Molybdenum and Tungsten Carbonyl Compounds Generate Carbonyl Sulfide (COS), but not Carbonyl Selenide (COSe), when Treated with Elemental Sulfur and Selenium

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Abstract

Carbonyl sulfide (COS) is implicated in prebiotic chemistry, and recent work on COS/H_2S donors has invigorated COS chemistry. We demonstrate that $[TpM(CO)_3]^-$ (M=Mo,W) react with S_8 to form COS, but form $[TpW(CO)_2]_2Se_3$ not COSe upon reaction with Se. These results advance the metal-mediated interconnectivity of CO and reactive S/Se species.
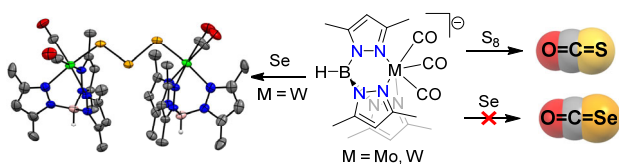
COS but not COSe Formation from Reaction of Metal Carbonyls with Elemental Chalcogens

Introduction

Metal chalcogenides play key roles in terrestrial chemistry and biology. Simple examples of this importance are found in common metal oxo motifs in metalloenzymes, ranging from the iron-based cytochrome P450 enzymes and methane monooxygenases to molybdenum-based sulfite oxidase and xanthine oxidase.[1-2] Each of these systems carry out specific chemical reactions that harness high-energy M=O motifs and enable oxidations that would not occur with molecular oxygen alone. Moving down one row in the periodic table, sulfur also plays key roles in biology, particularly during most of Earth's history that was devoid of atmospheric oxygen.[3] For example, the low solubility of metal sulfides helps to potentiate the bioavailability of metals dissolved in oceans and other bodies of water.[4] Similarly, sulfide lowers heavy metal ion toxicity in archaea native to hyperthermophilic vent environments, which were likely early locales capable of supporting life.[5] These reducing environments devoid of oxygen but rich in sulfur provided a home for early chemolithoautotrophic and sulfur-reducing microorganisms that likely built the cornerstones of bioinorganic metal-chalcogen chemistry still found today in modern biology.

Under such prebiotic conditions, carbon-containing sulfur compounds, such as carbonyl sulfide (COS), have also been hypothesized to play important roles in developing molecular complexity. For example, COS is the most prevalent sulfur-containing gas in Earth's atmosphere and is often found at elevated concentrations near volcanoes and hot springs. In the presence of amino acids, COS can act as a coupling agent to form dipeptides, aminoacyl phosphates, and aminoacyl adenylates, all of which are important building blocks for early life.[6-7] This potential prebiotic importance, coupled with a more reducing early-Earth environment that may have generated metal carbonyl motifs,[8-9] prompted us to investigate whether simple metal carbonyl compounds could play a role in COS generation, particularly under thermal rather than

photochemical reactions. Furthermore, we also viewed this as a viable platform to investigate whether similar chemistry could be observed from the heaver chalcogen congener Se as a platform for carbonyl selenide (COSe) formation. Both of these approaches would provide new insights into the metal-mediated crosstalk between CO and reactive sulfur and selenium species.

