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Synthesis of novel oxo complexes of tungsten and molybdenum with various chalcogen-bridged chelating bis(aryloxo) ligands and their catalytic behavior for ring-opening metathesis polymerization

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Abstract

Oxo tungsten complexes coordinated by O–E–O (E = S, Te, CH₂) chelating bis(aryloxo) ligands, WO[E(4-Me-6-^tBuC₆H₂O)₂]Cl₂ (**1**: E = S, **2**: E = Te, **3**: E = CH₂), were synthesized by the reaction of WOCl₄ with 2,2'-E(4-Me-6-^tBuC₆H₂OH)₂ [E = S (^tBu₂tbpH₂), E = Te (TebpH₂), E = CH₂ (mbpH₂)]. Similarly a molybdenum complex, MoO[S(4-Me-6-^tBuC₆H₂O)₂]Cl₂ (**4**), was also prepared. The structures of the oxodichloro tungsten complexes **1** and **3** were determined by single-crystal X-ray analysis to have pseudo C_s symmetry. A μ-oxo binuclear tungsten complex with two ^tBu₂tbp ligands, {WO[S(4-Me-6-^tBuC₆H₂O)₂]Cl₂}(μ-O) (**5**), was synthesized by refluxing a mixture of W₂O₃Cl₆ and two equivalents of ^tBu₂tbpH₂ in THF, whose structure was determined by single-crystal X-ray analysis. We study here the catalytic behavior of these complexes for the ring-opening metathesis polymerization (ROMP) of norbornene. In the catalytic systems, **1**–AlEt₃ and **2**–AlEt₃, *cis*–*trans* selectivity varies depending on the catalyst concentration and on the polymerization temperature. The resulting poly(norbornene) tend to have higher *cis*-content with increasing catalyst concentration and with lowering polymerization temperature. Oppositely, the polymerization under low catalyst concentration and at high polymerization temperature gave the *trans*-rich poly(norbornene). On the other hand, the complex **3** with the methylene-bridged bis(aryloxo) ligand did not show such a dependence of *cis*–*trans* selectivity. We proposed that these observations might come from oxotungsten–aluminum interaction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Group 6 transition metal complexes; Chalcogen-bridged bis(aryloxo) ligands; Ring-opening metathesis polymerization; Stereo selectivity

1. Introduction

Schrock and co-workers show the catalytic activity of the Group 6 metal alkylidene complexes bearing imido, alkoxy and other groups for ring-opening metathesis polymerization (ROMP) [1]. However, the systematic studies of controlling the stereoselectivity of the catalysts for ROMP of cyclic olefins are relatively rare [2]. We have prepared a series of new dialkyl tungsten complexes bearing diphenylacetylene and O–S–O tridentate chelating diaryloxo ligands, W(η²-PhC≡CPh)(^tBu₂tbp)R₂ (^tBu₂tbp = 2,2'-S(4-Me-6-^tBu-C₆H₂O)₂; R = CH₂SiMe₃, CH₂Ph, CH₃), which initiate the ROMP of norbornene to give poly(norbornene)

having high molecular weight ($M_n = 1.7 \times 10^6$) and high *cis*-content (*cis* 93%) at the early stage of the reaction [3]. The high *cis*-content could be attributed to the steric repulsion between the acetylene ligand and the five membered ring of the monomer. When the bridging atom of the chelating aryloxo ligand was changed from sulfur to tellurium, the resulting poly(norbornene) were found to be *trans*-rich [4]. Thus the *cis*-contents of the poly(norbornene) were controlled in the wide range by designing our catalyst precursors, although the activities of these catalyst systems were rather low.

On the other hand, various oxotungsten based catalysts such as WO(CHCM_e)(PEt₃)Cl₂ [5], WOCl₂(OC₆H₂Br₂-2,6)–PbEt₄ [6], WO(η²-diphenylcyclopropene)Cl₂(PX₃)₂ (PX₃ = P(OMe)₃, PMePh₂) [7], Tp'WO(=CHCMe₃)Cl (Tp' = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) [8], and WOCl₂(OAr)₂–ⁿBu₃SnH [9] have been known to show high activity for metathesis

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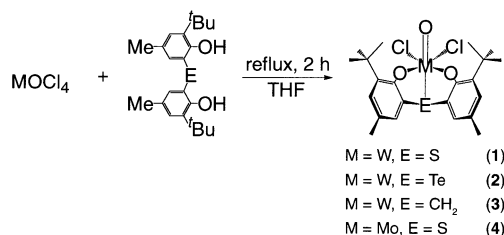
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reactions including ROMP. We have also reported that *trans*-dichloro(oxo)tungsten complexes and the *trans*-dialkyl(oxo)tungsten complex bearing O–N–O tridentate ligands, $\text{WOX}_2\{(\text{OCR}_1^1\text{CH}_2)(\text{OCR}_2^2\text{CH}_2)(\text{NC}_5\text{H}_3)\}$ ($\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{X} = \text{Cl}$; $\text{R}^1 = \text{R}^2 = i\text{-Pr}$, $\text{X} = \text{Cl}$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$, $\text{X} = \text{Cl}$; $\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{X} = \text{CH}_2\text{SiMe}_3$), catalyze the ROMP of norbornene upon activation with AlEt_3 to give poly(norbornene). These complexes enable the effective control of the *cis*–*trans* selectivity depending on the substituents on the ligands [10]. We recently reported an oxo tungsten complex coordinated with an O–S–O chelating bis(aryloxo) ligand, $\text{WO}(\text{}^t\text{Bu}_2\text{tbp})\text{Cl}_2$ (**1**), and its catalytic behavior for ROMP [11]. In order to elucidate the effect of the chalcogen bridging atom of bis(aryloxo) ligand in our catalyst system, we prepared the chelating bis(aryloxo) ligands bridged by various groups. Here we report the synthesis of a series of oxotungsten complex coordinated with O–E–O chelating bis(aryloxo) ligands, $\text{MO}[\text{E}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]\text{Cl}_2$ ($\text{M} = \text{Mo}$, W ; $\text{E} = \text{S}$, Te , CH_2), and their catalytic behavior for ROMP of norbornene. An μ -oxo binuclear derivative was also investigated as one of the rare examples of the tungsten complexes having an O–W–O–W=O unit.

