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Synthesis and Reactions of Group 6 Metal Half-Sandwich Complexes of 2,2-Dicyanoethylene-1,1-dichalcogenolates $[(Cp^*)M\{E_2C{=}C(CN)_2\}_2]^-$ (M = Mo, W; E = S, Se)

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A series of group 6 transition metal half-sandwich complexes with 1,1-dichalcogenide ligands have been prepared by the reactions of Cp^*MCl_4 ($Cp^* = \eta^5\text{-}C_5Me_5$; M = Mo, W) with the potassium salt of 2,2-dicyanoethylene-1,1-dithiolate, $(KS)_2C{=}C(CN)_2$ (K_2-i-mnt), or the analogous seleno compound, $(KSe)_2C{=}C(CN)_2$ (K_2-i-mns). The reaction of Cp^*MCl_4 with $(KS)_2C{=}C(CN)_2$ in a 1:3 molar ratio in CH_3CN gave rise to $K[Cp^*M\{S_2C{=}C(CN)_2\}_2]$ (M = Mo, **1a**, 74%; M = W, **2a**, 46%). Under the same conditions, the reaction of Cp^*MoCl_4 with 3 equiv of $(KSe)_2C{=}C(CN)_2$ afforded $K[Cp^*Mo\{Se_2C{=}C(CN)_2\}_2]$ (**3a**) and $K[Cp^*Mo\{Se_2C{=}C(CN)_2\}\{Se(Se_2)C{=}C(CN)_2\}]$ (**4**) in respective yields of 45% and 25%. Cation exchange reactions of **1a**, **2a**, and **3a** with Et_4NBr resulted in isolation of $(Et_4N)[Cp^*Mo\{S_2C{=}C(CN)_2\}_2]$ (**1b**), $(Et_4N)[Cp^*W\{S_2C{=}C(CN)_2\}_2]$ (**2b**), and $(Et_4N)[Cp^*Mo\{Se_2C{=}C(CN)_2\}_2]$ (**3b**), respectively. Complex **4** crystallized with one THF and one CH_3CN molecule as a three-dimensional network structure. Inspection of the reaction of Cp^*WCl_4 with $(KSe)_2C{=}C(CN)_2$ by ESI-MS revealed the existence of three species in CH_3CN, $[Cp^*W\{Se_2C{=}C(CN)_2\}_2]^-$, $[Cp^*W\{Se_2C{=}C(CN)_2\}\{Se(Se_2)C{=}C(CN)_2\}]^-$, and $[Cp^*W\{Se(Se_2)C{=}C(CN)_2\}_2]^-$, of which $[Cp^*W\{Se_2C{=}C(CN)_2\}\{Se(Se_2)C{=}C(CN)_2\}]^-$ (**5**) was isolated as the main product. Treatment of **2a** with $^1/_4$ equiv of S_8 in refluxing THF resulted in sulfur insertion and gave rise to $K[Cp^*W\{S_2C{=}C(CN)_2\}\{S(S_2)C{=}C(CN)_2\}]$ (**6**), which crystallized with two THF molecules forming a three-dimensional network structure. **6** can also be prepared by refluxing **2a** with $^1/_4$ equiv of S_8 in THF. **3a** readily added one Se atom upon treatment with 1 mol of Se powder in THF to give **4** in high yield, while the treatment of **3a** or **4** with 2 equiv of Na_2Se in THF led to formation of a dinuclear complex $[(Cp^*Mo)_2(\mu\text{-}Se)\{\mu\text{-}Se(Se_3)C{=}C(CN)_2\}]$ (**7**). The structure of **7** consists of two Cp^*Mo units bridged by a Se^{2-} and a $[Se(Se_3)C{=}C(CN)_2]^{2-}$ ligand in which the triselenido group is arranged in a nearly linear way (163°). The reaction of **2a** with 2 equiv of CuBr in CH_3CN yielded a trinuclear complex $[Cp^*WCu_2(\mu\text{-}Br)\{\mu_3\text{-}S_2C{=}C(CN)_2\}_2]$ (**8**), which crystallized with one CH_3CN and generated a one-dimensional chain polymer through bonding of Cu to the N of the cyano groups.

Introduction

During the past two decades, the investigation of the chalcogen chemistry of transition metals has continued to generate surprising results.[1,2] In particular, thiolato/sulfido complexes of transition metals are of long-standing interest in coordination chemistry, owing to the importance in metalloenzymes and in industrial processes, such as hydrodesulfurization and electro/photocatalysis,[3−6] where many molybdenum and tungsten complexes with a diverse range of structural features have been reported.[7,8]

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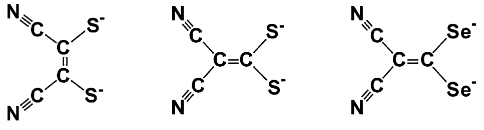
Among a range of thiolate complexes, those with unsaturated dithiolate ligands having planar geometry, such as 1,2-dicyanoethylene-1,2-dithiolate (malononitriledithiolate (mnt^{2-})) and 2,2-dicyanoethylence-1,1-dithiolate (iso-malononitriledithiolate (i-mnt^{2-})),[9,10] have received considerable renewed attention recently,[11] due to their high stability, intense color, and ability to undergo one-electron redox reactions, along with potential applications in new organic conductors.[11] The fascinating properties of these complexes are induced by the electronic structures characteristic of the ligands. Especially in square-planar complexes containing such ligands, the electron density on the metal center is almost independent of the oxidation state and the delocalization of the π electrons extends onto all of the ligand atoms. Thus the planar configurations are quite stable for varying oxidation states of the metal, and other bounded species do not alter appreciably the electronic structures.[9a]

As compared to the complexes with the mnt^{2-} ligand, those with the i-mnt^{2-} ligand have received less attention,[12,13] although i-mnt^{2-} has the two important features. First, i-mnt^{2-} may possess greater electron delocalization through the S−C, C=C, and C−CN bonds, which was suggested by studies of surface-enhanced Raman scattering.[14] Second, upon chelating to a metal atom, i-mnt^{2-} forms a four-membered chelating ring, different from the five-membered ring in mnt^{2-} complexes. Thereby, the intra- and interligand S−S separations, which are one of the main factors influencing the geometry of the complexes,[9a,15] would be very different. In fact, the adjacent S−S distances in $[Ni(mnt)_2]^{2-}$ are 3.101 and 3.022 Å, whereas those in $[Ni(i\text{-}mnt)_2]^{2-}$ are 2.836 and 3.410 Å. Furthermore, the i-mnt^{2-} ligand may exhibit variegated coordination modes, because it can coordinate to metal atoms through sulfur atoms only,[16] or through both sulfur and nitrogen atoms. Hence i-mnt^{2-} can be used as a versatile building block for the construction of polymeric structures. On the other hand, the use of the selenium analogue of i-mnt^{2-}, 2,2-dicyanoethylene-1,1-diselenolate (i-mns^{2-}), in coordination chemistry is still limited,[17] although the ligand was synthesized many years ago.[18]



mnt^{2-} **i-mnt^{2-}** **i-mns^{2-}**

Previously we reported the reactions of Cp*MCl$_4$ (M = Nb, Ta, Mo, W) with a range of monothiolates and 1,2-dithiolates, as well as Li$_2$S$_2$, to give a series of group 5 and 6 transition metal half-sandwich complexes with S-donor

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ligands.[19,20] The fascinating electron properties and rich coordination modes of 2,2-dicyanoethylene-1,1-dichalcogenolates (i-mnt^{2-} and i-mns^{2-}) prompted us to introduce these ligands into pentamethylcyclopentadienyl complexes of group 6 transition metals. This paper reports the synthesis and structures of a series of half-sandwich molybdenum and tungsten complexes with i-mnt^{2-} and i-mns^{2-} ligands, and their reactions with S_8, Na_2Se, and CuBr. One of our aims is to examine the unexplored coordination properties of the nitrogen atoms in i-mnt^{2-} and i-mns^{2-} ligands.

Experimental Section

General Procedures. All reactions and manipulations of air-sensitive compounds were performed under argon gas with standard Schlenk techniques. Solvents were predried over activated molecular sieves, degassed, and distilled from sodium/benzophenone ketyl (THF, hexane) or from CaH_2 (CH_3CN) under argon.

For UV−visible spectra, a JASCO V-560 spectrometer was used. FT-IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer with use of KBr pellets. ESI-mass spectra were collected on a Perkin-Elmer API 300 mass spectrometer. Elemental analyses were performed on LECO-CHN and LECO-CHNS microanalyzers where the crystalline samples were sealed in thin aluminum and tin tubes.

Cp^*MoCl_4 and Cp^*WCl_4 were prepared according to literature procedures.[21] $(KS)_2C{=}C(CN)_2$ and $(KSe)_2C{=}C(CN)_2$ were prepared by modified literature methods[18a,22] by using dioxane and ethanol instead of H_2O and ethanol as solvents, recrystallized in ethanol, and dried in a vacuum at 70 °C for 24 h. Carbon diselenide was prepared according to a literature method.[23] Na_2Se was prepared under argon by heating selenium powder and 2 equiv of sodium metal in DMF at 100 °C for 1 h, and the resulting violet-red precipitate was used for the reaction described in this paper. Other chemicals were used as purchased.

