide ligands tend to have their aryl planes roughly perpendicular while the aryl ring planes of the *cis* ligands have a dihedral angle of 56°, probably to minimize the isopropyl–isopropyl and isopropyl–chlorine repulsions. In W(O-2,6-$C_6H_3Ph_2)_2Cl_4$, the two phenoxide ligands are in a *cis* orientation. The W—O—C angles are significantly less than those in W(O-2,6-C_6H_3-*i*-$Pr_2)_3Cl_3$. This result suggests that steric crowding on account of the 2,6-phenyl groups as compared to isopropyl groups is less important than the relief of steric strain provided by the replacement of a bulky alkoxide by chloride on going from W(O-2,6-C_6H_3-*i*-$Pr_2)_3Cl_3$ to W(O-2,6-$C_6H_3Ph_2)_2Cl_4$.

A pertinent question is whether steric or electronic effects control the geometry of these two complexes. Because these are formally 12-electron W^{VI} complexes, it might be expected that ligand-to-metal π-donation would be of importance. The fact that in both complexes the W—Cl bond lengths are longer for Cl atoms *trans* to oxygen than for Cl atoms *trans* to Cl is consistent with the presence of $p\pi$–$d\pi$ bonding. This behaviour can be rationalized on the assumption that π-donation to W is possible for both oxygen and chlorine, but the oxygen atom is a slightly superior π-donor, thereby tying up the greater fraction of the W π-acceptor orbital shared with a *trans* Cl.

If Cl and O were very different in terms of their π-donating ability towards W^{VI}, the expectation would be that Cl and aryloxy ligands should be in the *cis* orientation, thereby avoiding competition between two molecules of the better π-donor ligand. On the other hand, bulky groups attached to the coordinating ligand favour the *trans* orientation of similar ligands.[10]

So, the simplest interpretation of the structures of these two complexes is that Cl and O aryl ligands are not greatly different in π-bonding capacity so that the balance between electronic and steric control is easy to tip. Thus, in W(O-2,6-$C_6H_3Ph_2)_2Cl_4$ the two O-2,6-$C_6H_3Ph_2$ ligands are in the electronically dictated *cis* orientation. In the other complex, the O-2,6-C_6H_3-*i*-Pr_2 ligands adopt meridional (*cis*, *cis*, *trans*) instead of facial (all *cis*) geometry because of the bulkiness of the isopropyl groups.

These aryloxide complexes are precursors of highly active metathesis catalysts in the two-component system (see below) and they are air stable and of easy practical use.[4,5] Obtention of more active and stereoselective catalysts can then be performed by obtention of the active species of the bi-component catalyst in a pure form, allowing then the preparation of a mono-component catalyst which should have very high activity. Modification of the coordination sphere of this complex should then lead to predictable catalytic properties. The next part of this review will describe our results in this field.

SYNTHESIS AND CHARACTERIZATION OF CYCLOMETALLATED ARYLOXY(CHLORO) NEOPENTYLIDENE-TUNGSTEN COMPLEXES

The most commonly used complex of this series is $\overline{\mathrm{W(OAr})}\mathrm{(OAr)({=}CHC(CH_3)_3)(OEt_2)Cl}$, with OAr = O-2,6-$C_6H_3Ph_2$. It has been characterized

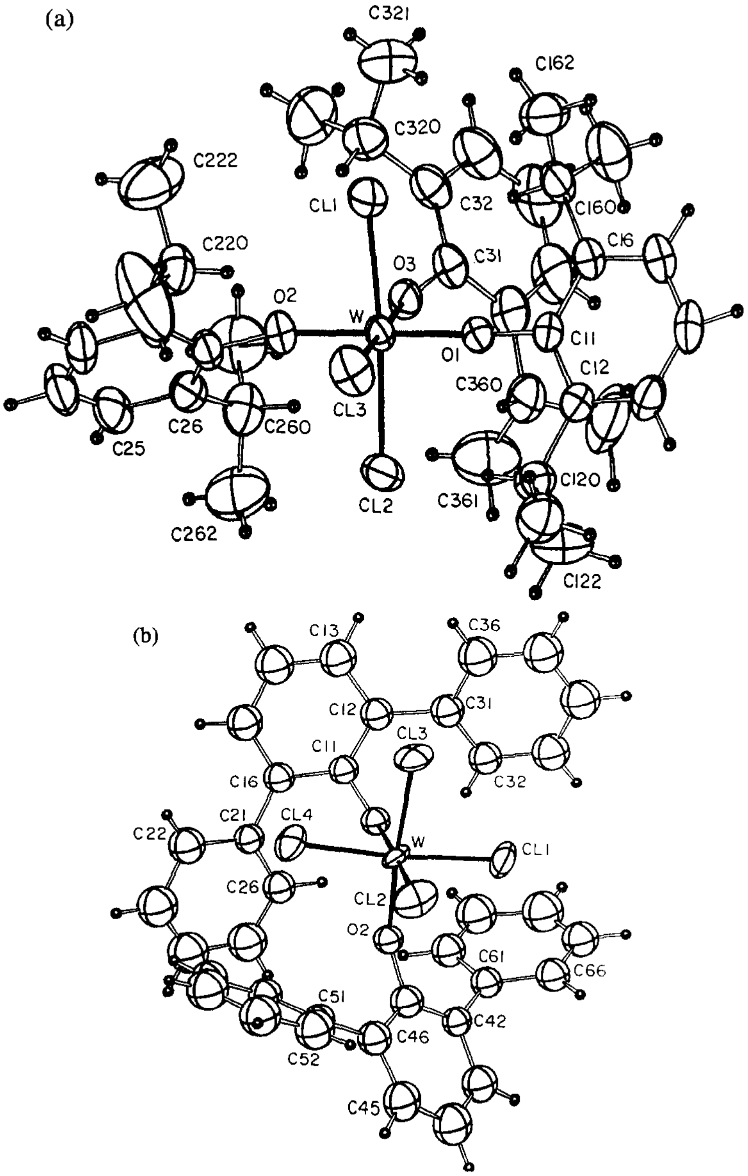


Fig. 1. ORTEP drawings with 50% probability ellipsoids of: (a) $W(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3Cl_3$; (b) $W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2Cl_4$.

by various physico-chemical techniques such as ^1H and ^{13}C NMR and mass spectroscopy. As an example, its ^{13}C NMR spectrum is given in Fig. 2 together with the attributions of the various peaks. The typical peak of the carbenic carbon atom can be seen at 296.7 ppm. Although no X-ray structure determination of this complex is available, the probable structure is that depicted at the bottom of Scheme 1.

This highly active complex can be prepared in two different ways (Scheme 1):

(a) Reaction of 2 molar equivalents of the bulky phenate LiOAr (Ar = 2,6-diphenyl-phenyl) with the Schrock carbyne complex $[WCl_3(CCMe_3)(dme)]$[11,12] in diethylether leads, by elimination of dimethoxyethane and of 2 equivalents of LiCl, to the formation of the carbene **1a**. It is expected that its formation occurs in two steps, first a double alkylation, via a coordinatively unsaturated intermediate, and then orthometallation of one phenyl substituent.

(b) A more classical approach is to alkylate $[WCl_4(O\text{-}2,6\text{-}C_6H_3Ph_2)]$ in diethylether with $[Mg(Np)_2(dioxane)]$. Elimination of HCl and neopentane leads to the product **1a**, which is then purified by exchange of diethylether for diisopropylether to give **1b**.

