

its properties, both structural and spectroscopic, are very similar to those previously reported for $\text{Re}_2\text{Cl}_6(\text{dppm})_2$.⁷ These compounds contain $\text{Re}=\text{Re}$ double bonds with the electronic configuration being $\sigma^2\pi^2\delta^*\delta^2$ as predicted by Shaik and Hoffmann.¹¹ Indeed, experimental evidence obtained from our recent study of a series of $\text{M}_2\text{Cl}_6(\text{L-L})_2$ compounds supports the molecular orbital ordering that places the δ^* orbital lower in energy than the δ orbital.¹⁰ The factors that influence the relative energies of these orbitals are not well-understood, however, and we are interested in preparing compounds that vary in a systematic manner, thereby allowing new trends to be established. Until recently, our efforts to "construct" homologous series have been thwarted by a general

lack of synthetic methods for the purposeful design of M_2L_{10} compounds. The present study documents the existence of a facile oxidative-addition chemistry for the electron-rich triple bond of dirhenium as found in $\text{Re}_2\text{X}_4(\text{L-L})_2$ compounds. This result is important because it provides the basis for a useful, predictable strategy for the preparation of new M_2L_{10} compounds with M-M double bonds. This approach, which is also applicable to triple and quadruple bonds, is sure to figure prominently in our future research involving the synthesis of new edge-sharing bioctahedral complexes.

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Supplementary Material Available: Full listings of bond angles, bond distances, and anisotropic equivalent displacement parameters (4 pages); a listing of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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Higher Oxidation State Chemistry of Osmocene: Dimeric Nature of the Osmocenium Ion

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A study of the oxidation chemistry of osmocene has led to the discovery of the metal-metal-bonded osmocenium dimer $[(\text{Cp}_2\text{Os})_2]^{2+}$. This complex has been characterized both in solution and in the solid state by determining the structure of the PF_6^- salt by X-ray diffraction. It is composed of two osmocenium cations joined by an Os-Os bond, with the rings tilted back away from the metal-metal bond and each half rotated by 90° with respect to the other. The complex serves as a key synthetic precursor to a variety of higher oxidation state Os(IV) metallocenes. The reaction chemistry of the dimer has been briefly surveyed, and the observed reaction pathways that result in new complexes include radical, disproportionation, and substitution routes. The isolation and characterization of new Os(IV) complexes include a structure determination by X-ray diffraction of the doubly metalated $[\{\text{Cp}(\text{C}_5\text{H}_4)\text{Os}\}_2][\text{PF}_6]_2$.

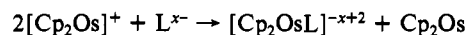
Introduction

In this report are described new higher oxidation state derivatives of osmocene. This chemistry stems in large part from discovery of the key precursor, $[(\text{Cp}_2\text{Os})_2][\text{PF}_6]_2$, which contains the metal-metal-bonded dimer of the osmocenium cation. A number of reactions of this dimer have been elucidated, and these provide routes to a variety of Os(IV) osmocene complexes. The synthesis, characterization, and some reactions of these new derivatives are described here.

Our interest in complexes of this type arose in part from the perception that the Os(IV)/Os(II) couples may be useful experimental probes of two-electron-transfer reactions. It should be recognized that many of the features that qualify pentaammineruthenium complexes as experimental probes of one-electron-transfer reactions are also present in osmium (and ruthenium) metallocenes. It is possible to prepare discrete molecular metallocene complexes that can be systematically modified, that are robust in solution, and that have appropriate oxidation states. We have already shown how simple haloruthenium(IV) and -osmium(IV) metallocenes, $[\text{Cp}_2\text{MX}]^+$ ($\text{M} = \text{Ru}, \text{Os}$; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), participate with osmocene in a two-electron-transfer reaction that is facilitated by halide atom transfer,¹ and there is interest in extending this work to potential multiatom bridges and possibly binuclear complexes.

Since the descriptive chemistry of these metallocenes is limited primarily to the halometallocene complexes,² we sought routes

by which ligands other than halide could be coordinated to the metal. One approach that we explored was formation of the osmocenium cation. This species is a desirable starting material for synthetic reactions since it is expected to react with donor ligands in a disproportionation reaction yielding osmium(IV) derivatives and osmocene:



The existing literature on osmocene,³ including that on the chemical and electrochemical oxidation, leads to no clear consensus on the accessibility of the osmocenium cation. We find that when osmocene reacts with cerium(IV), the metal-metal-bonded osmocenium dimer is formed instead of the expected osmocenium cation. This dimer then participates in a number of new reactions, including some that result in coordination of ligands other than halide to Os(IV).

Experimental Section

Materials. Osmocene was obtained from Strem Chemicals, Inc., and used as received. Reagent grade thiourea was recrystallized from hot water, vacuum-dried at 80°C , and stored under argon. Bis(triphenylphosphoranylidene)ammonium azide $[(\text{PNP})\text{N}_3]$ was prepared by metathesis of NaN_3 with $(\text{PNP})\text{Cl}$ in water. The resulting solid was collected, vacuum-dried at 80°C , and recrystallized by vapor diffusion of diethyl ether into a concentrated acetone solution of the salt under argon. The preparation of $[(\text{Cp}_2\text{Os})_2][\text{PF}_6]_2$ and $[\text{Cp}_2\text{OsNO}_3][\text{PF}_6]$ was performed under normal atmospheric conditions with use of standard

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reagent grade solvents. Although no extreme sensitivity to oxygen or water has been observed, as a precaution all other preparations were performed under an inert atmosphere (Ar-filled Vacuum Atmospheres Dri-Lab glovebox), with solvents that were dried by standard methods⁴ under either argon or vacuum, and transferred anaerobically to the glovebox. Infrared spectra were obtained on the IBM 98 FTIR system with samples prepared as KBr disks. ¹H NMR spectra were obtained with either a Nicolet NT-300WB or a Varian XL-400 spectrometer at 300 or 400 MHz, respectively, for proton resonances. Elemental analyses were obtained from either Stanford University or the Berkeley Micro-analytical Laboratory, University of California.

Syntheses. [(Cp₂Os)₂][PF₆]₂. A sample of osmocene (0.500 g, 1.56 mmol) was dissolved in 100 mL of hot CH₃CN with stirring. After the solution had cooled, solid [NH₄]₂[Ce(NO₃)₆] (0.941 g, 1.73 mmol) was added to the osmocene solution. A green solid precipitated as the ceric salt dissolved. After all the ceric salt had dissolved, the green solid was collected by filtration, leaving a red-brown filtrate.

The solid was washed with CH₃CN followed by diethyl ether and air-dried. This solid was then converted to its PF₆⁻ salt by metathesis according to the procedure to be described.⁵ The green solid was dissolved in 40 mL of a 3:1 glacial acetic acid/H₂O solution, resulting in a dark green solution. Excess solid NH₄PF₆ (1.0 g) was added, and a dark green solid precipitated. This solid was collected, washed first with about 50 mL of water, then with 50 mL of absolute ethanol, and finally with diethyl ether, and was dried under vacuum for 3 h. Note: the washing step is important in order to obtain a high-quality product. The yield was 0.406 g of a dark green powder (56% based on initial Cp₂Os). Anal. Calcd for C₁₀H₁₀OsPF₆: C, 25.81; H, 2.17; P, 6.66; F, 24.50. Found: C, 25.73; H, 2.06; P, 6.38; F, 24.43.

