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Communications to the Editor

Bromonium Ion Addition to Triruthenium and Triosmium Dodecacarbonyl: The Markedly Different Structures of the $[M_3(CO)_{12}(Br)]^+$ (M = Ru, Os) Ions

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Recently, Brown and co-workers reported the use of the bromonium ion of adamantylideneadamantane, as the triflate salt ([AdAdBr](OTf)), to transfer Br^+ to acceptor olefins.[1] On the other hand, work from this laboratory has shown that reaction of iodine with $Os_3(CO)_{12}$ proceeds via the $[Os_3(CO)_{12}(I)]^+$ cation, and it was suggested that bromination of $Os_3(CO)_{12}$ proceeded through a similar intermediate.[2] Here we report the use of the bromonium ion reagent to prepare the $[M_3(CO)_{12}(Br)]^+$ (M = Ru, Os) ions and the determination of their crystal structures. These ions are the first halonium ions of metal carbonyl cluster compounds to be structurally characterized. The two cations have markedly different structures: the ruthenium derivative can be considered as an organometallic analogue of the bromonium ion of ethylene, $[C_2H_4Br]^+$, whereas the osmium cation can be thought of as the corresponding ion of cyclopropane, $[C_3H_6Br]^+$. Furthermore, evidence is presented that the form of $[Os_3(CO)_{12}(Br)]^+$ characterized here is not an intermediate in the bromination of $Os_3(CO)_{12}$.

Addition of $[AdAdBr]\{B[C_6H_3(CF_3)_2]_4\}$[3] to $M_3(CO)_{12}$ (M = Ru, Os) in CH_2Cl_2 at or below room temperature readily afforded $[M_3(CO)_{12}(Br)]\{B[C_6H_3(CF_3)_2]_4\}$, which on addition of hexane formed air-stable, red-orange (M = Ru) or pale yellow (M = Os) crystals.[5] The structure of the ruthenium cation (**1**) as found in the X-ray structure determination of $[Ru_3(CO)_{12}(Br)]\{B[C_6H_3(CF_3)_2\text{-}3,5]_4\}$[6] is shown in Figure 1. It consists of a bent chain of three ruthenium atoms (Ru(1)Ru(2)Ru(3) = 157.19(4)°), one Ru−Ru bond of which is bridged by the bromonium ion. The Ru atom not bound to the bromine atom has five carbonyls coordinated to it. The $Ru(CO)_5$ moiety is therefore an 18-electron species, and the metal−metal bond involving the Ru atom of this fragment is an unusual donor−acceptor (dative) metal−metal bond.[7] Cation **1** may therefore be considered as derived from $[Ru_2(\mu\text{-}Br)(CO)_8]^+$ in which one of the carbonyl ligands has been replaced by $Ru(CO)_5$. Since $Ru(CO)_4$ is isolobal with CH_2,[8] the $[Ru_2(\mu\text{-}Br)(CO)_8]^+$ ion is an organometallic analogue of the classical bromonium ion of ethylene, $[C_2H_4Br]^+$. The Ru(μ-Br)Ru unit in **1** may be considered as consisting of either a closed three-center, two-electron RuBrRu bond, or two two-center, two-electron RuBr bonds, in each case augmented by a Ru−Ru bond. The Ru−Ru bond length of the Ru(μ-Br)Ru unit is short at 2.8067(14) Å. In $Ru_3(CO)_{12}$, the average Ru−Ru bond length is 2.8515 Å;[9] in $Ru_3(CO)_{12}(Br)_2$, described below, it is 2.8823(4) Å.[9,10] The unbridged, dative Ru−Ru bond in **1** is 2.8907(14) Å.

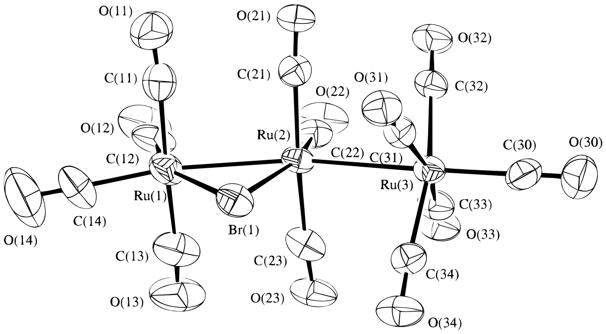

Figure 1. Molecular structure of $[Ru_3(CO)_{12}(Br)]^+$ (**1**).

