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Photochemistry of Bis[cyclopentadienyltricarbonyltungsten] with Diphenyl Diselenide To Produce (Benzeneselenato)cyclopentadienyltricarbonyltungsten

Harmon B. Abrahamson* and Heather Marxen

Department of Chemistry, University of North Dakota, Box 9024,
Grand Forks, North Dakota 58202

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Summary: Visible-light photolysis of [CpW(CO)$_3$]$_2$ with diphenyl diselenide in THF or toluene produces good yields of CpW(CO)$_3$SePh. Nonempirical Fenske–Hall MO calculations are used to compare the bonding in the CpW(CO)$_3$SePh product with its sulfur analog.

Introduction

Photolysis of single-bonded metal carbonyl dimers has been shown to give two types of intermediates, one from loss of a CO ligand and the other from cleavage of the metal–metal bond.[1] While the carbonyl-loss intermediates give substitution products, it is the latter type that is responsible for the bulk of the photoreactivity of unbridged dimers. The 17-electron radicals generated by metal–metal bond homolysis have been shown to participate in a variety of atom- and group-transfer reactions with substrates ranging from halogens and organic halides to organotin hydrides.[1,2]

We have been interested in the photochemistry of metal carbonyl dimers in the presence of electron-rich main group dimers and hydrides. For example, the reaction between [CpW(CO)$_3$]$_2$ (Cp = η^5-C_5H_5) and aryl disulfides in organic solvents can be driven by visible light photolysis:[3]

$$[\mathrm{CpW(CO)_3}]_2 + \mathrm{R_2S_2} \xrightarrow{h\nu} 2\mathrm{CpW(CO)_3SR} \qquad (1)$$

The related reaction with thiols is also fairly efficient:[4]

$$[\mathrm{CpW(CO)_3}]_2 + \mathrm{RSH} \xrightarrow{h\nu} \mathrm{CpW(CO)_3SR} + \mathrm{CpW(CO)_3H} \qquad (2)$$

In both cases, substituent effects allow one to infer that the reaction of the photoproduced radicals is electrophilic in nature.

To help test this hypothesis, we are examining the reaction of photoproduced metal radicals with a range of substrates. Below we report the results of reactions with an organic diselenide, Ph$_2$Se$_2$. Our results also suggest that previous, allegedly thermal, reactions of this diselenide with group 6 metal dimers were likely assisted by inadvertent visible light photochemistry.

Results and Discussion

Synthesis. The reaction between [CpW(CO)$_3$]$_2$ (Cp = η^5-C_5H_5) and Ph$_2$Se$_2$ in organic solvents, e.g., toluene or tetrahydrofuran (THF), is driven by photolysis at UV or visible wavelengths:

$$\underset{1}{[\mathrm{CpW(CO)_3}]_2} + \mathrm{Ph_2Se_2} \xrightarrow{h\nu} \underset{2}{2\mathrm{CpW(CO)_3SePh}} \qquad (3)$$

The metal dimer 1 absorbs very strongly in the near-UV and blue regions (see Table I). However, the other reactant, Ph$_2$Se$_2$, also has a strong absorbance in the near-UV at the concentrations used in this study (ϵ = 1020 M^{-1} cm^{-1} at 333 nm). To ensure that the tungsten dimer 1, and not the diselenide, is the excited species, visible rather than UV irradiation is used here to drive the photolysis. Efforts to drive the reaction to completion result in decomposition of the product 2, so the reaction typically is stopped when 10–15% of the original dimer remains. Control spectra of unirradiated solutions show no reaction.

The product CpW(CO)$_3$SePh, 2, has apparently been prepared once previously for use as a reagent in CO-substitution reactions,[5] but no data on its physical or spectral properties were reported. The Mo analogue of 2, CpMo(CO)$_3$SePh, was made using a supposedly thermal reaction of Ph$_2$Se$_2$ with the Mo dimer [CpMo(CO)$_3$]$_2$.[6] In view of the low temperature (10 °C) used and the lack of any provisions to protect the solution from light, it is likely that visible light-driven photochemistry was important in these previous preparations.

Only two other sets of tungsten carbonyl compounds are known with simple SeR ligands bonded to tungsten in a nonbridging mode. Those in the first set have the composition ArSeW(CO)$_4$(CNR$_2$), where Ar is phenyl or substituted phenyl and R is methyl or ethyl.[7,8] The second type is represented by (CHT)W(CO)$_2$SePh (CHT = η^7-C_7H_7).[9,10] Both classes of compounds also have several related selenato-bridged di- and trinuclear complexes.[7–9,11] Compounds in both classes are prepared by the reaction of selenolates, RSe$^-$, or selenols, RSeH, with metal carbonyl cations or halides. Other known organoselenato complexes of group 6 metal carbonyls are limited to analogous compounds of molybdenum[7,8,10,12] and chromium.[7,8] Ther-

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[1] Meyer, T. J.; Caspar, J. V. *Chem. Rev.* 1985, *85*, 187–218.

