Synthesis, Electrochemistry, and Oxygen-Atom Transfer Reactions of Dioxotungsten(VI) and -molybdenum(VI) Complexes with N_2O_2 and N_2S_2 Tetradentate Ligands

Yee-Lok Wong,[a] Jian-Fang Ma,[a] Wing-Fong Law,[a] Yan Yan,[a] Wing-Tak Wong,[b] Ze-Ying Zhang,[a] Thomas C. W. Mak,[a] and Dennis K. P. Ng*[a]

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A series of N_2O_2 tetradentate ligands with a range of substituents attached to the nitrogen atoms have been prepared (H_2L^n) (n = 1–9). Treatment of these ligands and the N_2S_2 tetradentate ligand H_2L^{10} with $[WO_2Cl_2(DME)]$ (DME = 1,2-dimethoxyethane) in the presence of triethylamine leads to the formation of *cis*-dioxotungsten(VI) complexes $[WO_2(L^n)]$ (n = 1–10). Reaction of the N_2O_2 tetradentate ligands H_2L^n (n = 1, 3–7) with ammonium molybdate tetrahydrate and dilute hydrochloric acid gives the corresponding molybdenum(VI) analogs $[MoO_2(L^n)]$ (n = 1, 3–7). These compounds have been spectroscopically characterized and the molecular structures of $[WO_2(L^n)]$ (n = 1, 2, 9) and $[MoO_2(L^5)]$ have been established by X-ray diffraction analysis. These high-valent compounds participate in oxygen-atom transfer reactions and can catalyze the oxidation of benzoin with dimethyl sulfoxide. The complex $[WO_2(L^{10})]$, which contains an S-donor ligand, has lower reduction potential and higher reactivity toward oxo-transfer reactions than analogous tungsten complexes having N_2O_2 ligands. The kinetics of these catalytic processes along with the structure and electrochemistry of these dioxotungsten and -molybdenum complexes are described and compared.

Introduction

Atom-transfer chemistry of tungsten has recently attracted considerable attention because of its relevance to some important oxidation processes promoted by high-valent tungsten species[1] and biological reactions mediated by tungsten oxotransferase enzymes, which catalyze the oxo-transfer reactions for a range of substrates such as aldehydes and carbon dioxide.[2] In contrast to the related molybdenum chemistry that has been well documented,[3] tungsten-mediated atom-transfer reactions have been little studied and, to our knowledge, not more than a dozen examples have been reported so far.[4] Of much current interest are those containing bidentate dithiolene-type ligands which mimic the pterin cofactors found in the tungstoenzymes.[4][5] Although the oxomolybdenum complexes with tetradentate N-, O- and S-donor ligands have been studied extensively and some of them participate in various atom-transfer reactions,[6] very little has been accomplished with regard to the analogous tungsten chemistry.[7] We describe herein the synthesis and characterization of a new series of dioxotungsten(VI) complexes with N_2O_2 and N_2S_2 tetradentate ligands. These compounds undergo an irreversible reduction at highly negative potentials, but are still active toward oxygen-atom transfer reactions. The structural, electrochemical and oxo-transfer properties of these tungsten complexes are discussed and compared with those of their molybdenum counterparts, some of which have also been synthesized for the first time.

Results and Discussion

Synthesis and Characterization

Deprotonation of the readily available tetradentate ligand H_2L^1[8] with *n*BuLi followed by *N*-methylation with methyl iodide or *N*-benzylation with various benzyl bromides led to the formation of a series of N_2O_2 tetradentate ligands H_2L^n (n = 2−7) in good yield (Scheme 1). These substituents, having different steric and electronic properties, were introduced to the nitrogen atoms with the goal of examining their effects on complex formation and properties of the resulting complexes. The ligand H_2L^2 was prepared previously by reductive amination from formaldehyde and glyoxalbis(2-hydroxyanil).[9] The new ligands H_2L^n (n = 3−7) were found to be rather unstable and the yellow oily liquids darkened gradually upon exposure to air over 1−2 days. The ligands should therefore be freshly prepared for complex formation. The ligands H_2L^n (n = 8−10) were synthesized according to literature methods.[10,11]

Treatment of these ligands with $[WO_2Cl_2(DME)]$ in the presence of triethylamine gave the corresponding dioxo complexes $[WO_2(L^n)]$ (n = 1−10, Scheme 2). In contrast to the commonly used starting material $[WO_2Cl_2]$,[12] this DME adduct, which can be prepared readily from $[WOCl_4]$, $(Me_3Si)_2O$ and DME,[13] possesses good solubility in or-

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[a] Department of Chemistry, The Chinese University of Hong Kong,
Shatin, N.T., Hong Kong
Fax: (internat.) + 852/2603-5057
E-mail: dkpn@cuhk.edu.hk
[b] Department of Chemistry, The University of Hong Kong,
Pokfulam Road, Hong Kong

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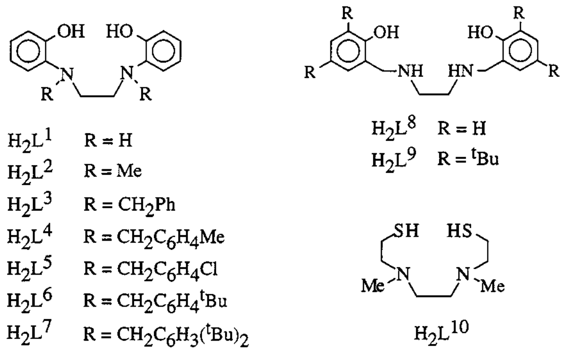
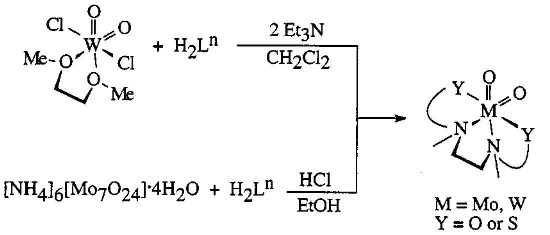


Scheme 1. Structures of tetradentate ligands

ganic solvents and undergoes facile ligand-substitution reactions.[14] It therefore appears to be a more versatile precursor to other high-valent tungsten complexes. The molybdenum counterparts [$MoO_2(L^n)$] (n = 1, 3−7) were also prepared in moderate yield by treating ammonium molybdate tetrahydrate with the ligands H_2L^n (n = 1, 3−7) in the presence of HCl and EtOH (Scheme 2).[15] The complex [$MoO_2(L^1)$] was prepared previously from [$MoO_2(acac)_2$] (acac = acetylacetonate) and H_2L^1 by Spence et al.[16] All these air-stable dioxotungsten and -molybdenum complexes could be purified by column chromatography and/or recrystallization, and were characterized with elemental analyses or accurate mass measurements, along with a range of spectroscopic methods.



Scheme 2. Preparation of dioxotungsten(VI) and -molybdenum(VI) complexes

All the tungsten compounds showed two characteristic *cis*-dioxo [WO_2] vibrational bands at 895−921 and 936−958 cm^{-1} in their IR spectra,[17] except [$WO_2(L^8)$] the IR spectrum of which exhibited only the higher frequency band at 941 cm^{-1} while the lower frequency band was embedded in a broad signal at 885 cm^{-1}. The IR spectra of the molybdenum analogs showed similar asymmetric and symmetric Mo=O stretches at 905−919 and 928−938 cm^{-1}, respectively; the latter band occurred at a 15−25 cm^{-1} lower frequency than that for the tungsten congeners. The ^{1}H- and ^{13}C-NMR spectra of these dioxo compounds were in accord with an octahedral structure having a C_2 rotation axis. Take compounds [$WO_2(L^n)$] (n = 8, 9) as examples; the two methylene protons next to the aromatic ring are no longer equivalent. Two doublets with a geminal coupling constant of ca. 14 Hz appeared at $\delta \approx 3.9$ and 4.7 in their ^{1}H-NMR spectra recorded in [D_6]DMSO. The two methylene protons in the benzyl groups in [$MO_2(L^n)$] (M = Mo, W; n = 3−6) are also diastereotopic and an AB quadruplet was observed for these protons in all the spectra. All these dioxo compounds were also characterized by fast atom bombardment (FAB) or liquid secondary ion (LSI) mass spectrometry. The M^+ or $[M+H]^+$ species were identified in all cases with predicted isotopic distribution pattern.