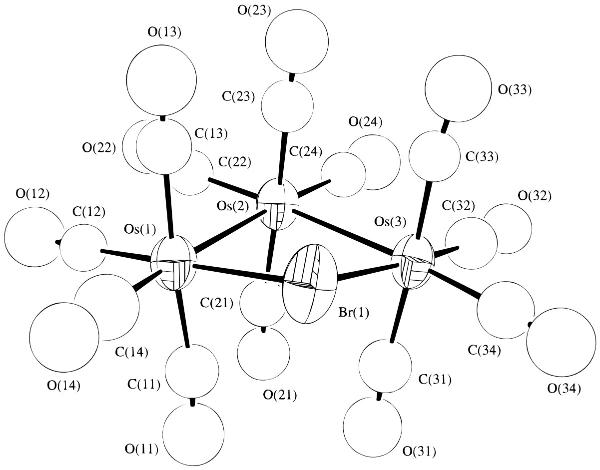

Figure 2. Molecular structure of $[Os_3(CO)_{12}(Br)]^+$ (**2**).

The structure (Figure 2) of $[Os_3(CO)_{12}\ (Br)]^+$ (**2**) as found in the $B[C_6H_3(CF_3)_2\text{-}3,5]_4$[6] salt is very different from that of **1**. The Os_3Br unit in **2** is a nearly planar, four-membered ring with only two Os−Os bonds, which are 2.952(3) and 2.964(3) Å. In $Os_3(CO)_{12}$, the average Os−Os bond distance is 2.877 Å;[11] for $Os_3(CO)_{12}(I)_2$, the Os−Os bonds are crystallographically equiva-

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(3) Prepared by metathesis of [AdAdBr][X] (X = Br_3^- or OTf^-)[1] and $Na\{B[C_6H_3(CF_3)_2\text{-}3,5]\}$[4] in CH_2Cl_2.

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(5) **1**·$B[C_6H_3(CF_3)_2]_4$: IR (CH_2Cl_2) ν(CO) 2165 (vw), 2137 (m-s), 2087 (s), 2057 (m) 2012 (m) cm^{-1}; ^{13}C NMR (CD_2Cl_2/CH_2Cl_2 3:1, −60 °C, CO region) δ 200.0 (2C), 196.0 (1C), 190.2 (4C), 189.0 (2C), 187.9 (1C), 178.9 (1C), 175.8 (1C) (major isomer, see text). **2**·$B[C_6H_3(CF_3)_2]_4$ IR (CH_2Cl_2) ν(CO) 2138 (s) 2099 (s) 2081 (vs) 2055 (m-s) 2023 (m) cm^{-1}; ^{13}C NMR (CD_2Cl_2/CH_2Cl_2 3:1, 21 °C, CO region) δ 177.0 (4C), 175.4 (2C), 167.6 (2C), 166.0 (2C), 155.5 (2C) (very weak peaks at δ 180.8 and 168.3 were also observed that may indicate traces of a second isomer.)

(6) Crystal data for **1**·$B[C_6H_3(CF_3)_2]_4$: formula $C_{44}H_{12}BBrF_{24}O_{12}Ru_3$, T = 210 K, triclinic, space group $P\bar{1}$, a = 11.655(2) Å, b = 11.952(3) Å, c = 19.640(6) Å, α = 77.64(2)°, β = 89.51(2)°, γ = 87.15(2)°; V = 2669.1 Å^3; Z = 2; 601 parameters; 4989 reflections with $I_o > 2.5\sigma(I_o)$; R_F = 0.049; R_{wF} = 0.057. Crystal data for **2**·$B[C_6H_3(CF_3)_2]_4$: formula $C_{44}H_{12}BBrF_{24}O_{12}Os_3$, T = 295 K, triclinic, space group $P\bar{1}$, a = 10.880(2) Å, b = 15.677(3) Å, c = 17.226(3) Å, α = 97.40(2)°, β = 100.34(2)°, γ = 103.80(2)°; V = 2761.3 Å^3; Z = 2; 356 parameters; 2870 reflections with $I_o > 2.5\sigma(I_o)$; R_F = 0.057; R_{wF} = 0.063.