[2] Abrahamson, H. B. In *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; VCH: Deerfield Beach, FL, 1986; Vol. 15, Chapter 13.3; pp 246–259.

[3] Brandenburg, K. L.; Heeg, M. J.; Abrahamson, H. B. *Inorg. Chem.* 1987, *26*, 1064–1069.

[4] Weinmann, D. J. Ph.D. Dissertation, University of North Dakota, Grand Forks, ND, Aug 1988.

[5] Carlton, L.; Davidson, J. L.; Shiralian, M. *J. Chem. Soc., Dalton Trans.* 1986, 1577–1586.

[6] Tillay, E. W.; Schermer, E. D.; Baddley, W. H. *Inorg. Chem.* 1968, 7, 1925–1927.

[7] Fischer, E. O.; Himmelreich, D.; Cai, R. *Chem. Ber.* 1982, *115*, 84–89.

[8] Fischer, E. O.; Wittmann, D.; Himmelreich, D.; Cai, R.; Ackermann, K.; Neugebauer, D. *Chem. Ber.* 1982, *115*, 3152–3166.

[9] Rettenmeier, A.; Weidenhammer, K.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* 1981, *473*, 91–100.

[10] Schulze, W.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* 1981, *481*, 78–94.

[11] Mohr, D.; Weinand, H.; Ziegler, M. L. *J. Organomet. Chem.* 1977, *134*, 281–296.

[12] Krauth-Siegel, L. R.; Schulze, W.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* 1980, *19*, 397–398.

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Table I. Carbonyl Stretching Frequencies and Electronic Spectral Data of Tungsten Complexes[a]

compd	solvent	infrared[b] ν(CO), cm^{-1} (ε, M^{-1} cm^{-1})	UV–vis[c] λ, nm (ε, M^{-1} cm^{-1})
Cp(CO)$_3$WSePh (**2**)	hexane	2026, 1946	280 (13 000), 400 (sh), 495 (1300)
	toluene	2021, 1935 (br)	400 (sh), 493 (1300)
	THF	2020 (4600), 1931 (4900)	282 (10 000), 343 (sh), 400 (sh), 491 (1600)
[Cp(CO)$_3$W]$_2$ (**1**)	toluene	2012 (*0.3*), 1953 (*13.5*), 1904 (*10.5*), 1896 (sh, *5.7*)	360 (21 000), 492 (2360)[d]
	THF	2009 (2400), 1953 (17 600), 1904 (13 200), 1896 (sh, 7000)	360 (20 600), 491 (2640)

[a] The extinction coefficients have been determined from fresh solutions of purified, isolated compound. [b] A 0.1-mm NaCl cell was used; numbers in italics are relative intensities. [c] A 1-cm quartz cell was used. [d] These values are from ref 18 and B. A. Van Vlierberge (personal communication).

mal reaction of group 7 carbonyl halides with Ph_2Se_2 gives complexes in which the intact diselenide bridges a pair of metal atoms. Both $Mn_2Br_2(CO)_6Se_2Ph_2$ and $Re_2X_2(CO)_6Se_2Ph_2$ (X = Br, I)[13,14] have been made.

Photochemical methods have been used to prepare group 7 complexes containing *N,N*-dialkyldiselenocarbamate coordinated to Mn or Re[15] from $M_2(CO)_{10}$ by using UV irradiation. These ligands from chelated mononuclear $M(CO)_4$ complexes or dinuclear bridged/chelated $M(CO)_3$ dimers. UV photolysis has also been used to prepare the dinuclear $[Mn(CO)_4SeCF_3]_2$[16] and the tetranuclear $[Mn(CO)_3SePh]_4$[17] from the parent dimers $Mn_2(CO)_{10}$ and R_2Se_2. In these cases, the ultraviolet irradiation used can cause homolysis of both parent dimers. In addition, the expected simple group transfer product $Mn(CO)_5SeR$ is not observed. Instead, carbonyl loss produces the observed dinuclear and tetranuclear products.

In contrast, our preparative method uses visible photolysis, which is possible because of the substantial visible absorption of the tungsten dimer. Visible photolysis gives primarily metal radicals[18] from metal–metal bond cleavage, which presumably attack the diselenide, leading to the observed group-transfer product **2**. We are able to isolate a mononuclear product because carbonyl loss from the product is drastically reduced by using visible rather than UV light. This has also proven true in the related $CpW(CO)_3SR$[3] and $CpW(CO)_3X$[19] systems.

In contrast to these reactions where photolysis is necessary to produce diselenide cleavage, either directly or indirectly, group 16 dimers R_2E_2 (E = S, Se, Te) react readily in thermal reactions with other main-group dimers, such as Ph_4Bi_2,[20] to produce unsymmetrical mixed dimers.

