

Synthesis and characterisation of tungsten siloxides including the crystal structure of $[\text{WO}\{\text{O}(\text{Ph}_2\text{SiO})_3\}_2(\text{thf})]$

Brian J. Brisdon,* Mary F. Mahon and Christopher C. Rainford

Department of Chemistry, University of Bath, Claverton Down, Bath, UK BA2 7AY

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Reactions of WOCl_4 with NaOSiPh_3 and $\text{Na}_2\text{O}_2\text{SiPh}_2$ gave respectively $[\text{WO}(\text{Cl})(\text{OSiPh}_3)_3]$ and $[\{\text{WO}_2[(\text{OSiPh}_2)_2\text{O}]\}_2]$. Under similar conditions NaOSiPh_3 reacted with $[\text{WO}_2\text{Cl}_2(\text{OSC}_4\text{H}_8)_2]$ to yield $[\text{WO}_2(\text{OSiPh}_3)_2(\text{OSC}_4\text{H}_8)_2]$. The novel spirocyclic tungstasiloxane $[\text{WO}\{\text{O}(\text{Ph}_2\text{SiO})_3\}_2(\text{thf})]$ was prepared from the reaction between equimolar quantities of $(\text{Ph}_2\text{SiO})_3$ and WOCl_4 in tetrahydrofuran. A crystal structure determination on this product revealed a distorted octahedral geometry about the central tungsten atom with the axially co-ordinated ether ligand *trans* to the oxo group, and puckered eight-membered siloxane rings oriented on opposite sides of the equatorial plane defined by the four co-ordinated siloxide O atoms. The W–O (Si) separations ranged from 1.851(7) to 1.896(8) Å and the W=O bond length was 1.675(13) Å. In dichloromethane WCl_6 reacted with $(\text{Ph}_2\text{SiO})_3$ to afford good yields of WOCl_4 , whereas in tetrahydrofuran the same reactants caused solvent polymerisation.

Species containing early transition metals supported on silica substrates are used extensively in heterogeneous catalysis. Despite the rapid evolution of surface science techniques, attempts to elucidate the exact nature of the active, surface-modified metal entities, and determine reaction mechanisms, have had limited success. As a consequence there is still considerable interest in the synthesis of metal complexes as mechanistic and structural models for these surfaces. The trisilanols $\text{R}_7\text{Si}_7\text{O}_9(\text{OH})_3$, $\text{R} = c\text{-C}_5\text{H}_9$, $c\text{-C}_6\text{H}_{11}$ or $c\text{-C}_7\text{H}_{13}$, are recognised as some of the best currently available molecular species for modelling the binding sites on silica surfaces,^{1–3} and several Group 6 metal derivatives have been prepared from them. These include both mono- and di-nuclear metallasilasesquioxanes $[\text{MO}_2\{(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{11})(\text{OSiMe}_3)\}]$, $\text{M} = \text{Cr}$ or Mo ,⁴ $[\text{Mo}_2\{(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{12})_2\}]$,⁵ $[\text{W}(\text{NMe}_2)_3\text{O}_3\{(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9\}]$ ⁶ and $[\text{W}_2(\mu\text{-H})(\mu\text{-O}^{\text{Bu}})\{(c\text{-C}_6\text{H}_{11})_7(\text{Si}_7\text{O}_{12})_2\}]$.⁷ Several of these complexes, as well as closely related metallasilasesquioxanes, are very active homogeneous catalysts.^{8–11} In addition many known molybda- and tungsta-siloxane model compounds derived from silanols containing ligand sets with only one or two binding sites also show catalytic activity.^{12–17} Despite the very considerable attention devoted to metallasiloxanes, structural data on tungsten derivatives are restricted to relatively few examples, many of which have been prepared by metathesis reactions involving either binuclear tungsten(III) alkoxide or amido complexes, W_2L_6 ($\text{L} = \text{OR}$ or NR_2), containing a metal–metal multiple bond, or mononuclear species, WX_2Y_2 ($\text{X} = \text{O}$ or NR ; $\text{Y} = \text{halide}$), containing two tungsten(VI)–non-metal multiple bonds.^{4,5,12,14}

In this paper we report the isolation and characterisation of several tungsten siloxides synthesized using either metal–halide metathesis reactions, or *via* ring opening of a cyclotrisiloxane. The first crystal structure of a cyclotungstasiloxane, $[\text{WO}\{\text{O}(\text{Ph}_2\text{SiO})_3\}_2(\text{thf})]$, is also described.

Results and discussion

Metal-halide metathesis reactions

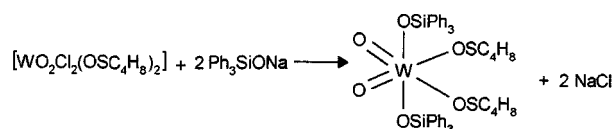
Reaction of WOCl_4 with 3 mol of NaOSiPh_3 afforded very high yields of $[\text{WO}(\text{Cl})(\text{OSiPh}_3)_3]$ **1**, as an extremely air and moisture sensitive white powder. In the IR spectrum of **1** $\nu(\text{W}=\text{O})$ and $\nu(\text{W}-\text{OSi})$ modes occur at 959 and 909 cm^{-1} respectively, with no evidence of a bridging W–O–W mode. The NMR spectrum



