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Reactions of Aminobis(phenolate)-Supported Dioxidotungsten(VI) and Dioxidomolybdenum(VI) Complexes

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The dioxidotungsten(VI) and -molybdenum(VI) complexes $[WO_2(O_2NO^{Me})]$ (**1**), $[MoO_2(O_2NO^{Me})]$ (**2**) and $[\{MoO_2(O_2N^{Me})\}_2]$ (**3**) [O_2NO^{Me} methoxyethylamino-*N*,*N*-bis(2-methylene-4,6-dimethylphenolate) dianion, O_2N^{Me} = methylamino-*N*,*N*-bis(2-methylene-4,6-dimethylphenolate) dianion] can react with chloride sources (Me_3SiCl, $SOCl_2$) to form resultant monooxido dichloro compounds $[WOCl_2(O_2NO^{Me})]$ (**4**), $[MoOCl_2(O_2NO^{Me})]$ (**5**) and $[MoOCl_2(O_2N^{Me})]$ (**6**), respectively. The reaction of tungsten complex yields of the mixture of *cis*-**4** and *trans*-**4**, which can be separated and characterized. The reactions of analogous molybdenum complexes with Me_3SiCl yield *trans* isomers of **5** and **6** as individual products. Reaction of dioxidotungsten complex **1** with isopropyl isocyanate was found to produce a tungsten(VI) complex $[W(O_2NO^{Me})(N\text{-}i\text{Pr})(L)]$ (**7**) (L = *N*,*N*′-diisopropylureate) with a terminal imido group and a bidentate ureate ligand.

Introduction

The research on early transition metal complexes with chelating aryloxide ligands is mostly motivated by their relevance in organometallic and catalytic chemistry.[1,2] For example, various oxidomolybdenum and oxidotungsten compounds with diverse aryloxide ligands have attracted considerable attention as they can catalyze scientifically and industrially interesting olefin metathesis reactions.[3] In particular, oxidotungsten complexes with various numbers of aryloxide and chloride ligands can form active catalysts when treated with alkylating aluminium or tin cocatalysts.[4] The chloride ligands seems to enhance the activity of these catalyst systems, as they allow the alkylation and formation of catalytically active carbene complexes.[3] The standard procedure for these oxidotungsten(VI) phenoxides comprises a straightforward reaction of $WOCl_4$ with a stoichiometric amount of phenolic ligand precursor in an appropriate solvent. On the other hand, reports on molybdenum complexes $[MoO(OAr)_{4-n}Cl_n]$ are very scarce in comparison with their tungsten congeners, which is most probably due to the poor stability of the starting material $MoOCl_4$. Some monooxidomolybdenum aryloxides, e.g. $[MoOCl_2(OAr)_2]$ (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) have been prepared from a commercially available precursor, MoO_2Cl_2 and parent phenols ArOH.[5] However, these preparations are rather delicate and they require sophisticated inert atmosphere techniques, while moisture and acidic impurities have to be rigorously excluded from the reaction medium.

Various cyclopentadienyl derivatives of dioxidotungsten(VI) and -molybdenum(VI) can be converted into the corresponding monooxido dichloro species using HCl as a chloride source.[6] This reaction proceeds probably via a stepwise addition of two HCl molecules across one of the M=O bonds, which yields one molecule of water as a by-product. Other efficient chlorination reagents are Me_3SiCl and PCl_5, which can initially react with proton sources, e.g. traces of water or alcohols, to generate the necessary amount of HCl for the reaction. Group 6 metallocenes Cp_2MO (M = Cr, Mo, W) were reported to undergo a direct silylation of M=O group with Me_3SiCl to yield Cp_2MCl_2 complexes.[7] Silylation of benzene-1,2-dithiolate (bdt) complex $[WO_2(bdt)_2]^{2-}$ leads to the formation of anionic chloro monooxido complex $[WO(bdt)_2Cl]^-$.[8] Molybdenum(VI) complex $[MoO_2(Sap)(EtOH)]$ (Sap = *N*-salicylidene-2-aminophenolate dianion) has been reported to react with $SOCl_2$ to yield the dichloro complex *trans*- $[MoO(Sap)Cl_2]$.[9] In this reaction, the active species are proposed to be $SOCl^+$ or Cl^-. Previously, we have prepared series of new dioxidomolybdenum(VI) and -tungsten(VI) complexes with dianionic aminobis(phenolato) ligands and studied their use as catalysts in oxotransfer reactions and ROMP of norbornene.[10] For example, $[WO_2(O_2NO^{Me})]$ (**1**), $[MoO_2(O_2NO^{Me})]$ (**2**) and $[\{MoO_2(O_2N^{Me})\}_2]$ (**3**) [O_2NO^{Me}-methoxyethylamino-*N*,*N*-bis(2-methylene-4,6-dimethylphenolate) dianion, O_2N^{Me} = methylamino-*N*,*N*-bis(2-methyl-

