

Synthesis and structural characterization of unsymmetrical osmocenes containing the pentamethylcyclopentadienyl ligand

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Abstract

Treatment of dibromo(pentamethylcyclopentadienyl)osmium(III) dimer with alkali metal salts of a variety of cyclopentadienyl derivatives provides a simple approach to the synthesis of unsymmetrical osmocenes containing the pentamethylcyclopentadienyl ligand. Furthermore, the reaction of dibromo(pentamethylcyclopentadienyl)osmium(III) with alkali metal salts of pyrrole and 3,5-di-*tert*-butylpyrazole afforded the corresponding pentamethylcyclopentadienylosmium complexes containing η^5 -pyrrolyl or η^5 -3,5-di-*tert*-butylpyrazolato ligands. This overall synthetic approach afforded pentamethylcyclopentadienyl(η^5 -indenyl)osmium (36%), (η^5 -pentamethylcyclopentadienyl)(η^5 -fluorenyl)osmium (30%), (η^5 -pyrrolyl)(η^5 -pentamethylcyclopentadienyl)osmium (30%), and (η^5 -3,5-di-*tert*-butylpyrazolato)(η^5 -pentamethylcyclopentadienyl)osmium (38%). The new complexes were characterized by spectroscopic and analytical techniques, and by single crystal X-ray structural determinations. In the solid state, all of the new complexes exist as eclipsed metallocenes.

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1. Introduction

In contrast to the well developed chemistry of ferrocenes and ruthenocenes [1,2], the chemistry of osmocenes has received little attention [2b,3–5]. A major impediment to development of this area remains the lack of starting materials that afford osmocenes with desired substitution patterns. We have recently described the synthesis and reactivity of a series of penta- and decametalated ruthenocenes [6] and have also prepared ruthenocene analogs that contain the previously unknown η^5 -pyrazolato ligand coordination mode [7a]. Progress in our studies was made possible by the availability of unsymmetrical ruthenocenes [7,8] from the starting materials [(C₅(CH₃)₅)RuCl₂]_n [9] and [(C₅(CH₃)₅)RuCl]₄ [10]. In seeking to expand our studies of permetalated

metallocenes and complexes containing η^5 -heterocyclic ligands beyond ruthenium, we required routes to unsymmetrical osmocenes such as pentamethylcyclopentadienyl ligand. Previous routes to symmetrical osmocenes have employed sodium hexachloroosmate, hexachloroosmic acid, or tetra-*n*-butylammonium hexachloroosmate as starting materials [3,4]. A few unsymmetrical osmocenes were obtained by electrophilic substitution at one of the cyclopentadienyl rings of osmocene [5c–5e].

Recent reports have described several potential starting materials for unsymmetrical osmocenes. (C₅H₅)OsCl(PiPr₃)₂, which affords entry into many half-sandwich cyclopentadienylosmium complexes, was described in 1997 [11]. [(C₅(CH₃)₅)OsCl]₄, which is the analogue of [(C₅(CH₃)₅)RuCl]₄ [10], remains unknown. While (C₅(CH₃)₅)RuCl(PiPr₃) was reported in 1988 [12], an analogous osmium complex, (C₅(CH₃)₅)OsBr(PiPr₃), was prepared only recently [13]. In 1994,

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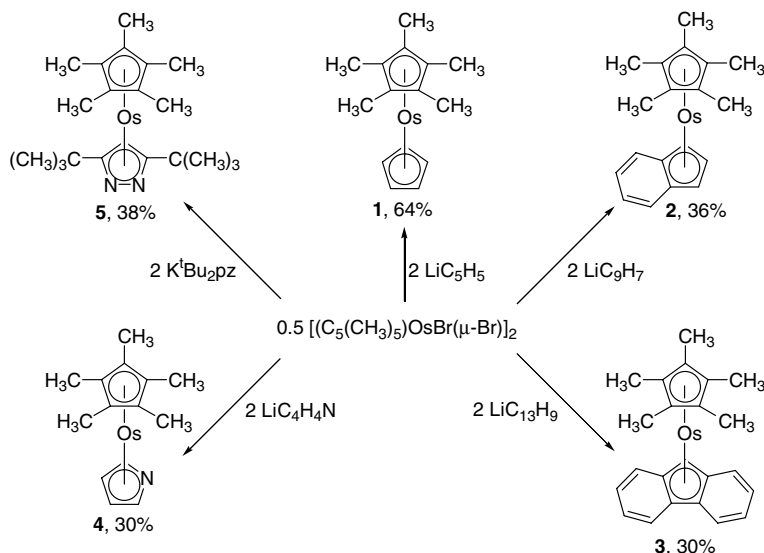
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Girolami and coworkers [14] reported the synthesis and characterization of dibromo(pentamethylcyclopentadienyl)osmium(III) dimer, $[(C_5(CH_3)_5)OsBr(\mu-Br)]_2$. This complex has served as a starting material for many half-sandwich pentamethylcyclopentadienylosmium complexes [13–15]. In addition, $[(C_5(CH_3)_5)OsBr(\mu-Br)]_2$ can be easily reduced to various complexes in the +2 oxidation state [13,15a,15d]. Based upon this facile reduction and the utility of $[(C_5(CH_3)_5)RuCl_2]_n$ in the synthesis of ruthenium complexes [8,16], it seemed likely that $[(C_5(CH_3)_5)OsBr(\mu-Br)]_2$ would serve as a suitable synthetic precursor for the synthesis of unsymmetrical osmocenes. Herein, we report a simple and general approach to unsymmetrical osmocenes and osmocene analogs containing one pentamethylcyclopentadienyl ligand, through treatment of $[(C_5(CH_3)_5)OsBr(\mu-Br)]_2$ with group 1 metal salts of cyclopentadienyl, substituted cyclopentadienyl, and heterocyclic cyclopentadienyl analogs.

