Synthesis and Chemistry of the 16-Electron Osmium Complex [OsBr(η^5-C_5Me_5)(P*i*Pr_3)]

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The isolable 16-electron half-sandwich Os complex [OsBr(η^5-C_5Me_5)(P*i*Pr_3)] has been synthesized and structurally characterized. This unsaturated complex binds N_2 reversibly at low temperature as determined by IR and multinuclear NMR spectroscopy. The reactions of the title complex with CO, H_2, $PhSiH_3$, and its thermolysis in C_6H_6 are reported.

The stable 16-electron complexes [RuClCp*(PR_3)] (Cp* = η^5-C_5Me_5; R = *i*Pr, Cy) were reported in 1988.[1] These complexes, prepared by addition of the appropriate phosphane in one step from the tetrameric ruthenium species [RuClCp*]$_4$,[2] have proven to be valuable starting materials for the synthesis of various silyl,[3] silene,[4] and metallacyclic[5] complexes. Analogous 16-electron complexes of osmium are also expected to be useful synthons, but they have yet to be reported. The synthesis of coordinatively unsaturated [OsXCp*(PR_3)] species would seem to require a method other than that used to prepare the related ruthenium complexes, as the osmium analog of [RuClCp*]$_4$ is not known. However, Esteruelas and co-workers have recently reported[6] the preparation of an 18-electron complex, [OsClCp(P*i*Pr_3)$_2$], which dissociates a phosphane ligand in solution to form an unsaturated species that activates E−H bonds (E = C, Si, Ge, Sn).[7,8]

Addition of two equiv. of triisopropylphosphane to a stirred CH_2Cl_2 solution of [$Os_2Br_4Cp^*_2$][9] effected a rapid color change from dark brown to black-cherry red. Removal of all volatile components of the mixture, washing with ether, and drying under vacuum afforded a pale pink-red solid which was soluble in toluene and dichloromethane. Three broad, featureless resonances spread over a range of greater than 30 ppm in the ^{1}H NMR spectrum (CD_2Cl_2, room temperature) were consistent with a paramagnetic 17-electron complex formulated as [$OsBr_2$Cp*(P*i*Pr_3)] (**1**); however, a CH_2Cl_2 solution of **1** gave no detectable EPR signal at room temperature, and only below 100 K was an extremely broad signal (with no detectable hyperfine coupling) observed. A Signer molecular weight determination[10,11] (room temperature, CH_2Cl_2 solution) confirmed the monomeric nature of the complex in solution.

Treatment of a THF solution of **1** with a stoichiometric amount of 0.3% Na/Hg amalgam resulted in a striking color change from red-black to purple. Removal of all volatile materials and recrystallization from pentane at −78 °C provided dendritic, translucent, red-orange crystals. Upon isolation and warming to room temperature, these crystals became purple and opaque. Repeated attempts to obtain X-ray diffraction data on these purple crystals failed. However, multinuclear NMR spectroscopy and combustion analysis allowed characterization of this compound as the 16-electron species [OsBrCp*(P*i*Pr_3)] (**2**).

To characterize the origin of the temperature-dependent color change associated with **2**, a [D$_8$]toluene solution of **2** was cooled to −78 °C under an atmosphere of nitrogen. This resulted in a color change from purple to red-orange. Variable temperature NMR spectroscopy experiments with **2** in [D$_8$]toluene under N_2 revealed disappearance of the ^{31}P{^{1}H} resonance for **2** as the temperature was lowered, and the appearance of two resonances at $\delta = 8.71$ and 8.10. After this sample was thoroughly degassed with a series of freeze-pump-thaw cycles, cooling to −78 °C did not afford a color change. The NMR spectroscopic properties of this degassed sample were essentially invariant from room temperature to −80 °C. On the basis of these observations, it was postulated that **2** reversibly binds N_2 at low temperature to give the terminal and bridging dinitrogen complexes **3** and **4**, respectively. The appearance of a relatively strong band at 2074 cm^{-1} in the low-temperature solution IR spectrum acquired under an N_2 atmosphere confirmed the presence of the end-on bound N_2 species **3**.[12] This diagnostic band did not appear when the solution was cooled under an argon atmosphere. When a sample of **2** in [D$_8$]toluene was cooled and sealed under an atmosphere of $^{15}N_2$, three resonances were observed in the ^{15}N NMR spectrum at low temperature, consistent with both terminal binding ($\delta = -47.9$ and -112.4) and a bridged structure ($\delta = -133$).[13,14] The ^{31}P{^{1}H} resonances associated with these structures also exhibited coupling to ^{15}N.