This solid is analytically pure and was used without further purification for all subsequent reactions. If desired, the complex may be crystallized as small black flakes by vapor diffusion of diethyl ether into a concentrated CH₃NO₂ solution under an inert atmosphere (see also X-ray Crystallography section), but the yield is low and there is some decomposition to [(Cp(C₅H₄)Os)₂][PF₆]₂ (see below).

[(Cp(C₅H₄)Os)₂][PF₆]₂. A sample of [(Cp₂Os)₂][PF₆]₂ (0.178 g) was added to 5 mL of CH₃NO₂. The mixture was warmed to 50–60 °C. The solid slowly dissolved on heating, resulting in a dark green solution. Heating was continued until the solution had changed from dark green to red-brown (about 15 min). The resulting complex was crystallized from this solution by vapor diffusion of diethyl ether for 3 days. A crude yellow-brown solid (0.070 g) was collected by filtration, leaving a pale yellow filtrate. Examination of this solid under a microscope revealed that it is a yellow microcrystalline product that has an occasional surface coating of a brown amorphous material. ¹H NMR spectra of this crude product showed only the signals of the desired product.

The complex can be obtained as a yellow crystalline solid free of the amorphous material, but in lower yield, by the following procedure: The salt is initially crystallized from a concentrated CH₃NO₂ solution of the crude product by vapor diffusion with acetone for 1 week followed by vapor diffusion with diethyl ether for 2 days. Large yellow plates are formed on treatment with acetone while small yellow plates formed during ether treatment. The total recovery was 0.044 g (63% recovery of the original 0.070-g sample). Anal. Calcd for C₁₀H₉OsPF₆: C, 25.87; H, 1.95; P, 6.67. Found: C, 25.74; H, 1.92; P, 6.08.

A composite white solid (0.072 g) containing Cp₂Os and HPF₆ was recovered from the filtrate. Identification of the solid was obtained by ¹H NMR for Cp₂Os (4.72 ppm in CD₃NO₂) and IR for HPF₆ (830 cm⁻¹ for PF₆⁻). The recovered solid amounts for 81% of that expected by stoichiometry (see eq 1; 0.061 g of Cp₂Os + 0.028 g of HPF₆). Overall yields based on total osmium for the main products were as follows: 35% (based on crude product) [(Cp(C₅H₄)Os)₂][PF₆]₂; 40%, Cp₂Os + HPF₆.

[Cp₂OsNCCH₃][PF₆]₂. A sample of [(Cp₂Os)₂][PF₆]₂ (0.124 g) was dissolved in about 10 mL of CH₃CN. The initially green solution was warmed to about 75 °C, at which point the solution had turned red-brown. The solution was set aside for crystallization by vapor diffusion with diethyl ether. Small red-brown crystals formed after 1 day. These crystals were collected, washed with ether, and allowed to dry by evaporation of any residual ether under the inert atmosphere. A nearly colorless filtrate remained.

Upon examination of the crystalline solid under a microscope, it was observed that a small amount of a pale yellow crystalline solid was mixed with the red-brown crystals of the acetonitrile complex. These two products were separated manually, resulting in 0.061 g of red-brown crystals (acetonitrile complex). Anal. Calcd for C₁₂H₁₃NOsP₂F₁₂: C, 22.13; H, 2.01; N, 2.15; P, 9.51. Found: C, 22.23; H, 2.08; N, 2.32; P, 9.20.

The pale yellow crystalline byproduct (0.008 g) has been identified by ¹H NMR as [(Cp(C₅H₄)Os)₂][PF₆]₂. It was also possible to separate these products by extracting the original crystalline solid with acetone, leaving the sparingly soluble [(Cp(C₅H₄)Os)₂][PF₆]₂ product behind.

Solvent removal from the filtrate resulted in isolation of 0.043 g of Cp₂Os (¹H NMR (CD₃NO₂) 4.72 ppm). Overall yields based on total osmium for the main products were as follows: 35%, [Cp₂OsNCCH₃][PF₆]₂; 50%, Cp₂Os.

[Cp₂OsSC(NH₂)₂][PF₆]₂. A sample of thiourea (0.013 g, 0.17 mmol) was dissolved in 3 mL of hot CH₃NO₂. After the solution had cooled to ambient temperature, solid [(Cp₂Os)₂][PF₆]₂ (0.140 g, 0.15 mmol) was added. Over a period of 5 min, the solution slowly turned color from dark green to orange-brown. A white solid (Cp₂Os) also separated. The solution was stirred for 1 h, whereupon diethyl ether was added gradually until the small amount of insoluble Cp₂Os had dissolved. The product was crystallized by ether vapor diffusion into this solution. Well-formed orange-bronze needles were obtained after 2 days. The needles were collected, washed with ether, and dried by evaporation of any residual ether under the inert atmosphere. A pale yellow filtrate remained. The yield was 0.08 g. Anal. Calcd for C₁₁H₁₄N₂SOsP₂F₁₂·CH₃NO₂: C, 19.28; H, 2.20; N, 5.62; S, 4.29. Found: C, 19.76; H, 2.30; N, 5.35; S, 4.65. The CH₃NO₂ molecule of crystallization is also observed in the ¹H NMR spectrum (in CD₃NO₂, 4.358 ppm), and the integration agrees with the empirical formula.

After removal of the solvent from the filtrate, the white solid of Cp₂Os (0.05 g; ¹H NMR (CD₃NO₂) 4.72 ppm) remained. Overall yields based on total osmium for the main products were as follows: 36%, [Cp₂OsSC(NH₂)₂][PF₆]₂; 50%, Cp₂Os.

Attempted Disproportionation of [(Cp₂Os)₂][PF₆]₂ with (PNP)N₃. Solid [(Cp₂Os)₂][PF₆]₂ (0.093 g, 0.1 mM) and (PNP)N₃ (0.116 g, 0.2 mM) were physically mixed in a flask. To this mixture was added 2–3 mL of CH₃NO₂. As the solids dissolved, the initial green color of [(Cp₂Os)₂][PF₆]₂ was quickly bleached and the solution became yellow-orange. After the solution stood for about 1 h, the color darkened to red-brown and a white to pale yellow solid crystallized from solution. This crystalline material was collected and washed with diethyl ether. Anal. Calcd for [C₁₀H₈Os]_n: C, 37.7; H, 2.53. Found: C, 36.9; H, 2.8. This crystalline solid is not osmocene itself. Its IR spectrum differs from that of osmocene in that splittings are observed on the peak near 3100 cm⁻¹. It is insoluble in all solvents tried: H₂O, alcohols, Me₂SO, ethyl acetate, CH₃CN, CH₃NO₂, benzene, THF, diethyl ether, and hexane. Osmocene itself is very soluble in diethyl ether. It is most likely that the solid is an oligomeric osmocene complex, [C₁₀H₈Os]_n·[C₁₀H₉Os].

The solvent was removed from the filtrate, and the resulting solid was extracted with diethyl ether. The ether extract contained only Cp₂Os (¹H NMR (CD₃NO₂) 4.7 ppm). The ether-insoluble fraction contained primarily (PNP)PF₆ and an intractable colored solid.

