$Os_5(CO)_{18}(CNBu^t)_2(Cl)_2$: A Complex with a Linear Chain of Five Osmium Atoms

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Summary: Complexes of formula $(X)Os_3(CO)_{12}Os(CO)_3(L)(X)$ *and* $(X)(L)(OC)_3OsOs_3(CO)_{12}Os(CO)_3(L)(X)$ *(L = CNBu*^{t}*; X = Cl, Br, I) have been prepared by the addition of* $Os(CO)_4(L)$ *to* $Os_3(CO)_{12}(X)_2$ *in solution at 60 °C. The structure of* $Os_5(CO)_{18}(CNBu^t)_2(Cl)_2$ *reveals it has an almost linear chain of five Os atoms.*

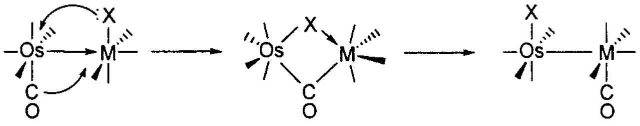
Introduction

Much of the work from this laboratory has described complexes in which an 18-electron organometallic compound acts as a two-electron donor ligand to a 16-electron organometallic fragment in much the same way as a conventional ligand such as PPh_3. Typical examples of molecules of this type are $(OC)_3(R_3P)_2OsW(CO)_5$ and $(R_3P)(OC)_4MRu(CO)_3(SiCl_3)_2$ (M = Ru, Os, but not Fe).[1] These complexes contain an unbridged dative bond between two transition metal atoms.

In some of our earliest studies of complexes of this type it was observed that isomerization often occurred for complexes with unbridged dative metal−metal bonds that also contained a halide or (especially) a hydride ligand coordinated to the acceptor metal atom.[2,3] The isomerization involved migration of the halide or hydride ligand to the donor atom with concomitant migration of a carbonyl ligand to the acceptor atom (Scheme 1; in this and the other scheme presented here the carbonyl ligands not involved in the isomerization have been omitted). If the halogen ligand is considered as a one-electron donor ligand, then the isomerization can be viewed as resulting in the conversion of the dative metal−metal bond to a nondative bond. In an interesting extension of this reaction we have recently reported the successive addition of 3 mol of $Os(CO)_4(L)$ (L = $CNBu^t$) to $Mn(CO)_5(I)$ to give $(I)[Os(CO)_3(L)]_3Mn(CO)_5$. The structure of the complex reveals it to contain a linear chain of four unbridged metal atoms.[4]

Here we describe the synthesis of $(X)Os_3(CO)_{12}Os(CO)_3(L)(X)$ and $(X)(L)(OC)_3OsOs_3(CO)_{12}Os(CO)_3(L)(X)$ (L = $CNBu^t$; X = Cl, Br, I) complexes containing linear chains of four and five unbridged Os atoms using this strategy. Organometallic complexes with linear chains of unbridged metal−metal bonds between heavy transition metals might be expected to show interesting electrical conduction and redox properties. This is because such chains should possess extended molecular orbitals with a small energy gap between the HOMO and LUMO.

Scheme 1



X = Cl, Br, I, H

Experimental Section

General Procedures. Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with the use of standard Schlenk techniques. Hydrocarbon solvents were refluxed over potassium, distilled, and stored over molecular sieves before use. Dichloromethane was dried in a similar manner except that CaH_2 was employed as the drying agent. The precursory compounds $Os(CO)_4(CNBu^t)$ and $Os_3(CO)_{12}(X)_2$ (X = Cl, Br, I) were prepared by literature procedures.[5,6] NMR spectra were recorded on a Bruker AMX400 spectrometer at the appropriate operating frequencies for ^1H and $^{13}C\{^1H\}$ NMR spectra. With the exception of **2Cl**, samples for $^{13}C\{^1H\}$ NMR spectra were enriched to ~30% ^{13}CO prepared from more highly ^{13}CO-enriched $Os_3(CO)_{12}$.[7] All new compounds gave a parent ion by MS (FAB).

