

Communication

Synthesis and structure of stable *cis*-dimethyl complex of oxotungsten(VI)

Ari Lehtonen ^{a,*}, Reijo Sillanpää ^b

^a *Laboratory of Materials Chemistry and Chemical Analysis, Department of Chemistry, University of Turku, FIN-20014 Turku, Finland*

^b *Laboratory of Inorganic Chemistry, Department of Chemistry, University of Jyväskylä, FIN-40351 Jyväskylä, Finland*

Received 9 January 2007; received in revised form 12 February 2007

Available online 23 February 2007

Abstract

Oxotungsten(VI) complex *cis*-[WO(L^{tBu})Me₂] (L^{tBu} = methylamino-*N,N*-bis(2-methylene-4-methyl-6-*tert*-butylphenolate) dianion) was prepared by the transmetallation reaction of [WO(L^{tBu})Cl₂] (either *cis* or *trans* isomer) with methyl magnesium iodide. This unexpectedly stable dialkyl complex can be activated by Et₂AlCl to catalyze the ring-opening metathesis polymerization of norbornene. © 2007 Elsevier B.V. All rights reserved.

Keywords: Alkoxide complexes; Phenolate ligands; Tungsten; Alkyl ligands

1. Introduction

A number of tungsten(VI) complexes with labile ligands can be activated by main-group organometallics to obtain active catalysts for olefin metathesis [1–4]. It is assumed that the main role of these activators is to substitute two labile ligands on tungsten with alkyl groups. The resultant organotungsten intermediate would then undergo an α -elimination reaction to give the corresponding alkylidene complex. Thus, dialkyl derivatives of high-valent tungsten are frequently regarded as intermediates in an activation process of two-component olefin metathesis catalysts.

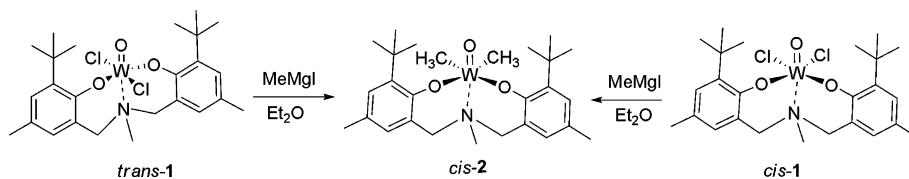
Aminobis(phenols) are known to react as tridentate ligands with various transition metals [5–8]. Recently, we have introduced the dianionic aminobis(phenolato) and diaminobis(phenolato) ligands to molybdenum(VI) and tungsten(VI) chemistry, and reported several catalytic applications of formed complexes [9]. For example, the *cis* and *trans* isomers of dichloro complex [WOC₂(L^{tBu})] (**1**) (L^{tBu} = methylamino-*N,N*-bis(2-methylene-4-methyl-6-*tert*-butylphenolate) dianion) can polymerize norbornene

when activated by Et₂AlCl at elevated temperature [9a]. The nature of active species in these two-component catalyst systems remains still unknown, but we may assume that alkylating agent replaces labile chloro ligands. However, no dialkylated intermediates were found during our experiments. In present paper, we report the dialkylation of **1** with methyl Grignard reagent to form a stable dimethyl complex.

2. Results and discussions

Scheme 1 presents the reaction of complexes **1** with MeMgI. In our initial experiment, a sample of *trans*-**1** was dissolved in anhydrous ether. Resulting red solution was treated with MeMgI while the reaction mixture turned rapidly orange. The orange solution was then stirred for an hour at room temperature. The solvent was evaporated and the yellow solid product was isolated in a 67% yield. The crystalline product is stable in air at room temperature and soluble in toluene, ether and chlorinated solvents. ¹H NMR spectrum in CDCl₃ showed a single resonance at 0.840 ppm for W–Me protons, whereas related signal in ¹³C NMR spectrum was seen at 40.90 ppm. IR spectrum showed strong absorptions in the range of 1150–1240 cm⁻¹, which are typical for phenoxide O–C stretching

* Corresponding author. Tel.: +358 2 3336733; fax: +358 2 333 6700.
E-mail address: ari.lehtonen@utu.fi (A. Lehtonen).



