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Synthesis and properties of homogeneous models of the Re_2O_7/Al_2O_3 metathesis catalyst

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Abstract

The aim of this work was to synthesize and to study homogeneous models of the rhenium oxide on alumina metathesis catalyst. A series of aluminium complexes, $(ArO)_2Al–Y$, has been synthesized, where ArO is a 4-substituted-2,6-di-*tert*-butylphenoxy ligand, or $(ArO)_2$ is a $–CH_2–$ or *–S-ortho* bridged-4,4′-di-*tert*-butyldiphenoxy ligand, and Y is an alkyl or chloride ligand. The reaction of $(ArO)_2Al–Cl$ with $AgReO_4$ led to new complexes $(ArO)_2Al–OReO_3$ (**A**). These complexes exhibit a low activity in the metathesis of 2-pentene. Complexes $(ArO)_2Al–R$ (R = iBu, Et) react with Re_2O_7 in THF or dioxane, giving type **B** complexes including oligomeric linkages like $O_3Re–[Al(OAr)–O]_2–ReO_3$. They show a fairly high activity in the metathesis of 2-pentene, with TOF values as high as 100 min^{-1}. Complexes of type **A** may be converted into complexes of type **B** upon reaction with $(ArO)_2Al–R$ in an ether solvent. The high activity of **B** complexes is tentatively related to the presence of Al–O–Al linkages that are known to induce a powerful bidentate Lewis acidity.

Keywords: Metathesis; Catalysis; Aluminium; Aryloxy; Rhenium

1. Introduction

The metathesis reaction occurs in the presence of both homogeneous and heterogeneous catalysts. The rhenium heptoxide on alumina heterogeneous catalyst is active even at low temperatures, allowing, in principle, comparisons with homogeneous catalysts. The activity of the catalyst increases with the amount of rhenium and a high rhenium loading is required to obtain a reasonably active catalyst. Besides, it has been demonstrated that less than 1% of the rhenium is involved at a given time in the metathesis [1]. Several studies demonstrated that the acidity of the alumina surface has a great importance on the activity even if the nature of this acidity (Lewis or Brönsted) is discussed [2–6].

There are only few rhenium complexes that are active for the olefin metathesis reaction. The methyltrioxorhenium complex of Herrmann [7,8] requires activation by a Lewis acid and alkylating cocatalyst. The alkylidene complexes of Schrock are active provided that an electron-attracting alkoxy ligand is coordinated to the rhenium [9–17]. Some kind of acidity is generally required in a metathesis catalyst, either a ligand in an homogeneous catalyst or the carrier itself in an heterogeneous catalyst.

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We have been interested to synthesize homogeneous models of the hypothetical surface species present in the heterogeneous catalyst. Such complexes should include an aluminium–perrhenate bridge, which is present at the surface of the alumina carrier. The ligands that we selected to complete the aluminium coordination sphere were substituted aryloxy ligands that exhibit well known advantages: changing the substituents of the aryloxy allows to modify the acidity of the aluminium and its steric crowding.

This paper reports the synthesis and the characterisation of soluble complexes including aluminium coordinated with a perrhenate and a 4-substituted-2,6-di-*tert*-butylphenoxy ligand or a CH_2– or *S-ortho* bridged-4,4′-di-*tert*-butyldiphenoxy ligand. Some of these complexes have been found to have a high activity for the metathesis of internal alkenes without the addition of any cocatalyst [18]. As far as we know, no complex of this kind has been described in the literature. A preliminary account of this work has been published [19].

2. Experimental

All operations were performed under an inert atmosphere of argon using standard Schlenk line or glove box techniques. Toluene, THF, dioxane and diethyl ether were distilled from sodium benzophenone. Pentane and heptane were purified by distillation from $LiAlH_4$.

Phenols, alkylaluminium and rhenium oxide were commercially available and used as received. Olefins were purified by distillation from sodium. Elemental analysis was performed by Mikroanalytisches Labor Pascher (Germany). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker CXP 200. Gas chromatography analyses were done on a HP 5890 series II.

2.1. Synthesis of bisaryloxyaluminium compounds

2.1.1. Alkylbis(aryloxy)aluminium: $(ArO)_2$ Al–R

*2.1.1.1. Bis(2,6-di-tert-butyl-4-methylphenoxy)-isobutylaluminium (**1a**).* To a solution of triisobutylaluminium (10 ml, 39.6 mmol) in 30 ml pentane under reflux was added a solution of 2,6-di-*tert*-butyl-4-methylphenol (17.46 g, 79.2 mmol) in 60 ml pentane with a canula. The addition was done in 30 min. The medium was stirred under reflux for 70 min then allowed to cool at room temperature (70 min). Pentane was removed under vacuum to give 20.55 g of a white powder. ^{1}H NMR showed that 98% of **1a** and 2% of phenol were obtained (η = 98%).

^{1}H NMR(C_6D_6): $\delta = 7.17$ ppm (s, Har); 2.28 ppm (s, H-Me); 1.70 ppm (t-hpt, $^3J = 6.5$–7.1 Hz, H-β); 1.61 ppm (s, H-^{t}Bu); 0.76 ppm (d, $^3J = 6.5$ Hz, H-γ); 0.46 ppm (d, $^3J = 7.1$ Hz, H-α).

*2.1.1.2. Bis(2,6-di-tert-butylphenoxy)isobutylaluminium (**1b**).* This compound was prepared as described for the synthesis of **1a**. ^{1}H NMR showed that 95% of **1b** and 5% of phenol were obtained (η = 69%).

^{1}H NMR (C_6D_6): $\delta = 7.30$ ppm (d, $^3J = 7.8$ Hz Har); 6.91 ppm (dd, $^3J = 7.8$ Hz Har′); 1.79 ppm (t-hpt, $^3J = 6.5$–7.2 Hz, H-β); 1.57 ppm (s, H-^{t}Bu); 0.73 ppm (d, $^3J = 6.5$ Hz, H-γ); 0.43 ppm (d, ^3J = 7.2 Hz, H-α).

*2.1.1.3. Bis(4-bromo-2,6-di-tert-butylphenoxy)-isobutylaluminium (**1c**).* This compound was prepared as described for the synthesis of **1a**. ^{1}H NMR showed that 98% of **1c** and 2% of phenol were obtained ($\eta = 72\%$).

^{1}H NMR (C_6D_6): $\delta = 7.40$ ppm (s, Har); 1.50 ppm (t-hpt, $^3J = 6.5$–7.2 Hz, H-β); 1.36 ppm (s, H-^{t}Bu); 0.51 ppm (d, $^3J = 6.5$ Hz, H-γ); 0.15 ppm (d, $^3J = 7.2$ Hz, H-α).

Elemental analysis: exp.: C 58.66%, H 7.65%, Br 24.5%, Al 4.31%; th.: C 58.90%, H 7.57%, Br 24.5%, Al 4.13% for **1c**.

*2.1.1.4. Bis(2,6-di-tert-butyl-4-methoxyphenoxy)-isobutylaluminium (**1d**).* This compound was prepared as described for the synthesis of **1a**. ^{1}H NMR spectrum showed that 97% of **1d** and 3% of phenol were obtained ($\eta = 70\%$).

^{1}H NMR (C_6D_6): $\delta = 7.03$ ppm (s, H-arom); 3.51 ppm (s, H-OMe); 1.84 ppm (t-hpt, $^3J = 6.6$–7.2 Hz, H-β); 1.58 ppm (s, H-^{t}Bu); 0.80 ppm (d, $^3J = 6.6$ Hz, H-γ); 0.47 ppm (d, $^3J = 7.2$ Hz, H-α).

*2.1.1.5. Bis(4-bromo-2,6-di-tert-butylphenoxy)-ethylaluminium (**1e**).* This compound was prepared as described for the synthesis of **1a**. The ^{1}H NMR showed that 100% of **1e** was obtained ($\eta = 79\%$).

