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New Chloro, μ-Oxo, and Alkyl Derivatives of Dioxomolybdenum(VI) and -Tungsten(VI) Complexes Chelated with N_2O Tridentate Ligands: Synthesis and Catalytic Activities toward Olefin Epoxidation

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A new series of *cis*-dioxomolybdenum(VI) complexes $MoO_2(L^n)Cl$ (n = 1–5) were prepared by the reaction of MoO_2Cl_2(DME) (DME = 1,2-dimethoxyethane) with 2-*N*-(2-pyridylmethyl)aminophenol (HL^1) or its *N*-alkyl derivatives (HL^n) (n = 2–5) in the presence of triethylamine. The new μ-oxo dimolybdenum compounds $[MoO_2(L^n)]_2O$ (n = 1, 4, 5, 7) were also prepared by treating the corresponding ligand HL^n with $MoO_2(acac)_2$ (acac = acetylacetonate) in warm methanolic solutions or $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ in the presence of dilute HCl. Treatment of $MoO_2(L^1)Cl$ or $[MoO_2(L^1)]_2O$ with the Grignard reagent Me_3SiCH_2MgCl gave the alkyl compound $MoO_2(L^1)(CH_2SiMe_3)$, which represents the first example of dioxomolybdenum(VI) alkyl complex supported by a N_2O-type ancillary ligand. The analogous chloro and μ-oxo tungsten derivatives $WO_2(L^n)Cl$ (n = 6, 7) and $[WO_2(L^n)]_2O$ (n = 1, 4, 6, 7) were prepared by the reaction of WO_2Cl_2(DME) with HL^n in the presence of triethylamine. Similar to their molybdenum analogues, the tungsten alkyl complexes $WO_2(L^n)(R)$ (n = 6, 7; R = Me, Et, CH_2SiMe_3, $C_6H_4{}^tBu$-4) were synthesized by treating $WO_2(L^n)Cl$ or $[WO_2(L^n)]_2O$ (n = 6, 7) with the appropriate Grignard reagents. The catalytic properties of selected dioxo-Mo(VI) and -W(VI) chloro and μ-oxo complexes toward epoxidation of styrene by *tert*-butyl hydroperoxide (TBHP) were also investigated.

Introduction

Organometallic oxo complexes have attracted considerable attention due to their relevance to the intermediate species involved in metal oxide- and peroxide-catalyzed reactions.[1] To reveal the nature and chemical behavior of such intermediates, a substantial number of organometallic oxometalates have been synthesized and examined as synthetic analogues.[2] High-valent organometallic dioxomolybdenum and -tungsten complexes with cyclopentadienyl ligands of the types $MO_2(\eta^5\text{-}C_5R_5)(Cl)$, $[MO_2(\eta^5\text{-}C_5R_5)]_2O$, and $MO_2(\eta^5\text{-}C_5R_5)(R')$ (M = Mo, W; R = H, Me; R′ = alkyl, alkynyl) have been extensively studied.[3] Apart from cyclopentadienyl ligands, 2,2′-bipyridine (bipy) has also been used as a supporting ligand to give the stable mononuclear dioxo complexes $MoO_2Br(bipy)R$[4] and $MO_2(bipy)R_2$ (M = Mo, W; R = alkyl).[5,6] Young et al. have also employed hydrotris(3,5-dimethylpyrazolyl)borate $[HB(Me_2pz)_3]^-$ as the ancillary ligand to generate a new class of organometallic dioxotungsten complexes $WO_2[HB(Me_2pz)_3]R$ (R = alkyl, phenyl, alkenyl).[7] To our knowledge, organometallic dioxomolybdenum and -tungsten complexes with other supporting

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(1) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981.
(2) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339.
(3) (a) Legzdins, P.; Rettig, S. J.; Sanchez, L. *Organometallics* **1985**, *4*, 1470. (b) Faller, J. W.; Ma, Y. *J. Organomet. Chem.* **1988**, *340*, 59. (c) Faller, J. W.; Ma, Y. *Organometallics* **1988**, *7*, 559. (d) Legzdins, P.; Phillips, E. C.; Sanchez, L. *Organometallics* **1989**, *8*, 940. (e) Shiu, C.-W.; Su, C.-J.; Pin, C.-W.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *J. Organomet. Chem.* **1997**, *545*−*546*, 151.
(4) (a) Schrauzer, G. N.; Moorehead, E. L.; Grate, J. H.; Hughes, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 4760. (b) Schrauzer, G. N.; Hughes, L. A.; Strampach, N. *Z. Naturforsch., B* **1982**, *37B*, 380.
(5) (a) Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Robinson, P. R.; Schlemper, E. O. *Organometallics* **1982**, *1*, 44. (b) Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Ross, F.; Ross, D.; Schlemper, E. O. *Organometallics* **1983**, *2*, 481. (c) Schrauzer, G. N.; Hughes, L. A.; Schlemper, E. O.; Ross, F.; Ross, D. *Organometallics* **1983**, *2*, 1163. (d) Schrauzer, G. N.; Schlemper, E. O.; Liu, N. H.; Wang, Q.; Rubin, K.; Zhang, X.; Long, X.; Chin, C. S. *Organometallics* **1986**, *5*, 2452.
(6) (a) Zhang, C.; Schlemper, E. O.; Schrauzer, G. N. *Organometallics* **1990**, *9*, 1016. (b) Zhang, C.; Zhang, X.; Liu, N. H.; Schrauzer, G. N.; Schlemper, E. O. *Organometallics* **1990**, *9*, 1307.
(7) (a) Eagle, A. A.; Tiekink, E. R. T.; Young, C. G. *J. Chem. Soc., Chem. Commun.* **1991**, 1746. (b) Eagle, A. A.; Young, C. G.; Tiekink, E. R. T. *Organometallics* **1992**, *11*, 2934.

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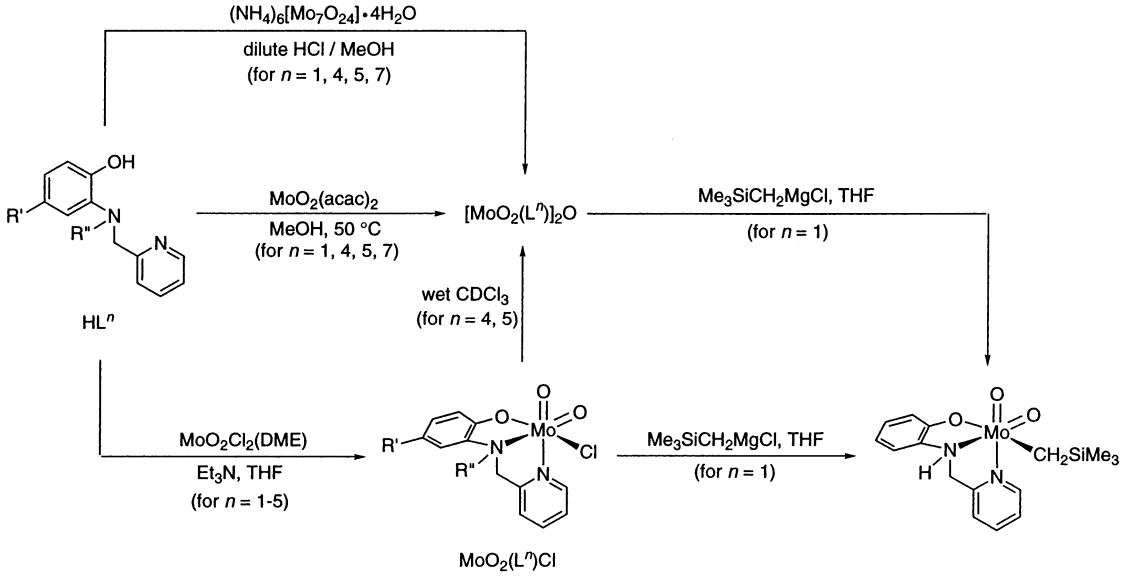
Scheme 1

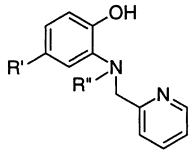


ligands remain scarce.[8] We have recently prepared a new series of N_2O-type ligands (HL^n) (n = 1−5), which can stabilize the high-valent dioxotungsten complexes $WO_2(L^n)$-Cl (n = 1−5) and $WO_2(L^1)(CH_2SiMe_3)$.[9] The molecular structure of the latter alkyl complex has been confirmed by X-ray diffraction analysis. As our continuing interest in the chemistry of dioxomolybdenum and -tungsten complexes, we report herein the synthesis of the analogous molybdenum complexes $MoO_2(L^n)Cl$ (n = 1−5) and $MoO_2(L^1)(CH_2SiMe_3)$, and the tungsten alkyl derivatives $WO_2(L^n)R$ (n = 6, 7; R = Me, Et, CH_2SiMe_3, $C_6H_4{}^tBu$-4). During the course of our study, the μ-oxo complexes $[MO_2(L^n)]_2O$ (M = Mo, W) have also been prepared and isolated. Reactions of these μ-oxo complexes with Grignard reagents provide a new synthetic route for the preparation of the alkyl derivatives $MO_2(L^n)R$. The catalytic activities of selected chloro and μ-oxo compounds toward epoxidation of styrene have also been examined.

Results and Discussion

Chloro Complexes. Treatment of the previously described ligands HL^n (n = 1−5)[9] (Chart 1) with MoO_2Cl_2(DME) in the presence of triethylamine gave the corresponding dioxo complexes $MoO_2(L^n)Cl$ (n = 1−5) (Scheme 1). Similar to its tungsten counterpart,[9] $MoO_2(L^1)Cl$ is only sparingly soluble in common organic solvents. Therefore, the compound could only be purified by repeated washing with methanol and hexanes, and characterized with IR spectroscopy. All the other dioxomolybdenum(VI) compounds, in particular $MoO_2(L^n)Cl$ (n = 3−5), possess a better solubility in common organic solvents which facilitates their purification by column chromatography and characterization by various spectroscopic methods. The ^{1}H NMR spectra of the

Chart 1



HL^1	R′ = R″ = H
HL^2	R′ = H, R″ = Me
HL^3	R′ = H, R″ = $CH_2C_6H_5$
HL^4	R′ = H, R″ = $CH_2C_6H_4{}^tBu$-4
HL^5	R′ = H, R″ = $CH_2C_6H_3(^tBu)_2$-3,5
HL^6	R′ = Me, R″ = H
HL^7	R′ = ^{t}Bu, R″ = H

chloro compounds $MoO_2(L^n)Cl$ (n = 2−5) showed two doublets at δ 4.30−5.20 ppm which can be assigned to the two diastereotopic methylene protons located adjacent to the pyridyl moiety. For the benzyl derivatives $MoO_2(L^n)Cl$ (n = 3−5), a second pair of doublets at δ 4.93−5.34 ppm was also observed due to the presence of two diastereotopic benzylic protons. It is evident that complexation of L^n to the Mo center results in the diastereotopicity of the two sets of methylene protons.