2. Results and discussion

2.1. Preparation and characterization of oxotungsten complexes 1–5

Refluxing a mixture of MOCl_4 ($\text{M} = \text{Mo}$, W) and one equivalent of $2,2'\text{-E}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{OH})_2$ [$\text{E} = \text{S}$ (${}^t\text{Bu}_2\text{tbpH}_2$), Te (TebpH_2), CH_2 (mbpH_2)] in THF generated the oxodichloro complexes, $\text{MO}[\text{E}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]\text{Cl}_2$ (**1**: $\text{M} = \text{W}$, $\text{E} = \text{S}$, **2**: $\text{M} = \text{W}$, $\text{E} = \text{Te}$, **3**: $\text{M} = \text{W}$, $\text{E} = \text{CH}_2$, **4**: $\text{M} = \text{Mo}$, $\text{E} = \text{S}$), as black or dark green crystals (Scheme 1). The ${}^1\text{H-NMR}$ spectra of the complexes **1–4** showed one singlet for the protons of the two *tert*-butyl substituents and one singlet for the protons of the two methyl substituents, while the aromatic protons at three- and five-positions appeared as two doublets. The signals for the methylene protons of the methylene-bridged bis(aryloxo) ligand in **3** appeared as two doublets (${}^2J_{\text{HH}} = 16.0$ Hz) at 3.99 and 3.69 ppm. These data together with the ${}^1\text{H-}^1\text{H}$ NOESY,



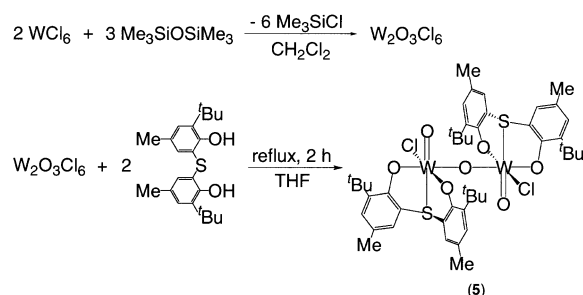
Scheme 1.

HMQC and HMBC spectra of **1–4** suggested that these complexes had C_s symmetric structure, which was also supported by X-ray crystallography of **1** [11] and **3** (vide infra).

A μ -oxo complex, $[\text{WO}(\text{}^t\text{Bu}_2\text{tbp})\text{Cl}]_2(\mu\text{-O})$ (**5**), was synthesized by the 2:1 reaction of ${}^t\text{Bu}_2\text{tbpH}_2$ with $\text{W}_2\text{O}_3\text{Cl}_6$ (Scheme 2), which was prepared from the reaction of three equivalents of hexamethyldisiloxane ($(\text{Me}_3\text{Si})_2\text{O}$) with two equivalents of WCl_6 in dichloromethane [12]. The ${}^1\text{H-NMR}$ spectrum of **5** showed two singlets for the protons of the *tert*-butyl substituents, two singlets for the methyl substituents, and four doublets (${}^4J_{\text{HH}} = 1.8$ Hz) for the aromatic protons.

2.2. Molecular structure of oxotungsten complexes 3 and 5 by X-ray analysis

Figs. 1–3 demonstrate the molecular structures of **1** [11], **3** and **5** elucidated by X-ray crystallographic analyses and Table 1 summarizes the selected bond distances and angles. The coordination sphere around the tungsten center in **1** and **5** can be described as pseudooctahedral in which the terminal oxo ligand is located at *trans*-position to sulfur. The complex **5** has a crystallographic center of symmetry at the $\mu\text{-O}$ atom. The crystal structure of **3** revealed the square pyramidal configuration in which the oxo ligand occupies an apical position. The tungsten–sulfur bond lengths in **1** (2.751(4) Å) and in **5** (2.749(1) Å) are the longest one among those in the reported tungsten thioether complexes [3,4]. This is probably due to the strong electron donation from the *trans*-oxo ligand. The ${}^t\text{Bu}_2\text{tbp}$ and *mbp* ligands in **1**, **3** and **5** adopts the typical boat conformations observed in other complexes with ${}^t\text{Bu}_2\text{tbp}$ or *mbp* ligands [13]. The W–O (aryloxo) distances in the ${}^t\text{Bu}_2\text{tbp}$ complexes **1** (av. 1.91 Å) are longer than those in the *mbp* complex **3** (av. 1.854 Å) and those found for tungsten complexes with monodentate aryloxo ligands such as *cis*- $\text{WCl}_4(\text{OC}_6\text{H}_3\text{-2,6-Ph}_2)_2$ (av. 1.846 Å) [14], $\text{WCl}_3(\text{OC}_6\text{H}_3\text{-2,6-Ph}_2)_2(\text{thf})$ (av. 1.856 Å) [14], *mer*- $\text{WCl}_3(\text{OC}_6\text{H}_3\text{-2,6-Pr}_2)_3$ (av. 1.840 Å) [15], *cis*- $\text{WCl}_2(\text{OPh})_4$ (av. 1.81 Å) [16], *cis*- $\text{WCl}_4(\text{OC}_6\text{H}_3\text{-2,6-Pr}_2)_2$ (av. 1.805 Å) [17], $\text{W}(\text{OC}_6\text{H}_3\text{-2,6-Pr}_2)_4$ (av. 1.854 Å) [18], $\text{WCl}_2(\text{OC}_6\text{H}_3\text{-2,6-Br}_2)_2$



Scheme 2.

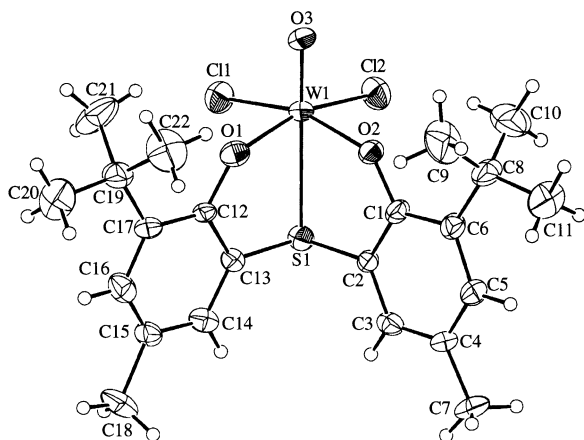


Fig. 1. ORTEP drawing of $\text{WO}(\text{t-Bu}_2\text{tbp})\text{Cl}_2$ (**1**) with numbering scheme.

