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Aminobis(phenolate)s of imidomolybdenum(VI) and -tungsten(VI)

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ABSTRACT

The reactions of *trans*-[MoO(ONO^{Me})Cl$_2$] **1** (ONO^{Me} = methylamino-*N*,*N*-bis(2-methylene-4,6-dimethylphenolate) dianion) and *trans*-[MoO(ONO^{tBu})Cl$_2$] **2** (ONO^{tBu} = methylamino-*N*,*N*-bis(2-methylene-4-methyl-6-*tert*-butylphenolate) dianion) with PhNCO afforded new imido molybdenum complexes *trans*-[Mo(NPh)(ONO^{Me})Cl$_2$] **3** and *trans*-[Mo(NPh)(ONO^{tBu})Cl$_2$] **4**, respectively. As analogous oxotungsten starting materials did not show similar reactivity, corresponding imido tungsten complexes were prepared by the reaction between [W(NPh)Cl$_4$] with aminobis(phenol)s. These reactions yielded *cis*- and *trans*-isomers of dichloro complexes [W(NPh)(ONO^{Me})Cl$_2$] **5** and [W(NPh)(ONO^{tBu})Cl$_2$] **6**, respectively. The molecular structures of **4**, *cis*-**6** and *trans*-**6** were verified by X-ray crystallography. Organosubstituted imido tungsten(VI) complex *cis*-[W(NPh)(ONO^{tBu})Me$_2$] **7** was prepared by the transmetallation reaction of **6** (either *cis* or *trans* isomer) with methyl magnesium iodide.

1. Introduction

The significance of transition metal imido complexes in organometallic chemistry and catalytic applications has increased while more pieces of information have gathered on their preparations, reactivities and structures [1]. Especially, the spectator ligand effect of the imido group contributes to the high reactivity of several active catalysts. For example, various molybdenum(VI) and tungsten(VI) compounds with such ligands have proven useful in a number of catalytic processes, including olefin [2] and imine [3] metathesis reactions. The π-donor property of the multiply bonded imido ligand is beneficial to stabilize the high oxidation state of a metal ion. Moreover, the electronic and steric effects of imido groups can be tuned by altering the organic part of the ligand [4]. On the synthetic point of view, the reaction of organic isocyanates with transition metal oxo compounds is frequently used to produce corresponding metal imido complexes [5,6].

We are currently looking for new synthetic methods with the aim of obtain air- and moisture-stable molybdenum(VI) and tungsten(VI) complexes as starting materials for catalytic applications [7–10]. During these investigations, we have, for example, prepared the *cis* and *trans* isomers of dichloro complexes [WO(ONO^{Me})Cl$_2$] (ONO^{Me} = methylamino-*N*,*N*-bis(2-methylene-4,6-dimethyl phenolate) dianion) and [WO(ONO^{tBu})Cl$_2$] (ONO^{tBu} = methylamino-*N*,*N*-bis(2-methylene-4-methyl-6-*tert*-butylphenolate) dianion) by a reaction of WOCl$_4$ with an appropriate aminobis(phenol) [7]. The corresponding molybdenum complex *trans*-[MoO(ONO^{Me})Cl$_2$] **1** was prepared by reaching the starting material [MoO$_2$Cl$_2$(dmf)$_2$] (dmf = dimethylformamide) with a stoichiometric amount of H$_2$ONO^{Me}, which leads to the condensation reaction of a Mo=O group with two phenol moieties of the ligand precursor [10]. All these complexes can catalyse ring-opening metathesis polymerization (ROMP) of norbornene derivatives when activated by Et$_2$AlCl co-catalyst. In present paper, we report seven new molybdenum(VI) and tungsten(VI) complexes with aminobis(phenolate) and imido ligands.

2. Results and discussion

2.1. Preparation of molybdenum complexes

The imido-for-oxo substitution reaction of transition metal compounds is typically carried out in inert solvents using organic isocyanates as imido sources. In order to prepare new molybdenum imido complexes, we selected phenyl isocyanate and monooxo complexes **1** and **2** as starting materials. Molybdenum precursors were heated with an excess of phenyl isocyanate in toluene solution at a reflux temperature. In this kind of substitution, the Mo=O fragment undergoes supposedly a [2+2] cycloaddition reaction with the N=C bond of phenyl isocyanate, which reaction is directly followed by an elimination of CO_2 to give the final imido complexes [3]. Under applied conditions, the reactions proceeded smoothly to give imido derivatives **3** and **4** in synthetically useful yields. Air-stable, deep blue complexes were isolated and purified by a silica column chromatography and finally crystallised from

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acetonitrile. The ^{1}H NMR spectra of **3** and **4** consist of sharp duplets at *ca.* 5.2 and 3.1 ppm due to the AX system for the Ar–CH_2–N methylene units, which indicates that the *trans* configuration of starting complexes has retained [10]. The molecular structure of **4** was verified also by XRD analysis (see below). Air-stable complexes **3** and **4** are soluble in common organic solvents i.e. aromatic hydrocarbons, chlorinated solvents and ethers, but they decompose slowly in alcohol solutions.

