Dioxotungsten(VI) Complexes with N_2O Tridentate Ligands. Synthesis and Structure of the Chloro and Alkyl Derivatives

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A new series of N_2O tridentate ligands HL^n (n = 2−5) have been prepared through *N*-methylation or *N*-benzylation of 2-*N*-(2-pyridylmethyl)aminophenol (HL^1). Treatment of these ligands with $WO_2Cl_2(DME)$ (DME = 1,2-dimethoxyethane) in the presence of triethylamine leads to the formation of *cis*-dioxotungsten(VI) complexes $WO_2(L^n)Cl$ (n = 1−5). Reaction of $WO_2(L^1)Cl$ with Me_3SiCH_2MgCl gives the alkyl derivative $WO_2(L^1)(CH_2SiMe_3)$, which has been structurally characterized.

Introduction

High-valent oxometalates have been widely used in various homogeneous and heterogeneous catalytic reactions such as oxidation, epoxidation, and ring-opening polymerization.[1] To reveal the nature of the catalytically active sites and understand the chemical behavior of the surface species, a substantial number of organometallic oxo complexes have been synthesized and studied as synthetic analogues.[2] The use of alkoxy and phenoxy groups and more recently the preorganized set of oxygen donor atoms from calix[4]arenes as ancillary ligands to mimic the oxo surfaces have also been described.[3] High-valent dioxotungsten complexes with hydrocarbon ligands have been reported sporadically, most of which contain cyclopentadienyl ligands of the types $WO_2(\eta\text{-}C_5R_5)Cl$, $[WO_2(\eta\text{-}C_5R_5)]_2O$, and $WO_2(\eta\text{-}C_5R_5)R'$ (R = H, Me; R′ = alkyl, alkynyl).[4] Bipyridine (bipy) and hydrotris(3,5-dimethylpyrazolyl)borate $[HB(Me_2pz)_3]$ have also been employed as the supporting ligands to give the complexes $WO_2(bipy)R_2$ (R = alkyl, phenyl) and $WO_2[HB(Me_2pz)_3]R$ (R = alkyl, phenyl, alkenyl), respectively.[5,6] To our knowledge, organometallic dioxotungsten complexes with other ancillary ligands are extremely rare.[7] We have recently reported several series of dioxotungsten(VI) complexes with N_2O_2 and N_2S_2 tetradentate ligands, which are active toward oxygen atom transfer reactions.[8] We describe herein a new series of dioxotungsten(VI) complexes containing N_2O tridentate ligands, which can be functionalized through *N*-alkylation. The molecular structure of an alkyl−dioxo complex, namely $WO_2(L^1)(CH_2SiMe_3)$, is also reported.

Results and Discussion

Treatment of 2-*N*-(2-pyridylmethyl)aminophenol (HL^1), which could be prepared readily by reductive amination from 2-aminophenol and 2-pyridinecarboxaldehyde,[9] with n-BuLi and methyl iodide or various benzyl bromides led to the formation of a new series of N_2O tridentate ligands HL^n (n = 2−5) (Scheme 1). The substituents, having different steric and electronic nature, were introduced to the nitrogen atom with a view to studying their effects on complex formation and properties of the resulting complexes. All the ligands were characterized spectroscopically, while for HL^3 the molecular structure was also confirmed by single-crystal X-ray analysis.[10] The bond distances and angles of this ligand are unexceptional, and the N_2O binding sites

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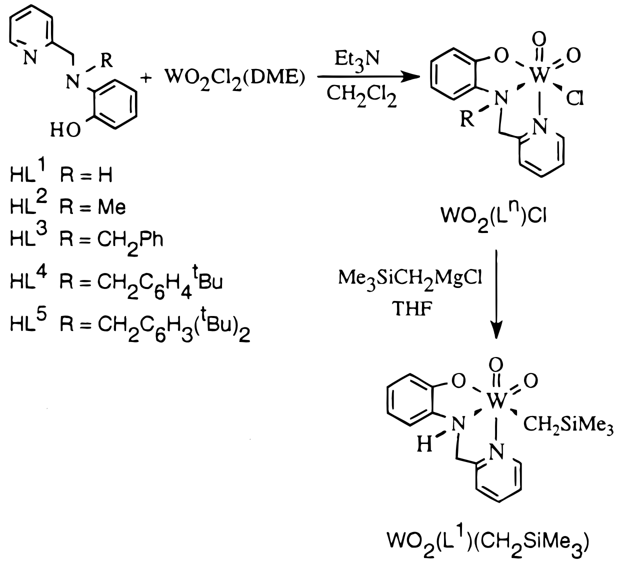
Scheme 1



adopt a favorable conformation to coordinate to a metal center in a facial manner. These tridentate ligands were found to be rather unstable, and the pale yellow solid darkened gradually upon exposure to air over a few days. The ligands should therefore be freshly prepared for complex formation.