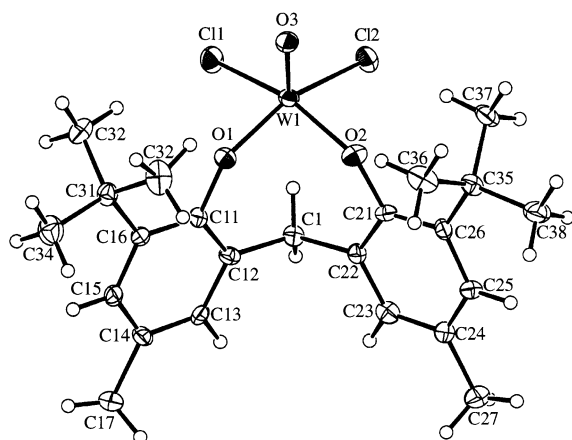


Fig. 2. ORTEP drawing of $\text{WO}(\text{mbp})\text{Cl}_2$ (**3**) with numbering scheme.

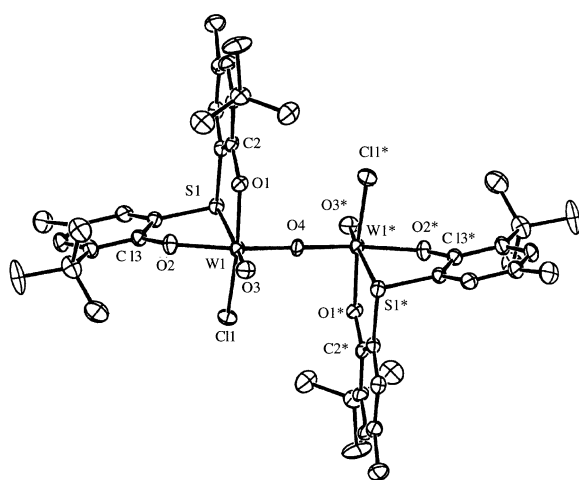


Fig. 3. ORTEP drawing of $[\text{WO}(\text{t-Bu}_2\text{tbp})\text{Cl}_2](\mu\text{-O})$ (**5**) with numbering scheme. Hydrogen atoms and solvent molecules are omitted for clarity.

(av. 1.857 Å) [6], and $\text{WOCl}_2(\text{OC}_6\text{H}_3\text{-2,6-Pr}_2)_2$ (av. 1.832 Å) [9]. The $\text{W}=\text{O}$ bond distance of **1** (1.69(1) Å) is also

Table 1
Selected bond distances (Å) and angles (°) for **1**, **3** and **5**

Complex	1 ^a	3	5
<i>Bond distances</i>			
W=O	1.69(1)	1.683(5)	1.682(3)
W–O	1.90(1) (O1) 1.92(1) (O2)	1.851(4) (O1) 1.857(4) (O2)	1.895(4) (O1) 1.907(4) (O2)
W–E (CH ₂ , S)	2.751(4)	3.172(6)	1.8687(2) (μ-O)
W–Cl	2.324(5) (Cl1) 2.324(5) (Cl2)	2.3214(18) (Cl1) 2.3250(18) (Cl2)	2.334(2)
<i>Bond angles</i>			
O–W–O	93.0(5)	89.9(2)	88.9(2)
C–E–C (CH ₂ , S)	102.9(3)	116.9(5)	104.0(2)
Cl–W–Cl	98.78(9)	85.29(7)	–
W–O–C	132(1) (O1) 133(1) (O2)	142.2(4) (O1) 143.6(4) (O2)	133.7(3) (O1) 132.0(3) (O2)

^a Reference [11].

longer than that of **3** (1.683(4) Å). The coordination of the bridging sulfur atom in **1** should make the tungsten center less electron-deficient to result in the decreased π -donation from the oxygen atoms to the metal center in **1**. The $\text{W}-\text{O}(\mu\text{-O})$ bond distance of **5** is 1.8687(2) Å, which is shorter than those of $\{\text{WO}(\text{CH}_2\text{CMe}_3)_2\}_2(\mu\text{-O})$ (**6**: 1.977 and 1.923 Å) [19], $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WO}_2(\mu\text{-O})\text{WO}(\text{CO})\{\text{HB}(\text{Me}_2\text{pz})_3\}$ (**7**: 1.912 Å) [20], and of $[\{\text{W}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CH}_2\text{CH}_3)\}(\mu\text{-O})\{\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{O})(\text{CH}_2\text{CH}_3)\}]\text{PF}_6$ (1.78 and 2.03 Å) [21].

2.3. Polymerization of norbornene by **1–5**– AlEt_3

Without cocatalyst, the complexes **1–5** showed no catalytic activity for the polymerization of norbornene at room temperature. The complexes **1–4** were found to be activated by AlEt_3 and Tables 2–5 summarized the results of polymerizations. In the polymerization of norbornene by the sulfur-bridged complex **1**– AlEt_3 system, the lower catalyst concentration ($[\text{W}] \leq 2.5$ mM) was more suitable to achieve high polymer yield (Table 2). The *cis*-content of the resulting polymer was found to decrease with decreasing catalyst concentration. As shown in Table 3, the resulting polymer had high *cis*-content (*cis* 88%) at lower polymerization temperature (–15 °C). By raising polymerization temperature, the *cis*-selectivity of the catalyst decreased and the *trans*-rich polymers were produced above ca. 90 °C [11]. The catalytic activity of **1**– AlEt_3 varies depending upon the Al–W ratio, and the 1:1 ratio of **1**: AlEt_3 gave the maximum yield (Table 4). The tellurium-bridged complex **2**– AlEt_3 system showed generally similar catalytic behaviors to those of the **1**– AlEt_3 system. The *cis*-content of the resulting polymer was found to decrease with decreasing catalyst concentration at 60 °C (Table 2), and with at rising the polymerization temperature (Table 3). Thus, in the **1**– AlEt_3 and **2**– AlEt_3 systems, *cis*-rich polymers were produced by the

Table 2

Effects of the concentration of **1**–**3** on the ROMP of norbornene by using $\text{WO}[\text{E}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]\text{Cl}_2$ [**1**: E = S, **2**: E = Te, **3**: E = CH_2], at 60 °C

Complex	[W] (mM)	Yield ^a (%)	$M_n/10^4$ ^b	M_w/M_n ^b	<i>cis</i> -Content ^c
1 ^d	10	70	47	1.6	58
1 ^d	5.0	69	26	2.0	54
1 ^d	2.5	99	13	2.3	52
1 ^d	1.0	96	6.0	1.7	37
1 ^d	0.1	98	6.6	1.7	32
2	10	63	19	1.2	57
2	5.0	62	68	1.8	52
2	2.5	52	130	1.2	41
2	1.0	53	170	3.4	36
2	0.5	47	110	1.3	30
3	10	65	43	1.6	65
3	5.0	63	52	1.4	65
3	2.5	61	45	1.7	66
3	1.0	65	35	1.8	65
3	0.5	64	21	1.6	68