2.2. Preparation of tungsten complexes

In a preliminary experiment, we tried to carry out the imido-for-oxo substitutions with oxotungsten complexes *trans*-[WO(ONO^R)Cl_2] in a similar manner as outlined for the reactions of molybdenum analogues. However, although the attempted syntheses were repeated in various solvents (toluene, chlorobenzene and hexane) even with prolonged reaction time, no reactions were observed. The tungsten imido complexes were finally prepared by the alcoholysis reaction of [W(NPh)Cl_4] with aminobis(phenol)s H_2ONO^R in toluene solutions at reflux temperature. Under these conditions, the reactions proceeded rapidly yielding the corresponding imido dichloro complexes **5** and **6** in *ca.* 50–60% yields. ^{1}H NMR spectra of isolated dark red materials indicated the presence of both *cis* and *trans* isomers in a *ca.* 1:4 ratio. Isomeric mixtures were separated by column chromatography to obtain individual isomers as intense red crystalline solids. Molecular structures of complexes **5** and **6** were characterised by ^{1}H and ^{13}C NMR data in addition to XRD determinations of *cis* and *trans* isomers of **6** (see below). The ^{1}H and ^{13}C NMR spectra of complexes **5** and **6** showed expected resonances for phenyl imido groups as well as for coordinated aminobis(phenolato) ligands. In the ^{1}H NMR spectra of *cis* isomers the Ar–CH_2–N protons were seen as broad overlapping signals at 3.6–3.2 ppm, which is typical for *cis* configuration of aminobis(phenolato) ligands [7,9]. For comparison, *trans* isomers presented sharp doublets at 5.2–5.3 and 3.2 ppm for the same methylene protons. On the whole, *trans* isomers have closely similar ^{1}H and ^{13}C NMR spectra than found for structurally identical molybdenum complexes **3** and **4**, although the signals for *ortho* and *para* hydrogens of phenylimido ligands were found to be shifted to down-field by 0.3 ppm compared to corresponding molybdenum complexes.

Complexes **5** and **6** are stable in air at room temperature and are soluble in typical organic solvents, but they decompose slowly in wet alcohol solutions. When *trans*-**6** was dissolved in anhydrous ether and treated with two equivalents of MeMgI, the reaction mixture turned yellow. The stable, yellow solid product was isolated by column chromatography and characterised by NMR spectroscopy to be *cis*-[W(NPh)(ONO^{tBu})Me_2] **7**. The strong *trans* influence of methyl group appears to make *cis* configuration thermodynamically more favoured, which leads to the reorientation of aminobis(phenolato) ligand during the transmetallation. Similar rearrangement is earlier seen in the reaction of *trans*-[WO(ONO^{tBu})Cl_2] [9]. The synthesis of **7** was repeated using *cis*-**6** as a precursor, in which case the reaction yielded an identical product. ^{1}H NMR of **7** in $CDCl_3$ showed a single resonance at 0.54 ppm for W–Me protons, whereas related signal in ^{13}C NMR spectrum was seen at 38.88 ppm. All other alkylation reactions of studied molybdenum and tungsten complexes with Grignard reagents RMgX (R = Et, Ph, CH_2CMe_2Ph) failed leading to the complex mixtures from which no single products could be isolated. To observe whether dimethyl complex **7** could decompose by α-elimination to produce a corresponding methylene complex, it was heated to 100 °C in a toluene solution, while the reaction was monitored by ^{1}H NMR. Although this complex seems to decompose upon heating, no evidence on carbene formation was observed.

It has been shown that amino(phenolate) complexes of Mo(VI) and W(VI) when activated with organoaluminium compounds exhibit high activity in ROMP of norbornene and its derivatives [10]. Especially, their stability on air represents an important advantage in comparison with metathesis catalysts based on W and Mo chlorides [11]. Therefore, dichloro complexes **3** and *trans*-**6** and dimethyl derivative **7** were tested as catalyst precursors for ROMP of norbornene. When the experiments were run without any co-catalyst, no activity was observed. This could be expected according to the high stability of the studied complexes. However, when the reaction mixtures in benzene were treated with a five-fold excess of organoaluminium reagent Et_2AlCl, the monomer conversions after 180 min reaction at room temperature were quantitative for precursors **3** and *trans*-**6** and 23% for **7**. At 60 °C, a system **7**/Et_2AlCl produced polynorbornene as an insoluble rubber-like material in an 80% yield during one hour. When activated, precursors **3** and **7** polymerised also 2-norbornen-5-yl acetate, however, in low yields (about 5%). As a consequence, it seems that the dichloro complexes can be activated by aluminium co-catalyst, probably due to Et for Cl exchange which is followed by an α-elimination reaction to yield active carbene species [12]. Significantly lower activity of dimethyl complex suggests another less efficient process of activation, e.g. coordination of organoaluminium compound as a Lewis acid [13] followed by primary carbene formation from norbornene molecule. The quite low activities of studied compounds in comparison with bidentate aminophenolate ligands [10] are supposedly due to the rigid tridentate chelate ligands, which may prevent the necessary reorganisation of the coordination sphere during the carbene formation and/or polymerization process.

