Synthesis, Characterization, and Halogenation of Decakis(acetoxymercurio)osmocene. Crystal and Molecular Structure of Decachloroosmocene

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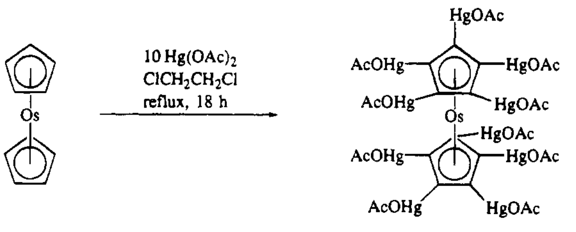
Introduction

The chemistry of osmocene remains largely unexplored, relative to the analogous situation for ferrocene and ruthenocene.[2] The available literature suggests several differences between osmocene and the lighter metallocenes. Osmocene is the least reactive of the group 8 metallocenes toward electrophilic substitution. For example, ferrocene is readily diacylated upon treatment with excess acetyl chloride and aluminum chloride, while ruthenocene affords a mixture of the monoacylated and diacylated products and osmocene affords only the monoacylated product.[3] Osmocene also possesses the highest tendency to form adducts with Lewis acids of the three metallocenes, even though the metal−carbon bond lengths are similar in the heavier metallocenes (Os−C 2.19 Å (average)[4] versus Ru−C 2.186 Å (average) for ruthenocene[5]). For example, treatment of equimolar amounts of ruthenocene and osmocene with 1 equiv of mercuric chloride affords a 3:1 mixture of $(C_5H_5)_2Os{\cdot}HgCl_2$ and $(C_5H_5)_2Ru{\cdot}HgCl_2$.[6,7] There have been no descriptions of the mercuration of osmocene. With these considerations in mind, we report the surprising finding that osmocene can be decamercurated under mild conditions using mercuric acetate. Treatment of the decamercurated osmocene with halogenating agents affords the decahaloosmocenes in moderate to good yields. Finally, the crystal structure of decachloroosmocene is described. This work constitutes the first mercuration of an osmocene and provides routes to the first perhaloosmocenes.

Results and Discussion

Treatment of osmocene with mercuric acetate (10 equiv) in refluxing 1,2-dichloroethane for 18 h afforded decakis(acetoxymercurio)osmocene (**1**, 84%) as a white solid that precipitated from the reaction medium (eq 1). Complex **1** was insoluble in all common organic solvents, which precluded analysis by solution NMR methods. It was characterized by melting point, microanalysis, and IR spectroscopy. The C, H microanalysis results were consistent with a decamercurated formulation. The infrared spectrum of **1** showed absorptions at 1564 (vs), 1402 (s), 1331 (m), 1040 (w), 1014 (m), 917 (w), 684 (m), 646 (m), and 613 (m) cm^{-1}. For comparison, mercuric acetate showed strong absorptions at 1555, 1400, 1330, and 653 cm^{-1}. Despite the acceptable microanalysis results, it was not possible to confidently assign a decamercurated structure for **1**, since the calculated microanalytical values were not strongly dependent on the degree of mercuration (Anal. Calcd for **1**: C, 12.40; H, 1.04. Calcd for octamercurated osmocene: C, 13.07; H, 1.10).



1, 84%

(1)

The fully mercurated nature of **1** was confirmed by its reaction with halogenating agents (Scheme 1). Treatment of **1** with cupric chloride (ca. 50 equiv) in refluxing acetone for 4 h afforded decachloroosmocene (**2**, 43%) as white crystals, after workup. Complex **2** was readily soluble in chloroform and dichloromethane and could be subjected to NMR analysis. The ^1H NMR of crude **2** did not show any resonances in the δ 4−6 region, which demonstrates that the crude product contained $\leq$2% of partially chlorinated osmocenes. This result also implied that **1** was $\geq$98% decamercurated. Analogous halogenations of **1** using cupric bromide in refluxing acetone or potassium triiodide in water/methanol afforded decabromoosmocene (**3**, 48%) and decaiodoosmocene (**4**, 61%) as tan and white solids, respectively. The proposed structures for **2**−**4** were based upon spectral and analytical data, and upon a crystal structure determination for **2** (vide infra). The $^{13}C\{^1H\}$ NMR data for **2**−**4** were particularly revealing. A steady shielding of the carbons was observed in going from chloride to iodide substituents (**2**, 86.20 ppm; **3**, 78.41 ppm; **4**, 62.37 ppm). For comparison, the $^{13}C\{^1H\}$ NMR spectrum of osmocene shows a singlet at 63.56 ppm in chloroform-*d*.

