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Preparation and Characterization of the Disulfur-Bridged Osmium(IV) Bis(osmocene) Complex $[(Cp_2OsS)_2][PF_6]_2$

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A reaction between $[(Cp_2Os)_2][PF_6]_2$ and elemental sulfur results in the disulfur-bridged, bis(metallocene) complex $[(Cp_2OsS)_2][PF_6]_2$. This new structural type of sulfur-containing metallocene has been fully characterized including a single-crystal X-ray diffraction structure determination. Crystal data for $C_{20}H_{20}Os_2S_2P_2F_{12}$: M_r 994.7, monoclinic, $P2_1/n$, $a = 14.667$ (7) Å, $b = 14.192$ (9) Å, $c = 12.385$ (16) Å, $\beta = 92.62$ (8)°, $V = 2577.1$ Å^3, $Z = 4$, $d_{obsd} = 2.54$ g/mL, $d_{calcd} = 2.56$ g/mL, $R = 0.052$, $R_w = 0.074$. Both spectroscopic and structural data support the description of the complex as two Os(IV) metallocene units linked by a disulfide (S_2^{2-}) bridge. Electrochemistry shows a reversible one-electron oxidation of the disulfide bridge to supersulfide (S_2^-); reaction with the nucleophile cyanide results in a redox reaction forming osmocene and thiocyanogen.

The study of polychalcogenide ligands (such as S_2^{2-}) is of considerable interest not only for fundamental reasons but also for the development of catalytic and solid–state materials. The synthesis and study of these ligands range from traditional coordination complexes to, more recently, organometallic compounds. In continuing our study on the reactivity of the metal–metal-bonded osmocenium dimer $[(Cp_2Os)_2][PF_6]_2$ (Cp = η^5-C_5H_5),[1] we have observed a reaction with elemental sulfur that produces a disulfur-bridged bis(metallocene) complex, $[(Cp_2OsS)_2][PF_6]_2$. Of the several known sulfur-containing metallocenes,[2] the common structural feature observed is a polysulfide chelate ring of variable size. The Os metallocene complex described here is a new structural type containing disulfide bridged between the metallocene units. Here we report the synthesis, characterization (including a single-crystal X-ray diffraction structure determination), and some observations on the reactivity of $[(Cp_2OsS)_2][PF_6]_2$.

Experimental Section

Materials and Procedures. All chemicals used were standard reagent grade. Bis(triphenylphosphoranylidene)ammonium cyanide ((PNP)CN) was prepared as previously described (method: in water, eq 1 of ref 3).[3] $[(Cp_2Os)_2][PF_6]_2$ was prepared as previously described.[1] As a precaution, the preparation of $[(Cp_2OsS)_2][PF_6]_2$ and its reaction with CN^- were preformed under an inert atmosphere (Ar-filled Vacuum Atmospheres Dri-Lab glovebox) with solvents that were dried by standard methods,[4] under argon, and transferred anaerobically to the glovebox. ^1H NMR spectra were obtained with either a Nicolet NT-300WB or a Varian XL-400 spectrometer. Elemental analyses were obtained from either the Stanford University or University of California, Berkeley, Microanalytical Laboratory. Electrochemical measurements were performed in the glovebox with a three-electrode cup cell and the PAR Model 175 universal programmer and Model 174 potentiostat/galvanostat. The working electrode was glassy carbon, the auxiliary electrode was platinum, and the reference electrode was a pseudoreference composed of a silver wire immersed in a salt bridge of the electrolyte solution. The electrolyte was 0.1 M Bu_4NPF_6 in CH_3CN, and sample concentrations were about 10^{-3} M. All potentials are referenced to SCE using ferrocene as an internal standard (+0.307 v).[5]

$[(Cp_2OsS)_2][PF_6]_2$. A sample (0.166 g, 0.178 mM) of $[(Cp_2Os)_2][PF_6]_2$ was stirred with excess elemental sulfur (0.114 g) in 5 mL of CH_3NO_2. As the osmocenium dimer salt dissolved, the solution became dark green. After about 10 min of stirring the solution color had changed to dark red-orange. The mixture was allowed to stir for 2 h more. It was then filtered to remove the insoluble sulfur, and the product was isolated by crystallization using vapor diffusion of diethyl ether into the clear red-orange filtrate. After several days, well-formed red needles of the product were collected, washed with diethyl ether, and allowed to dry under ambient conditions. The yield was 0.109 g (62%). Anal. Calcd for $C_{10}H_{10}OsSPF_6$: C, 24.15; H, 2.03; S, 6 45; P, 6.23. Found: C, 23.88; H, 2.06; S, 6.18; P, 6.81.