Scheme 1

indicates equivalence of the siloxide groups. It seems likely therefore that the siloxide ligands are disposed either in the equatorial plane of a trigonal bipyramidal arrangement, as observed for $[\text{MoO}_2(\text{OSiPh}_3)_2(\text{PPh}_3)]$,¹⁸ or in *trans* equatorial positions of the more usual square pyramidal arrangement found for the majority of WOL_4 complexes.¹⁹ Wilkinson and co-workers¹⁴ noted the formation of an oil on reaction of $[\text{WO}_2\text{Cl}_2(\text{dme})]$ with hexamethyldisilazane. This product readily formed a monoadduct with Lewis bases, and it was structurally characterised as the pyridine adduct $[\text{WCl}(\text{NSiMe}_3)(\text{OSiMe}_3)_3(\text{py})]$. We have noted that **1** also adds a sixth ligand on treatment with thf, to form the oxo-analogue of this product, $[\text{WO}(\text{Cl})(\text{OSiPh}_3)_3(\text{thf})]$ **1a**. On crystallising from toluene **1a** loses thf. Reaction of 4 equivalents of sodium triphenylsiloxide with tungsten tetrachloride oxide failed to generate $[\text{WO}(\text{OSiPh}_3)_4]$. The steric bulk of the siloxide ligand may not be the only factor determining the degree of halide replacement, as although completely substituted $[\text{WO}(\text{OR})_4]$ species containing sterically demanding alkoxide ligands have been prepared,²⁰ they are rarely accessible *via* metal halide metathesis reactions.

Reaction of NaOSiPh_3 with $[\text{WO}_2\text{Cl}_2(\text{OSC}_4\text{H}_8)_2]$ gave $[\text{WO}_2(\text{OSiPh}_3)_2(\text{OSC}_4\text{H}_8)_2]$ **2** (Scheme 2), the spectral properties of



Scheme 2 Formation of $[\text{WO}_2(\text{OSiPh}_3)_2(\text{OSC}_4\text{H}_8)_2]$.

which are in accord with a pseudo-octahedral geometry about tungsten. Two IR active $\nu(\text{WO}_2)$ modes appearing at 945 and 893 cm^{-1} confirm the presence of a *cis*- $[\text{WO}_2]^{2+}$ centre. A *trans*, *cis* disposition of siloxide and OSC_4H_8 ligands respectively is in keeping with the NMR data for **2**, and with the ligand arrangement found in many other structurally characterised six-co-ordinate dioxotungsten(VI) and dioxomolybdenum(VI) analogues.¹⁹

Reaction of WOCl_4 suspended in thf with 2 equivalents of

$\text{Na}_2\text{O}_2\text{SiPh}_2$, generated *in situ* from the reaction of $\text{Ph}_2\text{Si}(\text{OH})_2$ with sodium, yielded product **3** of empirical formula $\text{WO}_5\text{-Si}_2\text{Ph}_4$. Molecular weight measurements indicated that the complex was dimeric and either of the formulations $[\{\text{WO}(\text{OSiPh}_2\text{O})_2\}_2]$ or $[\{\text{WO}_2(\text{OSiPh}_2\text{O})\}_2]$ are possible. A strong IR absorption at 961 cm^{-1} may be assigned to either $\nu(\text{WO})$ or $\nu_{\text{sym}}(\text{WO}_2)$, but the spectrum at lower wavenumbers showed several strong absorptions which might have masked $\nu_{\text{asym}}(\text{WO}_2)$. The similarity in the spectra of compounds **3** and **4b** in the Si–O–Si region indicate that the formulation based on a disiloxane-1,3-diolate is likely for **3**. Neither ^1H nor $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectra were structurally diagnostic. Compound **3** readily and reproducibly formed a monohydrate **3a** on exposure to traces of moisture, with little spectral changes other than the appearance of new absorptions due to water. We are unaware of any complex in which the $[\text{R}_2\text{SiO}_2]^{2-}$ group acts as a chelating ligand, although structurally characterised complexes containing bridging, bidentate silanolate are widely documented for many transition metals.³ These include $[\{\text{MoO}_2(\text{O}_2\text{SiBu}^t)_2\}_2]$,¹⁶ $[\text{Mo}_2\{\text{O}_2\text{Si}(\text{OBu}^t)_2\}_3]$ ¹² and $[\text{W}(\text{NBU}^t)_2(\text{O}_2\text{SiBu}^t)_2]$.¹³ It is also well known that diphenylsilanediol, when treated with metal precursors, shows a strong tendency to self-condense and form tetraphenyldisiloxane-1,3-diolates.³ We were unable to grow crystals of **3** or **3a** suitable for X-ray crystallography, and so define unequivocally the bonding mode of the ligand in either complex, but based on infrared evidence we favour the diolate formulation.

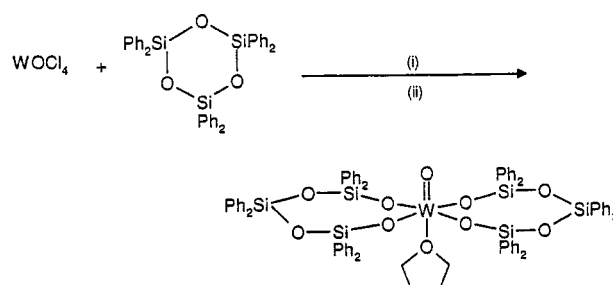
Ring opening reactions of cyclotrisiloxanes

