Synthesis of a Cp* Complex of Tungsten with Three Different Chalcogenido (O^{2-}, S^{2-}, and Se^{2-}) Ligands**

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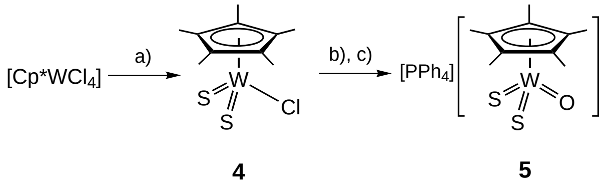
The number of compounds containing terminal chalcogenido ligands has been increasing during the last decade.[1] However, aside from derivatives of tetrachalcogenidometallates $[M(E)_4]^{n-}$, mixed chalcogenido complexes are rare.[2, 3] In particular, it is difficult to prepare mononuclear complexes having both M=S and M=Se multiple bonds. This is because of the lack of an appropriate synthetic route to such complexes, difficulty arises from the propensity of chalcogenide ligands to bridge metal atoms and from the tendency of metal chalcogenides to undergo complicated ligand-exchange reactions in solution.[3, 4] In this context, the title complex ion $[Cp^*W(O)(S)(Se)]^-$ ($Cp^* = \eta^5$-C_5Me_5) is unique in that three different atoms of Group 16 coordinate the Cp*W fragment. It is also noted that this anionic species is a new type of chiral transition metal compound. Recently we developed a new method to prepare a series of the trithio and triseleno complexes of Group 5 and 6 transition metals having a Cp* ligand, and reported high yield syntheses of $[Li(thf)]_2[Cp^*M(S)_3]$ (M = Nb, Ta),[5] $[PPh_4][Cp^*M(S)_3]$ (M = Mo, W),[6] and their seleno analogues for M = Ta, W.[7] We found by NMR spectroscopic analysis in CD_3CN that a mixture of $[PPh_4][Cp^*W(S)_3]$ (**1**) and $[PPh_4][Cp^*W(Se)_3]$ (**2**) remained intact for a prolonged period, and showed no sign of ligand exchange to form mixed seleno/thio complexes. This observation prompted us to seek the preparation of the mixed-chalcogenido complex $[PPh_4][Cp^*W(O)(S)(Se)]$ (**3**) which is reported here.

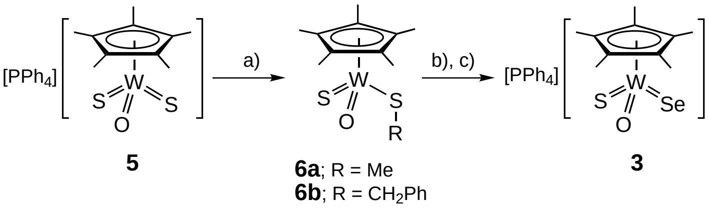
To synthesize the target molecule **3**, we first attempted the replacement of the terminal sulfide(s) of **1** by an oxygen or selenium atom. However, the reaction of **1** with a small amount of water caused partial decomposition of the complex, and the formation of a mononuclear oxo/thio complex was not discernible, while Li_2Se_2 did not react with **1**. Neither could we find a rational way to substitute the terminal selenide(s) of **2**. A successful, but less direct, route begins with the high yield (89%) synthesis of a dithio/chloro complex $[Cp^*W(S)_2Cl]$ (**4**) by the reaction of $[Cp^*WCl_4]$ with 1 equivalent of $Me_3SiSCH_2CH_2SSiMe_3$ (Scheme 1).[8] Apparently C–S bond cleavage occurs, along with the liberation of the Me_3Si group. This reaction contrasts to the formation of $[Cp^*W(S)_3]^-$ upon treatment of $[Cp^*WCl_4]$ with $LiSCH_2CH_2SLi$, in which all the chlorides are substituted by thio ligands.



Scheme 1. Synthesis of **4** and **5**; reagents: a) $Me_3SiSCH_2CH_2SSiMe_3$/THF; b) H_2O/Et_3N/THF; c) PPh_4Br/CH_3CN.

