

New Homogeneous Rhenium-based Metathesis Catalysts as Models of the Rhenium on Alumina Heterogeneous Catalyst

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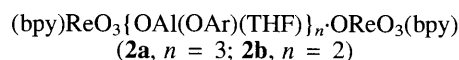
Bis(2,6-di-*tert*-butyl-4-methylphenoxy)isobutylaluminium reacts with dirhenium heptoxide to give complexes containing aluminium coordinated with perrhenate and 2,6-di-*tert*-butyl-4-methylphenoxy ligands which are active new catalysts for the metathesis of alkenes.

Almost since its origin, the metathesis reaction has been recognized to occur in the presence of both homogeneous and heterogeneous catalysts. The most common rhenium-based heterogeneous catalyst, rhenium heptoxide on alumina, is active at ambient temperature, allowing in principle comparisons with homogeneous catalysts. Unfortunately, rhenium complexes which are active as homogeneous catalysts for the metathesis reaction are relatively scarce.¹ The methyltrioxorhenium complex of Herrmann *et al.* requires activation by a Lewis acid and an alkylating cocatalyst,² unless it is deposited onto an acidic carrier.³ The alkylidene complexes described by Schrock *et al.* are active alone provided that the ancillary alkoxy ligands present electron-attracting properties.⁴ The requirement for the presence of some kind of acidic species in the metathesis catalysts appears quite general. This paper reports the synthesis of soluble complexes including aluminium coordinated with perrhenate and 2,6-di-*tert*-butyl-4-methylphenoxy ligands, which have been found to be active new catalysts for the metathesis of various alkenes without the help of any cocatalyst.

Bis(2,6-di-*tert*-butyl-4-methylphenoxy)isobutylaluminium (ArO)₂AlBuⁱ⁵ reacts with dirhenium heptoxide (molar ratio Al:Re = 1:1) in THF to give, after work-up,[†] an air- and water-sensitive red-brown solid **S1**, which is an active homogeneous catalyst for the metathesis of alkenes in hydrocarbon solvents, as shown in Table 1. The metathesis reaction is completely inhibited in THF or acetone. Pent-2-ene is transformed into the expected but-2-ene and hex-3-ene in a 1:1 molar ratio with 100% selectivity. Methyl oleate is also metathesized, although more slowly. Compound **S1** is much more active for the ring opening metathesis polymerization of cyclic alkenes. Cyclopentene is transformed into a living polymer, as ascertained by the depolymerization observed when the polymer solution still containing the catalyst is diluted with heptane. When the THF used in the synthesis is replaced by diethyl ether or diisopropyl ether, the same work-up sequence leads to more active catalysts [using Et₂O, TOF for pent-2-ene is 1235 h⁻¹, TOF for methyl oleate is 13 h⁻¹; using Pr₂O, TOF for pent-2-ene is 1800 h⁻¹ (TOF = turnover frequency)]. No reaction occurs between (ArO)₂AlBuⁱ and Re₂O₇ in toluene.

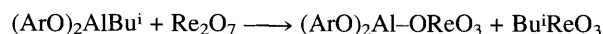
The complex‡ (ArO)₂Al(THF){OAl(OAr)(THF)}OReO₃ **1** is isolated from a heptane solution of **S1** on standing.† It can be redissolved easily in heptane and is itself a catalyst for the

metathesis of pent-2-ene under the same conditions as **S1**. The addition of 2,2'-bipyridine (bpy) to a toluene solution of **S1**† leads to the isolation of the complex **2a**:‡



When the reaction between (ArO)₂AlBuⁱ and Re₂O₇ is conducted in THF with the stoichiometry Al:Re = 0.5:1, the same work-up again gives a catalyst for the metathesis of pent-2-ene. On the addition of bpy, the complex **2b**‡ is isolated. Efforts to identify transitory rhenium-carbene complexes during catalysis have failed thus far.

The primary product of the reaction between (ArO)₂AlBuⁱ and Re₂O₇ is presumably (ArO)₂Al-OReO₃ arising from a reaction similar to that described by Herrmann *et al.* between ZnR₂ and Re₂O₇:⁶



Buⁱ-ReO₃ has not been characterized at any step of the reaction, but instead, its decomposition products, isobutane and isobutene, have been identified during the synthesis. (ArO)₂Al-OReO₃ reacts further, following pathways which are not elucidated at the present time, to give **1** and complexes leading to **2a** or **2b** in the presence of bpy, depending on the stoichiometry of the reactants.

When (ArO)₂Al-Cl(Et₂O)⁷ is contacted with AgO-ReO₃ in CH₂Cl₂ and in the presence of pent-2-ene at room temperature, a reaction occurs during which transitory metathesis of pent-2-ene is observed but ceases rapidly. (ArO)₂Al-OReO₃ is expected to be the primary product of this reaction (complex **1** is not identified), the formation of the coproduct AgCl being the driving force. Therefore, (ArO)₂Al-OReO₃ may also be active in metathesis.