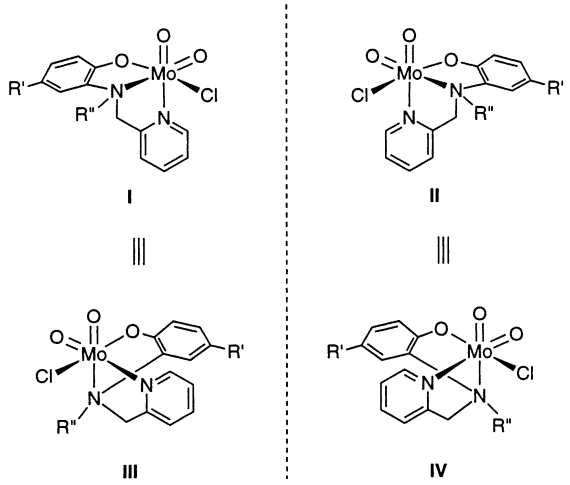
With reference to the structure of $WO_2(L^1)(CH_2SiMe_3)$, which has been determined by X-ray diffraction analysis,[9] and the similar spectroscopic properties, it is believed that the chloro complexes $[MoO_2(L^n)Cl]$ (and their alkyl derivatives) also adopt a distorted octahedral structure with the two nitrogen donor atoms being located trans to the oxo groups, with the phenolate oxygen opposite the chloro (or alkyl) ligand (Scheme 1). The trans orientation of oxo and nitrogen-donor ligands is in fact very common for related dioxo Mo(VI) and W(VI) complexes.[9−14] Apparently, there are two possible binding modes with trans oxo−nitrogen configurations (I and IV as shown in Chart 2), differing in the positions

(8) (a) Santini-Scampucci, C.; Riess, J. G. *J. Organomet. Chem.* **1974**, *73*, C13. (b) Santini-Scampucci, C.; Riess, J. G. *J. Chem. Soc., Dalton Trans.* **1976**, 195.

(9) Wong, Y.-L.; Ma, J.-F.; Xue, F.; Mak, T. C. W.; Ng, D. K. P. *Organometallics* **1999**, *18*, 5075.

(10) Wong, Y.-L. Ph.D. Thesis, The Chinese University of Hong Kong, 1999.

Chart 2



of the amino and pyridyl nitrogen ligands. Both of these structures are chiral and have their enantiomeric counterparts II and III, respectively. A close examination reveals that I and III (and II and IV as well) are, in fact, equivalent. In other words, only one pair of enantiomers for $MoO_2(L^n)Cl$ is present, which is consistent with a single set of signals in their NMR spectra.

Oxo Complexes. The μ-oxo dimolybdenum(VI) compounds $[MoO_2(L^n)]_2O$ (n = 1, 4, 5, 7) were prepared by treating $MoO_2(acac)_2$ with the corresponding ligands HL^n (n = 1, 4, 5, 7) in warm methanolic solutions. Alternatively, the μ-oxo complexes could also be synthesized by the reaction of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ in methanol with HL^n in the presence of dilute hydrochloric acid (Scheme 1). The pale yellow oxo-bridged dimolybdenum compounds are stable to air and moisture. Results of elemental analysis were consistent with their empirical formula. The compounds were also characterized by NMR spectroscopy.[15] The limited solubility of $[MoO_2(L^1)]_2O$ in common deuterated solvents renders its characterization difficult to carry out. On the other hand, the analogous $[MoO_2(L^4)]_2O$ and $[MoO_2(L^5)]_2O$ showed two sets of signals (in an approximately 1:1 ratio) in their ^1H and ^{13}C NMR spectra, which suggest the presence of two diastereomers (Chart 3). Similar stereochemistry has also been reported for μ-oxo dimolybdenum(V) complexes supported by the tridentate NO_2- and NOS− Schiff base ligands.[16] Attempts to separate the diastereomers for $[MoO_2(L^n)]_2O$ (n = 4 and 5) by column chromatography were not successful. However, separation seemed to be successful for $[MoO_2(L^7)]_2O$ as indicated by the appearance of a single set of NMR signals for the isolated product.

The corresponding μ-oxo tungsten complexes $[WO_2(L^n)]_2O$ (n = 1, 4, 6, 7) were prepared in satisfactory yields by the reaction of $WO_2Cl_2(DME)$ with the appropriate ligands HL^n and triethylamine in 1:1 CH_2Cl_2/MeOH solutions (Scheme 2). The μ-oxo tungsten complexes were isolated as white solids and are stable to air and moisture. Owing to the poor solubility of $[WO_2(L^n)]_2O$ (n = 1, 6, 7) in common organic solvents, the compounds could only be characterized with IR spectroscopy and elemental analysis. On the other hand, the analogous $[WO_2(L^4)]_2O$ possesses sufficient solubility in chlorinated solvents, facilitating its characterization by ^1H and ^{13}C NMR spectroscopy. Similar to the μ-oxo Mo derivative $[MoO_2(L^7)]_2O$, only one set of signals was observed for this complex, indicating that only one stereoisomer (probably together with its enantiomer) was isolated.[17]

Alkyl Complexes. The molybdenum alkyl $MoO_2(L^1)(CH_2SiMe_3)$ was readily prepared by treating $MoO_2(L^1)Cl$ with the Grignard reagent Me_3SiCH_2MgCl (Scheme 1). Young et al. have studied the reaction of $MoO_2[HB(Me_2pz)_3]Cl$ with various Grignard reagents.[18] Interestingly, the mixed-valence complex $[HB(Me_2pz)_3]Mo^{V}OCl(\mu\text{-}O)Mo^{VI}O_2[HB(Me_2pz)_3]$ was obtained, instead of the expected dioxomolybdenum(VI) alkyl compounds. In our study, attempts to prepare other dioxomolybdenum(VI) alkyl complexes by treating $MoO_2(L^n)Cl$ (n = 1, 2) with the Grignard reagents RMgX (R = Me, Et, CH_2SiMe_3, $C_6H_4{}^tBu$-4; X = Cl, Br) were unsuccessful (except for n = 1, R = CH_2SiMe_3). Reactions with other nucleophilic reagents such as sodium alkoxides and thiolates were also studied. Treatment of $MoO_2(L^n)Cl$ (n = 1−3) with NaER (E = O, S; R = Me, Et, Ph), in the presence of a catalytic amount of 18-crown-6, in refluxing toluene led to decomplexation and recovery of the free ligands. This is in contrast to the chemistry of $MoO_2[HB(Me_2pz)_3]Cl$, which can be converted to various alkoxy or thiolato derivatives through metathesis of the chloro ligand.[19]

The compound $MoO_2(L^1)(CH_2SiMe_3)$ is virtually insoluble in hydrocarbons and ether, and sparingly soluble in chlorinated solvents, but is readily soluble in dipolar aprotic solvents such as *N*,*N*-dimethylformamide (DMF) and dimeth-

(11) (a) Wong, Y.-L.; Yan, Y.; Chan, E. S. H.; Yang, Q.; Mak, T. C. W.; Ng, D. K. P. *J. Chem. Soc., Dalton, Trans.* **1998**, 3057. (b) Wong, Y.-L.; Ma, J.-F.; Law, W.-F.; Yan, Y.; Wong, W.-T.; Zhang, Z.-Y.; Mak, T. C. W.; Ng, D. K. P. *Eur. J. Inorg. Chem.* **1999**, 313.

(12) Schultz, B. E.; Gheller, S. F.; Muetterties, M. C.; Scott, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 2714.

(13) (a) Bruce, A.; Corbin, J. L.; Dahlstrom, P. L.; Hyde, J. R.; Minelli, M.; Stiefel, E. I.; Spence, J. T.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 917. (b) Subramanian, P.; Spence, J. T.; Ortega, R.; Enemark, J. H. *Inorg. Chem.* **1984**, *23*, 2564. (c) Küsthardt, U.; Albach, R. W.; Kiprof, P. *Inorg. Chem.* **1993**, *32*, 1838. (d) Shanmuga, S.; Raj, S.; Fun, H.-K.; Chen, Z.-F.; Zhang, J.; Xue, X.; Xiong, R.-G.; You, X.-Z. *Acta Crystallogr., Sect. C* **1999**, *55*, 2037.

(14) Herrmann, W. A.; Fridgen, J.; Lobmaier, G. M.; Spiegler, M. *New J. Chem.* **1999**, *23*, 5.

(15) It is worth noting that the chloro derivatives $MoO_2(L^n)Cl$ (n = 4, 5) could be converted to the μ-oxo dimers $[MoO_2(L^n)]_2O$ (n = 4, 5) in the presence of moisture, though the rate of conversion was rather slow. This phenomenon was revealed by NMR characterization of $MoO_2(L^n)Cl$ (n = 4, 5), in which signals ascribed to the μ-oxo dimolybdenum compounds were observed when wet $CDCl_3$ solutions were used.

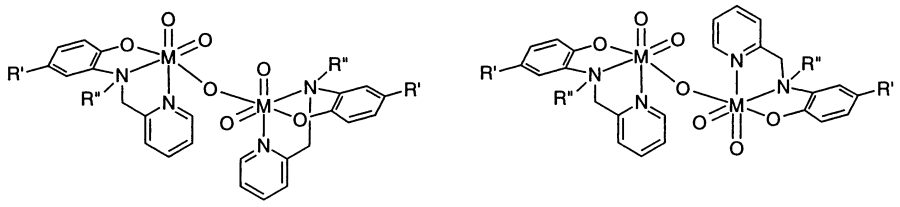
(16) Craig, J. A.; Harlan, E. W.; Snyder, B. S.; Whitener, M. A.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 2082.

(17) Like the molybdenum counterpart $[MoO_2(L^7)]_2O$, $[WO_2(L^4)]_2O$ is also expected to exist as a mixture of enantiomers and diastereomers. The latter could be separated by column chromatography. The ^1H NMR spectra of the isolated product showed only one set of signals, while two sets were observed for the crude product mixture. Attempts to purify and characterize the diastereomers were not successful.

(18) Eagle, A. A.; Mackay, M. F.; Young, C. G. *Inorg. Chem.* **1991**, *30*, 1425.

(19) (a) Roberts, S. A.; Young, C. G.; Kipke, C. A.; Cleland, W. E.; Yamanouchi, K.; Carducci, M. D.; Enemark, J. H. *Inorg. Chem.* **1990**, *29*, 3650. (b) Xiao, Z.; Bruck, M. A.; Doyle, C. Enemark, J. H.; Grittini, C.; Gable, R. W.; Wedd, A. G.; Young, C. G. *Inorg. Chem.* **1995**, *34*, 5950.

