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Preliminary communication

ACTIVATION OF SMALL MOLECULES BY TRANSITION METAL CLUSTER COMPOUNDS. OXIDATIVE CLEAVAGE OF A METAL-METAL BOND BY HCl IN AN OSMIUM CLUSTER COMPOUND

Richard D. Adams, Nancy M. Golembeski and John P. Selegue
Department of Chemistry, Yale University, New Haven, CT 06520 (U.S.A.)
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Summary

The complex $(\mu_3\text{-S})(\mu_3\text{-}\eta^2\text{-SCH}_2)\text{Os}_3(\text{CO})_8[\text{P(CH}_3)_2\text{C}_6\text{H}_5]$ reacts with HCl in an addition process to form the molecule $(\mu_3\text{-S})(\mu_3\text{-}\eta^2\text{-SCH}_2)(\text{H})\text{Os}_3(\text{CO})_8\text{-}[\text{P(CH}_3)_2\text{C}_6\text{H}_5]\text{Cl}$. The product was characterized by IR, ^{1}H NMR and x-ray crystallographic methods. The structural analysis shows that the HCl addition has caused a cleavage of one of the metal-metal bonds.

Considerable attention has now been focused on transition metal cluster compounds as a possible new class of homogeneous catalysts [1-4]. Interest has focused mainly on their ability to provide several sites for the activation of small molecules and on their ability to engage in polynuclear coordinations [5]. However another property of molecules containing metal-metal bonds is their ability to undergo cleavage reactions. While these reactions have been thoroughly studied in dinuclear complexes [6], reports of such reactions in cluster compounds have been comparatively few. Some recent reports have described nucleophilic cleavages [7-11]. Electrophilic cleavages are even more rare [12]. Here we wish to report an example of the cleavage of an osmium-osmium bond by the addition of HCl to a triosmium cluster.

We have recently reported the preparation of the complex $(\mu_3\text{-S})(\mu_3\text{-}\eta^2\text{-SCH}_2)Os_3(CO)_8[P(CH_3)_2C_6H_5]$, I, which is shown schematically in Figure 1 [13]. The complex contains two osmium-osmium bonds. In a typical reaction 37 mg

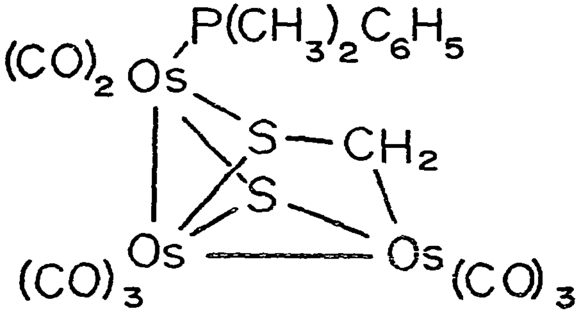
I

Fig. 1

of I were dissolved in 15 mL of dichloromethane and 10 drops of a 12 M HCl-ethanol (1:1) solution were added. After stirring for 15 hours at room temperature, the nearly colorless solution was reduced to ca 2 mL and 5 mL of pentane were added. Cooling to -20°C produced an off-white powder which was recrystallized from CH_2Cl_2-octane to give 20 mg (40%) of crystals of II, m.p. 151.0-151.5°.* The ^{1}H NMR spectrum of II shows resonances characteristic of a methylene group, δ4.40, 3.98 (AB, $^2J_{HH}$ = 11.0Hz, 2H), a dimethylphenylphosphine ligand, δ7.41m (5H), 2.11d ($^2J_{PH}$ = 9.8Hz, 6H), and a bridging metal hydride ligand, δ-15.12d ($^2J_{PH}$ = 8.55Hz, 1H). Details of the molecular structure were provided by an x-ray crystallographic analysis.

