Synthesis and Characterization of $(C_5Me_5)_2Os_2Br_4$ and the Osmium Polyhydride $(C_5Me_5)OsH_5$: A New Synthetic Entry into Mono(pentamethylcyclopentadienyl)osmium Chemistry

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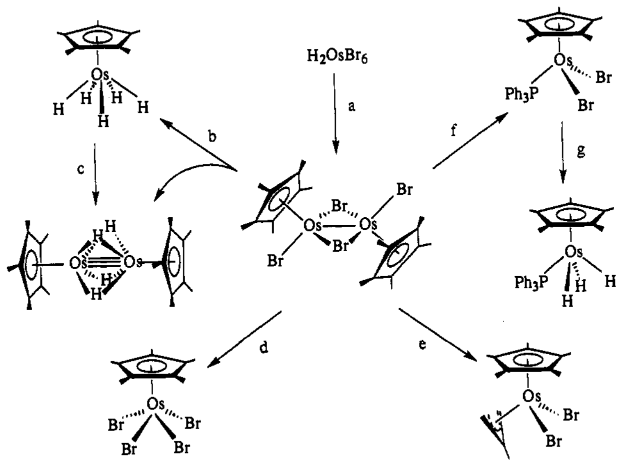
Received July 5, 1994

Molecules that contain $(C_5Me_5)M$ units exhibit a particularly rich and interesting chemistry, but corresponding $(C_5Me_5)Os$ complexes are extremely rare.[1] 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 $(C_5R_5)MX_n$, where X is a halide ligand (usually chloride).[2] 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 synthesis of a wide variety of $(C_5Me_5)OsL_n$ complexes (Scheme 1). We also describe the preparation, characterization, and reactivity of the novel osmium(VI) hydride $(C_5Me_5)OsH_5$.

Our attempts to prepare an osmium analogue of the widely-used ruthenium starting material $(C_5Me_5)_2Ru_2Cl_4$[3] from chloroosmium starting materials have been completely unsuccessful. We have found, however, that refluxing a mixture of hexabromoosmic acid, H_2OsBr_6,[4] and 1.5 equiv of C_5Me_5H in ethanol or *tert*-butyl alcohol for 45 min affords a brown-black precipitate, which has been identified as the osmium(III) dimer $(C_5Me_5)_2Os_2Br_4$, in 75% yield. The complex is weakly paramagnetic as judged from its ^1H and ^{13}C NMR resonances, which are shifted and broadened.[5] The field ionization mass spectrum of $(C_5Me_5)_2Os_2Br_4$ contains an envelope of peaks centered at *m/e* 890 due to the $[(C_5Me_5)_2Os_2Br_3]^+$ ion.

An X-ray crystallographic study[6] of $(C_5Me_5)_2Os_2Br_4$ 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, $Os–Br_t$ = 2.559(1) Å, $Os–Br_b$ = 2.482(1) Å, $Os–Br_b–Os$ = 73.51(4)°, $Br_b–Os–Br_b$ = 106.49(4)°, and $Br_b–Os–Br_t$ = 89.78(4)°. The structure is similar to that of $(C_5Me_5)_2Ru_2Br_4$ and to the deformational isomer of $(C_5Me_5)_2Ru_2Cl_4$ with the shorter Ru–Ru distance.[7] Interestingly, 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 $(C_5Me_5)_2Ru_2Br_4$ and the short-bond isomer of $(C_5Me_5)_2Ru_2Cl_4$ (but not in $(C_5Me_4Et)_2Ru_2Cl_4$!)[7] 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.[8]

Scheme 1. Interconversions of the New Osmium Compounds[a]



[a] (a) C_5Me_5H in EtOH or *t*-BuOH, reflux; (b) $LiAlH_4$ in Et_2O followed by addition of MeOH at −78 °C; (c) photolysis in C_6H_6; (d) Br_2 in CH_2Cl_2; (e) $BrCH_2CMe{=}CH_2$ and EtOH in CH_2Cl_2; (f) PPh_3 in EtOH, reflux; (g) $NaBH_4$ in EtOH.