Reaction of these ligands with $WO_2Cl_2(DME)$, which is a versatile precursor to other high-valent dioxotungsten(VI) complexes,[8] in the presence of triethylamine gave the corresponding dioxo complexes $WO_2(L^n)Cl$ (n = 1−5) (Scheme 1). Due to the poor solubility of $WO_2(L^1)Cl$ in common organic solvents, this compound could only be purified by washing with various solvents, and no characterizing data could be obtained. By contrast, all the other dioxo complexes, in particular $WO_2(L^n)Cl$ (n = 3−5), have sufficient solubility to be purified and characterized with a range of spectroscopic methods. Very convincing evidence for complex formation comes from the appearance of two doublets at δ 4.56−5.32 for the two methylene protons adjacent to the pyridine ring in the ^1H NMR spectra of these compounds, showing that the two protons become diastereotopic upon complexation. For the *N*-benzyl analogues $WO_2(L^n)Cl$ (n = 3−5), the two methylene protons in the benzyl groups are also diastereotopic, giving another two doublets in the spectra. It is worth noting that the solvent $CDCl_3$ used should be relatively dry. Some unidentified signals appeared in the ^1H NMR spectra for wet solutions of these compounds, indicating that although these chloro−dioxo complexes are air stable, they are slightly sensitive to moisture and decompose readily in the presence of water.

The IR spectra of all these dioxo compounds showed two strong bands within 913−918 and 946−961 cm^{-1} attributed to the asymmetric and symmetric W═O stretches, respectively, in a *cis*-dioxo moiety.[11] The compounds $WO_2(L^n)Cl$ (n = 2−5) were also characterized with liquid secondary ion (LSI) mass spectrometry. The protonated molecular ion (MH^+) was identified in all cases with a predicted accurate mass and isotopic distribution pattern.

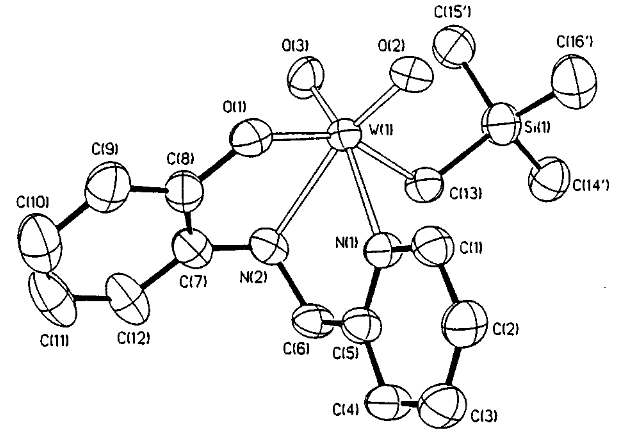


Figure 1. Molecular structure of $WO_2(L^1)(CH_2SiMe_3)$. Selected bond lengths (Å) and angles (deg) are as follows: W(1)−O(1) = 1.986(4), W(1)−O(2) = 1.709(4), W(1)−O(3) = 1.711(4), W(1)−N(1) = 2.333(4), W(1)−N(2) = 2.369(4), W(1)−C(13) = 2.149(6); O(1)−W(1)−O(2) = 97.66(18), O(1)−W(1)−O(3) = 100.89(17), O(2)−W(1)−O(3) = 106.96(19), O(1)−W(1)−N(1) = 78.87(15), O(2)−W(1)−N(1) = 89.11(16), O(3)−W(1)−N(1) = 163.73(18), O(1)−W(1)−N(2) = 74.27(16), O(2)−W(1)−N(2) = 157.53(16), O(3)−W(1)−N(2) = 95.25(17), N(1)−W(1)−N(2) = 68.89(12), O(1)−W(1)−C(13) = 154.13(19), O(2)−W(1)−C(13) = 98.6(2), O(3)−W(1)−C(13) = 93.5(2), N(1)−W(1)−C(13) = 81.38(18), N(2)−W(1)−C(13) = 83.12(19), W(1)−C(13)−Si(1) = 116.8(3).