Concentration and cooling of a diethyl ether solution of **2** under argon afforded large purple-black crystals suitable for an X-ray diffraction study. The solid-state structure of **2** is shown in Figure 1. The Cp*(centroid)−P−Os−Br unit is planar within experimental error and there is no evidence for agostic C−H interactions or close intermolecular contacts. It is noteworthy that samples of **2** obtained by recrystallization under N_2 had a completely different morphology to those crystallized under argon.

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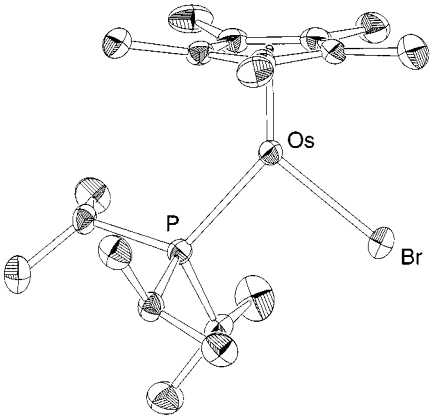


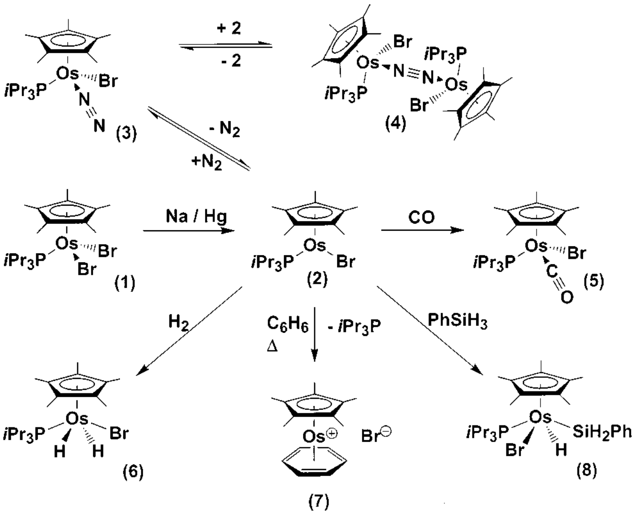
Figure 1. ORTEP diagram of **2** with 50% probability ellipsoids; hydrogens have been removed for clarity; selected bond lengths and angles (Cp* = C_5Me_5 centroid): Os−Br 2.4785(6) Å, Os−P 2.349(2) Å, Os−Cp* 1.7898(2) Å, Br−Os−P 93.52(4)°, P−Os−Cp* 137.13(4)°, Br−Os−Cp* 129.34(2)°

Exposure of a stirred pentane solution of **2** to an atmosphere of CO resulted in a rapid color change from purple to yellow. The resulting compound, [OsBrCp*(CO)(P*i*Pr$_3$)] (**5**), exhibited a CO stretching frequency of 1896 cm^{-1} (Nujol mull). This value compares to 1908 cm^{-1} for the closely related ruthenium complex [RuClCp*(CO)(P*i*Pr$_3$)][1] and is consistent with the more basic nature of the osmium center. Coordination of CO to the osmium center destroys the effective C_s symmetry of **2**, as indicated by NMR spectroscopy. Thus, the methyl groups of the triisopropylphosphane ligand in **5** are inequivalent in the ^{1}H NMR spectrum, appearing as two virtual quadruplets integrating to nine protons each.

