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Preliminary communication

Synthesis, structure and reactivity studies of triosmium complexes, $\text{Os}_3(\text{CO})_{10}(\mu\text{-Br})(\text{CH}=\text{CHPh})$ and $\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-Br})(\text{C}=\text{CHPh})$

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Abstract

Reaction of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with $\text{PhC}\equiv\text{CBr}$ produced a vinyltriosmium complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-Br})(\text{CH}=\text{CHPh})$ (**1**) in high yield. Thermolysis of complex **1** in refluxing toluene produced a hydrido-vinylidene complex $\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-Br})(\text{C}=\text{CHPh})$ (**2**); the crystal structure and reactivity of complexes **1** and **2** have been studied. Crystal data for complex **1**: space group $P2_1/c$, a 14.049(6), b 10.035(4), c 15.933(6) Å, β 93.06(4)°, $Z = 4$; R_F 6.32%, R_w 6.33%, GOF = 1.49. Crystal data for complex **2**: space group $P1/n$, a 14.047(4), b 10.439(3), c 15.636(4) Å, β 114.28(3)°, $Z = 4$; R_F 3.80%, R_w 4.38%, GOF = 0.73.

Halogen elements are routinely used in chemical technology to improve the activity, selectivity, and stability of metal catalysts [1]; however, their influence on the bonding and the reactivity of adsorbed hydrocarbons is poorly understood [2]. Recently, there seems to have been a growing research activity on this subject. Geoffroy and Morrison [3] have reported a halide-promoted insertion of carbon monoxide into the bridging methylene group in anionic triosmium clusters; Lin and coworkers [4] have reported a halogen induced cluster fragmentation of a carboxamide-substituted triosmium complex. Their investigations have underlined the progress on the studies of the influence of the halogen elements. Similarly, to examine the effect of halogen on the coordinated hydrocarbon fragments, we have synthesized a triosmium complex containing both a bromo fragment and a vinyl substituent, $\text{Os}_3(\text{CO})_{10}(\mu\text{-Br})(\text{CH}=\text{CHPh})$ (**1**). Here we report our studies on the reactivity and the structure of both complex **1** and its vinylidene derivative $\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-Br})(\text{C}=\text{CHPh})$ (**2**).

Treatment of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with 1.1 equivalent of freshly distilled $\text{PhC}\equiv\text{CBr}$ in toluene solution at 60°C for 10 min gives the vinyl complex **1** in about 75% yield. Complex **1** was separated by column chromatography and characterized by spectro-