Compound II crystallizes in the monoclinic space group $P2_1/c$, No. 14, a = 10.423(2), b = 11.014(5), c = 22.743(9)Å, β = 101.98(3)°, Z = 4. Diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer. All data were corrected for absorption. The structure was solved by the heavy atom method and refined by full-matrix least-squares techniques.** The final

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*ν(CO) hexanes solvent: 2105m, 2095s, 2035vs, 2025s, 2010sh, 2005m, 1990w, 1970w cm^{-1}.

**All calculations were done on a Digital Equipment PDP 11/45 computer using programs of the Enraf-Nonius SDP program library.

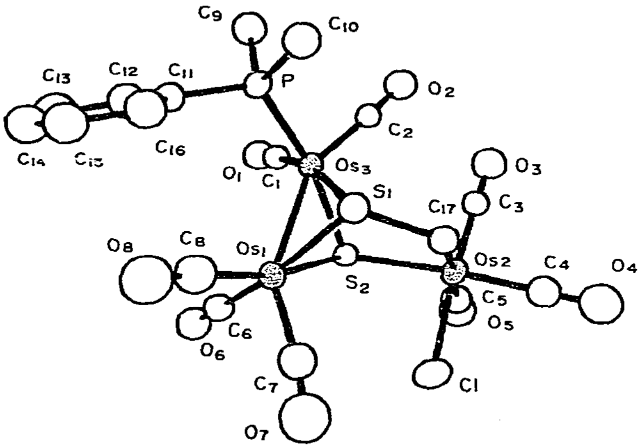

Fig. 2

values of the residuals R and R_w were 0.044 and 0.048, respectively, for 2689 reflections $(F_O^2 \geq 3\sigma(F_O^2))$ collected in the scan range $2\theta = 0\text{-}50°$. ***

An ORTEP diagram of **II** is shown in Figure 2. The molecule contains a triply bridging inorganic sulfide ligand, S(2) and a triply bridging, dihapto thioformaldehyde ligand C(17)-S(1) with the sulfur atom bridging the Os(1)-Os(3) bond and carbon atom C(17) bonded solely to Os(2). Most interestingly the molecule has only one osmium-osmium bond, Os(1)-Os(3) = 2.834(1)Å. The internuclear distances Os(1)···Os(2) = 4.037(1)Å and Os(2)···Os(3) = 4.005(1) are clearly outside the range of normal bonding distances. A chlorine atom was found bonded to Os(2), Os(2)-Cl = 2.423(4)Å. The hydride ligand was not observed crystallographically but probably bridges the Os(1)-Os(3) bond in the cavity circumscribed by the carbonyls C(1)-O(1), C(6)-O(6), and C(8)-O(8) and the phosphine ligand. Structural parameters are listed in Tables 1 and 2.

The mechanism of the addition of HCl to **I** is not known at this time.

***A table of final observed and calculated structure factor amplitudes has been deposited as NAPS document no. 03677 (20 pages). Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only $5.00 for photocopies or $3.00 for microfiche. Outside the U.S. and Canada add postage of $3.00 for photocopy and $1.00 for microfiche.

Table 1. Bond Distances with Errors for $(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(H)Os_3(CO)_8[P(CH_3)_2C_6H_5]Cl$, II.

Atoms	Distance (Å)	Atoms	Distance (Å)
Os(1)-Os(3)	2.834(1)	S(1)-C(17)	1.872(12)
Os(1)-S(1)	2.427(3)	C(1)-O(1)	1.158(14)
Os(1)-S(2)	2.445(3)	C(2)-O(2)	1.167(13)
Os(1)-C(6)	1.919(13)	C(3)-O(3)	1.162(14)
Os(1)-C(7)	1.926(16)	C(4)-O(4)	1.130(14)
Os(1)-C(8)	1.952(16)	C(5)-O(5)	1.134(15)
Os(2)-S(2)	2.457(3)	C(6)-O(6)	1.134(13)
Os(2)-Cl	2.423(4)	C(7)-O(7)	1.151(17)
Os(2)-C(17)	2.147(12)	C(8)-O(8)	1.125(16)
Os(2)-C(3)	1.852(13)	P-C(9)	1.853(15)
Os(2)-C(4)	1.911(14)	P-C(10)	1.851(14)
Os(2)-C(5)	1.949(15)	P-C(11)	1.835(12)
Os(3)-P	2.350(3)	C(11)-C(12)	1.371(17)
Os(3)-S(1)	2.436(3)	C(12)-C(13)	1.441(20)
Os(3)-S(2)	2.455(3)	C(13)-C(14)	1.348(20)
Os(3)-C(1)	1.864(13)	C(14)-C(15)	1.309(19)
Os(3)-C(2)	1.841(12)	C(15)-C(16)	1.422(19)
		C(11)-C(16)	1.382(18)