Preparation of $Os_4(CO)_{15}(CNBu^t)(Cl)_2$ (1Cl). A round-bottom flask (~100 mL; fitted with a Teflon valve) was furnished with $Os(CO)_4(CNBu^t)$ (34 mg, 0.088 mmol), $Os_3(CO)_{12}(Cl)_2$ (74 mg, 0.075 mmol), and toluene (70 mL). The solution was degassed with three freeze−pump−thaw cycles and then heated at 60 °C for 66 h. The solvent was removed on the vacuum-line and the residue dissolved in a minimum amount of CH_2Cl_2 (~3 mL). The solution was subjected to chromatography on silica gel (12 × 1 cm). Hexane was used as eluent to remove traces of $Os_3(CO)_{12}$; hexane/CH_2Cl_2 (1:1) to remove unreacted $Os_3(CO)_{12}(Cl)_2$; and hexane/CH_2Cl_2 (1:4) to elute $Os_4(CO)_{15}(CNBu^t)(Cl)_2$. The third fraction was collected, concentrated, and cooled to −25 °C to give yellow

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(1) (a) Jiang, F.; Jenkins, H. A.; Biradha, K.; Davis, H. B.; Pomeroy, R. K.; Zaworotko, M. J. *Organometallics* **2000**, *19*, 5049. (b) Jiang, F.; Male, J. L.; Biradha, K.; Leong, W. K.; Pomeroy, R. K.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 5810.

(2) Fleming, M. M.; Pomeroy, R. K.; Rushman, P. *J. Organomet. Chem.* **1984**, *273*, C33.

(3) Einstein, F. W. B.; Jennings, M. C.; Krentz, R.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Inorg. Chem.* **1987**, *26*, 1341.

(4) Jiang, F.; Jenkins, H. A.; Yap, G. P. A.; Pomeroy, R. K. *Inorg. Chem. Commun.* **2000**, *3*, 690.

(5) Shipley, J. A.; Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1991**, *10*, 3620.

(6) (a) Sanati, H. K.; Becalska, A.; Ma, A. K.; Pomeroy, R. K. *J. Chem. Soc., Chem. Commun.* **1990**, 197. (b) Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. (A)* **1968**, 2859.

(7) Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437.

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crystals of $Os_4(CO)_{15}(CNBu^t)(Cl)_2$ (26 mg, 32%). The bromo and the iodo analogues were prepared in a similar way in 32% and 19% yield, respectively. **1Cl**: IR (CH_2Cl_2) ν(CN) 2214 mbr; ν(CO) 2137 m, 2103 s, 2081 m, 2061 vwsh, 2053 vs, 2030 wsh, 2034 m, 2021 vs, 2009 m, 2000 w cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.61; $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 1:4) δ 190.0 (4C), 189.2 (4C), 182.2 (2C), 181.9 (1C), 174.5 (1C), 172.1 (1C), 166.0 (1C), 164.6 (1C); 31.6 (Me). Anal. Calcd for $C_{20}H_9Cl_2O_{15}Os_4N$: C, 17.99; H, 0.68; N, 1.05. Found: C, 17.88: H, 0.56; N, 1.23. **1Br**: IR (CH_2Cl_2) ν(CN) 2213 mbr; ν(CO) 2136 m, 2102 s, 2080 m, 2061 vwsh, 2052 vs, 2031 m, 2019 vs, 2009 s, 2003 w cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.59; $^{13}C\{^1H\}$ NMR ($C_2D_2Cl_4/C_2H_2Cl_4$, 1:4) δ 189.3 (4C), 188.4 (4C), 179.1 (1C), 178.8 (2C), 173.2 (1C), 170.8 (1C), 164.1 (1C) 162.3 (1C). Anal. Calcd for $C_{20}H_9Br_2O_{15}Os_4N$: C, 16.87; H, 0.64; N, 0.98. Found: C, 16.88; H, 0.68; N, 0.91. **1I**: IR (CH_2Cl_2) ν(CN) 2209 mbr; ν(CO) 2132 m, 2099 s, 2078 m, 2059 vwsh, 2048 s, 2040wsh, 2030 m, 2021vs, 2002 vwshw cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.58. Anal. Calcd for $C_{20}H_9I_2O_{15}Os_4N$: C, 15.82; H, 0.60; N, 0.92. Found: C, 16.14; H, 0.70; N, 0.96.