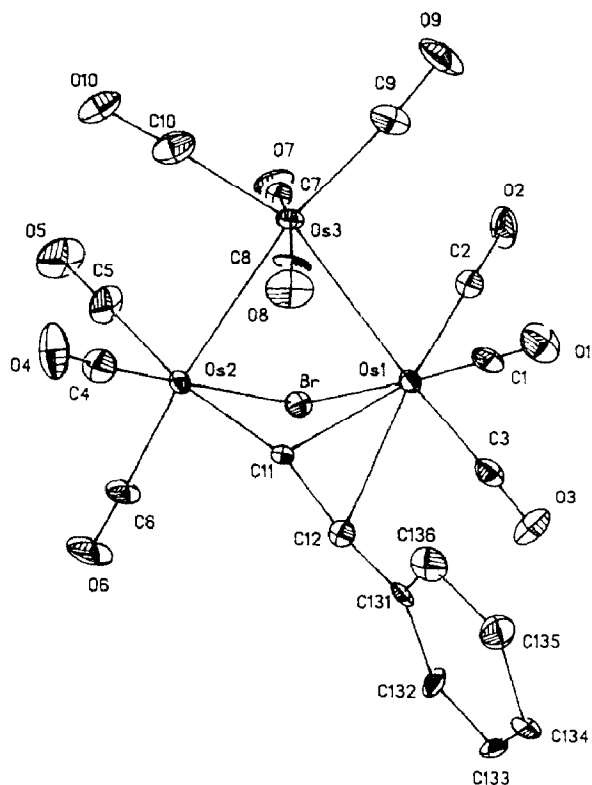


Fig. 1. Molecular structure of complex **1**. Important dimensions include: bond lengths (Å) Os(1)···Os(2) 3.277(2), Os(1)–Os(3) 2.925(2), Os(2)–Os(3) 2.865(2), Os(1)–Br 2.599(3), Os(2)–Br 2.624(3), Os(1)–C(11) 2.36(2), Os(2)–C(11) 2.12(2), Os(1)–C(12) 2.47(3), C(11)–C(12) 1.42(3); bond angle (°) Os(1)–C(11)–Os(2) 93.8(9), Os(1)–Br–Os(2) 77.7(1).

scopic methods [5*] and single-crystal X-ray diffraction [6*]. The ORTEP diagram together with important structural parameters of **1** are shown in Fig. 1. The molecule consists of an open triangle in which the non-bonded osmium atoms Os(1) and Os(2) are bridged by the bromo ligand (as a three-electron donor), while the third osmium atom is uniquely bonded to four terminal CO ligands. The vinyl group is σ -bonded to the atom Os(2) and π -bonded to the atom Os(1); the phenyl substituent is located *trans* to the Os(2)–C(11) bond, and the α -hydrogen is oriented *syn* to the unique Os(CO)₄ unit [7]. Therefore, the gross molecular geometry and ligand conformations of complex **1** are complementary to those of the analogous hydridovinyl complexes Os₃(CO)₁₀(μ -H)(CH=CHBu^t) [8] and Os₃(CO)₁₀(μ -H)(CH=CHEt) [9], and the sulfido-vinyl complex Os₃(CO)₁₀(μ -SPh)(CH=CH₂) [10].

Complex **1** also underwent facile intramolecular rearrangement in solution. Its ¹³C NMR spectrum (100.4 MHz, CD₂Cl₂, 294 K) displays six Os–CO signals at δ 181.2, 180.7, 177.8, 176.4, 174.9 and 167.5 with relative ratio 2/1/1/2/2/2, suggesting the presence of an extremely rapid $\pi \rightarrow \sigma$, $\sigma \rightarrow \pi$ exchange of the bridging vinyl ligand. The low temperature limiting spectrum was recorded while

* Reference number with asterisk indicates a note in the list of references.

