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Sugimoto, Itoh *et al.* A new series of bis(ene-1,2-dithiolato)tungsten(IV), -(V), -(VI) complexes as reaction centre models of tungsten enzymes: Preparation, crystal structures and spectroscopic properties



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The carbomethoxy substituted dithiolene ligand (L^{COOMe}) enabled us to develop a series of new bis(ene-1,2-dithiolato)tungsten complexes including W^{IV}O, W^{IV}(OSiBuPh₂), W^{VI}O₂, W^{VI}O(OSiBuPh₂) and W^{VI}O(S)

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enzymes: Preparation, crystal structures and

spectroscopic properties†

Minoru Kubo,^c Takashi Ogura^c and Shinobu Itoh*^a

core structures. By using these tungsten complexes, a systematic study of the terminal monodentate ligand effects has been performed on the structural, spectroscopic properties and reactivity. The structure and spectroscopic properties of the tungsten complexes have also been compared to those of the molybdenum complexes coordinated by the same ligand to investigate the effects of the metal ion (W vs. Mo). X-ray crystallographic analyses of the tungsten(IV) complexes have revealed that the tungsten centres adopt a distorted square pyramidal geometry with a dithiolene ligand having an ene-1,2-dithiolate form. On the other hand, the dioxotungsten(v) complex exhibits an octahedral structure consisting of the bidentate L^{COOMe} and two oxo groups, in which π -delocalization was observed between the $W^{VI}O_2$ and ene-1,2-dithiolate units. The tungsten(IV) and dioxotungsten(VI) complexes are isostructural with the molybdenum counter parts. DFT calculation study of the W^{VI}O(S) complex has indicated that the W=S bond of 2.2 Å is close to the bond length between the tungsten centre and ambiguously assigned terminal monodentate atom in aldehyde oxidoreductase of the tungsten enzyme. Resonance Raman (rR) spectrum of the W^{VI}O(S) complex has shown the two inequivalent L^{COOMe} ligands with respect to their bonding interactions with the tungsten centre, reproducing the appearance of two ν (C=C) stretches in the rR spectrum of aldehyde oxidoreductase. Sulfur atom transfer reaction from the W^{VI}O(S) complex to triphenylphosphines has also been studied kinetically to demonstrate that the tungsten complex has a lower reactivity by about one-order of magnitude, when compared with its molybdenum counterpart.

A new series of bis(ene-1,2-dithiolato)tungsten(IV), -(V),

-(vi) complexes as reaction centre models of tungsten

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Introduction

Molybdenum (Mo) and tungsten (W) are unique 4d (Mo) and 5d (W) transition metals found in biological systems. Mo and W enzymes exist in all forms of life from ancient archaea to humans, and catalyse a wide range of reactions in carbon,

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sulfur and nitrogen metabolism.¹⁻³ Some of the W enzymes are more available in locations where extremophiles live. Active sites of Mo and W enzymes feature the presence of metal binding pyranopterin ene-1,2-dithiolate (MPT).¹⁻³ Isostructural metal centres (metal = Mo and W) are found in some of the enzymes (Fig. 1). Molybdenum and tungsten containing enzymes such as dimethylsulfoxide reductases (Mo-DMSOR and W-DMSOR) have a bis(MPT)metal(IV) centre of a five coordinate structure with one serine oxygen atom at the apex in the reduced forms.4,5 In the oxidised state, an additional oxygen atom coordinates to the metal(vi) centre to form a six coordinate structure.4,5 In Mo- and W-containing FDH (FDH = formate dehydrogenase), both the metal centres adopt a five coordinate bis(MPT)sulfidemetal(IV) centre and a bis(MPT)sulfidemetal(vi) with a selenium substituted cysteine ligand.⁶⁻⁸ A dioxo metal(vi) centre is included in arsenite oxidase (AO) as an oxidised form and W-aldehyde

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[†]Electronic supplementary information (ESI) available: The optimized Cartesian coordinates (Tables S1 and S2). Kinetic data (Fig. S1–S4). Full Gaussian03 reference. CCDC reference numbers 883040–883042. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32179c



Fig. 1 Isostructural pairs of molybdenum and tungsten enzyme metal centers (M = Mo and W).

oxidoreductase as an inactive form.^{3,9} Thus, development of isostructural pairs of molybdenum and tungsten model complexes is highly desired for understanding the similarities and differences in the reactivity and electronic structure between the molybdenum and tungsten active sites.

In the modeling studies of the active sites of molybdenum and tungsten enzymes, structure and physicochemical properties of dithiolene complexes have been investigated extensively by using ene-1,2-dithiolate ligands that can provide stereochemical and electronic features related to the coordination environments of the enzyme active sites.¹⁰⁻¹⁴ A number of isostructural pairs of molybdenum and tungsten complexes of ene-1,2-dithiolate ligands have been synthesised and crystallographically characterised mainly by Holm and his coworkers.15 Most of the isostructural complexes are of dimethyl-1,2-dithiolate (L^{CH3}) and its diphenyl (L^{Ph}) derivative. They cover variety types of bis(ene-1,2-dithiolato)metal(IV) complexes with square pyramidal monooxo (M^{IV}O), alcoholato (M^{IV}(OR)), thiolato (M^{IV}(SR)), selenolato (M^{IV}(SeR)) and carboxylato $(M^{IV}(O_2CR))$ structures $(M^{IV} = MO^{IV} and W^{IV})$. Other isostructural pairs were reported by Garner and co-workers using phenyl-1,2-dithiolate ligand and its pyridyl derivatives, providing square pyramidal bis(dithiolene)M^{IV}O complexes.^{16,17} We also reported isostructural bis(dithiolene)M^{IV}O, -M^{IV}S and -M^{IV}Se complexes with cyclohexene-1,2-dithiolate.18-20 However, the above dithiolene ligands do not stabilise the molybdenum(vi) structures with an additional oxygen or sulfur atom owing to internal redox reaction between the molybdenum(vi) centre and ene-1,2-dithiolate ligand. Thus, isostructural pairs of bis(ene-1,2-dithiolato)molybdenum(vi) and -tungsten(vi) complexes are still very limited. So far, bis(L^{CN}) dioxomolybdenum(vi) (Mo^{VI}O₂) and -tungsten(vi) (W^{VI}O₂) complexes (L^{CN} = dicyanoethylene-1,2-dithiolato) reported by Sarkar' group are the unique example of isolated and crystallographically characterised isostructural bis(ene-1,2-dithiolato) metal(vi) complexes.^{21,22} In these complexes, the internal

redox reaction between L^{CN} and the metal(vi) centres is prevented by the strong electron-withdrawing CN groups. With L^{CN} ligand, two isostructural pairs of square pyramidal $bis(L^{CN})M^{IV}O$ and pseudo trigonal prismatic $bis(L^{CN})M^{IV}(SPh)_2$ complexes were also reported, even though the oxidation state of the metal centre is $+IV.^{21-23}$ The L^{CN} ligand, however, could not adopt the formation of six coordinate mono(oxo or sulfido)molybdenum(vi) and -tungsten(vi) complexes with an additional monodentate ligand such as RO^- , RS^- and RCO_2^- as found in oxidised DMSOR and oxidised FDH. Furthermore, square pyramidal desoxoMo^{IV} and desoxoW^{IV} complexes, found in the reduced DMSOR active sites, have not been synthesised yet, probably due to the high Lewis acidity of the central molybdenum(iv) and tungsten(iv) ions in the case of the less electron donating L^{CN} ligand.

On the basis of this information, we expect that dicarbomethoxyethylene-1,2-dithiolate ligand (L^{COOMe}), whose electron-donation nature lies between L^{R} (R = CH₃ or Ph) and L^{CN} , can stabilise both the five coordinate desoxo metal(w) and six coordinate (oxo or sulfido)molybdenum(vi) centres. Although bis(L^{COOMe})molybdenum complex has so far been limited to the monooxo molybdenum(IV) one,²⁴ we recently demonstrated that L^{COOMe} can stabilise various types of bis(L^{COOMe})molybdenum complexes such as the square pyramidal desoxo-,25 sulfido- and selenido-molybdenum(IV) complexes²⁶ as well as six coordinate dioxo-,27 monooxo-,25 oxosulfido- and oxoselenido-molybdenum(vi) complexes.²⁸ Along this line, we tried to synthesise their tungsten counterparts to complete isostructural pairs of complexes with the same ligand L^{COOMe}. Although bis(L^{COOMe})W^{IV}O complex was reported in the literature, the complex was obtained in a very low yield ($\sim 1\%$), and, therefore, detailed characterization has not been carried out yet.²⁹ Here, we report the preparation, characterization and reactivity of a series of tungsten complexes shown in Fig. 2, and compare some of the properties of the complexes with those of their molybdenum counterparts.

