DALTON
FULL PAPER

New organometallic dioxotungsten(VI) complexes containing N_2S tridentate ligands: the synthesis and reactivity of chloro and alkyl derivatives

Yee-Lok Wong and Jonathan R. Dilworth *

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, UK OX1 3QR. E-mail: jon.dilworth@chem.ox.ac.uk

Received 3rd October 2001, Accepted 11th April 2002
First published as an Advance Article on the web 1st May 2002

A new series of *N*-benzyl aliphatic N_2S tridentate proligands HL^n (n = 2–4) derived from 2-[(2-mercaptoethyl)-aminomethyl]pyridine (HL^1) has been prepared *via* the sequential reactions of trimethylsilylation, *N*-benzylation, and hydrolysis. A previously reported aromatic N_2S tridentate proligand, 2-[(2-mercaptophenyl)aminomethyl]-pyridine (HL^5), is also employed as an ancillary ligand. Reaction of these proligands HL^n (n = 1–5) 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). Treatment of the chloro derivatives $[WO_2(L^n)Cl]$ (n = 1, 5) with the Grignard reagents RMgX (R = CH_2SiMe_3, $C_6H_4{}^tBu$-4; X = Cl, Br) resulted in ligand substitution reaction and the formation of the first reported alkyl complexes of the type $[WO_2(L^n)R]$ (n = 1, 5; R = CH_2SiMe_3, $C_6H_4{}^tBu$-4).

Introduction

Applications of high-valent oxo-organometallic compounds as catalysts for various reactions such as ring-opening metathesis polymerisation (ROMP), epoxidation, and oxidation have received considerable attention.[1] Although some of these compounds have been widely used as catalysts in industrial processes, the exact nature and mechanism of the interaction between the catalyst and substrate have rarely been explored. In order to have a better understanding of their chemical behaviour, a substantial number of organometallic oxo-complexes have been synthesised and their chemistry investigated.[2] Alkoxy and phenoxy groups have most commonly been used as ancillary ligands.[3] Recently, calix[4]arenes containing pre-organized sets of alkoxy donor atoms have been employed to mimic metal oxide surfaces.[4] High-valent dioxotungsten complexes with hydrocarbon ligands have been reported sporadically. The most typical examples contain cyclopentadienyl ligands, *e.g.* $[WO_2(\eta^5\text{-}C_5R_5)Cl]$, $[\{WO_2(\eta^5\text{-}C_5R_5)\}_2O]$, and $[WO_2(\eta^5\text{-}C_5R_5)R']$ (R = H, Me; R′ = alkyl, alkynyl).[5] Apart from these, 2,2′-bipyridine (bipy) and hydridotris(3,5-dimethylpyrazolyl)borate $[HB(Me_2pz)_3]^-$ have also been used as co-ligands in complexes such as $[WO_2(bipy)R_2]$ (R = alkyl, phenyl) and $[WO_2HB(Me_2pz)_3R]$ (R = alkyl, phenyl, alkenyl).[6,7] However, examples of organometallic dioxotungsten complexes containing other types of supporting ligands are extremely rare.[8] Recently, a new series of N_2O-type ligands derived from 2-*N*-(2-pyridylmethyl)aminophenol [H(L–N_2O)] and its *N*-alkyl derivatives, which can stabilize the high-valent dioxotungsten complexes $[WO_2(L\text{–}N_2O)Cl]$ and $[WO_2(L\text{–}N_2O)(R)]$ (R = Me, Et, CH_2SiMe_3, $C_6H_4{}^tBu$-4) has been reported by Wong *et al.*[9] The molecular structure of the alkyl complex $[WO_2(L\text{–}N_2O)(CH_2SiMe_3)]$ has also been confirmed by X-ray diffraction analysis. In this paper, we describe the synthesis of a new series of dioxotungsten(VI) complexes containing new N_2S tridentate ligands which can be functionalised *via* *N*-benzylation.

Experimental

General procedures

All reactions were carried out using standard Schlenk-line techniques under an atmosphere of dinitrogen; workups were performed in air. Dichloromethane was pre-dried over 4 Å molecular sieves and distilled from calcium hydride. Diethyl ether, tetrahydrofuran (THF) and toluene were distilled from sodium–benzophenone. Methanol (MeOH) was distilled from magnesium methoxide. Silica gel (70–230 mesh) for flash column chromatography was purchased from Fluka. All other reagents and solvents were of reagent grade and used as received. $[WO_2Cl_2(DME)]$[10] (DME = 1,2-dimethoxyethane), 2-(2-mercaptoethyl)aminomethylpyridine[11] (HL^1), and 2-(2-mercaptophenyl)aminomethylpyridine[12] (HL^5) were prepared according to the literature procedures with minor modification. All ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Mercury VX300 spectrometer (^1H, 300; ^{13}C, 75.4 MHz). Chemical shifts were relative to internal $SiMe_4$ (δ = 0). IR spectra were recorded on a Perkin-Elmer 1710 spectrophotometer as KBr pellets. Atmospheric pressure chemical ionization (APCI) mass spectra were recorded on a Hewlett-Packard 1050 Series mass spectrometer. Liquid secondary ion (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 microanalysis laboratory of the Inorganic Chemistry Laboratory, University of Oxford, UK.

