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A Cyclometalated Aryloxy(chloro)neopentylidene-tungsten Complex: A Highly Active and Stereoselective Catalyst for the Metathesis of *cis*- and *trans*-2-Pentene, Norbornene, 1-Methylnorbornene, and Ethyl Oleate**

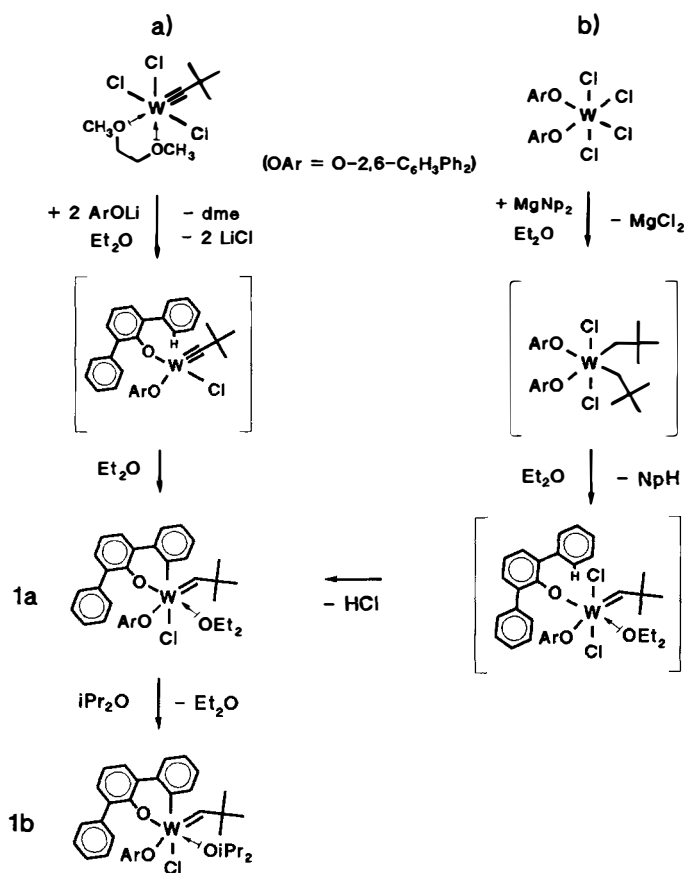
By *Jean-Luc Couturier, Christophe Paillet, Michel Leconte, Jean-Marie Basset,* and Karin Weiss*

The design of versatile, highly active, and well-characterized catalysts remains one of the main objectives of the research in olefin metathesis.^[1] In the past few years, it has been shown that some neopentylidene-tungsten(vi) complexes with alkoxide,^[2, 3] imido,^[3] or aryloxy ligands^[4] are efficient homogeneous metathesis catalysts. Aryloxides prove to be particularly useful ligands since their steric and electronic properties can be varied substantially by changing the nature, the number, and the position of the substituents on the phenoxide ligand. With these ligands, it has been possible to control both the activity and the stereoselectivity

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of the metathesis reaction.^[4,5] We report here the synthesis and the catalytic properties of a new 2,6-diphenylphenoxy (neopentylidene)tungsten derivative, which has the cyclometalated structure **1a**/**1b** (Scheme 1).



Scheme 1. Two routes for the synthesis of the cyclometalated complexes **1a** and **1b**. Because X-ray structure data are not available, the structures are still hypothetical and are derived from that proposed by R. R. Schrock et al. for the starting complex [WCl₃(CCMe₃)(dme)] [6] and from the known complex [WCl₄(O-2,6-C₆H₃Ph₂)] [7].

