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Reaction of [Cp*₂W₂O₅] with mercaptocarboxylic acids: addition rather than reduction. Isolation and characterization of Cp*WO₂(SCH₂CH₂COOH)

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Summary

The reaction of $\text{Cp}^*\text{W}_2\text{O}_5$ with $\text{HS}(\text{CH}_2)_n\text{COOH}$ ($n = 1, 2$) in MeOH or in CH_2Cl_2 solutions at room temperature proceeds in a slightly different way: for $n = 2$, the reaction selectively yields compound $\text{Cp}^*\text{WO}_2(\text{SCH}_2\text{CH}_2\text{CO}_2\text{H})$, which has been isolated and characterized by elemental analysis, NMR and single crystal X-ray diffraction. The reaction is equilibrated, being shifted to the product by absorption of water by anhydrous Na_2SO_4 in CH_2Cl_2 , and to the reactants by addition of water. Contrary to the Mo analogue, no products resulting from metal reduction are obtained. The corresponding reaction for $n = 1$ occurs similarly at low substrate/W ratios (<0.5), but proceeds further to several uncharacterized products for greater substrate amounts. The primary product could not be isolated, but its ^1H NMR spectrum suggests a different, asymmetric structure.

Keywords

Tungsten, oxido ligands, high-oxidation state organometallics, alkylsulfido ligands, pentamethylcyclopentadienyl ligands.

Introduction

High oxidation state organometallic chemistry has long attracted attention, particularly for its potential in oxidation catalysis [1-4]. We have explored for some time the chemistry of half-sandwich complexes of the heavier Group 6 metals Mo and W in high oxidation states [5-13] and recently reported on the activity of the dinuclear oxido complexes $\text{Cp}^*_2\text{M}_2\text{O}_5$ (M = Mo, W) as precatalysts in the oxidation of thiophene derivatives to sulfoxides and sulfones [14], and in cyclooctene epoxidation [15, 16]. Most of the studies have been centered on the molybdenum system because of its more straightforward preparation, but we have recently developed an improved and convenient synthesis of the tungsten compound [17] and have thus renewed our attention to this system, since its catalytic performance in oxidation processes appears to be far superior to that of the Mo congener, at least under certain conditions [14, 16].

A few years ago, we have reported on the interaction between $[\text{Cp}^*_2\text{Mo}_2\text{O}_5]$ and mercaptocarboxylic acids, $\text{HS}(\text{CH}_2)_n\text{COOH}$ ($n = 1$, mercaptoacetic or thioglycolic acid [18]; $n = 2$, mercaptopropionic acid [19]), which resulted in the isolation and characterization of dinuclear Mo^{IV} products, $[\text{Cp}^*_2\text{Mo}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{COO})_2]$ in the first case and $[\text{Cp}^*_2\text{Mo}_2(\mu\text{-O})(\mu\text{-SCH}_2\text{CH}_2\text{COO})_2]$ in the latter. One of the reasons for investigating the interaction of these substrates, in particular the thioglycolic acid, with the Mo^{VI} complex was as model for the action of cysteine in molybdenum hydroxylase enzymes [20]. In these reactions, the mercaptocarboxylic acid exerts three simultaneous functions: reducing agent, ligand, and (limited to the $n = 1$ case) substrate for the reductive cleavage of the S-C bond, leading to the incorporation of the sulphur atom in the isolated product as a bridging sulfido ligand. We have now extended these studies to the analogous W system, since the bioinorganic chemistry

of W^{VI} with sulphur donor ligands is also of interest [21], and report the results of this investigation in the present contribution.

Experimental Section

General procedures. All preparations and manipulations were carried out with Schlenk techniques under an oxygen-free argon atmosphere. All glassware was oven-dried at 120°C. Solvents were dried by standard procedures and distilled under dinitrogen prior to use. 1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker DPX 300 and ARX 250 instruments. Chemical shifts are expressed in ppm downfield from Me_4Si . Coupling constants are given in Hertz. The starting compound, $[Cp^*_2W_2O_5]$, was prepared as described in the literature [17]. The compounds 3-mercaptopropionic acid (99%, ACROS) and 2-mercaptoacetic acid (98%, Fluka) were used as received.