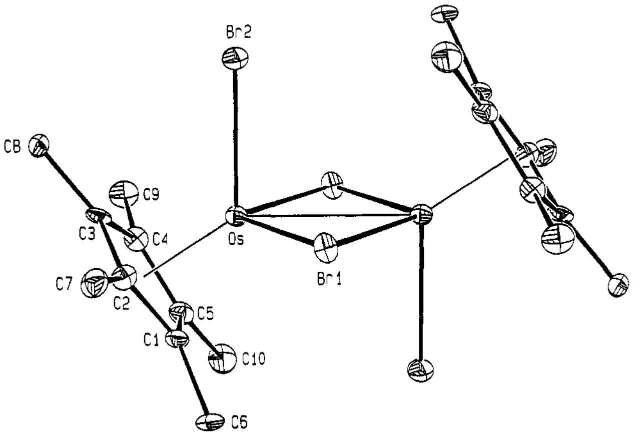


Figure 1. ORTEP view of the molecular structure of $(C_5Me_5)_2Os_2Br_4$; the 35% probability density surfaces are shown.

The dinuclear complex has proven to be an excellent starting material for the preparation of new organometallic complexes of osmium. Treatment of $(C_5Me_5)_2Os_2Br_4$ with $LiAlH_4$ in diethyl ether followed by methanolysis at −78 °C gives the colorless osmium(VI) hydride $(C_5Me_5)OsH_5$, which can be purified by sublimation at 50 °C in vacuum in 19% overall yield.[9] The pentahydride occupies a position intermediate between the known rhenium[10] and iridium[11] polyhydrides $(C_5Me_5)ReH_6$ and

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[1] Few osmium complexes of *any* kind with one cyclopentadienyl (or substituted cyclopentadienyl) ligand have been described. See: (a) Albers, M. O.; Robinson, D. J.; Singleton, E. *Coord. Chem. Rev.* **1987**, *79*, 1–96. (b) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Schaver, A.; Singleton, E.; Wiege, M. B.; Boeyens, J. C. A.; Levendis, D. C. *Organometallics* **1986**, *5*, 2321–2327. (c) Herrmann, W.; Herdtweck, E.; Schäfer, A. *Chem. Ber.* **1988**, *121*, 1907–1911. (d) Marshman, R. W.; Shusta, J. M.; Wilson, S. R.; Shapley, P. A. *Organometallics* **1991**, *10*, 1671–1676. (e) Weber, L.; Reizig, K.; Bungardt, D.; Boese, R. *Organometallics* **1987**, *6*, 110–114. (f) Weber, L.; Bungardt, D. *J. Organomet. Chem.* **1986**, *311*, 269–280. (g) Weber, L.; Reizig, K.; Bungardt, D.; Boese, R. *Chem. Ber.* **1987**, *120*, 1421–1426. (h) Sanderson, L. J.; Baird, M. C. *J. Organomet. Chem.* **1986**, *307*, C1–C4. (i) Johnston, L. J.; Baird, M. C. *J. Organomet. Chem.* **1988**, *358*, 405–409. (j) Johnston, L. J.; Baird, M. C. *Organometallics* **1988**, *7*, 2469–2475. (k) Pourreau, D. B.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1986**, *5*, 1337–1345. (l) Freedman, D. A.; Matachek, J. R.; Mann, K. R. *Inorg. Chem.* **1993**, *32*, 1078–1080.

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[4] The H_2OsBr_6 (prepared from OsO_4 and 48% HBr) must be thoroughly dried at 50 °C, or else the unusual salt $[Cp^*{}_2OsH]_2[Os_2Br_8]$ may be obtained. See: Gross, C. L.; Wilson, S. R.; Girolami, G. S. *Inorg. Chem.*, submitted.

[5] Spectroscopic data for $(C_5Me_5)_2Os_2Br_4$: ^1H NMR (CD_2Cl_2, 25 °C) δ 2.56 (s, C_5Me_5); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ 13.00 (C_5*Me*$_5$), 101.22 (*C*$_5$Me$_5$); MS (FI) *m/e* 890 ($M^+ - Br$).