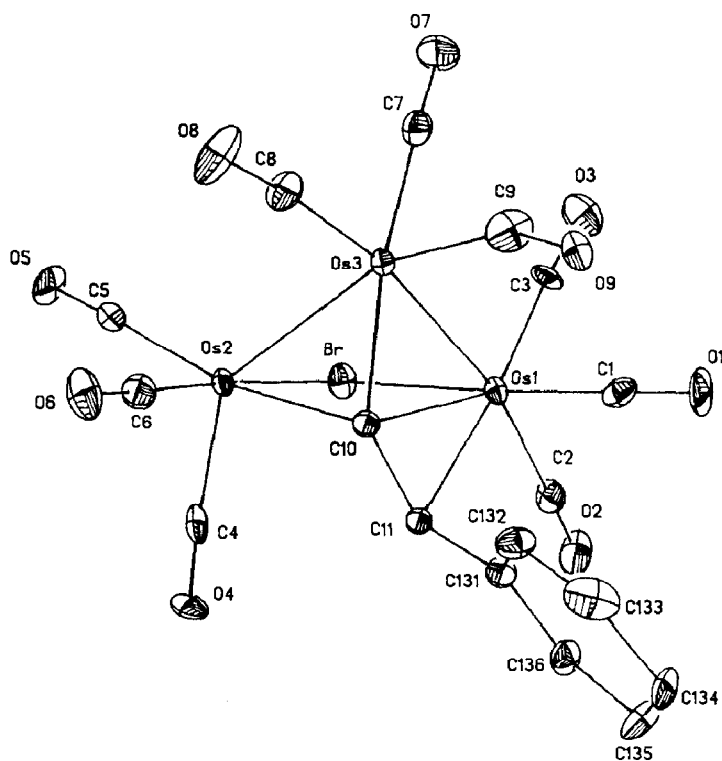
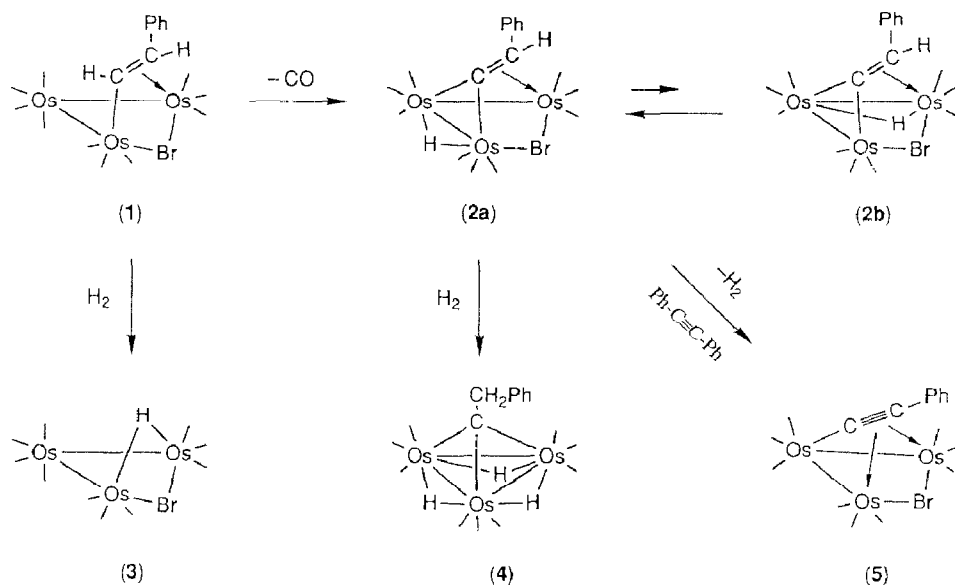


Fig. 2. Molecular structure of complex **2**. Important dimensions include: bond lengths (Å) Os(1)···Os(2) 3.547(1), Os(1)–Os(3) 2.851(1), Os(2)–Os(3) 2.883(1), Os(1)–Br 2.630(2), Os(2)–Br 2.593(2), Os(1)–C(10) 2.27(1), Os(2)–C(10) 2.16(1), Os(3)–C(10) 2.05(2), Os(1)–C(11) 2.34(2), C(10)–C(11) 1.37(2); bond angle (°) Os(3)–Os(2)–C(5) 123.4(6), Os(2)–Os(3)–C(7) 115.1(5), Os(3)–Os(1)–C(1) 90.7(4), Os(3)–Os(1)–C(3) 93.0(5), Os(1)–C(10)–Os(2) 106.6(5), Os(1)–C(10)–Os(3) 86.5(6), Os(1)–Br–Os(2) 85.6(1).

the temperature was being decreased to 168 K. At this temperature, ten relatively broad Os–CO signals were observed at δ 181.5, 180.3, 180.0, 177.9, 177.6, 177.3, 177.5, 170.7, 168.3 and 165.6. With use of the coalescence temperature of the signals at δ 168.3 and 165.6, the activation free energy (ΔG^\ddagger) for the dynamic process was calculated to be 8.3 kcal/mol. For comparison, its hydrido analogue exhibits an activation energy in the range 10.3–11.3 kcal/mol [11].

