

Synthesis and structures of half-sandwich W(VI) tri(selenido) and W(II) selenolato complexes

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The reaction of Cp^{*}WCl₄ with LiSeBu^t in THF in the presence of Bu^tNC gave rise to Cp^{*}W(SeBu^t)(CNBu^t)₃ **3**, while treatment of the Cp^{*}WCl₄/LiSeBu^t reaction mixture with Li₂Se₂ followed by cation exchange with PPh₄Br in MeCN afforded (PPh₄)[Cp^{*}WSe₃] **1**.

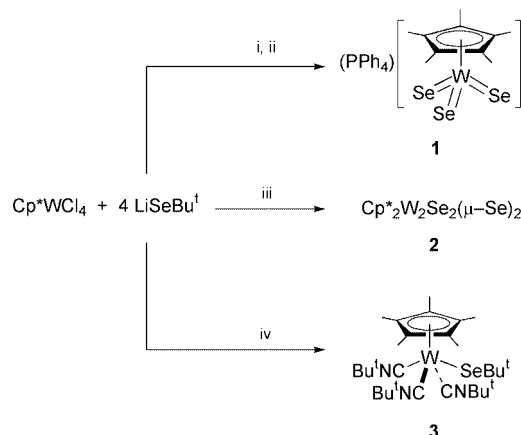
The chemistry of terminal selenido complexes is much less developed than that of the familiar metal oxides and sulfides.¹ This is mainly because many of the traditional reagents used in metal oxo and sulfido chemistry are not simply transferable to their selenido congeners.² In the course of our studies of group 6 transition metal chalcogenido chemistry, we previously isolated the half-sandwich tri(sulfido) complexes [Cp^{*}MS₃]⁻ (M = Mo, W).^{3,4} Carbon–sulfur bond rupture of thiolato complexes gives ready access to thiolato/sulfido derivatives and eventually [Cp^{*}MS₃]⁻. Here we report the synthesis of (PPh₄)[Cp^{*}WSe₃] **1** via C–Se bond cleavage.

For the selenolation reagent, the readily accessible LiSeBu^t was employed, which is prepared by the reaction of LiBu^t with 1 equiv. of selenium in THF at –78 °C. We have reported facile C–S bond cleavage of *tert*-butylthiolato complexes of group 5 and 6 metals,³ and C–Se bond activation was expected to occur for the analogous selenolato complexes. Addition of 4 equiv. of LiSeBu^t to Cp^{*}WCl₄ in THF at –78 °C gave a red solution. After stirring for 30 min, the solution turned brown, from which Cp^{*}W₂Se₂(μ-Se)₂ **2** was obtained in 40% yield (Scheme 1). Spectral data show that **2** is a mixture of *syn*- and *anti*-isomers. In a separate experiment, a freshly prepared Cp^{*}WCl₄/LiSeBu^t mixture was quickly transferred into a THF solution of Li₂Se₂ to give a dark red suspension. Cation exchange with PPh₄Br in MeCN provided the intriguing tri(selenido) complex **1** as dark red crystals in 23% yield concomitant with **2** (14%).[†] This synthetic route to **1** is reminiscent of the preparation of [Cp^{*}MoS₃]⁻ by the reaction of Cp^{*}MoS₂(SBU^t) with Li₂S₂ and supports the generation of the hypothetical Cp^{*}WSe₂(SeBu^t) intermediate in the Cp^{*}WCl₄/LiSeBu^t reaction.³ While the

reaction of Cp^{*}WCl₄ with LiSBU^t afforded Cp^{*}W(SBU^t)₃, Cp^{*}WS₂(SBU^t), and Cp^{*}W₂S₂(μ-S)₂, all attempts to isolate the expected Se analogues, such as Cp^{*}W(SeBU^t)₃ and Cp^{*}WSe₂(SeBU^t), have failed.