Preparation of $K[Cp^*Mo\{S_2C{=}C(CN)_2\}_2]$ (1a) and $(Et_4N)[Cp^*Mo\{S_2C{=}C(CN)_2\}_2]$ (1b). To a solution of Cp^*MoCl_4 (0.186 g, 0.50 mmol) in 30 mL of CH_3CN was added solid $(KS)_2C{=}C(CN)_2$ (0.327 g, 1.50 mmol). The reaction mixture turned purple gradually. After being stirred for 24 h at room temperature, the resulting solution was dried and the resulting dark-red residue was extracted with THF (10 mL). The purple solution was centrifuged to remove insoluble solid and covered with a layer of Et_2O in a Schlenk tube. After two weeks, dark-red crystalline plates of $K[Cp^*Mo\{S_2C{=}C(CN)_2\}_2]$ (**1a**) were collected and washed with THF/Et_2O (v/v 1:3). Yield: 74%. IR (cm^{-1}, KBr): ν(C$\equiv$N) 2214 (vs); ν(C=CS_2) 1401 (vs), 1375 (vs), 884 (m); ν(Cp*) 1022 (m). UV−vis (nm, THF): 567, 525 (sh), 380 (sh), 328. Purple-red crystals suitable for X-ray diffraction analysis of $(Et_4N)[Cp^*Mo\{S_2C{=}C(CN)_2\}_2]$ (**1b**) were obtained from layering hexane on a THF solution of **1a** and Et_4NBr. Anal. Calcd for $C_{26}H_{35}N_5S_4Mo$ (**1b**): C, 48.66; H, 5.50; N, 10.91; S, 19.98. Found: C, 49.21; H, 5.41; N, 10.93, S, 20.52.

Preparation of $K[Cp^*W\{S_2C{=}C(CN)_2\}_2]$ (2a) and $(Et_4N)[Cp^*W\{S_2C{=}C(CN)_2\}_2]$ (2b). The procedures followed were almost the same as those for the preparation of **1a** and **1b**. To a solution of Cp^*WCl_4 (0.230 g, 0.50 mmol) in 30 mL of CH_3CN was added solid $(KS)_2C{=}C(CN)_2$ (0.327 g, 1.50 mmol). The reaction mixture turned brown gradually and was stirred for 24 h at room temperature. The resulting solution with a large amount of precipitate was dried and the resulting brown residue was dissolved in THF (10 mL). Removing insoluble solid gave rise to a brown-red solution that was covered with a layer of Et_2O in a Schlenk tube. After three weeks, dark-red crystalline $K[Cp^*W\{S_2C{=}C(CN)_2\}_2]$ (**2a**) was collected and washed with THF/Et_2O (v/v 1:3). Yield: 46%. IR (cm^{-1}, KBr): ν(C$\equiv$N) 2204 (vs); ν(C=CS_2) 1405 (vs), 1375 (vs), 888 (m); ν(Cp*) 1025(m). UV−vis (nm, THF): 492, 463 (sh), 345 (sh), 311. $(Et_4N)[Cp^*W\{S_2C{=}C(CN)_2\}_2]$ (**2b**) was prepared by a cation exchange reaction of **2a** with Et_4NBr in THF. Red prismatic crystals suitable for X-ray diffraction analysis were obtained from covering the solution with a layer of hexane. Anal. Calcd for $C_{26}H_{35}N_5S_4W$ (**2b**): C, 42.80; H, 4.83; N, 9.60; S, 17.58. Found: C, 43.19; H, 4.90; N, 9.77, S, 17.97.

Reaction of Cp^*MoCl_4 with $\{(KSe)_2C{=}C(CN)_2\}_2$. A mixture of Cp^*MoCl_4 (0.186 g, 0.50 mmol) and $(KSe)_2C{=}C(CN)_2$ (0.467 g, 1.50 mmol) was dissolved in 30 mL of CH_3CN. The solution turned blue gradually and was stirred for 24 h at room temperature. The reaction mixture was evaporated to dryness. The resulting residue was dissolved in THF (10 mL) and centrifuged to remove insoluble solid. The final dark-blue solution was covered with a layer of Et_2O in a Schlenk tube. After two weeks, crystalline needles of $K[Cp^*Mo\{Se_2C{=}C(CN)_2\}_2]$ (**3a**) and rhombus-shape crystals of $[K(THF)(CH_3CN)][Cp^*Mo\{Se_2C{=}C(CN)_2\}\{Se(Se_2)C{=}C(CN)_2\}]$ (**4**) were collected and washed with THF/Et_2O (v/v 1:3). They were separated manually. For **3a**: Yield: 45%. IR (cm^{-1}, KBr): ν(C$\equiv$N) 2207 (vs); ν(C=CSe_2) 1398 (vs), 1362 (vs), 846 (m); ν(Cp*) 1025 (m). UV−vis (nm, THF): 589, 540 (sh), 380 (sh), 345. For **4**: Yield: 25%. IR (cm^{-1}, KBr): ν(C$\equiv$N) 2210 (vs); ν(C=CSe_2) 1385 (vs), 1358 (vs), 842 (m); ν(Cp*) 1025 (m). UV−vis (nm, THF): 546, 340, 328. Anal. Calcd for $C_{24}H_{26}N_5OKSe_5Mo$ (**4**): C, 30.98; H, 2.82; N, 7.53. Found: C, 30.47; H, 2.70; N, 7.38.

From the cation exchange reaction of **3a** with Et_4NBr in THF, red crystalline needles of $(Et_4N)[Cp^*Mo\{Se_2C{=}C(CN)_2\}_2]$ (**3b**) were obtained from covering the solution with a layer of Et_2O. Anal. Calcd for $C_{26}H_{35}N_5Se_4Mo$ (**3b**): C, 37.65; H, 4.25; N, 8.44. Found: C, 36.18; H, 4.40; N, 8.78.

Reaction of Cp^*WCl_4 with $\{(KSe)_2C{=}C(CN)_2\}_2$. A mixture of Cp^*WCl_4 (0.230 g, 0.50 mmol) and $(KSe)_2C{=}C(CN)_2$ (0.467 g, 1.50 mmol) was dissolved in 30 mL of CH_3CN. The reaction mixture turned dark-red gradually. After it was stirred for 24 h at room temperature, the solution was evaporated to dryness. The resulting dark-red residue was dissolved in THF (10 mL). The final brown-red solution was centrifuged to remove an insoluble solid and covered with a layer of hexane in a Schlenk tube. After three weeks, dark-red crystalline $[K(THF)_2][Cp^*W\{Se_2C{=}C(CN)_2\}\{Se(Se_2)C{=}C(CN)_2\}]$ (**5**) was collected (60%) and washed with THF/hexane (v/v 1:3). IR (cm^{-1}, KBr): ν(C$\equiv$N) 2207 (vs); ν(C=CSe_2) 1405 (vs), 1362 (vs), 846 (m); ν(Cp*) 1024 (m). UV−vis (nm,

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Table 1. Crystallographic Data for **1b**, **2b**, **3b**, **4**, **6**, **7**, and **8**

	1b	**2b**	**3b**	**4**	**6**	**7**	**8**
formula	$MoS_4N_5C_{26}H_{35}$	$WS_4N_5C_{26}H_{35}$	$MoSe_4N_5C_{26}H_{35}$	$MoSe_5KON_5C_{24}H_{26}$	$WKS_5O_2N_4C_{26}H_{31}$	$Mo_2Se_5N_2C_{24}H_{30}$	$WCu_2BrS_4N_5C_{20}H_{18}$
fw	641.78	729.69	829.38	930.34	814.80	933.19	847.48
T, °C	room temp.	room temp.	−100	room temp.	room temp.	−100	room temp
space group	*Cmcm* (no. 63)	*Cmcm* (no. 63)	*C*2/*m* (no. 12)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a, Å	9.236(9)	9.248(2)	21.821(4)	7.676(7)	13.676(9)	12.4408(7)	11.28(2)
b, Å	25.149(9)	25.124(4)	21.281(1)	27.28(3)	15.833(9)	15.4474(3)	14.758(6)
c, Å	13.805(9)	13.772(2)	7.4857(6)	15.211(8)	8.641(9)	15.2899(4)	9.597(3)
α, deg	90	90	90	90	105.28	90	98.21(3)
β, deg	90	90	103.125(2)	93.43	97.67	90	90.64(6)
γ, deg	90	90	90	90	66.75	109.8749(4)	74.84(4)
V, Å^3	3206(3)	3200.1(8)	3385.4(5)	3179(4)	1657(3)	2763.4(1)	1525(2)
Z	4	4	4	4	2	4	2
D_{calcd}, g/cm^3	1.329	1.514	1.429	1.943	1.633	2.243	1.844
μ(Mo Kα), cm^{-1}	6.19	38.97	47.10	62.93	39.59	75.10	67.49
R	0.043	0.028	0.089	0.036	0.045	0.039	0.033
Rw	0.060	0.038	0.097	0.041	0.056	0.050	0.049

THF): 510, 462, 375 (sh), 346. Anal. Calcd for $C_{26}H_{31}N_4KO_2Se_5W$: C, 29.76; H, 2.98; N, 5.34. Found: C, 29.48; H, 2.79; N, 5.42.