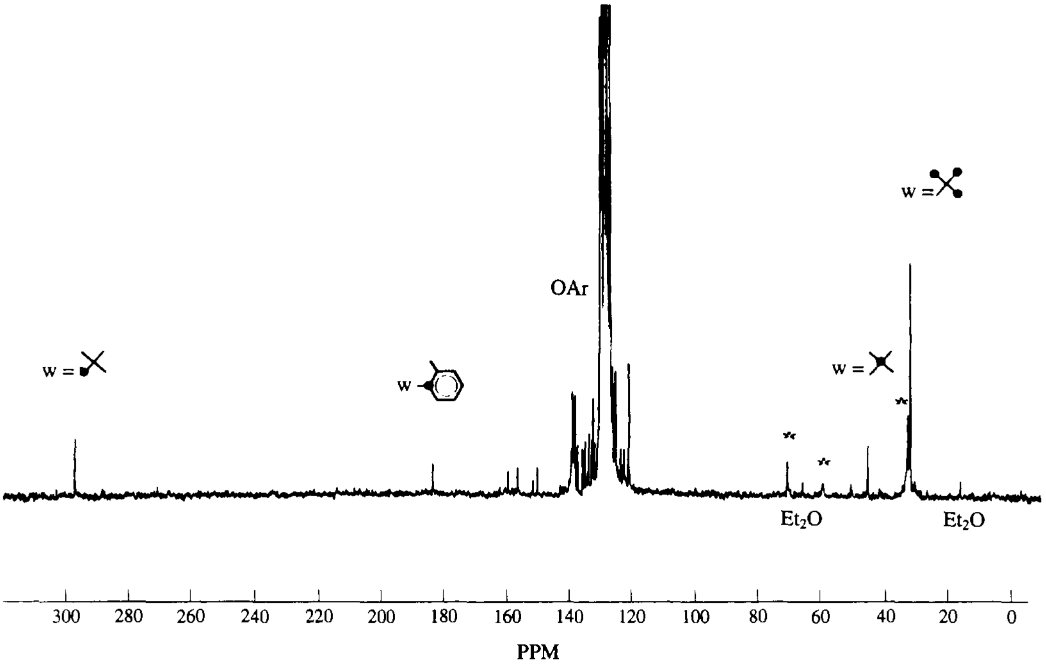


Fig. 2. ^{13}C NMR spectrum of W(OAr)(OAr)(=CHC(CH$_3$)$_3$)(OEt$_2$)Cl in C$_6$D$_6$ at 25°C.

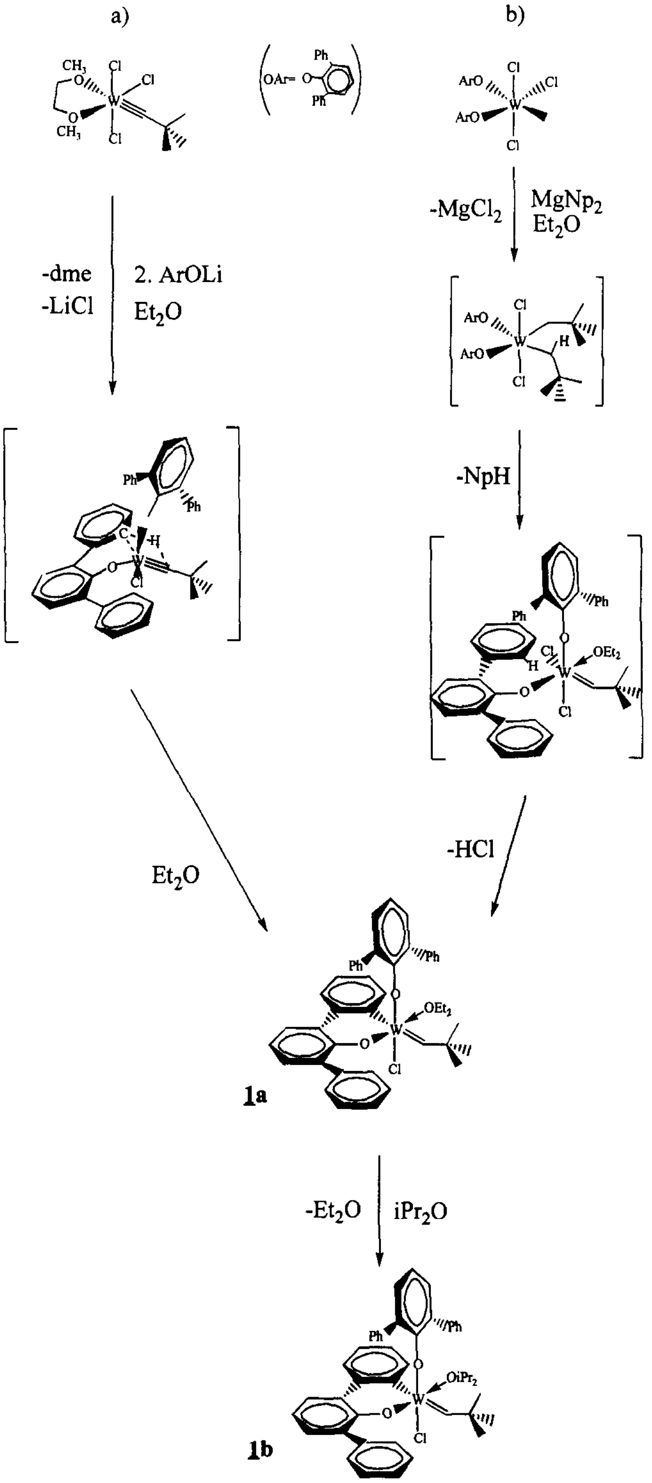
An interesting feature of these syntheses is the two different ways in which the intramolecular activation of the C—H bond of the arene substituent on the d^0 metal leads to a stable cyclometallated structure.[13-17] In the first case (path a), a C—H activation of the ligand leads to the addition of a hydrogen atom to the carbyne to form the carbene, concomitant with the orthometallation. Here, the role of the weakly coordinated ether is crucial to the tetracoordinated W^{VI}, where the C—H bonds of the phenyl group should coordinate to the metallocarbene and give the metallation via a four-centre transition state, as is now currently accepted for electrophilic activation of the C—H bond.[18] The situation is much less clear in path (b). Indeed, two reactions occur, the formation of the carbene by an α-H transfer between the two neopentyl groups and the orthometallation of the phenyl group, and we have no indication of what is the first step and so what reaction governs the second one.

Whatever the mode of formation, carbenes **1a** and **1b** are catalysts which are more active than the corresponding bicomponent systems for the metathesis of both functional and non-functional olefins. Indeed, it is expected that they are formed *in situ*, in small amounts, in these late catalysts. Below, we will denote the carbenes as **1**, as both **1a** and **1b** can be used for the reactions under study.

METATHESIS OF NON-FUNCTIONAL OLEFINS WITH W(OAr)$_x$Cl$_{6-x}$+MR$_4$ (M = Sn, Pb; R = Me, Bu) OR AlEtCl$_2$ AND WITH W(OAr)(OAr)(=CHC(CH$_3$)$_3$)(OEt$_2$)Cl (OAr = O-2,6-C$_6$H$_3$Ph$_2$ OR O-2,6-C$_6$H$_3$Cl$_2$)

We will only briefly discuss the metathesis of non-functional olefins by the aryloxy complexes of tungsten as it is not the purpose of this review article. However, some interesting features of the two-component system and the aryloxy (chloro)neopentylidene complex should be pointed out.