Molecular Structures

Single-crystal X-ray diffraction studies of [$WO_2(L^2)$] and [$MoO_2(L^5)$] revealed that the asymmetric unit consists of two crystallographically independent molecules. The former also contains solvated dichloromethane. Figures 1 and 2 display the molecular structure of one of the independent molecules for [$WO_2(L^2)$] and [$MoO_2(L^5)$], respectively. For [$WO_2(L^9)$] (Figure 3), the tungsten atom lies on a crystallographic 2-fold axis so that one-half of the molecule is present in the asymmetric unit. A perspective view of [$WO_2(L^1)$] is also presented in Figure 4. Each of these structures possesses C_2 {for [$WO_2(L^9)$]} or approximate C_2 symmetry and adopts distorted octahedral geometry, with the N atoms *trans* to the terminal oxo groups. The bond lengths and angles of these complexes are unexceptional and resemble those found in other six-coordinate dioxo−W^{VI}[12d,14a,17b,18] and −Mo^{VI} complexes.[9,10,19] Selected bond lengths and angles for these compounds, along with a brief description is available as Supporting Information on the WWW or from the author.

Electrochemistry

The electrochemical behavior of [$MoO_2(L^1)$] in *N*,*N*-dimethylformamide (DMF) was studied previously by cyclic voltammetry.[16] The voltammogram displayed an irreversible one-electron reduction peak at −1.41 V vs. SCE coupled to an oxidation peak at −0.02 V, together with a reversible one-electron reduction peak at −1.70 V assignable to the Mo^{VI}/Mo^{V} and Mo^{V}/Mo^{IV} couples, respectively. An oxo−Mo^{V} species with deprotonated amino ligand was postulated as the intermediate. The electrochemistry of [$MoO_2(L^n)$] (n = 4, 5, 7), which do not have ionizable protons, is somewhat different. Their voltammograms recorded in DMF showed only one redox couple attributable to a metal-based reduction. A weak cathodic peak at around −1 V was also observed for [$MoO_2(L^n)$] (n = 5, 7) but its origin is unclear at this stage. The electrochemical data are summarized in Table 1. Ferrocene was added in all measurements as an internal reference and its half-wave potential ($E_{1/2}$ = 0.08 V vs. Ag/Ag^+ in MeCN) remained virtually unchanged. By comparing the values of ΔE_p of the reduction couples of [$MoO_2(L^n)$] (n = 4, 5, 7) (102−160 mV) with that of ferrocene which ranges from 66 to 71 mV, and on considering the i_{pa}/i_{pc} values which are less than unity, these couples can be described as quasi-reversible processes. It is worth noting that the substituents attached to the nitrogen atoms of the ligands only have marginal effects on the redox potentials. The $E_{1/2}$ values follow the order

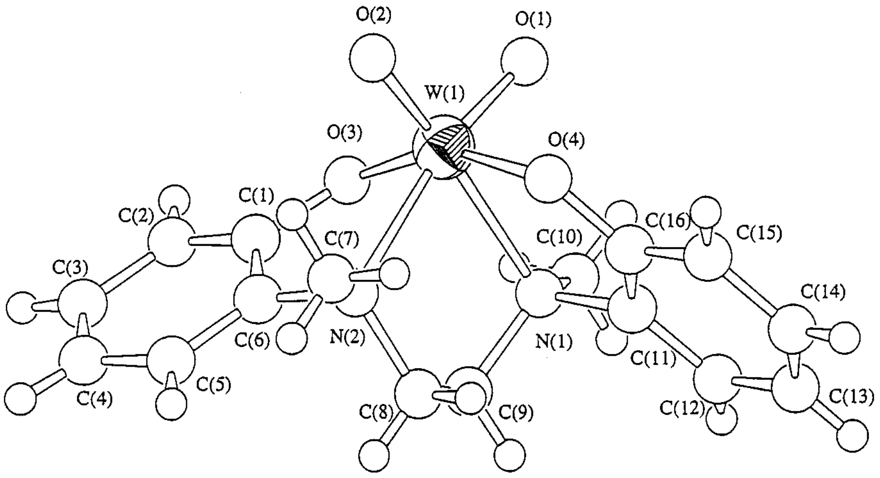


Figure 1. Molecular structure and atom-labeling scheme for $[WO_2(L^2)]$; the hydrogen atoms are shown with small arbitrary radii

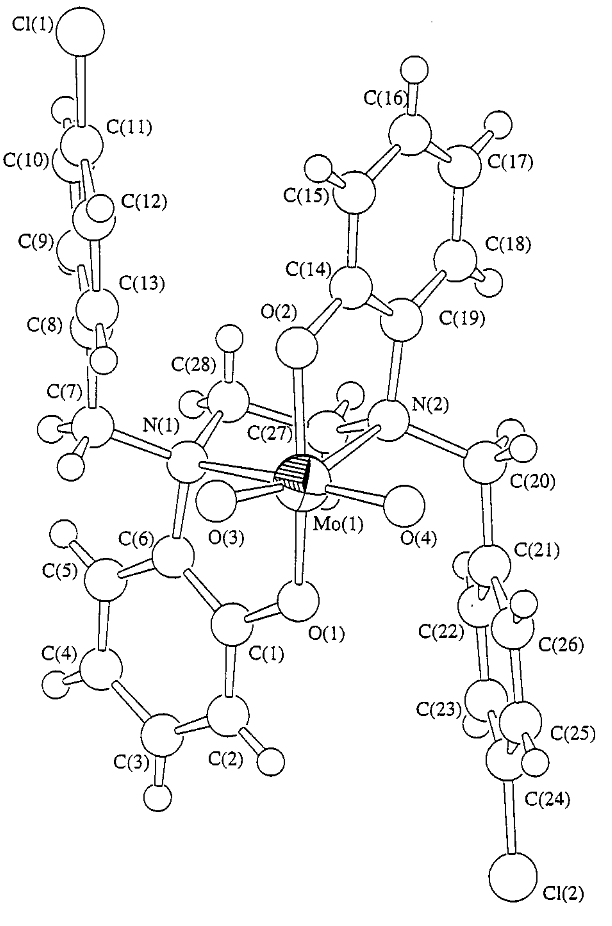


Figure 2. Molecular structure and atom-labeling scheme for $[MoO_2(L^5)]$; the hydrogen atoms are shown with small arbitrary radii

$[MoO_2(L^5)] > [MoO_2(L^4)] > [MoO_2(L^7)]$ as a result of the different electron-withdrawing abilities (Cl > Me > *t*Bu).

The voltammograms of the tungsten analogs $[WO_2(L^n)]$ (n = 1, 4, 5, 8) revealed a major irreversible process at highly negative potentials (E_{pc} ranged from −2.07 to −2.32 V vs. SCE) assignable to the reduction of the W^{VI} metal center. Some weak and unidentified signals were also seen for some of these complexes (Table 1). In accordance with previous studies,[5a,17b,20] the metal-based reduction potentials for the tungsten complexes were more negative than those of the corresponding molybdenum counterparts and the redox processes were less reversible.