Preparations

2-(2-Mercaptoethyl)aminomethylpyridine (HL^1). A colourless mixture of 2-aminomethylpyridine (0.54 g, 5.0 mmol) and ethylene sulfide (0.30 g, 5.0 mmol) in toluene (5 cm^3) was heated in a sealed ampoule at 110 °C for 38 h. After cooling to room temperature, the pale yellow mixture was loaded onto a silica gel column, which was eluted with ethyl acetate first followed by ethyl acetate–ethanol (1 : 1). The third band was collected and concentrated with a rotary evaporator to give a colourless pungent liquid. Yield: 0.57 g (68%). ^1H NMR ($CDCl_3$): δ 8.56 (d, J = 4.8 Hz, 1 H, PyH), 7.65 (dd, J = 1.8, 7.8 Hz, 1 H, PyH), 7.32 (d, J = 7.5 Hz, 1 H, PyH), 7.17 (t, J = 6.2 Hz, 1 H, PyH), 3.93 (s, 2 H, $PyCH_2$), 2.87 (t, J = 6.2 Hz, 2 H, NCH_2CH_2), 2.70 (t, J = 6.2 Hz, 2 H, NCH_2CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.5, 149.2, 136.4, 122.1, 121.9, 54.6, 51.9, 24.9. MS (APCI): m/z 169 (80%) $[M + H]^+$.

 DOI: 10.1039/b108994n

General procedure for the preparation of HL^n (n = 2–4). To a colourless mixture of HL^1 and triethylamine (1 equiv.) in THF was added chlorotrimethylsilane (1 equiv.) dropwise at 0 °C. A white solid began to form during the addition. The mixture was stirred at this temperature for 1 h, allowed to warm to ambient temperature and stirred for a further 12 h. A second portion of triethylamine (1 equiv.) and the appropriate substituted benzyl bromide (1 equiv.) in THF were added. After heating under reflux for 18 h, the resulting white solid was filtered off and discarded. The pale yellow filtrate was concentrated using a rotary evaporator and the residue was chromatographed on a silica gel column using CH_2Cl_2 followed by ethyl acetate as eluent. The second band was collected and concentrated to give a colourless liquid.

2-[N-Benzyl-N-(2-mercaptoethyl)]aminomethylpyridine (HL^2). According to the general procedure, HL^1 (0.57 g, 3.4 mmol) was stirred with triethylamine (0.47 cm^3, 3.4 mmol) and chlorotrimethylsilane (0.37 g, 3.4 mmol) in THF (40 cm^3) for 12 h. Then a second portion of triethylamine (0.47 cm^3, 3.4 mmol) and benzyl bromide (0.58 g, 3.4 mmol) were added, and the mixture was heated under reflux for 18 h to give HL^2 (0.48 g, 55%). ^{1}H NMR ($CDCl_3$): δ 8.51 (d, J = 4.2 Hz, 1 H, PyH), 7.66 (dt, J = 1.8, 7.7 Hz, 1 H, PyH), 7.55 (d, J = 8.1 Hz, 1 H, PyH), 7.22–7.40 (m, 5 H, ArH), 7.15 (t, J = 5.9 Hz, 1 H, PyH), 3.78 (s, 2 H, $PyCH_2$), 3.67 (s, 2 H, $ArCH_2$), 2.73–2.77 (m, 2 H, NCH_2CH_2), 2.61–2.68 (m, 2 H, NCH_2CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.6, 148.8, 138.8, 136.3, 128.8, 128.2, 127.0, 122.9, 121.9, 59.9, 58.5, 56.7, 22.4. MS (APCI): m/z 259 (15%) [M + H]$^+$.

2-[N-(4-tert-Butylbenzyl)-N-(2-mercaptoethyl)]aminomethylpyridine (HL^3). According to the general procedure, HL^1 (1.23 g, 7.3 mmol) was stirred with triethylamine (1.0 cm^3, 7.3 mmol) and chlorotrimethylsilane (0.92 g, 7.3 mmol) in THF (60 cm^3) for 12 h. Then a second portion of triethylamine (1.0 cm^3, 7.3 mmol) and 4-*tert*-butylbenzyl bromide (1.66 g, 7.3 mmol) were added, and the mixture was heated under reflux for 18 h to give HL^3 (0.69 g, 30%). ^{1}H NMR ($CDCl_3$): δ 8.51 (d, J = 4.2 Hz, 1 H, PyH), 7.67 (dt, J = 1.8, 7.7 Hz, 1 H, PyH), 7.57 (d, J = 7.5 Hz, 1 H, PyH), 7.29–7.36 (m, 4 H, ArH), 7.15 (t, J = 6.2 Hz, 1 H, PyH), 3.77 (s, 2 H, $PyCH_2$), 3.64 (s, 2 H, $ArCH_2$), 2.63–2.78 (m, 4 H, NCH_2CH_2), 1.31 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.7, 149.9, 148.7, 136.4, 135.5, 128.4, 125.1, 122.9, 121.9, 59.8, 58.0, 56.6, 34.4, 31.3, 22.4. MS (APCI): m/z 315 (20%) [M + H]$^+$.