2.3. Structural studies

Crystals of **4**, *cis*-**6**, *trans*-**6** and **7** were grown from acetonitrile solutions at 4 °C. All four complexes form mononuclear molecules, in which the dianionic aminobis(phenolato) group is coordinated to the metal ion as a tripodal O_2N ligand (see Figs. 1–4 and Table 1). The weakly bonded nitrogen donor of the chelate backbone is located *trans* to the imido ligand. The overall geometry and bonding parameters of **4** and *trans*-**6** are quite similar resembling those structures reported earlier for aminobis(phenolate) complexes of

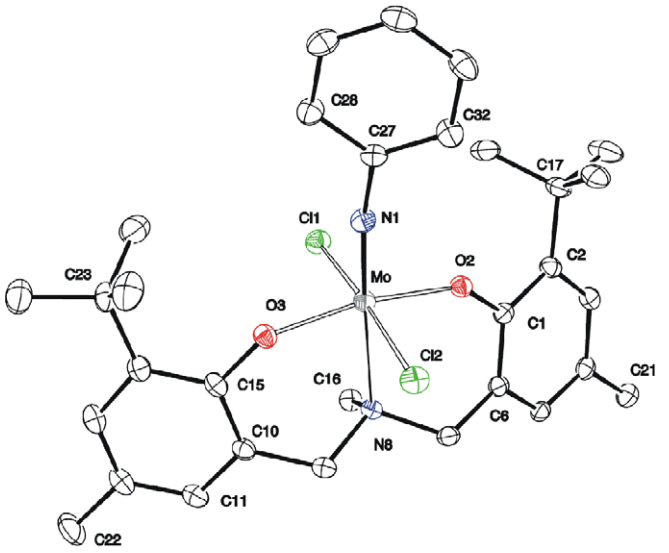


Fig. 1. A diagram of the molecular structure of *trans*-[Mo(NPh)(ONO^{tBu})Cl_2] **4**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

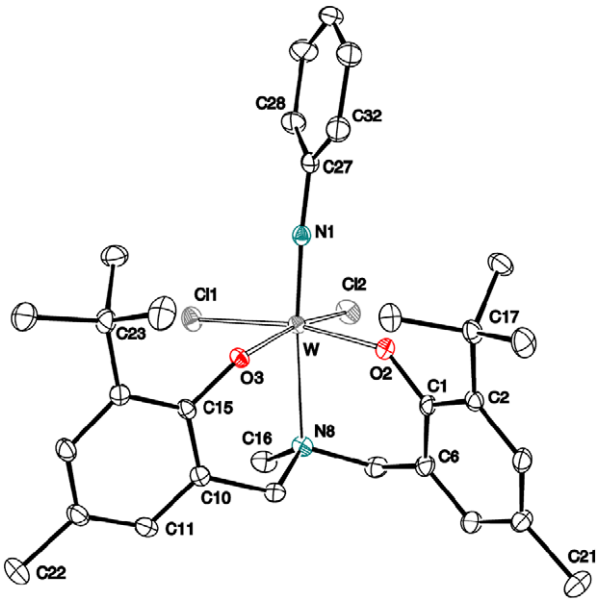


Fig. 2. A diagram of the molecular structure of cis-[W(NPh)(ONO^{tBu})Cl$_2$] *cis*-**6**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