Results and Discussion

Inspired by the prevalence of reactive a metal sulfide in xanthene oxidase enzymes and also the importance of Mo and W in enzymes in the iron-sulfur molybdoenzyme superfamily,[10] we wanted to investigate whether simple Mo and W carbonyl compounds could serve as potential precursors to COS formation. Hidai and coworkers previously studied the reactivity of zero valent $[TpMo(CO)_3]^-$ and $[TpW(CO)_3]^-$ and demonstrated that reaction of these complexes with elemental sulfur (S_8) resulted in the formation of $[TpMo(S)(S_4)]^-$ and $[TpW(S)_3]^-$, respectively.[11] The formation of $[TpMo(S)(S_4)]^-$ is the result of a $4e^-$ oxidation at the Mo metal center in $[TpMo(CO)_3]^-$ to reduce one S^0 equivalent to a terminal sulfide (S^{2-}) ligand and to reduce a tetresulfur moiety by $2e^-$ to form a tetrasulfide (S_4^{2-}) ligand. More recently using the same ligand platform, we demonstrated that introducing more reducing equivalents, either in the form HS^- or PPh_3, resulted in tandem oxidation of the Mo^{4+} to Mo^{6+} to form the *tris*(sulfide) $[TpMo(S)_3]^-$ product.[12] In contrast, the formation of $[TpW(S)_3]^-$ proceeds rapidly from the $6e^-$ oxidation of $[TpW(CO)_3]^-$ to reduce three S^0 equivalents to form the three terminal S^{2-} sulfide ligands in $[TpW(S)_3]^-$. Taken together, these results suggest that $[TpW(CO)_3]^-$ is a stronger reductant than $[TpMo(CO)_3]^-$, and that these two compounds may provide useful models to probe thermal COS formation from M-CO motifs based on the well-defined metal sulfide products.

To investigate the fate of the CO ligands in these complexes, we monitored the reactions [TpMo(CO)$_3$]$^-$ and [TpW(CO)$_3$]$^-$ with S$_8$ in sealed NMR tubes. Treatment of [TpMo(CO)$_3$]$^-$ with 1.0 equiv of S$_8$ in THF-d_8 at 50 °C for 16 h resulted in a color change from light yellow to dark green. Both the color change and the resultant ^{1}H NMR spectrum of the product were consistent with formation of [TpMo(S)(S$_4$)]$^-$ as expected. We next monitored the ^{13}C{^{1}H} NMR spectrum of the sealed tube to determine the other products of this reaction (Figure 1). Ligand substitution reactions in metal carbonyl compounds are known to typically release CO when heated or photochemically activated, however we did not observe any CO liberation in the ^{13}C{^{1}H} NMR spectrum (expected: δ = 185.2 ppm). Instead, we observed a new resonance at 154.3 ppm, which matched the chemical shift of independently synthesized COS in THF-d_8 (154.34 ppm).[13] No other carbonyl-containing compounds were observed, which suggested that each CO ligand is converted to COS.
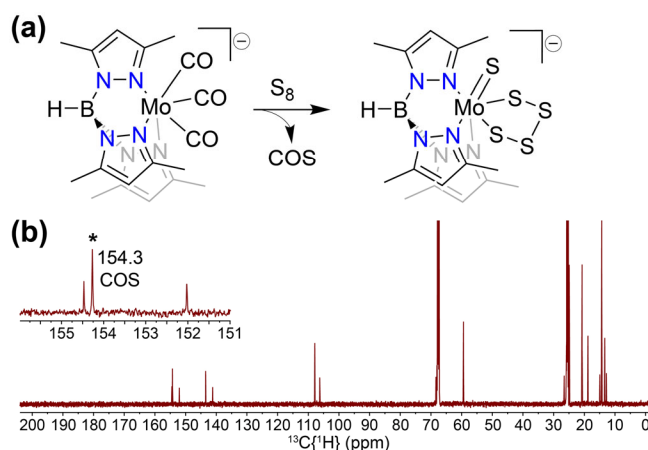
Figure 1. (a) Reaction scheme of [TpMo(CO)$_3$]$^-$ + S$_8$. (b) ^{13}C{^{1}H} NMR spectrum (THF-d_8) of the sealed tube reaction products showing COS formation at δ = 154.3 ppm.