The electrochemical behavior of $[WO_2(L^{10})]$ was remarkably different from that of other tungsten analogs. Its voltammogram recorded at a scan rate of 100 mV s^{-1} showed a reduction couple centered at −1.90 V and an oxidation peak at −0.06 V, both vs. SCE (Figure 5a). The anodic peak for the reduction couple was not observed at slower scan rates but this peak emerged and the peak current ratio (i_{pa}/i_{pc}) for this couple approached unity as the scan rate was increased. The peak-to-peak separation (ΔE_p) fell in the region 100 to 105 mV at scan rates between 100 and 700 mV s^{-1}. The value increased gradually to 197 mV with increasing scan rate to 10,000 mV s^{-1}. These results suggested that the reduction changed from an irreversible to a quasi-reversible process as the scan rate was increased. The peak current function ratio {peak current function: $i_p\nu^{-1/2}C^{-1}$, where i_p = peak current [A], ν = scan rate [V s^{-1}], C = concentration [M]} for the reduction of $[WO_2(L^{10})]$ with respect to the one-electron oxidation of ferrocene under identical conditions was 1.25 at 20 mV s^{-1}, which decreased to 0.76 at 800 mV s^{-1}. These data together with the plot showing the variation of $i_{pc}\nu^{-1/2}$ with ν (Figure 6) indicated that the process approaches an overall two-electron reduction at slow scan rates. This plot implied that the one-electron reduction product is somewhat unstable and a further removal of one electron occurs readily to the W^{IV} state. This will happen if the $W^{VI/V}$ potential is more negative than the $W^{V/IV}$ potential, as was observed for related molybdenum complexes.[10,21] It is also worth noting that the intensity of the oxidation peak at −0.06 V decreases with increasing scan rate and eventually vanishes at 800 mV s^{-1} (Figure 5b). This peak may thus be attributed to an electrochemically generated W^{IV} species and a purely one-electron quasi-reversible reduction seems to occur at scan rates over 800 mV s^{-1}. This behavior is very similar to that of the molybdenum counterpart $[MoO_2(L^{10})]$ with the ex-

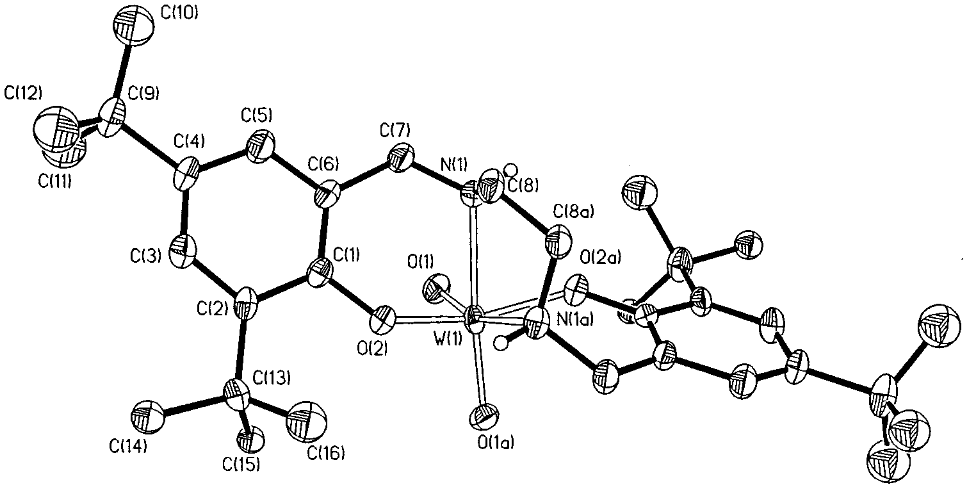


Figure 3. Perspective view and atom-labeling scheme for $[WO_2(L^9)]$

Table 1. Electrochemical data for selected dioxomolybdenum and -tungsten complexes[a]

Compound	E_{pc}	E_{pa}	$E_{1/2}$	ΔE_p[b]	$\lvert i_{pa}/i_{pc}\rvert$	Other processes
$[MoO_2(L^4)]$	−1.42	−1.32	−1.37	102	0.84	nil
$[MoO_2(L^5)]$	−1.43	−1.27	−1.35	160	0.48	$E_{pc} = -0.99$
$[MoO_2(L^7)]$	−1.48	−1.33	−1.41	156	0.85	$E_{pc} = -1.11$
$[WO_2(L^1)]$	−2.30	–	–	–	–	$E_{pc} = -1.57, -2.00$; $E_{pa} = -0.59$
$[WO_2(L^4)]$	−2.32	–	–	–	–	$E_{pa} = 0.94$
$[WO_2(L^5)]$	−2.27	–	–	–	–	$E_{pa} = 0.91$
$[WO_2(L^8)]$	−2.07	–	–	–	–	nil
$[WO_2(L^{10})]$	−1.96	−1.84	−1.90	118	0.51	$E_{pa} = -0.06$

[a] Recorded with $[Bu_4N][ClO_4]$ as electrolyte in DMF (0.1 M) at ambient temp. Scan rate = 100 mV s^{-1}. Potentials are expressed in V vs. SCE. – [b] $\Delta E_p = \lvert E_{pc} - E_{pa}\rvert$ in mV.

ception that the reduction of the latter occurs at a much more positive potential (−1.34 V vs. SCE).[22] It is interesting to note that incorporation of sulfur-containing ligand such as L^{10} lowers the reduction potential of the complex and increases its reversibility relative to the analogous oxygen-containing ligands. The reduction potential of $[WO_2(L^{10})]$ ($E_{pc} = -1.96$ V vs. SCE or −2.27 V vs. Ag/Ag^+ in MeCN), however, is still more negative than those of the synthetic models for tungstoenzymes such as $[Et_4N]_2[WO_2(bdt)_2]$ (bdt = 1,2-benzenedithiolate) ($E_{pc} = -1.34$ V vs. SCE)[5a] and $[Et_4N]_2[WO_2(mnt)_2]$ (mnt = 1,2-dicyanoethylenedithiolate) ($E_{pc} = -1.50$ V vs. Ag/Ag^+ in MeCN).[5c] It appears that these unsaturated dithiolene-type ligands are crucial for the complexes to reach physiologically accessible potentials.

Oxo-Transfer Reactions

As tungsten-mediated oxo-transfer reactions had been little studied, we were interested to examine the oxo-transfer properties of some of these dioxotungsten(VI) compounds, namely $[WO_2(L^n)]$ (n = 1, 8, 10) using benzoin as the common reductant. Typically, 7×10^{-3} mmol of the complexes and 20 equiv. of benzoin were dissolved in deoxygenated $[D_6]$DMSO (0.5 ml). The mixtures were sealed in NMR tubes and heated at 100°C. The kinetics of the systems were analyzed by ^{1}H-NMR spectroscopy which allowed the quantification of benzoin and its oxidized product, benzil, as well as the complexes. The concentration ratios of {[benzoin] + [benzil]} to $\{[WO_2(L^n)]\}$ (n = 1, 8, 10) remained constant during the course of the reactions. In the absence of the complexes, no reaction between benzoin and $[D_6]$DMSO was detected. The percentage conversion of benzoin to benzil was about 90% after 36 h when compound $[WO_2(L^{10})]$ was used. Reactions involving complexes $[WO_2(L^n)]$ (n = 1, 8) proceeded slowly and only ca. 50% of benzoin was consumed after 1 week. These results indicated that these dioxotungsten(VI) complexes can catalyze the