[6] Crystal data for $(C_5Me_5)_2Os_2Br_4$: monoclinic, space group $P2_1/c$, a = 9.597(2) Å, b = 13.821(4) Å, c = 9.773(3) Å, β = 117.26(2)°, V = 1152.3(5) Å^3, $Z = 2$, R_F ($I > 2\sigma(I)$) = 0.0336, and R_{wF^2} (all data) = 0.0942 for 124 parameters and 1962 observed and 2376 total data. All non-hydrogen atoms were refined with independent anisotropic thermal parameters; hydrogen atom positions were refined with idealized C–H distances and C–C–H and H–C–H angles, and their isotropic thermal parameters were set equal to $1.2U_{eq}$ for the attached carbon atom.

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$(C_5Me_5)IrH_4$. The ruthenium analogue of this pentahydride is not known, although recently two ruthenium tris(pyrazolyl)borate complexes have been described that are formulated as nonclassical molecular dihydrogen derivatives, $(L)RuH(H_2)_2$.[12,13]

The pentahydride $(C_5Me_5)OsH_5$ exhibits a ^{1}H NMR singlet at δ −11.16 which remains sharp even at −90 °C. The spin-lattice relaxation time (T_1) 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 ^{1}H NMR spectrum of $(C_5Me_5)OsH_5$ suggests that this molecule either adopts a unique five-legged piano stool geometry or is highly fluxional and adopts a pseudooctahedral 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 $(C_5Me_5)ReH_6$ were readily distinguishable by NMR spectroscopy.[10] The IR spectrum of $(C_5Me_5)OsH_5$ 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 C_6D_6. The pentahydride also does not react with D_2 (1 atm) under similar conditions.

The reaction of $(C_5Me_5)_2Os_2Br_4$ with $LiAlH_4$ and methanol yields a second product which can be isolated by crystallization from diethyl ether in 25% yield: the dinuclear tetrahydride $(C_5Me_5)_2Os_2H_4$. This species is analogous to the known[15] ruthenium complex $(C_5Me_5)_2Ru_2H_4$ and can also be prepared in high yield by photolysis of $(C_5Me_5)OsH_5$ in C_6H_6 with a mercury arc lamp. The dark red diosmium tetrahydride complex is characterized by an Os–H stretch at 1762 cm^{-1} and by a singlet in the ^{1}H NMR spectrum at δ −15.80.[16] The hydride ligands are equivalent in the ^{1}H NMR spectrum even at −90 °C, which suggests that all four bridge the metal–metal bond as seen in $(C_5Me_5)_2Ru_2H_4$.

Other high-valent organoosmium complexes can be prepared from $(C_5Me_5)_2Os_2Br_4$. Addition of Br_2 to $(C_5Me_5)_2Os_2Br_4$ in CH_2Cl_2 gives the osmium(V) halide complex $(C_5Me_5)OsBr_4$;[17] the corresponding bromination of the ruthenium analogue gives a ruthenium(IV) product $(C_5Me_5)RuBr_3$.[18] The reaction of $(C_5Me_5)_2Os_2Br_4$ with 3-bromo-2-methylpropene and ethanol in CH_2Cl_2 yields the methallyl complex $(C_5Me_5)OsBr_2(\eta^3\text{-}CH_2CMeCH_2)$,[17] which closely resembles the analogous ruthenium compound.[19] Treatment of $(C_5Me_5)_2Os_2Br_4$ with PPh_3 in ethanol gives $(C_5Me_5)Os(PPh_3)Br_2$,[17] which in turn reacts with $NaBH_4$ in ethanol to afford the osmium(IV) trihydride $(C_5Me_5)Os(PPh_3)H_3$.[17] Unlike its ruthenium analogues,[20] which are classical trihydrides but are fluxional and show large exchange couplings between the hydride nuclei, $(C_5Me_5)Os(PPh_3)H_3$ is nonfluxional and has a $^2J_{HH}$ 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 ($^2J_{PH}$ = 33.5 Hz) and δ −13.77 ($^2J_{PH}$ = 8 Hz), respectively, at 25 °C. Interestingly, the $^2J_{PH}$ couplings to the "cis"-hydrides are also the larger in the ruthenium $(C_5Me_5)Ru(L)H_3$ complexes.[20c]

The diosmium complex $(C_5Me_5)_2Os_2Br_4$ is clearly a versatile starting material for the synthesis of molecules containing the $(C_5Me_5)Os$ fragment, and increased interest in the organometallic chemistry of osmium can be expected as a result.