The analogous reaction was also performed with the W congener by treating $[TpW(CO)_3]^-$ with 1.0 equiv of S_8 in THF-d_8 at 50 °C for 16 h (Figure 2). Under these conditions, the reaction mixture turned from yellow to dark red, and the color change along with the resultant ^1H NMR spectrum was consistent with the formation of $[TpW(S)_3]^-$. Akin to the Mo system, the $^{13}C\{^1H\}$ NMR spectrum of the sealed tube reaction mixture revealed a peak at 154.3 ppm, which confirmed COS liberation. Attempts to measure COS directly by GC, either from pure COS or generated from this reaction, were unsuccessful likely due to the low TCD sensitivity of COS. No CO liberation was observed. In both the Mo and W systems, new intermediate species are transiently observed at ~5.5 ppm in the ^1H NMR spectrum during the course of the reaction, which disappear upon reaction completion. Taken together these data show that both the Mo/W-CO motifs can cleanly generate COS upon treatment with S_8 and to the best of our knowledge are the first examples of thermal COS generation from Mo/W-CO compounds.
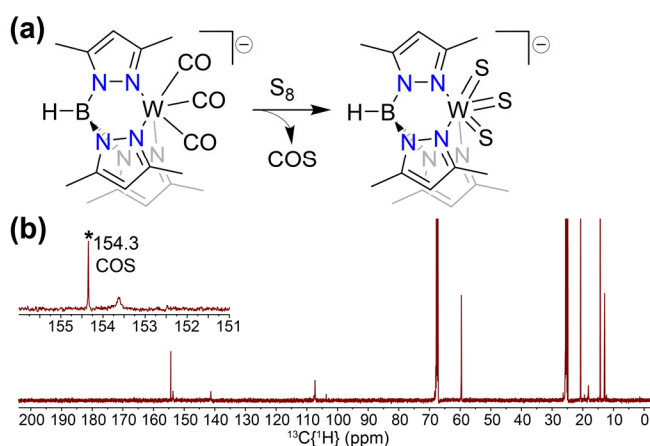
Figure 2. (a) Reaction scheme of $[TpW(CO)_3]^- + S_8$. (b) $^{13}C\{^1H\}$ NMR spectrum (THF-d_8) of the sealed tube reaction products showing COS formation at $\delta = 154.3$ ppm.

In a prior photochemical system, Sita and coworkers observed photocatalytic S atom transfer reaction to CO to form COS from Cp*Mo{N(iPr)-C(Ph)N(iPr)}(CO)S$_2$ in the presence of excess S$_8$ and CO.[14] To test for similar potential turnover, we treated isolated [TpMo(S)(S$_4$)]$^-$ and [TpW(S)$_3$]$^-$ with excess CO, but failed to observe any formation of M(CO)$_x$ products by ^{13}C{^{1}H} NMR spectroscopy. This lack of reactivity is not unexpected since both [TpMo(S)(S$_4$)]$^-$ and [TpW(S)$_3$]$^-$ are already coordinatively saturated at the metal center. Furthermore, the W in [TpW(S)$_3$]$^-$ in its most oxidized +6 oxidation state, which does not allow for further W oxidation to help facilitate the activation and reactivity with CO and S$_8$.