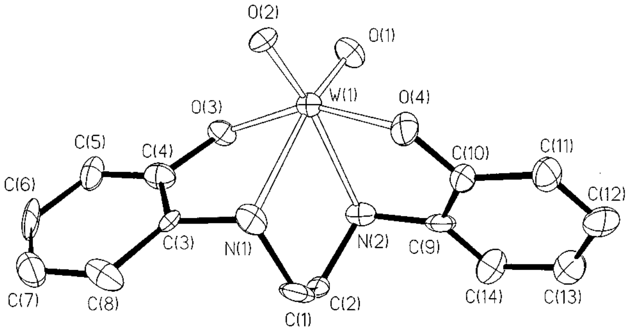


Figure 4. Molecular structure of $[WO_2(L^1)]$ showing the atom-labeling scheme

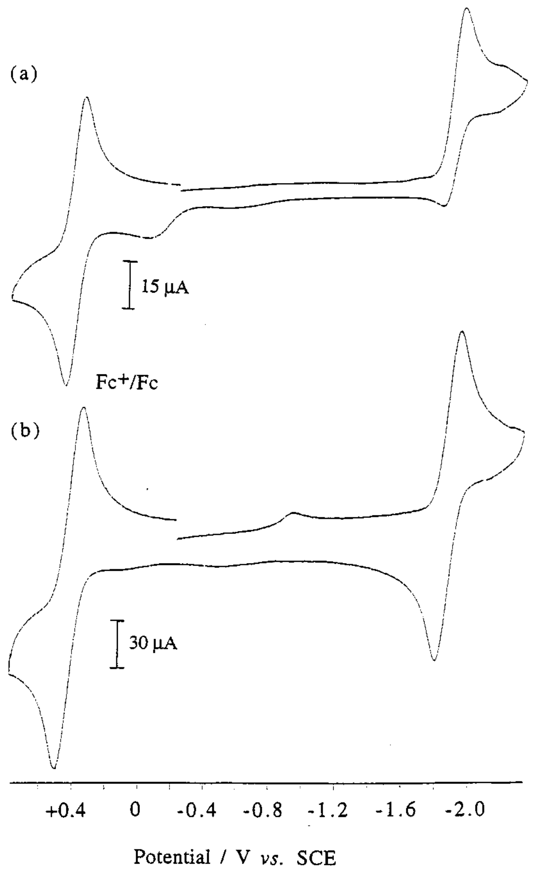


Figure 5. Cyclic voltammograms of $[WO_2(L^{10})]$ in DMF containing 0.1 M $[Bu_4N][ClO_4]$ recorded at (a) 100 mV s^{-1} and (b) 800 mV s^{-1}

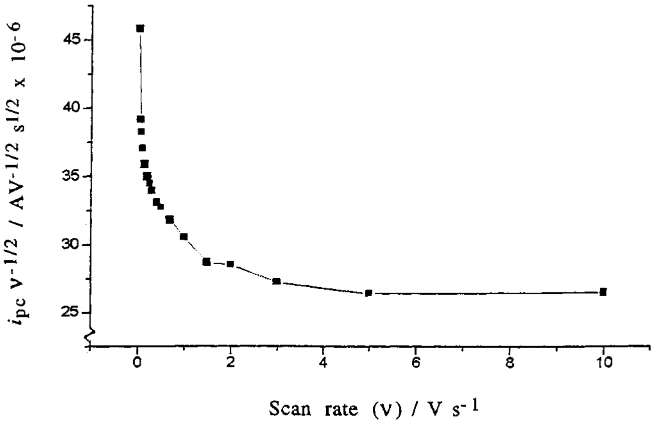
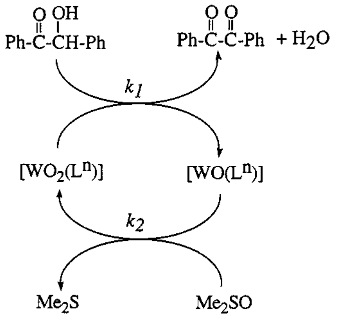


Figure 6. Plot of $i_{pc}v^{-1/2}$ vs. v for $[WO_2(L^{10})]$

oxidation of benzoin with $[D_6]$DMSO. The use of DMSO as oxo donor in this study has biological relevance to the molybdenum-containing DMSO reductases, which are able to utilize a variety of dialkyl- and alkylarylsulfoxides as oxidizing substrate.[23]

A plausible mechanism for this oxidation is suggested in Scheme 3 by analogy to that proposed for related catalytic systems.[24] Presumably, the W^{VI} complexes are reduced by benzoin to yield monomeric oxotungsten(IV) species, benzil and water. The W^{IV} complexes are then oxidized back to their parent dioxo compounds with $[D_6]$DMSO. Assuming that the regeneration of the W^{VI} species is fast ($k_2 \gg k_1$), their concentration should be essentially constant throughout the reactions. The rate of consumption of benzoin can thus be regarded as a pseudo-first-order reaction ($-d[\text{benzoin}]/dt = k_{obs}$ [benzoin], where $k_{obs} = k_1\{[WO(L^n)]\}$). Figure 7 shows the variation of ln{[benzoin]$_o$/[benzoin]} with time for $[WO_2(L^{10})]$, where [benzoin]$_o$ is the initial concentration of benzoin. From the slope of the best-fit straight line (1.86×10^{-5} s^{-1}), the value of k_1 can be determined (1.31×10^{-3} M^{-1} s^{-1}). For the other two N_2O_2 complexes $[WO_2(L^n)]$ ($n = 1, 8$), a gradual decrease in the catalytic activities was observed after prolonged heating. The respective k_1 values were calculated to be 1.28×10^{-4} and 9.43×10^{-5} M^{-1} s^{-1} based on the data collected in the first 85 h. The *S*-ligated complex $[WO_2(L^{10})]$ is therefore a better oxo donor than the *O*-ligated complexes $[WO_2(L^n)]$ ($n = 1, 8$) which is fully consistent with the electrochemical data (Table 1). A comparison of these dioxo complexes shows that the anionic complexes $[WO_2(bdt)_2]^{2-}$[5a,25] and $\{WO_2[O_2CC(S)Ph_2]_2\}^{2-}$[24a] are very efficient in promoting the oxidation of benzoin, while the complexes $[WO_2LX]$ [L = hydrotris(3,5-dimethyl-1-pyrazolyl)borate; X = OPh, S_2PPh_2-*S*] are inert toward oxygen-atom transfer reactions.[17b]



Scheme 3. Proposed mechanism for the oxidation of benzoin with DMSO using $[WO_2(L^n)]$ as a catalyst

In order to reveal whether the W^{IV} species $[WO(L^{10})]$ or the W^V dimer $[W_2O_3(L^{10})_2]$ were actually formed, a mixture of $[WO_2(L^{10})]$ and one equiv. of benzoin in deoxygenated $[D_7]$DMF was sealed in an NMR tube and heated at 100°C. The reaction was monitored by ^{1}H-NMR spectroscopy. Surprisingly, the spectra were essentially unchanged and no significant amount of benzil was detected even after 1 week.

The oxo-transfer properties of the molybdenum analogs $[MoO_2(L^n)]$ ($n = 5, 6$) were also investigated under identical conditions for comparison. These molybdenum-mediated reactions proceeded considerably faster and ca. 75% of benzoin was consumed after 25 h at 100°C. However, the {[benzoin] + [benzil]}-to-$\{[MoO_2(L^n)]\}$ ($n = 5, 6$) ratios increased gradually during the course of the reactions indicating that part of the catalysts was deactivated and consumed. Some unidentified signals were also observed in the NMR spectra which precluded a detailed kinetic analysis. Lowering the temperature to 50°C greatly retarded the oxo-transfer reactions; the benzoin conversion was only 5−7% after 95 h. The higher oxo-transfer reactivity of molybdenum complexes relative to their tungsten counterparts may be attributed to their lower reduction potentials and weaker M=O bond (bond dissociation energy = ca. 410 kJ mol^{-1} for Mo=O and > 580 kJ mol^{-1} for W=O).[4,17b]

In summary, we have synthesized a new series of dioxotungsten complexes with N_2O_2 and N_2S_2 tetradentate ligands which represent rare examples of tungsten compounds showing oxo-transfer activity. The S-donor atoms in the ligand seem to play an important role in lowering the reduction potential of the complex and thereby increasing its oxo-transfer reactivity toward the oxidation of benzoin with DMSO. The analogous molybdenum complexes are more active in this oxygen-atom transfer reaction which is in accord with the electrochemical data.