Preparation of $Os_5(CO)_{18}(CNBu^t)_2(I)_2$ (2I). A round-bottom flask (~50 mL; fitted with a Teflon valve) was charged with $Os(CO)_4(CNBu^t)$ (39 mg, 0.10 mmol), $Os_3(CO)_{12}(I)_2$ (58 mg, 0.050 mmol), and toluene (15 mL). The solution was degassed as described above and then heated at 60 °C for 19 h. The solvent was removed on the vacuum-line. The residue was washed with hexane and then dissolved in CH_2Cl_2 (30 mL). The same amount of hexane was added. The resulting solution was concentrated until solids just appeared, and it was then stored in the freezer (−25 °C) to give $Os_5(CO)_{18}(CNBu^t)_2(I)_2$ as a yellow crystalline solid (58 mg, 62%). The chloro and bromo analogues were prepared in a similar way in a yield of 35% and 72%, respectively. **2Cl**: IR (CH_2Cl_2) ν(CN) 2210w; ν(CO) 2120 w, 2092 m, 2078 w, 2066 w, 2030 m, 2009 s cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.62; $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 1:4) δ 191.5 (4C), 190.9 (8C), 182.6 (2C), 175.0 (2C), 166.2 (2C), 62.0 (*t*-C); 31.7 (Me). Anal. Calcd for $C_{28}H_{18}Cl_2O_{18}Os_5N_2$: C, 19.87; H, 1.07; N, 1.66; for $C_{29}H_{20}Cl_4O_{18}Os_5N_2$ (i.e., **2Cl**·CH_2Cl_2): C, 19.60; H, 1.13; N, 1.58. Found: C, 19.86; H, 1.19; N, 1.55. **2Br**: IR (CH_2Cl_2) ν(CN) 2211 w; ν(CO) 2119 w, 2091 m, 2077 w, 2066 w, 2029 m, 2010 s cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.60; $^{13}C\{^1H\}$ NMR ($C_2D_2Cl_4/C_2H_2Cl_4$, 1:4) δ 190.5 (4C), 190.3 (8C), 180.1 (2C), 173.9 (2C), 164.6 (2C), 61.3 (*t*-C); 31.4 (Me). Anal. Calcd for $C_{28}H_{18}Br_2O_{18}Os_5N_2$: C, 18.88; H, 1.02; N, 1.57. Found: C, 18.88; H, 1.05; N, 1.49. **2I**: IR (CH_2Cl_2) ν(CN): 2207w; ν(CO): 2119w, 2089m, 2074w, 2064w, 2027m, 2009s cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.58. Anal. Calcd for $C_{28}H_{18}I_2O_{18}Os_5N_2$: C, 17.93; H, 0.97; N, 1.49. Found: C, 17.82: H, 0.94; N, 1.45.

Structure Determination of 2Cl·CH_2Cl_2. A suitable crystal was selected, mounted on thin, glass fiber using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0°, 90°, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[8] Systematic absences in the diffraction data and unit-cell parameters were consistent with space groups *C*2/*c* and *Cc*. Initial exploration of the noncentrosymmetric space group *Cc* yielded solutions with inversion symmetry. The solution in the centrosymmetric space group option *C*2/*c* gave chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. The molecule is located at an inversion center with a disordered chloride/carbonyl ligand having a 50/50 site occupancy distribution. A molecule of cocrystallized dichloromethane solvent was located at a 2-fold axis. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion factors are contained in the SHELXTL v. 5.10 program library.[9]