Having established that [TpMo(CO)$_3$]$^-$ and [TpW(CO)$_3$]$^-$ react with S$_8$ to generate COS, we were also curious whether analogous reactivity would be observed with elemental Se to generate COSe. When compared to COS, the fundamental chemistry of COSe is much less investigated, with prior work primarily focusing on preparation,[15-16] carbonylation of amines,[17-18] and other related carbonylation reactions.[19] Treatment of [TpMo(CO)$_3$]$^-$ with 1 equiv of gray Se in THF-d_8 in a sealed NMR tube at 50 °C for 16 h failed to produce any reaction. Similarly, extended heating at 50 °C for up to 3 days did not result in any changes in the ^{1}H NMR spectrum of [TpMo(CO)$_3$]$^-$. By contrast, treatment of [TpW(CO)$_3$]$^-$ with Se under identical conditions resulted in a color change from black to deep green. Analysis of the ^{1}H NMR spectrum showed loss of C$_3$ symmetry and formation of new resonances consistent with a C$_2$ symmetric product (Figure 3), which was later identified as a bridged triselenide (*vide infra*). Analysis of the ^{13}C{^{1}H} NMR spectrum showed the formation of new peaks corresponding to the W-containing product, a peak for free CO at 185 ppm, but no new resonances for COSe were observed (expected chemical shift: 156.6 ppm).[20] We note that inability of [TpMo(CO)$_3$]$^-$ to react with Se is consistent with previous results suggesting that [TpMo(CO)$_3$]$^-$ is a weaker reductant than [TpW(CO)$_3$]$^-$.
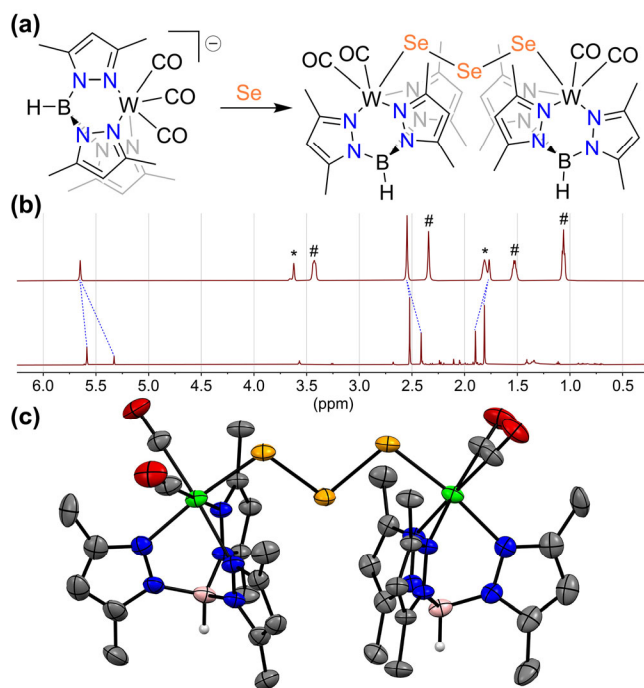
Figure 3. (a) Reaction of $[TpW(CO)_3]^-$ with Se. (b) ^1H NMR spectrum of the reaction product showing change from C_3 to C_2 symmetry. * = THF solvent resonances; # = NBu_4^+ resonances. (c) Solid-state structure of $[TpW(CO)_2]_2Se_3$. Ellipsoids are shown at 50% probability levels. Blue, red, orange, pink, and green ellipsoids represent N, O, Se, B, and W atoms, respectively. A residual toluene molecule and all the C-H bonds are omitted for clarity.

To further investigate the identity of the product, we scaled up the reaction by treating $[NBu_4][TpW(CO)_3]$ with excess gray Se powder at 80 °C for 16 hours in THF in a sealed tube under N_2. Filtration of the dark green reaction mixture through Celite and removal of the THF under vacuum afforded a green powder, which was recrystallized from a toluene solution layered with hexanes to yield crystals suitable for X-ray diffraction. Crystallographic analysis revealed that the structure was triselenide bridged $[TpW(CO)_2]_2Se_3$, which crystallized in C2/c with the central Se atom in the triselenide sitting on a 2-fold rotational axis. The W-Se-Se-Se dihedral (166.3°) deviates from complete co-planarity, and the W-Se-Se angle is 102.09(2)°. In the

trisulfide, the W-Se and Se-Se bond distances are 2.3942(6) and 2.3607(7) Å, respectively. The NMR spectrum of isolated crystals of $[TpW(CO)_2]_2Se_3$ matches that of the bulk material. To the best of our knowledge, $[CpW(CO)_3]_2Se_3$ is the only other crystallographically characterized compounds with an isolated W-Se$_3$-W motif.[21] $[CpW(CO)_3]_2Se_3$ was prepared by treatment of $[CpW(CO)_3][Li]$ with gray Se using O_2 as the oxidant, whereas in the $[TpW(CO)_2]_2Se_3$ we speculate that Se is serving as the oxidant. The W-Se bond distances in $[CpW(CO)_3]_2Se_3$ are 2.651(2) and 2.632(1) Å and Se-Se bond distances are 2.348(2) and 2.342(2) Å. The significantly shorter W-Se bond distances in $[TpW(CO)_2]_2Se_3$ are consistent with the different coordination environment of the $[CpW(CO)_3]^+$ and $[TpW(CO)_2]^+$ fragments. In the above $[CpW(CO)_3]_2Se_3$