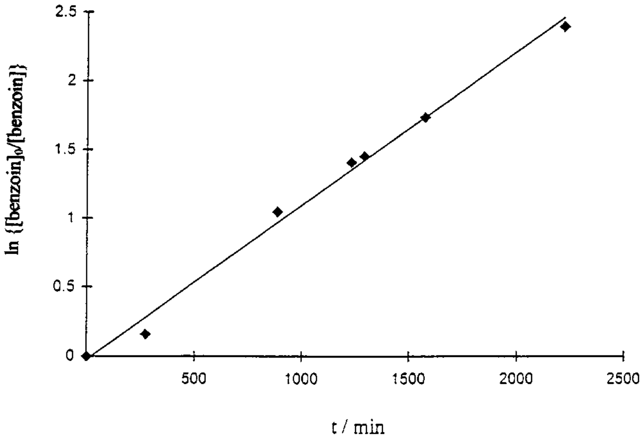


Figure 7. Plot of ln{[benzoin]$_o$/[benzoin]} vs. time for a system containing initially 0.28 M benzoin and 0.014 M [$WO_2(L^{10})$] in [D_6]DMSO at 100°C

Experimental Section

All reactions were carried out with standard Schlenk-line techniques under nitrogen; workups were performed in air. Dichloromethane was dried with 4-Å molecular sieves and distilled from calcium hydride. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. DMF for voltammetric studies was dried with barium oxide and distilled under reduced pressure. The electrolyte [Bu_4N][ClO_4] was recrystallized from dry acetone three times prior to use. All other reagents and solvents were of reagent grade and used as received. The ligands H_2L^n (n = 1,[8] 8, 9,[10] 10[11]) and the tungsten complex [WO_2Cl_2(DME)][13] were prepared by previously described methods. − NMR: Bruker WM 250 (^{1}H, 250; ^{13}C, 62.9 MHz), Bruker DPX 300 (^{1}H, 300; ^{13}C, 75.4 MHz) and Bruker ARX 500 (^{1}H, 500; ^{13}C, 125.8 MHz), $CDCl_3$ as solvent and TMS as internal standard unless otherwise stated, for [D_6]DMSO as solvent δ_H = 2.50, δ_C = 39.7, coupling constant J in Hz. − IR: Perkin Elmer 1600 FT-IR and Nicolet 550 FT-IR as KBr pellets. − MS: Hewlett Packard 5989B (FAB) and Bruker APEX 47e FT-ICR (LSI) with 3-nitrobenzyl alcohol as matrix. − Elemental analyses: Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. − Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a platinum-sphere working electrode, a silver-wire counter electrode and an Ag/$AgNO_3$ (0.1 M in MeCN) reference electrode which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode.[26] Typically, a 0.1 M solution of [Bu_4N][ClO_4] in DMF containing 1.0 mM of sample was purged with nitrogen for 20 min, then the voltammograms were recorded at scan rates ranging from 20 to 3000 mV s^{-1} at ambient temp. unless otherwise stated. All potentials were referred internally to the ferrocene/ferrocenium couple at +0.39 V vs. SCE.[27]

General Procedure for the Preparation of H_2L^n (n = 2−7): To a colorless solution of H_2L^1 (0.24 g, 1.0 mmol) in THF (10 ml) was added nBuLi (1.6 M solution in n-hexane, 2.6 ml, 4.1 mmol) dropwise at 0°C. The mixture was stirred at this temp. for 1 h, then allowed to warm to room temp. Iodomethane (0.13 ml, 2.0 mmol) or differently substituted benzyl bromides (2.0 mmol) were added slowly and stirring was continued for 18 h (only 6 h was required for the reaction with iodomethane). The volatiles were removed under reduced pressure and water (20 ml) was added. The mixture was extracted with CH_2Cl_2 (3 × 50 ml) and the combined extracts were dried with sodium sulfate and the solvent was removed using a rotary evaporater. The ligand H_2L^2 was collected as a white solid by washing the residual light brown solid with CH_2Cl_2/hexane (1:3), while the other ligands were purified by column chromatography using hexane followed by CH_2Cl_2 as eluent. These ligands were obtained as a pale yellow oil.

***N*,*N*′-Bis(2-hydroxyphenyl)-*N*,*N*′-dimethyl-1,2-diaminoethane (H_2L^2):** 0.20 g (73%); m.p. 110−112°C (ref.[9] 112°C). − ^{1}H NMR (250 MHz): δ = 2.87 (s, 6 H, CH_3), 3.02 (s, 4 H, CH_2), 6.86 (dt, J = 1.5, 7.6, 2 H, ArH), 6.94 (dd, J = 1.5, 8.0, 2 H, ArH), 7.06 (dt, J = 1.5, 7.6, 2 H, ArH), 7.17 (dd, J = 1.5, 8.0, 2 H, ArH).

***N*,*N*′-Dibenzyl-*N*,*N*′-bis(2-hydroxyphenyl)-1,2-diaminoethane (H_2L^3):** 0.30 g (71%). − ^{1}H NMR (300 MHz): δ = 2.90 (s, 4 H, CH_2CH_2), 3.84 (s, 4 H, PhCH_2), 6.73−6.79 (m, 2 H, ArH), 6.88 (dd, J = 1.5, 8.1, 2 H, ArH), 6.96−7.04 (m, 8 H, ArH), 7.13−7.20 (m, 6 H, ArH). − ^{13}C{^{1}H} NMR (75.4 MHz): δ = 52.1, 60.9, 114.5, 119.9, 123.3, 126.8, 127.3, 128.2, 129.1, 136.0, 136.8, 152.9. − HRMS (LSI): m/z = 425.2216 {calcd. for [M + H]$^+$ 425.2229}.

***N*,*N*′-Bis(2-hydroxyphenyl)-*N*,*N*′-bis(4-methylbenzyl)-1,2-diaminoethane (H_2L^4):** 0.35 g (77%). − ^{1}H NMR (300 MHz): δ = 2.38 (s, 6 H, CH_3), 3.02 (s, 4 H, CH_2CH_2), 3.93 (s, 4 H, ArCH_2), 6.86−6.91 (m, 2 H, ArH), 6.99−7.19 (m, 14 H, ArH). − ^{13}C{^{1}H} NMR (75.4 MHz): δ = 21.0, 52.1, 60.5, 114.4, 119.8, 123.3, 126.7, 128.8, 129.0, 133.8, 136.2, 136.8, 152.9. − HRMS (LSI): m/z = 453.2553 {calcd. for [M + H]$^+$ 453.2542}.

***N*,*N*′-Bis(4-chlorobenzyl)-*N*,*N*′-bis(2-hydroxyphenyl)-1,2-diaminoethane (H_2L^5):** 0.39 g (79%). − ^{1}H NMR (300 MHz): δ = 2.88 (s, 4 H, CH_2CH_2), 3.83 (s, 4 H, ArCH_2), 6.78 (dt, J = 1.5, 7.6, 2 H, ArH), 6.89 (dd, J = 1.5, 8.1, 2 H, ArH), 6.93−6.96 (m, 4 H, ArH), 6.99 (dd, J = 1.5, 8.0, 2 H, ArH), 7.02−7.07 (m, 2 H, ArH), 7.11−7.16 (m, 4 H, ArH). − ^{13}C{^{1}H} NMR (75.4 MHz): δ = 52.3, 60.3, 114.8, 120.1, 123.2, 127.1, 128.4, 130.4, 133.2, 135.1, 135.4, 152.9. − HRMS (LSI): m/z = 493.1458 {calcd. for [M + H]$^+$ based on ^{35}Cl 493.1449}.

***N*,*N*′-Bis(4-*tert*-butylbenzyl)-*N*,*N*′-bis(2-hydroxyphenyl)-1,2-diaminoethane (H_2L^6):** 0.40 g (75%). − ^{1}H NMR (300 MHz): δ = 1.27 (s, 18 H, tBu), 2.87 (s, 4 H, CH_2CH_2), 3.80 (s, 4 H, ArCH_2), 6.76 (dt, J = 1.5, 7.6, 2 H, ArH), 6.90−7.06 (m, 10 H, ArH), 7.20−7.23 (m, 4 H, ArH). − ^{13}C{^{1}H} NMR (75.4 MHz): δ = 31.3, 34.4, 51.3, 60.5, 114.5, 119.8, 123.2, 125.2, 126.7, 128.7, 133.8, 136.4, 150.2, 152.8. − HRMS (LSI): m/z = 537.3480 {calcd. for [M + H]$^+$ 537.3481}.