The structure of **2** was determined in order to establish its molecular geometry. X-ray data were collected under the conditions summarized in Table 1. Bond lengths and positional parameters are provided in Tables 2 and 3. A perspective view of **2** is shown in Figure 1. Further data are contained in the supplementary material.

Complex **2** crystallized with the cyclopentadienyl ligands in an eclipsed conformation. The osmium−carbon bond lengths ranged between 2.118 and 2.198 Å, with an average distance of 2.166 Å. The osmium−cyclopentadienyl (centroid) distance was 1.79(1) Å. The cyclopentadienyl ligands were coplanar with a cyclopentadienyl (centroid)−osmium−cyclopentadienyl (centroid)′ angle of 179.6(5)°. The carbon−chlorine bonds averaged 1.700 Å. Comparison can be made with the structures of several related metallocenes for which X-ray structure determinations have been carried out. Osmocene itself crystallizes with the cyclopentadienyl ligands in an eclipsed conformation, with an osmium−carbon bond length of 2.190 Å.[4]

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Scheme 1. Halogenation of **1**

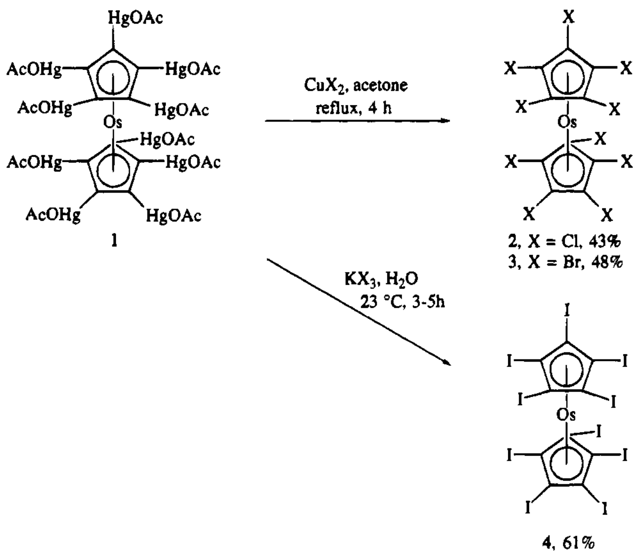

Table 1. Experimental Crystallographic Data for **2**

chem formula	$C_{10}Cl_{10}Os$	V (Å^3)	852.3(4)
fw	664.8	Z	2
space group	$P\bar{1}$	T (K)	296
a (Å)	7.396(2)	λ (Å)	0.710 73
b (Å)	8.5239(10)	ϱ_{calcd} (g·cm^{-3})	2.59
c (Å)	13.839(5)	μ (cm^{-1})	9.033
α (deg)	89.25(2)	transm coeff.	0.0611–0.1142
β (deg)	84.20(2)	$R(F)^a$ (%)	6.34
γ (deg)	79.120(10)	$R_w(F)^a$ (%)	7.89

$^a R = (\Sigma|\Delta F|)/\Sigma|F_o|$; $R_w = [(\Sigma w|\Sigma F|^2)/\Sigma wF_o^2]^{1/2}$.

