Synthesis and Characterization of (C₅Me₅)₂OsBr₄ and the Osmium Polyhydride (C₅Me₅)₂OsH₅: A New Synthetic Entry into Mono(pentamethylcyclopentadienyl)osmium Chemistry

Christopher L. Gross, Scott R. Wilson, and Gregory S. Girolami*

School of Chemical Sciences
503 South Mathews Avenue
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

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Molecules that contain (C₅Me₅)M units exhibit a particularly rich and interesting chemistry, but corresponding (C₅Me₅)Os complexes are extremely rare. In part, this situation reflects the lack of a convenient osmium starting material: for all of the transition elements except osmium and the radioactive element technetium, synthetic routes have been developed to prepare derivatives of the type (C₅R₅)MXₙ, where X is a halide ligand (usually chloride). We now describe our discovery of a convenient method to synthesize such “half-sandwich” complexes of osmium; this development affords for the first time a general route to the preparation of a wide variety of (C₅Me₅)OsLₙ complexes (Scheme 1). We also describe the preparation, characterization, and reactivity of the novel osmium(VI) hydride (C₅Me₅)₂OsH₅.

Our attempts to prepare an osmium analogue of the widely-used ruthenium starting material (C₅Me₅)₂Ru₂Cl₄ from chloroiridium starting materials have been completely unsuccessful. We have, however, that refluxing a mixture of CsMesH in ethanol or tert-butyl alcohol for 45 min affords a brown-black precipitate, which has been identified as the osmium(III) dimer (C₅Me₅)₂OsBr₄, in 75% yield. The complex is weakly paramagnetic as judged from its ¹H and ¹³C NMR resonances, which are shifted and broadened. The field ionization mass spectrum of (C₅Me₅)₂OsBr₄ contains an envelope of peaks centered at m/e 890 due to the [(C₅Me₅)₂OsBr₄]²⁺ ion.

An X-ray crystallographic study of (C₅Me₅)₂OsBr₄ shows that two of the bromide ligands bridge between the two osmium centers (Figure 1); selected distances and angles are as follows: Os-Os = 2.970(1) Å, Os-Br = 2.559(1) Å, Br-Br = 2.482(1) Å, Os-Br-Br = 73.5(1)°, Br-Os-Br = 106.4(1)°, and Br₃-Os-Br = 89.7(4)°. The structure is similar to that of (C₅Me₅)₂Ru₂Cl₄ and to the deformational isomer of (C₅Mes)₂Ru₂Cl₂ (but not in (C₅Me₅Et)₂Ru₂Cl₂). The Os-Br distances to the bridging bromide ligands are shorter than those to the terminal bromide ligands. This unusual structural feature is also seen in (C₅Me₅)₂Ru₂Cl₄ and the short-bond isomer of (C₅Me₅)₂Ru₂Cl₄ (but not in (C₅Me₅Et)₂Ru₂Cl₄) and may reflect the fact that the HOMO is nonbonding with respect to the bridging bromide atoms but antibonding with respect to the terminal bromides.

The dinuclear complex has proven to be an excellent starting material for the preparation of new organometallic complexes of osmium. Treatment of (C₅Me₅)₂OsBr₄ with LiAlH₄ in diethyl ether followed by methanolysis at -78 °C gives the colorless osmium(VI) hydride (C₅Me₅)₂OsH₅, which can be purified by sublimation at 50 °C in vacuum in 19% overall yield. The pentahydride occupies a position intermediate between the known rhenium¹⁰ and iridium¹¹ polyhydrides (C₅Mes)₂ReH₅ and (C₅Mes)₂IrH₅.

Scheme 1. Interconversions of the New Osmium Compounds

Figure 1. ORTEP view of the molecular structure of (C₅Me₅)₂OsBr₄, the 35% probability density surfaces are shown.


(2) (a) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. Organometallics 1984, 5, 274-278. (b) Oshima, N.; Suzuki, H.; Moro-oka, Y. Chem. Lett. 1984, 1152-1154. (c) (C₅Me₅)₂OsBr₄ (prepared from OsO₄ and 48% HBr) must be thoroughly dried at 50 °C, or else the usual salt (C₅Mes)₂[OsBr₄] may be obtained. See: Gross, C. L.; Wilson, S. R.; Girolami, G. S. Inorg. Chem., submitted. (d) (C₅Me₅)₂OsBr₄: ¹H NMR (CDCl₃, 25 °C) δ 2.56 (s, C₅Mes); ¹³C{¹H} NMR (CDCl₃, 25 °C) δ 13.00 (C₅Mes), 101.22 (C₅Mes); MS (FI) m/e 890 (M⁺ - Br).
(C5Me5)IrH2. The ruthenium analogue of this pentahydride is not known, although recently two ruthenium triis(pyrrozolyl)borate complexes have been described that are formulated as nonclassical molecular dihydrogen derivatives, (L)RuH(H2)2.