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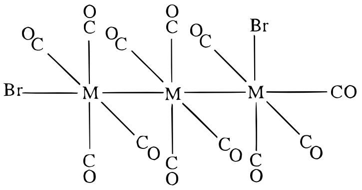
lent, at 2.935(2) Å.[12] The third Os−Os vector in **2** is completely nonbonding, at 4.011(3) Å. Inasmuch as $Os(CO)_4$ is isolobal with CH_2,[8] the structure for **2** is a model for that of $[C_3H_6Br]^+$, the bromonium ion adduct of cyclopropane. The structure of the latter cation is unknown, but the structure most favored does, indeed, have a configuration analogous to that found for **2**.[13]

The ^{13}C NMR spectra of **1** and **2** (^{13}CO-enriched samples) as the $B[C_6H_3(CF_3)_2]_4$ salts in CD_2Cl_2/CH_2Cl_2 at 0 °C indicate that the predominant form of each cation in solution has the same structure as found in the solid state, with rigid carbonyls.[5] A freshly prepared sample of **1** at −50 °C in CD_2Cl_2/CH_2Cl_2 exhibited four minor ^{13}C NMR resonances (at δ 196.3, 192.9, 188.1, and 173.7) attributed to the presence of a second form of **1** in solution. The spectrum was unchanged when a sample of **1** (from a different synthesis) had been allowed to stand in solution at room temperature before obtaining the low-temperature spectrum. In other words, the second species is not a transitory intermediate in the formation of **1**. In the spectrum of **1** at −20 °C, the minor peaks had collapsed to the base line, indicative of carbonyl exchange in the second isomer.

The first observable product (by ^{13}C NMR spectroscopy) in the reaction of $Os_3(CO)_{12}$ with Br_2 in CD_2Cl_2/CH_2Cl_2 at −20 °C is *cis, trans*-$Os_3(CO)_{12}(Br)_2$ (**3**, M = Os), which in solution at room temperature isomerizes over 3 h to the *cis,cis* isomer (**4**, M = Os).[2] We now report that the first detectable product (by ^{13}C NMR spectroscopy) in the reaction of $Ru_3(CO)_{12}$ with Br_2 at −50 °C is the previously unknown *cis,cis*-$Ru_3(CO)_{12}(Br)_2$ (**4Ru**). The identity of **4Ru** has been confirmed by a crystal structure determination.[10]



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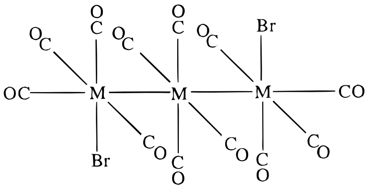

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The product from the treatment of **1** in CH_2Cl_2 at room temperature with Br^- has not been positively identified, but it is not **4Ru**. Furthermore, **2** under the same conditions immediately reacts with Br^- (or Br_3^-) to yield **4Os** (i.e., not **3Os**). These results indicate, surprisingly, that the bromination of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ does not proceed via the respective solvent-equilibrated forms of $[M_3(CO)_{12}(Br)]^+$ characterized here (i.e., **1** and **2**). This is in contrast to the reaction of $Os_3(CO)_{12}$ with iodine, where ^{13}C NMR spectroscopy clearly indicates proceeds via $[Os_3(CO)_{12}(I)]^+$ (analogous to **2**) to yield *cis,cis*-$Os_3(CO)_{12}(I)_2$, analogous to **4Os**. Studies are in progress in an attempt to further elucidate the mechanism of the initial reaction of $M_3(CO)_{12}$ with halogens, which is much more complex than had previously been thought.[2]

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Supporting Information Available: Experimental details of the synthesis of **1**·$B[C_6H_3(CF_3)_2]_4$ and **2**·$B[C_6H_3(CF_3)_2]_4$ and tables of crystallographic data and positional and thermal parameters (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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