Two-component catalysts derived from the chloro aryloxy complexes of tungsten are very active systems for the metathesis of internal and terminal olefins, which present an interesting feature as they are air-stable.[4-6] The most interesting systems are those of the series W(OAr)$_2$Cl$_4$ and specially those obtained with *ortho-ortho'* substituted phenols. For *cis*-2-pentene metathesis, many parameters play a role in the activity: the electron-withdrawing property of the aryloxide ligand, the nature of the cocatalyst and the time of interaction between the precursor and the cocatalyst. For a given catalyst and a given time of interaction, the activity varies with the nature of the



Scheme 1.

substituent in the *o,o'*-position on the aryloxide ($X = CH_3 < C_6H_5 < F < Cl < Br$). For a given precursor complex and a given time of interaction, the activity increases with the nature of the cocatalyst in the following order: $SnMe_4 < Sn(n\text{-}Bu)_4 < Pb(n\text{-}Bu)_4$. For a given catalyst and cocatalyst, there is an optimum time of interaction before introducing the olefin. This decline of activity, which is observed if the olefin is introduced after this optimum value, might be related to a bimolecular side reaction leading to a coupling of carbenes. It can be suppressed if diethylether is added

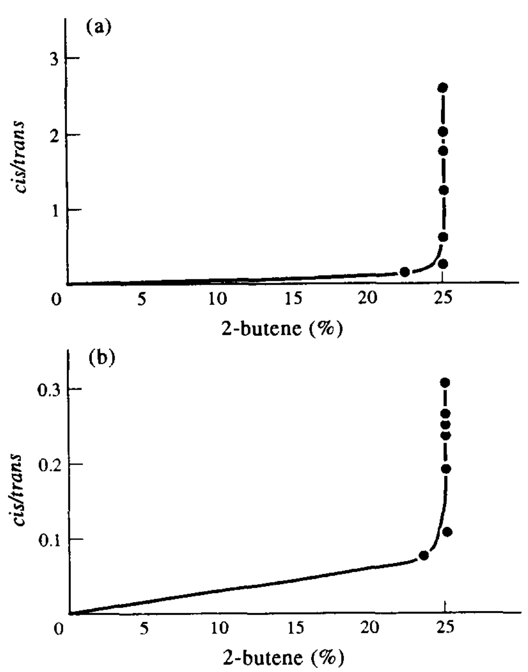


Fig. 3. *Cis/trans* ratio of 2-butene as a function of the yield of 2-butene in the metathesis of: (a) *cis*-2-pentene and (b) *trans*-2-pentene by **1a** (the thermodynamic equilibrium corresponds to *ca* 25% of butene).

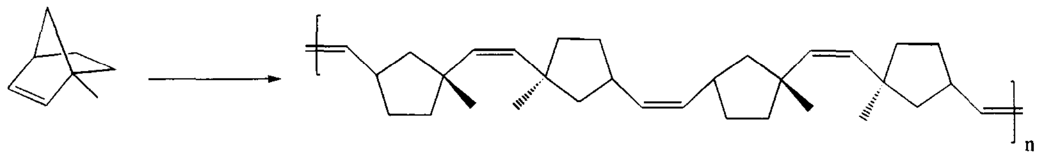
before the olefin. The stereochemical results obtained with $W(OAr)_2Cl_4$ and $Pb(n\text{-}Bu)_4$ show an increase of the stereoselectivity (defined as the retention of configuration of the starting olefin) with the nature of the aryloxide substituents in the following order: $F = Cl < Br = Me < Ph$. As already observed, the most active catalysts correspond to an almost statistical coordination and reaction of the olefin with the metallocarbene.

The results observed with the two-component systems show that the neopentylidene complex of tungsten should display very interesting properties in the metathesis of olefins. Indeed, the catalyst **1** has been shown to be simultaneously highly active and highly stereoselective for the self-metathesis of non-functional olefins. For example, metathesis of 1000 equivalents of *cis*-2-pentene with catalyst **1a** gives exclusively *cis*-2-butene and *cis*-3-hexene up to almost thermodynamic equilibrium, which is then reached in less than 2 min at room temperature, with an initial turnover of 800 min^{-1} (Fig. 3a). Similarly, *trans*-2-pentene reacts with catalyst **1a** to give almost exclusively *trans*-2-butene and *trans*-3-hexene up to thermodynamic equilibrium (Fig. 3b). When the conversion reaches thermodynamic values, a *cis–trans* or *trans–cis* isomerization occurs. This retention of configuration of the starting olefin has been explained upon considering the stability of the various possible metallacyclobutane intermediates.

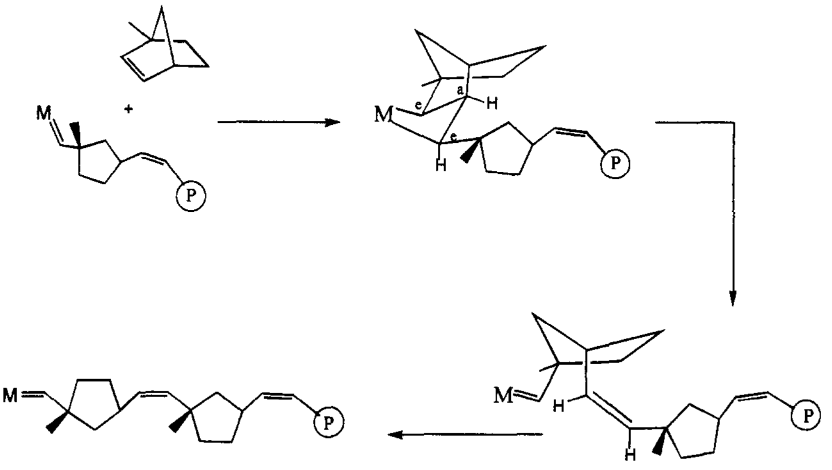
This high stereoselectivity of the aryloxy (chloro)neopentylidene complex can be used for the preparation of highly regular polymers by ring opening metathesis polymerization (ROMP). In the polymerization of norbornenes (bicyclo[2.2.1]hept-2-enes), catalyst **1** polymerizes 500 equivalents of monomer at −45°C in less than a minute to give approximately 80% *cis* distribution of the double bonds. The remarkable stereoselectivity of catalyst **1** can be verified with 1-methyl-norbornene: as compared to norbornene, a higher stereoregularity and an excellent tacticity can be obtained with this monomer[19] as can be determined by carbon-13 NMR. The presence of a methyl group at the 1-position sufficiently differentiates the double bonds on either side of the cyclopentane moieties to give different NMR signals (see Scheme 2). A completely head–tail structure, containing 100% *cis* C=C double bonds, and exclusively syndiotactic poly-1-methyl-norbornene, is obtained with **1a** or **1b** (Scheme 2).[19]

Such extremely high stereoselectivity (never reported up to date) can be explained on the same basis as with acyclic olefins: the structure of the olefin, especially in the vicinity of the double bond, is certainly a determining factor in the stereochemistry of metathesis of cyclic olefins; amongst all the possible metallacyclobutane intermediates, the most favoured tungstacyclobutane configuration is the one with the two bulkiest alkyl substituents in the 1-equatorial, 3-equatorial positions (Scheme 3).[20] The polymer resulting from this metallacyclobutane has a *cis* configuration with H-T structure and is syndiotactic.

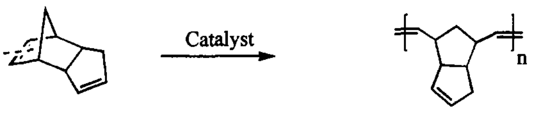
The chloro-aryloxide complexes of tungsten were also used in the polymerization of dicyclopentadiene.[5,21] Metathesis of dicyclopentadiene can lead, after cleavage of the double bond of the nor-



Scheme 2.