The pentahydride (C5Me5)OsH5 exhibits a 1H NMR singlet at δ -11.16 which remains sharp even at -90 °C. The spin-lattice relaxation time (T1) of this resonance at -90 °C is 1.6 s, which rules out the possibility that this molecule is a nonclassical hydride.14 The low-temperature 1H NMR spectrum of (C5Me5)OsH5 suggests that this molecule either adopts a unique five-legged piano stool geometry or is highly fluxional and adopts a pseudo-octahedral structure with one axial and four equatorial hydride ligands. The latter possibility seems less likely in view of the fact that the inequivalent axial and equatorial hydride sites in the rhenium complex (C5Me5)ReH5 were readily distinguishable by NMR spectroscopy.10 The IR spectrum of (C5Me5)OsH5 as a Nujol mull shows two bands at 2214 (w) and 2083 (s) cm⁻¹; these bands also appear in the Raman spectrum, and the latter is polarized. The pentahydride is a reasonably robust molecule: it neither decomposes nor undergoes H/D exchange after being heated at 100 °C for 24 h in C6D6. The pentahydride molecule: it neither decomposes nor undergoes H/D exchange.

The reaction of (C5Me5)2OsBr2 with LiAIH4 and methanol yields a second product which can be isolated by crystallization from diethyl ether in 25% yield: the dinuclear tetrahydride (C5Me5)2Os2H4. This species is analogous to the known15 ruthenium complex (C5Me5)2Ru2H4 and can also be prepared in high yield by photolysis of (C5Me5)OsH5 in C6H6 with a mercury arc lamp. The dark red ditosmium tetrahydride complex is characterized by an Os–H stretch at 1762 cm⁻¹ and by a singlet in the 1H NMR spectrum at δ -15.80.16 The hydride ligands are equivalent in the 1H NMR spectrum even at -90 °C, which suggests that all four bridge the metal–metal bond as seen in (C5Me5)2Ru2H4.

Other high-valent organoosmium complexes can be prepared from (C5Me5)2OsBr4. Addition of Br2 to (C5Me5)2OsBr4 in CH2Cl2 gives the osmium(V) halide complex (C5Me5)OsBr5;17 the corresponding bromination of the ruthenium analogue gives a ruthenium(V) product (C5Me5)RuBr5.18 The reaction of (C5Me5)2OsBr4 with 3-bromo-2-methylpropene and ethanol in CH2Cl2 yields the metallyl complex (C5Me5)OsBr3(q3-CH2CMCMe2),17 which closely resembles the analogous ruthenium compound.19 Treatment of (C5Me5)2OsBr4 with PPh3 in ethanol gives (C5Me5)Os(PPh3)2Br2 which in turn reacts with NaBH4 in ethanol to afford the osmium(IV) trihydride (C5Me5)Os(PPH3)3H2. Unlike its ruthenium analogues,20 which are classical trihydrides but are fluxional and show large exchange couplings between the hydride nuclei, (C5Me5)Os(PPH3)3H2 is nonfluxional and has a 2JHH coupling constant that is too small to be resolved. The hydride ligands " cis" and "trans" to the phosphine ligand in the square base of the four-legged piano stool appear as doublets at δ -14.28 (2JHH = 33.5 Hz) and δ -13.77 (2JHH = 8 Hz), respectively, at 25 °C. Interestingly, the 2JHH couplings to the "cis"-hydrides are also larger in the ruthenium (C5Me5)Ru(L)H2 complexes.

The ditosmium complex (C5Me5)2Os2Br4 is clearly a versatile starting material for the synthesis of molecules containing the (C5Me5)Os fragment, and increased interest in the organometallic chemistry of osmium can be expected as a result.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, and selected bond distances and angles (6 pages); listing of observed and calculated structure factors for (C5Me5)2Os2Br4 (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.