This reaction has been performed in a 1:1 molar ratio with similar results. Larger scale reactions (0.3–0.5 g of the dimer) reveal the release of gas from solution as the reaction occurs. This gas is assumed to be N₂.

[Cp₂OsNO₃][PF₆]. This complex was isolated directly from the filtrate of the original product mixture obtained in the preparation of [(Cp₂Os)₂][PF₆]₂. The filtrate was retained, and the CH₃CN was removed by rotavaporation. The resulting red-brown residue was dissolved in a minimum amount of water (50–100 mL). Then an excess of NH₄PF₆ (4 g) solid was added to the red-brown water solution. Two situations occur: If the solution is sufficiently concentrated in the product, a precipitate results. This solid was collected, washed with a small amount of water (this product is somewhat water-soluble) and with absolute ethanol, and air-dried. The product was crystallized by vapor diffusion of diethyl ether into a concentrated CH₃NO₂ solution of the product. Under these conditions, the salt has a crystal morphology of small red-brown spheres which consist of microcrystalline fibers. Anal. Calcd for C₁₀H₁₀NO₃OsPF₆: C, 22.78; H, 1.91; N, 2.66; P, 5.78. Found: C, 23.09; H, 1.90; N, 2.75; P, 5.34.

If the aqueous solution is less concentrated in the product, only a slight precipitate occurs on NH₄PF₆ addition. In this case, the product has been obtained by prolonged cooling in a refrigerator (1–2 weeks). The product crystallized directly as the red-brown spheres. The solid was collected, washed with a minimum amount of cold water, washed with absolute ethanol followed by diethyl ether, and air-dried. The product in both

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(5) Elemental analysis indicates the presence of a cerium-containing counterion. Since the cerium salt is soluble only in water, where it eventually decomposes, organic-solvent-soluble salts were prepared. In addition to the PF₆⁻ salt, the ClO₄⁻ and BF₄⁻ salts have also been prepared. However, only the PF₆⁻ salt has any appreciable solubility in polar aprotic solvents (CH₃CN, CH₃NO₂).

Table I. Summary of Crystallography Data for [(Cp₂Os)₂][PF₆]₂ and [(Cp(C₅H₄)Os)₂][PF₆]₂

	[(Cp ₂ Os) ₂][PF ₆] ₂	[(Cp(C ₅ H ₄)Os) ₂][PF ₆] ₂
formula	C ₂₀ H ₂₀ Os ₂ P ₂ F ₁₂	C ₂₀ H ₁₈ Os ₂ P ₂ F ₁₂
fw	930.7	928.7
space group	tetragonal, <i>P</i> 4̄ <i>n</i> 2	triclinic, <i>P</i> 1̄
cryst size, mm	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.08
color	black-green	yellow
<i>a</i> , Å	9.766 (7)	10.023 (7)
<i>b</i> , Å		8.139 (7)
<i>c</i> , Å	12.512 (4)	7.792 (8)
α , deg		101.65 (8)
β , deg		105.48 (7)
δ , deg		102.29 (6)
<i>V</i> , Å ³	1193 (1)	575.6 (9)
<i>Z</i>	2	1
<i>d</i> _{calcd} , g/mL	2.59	2.68
<i>d</i> _{obsd} , g/mL	2.57	2.69
μ , cm ⁻¹	108.9	112.8
transmission factor	<i>a</i>	36.3%, 99.9%
range: min, max		
2 θ limits, deg	2 ≤ 2 θ ≤ 70	2 ≤ 2 θ ≤ 55
data collected	+ <i>h</i> , + <i>k</i> , + <i>l</i>	± <i>h</i> , ± <i>k</i> , + <i>l</i>
unique observns	1207	1079
<i>F</i> _o > 3 σ (<i>F</i> _o)		
no. of variables	91	83
<i>R</i> ^b	0.070	0.070
<i>R</i> _w ^b	0.094	0.125

^aNo absorption correction. ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

instances was identical (by ¹H NMR and IR spectroscopy).

It should be noted that although [(Cp₂OsNO₃)⁺] has been isolated several times, the recovery of this product is quite erratic and the yields low and variable. It appears that best results are obtained when the product is recovered from a large-scale preparation of [(Cp₂Os)₂][PF₆]₂ (>0.5 g of initial Cp₂Os) and use of excess [(NH₄)₂Ce(NO₃)₆] (usually 2-fold).

Reaction of [(Cp₂OsNCCH₃)]PF₆ with X (X = Br⁻, I⁻, N₃⁻). These reactions were performed under an inert atmosphere in the glovebox on a scale suitable for NMR experiments.

X = Br⁻. The salts Bu₄NBr (0.006 g, 0.02 mM) and [(Cp₂OsNCCH₃)]PF₆ (0.013 g, 0.02 mM) were dissolved in 1 mL of CD₃NO₂. The red-brown solution was loaded into a NMR tube, and the tube was sealed and heated in a hot-water bath at 90–100 °C for 1 h outside the glovebox. During heating, the solution darkened to yellow-brown. After the solution was cooled to room temperature, the ¹H NMR spectrum was recorded.

X = I⁻. The salts Bu₄NI (0.007 g, 0.02 mM) and [(Cp₂OsNCCH₃)]PF₆ (0.012 g, 0.02 mM) were dissolved in 1 mL of CD₃NO₂. An orange solid precipitated from solution as the solids dissolved. This orange solid is presumably the I⁻ salt of the acetonitrile complex. The mixture was loaded into a NMR tube, and the tube was sealed and heated in a hot-water bath at 90–100 °C for 30 min. The orange solid quickly dissolved as the solution warmed, and on extended heating the solution changed from red-brown to green-brown. After the solution was cooled to room temperature, the ¹H NMR spectrum was recorded. A green crystalline product was isolated (4 mg) by vapor diffusion of ether into the NMR sample for 18 h. The complex was determined by ¹H NMR to be [(Cp₂OsI)]PF₆ by comparison with authentic [(Cp₂OsI)]PF₆.¹

X = N₃⁻. The salts (PNP)N₃ (0.014 g, 0.02 mM) and [(Cp₂OsNCCH₃)]PF₆ (0.014 g, 0.02 mM) were dissolved in 1 mL of CD₃NO₂. The resulting red-brown solution was loaded into a NMR tube, the tube was sealed, and the ¹H NMR spectrum was recorded.

X-ray Crystallography. Crystallographic and related data are summarized in Table I. Suitable crystals of [(Cp₂Os)₂][PF₆]₂ and [(Cp(C₅H₄)Os)₂][PF₆]₂ were grown by vapor diffusion of acetone into a CH₂NO₂ solution of the complex. Experimental densities were obtained by flotation using CH₂I₂/CCl₄. Crystal data were collected on a Syntex P2₁ computer-controlled four-circle diffractometer with graphite-monochromated Mo K α 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 2 θ . Intensity data were obtained by using the θ -2 θ scan method. The structures were 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. All atoms except H were refined anisotropically for

Table II. Positional Parameters and Their Estimated Standard Deviations for [(Cp₂Os)₂][PF₆]₂^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Os	0.390	0.110	0.250	3.48 (1)
P1	0.000	0.500	0.250	5.4 (1)
F11	0.146 (4)	0.555 (3)	0.214 (5)	11 (1)
F12	0.101 (2)	0.457 (3)	0.335 (2)	12.5 (6)
P2	0.500	0.500	0.000	4.6 (2)
F21	0.155 (2)	-0.038 (3)	0.512 (3)	14 (1)
F22	0.000	0.000	0.378 (3)	16 (2)
C1	0.225 (3)	-0.027 (3)	0.201 (3)	6.2 (7)
C2	0.328 (3)	-0.045 (3)	0.128 (2)	5.3 (6)
C3	0.356 (3)	0.079 (3)	0.076 (2)	5.1 (6)
C4	0.257 (3)	0.179 (3)	0.120 (2)	6.0 (6)
C5	0.183 (3)	0.098 (2)	0.201 (2)	5.5 (6)

^aStarred values are for atoms refined isotropically. Anisotropically refined atoms are given in the forms of the isotropic equivalent thermal parameter defined as $1/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$.