Scheme 3.

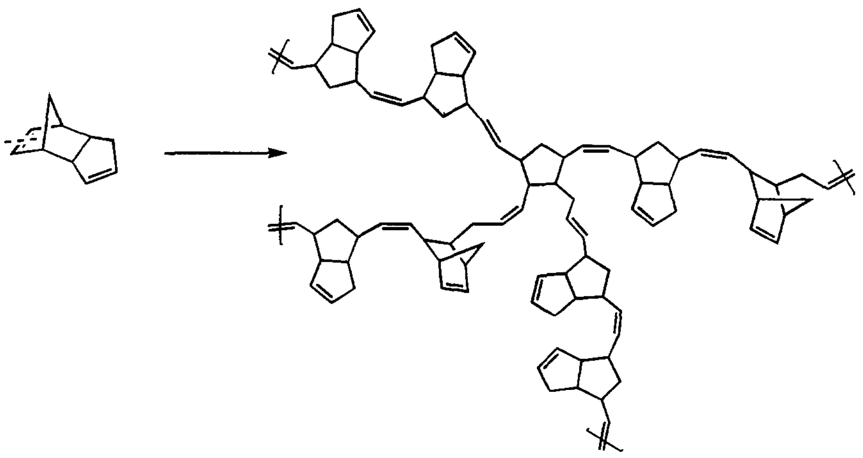


Scheme 4.

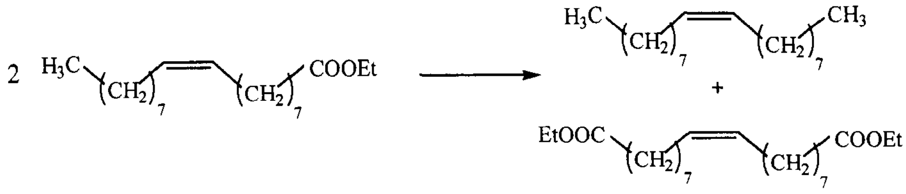
bornene unit, to the formation of an unsaturated linear polymer (Scheme 4). However, with some catalytic systems, the polymerization is very fast and gives highly cross-linked materials (Scheme 5) so that the reaction can be applied in Reaction Injection Moulding (RIM) techniques for manufacturing of impact-resistant and tough moulded parts. Depending on the nature of the aryloxide and of the cocatalyst, very different behaviour was observed in the metathesis of dicyclopentadiene with catalysts based on these systems.

With the catalytic systems $WCl_{6-x}(OAr)_x/EtAlCl_2$ and in the experimental conditions used, two main features were observed: (i) the polymerization reaction was fast and exothermic and resulted in the formation of a compact, very tough and insoluble polymer; (ii) the polymerization rate was greatly dependent on the nature of the catalyst and, more precisely, on the number and the nature of the aryloxide ligands. The most active catalysts were those with two aryloxide ligands and in this family an effect of the substituent of the phenoxide was observed: the activity increased in the order Ph < Cl < F.

The complexes $WCl_2(O\text{-}4\text{-}C_6H_4OMe)_4$ and WCl_3



Scheme 5.



Scheme 6.

(O-2,6-C_6H_3-*i*-Pr_2)$_3$ exhibited a very particular behaviour, easily applied for RIM technology: there was an induction priod of a few minutes which was followed by a very fast polymerization. The induction period depended on two parameters:

(i) the Al/W ratio; below an Al/W ratio of 6, the reaction proceeded very slowly, whereas above this value the induction period decreased until a limiting value of *ca* 10 min (for a length of interaction of 10 min);

(ii) the length of interaction between the catalyst and the cocatalyst before introduction of the dicyclopentadiene: the greater the length of interaction, the longer the induction period.

When the aryloxide was the *p*-methoxyphenol, it was proposed that the induction period was due to a competitive coordination of the *p*-methoxy group of one aryloxide and the dicyclopentadiene. In the case of the 2,6-di-isopropyl phenoxide, it was explained by a competition between the coordination of the dicyclopentadiene and an intramolecular C—H activation of a methyl group of one ligand.

When the polymerization was carried out with alkyl-tin or alkyl-lead as cocatalysts, the reaction proceeded more slowly and no solidification of the reaction mixture was observed. The polymerization depended on the cocatalyst and decreased in the order $PbBu_4 > SnBu_4 > SnMe_4$. Analysis of the polymer showed that it was linear with a low degree of cross-linking (as depicted in Scheme 3).

The ring-opening metathesis polymerization of dicyclopentadiene demonstrates the wide versatility of the chloro-aryloxide complexes of tungsten as olefin metathesis catalysts. Indeed, depending on the cocatalyst, a highly cross-linked insoluble or a linear soluble material can be obtained, the rate of polymerization being controlled by the nature of the aryloxide ligands and of the cocatalyst. Finally, some catalysts compatible with the RIM processes (very fast polymerization after an induction period) were obtained.

METATHESIS OF OLEFINIC ESTERS WITH $W(OAr)_xCl_{6-x}+MR_4$ (M = Sn, Pb; R = Me, Bu) AND WITH $\overline{W(OAr)}(OAr)({=}CHC(CH_3)_3)(OEt_2)Cl$ ($OAr = O$-2,6-$C_6H_3Ph_2$ OR O-2,6-$C_6H_3Cl_2$)

One of the challenges of organic chemistry is the metathesis of functional olefins. For example, this can lead to a simple one-step synthesis of difunctional olefins, useful starting materials which are sometimes difficult to obtain by the classical methods of organic chemistry. What has now virtually become a test of the tolerance of metathesis catalysts towards functional groups is the metathesis of an olefin bearing an ester group such as ethyl oleate (ethyl-9-octadecenoate) (Scheme 6).

The bis-aryloxide precursors $W(O\text{-}2,6\text{-}C_6H_3X_2)_2Cl_4$ (X = Cl, Br), when associated with homoleptic alkyl-tin or alkyl-lead derivatives, achieve metathesis of ethyl oleate with good activities and selectivities and rather high substrate/catalyst ratios. In most cases, the results are better than those reported for the conventional homogeneous catalyst WCl_6/SnR_4: for example, metathesis of ethyl oleate by the system $W(O\text{-}2,6\text{-}C_6H_3Cl_2)Cl_4/PbBu_4$ (reaction conditions: solvent C_6H_5Cl, temperature 85°C, $[W] = 10^{-4}$ mol, Pb/W = 2, substrate/catalyst = 50, catalyst–cocatalyst interaction time: 20 min) leads to 50% conversion after 30 min, with a 28% yield in the corresponding diester.[6] The chloro-aryloxide catalysts also appear particularly interesting for the cometathesis of unsaturated esters with olefins, since the selectivity in cross-metathesis can reach 90%.

As expected, much better results were obtained with **1**, as approximately 50% of 500 equivalents of ethyl oleate was selectively converted to 9-octadecene and diethyl-9-octadecenedioate, in 60 min at 25°C. The initial turnover rate for the conversion of ethyl oleate is higher than 800 h^{-1} (Fig. 4), a value which is, to our knowledge, one of the highest activities reported for the metathesis of that substrate[22] and the highest with a tungsten-based catalyst.[23,24]

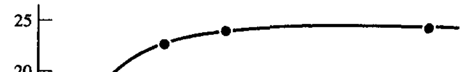


Fig. 4. Yield of 9-octadecene vs reaction time in the metathesis of ethyl oleate with **1** [ethyl oleate/**1** molar ratio = 500, $T = 25°C$; solvent: chlorobenzene (5 cm^3)].