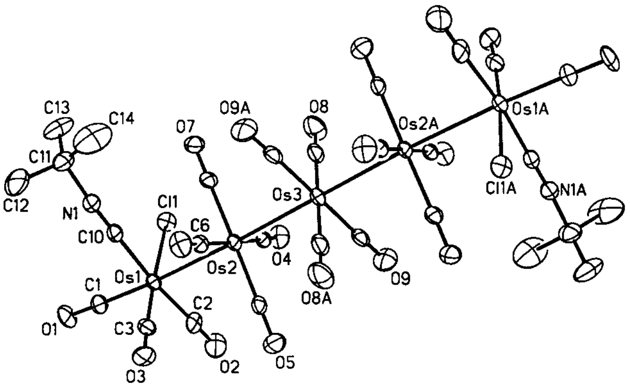
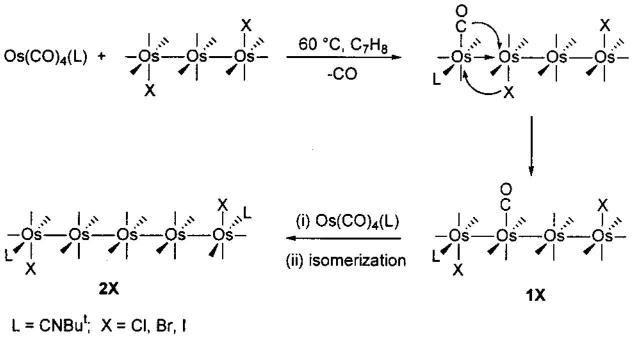


Figure 1. Molecular structure of $Os_5(CO)_{18}(CNBu^t)_2(Cl)_2$ (**2Cl**).

Scheme 2



Results and Discussion

The (X)$Os_3(CO)_{12}Os(CO)_3$(L)(X) (L = $CNBu^t$; X = Cl, Br, I; **1X**) and (X)(L)$(OC)_3OsOs_3(CO)_{12}Os(CO)_3$(L)(X) (**2X**) complexes were prepared by the reaction of $Os(CO)_4(CNBu^t)$ with (X)$Os_3(CO)_{12}$(X) in the correct molar ratio in toluene at 55−60 °C (Scheme 2). The compounds are yellow microcrystalline solids that appeared stable in air. Compound **2Br** showed no sign of decomposition after 16 h in toluene at 90 °C (under nitrogen). The corresponding reaction with (Br)$Ru_3(CO)_{12}$(Br)[10] in place of the Os analogue gave a product that was too unstable to characterize.

The structure of **2Cl**, as **2Cl**·CH_2Cl_2, was determined by X-ray crystallography (Figure 1). There was disorder between the Cl and CO(3) sites. The molecule possesses an inversion center, and therefore the Os(2)−Os(3)−Os(2A) angle is 180°. The independent Os_3 angle (Os(1)-Os(2)Os(3)) is 177.01(2)°. In other words, **2Cl** contains an almost linear chain of five unbridged Os atoms. The radial ligands on each Os atom are staggered with respect to the radial ligands on the adjacent Os atoms. The OsOs lengths are 2.8709(7) (Os(1)Os(2)) and 2.8907(5) Å (Os(2)Os(3)). These lengths may be compared to the average OsOs length in $Os_3(CO)_{12}$ of 2.877 Å.[11]

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[8] Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

[9] Sheldrick, G. M. *SHELXTL* v. 5.10; Bruker AXS: Madison, WI, 1997.

[10] Nagra, H. K.; Batchelor, R. J.; Bennet, A. J.; Einstein, F. W. B.; Lathioor, E. C.; Pomeroy, R. K.; Wang, W. *J. Am. Chem. Soc.* **1996**, *118*, 1207.

It is often found, however, that OsOs lengths in compounds with Os_3 chains are somewhat longer than these lengths.[1] For example, in $Os_3(CO)_{12}(I)_2$, $Os_3(CO)_{10}[P(OMe_3)]_2(Br)_2$, and $Os(CO)_{12}(SiCl_3)_2$ the OsOs bonds are 2.935(2), 2.916(1), and 2.912(1) Å, respectively.[12-14] The OsOs bonds in **2Cl** from a ground-state view therefore appear as strong OsOs single bonds. This was also observed for $(I)[Os(CO)_3(CNBu^t)]_3Mn(CO)_5$ (OsOs bond distances of 2.8894(5) and 2.8928(5) Å).[4] We tentatively ascribed this to stronger OsOs σ bonding brought about by more extensive delocation over more metal−metal bonds.[15] The other bonding parameters of **2Cl** do not show any unusual features.