In toluene, $[\text{Monomer}]_0/[\text{W}] = 100$, $[\text{AlEt}_3]/[\text{W}] = 1$, time = 1 h.^a Methanol-insoluble fraction.^b Determined by GPC analysis in THF calibrated with standard poly(styrene). Theoretical M_n value is less than the experimental one [29].^c *cis*-Content of double bonds in polymer as determined by ¹H-NMR spectra [29–31].^d Reference [11].

polymerization at low temperature and/or by that under high catalyst concentration. In sharp contrast to these behaviors, the polymerization under dilute condition and/or that at high temperature gave *trans*-rich polymers. These observations differ from that of the corresponding acetylene complexes, in which the *cis*–*trans* selectivity was not so affected by polymerization concentration and temperature [3,4]. In comparison with the corresponding acetylene complex, the **1**–

AlEt_3 and **2**– AlEt_3 systems showed higher catalytic activity to give poly(norbornene) with similar molecular weights. This **2**– AlEt_3 system gave the polymers with high *cis*-content at 0 °C regardless of the catalyst concentrations (Table 5). In general, **1**– AlEt_3 system showed higher *cis*–*trans* selectivity than that of the **2**– AlEt_3 system.

In contrast to **1** and **2**, the *cis*–*trans* selectivity of the methylene-bridged complex **3**– AlEt_3 was found to be

Table 3

Effects of polymerization temperature on the ROMP of norbornene by using $\text{MO}[\text{E}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]\text{Cl}_2$ [**1**: M = W, E = S, **2**: M = W, E = Te, **3**: M = W, E = CH_2 , **4**: M = Mo, E = S]

Complex	Temperature (°C)	Yield ^a (%)	$M_n/10^4$ ^b	M_w/M_n ^b	<i>Cis</i> -Content ^c
1 ^d	60	< 1	–	–	–
1 ^e	–15	37	23	2.6	88
1 ^e	0	42	25	2.1	80
1 ^e	60	70	47	1.6	58
1 ^e	110	64	11	2.0	31
2	–15	75	> 200	–	84
2	0	74	72	2.3	77
2	60	63	19	1.2	57
2	110	72	58	2.2	47
3	–15	< 1	–	–	–
3	0	64	55	1.7	67
3	60	65	43	1.6	65
3	110	67	120	1.3	33
4	30	51	7.4	2.1	48
4	60	52	20	2.0	44
5	60	< 1	–	–	–

In toluene, $[\text{M}] = 10$ mM, $[\text{Monomer}]_0/[\text{M}] = 100$, $[\text{AlEt}_3]/[\text{M}] = 1$, time = 1 h.^a Methanol-insoluble fraction.^b Determined by GPC analysis in THF calibrated with standard poly(styrene). Theoretical M_n value is less than the experimental one [29].^c *cis*-Content of double bonds in polymer as determined by ¹H-NMR spectra [29–31].^d The cocatalyst is not added.^e Reference [11].

Table 4
Effects of the amount of AlEt₃ on the ROMP of norbornene by using **1**-AlEt₃ at 60 °C

[AlEt ₃]/[W]	Yield ^a (%)	M _n /10 ⁴ ^b	M _w /M _n ^b	cis-Content ^c
0.5	< 1	–	–	–
0.67	60	94	1.4	60
1	70	47	1.6	57
2	61	22	1.5	44
3	56	22	1.9	53
4	39	19	2.0	67
5	33	2	15.3 ^d	52

In toluene, [W] = 10 mM, [Monomer]₀/[W] = 100, time = 1 h.

^a Methanol-insoluble fraction.

^b Determined by GPC analysis in THF calibrated with standard poly(styrene). Theoretical M_n value is less than the experimental one [29].

^c cis-Content of double bonds in polymer as determined by ¹H-NMR spectra [29–31].

^d Bimodal.

Table 5
Effects of concentration on the ROMP of norbornene by using **2**-AlEt₃ at 0 °C

[W] (mM)	Yield ^a (%)	M _n /10 ⁴ ^b	M _w /M _n ^b	cis-Content ^c
10	74	72	2.3	77
5	62	110	1.4	82
2.5	52	51	1.9	83
1	45	46	1.6	83
0.5	< 1	–	–	–

In toluene, [Monomer]₀/[W] = 100, [AlEt₃]/[W] = 1, time = 1 h.

^a Methanol-insoluble fraction.

^b Determined by GPC analysis in THF calibrated with standard poly(styrene). Theoretical M_n value is less than the experimental one [29].

^c cis-Content of double bonds in polymer as determined by ¹H-NMR spectra [29–31].

almost independent of the catalyst concentration (Table 2). The **3**-AlEt₃ also gave *trans* rich-polymers at higher temperature (110 °C), while *cis*-selectivity of **3**-AlEt₃ significantly lowered than those of **1**-AlEt₃ and of **2**-AlEt₃ at 0 °C (Table 3). The catalytic activity of **3**-AlEt₃ tends to be lower than those of **1**-AlEt₃ and **2**-AlEt₃ especially at –15 °C. Thus, the coordination of sulfur or tellurium in **1** and **2** enhanced catalytic activity of the catalyst metal center for ROMP. The molybdenum complex **4**-AlEt₃ system did not show such a dependence of the *cis*–*trans* selectivity on the polymerization conditions (Table 3). The μ-oxo complex **5** showed no polymerization activity even in the presence of AlEt₃. This can be attributed the hardness of chloride ligand in **5** to be used for generation of the alkylidene species.

In order to examine the effect of the cocatalyst, we investigated the catalytic behavior of **1** in combination with various alkylaluminum reagents. Activation effects of aluminum cocatalysts have been reported in the

metathesis reactions by oxo alkylidene tungsten systems such as WO(=CHCMe₃)(PEt₃)Cl₂ [5] and Tp'WO(=CHCMe₃)Cl (Tp' = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) [8]. A theoretical study indicated that the Lewis acidic aluminum cocatalysts decrease the activation energy gap between the metallacyclic intermediate and the alkylidene complex in oxotungsten catalyst system [22]. However, there was no report on the *cis*–*trans* selectivity which varies depending on the kinds of the aluminum cocatalyst. In the polymerization of norbornene by **1**-AlEtCl₂, the *cis*-content of the resulting polymer was about 40% independent from the polymerization temperature in the range from –15 to 30 °C. At high temperature (110 °C), the present system produces a slightly *trans*-rich polymer (Table 6). The **1**-AlEt₂Cl system gave *cis*-rich polymer (*cis* 77%) at low temperature (–15 °C), while *cis*-selectivity of **1**-AlEt₂Cl was almost constant at 40% in the temperature range, 0–110 °C. Thus, the *cis*-selectivity of **1**-AlEtCl₂ and **1**-AlEt₂Cl was less dependent on the polymerization conditions compared with the **1**-AlEt₃ system. We expected that the use of more bulky aluminum cocatalyst might enhance *cis*–*trans* selectivity of the catalyst system. However, the **1**-Al^{*i*}Bu₃ system showed no catalytic activity for the ROMP of norbornene at various temperature. The exceeded bulkiness of Al^{*i*}Bu₃ might hinder the generation of active species or coordination of the monomer to the active metal center.