Treatment of $WO_2(L^1)Cl$ with an excess of the Grignard reagent Me_3SiCH_2MgCl resulted in ligand substitution reaction and the formation of $WO_2(L^1)(CH_2SiMe_3)$ in 30% yield (Scheme 1). This high-valent alkyl tungsten complex is stable to air and moisture. It has limited solubility in hydrocarbons, ethers, and chlorinated solvents, but can be dissolved in dipolar aprotic solvents such as *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The ^1H NMR spectrum of $WO_2(L^1)(CH_2SiMe_3)$ in DMSO-d_6 showed, apart from the signals due to L^1 and the trimethylsilyl group, two upfield doublets at δ 1.19 and −0.13 with a geminal coupling constant of 12.4 Hz, which could be ascribed to the two diastereotopic methylene protons next to tungsten. No satellite resonances due to ^{183}W and ^{29}Si nuclei were observed probably due to the low intensity. The ^{13}C NMR spectrum recorded in DMSO-d_6 was also in accord with C_1 symmetry except that the carbon signal for the WCH_2 moiety was not seen. It is likely that the signal was obscured by the strong solvent septet.[12]

The structure of $WO_2(L^1)(CH_2SiMe_3)$ was established by single-crystal X-ray analysis. Figure 1 gives a perspective view of the structure together with selected bond distances and angles. The compound exhibits a distorted octahedral geometry with a facially coordinated tridentate ligand L^1 and *cis*-dioxo ligands that are trans to the two nitrogen atoms of the ligand. The W═

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(10) Crystallographic data for HL^3: $C_{19}H_{18}N_2O$, fw 290.4, monoclinic space group $P2_1/c$ (no. 14), with a = 14.624(3) Å, b = 11.306(2) Å, c = 9.878(2) Å, β = 101.12(3)°, V = 1602.6(5) Å^3, and D_{calcd} = 1.203 g cm^{-3} for Z = 4. The structure was solved by direct methods and refined by a full-matrix least-squares procedure using 3675 data to a conventional R value of 0.0571 (R_w = 0.1490).

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(12) The $^{13}C\{^1H\}$ NMR spectra of $WO_2(\eta\text{-}C_5R_5)(CH_2SiMe_3)$ and $WO(\eta^2\text{-}O_2)(\eta\text{-}C_5R_5)(CH_2SiMe_3)$ (R = H, Me) in C_6D_6 showed this carbon signal at δ 19.2−33.1 with $^1J_{CW}$ = 92.7−135.0 Hz (see ref 4d).

O bond distances [1.709(4)−1.711(4) Å] are virtually identical to the mean value of 1.709 Å determined for a number of dioxotungsten complexes.[13] The W−O single bond distance [1.986(4) Å] is in the range typical of W(VI) alkoxides.[14] The W−C bond [2.149(6) Å] is also comparable to those found in other alkyl−oxo tungsten complexes.[4a,c,5a,6a,b,15] The W−N bonds are relatively long (>2.33 Å) because of the strong trans influence of the oxo ligands.[11b,16] The angle subtended by the dioxo ligands [106.96(19)°] is typical of related dioxotungsten complexes.[4a,e,5,6b,11b,17]

Attempts to prepare other alkyl−dioxo complexes by treating $WO_2(L^n)Cl$ ($n = 1-3$) with RMgX (R = Me, Et, Ph, CH_2Ph, CH_2SiMe_3) were not successful (except for $n = 1$, R = CH_2SiMe_3, as shown in Scheme 1). For the reactions involving $WO_2(L^n)Cl$ ($n = 2, 3$), free ligands HL^n ($n = 2, 3$) were regenerated after the workup procedure, showing that the compounds underwent decomplexation rather than ligand substitution reactions. The reasons for the difference in reactivity remain elusive at this stage. To examine the reactivity of the chloro functionality in these complexes toward other anions, the compounds $WO_2(L^n)Cl$ ($n = 1, 3$) were also treated with NaOR (R = Me, Et, Ph) in tetrahydrofuran (THF), and thiophenol in the presence of triethylamine in CH_2Cl_2. Surprisingly, only the starting complexes were recovered with no indication of the formation of substituted products even after prolonged heating. This is in contrast with the chemistry of $WO_2[HB(Me_2pz)_3]Cl$, which can be converted to various alkyl, −OR, −SR, and −SeR derivatives through displacement of the chloro ligand.[6a,b,11b]