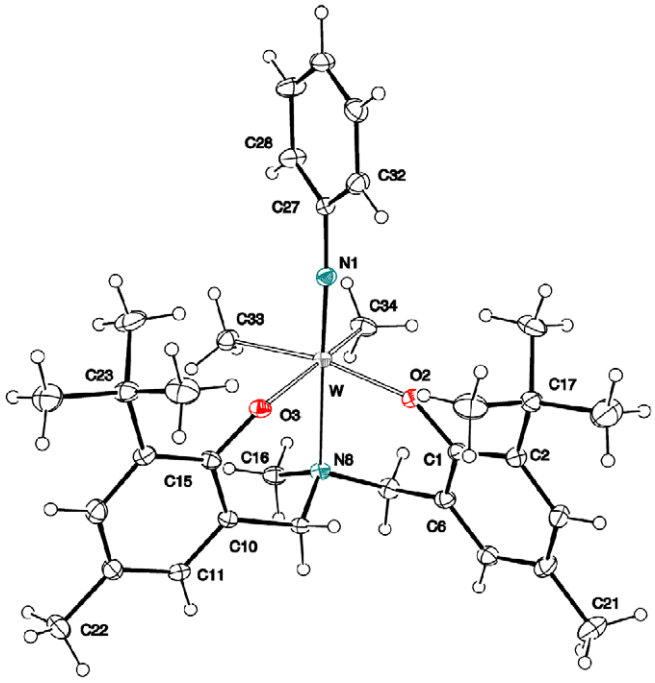


Fig. 4. A diagram of the molecular structure of *cis*-[W(NPh)(ONO^{tBu})Me$_2$] **7**. Thermal ellipsoids are drawn at the 30% probability level..

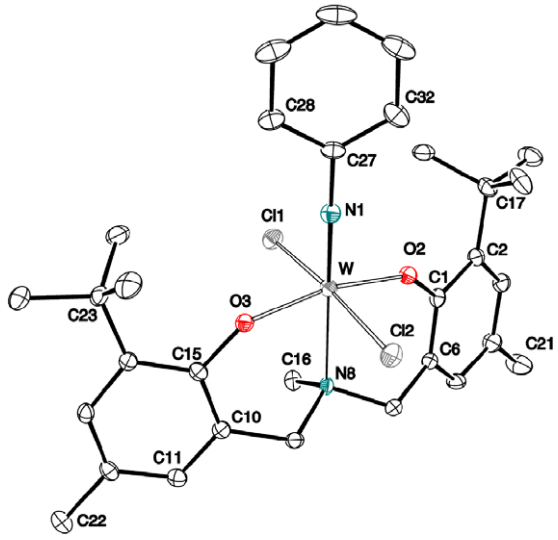


Fig. 3. A diagram of the molecular structure of *trans*-[W(NPh)(ONO^{tBu})Cl$_2$] *trans*-**6**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

oxomolybdenum(VI) and oxotungsten(VI) with a *trans* dichloro moiety [7,8]. Although the molecular structures of these two complexes are closely similar, they are not crystallographically identical, i.e. **4** crystallises in a triclinic system, whereas *trans*-**6** crystallises in a monoclinic space group. They show also some noticeable differences in their bonding parameters. In particular, the M–N$_{imido}$ distances are 1.732(2) Å for **4** and 1.751(3) Å for *trans*-**6**, whereas related M–N–C angles are 171.5(2)° and 176.9(3)°, respectively. As expected according to the spectral characterizations, complex *cis*-**6** is formed of molecular units in which two *cis*-aryloxide moieties and two *cis*-chlorides occupy the equatorial plane. The overall geometry of **7** is comparable to that found for *cis*-**6**. The W–C(methyl) bond lengths are 2.172(3) and 2.206(4) Å, which are typical values for tungsten(VI) alkyl complexes with a six-coordination. For both compounds, the coordination around the tungsten atom is similar than found for cis dichloro or dimethyl complexes of oxotungsten(VI) with related aminobis(phenolate)s. In all studied complexes, the M–N$_{imido}$–C bond angles are nearly linear, which suggest that the imido nitrogen is sp-hybridised. Accordingly, the M≡N bond order is three, which makes the imido ligand as a six-electron donor. The strong *trans* influence of the imido group is seen in the distortion of equatorial ligands, since the N$_{imido}$–M–O angles are in the range 95.16(8)–99.15(8) and the N$_{imido}$–M–Cl angles vary between 91.64(7) and 96.53(7). In all compounds, the M–N8 distances are *ca.* 0.1 Å short-

Table 1
Crystallographic data for *trans*-[Mo(NPh)(ONO^{tBu})Cl$_2$] **4**, *trans*-[W(NPh)(ONO^{tBu})Cl$_2$] *trans*-**6**, *cis*-[W(NPh)(ONO^{tBu})Cl$_2$] *cis*-**6** and *cis*-[W(NPh)(ONO^{tBu})Me$_2$] **7**.