[(Cp₂Os)₂][PF₆]₂ while only Os and P were refined anisotropically for [(Cp(C₅H₄)Os)₂][PF₆]₂. The hydrogen atoms were included in calculated positions with fixed temperature factors. All computations were performed by using the SDP structure determination software package obtained from Enraf-Nonius. The systematic absences of 0*kl*, *k* + *l* = 2*n* + 1, narrowed the possible space groups for [(Cp₂Os)₂][PF₆]₂ to the tetragonal groups *P*4₂/*mmm*, *P*4̄*n*2, and *P*4₂/*nm*. Solution of the Patterson map for the heavy atoms and subsequent refinement showed the correct space group to be *P*4̄*n*2. For the triclinic [(Cp(C₅H₄)Os)₂][PF₆]₂, solution of the Patterson map and successful refinement showed the correct space group to be *P*1̄.

In both of these crystals, the symmetric PF₆⁻ counterions showed considerable rotational motion and/or disorder, which is reflected in larger thermal parameters, in slightly altered bond lengths and angles of the PF₆⁻ group, and in higher final *R* values. Attempts to model these effects by the use of multiple PF₆⁻ 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. In the case of [(Cp(C₅H₄)Os)₂][PF₆]₂, this procedure resulted in a slightly distorted PF₆⁻ group with large temperature factors. A final difference map shows that the only remaining peaks of significance are diffusely clustered about phosphorus. For the [(Cp₂Os)₂][PF₆]₂ crystal, which has greater symmetry restrictions on the counterions, one PF₆⁻ group is well-behaved, showing only some rotational motion about the 4-fold axis as is often observed. The other PF₆⁻ group shows considerable disorder. Since phosphorus (P1) lies in a special position of 222 symmetry, only two F positions are required. One is a general position of the space group with an occupancy of 1.0, and the other is a special position with an occupancy of 0.5. Fourier synthesis indicates that these symmetry requirements are maintained with at least two separate orientations being observed. However, it was not possible to successfully model and refine the various orientations at fractional occupancy. In this case, the predominant orientation alone was allowed to refine to convergence. This procedure ultimately places the position of 0.5 occupancy in the vicinity of the special position but not on it. The result is a PF₆⁻ group that is characterized by diffuse fluorine electron density about phosphorus. A final difference map shows remaining electron density about the phosphorus atoms. Solution of the structure in the related orthorhombic space group *Pnn*2, where fewer symmetry restrictions are placed on the PF₆⁻ positions, led to no improvement in locating the PF₆⁻ group and resulted in substantially the same overall solution.

It is important to note that these approximations in modeling the PF₆⁻ groups have not had a significant effect on the cation portion of the structure solution, which is of most interest. We are confident of both the overall molecular structure of the cation and the observed bond lengths and angles. Both the bond lengths and angles are in excellent agreement with similar values for related metallocenes that do not suffer from disorder of the anions (see Results).

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

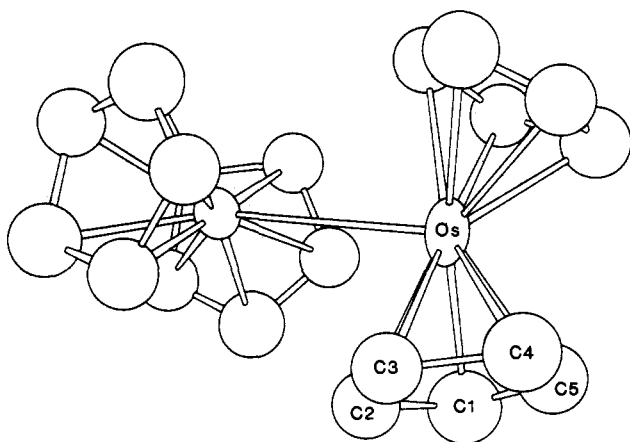
Results

Synthesis and Characterization of [(Cp₂Os)₂][PF₆]₂. The synthesis of the title compound is facilitated by its precipitation from solution before further reaction can occur. It has been observed

Table III. Positional Parameters and Their Estimated Standard Deviations for $[(\text{Cp}(\text{C}_5\text{H}_4)\text{Os})_2][\text{PF}_6]_2^a$

atom	x	y	z	B, Å ²
Os	0.1786 (1)	0.1587 (2)	0.0327 (2)	2.46 (3)
P	0.729 (1)	0.301 (1)	0.429 (1)	3.3 (2)
F1	0.835 (4)	0.188 (5)	0.484 (5)	10 (1)*
F2	0.609 (4)	0.391 (5)	0.426 (6)	11 (1)*
F3	0.839 (4)	0.400 (6)	0.338 (6)	12 (1)*
F4	0.646 (6)	0.249 (8)	0.536 (8)	17 (2)*
F5	0.159 (5)	-0.451 (6)	0.382 (6)	13 (1)*
F6	0.648 (4)	0.182 (5)	0.248 (5)	10 (1)*
C1	0.242 (4)	0.199 (5)	-0.202 (5)	3.4 (8)*
C2	0.144 (5)	0.300 (6)	-0.190 (6)	6 (1)*
C3	0.199 (5)	0.416 (6)	-0.011 (7)	6 (1)*
C4	0.361 (6)	0.423 (7)	0.086 (8)	7 (1)*
C5	0.383 (5)	0.293 (7)	-0.030 (7)	6 (1)*
C11	0.052 (4)	-0.047 (5)	0.120 (5)	4.2 (9)*
C12	0.106 (4)	0.122 (4)	0.257 (5)	2.9 (7)*
C13	0.256 (4)	0.143 (5)	0.325 (6)	4.8 (9)*
C14	0.286 (4)	0.009 (5)	0.201 (5)	3.2 (7)*
C15	0.159 (4)	-0.095 (5)	0.071 (5)	3.5 (8)*

^aSee footnote a of Table II.