2. Results and discussion

The general synthetic approach entailed treatment of $[(C_5(CH_3)_5)OsBr(\mu-Br)]_2$ with four or greater equivalents of a group 1 cyclopentadienyl, substituted cyclopentadienyl, or azacyclopentadienyl salt in refluxing tetrahydrofuran for 18 h (Scheme 1). Presumably, two of the anionic donor ligands served to reduce the osmium centers from the +3 to +2 oxidation state. Workup, as described below and in the Experimental section, afforded **1–5** in 30–64% isolated yields. Trace amounts of decamethylsmocene were observed in the crude reaction mixtures. Synthesis of pentamethylsmocene (**1**) and $(\eta^5\text{-pentamethylcyclopentadienyl})(\eta^5\text{-indenyl})$ osmium (**2**)

proceeded through treatment of $[(C_5(CH_3)_5)OsBr(\mu-Br)]_2$ with four equivalents of cyclopentadienyllithium and indenyllithium, respectively. Sublimation of the crude reaction mixtures at 60–62 °C (0.1 Torr) afforded analytically pure samples of **1** (64%) and **2** (36%) as colorless and orange crystals, respectively. Treatment of $[(C_5(CH_3)_5)OsBr(\mu-Br)]_2$ with fluorenyllithium afforded a crude product mixture that included the desired $(\eta^5\text{-pentamethylcyclopentadienyl})(\eta^5\text{-fluorenyl})$ osmium (**3**), fluorene, 1,1-bifluorenyl, lithium bromide, colored impurities, and ~6% of decamethylsmocene. The fluorene was removed by sublimation at 50 °C (0.1 Torr), and the remaining residue was sublimed at 110 °C (0.1 Torr) to afford analytically pure **3** (30%) as bright orange crystals. The syntheses of $(\eta^5\text{-pyrrolyl})(\eta^5\text{-pentamethylcyclopentadienyl})$ osmium (**4**) and $(\eta^5\text{-pentamethylcyclopentadienyl})(\eta^5\text{-3,5-di-tert-butylpyrazolato})$ osmium (**5**) proceeded through treatment of $[(C_5(CH_3)_5)OsBr(\mu-Br)]_2$ with pyrrolyllithium or 3,5-di-tert-butylpyrazolotopotassium. For the isolation of **4**, sublimation of the crude reaction mixture at 66 °C (0.1 Torr) afforded an analytically pure sample as colorless crystals (30%). Complex **5** was isolated as a white solid in 38% yield after column chromatography on silica gel. The structures of **1–5** were assigned using spectroscopic and analytical techniques, and by X-ray crystal structure determinations. The presence of decamethylsmocene in the crude reaction mixtures was confirmed by correlation of the 1H and $^{13}C\{^1H\}$ NMR resonances with those of authentic material [4b]. The identity of 1,1-bifluorenyl was established by comparison of its 1H and $^{13}C\{^1H\}$ NMR shifts in the crude reaction mixture with previously reported NMR data [17]. In the crude reaction mixtures, 1,1-bifluorenyl and **5** were consistently present in a 1:2 ratio. The observation



Scheme 1. Synthesis of **1–5**. All reactions were conducted in refluxing tetrahydrofuran for 18 h.

of 1,1-bifluorenyl as a reaction product provides insight into the mechanism by which the reduction from osmium(III) to osmium(II) occurs.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1–5** in dichloromethane- d_2 at ambient temperature were consistent with sandwich structures in which the anionic five-membered rings are coordinated to the $(\text{C}_5(\text{CH}_3)_5)\text{Os}$ fragment with the η^5 -coordination mode. In particular, the hydrogen and carbon resonances of the anionic five-membered rings in **1–5** showed significant upfield chemical shifts, relative to the protonated ligand precursors in dichloromethane- d_2 . The cyclopentadienyl ligand in **1** exhibited resonances at δ 4.18 and 65.41 ppm in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, respectively. For comparison, the related resonances in osmocene appear at δ 4.70 and 63.6 ppm in chloroform- d [4b]. In **2**, the indenyl five-membered ring moiety exhibited ^1H NMR resonances at δ 4.94 ($\text{H}_{1,3}$) and 4.50 (H_2) and resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR at 86.73 (C_{quat}), 68.85 (C_2), and 62.03 ($\text{C}_{1,3}$) ppm. Indene had ^1H NMR resonances at δ 3.45 (2H_1), 6.63 (H_2), and 6.96 (H_3). Thus, the chemical shift difference for the vinylic hydrogen atoms of indene and the corresponding atoms in **2** is 1.5–2.5 ppm. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of indene, resonances for the five-membered ring fragment were observed at 145.05 (C_9), 144.00 (C_8), 134.46 (C_2), 132.11 (C_3), and 39.24 (C_1) ppm. Thus, there are upfield chemical shifts in going from indene to **2** of 56.9–57.3, 63.3, and 72.5 ppm for $\text{C}_{8,9}$, C_3 , and C_2 , respectively. In **3**, the five-membered ring exhibited resonances for the C–H fragment at δ 5.50 and 57.03 ppm, respectively, in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. The quaternary carbon atoms of the five-membered ring showed resonances at 90.02 and 74.69 ppm, which are shifted 51.9–68.9 ppm

upfield from the same carbon atoms in fluorene. The ^1H NMR resonances for the six-membered rings of the fluorenyl ligand in **3** appeared between δ 6.78 and 7.15. Observation of four resonances with chemical shifts in the normal aromatic region rules out coordination of a six-membered ring of the fluorenyl ligand. In **4**, resonances for the pyrrolyl ligand were observed in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at δ 5.41 and 4.71 and 86.16 and 69.41 ppm, respectively. These resonances are δ 1.08–2.83 and 21.7–48.4 ppm upfield of the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR resonances observed for the same atoms in pyrrole. For **5**, resonances for the pyrazolato ligand core C–H fragment were observed at δ 5.06 and 67.15 ppm, respectively, in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. The quaternary carbon atoms in the pyrazolato ligand core resonated at 127.58 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. For comparison, the C–H fragment of 3,5-di-*tert*-butylpyrazole exhibited ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR resonances at δ 5.95 and 97.65 ppm, respectively, and the quaternary carbon atoms in the pyrazolato ligand core resonated at 154.59 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. We have recently reported the ruthenium analog of **5**, $\text{Ru}(\text{C}_5(\text{CH}_3)_5)(\text{C}_3\text{HN}_2(\text{C}(\text{CH}_3)_3)_2)$, which has pyrazolato ligand core C–H resonances at δ 4.73 and 71.23 ppm, respectively, in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in benzene- d_6 [7a].