Tungsten hexachloride reacts at ambient temperature with dichloromethane solutions of hexaphenylcyclotrisiloxane to afford tungsten tetrachloride oxide in yields approaching those obtained by Gibson *et al.*²¹ from hexamethyldisiloxane– WCl_6 reactions. However, prolonged reaction (24 h) of WCl_6 with a thf solution of this cyclotrisiloxane generated an intractable dark blue, viscous oil. Treatment of this oil with 20 volume hydrogen peroxide, in order to oxidise tungsten to the hexavalent state, followed by extraction with dichloromethane yielded a tungsten-free colourless oil on evaporation of the solvent. This oil was shown by microanalysis and spectroscopy to be polytetrahydrofuran, which is readily formed from the monomer in the presence of a wide range of electrophilic reagents.²² Previous studies have shown that WCl_6 causes oxygen abstraction from ethers, and several ether adducts of WOCl_3 , including $[\text{WOCl}_3(\text{thf})_2]$ ²³ and $[\text{WOCl}_3(\text{dme})]$,²⁴ have been synthesized by this route. In view of the intractable nature of the reaction mixture formed in the prolonged reaction of WCl_6 with thf, we have been unable to determine to date whether a tungstasiloxane intermediate is responsible for the ring opening polymerisation of this cyclic ether, but in the early stages of the reaction some WOCl_4 is formed. However, **4a**, whose preparation from WOCl_4 and hexaphenylcyclotrisiloxane in thf is described below, does not itself catalyse the room temperature ring opening polymerisation of thf.

Reaction of WOCl_4 with a thf solution of hexaphenylcyclotrisiloxane for 3 d, afforded after work-up a blue oil. Extraction of this oil with a dichloromethane–hexane (2:1) yielded an air-stable spirocyclic tungsten siloxide $[\text{WO}\{\text{O}(\text{OSiPh}_2)_3\}_2(\text{thf})]\cdot\text{thf}$ **4a** in low yield. The NMR measurements revealed that the two molecules of thf were inequivalent on dissolution in chloroform, and on recrystallisation of **4a** in the absence of excess of thf small colourless needles of $[\text{WO}\{\text{O}(\text{OSiPh}_2)_3\}_2(\text{thf})]$ **4b** were isolated (Scheme 3), from which a crystal suitable for an X-ray structure determination was selected. Compounds **4a** and **4b** both display strong, sharp bands in their IR spectra at 968 and 916 cm^{-1} , indicative of $\nu(\text{W}=\text{O})$ and $\nu(\text{W}=\text{OSi})$ modes. Absorptions at 1028 and 1076 cm^{-1} assigned to $\nu(\text{Si}=\text{O}=\text{Si})$ are consistent with the presence of a relatively unstrained cyclic siloxane framework. The ^{29}Si NMR spectrum of **4b**

Table 1 Selected bond lengths (Å) and angles (°) for $[\text{WO}\{\text{O}(\text{OSiPh}_2)_3\}_2(\text{thf})]$ **4b**

W(1)–O(10)	1.675(13)	W(1)–O(1)	1.851(7)
W(1)–O(4)	1.872(8)	W(1)–O(5)	1.896(8)
W(1)–O(8)	1.894(7)	W(1)–O(9)	2.326(10)
O(10)–W(1)–O(1)	96.2(4)	O(3)–Si(1)–O(4)	109.5(4)
O(10)–W(1)–O(4)	96.3(4)	O(3)–Si(2)–O(2)	109.4(4)
O(1)–W(1)–O(4)	89.9(3)	O(2)–Si(3)–O(1)	111.3(4)
O(10)–W(1)–O(5)	88.4(3)	O(6)–Si(4)–O(5)	109.9(4)
O(4)–W(1)–O(5)	166.3(4)	O(6)–Si(5)–O(7)	109.4(4)
O(10)–W(1)–O(8)	96.6(4)	O(8)–Si(6)–O(7)	112.7(4)
O(1)–W(1)–O(8)	167.1(4)	Si(3)–O(1)–W(1)	169.8(5)
O(4)–W(1)–O(8)	87.4(3)	Si(2)–O(2)–Si(3)	156.2(5)
O(5)–W(1)–O(8)	91.3(3)	Si(1)–O(3)–Si(2)	159.3(6)
O(10)–W(1)–O(9)	178.8(3)	Si(1)–O(4)–W(1)	165.7(6)
O(1)–W(1)–O(9)	84.9(3)	Si(4)–O(5)–W(1)	147.9(7)
O(4)–W(1)–O(9)	84.2(4)	Si(4)–O(6)–Si(5)	161.7(6)
O(5)–W(1)–O(9)	82.1(4)	Si(6)–O(7)–Si(5)	156.5(5)
O(8)–W(1)–O(9)	82.3(3)	Si(6)–O(8)–W(1)	155.9(6)



Scheme 3 Tungsten tetrachloride oxide mediated ring opening reaction of cyclo- $\text{Ph}_6\text{Si}_3\text{O}_3$. (i) thf, rt, 3 d; (ii) extraction with hexane-dichloromethane (1:2).

exhibits two distinct silicon environments with chemical shift data similar to those observed for the eight-membered metallasiloxanes $[\text{M}\{\text{O}(\text{Ph}_2\text{SiO})_3\}_2\text{L}_2]$ ($\text{M} = \text{Ti}$ or Hf , $\text{L} = \text{py}$; $\text{M} = \text{Sn}$, $\text{L} = \text{thf}$).^{25,26}

Reaction for several days between thf solutions of WOCl_4 and the less strained siloxane ring compound octaphenylcyclotetrasiloxane yielded, after work-up, only small quantities of a blue oil from which no tungstasiloxanes could be isolated. The propensity of highly strained cyclosiloxanes to react readily with oxophilic metal centres to yield metallasiloxanes, which exhibit a variety of structural motifs, has been noted previously in reports on the preparations of $[\{\{\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{thf})_2\}_2(\mu\text{-OSiMe}_2\text{OSiMe}_2\text{O})\}_2]$ ²⁷ and $[\{\{\text{Yb}(\eta^2\text{-C}_3\text{N}_2\text{HMe}_2\text{-3,5})-(\mu\text{-}\eta^1\text{-}\eta^2\text{-OSiMe}_2\text{C}_3\text{N}_2\text{HMe}_2\text{-3,5})(\eta\text{-C}_5\text{H}_4\text{Me})\}_2]$,²⁸ and the formation of long chain titanasiloxane polymers²⁹ and cyclic aluminosiloxanes.³⁰

No reaction was observed between $[\text{WO}_2\text{Cl}_2(\text{OSC}_4\text{H}_8)_2]$ and $(\text{Ph}_2\text{SiO})_3$ even after several hours under reflux in either thf or dichloromethane.