Chart 3

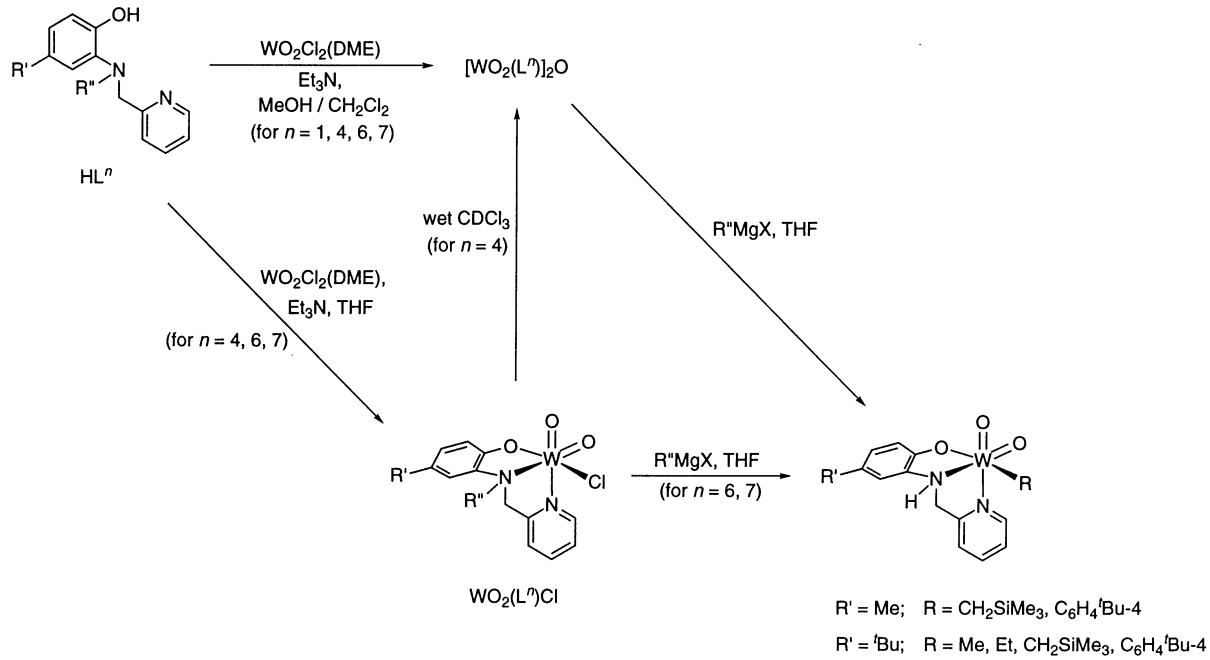


M = Mo, W

R' = H, R" = $CH_2C_6H_4{}^tBu$-4 (L^4)

R' = H, R" = $CH_2C_6H_3({}^tBu)_2$-3,5 (L^5)

Scheme 2



yl sulfoxide (DMSO). The ^{1}H NMR spectrum of MoO$_2$(L^1)(CH$_2$SiMe$_3$) in DMSO-d_6 showed, apart from the signals due to L^1 and the trimethylsilyl group, two upfield doublets at δ 0.34 and 1.77 ppm with a geminal coupling constant of 12 Hz assignable to the two diastereotopic methylene protons on the α-carbon of the CH$_2$SiMe$_3$ ligand.

The new chloro dioxotungsten(VI) complexes WO$_2$(L^n)Cl (n = 6, 7) are relatively more reactive. As shown in Scheme 2, they react with a variety of Grignard reagents RMgX (R = Me, Et, CH$_2$SiMe$_3$, C$_6$H$_4{}^t$Bu-4; X = Cl, Br), affording the corresponding alkyl derivatives WO$_2$(L^n)(R) (n = 6, 7; R = Me, Et, CH$_2$SiMe$_3$, C$_6$H$_4{}^t$Bu-4). However, for the NH derivative WO$_2$(L^1)Cl, the corresponding alkyl complexes WO$_2$(L^1)(R) could not be obtained except for R = CH$_2$SiMe$_3$.[9] It is believed that the alkyl substituent (Me or ^{t}Bu) on L^6 and L^7 enhances the solubility of the resulting complexes, thereby promoting the reactivity of WO$_2$(L^n)Cl (n = 6, 7) and facilitating the isolation and purification of WO$_2$(L^n)(R).

Alternatively, the dioxomolybdenum(VI) and -tungsten(VI) alkyls could also be synthesized via a new synthetic route. Treatment of the μ-oxo complexes [MO$_2$(L^n)]$_2$O (M = Mo, n = 1; M = W, n = 6, 7) with the appropriate Grignard reagents gave the corresponding organometallic dioxo complexes MO$_2$(L^n)(R) (M = Mo, n = 1, R = CH$_2$SiMe$_3$; M = W, n = 6, 7, R = Me, Et, CH$_2$SiMe$_3$, C$_6$H$_4{}^t$Bu-4) in moderate yields (5−25%).

All the molybdenum and tungsten chloro derivatives MO$_2$(L^n)Cl (M = Mo, W; n = 1−5) show similar stability toward air and moisture. However, the molybdenum alkyl complex MoO$_2$(L^1)(CH$_2$SiMe$_3$) is significantly more sensitive to moisture than its tungsten analogue. In the solid state, all the dioxotungsten(VI) alkyl complexes WO$_2$(L^n)(R) are stable in air. However, their solutions are sensitive to moisture to a different extent, following the order R = Me (least stable) > Et ≫ C$_6$H$_4{}^t$Bu-4 > CH$_2$SiMe$_3$ (most stable). The complex WO$_2$(L^7)(Me), for example, decomposes readily in predried DMSO-d_6 within 15 min, while WO$_2$(L^7)(CH$_2$SiMe$_3$) is apparently inert even in wet DMSO-d_6 over a period of 1 week.

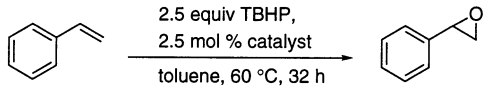
All the alkyl compounds reported in this work were characterized by NMR spectroscopy. The ^{13}C{^{1}H} NMR data of the methyl and ethyl derivatives, however, could not be obtained, probably due to the instability of these compounds in solution. All the dioxomolybdenum compounds showed two characteristic *cis*-dioxo (MoO$_2$) vibrational bands at

Table 1. Epoxidation of Styrene Using $MO_2(L^n)Cl$ or $[MO_2(L^n)]_2O$ as Catalysts[a]

entry	catalyst	yield[b] (%)
1	$MoO_2(L^4)Cl$	52
2	$MoO_2(L^5)Cl$	36
3	$WO_2(L^3)Cl$	31
4	$WO_2(L^4)Cl$	32
5	$WO_2(L^5)Cl$	30
6	$[MoO_2(L^4)]_2O$	27
7	$[MoO_2(L^7)]_2O$	34
8	$[WO_2(L^4)]_2O$	24
9	$[WO_2(L^7)]_2O$	19

[a] Reactions were performed in 3 mL of toluene with 0.4 mmol of styrene, 2.5 mol % catalyst, and 2.5 equiv of *tert*-butyl hydroperoxide under N_2 at 60 °C for 32 h. [b] Reaction yields were determined by GC−MS.

Scheme 3



897−915 and 932−940 cm^{-1} in their IR spectra which could be assigned to the asymmetric and symmetric Mo═O stretchings, respectively.[12,19a,20] The IR spectra of the tungsten analogues showed similar asymmetric and symmetric W═O stretching bands at 893−902 and 940−960 cm^{-1}, respectively.[21] The liquid secondary ion (LSI) mass spectra of all these compounds displayed the protonated molecular ion peaks (MH^+), which are in good agreement with the predicted accurate mass and isotopic distribution pattern.

Catalytic Activities. The catalytic activities of the chloro $MO_2(L^n)Cl$ (M = Mo, W; n = 3−5) and μ-oxo $[MO_2(L^n)]_2O$ (M = Mo, W; n = 4, 7) compounds toward epoxidation of styrene were examined. In a typical experiment, styrene (0.40 mmol) was mixed with 2.5 mol % of the catalyst and 2.5 equiv of *tert*-butyl hydroperoxide (TBHP) in toluene containing 4 Å molecular sieves with benzophenone as an internal standard.[22] The reaction mixture was heated at 60 °C under nitrogen for 32 h (Scheme 3), and the reaction yield of styrene oxide was determined by GC−MS analysis. As shown in Table 1, all these compounds are active toward oxidation of styrene to styrene oxide, despite the moderate reaction yields which range from 19 to 52%.[23]

The chemistry of molybdenum-catalyzed epoxidation of olefins by alkyl hydroperoxides has been extensively studied.[24,25] It is generally believed that the mechanism involves the formation of a Mo(VI) alkyl peroxide intermediate and the transfer of the distal oxygen atom of the coordinated alkyl peroxide instead of the oxo ligand to the olefins.[25] Recently, Finney et al. have reported a series of dioxo Mo(VI) compounds supported by tridentate ligands.[26] The catalytic reactivities of these compounds toward epoxidation of olefins by *tert*-butyl hydroperoxide have also been investigated. On the basis of NMR spectroscopy, it has been shown that the metal complexes are stable toward the alkyl hydroperoxide with the tridentate ligands remaining coordinated to the Mo(VI) center during the epoxidation reactions. Although a detailed kinetic and spectroscopic study of the epoxidation reactions has not been carried out in our work, it is conceivable that they may proceed by a mechanism similar to the one proposed by Finney et al.[26]

Conclusions

In conclusion, we have described the preparation and spectroscopic characterization of a series of new chloro dioxomolybdenum $MoO_2(L^n)Cl$ (n = 1−5) and -tungsten complexes $WO_2(L^n)Cl$ (n = 6, 7). The μ-oxo complexes $[MoO_2(L^n)]_2O$ (n = 1, 4, 5, 7) and $[WO_2(L^n)]_2O$ (n = 1, 4, 6, 7) have also been successfully prepared and characterized. The chloro and μ-oxo compounds react readily with Grignard reagents to give the corresponding alkyl derivatives. The alkyl complexes are rare and can be stabilized by the new N_2O tridentate ligands based on 2-*N*-(2-pyridylmethyl)-aminophenolate. The catalytic activities of selected chloro and μ-oxo compounds toward epoxidation of styrene by *tert*-butyl hydroperoxide have also been studied. To our knowledge, only one application of dioxotungsten(VI) complexes as epoxidation catalysts has been reported previously.[14]

Experimental Section

All reactions were carried out using standard Schlenk line techniques under an atmosphere of nitrogen; workups were performed in air. All reagents and solvents were of reagent grade and used as received. Dichloromethane was predried over 4 Å molecular sieves and distilled from calcium hydride. Diethyl ether, THF, and toluene were distilled from sodium benzophenone. Methanol was distilled from magnesium methoxide. All deuterated solvents as well as *tert*-butyl hydroperoxide (TBHP) in decane (5−6 M) were predried by storing over 4 Å molecular sieves. The free ligands HL^n (n = 1−5)[9,27] and the complexes $MO_2Cl_2(DME)$ (M = Mo, W)[28] were prepared according to literature procedures with minor modification. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DPX 300 spectrometer (^1H, 300 MHz; ^{13}C, 75.4 MHz) in $CDCl_3$ solutions unless stated otherwise. Chemical shifts were referenced to internal $SiMe_4$ (δ = 0 ppm). IR spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer as KBr pellets. EI mass spectra were obtained on a Hewlett-Packard 5989B Mass Engine spectrometer. LSI mass spectra were measured on a Bruker APEX 47e Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with 3-nitrobenzyl alcohol as matrix. GC−MS