Paper





Experimental

General

All reagents and solvents were used as received unless otherwise noted. All reactions and sample preparations were carried out under a dinitrogen atmosphere in a glovebox (Miwa DB0-1KP). $K_3Na[W^{IV}O_2(CN)_4]\cdot 6H_2O^{30}$ and 4,5-dicarbomethoxy-1,3-dithiol-2-one³¹ were prepared by following the established literature procedures.

Synthesis and characterisation of complexes

 $(Et_4N)_2[W^{IV}O(L^{COOMe})_2]$ ($W^{IV}OL^{COOMe}$). An ethanol solution (25 mL) containing 4,5-dicarbomethoxy-1,3-dithiol-2-one (660 mg, 2.82 mmol) and 3.76 mL of a methanol solution of Et₄NOH (5.64 mmol) was added to K₃Na[W^{IV}O₂(CN)₄]·6H₂O (801 mg, 1.41 mmol). The resulting suspension was refluxed for 3.5 h to give a black powder. After the powder was collected by filtration, it was dissolved in acetonitrile. The resulting brown mixture was filtered to remove any insoluble solid, and diethyl ether was introduced into the filtrate to yield dark-red microcrystals. The crystals were collected by filtration and dried under reduced pressure. Yield 453 mg (37%). Anal. Calcd for C₂₈H₅₂N₂O₉S₄W (mol wt. 872.82): C, 38.53; H, 6.01; N, 3.21. Found: C, 38.59; H, 5.75; N, 3.23. IR (KBr): 910 ν (W=O) cm⁻¹. ¹H NMR (CD₃CN): δ 3.70 (s, 12 H), 3.09 (q, *J* = 7.21 Hz, 16 H), 1.15 (t, J = 7.21 Hz, 24 H). UV-vis spectrum (CH₃CN): $\lambda_{max} =$ 342 (ε = 10100), 478 (903), 580 nm (600 M⁻¹ cm⁻¹). ESI-MS (CH₃CN): $m/z = 612 \text{ [M]}^-$. CV (0.1 V s⁻¹, CH₃CN): $E_{1/2}$ (quasirev.) = $-0.27 \text{ V} \nu s$. SCE.

 $(Et_4N)[W^{IV}(OSi^tBuPh_2)(L^{COOMe})_2]$ ($W^{IV}(OSiBuPh_2)L^{COOMe}$). To an acetonitrile solution (8 mL) of $W^{IV}OL^{COOMe}$ (40.1 mg, 0.046 mmol), ^{*t*}BuPh₂SiCl (23.5 mL, 0.092 mmol) was added to give an orange solution. The solvent was removed under reduced pressure to provide an orange solid. Diethyl ether (12 mL) was added to the solid, and a light green powder appeared after continuous stirring for several hours. The powder was collected by filtration, washed with ethanol (4 mL) and then, diethyl ether (4 mL), and dried under air. Yield: 29 mg (65%). Anal. Calcd for C₃₆H₅₁NO₉S₄SiW (mol wt. 981.98): C, 44.03; H, 5.23; N, 1.43. Found: C, 43.96; H, 5.04; N, 1.46. IR (KBr): 938 ν (O–Si) cm⁻¹. ¹H NMR (CD₃CN): δ 7.40–7.29 (m, 10 H), 3.81 (s, 12 H), 3.13 (q, *J* = 7.26 Hz, 8 H), 1.18 (t, *J* = 7.26 Hz, 12 H), 0.81 ppm (s, 9 H). UV-vis spectrum (CH₃CN): $\lambda_{max} = 375$ ($\varepsilon = 2400$, sh), 430 (969, sh), 516 (205), 568 nm (150 M⁻¹ cm⁻¹). ESI-MS (CH₃CN): *m/z* = 851 [M]⁻.

 $(Et_4N)_2[W^{VI}O_2(L^{COOMe})_2]$ ($W^{VI}O_2L^{COOMe}$). An acetone solution (1 mL) of Me₃NO (4.8 mg, 0.064 mmol) was added to an acetonitrile solution (2 mL) of W^{IV}OL^{COOMe} (47.2 mg, 0.054 mmol). The colour of the solution changed to redorange after stirring for 6 h. The solvent was removed under reduced pressure, and diethyl ether (8 mL) and ethanol (2 mL) were added to the resulting residue, from which a red-orange powder was precipitated by ultrasonic agitation. The powder was then collected by filtration. Recrystallization from acetonitrile/diethyl ether gave orange crystals. Yield: 27.9 mg (58%). Anal. Calcd for C₂₈H₅₂N₂O₁₀S₄W (mol wt. 888.82): C, 37.84; H, 5.90; N, 3.15. Found: C, 37.89; H, 5.61; N, 3.21. IR (KBr): 894 ν (W=O)_{sym}, 855 ν (W=O)_{asym} cm⁻¹. ¹H NMR (CD₃CN): δ 3.61 (s, 12 H), 316 (q, J = 7.04 Hz, 16 H), 1.20 (t, J = 7.04 Hz, 24H). UV-vis spectrum (CH₃CN): $\lambda_{max} = 319$ ($\epsilon = 7370$), 374 nm (11 800 M^{-1} cm⁻¹). ESI-MS (CH₃CN): $m/z = 628 [M]^{-}$, 758 $\{[M]^{2-} + Et_4N^+\}^-$.

 $(Et_4N)[W^{VI}O(OSiBuPh_2)(L^{COOMe})_2]$ $(W^{VI}O(OSiBuPh_2)L^{COOMe}).$ To a THF solution (14 mL) of W^{IV}(OSiBuPh₂)L^{COOMe} (83.4 mg, 0.085 mmol), an acetonitrile solution (1 mL) of Me₃NO (8.6 mg, 0.114 mmol) was added. The resulted green-black solution was concentrated to ca. 3-4 mL under reduced pressure. After removing insoluble solid by filtration, the filtrate was concentrated to ca. 0.5 mL. Addition of n-hexane (12 mL) to the solution yielded a black powder, which was collected by filtration and dried under air. Yield: 68.8 mg (81%). Anal. Calcd for C₃₆H₅₁NO₁₀S₄SiW (mol wt. 997.98): C, 43.33; H, 5.15; N, 1.40. Found: C, 43.20; H, 5.08; N, 1.59. IR (KBr): 891 ν(W=O), 930 ν(O-Si) cm⁻¹. ¹H NMR (CD₃CN): δ 7.77-7.80 (m, 4 H), 7.35–7.42 (m, 6 H), 3.70 (s, 12 H), 3.14 (q, J = 7.26 Hz, 8 H), 1.19 (t, J = 7.26 Hz, 12 H), 1.05 ppm (s, 9 H). UV-vis spectrum (CH₃CN): $\lambda_{max} = 335$ ($\epsilon = 9090$, sh), 401 (3940), 463 (3650), 628 nm (1410 M^{-1} cm⁻¹). ESI-MS (CH₃CN): m/z = 867 $[M]^{-}$. CV (CH₃CN): E^{pa} (quasi-rev.) = -0.78 V vs. SCE.

Quantification of tri-p-tolylphosphine sulfide obtained after reaction of $W^{VI}O(S)L^{COOMe}$ with tri-p-tolylphosphine

To $W^{VI}O(S)L^{COOMe}$ generated *in situ* by the reaction of $W^{VI}O(OSiBuPh_2)L^{COOMe}$ (17.9 mg, 0.018 mmol) and Et₄NSH (6.1 mg, 0.037 mmol) at room temperature in acetonitrile (2 mL) under an inert atmosphere, an acetone solution (0.7 mL) of tri-*p*-tolylphosphine (10.5 mg, 0.034 mmol) was added. After stirring for 1 h, the volume of the solution was reduced to dryness. The residue was extracted with diethyl ether (50 mL × 3) and the organic layer of diethyl ether was concentrated to give a pale yellow powder containing tri-*p*-tolylphosphine sulfide in ~100% yield based on $W^{VI}O(S)L^{COOMe}$. The ¹H NMR spectrum of the product was identical with that of tri-*p*-tolylphosphine sulfide reported in the literature.²⁸

DFT calculation

The molecular geometries of $W^{VI}O_2L^{COOMe}$ and $W^{VI}O(S)L^{COOMe}$ were fully optimized at the B3LYP level of theory. The correlation consistent basis set of double- ζ quality augmented with diffuse s and p functions (aug-cc-pVDZ) was adopted for O and S atoms, and the standard cc-pVDZ basis set for C and H atoms. The Stuttgart/Dresden MWB28 effective core potential (ECP) basis set was employed for molybdenum. All DFT calculations were performed using the Gaussian 03 program. The optimized Cartesian coordinates are listed in Tables S1 and S2.[†] Bond dissociation energies were calculated as differences in the sum of electronic energy.