Crystal structure of compound **4b**

Compound **4b** exhibits a monomeric structure with one molecule per asymmetric unit (Fig. 1 and Table 1). The six-coordinate tungsten displays a distorted octahedral geometry with the oxo group *trans* to the co-ordinated thf ligand [O(10)–W(1)–O(9) 178.8°]. The tungsten atom is raised out of the plane formed by the O-donor atoms of the two equatorial bidentate ligands, as is observed in WOCl_4 .³¹ The multiply bonded W–O distance in **4b** of 1.675(13) Å is typical of oxotungsten(vi) diolato species, and slightly shorter than analogous distances observed for mononuclear and dinuclear oxoalkoxide species [1.702(7)–1.817(7) Å].^{20,32} The strong *trans* influence of the multiply bonded oxo ligand accounts for the *trans* arrangement for the weakest π -donating ligand (thf). This is also reflected in the long W–O (thf) bond length [W(1)–O(9) 2.326(10) Å],

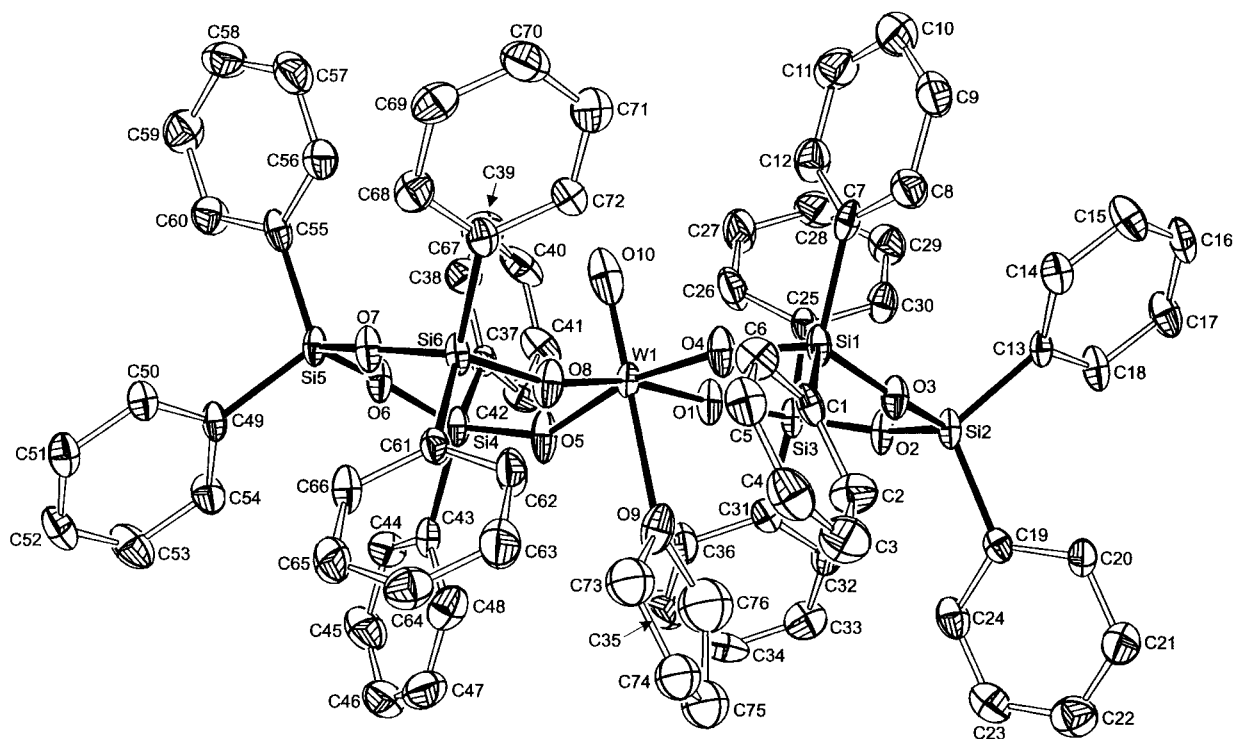


Fig. 1 Molecular structure of compound **4b** showing the atom labelling scheme adopted. Thermal ellipsoids are shown at the 30% probability level.

which is similar to that of 2.38(3) Å found in $[\text{WO}(\text{OBU})_4(\text{thf})]^{20}$. The W–O (Si) bond distances in **4b** are all similar [1.851(7)–1.896(8) Å, average 1.879 Å] and relatively short on average in comparison with those in other tungsten siloxides; 1.87–1.96 Å for $[\text{W}_2(\text{OSiBu}^t\text{Me}_2)_6]^{33}$ and related alkene adducts, 1.889 Å for $[\{\text{W}(\text{NBU}^t)_2(\mu\text{-OSiBu}^t\text{O})_2\}_2]^{13}$ and 1.947(4) Å for $[\text{W}(\text{NMe}_2)_3\text{O}_3\{\text{(}i\text{-C}_6\text{H}_{11}\text{)}_2\text{Si}_7\text{O}_9\}]^6$. The bond distances in **4b** are thus indicative of significant π donation by the siloxide oxygen lone pairs to the metal centre.