The tungsten complexes **1a**/**1b** can be obtained by two independent routes. Reaction of [WCl₃(CCMe₃)(dme)]^[6] (dme = dimethoxyethane) with two equivalents of LiOAr (OAr = O-2,6-C₆H₃Ph₂) in diethyl ether leads to the orange-brown solid **1a**, which likely arises from path a). The reaction of [WCl₄(O-2,6-C₆H₃Ph₂)]^[7] in diethyl ether with one equivalent of MgNp₂ · dioxane (Np = neopentyl) leads, after purification by exchange of diethyl ether with diisopropyl ether, to the orange-brown solid **1b**.^[8] The probable sequence of reactions leading to **1b** is path b). **1a** and **1b** were characterized by elemental analyses and ¹H and ¹³C NMR spectroscopy.^[9]

The key step of the two syntheses is the different intramolecular activation of the C–H bond of the arene substituent on the d⁰ metal which leads to a stable cyclometalated structure.^[10–12] In path a) C–H activation leads to the addition of a hydrogen atom to the carbyne ligand forming a carbene and simultaneous cyclometalation. In path b) the C–H activation leads to the elimination of HCl. The role of the weakly coordinated ether is probably crucial in path a) in which a pentacoordinated W^{VI} center with a possible agostic C–H bond is the precursor of the carbene complex formed via a four-center transition state; this type of sequence is

often discussed for the electrophilic activation of C–H bonds.^[13]

Complexes **1a** and **1b** are excellent catalysts for olefin metathesis. For example, with **1a** the metathesis equilibrium of 500 equivalents of *cis*-2-pentene or *trans*-2-pentene is reached in 1 min at 25 °C (the equilibrium mixture consists of 2-butene, 2-pentene, and 3-hexene in the approximate ratio of 1:2:1).^[14] **1a** is also highly stereoselective: Extrapolation to 0% conversion shows that the *trans*/*cis* ratios of 2-butene (C₄) and 3-hexene (C₆) in the metathesis of *cis*-2-pentene are 0.01 and 0.00, respectively^[14] (at equilibrium, *trans*/*cis* C₄ ≈ 3 and *trans*/*cis* C₆ ≈ 6). In the metathesis of *trans*-2-pentene, the *cis*/*trans* ratios of both C₄ and C₆ are equal to 0.004 at 0% conversion. These high stereoselectivities with retention of configuration of the starting olefin are maintained even at high conversions (Figs. 1 and 2). When the

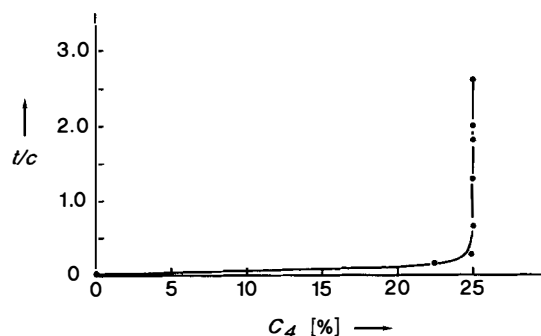


Fig. 1. Metathesis of *cis*-2-pentene catalyzed by **1a**: Plot of the ratio of *trans*- to *cis*-2-butene (*t/c*) versus the yield of 2-butene (C₄). *cis*-2-Pentene/**1a** molar ratio = 500/1, T = 25 °C, solvent C₆H₅Cl.

equilibrium of productive metathesis is nearly reached (roughly 25% yield in 2-butene), there is a dramatic change of the configuration of the products due to secondary metathetical isomerization reactions that progressively lead to the ultimate equilibrium *trans*/*cis* ratios.

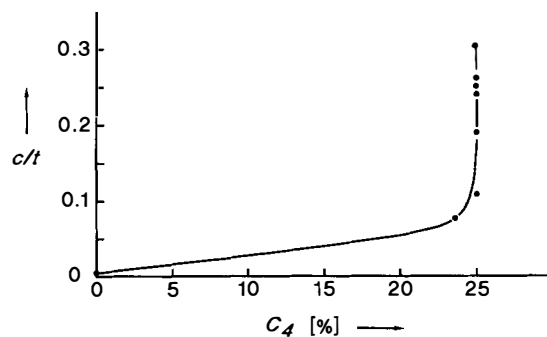
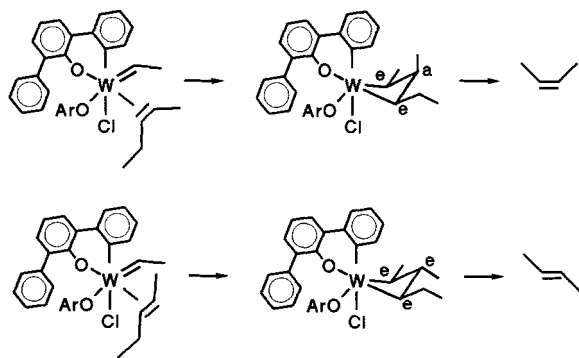