Experimental Section

General Information. All reactions were carried out using standard Schlenk-line techniques under an atmosphere of nitrogen; workups were performed in air. Dichloromethane was predried over 4 Å molecular sieves and distilled from calcium hydride. THF was distilled from sodium benzophenone ketyl. All other reagents and solvents were of reagent grade and used as received. The ligand HL^1 and the tungsten complex $WO_2Cl_2(DME)$ were prepared according to literature procedures with minor modification.[9,18] All ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer (^1H, 300; ^{13}C, 75.4 MHz) in $CDCl_3$ solutions unless otherwise stated. Chemical shifts were relative to internal $SiMe_4$ ($\delta = 0$). IR spectra were taken on a Nicolet Magna 550 FT-IR spectrometer as KBr pellets. Electron impact (EI) mass spectra were obtained on a Hewlett-Packard 5989B mass 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. Elemental analyses were performed by the Medac Ltd., Brunel Science Centre, and the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

General Procedure for the Preparation of HL^n ($n = 2-5$). To a light brown solution of HL^1 (0.20 g, 1.0 mmol) in THF (10 mL) was added n-BuLi (1.6 M solution in hexanes, 1.3 mL, 2.1 mmol) dropwise at 0 °C. The mixture was stirred at this temperature for 1 h, then allowed to warm to room temperature. Iodomethane or differently substituted benzyl bromides (1.0 mmol) were added slowly, and stirring was continued for 12 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 anhydrous magnesium sulfate before being concentrated with a rotary evaporator. The residue was chromatographed on a silica gel column using ethyl acetate/hexanes (1:3 for $n = 2-4$; 1:2 for $n = 5$) as eluent. HL^5 was isolated as a pale yellow oily solid, while the other ligands were further purified by recrystallization from CH_2Cl_2/hexanes (1:1), yielding pale yellow crystals.

2-*N*-Methyl-*N*-(2-pyridylmethyl)aminophenol (HL^2): 0.18 g (83%), mp 88−91 °C. ^1H NMR: δ 8.66 (d, $J = 4.5$ Hz, 1 H, ArH), 7.70 (dt, $J = 1.6$, 7.6 Hz, 1 H, ArH), 7.21−7.29 (m, 2 H, ArH), 7.10 (d, $J = 7.8$ Hz, 1 H, ArH), 6.95−7.02 (m, 2 H, ArH), 6.79−6.85 (m, 1 H, ArH), 4.02 (s, 2 H, CH_2), 2.73 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR: δ 158.5, 151.8, 149.0, 140.5, 137.2, 124.4, 122.8, 122.6, 119.8, 119.1, 116.0, 62.3, 39.8. HRMS (LSI): *m/z* 215.1180 (calcd for $C_{13}H_{15}N_2O$ (MH^+) 215.1184). Anal. Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.07. Found: C, 72.78; H, 6.61; N, 12.96.

2-*N*-Benzyl-*N*-(2-pyridylmethyl)aminophenol (HL^3): 0.17 g (60%), mp 97−99 °C. ^1H NMR: δ 8.60 (d, $J = 4.8$ Hz, 1 H, ArH), 7.49 (dt, $J = 1.7$, 7.7 Hz, 1 H, ArH), 7.06−7.17 (m, 7 H, ArH), 6.93−6.98 (m, 2 H, ArH), 6.87 (d, $J = 7.7$ Hz, 1 H, ArH), 6.73−6.79 (m, 1 H, ArH), 4.28 (s, 2 H, CH_2), 4.15 (s, 2 H, CH_2). $^{13}C\{^1H\}$ NMR: δ 158.9, 152.8, 148.3, 139.1, 138.0, 136.9, 128.7, 127.9, 126.9, 125.0, 122.6, 122.3, 121.9, 118.9, 116.3, 60.8, 57.6. MS (EI): *m/z* 290 (M^+). Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.49; H, 6.28; N, 9.57.