Reaction of 2a with S_8. A mixture of **2a** (0.128 g, 0.20 mmol) and S_8 (0.064 g, 0.40 mmol) in 15 mL of THF was stirred at room temperature for 1 h and excess zinc powder was added. The reaction solution turned from brown-red to yellow gradually. After it was stirred for 40 h at room temperature, the resulting solution was reduced to 5 mL, and centrifuged to remove an insoluble solid and unreacted zinc powder. The final yellow solution was covered with a layer of hexane in a Schlenk tube. After one week, the brown crystals of $[K(THF)_2][Cp^*W\{S_2C{=}C(CN)_2\}\{S(S_2)C{=}C(CN)_2\}]$ (**6**) were collected and washed with THF/Et_2O (v/v 1:3). Yield: 84%. IR (cm^{-1}, KBr): ν(C≡N) 2211 (vs); ν(C=CS_2) 1400 (vs), 1374 (vs), 889 (m); ν(Cp*) 1025 (m). UV−vis (nm,THF): 500 (sh), 440, 381, 336. Anal. Calcd for $C_{26}H_{31}N_4KO_2S_5W$: C, 38.33 H, 3.83; N, 6.88; S, 19.68. Found: C, 38.40; H, 3.70; N, 7.01, S, 20.29. Refluxing the reaction mixture in THF without the presence of zinc powder gave rise to a similar result.

Reaction of 3a with O_2. To a THF solution (15 mL) of **3a** (0.145 g, 0.20 mmol) was injected 20 mL of 1 atm dried oxygen. The reaction mixture turned from purple to dark-red gradually. After it was stirred for 12 h at room temperature, the resulting solution was reduced to 5 mL by evaporation and centrifuged to remove an insoluble solid. The final dark-red solution was covered with a layer of hexane in a Schlenk tube. After two weeks, dark-red crystalline plates were collected and washed with THF/hexane (v/v 1:3). Yield: 38%. IR, UV−vis spectra, and unit cell parameters showed the compound was identical to **4**.

Reaction of 3a with Se Powder. To a THF solution (15 mL) of **3a** (0.145 g, 0.20 mmol) was added Se powder (0.020 g, 0.25 mmol). The reaction mixture turned from purple to dark-red gradually. After it was stirred for 20 h at room temperature, the resulting solution was reduced to 5 mL and centrifuged to remove an insoluble solid. The final dark-red solution was covered with a layer of hexane in a Schlenk tube. After three weeks, dark-red plates were collected and washed with THF/hexane (v/v 1:3). Yield: 72%. IR, UV−vis spectra, and unit cell parameters showed the compound was identical to **4**.

Reaction of 4 with Na_2Se. To a THF (10 mL) slurry of Na_2Se, prepared from heating selenium powder (0.040 g, 0.5 mmol) and sodium metal (0.018 g, 0.8 mmol), was added a THF solution (10 mL) of **4** (0.160 g, 0.20 mmol). The reaction mixture turned from dark-red to brown-red gradually. After it was stirred at room temperature for 15 h, the resulting solution was reduced to 8 mL and centrifuged to remove an insoluble solid. The final brown-red solution was covered with a layer of hexane in a Schlenk tube. After one month, dark-red prismatic crystals of $[(Cp^*Mo)_2(\mu\text{-}Se)\{\eta_2\text{-}\mu\text{-}Se(Se_3)C{=}C(CN)_2\}]$ (**7**) were collected and washed with THF/ether (v/v 1:3). Yield: 28%. The compound is slightly soluble in THF, soluble in CH_2Cl_2, and insoluble in CH_3CN and toluene. IR (cm^{-1}, KBr): ν(C≡N) 2216 (vs); ν(C=CSe_2) 1390 (vs), 1375 (vs), 846(m); ν(Cp*) 1022 (m). UV−vis (nm, THF): 376 (sh), 328. Anal. Calcd for $C_{24}H_{30}N_2Se_5Mo_2$: C, 30.89; H, 3.24; N, 3.00. Found: C, 31.28; H, 3.49; N, 3.14. Replacing **4** by **3a** in the reaction gave rise to the same result.

Reaction of 2a with CuBr. Solid CuBr (0.056 g, 0.40 mmol) was added to a CH_3CN (15 mL) solution of **2a** (0.128 g, 0.20 mmol). After being stirred for 2 days at room temperature, the resulting solution was reduced to 6 mL and centrifuged to remove an insoluble solid. The final red solution was covered with a layer of Et_2O in a Schlenk tube. After two weeks, dark-red prismatic crystals of $[Cp^*WCu_2Br\{S_2C{=}C(CN)_2\}_2{\cdot}CH_3CN]_n$ (**8**) were collected and washed with THF/Et_2O (v/v 1:3). Yield: 43%. IR (cm^{-1}, KBr): ν(C≡N) 2218 (vs); ν(C=CS_2) 1430 (vs), 1372 (vs), 880 (m); ν(Cp*) 1024 (m). UV−vis (nm, THF): 563, 488, 464 (sh), 380 (sh), 328. Anal. Calcd for $C_{20}H_{18}N_5S_4Cu_2WBr$: C, 28.34; H, 2.14; N, 8.26, S, 15.13. Found: C, 28.01; H, 2.05; N, 8.03; S, 15.65.

X-ray Crystal Structure Determination. Crystal data, data collection, and refinement parameters for all structurally characterized complexes are summarized in Table 1. All the crystals were mounted in glass capillaries and sealed under argon. Diffraction data for **1b**, **2b**, **4**, **6**, and **8** were collected at room temperature on a Rigaku AFC7R diffractometer, while those for **3b** and **7** were collected at low room temperature (−100 °C) on a Rigaku CCD diffractometer; both employed graphate-monochromatized Mo Kα radiation (λ = 0.7069 Å) and used $\omega-2\theta$ scans. For Rigaku AFC7R data, refined cell dimensions and their standard deviations were obtained by least-squares refinements of 25 randomly selected centered reflections. Three standard reflections were monitored periodically for crystal decomposition and movement. The raw intensities were corrected for Lorenz and Polarization effects. Empirical absorption corrections based on φ scans were applied. Calculations were performed on a silicon graphics computer with the TEXSAN program package. The structures of **1b**, **3b**, **4**, **7**, and **8** were solved by direct methods,[24] while those of **2b** and **6** were solved by the Patterson method, where the metal and chalcogenide atom positions were located unequivocally. The remaining atoms

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(24) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *DIRDIF94*: The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

except for the hydrogen atoms were found in subsequent Fourier maps, and the structures were refined by full-matrix least squares. Anisotropic refinement was applied to all non-hydrogen atoms except solvent atoms of **8**, which were refined isotropically. The hydrogen atoms were put at calculated positions. Neutral atom scattering factors were taken from Cromer and Waber.[25] Anomalous dispersion effects were included in Fc.[26] Additional data are available as Supporting Information.

In the case of the crystal structure of **7**, due to the large residues of Fourier peaks associated with the selenium atoms and a larger value of goodness of fit, a number of alternative refinements were attempted. And two data sets were collected independently on a Rigaku AFC7R diffractometer and a Rigaku CCD diffractometer. Practically the same result was obtained from the two data sets, of which the CCD data set is presented in this paper. The five selenium atoms are obviously disordered over two sets of positions. According to the final average refined values of site occupancies of selenium atoms, there is a 9:1 ratio of the two sets of selenium atoms. The refinement with reasonable structure parameters as well as lower *R*, *Rw*, and goodness of fit values was considered to be final.

In the case of **8**, the solvent molecule was treated as disordered over three positions by refining the site occupancies of the solvent molecule atoms. The summation of the refined site occupancies led to nearly one as the total occupancy. The final refinement with fixed occupancies of the solvent atoms was performed upon finalizing the structure.

Results and Discussion

According to our previous work, d^1 Cp*Mo^{V}Cl$_4$ reacted with LiS^{t}Bu and Li$_2$(SCH$_2$CH$_2$S) generating the Mo(IV) thiolato complexes, Cp*Mo(S^{t}Bu)$_3$ and [Cp*Mo(SCH$_2$CH$_2$S)$_2$]$^-$, while the analogous reactions of d^1 Cp*W^{V}Cl$_4$ induced C−S bond cleavage of the thiolate ligands and gave rise to the W(VI) sulfido/thiolato complexes, Cp*W(S)$_2$(S^{t}Bu) and [Cp*W(S)$_3$]$^-$.[20] Keeping these results in our mind, we examined the reactions of d^1 Cp*MCl$_4$ (M = Mo, W) with the potassium salts of 2,2-dicyanoethylene-1,1-dicholcogenides, (KS)$_2$C=C(CN)$_2$ (K$_2$-i-mnt) and (KSe)$_2$C=C(CN)$_2$ (K$_2$-i-mns).