	4	*trans*-**6**	*cis*-**6**	**7**
Formula	$C_{31}H_{40}Cl_2MoN_2O_2$	$C_{31}H_{40}Cl_2N_2O_2W$	$C_{31}H_{40}Cl_2N_2O_2W$	$C_{33}H_{46}N_2O_2W$
M_r	639.49	727.4	727.4	686.57
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
Z	2	4	4	4
a (Å)	9.3686(2)	9.56030(10)	10.70850(10)	9.9696(2)
b (Å)	10.2573(2)	23.5055(4)	16.3339(2)	24.3566(6)
c (Å)	16.3306(3)	14.0927(2)	17.3987(2)	13.3218(2)
α (°)	97.0420(10)	90	90	90
β (°)	93.3910(10)	105.7630(10)	90.0500(10)	99.9140(10)
γ (°)	101.4940(10)	90	90	90
V (Å^3)	1520.60(5)	3047.81(7)	3043.23(6)	3186.57(11)
μ (cm^{-1})	3.654	6.37	3.995	4.001
D_{calc} (g cm^{-3})	1.431	1.397	1.585	1.588
2θ Range (°)	2.07–28.00	2.23–28.3	2.29–28.27	1.71–28.25
R_1, wR_2	0.0627, 0.0845	0.052, 0.0561	0.033, 0.044	0.034, 0.0694

Table 2
Selected distances (Å) and angles (°) for *trans*-[Mo(NPh)(ONO^{tBu})Cl$_2$] **4**, *trans*-[W(NPh)(ONO^{tBu})Cl$_2$] *trans*-**6**, *cis*-[W(NPh)(ONO^{tBu})Cl$_2$] *cis*-**6** and *cis*-[W(NPh)-(ONO^{tBu})Me$_2$] **7**.

	4	*trans*-**6**	*cis*-**6**	*cis*-**7**
M–N1	1.732(2)	1.751(3)	1.738(2)	1.734(3)
M–Cl1	2.3956(7)	2.3752(9)	2.3715(6)	2.206(4)[a]
M–Cl2	2.4245(7)	2.4025(9)	2.3682(6)	2.172(3)[a]
M–O2	1.9134(17)	1.907(2)	1.8991(16)	1.922(3)
M–O3	1.9033(17)	1.905(2)	1.9246(16)	1.954(2)
M–N8	2.3943(19)	2.399(3)	2.417(2)	2.471(3)
M–N1–C27	171.5(2)	176.9(3)	171.93(18)	174.0(2)
Cl1–M–Cl2	171.88(2)	172.00(3)	85.34(2)	79.60(15)
O2–M–O3	164.43(7)	163.25(9)	93.80(7)	99.94(10)
N1–M–N8	176.73(9)	178.95(11)	174.62(8)	176.98(10)

[a] W–C(33) and W–C(34) distances, C(33)–W–C(34) angle.

er and M–O_{Ar} distances are slightly longer than in corresponding oxo complexes [7–9] (see Table 2).

3. Experimental section

Starting compounds [W(NPh)Cl$_4$] and H$_2$ONO^R were prepared according published procedures [14,15]. *trans*-[MoO(ONO^{Me})Cl$_2$] was synthesised as described earlier by us [10], while *trans*-[MoO(ONO^{tBu})Cl$_2$] was prepared using analogous procedure. Other chemicals were from commercial sources and were used as purchased. Toluene and diethyl ether were distilled over CaH$_2$; other solvents were of HPLC grade. All syntheses and manipulations were performed under ambient laboratory atmosphere if not otherwise stated. The purity of isolated complexes as well as the progress of the reactions was monitored by thin-layer chromatography. ^{1}H NMR (500 MHz) and ^{13}C NMR spectra (200 MHz) were recorded at 20 °C using Bruker AV 500 spectrometer in CDCl$_3$ solutions and were referenced internally to SiMe$_4$. Elemental analyses were obtained using a Perkin–Elmer CHNS-Analyzer 2400. Catalytic tests were run similarly as presented in Ref. [10].

3.1. trans-[MoO(ONO^{tBu})Cl$_2$]

520 mg (92%). ^{1}H NMR (CDCl$_3$): δ 7.25 (s, 2H, Ar), 6.96 (s, 2H, Ar), 4.80 (d, J = 13 Hz, 2H , N-CH_2), 3.09 (d, J = 13 Hz, 2H, N-CH_2), 2.49 (s, 6H, Ar-CH_3), 1.99 (s, 3H, N-CH_3), 1.59 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (CDCl$_3$): δ 161.19, 140.76, 138.67, 130.75, 129.71, 127.60, 63.42, 47.21, 35.59, 30.85, 21.62. Anal. Calc. for C$_{25}$H$_{35}$Cl$_2$MoNO$_3$: C, 53.20; H, 6.25; N, 2.48. Found: C, 53.08; H, 6.12; N, 2.30%.

3.2. Preparation of Mo–imido complexes. General procedure

1.00 mmol of starting compound (480 mg of *trans*-[MoO(ONO^{Me})Cl$_2$] or 564 mg of *trans*-[MoO(ONO^{tBu})Cl$_2$]) was dissolved in 10 ml of toluene. An excess of phenyl isocyanate (0.20 ml, 1.6 mmol) was added and the blue solutions were stirred at reflux temperature for 2 h. The products were column chromatographed over silica gel using a hexane–toluene mixture (1:1) as an eluent. The intense blue solid products were crystallised from hot acetonitrile.