The siloxane skeletons of the eight-membered tungstasiloxane rings lie on opposite sides of the equatorial plane defined by the four oxygen donors of the siloxide ligands O(1), O(4), O(5), O(8). Distances of Si atoms (1)–(6) from the plane of these four oxygen atoms are +0.45, +1.45, +0.24, –0.65, –1.65 and –0.43 Å respectively. Of other compounds containing eight-membered siloxide rings a *trans* disposition has been noted in $[\text{Sn}\{\text{O}(\text{Ph}_2\text{SiO})_3\}_2(\text{thf})_2]$, whereas both $[\text{M}\{\text{O}(\text{Ph}_2\text{SiO})_3\}(\text{py})_2]$ (M = Ti or Hf) exhibit a *cis* arrangement.²⁵ The average M–O–Si angles in compound **4b** are some 5° larger than those observed in other eight membered metallasiloxide rings (154.3, Sn; 154.8, Ti; 153.9°, Hf) and considerably larger than those observed in six-membered oxometallasiloxides. The Si–O–W interbond angles in **4b** are also smaller than those observed in $[\text{W}(\text{NMe}_2)_3\text{O}_3\{\text{(}i\text{-C}_6\text{H}_{11}\text{)}_2\text{Si}_7\text{O}_9\}]$, which is considered to exhibit only weak Si–O–W π -bonding interactions. The flexibility of the metallasiloxide ring skeleton is demonstrated by comparing O–M–O and Si–O–Si angles in known compounds with various ring sizes. The (Si)O–M–O(Si) angles in **4b** [89.9(3) and 91.3(3)°, average 90.6(3)°] are not only very similar to the corresponding angles in the eight-membered ring system in $[\text{Sn}\{\text{O}(\text{SiPh}_2\text{O})_3\}_2(\text{thf})_2]$, 90.42(7)°, but they are also of a similar size to those found in the six-membered siloxane ring system in $[\text{VO}\{\text{O}(\text{SiPh}_2\text{O})_2\}_2\text{Li}(\text{thf})_2]$, 90.1(2)°.³⁴ However, they are significantly smaller than the (Si)O–M–O(Si) angles found in the eight-membered rings of either *cis*- $[\text{Hf}\{\text{O}(\text{SiPh}_2\text{O})_3\}_2(\text{py})_2]$, 94.6(2)°, or *cis*- $[\text{Ti}\{\text{O}(\text{SiPh}_2\text{O})_3\}_2(\text{py})_2]$, 95.5(2)°.²⁵ The Si–O–Si angles in **4b** [156.2(5)–161.7(6)°] also differ significantly from those in the closely related titanium [146.4(3) and 156.0(3)°], hafnium [149.6(4) and 156.6(4)°] and tin analogues [149.09(12) and 164.14(14)°] referred to above. A fairly close

match is found in the almost unstrained ring in $(\text{Ph}_2\text{SiO})_4$ which has Si–O–Si angles of 152.3(2) and 167.4(2)°.³⁵

Experimental

Unless stated otherwise all manipulations were carried out in an atmosphere of dried, purified nitrogen using standard Schlenk and cannula techniques. Hydrocarbon and ether solvents were dried in a nitrogen atmosphere over sodium and benzophenone. Dichloromethane and 1,2-dichloroethane were dried over calcium hydride and fractionated before use.

Hexaphenylcyclotrisiloxane, octaphenylcyclotetrasiloxane, potassium trimethylsilanolate, triphenylsilanol and diphenylsilanediol were purchased from Aldrich Chemical Company and used as supplied. Standard literature methods were utilised for the preparation of tungsten tetrachloride oxide, $[\text{WO}_2\text{Cl}_2(\text{OSC}_4\text{H}_9)_2]$, 1,3-dihydroxytetraphenyldisiloxane and sodium triphenylsilanolate.^{36,37}

Infrared spectra were recorded as Nujol mulls, NMR spectra on 270 and 400 MHz instruments; ¹H chemical shifts are reported in units of ppm downfield from tetramethylsilane, ¹³C- $\{^1\text{H}\}$ chemical shifts relative to residual ¹³C in the deuterated solvents and ²⁹Si chemical shifts relative to SiMe₄. Samples were 0.02 M with respect to [Cr(acac)]. Tungsten was determined gravimetrically on silicon-free samples following ignition in air to WO₃. Microanalyses were performed on a Carlo Erba 1106 Elemental Analyser. Samples of **1** and **3** rapidly absorbed traces of moisture during preparation for microanalysis, consequently analytical results for the anhydrous complexes invariably yielded slightly high hydrogen and low carbon contents. Infrared spectroscopy confirmed that no water was present in the samples when first isolated.

Crystal structure determination of complex **4b**

X-Ray diffraction quality crystals of complex **4b** were isolated from a dichloromethane–hexane (2:1) solution after storage at 0 °C for 1 week. They were air and moisture stable.

Crystallographic measurements were made at 293(2) K on a CAD4 automatic four-circle diffractometer in the range

2.04 < θ < 22.00°. Data were corrected for Lorentz-polarisation and also for absorption.³⁸ Careful scrutiny of the difference electron density map revealed that there was some disorder present in the region of the bound solvent molecule. Rigorous efforts failed to model this disorder successfully, and the best convergence was ultimately achieved by isotropic refinement of the carbons therein, C73–C76, while restraining the distances within the furan ring to ideal values. Remaining atoms were allowed to vibrate anisotropically. Phenyl groups were treated as rigid hexagons. Hydrogen atoms were included at calculated positions where relevant.