2.4. Examination of oxotungsten **1**–aluminum interaction

The ¹H-NMR spectra of **1** did not change in the temperature range from –60 to 30 °C, suggesting no significant structural change of **1** in this temperature range. We propose that such strong dependencies of the *cis*–*trans* selectivity on the polymerization conditions in **1**-AlEt₃ and in **2**-AlEt₃ systems could come from the interaction between the oxotungsten center and the aluminum compounds, possibly by AlEtCl₂, which should be released in the reaction of **1** with AlEt₃ (Scheme 3). For example, an oxotungsten–aluminum adduct, (t-BuCH₂)₃BrWO···AlBr₃, has been isolated and crystallographically characterized as an absolute evidence for the W=O···Al interaction [23]. At high concentration and/or low temperature, the oxotungsten center would coordinate to the Lewis acidic aluminum compounds, which should restrict the direction of the coordinating monomer on the tungsten center to produce *cis*-rich polymers. With diluting the polymerization system and/or with raising polymerization temperature, the oxotungsten center would dissociate from the aluminum compounds to decrease *cis*-selectivity for the ROMP of norbornene. In the **3**-AlEt₃ system, the oxotungsten–aluminum interaction would be much weaker than in the **1**-AlEt₃ due to the higher electron-deficiency of **3** as indicated by X-ray analysis, which

Table 6
Effects of cocatalysts on the ROMP of norbornene by using **1**

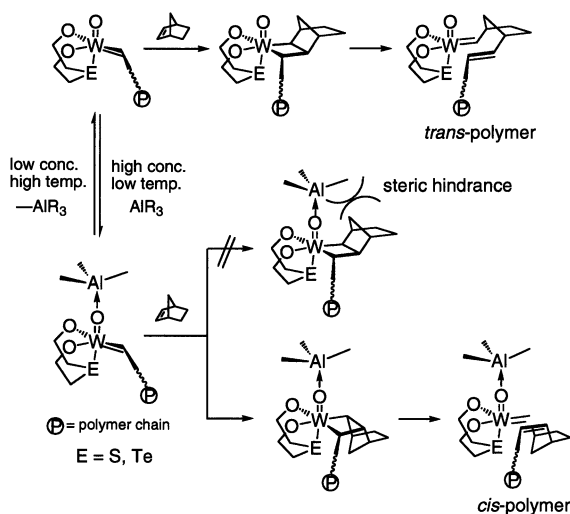
Cocatalyst	Temperature (°C)	Yield ^a (%)	$M_n/10^4$ ^b	M_w/M_n ^b	<i>cis</i> -Content ^c
EtAlCl ₂	-15	76	> 200	–	37
EtAlCl ₂	0	77	> 200	–	39
EtAlCl ₂	30	81	19	2.0	37
EtAlCl ₂	110	60	9.9	4.0	31
Et ₂ AlCl	-15	71	120	1.5	77
Et ₂ AlCl	0	72	110	1.7	39
Et ₂ AlCl	30	75	84	2.1	40
Et ₂ AlCl	110	82	19	1.5	40

In toluene, [W] = 10 mM, [Monomer]₀/[W] = 100, [EtAlCl₂]/[W] = 2, [Et₂AlCl]/[W] = 1, time = 1 h.

^a Methanol-insoluble fraction.

^b Determined by GPC analysis in THF calibrated with standard poly(styrene). Theoretical M_n value is less than the experimental one [29].

^c *cis*-Content of double bonds in polymer as determined by ¹H-NMR spectra [29–31].



Scheme 3.

should bring the weak dependence of the *cis*–*trans* selectivity on the polymerization conditions in the **3**–AlEt₃ system. The oxotungsten–aluminum interaction was investigated in a model system: **1** and Al(O^{*i*}Pr)₃. The ¹H–¹H NOESY spectrum of a 1:1 mixture of **1** and Al(O^{*i*}Pr)₃ in toluene-*d*₈ ([W] = [Al] = 20 mM) showed a correlation between *tert*-butyl protons of **1** and methyne protons of Al(O^{*i*}Pr)₃ at -50 °C (Fig. 4) but did not show such a correlation at 30 °C. Thus, **1** proved to associate reversibly with the aluminum compound depending on the conditions. This oxotungsten–aluminum interaction may enhance not only the *cis*-selectivity but also the catalytic activity.

3. Conclusion

We prepared new oxotungsten complexes having bis(aryloxo) ligands, WO[S(4-Me-6-^{*t*}BuC₆H₂O)₂]Cl₂ (**1**), WO[Te(4-Me-6-^{*t*}BuC₆H₂O)₂]Cl₂ (**2**), WO[CH₂(4-Me-6-^{*t*}BuC₆H₂O)₂]Cl₂ (**3**), MoO[S(4-Me-6-^{*t*}Bu-

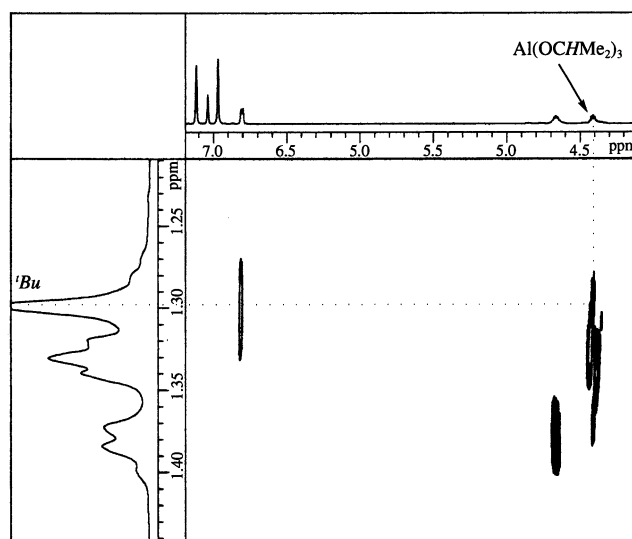


Fig. 4. NOESY spectrum of a 1:1 mixture of WO(*t*-Bu₂tbp)Cl₂ (**1**) and Al(O^{*i*}Pr)₃ at -50 °C.