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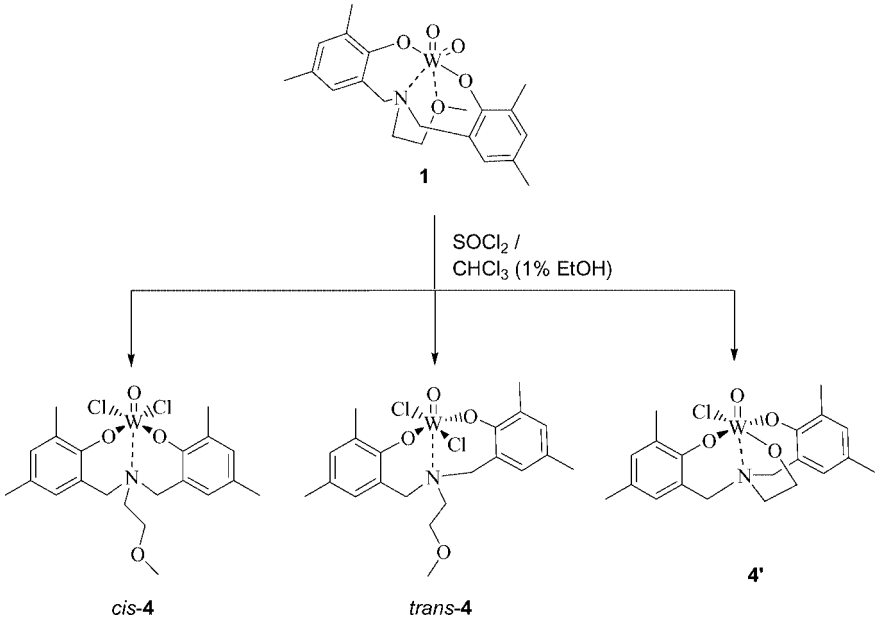
ene-4,6-dimethylphenolate) dianion] have been synthesized and structurally characterized.[10b,10c] We supposed that these air-stable dioxido compounds may also provide useful entries to the new monooxido-dichloro-tungsten(VI) and -molybdenum(VI) complexes, which would resemble well-known metathesis catalyst precursors. In present study we demonstrate a chloride-for-oxide substitution as a simple route to prepare dichloro oxidotungsten(VI) and oxidomolybdenum(VI) complexes with aminobis(phenolate) ligands. In addition, the reaction of tungsten complex **1** with isopropyl isocyanate is studied.

Results and Discussions

Chloride-for-Oxide Substitution of Dioxidotungsten(VI) Complex 1

In order to prepare aminobis(phenolate)-supported dichloro monooxido complex of tungsten(VI), we treated dioxidotungsten complex **1** with various potential chloride sources, i.e. HCl, $SOCl_2$, Me_3Cl and PCl_5. The stirred mixtures in various solvents ($CHCl_3$, THF, PhMe) were allowed to react with an excess of chlorinating reagents to obtain intense red solutions.[11] The reaction mixtures that formed were then heated to the reflux temperature while the reactions were monitored by TLC. As a result, complex **1** reacted smoothly to produce the mixtures of three distinct products (Scheme 1).

Dark red mixtures were separated by column chromatography to get two intense red solids and one yellow product as a minor component. The IR spectra of red solids presented strong absorption bands at ca. 950 cm^{-1} instead of characteristic doublet (939 and 899 cm^{-1}) for WO_2^{2+} moiety in complex **1**.[10c] NMR spectra of red solids were closely similar to those found for isomers of a related compound $[WOCl_2(O_2N^{Me})]$,[12] thus they were identified as *cis* and *trans* isomers of expected dichloro monooxido complex **4**. The third component in the reaction mixtures was a bright yellow complex **4′**, which was formed as trace amounts in all separate experiments. Spectroscopic studies of **4′** suggested some changes in the original aminobis(phenolate) ligand. Compound **4′** was finally identified by X-ray crystallography (see below) to be a mononuclear, monooxido chloro complex, in which the degraded aminobis(phenolato) ligand has coordinated as a tetradentate trianion. When the reaction parameters were optimized, it was found that the highest total conversion could be obtained when the starting compound **1** is dissolved in commercial chloroform with 1% of EtOH stabilizer and subsequently treated with excess of $SOCl_2$. Under these conditions, the reaction yielded a *trans* isomer of **4** as a major component. Although various amounts of both isomers were formed in all of these experiments, any selective reaction conditions for the preparation of *cis*-**4** could not be found.[13] As $SOCl_2$ reacts readily with EtOH to produce HCl, we can assume that the actual reaction is an addition of two HCl molecules across one of the W=O bonds, like reported by Legzdins[6a] and Schrock.[6b] Formation of the *trans* isomer as an eventual result of studied chloride-for-oxide substitution appears reasonable, seeing that two newly introduced chloride ligands replace one terminal oxido group and one neutral oxygen donor, which are at *trans* positions. Conversely, the development of the *cis* isomer is not so obvious, as it results in the substantial rearrangement of the aminobis(phenolate) ligand. Besides, the *cis* isomer appears to be thermodynamically less favourable, as it tends to isomerize in solutions. However, our attempts to isomerize quantitatively *cis*-**4** to *trans*-**4** by heating a sample in a xylene solution at reflux temperature failed, leading mainly to the decomposition of initial complex. Interestingly, the only isolable de-