2-*N*-(4-*tert*-Butylbenzyl)-*N*-(2-pyridylmethyl)aminophenol (HL^4): 0.24 g (70%), mp 103−105 °C. ^1H NMR: δ 8.54 (d, $J = 4.8$ Hz, 1 H, ArH), 7.34 (dt, $J = 1.8$, 7.7 Hz, 1 H, ArH), 7.15 (d, $J = 7.8$ Hz, 1 H, ArH), 7.02−7.07 (m, 5 H, ArH), 6.96−6.98 (m, 2 H, ArH), 6.74−6.80 (m, 1 H, ArH), 6.70 (d, $J = 7.5$ Hz, 1 H, ArH), 4.25 (s, 2 H, CH_2), 4.07 (s, 2 H, CH_2), 1.21 (s, 9 H, ^tBu). $^{13}C\{^1H\}$ NMR: δ 159.1, 152.6, 149.6, 148.1, 139.7, 136.5, 134.9, 128.4, 124.7 (two overlapping signals), 122.4, 121.9, 121.5, 118.8, 116.3, 60.8, 57.4, 34.2, 31.2. HRMS (LSI): *m/z* 347.2116 (calcd for $C_{23}H_{27}N_2O$ (MH^+) 347.2123). Anal. Calcd for $C_{23}H_{26}N_2O$: C, 79.73; H, 7.56; N, 8.09. Found: C, 79.53; H, 7.75; N, 7.78.

2-*N*-(3,5-Di-*tert*-butylbenzyl)-*N*-(2-pyridylmethyl)aminophenol (HL^5): 0.35 g (86%). ^1H NMR: δ 8.54 (d, $J = 4.5$ Hz, 1 H, ArH), 7.39 (dt, $J = 1.7$, 7.7 Hz, 1 H, ArH), 7.17 (d, $J = 8.0$, 1 H, ArH), 7.12 (t, $J = 1.8$ Hz, 1 H, ArH), 7.07 (dd, $J = 5.0$, 6.8 Hz, 1 H, ArH), 6.95−7.02 (m, 4 H, ArH), 6.74−6.82 (m, 2 H, ArH), 4.28 (s, 2 H, CH_2), 4.13 (s, 2 H, CH_2), 1.21 (s, 18 H, ^tBu). $^{13}C\{^1H\}$ NMR: δ 159.2, 152.7, 150.2, 148.0, 139.8, 137.0, 136.6, 124.9, 123.3, 122.5, 122.1, 121.8, 121.0, 118.9, 116.3, 60.8, 58.8, 34.6, 31.4. HRMS (LSI): *m/z* 403.2791 (calcd for $C_{27}H_{35}N_2O$ (MH^+) 403.2749). Satisfactory analytical data for this compound could not be obtained.

General Procedure for the Preparation of $WO_2(L^n)Cl$ ($n = 1-5$). A solution of $WO_2Cl_2(DME)$ in THF was added dropwise to a solution of HL^n ($n = 1-5$, 1 equiv) in THF with vigorous stirring. The pale yellow mixture turned to dark purple immediately. The mixture was stirred at room temperature for 15 min, then triethylamine (1 equiv) was added, and the mixture was kept stirring overnight. Due to the poor solubility of $WO_2(L^1)Cl$, this compound was collected by filtration, washed with EtOH, THF, and diethyl ether, and

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then dried in vacuo. For the other dioxo complexes, the resulting mixture was loaded onto a short bed of silica gel column, which was eluted with ethyl acetate. The dark purple band was collected and concentrated to give a pale purple solid. For $WO_2(L^2)Cl$, the solid was washed extensively with ethyl acetate and diethyl ether to give a pale gray solid, which was then dried in vacuo. For $WO_2(L^n)Cl$ ($n = 3-5$), the solid was further purified by column chromatography using $CHCl_3$ as eluent. The first band was collected and concentrated to give a white solid.