Table I. Summary of Crystallography Data for $[(Cp_2OsS)_2][PF_6]_2$

Formula	$C_{20}H_{20}Os_2S_2P_2F_{12}$	d_{obsd}	2.54 g/mL
fw	994.7 g/mol	μ	102.41 cm^{-1}
space group	monoclinic, $P2_1/n$	empirical abs cor	yes (ψ scan)
		transmission coeff (max, min)	99.88% 51.30%
cryst size	0.2 × 0.3 × 0.4 mm		
color	dark red	2θ limits	$2° \le 2\theta \le 55°$
a	14.677 (7) Å	data collected	$\pm h,+k,+l$
b	14.192 (9) Å	no. of observns, $F_o > 3\sigma(F_o)$	4083, 3599
c	12.385 (16) Å		
β	92.62 (8)°	no. of variables	243
V	2577.1 Å^3	R	0.052
Z	4	R_w	0.074
d_{calcd}	2.56 g/mL		

This complex has also been isolated in lower yield from the reaction of H_2S with $[(Cp_2Os)_2][PF_6]_2$ outside of the glovebox. Since a pale yellow precipitate developed during this reaction, we cannot rule out a reaction in which the osmocenium dimer initially oxidizes H_2S to elemental sulfur followed by reaction of the sulfur with remaining dimer as described above.

Reaction of $[(Cp_2OsS)_2][PF_6]_2$ with (PNP)CN. (1) A sample (0.011 g, 0.011 mM) of $[(Cp_2OsS)_2][PF_6]_2$ was dissolved in 1 mL of CD_3NO_2. Then (PNP)CN solid (0.0060 g, 0.011 mM) was added and dissolved at room temperature. When it was mixed, (t = seconds), the solution turned from orange-red to brown-yellow. The resulting solution was loaded in a NMR tube and sealed and the spectrum recorded. The ^1H NMR spectrum indicated that the reaction was completed within the time required to obtain the spectrum. (2) A sample (0.011 g, 0.011 mM) of $[(Cp_2OsS)_2][PF_6]_2$ was dissolved in 1 mL of CD_3NO_2. Then (PNP)CN solid (0.013 g, 0.023 mM) was added and dissolved at room temperature. When it was mixed, (t = seconds), the solution turned from orange-red to brown-yellow. The resulting solution was loaded in a NMR tube and sealed and the spectrum recorded. The ^1H NMR spectrum indicated that the reaction was completed within the time required to obtain the spectrum.

Subsequent to the initial rapid reaction of the disulfur-bridged complex with cyanide, in each case, a new product $[Cp_2OsSCN]^+$ was observed to form more slowly (see Results and Discussion).

Crystal Structure Determination. Crystallographic and related data are summarized in Table I. Suitable crystals of $[(Cp_2OsS)_2][PF_6]_2$ were obtained by the procedure described above. The experimental density was obtained by flotation in CH_2I_2/CCl_4. Crystal data were collected on a Syntex $P2_1$ computer-controlled four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The unit cell dimensions were obtained from a least-squares fit of 15 diffractometer-measured reflections varying from 5 to 20° in 2θ. Intensity data were measured by using the θ–2θ scan method. The structure was solved by using the heavy-atom method to locate Os. All other non-hydrogen atoms were located by alternating Fourier difference maps with full-matrix least-squares refinement. The Os, S, P, and F atoms were refined anisotropically while the C atoms were refined isotropically. The hydrogen atoms were included in calculated positions with fixed isotropic temperature factors. All computations were performed by using the SDP structure determination software package obtained from Enraf-Nonius. Scattering factors embedded in the SDP package were derived from ref 6. The systematic absences of $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n$