The metathesis activity of these new complexes may be attributed to the electron-attracting properties of the aluminium ligand. The pK_a of 2,6-di-*tert*-butyl-4-methylphenol is 11.2,⁸ and an ArO-Al ligand should behave as an electron donor toward the strongly acidic ReO₃ moiety.⁹ However, the steric crowding of the ArO ligand is such that the complex (ArO)₂Al-Me is a monomer¹⁰ with a three-coordinate, highly electron-deficient aluminium.¹¹ The intermediate (ArO)₂Al-OReO₃ may also include a three-coordinate aluminium for the same steric reasons. The aluminium atoms in **1** are coordinated by THF molecules in the solid state. A decomplexation equilibrium of the THF in hydrocarbon solution is suggested by its strong inhibiting effect when it is used as the solvent in metathesis. Accordingly, less coordinating ethers, like diethyl or diisopropyl ether, lead to more active catalysts. Such a decomplexation equilibrium in solution has already been reported in the chemistry of zinc aryloxides.¹² The steric crowding brought by the ArO ligands should thus favour three-coordinate aluminium in solution, providing an acidity which overcomes the opposite electronic effect, and making the perrhenate active for metathesis. In this way, the above complexes appear as good models of the heterogeneous rhenium-on-alumina catalyst in which the acidity of some sites of the alumina surface is thought to be responsible for the activity of the perrhenate anions anchored to the surface by means of Al-O-Re links.

This work is continuing in order to develop an understanding of the sequence of reactions leading to the complexes **1** and **2**,

Table 1 Catalysis of alkene metathesis with **S1**^a

Alkene	Conversion(%) [t/min]	TOF ^b /h ⁻¹
Pent-2-ene	40 [60]	50
Pent-2-ene ^c	50 [60]	60
Hex-1-ene	2 [60]	2
Methyl oleate	16 [60]	7
Cyclopentene	55 [4]	1275
Norbornene	^d	3500 ^e

^a Temperature: 25 °C, **S1**: 0.36 g, heptane: 20 ml (except^c), alkene: 5 ml (except norbornene: 1 g). ^b Turnover frequency calculated assuming that the active species is (ArO)₂AlOAl(OAr)OReO₃. ^c Solvent: chlorobenzene (20 ml). ^d Polymerization is immediate on the addition of the first drops of the catalyst solution. ^e Estimated value.

and to study in more detail the importance of the electronic unsaturation at the aluminium by changing the nature of the aryloxy ligands.

The experimental assistance of C. Halais and V. Noury, as well as the fruitful suggestions of Y. Chauvin, are gratefully acknowledged.

Received, 13th January 1995; Com. 5/00222B

Footnotes

† A solution of $(\text{ArO})_2\text{AlBu}^t$ (1.79 g) in THF is added under an argon atmosphere to a THF solution of Re_2O_7 (0.83 g) cooled at -78°C and the mixture is allowed to heat slowly up to room temperature. Evaporation of the THF under vacuum followed by extraction of the black residue with pentane give a brown solution, the evaporation of which leaves the air and water-sensitive red-brown solid **S1**, easily soluble in common organic solvents. A brown precipitate separates out from a heptane solution of **S1** on standing for 20 h at room temperature. After filtration and drying under vacuum, **1** is obtained as a light brown powder, unstable at room temperature even under an argon atmosphere. Addition of bpy to a toluene solution of **S1** followed by cooling at -20°C overnight lead to the isolation of **2a** as brown microcrystals with an overall yield of 20% based on rhenium.

‡ Complex **1** gave satisfactory elemental analysis for H, Al and Re, but deviation on C analysis is 2.3%, due to the poor stability of **1**. Complexes **2a** and **2b** gave satisfactory elemental analyses. *Selected data*: for $(\text{ArO})_2\text{Al}(\text{THF})\{\text{OAl}(\text{OAr})(\text{THF})\}\text{ReO}_3$ **1**: Molecular mass; found 1331, calc. 1121; ^1H NMR (CD_2Cl_2) (two different ArO ligands are observed): δ 6.98 (m, Ph), 4.1 (m, THF), 2.26 (s, *p*-CH₃), 2.18 (s, *p*-CH₃), 1.7–1.9 (m, THF), 1.44 (s, Bu^t), 1.37 (s, Bu^t); ^{13}C NMR (CD_2Cl_2) δ 151.8 (Ph, *ipso*-C), 136.2 (Ph, *o*-C), 128.7 (Ph, *p*-C), 125.8 (Ph, *m*-C), 70.9 (THF), 34.9 (Bu^t, C), 30.5 (Bu^t, CH₃), 21.2 (*p*-CH₃). For $(\text{bpy})\text{ReO}_3\{\text{OAl}(\text{OAr})(\text{THF})\}_3\text{-OReO}_3$ **2a**: ^1H NMR (CD_2Cl_2): δ 8.68, 8.46, 7.85 (m, bpy), 7.01 (m, Ph), 2.29 (s, *p*-CH₃), 1.46 (s, Bu^t). For $(\text{bpy})\text{ReO}_3\{\text{OAl}(\text{OAr})$

$(\text{THF})_2\text{OReO}_3(\text{bpy})$ **2b**: ^1H NMR (CD_2Cl_2): δ 8.64, 8.41, 7.81, 7.32 (m, bpy), 6.95 (m, Ph), 2.23 (s, *p*-CH₃), 1.40 (s, Bu^t).

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