The relatively mild reactivity of $Me_3SiSCH_2CH_2SSiMe_3$ toward $[Cp^*WCl_4]$ may be a reason for the formation of **4**. While an attempt to introduce seleno ligand(s) into **4** by reaction with Li_2Se_2 and subsequent cation exchange of the product with PPh_4Br resulted in a mixture of **1** (16%), $[PPh_4][Cp^*W(S)_2(Se)]$ (34%), and $[PPh_4][Cp^*W(S)(Se)_2]$ (5%),[9] addition of a small amount of H_2O to a THF solution of **4** in the presence of NEt_3 gave $[Cp^*W(O)(S)_2]^-$. This dithio/oxo complex anion was isolated as an analytically pure phosphonium salt $[PPh_4][Cp^*W(O)(S)_2]$ (**5**) in 77% yield. Geoffroy et al reported that the reaction of $[Cp^*WCl_4]$ with H_2S in the presence of NEt_3 produced $[NEt_3H][Cp^*W(O)(S)_2]$ in low yield along with $[Cp^*_2W_2(S)_2(\mu$-$S)_2]$, $[Cp^*_2W_2(S)_2(S_2)]$, and $[NEt_3H][Cp^*W(S)_3]$.[10]

We have reported that alkylation reactions of **1** occur readily with various alkylhalides (RX), producing a series of $[Cp^*W(S)_2(SR)]$ compounds.[6a] The remaining thio ligands are inert to alkylhalides, so that only one sulfide of **1** is alkylated. The reaction of **5** with CH_3I or $PhCH_2Br$ proceeded in a similar manner, and $[Cp^*W(O)(S)(SR)]$ (R = CH_3 (**6a**), CH_2Ph (**6b**)) were isolated in 98% and 92% yields, respectively. Finally, a terminal selenide was introduced successfully by the reaction of **6a** or **6b** with Li_2Se_2 and PPh_4Br, and the desired oxo/thio/seleno complex $[PPh_4][Cp^*W(O)(S)(Se)]$ (**3**) was obtained in 64% or 57% yield, respectively (Scheme 2). Elemental analysis of **3**–**6a**,**b** for H, C, S, and X-ray fluorescence microanalysis for P, S, Se, and W are satisfactory. The ^1H and ^{77}Se NMR (for **3**) ascertained their purity. The negative ion electrospray ionization mass spectrum (EI-MS) of **3** measured at room temperature in acetonitrile exhibits an intense isotope cluster corresponding to $[Cp^*W(O)(S)(Se)]^-$, which fits very well to the theoretical isotope pattern (Figure 1). The complex $[Cp^*_2V_2(\mu$-$O)(\mu$-$S)(\mu$-$SeTe)]$ containing four different chalcogenides in the bridge system between the two Cp*V units has been observed and characterized by NMR spectroscopy and mass spectrometry, although not isolated in a pure form.[2f]



Scheme 2. Synthesis of **3** and **6**; reagents: a) MeI or $PhCH_2Br/CH_3CN$; b) Li_2Se_2/THF; c) PPh_4Br/CH_3CN.

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[**] We thank Prof. Roger E. Cramer for careful reading of the manuscript; Cp = C_5Me_5.

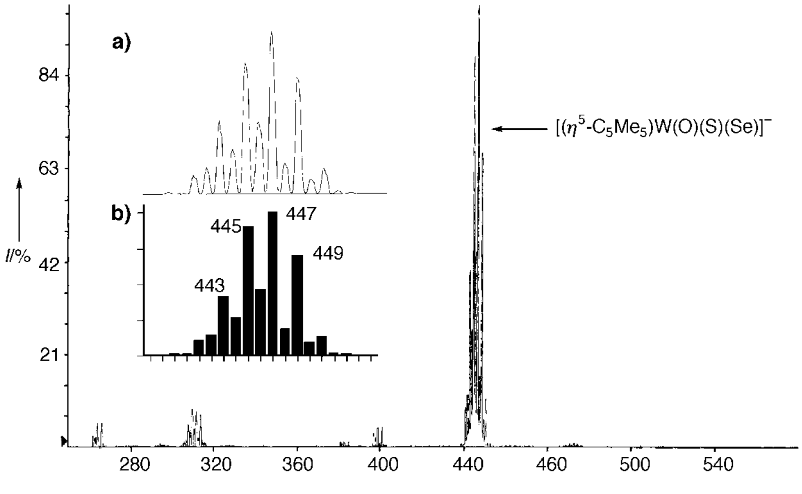

Figure 1. Negative ES mass spectrum of **3** in CH_3CN; a) observed spectrum of the mass ion, b) theoretical isotope pattern.