Characterization. The physical and spectroscopic characteristics of the product **2** are very similar to those of the sulfur analog $CpW(CO)_3SPh$ (**3**) and its substituted-phenyl relatives. Electronic and infrared spectral data are given in Table I. The visible absorption band occurs at lower energy in the Se complex **2** than in **3**[4] (493 vs 483 nm) in accord with the lower position of Se in the spectrochemical series.[21] Infrared stretching frequencies for the carbonyl ligands are slightly lower than in the sulfur analog[22] (see Table IV). This correlates with the lower electronegativity of Se (2.60) compared to S (2.69).[23] The relationship of these spectroscopic parameters to the results of the Fenske–Hall calculations is discussed below.

Table II. ^{13}C NMR Data for XSePh Compounds

	δ[a]				
		Ph			
compd	Cp	4-C	3,5-C	2,6-C	CO
Cp(CO)$_3$WSePh	93.1	126.3	128.3	135.8	211.7, 223.6
PhSeSePh[b]		127.7	129.2	131.5	
Ph$_2$BiSePh[c]		128.1	131.2	137.7	

[a] From TMS. The shifts were measured by reference to the ^{13}C values for the solvent, $CDCl_3$. [b] These values compare favorably with those of the diselenide measured previously: δ 130.9, 131.5, 129.1, and 127.6. See ref 25. [c] From ref 20.

In the ^1H NMR spectrum the tungsten dimer **1** has a Cp peak at 5.39 ppm; after reaction (eq 3) the Cp protons in the spectrum of **2** occur at 5.65 ppm. The Cp peak of the analogous sulfur compound **3** falls at 5.72 ppm,[24] and that of the corresponding *p*-nitrophenyl sulfide compound is found at 5.78 ppm.[24] The progression of downfield shifts in this series reflects the electron-withdrawing nature of the group bonded to W increasing in the order $W(CO)_3Cp$ < SePh < SPh < $SC_6H_4NO_2$.

In the phenyl region, unreacted Ph_2Se_2 has two multiplets with major peaks occurring at 7.68 and 7.65 and 7.34, 7.31, and 7.28 ppm, while the product **2** has peaks at 7.52, 7.49, 7.19, 7.17, and 7.14 ppm. The substitution of a $W(CO)_3Cp$ group for one of the SePh groups to make the product **2** causes an upfield shift due to an increase in the electron density in the phenyl ring, because the W group is less electronegative than the Se group and Se is formally reduced by one unit charge in the product (when compared to Ph_2Se_2).

Assignment of the phenyl carbon resonances in the ^{13}C spectrum of **2** (Table II) relies on the assignment of the diselenide.[25] The shifts of the more distant carbons are smaller than those carbons closer to Se. This increase in downfield shift as one approaches Se is again consistent with the electron-withdrawing nature of the atom. Note also that the magnitude of the increase in shift is larger in the compounds with more electropositive atoms (W, Bi) attached to the Se.

The mass spectrum of **2** has a moderately strong parent multiplet with its most intense peak at *m/e* 490, which corresponds to the combination of isotopes tungsten-184

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(13) Atwood, J. L.; Bernal, I.; Calderazzo, F.; Canada, L. G.; Poli, R.; Rogers, R. D.; Veracini, C. A.; Vitali, D. *Inorg. Chem.* **1983**, *22*, 1797–1804.

(14) Korp, J. D.; Bernal, I.; Atwood, J. L.; Calderazzo, F.; Vitali, D. *J. Chem. Soc., Dalton Trans.* **1979**, 1492–1496.

(15) DePlano, P.; Trogu, E. F. *J. Inorg. Nucl. Chem.* **1981**, *43*, 711–713.

(16) Chaudhuri, M. K.; Haas, A.; Wensky, A. *J. Organomet. Chem.* **1976**, *116*, 323–326.

(17) Jaitner, P. *J. Organomet. Chem.* **1981**, *210*, 353–355.

(18) Van Vlierberge, B. A.; Abrahamson, H. B. *J. Photochem. Photobiol. A, Chem.* **1990**, *52*, 69–81.

(19) Alway, D. G.; Barnett, K. W. *Inorg. Chem.* **1980**, *19*, 1533–1543.

(20) Calderazzo, F.; Morvillo, A.; Pelizzi, G.; Poli, R.; Ungari, F. *Inorg. Chem.* **1988**, *27*, 3730–3733.

(21) Jørgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon: Oxford, U.K., 1962; p 109.

(22) Weinmann, D. J.; Abrahamson, H. B. *Inorg. Chem.* **1987**, *26*, 2133–2137.

(23) Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 34–41.

(24) Duffy, D. E. Master's Thesis, University of North Dakota, Grand Forks, ND, Dec, 1991.

(25) Forchioni, A.; Galasso, V.; Irgolic, K. J.; Pappalardo, G. C. *J. Organomet. Chem.* **1977**, *135*, 327–331.