Physical measurements

FT-IR spectra were recorded with a Jasco FT-IR 4100 spectrometer. Resonance Raman scattering was excited at 363.8 nm with an Ar^+ ion laser (Spectra Physics, BeamLok 2080). Resonance Raman scattering was dispersed by a 75 cm single spectrometer (SPEX750M; Jovin Yvon) and was detected by a liquid nitrogen cooled CCD detector (Spec10:400B/LN; Roper Scientific). The resonance Raman measurement was carried out using a spinning NMR tube at -40 °C by flashing cooled dinitrogen gas. ¹H NMR spectra were recorded with a

JEOL Lambda 300 at 25 °C, and TMS signal was adjusted to 0 ppm. UV-vis spectra were recorded on a HP-8453 equipped with a Unisoku thermostat cell holder (USP-203).

Electrochemistry

Cyclic voltammetric measurements were performed under a dinitrogen atmosphere with a Hokuto Denko HZ-3000 potentiostat. A set of a glassy-carbon working electrode (circular, 3 mm diameter), a SCE reference electrode and a platinum counter electrode was employed in these experiments.

Kinetic measurements

Kinetic measurements for the reactions of W^{VI}O(S)L^{COOMe} and Mo^{VI}O(S)L^{COOMe} with triphenylphosphines were performed using a Hewlett Packard 8453 photodiode array spectrometer, with a magnetic stirrer, equipped with a Unisoku thermostated cell holder designed for low temperature measurements (USP-203, desired temperature can be fixed within ± 0.5 °C) in acetonitrile. To an acetonitrile solution of the complexes in a 1.0 cm path length UV-vis cell closed with a silicon rubber septum cap, an acetonitrile solution of the substrate was added using a microsyringe through the silicon rubber septum cap. The progress of the reaction was monitored by following a decrease of the absorption bands at 435 nm due to WVIO(S)-L^{COOMe} or 355 nm due to Mo^{VI}O(S)L^{COOMe}. The pseudo-firstorder rate constants for the reactions were calculated from the plots of $\ln(\Delta A)$ vs. time based on the time course of the absorbance change.

X-ray crystallography

Single crystals of $W^{VI}OL^{COOMe}$, $W^{VI}(OSi^{t}BuPh_2)L^{COOMe}$ and $W^{VI}O_2L^{COOMe}$ were obtained by vapor diffusion of diethyl ether into the acetonitrile solutions. Each single crystal obtained was mounted on a loop, and all measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-K α radiation. The structures were solved by direct methods (SIR2008³²) and refined anisotropically by full-matrix least squares on F^2 . The hydrogen atoms were attached at idealized positions on carbon atoms and were not refined. All structures in the final stages of refinement showed no movement in the atom positions. The calculations were performed using Single-Crystal Structure Analysis Software, version 3.8.³³ Crystallographic parameters are summarised in Table 1.

Results and discussion

Preparation, characterisation and crystal structural structures of $W^{IV}OL^{COOMe}$, $W^{IV}(OSiBuPh_2)L^{COOMe}$, $W^{VI}O_2L^{COOMe}$ and $W^{VI}O(OSiBuPh_2)L^{COOMe}$

The carbomethoxy substituted dithiolene ligand L^{COOMe} has often been employed in the modeling studies of molybdenum enzyme reaction centres. In such cases, $[Mo^{IV}(O)(S_4)_2]^{2-}$ is used as a precursor of $[Mo^{IV}O(L^{COOMe})_2]^{2-}$ and the oxo-molybdenum(IV) complex is converted to various derivatives, such as

Table 1 Crystallographic data of $W^{IV}OL^{COOMe},\ W^{VI}(OSiBuPh_2)L^{COOMe}$ and $W^{VI}O_2L^{COOMe}$

	W ^{IV} OL ^{COOMe}	W ^{IV} (OSiBuPh ₂)- L ^{COOMe}	$W^{VI}O_2L^{COOMe}$
Formula	$C_{28}H_{52}N_2O_9S_4W$	C ₃₆ H ₅₁ NO ₉ S ₄ SiW	$C_{56}H_{104}N_4O_{20}S_8W_2$
FW	872.82	981.98	1777.63
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2/ <i>n</i> (no. 13)	$P2_12_12_1$ (no. 19)	$P2_1/a$ (no. 14)
a (Å)	20.0069(8)	10.45548(19)	21.7443(7)
b (Å)	9.2346(4)	18.3525(3)	10.8658(3)
c (Å)	20.0827(7)	22.3689(4)	31.2865(8)
α (°)	90	90	90
$\beta(\circ)$	94.094(2)	90	98.9885(9)
γ (°)	90	90	90
$V(Å^3)$	3700.9(3)	4292.23(14)	7301.2(4)
Z	4	4	4
$\rho (\text{g cm}^{-3})$	1.566	1.519	1.617
μ (cm ⁻¹)	33.987	29.661	34.491
GOF	0.971	0.981	1.015
$R_1^a (I > 2.0\sigma I)$	0.0258	0.0280	0.0500
wR ₂ ^b	0.0549	0.0671	0.0951
(all data)			
$a R_1 = \Sigma(F_0 -$	$ F_{\rm c})/\Sigma F_{\rm o} $. ^b wR ₂ =	$= \{\Sigma(w(F_0^2 - F_c^2)^2)/\Sigma$	$\mathbb{E}w(F_0^2)^2\}^{1/2}.$

sulfido-, selenido- and desoxo-molybdenum(IV), oxo-molybdenum(V), and dioxo- and oxo-molybdenum(V) complexes.^{25–28} To our surprise, however, there is only one example of a tungsten model complex coordinated by L^{COOMe} ligand, $(Et_4N)_2[W^{IV}O(L^{COOMe})_2]$ ($W^{IV}OL^{COOMe}$).²⁹ The complex was obtained in only a 1% yield as a mixture with a dinuclear complex $(Et_4N)_2[W^{VI}S_4]$ with dimethylacetylenedicarboxylate and the sample purity was not determined, even though a few crystals were generated in the mixture.²⁹ Thus, the synthetic procedure of $W^{IV}OL^{COOMe}$, $[W^{IV}O_2(CN)_4]^{4-}$ was employed because a tungsten counter part, $[W^{IV}O(S_4)_2]^{2-}$, of $[Mo^{IV}O(S_4)_2]^{2-}$ is not available.¹⁷

The treatment of $K_3Na[W^{IV}O_2(CN)_4]$ with 4,5-dicarbomethoxy-1,3-dithiol-2-one under alkaline conditions in the presence of slightly excess Et₄NI yielded W^{IV}OL^{COOMe} in a 37% yield. The ν (W=O) stretch at 910 cm⁻¹ is between those of the L^{CH3} (897 cm⁻¹) and L^{CN} (935 cm⁻¹) derivatives, reflecting the fact that the electron donation from L^{COOMe} to the W(IV) centre is smaller and larger than those of L^{CH3} and L^{CN} ligands, respectively. Also, the $\nu(W=O)$ value is slightly larger than that of the molybdenum counter part Mo^{IV}OL^{COOMe} (905 cm⁻¹). W^{IV}OL^{COOMe} crystallised in a different space group and cell parameters (see Table 1) from those reported in the literature $(P2_1/n; a = 14.89794(2), b = 17.0217(2) \text{ and } c = 15.6206(2) \text{ Å}; \beta =$ $105.813(1)^{\circ}$).²⁹ The unit cell contains two crystallographically independent complexes (molecules a and b), the dimensions of which are very close to each other and nearly identical with those of the literature compound crystallized in $P2_1/n$. The crystal structure of the anionic part a is shown in Fig. 3 and the selected bond lengths and angles are listed in Table 2. The W1 atom is coordinated by one oxygen atom, O1, and four



Fig. 3 Crystal structure of the anionic part of $(Et_4N)_2[W^{IVO}(L^{COOMe})_2]$ $(W^{IVO}L^{COOMe})$ shown with 50% ellipsoids. The hydrogen atoms are omitted for clarity.