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Table II. Positional Parameters and Their Estimated Standard Deviations for $[(Cp_2OsS)_2][PF_6]_2$

atom	*x*	*y*	*z*
Os2	0.33467 (5)	0.08416 (5)	0.13664 (6)
Os1	0.82167 (5)	0.04186 (5)	0.20760 (6)
S1	0.7040 (3)	−0.0758 (3)	0.1681 (4)
S2	0.6155 (3)	−0.0405 (4)	0.0439 (4)
P1	0.5070 (4)	0.1866 (4)	0.5097 (5)
P2	0.8880 (3)	−0.1597 (4)	−0.4649 (5)
F11	0.5973 (9)	0.127 (1)	0.542 (1)
F12	0.450 (1)	0.103 (1)	0.490 (3)
F13	0.537 (1)	0.179 (2)	0.394 (1)
F14	0.4247 (8)	0.252 (1)	0.473 (2)
F15	0.5633 (8)	0.277 (1)	0.528 (2)
F16	0.514 (2)	−0.201 (1)	−0.628 (2)
F21	0.877 (1)	−0.093 (2)	−0.373 (2)
F22	0.800 (1)	−0.214 (1)	−0.438 (2)
F23	0.949 (1)	−0.219 (1)	−0.391 (2)
F24	0.823 (2)	−0.109 (2)	−0.543 (2)
F25	0.911 (1)	−0.240 (2)	−0.542 (2)
F26	0.977 (1)	−0.114 (1)	−0.490 (2)
C11	0.898 (1)	−0.083 (1)	0.178 (2)
C12	0.965 (2)	−0.019 (2)	0.240 (2)
C13	0.971 (1)	0.059 (1)	0.175 (2)
C14	0.914 (1)	0.047 (1)	0.074 (2)
C15	0.880 (1)	−0.042 (1)	0.077 (1)
C21	0.803 (1)	0.115 (2)	0.363 (2)
C22	0.829 (1)	0.179 (1)	0.288 (2)
C23	0.767 (1)	0.189 (1)	0.208 (2)
C24	0.700 (1)	0.128 (1)	0.237 (2)
C25	0.728 (1)	0.076 (1)	0.333 (2)
C31	0.610 (1)	−0.219 (1)	−0.070 (2)
C32	0.711 (1)	−0.215 (1)	−0.059 (2)
C33	0.747 (1)	−0.213 (1)	−0.160 (2)
C34	0.670 (1)	−0.211 (1)	−0.239 (2)
C35	0.584 (1)	−0.217 (1)	−0.179 (2)
C41	0.617 (1)	0.064 (1)	−0.159 (2)
C42	0.718 (1)	0.063 (2)	−0.126 (2)
C43	0.757 (1)	0.019 (1)	−0.210 (2)
C44	0.686 (2)	−0.007 (2)	−0.291 (3)
C45	0.608 (1)	0.019 (1)	−0.258 (2)

+ 1, indicated the nonstandard space group $P2_1/n$ (equivalent positions: $x, y, z; -x, -y, -z; {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z; {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$). Since this space group is commonly encountered and the SDP software is designed to accommodate this space group, the structure was solved by using $P2_1/n$.

The symmetric PF_6^- counterions show considerable rotational motion and/or disorder, which is the origin of the large thermal parameters, slightly altered bond lengths and angles of the PF_6^- group, and higher final *R* values. Attempts to model this disorder by the use of multiple PF_6^- orientations of fractional occupancy were unsuccessful. Instead, initial fluorine positions were obtained from the difference Fourier maps and these positions (and subsequently the temperature factors) were allowed to refine to convergence. The result of this approach was a slightly distorted PF_6^- group with large temperature factors. A final difference map shows that the only remaining peaks of significance are diffusely clustered about phosphorus.

Unfortunately, this disorder problem has apparently led to some difficulties in locating the carbon atomic positions. During attempts to model the PF_6^- disorder, it was observed that the C atomic positions were a function of the initial F positions and shifted as the F positions were refined to convergence. The atomic positions for the heavy atoms (Os, S, P) did not exhibit this behavior. This problem manifests itself primarily as an imprecision in the C–C distances of the Cp ring. However, as the C positions do lie on a common plane, as expected for the Cp ligand, and as the average C–C and Os–C distances are in excellent agreement with corresponding distances observed in related metallocenes, we believe that the imprecision noted in these distances is an artifact arising from the disorder inherent in this crystal. Furthermore, we are convinced that the overall molecular structure is correct and fully consistent with the supporting analytical and spectroscopic data presented here and that the bond distances and angles of most interest (Os–S, S–S) are accurate.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[(Cp_2OsS)_2][PF_6]_2$[a]