To understand the solid state geometries, the X-ray crystal structures of **1–5** were determined. Crystallographic data are summarized in Table 1. Selected bond lengths and angles are given in Tables 2–6. Perspective views of **1–5** are presented in Figs. 1–5. Complexes **3–5** each contain two independent molecules in the unit cells. The structural parameters of the two independent molecules in each structure are identical within the experi-

Table 1
Crystal data and data collection parameters for **1–5**

	1	2	3	4	5
Empirical formula	$\text{C}_{15}\text{H}_{20}\text{Os}$	$\text{C}_{19}\text{H}_{22}\text{Os}$	$\text{C}_{23}\text{H}_{24}\text{Os}$	$\text{C}_{14}\text{H}_{19}\text{NOs}$	$\text{C}_{21}\text{H}_{34}\text{N}_2\text{Os}$
Formula weight	390.51	440.57	490.62	391.50	504.70
space group	$P\bar{1}$	$P2(1)/n$	$P2(1)/n$	$P\bar{1}$	$P2(1)/n$
a (Å)	7.9266(5)	9.4928(3)	7.5220(4)	7.8910(2)	20.171(2)
b (Å)	8.1890(5)	12.5636(4)	30.6265(19)	12.0609(3)	12.1466(12)
c (Å)	12.0950(7)	12.7689(4)	15.7983(10)	14.1070(3)	20.348(2)
α (°)	100.746(3)			106.6910(10)	
β (°)	99.646(3)	96.4520(10)	101.402(2)	90.5220(10)	119.351(2)
γ (°)	118.220(3)			100.2590(10)	
V (Å ³)	649.32(7)	1513.22(8)	3567.7(4)	1262.88(5)	4345.5(8)
Z	2	4	8	4	8
T (K)	100(2)	100(2)	100(2)	100(2)	295(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (g/cm ³)	1.997	1.934	1.827	2.059	1.543
μ (mm ⁻¹)	9.790	8.414	7.149	10.070	5.873
$R(F)^a$ (%)	2.44	2.38	1.76	2.03	2.83
$Rw(F)^b$ (%)	6.22	6.76	4.11	4.74	5.84

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR = [\sum (wF_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ for $I > 2(I)$.

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Os–C(1)	2.182(3)
Os–C(2)	2.189(4)
Os–C(3)	2.185(4)
Os–C(4)	2.186(4)
Os–C(5)	2.179(4)
Os–C(11)	2.204(4)
Os–C(12)	2.197(4)
Os–C(13)	2.187(4)
Os–C(14)	2.195(4)
Os–C(15)	2.198(3)
Os–C ₅ Me ₅ centroid	1.809(4)
Os–C ₅ H ₅ centroid	1.827(4)
C ₅ Me ₅ –Os–C ₅ H ₅ centroid	179.3(2)

Table 3
Selected bond lengths (Å) and angles (°) for **2**

Os–C(1)	2.219(4)
Os–C(2)	2.189(4)
Os–C(3)	2.201(4)
Os–C(4)	2.202(4)
Os–C(5)	2.245(4)
Os–C(10)	2.165(4)
Os–C(11)	2.161(4)
Os–C(12)	2.182(4)
Os–C(13)	2.196(4)
Os–C(14)	2.177(4)
Os–C ₅ Me ₅ centroid	1.798(4)
Os–Ind centroid	1.842(4)
C ₅ Me ₅ –Os–Ind centroid	176.0(2)

Table 4
Selected bond lengths (Å) and angles (°) for **3**

Os(1)–C(1)	2.168(2)
Os(1)–C(2)	2.177(2)
Os(1)–C(3)	2.166(2)
Os(1)–C(4)	2.172(2)
Os(1)–C(5)	2.158(2)
Os(1)–C(11)	2.238(2)
Os(1)–C(16)	2.233(2)
Os(1)–C(17)	2.195(2)
Os(1)–C(18)	2.246(2)
Os(1)–C(19)	2.237(2)
Os(1)–C ₅ Me ₅ centroid	1.788(2)
Os(1)–fluorenyl centroid	1.861(2)
C ₅ Me ₅ –Os(1)–fluorenyl centroid	178.7(1)

mental errors of the diffraction experiments. Only the structural data for the molecule containing Os(1) are discussed below.

The molecular structures of **1–5** share a common (C₅(CH₃)₅)Os fragment. The osmium–carbon bond lengths associated with the C₅(CH₃)₅ ligand (**1**, 2.179(4)–2.189(4) Å; **2**, 2.161(4)–2.196(4) Å; **3**, 2.158(2)–2.177(2) Å; **4**, 2.172(3)–2.191(3) Å; **5**, 2.150(5)–2.172(5) Å) are identical within the experimental uncertainty of the diffraction experiments within each structure and also across the series **1–5**. The osmium–

Table 5
Selected bond lengths (Å) and angles (°) for **4**

Os(1)–C(1)	2.175(3)
Os(1)–C(2)	2.209(3)
Os(1)–C(3)	2.202(3)
Os(1)–C(4)	2.172(3)
Os(1)–N(1)	2.202(3)
Os(1)–C(5)	2.177(3)
Os(1)–C(6)	2.191(3)
Os(1)–C(7)	2.175(3)
Os(1)–C(8)	2.172(3)
Os(1)–C(9)	2.178(3)
Os(1)–C ₅ Me ₅ centroid	1.803(3)
Os(1)–pyrrolyl centroid	1.831(3)
C ₅ Me ₅ –Os(1)–pyrrolyl centroid	178.0(2)