**Figure 1.** ORTEP drawing of $[(\text{Cp}_2\text{Os})_2]^{2+}$.

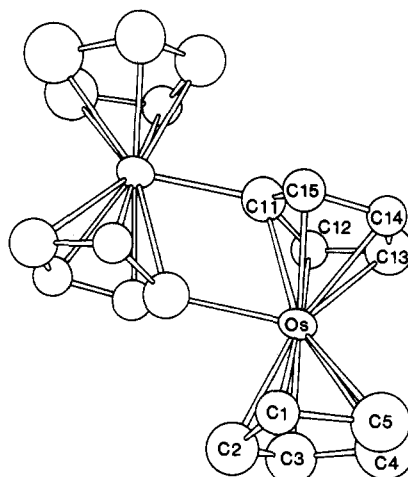
(see Discussion) that the cation is quite reactive, and it is likely that side reactions account for the diminished isolated yield. An example of this is the observation that both the acetonitrile and the nitrate complexes of $\text{Cp}_2\text{Os}^{\text{IV}}$ (see Discussion) have been isolated from the reaction mixture that produced the osmocenic dimer.

Elemental analysis of this green dimer salt shows that the empirical formula corresponds to the composition Cp_2OsPF_6 . The infrared spectrum is similar to that of osmocene and shows bands due only to the Cp rings and to PF_6^- .⁶ However, the ¹H NMR spectrum shows the compound to be diamagnetic. It consists of a sharp singlet, $\delta = 5.88$ in CD_3NO_2 , downfield from free osmocene (4.72 ppm). Analysis of the X-ray diffraction data reveals the true dimeric structure of the $[(\text{Cp}_2\text{Os})_2]^{2+}$ cation as shown in the ORTEP drawing (Figure 1). Pertinent bond lengths and angles are given in Table IV. Oxidation of the metal center to Os^{III} has caused an increase in the coordination number of osmium to 7, thus accommodating the Os–Os bond. The average Os–C bond of 2.19 (1) Å is similar to the 2.22-Å distance observed for Cp_2Os .⁷ The average C–C bond distance of 1.40 (2) Å and average C–C–C bond angle of 108 (2)° is the same as the 1.41 (1) Å distance and the 108 (2)° angle observed for $[\text{Cp}_2\text{RuI}]^+$.⁸ The Cp rings are tilted away from the Os–Os bond with the ring

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[(\text{Cp}_2\text{Os})_2][\text{PF}_6]_2^a$

atom 1	atom 2	dist	atom 1	atom 2	dist
Os	Os	3.038 (0)	C1	C2	1.38 (3)
Os	C1	2.18 (2)	C1	C5	1.29 (2)
Os	C2	2.23 (2)	C2	C3	1.40 (3)
Os	C3	2.23 (2)	C3	C4	1.48 (3)
Os	C4	2.19 (2)	C4	C5	1.47 (3)
Os	C5	2.12 (2)			
av Os–C = 2.19 (1); av C–C = 1.40 (2)					
atom 1	atom 2	atom 3	angle		
C2	C1	C5	110 (2)		
C1	C2	C3	110 (2)		
C2	C3	C4	105 (2)		
C3	C4	C5	103 (2)		
C1	C5	C4	111 (2)		
av C–C–C = 108 (2)					

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

**Figure 2.** ORTEP drawing of $[(\text{Cp}(\text{C}_5\text{H}_4)\text{Os})_2]^{2+}$.

planes forming a dihedral angle of 35.5° (dihedral angle 32.2° for $[\text{Cp}_2\text{RuI}]^+$).

The crystallography shows that osmium occupies a special position of the space group ($x, 1/2 - x, 1/4$). This position, determined from the Patterson synthesis, remained constant throughout refinement and as a result of the symmetry requirement fixes the Os–Os bond distance at 3.038 (0) Å. Solution of the structure in the absence of this symmetry requirement where Os occupies a general position (orthorhombic $Pnn2$) results in a slightly shorter Os–Os bond length of 2.991 (1) Å.

The observed Os–Os distance is somewhat longer than in other unbridged Os–Os-bonded complexes: The Os–Os distance in $\text{Os}_3(\text{CO})_{12}$ is 2.877 Å^{9a} and in $\text{Me}_3\text{P}(\text{CO})_4\text{OsOs}_3(\text{CO})_{11}$ is 2.94 Å.^{9b} However, the metal–metal bond distance is consistent with those observed for similar dimeric organometallic compounds: The metal–metal distance in $[\text{Re}(\text{CO})_5]_2$ is 3.041 Å^{10a} and in $[\text{CpW}(\text{CO})_3]_2$ is 3.222 Å.^{10b} The crystallographic symmetry at the midpoint of the Os–Os bond is 222, and the symmetry point group of the dimer is D_{2d} .

Reactivity of $[(\text{Cp}_2\text{Os})_2][\text{PF}_6]_2$. $[(\text{Cp}(\text{C}_5\text{H}_4)\text{Os})_2][\text{PF}_6]_2$. The dimer was found to react in and/or with any liquid in which it is soluble; of those tried, it persists longest in CH_3NO_2 . For the particular reaction of $[(\text{Cp}_2\text{Os})_2]^{2+}$ with the poor donor solvent CH_3NO_2 , a spontaneous reaction occurs slowly even in the absence

(6) Infrared spectrum of $[(\text{Cp}_2\text{Os})_2][\text{PF}_6]_2$ (cm^{-1}): Cp 3140, 1429, 1406, 1082, 1022; PF_6^- 950–800 (b), 559. Infrared spectrum of Cp_2Os (cm^{-1}):^{3a} 3108 ($\nu(\text{CH})$), 1400 ($\nu(\text{CC})$), 1098 ($\delta(\text{CC})$), 998 ($\eta(\text{CH})$), 989 ($\eta(\text{CH})$), 831 ($\eta(\text{CH})$), 823 ($\eta(\text{CH})$).

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Table V. Selected Bond Distances (Å) and Angles (deg) for $[(Cp(C_5H_4)Os)_2][PF_6]_2^a$

atom 1	atom 2	dist	atom 1	atom 2	dist
Os	C1	2.15 (2)	C1	C2	1.41 (3)
Os	C2	2.26 (2)	C1	C5	1.58 (3)
Os	C3	2.17 (2)	C2	C3	1.40 (3)
Os	C4	2.39 (3)	C3	C4	1.58 (4)
Os	C5	2.33 (3)	C4	C5	1.34 (4)
Os	C11	2.21 (2)	C11	C12	1.45 (3)
Os	C12	2.11 (2)	C11	C15	1.34 (3)
Os	C13	2.24 (2)	C12	C13	1.41 (3)
Os	C14	2.19 (2)	C13	C14	1.44 (3)
Os	C15	2.12 (2)	C14	C15	1.37 (3)
Os	C11	2.18 (2) ^b			
av Os-C(π) = 2.22 (1); av C-C = 1.43 (2)					
atom 1	atom 2	atom 3	angle		
C2	C1	C5	106 (2)		
C1	C2	C3	107 (2)		
C2	C3	C4	111 (2)		
C3	C4	C5	104 (2)		
C1	C5	C4	110 (2)		
av C-C-C = 108 (2)					

^aNumbers in parentheses are estimated standard deviations in the least significant digits. ^bOs-C(σ)(alkyl) bond.

of light at room temperature and rapidly at elevated temperatures, resulting in a yellow crystalline solid as one of the major products. Elemental analysis of the product gives the empirical formula $[Cp(C_5H_4)Os][PF_6]$. The ¹H NMR spectrum of this complex features three signals: a sharp singlet at 5.91 ppm (5 H) and apparent triplets centered at 6.19 ppm (2 H) and 5.27 ppm (2 H). These signals and their integrations are consistent with monosubstitution on one ring. Two possible structures are suggested by these results, one in which two metallocene units are coupled by a C-C bond and the other in which one ring from each of two metallocene units is σ bonded to the other Os (doubly metalated complex).