Scheme 1.

frequencies, whereas the W–O stretches were seen as medium to strong intensity peaks at 570–600 cm^{-1} [10,11]. Intense absorption band at 978 cm^{-1} is characteristic for W=O moiety [12]. The ^1H and ^{13}C NMR spectra of the studied compound showed anticipated resonances for coordinated aminobis(phenolato) ligands. Although a symmetrical structure would be expected to have signals for six aromatic and six aliphatic carbons, only five aromatic carbon peaks were observed due to some overlapping. The CH_2 protons were seen as broad overlapping signals at 3.4–3.6 ppm though corresponding resonances for C_s -symmetric *trans*-1 appear as sharp doublets at 4.93 and 3.15 ppm. Actually, the methylene protons of the dialkylated product gave similar NMR resonances as found in the spectra of $[\text{WO}(\text{eg})(\text{L}^{\text{tBu}})]$ ($\text{eg} = 1,2\text{-ethanediolato}$) and *cis*-1. This indicates that the methylation process is associated with a rearrangement of the aminobis(phenolato) ligand, which yields to the *trans* to *cis* isomerization of the reacting complex. The strong *trans* influence of methyl group seems to make *cis* configuration thermodynamically more favoured. The arrangement of two newly introduced methyl groups was finally verified by X-ray crystallography (see below). When the synthesis was repeated using *cis*-1 as a precursor the reaction yielded an identical product in a 42% isolated yield. Although, *cis*-2 is stable towards hydrolysis in a solid state, it seems to hydrolyze slowly in solutions to yield unidentified off-white solid (see Table 1. Especially, acidic impurities noticeably hasten this decomposition. Yellow solid *cis*-2 was crystallized from hot hexane and its molecular structure was verified by X-ray crystallography). The asymmetric unit contains two chemically identical molecules. As expected according to spectral characterization, the compound is formed of mononuclear units in which one oxo ligand, two phenolato oxygen atoms and two methyl groups (at *cis* positions) are bonded to the central tungsten atom. The weakly bonded nitrogen from the chelate ligand fulfils the distorted octahedral coordination around the W(VI) ion (Fig. 1, only one of the two molecules is presented). The W=O bond lengths are 1.697(3) and 1.703(3) Å, whereas W–O(phenolato) bond lengths are from 1.890(3) to 1.916(3) Å. Neutral N donors of the chelate backbones are bonded *trans* to the oxo ligands with the distances of 2.571(4) and 2.536(4) Å. All these bonding distances are slightly longer than found for the *cis*-dichloro precursor [9a]. The W–C(methyl) bond lengths are from 2.176(6) to 2.185(6) Å, which are typical values for tungsten(VI) alkyl complexes with oxygen-rich six-coordination [13–15]. In the high-valent transition metal aryloxides the M–O dis-

Table 1

Selected bond distances (Å) and angles ($^\circ$) for the two molecules of *cis*-2 in the asymmetric unit

	<i>cis</i> -2 ^a	<i>cis</i> -2 ^b
W–O1	1.697(3)	1.703(3)
W–O2	1.890(3)	1.916(3)
W–O3	1.913(3)	1.897(3)
W–C27	2.182(5)	2.178(5)
W–C28	2.176(6)	2.185(6)
W–N8	2.571(4)	2.536(4)
C1–O2	1.361(6)	1.364(6)
C15–O3	1.371(6)	1.364(6)
O2–W–O3	99.85(15)	103.40(14)
O2–W–C28	89.4(2)	86.62(19)
O2–W–C27	158.17(18)	159.09(19)
O3–W–C27	84.76(19)	86.2(2)
O3–W–C28	157.85(18)	155.50(18)
C27–W–C28	79.6(2)	77.8(2)
C1–O2–W	150.7(3)	141.7(3)
C15–O3–W	141.3(3)	148.8(3)
τ_1 vs τ_2	61.1(2) ^c	46.6(2) ^d

^a Parameters for a molecule labeled as W1, O1, O2, O3, C27 and so on.

^b Parameters for a molecule labeled as W2, O31, O32, O33, C47 and so on.

^c Dihedral angle between the planes C1, ..., C6 and C10, ..., C15.

^d Dihedral angle between the planes C31, ..., C36 and C40, ..., C45.