Table 6
Selected bond lengths (Å) and angles (°) for **5**

Os(1)–C(1)	2.196(4)
Os(1)–C(2)	2.211(4)
Os(1)–C(3)	2.191(4)
Os(1)–N(1)	2.165(3)
Os(1)–N(2)	2.167(3)
Os(1)–C(12)	2.172(5)
Os(1)–C(13)	2.164(5)
Os(1)–C(14)	2.150(5)
Os(1)–C(15)	2.161(5)
Os(1)–C(16)	2.171(5)
Os(1)–C ₅ Me ₅ centroid	1.818(5)
Os(1)–pyrazolato centroid	1.830(5)
C ₅ Me ₅ –Os(1)–pyrazolato centroid	177.5(3)

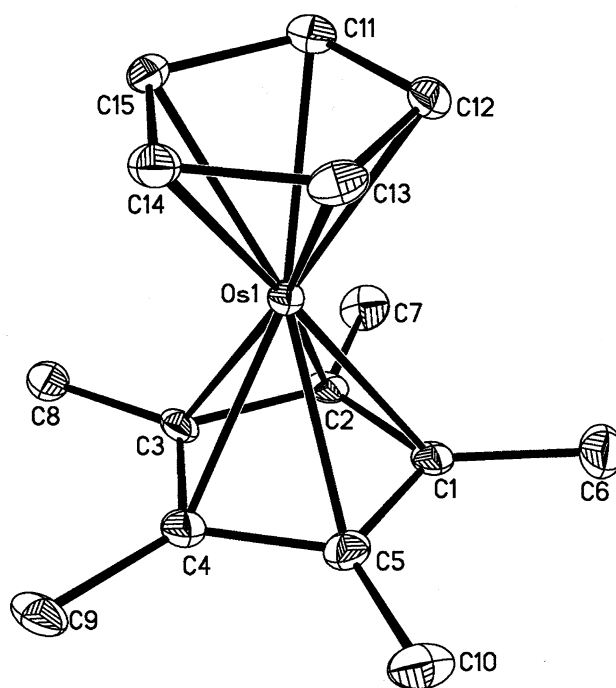


Fig. 1. Perspective view of **1** (50% probability ellipsoid; hydrogen atoms are omitted for clarity).

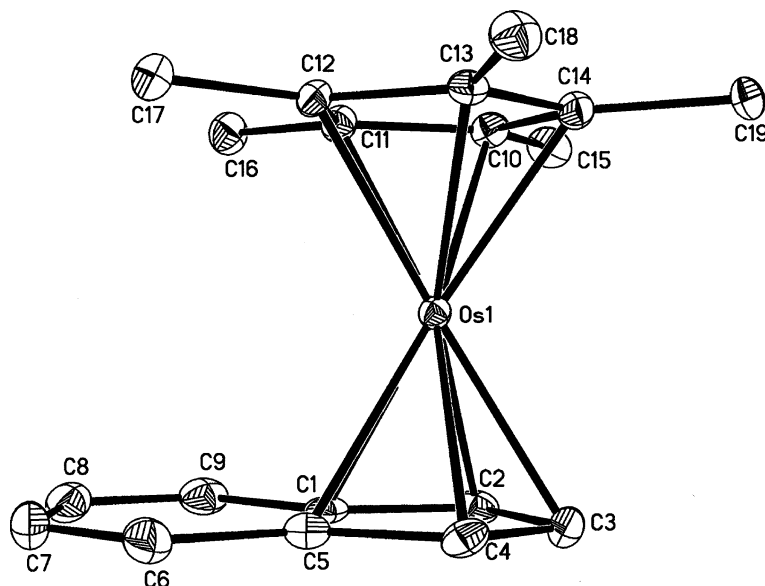


Fig. 2. Perspective view of **2** (50% probability ellipsoid; hydrogen atoms are omitted for clarity).

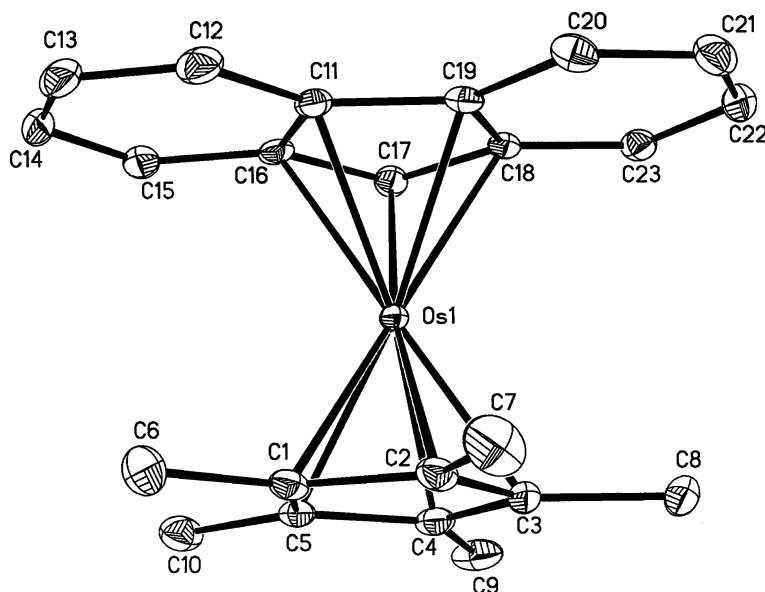


Fig. 3. Perspective view of **3** (50% probability ellipsoid; hydrogen atoms are omitted for clarity).

centroid distances to the $C_5(CH_3)_5$ ligand for **1–5** range between 1.788(2) and 1.818(5) Å, and are identical across the series within experimental uncertainty. The centroid–osmium–centroid angles in **1–5** are close to 180°. The osmium–carbon bond lengths and osmium–centroid distances associated with the other donor ligand in **1–5** (**1**, 2.187(4)–2.204(4), 1.827(4) Å; **2**, 2.189(4)–2.245(4), 1.842(4) Å; **3**, 2.195(2)–2.246(2), 1.861(2) Å; **4**, 2.175(3)–2.209(3), 1.831(3) Å; **5**, 2.191(4)–2.211(4), 1.830(5) Å) are slightly longer than the values associated with the $C_5(CH_3)_5$ ligand. The differences in the osmium–centroid distances between the

$C_5(CH_3)_5$ and other ligand are at the edge of experimental uncertainty for **2** and **3**. For complexes **1**, **4**, and **5**, the difference in the osmium–centroid distances within each molecule is less than the experimental uncertainty. The dihedral angles between the planes of the two five-membered rings within **1–5** are 1.22°, 5.36°, 1.66°, 2.34°, and 2.42°, respectively. The five-membered rings are approximately eclipsed within each molecule.