Based on the relatively unusual structure of $[TpW(CO)_2]_2Se_3$, we next sought to probe the basic reactivity of this motif as well as its byproducts by treatment with simple reductants and nucleophiles. Upon treatment of $[TpW(CO)_2]_2Se_3$ with 1 equiv of PPh$_3$, we observed rapid and stoichiometric formation of a new peak in the $^{31}P\{^1H\}$ NMR spectrum corresponding to Ph$_3$P=Se and decomposition of the resultant $[TpW(CO)_2Se]$ fragment into an intractable product mixture (Figure 4). Treatment of $[TpW(CO)_2]_2Se_3$ with the sulfur-based nucleophile BnSK resulted in rapid formation of a blue solution, which gradually bleached to green and then finally a red/brown color. We attribute the formation of these highly colored compounds to the transient formation polyselenide anions, which could be formed by triselenide cleavage by BnS$^-$ and subsequent reduction. Treatment of the reaction mixture with BnBr that resulted in Bn$_2$Se formation as evidenced by the major peak at 335.1 ppm in the ^{77}Se NMR spectrum, which matches the chemical shift of authentic Bn$_2$Se.[22] Alternatively, treatment of the reaction mixture with PPh$_3$ resulted in Ph$_3$P=Se formation. Taken together, these trapping experiments support that both Se^0 and Se^{2-} species are present, which is consistent with the formation of highly colored polyselenide anions.

Isolation of the W-containing product after BnSK treatment revealed formation of TpW(CO)₂(SBn), as evidenced by NMR spectroscopy and X-ray crystallography. Formation of this thiol adduct suggests either that the triselenide bridge to make the coordinatively-saturated W center available for substitution or that BnS⁻ attack on the W-Se motif generates an unstable TpW(CO)₂(SeSBn) intermediate that extrudes Se to form the more thermodynamically stable TpW(CO)₂(SBn) product. TpW(CO)₂(SBn) is a known compound that was prepared previously by treatment of TpW(CO)₂I with BnSH, and the NMR spectrum matches the previously reported spectrum.[23]
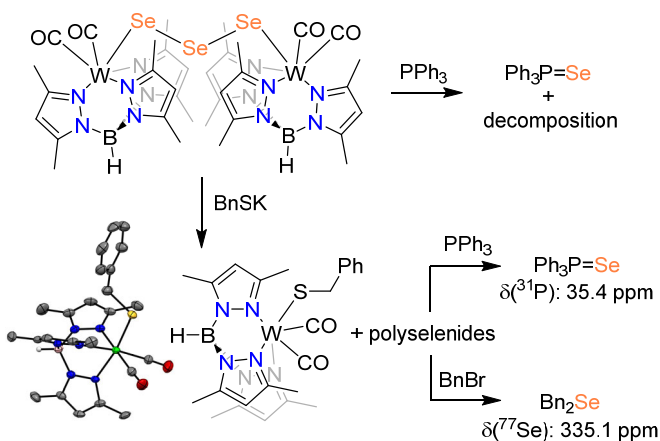
Figure 4. Summary of the reactivity of [TpW(CO)₂]₂Se₃ with PPh₃ and BnSK. The solid-state structure of TpW(CO)₂(SBn) includes ellipsoids at 50% probability levels. Blue, red, yellow, pink, and light blue ellipsoids represent N, O, Se, B, and W atoms, respectively.

Conclusions

We have demonstrated that simple Mo and W carbonyl compounds can react with elemental sulfur to generate COS. The atom economical nature of this chemistry provides an intriguing avenue by which COS can be generated from simple metal carbonyl compounds. Similar

reactions of the Mo and W carbonyl compounds with elemental grey selenium did not generate COSe. $[TpMo(CO)_3]^-$ was inert toward Se, whereas $[TpW(CO)_3]^-$ reacted with Se to form the unusual $[TpW(CO)_2]_2Se_3$ product, which was characterized by X-ray crystallography. Basic reactivity studies show that the triselenide bridge can be cleaved by both reductants and nucleophiles. More broadly, this work advances our understanding of the potential routes of metal-mediated interconnectivity between CO and reactive sulfur and selenium species.