C₆H₂O)₂]Cl₂ (**4**), and [WO{S(4-Me-6-^{*t*}BuC₆H₂O)₂}-Cl]₂(μ-O) (**5**). The molecular structures of **1**, **3** and **5** were determined by single-crystal X-ray analysis. The catalyst systems **1**–AlEt₃ and **2**–AlEt₃ showed strong dependence of *cis*–*trans* selectivity on the catalyst concentration and the polymerization temperature in the ROMP of norbornene. The *cis*-rich poly(norbornene) were produced under high monomer concentration and/or at low polymerization temperature, possibly due to the formation of oxotungsten–aluminum adducts. In the **3**–AlEt₃ system, such strong dependence of the *cis*–*trans* selectivity on the polymerization conditions was not observed. We suppose that these observations may be related to the bulkiness of cocatalyst and the kind of bridging atoms of the bis(aryloxo) ligands. In the comparison with the corresponding acetylene complex, W(η²-PhC≡CPh){S(4-Me-6-^{*t*}BuC₆H₂O)₂}Cl₂, the oxo complex **1** showed higher activity for the ROMP of norbornene to give the polymers with similar

molecular weight and with variable *cis*-content depending on the polymerization conditions.

4. Experimental

4.1. General considerations

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by the use of standard Schlenk techniques under an argon atmosphere. Hexane, THF, toluene, and *n*-pentane were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. Dichloromethane was distilled under argon after drying over phosphorus pentoxide. Benzene-*d*₆ and toluene-*d*₈ were distilled from Na–K alloy and thoroughly degassed by trap-to-trap distillation before use. Norbornene (bicyclo[2,2,1]hept-2-ene) purchased from the Aldrich Chemical Co. was refluxed over sodium and distilled prior to use. WOCl₄ [24] and 2,2'-tellurium bis(4-methyl-6-*tert*-butylphenol) [14] were prepared according to the literature. 2,2'-Thiobis(4-methyl-6-*tert*-butylphenol) was supplied by Ciba–Geigy AG, and 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol) was supplied by Nacal tesque.

The ¹H (500, 400 and 270 MHz), and ¹³C (125, 100 and 67.5 MHz) NMR spectra in benzene-*d*₆ and toluene-*d*₈ were measured on JEOL JNM-LA500, JEOL JNM-GSX400 and JEOL JNM-EX270 spectrometers. Assignments of ¹H and ¹³C-NMR peaks for some complexes were aided by 2D ¹H–¹H NOESY, 2D ¹H–¹H COSY, 2D HMQC and 2D HMBC spectra. Elemental analyses were performed at Elemental Analysis Center, Faculty of Science, Osaka University. All melting points of the complexes were measured in sealed tubes under an argon atmosphere and were not corrected. ESIMS measurements were performed on a Perkin–Elmer/Sciex API III plus spectrometer.

4.2. Preparation of WO[S(4-Me-6-*t*BuC₆H₂O)₂]Cl₂ (1)

A solution of 2,2'-S(4-Me-6-*t*BuC₆H₂OH)₂ (0.35 g, 0.97 mmol) in THF (5 ml) was added to a solution of WOCl₄ (0.33 g, 0.97 mmol) in THF (35 ml) at –78 °C. The reaction mixture was stirred for 10 min and then allowed to warm to ambient temperature. The color of the solution changed from red to dark red. After refluxing the mixture for the solution 2 h, all volatiles were removed under reduced pressure to give microcrystals. Recrystallization from a mixture of toluene and *n*-pentane gave WO[S(4-Me-6-*t*BuC₆H₂O)₂]Cl₂ (1) (0.32 g, 53%) as black crystals, m.p. 255–260 °C (dec.). ¹H-NMR (C₆D₆, 30 °C, 500 MHz): δ 7.18–7.05 (m, 7H, toluene), 7.03 (d, ⁴J_{HH} = 1.97 Hz, 2H, 3-C₆H₂O), 6.93

(d, ⁴J_{HH} = 1.96 Hz, 2H, 5-C₆H₂O), 2.16 (s, 4.2H, toluene), 2.00 (s, 6H, 4-Me), 1.37 (s, 18H, 6-*t*Bu). ¹³C-NMR (C₆D₆, 30 °C, 125 MHz): δ 160.3 (1-C₆H₂O), 143.2 (6-C₆H₂O), 137.5 (4-C₆H₂O), 130.4 (5-C₆H₂O), 132.0 (3-C₆H₂O), 132.0 (2-C₆H₂O), 35.5 (6-CMe₃), 29.9 (6-CMe₃), 20.1 (4-Me). Anal. Calc. for C₂₂H₂₈Cl₂O₃S₁W₁·1.4 C₇H₈: C, 50.50; H, 5.22. Found: C, 50.47; H, 5.51%. ESIMS (MeCN) *m/z* 628 [M⁺].

4.3. Preparation of WO[Te(4-Me-6-*t*BuC₆H₂O)₂]Cl₂ (2)

A solution of 2,2'-Te(4-Me-6-*t*BuC₆H₂OH)₂ (0.40 g, 0.875 mmol) in THF (5 ml) was added to a solution of WOCl₄ (0.30 g, 0.875 mmol) in THF (35 ml) at –78 °C. The reaction mixture was stirred for 10 min and then allowed to warm to ambient temperature. The color of the solution changed from blue to dark red. After refluxing the solution for 2 h, the color changed from dark red to dark green. All volatiles were removed under reduced pressure to give microcrystals. Recrystallization from a mixture of THF and hexane gave WO[Te(4-Me-6-*t*BuC₆H₂O)₂]Cl₂ (2) (0.39 g, 62%) as dark green crystals, m.p. 239–241 °C (dec.). ¹H-NMR (C₆D₆, 30 °C, 400 MHz): δ 7.19 (d, ⁴J_{HH} = 2.14 Hz, 2H, 3-C₆H₂O), 6.98 (d, ⁴J_{HH} = 2.06 Hz, 2H, 5-C₆H₂O), 2.00 (s, 6H, 4-Me), 1.44 (s, 18H, 6-*t*Bu). Anal. Calc. for C₂₂H₂₈Cl₂O₃Te₁W₁: C, 36.56; H, 3.90. Found: C, 36.48; H, 3.92%. ESIMS (THF) *m/z* 724 [M⁺].