Compound **2Cl** is an 82-electron compound and has the expected four metal−metal bonds.[16] This is the first complex with a linear chain containing five unbridged group 8 metal atoms. We have recently reported the synthesis and structure of $Os_5(\mu\text{-}Cl)_2(CO)_{16}(L)_2$, an Os_5 cluster with an 82e count, but with the triangular $Os_3(\mu\text{-}Cl)_2$unit.[17] There are also some Ru_5 clusters that have this electron count. Examples are $Ru_5(\mu_5\text{-}\eta^3\text{-}C_2PPh_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)(CO)_{13}$, $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{12}$, and $Ru_5(\mu\text{-}H)(\mu_5\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{:}\eta^2\text{:}\eta^6\text{-}C_{13}H_7CHC)(\mu\text{-}CO)(\mu_3\text{-}OH)(CO)_{11}$.[18,19] As indicated by their formulas, these clusters have a single ligand that bridges all five ruthenium atoms. Probably as a consequence of this interaction, the Ru_5 chain in each molecule is either doubly or triply bent.

The pattern of the resonances in the CO region of the $^{13}C\{^1H\}$ NMR spectra of **2Cl** and **2Br** indicates that each molecule has the same structure in solution as found in the solid state for **2Cl**, provided there is the typical free rotation about the OsOs bonds. The corresponding spectrum of **1Cl** (Figure 2) is likewise consistent with the idealized structure shown in Scheme 2 with three OsOs unbridged bonds. The other spectroscopic properties of the new complexes are also consistent with the structural assignments. The terminal Os atoms in **2X** are chiral centers. These molecules should therefore exist as a pair of enantiomers, and a meso form that is potentially distinguishable from the other diastereoisomers by NMR spectroscopy. There was however no evidence for two forms in the NMR spectra of **2X**. It is probable that because the chiral centers are far removed from each other, the spectral properties of each disastereoisomer are identical.

The samples used for the ^{13}C NMR spectra of **1Cl**, **1Br**, and **2Br** were prepared from the appropriate ^{13}CO-enriched $Os_3(CO)_{12}(X)_2$ and unenriched $Os(CO)_4(L)$. All carbonyl sites in the molecules were found by $^{13}C\{^1H\}$ NMR spectroscopy to be equally enriched (e.g., Figure 2). This indicates there is CO exchange on the synthetic time scale within these molecules. The $^{13}C\{^1H\}$ NMR spectrum of a mixture of **1Br** and **2Br** in CD_2Cl_4/CH_2Cl_4 at 90 °C, however, showed no significant line broadening indicative of CO-exchange on the NMR time scale.

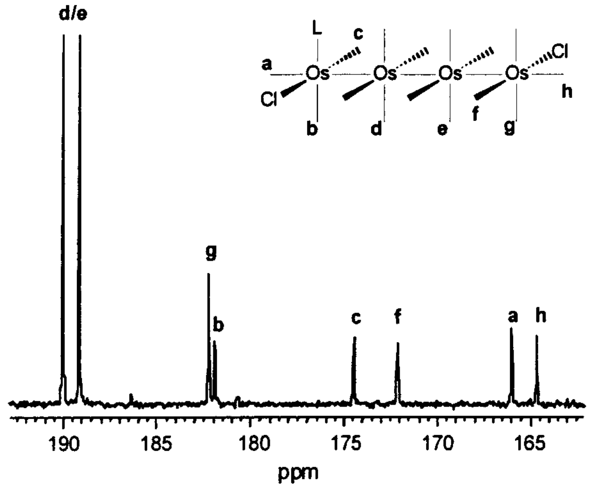

Figure 2. $^{13}C\{^1H\}$ NMR spectrum (carbonyl region) of $Os_4(CO)_{15}(CNBu^t)(Cl)_2$ (**1Cl**) in CD_2Cl_2/CH_2Cl_2. The tentative assignment of the signals is given in the inset.