^{1}H NMR(C_6D_6): $\delta = 7.51$ ppm (s, Har); 1.34 ppm (s, H-^{t}Bu); 0.86 ppm (t, $^3J = 8.0$ Hz, H-β); 0.27 ppm (q, $^3J = 8.0$ Hz, H-α).

*2.1.1.6. Bis(2,4,6-tri-tert-butylphenoxy)ethylaluminium (**1f**).* This compound was prepared as described for the synthesis of **1a**. ^{1}H NMR showed that 100% of **1f** was obtained ($\eta = 57\%$).

^{1}H NMR (C_6D_6): $\delta = 7.48$ ppm (s, Har); 1.63 ppm (s, H-^{t}Bu-*ortho*); 1.39 ppm (s, H-^{t}Bu-*para*); 0.81 ppm (t, $^3J = 7.9$ Hz, H-β); 0.33 ppm (q, $^3J = 7.9$ Hz, H-α).

*2.1.1.7. 2,2′-Methylene-bis(6-tert-butyl-4-methylphenoxy)isobutylaluminium(diethylether) (**1h**).* To a solution of triisobutylaluminium (5 ml, 19.8 mmol) in 20 ml diethylether was added a solution of 2,2′-methylene-bis(6-*tert*-butyl-4-methylphenol) (6.74 g, 19.8 mmol) in 75 ml diethylether with a canula. The addition was done in 5 min at room temperature. The medium was stirred for 2 h, a precipitate was then formed. Ether was removed to give a yellow solid that was recrystallised in diethylether. An amount of 6.15 g of white crystals was obtained ($\eta = 63\%$).

^{1}H NMR (C_6D_6): $\delta = 7.19$ ppm (AA′BB′, $^4J = 2$ Hz $\upsilon_0\delta = 28.0$ Hz, H-arom); 4.12 ppm (d, $^2J = 14$ Hz Hp′); 3.49 ppm (d, $^2J = 14$ Hz Hp); 3.49 ppm (q, $^3J = 7.0$ Hz *CH*$_2$–Et$_2$O); 2.24 ppm (s, H-Me); 2.22 ppm (t-hpt, $^3J = 6.5$–7.0 Hz, H-β); 1.57 ppm (s, H-^{t}Bu); 1.24 ppm (d, $^3J = 6.5$ Hz, H-γ); 0.74 ppm (t, $^3J = 7.0$ Hz, *CH*$_3$–Et$_2$O); 0.50 ppm (d, $^3J = 7.0$ Hz, H-α).

Elemental analysis: exp.: C 73.82%, H 9.92%, Al 5.30%; th.: C 74.96%, H 9.94%, Al 5.43% for **1h**.

*2.1.1.8. 2,2′-Methylene-bis(6-tert-butyl-4-methylphenoxy) isobutylaluminium (methyl -tert-butylether) (**1i**).* To a solution of 2,2′-methylene-bis(6-*tert*-butyl-4-methyl-phenol), 4.05 g (11.88 mmol), in 30 ml methyl-*tert*-butylether (MTBE) cooled at −30°C was added a solution of triisobutylaluminium (3 ml, 11.88 mmol) in 20 ml methyl-*tert*-butylether with a canula. The addition was done in 25 min. The medium was allowed to warm at room temperature. The resulting precipitate was filtered to afford 4.2 g of a white powder ($\eta = 69\%$).

^{1}H NMR (C_6D_6): $\delta = 7.22$ ppm (AA′BB′, $^4J = 2.2$ Hz $\upsilon_0\delta = 23.3$ Hz, H-arom); 4.07 ppm (d, $^2J = 13.6$ Hz Hp′); 3.46 ppm (d, $^2J = 13.6$ Hz Hp); 3.10 ppm (s, *CH*$_3$–MeOtBu); 2.28 ppm (t-hpt $^3J = 6.6$–7.2 Hz, H-β); 2.23 ppm (s, H-Me); 1.57 ppm (s, H-tBu); 1.27 ppm (d, $^3J = 6.6$ Hz, *H*-γ); 1.01 ppm (s, *tBu*-MeOtBu); 0.54 ppm (d, $^3J = 7.2$ Hz, H-α).

*2.1.1.9. 2,2′-Methylene-bis(6-tert-butyl-4-methylphenoxy)ethylaluminium(diethylether) (**1j**).* This compound was prepared as described for the synthesis of **1h** ($\eta = 85\%$).

^{1}H NMR (C_6D_6): $\delta = 7.16$ ppm (AA′BB′, $^4J = 2.2$ Hz $\upsilon_0\delta = 26.2$ Hz, H-arom); 4.10 ppm (d, $^2J = 13.6$ Hz Hp′); 3.50 ppm (d, $^2J = 13.6$ Hz Hp); 3.45 ppm (q, $^3J = 7.0$ Hz *CH*$_2$–Et$_2$O); 2.24 ppm (s, H-Me); 1.56 ppm (s, H-^{t}Bu); 1.40 ppm (t, $^3J = 8.0$ Hz H-β); 0.73 ppm (t, $^3J = 7.0$ Hz, *CH*$_3$–Et$_2$O); 0.40 ppm (d, $^3J = 8.0$ Hz, H-α).

2.1.2. Bis(aryloxy)choloroaluminium: (ArO)$_2$ AlCl, Et$_2$O

*2.1.2.1. Bis(2,6-di-tert-butyl-4-methylphenoxy)-chloroaluminium(diethylether) (**2a**).* An amount of 1.81 g (9.56 mmol) of anhydrous stannous chloride was added to a solution of **1a** (5.0 g, 9.56 mmol) in 50 ml diethylether. The medium was stirred for 5 days at room temperature.

Ether was removed under vacuum and 50 ml toluene was added to the residue. The resulting yellow suspension was filtered on celite. After the removal of the solvent, the residue is crystallised in ether to afford 3.75 g of a white solid ($\eta = 68\%$).

^{1}H NMR (C_6D_6): $\delta = 7.16$ ppm (s, H-arom); 3.91 ppm (q, $^3J = 7.0$ Hz *CH*$_2$–Et$_2$O); 2.26 ppm (s, H-Me); 1.52 ppm (s, H-^{t}Bu); 0.62 ppm (t, $^3J = 7.0$ Hz *CH*$_3$–Et$_2$O).

*2.1.2.2. Bis(2,6-di-tert-butylphenoxy)chloroaluminium(diethylether) (**2b**).* This compound was prepared as described for the synthesis of **2a** with **1b** starting material. ($\eta = 62\%$).

^{1}H NMR (C_6D_6): $\delta = 7.30$ ppm (d, $^3J = 7.7$ Hz Har′); 6.86 ppm (dd, $^3J = 7.7$ Hz Har); 3.87 ppm (q, $^3J = 7.0$ Hz CH_2–Et_2O); 1.49 ppm (s, H-^{t}Bu); 0.59 ppm (t, $^3J = 7.0$ Hz CH_3–Et_2O).

*2.1.2.3. Bis(4-bromo-2,6-di-tert-butylphenoxy)-chloroaluminium(diethylether) (**2c**).* This compound was prepared as described for the synthesis of **2a** with **1c** or **1e** starting material ($\eta = 40\%$).

^{1}H NMR(C_6D_6): $\delta = 7.52$ ppm (s, Har); 3.74 ppm (q, $^3J = 7.0$ Hz CH_2–Et_2O); 1.30 ppm (s, H-^{t}Bu); 0.53 ppm (t, $^3J = 7.0$ Hz CH_3–Et_2O).

*2.1.2.4. Bis-(2,4,6-tri-tert-butylphenoxy)chloroaluminium(diethylether) (**2d**).* This compound was prepared as described for the synthesis of **2a** with **1f** or **1g** starting material ($\eta = 53\%$).