2-[N-(3,5-Di-tert-butylbenzyl)-N-(2-mercaptoethyl)]aminomethylpyridine (HL^4). According to the general procedure, HL^1 (0.82 g, 4.9 mmol) was stirred with triethylamine (0.68 cm^3, 4.9 mmol) and chlorotrimethylsilane (0.54 g, 4.9 mmol) in THF (60 cm^3) for 12 h. Then a second portion of triethylamine (0.68 cm^3, 4.9 mmol) and 3,5-di-*tert*-butylbenzyl bromide (1.39 g, 4.9 mmol) were added, and the mixture was heated under reflux for 18 h to give HL^4 (0.58 g, 32%). ^{1}H NMR ($CDCl_3$): δ 8.50 (d, J = 4.5 Hz, 1 H, PyH), 7.65 (dt, J = 1.8, 7.7 Hz, 1 H, PyH), 7.58 (d, J = 7.5 Hz, 1 H, PyH), 7.22–7.29 (m, 3 H, ArH), 7.14 (t, J = 5.3 Hz, 1 H, PyH), 3.77 (s, 2 H, $PyCH_2$), 3.67 (s, 2 H, $ArCH_2$), 2.67–2.81 (m, 4 H, NCH_2CH_2), 1.32 (s, 18 H, ^{t}Bu). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.8, 150.5, 148.7, 137.8, 136.4, 136.2, 123.0, 122.9, 121.9, 120.9, 59.9, 59.1, 56.8, 34.7, 31.5, 22.6. MS (APCI): m/z 371 (25%) [M + H]$^+$.

General procedure for the preparation of [WO$_2$(L^n)Cl] (n = 1, 5). Triethylamine (1 equiv.) was added to a colourless solution of HL^n (n = 1, 5) in MeOH. After stirring at room temperature for 15 min, the mixture was then transferred to a solution of [WO_2Cl_2(DME)] (1 equiv.) in CH_2Cl_2 *via* a cannula. This colourless mixture turned yellow immediately and stirring was continued overnight. Due to the poor solubility of [WO$_2$(L^n)Cl] (n = 1, 5), the resulting solid was collected by filtration, washed with MeOH, ethyl acetate and hexanes, and dried *in vacuo*.

[WO$_2$(L^1)Cl]. According to the general procedure, [WO_2Cl_2(DME)] (3.32 g, 8.8 mmol) in CH_2Cl_2 (20 cm^3) was treated with HL^1 (1.48 g, 8.8 mmol) and triethylamine (1.2 cm^3, 8.8 mmol) in MeOH (30 cm^3) to give [WO$_2$(L^1)Cl] (1.14 g, 31%) as a yellow solid. IR (cm^{-1}): 3135m, 2925w, 1607m, 1484w, 1440m, 1340w, 1290m, 1227w, 1157w, 1106w, 1076w, 1025w, 943s ν(WO$_2$), 893s ν(WO$_2$), 819m, 773s, 731m, 645w, 425m. Anal. calc. for $C_8H_{11}ClN_2O_2SW$: C, 23.0; H, 2.7; N, 6.7%. Found: C, 22.6; H, 2.9; N, 6.5%.

[WO$_2$(L^5)Cl]. According to the general procedure, [WO_2Cl_2(DME)] (1.70 g, 4.5 mmol) in CH_2Cl_2 (20 cm^3) was treated with HL^5 (0.97 g, 4.5 mmol) and triethylamine (0.62 cm^3, 4.5 mmol) in MeOH (30 cm^3) to give [WO$_2$(L^5)Cl] (0.94 g, 45%) as a grey solid. IR (cm^{-1}): 3055w, 1708w, 1608m, 1585m, 1475m, 1439m, 1297m, 1249w, 1158w, 1083m, 1046m, 997w, 945s ν(WO$_2$), 905s ν(WO$_2$), 814m, 755s, 729m, 681w, 651w. Satisfactory analytical data for this compound could not be obtained.

General procedure for the preparation of [WO$_2$(L^n)Cl] (n = 2–4). A solution of [WO_2Cl_2(DME)] in THF was added dropwise to a solution of HL^n (n = 2–4, 1 equiv.) in THF with vigorous stirring. The pale yellow mixture turned dark purple immediately. This 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 loaded onto a silica gel column, which was then eluted with ethyl acetate. The yellow band was collected and concentrated to give a pale yellow solid.

[WO$_2$(L^2)Cl]. According to the general procedure, [WO_2Cl_2(DME)] (0.60 g, 1.6 mmol) was treated with HL^2 (0.41 g, 1.6 mmol) and triethylamine (0.22 cm^3, 1.6 mmol) in THF (50 cm^3) to give [WO$_2$(L^2)Cl] (0.39 g, 48%). ^{1}H NMR (DMSO-d_6): δ 9.23 (d, J = 4.5 Hz, 1 H, PyH), 8.13 (dt, J = 1.8, 7.8 Hz, 1 H, PyH), 7.60–7.69 (m, 4 H, PyH and ArH), 7.46–7.48 (m, 3 H, PyH and ArH), 4.89 (d, J = 14.1 Hz, 1 H, $ArCH_2$), 4.77 (d, J = 15.3 Hz, 1 H, $ArCH_2$), 4.68 (d, J = 14.1 Hz, 1 H, $ArCH_2$), 4.04 (d, J = 15.3 Hz, 1 H, $ArCH_2$), 3.85–3.89 (m, 1 H, NCH_2CH_2), 3.56–3.62 (m, 1 H, NCH_2CH_2), 3.18–3.22 (m, 1 H, NCH_2CH_2), 2.26–2.33 (m, 1 H, NCH_2CH_2). ^{13}C{^{1}H} NMR: δ 155.5, 150.4, 141.1, 132.5, 132.2, 129.1, 128.8, 125.6, 125.0, 62.3, 61.7, 61.4, 30.2. IR (cm^{-1}): 3032w, 2930w, 1608m, 1485w, 1440m, 1421m, 1366w, 1308w, 1294m, 1204w, 1160w, 1047m, 1028m, 951s ν(WO$_2$), 905s ν(WO$_2$), 847w, 783m, 764m, 751m, 723w, 697m, 604w, 546w. HRMS (LSI): m/z calc. for $C_{15}H_{18}ClN_2O_2SW$ [M + H]$^+$ 509.0287, found 509.0262. Anal. calc. for $C_{15}H_{17}ClN_2O_2SW$: C, 35.4; H, 3.4; N, 5.5%. Found: C, 36.0; H, 3.9; N, 5.3%.