Table 2. Bond Lengths (Å) for **2**

Os(1)–C(1)	2.150(17)	Os(1)–C(2)	2.136(20)
Os(1)–C(3)	2.176(17)	Os(1)–C(4)	2.160(17)
Os(1)–C(5)	2.190(16)	Os(1)–C(6)	2.159(17)
Os(1)–C(7)	2.187(18)	Os(1)–C(8)	2.118(20)
Os(1)–C(9)	2.198(18)	Os(1)–C(10)	2.183(14)
Cl(1)–C(1)	1.707(19)	Cl(2)–C(2)	1.742(21)
Cl(3)–C(3)	1.692(17)	Cl(4)–C(4)	1.735(18)
Cl(5)–C(5)	1.647(20)	Cl(6)–C(6)	1.726(18)
Cl(7)–C(7)	1.675(19)	Cl(8)–C(8)	1.757(19)
Cl(9)–C(9)	1.635(21)	Cl(10)–C(10)	1.682(18)
C(1)–C(2)	1.366(29)	C(1)–C(5)	1.477(30)
C(2)–C(3)	1.477(23)	C(3)–C(4)	1.370(25)
C(4)–C(5)	1.468(24)	C(6)–C(7)	1.365(26)
C(6)–C(10)	1.475(27)	C(7)–C(8)	1.471(28)
C(8)–C(9)	1.472(29)	C(9)–C(10)	1.452(26)
Cp(1)–Os(1)	1.79(1)	Cp(2)–Os(1)	1.79(1)

Decamethylosmocene[8] also exhibits an eclipsed structure, with an average osmium–carbon bond length of 2.170 Å. The structures of decachlororuthenocene[9] and decabromoruthenocene[10] have been determined and provide valuable comparisons to **2**. Both ruthenocenes adopt eclipsed conformations, with average ruthenium–carbon distances of 2.170 Å ($(C_5Cl_5)_2Ru$) and 2.170 Å ($(C_5Br_5)_2Ru$). In fact, the structure of **2** is isomorphous with those of decachlororuthenocene and decabromoruthenocene.

Despite the pronounced tendency of osmocene to form adducts with mercuric salts,[6,7] it can be decamercurated under the conditions described herein to provide **1** in 84% yield. The successful mercuration implies that adduct formation (i.e., a complex with a direct osmium–mercury bond), if a viable reaction path, is readily reversible under the reaction conditions. Alternatively, precoordination of the mercury may be required for mercuration at carbon. At present, we have no evidence that allows us to evaluate the importance of mercuric acetate–metallocene adducts in the decamercuration process, although the presence of such adducts is likely based upon the known ease of adduct formation[6] between osmocene and mercury salts. The decamercuration of osmocene should be evaluated in the context of the existing literature. We have previously reported that the cyclopentadienyl ligands in ferrocene,[11a] ruthenocene,[9,11a] pentamethylruthenocene,[11a,b] cyclopentadienylmanganese tricarbonyl,[11c] and cyclopentadienylrhenium tricarbonyl[11c] can be permercurated upon treatment with excess mercuric acetate in either ethanol/ether or refluxing 1,2-dichloroethane. Prior to our work, the only examples of cyclopentadienyl ligand perm-

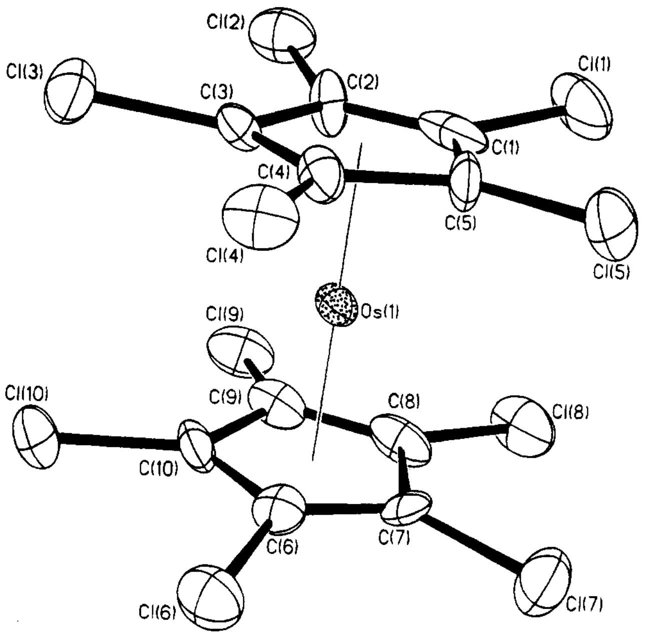

Figure 1. Perspective view of **2** drawn with 35% probability ellipsoids.