Fig. 1 shows the three-legged piano-stool structure of the anion of **1**.[‡] The average W–Se distance of 2.322 Å in **1** is similar to that of (PPh₄)₂[WSe₄] [2.314(1) Å].⁵ The IR spectrum of **1** shows the W=Se stretching frequency at 284 cm⁻¹ comparable to that of [WSe₄]²⁻.⁶ The ⁷⁷Se NMR signal (δ 1437) lies in the range of chemical shifts for terminal selenido ligands.⁷ The UV–VIS spectra of **2** and its sulfur congener (PPh₄)[Cp^{*}WS₃] are similar, showing a strong absorption at 437 and 377 nm, respectively, assignable to charge-transfer transitions from selenium and sulfur to the vacant d orbital of tungsten. The red shift on going from sulfide to selenide (0.45 eV) compares well with the difference in the first ionization potentials of S and Se.⁸

In another experiment, we carried out the Cp^{*}WCl₄/LiSeBu^t reaction in the presence of Bu^tNC, from which Cp^{*}W(SeBu^t)(CNBu^t)₃ **3** was isolated as brown crystals in 41% yield (Scheme 1).[§] The X-ray structure of **3**[‡] shows the metal surrounded in a distorted trigonal-bipyramidal geometry wherein the Se and C(20) atoms occupy axial positions, if the Cp^{*} ligand is viewed as a monodentate ligand (Fig. 1). While two of the three Bu^tNC ligands are nearly linear [C–N–C = 175.8(8), 164.3(7)°], the other contains essentially an sp²-type N atom with a C(15)–N(1)–C(16) angle of 128.7(6)° amongst the smallest of known bent isocyanides (122–156°).⁹ The presence of the bent isocyanide is ascribed to extensive π-back donation from the electron-rich W(II) metal ion to the isocyanide. The bent isocyanide also has a shorter W–C bond [1.984(7) Å] and a longer C_{ipso}–N bond [1.220(9) Å] relative to the corresponding values in two linear isocyanides (mean 2.032 and 1.151 Å). This structural feature is consistent with the two N–C stretching frequencies at 2038 and 1813 cm⁻¹ observed in the IR spectrum. The W–Se distance of 2.6271(7) Å is comparable to that of CpW(CO)₃(SeCH₂Ph) [2.623(1) Å].¹⁰ On the other hand, the ¹H NMR spectrum of **3** in C₆D₆ at room temperature shows three singlets assignable to *tert*-butyl groups in an intensity ratio of 2:1:1, indicating that the complex is fluxional in solution. Previously, we reported the isolation of



Scheme 1 Reagents and conditions: i, Li₂Se₂, THF; ii, PPh₄Br, MeCN; iii, 30 min, –78 °C, THF; iv, Bu^tNC, THF.

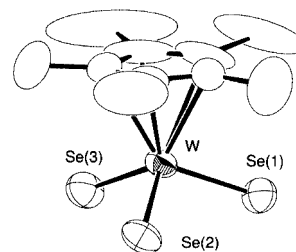


Fig. 1 Molecular structure of the anion of **1**. Selected bond lengths (Å) and angles (°): W–Se(1) 2.322(1), W–Se(2) 2.326(1), W–Se(3) 2.319(1); Se(1)–W–Se(2) 105.42(4), Se(1)–W–Se(3) 103.87(4), Se(2)–W–Se(3) 104.25(4).

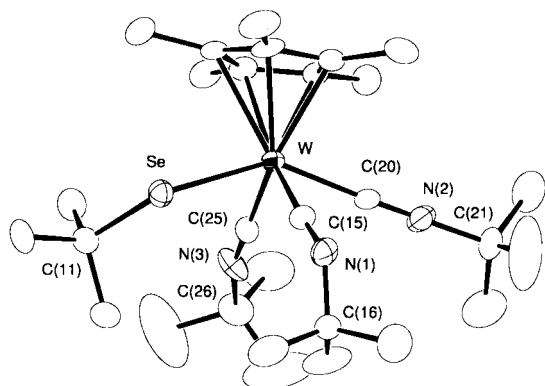


Fig. 2 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): W–Se 2.6271(7), W–C(15) 1.984(7), W–C(20) 2.039(7), W–C(25) 2.025(8), Se–C(11) 2.019(8), N(1)–C(15) 1.220(9), N(2)–C(20) 1.148(9), N(3)–C(25) 1.153(9); Se–W–C(5) 82.9(2), Se–W–C(15) 73.3(2), Se–W–C(20) 140.7(2), Se–W–C(25) 88.9(2), C(15)–W–C(20) 73.6(3), C(15)–W–C(25) 103.9(3), C(20)–W–C(25) 79.1(3).

the W(IV) thiolato complex Cp*W(SBu^t)₃(CNBu^t) from the Cp*WCl₄/LiS^tBu reaction in the presence of Bu^tNC.⁴ The isolation of a W(II) selenolato complex, **3**, is in accord with the tendency of selenolato complexes to favor lower oxidation states.