$WO_2(L^2)Cl$. According to the general procedure, $WO_2Cl_2(DME)$ (2.22 g, 5.9 mmol) was treated with HL^2 (1.27 g, 5.9 mmol) and triethylamine (0.83 mL, 5.9 mmol) in THF (50 mL) to give $WO_2(L^2)Cl$ (1.51 g, 55%). ^1H NMR: δ 9.39 (d, $J = 5.3$ Hz, 1 H, ArH), 7.87 (dt, $J = 1.6$, 7.7 Hz, 1 H, ArH), 7.51 (t, $J = 6.5$ Hz, 1 H, ArH), 7.39 (d, $J = 8.2$ Hz, 1 H, ArH), 7.27 (d, $J = 7.6$ Hz, 1 H, ArH), 7.12 (dt, $J = 1.4$, 7.8 Hz, 1 H, ArH), 6.92 (dt, $J = 1.3$, 7.8 Hz, 1 H, ArH), 6.69 (dd, $J = 1.3$, 8.2 Hz, 1 H, ArH), 4.89 (d, $J = 14.7$ Hz, 1 H, CH_2), 4.65 (d, $J = 14.7$ Hz, 1 H, CH_2), 3.62 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR: δ 157.9, 154.3, 151.2, 140.4, 138.8, 129.9, 125.2, 123.1, 121.9, 121.7, 119.7, 67.8, 50.4. IR: $\nu(WO_2) = 961$s, 913s cm^{-1}. HRMS (LSI): *m/z* 465.0165 (calcd for $C_{13}H_{14}ClN_2O_3W$ (MH^+) based on ^{35}Cl and ^{184}W 465.0182). Anal. Calcd for $C_{13}H_{13}ClN_2O_3W$: C, 33.61; H, 2.82; N, 6.03. Found: C, 33.74; H, 2.88; N, 5.98.

$WO_2(L^3)Cl$. According to the general procedure, $WO_2Cl_2(DME)$ (2.11 g, 5.6 mmol) was treated with HL^3 (1.61 g, 5.6 mmol) and triethylamine (0.78 mL, 5.6 mmol) in THF (50 mL) to give $WO_2(L^3)Cl$ (1.38 g, 46%). ^1H NMR: δ 9.38 (dd, $J = 0.9$, 5.4 Hz, 1 H, ArH), 7.83 (dt, $J = 1.7$, 7.7 Hz, 1 H, ArH), 7.37−7.51 (m, 6 H, ArH), 7.21 (d, $J = 7.3$ Hz, 1 H, ArH), 7.05 (dt, $J = 1.4$, 7.7 Hz, 1 H, ArH), 6.71 (dd, $J = 1.3$, 8.3 Hz, 1 H, ArH), 6.57 (dt, $J = 1.4$, 7.7 Hz, 1 H, ArH), 6.36 (dd, $J = 1.4$, 8.2 Hz, 1 H, ArH), 5.32 (d, $J = 14.1$ Hz, 1 H, CH_2), 5.22 (d, $J = 14.4$ Hz, 1 H, CH_2), 4.99 (d, $J = 14.1$ Hz, CH_2), 4.63 (d, $J = 14.4$ Hz, 1 H, CH_2). $^{13}C\{^1H\}$ NMR: δ 158.8, 155.3, 151.3, 140.5, 136.0, 133.0, 132.5, 129.9, 129.4, 128.6, 125.9, 125.0, 123.4, 120.3, 119.6, 65.8, 63.6. IR: $\nu(WO_2) = 946$s, 915s cm^{-1}. HRMS (LSI): *m/z* 541.0542 (calcd for $C_{19}H_{18}ClN_2O_3W$ (MH^+) based on ^{35}Cl and ^{184}W 541.0495). Anal. Calcd for $C_{19}H_{17}ClN_2O_3W$: C, 42.21; H, 3.17; N, 5.18. Found: C, 42.45; H, 3.21; N, 5.01.

$WO_2(L^4)Cl$. This compound was prepared from $WO_2Cl_2(DME)$ (1.66 g, 4.4 mmol), HL^4 (1.52 g, 4.4 mmol), and triethylamine (0.62 mL, 4.4 mmol) in THF (50 mL) by using the general procedure (1.99 g, 76%). ^1H NMR: δ 9.36 (d, $J = 5.3$ Hz, 1 H, ArH), 7.83 (dt, $J = 1.4$, 7.7 Hz, 1 H, ArH), 7.43−7.48 (m, 3 H, ArH), 7.31 (d, $J = 8.2$ Hz, 2 H, ArH), 7.23 (d, $J = 7.7$ Hz, 1 H, ArH), 7.05 (dt, $J = 1.2$, 7.8 Hz, 1 H, ArH), 6.69 (dd, $J = 1.1$, 8.2 Hz, 1 H, ArH), 6.59 (dt, $J = 1.1$, 7.7 Hz, 1 H, ArH), 6.42 (dd, $J = 1.2$, 8.2 Hz, 1 H, ArH), 5.29 (d, $J = 14.1$ Hz, 1 H, CH_2), 5.20 (d, $J = 14.5$ Hz, 1 H, CH_2), 4.93 (d, $J = 14.1$ Hz, 1 H, CH_2), 4.64 (d, $J = 14.5$ Hz, 1 H, CH_2), 1.39 (s, 9 H, ^tBu). $^{13}C\{^1H\}$ NMR: δ 158.7, 155.4, 152.5, 151.2, 140.5, 136.3, 132.2, 129.9, 129.8, 126.0, 125.5, 125.0, 123.4, 120.3, 119.4, 65.4, 63.6, 34.7, 31.3. IR: $\nu(WO_2) = 961$s, 918s cm^{-1}. HRMS (LSI): *m/z* 597.1154 (calcd for $C_{23}H_{26}ClN_2O_3W$ (MH^+) based on ^{35}Cl and ^{184}W 597.1121). Anal. Calcd for $C_{23}H_{25}ClN_2O_3W$: C, 46.29; H, 4.22; N, 4.69. Found: C, 46.53; H, 4.19; N, 4.68.