The only neutral osmocene containing a $C_5(CH_3)_5$ ligand that has been previously structurally characterized is $(C_5(CH_3)_5)_2Os$ [**4b**]. In $(C_5(CH_3)_5)_2Os$, the osmium–carbon bond lengths range between 2.145(10) and

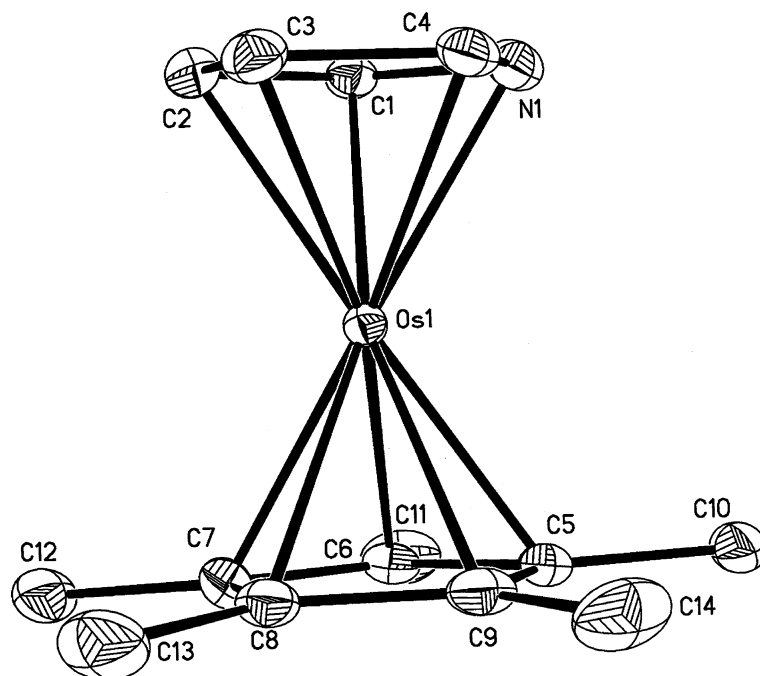


Fig. 4. Perspective view of **4** (50% probability ellipsoid; hydrogen atoms are omitted for clarity).

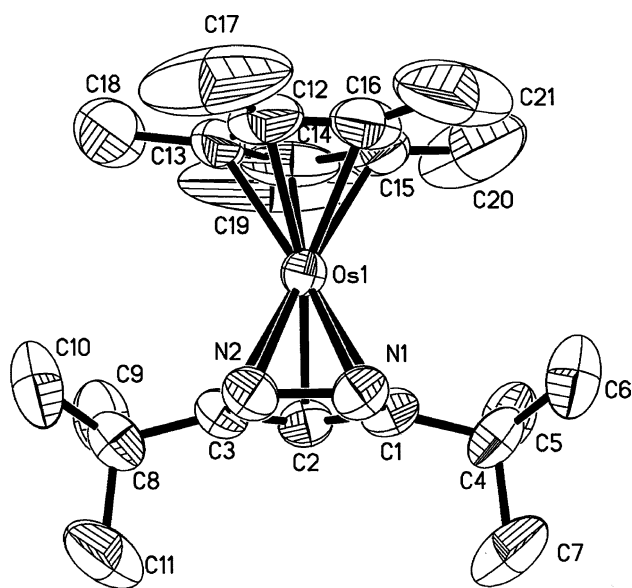


Fig. 5. Perspective view of **5** (50% probability ellipsoid; hydrogen atoms are omitted for clarity).

2.178(6) Å [4b], and are very similar to the related values observed in **1–5** (2.150–2.196 Å). In the molecular structure of osmocene [3c], the osmium–carbon bonds are between 2.179(8) and 2.20(2) Å. These bond distances are very similar to the osmium–carbon bond lengths associated with the cyclopentadienyl ligand in **1** (2.187(4)–2.204(4) Å). Like **1–5**, the cyclopentadienyl C₅ cores in (C₅(CH₃)₅)₂Os and osmocene are eclipsed. Several cationic osmocenes containing C₅(CH₃)₅ ligands have also been structurally characterized, including

[(C₅(CH₃)₅)₂Os]⁺BF₄[−] [18a], [(C₅(CH₃)₅)₂OsCl]₂[OsCl₆] [18b], [(C₅(CH₃)₅)Os(μ-C₅(CH₃)₅)Ru(C₅H₅)]⁺PF₆[−] [18c], and [(C₅(CH₃)₅)₂OsH]₂[Os₂Br₈] [18d].

Complexes **1–5** all have ruthenium analogs, several of which have been structurally characterized and have molecular structures that are very similar to those of **1–5**. (η⁵-Pentamethylcyclopentadienyl)(η⁵-indenyl)-ruthenium has ruthenium–centroid distances of 1.792 (C₅(CH₃)₅) and 1.840 Å (indenyl) [8a], compared to values of 1.798(4) (C₅(CH₃)₅) and 1.842(4) Å (indenyl) in **2**. (η⁵-Pentamethylcyclopentadienyl)(η⁵-fluorenyl)ruthenium has related values of 1.777 and 1.781 Å (C₅(CH₃)₅) and 1.857 and 1.865 Å (fluorenyl) [8a], compared to values of 1.788(2) and 1.861(2) Å in **3**. (η⁵-3,5-dimethylpyrazolato)(η⁵-pentamethylcyclopentadienyl)ruthenium has ruthenium–centroid values of 1.837(3) (C₃HN₂(CH₃)₂) and 1.785(3) (C₅(CH₃)₅) [7a], which are very similar to the values of 1.830(5) (C₃HN₂(C(CH₃)₃)₂) and 1.818(5) Å (C₅(CH₃)₅) in **5**. Complex **4** is the first structurally characterized osmium complex that contains an η⁵-pyrrolyl ligand. The pyrrolyl complex (η⁵-tetramethylpyrrolyl)(η⁵-pentamethylcyclopentadienyl)ruthenium has been reported, but was not crystallographically characterized [8d,8h]. Several other ruthenium(II) metallocenes containing substituted pyrrolyl ligands have been reported [8i,8j], and have been evaluated as nucleophilic catalysts [8h,8i,8j]. Interestingly, **5** is the third example of a crystallographically characterized complex that contains a terminal η⁵-pyrazolato ligand [7a,19].