Synthesis of [Cp*M{S$_2$C=C(CN)$_2$}$_2$]$^-$ (M = Mo, W). From the reactions of Cp*MCl$_4$ with 3 equiv of (KS)$_2$C=C(CN)$_2$ in CH$_3$CN, we isolated the diamagnetic bis(i-mnt) complexes K[Cp*M{S$_2$C=C(CN)$_2$}$_2$] (M = Mo, **1a**, 74%; W, **2a**, 46%) as dark-red crystals. Cation exchange of K$^+$ for Et$_4$N$^+$ resulted in (Et$_4$N)[Cp*M{S$_2$C=C(CN)$_2$}$_2$] (M = Mo, **1b**; W, **2b**), which were subjected to X-ray single crystal structure analyses. For both reactions, the metal center was reduced from M(V) to M(IV), where the reduction was presumably induced by (KS)$_2$C=C(CN)$_2$.

The crystals of **1b** and **2b** are isomorphic. Since their molecular structures are practically identical, only the ORTEP view of the molybdenum complex **1b** is shown in Figure 1. The selected bond distances and angles of **1b** and **2b** are compared in Table 2. In either of the structures, the metal atom adopts a distorted square-pyramidal coordination geometry. The Cp* ligand occupies the apical position, and the four sulfur atoms are coplanar, making up the base of the pyramid, which is parallel to the Cp* plane. Being crystallized in the orthorhombic *Cmcm* space group, there are two orthogonal mirror planes in the molecule, one of which runs through the metal atom and the olefinic carbons of i-mnt. As a result, the Cp* carbon atoms are disordered over two positions, and two conformations of Cp* are

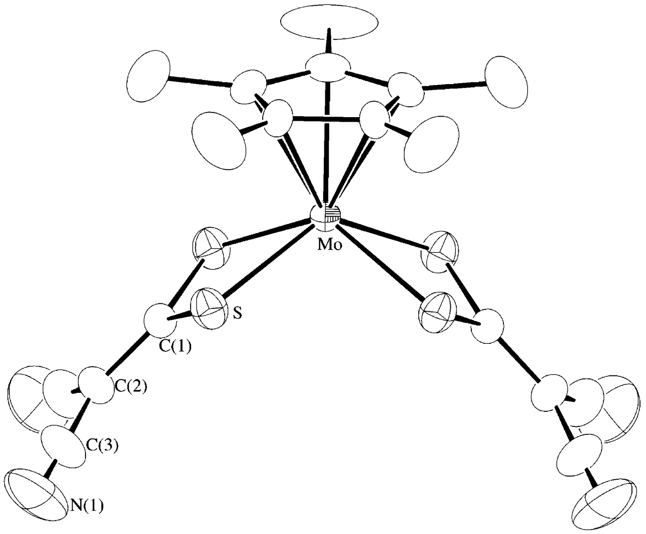
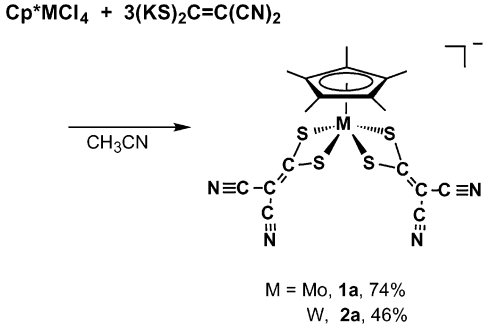


Figure 1. The anion of (Et$_4$N)[Cp*Mo{S$_2$C=C(CN)$_2$}$_2$] (**1b**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1b**, **2b**, and **3b**

1b, (Et$_4$N)[Cp*Mo{S$_2$C=C(CN)$_2$}$_2$]			
Mo−S	2.411(1)	S−C(1)	1.726(4)
C(1)−C(2)	1.369(8)		
S−Mo−S	71.78(7)	S−Mo−S	88.30(7)
Mo−S−C(1)	88.5(2)	S−C(1)−S	110.0(3)
S−C(1)−C(2)	124.9(2)		
2b, (Et$_4$N)[Cp*W{S$_2$C=C(CN)$_2$}$_2$]			
W−S	2.407(1)	S−C(1)	1.724(3)
C(1)−C(2)	1.381(8)		
S−W−S	71.74(6)	S−W−S	87.94(6)
W−S−C(1)	88.7(2)	S−C(1)−S	109.7(4)
S−C(1)−C(2)	125.0(2)		
3b, (Et$_4$N)[Cp*Mo{Se$_2$C=C(CN)$_2$}$_2$]			
Mo−Se(1)	2.545(2)	Mo−Se(2)	2.537(2)
Se(1)−C(1)	1.88(1)	Se(2)−C(1)	1.90(1)
C(1)−C(2)	1.36(2)		
Se(1)−Mo−Se(2)	73.50(6)	Se(1)−Mo−Se(1)	90.0(1)
Se(2)−Mo−Se(2)	85.5(1)	Mo−Se(1)−C(1)	89.4(5)
Mo−Se(2)−C(1)	89.3(4)	Se(1)−C(1)−Se(2)	107.1(6)
Se(1)−C(1)−C(2)	126(1)	Se(2)−C(1)−C(2)	126(1)



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[25] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *PATTY*: The DIRDIF program system, Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1992.

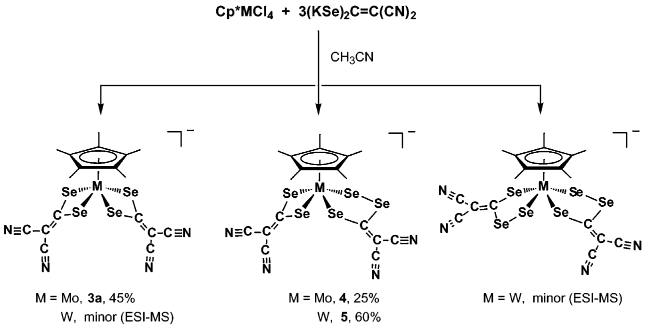
[26] Cromer, D.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

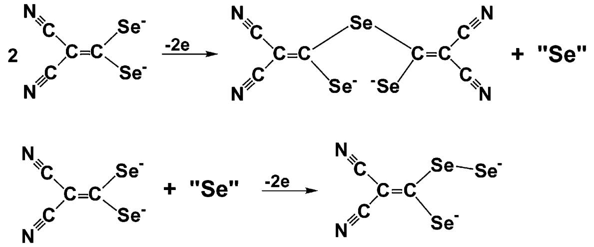
superimposed in the structure with an occupancy ratio of 50/50. Only one set of the disordered Cp* is depicted in Figure 1. The Mo−S distance of 2.411(1) Å in **1b** is very similar to the W−S distance (2.407(1) Å) in **2b**, and they are comparable to those in $(PPh_4)[CpMo(mnt)_2]$ (2.407 Å)[27a] and $[N(PPh_3)_2][CpMo(SC_6F_5)_4]$ (2.420 Å),[27b] but significantly longer than those found in $[Cp^*Mo(S^tBu)_3]^-$ (2.296(1) Å),[20b] $Mo(S^tBu)_4$ (2.235(3) Å),[27c] and $Mo[S\text{-}2,4,6\text{-}C_6H_2(CHMe_2)_3]_4$ (2.262(1) Å).[27d] This may be ascribed to the π electron delocalization on the i-mnt^{2-} ligand, and the somewhat long C═C bond distance of 1.369(8) Å corroborates this argument.

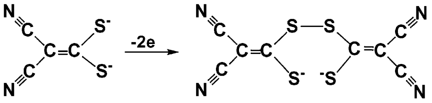
As was noted earlier in this section, the W center of Cp^*WCl_4 was oxidized from M(V) to M(VI) upon reacting it with LiS^tBu and $Li_2(SCH_2CH_2S)$, which was induced by C−S bond cleavage of the thiolate ligands.[20b] However, we did not observe C−S bond cleavage in the reaction of either Cp^*MoCl_4 or Cp^*WCl_4 with $K_2[S_2C{=}C(CN)_2]$. The high delocalization of π electrons in the i-mnt^{2-} ligand might have prevented the C−S bond rupture and oxidation of metal centers.