[WO$_2$(L^3)Cl]. According to the general procedure, [WO_2Cl_2(DME)] (0.83 g, 2.2 mmol) was treated with HL^3 (0.69 g, 2.2 mmol) and triethylamine (0.30 cm^3, 2.2 mmol) in THF (60 cm^3) to give [WO$_2$(L^3)Cl] (0.25 g, 20%). ^{1}H NMR ($CDCl_3$): δ 9.46 (d, J = 5.1 Hz, 1 H, PyH), 7.95 (dt, J = 1.8, 7.8 Hz, 1 H, PyH), 7.53 (t, J = 6.5 Hz, 1 H, PyH), 7.48 (d, J = 8.7 Hz, 2 H, ArH), 7.33–7.36 (m, 3 H, PyH and ArH), 4.93 (s, 2 H, $ArCH_2$), 4.89 (d, J = 15.0 Hz, 1 H, $PyCH_2$), 4.07–4.14 (m, 1 H, NCH_2CH_2), 3.86 (d, J = 15.0 Hz, 1 H, $PyCH_2$), 3.62–3.70 (m, 1 H, NCH_2CH_2), 3.30–3.35 (m, 1 H, NCH_2CH_2), 2.31–2.41 (m, 1 H, NCH_2CH_2), 1.37 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.8, 152.3, 151.3, 140.1, 131.7, 128.7, 125.8, 125.1, 123.8, 62.9, 61.6, 61.1, 34.7, 31.2, 30.8. IR (cm^{-1}): 2960m, 2869m, 1655w, 1609m, 1476m, 1445m, 1365m, 1297m, 1270w, 1218w, 1158w, 1109w, 1077w, 1051w, 1027m, 953s ν(WO$_2$), 910s ν(WO$_2$), 833m, 815w, 777m, 763w, 726w, 689w, 587w, 557w. HRMS (LSI): m/z calc. for $C_{19}H_{26}ClN_2O_2SW$ [M + H]$^+$ 565.0913, found 565.0889. Anal. calc. for $C_{19}H_{25}ClN_2O_2SW$: C, 40.4; H, 4.5; N, 5.0%. Found: C, 41.0; H, 4.7; N, 4.7%.

[WO$_2$(L^4)Cl]. According to the general procedure, [WO_2Cl_2(DME)] (0.60 g, 1.6 mmol) was treated with HL^4 (0.59 g, 1.6 mmol) and triethylamine (0.22 cm^3, 1.6 mmol) in THF (60 cm^3) to give [WO$_2$(L^4)Cl] (0.46 g, 46%). ^{1}H NMR ($CDCl_3$):

δ 9.48 (d, J = 5.4 Hz, 1 H, PyH), 7.94 (dt, J = 1.2, 7.8 Hz, 1 H, PyH), 7.50–7.56 (m, 2 H, PyH and ArH), 7.32 (d, J = 8.1 Hz, 1 H, PyH), 7.19 (d, J = 1.8 Hz, 2 H, ArH), 4.95 (s, 2 H, $ArCH_2$), 4.90 (d, J = 15.3 Hz, 1 H, $PyCH_2$), 4.04–4.08 (m, 1 H, NCH_2CH_2), 3.83 (d, J = 15.3 Hz, 1 H, $PyCH_2$), 3.64–3.71 (m, 1 H, NCH_2CH_2), 3.27–3.32 (m, 1 H, NCH_2CH_2), 2.32–2.40 (m, 1 H, NCH_2CH_2), 1.37 (s, 18, ^{t}Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.7, 151.4, 151.3, 140.1, 130.8, 126.2, 125.2, 123.7, 123.0, 62.8, 61.1 (one peak overlapping), 34.8, 31.4, 30.7. IR (cm^{-1}): 2962s, 2867m, 1609m, 1477m, 1459m, 1445m, 1363m, 1298m, 1249m, 1201m, 1158w, 1081w, 1053w, 1027w, 953s $\nu(WO_2)$, 911s $\nu(WO_2)$, 877w, 841w, 776m, 763m, 728m, 702w, 647w, 553w. HRMS (LSI): m/z calc. for $C_{23}H_{34}ClN_2O_2SW$ $[M + H]^+$ 621.1539, found 621.1602. Anal. calc. for $C_{23}H_{33}ClN_2O_2SW$: C, 44.5; H, 5.4; N, 4.5%. Found: C, 44.7; H, 5.4; N, 4.4%.

General procedure for the preparation of $[WO_2(L^n)(R)]$ (n = 1, 5; R = CH_2SiMe_3, $C_6H_4{}^tBu$-4). To an ice-cooled suspension of $[WO_2(L^n)Cl]$ (n = 1, 5) in THF was added a solution of Grignard reagent (3 equiv.) in diethyl ether over a period of 30 min. The mixture turned to dark brown during addition. The mixture was allowed to warm to room temperature and stirred overnight. The volatiles were then removed under reduced pressure, and water was added. The mixture was extracted with CH_2Cl_2 (3 × 80 cm^3) with vigorous shaking until a yellowish brown solution was achieved. The combined organic extracts were dried over anhydrous magnesium sulfate, then concentrated to *ca.* 2 cm^3 to afford a pale brown solid, which was collected by filtration and washed thoroughly with ethyl acetate–hexanes (1 : 1), and dried *in vacuo*.