(20) Hinshaw, C. J.; Peng, G.; Singh, R.; Spence, J. T.; Enemark, J. H.; Bruck, M.; Kristofzski, J.; Merbs, S. L.; Ortega, R. B.; Wexler, P. A. *Inorg. Chem.* **1989**, *28*, 4483.
(21) (a) Yu, S.-B.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 4385. (b) Oku, H.; Ueyama, N.; Nakamura, A. *Inorg. Chem.* **1995**, *34*, 3667. (c) Eagle, A. A.; Tiekink, E. R. T.; Young, C. G. *Inorg. Chem.* **1997**, *36*, 6315.
(22) Hanson and Sharpless have reported that molecular sieves not only increase the catalytic turnover of epoxidation reactions, but also suppress the partial conversion of epoxides to the corresponding diols, a common side reaction in Mo(VI)-catalyzed epoxidation reactions. See: Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922.
(23) It is expected that other oxidation products may also be present in the product mixtures. However, the complexity of the mixtures rendered their identification difficult to carry out.
(24) Sheldon, R. A. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; D. Reidel: Boston, 1981; Vol. 4.
(25) (a) Mimoun, H. *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 734. (b) Jørgensen, K. A. *Chem. Rev.* **1989**, *89*, 431. (c) Schurig, V.; Betschinger, F. *Chem. Rev.* **1992**, *92*, 873.
(26) Mitchell, J. M.; Finney, N. S. *J. Am. Chem. Soc.* **2001**, *123*, 862.
(27) Pitt, C. G.; Bao, Y.; Thompson, J.; Wani, M. C.; Rosenkrantz, H.; Metterville, J. *J. Med. Chem.* **1986**, *29*, 1231.
(28) (a) Kamenar, B.; Penavic, M.; Korpar-Colig, B.; Markovic, B. *Inorg. Chim. Acta* **1982**, *65*, L245. (b) Dreisch, K.; Andersson, C.; Stålhandske, C. *Polyhedron* **1991**, *10*, 2417.

analyses were carried out on a Hewlett-Packard GC(HP 6890)−MS(HP 5973) analyzer equipped with a HP-5MS (5% phenylmethylsiloxane) column. Elemental analyses were performed by MEDAC Ltd., Brunel University, UK.

4-Methyl-2-*N*-(2-pyridylmethyl)aminophenol (HL^6). A mixture of 2-amino-4-methylphenol (12.3 g, 100 mmol) and 2-pyridinecarboxaldehyde (9.5 mL, 100 mmol) in MeOH (200 mL) was refluxed in air for 2 h. After cooling to room temperature, $NaBH_4$ (7.57 g, 200 mmol) was slowly added with stirring and the reaction mixture was refluxed for a further period of 3 h. The volatiles were then removed under reduced pressure, and water (100 mL) was added to the resulting residue. The pH value of the mixture was adjusted to ca. 7 by adding glacial acetic acid, and the mixture was extracted with CH_2Cl_2 (3 × 150 mL). The combined extracts were dried over anhydrous magnesium sulfate before being concentrated with a rotary evaporator. The resulting dark brown solid was redissolved in CH_2Cl_2 (50 mL) and precipitated with hexanes (100 mL) to give a pale brown solid, which was isolated by filtration, washed with diethyl ether, and dried in vacuo. Yield: 16.3 g (76%). Mp: 96−98 °C. ^{1}H NMR: δ 8.58 (d, J = 3.9 Hz, 1 H, ArH), 7.66 (dt, J = 1.8, 7.7 Hz, 1 H, ArH), 7.36 (d, J = 7.5 Hz, 1 H, ArH), 7.20 (t, J = 6.2 Hz, 1 H, ArH), 6.67 (d, J = 7.2 Hz, 1 H, ArH), 6.41−6.44 (m, 2 H, ArH), 4.48 (s, 2 H, $ArCH_2$), 2.18 (s, 3 H, CH_3). ^{13}C{^{1}H} NMR: δ 159.1, 148.3, 142.7, 137.5, 137.0, 130.1, 122.4, 122.1, 118.6, 114.9, 113.8, 49.8, 21.0. MS-EI (70 eV): m/z 214 (M^+). Anal. Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07%. Found: C, 72.57; H, 6.62; N, 13.05%.

4-*tert*-Butyl-2-*N*-(2-pyridylmethyl)aminophenol (HL^7). This compound was prepared according to the above procedure using 2-amino-4-*tert*-butylphenol (16.5 g, 100 mmol) as the starting material. After the workup procedure, a dark brown oily residue was obtained which was dissolved in diethyl ether (50 mL) and precipitated with hexanes (100 mL). The pale brown solid was collected by filtration, washed thoroughly with hexanes, and dried in vacuo. Yield: 17.4 g (68%). Mp: 112−115 °C. ^{1}H NMR: δ 8.59 (d, J = 3.9 Hz, 1 H, ArH), 7.67 (dt, J = 1.8, 7.7 Hz, 1 H, ArH), 7.34 (d, J = 8.4 Hz, 1 H, ArH), 7.21 (t, J = 6.5 Hz, 1 H, ArH), 6.68−6.73 (m, 3 H, ArH), 4.51 (s, 2 H, $ArCH_2$), 1.22 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 158.9, 148.1, 143.8, 143.6, 137.7, 136.0, 122.5, 122.4, 116.2, 115.0, 112.5, 50.7, 34.1, 31.5. HRMS (LSI): m/z 257.1644 (calcd for $C_{16}H_{21}N_2O$ (MH^+): 257.1654). Anal. Calcd for $C_{16}H_{20}N_2O$: C, 74.97; H, 7.86; N, 10.93%. Found: C, 74.25; H, 7.93; N, 10.71%.[29]

Preparation of $MoO_2(L^1)Cl$. To a pale brown solution of HL^1 (0.60 g, 3.0 mmol) in CH_2Cl_2 (30 mL) was added triethylamine (0.42 mL, 3.0 mmol), and the mixture was stirred for 15 min. The resulting solution was transferred, via a cannula, to a colorless solution of MoO_2Cl_2(DME) (0.87 g, 3.0 mmol) in CH_2Cl_2 (20 mL). During the addition, the solution turned to dark brown immediately with the formation of a brown precipitate. The mixture was kept stirring overnight. The brown solid was collected by filtration, washed thoroughly with CH_2Cl_2 and hexanes, and then dried in vacuo to give the *title compound* as a yellowish brown solid.[30] Yield: 0.46 g (42%). IR (cm^{-1}): 1578m, 1482m, 1459m, 1365w, 1295m, 1268m, 1249w, 1149w, 1111w, 1029w, 947s ν(MoO_2), 907s ν(MoO_2), 867w, 815w, 747s, 620w, 559w, 508m.

General Procedure for the Preparation of $MoO_2(L^n)Cl$ (n = 2−5). A solution of MoO_2Cl_2(DME) in THF was added dropwise to a solution of HL^n (n = 2−5, 1 equiv) in THF with vigorous stirring. The resulting pale yellow mixture turned immediately to dark purple. The mixture was stirred at room temperature for 15 min; then triethylamine (1 equiv) was added and the mixture was kept stirring overnight. The resulting mixture was concentrated and then loaded onto a silica gel column with ethyl acetate as the eluent. The orange fraction was collected and then concentrated under reduced pressure to give a pale orange solid. For $MoO_2(L^2)Cl$, the orange solid was washed thoroughly with ethyl acetate and diethyl ether and then dried in vacuo. For $MoO_2(L^n)Cl$ (n = 3−5), the solid was further purified by column chromatography using $CHCl_3$ as eluent. The first band was collected and concentrated to give the desired product as an orange-yellow solid.

$MoO_2(L^2)Cl$. According to the general procedure, MoO_2Cl_2(DME) (0.87 g, 3.0 mmol) was treated with HL^2 (0.64 g, 3.0 mmol) and triethylamine (0.42 mL, 3.0 mmol) in THF (50 mL) to give $MoO_2(L^2)Cl$ (0.49 g, 43%). ^{1}H NMR: δ 9.33 (d, J = 5.4 Hz, 1 H, ArH), 7.81 (dt, J = 1.8, 7.7 Hz, 1 H, ArH), 7.48 (t, J = 6.5 Hz, 1 H, ArH), 7.38 (dd, J = 1.5, 8.1 Hz, 1 H, ArH), 7.20 (d, J = 7.5 Hz, 1 H ArH), 7.08 (dt, J = 1.5, 7.8 Hz, 1 H, ArH), 6.91 (dt, J = 1.5, 7.7 Hz, 1 H, ArH), 6.66 (dd, J = 1.5, 8.3 Hz, 1 H, ArH), 4.88 (d, J = 14.7 Hz, 1 H, CH_2), 4.39 (d, J = 14.7 Hz, 1 H, CH_2), 3.58 (s, 3 H, CH_3). ^{13}C{^{1}H} NMR: δ 159.1, 153.6, 150.6, 139.8, 138.8, 129.4, 125.0, 123.0, 121.7 (two overlapping signals), 118.4, 67.2, 50.1. IR (cm^{-1}): 3082w, 2978w, 2934w, 1732w, 1608m, 1586m, 1481s, 1442m, 1369w, 1267s, 1160w, 1107w, 1053w, 1025w, 932s ν(MoO_2), 912s ν(MoO_2), 859m, 763s, 720w, 636m, 574w, 492w. HRMS (LSI): m/z 378.9743 (calcd for $C_{13}H_{14}ClMoN_2O_3$ (MH^+) based on ^{35}Cl and ^{97}Mo: 378.9747). Anal. Calcd for $C_{13}H_{13}ClMoN_2O_3$: C, 41.46; H, 3.48; N, 7.44%. Found: C, 40.72; H, 3.44; N, 7.15%.[29]

$MoO_2(L^3)Cl$. According to the general procedure, MoO_2Cl_2(DME) (1.07 g, 3.7 mmol) was treated with HL^3 (1.07 g, 3.7 mmol) and triethylamine (0.51 mL, 3.7 mmol) in THF (50 mL) to give $MoO_2(L^3)Cl$ (0.87 g, 52%). ^{1}H NMR: δ 9.31 (d, J = 4.8 Hz, 1 H, ArH), 7.76 (dt, J = 1.6, 7.7 Hz, 1 H, ArH), 7.36−7.49 (m, 6 H, ArH), 7.14 (d, J = 7.7 Hz, 1 H, ArH), 7.02 (dt, J = 1.5, 7.7 Hz, 1 H, ArH), 6.67 (dd, J = 1.3, 8.2 Hz, 1 H, ArH), 6.57 (dt, J = 1.4, 7.7 Hz, 1 H, ArH), 6.39 (dd, J = 1.4, 8.2 Hz, 1 H, ArH), 5.34 (d, J = 14.1 Hz, 1 H, CH_2), 5.20 (d, J = 14.1 Hz, 1 H, CH_2), 4.97 (d, J = 14.1 Hz, 1 H, CH_2), 4.36 (d, J = 14.1 Hz, 1 H, CH_2). ^{13}C{^{1}H} NMR: δ 160.1, 154.6, 150.8, 139.9, 136.1, 133.3, 132.4, 129.5, 129.2, 128.5, 125.8, 124.8, 123.2, 120.1, 118.3, 65.5, 63.3. IR (cm^{-1}): 3440w, 3069w, 3032w, 2919w, 1606m, 1484s, 1450m, 1358w, 1276s, 1157w, 1107w, 1052w, 1022w, 938s ν(MoO_2), 911s ν(MoO_2), 861m, 764s, 707m, 645m, 571w, 508w. HRMS (LSI): m/z 455.0073 (calcd for $C_{19}H_{18}ClMoN_2O_3$ (MH^+) based on ^{35}Cl and ^{97}Mo: 455.0060). Anal. Calcd for $C_{19}H_{17}ClMoN_2O_3$: C, 50.40; H, 3.78; N, 6.19%. Found: C, 49.95; H, 3.91; N, 5.87%.