Table 1. Crystal Structure Data for $Os_5(CO)_{18}(CNBu^t)_2(Cl)_2\cdot CH_2Cl_2$ (2Cl·CH₂Cl₂)

empirical formula	$C_{29}H_{20}Cl_4N_2O_{18}Os_5$
fw	1777.44
color	yellow
temp	293(2) K
cryst syst	monoclinic
space group	$C2/c$
a (Å)	20.020(3)
b (Å)	11.760(2)
c (Å)	19.059(2)
β (deg)	100.171(2)
V (Å^3), Z	4416.7(9), 4
D(calcd) (Mg·m^{-3})	2.673
abs coeff (mm^{-1})	14.64
indpdt reflns ($I > 2\sigma(I)$)	4520 [R(int) = 0.090]
R_F[a]	0.0362
R_{wF}[b]	0.0789

[a] $R_F = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$. [b] $R_{wF} = [\Sigma(w(|F_o| - |F_c|)^2)/\Sigma(wF_o^2)]^{1/2}$ $w = [\sigma^2(F_o)^2 + kF_o^2]^{-1}$.

In Table 3 the UV−vis spectra in CH_2Cl_2 of $(X)(L)(OC)_3OsOs(CO)_4(X)$, $(X)[Os(CO)_4]_3(X)$, $(X)(L)(OC)_3OsOs(CO)_4Os(CO)_3(L)(X)$, $(X)(L)(OC)_3Os[Os(CO)_4]_2Os(CO)_4(X)$ (i.e., **1X**), and $(X)(L)(OC)_3Os[Os(CO)_4]_3Os(CO)_3(L)(X)$ (i.e., **2X**) are reported. The $(X)(L)(OC)_3OsOs(CO)_4(X)$ and $(X)(L)(OC)_3OsOs(CO)_4Os(CO)_3(L)(X)$ derivatives were prepared by the addition of $Os(CO)_4(L)$ to $Os(CO)_4(X)_2$; details of their preparation and characterization will be reported in a future publication.

The lowest energy band in the 340−390 nm region in each spectrum is assigned to transitions that involve electrons in mainly OsOs σ-bonding MOs being promoted to σ*-antibonding MOs, in accordance with earlier studies on molecules with metal−metal bonds.[20]

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[11] Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

[12] Cook, N.; Smart, L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 1744.

[13] Chen, Y.-S.; Wang, S.-L.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1986**, *25*, 1118.

[14] Willis, A. C.; van Buuren, G. N.; Pomeroy, R. K.; Einstein, F. W. B. *Inorg. Chem.* **1983**, *22*, 1162.

[15] Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 247.

[16] Cifuentes, M. P.; Humphrey, M. G. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1995; Vol. 7, p 907.

[17] Jiang, F.; Yap, G. P. A.; Pomeroy, R. K. *J. Clust. Sci.* **2001**, *12*, 433.

[18] Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1997**, 2937.

[19] Lau, C. S.-W.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.* **1999**, 607.

[20] (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979; p 20. (b) Tyler, D. R.; Altobelli, M.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 3022. (c) Meyer, T. J.; Casper, J. V. *Chem. Rev.* **1985**, *85*, 187. (d) Male, J. L.; Pomeroy, R. K.; Tyler, D. R. *Organometallics* **1997**, *16*, 3431.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2Cl

Bond Lengths

Os(1)−Os(2)	2.8709(7)	Os(2)−C(4)	1.94(1)
Os(2)−Os(3)	2.8907(5)	Os(2)−C(5)	1.89(1)
Os(1)−C(10)	2.01(1)	Os(2)−C(6)	1.94(1)
Os(1)−Cl	2.495(12), 2.502(14)[a]	Os(2)−C(7)	1.96(1)
Os(1)−C(1)	1.92(1)	Os(3)−C(8)	1.93(1)
Os(1)−C(2)	1.94(1)	Os(3)−C(9)	1.94(1)
Os(1)−C(3)	1.83(3), 1.84(3)[a]		

Bond Angles

Os(1)−Os(2)−Os(3)	177.01(2)	Os(2)−Os(1)−C(2)	87.3(3)
Os(2)−Os(1)−C(1)	177.2(4)	Os(2)−Os(1)−C(10)	86.4(3)
Os(2)−Os(1)−Cl	86.1(4), 88.0(4)[a]	Os(3)−Os(2)−C	89.5(3)−91.2(3)

[a] Cl and CO(3) are disordered.