METATHESIS OF UNSATURATED GLUCOSIDES WITH $W(OAr)_xCl_{6-x}+MR_4$ (M = Pb, R = Bu) AND WITH $\overline{W(OAr)}(OAr)(=CHC(CH_3)_3)(OEt_2)Cl$ ($OAr = O$-2,6-$C_6H_3Ph_2$)

The same kind of general strategy can be applied to the synthesis of any symmetrical disubstituted olefins bearing polar groups on either side of the double bond, one of the objectives being the synthesis of bolaamphiphilic compounds. The term bolaamphiphile describes a class of tensio-active compounds having two polar hydrophilic "head" moieties joined together by an hydrophobic alkyl chain. The interest in these compounds, along with their unusual surfactant properties, stems from their ability to form monolayer membranes.[25] Amongst others, one of the most interesting classes are the neutral bolaamphiphiles (uncharged hydrophilic moieties) that contain carbohydrate units at both ends of the long aliphatic chain. By analogy with the synthesis of unsaturated diesters above, one can envisage the synthesis of bolaamphiphiles by the self-metathesis of ω-unsaturated glucosides.

We studied the metathesis of unsaturated carbohydrates, both with the well defined neopentylidene monocomponent catalyst described previously, and the original bicomponent catalyst system, $WCl_4(OAR)_2/PbBu_4$. In order to avoid possible deactivation of the catalysts by hydroxyl groups, a series of substrates **2** (Scheme 7) bearing either acetylester, *t*-butyldimethylsilylether or benzyl ether protecting groups were prepared. Glycosylation[26] of 10-undecen-1-ol by tetra-*o*-acetyl glucopyranosyl bromide in the presence of silver triflate, followed by deprotection and reprotection procedures, afforded the starting olefins **2a**, **2b** and **2c**.[27]

Reaction of olefins protected by acetylester or *t*-butyldimethylsilylether with the neopentylidene complex in chlorobenzene at room temperature gave, after 12 h, good yields (> 50%) of the expected products.[27] Compound **2c** did not react with the carbene, showing that the nature of the protecting group has a non-negligible influence on the activity. This is the first example of the metathesis of sugar derivatives, and it demonstrates the effectiveness of the orthometallated neopentylidene complex even in the presence of numerous functional groups containing oxygen atoms.

In order to widen the scope of this type of reaction, other substrates (Scheme 8) were tested using the bicomponent catalyst system $WCl_4(OAr)_2/PbBu_4$.

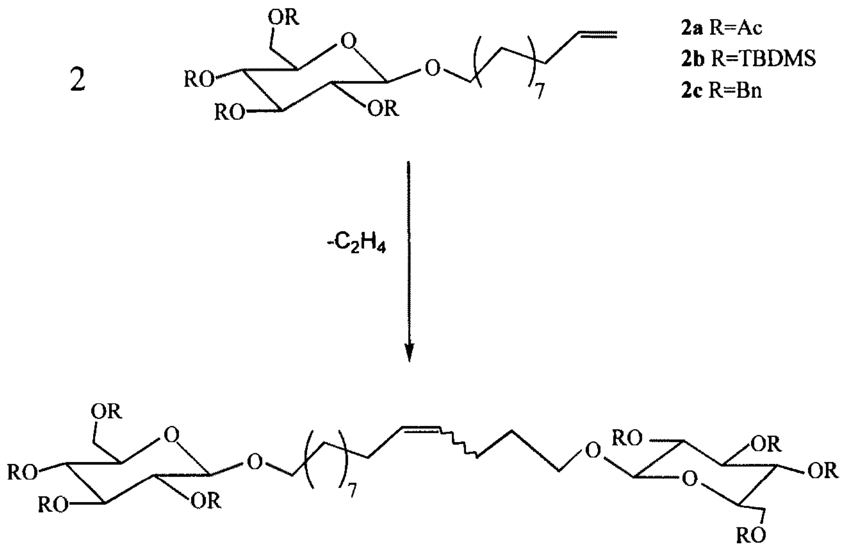
This also turned out to be a good system, for catalyst/substrate ratios ranging from 8 : 1 to 20 : 1, and giving similar yields of the expected products.[27] Only **3c**, the allyl ether glucoside, did not react. It seems that the proximity of the oxygen atom(s) to the double bond is an unfavoured parameter for metathetic activity, probably due to the competitive adsorption of the olefin on the tungsten complex by the heteroatom. However, metathesis of the allyl ether glucoside is expected to work using the more active monocomponent carbene catalyst, since the latter has already been used successfully in the metathesis of unsubstituted and substituted diallylethers.

METATHESIS OF UNSUBSTITUTED DIALLYLETHER WITH $\overline{W(OAr)}(OAr)(=CHC(CH_3)_3)(OEt_2)Cl$ ($OAr = O$-2,6-$C_6H_3Ph_2$ OR O-2,6-$C_6H_3Cl_2$)

To date, and to our knowledge, there have been no reports in the literature of the metathesis of unsubstituted allylic ethers. However, promising results were obtained for the metathesis of substituted allylic ethers by carbene catalysts,[28–30] where bulky groups at the α-position "protect" the metal from oxygen coordination. The tolerance of the orthometallated carbene catalyst **1** towards olefins bearing ester groups led us to test it in the metathesis of diallylether. Two metathesis reactions are possible, intra- or intermolecular, leading to the formation of either 2,5-dihydrofurane (DHF) or an olefinic polyether respectively (Scheme 9).

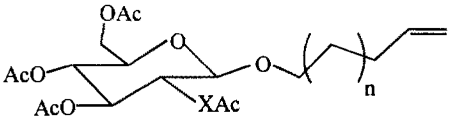
Figure 5 shows the rate of conversion of diallylether for substrate to catalyst ratios ranging from 40 : 1 to 190 : 1.[31] The experiments were carried out under argon in chlorobenzene at 70°C. The reaction was 100% selective for DHF, the intramolecular product, i.e. no intermolecular reaction was observed, and up to 80 equivalents of DHF were obtained per equivalent of catalyst.[31] This result is better than those obtained for the substituted allyl

2



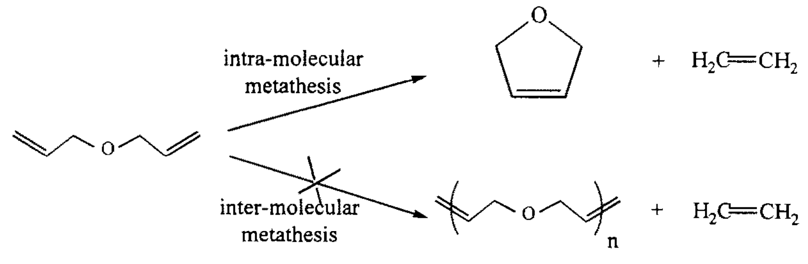
2a R=Ac
2b R=TBDMS
2c R=Bn

Scheme 7.



4a X = NH n=7
4b X = O n=1
4c X = O n=0

Scheme 8.



Scheme 9.

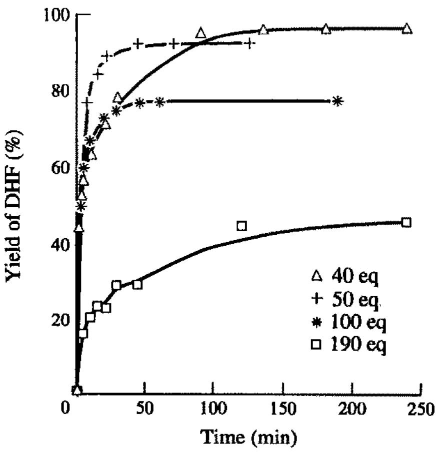


Fig. 5. Yield of DHF as a function of time in the metathesis of diallylether by **1** with various substrate/catalyst ratios.

ethers and so it can be expected that the aryloxy(chloro)neopentylidene complex should convert more than 100 equivalents of these substrates.