In summary, [(C₅(CH₃)₅)OsBr(μ-Br)]₂ serves as a useful starting material for the synthesis of osmocenes and

osmocene analogs that contain one pentamethylcyclopentadienyl ligand. A broad range of unsymmetrical osmocenes should be easily accessed by the approach outlined herein.

3. Experimental

3.1. General considerations

All reactions were performed under an inert atmosphere of argon using either glovebox or Schlenk line techniques. Tetrahydrofuran was distilled from sodium benzophenone ketyl, toluene was distilled from sodium, and hexane was distilled from P_2O_5 prior to use. $[(C_5(CH_3)_5)OsBr(\mu-Br)]_2$ [14], 3,5-di-*tert*-butylpyrazole [20a], and 3,5-di-*tert*-butylpyrazolato-potassium [20b] were prepared according to published procedures. Potassium hydride (35% dispersion in mineral oil) was purchased from Aldrich Chemical Company and was washed with hexane prior to use to remove the mineral oil. Sodium cyclopentadienide (2.0 M solution in tetrahydrofuran), indene, fluorene, pyrrole, methyl lithium (1.6 M solution in diethyl ether), and *n*-butyllithium (1.6 M solution in hexanes) were purchased from Aldrich Chemical Company and were used without further purification.

1H and $^{13}C\{^1H\}$ NMR were recorded at 500, 300, 121, or 75 MHz in dichloromethane- d_2 . Infrared spectra were obtained using KBr as the medium. Elemental analyses were performed by Desert Analytics Laboratory, Phoenix, AZ, USA. Melting points were obtained on a Haake-Buchler HBI digital melting point apparatus and are uncorrected.

3.2. Synthesis of (η^5 -pentamethylcyclopentadienyl)-(η^5 -cyclopentadienyl)osmium (**1**)

A 100-mL Schlenk flask was charged with $[(C_5(CH_3)_5)OsBr(\mu-Br)]_2$ (0.243 g, 0.250 mmol) and tetrahydrofuran (40 mL). To the stirred solution under argon was added 0.500 mL (1.00 mmol) of a 2.0 M solution of sodium cyclopentadienide in tetrahydrofuran. Upon addition of the sodium cyclopentadienide, the reaction mixture turned from dark brown to off white, and later to a deep red. The resultant mixture was stirred at ambient temperature for 18 h. The deep red solution was filtered through a 2-cm pad of Celite on a coarse glass frit. The volatile components were removed under reduced pressure to afford a deep red solid. The deep red solid was sublimed at 62 °C (0.1 Torr) to afford colorless crystals of **1** (0.125 g, 64%): mp 139 °C; IR (KBr, cm^{-1}) 3105 (m), 2967 (m), 2949 (m), 2896 (s), 2854 (m), 1742 (w), 1686 (m), 1654 (w), 1628 (w), 1470 (s), 1419 (m), 1397 (m), 1376 (vs), 1095 (vs), 1071 (m), 1035 (vs), 990 (vs), 814 (vs), 668 (w), 577

(w), 453 (w); 1H NMR (dichloromethane- d_2 , 23 °C, δ) 4.18 (s, 5H, C_5H_5), 2.03 (s, 15H, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ NMR (dichloromethane- d_2 , 23 °C, ppm) 80.42 (s, $C_5(CH_3)_5$), 65.41 (s, C_5H_5), 12.90 (s, $C_5(CH_3)_5$). Anal. Calcd. for $C_{15}H_{20}Os$: C, 46.13; H, 5.16. Found: C, 46.30; H, 5.28.

3.3. Synthesis of (η^5 -pentamethylcyclopentadienyl)-(η^5 -indenyl)osmium (**2**)

A 1.6 M solution of methyl lithium in diethyl ether (1.00 mL, 1.60 mmol) was added to a solution of indene (0.190 mL, 1.63 mmol) in tetrahydrofuran (20 mL), providing an orange solution. The reaction mixture was stirred at ambient temperature for 2 h, and was then transferred to a solution of $[(C_5(CH_3)_5)OsBr(\mu-Br)]_2$ (0.258 g, 0.265 mmol) in tetrahydrofuran (20 mL). The resultant mixture was stirred at ambient temperature for 18 h, and then the volatile components were removed under reduced pressure to afford a sticky brown solid. The brown solid was sublimed at 60 °C (0.1 Torr) to afford **2** as an orange oil, which crystallized upon cooling to room temperature to an orange solid (0.085 g, 36%): mp 72 °C; IR (KBr, cm^{-1}) 3043 (m), 2960 (m), 2940 (m), 2895 (s), 2850 (m), 1465 (s), 1418 (m), 1378 (s), 1331 (s), 1032 (s), 1021 (m), 817 (m), 739 (vs), 723 (m), 548 (m), 452(m); 1H NMR (dichloromethane- d_2 , 23 °C, δ) 6.98 (m, 2H, $CH(CH)_2CH$ of indenyl six-membered ring), 6.72 (m, 2H, $CH(CH)_2CH$ of indenyl six-membered ring), 4.94 (d, $J = 2.5$ Hz, 2H, $CHCHCH$ of indenyl five-membered ring), 4.50 (t, $J = 2.5$ Hz, 1H, $CHCHCH$ of indenyl five-membered ring), 1.70 (s, 15H, $C_5(CH_3)_5$); $^{13}C\{^1H\}$ NMR (dichloromethane- d_2 , 23 °C, ppm) 125.96 (s, $CH(CH)_2CH$ of indenyl six-membered ring), 121.32 (s, $CH(CH)_2CH$ of indenyl six-membered ring), 86.73 (s, quaternary C of indenyl), 77.53 (s, $C_5(CH_3)_5$), 68.85 (s, $CHCHCH$ of indenyl five-membered ring), 62.03 (s, $CHCHCH$ of indenyl five-membered ring), 11.22 (s, $C_5(CH_3)_5$). Anal. Calcd. for $C_{19}H_{22}Os$: C, 51.79; H, 5.03. Found: C, 51.97; H, 5.00.