Scheme 1. Reaction of $[WO_2(O_2NO^{Me})]$ with $SOCl_2$.

composition product was abovementioned **4′**. The formation of this complex is appealing, as the emergence of the atrane-type ligand[14] requires a breaking of the ether C–O bond upon formation of the metal alkoxide bond. Such an ether cleavage as this is a well-known transformation in organic synthesis, and it can be catalyzed by various Lewis and Brönstedt acids.[15] For example; WCl_6 can catalyze acylative cleavage of ether C–O bonds, while the reaction is supposed to proceed via a metal alkoxide intermediate.[16] Similar demethylation of the methoxy group upon coordination is earlier observed in the reaction of $TaCl_5$ with *p-tert*-butylcalix[4]arene dimethyl ether.[17] Correspondingly, we can assume that in present experiments, the ether functionality of the ligand side-arm reacts with the metal centre leading to the formation of W–O bond associated with evolution of CH_3Cl.

Chloride-for-Oxide Substitution of Dioxidomolybdenum(VI) Complexes 2 and 3

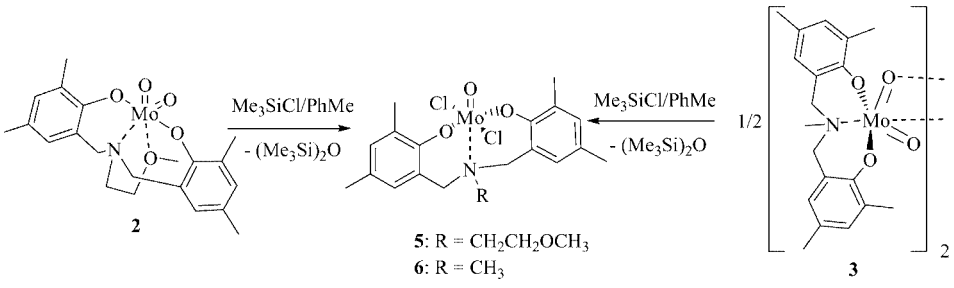
The reactions of the monomeric molybdenum complex **2** and the dimeric complex **3** with selected chlorinating agents in various solvents were conducted identically as described for tungsten complex **1** (see above). To our discontent, when chloride sources $SOCl_2$ or PCl_5 were added to the stirred solutions of dioxidomolybdenum(VI) complexes in $CHCl_3$, the vigorous reactions yielded predominantly to the swift decomposition of starting complexes, whereas only minor amounts of chlorinated products **5** or **6** could be isolated. However, the silylation of Mo=O moiety with Me_3SiCl in toluene proved a convenient procedure for the chloride-for-oxide substitution of these reactive molybdenum complexes. The reaction of complex **2** with Me_3SiCl in a toluene suspension at room temperature led to the formation of dark blue solution, from which the dichloro monooxido complex **5** was obtained in a high yield (Scheme 2).

The IR spectrum of dark purple solid indicated the absence of initial MoO_2^{2+} moiety, whereas the NMR spectra of complex were practically identical to those of *trans*-**4**. Consequently, this isolable reaction product was identified as the *trans* isomer of the expected dichloro derivative. The reaction of **2** appeared to yield also a minor amount of *cis* isomer (according to TLC and ^1H NMR analyses), but it could not be isolated, probably due to its tendency to isomerize during processing. The reaction of practically insoluble **3** in a toluene suspension led correspondingly to the intense blue solution, from which the complex **6** was obtained in practically quantitative yield as a dark blue solid. This solid has closely analogous IR and NMR spectra to **2** and tungsten complexes *trans*-[$WOCl_2(O_2N^{Me})$],[12] therefore it was identified as *trans*-[$MoOCl_2(O_2N^{Me})$]. The suspected structure was also verified by X-ray crystallography (see below).