Analysis of the X-ray diffraction data reveals that the latter description is the actual structure as shown in the ORTEP drawing (Figure 2). Pertinent bond lengths and angles are given in Table V. This C_{2h} -symmetry dimer has Os both π and σ bonded to Cp rings. The high-valent osmium(IV) atoms are again formally seven-coordinate. The average Os-C(π) distance of 2.22 (1) Å and average C-C bond of 1.43 (2) Å are the same as those observed for $[(Cp_2Os)_2]^{2+}$. The Cp rings are tilted away from the Os-Os bond with the ring planes forming a dihedral angle of 18.0°. This dihedral angle is nearly a factor of 2 less than the angle observed for $[(Cp_2Os)_2]^{2+}$ and is probably a consequence of the bond formation between the ring and the metal. The average Os-C(σ) bond of 2.18 (2) Å is slightly longer than the Os-C(σ) (naphthyl) bond of 2.134 (17) Å in $OsH(C_{10}H_7)(dmpe)_2$.¹¹

Mass balance indicates that the reaction proceeds by net two-electron oxidation of $[(Cp_2Os)_2]^{2+}$ yielding the metalated product, osmocene, and protons (eq 1). Both products, $[(Cp(C_5H_4)Os)_2]^{2+}$ and Cp_2Os , have been isolated and characterized. The acid equivalents (as HPF_6) are inferred from mass recovery and from IR absorption characteristic of PF_6^- observed in an ether extract.

The product $[(Cp(C_5H_4)Os)_2]^{2+}$ is very stable and has not been observed to undergo further reaction. The formation of this product from $[(Cp_2Os)_2]^{2+}$ appears to be an important reaction pathway in the absence of any suitable donor ligands.

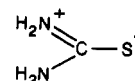
$[Cp_2OsNCCH_3][PF_6]_2$. In a good donor solvent such as acetonitrile, the dimer reacts readily at room temperature (faster at elevated temperatures). The major products of the reaction have been isolated and identified. Elemental analysis of the red-brown

crystalline product is consistent with the empirical formula $[Cp_2OsNCCH_3][PF_6]_2$. The infrared spectrum shows, in addition to Cp and PF_6 bands, the CH and CN stretches of CH_3CN .¹² The CN bands are shifted 60 and 70 cm^{-1} to higher energy as compared to those of free CH_3CN , consistent with the donating character of this ligand. The ¹H NMR spectrum (CD_3NO_2) contains only two singlets, one for the Cp rings ($\delta = 6.29, 10 H$) and one assignable to coordinated CH_3CN ($\delta = 2.92, 3 H$). The latter line is shifted about 1 ppm downfield from that of free CH_3CN .

The only other major product observed is osmocene. Both the products and the mass balance of this reaction indicate that the reaction with CH_3CN must be disproportionation (eq 2).



$[Cp_2OsSC(NH_2)_2][PF_6]_2$. A disproportionation reaction also occurs with $[(Cp_2Os)_2]^{2+}$ and thiourea. Elemental analysis of the crystalline product indicates the empirical formula $[Cp_2OsSC(NH_2)_2][PF_6]_2$. The IR spectrum shows the absence of the normally strong band at about 1100 cm^{-1} . This is taken to indicate a significant contribution of the dipolar thiourea structure and suggests that thiourea is coordinated to the metal through sulfur.¹³



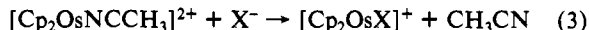
The diagnostic bands of thiourea in the region from 1600 to 1400 cm^{-1} are of little utility in determining the mode of coordination due to overlapping with bands of Cp and of the CH_3NO_2 molecule of crystallization.

The ¹H NMR spectrum shows a sharp singlet for the Cp rings at 6.15 ppm (10 H) and a broad peak for thiourea from 6.6 to 7.7 ppm (4 H) that is composed of two overlapping peaks of equal intensity centered at 7.0 and 7.3 ppm. Free thiourea shows a broad singlet at 6.74 ppm ($CD_3NO_2/(CD_3)_2CO$) under these conditions. At low temperatures two resonances of equal intensity, with a coalescence temperature of about -30 °C, are observed for free thiourea. This behavior is ascribable to a significant contribution to the ground state of the dipolar structure, resulting in hindered rotation about the C-N bond.¹⁴ It is also known that, on coordination of thiourea to a metal, the coalescence temperature rises significantly (an increase of 40 °C for $[(NH_2)_2CSCr(CO)_5]$).^{14b} Therefore, it seems likely that thiourea acts as a strongly donating ligand coordinated through sulfur to the Cp_2Os^{IV} fragment. This would favor the dipolar structure, and the resulting hindered C-N bond rotation is consistent with the observed NMR results. These results are also in agreement with the IR data suggesting sulfur coordination and significant contribution of the dipolar structure.

Reaction of $[Cp_2OsNCCH_3][PF_6]_2$ with X (X = Br⁻, I⁻, N₃⁻). The results indicate that in each case examined a reaction occurs between the added nucleophile and the Os(IV) acetonitrile complex. The reaction with bromide after heating results in quantitative displacement of the coordinated CH_3CN ligand (2.92 ppm) and the corresponding appearance of free CH_3CN (2.00 ppm) under these conditions) as observed by ¹H NMR spectroscopy. A sharp Cp resonance corresponding to $[Cp_2OsBr]^+$ (5.97 ppm) also appears. This resonance is shifted upfield from the Cp resonance of the Os(IV) acetonitrile complex (6.29 ppm). The reaction with iodide shows similar NMR changes. The Os(IV) iodo complex $[Cp_2OsI]^+$ was isolated from the reaction solution and identified by ¹H NMR (6.06 ppm). The results indicate a net substitution reaction between the Os(IV) acetonitrile complex and the halides (eq 3).

- (12) Infrared spectrum (cm^{-1}) for $[Cp_2OsNCCH_3][PF_6]_2$: 3138 (CH, Cp); 2959 (CH, CH_3CN); 2343, 2316 (CN, CH_3CN); 1442, 1408 (CC, Cp); 1366, 1124, 1083, and 1029 (not assigned); 950-800 br, 559 (PF_6^-).
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The situation is different, however, when azide is the nucleophile. Instead of simple substitution, proton NMR shows that azide reacts with the Os(IV) acetonitrile complex by attacking the Cp ring. The Cp resonance of the acetonitrile complex is completely replaced by three new Cp resonances. Two are apparent quartets centered at 5.77 ppm (2 H) and 4.58 ppm (2 H), and the remaining resonance is a sharp singlet at 5.55 ppm (5 H). Coordinated acetonitrile is still observed, but the resonance has shifted upfield to 2.82 ppm (3 H) from 2.92 ppm for the original acetonitrile complex. Integration of the new resonances agrees with that expected for a ring-attacked product, and both the new Cp resonances and the integration follow the general pattern observed for $[\{\text{Cp}(\text{C}_5\text{H}_4)\text{Os}\}_2]^{2+}$, where substitution of the ring has been observed. The exact molecular composition of this new product has not yet been fully determined.