The mononuclear nature of these complexes has been established by single-crystal X-ray diffraction analyses for **3**–**5**, and **6b**,[11] and they assume a common three-legged piano-stool geometry. In the X-ray structure of **3** (Figure 2), disorder between thio and seleno groups was observed, as is often the case, the chloro and thio groups of **4** are also disordered. Therefore we could not obtain accurate lengths for the W–Cl, W=S, and W=Se bonds of **3** and **4**. However, the oxo position is unique in the structure of **3**, and the oxo and thio groups of **5** are not disordered. Noteworthy here is that the centroid of the C_5Me_5 pentagon of **3** and **5** is not situated exactly above the metal atom, but is shifted toward the oxo ligand.[12] Thus the two W–C bonds approximately *trans* to the W=O unit are longer by 0.071 Å (for **3**) or by 0.065 Å (for **5**) than the other W–C bonds. We attribute this deformation to the stronger *trans* influence of the oxo ligand relative to the thio/seleno ligands. The W=O and W=S bonds of **5** are 1.755(6) and 2.205(3) Å, respectively, which fall in the normal range of those found for terminal oxo and thio ligands bound to tungsten.[13] The W=O and W=S bond lengths are somewhat longer than those of **6b** (1.732(9) and 2.150(4) Å), because one thio group of **5** is replaced by a thiolato ligand. The W=S bond length of **5** is also slightly longer than the W=S bond of **1** (2.188(2)–2.199(2) Å), indicating that the *trans* influence of the oxo ligand is in fact stronger than that of the thio ligand. The infrared and Raman spectra of **3** show strong absorptions can be assigned to the W=O stretch at $\tilde{\nu} = 871$ and 870 cm^{-1}, the corresponding band of **5** both appear at $\tilde{\nu} = 869$ cm^{-1}. The difference between thio- and seleno-coordination does not affect the W=O stretching frequencies. We observed two W=S stretching bands in the infrared and Raman spectra of **3**, both at 450 and 444 cm^{-1}, while those infrared bands of **4** and **5** are at 499, 486 cm^{-1}, and 454, 434 cm^{-1}, respectively. The W=Se stretching band for **3** appears at 287 cm^{-1} (infrared) or 286 cm^{-1} (Raman), comparable to those of $[PPh_4][Cp^*W(Se)_3]$ (**2**) and $[W(Se)_4]^{2-}$.[2a, 7b]

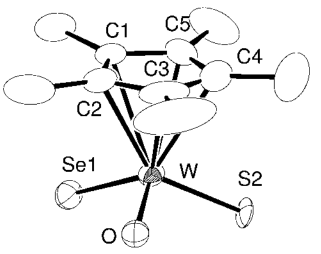

Figure 2. X-ray structure of the anion of **3**, only the major components of the disordered S and Se atoms are shown.

Complex **3** is thermodynamically stable, and does not show a propensity for chalcogenide scrambling reactions in CH_3CN. Determination of the stereochemistry at tungsten in the reaction of **6a**,**b** → **3**, and the separation of the enantiomers of **3** and **6a**,**b** are in progress.

Experimental Section

3: Addition of **6a** (0.28 g, 0.68 mmol) in THF (10 mL) to Li_2Se_2 (0.31 g, 1.80 mmol) in THF (10 mL) at 0 °C gave a red suspension. The mixture was stirred for 1 h at room temperature. After centrifugation to remove insoluble material, the red supernatant solution was evaporated to dryness. The residue was dissolved in CH_3CN (10 mL), and a solution of PPh_4Br (0.26 g, 0.62 mmol) in CH_3CN (5 mL) was added. Concentration and cooling to −20 °C afforded of **3** (0.34 g, 64 % yield) as red crystals; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.6-8.0$ (m, 20H; PPh_4), 2.10 (s, 15H; Cp*); ^{77}Se NMR (95.3 MHz, $CDCl_3$, Me_2Se): $\delta = 1027$; IR (Nujol): $\tilde{\nu} = 871$ (W=O), 450, 444 (W=S), 287 (W=Se) cm^{-1}; Raman: $\tilde{\nu} = 870$ (W=O), 450, 444 (W=S), 286 (W=Se) cm^{-1}; ESI-MS (negative mode, CH_3CN); *m/z* 447 ($[Cp^*W(O)(S)(Se)]^-$); X-ray fluorescence: W:S:Se:P = 1.00:0.98:1.06:1.10; elemental analysis calcd (%) for $C_{34}H_{35}OPSSeW$: C 51.99, H 4.49, S 4.08; found: C 52.24, H 4.36, S 4.22. A THF (10 mL) solution of **6b** (0.35 g, 0.71 mmol) was treated with Li_2Se_2 (0.36 g, 2.10 mmol) in THF (10 mL), and a workup similar to the one described above, using PPh_4Br (0.27 g, 0.64 mmol), yielded **3** (0.32 g, 57 %).

