# Synthesis and Catalytic Properties of $W(OAr)_2Cl_2(CHCMe_3)(OR_2)$ and $W(OAr)_2Cl(CHCMe_3)(CH_2CMe_3)(OR_2)$ (Ar = 2,6-disubstituted phenyl; R = Et or $Pr^i$), New Uni-component Catalysts for Metathesis of Acyclic and Cyclic Olefins, with or without Functional Groups

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The synthesis of $W(OAr)_2Cl(CHR)(CH_2R^1)(OR^2{}_2)$ (Ar = 2,6-disubstituted phenyl; $R^2$ = Et or $Pr^i$) illustrates one of the first examples of a well defined, Lewis acid-free, homogeneous olefin metathesis catalyst, for which the activity and stereoselectivity can be governed by the nature of the aryloxide ligands and of the co-ordinated ether and which shows a wide range of potential applications.

Aryloxide complexes of tungsten(VI), such as $W(OAr)_2Cl_4$ (OAr = $OC_6H_3Me_2$-2,6, $OC_6H_2Me_3$-2,4,6, $OC_6H_3Ph_2$-2,6, $OC_6H_3Br_2$-2,6, $OC_6H_3Cl_2$-2,6, or $OC_6H_3F_2$-2,6), are active in olefin metathesis when associated with alkyl-aluminium, alkyl-tin, or alkyl-lead complexes.[1] With the last two co-catalysts, the catalytic systems are highly efficient for metathesis of unsaturated esters.[2] A detailed study of the interaction between the precursor complex and $SnR_4$ (R = Me or Bu) or $PbBu_4$ suggested a co-ordination sphere of the type $W(OAr)_2Cl_2(CHR')$, similar to the co-ordination sphere derived from tungsten(VI) and alkylating agents.[3—7] It was therefore logical to try to synthesise such chloro–aryloxide–carbene complexes of tungsten for which the substituted aryloxide ligand would behave as a two-electron-ligand with versatile electronic and steric properties.[8]

We report here the synthesis and catalytic properties of two families of chloro–aryloxide complexes of tungsten(VI): $W(OAr)_2Cl_2(CHCMe_3)(OR_2)$ (**A**) and $W(OAr)_2Cl(CHCMe_3)(CH_2CMe_3)(OR_2)$ (**B**). The complexes of type (**B**) proved to be active without any co-catalyst for metathesis of various kinds of olefin: acyclic and cyclic, terminal and internal, linear and branched with or without functional groups (esters and nitriles). Also, depending on the nature of the aryloxide ligand, or of the co-ordinated ether ($OR_2$), they exhibit for a given olefin various degrees of activity and/or stereoselectivity.

**Table 1.** Activities and stereoselectivities of the chloro–aryloxide–carbene tungsten complexes (**A**) and (**B**) in the metathesis of *cis*-pent-2-ene.[a]

| Catalyst | % Yield of but-2-ene[b] | *trans*/*cis* at 0% conversion[c] $C_4$ | $C_6$ |
|---|---|---|---|
| (**A1**) | 0 | — | — |
| (**A2**) | 5 | 0.67(2) | — |
| (**A3**) | 8 | 0.62(2) | — |
| (**B1**) | 12 | 0.20(1) | 0.35(2) |
| (**B2**) | 3 | 0.18(1) | 0.40(2) |
| (**B3**) | 17.5 | 0.80(2) | 1.40(2) |
| (**B4**) | 20 | 0.90(2) | 1.50(2) |
| (**B5**) | 25 | 0.30(10) | 0.50(5) |
|  | 15[d] | 0.06(1)[d] | 0.11(2)[d] |
|  | 5[e] | 0.06(1)[e] | 0.10(2)[e] |
| (**B6**) | 6.5 | 0.80(2) | 1.10(2) |
| (**B7**) | 3 | 0.80(2) | 1.10(2) |

[a] Conditions: PhCl solvent, temp. 85 °C; molar ratio pentene/catalyst 100; reaction times 14 h for (**A1**) and (**A2**), 1 h for (**A3**), 5 min for (**B1**)—(**B7**). [b] Equilibrium value = 25%. [c] Standard deviations of the least significant figure in parentheses. [d] At 25 °C. [e] At 0 °C.