Notes and references

† All manipulations were carried out under an atmosphere of argon using solvents purified by standard methods. A mixture of LiSeBu^t (7.60 mmol) and Cp*WCl₄ (0.86 g, 1.87 mmol) in THF (50 mL) was quickly added to a slurry of Li₂Se₂ (1.40 mmol) in THF (20 mL) at –78 °C. The solution was warmed up to room temperature and stirred for 2 h. After centrifugation, the solution was evaporated to dryness. The residue was dissolved in MeCN (30 mL) to give a dark red solution and a brown solid. A solution of PPh₄Br (0.47 g, 1.12 mmol) in MeCN (20 mL) was added to the dark red supernatant. Concentration and cooling to –20 °C afforded 0.38 g of **1** as dark red crystals in 23% yield. The brown solid which was insoluble in MeCN was recrystallized from toluene to provide **2** in 14% yield. Data for **1**: ¹H NMR (500 MHz, CDCl₃), δ 2.20 (s, 15H, Cp*), 7.6–8.0 (m, 20H, PPh₄). ⁷⁷Se NMR (95.3 MHz, CDCl₃, Me₂Se), δ 1437. IR ν/cm⁻¹: 284m (W=Se). UV–VIS (MeCN): λ_{max}/nm(ε/M⁻¹ cm⁻¹) 299 (19000), 350 (sh), 437 (38000), 530 (sh). Anal. calc.: C, 45.61, H, 3.94. Found: C, 45.57; H, 3.98%. Data for **2**: ¹H NMR (500 MHz, CDCl₃), δ 2.27 (s, Cp*), 2.33 (s, Cp*). IR ν/cm⁻¹: 315m, 298m (W=Se). FAB–MS: 954 (M⁺). Anal. calc.: C, 25.18; H, 3.17. Found: C, 25.01; H, 3.30%.

‡ Crystal data: for **1**: C₃₄H₃₅Se₃PW, *M* = 895.35, orthorhombic, space group *Pbca*, *a* = 18.284(5), *b* = 20.171(7), *c* = 17.758(5) Å, *V* = 6549(2) Å³, *Z* = 8, *T* = 293 K, μ(Mo–Kα) = 69.37 cm⁻¹, Rigaku-AFC7R, 6360 measured reflections (2θ_{max} = 50°). The structure was solved by Patterson methods and refined by full-matrix least squares. At convergence, *R* = 0.057, *R_w* = 0.058, and GOF = 1.44 for 352 variables refined against 4341 unique reflections [*I* > 1σ(*I*)].

§ For **3**: C₂₉H₅₁N₃SeW, *M* = 704.55, monoclinic, space group *P2₁/n*, *a* = 9.7349(8), *b* = 18.9776(5), *c* = 17.4477(3) Å, β = 97.1791(7)°, *V* = 3198.1(2) Å³, *Z* = 4, *T* = 173 K, μ(Mo–Kα) = 47.74 cm⁻¹, Rigaku-AFC7 equipped with a MSC/ADSC Quantum1 CCD detector, 20472 measured reflections (2θ_{max} = 55°). The structure was solved by Patterson methods and refined by full-matrix least squares (TEXSAN). At convergence, *R* = 0.077, *R_w* = 0.063, and GOF = 1.47 for 307 variables refined against all 7147 unique reflections.

CCDC 182/1672. See <http://www.rsc.org/suppdata/cc/b0/b003303k/> for crystallographic files in .cif format.

§ Bu^tNC (1.0 mL, 8.8 mmol) was added to a mixture of Cp*WCl₄ (0.46 g, 1.06 mmol) and LiSeBu^t (4.24 mmol) in THF (30 mL) at –78 °C. The solution was warmed to room temperature and stirred for 0.5 h. The resulting brown solution was evaporated to dryness. The residue was crystallized from hexane to give **3** (0.31 g, 41%). ¹H NMR (400 MHz, C₆D₆), δ 1.36 (s, 18H, Bu^t), 1.44 (s, 9H, Bu^t), 1.86 (s, 9H, Bu^t), 1.93 (s, 15H, Cp*). IR ν/cm⁻¹: 2038s, 1813s. Anal. calc.: C, 49.44; H, 7.30; N, 5.96. Found: C, 49.07; H, 7.31; N, 5.61%.

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