Reactions of Cp^*MCl_4 with $(KSe)_2C{=}C(CN)_2$ (M = Mo, W). The successful isolation of $[Cp^*M\{S_2C{=}C(CN)_2\}_2]^-$ led us to examine the reactions of Cp^*MCl_4 with $(KSe)_2C{=}C(CN)_2$ (K_2-i-mns). The reaction of Cp^*MoCl_4 with 3 equiv of $(KSe)_2C{=}C(CN)_2$ in CH_3CN generated a dark-blue solution. ESI-MS spectra of the reaction mixture showed two sets of isotopic clusters at 699 and 779, corresponding to $[Cp^*Mo\{Se_2C{=}C(CN)_2\}_2]^-$ and $[Cp^*Mo\{Se_2C{=}C(CN)_2\}\{Se_3C{=}C(CN)_2\}]^-$, respectively. By diffusion of ether into the THF solution of the reaction mixture, we were able to isolate crystals with two different habits, needles of $K[Cp^*Mo\{Se_2C{=}C(CN)_2\}_2]$ (**3a**) and rhombs of $[K(THF)(MeCN)][Cp^*Mo\{Se_2C{=}C(CN)_2\}\{Se(Se_2){=}C(CN)_2\}]$ (**4**). Furthermore, recrystallization of **3a** in THF in the presence of Et_4NBr gave $(Et_4N)[Cp^*Mo\{Se_2C{=}C(CN)_2\}_2]$ (**3b**) as crystalline plates.

The similar reaction of Cp^*WCl_4 with 3 equiv of $(KSe)_2C{=}C(CN)_2$ in CH_3CN gave rise to a dark-red solution. ESI-MS spectra showed one strong signal at 867, corresponding to $[Cp^*W\{Se_2C{=}C(CN)_2\}\{Se(Se_2){=}C(CN)_2\}]^-$, and two weak signals at 780 and 946, probably arising from $[Cp^*W\{Se_2C{=}C(CN)_2\}_2]^-$ and $[Cp^*W\{Se(Se_2)C{=}C(CN)_2\}_2]^-$. By diffusion of hexane into the THF solution of the reaction mixture, crystalline plates of the major diamagnetic product $[K(THF)_2][Cp^*W\{Se_2C{=}C(CN)_2\}\{Se(Se_2){=}C(CN)_2\}]$ (**5**) were obtained. The oxidation states of both molybdenum and tungsten were again reduced from (V) to (IV) during the reactions between Cp^*MCl_4 and $(KSe)_2C{=}C(CN)_2$. The reduction is assumed to be induced by $(KSe)_2C{=}C(CN)_2$, similar to the case of $(KS)_2C{=}C(CN)_2$. However, the products are more complicated than those of the reactions with $(KS)_2C{=}C(CN)_2$, and the most intriguing feature is the presence of the perselenide ligand. Although a detailed study of mechanism is needed, we think that the oxidative coupling of $Se_2C{=}C(CN)_2$ (2−) would release free selenium in the reaction system.[28] Then the free selenium might insert into an M−Se bond with the $[Se_2C{=}C(CN)_2]^{2-}$ ligand, leading to the formation of the perselenide ligand. Thus, there would exist at least two different selenium ligands, $[Se_2C{=}C(CN)_2]^{2-}$ (i-mns^{2-}) and $[Se(Se_2)C{=}C(CN)_2]^{2-}$ (Se-i-mns^{2-}), in the reaction system and the product formed from either the molybdenum or the tungsten system is not unique. In the case of $[S_2C{=}C(CN)_2]^{2-}$, oxidative coupling may occur only upon reducing the metal centers, and no persulfide ligand could be formed in the reaction.







X-ray crystal analyses were carried out for **3b** and **4**. The molybdenum atom in **3b** adopts a distorted square based pyramidal coordination geometry, where the four selenium atoms make up the base of the pyramid. Because the structure of **3b** is similar to those of **1b** and **2b**, its ORTEP view is not shown here. Being crystallized in the monoclinic *C*2/*m* space group, the complex anion possesses a crystallographic mirror plane passing through the molybdenum atom and the middle of the Cp* ring. Selected bond distances and angles are given in Table 2. Note that the numbering scheme of **3b** is slightly different from those of **1b** and **2b**, where the two Se atoms within the i-mns ligand are crystallographically independent for **3b**. The mean Mo−Se distance of 2.541 Å is longer than the Mo−S distances of **1b** and the structurally related Mo(IV) thiolato complexes, simply due to the larger atomic radius of selenium.

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[27] (a) Churchill M. R.; Cooke, J. *J. Chem. Soc., A* **1970**, 2046−2053. (b) Bakar, W. A.; Davidson, J. L.; Lindsell, W. E.; McCullough *J. Chem. Soc., Dalton Trans.* **1990**, 61−71. (c) Otsuka, S.; Kamata, M.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 3011−3014. (d) Roland, E.; Walborsky, E. C.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5795−5797.

[28] (a) Barnardries, D. C.; Woodbridge, D. T. *J. Chem. Soc.* **1961**, 2922−2926. (b) Bao, M. T.; Cao, R.; Su, W. P.; Hong, M. C. *Acta Crystallogr.* **1998**, *C54*, 1622.

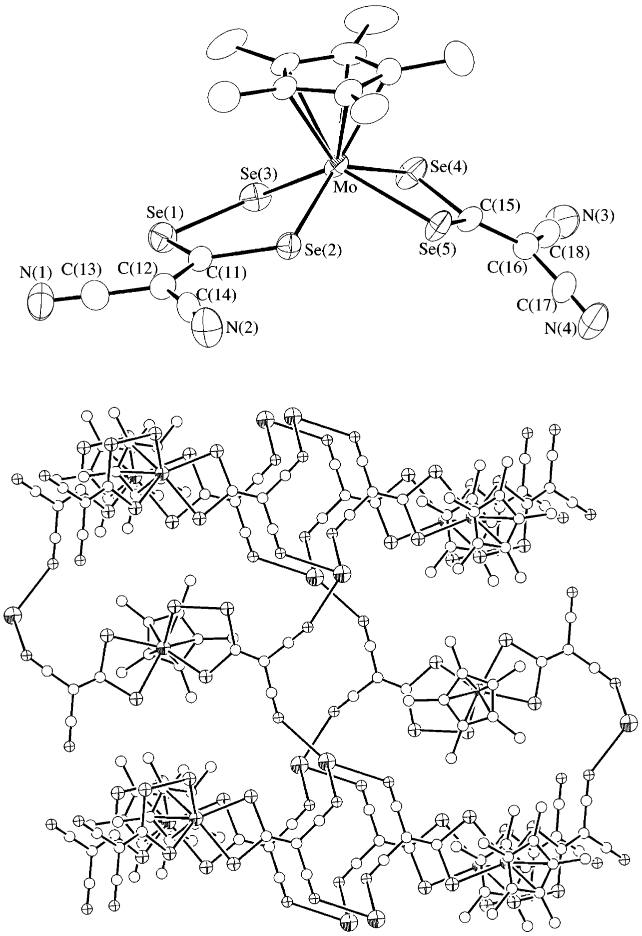

Figure 2. The anion of [K(THF)(MeCN)][Cp*Mo{$Se_2C=C(CN)_2$}{Se-(Se_2)C=$C(CN)_2$}] (**4**) (top) and its three-dimensional network structure (bottom).

The complex anion of **4** is illustrated in Figure 2 (top), and Table 3 lists the selected bond distances and angles. The square pyramidal coordination geometry at the molybdenum atom resembles those of **1b**, **2b**, and **3b**, except that one Se atom is inserted into a Mo−Se bond. The Mo atom is coplanar with the i-mns^{2-} group, while the five-membered $MoSe_3C$ ring formed with the Se-i-mns^{2-} ligand is slightly puckered. The Mo−Se distance of the perselenide portion of Se-i-mns^{2-} is substantially longer by 0.11 Å compared with the other Mo−Se distance (2.393(1) vs 2.502(1) Å), both of which are shorter than those for i-mns^{2-} (2.5740(8) and 2.5881(8) Å) and those in **3b** (av 2.541 Å). It appears that π-electron delocalization in Se-i-mns^{2-} does not extend much to the terminal perselenide Se atom, thereby giving rise to a stronger π donation from the Se atom to the electron-deficient metal center. The Se−Se distance of 2.410(1) Å is slightly longer than normal Se−Se single bond distances (2.30−2.36 Å).[5b] Another interesting facet of the crystal structure of **4** is that the mononuclear anions [Cp*Mo{$Se_2C=C(CN)_2$}{Se(Se_2)=$C(CN)_2$}]$^-$ and the [K(THF)(CH_3CN)]$^+$ cations are linked together through interactions between K$^+$ and the N atoms of the i-mns^{2-} and Se-i-mns^{2-} ligands. The three-dimensional network structure is given in Figure 2 (bottom), where the coordination sphere at K$^+$ is not completely shown for clarity. Each K$^+$ ion is bound by one THF oxygen, one CH_3CN nitrogen, two i-mns^{2-} nitrogens, and two Se-i-mns^{2-} nitorogens, forming a distorted octahedral coordination sphere. In other words, all the nitrogen atoms of i-mns^{2-} and Se-i-mns^{2-} interact with K$^+$ ions.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **4** and **6**