The solution of the structure (SHELXS 86)³⁹ and refinement (SHELXL 93)⁴⁰ converged to a conventional limit. The asymmetric unit (shown in Fig. 1), along with the labelling scheme used, was produced using ORTEP.⁴¹

Crystal data. C₇₆H₆₈O₁₀Si₆W, $M = 1493.69$, triclinic, $a = 9.915(5)$, $b = 13.865(3)$, $c = 25.712(6)$ Å, $\alpha = 82.47(2)$, $\beta = 83.83(3)$, $\gamma = 87.76(3)^\circ$, $U = 3483(2)$ Å³, space group $P\bar{1}$ (no. 2), $Z = 2$, $D_c = 1.42$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.82$ mm⁻¹, $F(000) = 1.524$, 10871 reflections measured, 8582 unique which were used in all calculations. Data corrected for absorption using DIFABS (maximum and minimum absorption corrections 1.00, 0.608 respectively). Final residuals [based on 5864 data with $F_o > 4\sigma(F_o)$], $R1 = 0.0573$ and $wR2 = 0.1436$. Goodness of fit = 1.084. The maximum and minimum residual densities were 1.431 and -1.099 e Å⁻³ respectively.

CCDC reference number 186/1119.

Synthesis

[WO(Cl)(OSiPh₃)₃] 1. A solution of Ph₃SiONa (1.02 g, 3.42 mmol) in thf (35 cm³) was added dropwise to an ice cold, stirred suspension of WOCl₄ (0.39 g, 1.14 mmol) in thf (20 cm³). An immediate reaction ensued with the initial orange suspension fading to a colourless solution which finally became pale blue upon reaching room temperature. Stirring was continued overnight and the volatiles removed *in vacuo* to yield a pale blue residue which was extracted with toluene (75 cm³). The product **1** was isolated from the filtrate following evaporation of the solvent (1.1 g, 91%). The product formed a thf adduct, **1a**, on treatment with thf (Found for **1**: C, 60.7; H, 4.44. C₅₄H₄₅ClO₄Si₃W requires C, 61.0; H, 4.28%; $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 3182, 3069, 3044, 1484, 1428, 1117, 1030, 999, 959, 909, 874, 739, 712 and 698; δ_{H} (270 MHz, C₆D₆, SiMe₄) 7.22 (27 H, m, *o*-, *p*-H of C₆H₅) and 7.73 (18 H, m, *m*-H of C₆H₅); δ_{C} (270 MHz, C₆D₆) 136.4, 136.0, 135.8, 131.3 and 130.5 (C₆H₅) (Found for **1a**: C, 61.6; H, 4.81. C₃₅H₅₃ClO₄Si₃W requires C, 61.4; H, 4.71%).

[WO₂(OSiPh₃)₂(OSC₄H₈)₂] 2. A solution of Ph₃SiONa (1.57 g, 5.26 mmol) in thf (40 cm³) was added dropwise to an ice cold, stirred suspension of [WO₂Cl₂(OSC₄H₈)₂] (1.3 g, 2.62 mmol). The mixture was allowed to warm to room temperature and stirring continued overnight. Volatiles were removed *in vacuo* and the residue extracted with toluene (80 cm³). Evaporation of the extract yielded the title product (1.96 g, 77%) (Found: C, 54.2; H, 5.07. C₄₄H₄₆O₆S₂Si₂W requires C, 54.2; H, 4.76%; $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 1460, 1428, 1306, 1262, 1186, 1115, 1035, 1022, 1001, 945, 931, 893, 833, 740, 708 and 700; δ_{H} (270 MHz, CD₂Cl₂, SiMe₄) 0.90 (4 H, m, C₄H₈SO), 1.92 (4 H, m, C₄H₈SO), 2.33 (4 H, m, C₄H₈SO), 2.71 (4 H, m, C₄H₈SO), 7.1–7.5 (18 H, m, *m*-, *p*-H of C₆H₅) and 7.8–8.0 (12 H, m, *o*-H of C₆H₅); δ_{C} (270 MHz, CD₂Cl₂) 25.9, 29.9, 34.2, 37.5 (C₄H₈SO), 127.9 (*m*-C of C₆H₅), 129.9 (*p*-C of C₆H₅), 136.4 (*o*-C of C₆H₅) and 137.9 (*ipso*-C of C₆H₅).

[{WO₂(OSiPh₂O)}₂] 3. A solution of Ph₂Si(ONa)₂ (0.73 g, 2.8 mmol) prepared *in situ* was added dropwise to an ice-cold, stirred orange suspension of WOCl₄ (0.48 g, 1.4 mmol) in thf (20 cm³). An immediate reaction ensued producing a slightly

blue solution. The mixture was allowed to warm to room temperature overnight, and then volatiles were removed *in vacuo*. Extraction with toluene (50 cm³) followed by removal of the solvent yielded the product **3** (0.65 g, 77%) (Found: C, 45.2; H, 3.40. C₂₄H₂₀O₅Si₂W requires C, 45.8; H, 3.20%; $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 1591, 1429, 1306, 1119, 1055, 1026, 997, 961, 916, 775, 741, 720, 700 and 660; δ_{H} (270 MHz, CD₂Cl₂, SiMe₄) 7.0–7.15 (8 H, m, *m*-H of C₆H₅), 7.2–7.3 (4 H, m, *p*-H of C₆H₅) and 7.4–7.6 (8 H, m, *o*-H of C₆H₅); δ_{C} (270 MHz, CD₂Cl₂) 127.9, 130.1, 134.7, 135.0, 135.4 and 135.7 (C₆H₅). Brief exposure of the toluene solution to atmospheric moisture resulted in the formation of a monohydrate, **3a**, on evaporation of the solvent (Found: C, 44.6; H, 3.65. C₂₄H₂₂O₆Si₂W requires C, 44.6; H, 3.44%).