$WO_2(L^5)Cl$. This compound was prepared from $WO_2Cl_2(DME)$ (2.00 g, 5.3 mmol), HL^5 (2.15 g, 5.3 mmol), and triethylamine (0.74 mL, 5.3 mmol) in THF (50 mL) by using the general procedure (2.01 g, 58%). ^1H NMR: δ 9.38 (d, $J = 4.8$ Hz, 1 H, ArH), 7.82 (dt, $J = 1.5$, 7.7 Hz, 1 H, ArH), 7.52 (t, $J = 1.8$ Hz, 1 H, ArH), 7.46 (t, $J = 6.5$ Hz, 1 H, ArH), 7.20 (d, $J = 7.8$ Hz, 1 H, ArH), 7.15 (d, $J = 1.8$ Hz, 2 H, ArH), 7.04 (dt, $J = 1.5$, 7.7 Hz, 1 H, ArH), 6.70 (dd, $J = 1.5$, 8.3 Hz, 1 H, ArH), 6.52 (dt, $J = 1.2$, 7.7 Hz, 1 H, ArH), 6.27 (dd, $J = 1.2$, 8.3 Hz, 1 H, ArH), 5.27 (d, $J = 13.8$ Hz, 1 H, CH_2), 5.19 (d, $J = 14.4$ Hz, 1 H, CH_2), 4.99 (d, $J = 13.8$ Hz, 1 H, CH_2), 4.56 (d, $J = 14.4$ Hz, 1 H, CH_2), 1.35 (s, 18 H, ^tBu). $^{13}C\{^1H\}$ NMR: δ 158.8, 155.4, 151.3, 151.0, 140.4, 135.9, 131.9, 129.8, 127.0, 126.3, 125.0, 123.4, 122.8, 120.0, 119.3, 66.6, 63.6, 34.8, 31.4. IR: $\nu(WO_2) = 957$s, 917s cm^{-1}. HRMS (LSI): *m/z* 653.1747 (calcd for $C_{27}H_{34}ClN_2O_3W$ (MH^+) based on ^{35}Cl and ^{184}W 653.1747). Anal. Calcd for $C_{27}H_{33}ClN_2O_3W$: C, 49.67; H, 5.09; N, 4.29. Found: C, 49.86; H, 5.05; N, 4.37.

Table 1. Crystallographic Data for $WO_2(L^1)(CH_2SiMe_3)$

formula	$C_{16}H_{22}N_2O_3SiW$
fw	502.3
cryst size (mm^3)	0.02 × 0.12 × 0.20
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a (Å)	11.800(1)
b (Å)	21.896(3)
c (Å)	7.768(2)
β (deg)	98.78(1)
V (Å^3)	1983.5(6)
Z	4
F(000)	976
D_{calcd} (g cm^{-3})	1.682
μ (mm^{-1})	5.897
total no. of reflns	6671
no. of indep reflns	3856 ($R_{int} = 0.0429$)
no. of params, p	236
R^a	0.0419
$R_w{}^b$	0.0911
S(GOF)^c	1.097
largest diff peak and hole (e Å^{-3})	+0.89 and −1.17

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{[\sum w(F_o{}^2 - F_c{}^2)^2]/[\sum w(F_o{}^2)^2]\}^{1/2}$. [c] $S = \{[\sum w(F_o{}^2 - F_c{}^2)^2]/(n - p)\}^{1/2}$; weighting scheme, $w = [\sigma^2(F_o{}^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