Os1–C11	2.14 (2)	Os1–S1	2.436 (4)
Os1–C12	2.29 (2)	Os2–S2	2.463 (4)
Os1–C13	2.256 (15)	S1–S2	2.030 (5)
Os1–C14	2.18 (2)	C11–C12	1.52 (2)
Os1–C15	2.208 (13)	C11–C15	1.39 (2)
Os1–C21	2.21 (2)	C12–C13	1.37 (2)
Os1–C22	2.19 (2)	C13–C14	1.48 (2)
Os1–C23	2.231 (15)	C14–C15	1.36 (2)
Os1–C24	2.21 (2)	C21–C22	1.36 (2)
Os1–C25	2.18 (2)	C21–C25	1.27 (2)
Os2–C31	2.25 (2)	C22–C23	1.32 (2)
Os2–C32	2.183 (15)	C23–C24	1.37 (2)
Os2–C33	2.206 (15)	C24–C25	1.44 (2)
Os2–C34	2.210 (15)	C31–C32	1.47 (2)
Os2–C35	2.28 (2)	C31–C35	1.39 (2)
Os2–C41	2.237 (14)	C32–C33	1.38 (2)
Os2–C42	2.24 (2)	C33–C34	1.45 (2)
Os2–C43	2.205 (14)	C34–C35	1.50 (2)
Os2–C44	2.23 (2)	C41–C42	1.52 (2)
Os2–C45	2.24 (2)	C41–C45	1.38 (2)
		C42–C43	1.36 (2)
		C43–C44	1.46 (2)
		C44–C45	1.28 (2)

Os1–S1–S2	114.0 (2)	C21–C25–C24	103 (2)
Os2–S2–S1	114.8 (2)	C32–C31–C35	109 (1)
C12–C11–C15	107 (1)	C31–C32–C33	110 (1)
C11–C12–C13	104 (2)	C32–C33–C34	107 (1)
C12–C13–C14	111 (1)	C33–C34–C35	108 (1)
C13–C14–C15	106 (1)	C31–C35–C34	106 (1)
C11–C15–C14	111 (1)	C42–C41–C45	107 (1)
C22–C21–C25	111 (2)	C41–C42–C43	103 (1)
C21–C22–C23	112 (2)	C42–C43–C44	110 (2)
C22–C23–C24	102 (2)	C43–C44–C45	109 (2)
C23–C24–C25	111 (2)	C41–C45–C44	111 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Final positional parameters for the complex are given in Table II. Listings of observed and calculated structure factors, anisotropic temperature factors, complete bond lengths and angles, calculated atomic positions, and Cp ring plane calculations are available as supplementary material.

Results and Discussion

At room temperature, a reaction readily occurs between elemental sulfur and $[(Cp_2Os)_2]^{2+}$, resulting in a color change from dark green to dark red. Elemental analysis of the resulting red crystalline complex shows the empirical formula Cp_2OsSPF_6. The ^1H NMR spectrum contains only a sharp singlet at 5.90 ppm (CD_3NO_2), which is consistent with the observed chemical shift of Os(IV) metallocene derivatives.[1]

Analysis of the X-ray diffraction data reveals the dimeric structure of the $[(Cp_2OsS)_2]^{2+}$ cation (Figure 1). Pertinent bond lengths and angles are given in Table III. The structure of the cation consists formally of two Os(IV) osmocene units joined by a disulfide (S_2^{2-}) bridge. The average Os–C bond of 2.22 (1) Å is similar to that observed for $[(Cp_2Os)_2]^{2+}$ and osmocene (2.19 and 2.22 Å, respectively).[1] The average C–C bond distance of 1.40 (1) Å and average C–C–C bond angle of 108 (2)° have a similar correspondence to $[(Cp_2Os)_2]^{2+}$. The average Os–S bond of 2.45 (2) Å is typical of osmium–sulfur bonds.[7,11b] The observed S–S distance is 2.030 (5) Å and is in the range expected for a disulfide bridging unit.[8] The Cp ring planes form an average dihedral angle of 28° compared to the dihedral angle of 35.5° for $[(Cp_2Os)_2]^{2+}$. The Os–S–S–Os torsion angle of 99.5° is characteristic of disulfide (S_2^{2-}) complexes and is to be contrasted with the torsion angle (180°) observed for $[(NH_3)_5RuS]_2^{4+}$, where the complex is formulated as a Ru(II)/Ru(III) mixed-valence species with a supersulfide (S_2^-) unit linking the ruthenium atoms.[9]