In boiling toluene complex **1** loses a CO ligand and cleavage of the α C–H bond is induced, to give a vinylidene complex Os₃(CO)₉(μ -H)(μ -Br)(C=CHPh) (**2**) [5*] in 65% yield. The structure of **2** has also been determined by X-ray diffraction [6*]. As indicated in Fig. 2, the molecule consists of three osmium atoms rearranged in open triangular geometry; the open edge is bridged by a bromine atom. The α -carbon of the vinylidene fragment is bonded to all three osmium atoms where the β -carbon is within the bonding distance of the atom Os(1). Therefore, the bonding mode of the vinylidene ligand can be considered to be σ -bonded to the atoms Os(2) and Os(3) and π -bonded to the third Os atom via an asymmetric η^2 interaction [12*]. Finally, the bridging hydride was not located on the Fourier map but is assumed to be associated with the Os(2)–Os(3) edge, because the Os(2)–Os(3) bond (2.883 Å) is longer than the Os(1)–Os(3) bond (2.851 Å) and the respective equatorial carbonyl ligands, C(5)–O(5) and C(7)–O(7) are both tilted away from the Os–Os bond (angle Os(3)–Os(2)–C(5) 123.4(6)°, angle Os(2)–Os(3)–C(7) 115.1(5)°).



Scheme 1

In solution, the ^1H NMR spectrum of **2** exhibits one set of olefinic and hydride proton signals at δ 9.11 and -11.25 and another set at δ 5.09 and -11.85 with a relative intensity 5/1, suggesting the presence of two rapidly interconvertible isomers (**2a**/**2b** 5/1). We propose that the isomerization is attributable to hydride migration (Scheme 1) but the 1,2-hydrogen migration from the vinylidene β -carbon to the α -carbon [13]. Consistent with our postulate, the ^{13}C NMR spectrum of **2** showed two signals at δ 184.8 (**2a**) and 203.4 (**2b**) assigned to the α -carbon of the vinylidene fragments and further confirmed by a ^{13}C labeling experiment. Furthermore, in the related hydrido vinylidene complex $\text{Os}_3(\text{CO})_9(\mu\text{-H})_2(\text{C}=\text{CH}_2)$, Lewis and Johnson have also demonstrated by isotopic substitution that the dynamic process is due to the hydride migration [14].

The vinyl complex **1** and vinylidene complex **2** behave quite differently when they are thermolyzed under hydrogen. Hydrogenation of **1** in refluxing toluene led to elimination of the coordinated vinyl group and produced $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-Br})$ (**3**) (30 min, 45%) as sole osmium cluster characterized. In contrast, reaction of **2** with hydrogen in refluxing benzene removed the bridging bromo fragment, to give an alkylidyne complex $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CCH}_2\text{Ph})$ (**4**) (4 h, 40%) [5*]. Analogous reactions have been reported for their hydrido analogues: Kaesz and coworkers and Deeming and coworkers have reported that hydrogenation of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{CH}=\text{CH}_2)$ and $\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}=\text{CH}_2)$ yields $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CCH}_3)$, respectively [15].

In addition, complexes **1** and **2** react with an excess of diphenylacetylene to give an acetylide complex $\text{Os}_3(\text{CO})_9(\mu\text{-Br})(\text{C}\equiv\text{CPh})$ (**5**) [5*,16] as the only isolable triosmium cluster, except that the required reaction conditions for complex **1** (110°C , 1 h, 30%) are more rigorous than that for **2** (70°C , 3 h, 41%). As the required reaction conditions for the dehydrogenation of the vinyl complex **1** are comparable to those of its decarbonylation reaction mentioned previously, we conclude that the active intermediate is the vinylidene complex **2**. Therefore, the

sequence of dehydrogenation of the vinyl fragment can be understood as an activation of the α -hydrogen to produce the hydride plus the vinylidene, followed by removal of the hydride and the β -hydrogen to produce the final acetylide fragment. In accord with our conclusion, Lewis and Johnson have reported that the reaction of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with excess terminal alkyne first produces a hydridovinyl complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{CH}=\text{CHR})$, and then an acetylide complex $\text{Os}_3(\text{CO})_9(\mu\text{-H})(\text{C}\equiv\text{CR})$ [17] as the reaction proceeds. However, the pivotal role of the vinylidene complexes was not clearly established in their system. The experiments we have described here suggest that a mechanism involving the formation of not only the vinyl but also the vinylidene complexes seems to be the most plausible reason for their presence.