***N*,*N*′-Bis(3,5-di-*tert*-butylbenzyl)-*N*,*N*′-bis(2-hydroxyphenyl)-1,2-diaminoethane (H_2L^7):** 0.45 g (69%). − ^{1}H NMR (300 MHz): δ = 1.22 (s, 36 H, tBu), 2.95 (s, 4 H, CH_2CH_2), 3.89 (s, 4 H, ArCH_2), 6.75 (dt, J = 1.2, 7.7, 2 H, ArH), 6.85−6.87 (m, 6 H, ArH), 6.92

(dd, *J* = 1.2, 7.7, 2 H, Ar*H*), 7.00 (dt, *J* = 1.2, 7.7, 2 H, Ar*H*), 7.23−7.24 (m, 2 H, Ar*H*). − $^{13}C\{^1H\}$ NMR (75.4 MHz): δ = 31.3, 34.6, 52.3, 61.4, 114.4, 119.7, 121.1, 123.7, 124.2, 126.7, 128.9, 135.5, 150.4, 153.1. − HRMS (LSI): *m/z* = 649.4773 {calcd. for $[M + H]^+$ 649.4733}.

General Procedure for the Preparation of $[WO_2(L^n)]$ (*n* = 1−10): To a mixture of $[WO_2Cl_2(DME)]$ (0.38 g, 1.0 mmol) and H_2L^n (*n* = 1−10, 1.0 mmol) in CH_2Cl_2 (30 ml) was added triethylamine (0.28 ml, 2.0 mmol). The mixture was allowed to reflux overnight then the volatiles were removed in vacuo. The complex $[WO_2(L^2)]$ was purified by chromatography with CH_2Cl_2/ethyl acetate (1:1) as eluent followed by recrystallization from acetone/hexane. The complexes $[WO_2(L^n)]$ (*n* = 3−7) were purified by chromatography with $CHCl_3$ as eluent. The remaining complexes were obtained by washing the residue with ethanol and hexane followed by recrystallization from MeCN {for $[WO_2(L^9)]$} or CH_2Cl_2 {for $[WO_2(L^{10})]$}, or diffusion of water into a DMF solution of the crude product {for $[WO_2(L^n)]$ (*n* = 1, 8)}.

$[WO_2(L^1)]$: 0.22 g (50%), light pink solid. − ^1H NMR ($[D_6]$DMSO, 250 MHz): δ = 2.85−3.01 (m, 4 H, CH_2CH_2), 6.83 (d, *J* = 7.5, 2 H, Ar*H*), 6.91 (t, *J* = 7.5, 2 H, Ar*H*), 7.20 (d, *J* = 7.5, 2 H, Ar*H*), 7.21 (t, *J* = 7.5, 2 H, Ar*H*), 8.04 (br s, 2 H, N*H*). − $^{13}C\{^1H\}$ NMR ($[D_6]$DMSO, 125.8 MHz): δ = 50.4, 117.0, 121.4, 125.6, 129.0, 134.1, 161.6. − IR: $\nu(WO_2)$ = 911 s, 951 s cm^{-1}. − MS (LSI): Cluster peak at *m/z* = 459 (27%) $[M + H]^+$. − $C_{14}H_{14}N_2O_4W$ (458.13): calcd. C 36.70, H 3.08, N 6.11; found C 36.68, H 3.00, N 5.88.

$[WO_2(L^2)]$: 0.34 g (70%), white crystals. − ^1H NMR ($[D_6]$DMSO, 300 MHz): δ = 2.62 (d, *J* = 10.0, 2 H, CH_2), 3.06 (d, *J* = 10.0, 2 H, CH_2), 3.26 (s, 6 H, CH_3), 6.94 (dd, *J* = 1.5, 8.1, 2 H, Ar*H*), 7.02 (dt, *J* = 1.5, 7.7, 2 H, Ar*H*), 7.30 (dt, *J* = 1.5, 7.7, 2 H, Ar*H*), 7.60 (dd, *J* = 1.5, 8.1, 2 H, Ar*H*). − $^{13}C\{^1H\}$ NMR ($[D_6]$DMSO, 75.4 MHz): δ = 48.3, 59.5, 117.8, 122.3, 122.7, 129.7, 138.6, 159.6. − IR: $\nu(WO_2)$ = 914 s, 950 s cm^{-1}. − MS (FAB): Cluster peak at *m/z* = 487 (24%) $[M + H]^+$. − $C_{16}H_{18}N_2O_4W$ (486.18): calcd. C 39.53, H 3.73, N 5.76; found C 40.09, H 4.05, N 5.13.

$[WO_2(L^3)]$: 0.46 g (72%), white crystals. − ^1H NMR (300 MHz): δ = 2.90 (d, *J* = 9.0, 2 H, CH_2CH_2), 3.06 (d, *J* = 9.0, 2 H, CH_2CH_2), 4.91−5.04 (AB q, 4 H, ArCH_2), 6.66 (d, *J* = 8.1, 2 H, Ar*H*), 6.75 (t, *J* = 7.7, 2 H, Ar*H*), 6.83 (d, *J* = 8.1, 2 H, Ar*H*), 7.21 (t, *J* = 7.7, 2 H, Ar*H*), 7.34−7.41 (m, 10 H, Ar*H*). − $^{13}C\{^1H\}$ NMR (75.4 MHz): δ = 56.2. 64.9, 118.7, 121.3, 124.4, 128.4, 128.9, 129.6, 132.4, 133.8, 137.1, 160.5. − IR: $\nu(WO_2)$ = 916 s, 953 s cm^{-1}. − MS (FAB): Cluster peak at *m/z* = 639 (100%) $[M + H]^+$. − $C_{28}H_{26}N_2O_4W$ (638.38): calcd. C 52.68, H 4.11, N 4.39; found C 52.95, H 4.05, N 4.12.

$[WO_2(L^4)]$: 0.47 g (71%), white crystals. − ^1H NMR (300 MHz): δ = 2.37 (s, 6 H, CH_3), 2.91 (d, *J* = 9.0, 2 H, CH_2CH_2), 3.04 (d, *J* = 9.0, 2 H, CH_2CH_2), 4.87−4.98 (AB q, 4 H, ArCH_2), 6.69 (dd, *J* = 1.5, 8.1, 2 H, Ar*H*), 6.74 (dt, *J* = 1.5, 7.7, 2 H, Ar*H*), 6.82 (dd, *J* = 1.5, 8.1, 2 H, Ar*H*), 7.13 (d, *J* = 7.7, 4 H, Ar*H*), 7.17−7.22 (m, 6 H, Ar*H*). − $^{13}C\{^1H\}$ NMR (75.4 MHz): δ = 21.1, 56.1, 64.5, 118.4, 121.2, 124.6, 129.0, 129.4, 130.6, 132.2, 137.1, 138.6, 160.4. − IR: $\nu(WO_2)$ = 918 s, 956 s cm^{-1}. − MS (FAB): Cluster peak at *m/z* = 667 (63%) $[M + H]^+$. − $C_{30}H_{30}N_2O_4W$ (666.43): calcd. C 54.07, H 4.54, N 4.20; found C 53.98, H 4.59, N 4.21.

$[WO_2(L^5)]$: 0.46 g (65%), silvery grey crystals. − ^1H NMR (300 MHz): δ = 2.84 (d, *J* = 9.0, 2 H, CH_2CH_2), 3.04 (d, *J* = 9.0, 2 H, CH_2CH_2), 4.81−4.95 (AB q, 4 H, ArCH_2), 6.71−6.82 (m, 6 H, Ar*H*), 7.20−7.25 (m, 2 H, Ar*H*), 7.32 (s, 8 H, Ar*H*). − $^{13}C\{^1H\}$ NMR (75.4 MHz): δ = 55.8, 64.0, 118.7, 121.5, 123.7, 128.6, 129.8, 131.9, 133.8, 135.1, 136.8, 160.3. − IR: $\nu(WO_2)$ = 908 s, 949 m cm^{-1}. − HRMS (LSI): *m/z* = 707.0688 {calcd. for $[M + H]^+$ based on ^{35}Cl and ^{184}W 707.0680}.