Compound **2** reacted under an atmosphere of hydrogen in pentane solution, as indicated by a rapid color change of the solution from purple to yellow. The ^{1}H NMR spectrum of a C_6D_6 solution of the resulting pale yellow product contained a new doublet at $\delta = -10.7$ consistent with oxidative addition of dihydrogen to the Os center to give a product formulated as [OsH$_2$BrCp*(P*i*Pr$_3$)] (**6**). $T_{1(\min)}$ measurements made by the null method revealed a value of 475 ms at −81 °C for the two hydrides of **6**, demonstrating that they are "classical" in nature. The ^{1}H NMR spectrum of **6** exhibited only one set of peaks for the isopropyl methyl groups, consistent with a *trans* disposition for the hydride ligands in a "four-legged piano stool" complex. A *cis* geometry for the hydride ligands would render the isopropyl methyl groups diastereotopic and can therefore be ruled out. It is interesting to note that [RuClCp*(PR$_3$)] complexes do not react with H$_2$ under comparable conditions.[1]

In an experiment intended to probe the thermal stability of **2**, an NMR tube fitted with a PTFE valve was charged with a benzene solution of **2** and heated in an oil bath at 80 °C. Colorless crystals were deposited on the bottom of the tube after a few days. Although insoluble in aliphatic hydrocarbons and benzene, the crystals were soluble in CD_2Cl_2 and were determined to be the arene complex [OsCp*(η^6-C$_6$H$_6$)]Br (**7**) by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The formation of this species presumably involves thermal dissociation of the phosphane ligand from the osmium center followed by coordination of the arene solvent to the metal center with displacement of the halide substituent. Characterization of **7** as an arene complex is supported by a comparison with the related species [RuCp*(η^6-toluene)]Cl which has been synthesized and fully characterized in these laboratories by crystallographic and spectroscopic techniques.[15]

The reaction of **2** with 1 equiv. of PhSiH$_3$ in pentane caused an immediate color change from purple to yellow. The resulting compound, [Os(H)(Br)Cp*(SiH$_2$Ph)(P*i*Pr$_3$)] (**8**), was isolated as a yellow microcrystalline solid from pentane. The ^{1}H NMR spectrum includes two resonances at δ = 6.60 and 4.71 for the diastereotopic silicon-bound protons. The stereochemistry of **8** depicted in Scheme 1 was assigned based on comparison to similar ruthenium complexes[1,4] and the structurally characterized analogue [Os(H)(Br)Cp*(SiHPh$_2$)(P*i*Pr$_3$)].[11]



Scheme 1

We are currently probing the utility of **2** as a synthon in osmium chemistry, especially its use in generating unsaturated metal−ligand interactions. We believe that the isolable nature of **2** makes it an ideal starting material for a series of studies involving the electron rich OsCp*(R$_3$P)$^+$ fragment.

Experimental Section

All solvents were distilled under N$_2$ from appropriate drying agents and stored in PTFE-valved flasks. Synthetic manipulations were performed under an atmosphere of purified N$_2$ or argon using standard Schlenk techniques. P*i*Pr$_3$ was obtained from Strem Chemicals, Inc. and was used as received. CO was obtained from Mattheson Gas and used without further purification. [Os$_2$Br$_4$Cp*$_2$] was prepared by the published method.[8] PhSiH$_3$ was made by the reduction of PhSiCl$_3$ with LiAlH$_4$ in ether and purified by fractional distillation under N$_2$. ^{1}H (500.1 MHz), ^{13}C{^{1}H} (124.7 MHz), ^{31}P{^{1}H} (202.4 MHz), ^{29}Si{^{1}H} (99.3 MHz), and ^{15}N{^{1}H} (50.7 MHz) NMR spectra were acquired on a Bruker DRX-500 spectrometer equipped with a BBI probe. Spectra were recorded at room temperature in C_6D_6 unless otherwise noted and were referenced to protic impurities in the deuterated solvent for ^{1}H, solvent peaks for ^{13}C, $SiMe_4$ for ^{29}Si, neat $MeNO_2$ for ^{15}N, and 85% H_3PO_4 for ^{31}P. Elemental analyses were performed by the University of California, Berkeley College of Chemistry Microanalytical Facility. IR absorptions are reported in units of cm^{-1} and were recorded with a Mattson Infinity 60 MI FTIR spectrometer as Nujol mulls for room temperature measurements and with an ASI React-IR apparatus for low-temperature measurements.