4.4. Preparation of WO[CH₂(4-Me-6-*t*BuC₆H₂O)₂]Cl₂ (3)

A solution of 2,2'-CH₂(4-Me-6-*t*BuC₆H₂OH)₂ (0.36 g, 1.05 mmol) in toluene (5 ml) was added to a solution of WOCl₄ (0.36 g, 1.05 mmol) in a mixture of toluene (35 ml) and THF (5 ml) at –78 °C. The reaction mixture was stirred for 10 min and then allowed to warm to ambient temperature followed by refluxing for 2 h. The color of the solution changed from orange to black. All volatiles were removed under reduced pressure to give microcrystals. Recrystallization from a mixture of toluene and hexane gave WO[CH₂(4-Me-6-*t*BuC₆H₂O)₂]Cl₂ (3) (0.11 g, 18%) as black crystals, m.p. 240–245 °C (dec.). ¹H-NMR (C₆D₆, 30 °C, 500 MHz): δ 6.90 (d, ⁴J_{HH} = 1.60 Hz, 2H, 3-C₆H₂O), 6.62 (d, ⁴J_{HH} = 1.50 Hz, 2H, 5-C₆H₂O), 3.99 (d, ²JH²H¹ = 16.03 Hz, 1H, CH²H¹), 3.69 (d, ²JH¹H² = 16.03 Hz, 1H, CH¹H²), 2.11 (s, 6H, 4-Me), 1.40 (s, 18H, 6-*t*Bu). ¹³C-NMR (C₆D₆, 30 °C, 125 MHz): δ 157.9 (1-C₆H₂O), 142.0 (6-C₆H₂O), 137.6 (4-C₆H₂O), 134.0 (2-C₆H₂O), 128.3 (3-C₆H₂O), 126.7 (5-C₆H₂O), 40.35 (–CH₂–), 35.2 (6-CMe₃), 30.5 (6-CMe₃), 21.0 (4-Me). Anal. Calc. for C₂₃H₃₀Cl₂O₃W₁: C, 45.34; H, 4.96. Found: C, 45.04; H, 5.04%. ESIMS (THF) *m/z* 609 [M⁺].

4.5. Preparation of $\text{MoO}[S(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]_2\text{Cl}_2$ (**4**)

A solution of MoOCl_4 (0.28 g, 1.11 mmol) was added to toluene (30 ml) at -78°C , and a mixture was added to a solution of $2,2'\text{-S}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{OH})_2$ (0.40 g, 1.11 mmol) in toluene (5 ml) at -78°C . The reaction mixture was stirred for 10 min and then allowed to warm to ambient temperature, followed by refluxing for 2.5 h. The color of the solution changed from purple to dark red. The precipitates were removed by centrifugation. All volatiles were removed under reduced pressure to give microcrystals. Recrystallization from a mixture of toluene and hexane gave $\text{MoO}[S(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]_2\text{Cl}_2$ (**4**) (0.53 g, 88%) as black crystals, m.p. $229\text{--}231^\circ\text{C}$ (dec.). $^1\text{H-NMR}$ (C_6D_6 , 30°C , 500 MHz): δ 7.18–7.05 (m, 1.5H, *toluene*), 6.94 (d, $^4J_{\text{HH}} = 1.37$ Hz, 2H, 3- $\text{C}_6\text{H}_2\text{O}$), 6.81 (d, $^4J_{\text{HH}} = 1.37$ Hz, 2H, 5- $\text{C}_6\text{H}_2\text{O}$), 2.16 (s, 0.9H, *toluene*), 1.89 (s, 6H, 4-*Me*), 1.30 (s, 18H, 6- ^tBu). $^{13}\text{C-NMR}$ (C_6D_6 , 30°C , 125 MHz): δ 162.6 (1- $\text{C}_6\text{H}_2\text{O}$), 142.2 (6- $\text{C}_6\text{H}_2\text{O}$), 139.8 (4- $\text{C}_6\text{H}_2\text{O}$), 130.1 (5- $\text{C}_6\text{H}_2\text{O}$), 132.9 (3- $\text{C}_6\text{H}_2\text{O}$), 129.0 (2- $\text{C}_6\text{H}_2\text{O}$), 36.0 (6- CMe_3), 29.9 (6- CMe_3), 21.3 (4-*Me*). Anal. Calc. for $\text{C}_{22}\text{H}_{28}\text{Cl}_2\text{MoO}_1\text{O}_3\text{S}_1 \cdot 0.3\text{C}_7\text{H}_8$: C, 51.05; H, 5.40. Found: C, 51.12; H, 5.29%. ESIMS (THF) m/z 540 [M^-].

4.6. Preparation of $\{\text{WO}[S(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]_2\text{Cl}\}_2(\mu\text{-O})$ (**5**)

A dichloromethane solution of $(\text{Me}_3\text{Si})_2\text{O}$ (0.19 g, 1.20 mmol) was added dropwise to a suspension of WCl_6 (0.32 g, 0.80 mmol) in dichloromethane (20 ml) at room temperature (r.t.) over a period of 15 min. An immediate reaction ensued leading to deposition of $\text{W}_2\text{O}_3\text{Cl}_6$ in the form of yellow powder. The mixture was stirred for further 60 min. The supernatant liquor was then removed by cannula and the solid was collected, washed with hexane and dried in vacuo. A solution of $\text{W}_2\text{O}_3\text{Cl}_6$ (0.35 g, 0.56 mmol) in toluene (30 ml) was added to a solution of $2,2'\text{-S}(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{OH})_2$ (0.45 g, 1.11 mmol) in toluene (5 ml) at -78°C . The reaction mixture was stirred for 10 min and then allowed to warm to ambient temperature, followed by refluxing for 2.5 h. The color of the solution changed from purple to black. The precipitates were removed by a centrifugation. All volatiles were removed under reduced pressure to give microcrystals. Recrystallization from a mixture of toluene and hexane gave $\{\text{WO}[S(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]_2\text{Cl}\}_2(\mu\text{-O})$ (**5**) (0.087 g, 13%) as black crystals. $^1\text{H-NMR}$ (C_6D_6 , 30°C , 400 MHz) δ 7.0–7.2 (10H, *toluene*), 7.11 (d, $^4J_{\text{HH}} = 1.84$ Hz, 2H, 3- $\text{C}_6\text{H}_2\text{O}$), 7.08 (d, $^4J_{\text{HH}} = 1.81$ Hz, 2H, 3- $\text{C}_6\text{H}_2\text{O}$), 6.98 (d, $^4J_{\text{HH}} = 1.87$ Hz, 2H, 5- $\text{C}_6\text{H}_2\text{O}$), 6.95 (d, $^4J_{\text{HH}} = 1.59$ Hz, 2H, 5- $\text{C}_6\text{H}_2\text{O}$), 2.15 (s, 6H, *toluene*), 1.99 (s, 6H, *Me*), 1.94 (s, 6H, *Me*), 1.57 (s, 18H, ^tBu), 1.39 (s, 18H, ^tBu). Anal. Calc. for $\{\text{WO}(^t\text{Bu}_2\text{tpb})\text{Cl}\}_2(\mu\text{-O}) \cdot 2\text{C}_7\text{H}_8 \cdot 0.33\text{C}_6\text{H}_{14}$ C,

51.01; H, 5.47. Found: C, 50.61; H, 5.63%. ESIMS (MeCN) m/z 1200 [M^-].