$[\text{Cp}_2\text{OsNO}_3][\text{PF}_6]$. This unexpected complex was isolated from the filtrate of the $[(\text{Cp}_2\text{Os})_2]^{2+}$ synthetic reaction. Elemental analysis of the red-brown crystalline product is consistent with the empirical formula $[\text{Cp}_2\text{OsNO}_3][\text{PF}_6]$. The infrared spectrum is similar to that observed for $[(\text{Cp}_2\text{Os})_2]^{2+}$ except that two intense additional bands at 1554 and 1271 cm^{-1} are now observed. These bands are indicative of coordinated NO_3^- .¹⁵ The ^1H NMR spectrum features only a sharp singlet for the Cp rings at 6.03 ppm (CD_3NO_2).

The mechanism by which the nitrate complex forms is not understood. Efforts to prepare it by disproportionation of $[(\text{Cp}_2\text{Os})_2]^{2+}$ in the presence of NO_3^- in water were unsuccessful. Further, it appears that appreciable yields of this complex are formed only in the presence of excess $[\text{Ce}(\text{NO}_3)_6]^{2-}$. The further oxidation of an intermediate Os^{III} species or $[(\text{Cp}_2\text{Os})_2]^{2+}$ to a reactive Os^{IV} species followed by capture of NO_3^- is one possible route of formation. Alternately, substitution of a side-reaction product, such as $[\text{Cp}_2\text{OsNCCH}_3]^{2+}$, by NO_3^- is also a possible route.

Discussion

Synthesis and Characterization of $[(\text{Cp}_2\text{Os})_2][\text{PF}_6]_2$. $[(\text{Cp}_2\text{Os})_2]^{2+}$ is the first example of a dimeric metallocene of the Fe, Ru, Os triad. This is unlike metallocenes of other metals, where formally dimeric species are known (characterized by $\text{M}-\text{C}(\sigma)$ or $\text{M}-\text{C}(\sigma)$ and $\text{M}-\text{M}$ bonding). After the very recently reported isoelectronic rhenocene dimer $[\text{Cp}_2\text{Re}^{\text{II}}]_2$,¹⁶ $[(\text{Cp}_2\text{Os}^{\text{III}})]_2^{2+}$ is the only other example of an unsupported metal-metal-bonded metallocene dimer. Two factors probably contribute to the formation of this dimer: (i) Oxidation of the parent metallocene by one electron results in a reactive 17-electron species, which by formation of a simple metal-metal bond forms a more stable overall 18-electron complex. (ii) The fact that the third-row metals Os and Re constitute the only known stable examples of these dimeric complexes suggests that the greater orbital extension of the 5d elements is necessary for effective overlap in the presence of the bulky Cp substituents. Though the halves of the $[(\text{Cp}_2\text{Os})_2]^{2+}$ dimer are rotated by 90° , presumably to minimize steric interactions, the observed Os-Os bond is quite long, which is consistent with the complex being quite reactive, as exemplified by the reactions that have been described. The crystal structure also shows that, on oxidation of Cp_2Os to form $[(\text{Cp}_2\text{Os})_2]^{2+}$, the metal coordination spheres expand and the Cp rings tilt. These observations are consistent with the conclusions of a molecular orbital study of similar metallocenes.¹⁷

In light of the above results on $[(\text{Cp}_2\text{Os})_2]^{2+}$, we wish to comment on two related literature reports. Gubin and co-workers^{3c} described the precipitation of a dark green salt during the oxidation of Cp_2Os at a platinum electrode and characterized it as Cp_2OsBF_4 on the basis of elemental analysis and infrared spectroscopy. We

suggest that this compound is actually the BF_4^- salt of $[(\text{Cp}_2\text{Os})_2]^{2+}$. More recently, Mueller-Westerhoff and co-workers¹⁸ reported the two-electron oxidation of [1.1]ruthenocenophane and, primarily on the basis of ^1H NMR data, concluded that the product is a mixed-valence Ru(II)-Ru(IV)-containing complex. We suggest the possibility that a Ru-Ru bond is formed on oxidation of the complex, in analogy to the results described here for Cp_2Os .¹⁹ A molecular model of the methylene-bridged Cp ligands for [1.1]ruthenocenophane indicates that the Cp rings can easily tilt away, thus accommodating the Ru-Ru bond. The ^1H NMR spectrum predicted for this structure (mirror plane bisects Ru-Ru bond and bridging methylenes) will consist of four Cp resonances, which should all be shifted downfield as is observed for $[(\text{Cp}_2\text{Os})_2]^{2+}$ and one methylene resonance. This prediction is consistent with the observed results. In this case, the inequivalence of the ruthenocenophane protons would be due to the rigid structure imposed by the Ru-Ru bond rather than to different oxidation states of the metals.

Reactivity of $[(\text{Cp}_2\text{Os})_2][\text{PF}_6]_2$, $[\{\text{Cp}(\text{C}_5\text{H}_4)\text{Os}\}_2][\text{PF}_6]_2$. As with the formation of the dimer $[(\text{Cp}_2\text{Os})_2]^{2+}$ itself, the thermolysis reaction that produces the doubly metalated complex apparently is also paralleled by the rhenocene dimer, forming a similar doubly metalated product.¹⁶ Although the structure of the rhenium complex was inferred only from its ^{13}C NMR spectrum, it undoubtedly has a structure very similar to that of $[\{\text{Cp}(\text{C}_5\text{H}_4)\text{Os}\}_2]^{2+}$.

In considering the mechanism of formation of $[\{\text{Cp}(\text{C}_5\text{H}_4)\text{Os}\}_2]^{2+}$, it seems reasonable to assume that the initial step is homolysis of the Os-Os bond. The resulting $[\text{Cp}_2\text{Os}]^+$ radical then abstracts a hydrogen atom from a similar fragment, forming a Cp-centered and Os-centered diradical and $[\text{Cp}_2\text{OsH}]^+$ as an intermediate. The diradical can then couple with itself and form $[\{\text{Cp}(\text{C}_5\text{H}_4)\text{Os}\}_2]^{2+}$ directly or react with $[(\text{Cp}_2\text{Os})_2]^{2+}$ and straightforwardly form the metalated product and a hydride intermediate. The hydride is not isolated, and it is assumed to decompose to Cp_2Os and H^+ . This series of steps account for $[\{\text{Cp}(\text{C}_5\text{H}_4)\text{Os}\}_2]^{2+}$, Cp_2Os , and H^+ as the only observed products. It should be noted that, in the case of the analogous rhenium system, the hydride $[\text{Cp}_2\text{ReH}]$ is a stable, well-known species and, in addition to the metalated complex, was isolated as the only other product.

$[\text{Cp}_2\text{OsNCCH}_3][\text{PF}_6]_2$ and $[\text{Cp}_2\text{OsSC}(\text{NH}_2)_2][\text{PF}_6]_2$. One major route of reactivity available to $[(\text{Cp}_2\text{Os})_2]^{2+}$ is reaction by disproportionation of the Os-Os bond. In the presence of suitable ligands, a simple reaction occurs that partitions between coordination of the ligand to an Os^{IV} metallocene and the formation of osmocene. This reaction appears to be somewhat general (however, see following discussion) and to be a useful route to the synthesis of a number of higher valent Os metallocene derivatives. Qualitatively, similar disproportionation reactions have been observed in the presence of nucleophiles such as I^- and SCN^- . The major products are osmocene and $[\text{Cp}_2\text{OsI}]^+$ or $[\text{Cp}_2\text{OsSCN}]^+$, respectively.²⁰ However, only a small number of potential ligands have been tested. Besides those described above, simple ligands such as H_2O , NH_3 , pyrazine, pyridine, and azide have been examined.