3.3. trans-[Mo(NPh)(ONO^{Me})Cl$_2$]

400 mg (72%). ^{1}H NMR (CDCl$_3$): δ 7.74 (d, J = 7.5 Hz, 2H, *NAr*-H_{ortho}), 7.57 (t, J = 7.7 Hz, 2H, *NArH*$_{meta}$), 7.39 (t, J = 7.5 Hz, 1H, *NArH*$_{para}$), 7.06 (s, 2H, O*ArH*), 6.89 (s, 2H, O*ArH*), 5.20 (d, J = 12.9 Hz, 2H, N-CH_2), 3.13 (d, J = 12.9 Hz, 2H, N-CH_2), 2.42 (s, 6H, Ar-CH$_3$), 2.39 (s, 6H, Ar-CH$_3$) 2.09 (s, 3H, NCH_3) ppm. ^{13}C NMR (CDCl$_3$): δ 160.02, 155.52, 135.46, 132.11, 128.82, 128.74, 128.63, 127.07, 126.42, 63.16, 46.48, 21.05, 16.51 ppm. Anal. Calc. for C$_{25}$H$_{28}$Cl$_2$MoN$_2$O$_2$: C, 54.07; H, 5.08; N, 5.04. Found: C, 53.78; H, 5.24; N, 5.05%.

3.4. trans-[Mo(NPh)(ONO^{tBu})Cl$_2$]

335 mg (55%). ^{1}H NMR (CDCl$_3$): δ 7.80 (d, J = 7.5 Hz, 2H, *NAr*-H_{ortho}), 7.53 (t, J = 7.9 Hz, 2H, *NArH*$_{meta}$), 7.34 (t, J = 7.5 Hz, 1H, *NArH*$_{para}$), 7.19 (s, 2H, O*ArH*), 6.93 (s, 2H, O*ArH*), 5.16 (d, J = 12.9 Hz, 2H, N-CH_2), 3.13 (d, J = 12.9 Hz, 2H, N-CH_2), 2.39 (s, 6H, Ar-CH$_3$), 2.22 (s, 3H, NCH_3) 1.53 (18 H, s, C(CH_3)$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ 160.66, 155.39, 139.03, 135.29, 131.50, 129.21, 129.14, 128.61, 127.66, 126.89, 63.59, 46.88, 35.41, 30.76, 21.39 ppm. Anal. Calc. for C$_{31}$H$_{40}$Cl$_2$MoN$_2$O$_2$: C, 58.22; H, 6.30; N, 4.38. Found: C, 58.27; H, 6.48; N, 4.05%.

3.5. Preparation of W–imido complexes. General procedure

0.50 mmol (210 mg) of [W(NPh)Cl$_4$] was suspended in 10 ml of toluene and subsequently treated with 0.50 mmol of H$_2$ONO^R. The dark mixture that formed was then stirred for 3 h at reflux temperature. The mixtures of *cis*- and *trans*-isomers of [W(NPh)Cl$_2$(L^R)] thus obtained were separated by silica column chromatography using a hexane–toluene mixture (1:1) as an eluent.

3.6. cis-[W(NPh)(ONO^{Me})Cl$_2$]

42 mg (13%). ^{1}H NMR (CDCl$_3$): δ 7.60 (t, 2H, J = 7.6 Hz, *NArH*$_{meta}$), 7.36 (d, J = 7.4 Hz, 2H, *NArH*$_{ortho}$), 7.10 (s, 2H, O*ArH*), 7.08 (t, J = 7.6 Hz, 1H, *NArH*$_{para}$), 6.86 (s, 2H, O*ArH*), 4.17 (br, 2H, N-CH_2), 3.71 (br, 2H, N-CH_2), 2.70 (s, 3H, N-CH_3), 2.40 (s, 6H, Ar-CH_3), 2.39 (s, 6H, Ar-CH_3) ppm. ^{13}C NMR (CDCl$_3$): δ 155.46, 133.46, 131.39, 129.74, 128.64, 128.43, 127.75, 127.67, 125.29, 111.08, 61.73, 48.97, 20.73, 16.15 ppm. Anal. Calc. for C$_{25}$H$_{28}$Cl$_2$N$_2$O$_2$W: C, 46.68; H, 4.39; N, 4.35. Found: C, 46.80; H, 4.27; N, 4.11%.