^{1}H NMR (C_6D_6): $\delta = 7.47$ ppm (s, Har); 3.87 ppm (q, $^3J = 7.0$ Hz CH_2–Et_2O); 1.55 ppm (s, H-^{t}Bu-*ortho*); 1.37 ppm (s, H-^{t}Bu-*para*); 0.57 ppm (t, $^3J = 7.0$ Hz CH_3–Et_2O).

*2.1.2.5. 2,2′-Methylene-bis(6-tert-butyl-4-methylphenoxy)chloroaluminium(diethylether) (**2e**).* To a solution of 2,2′-methylene-bis(6-*tert*-butyl-4-methylphenol) (27.15 g, 79.7 mmol) in 100 ml diethylether was added a solution of chlorodiethylaluminium (10 ml, 7.97 mmol) in 15 ml diethylether. The addition was done in 5 min. The medium was stirred for 1.5 h. The solvent was removed and the resulting white grey solid was washed with pentane to afford 37.1 g of an orange powder.

^{1}H NMR (C_6D_6): $\delta = 7.14$ ppm (AA′BB′, $^4J = 2.1$ Hz $\upsilon_0\,\delta = 19.1$ Hz, Har); 4.02 ppm (d, $^2J = 14.0$ Hz Hp′); 3.58 ppm (d, $^2J = 14.0$ Hz Hp); 3.49 ppm (q, $^3J = 6.8$ Hz CH_2–Et_2O); 2.21 ppm (s, H-Me); 1.59 ppm (s, H-^{t}Bu); 0.83 ppm (t, $^3J = 6.8$ Hz, CH_3–Et_2O).

*2.1.2.6. 2,2′-Thia-bis(6-tert-butyl-4-methylphenoxy)chloroaluminium(diethylether) (**2f**).* To a solution of 2,2′-thia-bis(6-*tert*-butyl-4-methylphenol) (28.58 g, 79.7 mmol) in 100 ml diethylether was added a solution of chlorodiethylaluminium (10 ml, 7.97 mmol) in 20 ml diethylether. The addition was done in 5 min. The medium was stirred under argon for 1.5 h. The solvent was removed and the resulting white solid was washed with pentane to afford 38.0 g of an orange powder ($\eta = 97\%$).

^{1}H NMR(C_6D_6): $\delta = 7.14$ ppm (AA′BB′, $^4J = 2.3$ Hz $\upsilon_0\,\delta = 47.6$ Hz, Har); 4.19 ppm (q, $^3J = 6.7$ Hz CH_2–Et_2O); 2.03 ppm (s, H-Me); 1.41 ppm (s, H-^{t}Bu); 1.07 ppm (t, $^3J = 6.7$ Hz, CH_3–Et_2O).

Elemental analysis: exp.: C 61.73%, H 7.84%, Cl 6.87%, S 6.91%, Al 5.86%; th.: C 63.33%, H 7.77%, Cl 5.47%, S 6.50%, Al 5.47% for **2f**.

2.2. Synthesis of aryloxyaluminium perrhenate complexes

2.2.1. $AgReO_4$ path

*2.2.1.1. Bis(2,6-di-tert-butyl-4-methylphenoxy)aluminium perrhenate, quinuclidine (**A-1**).* Silver perrhenate (0.62 g, 1.7 mmol) was added to a solution of **2a** (1.00 g, 1.7 mmol) in 60 ml diethylether under an argon stream at room temperature. The medium was stirred in the dark for 24 h. Then it was filtered and ether was removed. The residue was crystallised with cold diethylether to afford 0.70 g of an orange powder. ^{1}H NMR analysis showed that 86% of a new product and 14% of phenol are obtained ($\eta = 54\%$).

^{1}H NMR (C_6D_6): $\delta = 7.13$ ppm (s, H-arom); 2.22 ppm (s, H-Me); 1.46 ppm (s, H-^{t}Bu).

Stabilisation with quinuclidine: to a solution of the above product (0.5 g, 0.8 mmol) in 10 ml pentane was added a solution of quinuclidine (0.15 g, 1.3 mmol) in 10 ml pentane at room temperature. A precipitate was immediately formed. After filtration and drying, the product was washed with pentane to afford 0.5 g of a grey powder ($\eta = 86\%$).

Elemental analysis after stabilisation with quinuclidine: exp.: C 50.08%, H 6.57%, N 1.65%, Al 2.79%, Re 21.3%; th.: C 53.73%, H 7.19%, N 1.69%, Al 3.26%, Re 22.5% for **A-1**.

*2.2.1.2. Bis(di-tert-butyl-2,6-phenoxy)aluminium perrhenate, quinuclidine (**A-2**).* This compound was prepared as described for the synthesis of **A-1** with **2b** starting material. NMR analysis showed that 97% of a new product and 3% of phenol are obtained ($\eta = 59\%$).

^{1}H NMR (C_6D_6): $\delta = 7.25$ ppm (d, $^3J = 7.7$ Hz Har′); 6.85 ppm (dd, $^3J = 7.7$ Hz Har); 1.42 ppm (s, H-^{t}Bu).

Stabilisation with quinuclidine: the above new product was stabilised with quinuclidine in a manner analogous to that described for **A-1** ($\eta = 89\%$) to give **A-2**.

Elemental analysis after stabilisation with quinuclidine: exp.: C 50.34%, H 7.05%, N 1.82%, Al 3.31%, Re 21.5%; th.: C 52.61%, H 6.94%, N 1.75%, Al 3.38%, Re 23.3% for **A-2**.

*2.2.1.3. Bis(4-bromo-2,6-di-tert-butyl-phenoxy)-aluminium perrhenate (diethylether) (**A-3**).* This compound was prepared as described for the synthesis of **A-1** with **2c** starting material. NMR analysis indicated that we obtained 96% of a new product that seemed to be a dimeric species of **A-3** according to integration and 4% of phenol. We also noticed the presence of a coordinated ether and two free ether in solution in C_6D_6.

^{1}H NMR (C_6D_6): $\delta = 7.49$ ppm (s, H-arom); 7.46 ppm (s, H-arom); 3.64 ppm (q, $^3J = 6.9$ Hz *CH*$_2$-coord. Et_2O); 3.25 ppm (q, $^3J = 7.1$ Hz *CH*$_2$-free Et_2O); 1.28 ppm (s, H-^{t}Bu); 1.07 ppm (t, $^3J = 7.1$ Hz *CH*$_3$-free Et_2O); 0.52 ppm (t, $^3J = 6.9$ Hz *CH*$_2$-coord. Et_2O).

*2.2.1.4. 2,2′-Methylene-bis(6-tert-butyl-4-methylphenoxy)aluminium perrhenate (diethylether) (**A-4**).* This compound was prepared as described for the synthesis of **A-1** with **2e** starting material. ^{1}H NMR indicated that we obtained 98% of **A-4** and 2% of **2e** ($\eta = 56\%$).

^{1}H NMR (C_6D_6): $\delta = 7.09$ ppm (AA′BB′, $^4J = 2$ Hz $\upsilon_0\,\delta = 18.8$ Hz, H-arom); 3.85 ppm (d, $^2J = 14$ Hz Hp′); 3.57 ppm (d, $^2J = 14$ Hz Hp); 3.43 ppm (q, $^3J = 7.0$ Hz *CH*$_2$–Et_2O); 2.18 ppm (s, H-Me); 1.49 ppm (s, H-^{t}Bu); 0.77 ppm (t, $^3J = 7.0$ Hz, *CH*$_3$–Et_2O).

Elemental analysis: exp.: C 45.64%, H 5.70%, Al 4.02%, Re 26.8%; th.: C 47.01%, H 5.84%, Al 3.91%, Re 27.0% for **A-4**.