METATHESIS OF DIALLYLDIMETHYLSILANE AND DIALLYLDIBUTYLTIN WITH $\mathbf{W(OAr)_xCl_{6-x}+PbBu_4}$ AND WITH $\mathbf{W(OAr)(OAr)({=}CHC(CH_3)_3)(OEt_2)Cl}$ $\mathbf{(OAr = O\text{-}2,6\text{-}C_6H_3Ph_2)}$

The metathesis of allyl silyl ethers has been reported for some monocomponent carbene catalysts.[32,33] Comparison of analogous tungsten and molybdenum carbene catalysts, ($[(CF_3)_2(CH_3)CO]_2(NAr)M{=}CHC(CH_3)_3$), gave slightly different reactivities. The molybdenum-based catalyst led to a mixture of inter- and intramolecular products of metathesis,[32] whereas the tungsten catalyst appeared to form exclusively intermolecular, i.e. polymer, products.[33]

We studied the metathesis of diallyldimethylsilane with the bicomponent system $WCl_4(OAr)_2/PbBu_4$ for a range of substrate/catalyst ratios varying from 10:1 to 100:1 (Fig. 6).[34] Only the cyclized product (the silacyclopentene; Scheme 10) was observed.

Increasing the substrate/catalyst ratio did not increase the rate, showing an inhibition of the reaction by the reactants. There are two explanations for this: (i) the reactants contain impurities which deactivate the catalyst or (ii) there is an effect of the silicon compound itself, which can be inhibition or a side-reaction.

Diallyldibutyltin is also metathesized by the neopentylidene complex of tungsten, even if the reaction is less efficient: 10 equivalents can be converted into the corresponding cyclic olefin (see Scheme 11).[34] However, it should be pointed out that there are side reactions which deactivate the catalyst, as can be deduced from the evolution of propene during the reaction.

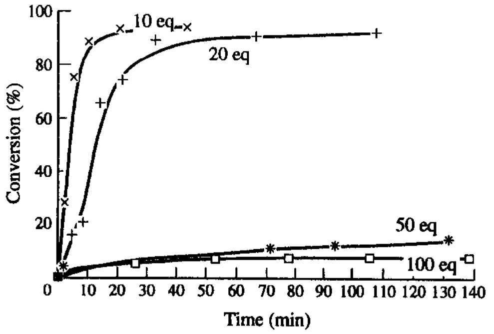


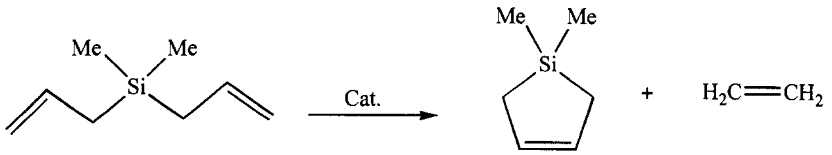
Fig. 6. Conversion of diallyldimethylsilane as a function of time during the metathesis by **1** with various substrate/catalyst ratios.

METATHESIS OF SULPHUR-CONTAINING OLEFINS WITH $W(OAr)(OAr)(=CHC(CH_3)_3)(OEt_2)Cl$ ($OAr = O\text{-}2,6\text{-}C_6H_3Ph_2$ OR $O\text{-}2,6\text{-}C_6H_3Cl_2$)

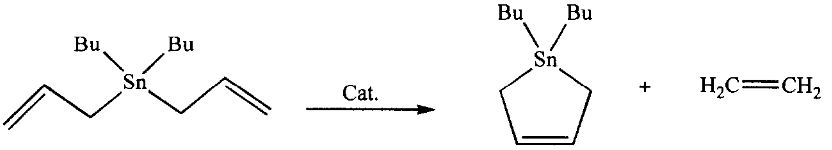
Up to very recently, the metathesis of functionalized olefins has been known for olefins bearing oxygen, nitrogen, halogen or silicon atoms, but, to our knowledge, there have been only two reports of successful metathesis reactions involving sulphur-containing acyclic or unstrained cyclic olefins by other groups.[35,36] This lack of data is probably due to a poisoning of the catalysts by the sulphur atoms, as reported previously in the case of some classical heterogeneous[37] or homogeneous[38] catalytic systems. However, this specific application of olefin metathesis could present a particular interest in enlarging the field of thiochemistry, and offering the possibility of synthesizing known or new olefinic compounds containing sulphur, via a novel and simple route.

We have found that metathesis of olefinic sulphides can be successfully achieved by using **1** as a homogeneous catalyst.[38–41] Thus, the self-metathesis of allyl methyl sulphide (**4**) and of 5-alkylthiocyclooctenes (**5**) (or their co-metathesis with various acyclic or cyclic olefins without functional groups such as 2-butene or 2-pentene) leads to a family of new olefins, dienes or unsaturated polymers containing one or more thioether groups (Scheme 12).

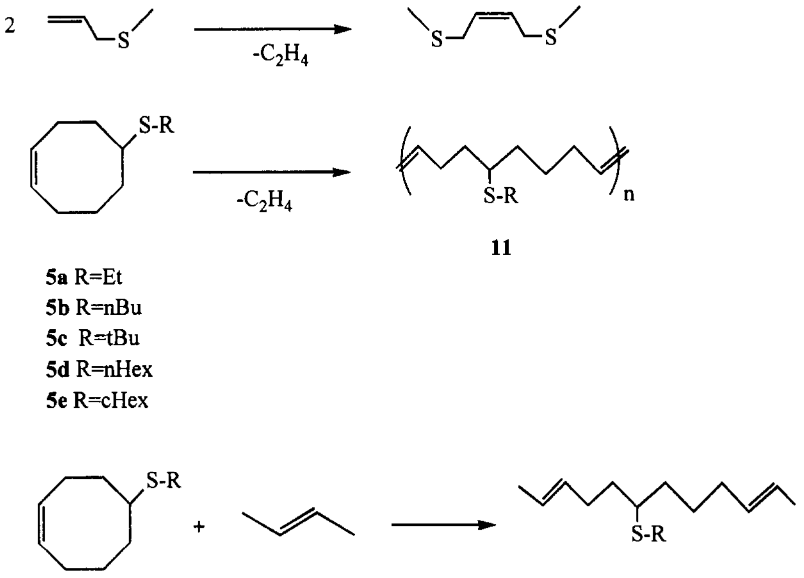
The turnover rates (Table 2) are lower than those obtained with the same catalyst in the metathesis of 2-pentene or ethyl oleate, suggesting a competitive coordination of the sulphur atom compound to the



Scheme 10.



Scheme 11.



Scheme 12.

Table 2. Self-metathesis of allyl methyl sulphide (**4**) and its co-metathesis with 2-butene (**6a**) or 2-pentene (**6b**) catalysed by **1**[a]

[Substrate]/[Catalyst][b]			Temp.[c]	Time[d]	Conversion	Product yield (%)[e]			
4:1	**6a**:1	**6b**:1	(°C)	(h)	(%)	**7**[f]	**8**[f]	**9**[f]	**10**[f]
25	—	—	80	15	40	20	20	—	—
25	100	—	20	15	95	—	—	95	—
20	—	20	80	15	60	5	5	30	20

[a] Typically, the metathesis reactions were carried out by using 0.025 mmol of **1** and 5 cm^3 of C_6H_5Cl as solvent.
[b] Initial molar ratios.
[c] Reaction temperature.
[d] Reaction time.
[e] Yields based on initial **4**.
[f] **7**: ethylene; **8**: $CH_3SCH_2CH{=}CHCH_2SCH_3$; **9**: $CH_3CH{=}CHCH_2SCH_3$; **10**: $EtCH{=}CHCH_2SCH_3$.

metallocarbene, leading to a partial deactivation of the catalyst. Nevertheless, the reaction is highly selective (only the expected metathesis products are detected) and the conversion of **4** can reach a high value when an excess of the co-reactant olefin is used.