Reaction of $W(OC_6H_3Ph_2\text{-}2,6)_2Cl_4$ (0.22 mmol) in diethyl ether (20 ml) at 25 °C with $Mg(neopentyl)_2(dioxane)$ (1 equiv.) gave a red-brown solution from which $MgCl_2(dioxane)$ precipitated in a few minutes, with evolution of *ca.* 0.9 mol of neopentane/mol of W. After 1 h, the red solution was decanted, filtered, and evaporated to dryness. The resulting red-brown essentially pure product (85% yield based on W), is extremely soluble in most organic solvents, and has the formula $W(OC_6H_3Ph_2\text{-}2,6)_2Cl_2(CHCMe_3)(OEt_2)$ (**A1**);† $^1H$ n.m.r. ($CDCl_3$, 25 °C): δ 8.68 (s, 1H, $J_{W-H}$ 10 Hz, $C\mathit{H}CMe_3$), 7.23 (m, 26H, $OC_6\mathit{H}_3\mathit{Ph}_2$), 3.42 (m, 4H, $OC\mathit{H}_2Me$), 1.12 (t, 6H, $OCH_2\mathit{Me}$), and 0.85 (s, 9H, $CHC\mathit{Me}_3$). A similar reaction with $W(OC_6H_3X_2\text{-}2,6)_2Cl_4$ (X = Cl or Br) gave the related products $W(OC_6H_3X_2\text{-}2,6)_2Cl_2(CHCMe_3)(OEt_2)$ (**A2**) (X = Cl) and (**A3**) (X = Br) as oils.

$W(OC_6H_3R^1{}_2\text{-}2,6)_2Cl(X)(CHCMe_3)(OR^2{}_2)$

X = Cl, $R^2$ = Et: (**A1**) $R^1$ = Ph
(**A2**) $R^1$ = Cl
(**A3**) $R^1$ = Br

X = $CH_2CMe_3$, $R^2$ = Et: (**B1**) $R^1$ = Ph
(**B2**) $R^1$ = Me
(**B3**) $R^1$ = Cl
(**B4**) $R^1$ = F

X = $CH_2CMe_3$, $R^2$ = $Pr^i$: (**B5**) $R^1$ = Ph
(**B6**) $R^1$ = Cl
(**B7**) $R^1$ = F

The reaction of $Mg(neopentyl)_2(dioxane)$ (1.5 equiv.) in diethyl ether at room temperature with $W(OC_6H_3Ph_2\text{-}2,6)_2Cl_4$ led in the gas phase to *ca.* 1 mol of neopentane/mole of W and a yellow-brown solution from which $MgCl_2(dioxane)$ precipitated. After decantation and filtration, the solution was evaporated to dryness. The resulting golden-brown essentially pure compound (75% yield based on W), $W(OC_6H_3Ph_2\text{-}2,6)_2Cl(CHCMe_3)(CH_2CMe_3)(OEt_2)$ (**B1**),† is highly soluble in most organic solvents, $^1H$ n.m.r. ($CD_2Cl_2$, 25 °C): δ 9.96 (s, 1H, $C\mathit{H}CMe_3$), 7.48 (m, 26H, $OC_6\mathit{H}_3\mathit{Ph}_2$), 3.42 (m, 4H, $OC\mathit{H}_2Me$), 1.26 (s, 2H, $C\mathit{H}_2CMe_3$), 1.12 (t, 6H, $OCH_2\mathit{Me}$), 0.86 (s, 9H, $CHC\mathit{Me}_3$), and 0.56 (s, 9H, $CH_2C\mathit{Me}_3$). Exchange with di-isopropyl ether at room temperature gave the analogue (**B5**), $^1H$ n.m.r. ($CD_2Cl_2$, 25 °C): δ 9.96 (s, 1H, $C\mathit{H}CMe_3$), 7.48 (m, 26H, $OC_6\mathit{H}_3\mathit{Ph}_2$), 3.62 (m, 2H, $OC\mathit{H}Me_2$), 1.26 (s, 2H, $C\mathit{H}_2CMe_3$), 1.11—1.036 (d, 12H, $OCH\mathit{Me}_2$), 0.86 (s, 9H, $CHC\mathit{Me}_3$), and 0.56 (s, 9H, $CH_2C\mathit{Me}_3$). Compounds (**B1**)—(**B7**) (Table 1) were synthesized by the same procedure, containing either $OEt_2$ or $OPr^i{}_2$

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† Satisfactory elemental analyses were obtained.

**Table 2.** Activities of chloro–aryloxide–carbene complexes (**B**) of tungsten in metathesis of various olefinic substrates.

| Catalyst | Substrate | Molar ratio substrate/catalyst | Temp./°C | Reaction time | Product analysed | % Yield |
|---|---|---|---|---|---|---|
| (**B5**) | Norbornene | 500 | 25 | 10 s | Polynorbornene | 100 |
| (**B5**) | Norborn-5-ene-2-yl acetate | 100 | 25 | 10 s | Polynorbornene acetate | 100 |
| (**B5**) | Norborn-5-ene-2-carbonitrile | 100 | 25 | 10 s | Polynorbornene nitrile | 100 |
| (**B1**) | Dec-1-ene | 100 | 85 | 1 h | Octadec-9-ene | 45 |
| (**B1**) | 2-Methylbut-2-ene/ hex-3-ene (1/3) | 200 | 85 | 1 h | Pent-2-ene | 35 |
| (**B1**) | Ethyl oleate | 100 | 85 | 1 h | Diester | 32 |
| (**B5**) | Ethyl oleate/dec-5-ene (1/2) | 150 | 85 | 30 min | Ethyl-tetradec-9-enoate | 70 |
| | | 300 | 85 | 30 min | ,, | 52 |