4: $Me_3SiSCH_2CH_2SSiMe_3$ (3.93 mmol) in THF (40 mL) was added to a slurry of $[Cp^*WCl_4]$ (1.81 g, 3.93 mmol) in THF (50 mL) at room temperature. The mixture was stirred at room temperature for 3 h, producing a dark brown homogeneous solution. After removal of the volatiles, the residue was extracted with toluene (60 mL × 2). The toluene solution was concentrated and allowed to stand overnight at −20 °C producing **4** as dark red crystals (1.46 g, 89 %); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.35$ (s; Cp*); IR (Nujol): $\tilde{\nu} = 499$, 486 (W=S) cm^{-1}; EI-MS; *m/z* 418 [M^+]; X-ray fluorescence: W:S:Cl = 1.00:2.03:0.92; elemental analysis calcd (%) for $C_{10}H_{15}ClS_2W$: C 28.69, H 3.61, S 15.32; found: C 28.77, H 3.58, S 15.30.

5: A mixture of NEt_3 (1.0 mL, 7.2 mmol) and H_2O (0.10 mL, 5.5 mmol) was added to a THF (80 mL) solution of **4** (1.06 g, 2.53 mmol) at room temperature. This immediately produced an orange suspension. After 30 min of stirring, the solution was dried over $MgSO_4$. After centrifugation to remove insoluble material a solution of PPh_4Br (0.95 g, 2.27 mmol) in CH_3CN (20 mL) was added to the supernatant solution. Concentration and cooling to −20 °C afforded **5** (1.44 g, 77 %) as orange crystals; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.6-8.0$ (m, 20H; PPh_4), 2.09 (s, 15H; Cp*); IR (Nujol): $\tilde{\nu} = 869$ (W=O), 454, 434 (W=S) cm^{-1}; Raman: $\tilde{\nu} = 869$ (W=O), 454, 434 (W=S) cm^{-1}; ESI-MS (negative mode, CH_3CN); *m/z* 399 ($[Cp^*W(O)(S)_2]^-$); X-ray fluorescence: W:S:P = 1.00:1.98:0.91; elemental analysis calcd (%) for $C_{36}H_{35}OPS_2W$: C 55.29, H 4.78, S 8.68; found: C 54.97, H 4.56, S 8.31.

6a: Iodomethane (90 µL, 1.44 mmol) was added to a solution of **5** (0.97 g, 1.31 mmol) in CH_3CN (40 mL) at room temperature. The reaction mixture immediately formed a red solution and was stirred for 30 min. The solvent was removed in vacuo. The resulting solid was extracted with toluene (20 mL) and PPh_4I was removed by centrifugation. The supernatant solution was evaporated to leave **6a** (0.53 g, 98 %) as a red crystalline powder; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 3.05$ (s, 3H; SMe), 2.23 (s, 15H; Cp*); IR (Nujol): $\tilde{\nu} = 910$ (W=O), 482 (W=S) cm^{-1}; EI-MS; *m/z* 414 [M^+], 399 [$M^+ - CH_3$]; elemental analysis calcd (%) for $C_{11}H_{18}OS_2W$: C 31.90, H 4.38, S 15.48; found: C 31.77, H 4.28, S 15.19.

6b: A CH_3CN solution of **5** (0.81 g, 1.10 mmol) was treated with benzyl bromide (0.14 mL, 1.18 mmol), and a workup similar to the one described above yielded **6b** (0.49 g, 92 %) as red microcrystals; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.1-7.4$ (m, 5H; SCH_2Ph), 4.63 (d, $J = 12.5$ Hz, 1H; SCH_2Ph), 4.33 (d, $J = 12.5$ Hz, 1H; SCH_2Ph), 2.23 (s, 15H; Cp*); IR (Nujol): $\tilde{\nu} = 911$ (W=O), 482 (W=S) cm^{-1}; EI-MS; m/z 490 [M^+], 399 [$M^+ - CH_2Ph$]; elemental analysis calcd (%) for $C_{17}H_{22}OS_2W$: C 41.64, H 4.52, S 13.08; found: C 41.72, H 4.66, S 12.98.