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Both the ^1H NMR and the structural results suggest that osmium is best described as Os(IV) and the disulfur bridge as S_2^{2-}. The overall net reaction can be considered as oxidation of each Os(III) of the osmocenium dimer to Os(IV) and corresponding reduction of disulfur to S_2^{2-}, which then serves as a ligand to the oxidized metal centers, forming the disulfide-bridged dimer. This is analogous to the net reaction observed when $[Co(CN)_5]^{3-}$ is oxidized by sulfur, forming the disulfur-bridged complex $[Co_2S_2(CN)_{10}]^{6-}$.[10]

The electrochemistry of $[(Cp_2OsS)_2]^{2+}$ exhibits only two features. One is an irreversible reduction of the complex to osmocene and sulfur, and the other is a reversible ($i_a/i_c = 1.05$) one-electron oxidation (determined by ΔE_p as compared to that of ferrocene under the same conditions) at $E_{1/2} = +0.9$ V (vs. SCE). This oxidation shows no scan rate dependence over the range of 20–200 mV/s, and we can thus conclude that the oxidized species appears to persist for some time. However, an attempt to produce this product by bulk electrolysis was unsuccessful with, apparently, product decomposition occurring over the extended time period (30–60 min) required for electrolysis. Since osmium is considered to be Os(IV) in this case, the most reasonable explanation of the electrochemistry is oxidation of the disulfide to a supersulfide bridge ($S_2^{2-} \rightarrow S_2^- + e^-$) rather than oxidation of Os(IV) to Os(V), for which there is no precedent on the basis of other work with related Os(IV) species.

The reaction of $[(Cp_2OsS)_2]^{2+}$ and CN^- was studied in an attempt to prepare a sulfido (S^{2-})-bridged complex by abstraction of a sulfur atom, forming SCN^-. This type of reaction is characteristic of disulfur ligands and is especially well-known for molybdenum disulfur complexes.[8] In the present case, however, when a reaction (1:1) between $[(Cp_2OsS)_2]^{2+}$ and CN^- was monitored by ^1H NMR, only Cp resonances due to the disulfur complex and to osmocene in a 0.5:1 molar ratio (1:1 integration ratio), respectively, were observed as the major products. In addition, a new resonance that gradually grew in intensity was observed ($t_{1/2}$ = approximately 1 day; reaction was monitored by ^1H NMR and appeared to be complete in at least 3 days). This resonance corresponds to $[Cp_2OsSCN]^+$ (6.08 ppm) and is a product that is known to us and has been prepared independently by the oxidation of Cp_2Os with $(SCN)_2$.[11] Therefore, the net reaction of $[(Cp_2OsS)_2]^{2+}$ in the presence of cyanide appears to be reduction of the disulfur complex to 2 equiv of osmocene and oxidation of the resulting SCN^- to thiocyanogen:

$$[(Cp_2OsS)_2]^{2+} + 2CN^- \rightarrow 2Cp_2Os + (SCN)_2$$

Thiocyanogen can then further react with the osmocene that is produced and generate $[Cp_2OsSCN]^+$ or, since $(SCN)_2$ is unstable at room temperature, it can polymerize or otherwise decompose. The above stoichiometry has also been confirmed by the reaction of the disulfur complex with CN^- in a 1:2 molar ratio, respectively. The ^1H NMR spectrum shows a complete absence of disulfur Cp resonance and only the appearance of the Cp resonance of osmocene. The slow appearance of $[Cp_2OsSCN]^+$ is also observed. The reactions of other nucleophiles have not been examined.

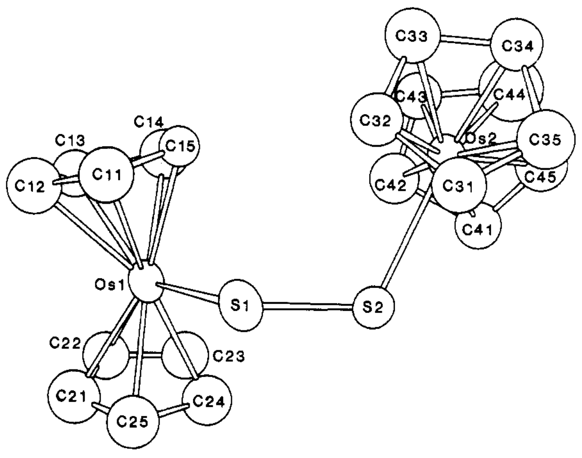

Figure 1. ORTEP drawing of $[(Cp_2OsS)_2]^{2+}$.