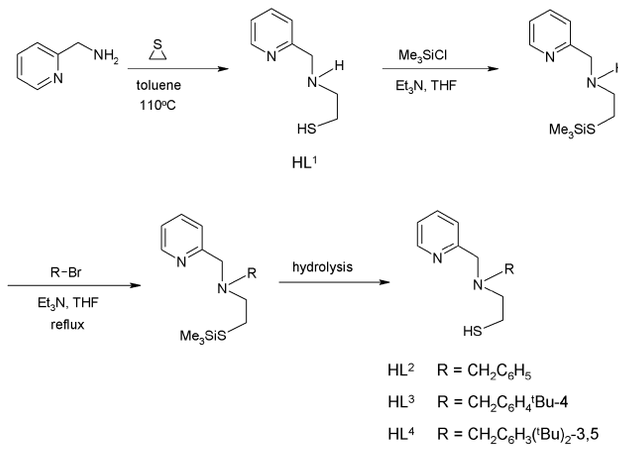
$[WO_2(L^1)(CH_2SiMe_3)]$. According to the general procedure, $[WO_2(L^1)Cl]$ (0.42 g, 1.0 mmol) in THF (30 cm^3) was treated with Me_3SiCH_2MgCl (3.0 mmol) in diethyl ether (20 cm^3) to give $[WO_2(L^1)(CH_2SiMe_3)]$ (85 mg, 18%). ^{1}H NMR (DMSO-d_6): δ 8.97 (d, J = 5.1 Hz, 1 H, PyH), 7.99 (t, J = 7.7 Hz, 1 H, PyH), 7.47–7.54 (m, 3 H, PyH and NH), 4.41–4.50 (m, 1 H, $PyCH_2$), 4.11 (d, J = 17.7 Hz, 1 H, $PyCH_2$), 3.48–3.52 (m, 1 H, NCH_2CH_2), (two aliphatic proton signals obscured by the residual solvent peaks), 1.91–2.00 (m, 1 H, NCH_2CH_2), 1.20 (d, J = 12.9 Hz, 1 H, WCH_2), −0.01 (s, 9 H, CH_3), −0.36 (d, J = 12.9 Hz, 1 H, WCH_2). IR (cm^{-1}): 2946w, 1607m, 1438m, 1291w, 1241m, 1158w, 1055w, 1025w, 945s $\nu(WO_2)$, 904s $\nu(WO_2)$, 850s, 832s, 761m, 713w, 682w, 499w. HRMS (LSI): m/z calc. for $C_{12}H_{23}N_2O_2SSiW$ $[M + H]^+$ 471.0759, found 471.0720. Anal. calc. for $C_{12}H_{22}N_2O_2SSiW$: C, 30.7; H, 4.7; N, 6.0%. Found: C, 31.1; H, 3.9; N, 6.6%.

$[WO_2(L^5)(CH_2SiMe_3)]$. According to the general procedure, $[WO_2(L^5)Cl]$ (0.47 g, 1.0 mmol) in THF (30 cm^3) was treated with Me_3SiCH_2MgCl (3.0 mmol) in diethyl ether (20 cm^3) to give $[WO_2(L^5)(CH_2SiMe_3]$ (0.14 g, 28%). ^{1}H NMR (DMSO-d_6): δ 9.09 (d, J = 5.4 Hz, 1 H, ArH), 8.28 (d, J = 6.6 Hz, 1 H, ArH), 7.99 (t, J = 7.5 Hz, 1 H, ArH), 7.58 (t, J = 6.5 Hz, 1 H, ArH), 7.49 (d, J = 7.8 Hz, 1 H, ArH), 7.30 (t, J = 4.2 Hz, 1 H, ArH), 7.00–7.03 (m, 3 H, ArH and NH), 4.84–4.92 (m, 1 H, $PyCH_2$), 4.40 (d, J = 17.7 Hz, 1 H, $PyCH_2$), 1.37 (d, J = 12.3 Hz, 1 H, WCH_2), 1.13 (d, J = 12.3 Hz, 1 H, WCH_2), 0.04 (s, 9 H, CH_3). IR (cm^{-1}): 3433w, 3067w, 2950w, 2894w, 1608m, 1481m, 1443m, 1363w, 1297w, 1281w, 1244m, 1185w, 1157w, 1132w, 1105w, 1025w, 995w, 948s $\nu(WO_2)$, 897s $\nu(WO_2)$, 852s, 832m, 757m, 728w, 713w, 683w, 649w. HRMS (LSI): m/z calc. for $C_{16}H_{23}N_2O_2SSiW$ $[M + H]^+$ 518.0681, found 518.0461. Anal. calc. for $C_{16}H_{22}N_2O_2SSiW$: C, 37.1; H, 4.3; N, 5.4%. Found: C, 36.8; H, 5.1; N, 5.2%.