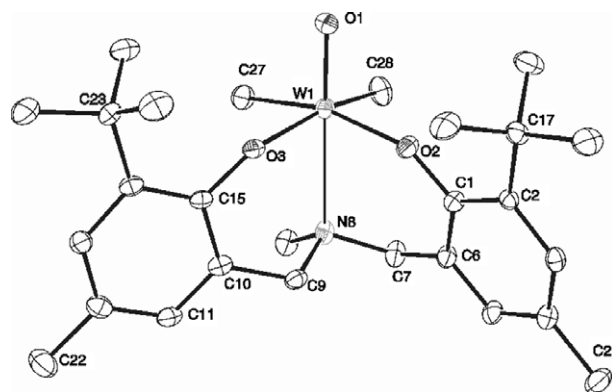


Fig. 1. Molecular structure of *cis*- $[\text{WO}(\text{L}^{\text{tBu}})\text{Me}_2]$ (*cis*-2). Thermal ellipsoids have been drawn at 30% probability level. The hydrogen atoms are omitted for the clarity.

tances are generally shorter than the values expected solely based on σ -bonding, which indicates that π -bonding (i.e. electron donation from the p-orbital of oxygen to the d-orbitals of metal) is present. Therefore, the relationship between the M–O bond distances and the degree of π -bonding for the terminal phenoxides has been widely discussed [11]. The value of the M–O–C angle can also, in theory, reflect the degree of π -donation to the metal, therefore

it has been used as an estimate of double bond character of the M–O bond. However, these parameters has proven to be particularly flexible and they may be controlled by steric properties [16,17]. In the structures presented here the W–O–C(phenyl) angles vary from 141.3(3)° to 150.7(3)°, while the relevant W–O distances are 1.913(3) Å and 1.890(3) Å, respectively. However, no clear correlation between W–O distances and W–O–C angles can be seen, thus crystal-packing forces seem to have strong effects on the bending of these bonds.

To observe whether synthesized dimethyl complex could decompose by α -elimination to produce a corresponding methylene complex we heated a toluene solution of *cis*-**2** to 100 °C in a sealed NMR tube, while the reaction was monitored by ¹H NMR. Still, this complex seems to be exceptionally stable, as no decomposition was observed after 96 h heating. Catalytic activity of *cis*-**2** in ROMP of norbornene was studied in a toluene–norbornene mixture while the overall conversion of monomer to insoluble polymers was used as a measure of activity. In our initial experiment, complex *cis*-**2** was used at 80 °C without any co-catalyst. No activity was observed under these conditions, which could be expected according to the high thermal stability of dimethyl complex. Though, when the reaction mixture was treated with a fivefold excess of organoaluminium reagent Et₂AlCl, the monomer conversions after 60 min reaction at 25 °C was *ca.* 20%. At 80 °C, *cis*-**2**/Et₂AlCl produced polynorbornene as an insoluble rubber-like material in a practically quantitative yield, which resembles the reactivity of starting complexes **1**. Thus, it seems that the non-active dimethyl complex can be activated by aluminium co-catalyst, possibly due to Et for Me exchange at high temperature. On the other hand, the Lewis acidic compounds of the main group metals are known to coordinate to the W=O moiety [18]. For example, oxotungsten–aluminium adduct [(*t*BuCH₂)₃Br–WO(AlBr₃)] with a O···Al distance of 1.79(1) Å has been structurally characterized [18b]. Related activation effects of aluminium co-catalysts have been reported in several oxo alkylidene and oxo dialkyl complexes [19–21]. Conceivably, the role of alkylaluminium co-catalysts in multi-component catalyst systems is not only to replace the labile chloro ligands, but also to improve the catalytic process by decreasing the activation energy of a catalytic cycle.

In conclusion, we have prepared stable *cis*-dimethyl complexes of oxotungsten(VI) using either *trans* or *cis* isomers of corresponding dichloro complexes as precursors. We also demonstrated that dimethyl complex do not catalyze ROMP of norbornene, but it can be activated by using Et₂AlCl as a co-catalyst.

3. Experimental section

3.1. Preparation of *cis*-[WO(ONO^{*t*Bu})Me₂] (*cis*-**2**)

Complexes *trans*-**1** and *cis*-**1** were prepared as published earlier [9a]. Other chemicals were of reagent grade and

were used as purchased. Alkylation reactions were carried out under a nitrogen atmosphere (99.999% purity) using standard bench-top techniques [22]. ¹H (500 MHz) and ¹³C NMR spectra (100 MHz) were recorded at 20 °C in CDCl₃ solutions and were referenced internally to residual solvent signal. Analytical samples were dried in vacuum at 40 °C for 2 h prior to elemental and spectral analyses.