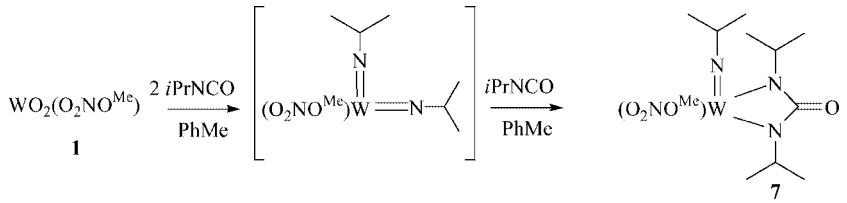
Reaction of Dioxidotungsten(VI) Complex with Isopropyl Isocyanate

Some transition metal oxido compounds are known to react with alkyl and aryl isocyanates to produce corresponding metal imido complexes.[18,19] In our experiment, dioxidotungsten complex **1** was treated with an excess of isopropyl isocyanate in toluene and the reaction mixture was heated for 120 min at 100 °C in a screw cap vial. As a result, the reaction mixture turned red while complex **1** dissolved. This red solution was subsequently cooled to the room temperature to obtain complex **7** as orange-red crystals. Somehow, identical reaction involving molybdenum complex **2** did not yield any isolable products. IR spectrum of complex **7** presented a strong absorption band at 1634 cm^{-1}, which can be assigned as a C=O stretch. X-ray crystal structure analysis verified that the product contains one imido group and one diisopropylureate ligand. The ureate ligand is supposedly formed via bis-imido intermediate, which reacts further with the additional molecule of isocyanate (Scheme 3).[18,20]

Legzdins et al. have studied analogous reactivity of dioxidotungsten complex $Cp^*WO_2(CH_2SiMe_3)$ with *p*-tolyl isocyanate, and reported that the use of hexanes as a reaction medium yields mono- and bis(imido) complexes, whereas the reaction in toluene solution affords an imido ureate complex.[18a] In our experiments, the reaction was conducted in a toluene solution, while the tungsten precursor dissolved slowly upon reaction. Thus, the stoichiometry of starting materials was unfeasible to control and the reaction yielded the ultimate ureate complex without any isolable intermediates. Complex **7** is stable in air as crystalline solid, but it decomposes in organic solvents, therefore adequate NMR spectroscopic data were not obtained.



Scheme 2. Reactions of [$MoO_2(O_2NO^{Me})$] and [{$MoO_2(O_2N^{Me})$}$_2$] with Me_3SiCl.



Scheme 3. Reaction of $[WO_2(O_2NO^{Me})]$ with isopropyl isocyanate.

Structural Studies

X-ray structure determinations were carried out for complexes *trans*-**4**, **4′**, **6** and **7**. In t*rans*-**4** the tungsten(VI) cation has adopted a distorted octahedral coordination geometry, whereas the aminobis(phenolate) ligand is coordinated as a tridentate O_2N donor (Figure 1). Two chloro ligands are in *trans* orientation. General structural parameters, e. g. W–O and W–Cl distances along with O–W–O and Cl–W–Cl angles, are of the same magnitude as usually found in $[WOCl_2(OAr)_2]$ complexes.[4,21] Consequently, the overall structure of *trans*-**4** is essentially similar to that found in related complexes with methylamino-*N*,*N*-bis(2-methylene-4,6-dialkylphenolate) ligands.[12] Complex **4′** forms monomeric molecules in which the aminobis(phenolate)ethanolate group has coordinated as a tetradentate trianionic ligand through three oxygen donors and one nitrogen donor (Figure 2). The nitrogen donor is located t*rans* to the terminal oxido group, while the chloro ligand is sited *trans* to the alkoxide oxygen. In the solid-state structure of **4′**, the $W–O_{aryloxide}$ bond lengths are 1.896(5) and 1.918(5) Å, whereas the $W–O_{alkoxide}$ bond is 1.909(4) Å. The bonding parameters between the metal centre and the aminobis(phenolato)ethanolato ligand is rather expected, although the W–O bond lengths are slightly longer and W–N distances are slightly shorter than in comparable oxidotungsten(VI) complexes with tridentate aminobis(phenolates). In general, the solid-state structure of **4′** resembles those found in oxidotungsten(VI) complexes with tripodal aminotris(phenolate)s.[22]

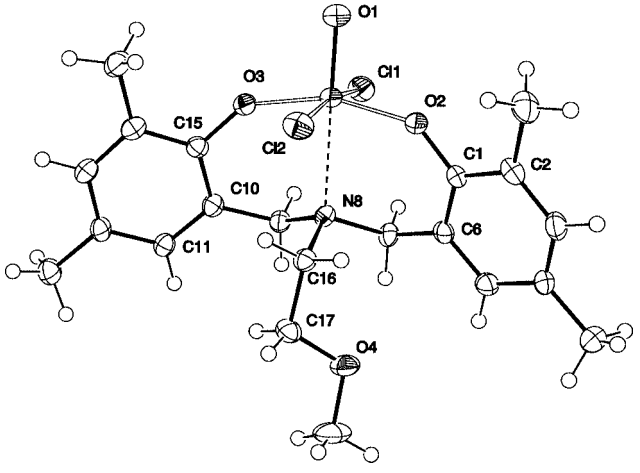


Figure 1. Molecular structure of *trans*-**4**. Thermal ellipsoids have been drawn at 30% probability level.