Preparation of $[Cp^*WO_2(SCH_2CH_2COOH)]$. To a solution of $Cp^*_2W_2O_5$ (100 mg, 0.14 mmol) in 10 mL MeOH was added 3-mercaptopropionic acid (23 μ L, 0.28 mmol). The solution stirred at room temperature for 24 hours. The reaction mixture was then evaporated to dryness leaving an oily pale-yellow residue, which was washed with 5x3 mL of pentane. The product was then crystallized from CH_2Cl_2 /pentane as white crystals. Yield: 96 mg (81.6 %). Elem. Anal.: C, 34.40; H, 4.10%. Calcd for $C_{13}H_{20}O_4SW$ (MW 456.201 $g\ mol^{-1}$): C, 34.23; H, 4.42%. 1H NMR ($CDCl_3$): δ 3.51 (t, 2H, $J = 7.1$ Hz, CH_2), 2.84 (t, 2H, $J = 7.1$ Hz, CH_2), 2.21 (s, 15H, Cp^*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 175.0 (COOH); 119.6 (Cp^* , C_{ring}); 34.9 (CH_2); 31.9 (CH_2); 10.9 (Cp^* , $-CH_3$).

1H NMR monitoring of the reaction between $Cp^*_2W_2O_5$ and $HSCH_2CH_2COOH$.
(a) In CD_3OD . In an NMR tube, compound $Cp^*_2W_2O_5$ (10 mg, $1.4 \cdot 10^{-2}$ mmol) was dissolved in CD_3OD (0.5 mL) and to the resulting solution was added 3-mercaptopropionic acid (2.3

μL , $2.8 \cdot 10^{-2}$ mmol). ^1H NMR spectra of the resulting solution were taken immediately, after 4 hours and after 1 day (see Results and Discussion section).

(b) In CH_2Cl_2 . In a Schlenk tube, compound $\text{Cp}^*\text{W}_2\text{O}_5$ (177 mg, 0.246 mmol) was dissolved in CH_2Cl_2 (15 mL). To this solution was added anhydrous Na_2SO_4 (1.5 g) and subsequently 3-mercaptopropionic acid (40 μL , 0.49 mmol). The solution was stirred at room temperature for 18 h, then the solid Na_2SO_4 was filtered off and the solution dried under vacuum. The residue was used for an NMR investigation in CDCl_3 , showing the complete conversion to compound $\text{Cp}^*\text{WO}_2(\text{SCH}_2\text{CH}_2\text{COOH})$ (NMR properties identical to the authentic sample described above). To this solution in the NMR tube, a drop of D_2O was subsequently added and the solution monitored by ^1H NMR (see Results and Discussion section).

^1H NMR monitoring of the reaction between $\text{Cp}^*\text{W}_2\text{O}_5$ and HSCH_2COOH . **(a) In CD_3OD .** In a NMR tube, $\text{Cp}^*\text{W}_2\text{O}_5$ (11.1 mg, $1.54 \cdot 10^{-2}$ mmol) was dissolved in CD_3OD (0.5 mL). Then thioglycolic acid was added in five incremental portions of 0.5 μL ($0.71 \cdot 10^{-2}$ mmol). After each addition, the progress of the reaction was monitored by ^1H NMR.

(b) In CDCl_3 . In a NMR tube, $\text{Cp}^*\text{W}_2\text{O}_5$ (13.1 mg, $1.82 \cdot 10^{-2}$ mmol) was dissolved in CDCl_3 (0.5 mL) and to the resulting solution was added thioglycolic acid (2.5 μL , $3.64 \cdot 10^{-2}$ mmol). ^1H NMR spectra of the resulting solution were recorded immediately, after 1 h 45 min and after 4 h (see Results and Discussion section).