Table 3. UV−Vis Spectra (in CH_2Cl_2) of Complexes with Linear Chains of Os Atoms

compound	X = Cl	X = Br[a]	X = I
$(X)(L)Os_2(CO)_7(X)$	295 m, 326 w,[b] 359 w[b]	301 (0.81), 337 (0.40), 368 (0.25)	321 s, 356 vvw, 386 vvw
$(X)Os_3(CO)_{12}(X)$	256 m, 341 s	259 (1.7), 297 (1.0), 348 (2.6)	255 m, 280 w,[b] 358 s
$(X)(L)Os_3(CO)_{10}(L)(X)$	281 vw,[b] 332 s, 357 m[b]	251 (1.7),[b] 334 (95), 365 (13)[b]	264 w,[b] 341 s, 374 m[b]
$(X)(L)Os_4(CO)_{15}(X)$, **1X**	255 w, 286 m, 353 s,br	259 (2.6), 293 (2.1), 355 (3.6)	276 w, 360 s,br
$(X)(L)Os_5(CO)_{18}(L)(X)$, **2X**	266 m, 317 vw,[b] 348 s,br	267 (39), 322 (43),[b] 350 (50)	275 m, 348 s,br

[a] Approximate ϵ, $\times 10^{-4}$ L mol^{-1} cm^{-1} in parentheses. [b] Shoulder.

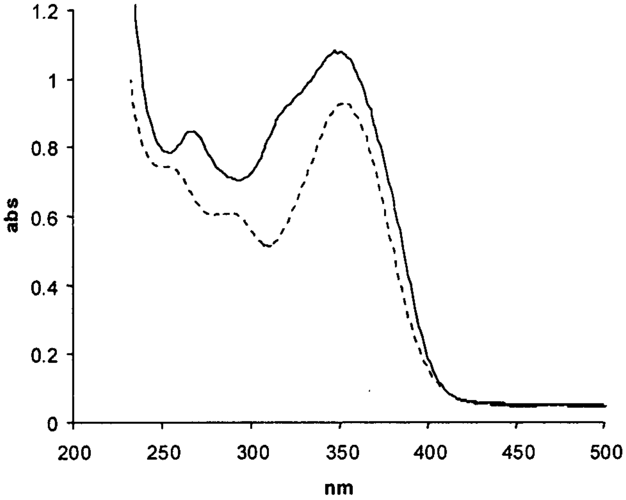

Figure 3. UV−vis spectra of approximately equimolar concentrations of **2Br (**upper trace) and **1Br** (lower trace) in CH_2Cl_2.

As the number of OsOs bonds increases, this absorption increases in intensity and becomes broader and the maximum shifts slightly to shorter wavelengths (e.g., Figure 3). The shifts are small and smaller than the shifts that occur when the halide is changed or a CO is replaced with a Bu^tNC ligand. The shift to lower frequency of the maxima as the Os chain length increases is also contrary to what might be expected if the transition was entirely due to the highest lying HOMO−LUMO transition associated with the metal−metal bonds. It may be however that all of the occupied molecular orbitals associated with the OsOs bonds are close in energy and the maximum represents the transition from the MO that is lowest in energy. The energy of this MO might be expected to get lower as the metal chain length increases.

Conclusions

The previous absence of reports describing molecules with more than three Os (or Ru) atoms in a linear chain suggested to us that such molecules were intrinsically unstable. (The little-studied polymeric $[Ru(CO)_4]_n$ is reported to possess a chain of unbridged RuRu bonds with lengths comparable to those in $Ru_3(CO)_{12}$.)[21] The synthesis of the **1X** and **2X** molecules with four and five unbridged Os atoms bound in a row as robust, air-stable crystals indicates this is not the case. Indeed, that the OsOs lengths in **2Cl** are somewhat shorter than in compounds with Os_3 chains indicates that chains with more than three atoms may be more stable than those with three atoms. The UV−vis spectra of the complexes are also in agreement with this view. The presence of the halide ligands in **1X** and **2X** may allow the synthesis of compounds with still longer Os chains.

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Supporting Information Available: Tables of crystal structure and refinement data, atomic coordinates, thermal parameters, and bond lengths and angles for **2Cl**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Masciocchi, N.; Moret, M.; Cairati, P.; Regaini, F.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1993**, 471.