Table III. Comparison of Calculated Electronic Structure Data for $CpW(CO)_3EPh$ (E = S, Se) and $[CpW(CO)_4]^+$

	orbital energies, eV						
compd	HOMO	LUMO	HOMO/LUMO gap, eV	charge[a] on W	av charge[a] on C[b]	av charge[a] on O	charge[a] on E
$CpW(CO)_3SePh$ (**2**)	−7.13	−1.68	5.45	0.088	0.156	−0.117	−0.182
$CpW(CO)_3SPh$ (**3**)	−7.31	−1.77	5.54	0.146	0.157	−0.109	−0.295
$[CpW(CO)_4]^+$ (**4**)	−14.85	−7.13	7.72	0.002	0.242	−0.054	

[a] Atom charges derived from Mulliken populations. Other atom charges are <0.1 electron. [b] Carbonyl carbon atom.

Table IV. Comparison of Mulliken Populations and Carbonyl Stretching Frequencies

	Mulliken populations, cis-CO ligands[a]		Mulliken populations, unique CO ligands		
compd	5σ	2π(tot.)	5σ	2π(tot.)	ν(CO),[b] cm^{-1}
$CpW(CO)_3SePh$ (**2**)	1.378	0.609	1.357	0.633	2021, 1939, 1934
$CpW(CO)_3SPh$ (**3**)	1.380	0.590	1.360	0.634	2028, 1941, 1937
$[CpW(CO)_4]^+$ (**4**)	1.326	0.524	1.325	0.526	
			1.327	0.522	

[a] The two symmetry-equivalent CO ligands in the *y,z* plane, cis to the EPh group. [b] In toluene solution, 1-cm^{-1} resolution.

and selenium-80. Other strong multiplets are seen at *m/e* 462, 434, and 406, corresponding to the loss of one, two, and three carbonyl ligands, respectively. All multiplets show the expected tungsten–selenium isotope pattern and match the multiplets calculated with a simulation program.[26] Other less intense multiplets with *m/e* between 400 and 200 are consistent with higher degrees of fragmentation of the compound.

Reactivity. Some minor decomposition occurs in solutions of **2** in toluene that are either exposed to ambient lighting for 24 h or saturated with air but kept in the dark. Formation of a cloudy suspension in the liquid is accompanied by the growth of weak peaks in the IR (1861, 1878 cm^{-1}). In contrast, decomposition occurs rapidly in solutions exposed to light and air simultaneously, as evidenced by a decrease in IR absorption intensity and a bleaching of the orange color of the solution.

UV irradiation of **2** in THF solution under N_2 produces gas bubbles and new peaks in the IR spectrum at 1871 and 1853 cm^{-1}. This is consistent with carbonyl loss to form $[CpW(CO)_2SePh]_2$ or $[CpW(CO)SePh]_2$. Analogous sulfur compounds[22] give absorptions between 1840 and 1890 cm^{-1} after similar photolysis. Dimeric compounds $[CpMo(CO)_xSePh]_2$ ($x = 1, 2$) are formed even more easily in the related Mo compounds.[6,22] The decomposition seen on irradiation in air-saturated solutions is in accord with the known air sensitivity of carbonyl-loss intermediates.[27]

Quantitative Photochemistry. A solution of **1** (7 mM) and Ph_2Se_2 (80 mM) in tetrahydrofuran (THF) is irradiated using 546-nm light to restrict excitation to **1**. Attempts to follow reaction progress by quantitative UV–vis spectroscopy as in previous studies[3] run afoul of the identical absorption maxima of **2** and **1** in THF. Concentration changes are best followed by using FTIR spectroscopy (in absorbance mode) in the carbonyl stretching region. The appearance of **2** is monitored at 2020 cm^{-1}, and the disappearance of **1** is followed at 2009 and 1904 cm^{-1}. These absorptions follow Beer's law in the concentration range used here (<10 mM).

The quantum yields were calculated using methods outlined in the Experimental Section, which include corrections for absorption by product. The value of 0.45 ± 0.15 for the disappearance quantum yield of **1** with diphenyl diselenide is the same as that seen for reaction with diphenyl disulfide (0.42 ± 0.10) at similar concentrations (30 mM) in toluene.[4] However, the appearance quantum yield for **2** of 1.33 ± 0.19 is somewhat higher than the 0.99 ± 0.10 found for the reaction with Ph_2S_2 to produce **3**.[4] The ratio of appearance/disappearance yields that we observe, 2.9, is higher than the value of 2.0 expected from eq 3 but is consistent with it within the experimental error. Both the efficiency and the stoichiometry for reaction 3 are somewhat, but not significantly, higher than those seen for the related reaction with diphenyl disulfide. Thus, the effects on the photochemistry that are seen on replacing a disulfide with a diselenide are consistent with the postulated electrophilic nature of the intermediate $CpW(CO)_3$ radical; unfortunately, the changes are not very large.