$MoO_2(L^4)Cl$. According to the general procedure, MoO_2Cl_2(DME) (0.95 g, 3.3 mmol) was treated with HL^4 (1.14 g, 3.3 mmol) and triethylamine (0.46 mL, 3.3 mmol) in THF (50 mL) to give $MoO_2(L^4)Cl$ (1.06 g, 63%). ^{1}H NMR: δ 9.31 (d, J = 5.1 Hz, 1 H, ArH), 7.76 (dt, J = 1.5, 7.7 Hz, 1 H, ArH), 7.40−7.46 (m, 3 H, ArH), 7.27−7.31 (m, 2H, ArH), 7.14 (d, J = 7.7 Hz, 1 H, ArH), 7.02 (dt, J = 1.4, 7.7 Hz, 1 H, ArH), 6.67 (dd, J = 1.2, 8.2 Hz, 1 H, ArH), 6.58 (dt, J = 1.4, 7.7 Hz, 1 H, ArH), 6.45 (dd, J = 1.4, 8.1 Hz, 1 H, ArH), 5.31 (d, J = 14.1 Hz, 1 H, CH_2), 5.19 (d, J = 14.4 Hz, 1 H, CH_2), 4.93 (d, J = 14.1 Hz, 1 H, CH_2), 4.36 (d, J = 14.4 Hz, 1 H, CH_2), 1.39 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 160.1, 154.7, 152.3, 150.7, 139.9, 136.3, 132.1, 130.2, 129.4, 126.0, 125.4, 124.7, 123.2, 120.1, 118.2, 65.1, 63.2, 34.7, 31.3. IR (cm^{-1}): 3067w, 2962m, 2863w, 1607m, 1481s, 1450m, 1361w, 1277s, 1108w, 1027w, 940s ν(MoO_2), 915s ν(MoO_2), 862m, 761m, 637w,

(29) Attempts to obtain better analytical data were not successful.
(30) Satisfactory elemental analysis data for this compound could not be obtained.

567w. HRMS (LSI): *m*/*z* 511.0704 (calcd for $C_{23}H_{26}ClMoN_2O_3$ (MH^+) based on ^{35}Cl and ^{97}Mo: 511.0686). Anal. Calcd for $C_{23}H_{25}ClMoN_2O_3$: C, 54.29; H, 4.95; N, 5.51%. Found: C, 54.43; H, 4.98; N, 5.43%.

$MoO_2(L^5)Cl$. According to the general procedure, MoO_2Cl_2(DME) (0.87 g, 3.0 mmol) was treated with HL^5 (1.21 g, 3.0 mmol) and triethylamine (0.42 mL, 3.0 mmol) in THF (50 mL) to give $MoO_2(L^5)Cl$ (0.76 g, 45%). ^1H NMR: δ 9.31 (d, $J = 4.8$ Hz, 1 H, ArH), 7.76 (dt, $J = 1.6$, 7.7 Hz, 1 H, ArH), 7.51 (t, $J = 1.7$ Hz, 1 H, ArH), 7.42 (t, $J = 6.5$ Hz, 1 H, ArH), 7.11−7.15 (m, 3 H, ArH), 7.01 (dt, $J = 1.4$, 7.7 Hz, 1 H, ArH), 6.66 (dd, $J = 1.3$, 8.2 Hz, 1 H, ArH), 6.53 (dt, $J = 1.3$, 7.7 Hz, 1 H, ArH), 6.33 (dd, $J = 1.4$, 8.2 Hz, 1 H, ArH), 5.29 (d, $J = 13.8$ Hz, 1 H, CH_2), 5.18 (d, $J = 14.4$ Hz, 1 H, CH_2), 4.98 (d, $J = 13.8$ Hz, 1 H, CH_2), 4.30 (d, $J = 14.4$ Hz, 1 H, CH_2), 1.35 (s, 18 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 160.1, 154.6, 150.8, 150.6, 139.9, 135.9, 132.0, 129.4, 126.9, 126.2, 124.7, 123.3, 122.6, 119.9, 118.1, 66.1, 63.2, 34.8, 31.4. IR (cm^{-1}): 3067w, 2958s, 2869w, 1603m, 1484s, 1450m, 1360w, 1277s, 1252m, 1201w, 1157w, 1108w, 1055w, 1023w, 940s $\nu(MoO_2)$, 913s $\nu(MoO_2)$, 862m, 760m, 721w, 645m, 506w. HRMS (LSI): *m*/*z* 567.1373 (calcd for $C_{27}H_{34}ClMoN_2O_3$ (MH^+) based on ^{35}Cl and ^{97}Mo: 567.1312). Anal. Calcd for $C_{27}H_{33}ClMoN_2O_3$: C, 57.40; H, 5.89; N, 4.96%. Found: C, 57.56; H, 5.92; N, 4.90%.

General Procedure for the Preparation of $[MoO_2(L^n)]_2O$ ($n = 1, 4, 5, 7$). Method A. To a pale brown solution of HL^n ($n = 1, 4, 5, 7$) in MeOH was added $MoO_2(acac)_2$ (1 equiv) in a single portion, and the mixture was heated at 50 °C for 3 h. The resulting yellowish brown solid was collected by filtration, washed thoroughly with MeOH and hexanes, and then dried in vacuo to give the desired complexes $[MoO_2(L^n)]_2O$ ($n = 1, 4, 5, 7$) as a pale yellow solid.

Method B. To a mixture of HL^n ($n = 1, 4, 5, 7$) (2.0 mmol) and $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (1/7 equiv) in MeOH was added dilute hydrochloric acid (0.5 equiv, 0.1 M). A pale yellow suspension was obtained after stirring for 30 min. Stirring was continued at room temperature for overnight, and the resulting yellow solid was isolated by filtration, washed with MeOH, diethyl ether, and hexanes, and then dried in vacuo to give the desired complexes.

$[MoO_2(L^1)]_2O$. According to the general procedure of method A, $MoO_2(acac)_2$ (0.65 g, 2.0 mmol) was treated with HL^1 (0.40 g, 2.0 mmol) in MeOH (40 mL) at 50 °C to give $[MoO_2(L^1)]_2O$ (0.39 g, 58%). By employing method B, a mixture of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (0.36 g, 0.29 mmol) and HL^1 (0.40 g, 2.0 mmol) in MeOH (50 mL) was treated with dilute hydrochloric acid (10 mL, 0.1 M) to give the *title compound* as a pale yellow solid (0.44 g, 65%).[30] IR (cm^{-1}): 3445m, 3184m, 1607m, 1591m, 1489s, 1458w, 1445m, 1347w, 1284s, 1112w, 1024w, 933s $\nu(MoO_2)$, 898s $\nu(MoO_2)$, 864m, 804s, 776s, 752s, 738s, 648m, 628s, 582w, 489w, 429w.

$[MoO_2(L^4)]_2O$. According to the general procedure of method A, $MoO_2(acac)_2$ (0.65 g, 2.0 mmol) was treated with HL^4 (0.69 g, 2.0 mmol) in MeOH (35 mL) to give $[MoO_2(L^4)]_2O$ (0.50 g, 52%). By employing method B, a mixture of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (0.36 g, 0.29 mmol) and HL^4 (0.69 g, 2.0 mmol) in MeOH (30 mL) was treated with dilute HCl (10 mL, 0.1 M) to give the *title compound* as a pale yellow solid (0.56 g, 58%). ^1H NMR (two isomers existed): δ 9.17 (d, $J = 5.1$ Hz, ArH), 8.68 (d, $J = 4.2$ Hz, ArH), 7.62−7.69 (m, ArH), 7.35−7.46 (m, ArH), 7.14−7.31 (m, ArH), 6.91−6.98 (m, ArH), 6.61−6.66 (m, ArH), 6.36−6.57 (m, ArH), 5.50 (d, $J = 14.7$ Hz, $ArCH_2$), 5.43 (d, $J = 14.7$ Hz, $ArCH_2$), 5.33 (d, $J = 14.1$ Hz, $ArCH_2$), 4.95 (d, $J = 13.5$ Hz, $ArCH_2$), 4.89 (d, $J = 14.1$ Hz, $ArCH_2$), 4.58 (d, $J = 13.5$ Hz, $ArCH_2$), 4.34 (d, $J = 14.7$ Hz, $ArCH_2$), 4.31 (d, $J = 14.7$ Hz, $ArCH_2$), 1.40 (s, ^{t}Bu), 1.35 (s, ^{t}Bu). $^{13}C\{^1H\}$ NMR (two isomers existed): δ 161.2, 161.1, 155.2, 155.0, 152.0, 151.9, 149.8, 149.6, 139.3, 139.1, 136.5, 136.2, 132.5, 132.4, 130.6, 130.5, 128.9, 125.8, 125.2, 125.1, 124.1, 123.6, 123.1, 123.0, 118.3, 118.2, 118.0, 64.6, 63.9, 63.1, 62.6, 34.7, 34.6, 31.4, 31.3. IR (cm^{-1}): 3477w, 3066w, 3031w, 2960m, 2905w, 2867w, 1607m, 1588m, 1485s, 1454s, 1357w, 1299s, 1283s, 1168w, 1109m, 1054w, 1024m, 936s $\nu(MoO_2)$, 909s $\nu(MoO_2)$, 864m, 834w, 811w, 786s, 768s, 748s, 717s, 686w, 630s, 574w, 563w, 528w, 509w, 498w, 438w. HRMS (LSI): *m*/*z* 967.1818 (calcd for $C_{46}H_{51}Mo_2N_4O_7$ (MH^+) based on ^{35}Cl and ^{97}Mo: 967.1866). Anal. Calcd for $C_{46}H_{50}Mo_2N_4O_7$: C, 57.38; H, 5.23; N, 5.82%. Found: C, 57.43; H, 5.61; N, 5.82%.