3.4. Synthesis of (η^5 -pentamethylcyclopentadienyl)-(η^5 -fluorenyl)osmium (**3**)

A 1.6 M solution of methyl lithium in diethyl ether (0.750 mL, 1.200 mmol) was added to a solution of fluorene (0.199 g, 1.197 mmol) in tetrahydrofuran (20 mL), providing an orange solution. The reaction mixture was stirred at ambient temperature for 2 h, and was then transferred to a solution of $[(C_5(CH_3)_5)OsBr(\mu-Br)]_2$ (0.194 g, 0.199 mmol) in tetrahydrofuran (20 mL). The resultant mixture was stirred at ambient temperature for 18 h, and then the volatile components were removed under reduced pressure to afford a sticky red-brown solid. The excess fluorene was removed by sublimation at 50 °C (0.1 Torr), and the residue was sublimed

at 110 °C (0.1 Torr) to afford **3** as bright orange crystals (0.059 g, 30%): mp 130 °C; IR (KBr, cm^{-1}) 3046 (m), 2960 (m), 2943 (m), 2899 (s), 2850 (m), 1457 (s), 1421 (m), 1384 (m), 1374 (vs), 1349 (m), 1328 (m), 1317 (m), 1192 (m), 1033 (s), 971 (m), 870 (m), 731 (s), 716 (m); ^1H NMR (dichloromethane- d_2 , 23 °C, δ) 7.50 (m, 2H, CHCH'CH''CH''' of fluorenyl six-membered ring), 7.15 (m, 2H, CHCH'CH''CH''' of fluorenyl six-membered ring), 6.90 (m, 2H, CHCH'CH''CH''' of fluorenyl six-membered ring), 6.78 (m, CHCH'CH''CH''' of fluorenyl six-membered ring), 5.50 (s, 1H, fluorenyl CH of five-membered ring), 1.36 (s, 15H, $\text{C}_5(\text{CH}_3)_5$); $^{13}\text{C}\{^1\text{H}\}$ NMR (dichloromethane- d_2 , 23 °C, ppm) 125.63 (s, CHCH'CH''CH''' of fluorenyl six-membered ring), 124.78 (s, CHCH'CH''CH''' of fluorenyl six-membered ring), 122.58 (s, CHCH'CH''CH''' of fluorenyl six-membered ring), 120.03 (s, CHCH'CH''CH''' of fluorenyl six-membered ring), 90.02 (s, quaternary C of fluorenyl), 83.45 (s, $\text{C}_5(\text{CH}_3)_5$), 74.69 (s, quaternary C of fluorenyl), 57.03 (s, CH of fluorenyl five-membered ring), 9.80 (s, $\text{C}_5(\text{CH}_3)_5$). Anal. Calcd. for $\text{C}_{23}\text{H}_{24}\text{Os}$: C, 56.30; H, 4.93. Found: C, 56.50; H, 4.98.

3.5. Synthesis of (η^5 -pentamethylcyclopentadienyl)-(η^5 -pyrrolyl)osmium (**4**)

A 1.6 M solution of *n*-butyllithium in hexanes (0.810 mL, 1.30 mmol) was added to a solution of pyrrole (90 μL , 1.3 mmol) in tetrahydrofuran (20 mL), providing a light-yellow solution. The reaction mixture was stirred at ambient temperature for 1 h, and was then transferred to a solution of $[(\text{C}_5(\text{CH}_3)_5)\text{OsBr}(\mu\text{-Br})_2]$ (0.252 g, 0.259 mmol) in tetrahydrofuran (20 mL). The resultant mixture was refluxed for 18 h. Upon cooling of the reaction mixture, the volatile components were removed under reduced pressure to afford a sticky red-brown solid. The red-brown solid was sublimed at 66 °C (0.1 Torr) to afford **4** as colorless crystals (0.060 g, 30%): mp 163 °C; IR (KBr, cm^{-1}) 3085 (m), 2969 (m), 2950 (m), 2899 (s), 2855 (m), 1471 (s), 1377 (vs), 1343 (m), 1265 (m), 1186 (m), 1097 (vs), 1064 (m), 1039 (s), 998 (vs), 853 (m), 839 (m), 813 (s), 628 (m), 457 (w); ^1H NMR (dichloromethane- d_2 , 23 °C, δ) 5.41 (s, 2H, $(\text{CH})_2(\text{C}'\text{H}')_2\text{N}$), 4.71 (s, 2H, $(\text{CH})_2(\text{C}'\text{H}')_2\text{N}$), 2.02 (s, 15H, $\text{C}_5(\text{CH}_3)_5$); $^{13}\text{C}\{^1\text{H}\}$ NMR (dichloromethane- d_2 , 23 °C, ppm) 86.16 (s, $(\text{CH})_2(\text{C}'\text{H}')_2\text{N}$), 81.22 (s, $\text{C}_5(\text{CH}_3)_5$), 69.41 (s, $(\text{CH})_2(\text{C}'\text{H}')_2\text{N}$), 12.38 (s, $\text{C}_5(\text{CH}_3)_5$). Anal. Calcd. for $\text{C}_{14}\text{H}_{19}\text{NOs}$: C, 42.95; H, 4.89; N, 3.58. Found: C, 43.07; H, 4.76; N, 3.55.