Fig. 2. Metathesis of *trans*-2-pentene catalyzed by **1a**: Plot of the ratio of *cis*- to *trans*-2-butene (*c/t*) versus the yield of 2-butene (C₄). *trans*-2-Pentene/**1a** molar ratio = 500/1, T = 25 °C, solvent C₆H₅Cl.

To our knowledge such high stereoselectivities observed almost up to thermodynamic metathesis equilibrium have never been reported in metathesis of 2-pentene with any highly active tungsten-based catalyst. The extremely high retention of configuration of the starting olefin is easily explained on the basis of the favored configuration of the tungstacyclobutane intermediate with two equatorial (e) alkyl groups in the 1 and 3 positions (Scheme 2).^[15] One can

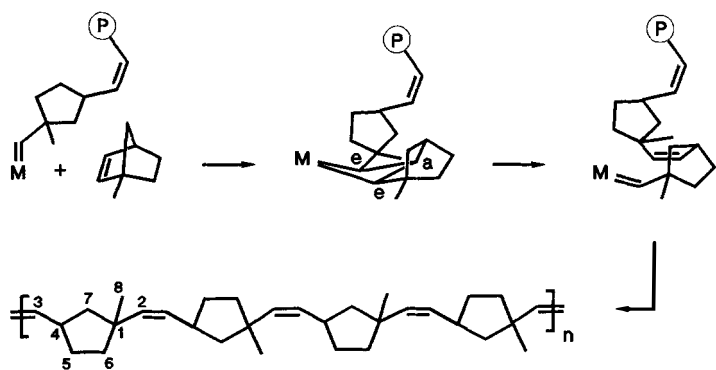


Scheme 2. The two favored tungstacyclobutane intermediates with 1,3-diequatorial alkyl substituents that lead to *cis*-2-butene (in the metathesis of *cis*-2-pentene) and to *trans*-2-butene (in the metathesis of *trans*-2-pentene).

assume that these favored conformations are particularly stabilized by the bulky ligands on tungsten and/or by the rigidity generated by the cyclometalation.

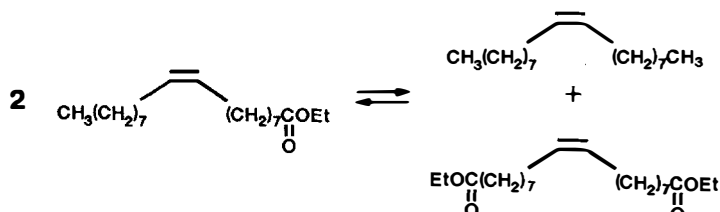
With **1a**, 500 equivalents of norbornene are polymerized at 25 °C in less than one minute.^[16] ¹H and ¹³C NMR spectra (CDCl₃, 25 °C) indicate that 70% of the C=C bonds have *cis* configuration. This value is in agreement with earlier results found in norbornene metathesis with other stereoselective aryloxy(chloro)carbene-tungsten catalysts.^[17]

Polymerization of 1-methylnorbornene with **1a** or **1b** provides a completely head-tail, predominantly syndiotactic poly-1-methylnorbornene with 100% *cis* C=C bonds.^[18] Such extremely high stereoselectivity can also be explained on the basis of the favored configuration of the tungstacyclobutane intermediate with the two bulkiest alkyl substituents in 1,3-diequatorial positions (Scheme 3).^[20]



Scheme 3. In the ring-opening metathesis polymerization of 1-methylnorbornene with **1a** or **1b** the favored reaction path leads to the formation of a head-tail, *cis* polymer.