2.2.2. Re_2O_7 path

Unless otherwise stated, the following syntheses are described for an initial atomic ratio Al/Re = 0.5. For ratio Al/Re = 1 and 2, the initial proportion of $Al(OAr)_2R$ was increased.

*2.2.2.1. **1a** + Re_2O_7*

THF solvent. A solution of Re_2O_7 (1.00 g, 2.06 mmol) in 20 ml THF was cooled at −78°C. A solution of **1a** (1.08 g, 2.06 mmol) in 20 ml THF was added through a canula. The medium was allowed to warm at room temperature. At −35°C, a black precipitate appeared. The medium was stirred for 1 h at room temperature then THF was removed under vacuum and the residue was dried for 2 h. The residue was extracted with pentane to afford 1.41 g of a brown-red oil that was used in metathesis. ^{1}H NMR mainly showed phenol.

Elemental analysis after stabilisation with bipyridine (**B-1**): exp.: C 47.46%, H 5.66%, N 3.17%, Al 4.33%, Re 26.4%; th.: C 47.53%, H 5.36%, N 3.82%, Al 3.68%, Re 25.4% for **B-1** (see Table 2).

Dioxane solvent. To a solution of Re_2O_7 (1.00 g, 2.06 mmol) in 25 ml dioxane was added a solution of **1a** (1.08 g, 2.06 mmol) in 25 ml dioxane through a canula. A black precipitate immediately formed. The addition was done slowly for 35 min and the medium was stirred at room temperature for 2 h. Dioxane was removed under vacuum and the resulting residue was extracted with pentane to afford 1.38 g of a brown-red oil that was used in metathesis. ^{1}H NMR showed mainly the presence of phenol.

Stabilisation with quinuclidine: after the extraction with pentane, 0.23 g (2.1 mmol) of quinuclidine was added. A precipitate was then formed. After filtration, we obtained 0.40 g of a ochre powder that was washed with pentane.

Elemental analysis after stabilisation with quinuclidine (**B-3**): exp.: C 53.42%, H 7.53%, N 2.44%, Al 3.51%, Re 21.3%; th.: C 55.08%, H 7.56%, N 2.27%, Al 2.91%, Re 20.1% for **B-3** (see Table 2).

*2.2.2.2. **1b** + Re_2O_7*

THF solvent. This compound was prepared as described for the synthesis of **B-1** with **1b** starting material.

Elemental analysis after stabilisation with quinuclidine (**B-2**): exp.: C 44.87%, H 6.68%, N 2.08%, Al 3.31%, Re 28.2%; th.: C 44.56%, H 6.28%, N 2.08%, Al 4.00%, Re 27.6% for **B-2** (see Table 2).

Dioxane solvent. This compound was prepared as described for the synthesis of **B-3**. The crude product was used directly in metathesis.

2.2.2.3. ***1c*** *+* Re_2O_7

THF solvent. This compound was prepared as described for the synthesis of **B-1** with **1c** starting material. The crude product was used directly in metathesis.

2.2.2.4. ***1d*** *+* Re_2O_7

THF solvent. This compound was prepared as described for the synthesis of **B-1** with **1d** starting material. The crude product was used directly in metathesis.

Dioxane solvent. This compound was prepared as described for the synthesis of **B-3** with **1d** starting material. The crude product was used directly in metathesis.

2.2.2.5. ***1f*** *+* Re_2O_7

THF solvent. This compound was prepared as described for the synthesis of **B-1** with **1f** starting material, but with a molar ratio Al/Re = 1.

Elemental analysis after stabilisation with quinuclidine (**B-4**): exp.: C 52.80%, H 6.66%, N 2.53%, Al 4.01%, Re 22.0%; th.: C 53.64%, H 6.60%, N 2.91%, Al 4.21%, Re 19.4% for **B-4** (see Table 2).

Dioxane solvent. This compound was prepared as described for the synthesis of **B-3** with **1f** starting material, but with a molar ratio Al/Re = 1 and 2.

Elemental analysis after stabilisation with bipyridine: ratio Al/Re = 1 (**B-5**): exp.: C 54.79%, H 6.76%, N 2.80%, Al 4.15%, Re 20.1%; th.: C 52.21%, H 6.25%, N 3.04%, Al 4.40%, Re 20.2% for **B-5** (see Table 2).

Ratio Al/Re = 2 (**B-6**): exp.: C 56.43%, H 7.13%, N 2.48%, Al 4.52%, Re 16.2%; th.: C 54.83%, H 6.81%, N 2.56%, Al 4.93%, Re 17.0% for **B-6**(see Table 2).

2.2.2.6. ***1h*** *+* Re_2O_7. This compound was prepared as described for the synthesis of **B-3** with **1h** starting material in dioxane.

2.2.2.7. ***1j*** *+* Re_2O_7. This compound was prepared as described for the synthesis of **B-1** with **1j** starting material in THF. ^{1}H NMR analysis of the two last compounds showed mainly phenol but also a new product with a signal at 1.49 ppm as for the ^{t}Bu signal of the **A-4** complex (cf. $AgReO_4$ path).

2.2.3. Oligomerisation of $AgReO_4$ *path complexes (type* ***A*** *complexes)*

To a solution of **A-1** (2.71g, 3.8 mmol) in 35 ml dioxane was added a solution of **1a** (2.00 g, 3.8 mmol) in 35 ml dioxane. The medium was stirred for 2 h. The dioxane was removed to afford 5.71 g of a brown-red powder looking like products obtained with the Re_2O_7 path. The product was used as such in metathesis.

Elemental analysis after stabilisation by quinuclidine (complex **AB**): exp.: C 54.34%, H 7.46%, N 1.73%, Al 4.49%, Re 19.0%; th.: C 55.27%, H 7.40%, N 1.45%, Al 4.19%, Re 19.3% for **AB** (see Section 3.4).

2.3. Olefin metathesis

2.3.1. Non-functional olefins

In a double wall glass reactor, 0.10 g of the aluminium perrhenate complex was introduced (the initial Al/Re ratio used in the synthesis of the complex had no influence over its activity in metathesis). The complex was dissolved in 40 ml toluene. The medium was stirred for half an hour at 25°C under argon. Distilled olefin, 1.0 ml, was added. The evolution of the reaction was followed by taking samples with time. These samples were hydrolysed with an aqueous solution of 10% nitric acid. The organic phase was analysed by gas chromatography.

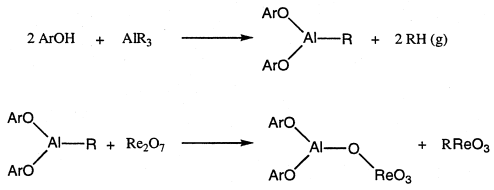
2.3.2. Functional olefins

An amount of 0.10 g of the aluminium perrhenate complex was introduced in a Schlenk then dissolved in 5 ml toluene. The medium was stirred under argon for half an hour at 25°C. Distilled olefin, 1.0 ml, was added. The evolution of the reaction was followed by taking samples with time. These samples were hydrolysed with an aqueous solution of 10% nitric acid. The organic phase was analysed by gas chromatography (toluene was used as an internal standard).