Reaction of WCl₆ with (Ph₂SiO)₃. (a) A Schlenk tube was charged with WCl₆ (0.20 g, 0.50 mmol), (Ph₂SiO)₃ (0.91 g, 1.53 mmol) and thf (25 cm³), and the mixture stirred at room temperature. An immediate reaction ensued, the initial brown suspension becoming orange. The reaction mixture then changed to pale green over the next 2 h. Stirring was continued overnight to afford a viscous blue solution, at which stage the volatiles were removed *in vacuo* to yield a viscous blue oil. Treatment of the oil with an excess of toluene and storing at -30°C resulted in the precipitation of unchanged cyclotrisiloxane. The residual oil was separated from the solid and supernatant solvent, dissolved in acetone (25 cm³) and treated with sufficient H₂O₂ (20 vol.) to discharge the blue colouration. Storing at -30°C for 7 d yielded a ring-opened thf polymer containing no tungsten (Found: C, 66.7; H, 11.2. C₄H₈O requires 66.6, 11.2%; δ_{H} (270 MHz, CDCl₃, SiMe₄) 1.63 (4 H, q, OCH₂CH₂CH₂CH₂O) and 3.47 (4 H, t, OCH₂CH₂CH₂CH₂O); δ_{C} (270 MHz, CDCl₃) 26.5 (OCH₂CH₂CH₂CH₂O) and 34.1 (OCH₂CH₂CH₂CH₂O).

(b) The reaction was repeated using finely divided WCl₆ (0.31 g, 0.78 mmol) and (Ph₂SiO)₃ (0.47 g, 0.78 mmol) in CH₂Cl₂ (30 cm³). After 1 h at room temperature *ca.* 20 cm³ of solvent were evaporated and the solid formed on standing at 0°C for 1 h was isolated, washed with ice-cold CH₂Cl₂ (2×10 cm³) and dried *in vacuo* (0.18 g, 67%) (Found: W, 53.6. Cl₄OW requires W, 53.8%; $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 960.

[WO{(OSiPh₂OSiPh₂OSiPh₂O)}₂(thf)] 4b. A Schlenk tube containing WOCl₄ (1.12 g, 3.28 mmol) and (Ph₂SiO)₃ (3.90 g, 6.56 mmol) in thf (50 cm³) was stirred at room temperature for 3 d. The resulting viscous blue solution was concentrated to one third of its original volume, and cooled to -30°C for 4 d. Crystals of unchanged hexaphenylcyclotrisiloxane were then separated and washed free of blue oil with cold hexane–dichloromethane (2:1, 30 cm³). The filtrate and the washings were combined and solvent evaporated to yield a viscous blue oil which was treated with dichloromethane–hexane (2:1, 30 cm³). Filtration removed insoluble tungsten containing species, and on cooling the filtrate to 0°C small colourless needles of the product [WO{(OSiPh₂OSiPh₂OSiPh₂O)}₂(thf)]·thf **4a** separated (0.92 g, 18%) (Found: C, 61.4; H, 4.89. C₈₀H₈₆O₁₁Si₆W requires C, 61.4; H, 4.90%; $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 1694, 1591, 1306, 1227, 1123, 1076, 1028, 997, 968, 914, 741, 720 and 698; δ_{H} (270 MHz, CDCl₃, SiMe₄) 1.18 (4 H, s, β -CH₂ of thf1), 1.54 (4 H, s, β -CH₂ of thf2), 3.34 (4 H, t, α -CH₂ of thf1), 3.42 (4 H, t, α -CH₂ of thf2) and 6.97–7.54 (60 H, m, C₆H₅); δ_{C} (270 MHz, C₆D₆) 23.9 (β -CH₂ of thf1), 25.5 (β -CH₂ of thf2), 68.1 (α -CH₂ of thf1), 69.6 (α -CH₂ of thf2), 126.5, 126.6, 126.8, 128.9, 129.0, 133.3, 133.4, 133.5, 133.8, 134.0 and 134.2 (C₆H₅); δ_{Si} (400 MHz, CDCl₃, [Cr(acac)₃], -21.8 , -40.4 (WOSiPh₂O) and -43.9 (WOSiPh₂OSiPh₂O). A second recrystallisation from dichloromethane–hexane (2:1) yielded crystals of **4b** suitable for a structural determination (0.44 g, 57% based on **4a**) (Found: C, 61.1; H, 4.66. C₇₆H₆₈O₁₀Si₆W requires C, 61.1; H, 4.60%; $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ 1962, 1894, 1825, 1590, 1568, 1428, 1306, 1117, 1076, 1028, 997, 968, 918, 743, 718 and 698 cm⁻¹; δ_{H} (270 MHz, CDCl₃, SiMe₄) 1.28 (4 H, s, β -CH₂ of thf), 3.50 (4 H, s,

α -CH₂ of thf) and 7.06–7.61 (60 H, m, C₆H₅); δ_{C} (270 MHz, C₆D₆) 24.9 (β -CH₂ of thf), 69.1 (α -CH₂ of thf), 127.6, 127.7, 129.9, 130.0, 134.3, 134.4, 134.9 and 135.2 (C₆H₅); δ_{Si} {400 MHz, CDCl₃, [Cr(acac)₃]} -40.5 (WOSiPh₂O) and -44.1 (WOSiPh₂OSiPh₂O).