Experimental Section

Materials and Methods. All manipulations were performed under an inert atmosphere using an Innovative Technology N_2-filled glove box unless otherwise noted. C_6D_6 was degassed with N_2 and stored in an inert atmosphere glove box over 4 Å molecular sieves. THF-d_8 was degassed with N_2, distilled from Na/benzophenone, and stored in an inert atmosphere glove box over 4 Å molecular sieves. All commercially available chemicals were used as received and purchased from Strem. $[NBu_4][TpMo(CO)_3]$,[24] $[NBu_4][TpW(CO)_3]$,[24] BnSK,[25] and COS[13] were synthesized from established procedures. C_6D_6 and THF-d_8 were purchased from Cambridge Isotope Laboratories. UV/Vis spectra were acquired on an Agilent Cary 60 UV/Vis spectrophotometer equipped with a Quantum Northwest TC-1 temperature controller set at 25.0 ± 0.05 °C. NMR spectra were acquired on a Varian 500 MHz spectrometer ([1]H: 500 MHz, [13]C: 126 MHz, [31]P: 202 MHz, [77]Se: 95 MHz). Chemical shifts are reported in parts per million (δ) and are referenced to an internal or external standard (PPh$_3$ for ^{31}P, δ = -6.00 ppm). IR spectra were acquired on a Nicolet 6700 IR Spectrometer as ATR or KBr pellet samples.

X-Ray Crystallography. Diffraction intensities for $[TpW(CO)_2]_2Se_3$ and $TpW(CO)_2(SBn)$ were collected at 173 K on a Bruker Apex2 CCD diffractometer using an

Incoatec Cu *IμS* source with CuK$_\alpha$ radiation (1.54178 Å). The space groups were determined based on systematic absences and intensity statistics. Absorption corrections were applied by SADABS.[26] Structures were solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms in both structures were refined in calculated positions in a rigid group model, except the H atoms at the B atoms which were found on the residual density map and refined with isotropic thermal parameters. Both structures include solvent molecules: toluene in [TpW(CO)$_2$]$_2$Se$_3$ and tetrahydrofuran in TpW(CO)$_2$(SBn). All calculations were performed using the Bruker SHELXL-2014/7 package.[27]

COS generation from [NBu$_4$][TpMo(CO)$_3$]. A J-young NMR tube was charged with [NBu$_4$][TpMo(CO)$_3$] (0.020 g, 0.029 mmol), S$_8$ (0.010 g, 0.31 mmol "S^0") and 0.5 mL THF-d_8. The Teflon screw top was closed on the J-young NMR tube, and the solution was heated at 50 °C on a hot plate in a heating container containing metal beads for 24 hrs. The solution turned from a yellow color to a dark green color over this time, and the reaction was analyzed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. As previously described, the [NBu$_4$][TpMo(S)(S$_4$)] product formed, and the spectral data matched previously reported data for [NBu$_4$][TpMo(S)(S$_4$)]. The ^{13}C{^{1}H} NMR spectrum was analyzed to determine the CO-containing by products of the reaction. A peak at 154.3 ppm was observed, which matches that of independently prepared COS.

COS generation from [NBu$_4$][TpW(CO)$_3$]. A J-young NMR tube was charged with [NBu$_4$][TpW(CO)$_3$] (0.0249 g, 0.031 mmol), S$_8$ (0.0088 g, 0.275 mmol "S^0"), and 0.5 mL THF-d_8. The Teflon screw top was closed on the J-young NMR tube, and the solution was heated at 50 °C on a hot plate with a container containing metal beads for 24 hrs. The solution immediately began changing color from yellow to a dark red. The reaction was analyzed by ^{1}H and ^{13}C{^{1}H}

NMR spectroscopy. As previously described, the [NBu4][TpW(S)3] product was formed, and the spectral data matched previously reported data for [NBu4][TpW(S)3]. The $^{13}C\{^1H\}$ NMR spectrum was analyzed to determine the CO containing by products. A peak was observed at 154.3 ppm, which matches that of independently prepared COS.