The indications are that the disproportionation reaction is quite ligand-specific. Those ligands that do not stabilize the resulting Os(IV) species have the option of reaction by alternate redox pathways. Thus, in the case of the symmetric, potentially bridging ligand N_3^- , a complex redox reaction occurs, producing among the major products Cp_2Os , N_2 , and an oligomeric osmocene Os(II) compound. Other ligands, such as water (70 °C suspension) and

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(19) Qualitatively, we have observed that Cp_2Ru reacts with $\text{Ce}(\text{IV})$ to give a short-lived green color. We take this to indicate the transient formation of the metal-metal-bonded ruthenocenium dimer. The instability of this complex probably reflects poorer overlap of the 4d orbitals of Ru as opposed to the 5d orbitals of Os in the presence of the bulky Cp rings.

(20) $[\text{Cp}_2\text{OsI}]^+$ and $[\text{Cp}_2\text{OsSCN}]^+$: Droege, M. W., unpublished results.

pyrazine (molten, 50 °C), react with the osmocenium dimer, yielding the metalated complex $[(Cp(C_5H_4)Os)_2]^{2+}$, osmocene, and noncrystalline intractable materials, while NH_3 and pyridine yield only intractable materials. As a result, these reactions have not been pursued further.

Reaction of $[Cp_2OsNCCH_3][PF_6]_2$ with X ($X = Br^-, I^-, N_3^-$). One other possible route toward new Os(IV) derivatives is to use existing Os(IV) complexes in substitution reactions. It is expected that these reactions would be less likely to follow alternate pathways that are apparently available to the more reactive $[(Cp_2Os)_2]^{2+}$. The substitution of Br^- and I^- for CH_3CN in $[Cp_2OsNCCH_3]^{2+}$ yielding $[Cp_2OsX]^+$ ($X = Br, I$) derivatives suggests that this approach has merit. The scope of this substitution reaction has not yet been fully explored.

On the other hand, reaction with N_3^- does not result in substitution. This appears to confirm the implication that N_3^- does not sufficiently stabilize Os(IV) and prefers to react by alternate pathways as was observed in the attempted disproportionation of $[(Cp_2Os)_2]^{2+}$ with azide. In this case, alternate redox pathways involving the metal are not readily available and instead the nucleophile attacks the Cp ring. The Cp ring in these higher valent Os metallocenes is activated toward nucleophilic attack. Such ring attack is preceded by the reaction of $[Cp_2RuBr]^+$ with water, where one cyclopentadienyl ring is converted to a cyclopentadienone ligand.²¹

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Summary

The complex $[(Cp_2Os)_2]^{2+}$ is an important synthetic entry into the study of higher oxidation state Os metallocenes. The chemistry surveyed indicates that a variety of ligand-dependent reaction pathways are available to this complex or its derivatives. These include radical, disproportionation, and substitution routes. As a result, a number of previously unknown Os metallocene derivatives have been discovered and routes toward new complexes have been outlined. Additionally, the close analogy between $[(Cp_2Os)_2]^{2+}$ and $[Cp_2Re]_2$ suggests that similar chemistry may be developed for Re metallocenes.

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Registry No. $[(Cp_2Os)_2][PF_6]_2$, 107272-09-3; $[(Cp(C_5H_4)Os)_2][PF_6]_2$, 107272-11-7; Cp_2Os , 1273-81-0; $[NH_4]_2[Ce(NO_3)_6]$, 16774-21-3; $[Cp_2OsNCCH_3][PF_6]_2$, 107272-13-9; $[Cp_2OsSC(NH_2)_2][PF_6]_2$, 107272-15-1; $SC(NH_2)_2$, 62-56-6; $[C_{10}H_8Os]_n$, 107272-16-2; $(PNP)N_3$, 38011-36-8; $[Cp_2OsNO_3][PF_6]$, 107272-18-4.

Supplementary Material Available: Listings of anisotropic temperature factors and root-mean-square amplitudes of thermal vibration, complete listings of bond lengths and bond angles, and listings of calculated H atom positions and Cp ring plane calculations (12 pages); listings of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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The Titanyl Question Revisited

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The qualitative and quantitative composition of acidic aqueous solutions of dilute hydrolyzed Ti(IV) has been investigated by ¹⁷O NMR spectroscopy supported by light-scattering experiments and UV, FTIR, and Raman spectroscopy. $[H^+]$ - and $[Ti(IV)]_{total}$ -dependent ¹⁷O NMR experiments show unambiguously that oligomeric Ti(IV) species are formed at low $[H^+]$ and relatively high $[Ti(IV)]_{total}$ ($\geq 0.05 M$). The data are analyzed on the basis of a model system containing two trimers ($Ti_3O_4^{4+}$ (A) and $Ti_3O_3O_2H_3^{5+}$ (B)) and a tetramer ($Ti_4O_4O_2H_4^{8+}$ (C)) apart from monomeric species. The formation constants for the oligomer formations from TiO^{2+} in aqueous $HClO_4$ at 298 K and $\mu = 4.0 M$ are $K_3^1 = 0.38 \pm 0.06$, $K_3^2 = 1.64 \pm 0.06 M^{-1}$, and $K_4^1 = 2.31 \pm 0.03 M^{-3}$, respectively. Possible implications for substitution and electron-transfer reactions of Ti(III) and Ti(IV) are discussed. Oxygen-exchange rates of the oxo, hydroxo, and aqua ligands of all the species involved have been determined qualitatively by the analysis of the temperature-dependent line widths of the ¹⁷O NMR signals (oxo and hydroxo bridges, $k_{ex}^{298} \approx 100 \pm 50 s^{-1}$; terminal H_2O or OH^- of oligomers, $k_{ex}^{298} \approx 3400 \pm 200 s^{-1}$ (limit for slowest exchanging terminal H_2O or OH^- ligands); TiO^{2+} (rate measured in 68% aqueous methanol), $k_{ex}^{298} \approx 16000 \pm 5000 s^{-1}$). This is a surprising result in terms of the yl oxygen since it is exchanging about 9 orders of magnitude faster than the yl oxygen in the thoroughly investigated VO^{2+} ion. This enormous difference is explained by a change of the exchange mechanism, and some theoretical and experimental indications for protonation of the yl oxygen of TiO^{2+} are presented.

Introduction

Yl-type metal oxo ions (MO_n^{m+} , $n = 1, 2$) are well-known for many metal centers, in particular for highly oxidized ions (e.g. V(IV),²⁻⁴ Cr(V),⁵ Mo(V) and -(VI),^{6,7} W(V) and -(VI),⁸ Os(VI),⁹

Re(V),^{10,11} U(VI),¹² etc.). However, simple monomeric and first-row transition-metal oxo ions seem not to be very common. The probably best known and thoroughly studied vanadyl ion²⁻⁴ is quite special in both respects. It is then an obvious question whether Ti(IV), the highly oxidized neighbor of V(IV), does form

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