Acknowledgment. We thank the Exxon Educational Foundation for support, Prof. Paul Bohn and Eva Thurman for assistance with the Raman experiments, and Theresa Prussak-Wieckowska for assistance with the X-ray crystallographic study. C.L.G. is the recipient of a Department of Education Fellowship from the Chemistry Department at the University of Illinois.

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 $(C_5Me_5)_2Os_2Br_4$ (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.

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(9) Spectroscopic data for $(C_5Me_5)OsH_5$: ^{1}H NMR (toluene-d_8, 25 °C) δ 2.04 (s, C_5Me_5), −11.16 (s, OsH) (the relative intensities of the ^{1}H NMR resonances clearly show that five hydride ligands are present); MS (FI) *m/e* 332 (M^+); IR (Nujol) 2214 (w), 2083 (s) cm^{-1}; Raman (pentane) 2214 (w), 2096 (s) cm^{-1}. For the Os–H stretches of $(C_5Me_5)OsH_5$, the C_{5v} structure should exhibit two IR and three Raman bands, while the pseudo-C_{4v} structure should exhibit three IR and four Raman bands. The presence of two bands in both the IR and Raman spectra is more consistent with the C_{5v} alternative, although the assignment of structures based on counting the number of M–H stretching bands is often unreliable. An X-ray crystal structure refined well but did not afford positions for the hydrogen atoms.

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(16) Spectroscopic data for $(C_5Me_5)_2Os_2H_4$: ^{1}H NMR (toluene-d_8, 25 °C) δ 2.01 (s, C_5Me_5), -15.80 (s, OsH); MS (FD) *m/e* 656 (M^+); IR (Nujol) 1762 cm^{-1}.

(17) Yields and spectroscopic data: (a) for $(C_5Me_5)OsBr_4$, yield, 70%; MS (FD) *m/e* 647 (M^+); (b) $(C_5Me_5)OsBr_2(\eta^3\text{-}CH_2CMeCH_2)$, yield, 56%; ^{1}H NMR (CD_2Cl_2, 25 °C) δ 3.60 (s, CH_2), 2.86 (s, CH_2), 2.84 (s, CMe), 1.68 (s, C_5Me_5); (c) $(C_5Me_5)OsBr_2(PPh_3)$, yield, 67%; MS (FD) *m/e* 747 (M^+); ^{1}H NMR (CD_2Cl_2, 25 °C) δ 28.0 (br s, C_5Me_5, 15H), 21.5 (br s, *o*-CH, 2H), 12.2 (br s, *m*-CH, 2H), 11.0 (br s, *p*-CH, 1H), 3.7 (br s, *m′*-CH, 4H), 3.2 (br s, *p′*-CH, 2H), −11.2 (br s, *o′*-CH, 4H) (evidently, rotation about the Os–P bond is slow on the NMR time scale so that two different phenyl environments (in a ratio of 2:1) are seen); (d) $(C_5Me_5)OsH_3(PPh_3)$, yield, 73%; ^{1}H NMR (CD_2Cl_2, 25 °C) δ 7.36 (m, PPh_3, 15H), 1.91 (s, C_5Me_5, 15H), −13.77 (d, $^2J_{PH}$ = 8 Hz, OsH, 1H), −14.28 (d, $^2J_{PH}$ = 33.5 Hz, OsH, 2H); IR (Nujol) 2101 (m, sh), 2068 (s), 2049 (s) cm^{-1}.

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