[OsBr$_2$Cp*(P*i*Pr$_3$)] (1): A stirred CH_2Cl_2 solution of $[Os_2Br_4Cp^*_2]$ (1.23 g, 1.27 mmol) was treated with 2.1 equiv. of neat P*i*Pr$_3$ at room temperature. The solution was stirred for 60 minutes, by which time it turned from brown to deep black-red. All volatile components of the mixture were removed in vacuo, and the resulting black-red solid was washed with Et_2O at 0 °C (2 × 20 mL) and dried in vacuo to give a red-pink powder. 1.36 g (83%) isolated, m.p. 205−210 °C. ^{1}H NMR (CD_2Cl_2): $\delta = -2.26$ [fwhh 205 Hz, 18 H, $PCH(CH_3)_2$], 6.6 [fwhh 420 Hz, 3 H, $PCH(CH_3)_2$], 23.9 [fwhh 350 Hz, 15 H, C_5Me_5). − $\mu_{eff} = 1.37$ B.M (Evans' method,[16] CH_2Cl_2, room temperature.) Solution molecular weight (CH_2Cl_2, Signer method) 580 (645 ideal). − $C_{19}H_{36}Br_2OsP$ (645.48): calcd. C 35.35, H 5.62; found, C, 35.19, H 5.76.

[OsBrCp*(P*i*Pr$_3$)] (2): A solution of **1** (4.1 g, 6.36 mmol) in THF was added to a flask containing a stirred Na/Hg amalgam (0.3% Na, 1 equiv.) and THF at room temperature. The solution became violet after a few minutes of vigorous stirring, and a white precipitate formed. The reaction mixture was allowed to settle after approximately 60 minutes. The supernatant was filtered away from the amalgam and precipitated solids, then was pumped dry to give a black-purple solid. Extracting the solid with pentane (5 × 20 mL) gave a purple solution, which afforded red-orange crystals of the dinitrogen adduct after concentrated cooling to −78 °C under N_2. 2.3 g (64%) isolated, m.p. 132−136 °C. X-ray quality crystals were grown from a concentrated diethyl ether solution of **2** under argon at −78 °C. ^{1}H NMR: $\delta = 1.15-1.09$ [vq, 18 H, $PCH(CH_3)_2$], 1.45 (s, 15 H, C_5Me_5), 2.54 [m, 3 H $PCH(CH_3)_2$]. − $^{13}C\{^{1}H\}$ NMR: $\delta = 13.4$ (C_5Me_5), 20.5 [$PCH(CH_3)_2$], 25.7 [d, $^{1}J_{PC} = 24.3$ Hz, $PCH(CH_3)_2$], 72.8 (C_5Me_5). − $^{31}P\{^{1}H\}$ NMR: $\delta = 42.63$. − $^{15}N\{^{1}H\}$ NMR (220 K): $\delta = -47.0$. − $C_{19}H_{36}BrOsP$ (565.57): calcd. C 40.35, H 6.42; found C 40.45, H 6.10.