3.7. trans-[W(NPh)(ONO^{Me})Cl$_2$]

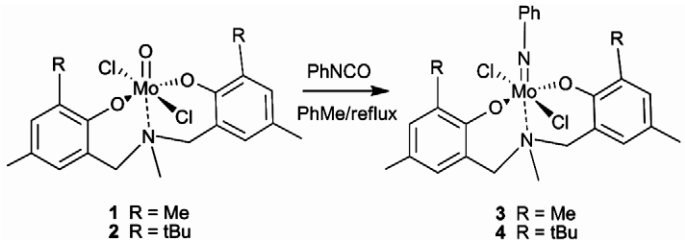
135 mg (42%). ^{1}H NMR (CDCl$_3$): δ 7.60 (t, J = 7.9 Hz, 2H, *NarH*$_{meta}$), 7.34 (d, J = 7.5 Hz, 2H, *NarH*$_{ortho}$), 7.11 (t, J = 7.4 Hz, 1H, *NArH*$_{para}$), 7.10 (s, 2H, O*ArH*), 6.85 (s, 2H, O*ArH*), 5.31 (d, J = 12.9 Hz, 2H, N-CH_2), 3.20 (d, J = 12.9 Hz, 2H, N-CH_2), 2.43 (s, 6H, Ar-CH_3), 2.41 (s, 6H, Ar-CH_3) 2.22 (s, 3H, N-CH_3) ppm. ^{13}C NMR (CDCl$_3$): δ 155.45, 152.83, 133.98, 131.41, 130.70, 129.49, 128.10, 127.98, 127.70, 125.36, 62.91, 46.80, 20.75, 16.08 ppm. Anal. Calc. for C$_{25}$H$_{28}$Cl$_2$N$_2$O$_2$W: C, 46.68; H, 4.39; N, 4.35. Found: C, 46.88; H, 4.64; N, 4.25%.

3.8. cis-[W(NPh)(ONO^{tBu})Cl$_2$]

55 mg (15%). ^{1}H NMR (CDCl$_3$): δ 7.58 (t, J = 8.2 Hz, 2H, *NArH*$_{meta}$), 7.39 (d, J = 7.3 Hz, 2H, *NArH*$_{ortho}$), 7.21 (s, 2H, O*ArH*), 7.06 (t, J = 7.5 Hz, 1H, *NArH*$_{para}$), 6.91 (s, 2H, O*ArH*), 4.22 (s, br, 2H, N-CH_2), 3.65 (s, br, 2H, N-CH_2), 2.85 (s, 3H, NCH_3), 2.42 (s, 6H, Ar-CH_3), 1.43 (s, 18H, C(CH_3)$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ 156.91, 152.07, 140.28, 133.16, 129.49, 128.67, 128.25, 127.76, 127.62, 126.82, 61.21, 49.26, 40.85, 34.91, 30.26, 21.07 ppm. Anal. Calc. for C$_{31}$H$_{40}$Cl$_2$N$_2$O$_2$W: C, 51.23; H, 5.55; N, 3.86. Found: C, 51.60; H, 5.24; N, 4.00%.

3.9. trans-[W(NPh)(ONO^{tBu})Cl$_2$]

170 mg (55%). ^{1}H NMR (CDCl$_3$): δ 7.57 (t, J = 8.0 Hz, 2H, *NArH*$_{meta}$), 7.40 (d, J = 7.9 Hz, 2H, *NArH*$_{ortho}$), 7.24 (s, 2H, O*ArH*), 7.06 (t, J = 7.5 Hz, 1H, *NArH*$_{para}$), 6.90 (s, 2H, O*ArH*), 5.2 (d, 2H, J = 12.9 Hz, N-CH_2), 3.20 (d, J = 12.9 Hz, 2H, N-CH_2), 2.37 (s, 6H, Ar-CH_3), 2.02 (s, 3H, NCH_3) 1.51 (18 H, s, C(CH_3)$_3$) ppm. ^{13}C NMR



Scheme 1. Preparation of *trans*-[Mo(NPh)(ONO^{R})Cl$_2$].

(CDCl$_3$): δ 156.10, 152.80, 139.99, 133.80, 130.08, 129.68, 128.68, 127.92, 127.62, 126.51, 63.34, 47.33, 35.12, 30.58, 21.09 ppm. Anal. Calc. for $C_{31}H_{40}Cl_2N_2O_2W$: C, 51.23; H, 5.55; N, 3.86. Found: C, 50.98; H, 5.44; N, 4.01%.