Electronic Structure Calculations. Calculations of the electronic structure of $CpW(CO)_3SePh$ (**2**) and its sulfur analog $CpW(CO)_3SPh$ (**3**), along with the reference compound $[CpW(CO)_4]^+$ (**4**), were performed using the nonempirical Fenske–Hall method.[28] Details of the calculation are described in the Experimental Section. Selected results of the calculations (HOMO and LUMO energies, largest atomic charges, and carbonyl ligand 5σ and 2π orbital populations) are collected in Tables III and IV.

It is relatively easy to understand the ordering of the frontier orbitals in $CpW(CO)_3SePh$ (**2**) if one uses the more symmetrical $[CpW(CO)_4]^+$ (**4**) as a basis for comparison (see Figure 1). While **4** has effective C_{4v} symmetry and all CO ligands are equivalent, substitution to form **2** reduces the symmetry to C_s, which makes the CO ligand trans to the SePh group unique. In **2**, orbital 29a′ (the SHOMO) has composition and energy similar to the HOMO ($8a_1$) in the tetracarbonyl **4**. The HOMO in **2** (19a″) is of similar composition to the SHOMO ($3b_2$) in **4**, except that it has almost 50% contribution from the highest-energy Se π long pair. This substitution of a π-donor orbital contribution in **2** for the π-acceptor contribution seen in **4** leads to a substantial destabilization of the 19a″ MO. A similar effect operates in reverse in the LUMO; the addition of π-donor character leads to a stabilization of one component of the doubly degenerate (in **4**) 10e set to create the 30a′ MO in **2**. Both effects lead to a decrease in the HOMO–LUMO gap in **2** compared to **4** (5.45 vs 7.72 eV).

The nature of the orbitals in the S compound **3** is almost identical with that in the Se compound **2**; differences can

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(26) Abrahamson, H. B. Mass Spec Simulator, Ver. 0.6, 1990.

(27) Abrahamson, H. B. In *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; Vol. 15; VCH: Deerfield Beach, FL, 1986; Vol. 15, Chapter 13.2.4; pp 204–230.

(28) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768–775.

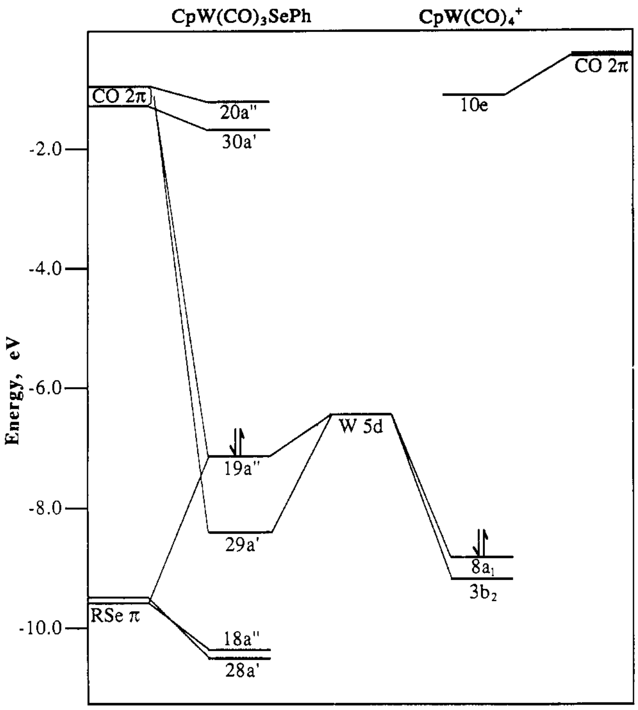

Figure 1. Comparison of the frontier orbitals of CpW(CO)$_3$SePh (A, left) with those of [CpW(CO)$_4$]$^+$ (B, right). The energy scale is correct for (A); the right side of the diagram has been shifted up by 6.05 eV to match the energies of the W 5d orbitals in the two calculations.

be traced to the differing electronegativities of S and Se. This means that the SHOMOs in the two compounds, which have little π-donor lone pair character, differ by only 1% in orbital contributions. On the other hand, the HOMOs differ considerably. In the Se compound **2**, the HOMO is 35% W 5d$_{xy}$, 47% Se lone pair, and 13% CO 2π, while, in the S compound **3**, the corresponding contributions are 39% d$_{xy}$, 40% S lone pair, and 16% CO 2π. The lower electronegativity of S compared to Se lowers the energies of the thiolate lone pairs in **3** compared to the Se lone pairs in **2** and thus reduces the mixing of lone pair character in the HOMO in **3**. Simultaneously, the lone pair character of the lower-lying 18a'' and 28a' orbitals increases in the S compound **3** (from 47 to 53% and 57 to 62%, respectively, in **2** compared to **3**). The same difference in electronegativity also accounts for the differences in atom charges as calculated from Mulliken populations (Table III). As expected, the W–S bond is seen to be more polar than the corresponding W–Se bond.