$[WO_2(L^5)(C_6H_4{}^tBu$-4$)]$. According to the general procedure, $[WO_2(L^5)Cl]$ (0.47 g, 1.0 mmol) in THF (30 cm^3) was treated with 4-$^tBuC_6H_4MgBr$ (3.0 mmol) in diethyl ether (20 cm^3) to give $[WO_2(L^5)(C_6H_4{}^tBu$-4$)]$ (0.12 g, 22%). ^{1}H NMR (DMSO-d_6): δ 9.35 (d, J = 5.1 Hz, 1 H, ArH), 8.18 (d, J = 6.6 Hz, 1 H, ArH), 8.00 (t, J = 5.9 Hz, 1 H, ArH), 7.71 (t, J = 5.9 Hz, 1 H, ArH), 7.60 (d, J = 7.8 Hz, 2 H, ArH), 7.37–7.44 (m, 2 H, ArH), 7.15 (d, J = 7.8 Hz, 2 H, ArH), 7.04–7.10 (m, 3 H, ArH and NH), 4.41 (d, J = 16.2 Hz, 1 H, $PyCH_2$), 3.87–3.93 (m, 1 H, $PyCH_2$), 1.18 (s, 9 H, ^{t}Bu). IR (cm^{-1}): 3386m, 3110w, 2966w, 1610m, 1491s, 1284s, 1058w, 1025w, 949s $\nu(WO_2)$, 900s $\nu(WO_2)$, 867m, 820w, 780m, 752m, 635m, 562w. HRMS (LSI): m/z calc. for $C_{22}H_{25}N_2O_2SW$ $[M + H]^+$ 565.1146, found 565.0991. Anal. calc. for $C_{22}H_{24}N_2O_2SW$: C, 46.8; H, 4.3; N, 5.0%. Found: C, 46.7; H, 3.8; N, 4.6%.

Results and discussion

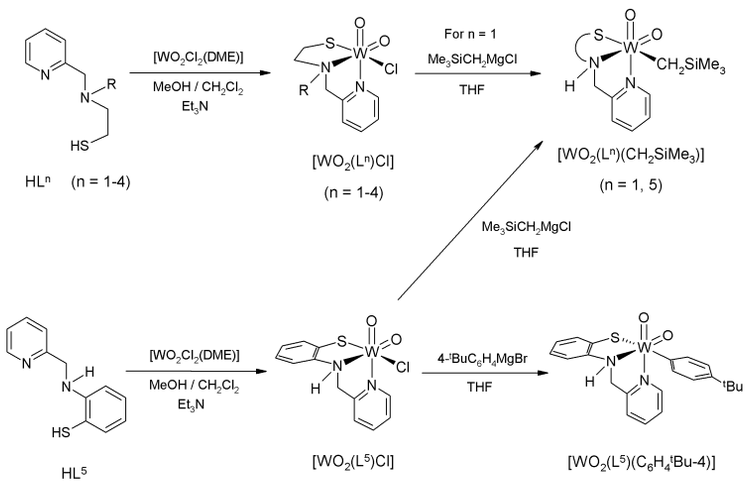
A new series of aliphatic N_2S tridentate proligands HL^n (n = 2–4), derived from the previous reported 2-[(2-mercaptoethyl)-aminomethyl]pyridine (HL^1), were synthesised by a reaction involving four steps, two of which were performed *in situ* (Scheme 1). The first step was based on the literature procedure



Scheme 1

with minor modifications.[11] Reaction of 2-aminomethylpyridine with 1 equivalent of ethylene sulfide gave 2-[(2-mercaptoethyl)-aminomethyl]pyridine (HL^1) in 68% yield. This compound was purified by flash column chromatography rather than vacuum distillation in order to prevent the possibility of regenerating the starting materials by decomposition during prolonged heating. Treatment of HL^1 with chlorotrimethylsilane in the presence of triethylamine gave the silyl thioether adduct which was then *N*-alkylated with a variety of benzyl bromides to afford the silyl-protected N_2S proligands. Hydrolysis of these potential ligands during workup and purifying procedures led to the formation of a new series of N_2S tridentate proligands HL^n (n = 2–4) in 30–55% yield. Although silyl reagents have been conventionally used as protecting groups for alcohols and amines, they are seldom used for thiol protection, mainly due to the instability of the silyl thioether type compounds in protic media.[13] By employing this synthetic scheme with the silyl reagent, we were able to introduce a wide range of substituents on the nitrogen donor atom having different steric and electronic requirements with the goal of studying their effects on complex formation and properties of the resulting complexes. The versatility of this synthetic route using silyl reagents has been further explored through the preparation of a new class of asymmetric N_2OS tripodal ligands.[14] Apart from the aliphatic analogues, the previously reported aromatic N_2S tridentate proligand 2-[(2-mercaptophenyl)aminomethyl]pyridine[12] (HL^5) has also been investigated as a comparison to the aliphatic analogues. All these tridentate proligands HL^n (n = 1–5) were found to be rather unstable, and the colourless oily liquids darkened gradually upon exposure to air over 1–2 days. The proligands were therefore freshly prepared and stored under dinitrogen.