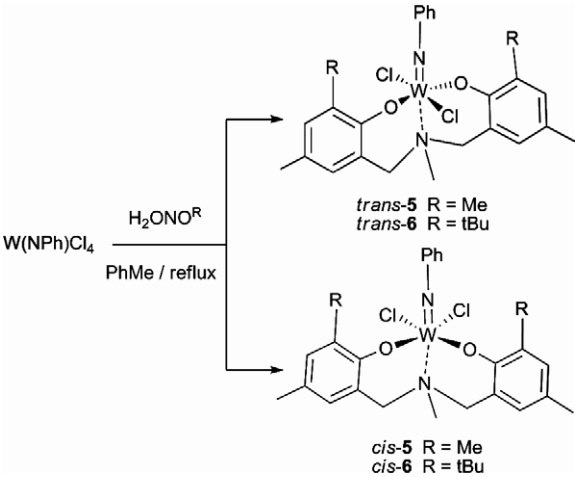
3.10. Preparation of *cis*-[W(NPh)(ONO^{tBu})Me$_2$]

3.10.1. From *trans*-[W(NPh)(ONO^{tBu})Cl$_2$]

0.20 mmol (146 mg) of *trans*-[W(NPh)(ONO^{tBu})Cl$_2$] was dissolved in 10 ml of anhydrous diethyl ether under N_2 atmosphere. The red solution was treated with freshly prepared MeMgI (ca. 0.6 mmol) in diethyl ether (0.6 ml) while the reaction mixture turned rapidly yellow. The yellow solution was then stirred for an hour at room temperature. The solvent was evaporated and the yellow-orange solid product was isolated by a silica column chromatography using a hexane-toluene mixture (1:1) as an eluent. 95 mg (69%). ^{1}H NMR (CDCl$_3$): δ 7.46 (2H, t, J = 7.8 Hz, *NArH$_{meta}$*), 7.32 (2H, d, J = 7.4 Hz, *NArH$_{ortho}$*), 7.17 (2H, s, O*ArH*), 7.11 (1H, t, J = 7.4 Hz, *NArH$_{para}$*), 6.85 (2H, s, O*ArH*), 3.6–4.0 (4H, br, N-*CH$_2$*), 2.45 (3H, s, N*CH$_3$*), 2.36 (6H, s, Ar-*CH$_3$*), 1.42 (18H, s, C(*CH$_3$*)$_3$), 0.54 (6H, s, W-*CH$_3$*). ^{13}C NMR (CDCl$_3$) δ: 155.25, 154.03, 140.75, 130.39, 128.46, 128.04, 127.50, 126.54, 125.96, 125.68, 61.68, 47.57, 38.88, 34.86, 29.87, 21.09. Anal. Calc. for $C_{33}H_{46}N_2O_2W$: C, 57.73; H, 6.75; N, 4.08. Found: C, 57.78; H, 6.91; N, 4.04%.

3.10.2. From *cis*-[WO(ONO^{tBu})Cl$_2$]

The reaction was carried out using 0.10 mmol (73 mg) of *cis*-[W(NPh)(ONO^{tBu})Cl$_2$] and 0.3 mmol of MeMgI in diethyl ether to yield 52 mg (75%) of a yellow product. The ^{1}H and ^{13}C NMR spectra of the product were identical with those described above.



Scheme 2. Preparation of *cis* and *trans* isomers of [W(NPh)(ONO^{R})Cl$_2$].

4. X-ray crystallography

Crystals of **4**, *cis*-**6** and *trans*-**6** were grown from concentrated acetonitrile solutions upon slow cooling to 4 °C. The crystal data for the compounds are summarized in Table 1. The crystallographic data were collected at 173 K on an Enraf Nonius Kappa CCD area-detector diffractometer using graphite monochromatised Mo Kα radiation (λ = 0.71073 Å). Data collection was performed using ϕ and ω scans and the data were processed using *DENZO-SMN* v0.93.0 [16]. SADABS [17] absorption correction was applied to the data of all compounds. The structures were solved by direct methods using the SHELXS-97 program and full-matrix least-squares refinements on F^2 were performed using the SHELXL-97 program [18]. Structure figures were drawn using *Ortep-3* for *Windows* [19].

5. Conclusions

In conclusion, we have found that the aminobis(phenolato) complexes *trans*-[MoO(ONO^{R})Cl$_2$] can react with PhNCO to yield air-stable imido molybdenum complexes *trans*-[Mo(NPh)(ONO^{R})Cl$_2$]. Regardless their structural similarities, analogous oxotungsten complexes do not show the same reactivity, but corresponding imido tungsten complexes can be prepared by the reaction of [W(NPh)Cl$_4$] with aminobis(phenol)s. These reactions yield *cis*- and *trans*-isomers of dichloro complexes [W(NPh)(ONO^{R})Cl$_2$] in a *ca.* 1:4 ratio. Moreover, *cis* and *trans* isomers of tungsten complex [W(NPh)(ONO^{tBu})Cl$_2$] react with methyl Grignard reagent to yield corresponding dimethyl complex *cis*-[W(NPh)(ONO^{tBu})(Me)$_2$] (see Schemes 1 and 2).

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Appendix A. Supplementary material

CCDC 699861–699864 (for **4**, *trans*-**6**, *cis*-**6** and *cis*-**7**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.047.

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