Note that the ordering and composition of the highest occupied orbitals in the two CpW(CO)$_3$EPh (E = S, Se) compounds **2** and **3** are strikingly similar to those calculated for [Cr(CO)$_5$Br]$^-$.[29] In our compounds, the lower symmetry and presence of the cyclopentadienyl group provide more opportunities for mixing than are present in the mono- and disubstituted octahedral carbonyl halides studied by Hall and Fenske. The similarity is even more remarkable when one considers that the CpW(CO)$_3$EPh compounds are formally d^4, while [Cr(CO)$_5$Br]$^-$ and its congeners have d^6 configurations. However, there is a strong correspondence between the relative position of metal d orbitals and the lone pairs on the π-donor ligand in our compounds and [Cr(CO)$_5$Br]$^-$. (Compare the left side of Figure 1 to Figure 3 in ref 29.)

The order of lowest-energy electronic absorption band maxima in **2** and **3** is consistent with the results of our Fenske–Hall calculations, which show a smaller HOMO/LUMO gap for the Se complex (5.45 vs 5.54 eV; see Table III). The calculated difference in band maxima (0.091 eV) is larger than that observed (0.052 eV; see above), in harmony with the usual phenomenon in MO theory that the HOMO/LUMO gap overestimates the energy of the lowest electronic excited state.

The lower IR frequencies in **2** compared to **3** imply that there are weaker C–O bonds in the former (Se) complex; the larger calculated 2π orbital population in CO ligands cis to the phenyl selenide ligand in **2** as compared to the corresponding population in the sulfur analog **3** is consistent with this (see Table IV). A more quantitative treatment of the relation between orbital populations and carbonyl bond stretching force constants is being undertaken.[30]

Experimental Section

Materials. Toluene and tetrahydrofuran (THF) were refluxed over sodium and benzophenone and distilled under nitrogen directly prior to use. Diphenyl diselenide, dicyclopentadiene, and CDCl$_3$ were obtained from Aldrich Chemical Co., W(CO)$_6$ was obtained from Pressure Chemical Co., all were used without further purification. Neutral silica gel was obtained from Davison Chemicals and activated to grade I by heating at 200 °C under dynamic vacuum overnight. The activated silica gel was stored under vacuum until needed for dry column chromatography[31] (DCC). DCC tubing was obtained from Universal.

Methods. All reactions were run under an inert atmosphere of dinitrogen, unless otherwise noted. Melting points were taken on a MEL-TEMP melting point apparatus, in melting point tubes that were either flame-sealed or plugged with stopcock grease. Infrared (IR) spectra were run on a Biorad FTS-40 spectrometer in a 0.1 mm path length solution cell with NaCl windows. All spectra were of the carbonyl stretching region (2200–1700 cm^{-1}) in the absorbance mode; solvents used were THF, toluene, and hexane. NMR spectra were run on a Varian VXR-300 in CDCl$_3$ and referenced to TMS (tetramethylsilane). UV–vis absorbance spectra were run on a Shimadzu 260 spectrometer; solvents used were THF, toluene, and hexane. Mass spectra were run on a Dupont 21-491B mass spectrometer (probe temperature = 110 °C, sweep width = 0–600 amu, scan rate = 40 s/decade). Isotope patterns were modeled using Mass Spectrum simulator,[26] a Pascal program for the Macintosh based on an algorithm by San Filippo.[32]

Synthesis of [CpW(CO)$_3$]$_2$ (1). This dimer was made using modified literature methods. NaCp (Cp = C$_5$H$_5$) was synthesized from Cp$_2$H$_2$ (dicyclopentadiene) and sodium metal. The Cp$_2$H$_2$ was cracked into CpH and distilled into a flask held at −78 °C. The sodium was heated in xylene until it was liquid, then made into sodium sand using a mechanical stirrer. The sodium sand was rinsed with THF, and Na and CpH were reacted in THF to give the NaCp salt.[33]

W(CO)$_6$ was heated at reflux in an excess of acetonitrile[34] to yield W(CO)$_3$(CH$_3$CN)$_3$. This tris(acetonitrile) intermediate was isolated under dinitrogen by evaporation of acetonitrile under reduced pressure. The resulting yellow-green solid was redissolved in THF and was reacted[33] with a freshly prepared THF solution of NaCp to yield [CpW(CO)$_3$]$^-$. This reactive anionic

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[29] Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 1619–1624.

[30] Abrahamson, H. B.; Duffy, D. E. Manuscript in preparation, 1992.

[31] Pavia, D. L.; Lampman, G. M.; Kriz, G. S. *Introduction to Organic Laboratory Techniques*: *A Contemporary Approach.*, 3rd ed.; Saunders: New York, 1988; pp 612.

[32] San Filippo, J. A Program for the Synthesis of Mass Spectral Ions, 1979. Personal communication.

[33] Birdwhistell, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239–241.