$[MoO_2(L^5)]_2O$. According to the general procedure of method A, $MoO_2(acac)_2$ (0.65 g, 2.0 mmol) was treated with HL^5 (0.80 g, 2.0 mmol) in MeOH (35 mL) to give $[MoO_2(L^5)]_2O$ (0.52 g, 48%). By employing method B, a mixture of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (0.36 g, 0.29 mmol) and HL^5 (0.80 g, 2.0 mmol) in MeOH (30 mL) was treated with dilute HCl (10 mL, 0.1 M) to give the *title compound* as a pale yellow solid (0.56 g, 52%). ^1H NMR (two isomers existed): δ 9.19 (d, $J = 4.8$ Hz, ArH), 8.78 (d, $J = 5.4$ Hz, ArH), 7.63−7.68 (m, ArH), 7.44−7.50 (m, ArH), 7.13−7.29 (m, ArH), 6.91−6.96 (m, ArH), 6.62−6.68 (m, ArH), 6.30−6.50 (m, ArH), 5.39−5.53 (m, $ArCH_2$), 4.95−5.02 (m, $ArCH_2$), 4.64 (d, $J = 14.1$ Hz, $ArCH_2$), 4.25 (d, $J = 14.7$ Hz, $ArCH_2$), 1.38 (s, ^{t}Bu), 1.31 (s, ^{t}Bu). $^{13}C\{^1H\}$ NMR (two isomers existed): δ 161.3, 161.1, 155.2, 155.0, 150.7, 149.8, 149.7, 139.3, 139.1, 136.2, 136.0, 132.5, 129.0, 127.3, 126.1, 124.1, 123.6, 123.1, 122.2, 118.3, 118.2, 117.9, 117.7, 65.6, 64.9, 62.8, 62.5, 34.9, 34.8, 31.5, 31.4. IR (cm^{-1}): 3502w, 3066w, 2962s, 2866w, 1607m, 1589m, 1486s, 1454m, 1394w, 1363m, 1298s, 1286s, 1250m, 1203w, 1154w, 1109w, 1054w, 1024w, 938s $\nu(MoO_2)$, 908s $\nu(MoO_2)$, 864m, 760s, 738s, 716s, 627s, 582w, 503m. HRMS (LSI): *m*/*z* 1079.3863 (calcd for $C_{54}H_{67}Mo_2N_4O_7$ (MH^+) based on ^{35}Cl and ^{97}Mo: 1079.3118). Anal. Calcd for $C_{54}H_{66}Mo_2N_4O_7$: C, 60.33; H, 6.19; N, 5.21%. Found: C, 60.13; H, 6.39; N, 5.07%.

$[MoO_2(L^7)]_2O$. According to the general procedure of method A, $MoO_2(acac)_2$ (0.65 g, 2.0 mmol) was treated with HL^7 (0.51 g, 2.0 mmol) in MeOH (35 mL) to give $[MoO_2(L^7)]_2O$ (0.41 g, 53%). By employing method B, a mixture of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (0.36 g, 0.29 mmol) and HL^7 (0.51 g, 2.0 mmol) in MeOH (30 mL) was treated with dilute HCl (10 mL, 0.1 M) to give the *title compound* as a pale yellow solid (0.43 g, 55%). ^1H NMR: δ 9.01 (d, $J = 5.4$ Hz, 1 H, ArH), 7.73 (t, $J = 8.6$ Hz, 1 H, ArH), 7.23−7.33 (m, 3 H, ArH), 7.12 (d, $J = 8.1$ Hz, 1 H, ArH), 6.61 (d, $J = 8.7$ Hz, 1 H, ArH), 6.15 (d, $J = 4.7$ Hz, 1 H, ArH), 5.39 (dd, $J = 4.7$, 15.9 Hz, 1 H, $ArCH_2$), 4.35 (d, $J = 15.9$ Hz, 1 H, $ArCH_2$), 1.26 (s, 9 H, ^{t}Bu). IR (cm^{-1}): 3447m, 3204w, 2959m, 2866w, 1607m, 1503s, 1436w, 1363w, 1283s, 1131w, 1023w, 928s $\nu(MoO_2)$, 897s $\nu(MoO_2)$, 837m, 798w, 768s, 685m, 629m, 537m, 488w, 427w. MS-LSI: *m*/*z* 787 (MH^+). Anal. Calcd for $C_{32}H_{38}Mo_2N_4O_7$: C, 49.11; H, 4.89; N, 7.16%. Found: C, 48.88; H, 5.22; N, 6.98%.

Preparation of $MoO_2(L^1)(CH_2SiMe_3)$. Method A. To an ice-cooled suspension of $MoO_2(L^1)Cl$ (0.36 g, 1.0 mmol) in THF (30 mL) was added a solution of freshly prepared Me_3SiCH_2MgCl (3.0 mmol) in diethyl ether (30 mL) over a period of 30 min. The mixture turned from a brown suspension to a dark purple solution. The solution was stirred overnight at room temperature. All the volatiles were then removed under reduced pressure, and water (100 mL) was added to the residue. The resulting mixture was extracted by vigorous shaking with CH_2Cl_2 (3 × 80 mL). The extracts were combined, dried over anhydrous magnesium sulfate, and then concentrated to ca. 3 mL to afford a brown solid, which was collected and washed thoroughly with ethyl acetate, diethyl ether, and hexanes. Yield: 87 mg (21%). Mp: 216−218 °C. ^1H NMR

(DMSO-d_6): δ 9.07 (d, J = 4.5 Hz, 1 H, ArH), 7.92 (t, J = 7.1 Hz, 1 H, ArH), 7.72−7.75 (m, 1 H, ArH), 7.55 (t, J = 6.2 Hz, 1 H, ArH), 7.43 (d, J = 7.8 Hz, 1 H, ArH), 7.27 (d, J = 7.8 Hz, 1 H, ArH), 6.95 (t, J = 7.4 Hz, 1 H, ArH), 6.70 (t, J = 7.1 Hz, 1 H, ArH), 6.49 (d, J = 7.8 Hz, 1 H, ArH), 4.58 (dd, J = 4.7, 16.2 Hz, 1 H, ArCH$_2$), 4.32 (d, J = 16.2 Hz, 1 H, ArCH$_2$), 1.77 (d, J = 12.0 Hz, 1 H, MoCH$_2$), 0.34 (d, J = 12.0 Hz, 1 H, MoCH$_2$), 0.02 (s, 9 H, CH$_3$). IR (cm^{-1}): 3176m, 3068w, 2945w, 2889w, 1591m, 1488s, 1442m, 1285s, 1243m, 934s ν(MoO$_2$), 900s ν(MoO$_2$), 850s, 752m, 630w. HRMS (LSI): m/z 417.0517 (calcd for $C_{16}H_{23}MoN_2O_3Si$ (MH$^+$) based on ^{97}Mo: 417.0532). Anal. Calcd for $C_{16}H_{22}MoN_2O_3Si$: C, 46.38; H, 5.35; N, 6.76%. Found: C, 47.01; H, 5.37; N, 5.82%.[29]

Method B. To an ice-cooled suspension of [MoO$_2$(L^1)]$_2$O (0.34 g, 0.5 mmol) in THF (30 mL) was added a solution of freshly prepared Me$_3$SiCH$_2$MgCl (3.0 mmol) in diethyl ether (30 mL) over a period of 30 min. The mixture was stirred at room temperature overnight. The workup and purification procedures were analogous to those of method A. Yield: 50 mg (12%).

General Procedure for the Preparation of WO$_2$(L^n)Cl (n = 6, 7). To a pale brown solution of HL^n (n = 6, 7) in CH_2Cl_2 was added triethylamine (1 equiv). After being stirred at room temperature for 30 min, the solution was transferred to a colorless solution of WO$_2$Cl$_2$(DME) (1 equiv) in CH_2Cl_2 via a cannula. A dark purple suspension was immediately obtained. Stirring was continued overnight, and the dark gray solid formed was collected by filtration, washed thoroughly with CH_2Cl_2, diethyl ether, and hexanes, and then dried in vacuo to give the desired complexes WO$_2$(L^n)Cl (n = 6, 7).

WO$_2$(L^6)Cl. According to the general procedure, WO$_2$Cl$_2$(DME) (1.13 g, 3.0 mmol) in CH_2Cl_2 (20 mL) was treated with a solution of HL^6 (0.64 g, 3.0 mmol) and triethylamine (0.42 mL, 3.0 mmol) in CH_2Cl_2 (30 mL) to give WO$_2$(L^6)Cl (0.80 g, 58%) as a gray solid.[30] IR (cm^{-1}): 3452w, 3069m, 2934w, 2870w, 1609m, 1505s, 1447m, 1350w, 1282s, 1220w, 1125w, 1026w, 951s ν(WO$_2$), 903s ν(WO$_2$), 841s, 792m, 631m, 538m, 508w.

WO$_2$(L^7)Cl. According to the general procedure, WO$_2$Cl$_2$(DME) (1.89 g, 5.0 mmol) in CH_2Cl_2 (30 mL) was treated with a solution of HL^7 (1.28 g, 5.0 mmol) and triethylamine (0.70 mL, 5.0 mmol) in CH_2Cl_2 (30 mL) to give WO$_2$(L^7)Cl (1.65 g, 65%) as a gray solid.[30] IR (cm^{-1}): 3438w, 3069m, 2957m, 2869w, 2827w, 1608m, 1505s, 1489m, 1458m, 1439m, 1364m, 1303s, 1287s, 1160w, 1133m, 1085m, 1058m, 1026m, 939s ν(WO$_2$), 895s ν(WO$_2$), 839m, 827m, 793w, 775w, 747w, 540m.

General Procedure for the Preparation of [WO$_2$(L^n)]$_2$O (n = 1, 4, 6, 7). To a pale brown solution of HL^n (n = 1, 4, 6, 7) in MeOH was added triethylamine (1 equiv). After being stirred at room temperature for 15 min, the solution was transferred to a colorless solution of WO$_2$Cl$_2$(DME) (1 equiv) in CH_2Cl_2 via a cannula. A dark brown solution was immediately obtained, and a pale brown solid appeared after stirring at room temperature for 2 h. Stirring was continued overnight, and the brown solid was collected by filtration, washed thoroughly with MeOH and hexanes, and then dried in vacuo to give the desired complexes [WO$_2$(L^n)]$_2$O (n = 1, 4, 6, 7).

[WO$_2$(L^1)]$_2$O. According to the general procedure, WO$_2$Cl$_2$(DME) (2.26 g, 6.0 mmol) in CH_2Cl_2 (30 mL) was treated with a solution of HL^1 (1.20 g, 6.0 mmol) and triethylamine (0.83 mL, 6.0 mmol) in MeOH (30 mL) to give [WO$_2$(L^1)]$_2$O (1.70 g, 67%) as a white solid. IR (cm^{-1}): 3438w, 3232w, 3072w, 1609m, 1595m, 1491s, 1459m, 1447m, 1288s, 1182w, 1154w, 1109w, 1057w, 1027m, 956s ν(WO$_2$), 894s ν(WO$_2$), 866m, 819s, 775s, 633s, 583w, 537w, 495w. Anal. Calcd for $C_{24}H_{22}N_4O_7W_2$: C, 34.07; H, 2.62; N, 6.62%. Found: C, 33.87; H, 3.10; N, 6.48%.