Synthesis of [TpW(CO)2]2Se3. In the glovebox, a Schlenk tube with a Teflon screw top was charged with [NBu4][TpW(CO)3] (0.104 g, 0.128 mmol), excess grey Se powder (0.136 g, 1.72 mmol), and 5 mL of THF to form a black slurry. The Schlenk tube was closed and heated at 50 °C on a hot plate with metal beads for 16 hours, during which the black slurry turned a deep green color. The slurry was filtered over a pad of Celite, and solvent from the resulting green filtrate was removed *in vacuo* to yield [TpW(CO)2]2Se3 (48.0 mg, 57% yield) as a powder. Green crystals suitable for X-ray diffraction studies were grown from a concentrated toluene solution that was layered with hexanes and stored overnight at room temperature. [TpW(CO)2]2Se3 is thermally unstable and appears to decompose slowly in solution even under aerobic conditions at -30 °C in the dark, but can be readily be prepared reproducibly from the [TpW(CO)3]$^-$ precursor immediately prior to use in subsequent experiments. ^1H NMR (600 MHz, C6D6) δ: 5.59 (s, 2H), 5.33 (s, 1H), 2.52 (s, 6H), 2.41 (s, 3H), 1.90 (s, 3H), 1.81 (s, 6H). $^{13}C\{^1H\}$ NMR (151 MHz, C6D6) δ: 244.8, 159.0, 150.4, 147.1, 144.2, 109.2, 106.6, 17.6, 16.3, 12.4, 12.2. UV-vis spectrum (THF) λ_{max} (ε_M, M^{-1}cm^{-1}): 328 (25,670), 327 (25,800), 594 (8,340). FTIR (KBr, cm^{-1}): 2545 (w, v_{B-H}), 1942 (sh, v_{CO}), 1918 (s, v_{CO}), 1842 (s, v_{CO}).

Reaction of [TpW(CO)2]2Se3 with PPh3. [TpW(CO)2]2Se3 (0.0030 g, 0.0023 mmol) was dissolved in 0.5 mL of C6D6 in an NMR tube. To this solution was added 11 μL of a 0.199 M PPh3 solution in C6D6. Upon addition of the PPh3 solution, a purple-red precipitate formed, and a ^{31}P NMR spectrum was acquired. The NMR spectrum revealed formation of Ph3P=Se at -34.7 ppm.

Reaction of [TpW(CO)$_2$]$_2$Se$_3$ with BnSK to form TpW(CO)$_2$SBn. A scintillation vial was charged with [TpW(CO)$_2$]$_2$Se$_3$ (0.010 g, 0.0076 mmol) and 3 equiv. of BnSK (0.0040 g, 0.025 mmol). THF (5 mL) was added to the vial, and the resultant mixture was stirred. The solution turned from dark green to bright blue within seconds, and the blue color dissipated over the next hour to afford a yellow-brown solution. The solution was filtered over a pad of Celite, concentrated under vacuum, layered with hexanes, and placed in the freezer at -25 °C. Yellow crystals formed overnight and were analyzed by single crystal X-ray diffraction revealing the formation of TpW(CO)$_2$SBn. The crystals were further analyzed by ^{1}H NMR and IR spectroscopy, and the resultant spectral data matched those previously reported for TpW(CO)$_2$(SBn).[23]

Reaction of [TpW(CO)$_2$]$_2$Se$_3$ with BnSK in the presence of BnBr. A scintillation vial was charged with [TpW(CO)$_2$]$_2$Se$_3$ (0.008 g, 0.006 mmol), BnSK (0.0040 g, 0.025 mmol), and excess BnBr (0.012 g, 0.071 mmol). THF (5 mL) was added to the vial, and the resultant reaction mixture was stirred. The solution quickly turned color from dark green to yellow. The solution was filtered, the solvent was removed under reduced pressure, and the residue was analyzed by ^{1}H and ^{77}Se NMR spectroscopy. The ^{1}H NMR spectrum revealed the formation of TpW(CO)$_2$(SBn) and Bn$_2$(Se)$_n$ products. The ^{77}Se NMR spectrum agreed with the Se containing product being Bn$_2$Se observed at 335.1 ppm.[22]

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