4.7. Polymerization of norbornene

A solution of AlEt_3 (0.01 mmol) in toluene (50 μl) was added to a solution of $\text{WO}[S(4\text{-Me-6-}^t\text{BuC}_6\text{H}_2\text{O})_2]_2\text{Cl}_2$ (**1**) (6.3 mg, 0.01 mmol) in toluene (0.5 ml) at -78°C . The reaction mixture was stirred for 10 min and then allowed to be stirred at ambient temperature for 15 min, followed by cooling to -78°C . To this solution of **1**– AlEt_3 in toluene was added a solution of norbornene (100 equivalent, 1 mmol) in toluene (0.2 ml) and toluene (0.25 ml) at -78°C . The reaction mixture was stirred for 5 min and then allowed to raise to ambient temperature. After the solution was stirred at the temperature for 1 h, a large excess of methanol was added to the resulting reddish viscous solution to precipitate a white polymer. The polymer was washed with methanol and then dried in vacuo. $^1\text{H-NMR}$ (CDCl_3 , 30°C , 270 MHz): δ 5.39(br), 2.95(br), 2.09(br), 1.92(br), 1.49(br), 1.21 (q(br)).

4.8. GPC analysis of the polymers

GPC analyses were carried out using Tosoh TSKgel HXL-H and HXL-L columns connected to a Tosoh RI-8012 detector. Samples were prepared in THF (0.1–0.3% (w/v)) and were filtered through an Advantec DISMIC-25JP filter in order to remove particulates before injection. GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) whose molecular weight ranged from 500 to 2.15×10^6 .

4.9. Crystallographic data collections and structure determination of **3** and **5**

A crystal of **3** suitable for X-ray diffraction studies was mounted on a cryoloop. The measurement of **3** was made on a Rigaku R-AXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$). Relevant crystal and data statistics are summarized in Table 7. Indexing was performed from one oscillations which were exposed for 5.0 min. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. In the case of R-AXIS Rapid imaging plate diffractometer, a symmetry-related absorption correction using the program ABCOR [25] was applied. The data were corrected for Lorentz and polarization effects. The structures of complex **3** was solved by direct methods (SHELXS-86) [26], expanded using Fourier techniques (DIRDIF-94) [27], and refined by full-matrix least-squares refinement (SHELXL-97) [28]. In the subsequent refinement the function $\sum \omega(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$

Table 7
Crystal data and collection parameters of **3** and **5**

Complex	3	5
Formula	C ₂₃ H ₃₀ Cl ₂ O ₃ W	C ₆₀ H _{62.67} Cl ₂ O ₇ S ₂ W ₂
Formula weight	609.22	1398.55
Crystal system	Monoclinic	Trigonal
Space group	C ₂ /c (#15)	R $\bar{3}$ (#148)
<i>a</i> (Å)	29.791(2)	36.378(8)
<i>b</i> (Å)	10.9653(13)	–
<i>c</i> (Å)	19.1266(13)	13.194(8)
α (°)	–	–
β (°)	128.610(2)	–
γ (°)	–	120
<i>V</i> (Å ³)	4882.2(8)	15120(9)
<i>Z</i>	8	9
<i>D</i> _{calc.} (g cm ^{−3})	1.658	1.592
<i>F</i> (000)	2400.00	6234.03
μ [Mo–K α] (cm ^{−1})	49.71	36.09
Diffractometer	R-AXIS-RAPID	AFC-5R
Temperature (K)	193 (1)	296 (1)
Scan speed (° min ^{−1})	–	16.0
Scan width (°)	–	1.00+0.3 tan θ
2 θ _{max} (°)	55.0	54.9
Unique data (<i>R</i> _{int})	5507 (0.0474)	7749 (0.018)
Number of observations	3437	4969
Number of variables	270	293
<i>R</i>	0.0418	0.033
<i>R</i> _w	0.0803 (all data)	0.033
Goodness-of-fit	0.914	1.32

and $|F_c|$ are the observed and calculated structure factors amplitudes, respectively. The agreement indices are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum \omega (F_o^2 - F_c^2)^2 / \sum \omega (F_o^2)^2]^{1/2}$. The positions of all non-hydrogen atoms for the complex was found from a difference Fourier electron density maps and refined anisotropically. All hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and kept fixed.

A crystal of **5** was sealed in a glass capillary under argon. The measurement of **5** was made on a Rigaku AFC-5R four-circle diffractometer for data collection using Mo–K α radiation. Relevant crystal and data statistics are summarized in Table 7. The unit cell parameters and the orientation matrix at 23 °C were determined by a least-squares fit to 2 θ values of 25 strong higher reflections for complex **5**. Three standard reflections were chosen and monitored every 150 reflections. Empirical absorption correction was carried out on the basis of an azimuthal scan. The unit cell parameters at 23 °C were determined by a least-squares fit to 2 θ values of 25 strong higher reflections for complex **5**. Complex **5** showed no significant intensity decay during the data collection. The structures of complex **5** was solved by direct methods (SHELXS-86 [26], expanded using Fourier techniques (DIRDIF-94) [27], refined by the full-matrix least-square method. Measured non-equivalent reflections with $I > 2.0\sigma(I)$ were used for the structure determination. In the subsequent

refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors amplitudes, respectively. The agreement indices are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum \omega (|F_o| - |F_c|)^2 / \sum \omega (|F_o|)^2]^{1/2}$ where $\omega^{-1} = \sigma^2(F_o) = [\sigma_c^2(F_o) + p^2/4(F_o^2)]$. The positions of all non-hydrogen atoms for complex **5** were found from a difference Fourier electron density map and refined anisotropically. Hydrogen atoms were refined isotropically, and the hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and constrained to ride on their respective carbon atoms.

All calculations were performed using the TEXSAN crystallographic software package, and illustrations were drawn with ORTEP.

5. Supplementary material

Crystallographic data for the structural analysis of **3** and **5** have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 172718 and 172719, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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