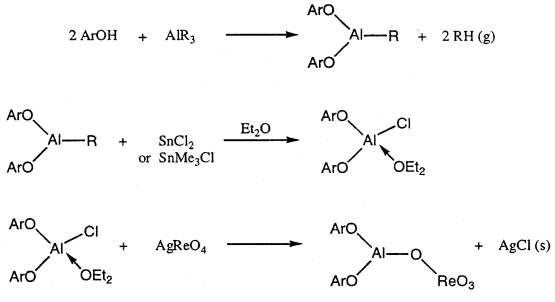
3. Results and discussion

3.1. Strategy for the synthesis of complexes including aluminium perrhenate

Two reaction pathways were considered to achieve the synthesis of complexes comprising an aluminium perrhenate bonding. Herrmann [7] and Romão et al. [8] have described the reaction between rhenium oxide and tetramethylin to synthesize methyltrioxorhenium. We have transposed this reaction to an alkyl-bis(aryloxy)-
aluminium compound according to the following reactions, where the alkyltrioxorhenium formed would appear here as a by-product:



The metathetical exchange between silver perrhenate and chlorotrimethylsilane was described by Schmidt and Schmidbaur [20,21]. By analogy, we have performed the following sequence of reactions:



These two reaction paths first require the synthesis of bis(aryloxy)aluminium-alkyl or -chloride precursors.

3.2. Aryloxy complexes of aluminium

3.2.1. Alkyl-bis(aryloxy)aluminium complexes $(AoO)_2$ Al–R

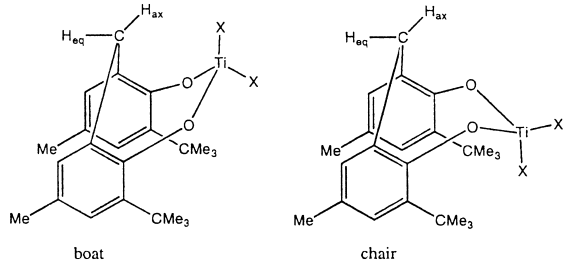
We have chosen the method described by Schreve et al. [22] which is the fastest:

$$2\mathrm{ArOH} + \mathrm{AlR_3} \xrightarrow[\Delta]{\text{heptane}} \mathrm{Al(OAr)_2R} + 2\mathrm{RH(g)}$$

OAr	R	
2,6-Di-*tert*-butyl-4-methyl phenoxy	isoButyl	**1a**
2,6-Di-*tert*-butyphenoxy	isoButyl	**1b**
4-Bromo-2,6-di-*tert*-butyl phenoxy	isoButyl	**1c**
2,6-Di-*tert*-butyl-4-methoxy phenoxy	isoButyl	**1d**
4-Bromo-2,6-di-*tert*-butyl phenoxy	ethyl	**1e**
2,4,6-Tri-*tert*-butylphenoxy	ethyl	**1f**

After refluxing in heptane or pentane and recrystallisation, we obtained the expected products with a purity of 95–98% (the other product being the starting phenol) with yields between 57% and 98%. As far as we know, **1c**, **1d** and **1f** complexes have not been described in the literature until now (the methyl analog of **1c** was described but not isolated [23]). All of the complexes were characterized with ^{1}H NMR. Complex **1c** was also characterized by elemental analysis.

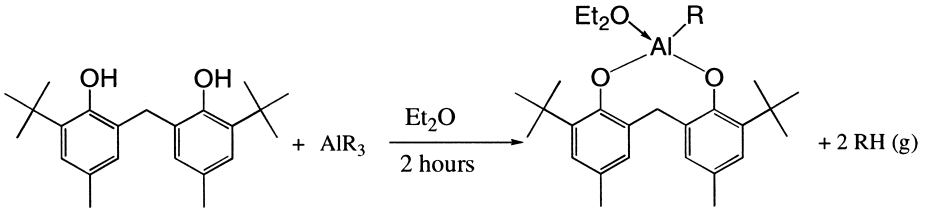
The 2-2′-methylene-bis(6-*tert*-butyl-4-methyl-phenol) exhibited a specific behaviour. When this work started, the corresponding complexes **1h** and **1j** were not described in the literature. Only titanium [24–27] and silicon [28] complexes of



Scheme 1. 2-2′-Methylene-bis(6-*tert*-butyl-4-methyl-phenoxy) complexes of titanium.

2-2′-methylene-bis(6-*tert*-butyl-4-methyl-phenol) were described.

In our hands, the reaction of 2-2′-methylene-bis(6-*tert*-butyl-4-methyl-phenol) with a trialkylaluminium complex using the Ittel method did not lead to the expected product. We obtained a white powder soluble only in hot toluene, maybe an oligomer arising from an intermolecular reaction. Thus, we modified the Ittel method using diethylether as a solvent:



R=iBu **1h**

R=Et **1j**

We were then able to isolate the complexes **1h** and **1j** 99% pure after crystallisation in ether in good yields (63% and 85%). They were characterized by NMR and elemental analysis. During this work, a Taiwan team published a study of those compounds that confirmed our results [29,30].

Studies of titanium complexes showed that the protons of the CH_2 bridge present an AB signal ($\delta = 3.14$ and 3.52 ppm). NOE allowed to assign the resonance in high fields to H_{ax} pointing toward the Ti centre (Scheme 1). The signal in low fields was assigned to H_{eq}. We noticed that **1h** and **1j** also present an AB signal ($\delta \sim 3.5$ and 4.1 ppm, Hp, Hp′). We propose that the same attributions as for titanium complexes may be done.

3.2.2. Bis(aryloxy)chloroaluminium $(ArO)_2$ Al–Cl complexes

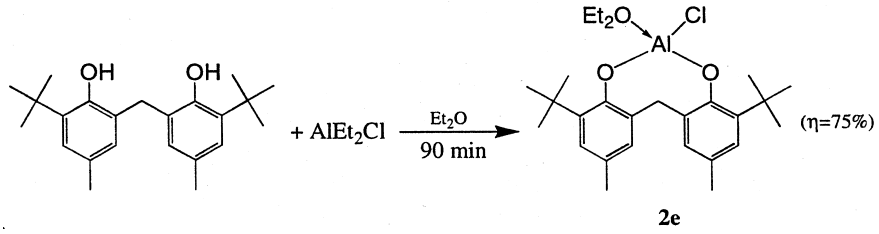
Using the method of Healy, involving the reaction of methyl- and ethyl-bis(aryloxy)-aluminium complexes and either tin (II) chloride or trimethyltin chloride [31], with the bulkier isobutyl-bis (aryloxy)aluminium, trimethyltin chloride was inactive, while tin (II) chloride allowed to isolate the expected products but with a slower kinetics (5–8 days of reaction).

Concerning monophenols, we could isolate the products after crystallisation in ether in good yields (53–68%) except the *para*-bromo-substituted aryloxy complex **2c** ($\eta = 40\%$). Monophenols did not react with $Sn(nBu)_3Cl$ or with $AlEt_2Cl$ even under reflux:

$$Al(OAr)_2R + SnCl_2 \xrightarrow[3\,days]{Et_2O} Al(OAr)_2Cl,Et_2O + RSnCl$$

OAr	R	
2,6-Di-*tert*-butyl-4-methyl phenoxy	isoButyl	**2a**
2,6-Di-*tert*-butylphenoxy	isoButyl	**2b**
4-Bromo-2,6-di-*tert*-butyl phenoxy	isoButyl	**2c**
4-Bromo-2,6-di-*tert*-butyl phenoxy	ethyl	**2c**
2,4,6-Tri-*tert*-butylphenoxy	ethyl	**2d**

As concerns the complexes **1h** and **1j** derived from 2-2′-methylene-bis(6-*tert*-butyl-4-methylphenol), $SnCl_2$ reacted very slowly (80% yield after 15 days), $SnMe_3Cl$ reacted faster, but the best way was starting from the phenol itself and diethylaluminium chloride. The complex **2e** and the analogous *S*-bridged complex **2f** were obtained in good yields.



2e

3.3. Aryloxy aluminium perrhenate complexes

*3.3.1. The $AgReO_4$ path (conducting to type **A** complexes)*

3.3.1.1. Synthesis and characterisation of the complexes. The bis(aryloxy)chloroaluminium complexes **2a** and **2b** reacted with $AgReO_4$ in the dark, in diethylether or methylene dichloride solvent. After filtration and removal of the solvent, a powder was isolated which was unstable even under an inert atmosphere. ^{1}H NMR of these crude products showed that they were composed of various amounts of phenol and another compound.