$[WO_2(L^6)]$: 0.50 g (67%), white crystals. − ^1H NMR (300 MHz): δ = 1.33 (s, 18 H, *t*Bu), 2.85 (d, *J* = 9.3, 2 H, CH_2CH_2), 3.05 (d, *J* = 9.3, 2 H, CH_2CH_2), 4.83−5.00 (AB q, 4 H, ArCH_2), 6.74−6.77 (m, 6 H, Ar*H*), 7.15−7.19 (m, 2 H, Ar*H*), 7.27−7.36 (m, 8 H, Ar*H*). − $^{13}C\{^1H\}$ NMR (75.4 MHz): δ = 31.3, 34.6, 55.9, 64.4, 118.6, 121.2, 124.2, 125.2, 129.4, 130.5, 132.3, 137.4, 151.8, 160.4. − IR: $\nu(WO_2)$ = 919 s, 958 s cm^{-1}. − HRMS (LSI): *m/z* = 751.2749 {calcd. for $[M + H]^+$ based on ^{184}W 751.2712}.

$[WO^2(L^7)]$: 0.54 g (63%), white crystals. − ^1H NMR (300 MHz): δ = 1.27 (s, 36 H, *t*Bu), 2.86 (d, *J* = 9.3, 2 H, CH_2CH_2), 3.06 (d, *J* = 9.3, 2 H, CH_2CH_2), 4.93 (s, 4 H, ArCH_2), 6.54 (dd, *J* = 1.2, 8.1, 2 H, Ar*H*), 6.69 (dt, *J* = 1.2, 7.7, 2 H, Ar*H*), 6.80 (dd, *J* = 1.2, 8.1, 2 H, Ar*H*), 7.14 (s, 2 H, Ar*H*), 7.15 (s, 2 H, Ar*H*), 7.19 (dt, *J* = 1.2, 7.7, 2 H, Ar*H*), 7.42 (s, 2 H, Ar*H*). − $^{13}C\{^1H\}$ NMR (75.4 MHz): δ = 31.4, 34.7, 56.1, 65.7, 118.5, 120.8, 122.3, 124.7, 126.9, 129.5, 132.7, 137.1, 150.7, 160.7. − IR: $\nu(WO_2)$ = 921 s, 956 s cm^{-1}. − MS (FAB): Cluster peak at *m/z* = 862 (11%) $[M^+]$. − $C_{44}H_{58}N_2O_4W$ (862.81): calcd. C 61.25, H 6.78, N 3.25; found C 61.36, H 6.98, N 3.05.

$[WO^2(L^8)]$: 0.36 g (74%), white crystalline solid. − ^1H NMR ($[D_6]$DMSO, 250 MHz): δ = 2.32 (br s, 2 H, N*H*), 2.87 (br s, 2 H, CH_2), 3.87 (d, *J* = 14.3, 2 H, CH_2), 4.74 (d, *J* = 14.3, 2 H, CH_2), 5.46 (br s, 2 H, CH_2), 6.76 (d, *J* = 8.0, 2 H, Ar*H*), 6.83 (t, *J* = 7.5, 2 H, Ar*H*), 7.11 (d, *J* = 7.5, 2 H, ArH), 7.18 (t, *J* = 7.5, 2 H, ArH). − $^{13}C\{^1H\}$ NMR ($[D_6]$DMSO, 62.9 MHz): δ = 46.1, 52.6, 119.2, 120.3, 122.4, 128.0, 129.5, 158.2. − IR: $\nu(WO_2)$ = 941 s cm^{-1}. − MS (LSI): Cluster peak at *m/z* = 487 (17%) $[M + H]^+$. − $C_{16}H_{18}N_2O_4W$ (486.18): calcd. C 39.53, H 3.73, N 5.76; found C 39.63, H 3.42, N 5.74.

$[WO^2(L^9)]$: 0.42 g (59%), colorless crystals. − ^1H NMR (250 MHz): δ = 1.28 (s, 9 H, *t*Bu), 1.45 (s, 9 H, *t*Bu), 2.79 (br s, 2 H, N*H*), 3.00 (br s, 4 H, CH_2CH_2), 3.95 (d, *J* = 13.6, 2 H, ArCH_2), 5.22 (d, *J* = 13.6, 2 H, ArCH_2), 6.86 (s, 2 H, Ar*H*), 7.32 (s, 2 H, Ar*H*). − $^{13}C\{^1H\}$ NMR (62.9 MHz): δ = 30.0, 31.6, 34.3, 35.2, 46.7, 54.3, 120.7, 123.6, 124.1, 138.9, 142.9, 154.9. − IR: $\nu(WO_2)$ = 897 s, 939 s cm^{-1}. − MS (LSI): Cluster peak at *m/z* = 711 (21%) $[M + H]^+$. − $C_{32}H_{50}N_2O_4W$ (710.62): calcd. C 54.09, H 7.09, N 3.94; found C 53.49, H 7.14, N 3.74.

$[WO^2(L^{10})]$: 0.14 g (33%), yellow crystals. − ^1H NMR (250 MHz): δ = 3.26 (s, 6 H, CH_3), 3.04−3.39 (m, 10 H, CH_2), 3.54−3.64 (m, 2 H, CH_2). − $^{13}C\{^1H\}$ NMR ($[D_6]$DMSO, 125.8 MHz): δ = 27.6, 52.0, 56.2, 67.0. − IR: $\nu(WO_2)$ = 895 s, 936 s cm^{-1}. − MS (LSI): Cluster peak at *m/z* = 423 (15%) $[M + H]^+$. − $C_8H_{18}N_2O_2S_2W$ (422.21): calcd. C 22.76, H 4.30, N 6.63, S 15.19; found C 23.00, H 4.21, N 6.56, S 15.74.

General Procedure for the Preparation of $[MoO_2(L^n)]$ (*n* = 1, 3−7): A mixture of ammonium molybdate tetrahydrate $[NH_4]_6[Mo_7O_{24}] \times 4\ H_2O$ (0.18 g, 0.14 mmol), H_2L^n (*n* = 3−7, 1.0 mmol) and dilute hydrochloric acid (0.1 м, 5 ml, 0.5 mmol) in ethanol (30 ml) was stirred at room temp. overnight. $[MoO_2(L^1)]$ was collected by filtration as a yellow solid which was washed with ethanol and hexane, and dried in vacuo. For the other molybdenum complexes, the solid was collected by filtration and the filtrate was extracted with CH_2Cl_2 (3 × 20 ml). The solid and the extracts were combined, dried with sodium sulfate and the solvent removed using a rotary evaporator. The residue was chromatographed with $CHCl_3$ as eluent to develop a bright yellow band which was collected and evaporated to give a yellow solid.

[MoO$_2$(L^1)]:[16] 0.26 g (70%). − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 2.78−2.91 (m, 4 H, C*H*$_2$C*H*$_2$), 6.79 (dd, *J* = 1.2, 8.0, 2 H, Ar*H*), 6.89 (dt, *J* = 1.2, 7.6, 2 H, Ar*H*), 7.16−7.22 (m, 4 H, Ar*H*), 7.78 (s, 2 H, N*H*). − ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 75.4 MHz): δ = 50.0, 115.7, 121.0, 125.4, 128.6, 134.2, 162.7. − IR: $\nu(MoO_2)$ = 910 s, 932 m cm^{-1}. − MS (LSI): Cluster peak at *m/z* = 373 (13%) [M + H]$^+$.

[MoO$_2$(L^3)]: 0.30 g (55%). − ^{1}H NMR (300 MHz): δ = 2.77 (d, *J* = 9.0, 2 H, C*H*$_2$C*H*$_2$), 3.05 (d, *J* = 9.0, 2 H, C*H*$_2$C*H*$_2$), 4.87−5.02 (AB q, 4 H, ArC*H*$_2$), 6.66−6.82 (m, 6 H, Ar*H*), 7.17 (t, *J* = 7.5, 2 H, Ar*H*), 7.33−7.38 (m, 10 H, Ar*H*). − ^{13}C{^{1}H} NMR (75.4 MHz): δ = 55.9, 64.6, 117.4, 120.8, 124.5, 128.3, 128.7, 129.2, 132.3, 134.1, 137.1, 161.5. − IR: $\nu(MoO_2)$ = 905 s, 928 m cm^{-1}. − MS (FAB): Cluster peak at *m/z* = 553 (54%) [M + H]$^+$. − $C_{28}H_{26}MoN_2O_4$ (550.47): calcd. C 61.10, H 4.76, N 5.09; found C 61.03, H 4.80, N 4.88.