X-ray diffraction study. A single crystal of the compound was mounted under inert perfluoropolyether on the tip of glass fibre and cooled in the cryostream of the Oxford-Diffraction XCALIBUR CCD diffractometer. Data were collected using the monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$). The structure was solved by direct methods (SIR97) [22] and refined by least-squares procedures on F^2 using SHELXL-97 [23]. All H atoms attached to carbon and oxygen (OH) were introduced in calculation in idealised positions and treated as

riding on their parent atoms. The value of the Flack's parameter, 0.25(1), indicates the occurrence of a twin by inversion. The drawing of the molecules was realised with the help of ORTEP32 [24]. Crystal data and refinement parameters are shown in Table 1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 795729. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

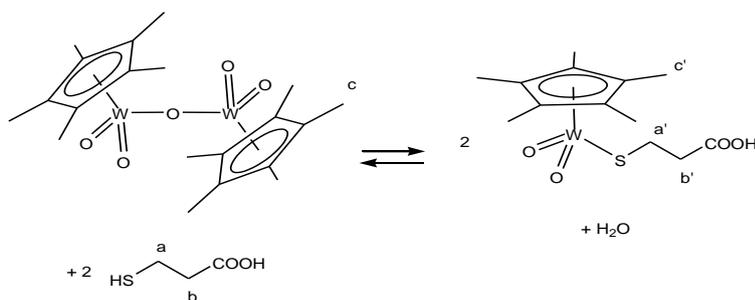
Table 1. Selected crystallographic and refinement parameters for compound [Cp*WO₂(SCH₂CH₂COOH)].

Identification code	Cp*WO₂(SCH₂CH₂COOH)	
Empirical formula	C ₁₃ H ₂₀ O ₄ S W	
Formula weight	456.20	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n a 2 ₁	
Unit cell dimensions	a = 15.223(3) Å	α = 90°.
	b = 8.8749(18) Å	β = 90°.
	c = 11.337(2) Å	γ = 90°.
Volume	1531.6(5) Å ³	
Z	4	
Density (calculated)	1.978 Mg/m ³	
Absorption coefficient	7.685 mm ⁻¹	
F(000)	880	
Crystal size	0.462 x 0.318 x 0.231 mm ³	
Theta range for data collection	2.66 to 30.03°.	
Index ranges	-21 ≤ h ≤ 21, -12 ≤ k ≤ 8, -15 ≤ l ≤ 15	
Reflections collected	14393	
Independent reflections	4444 [R(int) = 0.0323]	
Completeness to theta = 30.00°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0 and 0.28413	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4444 / 1 / 179	
Goodness-of-fit on F ²	1.026	
Final R indices [I > 2σ(I)]	R1 = 0.0254, wR2 = 0.0583	
R indices (all data)	R1 = 0.0316, wR2 = 0.0612	
Absolute structure parameter	0.25(1)	
Largest diff. peak and hole	2.410 and -2.113 e.Å ⁻³	

Results and Discussion

(a) Mercaptopropionic acid

The reaction between $\text{Cp}^*_2\text{W}_2\text{O}_5$ and $\text{HSCH}_2\text{CH}_2\text{COOH}$ proceeded as shown in Scheme 1. The product was isolated in good yields from the reaction run in methanol. It was characterized by NMR spectroscopy, elemental analysis, and by an X-ray structural determination (*vide infra*). However, a ^1H NMR monitoring of the reaction in CD_3OD showed an incomplete conversion, see Figure 1. The spectrum of the free thiol, Figure 1 (I), shows the COOH proton position averaged with that of the solvent by fast exchange. The immediate NMR analysis after mixing yields spectrum (II), featuring essentially the mixture of the two reagents (Cp^* resonance of $\text{Cp}^*_2\text{W}_2\text{O}_5$ at δ 2.19), although the presence of small quantities of the product is already evidenced by a small triplet at δ 3.46. Formation of the reaction product occurs slowly and equilibrium is achieved with incomplete conversion within 24 hours. The spectrum obtained after 4 h, (III) in Figure 1, is already close to the final one. The conversion at equilibrium is ca. 64%.