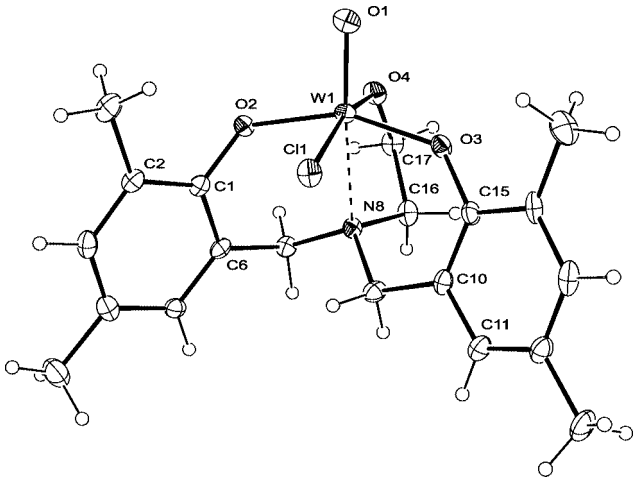


Figure 2. Molecular structure of **4′**. Thermal ellipsoids have been drawn at 30% probability level.

The coordination sphere around the metal centre in the molybdenum complex **6** (Figure 3.) is very similar to that in *trans*-**4** and other related tungsten complexes. Essentially, complex **6** is isostructural with the equivalent tungsten compound $[WOCl_2(O_2N^{Me})]$.[12] Only small structural differences are found between these two complexes, e.g. the M=O and M–N bond lengths are 1.672(4) and 2.536(4) for the Mo complex, whereas corresponding distances for the tungsten analogue are 1.696(5) Å and 2.512(5) Å, respectively.

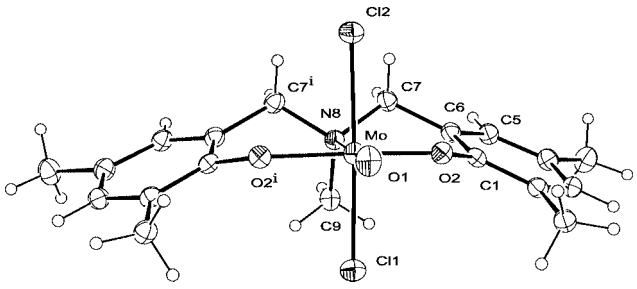


Figure 3. Molecular structure of **6**. Thermal ellipsoids have been drawn at 30% probability level.

In complex **7** the metal centre is surrounded by two phenoxides oxygen atoms, one neutral nitrogen donor, one imido group and two amido nitrogen donors (Figure 4.). The phenoxides oxygen atoms of aminobis(phenolato) ligand have arranged in a *cis* fashion [the O–W–O angle is 107.51(19)°], while the neutral amino nitrogen has located

trans to the imido nitrogen atom. Amido nitrogen atoms of the ureate group are in *cis* positions by necessity [the N–W–N angle is 63.4(2) °]. The $W{=}N_{imido}$ and two $W{-}N_{ureate}$ distances [1.723(6), 1.926(4) and 1.939(5) Å, respectively] are slightly shorter than found in related high-valent metal complexes derived from aromatic isocyanates.[18]

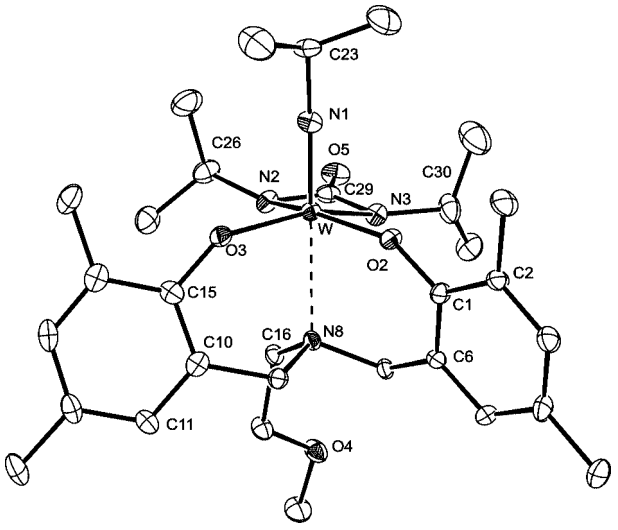


Figure 4. Molecular structure of **7**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids have been drawn at 30% probability level. Selected bond lengths [Å] and angles [°]: W–N1, 1.723(6); W–N2, 2.062(5); W–N3, 2.063(5); W–O2, 1.926(4); W–O3, 1.939(5); W–N(3), 2.064(5); W–N8, 2.458(5); W–N1–C23, 172.0(5); N2–W–N3, 63.4(2); O2–W–O3, 107.51(19); N1–W–N8, 170.2(2).