4, [K(THF)(MeCN)][Cp*Mo{$Se_2C=C(CN)_2$}{Se(Se_2)C=$C(CN)_2$}]			
Mo−Se(2)	2.502(1)	Mo−Se(3)	2.393(1)
Mo−Se(4)	2.5881(8)	Mo−Se(5)	2.5740(7)
Se(1)−Se(3)	2.410(1)	Se(1)−C(11)	1.873(6)
Se(2)−C(11)	1.894(6)	Se(4)−C(15)	1.873(6)
Se(5)−C(15)	1.875(6)		
C(11)−C(12)	1.372(8)	C(15)−C(16)	1.361(8)
K−O(1)	2.648(7)	K−N(1)	2.827(7)
K−N(2)	2.874(6)	K−N(3)	2.888(7)
K−N(4)	2.851(6)	K−N(5)	2.879(7)
Se(2)−Mo−Se(3)	87.09(5)	Se(2)−Mo−Se(5)	79.71(2)
Se(3)−Mo−Se(4)	83.62(3)	Se(4)−Mo−Se(5)	72.51(2)
Se(3)−Se(1)−C(11)	100.1(2)	Mo−Se(2)−C(11)	111.9(2)
Mo−Se(3)−Se(1)	110.10(4)	Mo−Se(4)−C(15)	89.0(2)
Mo−Se(5)−C(15)	89.4(2)		
6, [K(THF)$_2$][Cp*W{$S_2C=C(CN)_2$}{S(S_2)C=$C(CN)_2$}]			
W−S(2)	2.354(2)	W−S(3)	2.258(2)
W−S(4)	2.464(2)	W−S(5)	2.450(2)
S(1)−S(3)	2.139(3)	S(1)−C(11)	1.730(7)
S(2)−C(11)	1.719(7)	S(4)−C(15)	1.714(7)
S(5)−C(15)	1.721(7)		
C(11)−C(12)	1.393(9)	C(15)−C(16)	1.397(9)
K−O(1)	2.768(7)	K−O(2)	2.64(1)
K−N(1)	2.879(7)	K−N(2)	2.810(8)
K−N(3)	2.935(9)	K−N(4)	2.833(8)
S(2)−W−S(3)	86.71(6)	S(2)−W−S(5)	83.51(7)
S(3)−W−S(4)	83.37(7)	S(4)−W−S(5)	69.92(6)
S(3)−S(1)−C(11)	102.6(2)	W−S(2)−C(11)	112.0(2)
W−S(3)−S(1)	111.87(9)	W−S(4)−C(15)	90.0(2)
W−S(5)−C(15)	90.0(2)		

The unit cell measurement[29] showed that the structure of **5** is isomorphous and probably isostructural to **6**, which will be described later. Unfortunately, X-ray data collection for **5** was hampered by decomposition of the crystal.

Reaction of K[Cp*W{$S_2C=C(CN)_2$}$_2$] (2a) with S_8. Since the oxidation state of the metal center in the half-sandwich complexes isolated from our reactions is IV, we attempted possible oxidation reactions of **2a** and **3a**. The reaction of **2a** with $^1/_4$ equiv of S_8 in THF at room temperature did not take place. However, the reaction proceeded with gradual color change from orange-red to yellow upon refluxing at about 70 °C or upon addition of zinc powder at room temperature. A brown crystalline compound was isolated from the yellow reaction solution in nearly quantitative yield. The product was characterized as a mononuclear complex with a persulfide ligand [K(THF)$_2$]-[Cp*W{$S_2C=C(CN)_2$}$_2$]{S(S_2)C=$C(CN)_2$} (**6**), where the oxidation state of tungsten remains IV. This sulfur insertion reaction may be similar to that observed in nickel(II) and zinc(II) dithiobenzoate systems,[30] although a more detailed study of the mechanism may be needed.

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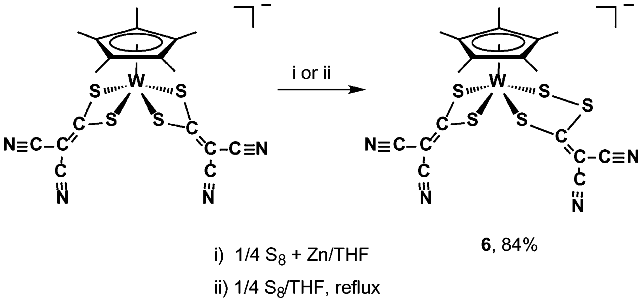
(29) The unit cell parameters of **5**: $a = 16.088(1)$ Å, $b = 13.899(8)$ Å, $c = 8.780(6)$ Å, $\alpha = 97.14(6)°$, $\beta = 105.86(6)°$, $\gamma = 65.97(5)°$, $V = 1724.9(23)$ Å^3.

(30) (a) Fries, D. C.; Fackler, J. P., Jr. *Chem Commun.* **1971**, 276−277. (b) Fackler, J. P., Jr.; Fetchin, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 2912−2913. (c) Fackler, J. P., Jr.; Fetchin, J. A.; Smith, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 2910−2912.



6, 84%

The X-ray analysis of **6** shows that the complex anion is isostructural with that in **4**. Table 3 compares selected bond distances and angles with those of **4**. In the square pyramidal coordination geometry at W, the five-membered WS_3C ring formed by chelation of the persulfide ligand, S-i-mnt^{2-}, is slightly puckered, as was observed for the Se-i-mns^{2-} coordination at Mo of **4**. Due to the decrease of π-electron delocalization within S-i-mnt^{2-},[30a] substantial shortening of the W−S bond of the persulfice site of S-i-mnt^{2-} was again noticed (2.257 vs 2.356 Å). Interestingly, both of the W−S bonds with S-i-mnt^{2-} are much shorter than those for i-mnt^{2-} ligand and those in **2b**. They are comparable to the W−S distances in $[\mathrm{Cp^*Mo(S^tBu)_3}]^-$ (2.296(1) Å), $\mathrm{Mo(S^tBu)_4}$ (2.235(3) Å), and $\mathrm{Mo[S\text{-}2,4,6\text{-}C_6H_2(CHMe_2)_3]_4}$ (2.262(1) Å). The S−S distance is slightly longer than normal single S−S bond distances, which ranges from 2.03(2) to 2.07(3) Å.[31] In the crystal, all the N atoms of the cyano groups interact with K^+ ions, and the complex anions $[\mathrm{Cp^*W\{S_2C{=}C(CN)_2\}\{S(S_2)C{=}C(CN)_2\}}]^-$ and the $[\mathrm{K(THF)_2}]^+$ cations are linked together forming a three-dimensional network structure. Each K^+ ion is coordinated octahedrally by two THF oxygens, and four cynanide N atoms of i-mnt^{2-} and S-i-mnt^{2-}.

Reaction of K[Cp*Mo{Se$_2$C=C(CN)$_2$}$_2$] (3a) with O$_2$ or Selenium. We then investigated the reaction of **3a** with O_2, anticipating that the Mo(IV) center might be oxidized. However, formation of a Mo(V) or Mo(VI) complex was not observed. Instead, one of the i-mns^{2-} ligands in **3a** was converted into Se-i-mns^{2-}, and complex **4** was isolated in 38% yield. Although the reaction mechanism is not clear, we suppose that the i-mns^{2-} ligand was oxidized by O_2 leading to cleavage of the C−Se bond and release of free selenium. The free selenium inserted into an i-mns^{2-} ligand, similar to the reaction of **2a** and S_8. Taking account of this, we expected that **4** might be isolated in high yield, if selenium was introduced externally into the reaction. In fact, **4** was isolated in nearly qualitative yield from the reaction of **3a** with 2 equiv of Se in THF at room temperature. These results illustrate that the metal centers in half-sandwich complexes containing i-mnt^{2-} or i-mns^{2-} are not oxidized readily, and also give some support for our rationale for the formation of **4** and **5**.

Reaction of 3a or [K(THF)(MeCN)][Cp*Mo{Se$_2$C=C(CN)$_2$} {Se(Se$_2$)=C(CN)$_2$}] (4) with Na$_2$Se. In an attempt to insert another selenium into the i-mns^{2-} ligand, **4** was reacted with excess selenium powder. However, no reaction took place. When Na_2Se was used in place of selenium powder, a brown reaction solution was obtained, with the disappearance of the typical UV−visible siganl at 540 nm of **4**, and the neutral diamagnetic binuclear complex with a "selenide-rich" ligand system, $[\mathrm{(Cp^*Mo)_2(\mu\text{-}Se)\{Se(Se_3)C{=}C(CN)_2\}}]$ (**7**), was isolated as needlelike crystals. The oxidation state of the molybdenum in **7** is III, indicating that Na_2Se reduced the molybdenum center and induced the dimerization. Complex **7** was also generated by the reaction of **3a** with Na_2Se.