Scheme 1

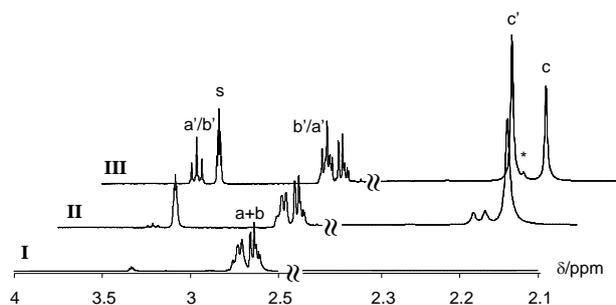


Figure 1. ^1H NMR monitoring of the reaction between $\text{Cp}^*\text{W}_2\text{O}_5$ and $\text{HSCH}_2\text{CH}_2\text{COOH}$ in CD_3OD at room temperature: (I) free $\text{HSCH}_2\text{CH}_2\text{COOH}$ before addition of $\text{Cp}^*\text{W}_2\text{O}_5$; (II) Immediately after $\text{Cp}^*\text{W}_2\text{O}_5$ addition; (III) after 4 hours. Refer to Scheme 1 for the peak assignments; s = solvent CHD_2 resonance; * = unknown impurity in $\text{Cp}^*\text{W}_2\text{O}_5$.

A similar NMR monitoring was also carried out in CDCl_3 , where an equilibrium conversion of ca. 40% was reached in 3 days. This shows a slight solvent effect both on the kinetics and the thermodynamics of the reaction. The reaction is a bit slower and the equilibrium slightly less displaced toward the product in CDCl_3 . The isolation of the pure product from the synthesis in MeOH in ca. 80% yield may be attributed to the less hydrated nature of the solvent relative to the CD_3OD used in the NMR experiment.

In order to displace the equilibrium toward the product, anhydrous Na_2SO_4 was added to the reaction mixture in CH_2Cl_2 . Indeed, a complete conversion could be achieved under these conditions according to NMR. Subsequent addition of water to the solution after filtration of Na_2SO_4 slowly regenerated the starting materials, see Figure 2. It is important to underline that the solution color during all these manipulation remained pale yellow, consistent with the fact that the metal maintains its d^0 configuration for the oxidation state +6. During the analogous reaction of the Mo congener, on the other hand, the metal reduction to Mo^{IV} was accompanied by a color change to deep red [19].

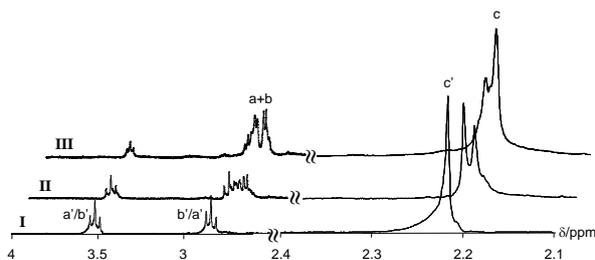


Figure 2. ^1H NMR spectra of compound $\text{CpWO}_2(\text{SCH}_2\text{CH}_2\text{COOH})$ in CDCl_3 : **(I)** anhydrous solution; **(II)** immediately after addition of D_2O ; **(III)** 24 h after addition of D_2O . Refer to Scheme 1 for the peak assignments.

The NMR characterization of the isolated compound is fully consistent with the mononuclear formula proposed in Scheme 1 and with a symmetric arrangement of the $\text{SCH}_2\text{CH}_2\text{COOH}$ ligand, as shown by the equivalence of each geminal pair of methylene H atoms, which give rise to mutual coupling as two triplets in the ^1H NMR. The SCH_2 protons are downfield shifted upon coordination by almost 1 ppm relative to the free substrate, whereas the CH_2COO protons are nearly unaffected, in agreement with the proposed coordination of only one of the two functions. The two corresponding ^{13}C NMR resonances are observed at δ 34.9 and 31.9. The substrate binding via the S function, rather than via the COO function, is suggested by the loss, upon coordination, of the SH resonance. This resonance is clearly discernible for the free substrate in CD_3OD as well as in CDCl_3 , indicating slow exchange with methanol. Hence, if the SH function would remain intact in the product, its resonance should still be visible. The carboxylic acid function, on the other hand, exchanges rapidly with CD_3OD and hence no positive information can be obtained from ^1H NMR about its presence in the product.