We stabilised this compound by addition of a Lewis base, like quinuclidine or bipyridine. ^{1}H NMR of the stabilised complexes is in agreement with the expected formulae **A-1** and **A-2**. The elemental analysis matched correctly except for the carbon analysis. A first explanation is that, despite the addition of a stabilising ligand, the complex was still unstable. Such a phenomenon has already been observed by Herrmann: quinuclidine adducts of several allyltrioxorhenium complexes are less stable than the uncoordinated allyl starting complexes [32]. Another explanation is the presence of trace amounts of AgCl even in the stabilised complexes that we were not able to crystallise pure without decomposition.

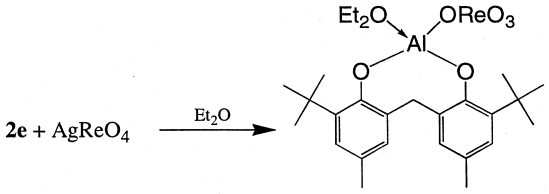
When the complex **2c** including a *para*-bromo-substituted aryloxy ligand was reacted with $AgReO_4$ in diethylether in the dark, the complex was identified as a dimeric species **A-3** by analogy with the complexes described above and according to NMR. In the same reaction, the complex **2d** including a *para-tert*-butyl-substituted aryloxy ligand only led to a decomposition into phenol.

$$Al(OAr)_2Cl,Et_2O + AgReO_4 \xrightarrow{Et_2O} (ArO)_2Al{-}O{-}ReO_3\ (\text{unstable, immediately used in metathesis})$$

$$(ArO)_2Al{-}O{-}ReO_3 \xrightarrow{\text{quinuclidine}} (ArO)_2Al{-}O{-}ReO_3\ (\text{quin})$$

OAr	
2,6-Di-*tert*-butyl-4-methyl phenoxy	**A-1**
2,6-Di-*tert*-butylphenoxy	**A-2**
4-Bromo-2,6-di-*tert*-butyl phenoxy	**A-3**

The complex **2e** derived from the 2-2′-methylene-bis(6-*tert*-butyl-4-methyl-phenol) reacted more slowly. After 4 days, we could isolate the expected complex **A-4** as a white powder with a purity of 98%. Unlike monophenoxy-containing complexes, a Lewis base was not necessary to stabilise the complex, but an ether molecule remains coordinated, most probably on aluminium. Actually, when a complex containing an ether coordinated to rhenium is dried, the ether is generally decoordinated under vacuum. Thus, it appears that using a bidentate bis(aryloxy) ligand on the aluminium increases the stability of the corresponding perrhenate:



A-4

When the similar complex **2f**, derived from the 2-2′-thia-bis(6-*tert*-butyl-4-methyl-phenol), was reacted with $AgReO_4$ in diethylether or dioxane, a purple solid is obtained. However, ^{1}H NMR showed that the crude product was constituted mainly by the starting phenol and unidentified by-products. Stabilisation with quinuclidine did not allow to isolate any rhenium complex.

3.3.1.2. Catalytic activity in metathesis. The metathesis of 2-pentene (a *cis–trans* mixture) to 2-butene and 3-hexene has been chosen as a test reaction for the activity of the new complexes. These complexes are used before their stabilisation with a Lewis base and immediately after their synthesis, owing to their unstability. The reaction was conducted at 25°C and started without the addition of any cocatalyst. Detailed conditions are given in Section 2.

The activity of each complex is expressed by the kinetic constant calculated according to a second-order equilibrated reaction [18], with conversion being 50% at the equilibrium. Results are given in Table 1.

Table 1
Activity of complexes synthesized by the $AgReO_4$ path (type **A**) in 2-pentene metathesis

Corresponding stabilised complex	Substituent in *para* position of the aryloxy ligand	Activity k ($mol^{-1}l^2\ h^{-1}g_{cat}^{-1}$) of the unstabilised complex
A-1	Me	0.4
A-2	H	0.04
A-3	Br	0
A-4		0.007

These type **A** complexes have a poor catalytic activity in 2-pentene metathesis. The most active complex is **A-1** with a *para*-methyl-substituted aryloxy ligand. When an electron-attracting group such as bromine is in *para* position, the complex (**A-3**) has no activity. The activity of the complex comprising the 2-2′-methylene-bis(6-*tert*-butyl-4-methyl-phenoxy) ligand is very weak. However, we ignore how the presence of a coordinated ether influences the catalytic activity.

We tried to improve the activity of these type **A** complexes by adding a Lewis acid cocatalyst such as $AlEtCl_2$, $Al(OAr)_2R$, $Al(OAr)_2Cl,Et_2O$, $GaBr_3$ and $AlCl_3$, in toluene solution. No effect on the catalytic activity was observed. However, with $AlCl_3$ in chlorobenzene, the medium became black and activity was no more observed. Aluminium chloride is well known to decompose aryloxyaluminium complexes [31]. An alkylating cocatalyst such as tetramethyltin did not improve the catalytic activity.

*3.3.2. Oligomeric complexes synthesized by the Re_2O_7 path (type **B** complexes)*

3.3.2.1. Synthesis and characterisation. The reaction of an alkyl-bis(aryloxy)aluminium complex with Re_2O_7 was performed in two different solvent: THF or dioxane. No reaction occurred in toluene:

$$Al(OAr)_2R + Re_2O_7 \xrightarrow[(2)\,\text{extraction with pentane}]{(1)\,\text{THF}\ -35^\circ\text{C}\ldots20^\circ\text{C}} \text{used in metathesis},$$

$$Al(OAr)_2R + Re_2O_7 \xrightarrow[(2)\,\text{extraction with pentane}]{(1)\,\text{Dioxane}\ 20^\circ\text{C}} \text{used in metathesis}.$$

Using THF as a solvent, the aluminium complex and Re_2O_7 are mixed at −78°C. The medium is allowed to warm slowly to room temperature. At −35°C, a black precipitate appears, due to the decomposition of the alkyltrioxorhenium complex $RReO_3$ that is formed as a by-product. Indeed, isobutane and isobutene were identified by gas chromatography and ^{1}H NMR during the reaction between $Al(OAr)_2iBu$ and Re_2O_7 (ethane and ethylene are found with $Al(OAr)_2Et$ and Re_2O_7). The black colour was attributed to ReO_3 (usually red, but black when finely divided).

When the reaction medium reached room temperature, it was allowed to stir again for 1 h then THF was removed. The time of stirring at room temperature mainly determines the final activity of the catalyst. If the medium was stirred for too long a time (more than 2 h) or when the reaction was performed from the beginning at room temperature, THF polymerised.

Once the solvent was removed, the residue was extracted with pentane in order to separate the soluble complex from the rhenium oxide precipitate. After removal of the pentane, brown-red oils (sometimes powders) were obtained. If the oils were dissolved in pentane, a brown-red precipitate appeared after a few hours. Nonetheless, the solutions did not seem to be colloidal because no sedimentation was observed by centrifugation. On the other hand, the solutions of the oils in toluene are much more stable. They did not conduct to a precipitation and gave reproducible results in catalysis.

In dioxane as a solvent, the reaction medium was allowed to stir for 2 h at room temperature, then it was treated as described above. Brown-red powders were obtained. The black precipitate separated during the pentane extraction was found to be $ReO_3(C_4H_8O_2)$ (satisfactory elemental analysis), confirming the decomposition of the alkyltrioxorhenium into alkane, alkene and ReO_3(solvent) under our conditions.