[34] Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433–434.

complex was not isolated but was oxidized in situ with an aqueous solution of ferric sulfate to give 1, which precipitated out of solution. The reddish-purple solid was filtered out on a fine frit and washed twice with distilled water, once with methanol, and repeatedly with hexane to remove the last traces of $W(CO)_6$. The solid was dried by aspiration for 30 min and then stored in a desiccator in the dark.

Synthesis of $CpW(CO)_3SePh$ (2). In the bottom of a three-necked, 200-mL, round-bottom flask was placed 0.310 g (0.993 mmol) of Ph_2Se_2, along with a magnetic stirring bar. To one neck of the flask was attached a bent side-arm tube containing 0.507 g (0.761 mmol) of 1. The flask was connected to a Schlenk line and was degassed (pump-backfill method) three times, after which 50 mL of dry, O_2-free toluene was added by cannula. After the dimer 1 had been added and mixed into solution, the side arm was replaced, under positive pressure, with a septum. The solution was kept at 0 °C with an ice bath and irradiated using a 67-W tungsten lamp from a distance of 5 cm. Progress of the reaction was monitored by IR spectroscopy on small aliquots for the disappearance of the peaks due to 1 (at 1953 and 1904 cm^{-1}) and the appearance of product peaks. Irradiation was stopped after 5 h when there was no further decrease of the 1 peaks. The solution was concentrated to about 10 mL by rotary evaporation in the absence of light and applied to the top of a dry column (2.5 × 100 cm) of neutral silica gel;[31] toluene was used as the eluent in the subsequent dry column chromatography. Three individual bands were cut out of the column, and each was extracted with toluene. The fastest moving band (purple) proved to contain unreacted 1. A dark brown band, insoluble in organic solvents, remained at the top of the column. The solution from the orange (middle) band was evaporated completely on a rotary evaporator and yielded an orange solid identified as 2; it was obtained in a 68.1% yield (0.507 g, 1.037 mmol). Elemental analysis was determined by Oneida Research Services. Anal. Calcd for $C_{14}H_{10}O_3SeW$: C, 34.38; H, 2.06; O, 9.18; Se, 16.15; W, 37.59. Found: C, 33.53; H, 2.06; Se, 16.34; W, 37.38; O (by difference), 10.69. NMR ($CDCl_3$; δ, ppm): ^1H, 7.5 (m, 2H, Ph), 7.17 (m, 3H, Ph), 5.65 (s, 5H, Cp); ^{13}C, see Table II. UV-vis and IR: see Table I. Mp: 99–102 °C (dec, grease-sealed), 134 °C (dec, flame-sealed).

Decomposition of $CpW(CO)_3SePh$. Qualitative decomposition studies were conducted by dissolving the compound 2 in toluene (~3 mM) and exposing the solution to either air, room light (fluorescent), or both, for periods of 1 and 24 h. Infrared spectra showed no obvious decline in absorptions of 2, except for exposure to air and light together. In all cases, weak peaks appeared at 1808, 1861, and 1878 cm^{-1}. A slight cloudiness of the solutions was also noted.

A solution of 2 in THF (~5 mM) was made and irradiated in a 0.1 mm path length NaCl cell using 366-nm light for 0.5, 1, 5, and 10 min. Only after 5 min was significant intensity noted in peaks at 1800, 1853, and 1871 cm^{-1}, while, after 10 min of irradiation, most of the volume of the cell was occupied with gas bubbles.

Quantum Yield Determinations. A stock solution of diselenide was made by dissolving 1.252 g of Ph_2Se_2 (4.011 mmol) in 50 mL of THF to make an 80.2 mM solution. In a typical run, 0.0235 g of 1 was dissolved in 5 mL of the diselenide solution, giving a solution that was 7.06 mM in tungsten dimer. The solution was placed in a septum-sealed Pyrex test tube, purged with N_2, and irradiated using 546-nm light for 2-min periods; a 0.2-mL aliquot was removed after each interval, and an IR spectrum was taken. After subtraction of the solvent spectrum, the concentration of each species was calculated from the absorbance at characteristic frequencies (2009 and 1904 cm^{-1} for 1, 2020 cm^{-1} for 2) using the extinction coefficients in Table I. Photolysis was stopped after a total of 10 min of irradiation, when the reaction had been taken to about 25% completion.

The volume of solution and the changes in concentrations were combined to give changes in reactant and product amounts (in mmol) for each irradiation period. Ferrioxalate actinometry[35–38] was used to find the intensity of the 546-nm light source, which was 2.7×10^{-8} einstein/s. The quantum yield was determined differentially,[39] calculating intermediate values for each interval and averaging them. The results from three runs were combined using the standard deviation of each run to weight the average.