Final confirmation of the binding mode was obtained from the X-ray study, see Figure 3. Besides this confirmation, the most interesting structural feature is the presence of an intermolecular H-bond between the carboxylic acid of one molecule and atom O2 of a second molecule, building infinite zig-zag chain parallel to the a axis. This is also reflected in the fact

that the W-O2 bond is slightly longer than the W-O1 bond. According to the Cambridge Data Base, this is the first reported structure where W is surrounded by a “CpO₂(SR)” ligand set, whereas only one is available for molybdenum, Cp*MoO₂(*St*Bu) [25]. The CpWO₂X structure has been previously reported for crystallographically characterized compounds only with O-based or C-based X ligands. The W=O distances observed for Cp*WO₂(SCH₂CH₂COOH) are as expected [average of 1.74(2) Å for the 38 previously reported CpWO₂X structures]. The W-S distance is quite short compared to other distances in W^{VI}O₂(SR) compounds, e.g. 2.440(5) and 2.464(5) Å in WO₂(SPh)₂(terpy) [26], 2.405(4) and 2.434(4) Å in [WO₂(SCPh₂COO)₂]²⁻ [27], 2.419(2) and 2.422(2) for the *cis* S donors in [WO₂(S₂C₂Me₂)₂]²⁻ [28] and 2.426(4) Å for the *cis* S donors in [WO₂{2,3-S₂-1,4-C₆H₂(NHCOMe)₂]₂]²⁻ [29]. In the two latter compounds, the *trans* S donors (*trans* to an oxo ligand) show ever longer W-S bonds, 2.581(2), 2.586(2) [28] and 2.607(3) Å [29]. In all the other above-cited molecules, the SR donors are mutually *trans*. Hence, the *trans* effect of the Cp* ligand is weaker than those of the SR and O ligands.

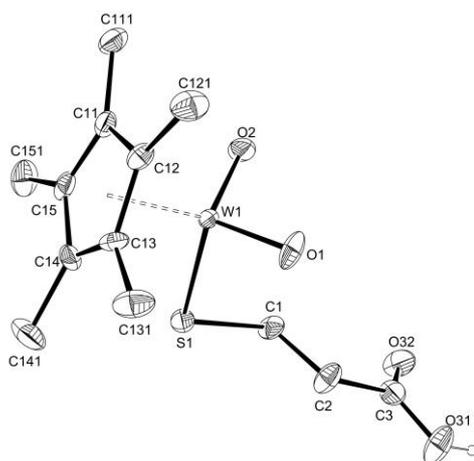


Figure 3. An ORTEP view of the CpWO₂(SCH₂CH₂COOH) molecule with the numbering scheme used. The ellipsoids are drawn at the 50% probability level. Relevant distances (Å): W-CNT (Cp* ring centroid), 2.094(4); W-S1, 2.3476(15); W-O1, 1.723(4); W-O2, 1.734(2); C3-O31, 1.319(7); C3-O32, 1.208(6). Relevant angles (°): CNT-W-S1, 105.8(6); CNT-W-O1, 119.5(6); CNT-W-O2, 116.22(10); S-W-O1, 103.78(15); S-W-O2, 103.42(18); O1-W-O2, 106.3(2). H-bonding interaction

[O(31)-H(31)···O(2)ⁱ]: D-H, 0.82; H···A, 1.86; D···A, 2.670(4); D-H···A, 167.6
(Symmetry code : (i) x+1/2, -y+1/2, z).