3.6. Synthesis of (η^5 -3,5-di-*tert*-butylpyrazolato)-(η^5 -pentamethylcyclopentadienyl)osmium (**5**)

A 50-mL Schlenk flask was charged with $[(\text{C}_5(\text{CH}_3)_5)\text{OsBr}(\mu\text{-Br})_2]$ (0.100 g, 0.103 mmol), 3,5-di-*tert*-butylpyrazolatopotassium (0.180 g, 0.824 mmol),

and tetrahydrofuran (30 mL). The resultant mixture was refluxed for 18 h. Upon cooling, the dark brown solution was filtered through a 2-cm pad of Celite on a coarse glass frit. The volatile components were removed under reduced pressure to afford a sticky, brown solid. The dark brown solid was extracted with hexane (15 mL), concentrated to 5 mL under reduced pressure, and separated by column chromatography on silica gel. The column was initially eluted with hexane, then with ethyl acetate/hexane (20:80) to remove the 3,5-di-*tert*-butylpyrazole, and finally with ethyl acetate/hexane (30:70) to afford **5** as a white crystalline solid (0.040 g, 38%). An analytical sample and single crystals for the X-ray diffraction analysis were obtained by slow evaporation of a hexane solution of **5**: mp 135 °C; IR (KBr, cm^{-1}) 3049 (w), 2976 (m), 2959 (s), 2904 (s), 2863 (m), 1487 (m), 1456 (m), 1384 (s), 1363 (m), 1248 (m), 1181 (w), 1035 (s), 1006 (w), 805 (w), 692 (m); ^1H NMR (dichloromethane- d_2 , 23 °C, δ) 5.06 (s, 1 H, $\text{tBu}_2\text{pz CH}$), 1.93 (s, 15H, $\text{C}_5(\text{CH}_3)_5$), 1.22 (s, 18H, $\text{tBu}_2\text{pz C}(\text{CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (dichloromethane- d_2 , 23 °C, ppm) 127.58 (s, $\text{tBu}_2\text{pz CC}(\text{CH}_3)_3$), 81.95 (s, $\text{C}_5(\text{CH}_3)_5$), 67.15 (s, $\text{tBu}_2\text{pz CH}$), 31.15 (s, $\text{tBu}_2\text{pz C}(\text{CH}_3)_3$), 29.94 (s, $\text{tBu}_2\text{pz C}(\text{CH}_3)_3$), 12.55 (s, $\text{C}_5(\text{CH}_3)_5$). Anal. Calcd. for $\text{C}_{21}\text{H}_{34}\text{N}_2\text{Os}$: C, 49.97; H, 6.79; N, 5.55. Found: C, 50.46; H, 6.64; N, 5.43.

3.7. X-ray crystallographic structure determination for **1–5**

Diffraction data for **1–4** were measured on a Bruker X8 APEX-II kappa geometry diffractometer with Mo radiation and a graphite monochromator at 100 K. Frames were collected as a series of sweeps with the detector at 40–50 mm and 0.2–0.3° between each frame. The manufacturer's APEX II software [21] was used for processing. All structures were refined using Sheldrick's SHELX-97 software [22].

Complex **1** crystallized as colorless tablets. Eight separate datasets were collected on eight different samples in a search for an untwined specimen. All datasets solved poorly, characteristically exhibiting a 7 e- peak at $1/2 + x, y, z$, from the osmium atom near the cyclopentadienyl ligand. This anomalous peak interfered with the cyclopentadienyl ligand refinement, causing non-positive definite thermal parameters for most carbon atoms. To solve the twin dilemma, the best dataset was processed using Sheldrick's CELL_NOW software [22] and the data were integrated (via SAINTPLUS and TWINABS) with two simultaneous matrices that represented a 180° rotation about the (1/2, 1, 0) axis in reciprocal space. The refinement then proceeded normally [22] and the minor twin component was refined to represent 13% of the total volume. A sample with dimensions of $0.25 \times 0.25 \times 0.15 \text{ mm}^3$ was used for the data collection. 1531 frames were collected at 2 s/frame, yielding

13,538 reflections, of which 5427 were independent. Hydrogen atom positions were calculated. The neutral molecule crystallized without solvent.

Complex **2** crystallized as orange irregular fragments and a crystal with dimensions of $0.14 \times 0.12 \times 0.12 \text{ mm}^3$ was used for the data collection. 2003 frames were collected at 10 s/frame, yielding 17,512 reflections, of which 4712 were independent. Hydrogen atom positions were observed and held invariant. The asymmetric unit consists of one neutral molecule.

Complex **3** crystallized as orange blocks and a large crystal with dimensions of $0.28 \times 0.26 \times 0.20 \text{ mm}^3$ was used for the data collection. 4128 frames were collected at 5 s/frame, yielding 41,094 reflections, of which 9966 were independent. Hydrogen atom positions were observed or calculated. The asymmetric unit consists of two independent neutral molecules.

Complex **4** crystallized as colorless beads and a sample with dimensions of $0.16 \times 0.14 \times 0.12 \text{ mm}^3$ was used for data collection. 2270 frames were collected at 10 s/frame, yielding 17,897 reflections, of which 7066 were independent. Hydrogen atom positions were observed or calculated. Within the five-membered heterocyclic ring, the nitrogen atom was located on the basis of observed hydrogen atoms. The asymmetric unit consists of two independent neutral molecules.

Diffraction data for compound **5** were collected on a Bruker P4/CCD diffractometer equipped with Mo radiation and a graphite monochromator at 295 K. A sphere of data was measured at 10 s/frame and 0.2° between frames. The frame data were indexed and integrated with the manufacturer's SMART software [21]. The complex crystallized as colorless plates and a crystal with dimensions of approximately $0.2 \times 0.2 \times 0.1 \text{ mm}^3$ was used for data collection. 1850 frames were collected, yielding 30,610 reflections, of which 10,239 were independent. The hydrogen atoms were placed in calculated positions. The asymmetric unit contains two independent neutral molecules. The model exhibits large thermal ellipsoids for the methyl groups, which is typical for $\text{C}_5(\text{CH}_3)_5$ groups and *tert*-butyl groups when the data are collected at room temperature. A summary of all crystal structure parameters is contained in Table 1.

4. Supporting information available

X-ray crystallographic files reported in this paper in CIF format for the structure determinations of **1–5** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 274689 (**1**), 274690 (**2**), 274691 (**3**), 274692 (**4**), and 274693 (**5**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax +44-1223-336033; email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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