[MoO$_2$(L^4)]: 0.39 g (67%). − ^{1}H NMR (300 MHz): δ = 2.37 (s, 6 H, C*H*$_3$), 2.74 (d, *J* = 9.9, 2 H, C*H*$_2$C*H*$_2$), 3.02 (d, *J* = 9.9, 2 H, C*H*$_2$C*H*$_2$), 4.86−5.00 (AB q, 4 H, ArC*H*$_2$), 6.68 (dd, *J* = 1.2, 8.4, 2 H, Ar*H*), 6.74 (dt, *J* = 1.2, 7.6, 2 H, Ar*H*), 6.84 (dd, *J* = 1.2, 8.4, 2 H, Ar*H*), 7.11−7.22 (m, 10 H, Ar*H*). − ^{13}C{^{1}H} NMR (75.4 MHz): δ = 21.2, 56.0, 64.4, 117.4, 120.7, 124.7, 129.0, 129.2, 131.2, 132.2, 137.2, 138.5, 161.7. − IR: $\nu(MoO_2)$ = 919 s, 938 s cm^{-1}. − MS (FAB): Cluster peak at *m/z* = 581 (45%) [M + H]$^+$. − $C_{30}H_{30}MoN_2O_4$ (578.52): calcd. C 62.29, H 5.23, N 4.84; found C 61.98, H 5.27, N 4.72.

[MoO$_2$(L^5)]: 0.44 g (71%). − ^{1}H NMR (300 MHz): δ = 2.71 (d, *J* = 9.0, 2 H, C*H*$_2$C*H*$_2$), 3.02 (d, *J* = 9.0, 2 H, C*H*$_2$C*H*$_2$), 4.77−4.94 (AB q, 4 H, ArC*H*$_2$), 6.71−6.81 (m, 6 H, Ar*H*), 7.19 (dt, *J* = 1.5, 7.6, 2 H, Ar*H*), 7.30 (s, 8 H, Ar*H*). − ^{13}C{^{1}H} NMR (75.4 MHz): δ = 55.6, 63.7, 117.5, 121.0, 123.8, 128.5, 129.4, 132.2, 133.7, 134.9, 136.8, 161.4. − IR: $\nu(MoO_2)$ = 911 s, 934 m cm^{-1}. − MS (FAB): Cluster peak at *m/z* = 620 (63%) [M$^+$]. − $C_{28}H_{24}Cl_2MoN_2O_4$ (619.36): calcd. C 54.30, H 3.91, N 4.52; found C 53.95, H 3.79, N 4.28.

[MoO$_2$(L^6)]: 0.43 g (65%). − ^{1}H NMR (300 MHz): δ = 1.33 (s, 18 H, *t*Bu), 2.70 (d, *J* = 9.6, 2 H, C*H*$_2$C*H*$_2$), 3.04 (d, *J* = 9.6, 2 H, C*H*$_2$C*H*$_2$), 4.79−4.99 (AB q, 4 H, ArC*H*$_2$), 6.72−6.79 (m, 6 H, Ar*H*), 7.12−7.17 (m, 2 H, Ar*H*), 7.29−7.35 (m, 8 H, Ar*H*). − ^{13}C{^{1}H} NMR (75.4 MHz): δ = 31.3, 34.6, 55.7, 64.2, 117.4, 120.8, 124.2, 125.1, 129.1, 131.0, 132.2, 137.5, 151.7, 161.6. − IR: $\nu(MoO_2)$ = 916 s, 937 m cm^{-1}. − MS (FAB): Cluster peak at *m/z* = 664 (18%) [M$^+$]. − $C_{36}H_{42}MoN_2O_4$ (662.69): calcd. C 65.25, H 6.39, N 4.23; found C 65.73, H 6.71, N 3.94.

[MoO$_2$(L^7)]: 0.46 g (59%). − ^{1}H NMR (300 MHz): δ = 1.26 (s, 36 H, *t*Bu), 2.71 (d, *J* = 10.5, 2 H, C*H*$_2$C*H*$_2$), 3.04 (d, *J* = 10.5, 2 H, C*H*$_2$C*H*$_2$), 4.92 (s, 4 H, ArC*H*$_2$), 6.56 (d, *J* = 8.1, 2 H, Ar*H*), 6.68 (t, *J* = 7.7, 2 H, Ar*H*), 6.79 (d, *J* = 8.1, 2 H, Ar*H*), 7.12 (s, 2 H, Ar*H*), 7.13 (s, 2 H, Ar*H*), 7.15 (t, *J* = 7.8, 2 H, Ar*H*), 7.40 (s, 2 H, Ar*H*). − ^{13}C{^{1}H} NMR (75.4 MHz): δ = 31.4, 34.7, 55.8, 65.5, 117.3, 120.4, 122.2, 124.7, 126.8, 129.1, 133.1, 137.1, 150.6, 161.8. − IR: $\nu(MoO_2)$ = 913 s, 935 s cm^{-1}. − MS (FAB): Cluster peak at *m/z* = 777 (3%) [M + H]$^+$. − $C_{44}H_{58}MoN_2O_4$ (774.90): calcd. C 68.20, H 7.54, N 3.62; found C 68.31, H 7.74, N 3.53.

X-ray Crystallographic Analysis of [WO$_2$(L^1)] and [WO$_2$(L^9)] · MeCN · EtOH: Crystal data and data-processing parameters are given in the Supporting Information on the WWW or may be obtained from the author. Data collection was performed in the variable ω-scan mode with a Rigaku AFC7R diffractometer using Mo-K_α radiation (λ = 0.71073 Å) at 294 K. Unit-cell parameters were calculated from least-squares fitting of the 2θ angles for 25 selected strong reflections. Three standard reflections were monitored periodically after every 150 reflections and showed no significant decay during the data collection. The tungsten atom {of site symmetry 2 for [WO$_2$(L^9)] · MeCN · EtOH} was located by the Patterson method and the remaining non-hydrogen atoms were derived from subsequent Fourier difference syntheses. For [WO$_2$(L^9)] · MeCN · EtOH, both *tert*-butyl groups exhibit twofold orientational disorder, and the ethanol molecule is likewise twofold disordered with a common methylene group. The acetonitrile molecule lies on a crystallographic twofold axis. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedures. The hydrogen atoms were placed in idealized positions (C−H 0.96 Å, N−H 0.90 Å) with fixed isotropic thermal parameters and allowed to ride on their respective parent carbon and nitrogen atoms. All calculations were performed with a PC-486 computer using the SHELXL-PLUS program package.[28] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[29]

X-ray Crystallographic Analysis of [WO$_2$(L^2) · 1/4CH$_2$Cl$_2$] and [MoO$_2$(L^5)]: All pertinent crystallographic data and other experimental details are also summarized in the Supporting Information. Intensity data were collected at 298 K with an Enraf-Nonius diffractometer using graphite monochromated Mo-K_α radiation and the ω-2θ scan technique. Three checked reflections were monitored periodically throughout data collection and showed no significant variations. All intensity data were corrected for Lorentz and polarization effects. An absorption correction by the ψ-scan method[30] was applied for [WO$_2$(L^2) · 1/4CH$_2$Cl$_2$]. Both structures were solved by direct methods (SIR 92)[31] and expanded using Fourier techniques.[32] Some non-hydrogen atoms were refined anisotropically, while the rest was refined isotropically by full-matrix least-squares analysis. Hydrogen atoms were generated in their idealized positions but not refined. All calculations were performed with a Silicon-Graphics computer using the program package TEXSAN.[33]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-102337 {for [WO$_2$(L^2)]}, 101953 {for [WO$_2$(L^2) · 1/4CH$_2$Cl$_2$]}, 102338 {for [WO$_2$(L^9)] · MeCN · EtOH} and 101952 {for [MoO$_2$(L^5)]}. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int.code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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