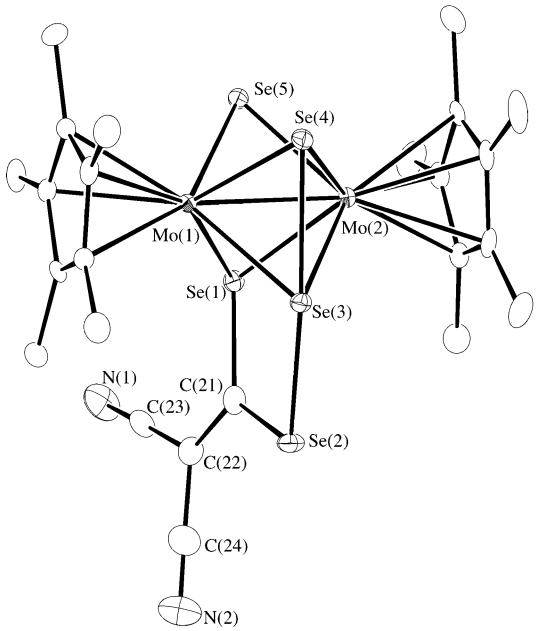


Figure 3. Molecular structure of $[\mathrm{(Cp^*Mo)_2(\mu\text{-}Se)\{\mu\text{-}Se(Se_3)C{=}C(CN)_2\}}]$ (**7**).

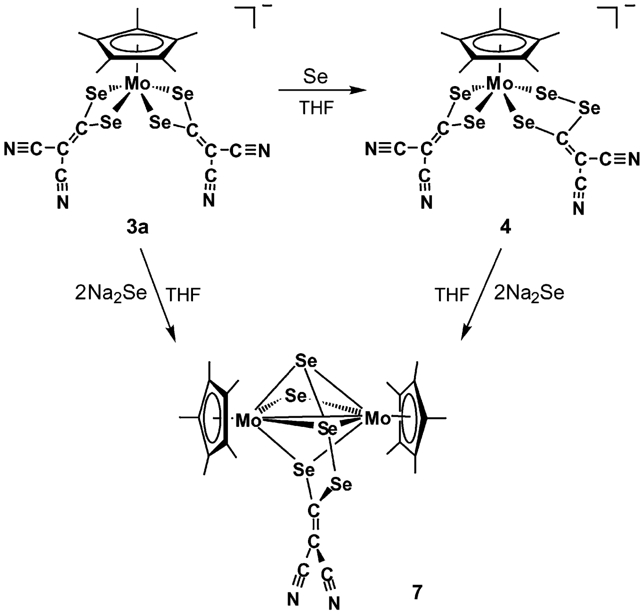


Figure 3 shows the X-ray-derived molecular structure of **7**, and Table 4 summarizes its selected bond distances and angles. The molecular structure consists of two Cp*Mo fragments bridged by one μ_2-Se and one newly formed μ_2-η_2-$[\mathrm{Se(Se_3)C{=}C(CN)_2}]^-$ ligand. Similar to those in **3b** and

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(31) Cohen, S. A.; Stiefel, E. I. *Inorg. Chem.* **1985**, *24*, 4657−4662.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $(Cp^*Mo)_2(\mu\text{-}Se)\{\mu\text{-}Se(Se_3)C{=}C(CN)_2\}$ (**7**)

Mo(1)−Mo(2)	2.6701(6)	Mo(1)−Se(1)	2.5760(8)
Mo(1)−Se(3)	2.5670(6)	Mo(1)−Se(4)	2.5266(9)
Mo(1)−Se(5)	2.461(3)	Mo(2)−Se(1)	2.5917(8)
Mo(2)−Se(3)	2.5436(8)	Mo(2)−Se(4)	2.5450(9)
Mo(2)−Se(5)	2.467(3)	Se(2)−Se(3)	2.5210(8)
Se(3)−Se(4)	2.640(1)	Se(1)−C(21)	1.936(6)
Se(2)−C(21)	1.877(5)	C(21)−C(22)	1.342(8)
Mo(1)−Se(1)−Mo(2)	62.22(2)	Mo(1)−Se(3)−Mo(2)	62.99(2)
Mo(1)−Se(4)−Mo(2)	63.53(2)	Mo(1)−Se(5)−Mo(2)	65.63(2)
Mo(1)−Se(1)−C(21)	107.1(2)	Mo(2)−Se(1)−C(21)	113.0(2)
Se(3)−Se(2)−C(21)	94.4(2)	Mo(1)−Se(3)−Se(2)	109.42(3)
Mo(1)−Se(3)−Se(4)	58.02(2)	Mo(2)−Se(3)−Se(2)	106.33(3)
Mo(2)−Se(3)−Se(4)	58.77(2)	Se(2)−Se(3)−Se(4)	163.06(3)

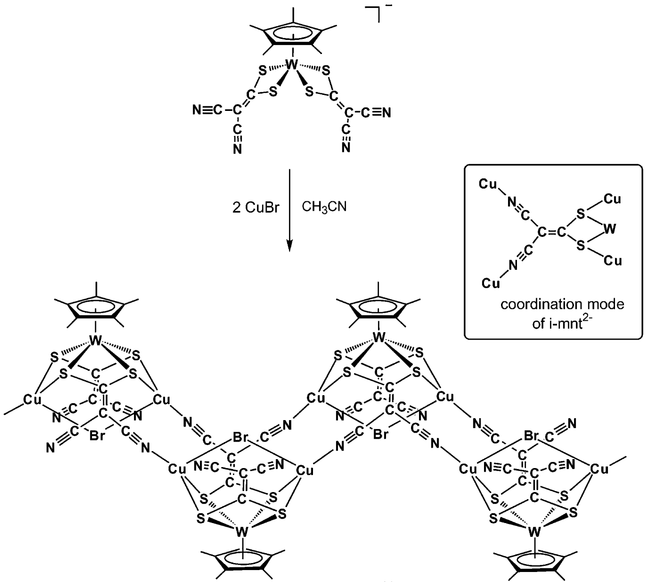
4, the Mo atoms adopt a distorted square pyramidal coordination geometry. The four Se atoms bonded to the Mo atom form a basal plane, which is shared by the two Mo atoms and is nearly parallel to the two Cp* rings. Each Mo atom is 1.33 Å from the Se_4 plane. Interestingly the μ_2-η_2-$[Se(Se_3)C{=}C(CN)_2]^-$ group is essentially planar. The most striking aspect of this ligand is that the Se_3 portion is almost linear (Se−Se−Se = 163°) with two nearly equal Se−Se bond lengths (2.592 and 2.639 Å). This coordination mode is unique in transition metal compounds, although a similar inorganic triselenido (Se_3^{2-}) coordination was reported by Kanatzdis and co-workers in the solid state made up with the $[Mo_3Se_7]^{4+}$ building unit.[5b] However, in that case, the two Se−Se distances are quite different, where the short Se−Se distance is 2.3−2.4 Å and the long one is 2.9−3.2 Å. The Mo−Mo distance of 2.6695(7) Å in **7** is slightly shorter than those in $[Mo_3Se_7]^{4+}$ (2.75 to 2.78 Å). There are two kinds of Mo−Se distances: 2.464 Å for the average distance from Mo to μ_2-Se and 2.558 Å for the distance from Mo to Se of μ_2-η_2-$[Se(Se_3)C{=}C(CN)_2]^-$.

Reaction of $K[Cp^*W\{S_2C{=}C(CN)_2\}_2]$ (2a) with CuBr. The coordination power of i-mnt^{2-} and i-mns^{2-} in the mononuclear compounds **1a**, **2a**, or **3a** does not appear to be saturated, and heterometallic compounds may be reasonably expected through adding other metal atoms via the further coordination of sulfur, selenium, and/or nitrogen atoms of the ligands. Therefore we examined the reaction of **2a** with 2 equiv of CuBr in CH_3CN at room temperature to find that a brown-red solution was generated. A new UV−visible band at 563 nm was observed for the reaction solution, in addition to the two typical absorption bands of **2a** at 491 and 453 nm. And brown-red crystals of $[Cp^*WCu_2(\mu\text{-}Br)\{S_2C{=}C(CN)_2\}_2 \cdot CH_3CN]_n$ (**8**) were isolated from the reaction in 43% yield.