Computational Details. Molecular orbital calculations were performed on a Digital Equipment Corp. DECstation 3100 workstation using the Fenske–Hall method.[28,40] Slater-type orbital (STO) atomic basis functions were derived from numerical atomic calculations.[41] Contracted double-ζ representations were used for the W 5d, Se 4p, S 3p, and C and O 2p AO's. The basis functions for W were calculated for the 1+ oxidation state with the 6s and 6p exponents both fixed at 2.0. The basis functions for S and Se were calculated for a –0.5 oxidation state. An exponent of 1.16 was used for the hydrogen 1s AO.

The geometric parameters of the $CpW(CO)_3$ fragment were held constant; distances and angles used are (E = S, Se) as follows: W–Cp(centroid) = 2.004 Å, W–C (CO cis to EPh) = 2.003 Å, W–C (CO trans to EPh) = 1.998 Å, C–O = 1.146 Å; C–W–C (CO groups cis to EPh) 110°, C–W–E = 134°, W–C–O = 180°. Local D_{5h} symmetry was imposed upon the cyclopentadienyl ring; a C–C distance of 1.415 Å and a C–H distance of 1.10 Å were used in each compound. The parameters used for the $CpW(CO)_3$ fragment are consistent with the structures of $CpW(CO)_3Cl$,[42] $CpW(CO)_3SBtz$ (Btz = benzothiazolyl),[3] and $CpW(CO)_3SC(S)NMe_2$.[43]

For 3, W–S was set at 2.496 Å, S–C was set at 1.769 Å, and the W–S–C angle was set at 113°. For 2, this angle was maintained, and the W–Se and Se–C distances were increased by 0.13 Å over the corresponding bonds in the sulfur analog. Metal–ligand distances used here agree with the averages determined by Orpen et al.[44] Phenyl rings were constructed on the basis of an idealized hexagon using a C–C distance of 1.395 Å and a C–H distance of 1.10 Å. The plane of the phenyl ring was oriented perpendicular to the plane containing the Cp centroid, W atom, and heteroatom (S or Se).

The master coordinate system is defined with the positive z-axis pointing from tungsten toward the centroid of the Cp ring and the x- and y-axes are oriented so that the other atoms coordinated to W fall in the x,z and y,z planes, with the heteroatom (S or Se), if present, in the (–,–) quadrant of the x,z plane. The local coordinate system on tungsten is the same as the master coordinate system. On the E atom (S, Se) and the C atoms of the CO ligands, the z-axis points toward W, while the y-axis points toward the negative z direction on W. On the E atom and the CO trans to it, the x-axis is parallel to the y-axis on W, while, on the two equivalent CO ligands (called here the cis CO ligands), the x-axis is parallel to the x-axis on W.

The calculations were done using a fragment approach. Calculations were first done on an atomic basis. Multiatom ligands were then converged as separate fragments and allowed to interact with the W atom in a transformed calculation. The CO ligand was converged as a neutral molecule, and the Cp, SR, and SeR ligands were each converged as a monoanion. All calculations were converged using a self-consistent-field iterative approach that had the largest deviation between atomic orbital populations on successive cycles of 0.001 as a convergence

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(35) Bowman, W. D.; Demas, J. N. *J. Phys. Chem.* **1976**, *80*, 2434–2435.

(36) Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966; pp 783–786.

(37) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. (London)* **1956**, *A235*, 518–536.

(38) Parker, C. A. *Proc. R. Soc. (London)* **1953**, *A220*, 104–116.

(39) Abrahamson, H. B.; Brandenburg, K. L.; Lucero, B.; Martin, M. E.; Dennis, E. *Organometallics* **1984**, *3*, 1379–1386.

(40) Bursten, B. E. *Pure Appl. Chem.* **1991**, *63*, 839–844.

(41) Bursten, B. E.; Jensen, J. R.; Fenske, R. F. *J. Chem. Phys.* **1978**, *68*, 3320–3321.

(42) Bueno, C.; Churchill, M. R. *Inorg. Chem.* **1981**, *20*, 2197–2202.

(43) Abrahamson, H. B.; Freeman, M. L.; Hossain, M. B.; van der Helm, D. *Inorg. Chem.* **1984**, *23*, 2286–2293.

(44) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.

criterion. A mixing factor of 0.65 was used, and calculations for complete molecules typically converged in 10–15 cycles.

Note Added in Proof: Diphenyl diselenide reacts with the coordinatively unsaturated mixed-metal complex (η^5-C_5Me_5)Ni–W(CO)$_3$(η^5-C_5H_4Me) at low temperature to produce the bridged species (η^5-C_5Me_5)Ni(μ-CO)(μ-SePh)W(CO)(SePh)(η^5-C_5H_4Me).[45] The ^{1}H and ^{13}C NMR spectral parameters for the phenylselenate groups are very close to those reported here for the same ligand in complex **2**.

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(45) Bartlone, A. F.; Chetcuti, M. J.; Fanwick, P. E.; Haller, K. J. *Inorg. Chem.* **1993**, 32, 1435–1441.