In the preparation of the dioxo complexes, $[WO_2Cl_2(DME)]$[10] was employed as the starting material. The versatility of this



Scheme 2

DME adduct as a precursor to a number of *cis*-dioxotungsten(VI) complexes has been recently reported by Wong and co-workers.[9,15] Treatment of the proligands HL^n (n = 1–5) with $[WO_2Cl_2(DME)]$ in the presence of triethylamine gave the corresponding dioxo compounds $[WO_2(L^n)Cl]$ (n = 1–5) (Scheme 2) in moderate yield. Due to the poor solubility of $[WO_2(L^n)Cl]$ (n = 1, 5) in common organic solvents, these compounds were isolated by filtration and could only be purified by washing thoroughly with various solvents, thus no solution characterisation data could be obtained. By contrast, the dioxo complexes $[WO_2(L^n)Cl]$ (n = 2–4) containing various benzyl groups possess sufficient solubility to be purified by column chromatography and have been characterized with a wide range spectroscopic methods. The ^{1}H NMR spectra of these chloro compounds $[WO_2(L^n)Cl]$ (n = 2–4) show two doublets at δ 3.81–4.92 which are assignable to the two diastereotopic methylene protons adjacent to the pyridine ring. Similarly to the dioxotungsten(VI) analogues with N_2O ancillary ligands,[9] these high-valent dioxo compounds are stable to air, however they are slightly sensitive to moisture. Some unidentified peaks appeared in the ^{1}H NMR spectra after prolonged dissolution of these compounds in undried solvent, showing that these dioxo compounds decomposed in the presence of moisture.

Treatment of $[WO_2(L^n)Cl]$ (n = 1, 5) with an excess of a Grignard reagent RMgX (R = CH_2SiMe_3, $C_6H_4{}^tBu$-4; X = Cl, Br) resulted in a chloride ligand substitution reaction and the formation of $[WO_2(L^n)(R)]$ (n = 1, 5; R = CH_2SiMe_3, $C_6H_4{}^tBu$-4) in 18–28% yield (Scheme 2). Numerous attempts were made to improve the yield by modifying the reaction conditions without success. These high-valent alkyl and aryl tungsten complexes are stable to oxygen; but they are sensitive to moisture to different extents. Those containing a CH_2SiMe_3 group are more stable than the one with $C_6H_4{}^tBu$-4. These complexes are completely insoluble in hydrocarbons and ether; and showed only limited solubility in chlorinated solvents, but are soluble in dipolar aprotic solvents such as *N*,*N*-dimethylformamide (DMF) or dimethylsulfoxide (DMSO). Similarly to $[WO_2(L–N_2O)(CH_2SiMe_3)]$ [L–N_2O = 2-*N*-(2-pyridylmethyl)aminophenolato],[9] the ^{1}H NMR spectrum of $[WO_2(L^5)(CH_2SiMe_3)]$ in DMSO-d_6 showed two upfield doublets at δ 1.37 and 1.13 with a geminal coupling constant of 12.3 Hz, which could be attributed to the two diastereotopic methylene protons next to tungsten. Moreover, no satellite resonances due to ^{183}W and ^{29}Si nuclei were observed probably due to relatively poor solubility. The complexes decomposed over the period required to acquire ^{13}C NMR spectra. Attempts to prepare other alkyl or aryl dioxo complexes by treating $[WO_2(L^n)Cl]$ (n = 1, 2, 5) with RMgCl (R = Me, Et, *i*-Pr, CH_2Ph, mesityl) were not successful. Free proligands were regenerated after the workup procedure, suggesting that the compounds underwent decomposition. The stability of the organometallic compounds is significantly enhanced by increasing the steric bulk of the alkyl or aryl group. An absence of β-hydrogens may also improve stability.

The reactivity of the chloro functionality in these complexes towards other anions has also been examined. Treatment of the compounds $[WO_2(L^n)Cl]$ (n = 1, 2, 5) with NaXR (X = O, S, Se; R = Me, Et, Ph) in the presence of 18-crown-6 (cat.) in toluene under reflux conditions caused complete decomplexation. This is in contrast with the behaviour of $[WO_2HB(Me_2pz)_3Cl]$, which can be converted to various –OR, –SR, and –SeR derivatives by displacement of the chloro ligand.[16]

The IR spectra of these dioxo compounds show two characteristic vibrational bands in the regions 893–911 and 943–953 cm^{-1} which were assignable to the asymmetric and symmetric W=O stretches respectively.[17] The liquid secondary ion (LSI) mass spectra of all these compounds exhibited the corresponding protonated molecular ion $[M + H]^+$ which was in good agreement with a predicted accurate mass and isotopic distribution pattern. Despite strenuous efforts we were unable to obtain crystals of any of the dioxo complexes suitable for X-ray structure determination.

In conclusion, a new series of chloro dioxotungsten(VI) complexes of general type $[WO_2(L^n)Cl]$ (n = 1–5) have been prepared from the reaction of $[WO_2Cl_2(DME)]$ with the N_2S tridentate ligands (HL^n) (n = 1–5) in the presence of triethylamine. Reaction of $[WO_2(L^n)Cl]$ (n = 1, 5) with an excess of the Grignard reagent RMgX (R = CH_2SiMe_3, $C_6H_4{}^tBu$-4; X = Cl, Br) gave the alkyl or aryl compounds $[WO_2(L^n)(R)]$. To our knowledge, these compounds are the first example of organometallic dioxotungsten(VI) complexes with N_2S ancillary ligands. The chloro derivatives show similar stability to air and moisture to the tungsten N_2O analogues, while the alkyl or aryl compounds $[WO_2(L^n)(R)]$ (n = 1, 5; R = CH_2SiMe_3, $C_6H_4{}^tBu$-4) are relatively less stable than their counterparts with N_2O ligands. Although all these high-valent alkyl or aryl dioxotungsten complexes $[WO_2(L^n)(R)]$ are stable to oxygen; they are sensitive to moisture to different extents [CH_2SiMe_3 > $C_6H_4{}^tBu$-4 (less stable)]. The degree of sensitivity may reflect the difference in steric bulk of the organometallic ligands.