(b) Thioglycolic acid

The analogous reaction of mercaptoacetic (or thioglycolic) acid with Cp*₂W₂O₅ in a 2:1 ratio (S/W ratio of 1) revealed interesting differences relative to that of mercaptopropionic acid described in the previous section. The NMR monitoring in CDCl₃ did not exhibit any major change, leaving a substantial amount of starting materials unreacted but revealing also a number of new Cp* peaks and a slight color deepening. This suggests an equilibrated and unselective process. The shape of the NMR spectrum was the same after immediate recording following mixing, and several hours later, showing that the equilibration is rapid. Since the related mercaptopropionic acid addition was found to be favored by methanol (see previous section), a second experiment was conducted in this solvent and found to lead to complete consumption of the starting materials, but once again at least 4 different Cp*-containing products were obtained (resonances at δ 2.55, 2.52, 2.34, 2.30 (major peak), and 2.25) and the solution color darkened.

In order to learn more about this transformation, the ¹H NMR monitoring experiment in CD₃OD was repeated with stepwise addition of substoichiometric amounts of substrate (total S/W ratios of 0.23, 0.46, 0.70, 0.93, 1.16, and 1.40 equivalents, respectively), see results in Figure 4. After the first and second addition, only the major product with the Cp* resonance at δ 2.30 was formed. The amount of this product approximately doubled from the first to the second addition. After the third addition, while the depletion of Cp*₂W₂O₄ continued to be linear, the δ 2.30 resonance increased less than proportionally and the other by-products started to form. Note that the interpolation of the starting material data cuts the axis at an S/W ratio of 1, indicating the essentially quantitative nature of the transformation in CD₃OD. The

slope observed for the growth of the major product is identical in value and opposite in sign to the slope of the starting material decrease, showing that this main product has an S/W stoichiometry of 1:1. The lack of disappearance of the starting material beyond the 1:1 stoichiometry indicates that the minor by-products are characterized by a higher S/W stoichiometry. After the addition of 1.4 equivalents of the substrate, the combined minor products remained under 20% of the total according to integration of the Cp* peaks, whereas the main product reached a maximum of 67% and slightly less than 20% of the starting compound remained unreacted. The NMR monitoring was not pursued for higher S/W ratios.

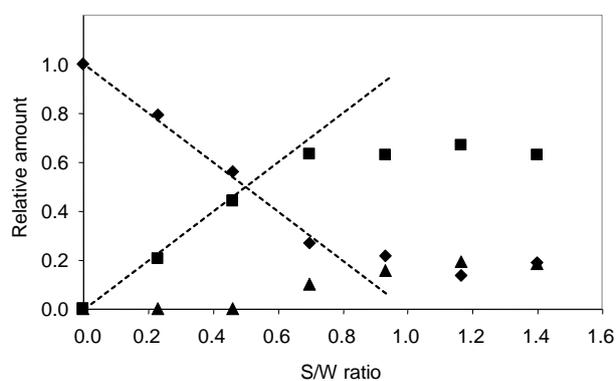


Figure 4. Relative amounts (in moles of W) of starting compound, Cp*₂W₂O₅ (diamonds), main product (squares), and the sum of all other products (triangles) as a function of the S/W ratio.

However, on the basis of the evidence that the by-products are likely resulting from the reducing action of the substrate (deepening of the solution color, higher S/W stoichiometry) we run an experiment with a larger excess of thioglycolic acid (10 equivalents) at the methanol reflux temperature. This experiment led to a deep green colored final solution, the ¹H NMR of which showed the complete consumption of the starting material but many products were again observed (same Cp* resonances observed in the NMR titration experiments, see above), with the major product being that with δ 2.34. The resonance of the primary 1:1 addition product was not visible in this product mixture. Unfortunately, all our

efforts to crystallize one or more of the resulting products were unsuccessful. The stronger color that develops, however, suggests that one or more of these by-products derive from a reduction process. Any further speculation on their molecular constitution is unjustified.