The above results describe the synthesis and characterization of a new structural type of sulfur-containing metallocene. The close analogy observed between the chemistry of $[(Cp_2Os)_2]^{2+}$ and that of the isoelectronic rhenium complex $[(Cp_2Re)_2]^1$ suggests that similar chemistry with rhenium as described here for osmium should be expected. A reaction of considerable interest would be that of $[(Cp_2Os)_2]^{2+}$ with oxygen, forming an analogous bis(metallocene) dioxygen-bridged complex. Although a relatively rapid reaction occurs between $[(Cp_2Os)_2]^{2+}$ and pure oxygen under pressure,[12] the dioxygen-bridged complex has not been observed.

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Registry No. $[(Cp_2Os)_2][PF_6]_2$, 107272-09-3; $[(Cp_2OsS)_2][PF_6]_2$, 109336-14-3; Cp_2Os, 1273-81-0; $[Cp_2OsSCN]^+$, 109336-15-4; $[Cp_2OsSCN][PF_6]$, 109336-16-5; $(SCN)_2$, 505-14-6.

Supplementary Material Available: Tables SI–SV listing anisotropic temperature factors, complete bond lengths, complete bond angles, calculated atomic positions, and Cp ring plane calculations (7 pages); a table of calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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(11) (a) $[Cp_2OsSCN][SCN]$ was precipitated as a yellow-orange salt on reaction of Cp_2Os with $(SCN)_2$ in CCl_4. Anal. Calcd for $C_{12}H_{10}OsS_2N_2$: C, 33.02; H, 2.31; N, 6.42; S, 14.89. Found: C, 32.46; H, 2.40; N, 6.33; S, 15.24. ^1H NMR (CD_3CN): 5.90 ppm (singlet for Cp) IR 2140 (ν(CN) of coordinated SCN), 2053 cm^{-1} (K(SCN)).[13] The more stable PF_6^- salt was prepared by resin anion exchange (Amberlyst IRA-900) in CH_3NO_2 (^1H NMR: 5.83 ppm in CD_3CN). The complex, $[Cp_2OsSCN][PF_6]$, was also prepared by the disproportionation of $[(Cp_2Os)_2][PF_6]_2$ in the presence of SCN^-.[1] (b) A preliminary single-crystal X-ray diffraction structure determination of $[Cp_2OsSCN][PF_6]$ has been completed. Crytal data for $C_{11}H_{10}OsSNPF_6$: M_r 523.4, orthorhombic, *Pbca*, $a = 15.39$ Å, $b = 14.06$ Å, $c = 26.55$ Å, $V = 2577.1$ Å^3, $Z = 16$, $d_{obsd} = 2.42$ g/mL, $d_{calcd} = 2.41$ g/mL, $R = 0.059$, $R_w = 0.070$. The asymmetric unit contained two independent salt molecules, each of which was solved. Crystallography shows that the asymmetric unit is composed of discrete $[Cp_2OsSCN]^+$ cations and PF_6^- anions. The SCN ligand is coordinated to Os through the sulfur end with an Os–S distance of 2.411 Å. The other distances and angles are consistent with those commonly encountered in Os metallocene and SCN structures.

(12) In the glovebox under argon, a Fischer–Porter bottle was loaded with 0.13 g of $[(Cp_2Os)_2][PF_6]_2$, 6 mL of CH_3NO_2, and a teflon-coated magnetic stirbar. The bottle was sealed, removed from the glovebox, and thoroughly flushed with pure oxygen while the dark green solution was being stirred for 5 min. The bottle was pressured to 50 psig oxygen, and the solution was stirred vigorously. After several minutes, the solution color had changed from dark green to red-brown and a drop in pressure occurred, indicating oxygen consumption. The reaction was continued until no further change in oxygen pressure was observed. The fianl pressure reading of 32 psig was obtained after about 4–5 h. Vapor diffusion of diethyl ether into the red-brown CH_3NO_2 solution was performed in an attempt to isolate any crystalline products. After 2 days only a gray-brown amorphous solid was obtained (0.11 g). ^1H NMR (CD_3NO_2) showed that the solid was inhomogeneous and was characterized by a set of complex, broad Cp peaks in the vicinity of 5–6 ppm. This solid proved to be quite intractable, and as a result, the investigation was not pursued further.

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