	W ^{VI} OL ^{COOMe}	W ^{IV} (OSiBuPh ₂)L ^{COOMe}
W(1)-O(1)	1.725(3)	1.835(2)
W(1) - S(1)	2.3643(6)	2.3242(9)
W(1) - S(2)	2.3720(7)	2.3428(9)
W(1)-S(3)	2.3643(6)	2.3335(9)
W(1)-S(4)	2.3720(7)	2.3297(8)
S(1) - C(1)	1.760(3)	1.766(3)
S(2) - C(2)	1.782(3)	1.772(3)
S(3) - C(7)	1.760(3)	1.757(3)
S(4) - C(8)	1.782(3)	1.773(3)
C(1) - C(2)	1.349(4)	1.329(5)
C(7) - C(8)	1.349(4)	1.344(5)
O(1) - W(1) - S(1)	107.116(16)	109.81(8)
O(1) - W(1) - S(2)	109.820(16)	110.44(8)
O(1) - W(1) - S(3)	107.116(16)	110.75(8)
S(1) - W(1) - S(3)	145.77(3)	139.44(3)

sulfur atoms, S1–S4, of the two dithiolene ligands, providing a square-pyramidal geometry with the O1 atom at the apex. The structure is isostructural with that of the molybdenum counter part, **Mo**^{IV}OL^{COOMe}.²⁴

Silvlation of the apical oxygen atom of W^{IV}OL^{COOMe} with ^tBuPh₂SiCl afforded a desoxo derivative, W^{IV}(OSiBuPh₂)L^{COOMe}. The crystal structure of the anionic part is shown in Fig. 4 and the selected bond distances and angles are listed in Table 2. The W1 atom also exhibits a square pyramidal geometry with the OSi^tBuPh₂ group at an axial position. The W1 centre is isostructural with that of its molybdenum counter part, Mo^{IV}(OSiBuPh₂)L^{COOMe.25} By the silvlation, W1-O1 bond length is elongated by ca. 0.1 Å when compared with W^{IV}OL^{COOMe} and the W1 atom is raised above the basal plane by 0.80 Å, which is somewhat larger than that of the oxoprecursor (0.75 Å). The C1–C2 and C7–C8 bond lengths (1.329(5) and 1.344(5) Å, respectively) as well as the C-S (mean value 1.77 Å) bond length clearly indicate that L^{COOMe} ligands take an ene-1,2-dithiolate form as found in all the square pyramidal [W^{IV}(OR)(L^{CH3} or L^{Ph})₂]⁻ complexes.³⁴⁻³⁹

The dioxotungsten(v₁) complex, $W^{VI}O_2L^{COOMe}$, was prepared by oxidizing $W^{IV}OL^{COOMe}$ with Me₃NO, and single crystals suitable for X-ray crystallographic analysis were obtained by

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Fig. 4 Crystal structure of the anionic part of $Et_4N[W^{IV}(OSi^FBuPh_2)(L^{COOMe})_2]$ ($W^{IV}(OSiBuPh_2)L^{COOMe}$) shown with 50% ellipsoids. The hydrogen atoms are omitted for clarity.



Fig. 5 Crystal structure of the anionic part of $(Et_4N)_2[W^{VI}O_2(L^{COOMe})_2]$ $(W^{VI}O_2L^{COOMe})$ shown with 50% ellipsoids. The hydrogen atoms are omitted for clarity.

recrystallization from acetonitrile/diethyl ether. Although two crystallographically independent complexes (molecules a and b) are found in the unit cell, the dimensions of the two complexes are very close to each other. The crystal structure of the anionic part of complex a is shown in Fig. 5 and the selected bond lengths and angles are listed in Table 3. The W1 atom is coordinated by two oxo oxygen atoms (O1 and O2) and four sulfur atoms (S1-S4) from the two dithiolene ligands. The S2-S1-S3-S4 torsion angle describing the twist of the two L^{COOMe} ligands is 95.5°, indicative of a slightly distorted octahedral geometry around the W centre. The stereochemistry is similar to those of $(Ph_4P)_2[W^{VI}O_2(L^{CN})_2]$,²² $(Et_4N)_2[W^{VI}O_2-W^{VI}$ $(L^{CH3})_2$ ³⁶ and $(Et_4N)_2[W^{VI}O_2(S_2C_5OH_6)_2]$,⁴⁰ and isostructural with the molybdenum counter part, $Mo^{VI}O_2L^{COOMe}$.²⁷ The W1-S2 and W1-S4 bond lengths (2.6074(19) and 2.626(2) Å) are longer than the W-S1 and W1-S3 lengths (2.4222(19) and 2.4332(19) Å) due to the fact that S2 and S4 are oriented *trans* to the O1 and O2 oxygen atoms. This trans influence causes dimensional differences of the coordinating two L^{COOMe}

Table 3 Selected bond lengths (Å) and angles (°) of $W^{Vl}O_2L^{COOMe}$ (molecule a)

	$W^{VI}O_2L^{COOMe}$
W(1)-O(1)	1.741(5)
W(1) - O(2)	1.735(5)
W(1)-S(1)	2.4222(19)
W(1) - S(2)	2.6074(19)
W(1) - S(3)	2.4332(19)
W(1)-S(4)	2.626(2)
S(1)-C(1)	1.756(7)
S(2) - C(2)	1.711(8)
S(3)-C(7)	1.755(8)
S(4)-C(8)	1.708(7)
C(1)-C(2)	1.355(10)
C(7)-C(8)	1.357(9)
O(1)-W(1)-O(2)	102.1(2)
O(1)-W(1)-S(1)	84.19(15)
O(1)-W(1)-S(3)	110.44(15)
S(1)-W(1)-S(3)	158.55(6)
$S(2)-S(1)-S(3)-S(4)^{a}$	95.5
$S(1)C(1)C(2)S(2)-O(5)C(5)O(6)^{b}$	84.5
$S(3)C(7)C(8)S(4)-O(9)C(11)O(10)^{b}$	82.7
$S(1)C(1)C(2)S(2)-O(3)C(3)O(4)^{b}$	3.1
$S(3)C(7)C(8)S(4)-O(7)C(9)O(8)^{b}$	1.6

^{*a*} Torsion angle. ^{*b*} Dihedral angle.

ligands. The S2-C2 (1.711(8) Å) and S4-C8 (1.708(7) Å) bonds oriented trans to O1 and O2 are shorter than the S-C bonds oriented cis to O1 and O2 (1.756(7) Å and 1.755(8) Å, respectively). In addition, the S2-C4 and S4-C8 bond lengths are shorter than the four S-C bonds (average distance, 1.77 Å) of the corresponding W^{IV}O complex, W^{IV}OL^{COOMe}, and C1-C2 and C7–C8 (1.355(10) and 1.357(9) Å) bond lengths are longer than the two C=C bonds (1.349(4) and 1.350(4) Å) in W^{IV}OL^{COOMe}. Regarding to the orientation of the methyl ester groups, the ones situated at trans to the two oxygen atoms, O1 and O2, have larger dihedral angles with respect to the chelating S-C-C-S planes (84.5° and 82.7° for S1C1C2S2-O5C5O6 and S3C7C8S4-O9C11O10, respectively), whereas smaller dihedral angles between the other -COOMe groups and the chelating S-C-C-S planes were observed (3.1° for S1C1C2S2-O3C3O4 and 1.6° for S3C7C8S4-O7C9O8). Thus, the conjugation of the ene-1,2-dithiolate ligands situated at trans positions with respect to W=O bonds is larger than those existing at *cis* position to the W=O bonds.