[WO$_2$(L^4)]$_2$O. According to the general procedure, WO$_2$Cl$_2$(DME) (1.13 g, 3.0 mmol) in CH_2Cl_2 (10 mL) was treated with a solution of HL^4 (1.04 g, 3.0 mmol) and triethylamine (0.42 mL, 3.0 mmol) in MeOH (30 mL) to give [WO$_2$(L^4)]$_2$O (0.79 g, 46%) as a white solid. ^{1}H NMR: δ 9.22 (d, J = 4.5 Hz, 1 H, ArH), 7.70 (dt, J = 1.8, 7.7 Hz, 1 H, ArH), 7.45−7.52 (m, 3 H, ArH), 7.23−7.30 (m, 3 H, ArH), 6.98 (dt, J = 1.8, 7.7 Hz, 1 H, ArH), 6.66 (d, J = 8.1 Hz, 1 H, ArH), 6.47 (t, J = 7.7 Hz, 1 H, ArH), 6.40 (d, J = 8.1 Hz, ArH), 5.75 (d, J = 14.4 Hz, 1 H, ArCH$_2$), 5.00 (d, J = 13.5 Hz, 1 H, ArCH$_2$), 4.52−4.58 (m, 2 H, ArCH$_2$), 1.40 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR: δ 159.8, 155.8, 152.1, 150.1, 139.9, 136.5, 132.7, 130.1, 129.3, 125.9, 125.2, 124.3, 123.3, 119.3, 118.6, 64.0, 62.9, 34.7, 31.4, 31.3. IR (cm^{-1}): 3460m, 3058w, 3030w, 2961m, 2905w, 2869w, 1610m, 1589m, 1488s, 1457m, 1362w, 1299s, 1287s, 1168w, 1110m, 1054w, 1027w, 960s ν(WO$_2$), 912s ν(WO$_2$), 868m, 811s, 756s, 720m, 685w, 636s, 574w, 564w, 528w, 502w. Anal. Calcd for $C_{46}H_{50}N_4O_7W_2$: C, 48.52; H, 4.43; N, 4.92%. Found: C, 48.87; H, 4.37; N, 4.95%.

[WO$_2$(L^6)]$_2$O. According to the general procedure, WO$_2$Cl$_2$(DME) (3.02 g, 8.0 mmol) in CH_2Cl_2 (20 mL) was treated with a solution of HL^6 (1.71 g, 8.0 mmol) and triethylamine (1.11 mL, 8.0 mmol) in MeOH (20 mL) to give [WO$_2$(L^6)]$_2$O (2.53 g, 72%) as a white solid. IR (cm^{-1}): 3452w, 3069m, 2934w, 2870w, 1609m, 1505s, 1447m, 1350w, 1282s, 1220w, 1125w, 1026w, 953s ν(WO$_2$), 901s ν(WO$_2$), 841s, 793s, 633s, 538m, 508w. Anal. Calcd for $C_{26}H_{26}N_4O_7W_2$: C, 35.72; H, 3.00; N, 6.41%. Found: C, 35.65; H, 3.21; N, 6.31%.

[WO$_2$(L^7)]$_2$O. According to the general procedure, WO$_2$Cl$_2$(DME) (3.77 g, 10.0 mmol) in CH_2Cl_2 (30 mL) was treated with a solution of HL^7 (2.56 g, 10.0 mmol) and triethylamine (1.4 mL, 10.0 mmol) in MeOH (30 mL) to give [WO$_2$(L^7)]$_2$O (4.00 g, 84%) as a white solid. IR (cm^{-1}): 3438w, 3069m, 2957m, 2869w, 2827w, 1608m, 1505s, 1489m, 1458m, 1439m, 1364m, 1303s, 1287s, 1160w, 1133m, 1085m, 1058m, 1026m, 940s ν(WO$_2$), 893s ν(WO$_2$), 839m, 827m, 799m, 778w, 747w, 540m. Anal. Calcd for $C_{32}H_{38}N_4O_7W_2$: C, 40.10; H, 4.00; N, 5.85%. Found: C, 40.40; H, 4.31; N, 5.53%.

General Procedure for the Preparation of WO$_2$(L^7)(R) (R = Me, Et). Method A. To an ice-cooled suspension of WO$_2$(L^7)Cl (1.0 mmol) in THF (30 mL) was added a solution of RMgCl (R = Me, Et) (2.0 mmol) in THF (20 mL) over a period of 30 min. During the addition, the reaction mixture turned from a yellowish orange to a pale brown suspension, and finally to a dark brown solution. The solution was stirred overnight at room temperature. Then all the volatiles were removed under reduced pressure, followed by the addition of water (100 mL). The mixture was extracted by vigorous shaking with CH_2Cl_2 (3 × 80 mL) to give a bright yellow extract. The combined organic extracts were dried over anhydrous magnesium sulfate, and then concentrated to ca. 3 mL to afford a pale yellow solid, which was filtered and washed thoroughly with ethyl acetate, diethyl ether, and hexanes.

Method B. The alkyl complexes were prepared by a procedure analogous to that described in method A by the reaction of [WO$_2$(L^n)]$_2$O (n = 6, 7), instead of WO$_2$(L^7)Cl, with 4 equiv of RMgCl (R = Me, Et).

WO$_2$(L^7)(Me). According to the general procedure of method A, WO$_2$(L^7)Cl (0.51 g, 1.0 mmol) was treated with MeMgCl (2.0 mmol) in THF (20 mL) to give the *title compound* (88 mg, 18%). By employing method B, [WO$_2$(L^7)]$_2$O (0.48 g, 0.5 mmol) was reacted with MeMgCl (2.0 mmol) in THF (30 mL) to give WO$_2$(L^7)(Me) (24 mg, 5%). Mp: 249−251 °C (dec). ^{1}H NMR (DMSO-

d_6): δ 9.06 (d, J = 5.1 Hz, 1 H, ArH), 7.97−8.02 (m, 2 H, ArH), 7.57 (t, J = 6.5 Hz, 1 H, ArH), 7.52 (d, J = 7.8 Hz, 1 H, ArH) 7.27 (s, 1 H, ArH), 7.06 (d, J = 8.4 Hz, 1 H, ArH), 6.47 (d, J = 8.4 Hz, 1 H, ArH), 4.55−4.63 (m, 2 H, $ArCH_2$), 1.23 (s, 9 H, ^{t}Bu), 0.60 (s, 3 H, WCH_3). IR (cm^{-1}): 3071m, 2967m, 1608m, 1503m, 1440w, 1365w, 1284s, 1132 m, 1026w, 951s $\nu(WO_2)$, 904s $\nu(WO_2)$, 824m, 840m, 800m, 747w, 669w, 648w, 541w, 515w. HRMS (LSI): m/z 487.1208 (calcd for $C_{17}H_{23}N_2O_3W$ (MH^+) based on ^{184}W: 487.1218). Anal. Calcd for $C_{17}H_{22}N_2O_3W$: C, 41.99; H, 4.56; N, 5.76%. Found: C, 41.71; H, 4.49; N, 5.74%.

$WO_2(L^7)$(Et). According to the general procedure of method A, $WO_2(L^7)Cl$ (0.51 g, 1.0 mmol) was treated with EtMgCl (2.0 mmol) in THF (20 mL) to give $WO_2(L^7)$(Et) (0.11 g, 21%). By employing method B, $[WO_2(L^7)]_2O$ (0.48 g, 0.5 mmol) was reacted with EtMgCl (2.0 mmol) in THF (30 mL) to give the *title compound* (40 mg, 8%).[30] Mp: 248−250 °C (dec). ^{1}H NMR (DMSO-d_6): δ 9.09 (d, J = 4.8 Hz, 1 H, ArH), 8.00 (t, J = 7.7 Hz, 1 H, ArH), 7.95 (d, J = 4.8 Hz, 1 H, ArH), 7.58 (t, J = 6.8 Hz, 1 H, ArH), 7.52 (d, J = 8.4 Hz, 1 H, ArH), 7.27 (d, J = 2.4 Hz, 1 H, ArH), 7.04 (dd, J = 2.4, 8.1 Hz, 1 H, ArH), 6.45 (d, J = 8.7 Hz, 1 H, ArH), 4.56−4.62 (m, 2 H, $ArCH_2$), 1.62−1.78 (m, 2 H, WCH_2), 1.21−1.27 (m, 12 H, ^{t}Bu and CH_3). IR (cm^{-1}): 3422w, 3069w, 2961w, 2904w, 2865w, 1608m, 1507m, 1458w, 1364w, 1283s, 1132w, 1025w, 951s $\nu(WO_2)$, 899s $\nu(WO_2)$, 839m, 798w, 669w, 647w, 541w, 513w. HRMS (LSI): m/z 501.1357 (calcd for $C_{18}H_{25}N_2O_3W$ (MH^+) based on ^{184}W: 501.1375).

General Procedure for the Preparation of $WO_2(L^n)$(R) (n = 6, 7; R = CH_2SiMe_3, $C_6H_4{}^t$Bu-4). Method A. To an ice-cooled suspension of $WO_2(L^n)Cl$ (n = 6, 7) (1.0 mmol) in THF (30 mL) was added a solution of freshly prepared RMgX (R = CH_2SiMe_3, $C_6H_4{}^t$Bu-4; X = Cl, Br) (3.0 mmol) in diethyl ether (30 mL) over a period of 30 min. During the addition, the reaction mixture turned from a yellowish orange to a pale brown suspension, and finally to a dark brown solution. The solution was allowed to warm to room temperature and stirred overnight. The volatiles were then removed under reduced pressure, followed by quenching with water (100 mL). The mixture was extracted by vigorous shaking with CH_2Cl_2 (3 × 80 mL) to give a bright yellow extract. The organic portions were combined, dried over anhydrous magnesium sulfate, and then concentrated to ca. 3 mL to afford a pale yellow solid, which was filtered and washed thoroughly with ethyl acetate, diethyl ether, and hexanes.

Method B. This procedure is analogous to that of method A except for the use of $[WO_2(L^n)]_2O$ (n = 6, 7), instead of $WO_2(L^n)Cl$ (n = 6, 7), and 6 equiv of RMgX (R = CH_2SiMe_3, $C_6H_4{}^t$Bu-4; X = Cl, Br) as the starting materials.