Similarly, the ring-opening metathesis polymerization of various 5-alkylthiocyclooctenes (**5a–e**) leads to the corresponding sulphur polymers **11** (Scheme 12),[43] with turnover rates higher than those observed in the metathesis of allyl methyl sulphide (Table 3). Table 3 and Fig. 7 show that there is a strong effect of the nature of the thioalkyl substituent on the rate of polymerization: the higher the steric crowding of the alkyl substituent, the higher the rate of polymerization; this confirms the hypothesis that steric hindrance around the sulphur atom could decrease the inhibiting effect induced by a possible coordination of the sulphur to the tungsten. The turnover rates can be increased by increasing reaction temperature and/or by performing the polymerization in the absence of a solvent.

METATHESIS OF DIALLYL SULPHIDES WITH $W(OAr)_xCl_{6-x}+MR_4$ ($M = Sn, Pb$; $R = Me, Et, Bu$) AND WITH $\overline{W(OAr)}(OAr)({=}CHC(CH_3)_3)(OEt_2)Cl$ ($OAr = O\text{-}2,6\text{-}C_6H_3Ph_2$ OR $O\text{-}2,6\text{-}C_6H_3Cl_2$)

As for diallyl ether, two reactions are expected (intra- or intermolecular) in the case of diallyl thioether. We studied the metathesis of this olefin for a

Table 3. Ring-opening metathesis polymerizations of 5-alkylthiocyclooctenes (**5a–e**) catalysed by **1**[a]

	R	5 : 1[b]	Temp.[c] (°C)	Time[d] (min)	Conversion of 5 (%)
5a	Et	100	20	200	97
5b	*n*-Bu	100	20	120	97
5c	*t*-Bu	100	20	10	99
		100	80	5	99
		500	80	30	96
		100[e]	20	2	65[f]
5d	*n*-hex	100	20	100	99
5e	*c*-hex	100	20	30	99

[a] Typically, the metathesis reactions were carried out by using 0.025 mmol of **1** and 5 cm^3 of C_6H_5Cl as solvent.
[b] Initial molar ratios.
[c] Reaction temperature.
[d] Reaction time.
[e] Polymerization performed without solvent.
[f] Yield of isolated polymer **11** ($M_W = 140\,100$, $M_N = 39\,700$, $M_W/M_N = 3.5$, $T_g = -26°C$).

range of molecular ratios from 250 : 1 to 500 : 1. Total selectivity for intramolecular reaction (leading to the corresponding 2,5-dihydrothiophen; Scheme 13) was proved by GC standardization. Using complex **1** it is possible to metathesize 350 equivalents of diallyl thioether to 2,5-dihydrothiophen at 80°C in 1 h.[44] The high turnover rates observed are probably best explained by the thermodynamic aspects of the cyclization.

In order to broaden the scope of ADMET with allylic sulphides we tested the activity of complex **1** toward some alkylated substrates.[44] In Table 4 are given results for diallyl sulphide (**12a**), allylmethallyl sulphide (**12b**), allylcrotyl sulphide (**12c**) and dimethallyl sulphide (**12d**).

It is clear that steric hindrance on the double bond decreases the activity (conversion of only 100 equivalents for **12b**, 90 equivalents for **12c** and no reaction for **12d**) of the catalyst. This is probably due to the bulkiness of *o,o′*-diphenyl(phenoxo) ligands and the resulting rigidity of ortho-metallation.

Bicomponent systems $WCl_4(OAr)_2$ (with Ar = 2,6-diphenyl(phenyl)) also show some interesting activity for the diallyl suphide metathesis.[44] Results with various molar ratios and various substrates are shown in Table 5.

Total conversion of 40 equivalents of diallyl sulphide (**12a**) is reached in 8 h with such a system.[44] In addition it is possible to convert 20 equivalents of allylmethallyl suphide (**12b**) but no reaction occurs with dimethallyl suphide (**12d**). This is in agreement with studies on other functionalized olefins, the concentration of carbene being smaller than when complex **1** is used.

These results provide a novel route to thiophen and its alkylated derivatives by subsequent dehydrogenation of the 2,5-dihydrothiophen prepared in this metathetical way.

METATHESIS OF ALLYL PHOSPHANES WITH $\overline{W(OAr})(OAr)(=CHC(CH_3)_3)(OEt_2)Cl$ $(OAr = O\text{-}2,6\text{-}C_6H_3Ph_2)$

To our knowledge, metathesis of phosphorus-containing olefins has never been investigated. As the aryloxide neopentylidene tungsten complex displays very high activity in the metathesis of functionalized olefins, it was logical to study it in the metathesis of a series of allylic phosphanes, allyldiphenyl phosphane and diallylphenyl phosphane. Typically the experiments were performed in chlorobenzene with a substrate/catalyst ratio of 20, at 80°C and under standard conditions. After 12 h the solvent was removed by evaporation at room temperature. The products were isolated and characterized by GC-MS and NMR.

As soon as the olefin is contacted by the catalyst, ethylene begins to evolve. Chromatographic monitoring showed the formation of a single product, identified by physiochemical methods (^1H, ^{13}C, ^{31}P NMR, MS, etc.) as 1,4-bis(diphenylphosphino)-2-butene (c + t) when the olefin was the allyldiphenyl phosphane, and 1-phenyl-3-phospholen when it was diallylphenyl phosphane.[45] The corresponding metathesis reactions can be written as in Scheme 14.

By studying the kinetics of the reaction it is possible to evaluate the respective reactivity of each substrate. Figure 8 gives the conversion of the two substrates with time for the same experimental con-

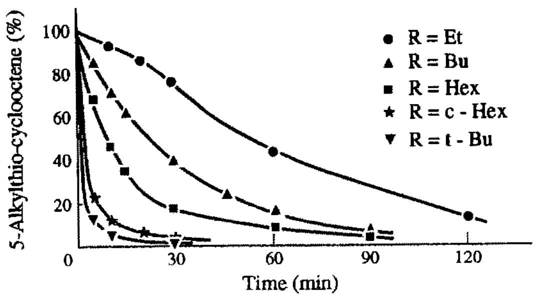
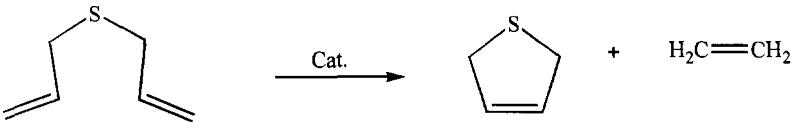


Fig. 7. Conversion of various 5-alkylthiocyclooctenes vs time during the metathesis by **1** as a function of the nature of the substituent on sulphur.



Scheme 13.