According to the X-ray diffraction analysis, **8** has a one-dimensional polymer structure in crystals as shown in Figure 4 and the repeating unit is a neutral trinuclear cluster complex, $[Cp^*WCu_2(\mu\text{-}Br)\{S_2C{=}C(CN)_2\}_2]$. Table 5 summarizes the selected bond distances and angles. The cluster skeleton of the repeating unit consists of a WS_4Cu_2Br butterfly, in which the two Cu atoms are bridged by one bromide and two sulfur atoms of the i-mnt^{2-} ligand. The average W−Cu distance of 3.051 Å is much longer than those found in other W/Cu/S complexes (2.60−2.85 Å), while the mean Cu−Br distance (2.394(2) Å) and the Cu−Br−Cu angle (90.41(9)°) are typical.[3c,32] Each Cu atom is further coordinated by the cyano N atoms of i-mnt^{2-} in an adjacent trinuclear cluster complex, completing a tetrahedral coordination geometry. Interestingly CH_3CN crystal solvent molecules are not bound to Cu. Thus the Cu−N bonds link the trinuclear cluster units, generating a zigzag one-dimensional chain polymer. There are two types of coordination modes of i-mnt^{2-} in the structure: one is a μ_3-bridging mode connecting three metal centers of 2Cu + W via sulfur atoms, and the other adopts an unusual μ_5-bridging mode connecting five metal centers, 4Cu + W, via sulfur and nitrogen atoms, the latter of which is emphasized in the scheme. To our knowledge, this is the first example of μ_5-i-mnt coordination geometry.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $(Cp^*WCu_2Br\{(S_2CC(CN)_2)_2\}$ (**8**)

W−Cu(1)	3.032(2)	W−Cu(2)	3.068(2)
W−S(1)	2.435(2)	W−S(2)	2.436(2)
W−S(3)	2.436(2)	W−S(4)	2.437(2)
Cu(1)−Br	2.392(2)	Cu(2)−Br	2.395(2)
Cu(1)−S(1)	2.377(2)	Cu(1)−S(4)	2.322(2)
Cu(1)−N(1)	1.955(6)	Cu(2)−S(2)	2.373(2)
Cu(2)−S(3)	2.326(2)	Cu(2)−N(2)	1.934(6)
S(1)−C(1)	1.731(7)	S(2)−C(1)	1.745(7)
S(3)−C(5)	1.740(8)	S(4)−C(5)	1.756(8)
C(1)−C(2)	1.386(9)	C(5)−C(6)	1.363(9)
S(1)−W−S(2)	71.37(9)	S(1)−W−S(4)	90.82(8)
S(2)−W−S(3)	89.72(8)	S(3)−W−S(4)	71.55(9)
Cu−(1)−W−Cu(2)	67.66(8)	Cu(1)−Br−Cu(2)	90.37(9)
S(1)−Cu(1)−S(4)	95.20(6)	S(2)−Cu(2)−S(3)	93.98(6)
W−S(1)−Cu(1)	78.11(6)	W−S(2)−Cu(2)	79.27(6)
W−S(3)−Cu(2)	80.17(6)	W−S(4)−Cu(1)	79.12(6)
W−S(1)−C(1)	89.2(2)	W−S(2)−C(1)	88.8(2)
W−S(3)−C(5)	89.2(3)	W−S(4)−C(5)	88.9(2)
S(1)−C(1)−S(2)	109.6(4)	S(3)−C(5)−S(4)	109.2(3)



8, 43%

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[32] (a) Lang, J.-P.; Kawaguchi, H.; Ohnishi, S.; Tatsumi, K. *J. Chem. Soc., Chem. Commun.* **1997**, 405−406. (b) Lang, J.-P.; Kawaguchi, H.; Ohnishi, S.; Tatsumi, K. *Inorg. Chim. Acta* **1998**, *283*, 136−144. (c) Lang, J.-P.; Tatsumi, K. *J. Organomet. Chem.* **1999**, *579*, 332−337. (d) Guo, J.; Sheng, T. L.; Zhang, W. J.; Wu, X. T.; Lin, P.; Wang, Q. M.; Lu, J. X. *Inorg. Chem.* **1998**, *37*, 3689−3697. (e) Hong, M. C.; Wu, D. X.; Cao, R.; Lei, X. J.; Liu, H. Q.; Lu, J. X. *Inorg. Chim. Acta* **1997**, *258*, 25−35.

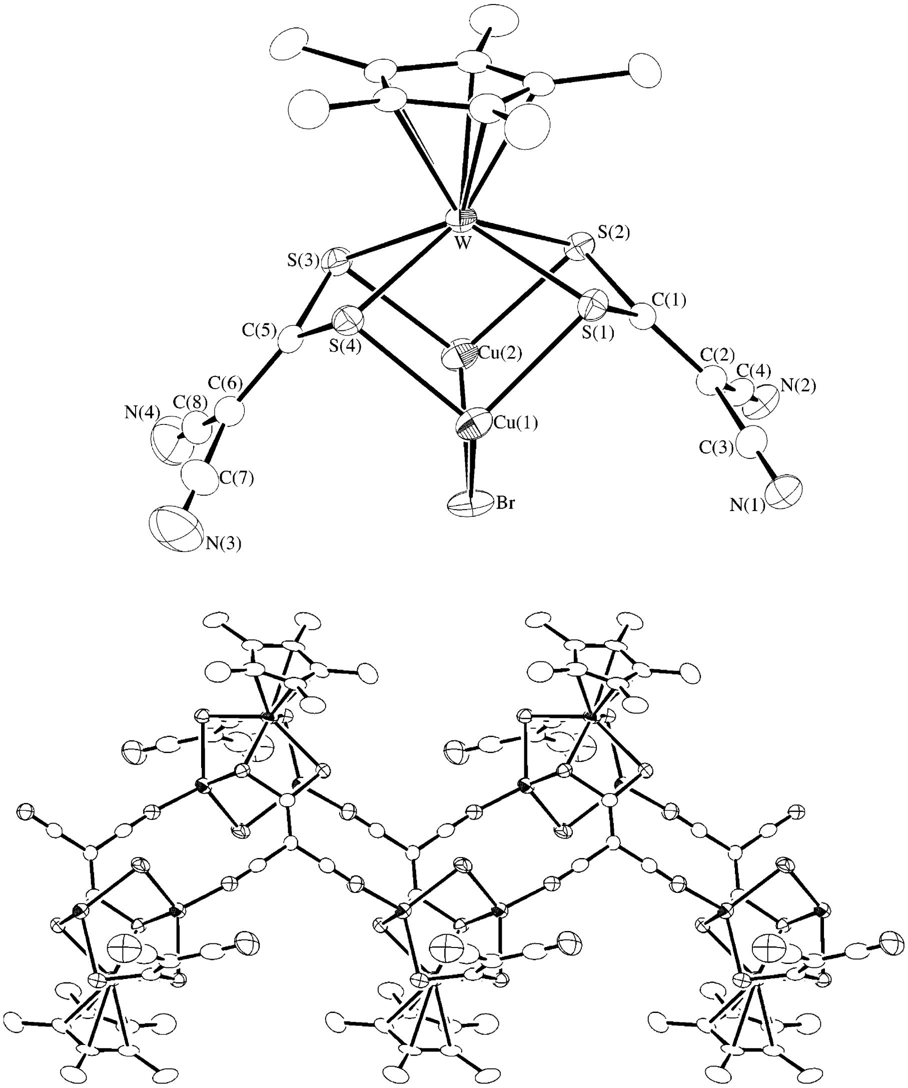

Figure 4. The structure of a repeating unit [Cp*$WCu_2Br\{S_2C{=}C(CN)_2\}_2$] (**8**) (top) and its one-dimensional chain structure (bottom).

Conclusions

We have shown that reactions of Cp*MCl_4 (M = Mo, W) with $(KS)_2C{=}C(CN)_2$ (K_2-i-mnt^{2-}) yielded anionic bis(i-mnt) complexes, [Cp*$M\{S_2C{=}C(CN)_2\}_2]^-$, while the analogous reactions with $(KSe)_2C{=}C(CN)_2$ (K_2-i-mns^{2-}) gave rise to a mixture of [Cp*$M\{Se_2C{=}C(CN)_2\}_2]^-$, [Cp*$M\{Se_2C{=}C(CN)_2\}\{Se(Se_2)C{=}C(CN)_2\}]^-$, and [Cp*$M\{Se(Se_2)C{=}C(CN)_2\}_2]^-$. In the case of K_2-i-mns^{2-}, the oxidative coupling of the ligand might have occurred, liberating free selenium in the reaction systems. The metal centers were reduced from M(V) to M(IV) during these reactions, and no C−S(Se) bond cleavage took place, presumably due to the delocalization of π electrons in the i-mnt^{2-} and i-mns^{2-} ligands. Further reduction of the molybdenum center to Mo(III) occurred, when [Cp*$Mo\{Se_2C{=}C(CN)_2\}_2]^-$ or [Cp*$Mo\{Se_2C{=}C(CN)_2\}\{Se(Se_2){=}C(CN)_2\}]^-$ was treated with Na_2Se, from which we isolated an intriguing dinuclear complex (Cp*$Mo)_2(\mu$-Se)$\{\eta_2$-μ-$Se(Se_3)C{=}C(CN)_2\}$. Our work also demonstrates that [Cp*$M\{E_2C{=}C(CN)_2\}_2]^-$ (E = S, Se) may serve as versatile building blocks for heterometallic olygomers/polymers, by utilizing the coordination power of the ligands at both S and N sites, which was incarnated by the formation of the one-dimensional chain structure of [Cp*$WCu_2(\mu$-Br)$\{S_2C{=}C(CN)_2\}_2{\cdot}CH_3CN]_n$ upon treating [Cp*$W\{S_2C{=}C(CN)_2\}_2]^-$ with 2 equiv of CuBr.

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Supporting Information Available: An X-ray crystallographic file in CIF format of compounds **1b**, **2b**, **3b**, **4**, **6**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org. This file also has been deposited with the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K.

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