$WO_2(L^6)(CH_2SiMe_3)$. According to the general procedure of method A, $WO_2(L^6)Cl$ (0.47 g, 1.0 mmol) was treated with Me_3SiCH_2MgCl (3.0 mmol) in THF (20 mL) to give $WO_2(L^6)(CH_2SiMe_3)$ (0.18 g, 35%). By employing method B, $[WO_2(L^6)]_2O$ (0.44 g, 0.5 mmol) was reacted with Me_3SiCH_2MgCl (3.0 mmol) in THF (30 mL) to give the *title compound* (93 mg, 18%). Mp: 234−236 °C (dec). ^{1}H NMR (DMSO-d_6): δ 9.07 (d, J = 6.0 Hz, 1 H, ArH), 7.93−8.01 (m, 2 H, ArH), 7.57 (t, J = 6.5 Hz, 1 H, ArH), 7.50 (d, J = 6.9 Hz, 1 H, ArH), 7.08 (s, 1 H, ArH), 6.80 (d, J = 7.5 Hz, 1 H, ArH), 6.42 (d, J = 8.1 Hz, 1 H, ArH), 4.67 (d, J = 16.2 Hz, 1 H, $ArCH_2$), 4.55 (d, J = 16.2 Hz, 1 H, $ArCH_2$), 2.20 (s, 3 H, $ArCH_3$), 1.17 (d, J = 12.9 Hz, 1 H, WCH_2), 0.03 (s, 9 H, CH_3), −0.16 (d, J = 12.9 Hz, 1 H, WCH_2). $^{13}C\{^1H\}$ NMR: δ 158.8, 157.1, 149.8, 140.0, 135.7, 129.3, 128.2, 126.1, 124.8, 124.4, 117.3, 58.4 (the signal due to the α-carbon of the CH_2SiMe_3 ligand may be obscured by the strong solvent septet),[31] 20.3, 1.8. IR (cm^{-1}): 3424w, 3106w, 2947w, 2894w, 1609m, 1561w, 1543w, 1506s, 1438w, 1406w, 1354w, 1284s, 1243m, 1126w, 988w, 951s $\nu(WO_2)$, 902s $\nu(WO_2)$, 853m, 825m, 763w, 716w, 633w, 539w, 505w. HRMS (LSI): m/z 517.1105 (calcd for $C_{17}H_{25}N_2O_3SiW$ (MH^+) based on ^{184}W: 517.1144). Anal. Calcd for $C_{17}H_{24}N_2O_3SiW$: C, 39.55; H, 4.69; N, 5.43%. Found: C, 39.06; H, 5.24; N, 5.39%.[29]

$WO_2(L^7)(CH_2SiMe_3)$. According to the general procedure of method A, $WO_2(L^7)Cl$ (0.51 g, 1.0 mmol) was treated with Me_3SiCH_2MgCl (3.0 mmol) in THF (20 mL) to give $WO_2(L^7)(CH_2SiMe_3)$ (0.21 g, 38%). By employing method B, $[WO_2(L^7)]_2O$ (0.48 g, 0.5 mmol) was treated with Me_3SiCH_2MgCl (3.0 mmol) in THF (30 mL) to give the *title compound* (89 mg, 16%). Mp: 216−218 °C (dec). ^{1}H NMR (DMSO-d_6): δ 9.09 (d, J = 6.0 Hz, 1 H, ArH), 8.00 (dt, J = 1.5, 7.7 Hz, 1 H, ArH), 7.93 (d, J = 4.5 Hz, 1 H, ArH), 7.59 (t, J = 6.2 Hz, 1 H, ArH), 7.52 (d, J = 7.8 Hz, 1 H, ArH), 7.26 (d, J = 2.4 Hz, 1 H, ArH), 7.04 (dd, J = 2.4, 8.6 Hz, 1 H, ArH), 6.46 (d, J = 8.4 Hz, 1 H, ArH), 4.68 (dd, J = 4.5, 16.8 Hz, 1 H, $ArCH_2$), 4.60 (d, J = 16.8 Hz, 1 H, $ArCH_2$), 1.24 (s, 9 H, ^{t}Bu), 1.14 (d, J = 12.3 Hz, 1 H, WCH_2), 0.03 (s, 9 H, CH_3), −0.16 (d, J = 12.3 Hz, 1 H, WCH_2). $^{13}C\{^1H\}$ NMR: δ 158.6, 157.2, 149.8, 141.9, 140.1, 135.5, 125.6, 124.8, 124.3, 122.3, 116.9, 58.5 (the signal due to the α-carbon of the CH_2SiMe_3 ligand may be obscured by the strong solvent septet),[31] 34.0, 31.6, 1.8. IR (cm^{-1}): 3422w, 3076w, 2955m, 2904w, 2868w, 1609m, 1502m, 1447w, 1364w, 1301m, 1285s, 1240w, 1131w, 1026w, 993w, 950s $\nu(WO_2)$, 899s $\nu(WO_2)$, 840s, 797w, 718w, 689w, 634w, 555w, 493w. HRMS (LSI): m/z 559.1555 (calcd for $C_{20}H_{31}N_2O_3SiW$ (MH^+) based on ^{184}W: 559.1613). Anal. Calcd for $C_{20}H_{30}N_2O_3SiW$: C, 43.02; H, 5.42; N, 5.02%. Found: C, 43.15; H, 5.45; N, 5.05%.

$WO_2(L^6)(C_6H_4{}^t$Bu-4). According to the general procedure of method A, $WO_2(L^6)Cl$ (0.47 g, 1.0 mmol) was treated with 4-^{t}BuC_6H_4MgBr (3.0 mmol) in THF (20 mL) to give $WO_2(L^6)(C_6H_4{}^t$Bu-4) (0.20 g, 36%). By employing method B, $[WO_2(L^6)]_2O$ (0.44 g, 0.5 mmol) was reacted with 4-^{t}BuC_6H_4MgBr (3.0 mmol) in THF (30 mL) to give the *title compound* (0.14 g, 25%). Mp: 230−232 °C (dec). ^{1}H NMR (DMSO-d_6): δ 9.33 (d, J = 4.5 Hz, 1 H, ArH), 7.97−8.03 (m, 2 H, ArH), 7.68 (t, J = 6.2 Hz, 1 H, ArH), 7.61 (d, J = 8.4 Hz, 2 H, ArH), 7.39 (d, J = 7.8 Hz, 1 H, ArH), 7.12−7.15 (m, 3 H, ArH), 6.86 (dd, J = 1.8, 8.1 Hz, 1 H, ArH), 6.49 (d, J = 8.1 Hz, 1 H, ArH), 4.51 (d, J = 15.9 Hz, 1 H, $ArCH_2$), 3.55 (dd, J = 4.5, 15.9 Hz, 1 H, $ArCH_2$), 2.21 (s, 3 H, CH_3), 1.19 (s, 9 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 175.3, 158.8, 157.1, 150.2, 149.5, 141.9, 140.7, 135.0, 129.6, 128.8, 126.5, 125.3, 124.7, 124.2, 117.5, 58.2, 34.8, 31.2, 20.2. IR (cm^{-1}): 3404m, 3090m, 3069m, 2961m, 2866w, 1609m, 1504s, 1488w, 1447w, 1355w, 1281s, 1125w, 1061m, 1025w, 951s $\nu(WO_2)$, 901s $\nu(WO_2)$, 819s, 767w, 635m, 561w, 537w, 506w. HRMS (LSI): m/z 563.1517 (calcd for $C_{23}H_{27}N_2O_3W$ (MH^+) based on ^{184}W: 563.1531). Anal. Calcd for $C_{23}H_{26}N_2O_3W$: C, 49.13; H, 4.66; N, 4.98%. Found: C, 48.89; H, 4.99; N, 5.03%.

$WO_2(L^7)(C_6H_4{}^t$Bu-4). According to the general procedure of method A, $WO_2(L^7)Cl$ (0.51 g, 1.0 mmol) was treated with 4-^{t}BuC_6H_4MgBr (3.0 mmol) in THF (20 mL) to give $WO_2(L^7)(C_6H_4{}^t$Bu-4) (0.24 g, 39%). By employing method B, $[WO_2(L^7)]_2O$ (0.48 g, 0.5 mmol) was reacted with 4-^{t}BuC_6H_4MgBr (3.0 mmol) in THF (30 mL) to give the *title compound* (0.13 g, 22%).[30] Mp: 258−260 °C (dec). ^{1}H NMR (DMSO-d_6): δ 9.34 (d, J = 5.4 Hz, 1 H, ArH), 8.01 (dt, J = 1.5, 7.7 Hz, 1 H, ArH), 7.97 (d, J = 4.8 Hz, 1 H, ArH), 7.69 (t, J = 6.5 Hz, 1 H, ArH), 7.62 (d, J = 8.4 Hz, 2 H, ArH), 7.40 (d, J = 7.5 Hz, 1 H, ArH), 7.32 (d, J = 2.4

(31) The $^{13}C\{^1H\}$ NMR spectra of $WO_2(\eta^5\text{-}C_5R_5)(CH_2SiMe_3)$ and $WO(\eta^2\text{-}O_2)(\eta^5\text{-}C_5R_5)(CH_2SiMe_3)$ (R = H, Me) in C_6D_6 solution show this carbon signal at δ 19.2−33.1 with $^1J_{CW}$ = 92.7−135.0 Hz (see refs 3d and 9).

Hz, 1 H, ArH), 7.13 (d, $J = 8.4$ Hz, 2 H, ArH), 7.09 (dd, $J = 2.4$, 8.7 Hz, 1 H, ArH), 6.52 (d, $J = 8.7$ Hz, 1 H, ArH), 4.55 (d, $J = 15.9$ Hz, 1 H, $ArCH_2$), 3.48 (d, $J = 15.9$ Hz, 1 H, $ArCH_2$), 1.24 (s, 9 H, ^{t}Bu), 1.19 (s, 9 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 175.3, 158.6, 157.2, 150.1, 149.5, 142.5, 141.9, 140.8, 134.8, 125.9, 125.2, 124.7, 124.1, 122.9, 117.1, 58.1, 34.5, 34.1, 31.5, 31.2. IR (cm^{-1}): 3423w, 3153w, 3064w, 2962m, 2903w, 2867w, 1608m, 1507s, 1459w, 1440w, 1363w, 1282s, 1203w, 1130w, 1060w, 1025w, 950s $\nu(WO_2)$, 901s $\nu(WO_2)$, 839m, 821m, 797m, 689w, 668w, 636w, 558w, 511w. HRMS (LSI): *m*/*z* 605.1967 (calcd for $C_{26}H_{33}N_2O_3W$ (MH^+) based on ^{184}W: 605.2001).

General Procedure for Epoxidation Experiments. In a typical epoxidation experiment, an ampule equipped with a Young's tap was charged with a mixture of the catalyst (0.01 mmol), *tert*-butyl hydroperoxide (0.20 mL, 1.0 mmol, 5−6 M in decane), benzophenone (0.0091 g, 0.050 mmol), and 4 Å molecular sieves (ca. 0.05 g) in toluene (3.0 mL). The mixture was gently warmed to 35 °C under a nitrogen atmosphere for 30 min, followed by the addition of styrene (0.042 g, 0.40 mmol), and the reaction mixture was heated at 60 °C under nitrogen for 32 h. The resulting mixture was filtered through a column containing a short bed of silica gel using *i*-PrOH/hexanes (1:5) as eluent to remove all metal compounds. The amount of styrene oxide in the product mixture was quantified by GC−MS analysis, using benzophenone as an internal standard.

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