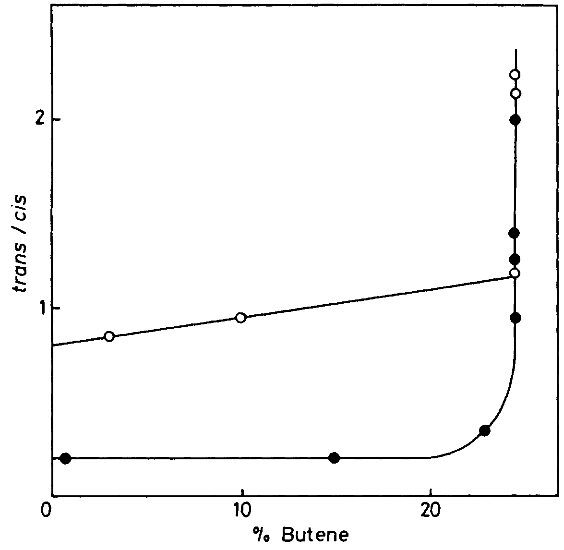

**Figure 1.** *trans*/*cis*-But-2-ene ratio *vs.* but-2-ene yield in metathesis of *cis*-pent-2-ene with (**B1**) (●) and (**B3**) (○) catalysts.

as co-ordinated ether. The total replacement of diethyl ether by di-isopropyl ether could be carried out at 25 °C, which indicates that the co-ordinated ether is very labile in this kind of complex. The 2,6-diphenyl-phenoxide derivatives are solids, whereas the other aryloxide ligands give rise to oily compounds.

Reaction of (**A1**) or (**B1**) with an excess of acetone in diethyl ether at room temperature gave the 2,4,4-trimethylpent-2-ene in 66 or 70% yield respectively, in agreement with the known reactivity of carbenes with ketones.[9]

Complexes (**A1**)—(**A3**) proved to be very poor catalysts in metathesis of *cis*-pent-2-ene, as are related complexes $W(O\text{-}neopentyl)_2X_2(CHCMe_3)$ which show no metathesis activity in the absence of Lewis acid co-catalyst.[10]

Interestingly, complexes (**B1**)—(**B7**) are fairly active in *cis*-pent-2-ene metathesis, even without any co-catalyst (Table 1). The activity and stereoselectivity depend markedly on the 2,6-substituents R of the phenoxide ligands; the activity also depends on the co-ordinated ether. For complexes (**B1**)—(**B4**), the activity increases in the order: $R = Me \ll Ph < Cl < F$. The stereoselectivity increases in the order: $F \leqslant Cl < Ph \sim Me$. The fact that both activity and stereoselectivity [(**B1**)—(**B4**)] change with the nature of the aryloxide ligand supports the hypothesis that this ligand remains co-ordinated in the catalytic cycle. The fact that the activity changes with the bulk of the ether whereas the stereoselectivity remains unchanged (for a given aryloxide ligand) [(**B1**)—(**B7**)] suggests (i) that the ether is deco-ordinated during the catalytic cycle and (ii) that this deco-ordination is governed, *inter alia*, by steric factors (repulsion between the bulky aryloxide and the bulky ether). The results of Table 1 indicate that the major factor which governs the stereoselectivity is the electronic effect of the aryloxide ligands [(**B1**)—(**B4**)]. Further, with complexes (**B1**) or (**B5**), extremely high stereoselectivites can be achieved even for very high conversion which make these catalysts useful in organic synthesis (Figure 1).

Table 2 illustrates the various synthetic possibilities for catalysts (**B1**) and (**B5**). As expected, it appears that the absence of a Lewis acid in metathesis allows a variety of uses. The weak Lewis acidity of the catalyst avoids many side reactions which were observed with conventional systems: double bond migration, cationic oligomerisation, solvent alkylation, acid–base complexation between heteroatoms and Lewis acid co-catalysts. Additionally, the turnover numbers reached with unsaturated esters are higher than classical values.[11,12] This may be due to a 'protecting' effect of the bulky aryloxide ligands which may prevent dimerisation of carbene,[6] or co-ordination of the functional groups which could poison the catalysts by Wittig type reactions.

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