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References

- 1 R. Murugavel, V. Chandrasekhar and H. W. Roesky, *Acc. Chem. Res.*, 1996, **26**, 183.
- 2 F. J. Feher and T. A. Budzichowski, *Polyhedron*, 1995, **14**, 3239.
- 3 R. Murugavel, A. Voigt, M. G. Walawalkar and H. W. Roesky, *Chem. Rev.*, 1996, **96**, 2205.
- 4 F. J. Feher, K. Rahimian, T. A. Budzichowski and J. W. Ziller, *Organometallics*, 1995, **14**, 3920.
- 5 F. J. Feher, D. N. Newman and J. F. Walzer, *J. Am. Chem. Soc.*, 1989, **111**, 1741.
- 6 M. H. Chisholm, F. J. Feher, T. A. Budzichowski and J. W. Ziller, *Polyhedron*, 1992, **11**, 1575.
- 7 M. H. Chisholm, C. M. Cook, J. C. Huffman and W. E. Strieb, *J. Chem. Soc., Dalton Trans.*, 1991, 929.
- 8 K. Wada, M. Nakashita, A. Yamamoto and T. Mitsudo, *Chem. Commun.*, 1998, 133.
- 9 F. J. Feher and T. L. Tajima, *J. Am. Chem. Soc.*, 1994, **116**, 2145.
- 10 H. C. L. Abbenhuis, S. Krijnen and R. A. van Santen, *Chem. Commun.*, 1997, 331; M. Crocker, R. H. M. Herold and A. G. Orpen, *Chem. Commun.*, 1997, 2411.
- 11 F. J. Feher and R. L. Blanski, *J. Chem. Soc., Chem. Commun.*, 1990, 1614.
- 12 K. Su and T. D. Tilley, *Chem. Mater.*, 1997, **9**, 588.
- 13 H.-J. Gosink, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, E. Irmer and R. Herbst-Irmer, *Organometallics*, 1994, **13**, 3420.
- 14 H.-W. Lam, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1993, 1477.
- 15 M. Weidenbruch, C. Pierrard and H. Pesel, *Z. Naturforsch., Teil B*, 1978, **33**, 1468.
- 16 H. J. Gosink, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, C. Freire-Edbrugger and G. M. Sheldrick, *Chem. Ber.*, 1993, **126**, 279.
- 17 M. S. Rau, C. M. Cretz, G. L. Geffroy, A. L. Rheingold and B. S. Haggerty, *Organometallics*, 1994, **13**, 1624.
- 18 M. Huang and C. W. Decock, *Inorg. Chem.*, 1993, **32**, 2287.
- 19 W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley-Interscience, New York, 1988 and refs. therein.
- 20 F. A. Cotton, W. Schwotzer and E. S. Shaushoum, *J. Organomet. Chem.*, 1985, **296**, 55; D. C. Bradley, M. H. Chisholm, M. W. Extine and M. E. Stager, *Inorg. Chem.*, 1977, **16**, 1794; V. G. Kessler, A. V. Mironov, N. Y. Turova, A. I. Yanovsky and Y. T. Struchkov, *Polyhedron*, 1993, **12**, 1573.
- 21 V. C. Gibson, T. P. Kee and A. Shaw, *Polyhedron*, 1990, **9**, 2293.
- 22 P. Dreyfus, M. P. Dreyfus and G. Pruckayr, in *Encyclopedia of Polymer Science and Engineering*, ed. J. I. Kroschwitz, Wiley, New York, 2nd edn., 1989, vol. 16, p. 649.
- 23 P. C. Crouch, G. W. A. Fowles, P. R. Marshall and R. A. Walton, *J. Chem. Soc. A*, 1968, 1634; W. Levason, C. A. McAuliffe and F. P. McCullough, *Inorg. Chem.*, 1977, **16**, 2911.
- 24 C. Persson and C. Andersson, *Polyhedron*, 1991, **10**, 2089.
- 25 M. A. Hossain, M. B. Hursthouse, A. Ibrahim, M. Mazid and A. C. Sullivan, *J. Chem. Soc., Dalton Trans.*, 1989, 2347.
- 26 M. Lazell, M. Motevalli, S. A. A. Shah, C. K. S. Simon and A. C. Sullivan, *J. Chem. Soc., Dalton Trans.*, 1996, 1449.
- 27 W. J. Evans, T. A. Ulibarri and J. W. Ziller, *Organometallics*, 1991, **10**, 134.
- 28 X. Zhou, H. Ma, X. Huang and X. You, *J. Chem. Soc., Chem. Commun.*, 1995, 2483.
- 29 K. A. Andrianov, *Metalorganic Polymers*, Interscience, New York, 1965, ch. 41, p. 276.
- 30 C. C. Landry, J. A. Davis, A. W. Apblett and A. R. Barron, *J. Mater. Chem.*, 1993, **3**, 597; R. Mulhapaup, J. Calabrese and S. D. Ittel, *Organometallics*, 1991, **10**, 3403.
- 31 H. Hess and H. Hartung, *Z. Anorg. Allg. Chem.*, 1966, **344**, 157.
- 32 W. Clegg, R. J. Errington, P. Kraxner and C. Redshaw, *J. Chem. Soc., Dalton Trans.*, 1992, 1431.
- 33 M. H. Chisholm, C. M. Cook, J. C. Huffman and W. E. Strieb, *J. Chem. Soc., Dalton Trans.*, 1991, 929.
- 34 M. Motevalli, D. Shah, S. A. A. Shah and A. C. Sullivan, *Organometallics*, 1994, **13**, 4109.
- 35 J. M. Barrow, V. Ebsworth and M. Harding, *Acta Crystallogr., Sect. B*, 1979, **35**, 2093.
- 36 B. J. Brisdon, *Inorg. Chem.*, 1967, **6**, 1791.
- 37 G. Harris, *J. Chem. Soc.*, 1963, 5978.
- 38 N. Walker and D. Stewart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
- 39 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 40 G. M. Sheldrick, SHELXL 93, A Computer Program for Crystal Structure Refinement, University of Göttingen, 1993.
- 41 P. McArdle, *J. Appl. Crystallogr.*, 1994, **27**, 438.

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