Table 3. Atomic Coordinates (×10^4) for **2**

	x	y	z
Os(1)	47.9(9)	2200.1(8)	2474.1(6)
Cl(1)	−2528(8)	6030(5)	2209(6)
Cl(2)	−1524(7)	3496(6)	243(4)
Cl(3)	−1884(7)	−254(5)	1037(4)
Cl(4)	−3131(6)	−69(6)	3495(4)
Cl(5)	−3498(7)	3817(7)	4224(4)
Cl(6)	2030(7)	−886(5)	3958(4)
Cl(7)	1580(8)	3011(7)	4685(4)
Cl(8)	2566(8)	5226(6)	2675(5)
Cl(9)	3618(7)	2688(7)	707(4)
Cl(10)	3248(7)	−1085(5)	1505(4)
C(1)	−2316(23)	4001(21)	2229(19)
C(2)	−1919(26)	2971(19)	1456(15)
C(3)	−2099(20)	1345(18)	1781(12)
C(4)	−2603(22)	1482(19)	2761(14)
C(5)	−2775(23)	3122(20)	3119(14)
C(6)	2178(22)	754(20)	3231(13)
C(7)	2003(22)	2291(22)	3548(13)
C(8)	2405(25)	3195(21)	2665(17)
C(9)	2872(25)	2170(22)	1794(16)
C(10)	2718(22)	600(19)	2176(16)

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ercuration were limited to poorly characterized products derived from the decamercuration of ferrocene[12a] and the pentamercuration of cyclopentadienylmanganese tricarbonyl.[12b] It is clear that the permercuration of transition metal cyclopentadienyl complexes is a general process, provided that the complex can withstand the reaction conditions.

One of the continuing problems in the development of osmocene chemistry is the lack of high-yield, convenient syntheses of new complexes. The present synthesis of **1** in nearly quantitative yield provides a flexible synthon for further elaboration to persubstituted osmocenes. Halogenation of **1** with chlorinating, brominating, and iodinating agents affords the previously unknown decahaloosmocenes **2**−**4** in moderate to good yields. The crystal structure of **2** provides the first structural data for an osmocene bearing pentahalocyclopentadienyl ligands. In general, complexes bearing pentahalocyclopentadienyl ligands have been difficult to prepare and have remained accordingly rare.[13,14] The present preparation of **2**−**4** can be compared with the synthesis of decachloroferrocene and decachlororuthenocene. Hedberg and Rosenberg first prepared these chlorinated metallocenes by repetitive lithiation/chlorination of ferrocene and ruthenocene in 7% and 14% yields, respectively.[13] By contrast, our methodology affords **2**−**4** in 36−51% overall yields, for a two-step sequence from osmocene. Carbon−mercury bonds represent extremely flexible synthetic intermediates,[15] and it is likely that osmocenes bearing many new functional groups should be readily accessible from **1**.

We are continuing to explore the permercuration of organometallic complexes and aromatic molecules, as well as their transformation to functionalized compounds. These studies will be published in due course.

Experimental Section

General Considerations. The mercuration reactions were performed under an atmosphere of nitrogen using Schlenk techniques. Dichloromethane was distilled from calcium hydride. Hexane was distilled from sodium. Reagent grade 1,2-dichloroethane and acetone were used as received. Chloroform-*d* was purified by vacuum-transfer from 4-Å molecular sieves. Osmocene was used as received from Strem Chemicals. Mercuric acetate, cupric chloride, cupric bromide, sodium thiosulfate, potassium iodide, and iodine were used as received from Aldrich Chemical Co.

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained at 500, 300, 121, or 75 MHz in chloroform-*d*, unless otherwise noted. Infrared spectra were obtained using potassium bromide as the medium. Mass spectra were obtained in the electron impact mode. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected.

Decakis(acetoxymercurio)osmocene (1). A 100-mL Schlenk flask, equipped with a condenser, stir bar, and rubber septum, was charged with osmocene (0.108 g, 0.337 mmol), mercuric acetate (1.08 g, 3.39 mmol), and 1,2-dichloroethane (20 mL). The mixture was refluxed for 18 h, during which time a white precipitate formed. The precipitate was collected on a medium-porosity glass frit and was washed with dichloromethane (100 mL) and acetone (100 mL). Vacuum-drying afforded **1** as a white powder (0.825 g, 84%): dec range 243−250 °C; IR (KBr, cm^{-1}) 1564 (ν_{CO}, vs), 1402 (ν_{CO}, s), 1331 (m), 1040 (w), 1014 (m), 917 (w), 684 (m), 646 (m), and 613 (m).