Conclusions

In summary, we have shown that aminobis(phenolate)-supported dioxidotungsten(VI) and -molybdenum(VI) complex can be used as starting materials for new dichloro monooxido complexes. The chloride-for-oxide substitution can be easily carried out using $SOCl_2$ or Me_3SiCl as chloride sources. Particularly, the chlorination of molybdenum complexes can be easily carried out in synthetically useful yields. Resulting oxidometal(VI) complexes carry primarily a *trans* dichloro functionality. These complexes resemble potential metathesis catalyst precursors; therefore their use in catalytic applications will be probed in future. The aminobis(phenolate)-supported dioxidotungsten(VI) can also react with isopropyl isocyanate to generate corresponding imido ureate complex.

Experimental Section

Starting complexes **1**, **2** and **3** were prepared according published procedures.[10b,10c] Other chemicals were from commercial sources and were used as purchased. Solvents were of HPLC grade. All syntheses and manipulations were performed under ambient laboratory atmosphere if not otherwise stated. ^1H and ^{13}C NMR spectra (500 MHz) were recorded at 20 °C using Bruker AV 500 spectrometer in $CDCl_3$ solutions and were referenced internally to $SiMe_4$. IR spectra were recorded as Nujol mulls using a Mattson Galaxy FTIR spectrometer. Elemental analyses were obtained using a Perkin–Elmer CHNS Analyzer 2400. Crystalline samples were dried in vacuo at 40 °C for 4 h prior to elemental analyses.

Chloride-for-Oxide Substitutions of 1: Complex **1** (110 mg, 0.20 mmol) was mixed with $CHCl_3$ (10 mL, stabilized with 1% of EtOH) and subsequently treated with $SOCl_2$ (0.10 mL, 1.4 mmol). The reaction mixture was then heated at reflux temperature under dynamic N_2 atmosphere for two hours while the reaction was monitored by TLC (toluene as an eluent). As a result, complex **1** reacted completely to produce a mixture of two red products and one yellow product. The dark red mixture was separated by silica column chromatography using toluene as an eluent to get *trans* and *cis* isomers, in that order, of dichloro complex **4** as intense red solids. The third component in the reaction mixture was a bright yellow complex **4′**.

***cis*-4:** Yield: 8 mg (7%). $C_{21}H_{27}Cl_2NO_4W$ (M = 612.19 g mol^{-1}): calcd. C 41.20, H 4.45, N 2.29; found C 40.80, H 4.27, N 2.11. ^1H NMR ($CDCl_3$): δ = 7.13 (s, 2 H, Ar), 6.91 (s, 2 H, Ar), 3.75–3.78 (overlapping d + s, 6 H, CH_2), 3.36 (s, 3 H, OCH_3), 2.95 (s, 2 H, CH_2), 2.50 (s, 6 H, $ArCH_3$), 2.47 (s, 6 H, $ArCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 155.91, 135.83, 131.16, 129.46, 128.24, 127.42, 68.23, 58.81, 57.90, 56.98, 20.80, 16.00 ppm. IR (Nujol): $\tilde{\nu}$ = 1304 (w), 1236 (s), 1220 (s), 1156 (s), 1144 (m), 1082 (w), 1038 (w), 976 (s), 966 (vs), 941 (s), 880 (s), 862 (vs), 835 (m), 745 (w), 665 (w), 604 (m), 560 (m) cm^{-1}.

***trans*-4:** Yield: 79 mg (65%) $C_{21}H_{27}Cl_2NO_4W$ (M = 612.19 g mol^{-1}): calcd. C 41.20, H 4.45, N 2.29; found C 40.88, H, 4.22, N 2.02. ^1H NMR ($CDCl_3$): δ = 7.15 (s, 2 H, Ar), 6.92 (s, 2 H, Ar), 4.83 (d, J = 13.4 Hz,2 H, Ar-CH_2), 3.90 (d, J = 13.4 Hz,2 H, Ar-CH_2), 3.50 (t, J = 5.2 Hz,2 H, CH_2), 3.28 (s, 3 H, OCH_3), 2.57 (t, J = 5.2 Hz,2 H, CH_2), 2.55 (s, 6 H, $ArCH_3$), 2.48 (s, 6 H, $ArCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 155.20, 136.38, 131.15, 128.97, 128.68, 127.17, 66.87, 58.95, 56.12, 50.71, 20.87, 15.93 ppm. IR (Nujol): $\tilde{\nu}$ = 1312 (w), 1240 (s), 1227 (s), 1157 (s), 1140 (w), 1090 (w), 964 (vs), 951 (s), 876 (vs), 843 (m), 745 (s), 728 (m), 667 (w), 600 (m), 571 (m) cm^{-1}.