 $W^{VI}O(OSiBuPh_2)L^{COOMe}$ was synthesised by the oxidation of $W^{IV}(OSiBuPh_2)L^{COOMe}$ with Me₃NO. Although we were not able to obtain a single crystal of $W^{VI}O(OSiBuPh_2)L^{COOMe}$, the ¹H NMR, IR and ESI-mass spectra and elemental analysis definitely support its structure. In the ¹H NMR spectra measured in a range from 25 to -40 °C, protons of the four carbomethoxy groups appeared as one singlet peak although the singlet became somewhat broad at -40 °C, suggesting that the rearrangements of the oxo, silanolate and two L^{COOMe} ligands as well as the intramolecular SiBuPh_2-group shift between the two oxygen atoms on the octahedral metal centre are faster than the ¹H NMR timescale. The absorption spectrum has a similar profile to that of the molybdenum counterpart, Mo^{VI}O (OSiBuPh_2)L^{COOMe}, with the λ_{max} -values blue-shifted (W: 401,

463 and 628 nm *vs.* Mo: 426, 563 and 729 nm).²⁵ In **Mo^{VI}O**-(**OSiBuPh**₂)**L**^{COOMe}, the absorption bands at $\lambda_{max} = 729$ and 563 have been assigned to dithiolate ligands-to-molybdenum(vi) charge-transfer transitions.²⁵ Thus, the two bands centered at 628 and 563 nm can be assignable to dithiolate ligands-to-tungsten(vi) charge-transfer transitions. Similar blue shifts have been observed in the absorption spectra of Mo-DMSOR_{oxidised} and W-DMSOR_{oxidised}.¹⁷ The less blue-shifted band at $\lambda_{max} = 401$ nm as compared with that of the molybdenum counterpart may involve ligand-to-ligand charge transitions.

Preparation and characterization of WVIO(S)LCOOMe

We have previously reported that the oxo-sulfido-tungsten(vi) complex of L^{Ph} was produced by the reaction of 5-coordinate tungsten(v) complex, $[W^{V}O(L^{Ph})_2]^-$ with an equimolar amount of SH⁻ ion of (Et₄NSH).⁴² In this case, however, an equimolar amount of the corresponding oxo-tungsten(IV) complex, [WIVO- $(L^{Ph})_2^{2^{2-}}$, was also produced *via* disproportionation of a putative intermediate $[W^{VO}(SH)(L^{Ph})_2]^{2-}$. The targeted $W^{VI}O(S)$ complex could not be purified owing to the low solubility of the by-products, preventing us investigating the spectroscopic properties and reactivities. When W^{IV}OL^{COOMe} was treated with elemental sulfur, the disulfido-tungsten(vi) complex, $[W^{VI}O(S_2) (L^{COOMe})_2$ ²⁻ was formed as found in the reactions of $[W^{IV}O$ - $(L^{bdts})_2^{2-}$ (bdts = benzene-1,2-dithiolates),^{43,44} but the targeted compound W^{VI}O(S)L^{COOMe} was not obtained. The UV-vis spectral change of W^{IV}OL^{COOMe} was close to that of the W^{IV}O complexes with bdts. On the other hand, we found that oxo-sulfido-molybdenum(vi) complex, $[Mo^{VI}O(S)(L^{COOMe})_2]^{2-1}$ $(Mo^{VI}O(S)L^{COOMe})$ was formed from $[Mo^{VI}O(OSi^{t}BuPh_{2}) (L^{COOMe})_2$]⁻ by reaction with an equimolar amount of SH⁻, where undesirable by-products such as the Mo^{IV}O complex were not generated.²⁸ Thus, we investigated a reaction of W^{VI}O(OSi^tBuPh₂)L^{COOMe} with SH⁻ to obtain the expected $W^{VI}O(S)$ complex.

Addition of Et₄NSH in acetonitrile to an acetonitrile solution of W^{VI}O(OSiBuPh₂)L^{COOMe} at room temperature resulted in a colour change from grey to orange, which could be monitored spectroscopically. Fig. 6 shows a UV-vis spectral change observed upon addition of Et₄NSH to W^{VI}O(OSiBuPh₂)L^{COOMe}, where the absorption bands at 463 and 628 nm due to W^{VI}O(OSiBuPh₂)L^{COOMe} decrease in intensity. The final spectrum exhibiting absorption bands at λ_{max} = 437, 516 and 681 nm, was similar to that of $W^{VI}O(S)L^{Ph}$ ($\lambda_{max} = 455$, 529 and 699 nm in acetonitrile), suggesting the formation of the expected product W^{VI}O(S)L^{COOMe}. The titration plot based on the absorbance changes at 463 and 628 nm against equivalence of SH⁻ added clearly indicates that the stoichiometry of $W^{VI}O(OSiBuPh_2)L^{COOMe}$: SH⁻ is 1:2. The ESI-mass spectrum of an acetonitrile solution of $W^{VI}O(OSiBuPh_2)L^{COOMe}$ in the presence of Et4NSH exhibited a peak cluster at m/z = 774, which is consistent with the molecular formula of the oxosulfido-tungsten(vi) complex, $\{Et_4N^+ + [W^{VI}O(S)(L^{COOMe})_2]^{2-}\}^{-}$ (Fig. 7(a)). The ¹H NMR spectrum of a CD₃CN solution containing W^{VI}O(OSiBuPh₂)L^{COOMe} and 2 equiv of Et₄NSH showed



Fig. 6 (a) Spectral changes observed upon addition of 0, 1/2, 2/2, 3/2, 4/2, 5/2 equiv. of Et_4NSH to $W^{VI}O(OSiBuPh_2)L^{COOMe}$ (0.30 mM) in CH₃CN at room temperature. (b) Plots of absorbance at 463 and 628 nm against the molar ratio of [SH⁻]/[W].



Fig. 7 (a) ESI-MS and (b) ¹H NMR spectra of $W^{VI}O(S)L^{COOMe}$ formed by the reaction of $W^{VI}O(OSiBuPh_2)L^{COOMe}$ and Et₄NSH.

peaks of four methyl groups of the two L^{COOMe} ligands at 3.60, 3.61 and 3.62 ppm in a 1:2:1 integral ratio as shown in Fig. 7(b), indicating its diamagnetic nature. Appearance of such three different methyl signals can be explained by the formation of oxo-sulfido tungsten(vi) complex with an octahedral geometry, where two of the four methyl groups of the two

ligands are oriented *trans* to each other whereas one of the remaining two methyl groups is situated in the *trans* position to the oxo group and the other methyl group is located at *trans* to the sulfido group. Taking into account a fact that the four methyl groups of the two L^{COOMe} ligands of W^{VI}O(OSiBuPh₂)-L^{COOMe} appeared as one singlet peak, rates of the ligand rearrangements on the octahedral metal centre of WO(S)-L^{COOMe} is slower than that of W^{VI}O(OSiBuPh₂)L^{COOMe}. On the basis of these spectroscopic data (UV-vis, ESI-mass and ¹H NMR spectra), we concluded that oxo-sulfido-tungsten(vi) complex of L^{COOMe}, W^{VI}O(S)L^{COOMe}, was generated by the treatment of W^{VI}O(OSiBuPh₂)L^{COOMe} with SH⁻.

Judging from the observed stoichiometry of WVIO- $(OSiBuPh_2)L^{COOMe}: SH^- = 1:2$, the formation mechanism of W^{VI}O(S)L^{COOMe} from W^{VI}O(OSiBuPh₂)L^{COOMe} can be drawn as follows. Ligand substitution of the -OSiBuPh₂ group with SH⁻ may take place on the tungsten(vi) centre of W^{VI}O(OSiBuPh₂)- L^{COOMe} to give $W^{VI}O(SH)L^{COOMe}$. Then, the second SH⁻ ion works as a base to abstract proton from the W-SH unit to give the final product W^{VI}O(S)L^{COOMe}. In spite of our great efforts, W^{VI}O(S)L^{COOMe} could not be isolated, but the monooxo-tungsten(v) complex, $W^{IV}OL^{COOMe}$, was obtained, when the solution was concentrated. Intramolecular reactions may proceed under concentrated conditions to give W^{IV}OL^{COOMe} together with elemental sulfur. Some $M^{VI}O(S)$ complexes (M = Mo and W) with a neutral charge have been reported to dimerise into M^V-S-S-M^V species by an intermolecular redox reaction.⁴⁵ The five coordinate structure of W^{IV}OL^{COOMe} is stabilized by its dianionic charge whereas a five coordinate structure of the M^{IV} complexes formed by dissociation of the sulfur atom is less stable due to its high Lewis acidic character.