Another interesting observation concerns the structure and symmetry of the first product obtained at low S/W ratios. The absence of a visible SH resonance suggests, like for the mercaptopropionic acid reaction described above, that the substrate has reacted with the metal atom via the SH function, presumably to yield a similar product to that obtained with the mercaptopropionic acid. The methylene resonance is downfield shifted by nearly 1 ppm relative to the free substrate, a similar shift also experienced by the mercaptopropionic substrate (see above). However, the CH₂ resonance in the product is visible as an AB pattern ($J_{\text{HH}} = 18.1$ Hz) rather than as a singlet (see Figure 5), clearly indicating that the two methylene protons are inequivalent and hence that the structure is asymmetric. Therefore, a structure related to that of Cp*WO₂(SCH₂CH₂COOH) shown in Figure 3 cannot be adopted by this compound.

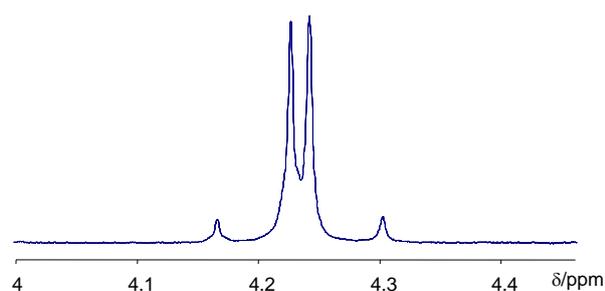
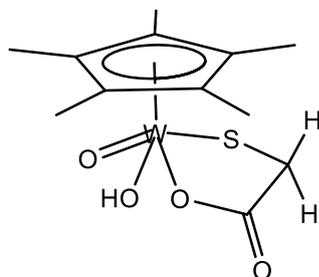


Figure 5. Expansion of the CH₂ resonance of the thioglycolate ligand in the major product obtained from Cp*₂W₂O₅ and thioglycolic acid.

A tentative formulation for this product is proposed in Scheme 2. The aptitude to form a metallacycle would presumably be higher in the thioglycolate derivative because of the formation of a more favored 5-membered ring. Clearly, the conversion of this structure to the symmetric Cp*WO₂(SCH₂COOH) structure similar to that of the mercaptopropionato

derivative, if energetically accessible, must be slow on the NMR time scale in order to maintain the inequivalence of the methylene protons. Unfortunately, all our attempts to crystallize this product, in order to confirm its structure, were also unsuccessful.



Scheme 2

(c) Comparison with the Cp*₂Mo₂O₅ system.

One interesting result of this investigation is the different behavior of the Mo and W complexes. The reaction between Cp*₂Mo₂O₅ and HS(CH₂)_nCOOH resulted in metal reduction and formation of dinuclear Mo(IV) products as the sole isolated materials, without any evidence of simple Cp*Mo^{VI} addition products. For both reactions, the reducing action of the substrate SH function was proven by the observation of HOOC(CH₂)_nS-S(CH₂)_nCOOH (n = 1, 2) in the product mixture. For the W complex, on the other hand, a reversible reaction gives rise to simple Cp*W^{VI} addition products. The primary Cp*W^{VI} addition product for the reaction with thioglycolic acid appears more susceptible to reduction than the corresponding product of the reaction with mercaptopropionic acid, perhaps because the greater aptitude of the thioglycolate ligand to chelate in a structure such as that shown in Scheme 2 provides a more suitable coordination environment to stabilize a W^V intermediate, favoring electron transfer from S to W and the departure of the alkylthiyl radical in a first step of the reduction process. It is appropriate to mention that other half-sandwich W^{VI} compounds with S-based ligands exist, although they are rare. A notable example is [Cp*WS₃]⁻ [25, 30], which is also

paralleled by the molybdenum analogue, $[\text{Cp}^*\text{MoS}_3]^-$ [25]. Neutral species with alkylthiolato ligands are $[\text{Cp}^*\text{MS}_2(\text{S}t\text{Bu})]$ ($\text{M} = \text{Mo}, \text{W}$) [25] $[\text{Cp}^*\text{MoOS}(\text{S}t\text{Bu})]$ and $[\text{Cp}^*\text{WOS}(\text{SR})]$ ($\text{R} = \text{Me}, \text{Bz}$) [31]. Those compounds, however, are obtained starting from Cp^*MCl_4 and thiolate or sulphur delivering reagents in a non aqueous environment.