Acknowledgements

We thank Prof. Hung Kay Lee of the Chinese University of Hong Kong for recording the HRMS (LSI) spectra and the Croucher Foundation for financial support (Dr. Yee-Lok Wong).

References

1 R. A. Sheldon and J. K. Kochi, *Metal-catalyzed Oxidation of Organic Compounds*, Academic Press, New York, 1981; F. J. de la Mata and R. H. Grubbs, *Organometallics*, 1996, **15**, 577; M. B. O'Donoghue, R. R. Schrock, A. M. LaPointe and W. M. Davis, *Organometallic*, 1996, **15**, 1334; K. J. Ivin and J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, 1997; Y. Nakayama, N. Ikushima and A. Nakamura, *Chem. Lett.*, 1997, 861; J.-Y. Piquemal, S. Halut and J.-M. Brégeault, *Angew. Chem., Int. Ed.*, 1998, **37**, 1146 and references therein; Y. Nakayama, N. Ikushima, N. Ueyama, A. Nakamura and A. Harada, *Chem. Lett.*, 2000, 434.

2 F. Bottomley and L. Sutin, *Adv. Organomet. Chem.*, 1988, **28**, 339.

3 W. Kläui, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 627; M. H. Chisholm, *Chemtracts: Inorg. Chem.*, 1992, **4**, 273; M. Pohl, D. K. Lyon, N. Mizuno, K. Nomiya and R. G. Finke, *Inorg. Chem.*, 1995, **34**, 1413; F. J. Feher and T. A. Budzichowski, *Polyhedron*, 1995, **14**, 3239; T. Nagata, M. Pohl, H. Weiner and R. G. Finke, *Inorg. Chem.*, 1997, **36**, 1366.

4 L. Giannini, S. Dovesi, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Angew. Chem., Int. Ed.*, 1999, **38**, 807 and references therein; L. Giannini, G. Guillemot, E. Solari, C. Floriant, N. Re, A. Chiesi-Villia and C. Rizzoli, *J. Am. Chem. Soc.*, 1999, **121**, 2797 and references therein.

5 P. Legzdins, S. J. Rettig and L. Sánchez, *Organometallics*, 1985, **4**, 1470; J. W. Faller and Y. Ma, *J. Organomet. Chem.*, 1988, **340**, 59; J. W. Faller and Y. Ma, *Organometallics*, 1988, **7**, 559; P. Legzdins, E. C. Phillips and L. Sánchez, *Organometallics*, 1989, **8**, 940; C.-W. Shiu, C.-J. Su, C.-W. Pin, Y. Chi, S.-M. Peng and G.-H. Lee, *J. Organomet. Chem.*, 1997, **545–546**, 151.

6 C. Zhang, E. O. Schlemper and G. N. Schrauzer, *Organometallics*, 1990, **9**, 1016; C. Zhang, X. Zhang, N. H. Liu, G. N. Schrauzer and E. O. Schlemper, *Organometallics*, 1990, **9**, 1307.

7 A. A. Eagle, E. R. T. Tiekink and C. G. Young, *J. Chem. Soc., Chem. Commun.*, 1991, 1746; A. A. Eagle, C. G. Young and E. R. T. Tiekink, *Organometallics*, 1992, **11**, 2934; J. Sundermeyer, J. Putterlik and H. Pritzkow, *Chem. Ber.*, 1993, **126**, 289; W. Adam, J. Putterlik, R. M. Schuhmann and J. Sundermeyer, *Organometallics*, 1996, **15**, 4586.

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

9 Y.-L. Wong, J.-F. Ma, F. Xue, T. C. W. Mak and D. K. P. Ng, *Organometallics*, 1999, **18**, 5057; Y.-L. Wong, D. K. P. Ng and H. K. Lee, submitted.

10 K. Dreisch, C. Andersson and C. Stålhandske, *Polyhedron*, 1991, **10**, 2417.

11 U. Brand and H. Vahrenkamp, *Inorg. Chem.*, 1995, **34**, 3285.

12 J. L. Corbin and D. E. Work, *Can. J. Chem.*, 1974, **52**, 1054.

13 T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, Wiley, New York, 2nd edn., 1991.

14 Y.-L. Wong, A. C. Cowley and J. R. Dilworth, unpublished work.

15 Y.-L. Wong, Y. Yan, E. S. H. Chan, Q. Yang, T. C. W. Mak and D. K. P. Ng, *J. Chem. Soc., Dalton Trans.*, 1998, 3057; Y.-L. Wong, J.-F. Ma, W.-F. Law, Y. Yan, W.-T. Wong, Z.-Y. Zhang, T. C. W. Mak and D. K. P. Ng, *Eur. J. Inorg. Chem.*, 1999, 313; H. K. Lee, Y.-L. Wong, Z.-Y. Zhou, Z.-Y. Zhang, D. K. P. Ng and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 2000, 539; Y.-L. Wong, Q. Yang, Z.-Y. Zhou, H. K. Lee, T. C. W. Mak and D. K. P. Ng, *New J. Chem.*, 2001, **25**, 353.

16 A. A. Eagle, E. R. T. Tiekink and C. G. Young, *Inorg. Chem.*, 1997, **36**, 6315.

17 S.-B. Yu and R. H. Holm, *Inorg. Chem.*, 1989, **28**, 4385; S. Lee, D. L. Staley, A. L. Rheingold and N. J. Cooper, *Inorg. Chem.*, 1990, **29**, 4391; H. Oku, N. Ueyama and A. Nakamura, *Inorg. Chem.*, 1995, **34**, 3667.