The characterisation of the products was difficult because of the extreme unstability of these type **B** complexes even under an inert atmosphere. ^{1}H NMR most often showed the presence of phenol mainly. By analogy with the work of Kühn et al. [33] on alkylrhenium complexes, we tried purifications by chromatography on grafted silica (C18) or polystyrene resins at low temperature under argon but this did not improve the purity of the product.

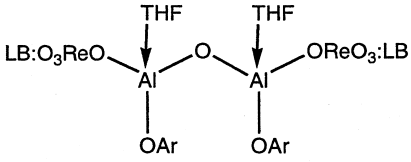
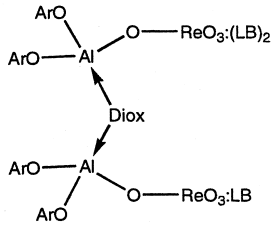
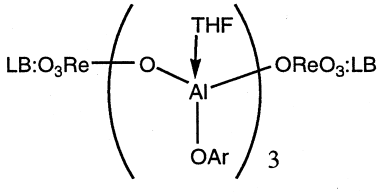
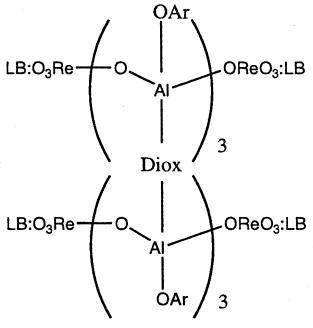
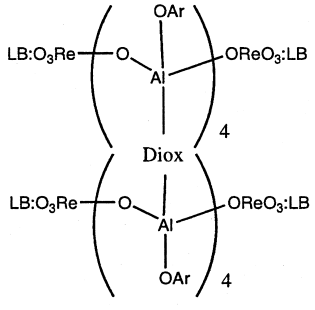
We stabilised these products by the addition of a Lewis base (bipyridine or quinuclidine) like in the case of type **A** complexes. After stabilisation, the elemental analysis for C, H, N, Al, Re was performed. The formulae that we could derive are more complicated than those obtained in the $AgReO_4$ path. The complexes contained one or more Al–O–Al linkages. The formulae are summarised in the Table 2, depending on the initial atomic ratio Al/Re used in the synthesis and the nature of the solvent.

The product of the synthesis starting with complexes **1h** or **1j** is different from those obtained with the monodentate bis(aryloxy)aluminium complexes. In THF, dioxane, Et_2O, we obtained a purple solid. Its ^{1}H NMR spectrum showed the presence of phenol and of an unknown product of which the chemical shift of *tert*-butyls was close to the one of the complex **A-4** synthesized by the $AgReO_4$ path ($\delta =$ 1.49 ppm). We were not able to isolate any complex. However, it seemed that the presence of a bidentate bis(phenoxy) ligand did not allow the synthesis of a complex containing multiple Al–O–Al linkages.

3.3.2.2. Catalytic activity in the metathesis of 2-pentene. The catalytic experiments were conducted in the same conditions as for the type **A** complexes. Again, complexes were used in metathesis before their stabilisation with a base and immediately after their synthesis. Table 3 summarises the results according to the solvent of the synthesis. We noticed that the atomic ratio Al/Re (i.e. one, two or three Al–O linkages) had no influence on the final activity of the complex.

The complexes of type **B** obtained through the Re_2O_7 path are generally much more active in metathesis catalysis than the type **A** complexes. As an example, 0.1 g catalyst (90 μmol with **B-2** formula without quinuclidine) in 1 ml of toluene brought about the metathesis of 10 ml (93 mmol) of 2-pentene to equilibrium in 5 min (TOF 100 min^{-1}). Strong differences are observed according to the nature of the aryloxy groups. The catalyst synthesized by the reaction of **1f** and Re_2O_7 in dioxane gave the best results.

Table 2
Complexes synthesized by the Re_2O_7 path (type **B** complexes)

	Solvent THF	Solvent dioxane
Al/Re=0,5		
	B-1, B-2	**B-3**
Al/Re=1		
	B-4	**B-5**
Al/Re=2		
		B-6

3.3.2.3. Influence of the nature of the olefin We compared the reactivity in metathesis of different non-functional olefins with a type **B-4** catalyst before its stabilisation with a base. Functional olefins were tested with a type **B-5** catalyst before its stabilisation (Table 4).

1-Hexene is much less reactive than 2-pentene. Steric crowding around the double bond strongly hinders metathesis. Indeed, 2-methyl-2-pentene and 2,4,4-trimethyl-2-pentene were not converted even after 3 days of reaction. However, when 2-pentene was added at that time, it was readily converted. The lack of activity with bulky olefins is then due to an impossibility of coordination rather than to an inhibition of the catalyst.

Our catalysts are active in the metathesis of some functional olefins. When diallylether (respectively, diallylsulphide) was added to a typical solution of catalyst, a violent gas emission was observed. It was identified as ethylene by gas chromatography. The reaction was not selective, dihydrofurane and oligomers were formed together. In the case of the diallylsulphide, we only observed the formation of ethylene and oligomers.

3.4. Oligomerisation of type **A** complexes

The type **A** complexes prepared through the $AgReO_4$ path exhibit a much lower activity in metathesis than type **B** complexes synthesized via the Re_2O_7 path. The main difference between the two kinds of complexes is the presence of Al–O–Al linkages in **B** complexes. However, Al–O–Al linkages are not created when the aryloxy ligand is a bidentate bis(phenoxy) ligand. A partial evidence was the observation by ^{1}H NMR of the same signals in the products of the two paths when the 2-2′-methylene-bis(6-*tert*-butyl-4-methyl-phenoxy) ligand was involved. Generation of Al–O–Al linkages would imply the elimination of an aryloxy ligand, a process which is forbidden by the CH_2 bridge in the bis(phenoxy) ligand. We tried to demonstrate that type **A** complexes are intermediates of type **B** complexes in the Re_2O_7 path. With this aim, we performed the following experiments.

- Complex **A-1** was stirred with the ReO_3 (coming from Re_2O_7 path) black precipitate in dioxane for 2 h and the medium was then extracted with pentane after removal of dioxane. ^{1}H NMR showed that **A-1** was not modified and there was no improvement in catalysis. Thus, ReO_3 do not interact with a type **A** complex.
- Complex **A-1** was allowed to stir with the aluminium complex **1a** (1 Eq) in dioxane for 2 h. After removal of dioxane, the product looks like the one observed at the end of the Re_2O_7 path. Moreover, its catalytic activity was considerably improved ($k = 100$ mol^{-1} l^2 g$_{cat}^{-1}$ instead of 0.4 mol^{-1} l^2 g$_{cat}^{-1}$). When the same reaction was done in toluene, there was no improvement in metathesis.

The complex resulting from the above reaction in dioxane was stabilised by quinuclidine (complex

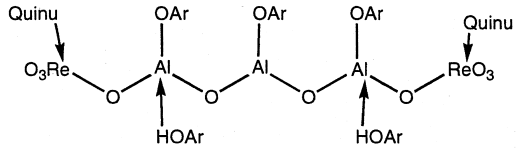
Table 3
Activity of complexes synthesized by the Re_2O_7 path (type **B**) in 2-pentene metathesis

Corresponding stabilised complex	Substituent in *para* position of the aryloxy ligand	Activity k (mol^{-1}l^2 h^{-1} g$_{cat}^{-1}$) of the unstabilised complex
Synthesis of the complex in THF		
Non-isolated	Br	2.4
Non-isolated	OMe	1.9
B2	H	75
B1	Me	125
Non-isolated	tBu	35
Synthesis of the complex in dioxane		
Non-isolated	OMe	8
Non-isolated	H	14
B3	Me	160
B6	tBu	450

Table 4
Activity of complexes synthesized by the Re_2O_7 path (type **B**) in the metathesis of various olefins