(d) Hard vs. soft ligand exchange

Another interesting aspect of the reactions reported in this contribution is the fact that a hard ligand, the bridging oxido ligand in $\text{Cp}^*_2\text{W}_2\text{O}_5$, is exchanged by a softer ligand, the thiolate. Although the reaction is not quantitative, it proceeds to high conversions at equilibrium with the production of water. This is an unusual behaviour for the oxophilic W^{VI} center. Other related $\text{W}^{\text{VI}}\text{O}_2(\text{SR})$ systems, notably the hydrotris(3,5-dimethylpyrazolyl)borate complex $\text{Tp}^*\text{WO}_2(\text{SPh})$ which may be prepared by salt metathesis under strictly anhydrous conditions, reacts with hard donors such as phenol, methanol, and formic acid to yield $\text{Tp}^*\text{WO}_2(\text{OPh})$, $\text{Tp}^*\text{WO}_2(\text{OMe})$ and $\text{Tp}^*\text{WO}_2(\text{O}_2\text{CH})$, respectively [32]. The latter transformation is particularly relevant, because the reactions reported here implicate the direct competition of SH and COOH functions for addition to W^{VI} , with a clear preference for the former. Hard-for-soft ligand exchange may also account for the moisture sensitivity of other dioxo- W^{VI} S-donor complexes such as $(\text{phen})\text{WO}_2(\text{SPh})_2$ [26], $\text{WO}_2(\text{S}_2\text{CNR}_2)_2$ [33], and $[\text{WO}_2(\text{bdt})_2]^{2-}$ [34]. The reason for this switch of preference between a hard and a soft donor ligand is probably related to the presence of the soft Cp^* ligand, leading to a “softening” of the tungsten Lewis acidity. Hence, the use of the $\text{Cp}^*\text{W}^{\text{VI}}$ system has opened a new and simpler route for the assembly of sulphur-containing W^{VI} complexes that are of potential interest as models of W-containing biological systems.

Conclusions

Contrary to Cp*₂Mo₂O₅, the W congeners reacts with HS(CH₂)_nCOOH (n = 1, 2) to yield observable substrate addition products with displacement of water in equilibrated processes. This can certainly be attributed to the lower susceptibility of the heavier metal to undergo reductive processes. Oxo-bridge splitting is more favourable for the S-H function to yield an alkylthiolato derivative than for the COOH function to yield a carboxylato derivative. The unusual and unexpected preference of Cp*W^{VI} for a soft donor (RS) vs. a hard one (RCOO) may be attributed to a “softening” effect of the Cp* ligand. It is quite possible that the compounds obtained for the W system represent models of the first generated intermediates in the corresponding reaction of the Mo system.

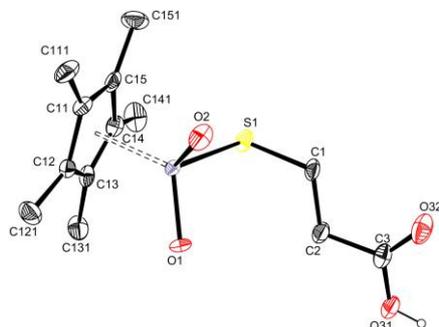
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Graphical Abstract:**Pictogram****Synopsis**

Contrary to $\text{Cp}^*_2\text{Mo}_2\text{O}_5$, the tungsten analogue is not reduced by the thiol function in mercaptocarboxylic acid reagents, leading to equilibrated addition processes with release of water. The addition of the SH function yielding an alkylthiolato derivative is more favourable than addition of the COOH function yielding a carboxylato derivative.