Overall, however, it can be described formally as an oxidative cleavage of the Os(1)-Os(2) metal-metal bond as it existed in I. The chemistry of the thioformaldehyde cluster complex I contrasts with that of the mononuclear thioformaldehyde osmium complex $Os(\eta^2\text{-}SCH_2)(CO)_2[P(C_6H_5)_3]_2$. Treatment of this complex with HCl led first to the formation of $OsCl(SCH_3)(CO)_2[P(C_6H_5)_3]_2$ and subsequently to $OsCl_2(CO)_2[P(C_6H_5)_3]_2$ and methanethiol upon heating [14].

It is becoming increasingly evident that metal-metal bonds in clusters can be viewed as elements of unsaturation, and their cleavage can be used as a means of activating small molecules. Unlike unbridged dinuclear metal

Table 2. Selected Bond Angles with Errors for $(\mu_3\text{-S})(\mu_3\text{-}\eta^2\text{-SCH}_2)(\text{H})\text{Os}_3(\text{CO})_8[\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5]\text{Cl}$, **II**.

Atoms	Angle (deg)	Atoms	Angle (deg)
S(1)-Os(1)-Os(3)	54.51(7)	C(3)-Os(2)-C(4)	90.8(6)
S(1)-Os(1)-S(2)	79.1(1)	C(3)-Os(2)-C(5)	90.8(6)
S(1)-Os(3)-Os(1)	54.21(8)	C(3)-Os(2)-Cl	175.7(4)
S(1)-Os(3)-S(2)	78.7(1)	C(4)-Os(2)-C(5)	92.4(6)
S(1)-Os(3)-P	93.2(1)	C(4)-Os(2)-C(17)	90.5(5)
S(2)-Os(3)-P	165.5(1)	C(5)-Os(2)-C(17)	175.2(5)
Os(1)-S(1)-Os(3)	71.28(9)	P-Os(3)-C(1)	95.9(4)
Os(1)-S(1)-C(17)	109.6(4)	P-Os(3)-C(2)	86.2(4)
Os(3)-S(1)-C(17)	110.2(4)	C(1)-Os(3)-C(2)	89.4(5)
S(2)-Os(2)-C(17)	88.0(3)	Os(1)-C(6)-O(6)	174.5(12)
S(1)-C(17)-Os(2)	119.7(6)	Os(1)-C(7)-O(7)	169.7(14)
C(17)-Os(2)-Cl	88.4(3)	Os(1)-C(8)-O(8)	173.0(16)
S(2)-Os(2)-Cl	89.6(1)	Os(2)-C(3)-O(3)	178.3(14)
C(6)-Os(1)-C(7)	90.9(6)	Os(2)-C(4)-O(4)	178.3(14)
C(6)-Os(1)-C(8)	93.2(6)	Os(2)-C(5)-O(5)	174.8(14)
C(7)-Os(1)-C(8)	88.6(6)	Os(3)-C(1)-O(1)	176.5(12)
C(3)-Os(2)-C(17)	92.9(5)	Os(3)-C(2)-O(2)	176.0(10)

complexes, cleavage of one metal-metal bond in a cluster does not necessarily result in disintegration of the molecule. Thus, the activation of small molecules through the cleavage of metal-metal bonds may play a key role in the development of cluster compounds as catalysts.

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