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- Complex 1: MS (EI, ^{192}Os , ^{81}Br), m/z 1040 (M^+); IR(C_6H_{12}) $\nu(\text{CO})$ 2105(m), 2068(vs), 2057(s), 2020(vs), 2012(s), 2000(s), 1993(w), 1987(m), 1980(m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 294 K) δ 7.44–7.24 (m, 5H), 6.93 (d, 1H, $J(\text{H}-\text{H})$ 16.2 Hz), 6.39 (d, 1H, $J(\text{H}-\text{H})$ 16.2 Hz); Elemental analysis: Found: C, 2098; H, 0.77. $\text{Os}_3\text{Br}_1\text{C}_{18}\text{H}_7\text{O}_{10}$ calcd.: C, 20.91; H, 0.68%. Complex 2: MS (EI, ^{192}Os , ^{81}Br), m/z 1012 (M^+); IR(C_6H_{12}) $\nu(\text{CO})$ 2114(w), 2094(vs), 2067(vs), 2040(s), 2027(vs), 2023(sh), 2017(s), 1193(m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 194 K) δ 9.11 (s, 0.83H), 7.75–7.08 (m, 5H), 5.09 (s, 0.17H), –11.25 (s, 0.83H), –11.85 (s, 0.17H); Elemental analysis: Found: C, 2042; H, 0.81. $\text{Os}_3\text{Br}_1\text{C}_{17}\text{H}_7\text{O}_9$ calcd.: C, 20.26; H, 0.70%. Complex 4: MS (EI, ^{192}Os), m/z 934 (M^+); IR(C_6H_{12}) $\nu(\text{CO})$ 2077(vs), 2069(vw), 2016(vs), 2007(w), 2004(m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 294 K) δ 7.34–7.23 (m, 5H), 5.23 (s, 2H), –18.86 (s, 3H); Complex 5: MS (EI, ^{192}Os , ^{81}Br), m/z 1010 (M^+); IR(C_6H_{12}) $\nu(\text{CO})$ 2101(w), 2081(vs), 2074(sh), 2053(vs), 2046(sh), 2021(vs), 2010(vs), 1987(m) 1983(s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 294 K) δ 7.86 (d, 2H, $J(\text{H}-\text{H})$ 7.7 Hz), 7.50 (t, 2H, $J(\text{H}-\text{H})$ 7.7 Hz), 7.32 (t, 1H, $J(\text{H}-\text{H})$ 7.7 Hz); Elemental analysis: Found: C, 2032; H, 0.64. $\text{Os}_3\text{Br}_1\text{C}_{17}\text{H}_5\text{O}_9$ calcd.: C, 20.32; H, 0.50%.
- (a) Crystal data for complex 1: $\text{C}_{18}\text{H}_7\text{O}_{10}\text{Os}_3\text{Br}$, $M = 1033.7$, monoclinic, space group $P2_1/c$, a 14.049(6), b 10.035(4), c 15.933(6) Å, β 93.06(4)°, U 2243.5(16) Å³, $Z = 4$, D_c 3.061 g/cm³, $F(000) = 1832$, Mo- K_α radiation with λ 0.71073 Å, ψ scan absorption correction was made and 3981 unique reflections were measured of which 2638 were considered observed with $I > 3\sigma(I)$. The structure was solved by a direct method and refined by full matrix least-square refinement. Final R 6.32%, R_w 6.33%, GOF = 1.49. (b) Crystal data for complex 2: $\text{C}_{17}\text{H}_7\text{O}_9\text{Os}_3\text{Br}$, $M = 1004.7$, monoclinic, space group $P2_1/n$, a 14.047(4), b 10.439(3), c 15.636(4) Å, β 114.28(3)°, U 2153.2(9) Å³, $Z = 4$, D_c 3.099 g/cm³, $F(000) = 1772$, Mo- K_α radiation with λ 0.71073 Å, ψ scan absorption correction was made and 3439 unique reflections were measured of which 2709 were considered observed with $I > 3\sigma(I)$. Final R 3.80%, R_w 4.38%, GOF = 0.73.
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