$WO_2(L^1)(CH_2SiMe_3)$. To an ice-cooled suspension of $WO_2(L^1)Cl$ (0.45 g, 1.0 mmol) in THF (30 mL) was added a solution of Me_3SiCH_2MgCl (3.0 mmol) in diethyl ether (20 mL) over a period of 30 min. The mixture was then allowed to warm to room temperature and stirred overnight. The volatiles were then 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 over anhydrous magnesium sulfate, then concentrated to ca. 5 mL to afford a pale brown solid, which was filtered off and washed thoroughly with chloroform and diethyl ether. The product was further purified by recrystallization using DMF/hexanes to yield pale yellow crystals (0.15 g, 30%). ^1H NMR (DMSO-d_6): δ 9.08 (d, $J = 5.2$ Hz, 1 H, ArH), 8.03 (d, $J = 4.4$ Hz, 1 H, ArH), 7.98 (dt, $J = 1.4$, 7.7 Hz, 1 H, ArH), 7.58 (t, $J = 6.4$ Hz, 1 H, ArH), 7.50 (d, $J = 7.8$ Hz, 1 H, ArH), 7.29 (d, $J = 7.1$ Hz, 1 H, ArH), 6.99 (t, $J = 7.7$ Hz, 1 H, ArH), 6.73 (t, $J = 7.2$ Hz, 1 H, ArH), 6.53 (d, $J = 8.0$ Hz, 1 H, ArH), 4.67 (dd, $J = 4.7$, 16.6 Hz, 1 H, $ArCH_2$), 4.56 (d, $J = 16.6$ Hz, 1 H, $ArCH_2$), 1.19 (d, $J = 12.4$ Hz, 1 H, WCH_2), 0.03 (s, 9 H, CH_3), −0.13 (d, $J = 12.4$ Hz, 1 H, WCH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 161.1, 157.1, 149.9, 140.1, 136.2, 128.9, 126.1, 124.9, 124.4, 119.4, 117.9, 58.6, 1.8. IR: $\nu(WO_2) = 951$s, 906s cm^{-1}. MS (LSI): a cluster peaking at *m/z* 503.10 (MH^+). Anal. Calcd for $C_{16}H_{22}N_2O_3SiW$: C, 38.26; H, 4.41; N, 5.58. Found: C, 38.11; H, 4.25; N, 5.39.

X-ray Crystallographic Analysis of $WO_2(L^1)(CH_2SiMe_3)$. Crystal data and data processing parameters are given in Table 1. Data collection was performed at 294 K on a MSC/Rigaku RAXIS IIc imaging-plate system using Mo Kα radiation ($\lambda = 0.71073$ Å) from a Rigaku RU-200 rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{min} = 3°$, $2\theta_{max} = 55°$, 30 6° oscillation frames in the range of 0−180°, exposure 10 min per frame).[19] A self-consistent semiempirical absorption

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[19] (a) Tanner, J.; Krause, K. *Rigaku J.* **1994**, *11*, 4. (b) Tanner, J.; Krause, K. *Rigaku J.* **1990**, *7*, 28. (c) Krause, K. L.; Phillips, G. N., Jr. *J. Appl. Crystallogr.* **1992**, *25*, 146. (d) Sato, M.; Yamamoto, M.; Imada, K.; Katsube, Y.; Tanaka, N.; Higashi, T. *J. Appl. Crystallogr.* **1992**, *25*, 348.

correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied by using the ABSCOR program.[20] The structure was solved by direct methods, which yielded the positions of all non-hydrogen atoms, which were refined anisotropically. The methyl groups were disordered with a site occupancy 0.5. Hydrogen atoms were placed in their idealized positions (C−H 0.96 Å) with fixed isotropic thermal parameters and allowed to ride on their parent carbon or nitrogen atoms. All the H atoms were held stationary and included in structure factor calculations in the final stage of full-matrix least-squares refinement. All computations were performed with a PC-486 computer using the SHELX-97 program package.[21] Further details are included in the Supporting Information.

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Supporting Information Available: Listings of non-hydrogen coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters for HL^3 and $WO_2(L^1)(CH_2SiMe_3)$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990464+

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(20) Higashi, T. *ABSCOR−An Empirical Absorption Correction Based on Fourier Coefficient Fitting*; Rigaku Corporation: Tokyo, 1995.

(21) Sheldrick, G. M. *SHELX-97: Package for Crystal Structure Solution and Refinement*; University of Gottingen: Germany, 1997.