Anal. Calcd for $C_{30}H_{30}Hg_{10}O_{20}Os$: C, 12.40; H, 1.04 . Found: C, 12.68; H, 1.26.

Decachloroosmocene (2). A 250-mL round-bottomed flask was charged with **1** (0.380 g, 0.131 mmol), copper(II) chloride (0.884 g, 6.53 mmol), acetone (50 mL), and a stir bar and was fitted with a reflux condenser. The mixture was refluxed for 4 h. The solvent was removed under reduced pressure to give a dark oily solid. The solid was extracted with hexane (150 mL). The hexane extract was applied to a 30-cm column of silica gel on a coarse glass frit, and the column was eluted with hexane to afford a pale yellow solution. Removal of the solvent under reduced pressure, followed by vacuum-drying and crystallization from hexane at −20 °C, afforded **2** as white crystals (0.0378 g, 43%): sublimes at 225 °C; IR (KBr, cm^{-1}) 692 (ν_{C-Cl}, s); ^{13}C{^{1}H} NMR (CDCl$_3$, ppm) 86.20 (s, C_5Cl_5); LRMS calcd for $C_{10}Cl_{10}Os$ 661.6, found 661.6. The isotope distribution of the parent mass envelope was identical with the calculated pattern.

Anal. Calcd for $C_{10}Cl_{10}Os$: C, 18.07; H, 0.00. Found: C, 18.28; H, 0.06.

Decabromoosmocene (3). In a fashion similar to the preparation of **2**, **1** (0.167 g, 0.0574 mmol) and copper(II) bromide (0.642 g, 2.87 mmol) were reacted to afford **3** as a tan powder (0.0305 g, 48%): mp 244 °C (dec); IR (KBr, cm^{-1}) 578 (ν_{C-Br}, s); ^{13}C{^{1}H} NMR (CDCl$_3$, ppm) 78.41 (s, C_5Br_5); LRMS calcd for $C_{10}Br_{10}Os$ 1101.2; found 1101. The isotope distribution of the parent mass envelope was identical with the calculated pattern.

Anal. Calcd for $C_{10}Br_{10}Os$: C, 10.83; H, 0.0. Found: C, 10.75; H, 0.25.

Decaiodoosmocene (4). A 250-mL round-bottomed flask was charged with potassium iodide (0.435 g, 2.62 mmol), iodine (0.708 g, 2.79 mmol), water (25 mL), and methanol (25 mL). The resultant mixture was stirred at ambient temperature for 0.5 h, and then **1** (0.809 g, 0.278 mmol) was added. The mixture was stirred at ambient temperature for 6 h, during which time a red solid formed. The crude product was collected on a medium-porosity glass frit and was washed with saturated aqueous sodium thiosulfate (250 mL), saturated aqueous potassium iodide (250 mL), and dichloromethane (100 mL) to remove mercury impurities. The resultant solid was vacuum-dried to afford **4** as a white solid (0.269 g, 61%): mp 295 °C dec; IR (KBr, cm^{-1}) 497 (ν_{C-I}, vs); ^{13}C{^{1}H} NMR (dmso-d_6, ppm) 62.37 (s, C_5I_5).

Anal. Calcd for $C_{10}I_{10}Os$: C, 7.61; H, 0.00. Found: C, 7.29; H, 0.10.

Crystal Structure Determination of 2. The single-crystal X-ray diffraction experiment was performed on a Siemens P4 diffractometer with Mo Kα radiation and graphite monochromator at ambient temperature. The space group was assigned using photographic methods and from the systematic absences in the diffraction data. An empirical correction for absorption using ψ-scan data was applied. The osmium atom location was obtained from a Patterson projection. All atoms were anisotropically refined. All computations used the SHELX-TL-PC program library (G. Sheldrick, verersion 4.2, Siemens XRD, Madison, WI). Further data are contained in the supplementary material.

Acknowledgment. We are grateful to the Air Force Office of Scientific Research (Grant F49620-93-1-0072) for support of this research.

Supplementary Material Available: Tables S1−S3, listing full experimental details for data collection and refinement, bond angles, and thermal parameters, for **2** (5 pages). Ordering information is given on any current masthead page.

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