3.1.1. From *trans*-[WO(ONO^{*t*Bu})Cl₂]

0.25 mmol (163 mg) of *trans*-**1** was dissolved in 20 ml of anhydrous diethyl ether. This red solution was treated with a solution of freshly prepared MeMgI (*ca.* 1 mmol) in diethyl ether (1 ml) while the reaction mixture turned rapidly orange. The orange solution was then stirred for an hour at room temperature. The solvent was evaporated and the orange product was purified by a silica column chromatography using a hexane–toluene mixture (1:1) as an eluent to yield 102 mg (67%) of yellow, air-stable solid product. For *cis*-**2**: Anal. Calc. for C₂₇H₄₁NO₃W: C, 53.04; H, 6.76; N, 2.29. Found C, 52.78; H, 6.44; N, 2.05%. IR (KBr): 1460 s, 1377 s, 1288 m, 1240 vs, 1213 m, 1155 s, 1135 w, 1090 w, 978 s, 934 m, 921 m, 900 m, 862 vs (br), 842 s, 765 m, 725 m, 693 w, 598 m, 573 vs, 516 m, 489 w cm⁻¹. NMR (CDCl₃, standard SiMe₄) δ_{H} : 7.205 (2H, ArH), 6.844 (2H, ArH), 3.533 (2H, br, CH₂), 3.466 (1H, CH₂), 3.440 (1H, CH₂), 2.370 (6H, ArCH₃), 2.243 (3H, NCH₃), 1.464 (18 H, C(CH₃)₃), 0.840 (6H, W(CH₃)₂). δ_{C} : 152.71, 141.36, 132.39, 128.69, 127.58, , 61.27, 47.17, 40.90, 34.90, 30.01, 21.09. M.p. > 180 °C (decomp.).

3.1.2. From *cis*-[WO(ONO^{*t*Bu})Cl₂]

0.20 mmol (130 mg) of *cis*-**1** was dissolved in 20 ml of anhydrous diethyl ether. This red solution was treated with a solution of freshly prepared MeMgI (*ca.* 1 mmol) in diethyl ether (1 ml) while the reaction mixture turned rapidly orange. The orange solution was then stirred for an hour at room temperature. The solvent was evaporated and the orange product was purified by a silica column chromatography using a hexane–toluene mixture (1:1) as an eluent to yield 51 mg (42%) of a yellow product. The ¹H and ¹³C NMR spectra of the product were identical with *cis*-**2** described above.

3.2. Catalyst studies

Polymerizations were performed at 20 °C as well as at 80 °C under a nitrogen atmosphere. Complex *cis*-**2** (2 × 10⁻⁵ mol) was dissolved in 4 ml of 1 M norbornene monomer (4.0 mmol) solution in toluene. The reaction mixture was stirred for 5 min and subsequently treated with 0.05 ml of Et₂AlCl solution (1.8 M in toluene, 9 × 10⁻⁵ mol). After 60 min stirring (at 25 °C or 80 °C) the viscous solution was treated with 10 ml of methanol to precipitate formed polymer as a white solid. Polymers were swelled in toluene, re-precipitated by methanol and dried in vacuum at 40 °C for 4 h.

3.3. X-ray crystallography

Crystals of *cis-2* suitable for single crystal X-ray were grown upon slow cooling from hot hexane (50 mg of complex in 5 ml of solvent). Single-crystal data collections, reduction and subsequent calculations were essentially as described in other related papers from our laboratory [9]. *Crystal data*: C₂₇H₄₁NO₃W (*cis-2*); MW 611.46; orange blocks; size (mm) 0.24 × 0.22 × 0.18, monoclinic; space group *P*2₁/*c*; *Z* = 8; *a* = 11.5770(2) Å; *b* = 16.0458(2) Å; *c* = 29.3642(4) Å; β = 99.6770(10)°; *V* = 5377.14(14) Å³; *D*_c = 1.511 Mg m⁻³; 12051 unique reflections (*R*(int) = 0.0618), 9436 observed (*I* > 2σ(*I*)), data/restraints/parameters = 12051/0/599, *R*₁ = 0.0437, *wR*₂ = 0.0653 (on *I* > 2σ(*I*)), *R*₁ = 0.0665, *wR*₂ = 0.0717 on all data.

Appendix A. Supplementary material

CCDC 632606 contains the supplementary crystallographic data for *cis-2*. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.02.018](https://doi.org/10.1016/j.jorganchem.2007.02.018).

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