4′: Yield: 8 mg (7%). $C_{20}H_{24}ClNO_4W$ (M = 561.70 g mol^{-1}): calcd. C 42.77, H 4.31, N 2.49; found C 42.40, H 4.07, N 2.47. ^1H NMR ([D$_6$]DMSO): δ = 7.07 (s, 2 H, Ar), 6.78 (s, 2 H, Ar), 4.99 (t, J = 5.8 Hz, 2 H, CH_2), 4.11 (d, J = 14.6 Hz, 2 H, Ar-CH_2), 3.91 (d, J = 14.1 Hz, 2 H, Ar-CH_2), 2.98 (d, J = 7.4 Hz, 2 H,CH_2), 2.30 (s, 6 H, $ArCH_3$), 2.20 (s, 6 H,$ArCH_3$) ppm. IR (Nujol): $\tilde{\nu}$ = 1300 (m), 1240 (s), 1223 (s), 1159 (s), 1092 (m), 1038 (w), 956 (vs), 945 (s), 860 (vs), 842 (s), 748 (m), 734 (m), 696 (w), 665 (m), 599 (m), 572 (m) cm^{-1}.

Chloride-for-Oxide Substitutions of 2 and 3: Stirred suspensions of **2** (1.410 g, 3.00 mmol) and **3** (1.284 g, 1.50 mmol) in toluene (50 mL) were treated with Me_3SiCl (2.0 mL, 12 mmol). The intense blue reaction mixtures were stirred at room temperature for 18 h. The resulting dark blue solutions were filtered through a short pad of silica. The volatiles were then removed in a vacuum and remaining dark purple solids were washed with cold hexane (20 mL) and dried in air.

5: Yield: 1.330 g (85%). $C_{21}H_{27}Cl_2MoNO_4$ (M = 524.30 g mol^{-1}): calcd. C 48.11, H 5.19, N 2.67; found C 48.41, H 5.07, N 2.48. ^1H NMR ($CDCl_3$): δ = 7.10 (s,2 H, Ar), 6.97 (s,2 H, Ar), 4.69 (d, J = 13.3 Hz,2 H, Ar-CH_2), 3.89 (d, J = 13.3 Hz, 2 H, Ar-CH_2), 3.49 (t, J = 5.1 Hz, 2 H,CH_2), 3.28 (s, 3 H, OCH_3), 2.56 (s, 6 H,$ArCH_3$), 2.48 (s, 6 H, $ArCH_3$) 2.38 (t, J = 5.1 Hz, 2 H,CH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 161.21, 138.86, 130.83, 129.83, 129.68, 128.03, 66.82,

Table 1. Summary of Crystallographic data for *trans*-**4**, **4′**, **6** and **7** at 173(2) K.

	trans-**4**	**4′**	**6**	**7**
Formula	$C_{21}H_{27}Cl_2NO_4W$	$C_{20}H_{24}ClNO_4W$	$C_{19}H_{23}Cl_2MoNO_3$	$C_{31}H_{48}N_4O_4W$
M_r	612.19	561.70	480.22	724.58
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group (no.)	*C*2/*c* (15)	$P2_1/c$ (14)	$P2_1/m$ (11)	$P2_1/n$ (14)
a [Å]	35.7507(12)	8.1556(2)	7.6901(13)	9.1641(3)
b [Å]	8.0281(4)	34.1160(10)	16.014(3)	17.1466(6)
c [Å]	15.7217(7)	14.8612(4)	8.0501(8)	20.5434(7)
α [°]	90	90	90	90
β [°]	93.821(2)	104.5020(10)	93.171(9)	102.645(2)
δ [°]	90	90	90	90
V [Å^3]	4502.3(3)	4003.18(19)	989.8(3)	3149.75(19)
Z	8	8	2	4
D_c [g cm^{-1}]	1.806	1.864	1.611	1.528
μ(Mo-K_α) [cm^{-1}]	53.95	59.30	9.51	37.08
Observed reflections	5600	9233	2015	7701
R_{int}	0.0320	0.0483	0.0331	0.0447
Parameters	268	495	127	372
R_1[a]	0.0421 (0.0307)	0.0635 (0.0449)	0.058 (0.048)	0.0713 (0.0524)
wR_2[a]	0.0613 (0.0572)	0.0836 (0.0769)	0.100 (0.095)	0.1132 (0.1025)

[a] Values in parentheses for reflections with $I > 2.0\sigma(I)$: $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$, where $P = (2F_c^2+F_o^2)/3$.