[OsBrCp*(^{15}N$_2$)(P*i*Pr$_3$)] (3-^{15}N$_2$) and [OsBrCp*(P*i*Pr$_3$)]$_2$(μ-η^1:η^1-^{15}N$_2$) (4-^{15}N$_2$): A [D$_8$]toluene solution of **2** in a 5 mm O.D. PTFE-valved NMR tube was degassed by several freeze-pump-thaw cycles, exposed to 2 atm. of $^{15}N_2$ (Aldrich, 98%), and slowly cooled to −78 °C. The tube was then sealed and carefully brought to room temperature. $^{15}N\{^{1}H\}$ NMR spectra were recorded as the sample was cooled in the spectrometer. At 220 K, resonances assignable to **3**-$^{15}N_2$ [$\delta = -72.4$ (dd, $^{2}J_{NP} = 2.5$ Hz, $^{1}J_{NN} = 4.5$ Hz, Os−*N*N), −47.9 (d, $^{1}J_{NN} = 5$ Hz, Os−N*N*)] and **4**-$^{15}N_2$ [$\delta = -133.6$ (d, $^{2}J_{NP} = 2.0$ Hz)] were observed. − $^{31}P\{^{1}H\}$ NMR: (220 K): **4**-$^{15}N_2$ $\delta = 8.10$ (d, $^{2}J_{NP} = 2.0$ Hz); **3**-$^{15}N_2$ $\delta = 8.71$ (d, $^{2}J_{NP} = 2.5$ Hz).

[OsBrCp*(CO)(P*i*Pr$_3$)] (5): A flask containing a stirred pentane solution of 125 mg of **2** (0.220 mmol) was briefly evacuated, and then filled with an atmosphere of CO. The solution changed color from purple to yellow-orange within 20 seconds at room temperature. The solution was filtered, concentrated, and cooled to −78 °C, affording a crop of well-formed orange crystals of **5**. 97 mg (75%) isolated, m.p. 209−212 °C. ^{1}H NMR: $\delta = 0.96-1.00$ [vq, 9 H, $PCH(CH_3)_2$], 1.29−1.24 [vq, 9 H, $PCH(CH_3)_2$], 1.63 (s, 15 H, C_5Me_5), 2.30 [m, 3 H, $PCH(CH_3)_2$]. − $^{13}C\{^{1}H\}$ NMR: $\delta = 10.4$ (C_5Me_5), 19.6 [d, $^{2}J_{PC} = 23$ Hz, $PCH(CH_3)_2$], 20.8 [$PCH(CH_3)_2$], 27.2 [d, $^{1}J_{PC} = 27$ Hz, $PCH(CH_3)_2$], 92.2 (d, $J_{PC} = 2$ Hz, C_5Me_5), 190.1 (d, $^{1}J_{PC} = 12$ Hz, Os−*CO*). − $^{31}P\{^{1}H\}$ NMR: $\delta = 16.3$. − IR: $\nu_{CO} = 1896$ s. − $C_{20}H_{36}BrOOsP$ (593.58): calcd. C 40.47, H 6.11; found C 40.51, H 6.01.

[OsH$_2$BrCp*(P*i*Pr$_3$)] (6): A flask containing a stirred pentane solution of 100 mg (0.176 mmol) of **2** was briefly evacuated, and then filled with an atmosphere of H_2. The solution changed color from purple to very pale yellow within 50 seconds at room temperature. The solution was filtered, concentrated and cooled to −78 °C, affording solid **6** as feathery, pale yellow crystals. 62 mg (62%) isolated, m.p. 152 °C (color change) 172 °C melting complete. ^{1}H NMR: $\delta = -10.7$ [d, 2 H, $^{2}J_{PH} = 34.8$ Hz, Os−H; $T_{1(\text{ambient T})} = 1.73$ s, $T_{1(\min)} = 475$ ms, CD_2Cl_2, −81 °C), 1.12−1.03 [vq, 18 H, $PCH(CH_3)_2$], 1.80 (s, 15 H, C_5Me_5), 2.07 [m, 3 H, $PCH(CH_3)_2$]. − $^{13}C\{^{1}H\}$ NMR: $\delta = 11.3$ (C_5Me_5), 19.2 [$PCH(CH_3)_2$], 28.2 [d, $^{1}J_{PC} = 31$ Hz, $PCH(CH_3)_2$], 90.2 (C_5Me_5). − $^{31}P\{^{1}H\}$ NMR: $\delta = 42.63$. − IR: $\nu_{SiH} = 2105$ ws, 2042 s. − $C_{19}H_{38}BrOsP$ (567.59): calcd. C 40.35, H 6.42; found C 40.45, H 6.10.