Resonance Raman spectrum (rR) of $\mathbf{W^{VIO}(S)L^{COOMe}}$ generated *in situ* was measured in CD₃CN using an Ar⁺ ion laser at $\lambda_{ex} = 363.8 \text{ nm}$ (Fig. 8). In a region from 400 to 1000 cm⁻¹, two bands appeared at 899 and 449 cm⁻¹. The band at 899 cm⁻¹ is assignable to $\nu(W=O)$ stretch whereas that at 449 cm⁻¹ can be assigned to $\nu(W=S)$ stretch based on a comparison with those of $\mathbf{W^{VIO}(S)L^{Ph}}$ (865 and 465 cm⁻¹).⁴² In addition, two bands appeared at 1477 and 1509 cm⁻¹ in a region from 1000 to 1600 cm⁻¹ upon formation of $\mathbf{W^{VIO}(S)L^{COOMe}}$, which could be

Fig. 8 Resonance Raman spectrum (363. 8 nm excitation) of $W^{VI}O(S)L^{COOMe}$ formed by the reaction of $W^{VI}O(OSiBuPh_2)L^{COOMe}$ and Et_4NSH in CD₃CN. Asterisks indicate solvent peaks.

Raman shift / cm⁻¹

800

600

400

1200 1000

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Fig. 9 DFT optimised structures of $W^{VI}O(S)L^{COOMe}$ (left) and $W^{VI}O_2L^{COOMe}$ (right) calculated at the (U)B3LYP level of theory.

assigned to the ν (C==C) stretches of the inequivalent dithiolate ligands.

In order to obtain structural information for $W^{VI}O(S)$ -L^{COOMe}, DFT calculations at the (U)B3LYP level of theory were performed using the X-ray crystal structure of $W^{VI}O_2L^{COOMe}$ as a starting point for structural optimization.⁴⁶ The optimized structure of $W^{VI}O(S)L^{COOMe}$ is given in Fig. 9 together with that of $W^{VI}O_2L^{COOMe}$. The tungsten centre exhibits a distorted octahedron as in the case of WO_2L^{COOMe} . The W=S bond length of 2.24 Å is comparable to those of the six-coordinate oxo-sulfidotungsten(vı) complexes with hydrotris(3,5-dimethyl-pyrazolyl)borate (2.102(5)–2.132(5) Å)^{47,48} and phenanthroline derivatives (2.222(2) Å).⁴⁹

Comparison of atom transfer reactivity of $W^{VI}O(S)L^{COOMe}$ with the molybdenum counterpart

The atom transfer reaction from W^{VI}O(S)L^{COOMe} to triphenylphosphine derivatives was investigated. In a preparative scale reaction, $W^{VI}O(S)L^{COOMe}$ reacted with $P(p-CH_3-C_6H_4)_3$ in acetonitrile at room temperature. The ¹H NMR and GC-MS analyses of the product obtained after the extraction revealed that S= $P(p-CH_3-C_6H_4)_3$ was formed almost quantitatively. In this reaction, the oxygen atom transfer product $O = P(p-CH_3-C_6H_4)_3$ was not produced at all (see Experimental section). Further, $S=P(p-CH_3-C_6H_4)_3$ was not obtained by a reaction of Et_4NSH with $P(p-CH_3-C_6H_4)_3$ under the same conditions. The result clearly demonstrated that the terminal sulfide group is more reactive than the terminal oxo group as shown in Scheme 1. Indeed, $W^{VI}O_2L^{COOMe}$ was intact in the presence of a large excess amount of $P(C_6H_5)_3$ (1000 equiv.) although $W^{VI}O_2L^{CN}$ transfers the one oxygen atom to Ph₃P.⁴¹ The less oxygen atom transfer reactivity of W^{VI}O₂L^{COOMe} is reflected by the smaller ν (W=O) stretching values (894 and 855 cm⁻¹) in comparison to those of $W^{VI}O_2L^{CN}$ (906 and 860 cm⁻¹).²²

Then, the sulfur transfer reaction was followed by UV-vis spectroscopy. Fig. 10(a) shows a typical example of the UV-vis spectral change of the reaction between $W^{VI}O(S)L^{COOMe}$ and $P(C_6H_5)_3$ in acetonitrile at 0 °C. Upon addition of 20 equiv. of $P(C_6H_5)_3$ to $W^{VI}O(S)L^{COOMe}$ in acetonitrile, the absorption bands at 435 and 663 nm due to $W^{VI}O(S)L^{COOMe}$ decreased in intensity, keeping an isosbestic point at 585 nm. The λ_{max} and ε values of the final spectrum were identical with those of $W^{IV}OL^{COOMe}$, indicating that $W^{VI}O(S)L^{COOMe}$ exhibited a clean sulfur atom transfer reactivity. The decay of the absorption band at 435 nm due to $W^{VI}O(S)L^{COOMe}$ obeyed first-order

1477

1509

1600 1400



Scheme 1 Sulfur atom transfer from $M^{VI}O(S)L^{COOMe}$ (M = Mo and W) to P(p-X-C₆H₄)₃ (X = OMe, Me, H, F, Cl).



Fig. 10 Time dependent UV-vis spectral changes observed upon addition of Ph₃P (20 equiv.) to **W^{VI}O(S)L**^{COOMe} (0.1 mM) in CH₃CN at 0 °C. Inset shows the first-order plot based on the decay of absorption at 435 nm. (b) Plot of k_{obs} vs. [Ph₃P].

4 6

kinetics as shown in the inset of Fig. 10(a). The apparent firstorder rate constant kobs exhibited first-order dependence on the concentration of $P(C_6H_5)_3$ (Fig. 10(b)). Thus, the sulfur atom transfer reaction can be expressed by the second-order rate law of $v = k_2 [\mathbf{W^{VI}O(S)L^{COOMe}}] [P(C_6H_5)_3]$, where k_2 was calculated to be 1.1 M⁻¹ s⁻¹. The sulfur atom transfer reactions from $W^{VI}O(S)L^{COOMe}$ to para-substituted $P(p-X-C_6H_4)_3$ (X = OMe, Me, F, Cl) were also examined kinetically under the same experimental conditions and the rate constants were determined as 6.3 for OMe, 1.7 for Me, 4.1 for F and 4.7 $M^{-1} s^{-1}$ for Cl, respectively (Fig. S1[†]).

The results clearly indicate that the reactivity of the *p*-substituted triphenylphosphine derivatives are relatively similar,

even though there is a tendency that the reactivity of the substrate slightly increases in going from H to Me to OMe, and that the rate constant also slightly increases in going from H to F to Cl. Such a kinetic behavior may indicate that the reaction involves two steps; (i) reversible addition of the phosphorous atom of the substrate to the terminal sulfide atom of WVIO-(S) L^{COOMe} to give intermediate A (k_a and k_{-a} processes) and (ii) dissociation of the product $S = P(p-X-C_6H_4)_3$ from intermediate A (k_d process) as shown in Scheme 2. In such a case, the kinetic equation can be written as:

$$\nu = k_{d} [\mathbf{M}^{\mathbf{VI}} \mathbf{O}(\mathbf{S}) \mathbf{L}^{\mathbf{COOMe}}]_{\mathrm{T}} [\mathbf{P}(p \cdot \mathbf{X} - \mathbf{C}_{6} \mathbf{H}_{4})_{3}] / (K + [\mathbf{P}(p \cdot \mathbf{X} - \mathbf{C}_{6} \mathbf{H}_{4})_{3}])$$
(1)

where $K = (k_{-a} + k_d)k_a$.

In the case of M = W (tungsten), the apparent first-order rate constant k_{obs} , which is equal to $k_d [P(p-X-C_6H_4)_3]/$ $(K + [P(p-X-C_6H_4)_3])$, showed a linear dependence on the substrate concentration $[P(p-X-C_6H_4)_3]$. Thus, it can be regarded that K, which is equal to $(k_{-a} + k_d)k_a$, is much larger than $[P(p-k_a)k_a]$ $X-C_6H_4)_3$], simplifying the equation as:

$$k_2 = k_d/K = k_a k_d/(k_{-a} + k_d)$$
 (2)

Apparently, both the addition of phosphine to the sulfur atom (k_a process) and the dissociation of the product (k_d process) contribute to the reaction rate k_2 , and the electronic (electron-donating and electron-withdrawing) nature of the *p*-substituents (X) affect oppositely to the k_a and k_d processes, thus canceling out the electronic effects of X on the overall reaction rate. This may be the reason why the second-order rate constant k_2 are nearly the same among the series of substrates. The Eyring plot for the sulfur transfer to P(p-Cl-C₆H₄)₃ $(k_2 = 3.8, 4.7, 5.7 \text{ and } 7.4 \text{ M}^{-1} \text{ s}^{-1} \text{ at } 268, 273, 278 \text{ and } 283 \text{ K},$ respectively) gave the activation parameters of $\Delta H^{\dagger} = 6.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -33$ cal K^{-1} mol^{-1} (Fig. S2[†]). Such a negative activation entropy is consistent with the contribution of the association process k_a .