58.92, 56.45, 50.53, 21.33, 16.43 ppm. IR (Nujol): ṽ = 1306 (w), 1239 (s), 1219 (s), 1171 (vs), 1117 (s), 1090 (m), 959 (vs), 882 (vs), 873 (m), 746 (s), 731 (m), 681 (w), 661 (m), 598 (m), 574 (m) cm^{-1}.

6: Yield: 1.325 g (92%). $C_{19}H_{23}Cl_2MoNO_3$ (M = 480.22 g mol^{-1}): calcd. C 47.52, H 4.83, N 2.92; found C 47.81, H 5.05, N 2.78. ^{1}H NMR ($CDCl_3$): δ = 7.11 (s, 2 H, Ar), 6.94 (s, 2 H, Ar), 4.86 (d, J = 13.0 Hz, 2 H,Ar-CH_2), 3.08 (d, J = 13.0 Hz, 2 H,Ar-CH_2), 2.56 (s, ArCH_3, 6 H), 2.48 (s, 6 H,ArCH_3) 1.86 (s, 3 H,N–CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 160.78, 138.95, 131.03, 129.56, 129.20, 128.25, 62.80, 46.83, 21.23, 16.43 ppm. IR (Nujol): ṽ = 1300 (m), 1240 (s), 1223 (s), 1157 (s), 1132 (m), 1082 (vs, br), 955 (vs), 937 (m), 866 (vs), 844 (m), 748 (w), 696 (w), 666 (w), 600 (m), 573 (w) cm^{-1}.

Reaction of 1 with Isopropyl Isocyanate: Complex **1** (110 mg, 0.20 mmol) was mixed with toluene (3.0 mL) in a screw cap vial and subsequently treated with isopropyl isocyanate (0.10 mL, 1.0 mmol). The reaction mixture was then heated at 110 °C for 16 hours. The red solution formed was cooled to the room temperature and hexane (3.0 mL) was added to enhance the crystallization. The solution was then kept at –18 °C overnight, after that the orange-red crystals (85 mg, 60%) were separated by decantation and washed by hexane. Crystals were stable in air for several days, but they decompose quickly upon dissolution.

Table 2. Selected bond lengths [Å] and angles [°] for *trans*-**4**, **4′** and **6**.

	trans-**4**	**4′**[a]	**6**
M–O1	1.693(3)	1.714(5)	1.672(4)
M–O2	1.868(3)	1.918(5)	1.862(3)
M–O3	1.869(3)	1.896(5)	1.862(3)[b]
M–Cl1	2.3699(11)	2.3701(16)	2.3692(17)
M–Cl2/O4	2.3713(11)	1.909(4)	2.3822(18)
M–N8	2.534(3)	2.407(5)	2.536(4)
O1–M–N8	177.67(13)	168.2(2)	178.4(2)
O2–M–O3	159.21(11)	154.46(18)	158.76(16)[b]
Cl1–M–Cl2/O2	170.96(4)	165.60(14)	167.88(6)

[a] Parameters for the W1-centered molecule. [b] O3 corresponds to O2^i, where $i = x, -y+1/2, z$.

7: Yield: 54 mg (37%). $C_{31}H_{48}N_4O_4W$ (M = 724.58 g mol^{-1}): C 51.39, H 6.68, N 7.73; found C 50.99, H 6.35, N 7.59. IR: ṽ = 1634 (vs, br), 1283 (vs), 1245 (vs), 1221 (vs), 1159 (s), 1113 (s), 1094 (m), 1055 (m), 1038 (w), 988 (m), 961 (m), 932 (m), 860 (s), 855 (vs), 783 (m), 750 (m), 733 (m), 690 (w), 598 (m), 556 (m), 422 (w) cm^{-1}.

X-ray Crystallography: Crystals of *trans*-**4** and **4′**, suitable for X-ray measurements were grown at 4 °C from acetonitrile. Crystals of **6** were obtained from concentrated toluene solution at room temperature. Crystals of **7** precipitated from the reaction mixture at –18 °C. Crystal data for the compounds *trans*-**4**, **4′**, **6** and **7** along with other experimental details are summarized in Table 1. Single-crystal data collections, reduction, and subsequent calculations were performed essentially as described in our earlier papers.[12,22] Figures were drawn with *Ortep-3 for Windows*[23] (Table 2).

CCDC-601925, -601926, -601927 and -601928 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.

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