Table 4. Cyclization metathesis of diallyl sulphides with **1** (**12a–d**)

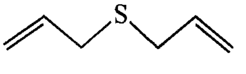
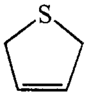
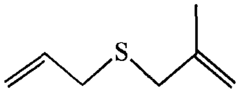
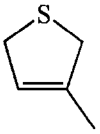
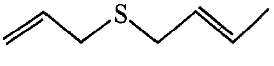
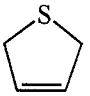
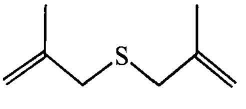
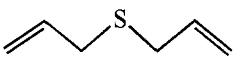
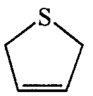
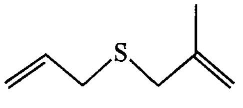
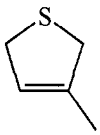
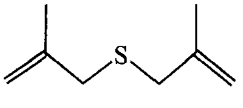
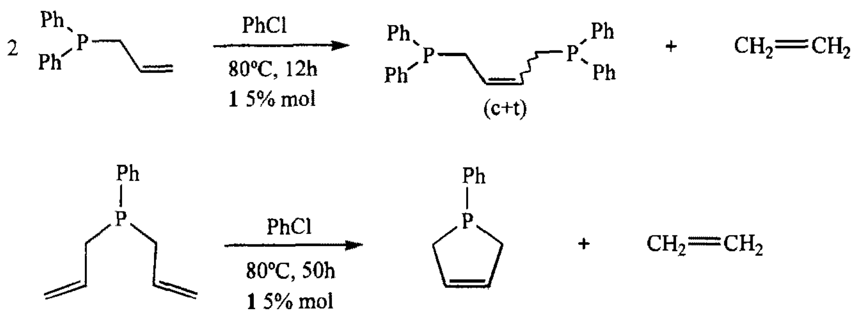
	Substrate	S/W	Conversion, h	Product
12a		500:1	75%, 3 h	
12b		100:1	100%, 3 h	
12c		100:1	90%, 3 h	
12d		100:1 20:1	0% 0%	

Table 5. Cyclization metathesis of diallyl suphides with bicomponent system (**12a–d**)

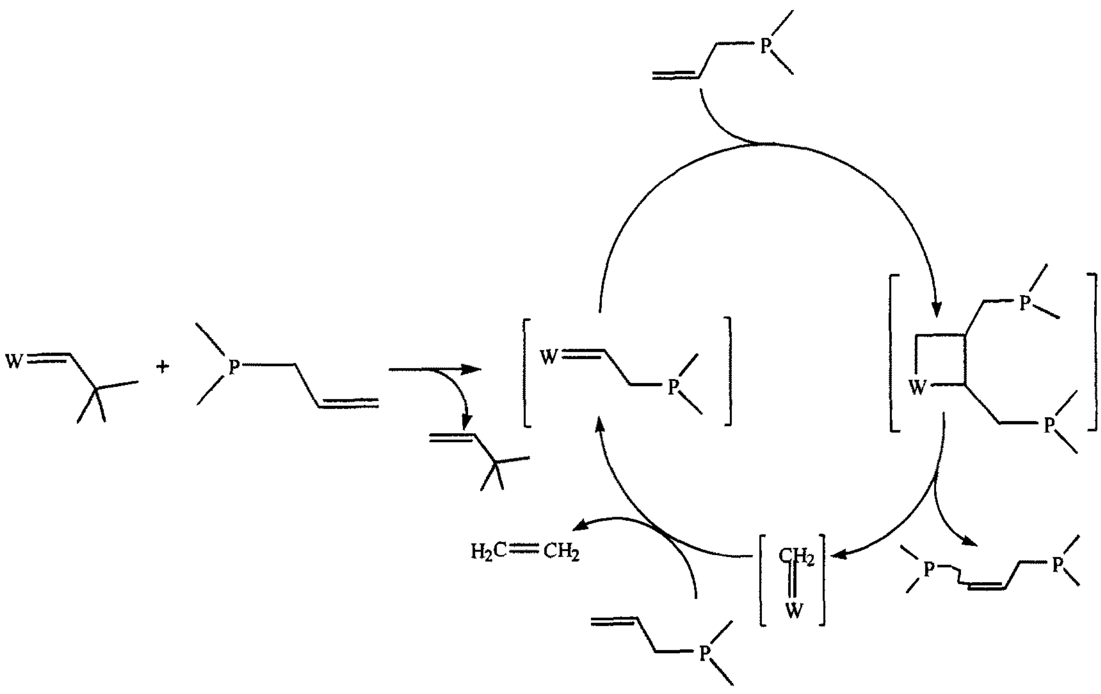
	Substrate	S/W	Conversion, h	Product
12a		100:1 50:1 40:1	50%, 8 h 90%, 8 h 100%, 8 h	
12b		20:1	100%, 3 h	
12d		20:1	0%	

ditions (80°C, substrate/catalyst ratio = 20). Apparently the two substrates show very different kinetic behaviour : in the case of diallyl phosphane, 95% conversion is obtained in 5 h compared to only 10% for the monoallyl phosphane.[45] These results are in agreement with the mechanism of metathesis displayed in Scheme 15 for the allyldiphenyl phosphane.

The initiation rate is probably the same for the two phosphanes, due to their similar structures. The differences in the kinetic rates are related to the intermediate carbene structure in the catalytic cycle.



Scheme 14.



Scheme 15.

Due to their similar structures, the rate of initiation should be the same for the two phosphines under study. The differences in the kinetic rates are more probably related to the intermediate carbene structure in the catalytic cycle: for the diallyl phosphane an intramolecular cyclization occurs while for the monoallyl phosphane it is necessary to coordinate another olefin molecule. In addition, thermodynamic considerations are also in agreement with higher reactivity for diallyl phosphane.

This is a supplementary proof of the high activity of this carbene with functionalized olefins. It is therefore possible, by metathesis, to synthesize various diphosphanes by varying the size of the sub-

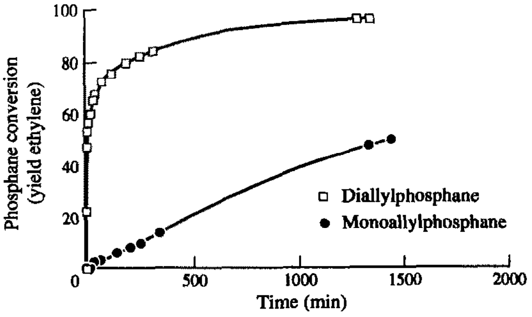


Fig. 8. Conversion of diallylphenyl phosphane and allyldiphenyl phosphane with time during the metathesis by **1**.

stituents on the phosphorus atom and to obtain as desired homoleptic or crossed diphosphanes.

CONCLUSIONS

In the course of this review article we have shown the very versatile properties of the aryloxide ligand in the metathesis of non-functionalized or functionalized olefins. One can monitor stereoselectivity and activity by the proper choice of the substituents on the aryloxide ligands. Electron withdrawing substituents have a tendency to make the bicomponent catalysts extremely active for non-functionalized olefins. The monocomponent system $\overline{\mathrm{W(OA}}\mathrm{r)}$ $(OAr)({=}CHC(CH_3)_3)(OEt_2)Cl$ ($OAr = O\text{-}2,6\text{-}C_6H_3Ph_2$ or $O\text{-}2,6\text{-}C_6H_3Cl_2$) is probably both very active and stereoselective for steric reasons. The metallation of the tungsten atom by one phenyl substituent renders the system rather rigid and may prevent relaxation from octahedral geometry to pentacoordinated structure. Secondly, the steric crowding around the tungsten atom due to the two bulky aryloxide substituents probably slows down dimerization to inactive complexes and prevents to an extent the coordination of the functional group to the tungsten (this is demonstrated in the polymerization of cyclo-octene with thio-ether functionality). This may explain why olefin glucosides can be metathetized with our catalytic systems.

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