On the other hand, the sulfur atom transfer reaction from the isostructural molybdenum complex Mo^{VI}O(S)L^{COOMe} to $P(p-X-C_6H_4)_3$ was examined at lower temperature (-20 °C), since internal redox reaction of the complex occurred at 0 °C to give Mo^{IV}OL^{COOMe} and elemental sulfur as mentioned above.²⁸ In contrast to the tungsten system, all the reactions exhibited saturation kinetics as in the case of the reaction with $P(C_6H_5)_3$ reported previously.²⁸ This clearly indicates that the

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Scheme 2 Reaction mechanism for sulfur atom transfer from $M^{VI}O(S)L^{COOMe}$ (M = Mo and W) to P(p-X-C₆H₄)₃ (X = OMe, Me, H, F, CI).



Fig. 11 Hammett plot for the sulfur atom transfer of $Mo^{VI}O(S)L^{COOMe}$ to $P(\textit{p-X-C}_6H_4)_3.$

dissociation step (k_d) becomes rate-limiting in the presence of a large excess of the substrate ($K \ll [P(p-X-C_6H_4)_3]$). Thus, the double reciprocal plots of k_{obs}^{-1} against the substrate concentration [P(p-X-C₆H₄)₃] (Fig. S3†) gave the k_d values as the intercepts: $k_d = 1.2 \times 10^{-2}$ for OMe, 1.3×10^{-2} for Me, 1.7×10^{-2} for H, 1.8×10^{-2} for F and 2.1×10^{-2} s⁻¹ for X = Cl, respectively. In this case, the k_d value increased as the p-substituent X became more electron-withdrawing, and the plot of log k_d at -20 °C against the Hammett constant σ gave a positive correlation with a slope of $\rho = +0.48$ as indicated in Fig. 11. This result is consistent with the mechanism that the dissociation of the product S=P(p-X-C₆H₄)₃ from the adduct intermediate **A** is the rate-determining step in the molybdenum system, since the electron-withdrawal may enhance the Mo–S cleavage in intermediate **A**.

To compare the sulfur atom transfer reactivity between the tungsten and the molybdenum systems, the second order rate constant, k_2 , at -20 °C for the reaction of $W^{IVO}(S)L^{COOMe}$ with $P(p\text{-}Cl-C_6H_4)_3$ was estimated to be 1.7 M⁻¹ s⁻¹ from the extrapolation of the Eyring plot shown in Fig. S3.[†] For the reaction of $Mo^{VI}O(S)L^{COOMe}$ with $P(p\text{-}Cl-C_6H_4)_3$, the k_2 values at -20 °C was estimated to be 15.4 M⁻¹ s⁻¹ as the slope of the initial linear portion of the saturation curve as shown in Fig. S4.[†] As a result, it became clear that the Mo-complex is more reactive by about one-order of magnitude as compared with the W-complex, which may reflect the higher electrophilicity of the sulfide group in the Mo-complex as compared with that in the W-complex.

Comparison of properties of $W^{VI}O(S)L^{COOMe}$ and AOR tungsten centre

The oxo-sulfidobis(dithiolene)tungsten(vi) complex exhibits some similarities in the structure and reactivity to the tungsten centre of AOR family of tungsten enzymes. WVIO(S)LCOOMe exhibits a W=S bond distance of 2.23 Å in the DFT calculations, which is close to the distance between the tungsten and ambiguously assigned terminal monodentate atoms in the reaction centre of the active AOR family.³ Thus, the terminal monodentate atom of the reaction centre in the enzyme can be assigned to a sulfur atom. The observation of inequivalent dithiolene units of W^{VI}O(S)L^{COOMe} (1509 and 1477 cm⁻¹) in the rR spectrum also mimics the appearance of the two independent ν (C=C) stretches in AOR (1595 and 1576 cm⁻¹).⁵⁰ The selective sulfur atom transfer from W^{VI}O(S)L^{COOMe} to triphenylphosphines indicating that the sulfido group works as a good electrophile. The relevant frontier molecular orbitals of WVIO(S)LCOOMe are shown in Fig. 12, and the fragment orbital contributions to these MO's are listed in Table 4. The S (sulfido) character is significant in the LUMO orbital, occupying 34.5% of the orbital. On the other hand, the orbital has only 1.37% of contribution of the oxo group. This calculation strongly supports the sulfido group functions as good electrophiles for the selective sulfur atom transfer. In the AOR family, dioxo-molybdenum(vi) centre is an inactive form, which is well explained by the small contributions of the two oxo groups into the LUMO orbital of $W^{VI}O_2L^{COOMe}$ (1.41% × 2). Thus, our present results strongly suggest that the sulfido group on the tungsten(vi) centre in the AOR family also works as a good electrophile (hydride acceptor) to include the aldehyde oxidation in the enzyme.

Conclusions

In this study, we have synthesised and characterised a series of new bis(ene-1,2-dithiolato)tungsten complexes coordinated with the L^{COOMe} ligand which have enabled a systematic study of the effects of the additional monodentate ligand such as oxo, sulfide and silanolate groups on the geometry and electronic structure of the complexes. This successful preparation suggests that electronic effects of the dithiolene ligand are similar to those of the pyranopterin cofactor ligand in the molybdenum enzymes. By comparing the physicochemical



Fig. 12 Frontier Kohn–Sham orbitals for W^{VI}O₂L^{COOMe} and W^{VI}O(S)L^{COOMe}.

 Table 4
 The contributions (%) of terminal oxo and sulfido groups to each molecular orbital

	W ^{VI} O ₂ L ^{COOMe} Oxo group (%)	W ^{VI} O(S)L ^{COOMe}	
		Oxo group (%)	Sulfido group (%)
LUMO + 1	5.34	3.77	2.32
LUMO	1.41	0.27	34.45
HOMO	1.54	1.37	14.04
HOMO – 1	1.50	2.59	8.18

properties and reactivity of the tungsten complexes with those of the known isostructural molybdenum counterparts, the effects of the metal center has also been explored. The crystal-lographic data have indicated the presence of π -delocalization between the W^{VI}O₂ and L^{COOMe} units in W^{VI}O₂L^{COOMe} whereas a lesser contribution of π -delocalization is involved between the W^{IV}O or W^{IV}(OSiBuPh₂) and L^{COOMe} ligands. This may be due to the greater W^{VI}–S bond covalency in W^{VI}O₂L^{COOMe} as compared with the W^{IV}–O bond in W^{IV}OL^{COOMe} and W^{IV}(OSiBuPh₂)L^{COOMe}.

 $W^{VI}O(S)L^{COOMe}$ has been successfully prepared from $W^{VI}O(OSiBuPh_2)L^{COOMe}$ and Et_4NSH . $W^{VI}O(S)L^{COOMe}$ is thermally stable at room temperature whereas its molybdenum counterpart, $Mo^{VI}O(S)L^{COOMe}$, is changed to $Mo^{IV}OL^{COOMe}$ and elemental sulfur above –20 °C. This fact is consistent with that

AOR family of a tungsten enzyme is found in hyperthermophilic archaea that thrive near 100 °C whereas molybdenum enzymes containing an oxo-sulfido-molybdenum(vi) centre do not exist in such environments. The rR spectrum of $W^{VI}O(S)$ - $\mathbf{L}^{\text{COOMe}}$ has also shown the inequivalence of the two $\mathbf{L}^{\text{COOMe}}$ ligands with respect to their bonding interactions with the tungsten centre. Sulfur atom transfer from W^{VI}O(S)L^{COOMe} to triphenylphosphines occurred selectively, where kinetic studies have suggested that the reaction consists of two steps; addition of the phosphine to the sulfur atom of the tungsten centre producing a W^{IV} -S-PAr₃ type intermediate A and then the W–S bond breaking occurs to release the S=PAr₃ product. The reactivity of W^{VI}O(S)L^{COOMe} is slower than that of Mo^{VI}O-(S)L^{COOMe} by about one-order of magnitude, which can be attributed to the higher electrophilicity of Mo=S as compared with W=S. This kinetically favorable reactivity for the sulfur atom transfer of the molybdenum complex may make molybdenum enzymes advantageous to occur in a wider range of organisms. On the other hand, it is suggested that nature has developed tungsten systems in extremophiles by the thermal and kinetic stability of oxo-sulfido-tungsten(vi) sites. Also, the present results will provide important insights into the reaction mechanism of the reaction cycle as well as spectroscopic properties of the reaction centres in the molybdenum and tungsten enzymes.