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[8] $Me_3SiSCH_2CH_2SSiMe_3$ was prepared from the reaction of $LiSCH_2CH_2SLi$ with 2 equivalents of Me_3SiCl in THF at 0 °C and used immediately.

[9] The ^{1}H NMR spectrum of the mixture in $CDCl_3$ shows three singlets arising from the Me Cp* protons, and the IR spectrum exhibits W=S and W=Se stretching bands. The negative electrospray (ES) mass spectrum of a CH_3CN solution of the mixture shows signals attributed to three isotopic clusters corresponding to $[Cp^*W(S)_3]^-$, $[Cp^*W(S)_2(Se)]^-$, and $[Cp^*W(S)(Se)_2]^-$.

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[11] Crystal data for **3**: $C_{34}H_{35}POSSeW$ ($M_r = 785.49$); crystal size $0.20 \times 0.15 \times 0.10$ mm, orthorhombic, *Pbca* (no. 61), $a = 16.9788(3)$, $b = 17.5295(2)$, $c = 20.6088(8)$ Å, $V = 6133.8(2)$ Å^3, $\rho_{calcd} = 1.701$ g cm^{-3}, $Z = 8$, $\mu(Mo_{K\alpha}) = 51.04$ cm^{-1}, 46199 measured, 5022 unique with $I > 2\sigma(I)$, 370 variables, $R = 0.043$, $R_w = 0.051$, residual electron density max./min. 2.49/ − 1.23 e Å^{-3}. The S and Se atoms were disordered over two positions with occupancy factors of 65:35. Diffraction data for **3** were collected at − 100 °C on a Rigaku RASA-7 Quantum system equipped with an ADSC CCD detector ($Mo_{K\alpha}$ radiation, $\lambda = 0.71067$ Å; graphite-monochromated). The structure was solved by employing TEXSAN software package. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151942 (**3**), -151943 (**4**), -151944 (**5**), and -151945 (**6b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Combination of Electrografting and Ring-Opening Metathesis Polymerization: An Efficient Way to Prepare Polynorbornene Brushes on Conducting Substrates[**]

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Nowadays, increasing attention is paid to films of polymer chains covalently bonded to solid surfaces.[1, 2] This strategy is very useful to modify the surface properties of inorganic materials, to improve the interfacial bonding in composites, and to prepare novel inorganic – organic hybrids.[3, 4] In addition to this technique that consists of the chemical bonding of preformed end-reactive chains to the surface ("grafting onto" method), polymer brushes can be formed by the "grafting from" method, that is, the initiation and growth of the chains from the solid surface. When this substrate is electrically conducting, electropolymerization has proved to be a powerful method to deposit polymers that highly adhere to the substrate.[5–7] Indeed, the electroreduction of monomers of the (meth)acrylate type at an appropriate potential leads to the rapid formation of an homogeneous polymer film on the cathode whatever its shape (plate, fiber) and nature (metal, carbon, indium tin oxide (ITO) glass).[8, 9] That the polymer is chemisorbed onto the substrate is confirmed by insolubility in a good solvent for the polymer and by peeling tests.[10, 11]

However, as a result of the formation of an insulating poly(meth)acrylate film on the cathode, the substrate is rapidly passivated (rendered inactive) which limits the film thickness (< 100 nm). Moreover, monomers that contain protic functions (alcohol, amine, carboxylic acid, etc.) cannot be electrografted because of their reduction at the same or at a less cathodic potential than the (meth)acrylate.

The recent development of well-defined and highly active catalysts by the groups of Schrock[12] and Grubbs,[13] has also reactivated interest in the ring-opening metathesis polymerization (ROMP) of cycloolefins, particularly for applications in solid-phase chemistry.[14–17] Therefore, a combination of living ROMP and electrografting appears to be a promising strategy to overcome the limitations of the electrografting process. Indeed, the thickness of the polymer film "grafted" to the electrode could be easily tuned by a second step of "grafting from" polymerization of cycloolefins. Moreover, advantage can be taken of the compatibility of the Grubbs

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