Olefin	Corresponding stabilised complex	Activity k (mol^{-1}l^2 h^{-1} g$_{cat}^{-1}$) of the unstabilised complex
2-Pentene	**B4**	160
1-Hexene	**B4**	3
2-Methyl-2-pentene	**B4**	0
2,4,4-Trimethyl-2-pentene	**B4**	0
Allyl acetate	**B5**	0
Diallyl ether	**B5**	1400
Diallyl sulphide	**B5**	1200

AB). Elemental analysis is close to the analysis of the complex **B-5** synthesized by Re_2O_7 path in dioxane with an Al/Re ratio equal to 1. The Al content in **AB** is found in the 4–5% by weight range (2.79% in **A-1**), a value which implies the presence of Al–O–Al linkages. The following tentative formula is proposed on the basis of the best fit for the C, H, N, Al, Re analyses. The phenols could be coordinated through the lone pairs of their oxygen to the electron-deficient aluminium atoms. Then it seems that there is a relation between the presence of Al–O–Al linkages in the complex and a high activity in metathesis:



AB

3.5. Possible origin of the metathesis activity

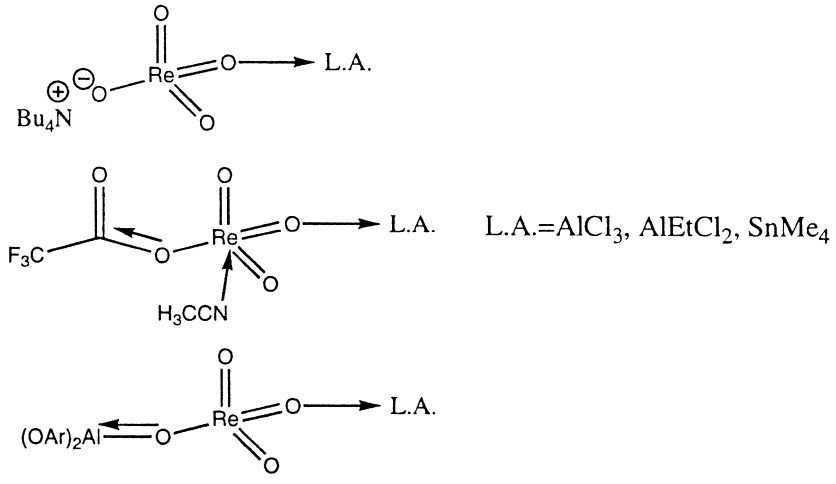
3.5.1. The respective roles of the aryloxy ligands and aluminium

In our homogeneous catalysts, either of **A** or **B** type, there is no correlation between the acidity of the aryloxy ligand (controlled by its *para* substituent) and the activity in metathesis. The isobutyl–aluminium complex **1a** is most probably monomeric with a tricoordinated aluminium as is known to be the methyl analog [34], due to the bulky *ortho* substituents. This steric bulk is likely to be found also in the **A** and **B** type complexes. The situation is more complicated because the syntheses were done in an ether medium. The complexes isolated from pentane extraction that are active in metathesis comprise THF or dioxane molecules coordinated to aluminium (and maybe to rhenium). On the other hand, we have observed that an excess of THF inhibits the catalysis. This suggests an equilibrium of coordination–decoordination of the ether. Such equilibria have been described in the literature [35–37].

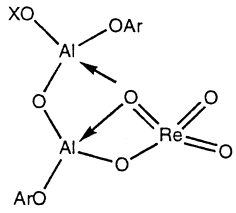
The acidity of a bis(aryloxy)aluminium moiety acting as a ligand for the perrhenate should then be attributed to the tricoordination of the aluminium center stabilised and protected by the bulky *ortho* substituents of the aryloxy ligands. This conclusion may explain the activity of these catalysts toward functional olefins because the acidic function cannot interact with the basic functional groups of the olefin because of the steric bulk of aryloxy ligands.

3.5.2. The difference of activity between **A** complexes and oligomeric **B** complexes

The above conclusion cannot explain why **A** complexes have a lower activity than **B** complexes. We observed that the only way to activate **A** complexes is to make them react with an alkyl-bis (aryloxy)aluminium in an ether solvent.



Scheme 2. Inactive or low active complexes in metathesis catalysis.



X=Ar, ReO_3

Scheme 3. Highly active complex in metathesis catalysis.

On the other hand, we tried to activate a perrhenate by the addition of a Lewis acid (Scheme 2). Tetrabutylammonium perrhenate, associated with a Lewis acid ($AlCl_3$, $AlEt_2Cl$, $SnMe_4$) in chlorobenzene, was inactive in metathesis. This result shows that a simple enhancement of the acidity at the rhenium (assuming coordination of the Lewis acid to an oxo ligand) was not sufficient to obtain an active catalyst. Even the trifluoroacetyl perrhenate (containing the trifluoroacetate electron-withdrawing group, but unfortunately isolated with an acetonitrile ligand), in the presence of a few equivalents of Lewis acid, was inactive in metathesis catalysis.

As a conclusion, favourable conditions for a high activity in metathesis seem to be met only when Al–O–Al linkages are present in the rhenium environment. Such linkages exhibit a strong Lewis acidity related to the possibility of a double coordination of two neighbouring aluminium atoms to a substrate, as suggested by Hanawa et al. [38], Ooi et al. [39] and Wuest [40]. In our case, according to Scheme 3, an Al–O–Al linkage attached to the perrhenate may induce a strong electrophilic activation of an oxo ligand of the rhenium.

The competition of acidity between the aluminium and the trioxorhenium parts in the molecule is then in favour of the aluminium, which at the end extracts an oxo ligand out of the coordination sphere of the rhenium, opening a vacant site where a carbene may be generated later from an incoming olefin.

4. Conclusion

A series of aluminium complexes $(ArO)_2$-Al–Y was synthesized, where ArO is a di-*tert*-butyl-2,6-phenoxy ligand or $(ArO)_2$ is an *ortho*-CH_2– or –*S*-bridged di-*tert*-butyl-2,6-bisphenoxy ligand, and Y is an alkyl or chlorine ligand. The reaction of bis(aryloxy)chloroaluminium $(ArO)_2Al–Cl,Et_2O$ complexes with $AgReO_4$ in ether leads to new complexes $(ArO)_2Al–OReO_3$ (type **A** complexes). These complexes were stabilised by coordination with a Lewis base such as quinuclidine. In the absence of this base, **A** complexes are poorly active 2-pentene metathesis catalysts. Alkylbis(aryloxy)aluminium $(ArO)_2Al–R$ (R = iBu, Et) complexes react with Re_2O_7 in THF or dioxane, leading to complexes that contain Al–O–Al oligomeric linkages such as in $O_3Re–[Al(OAr)–O]_2–ReO_3$ (type **B** complexes). Some of these complexes, unstable even under an argon atmosphere, were identified after stabilisation with a Lewis base such as quinuclidine or bipyridine. Before their stabilisation, they show a fairly high activity in the metathesis of 2-pentene ($TOF = 100\ min^{-1}$) and functional olefins (diallylether, diallylsulphide). As far as we know, they are the most active homogeneous rhenium-based catalysts for the metathesis of internal olefins.

We have demonstrated that **A** type complexes may be activated by reaction with alkylbis(aryloxy)aluminium complexes in an ether solvent. Al–O–Al linkages were then created, giving a **B** complex-like structure. We propose that the possible origin of the high catalytic activity is related to the presence of these oligomeric Al–O–Al linkages. The aluminium sites are protected by the steric hindrance of the aryloxy ligands and they show a strong Lewis acidity, eventually latent if the decoordination of a solvent molecule should occur first. These results exemplify again the determining role of the Lewis acidity in such catalysts.

The application of the bis(aryloxy)aluminium complexes to the activation of the Re_2O_7/Al_2O_3 heterogeneous catalyst is the object of our current investigations.

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