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References

- 1 R. H. Holm, P. Kennepohl and E. I. Solomon, *Chem. Rev.*, 1996, **96**, 2239.
- 2 R. Hille, Chem. Rev., 1996, 96, 2757.
- 3 M. K. Johnson, D. C. Rees and M. W. W. Adams, *Chem. Rev.*, 1996, **96**, 2817.
- 4 H. Schindelin, C. Kisker, J. Hilton, K. V. Rajagopalan and D. C. Rees, *Science*, 1996, 272, 1615.
- J. Stewart, S. Bailey, B. Bennett, J. M. Charnock, C. D. Garner and A. S. McAlpine, *J. Mol. Biol.*, 2000, 299, 593.
- 6 J. C. Boyington, V. N. Gladyshev, S. V. Khangulov, T. C. Stadtman and P. D. Sun, *Science*, 1997, **275**, 1305.
- 7 H. C. A. Raaijimakers and M. J. Romao, *J. Biol. Inorg. Chem.*, 2006, **11**, 1261.

- 8 H. Raaijimakers, S. Macieira, J. M. Dias, S. Teixeira, S. Bursakov, R. Huber, J. J. G. Moura, I. Moura and M. J. Romao, *Structure*, 2002, **10**, 1261.
- 9 T. Conrads, C. Hemann, G. N. George, I. J. Pickering, R. C. Prince and R. Hille, *J. Am. Chem. Soc.*, 2002, 124, 11276.
- 10 J. H. Enemark, J. J. A. Cooney, J.-J. Wang and R. H. Holm, *Chem. Rev.*, 2004, **104**, 1175.
- 11 J. McMaster, J. M. Tunney and C. D. Garner, *Prog. Inorg. Chem.*, 2004, **52**, 539.
- 12 H. Sugimoto and H. Tsukube, Chem. Soc. Rev., 2008, 37, 2609.
- 13 F. J. Hine, A. J. Taylor and C. D. Garner, *Coord. Chem. Rev.*, 2010, 254, 1570.
- 14 C. Schulzke, Eur. J. Inorg. Chem., 2011, 1189.
- 15 R. H. Holm, E. I. Solomon, A. Majumdar and A. Tenderholt, *Coord. Chem. Rev.*, 2011, 255, 993.
- 16 E. S. Davies, R. L. Beddoes, D. Collison, A. Dinsmore, A. Docrat, J. A. Joule, C. R. Wilson and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1997, 3985.
- 17 E. S. Davies, G. M. Aston, R. L. Beddoes, D. Collison, A. Dinsmore, A. Docrat, J. A. Joule, C. R. Wilson and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1998, 3647.
- 18 H. Sugimoto, M. Harihara, M. Shiro, K. Sugimoto, K. Tanaka, H. Miyake and H. Tsukube, *Inorg. Chem.*, 2005, 44, 6386.
- 19 H. Sugimoto, T. Sakurai, H. Miyake, K. Tanaka and H. Tsukube, *Inorg. Chem.*, 2005, 44, 6927.
- 20 H. Tano, R. Tajima, H. Miyake, S. Itoh and H. Sugimoto, *Inorg. Chem.*, 2008, **47**, 7465.
- 21 S. K. Das, P. K. Chaudhury, D. Biswas and S. Sarkar, J. Am. Chem. Soc., 1994, **116**, 9061.
- 22 S. K. Das, D. Biswas, R. Maiti and S. Sarkar, J. Am. Chem. Soc., 1996, 118, 1387.
- 23 A. Majumdar, K. Pal, K. Nagarajan and S. Sarkar, *Inorg. Chem.*, 2007, **46**, 6136.
- 24 D. Coucouvanis, A. Hadjikyriacou, A. Toupadakis, S. M. Koo, O. Ileperuma, M. Draganjac and A. Salifoglou, *Inorg. Chem.*, 1991, 30, 754.
- 25 H. Sugimoto, S. Tatemoto, K. Suyama, H. Miyake, R. P. Mtei, S. Itoh and M. L. Kirk, *Inorg. Chem.*, 2010, **49**, 5368.
- 26 H. Sugimoto, H. Tano, K. Suyama, T. Kobayashi, H. Miyake, S. Itoh, R. P. Mtei and M. L. Kirk, *Dalton Trans.*, 2011, 40, 1119.
- 27 H. Sugimoto, S. Tatemoto, K. Suyama, H. Miyake, S. Itoh, C. Dong, J. Yang and M. L. Kirk, *Inorg. Chem.*, 2009, 48, 10581.

- 28 H. Sugimoto, S. Tatemoto, K. Toyota, M. Kubo, T. Ogura and S. Itoh, *Chem. Commun.*, 2012, DOI: 10.1039/ c2cc35345h, Advanced View.
- 29 A. Mallard, C. Simmonnet-Jegat, H. Lavanant, J. Marrot and F. Secheresse, *Transition Met. Chem.*, 2007, **33**, 143.
- 30 R. P. Parg, J. D. Kilburn, M. C. Petty, C. Pearson and T. G. Ryan, *Synthesis*, 1994, 613.
- 31 A. Roodt, S. S. Basson and J. G. Leipoldt, *Polyhedron*, 1994, 13, 599.
- 32 SIR2008: M. Burla, R. Caliandro, M. Camalli, B. Carrozzini, C. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi and R. Spagna, 2007.
- 33 Crystal Structure 3.8: Crystal Structure Analysis Package, Rigaku Corporation, 9009 New Trails Dr., The Woodlands, TX 77381, USA, 2000–2006.
- 34 K.-M. Sung and R. H. Holm, Inorg. Chem., 2000, 39, 1275.
- 35 K.-M. Sung and R. H. Holm, J. Am. Chem. Soc., 2001, 123, 1931.
- 36 K.-M. Sung and R. H. Holm, *Inorg. Chem.*, 2001, 40, 4518.
- 37 J. Jiang and R. H. Holm, Inorg. Chem., 2004, 43, 1302.
- 38 J. Jiang and R. H. Holm, Inorg. Chem., 2005, 44, 1068.
- 39 J. Wang, C. Tessier and R. H. Holm, *Inorg. Chem.*, 2006, 45, 2979.
- 40 H. Sugimoto and K. Sugimoto, *Inorg. Chem. Commun.*, 2008, **11**, 77.
- 41 G. C. Tucci, J. P. Donahue and R. H. Holm, *Inorg. Chem.*, 1998, 37, 1602.
- 42 H. Sugimoto, H. Tano, R. Tajima, H. Miyake, H. Tsukube, H. Ohi and S. Itoh, *Inorg. Chem.*, 2007, **46**, 8460.
- 43 H. Sugimoto, R. Tajima, T. Sakurai, H. Ohi, H. Miyake, S. Itoh and H. Tsukube, *Angew. Chem., Int. Ed.*, 2006, 45, 3520.
- 44 H. Sugimoto, H. Tano, K. Toyota, R. Tajima, H. Miyake, I. Takahashi, S. Hirota and S. Itoh, *J. Am. Chem. Soc.*, 2010, 132, 8.
- 45 C. J. Doonan, D. J. Nielsen, P. D. Smith, J. M. White, G. N. George and C. G. Young, *J. Am. Chem. Soc.*, 2006, **128**, 305.
- 46 Gaussian 03, R. C. G., Inc., Pittsburgh, PA, 2003, Inc (full reference is given in ESI[†]).
- 47 A. A. Eagle, S. M. Harben, E. R. T. Tienk and C. G. Young, J. Am. Chem. Soc., 1994, 116, 9749.
- 48 A. A. Eagle, E. R. T. Tienk, G. N. George and C. G. Young, *Inorg. Chem.*, 2001, 40, 4563.
- 49 M. Miao, M. W. Willer and R. H. Holm, *Inorg. Chem.*, 2000, 39, 2843.
- 50 M. K. Johnson, Prog. Inorg. Chem., 2004, 52, 213.