Very promising preliminary results were obtained in the metathesis of ethyl oleate (ethyl-9-octadecenoate), an olefin bearing a functional group (Scheme 4). **1a** can convert selec-



Scheme 4. The equilibrium metathesis reaction of ethyl oleate leads to 9-octadecene and diethyl 9-octadecenedioate.

tively roughly 50% of 500 equivalents of ethyl oleate^[21] into 9-octadecene and diethyl 9-octadecenedioate in 60 min at 25 °C (Fig. 3; the equilibrium mixture consists of ethyl oleate, 9-octadecene, and the diester in the approximate ratio of 2:1:1). To our knowledge, this is the highest activity re-

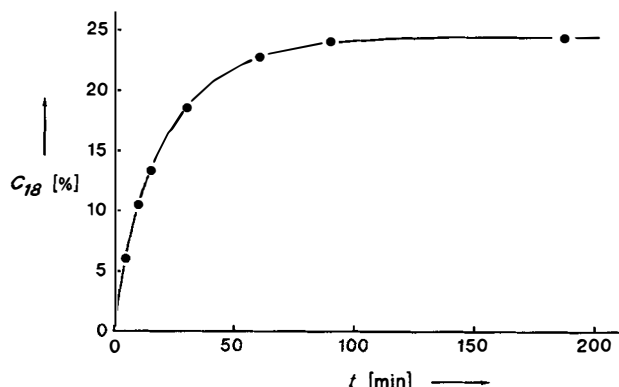


Fig. 3. Metathesis of ethyl oleate catalyzed by **1a**: Plot of the yield of 9-octadecene (C₁₈) versus the reaction time. Ethyl oleate/**1a** molar ratio = 500/1, T = 25 °C, solvent C₆H₅Cl.

ported so far for homogeneous catalysts in the metathesis of this type of substrate.^[3, 22]

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- [8] In our first study [4] we found that reaction of one equivalent of MgNp₂ with [WCl₄(O-2,6-C₆H₃Ph₂)₂] in Et₂O led to a compound **A1** whose ¹H NMR spectrum (CDCl₃) showed a signal at δ = 8.7 for a hydrogen atom bound to a carbene; **A1** proved essentially inactive in the metathesis of *cis*-2-pentene. We have now some indications that suggest that **A1** is a dimeric neopentylidene species (not yet totally identified) resulting from the dimerization of **1a** or **1b**. This dimerization seems to be rather fast in solution (especially in CHCl₃ and CH₂Cl₂) but can also be observed in the solid state where the reaction is slower.
- [9] Characteristic ¹H (100 MHz) and ¹³C (25 MHz) NMR data for **1a** (C₆D₆, 25 °C): δ(W = CHCMe₃) = 10.11 (J_{w,h} = 14 Hz), δ(W = CHCMe₃) = 0.57; δ(W = CH) = 296.66 (J_{c,h} = 130.5, J_{c,w} = 166 Hz), δ(W-C_{ipso}) = 183.15 (J_{c,w} = 115 Hz), δ(W = CHCMe₃) = 45.24, δ(W = CHCMe₃) = 31.82. The corresponding data for **1b** are practically identical.
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- [18] The 100% head-tail, 100% *cis* structure of the poly-1-methylnorbornene obtained with **1a** or **1b** was deduced from ¹H and ¹³C NMR spectra of the polymer; ¹⁹F ¹³C{¹H} NMR (62.8 MHz, CDCl₃): δ = 29.29 (C-8), 33.02 (C-5), 38.14 (C-4), 41.82 (C-6), 44.13 (C-1), 50.02 (C-7), 135.08 (C-3), 139.47 (C-2) (see Scheme 3 for the numbering of the carbon atoms). The predominantly syndiotactic structure was deduced from the ¹³C NMR spectrum of the hydrogenated polymer [19].
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