[OsCp*(η^6-C$_6$H$_6$)]Br (7): A 5 mm O.D. PTFE-valved NMR tube was charged with a C_6H_6 solution of **2**, degassed, sealed, and immersed in an oil bath maintained at approximately 80 °C. After 1 week, several crystals were deposited at the bottom of the tube. The crystals were removed from the tube inside the drybox, washed with a little pentane at ambient temperature and dried. ^{1}H NMR: $\delta = 2.19$ (15 H, C_5Me_5), 5.90 (6 H, C_6H_6). − $^{13}C\{^{1}H\}$ NMR: $\delta = 11.7$ (C_5Me_5), 78.1 (C_5Me_5), 94.4 (C_6H_6). Compound **7** was not prepared on a large enough scale to facilitate further characterization.

[Os(H)(Br)Cp*(SiH$_2$Ph)(P*i*Pr$_3$)] (8): A stirred pentane solution of **2** (202 mg, 0.356 mmol) was treated with 1.1 equiv. of $PhSiH_3$ dissolved in pentane. The solution immediately changed color from purple to yellow. The solution was filtered, concentrated, and cooled to −78 °C, affording a crop of polycrystalline **8**. 195 mg (81%) isolated, m.p. 163−165 °C. ^{1}H NMR: $\delta = 8.16$ (d, 2 H, *o*-Ph), 7.33 (t, 2 H, *m*-Ph), 7.21 (t, 1 H, *p*-Ph), 6.60 (d, $^{1}J_{SiH} = 189$ Hz, $^{2}J_{HH} = 4$ Hz, 1 H, SiH), 4.71 (vq, $^{1}J_{SiH} = 182$ Hz, 1 H, SiH), 2.49 [m, 3 H, $PCH(CH_3)_2$], 1.52 (s, 15 H, C_5Me_5), 1.04−1.08 [vq, 9 H, $PCH(CH_3)_2$], 0.97−1.00 [vq, 9 H, $PCH(CH_3)_2$], −14.8 (d, 1 H, $^{2}J_{PH} = 32$ Hz, Os−*H*). − $^{13}C\{^{1}H\}$ NMR: $\delta = 143.39$, 136.42, 127.53, 93.9 (d, $^{2}J_{PC} = 2.1$ Hz, C_5Me_5), 28.04 [d, $^{1}J_{PC} = 26.7$ Hz, $PCH(CH_3)_2$], 20.50 [$PCH(CH_3)_2$], 19.79 [d, $^{2}J_{PC} = 3$ Hz, $PCH(CH_3)_2$], 10.35 (C_5Me_5). − $^{31}P\{^{1}H\}$ NMR: $\delta = 8.98$. − $^{29}Si\{^{1}H\}$ NMR: $\delta = -26.0$ (d, $^{2}J_{PSi} = 17$ Hz). − IR: $\nu_{SiH} = 2061$ s, 2081 s. − $C_{19}H_{38}BrOsP$ (567.59): calcd. C 44.56, H 6.58; found C 44.66, H 6.66.

X-ray Crystallographic Study: Data were collected on a Siemens SMART system using Mo-K_α graphite monochromated radiation. Structure solution and refinement was performed with the TeXsan software package.[17] $C_{19}H_{36}BrOsP$ mol. weight 565.57, purple block, cryst. size 0.35 × 0.12 × 0.20 mm, $a = 16.1302(2)$, $b = 15.5831(2)$, $c = 16.7732(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 4216.09(9)$ Å^3, orthorhombic, *Pbca*, $Z = 8$, $d_{calcd.} = 1.782$ Mg m^{-3}, $F_{000} = 2208.00$, index ranges: $0 < h < 19$, $-17 < k < 17$, $-20 < l < 20$; 2Θ range 3.5−45.0°, $T = -115$ °C; refl. collected: 19152; refl. unique: 4124; $R_{int} = 0.055$, no. variables: 199, GOOF = 0.62, $R = 0.019$, $R_w = 0.020$, $R_{all} = 0.052$. Largest residual peak/hole = 0.080/−0.39 e/Å^3.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158416. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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