Inorganica Chimica Acta
LETTER

Triply Bonded Diosmium(III) Complexes That Contain Os–Br Bonds

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(Received July 4, 1989)

Diosmium(III) bromide complexes that contain an osmium–osmium triple bond are rare in comparison to the growing number of chloride derivatives of this type [1]. The only well-documented bromide derivatives are salts of the octabromodiosmate(III) anion [2, 3] and the complex $Os_2(NHCOPh)_4Br_2$ [4]. We have utilized a simple procedure, which we believe will be of general synthetic utility, to convert the complexes $Os_2(O_2CR)_4Cl_2$ (R = Et or n-Pr) [5, 6] and $Os_2(hp)_4Cl_2$ (hp is the monoanion of 2-hydroxypyridine) [5, 7, 8] to their bromo analogues. This involves the reaction of the aforementioned chloride complexes with liquid HBr, a strategy we have used previously to prepare the dirhenium(III) carboxylates $Re_2(O_2CR)_4X_2$ (X = Br or I) from $Re_2(O_2CR)_4Cl_2$ [9].

Experimental

A representative general synthetic procedure is as follows.

$Os_2(O_2CEt)_4Br_2$

A sample of $Os_2(O_2CEt)_4Cl_2$ (0.159 g, 0.214 mmol) was placed in a test tube equipped with a side arm. Nitrogen was flushed through this system for 15 min, after which time the test tube and its contents were cooled in a dry ice/acetone slush bath (–78 °C). Hydrogen bromide gas was then introduced into the test tube until 5 ml of liquid HBr had condensed onto the sample. This solution was stirred for *c.* 1 h. The reaction mixture was then slowly warmed to room temperature and purged with nitrogen to remove the HBr gas. The brown solid that remained was dissolved in dichloromethane and filtered. The brown filtrate that resulted was reduced in volume to 15 ml and diethyl ether was added slowly to precipitate $Os_2(O_2CEt)_4Br_2$ as dark red–brown microcrystals. This solid was collected by filtration, washed with diethyl ether several times, and vacuum dried; yield 0.153 g (86%). *Anal.* Calc. for $C_{12}H_{20}Br_2O_8Os_2$: C, 17.31; H, 2.42. Found: C, 18.18; H, 2.50%.

$Os_2(O_2C\text{-n-}Pr)_4Br_2$

This complex was prepared from $Os_2(O_2C\text{-n-}Pr)_4Cl_2$ (0.125 g, 0.156 mmol) in an identical manner to that described for $Os_2(O_2CEt)_4Br_2$; yield 0.118 g (85%). *Anal.* Calc. for $C_{16}H_{28}Br_2O_8Os_2$: C, 21.63; H, 3.18. Found: C, 21.48; H, 3.25%.

$Os_2(hp)_4Br_2$

An analogous procedure was used to prepare this complex from $Os_2(hp)_4Cl_2$ (0.25 g, 0.302 mmol); yield 0.24 g (87 %). *Anal.* Calc. for $C_{22}H_{23}Br_2N_4O_{5.5}Os_2$ (i.e. $Os_2(hp)_4Br_2 \cdot H_2O \cdot 0.5(C_2H_5)_2O$): C, 27.19; H, 2.39. Found: C, 26.44; H, 2.88%.

Results and Discussion

The red–brown microcrystalline carboxylate complexes have spectral and electrochemical properties that are similar to those of their previously reported chloro analogues [5, 8]. Cyclic voltammetric (CV) measurements were recorded on 0.1 M $n\text{-}Bu_4NPF_6/CH_2Cl_2$ solutions of the complexes and revealed the presence of a reversible one-electron process corresponding to a reduction of the bulk complex ($E_{1/2}$(red) = +0.43 V for R = Et, and $E_{1/2}$(red) = +0.40 V for R = n-Pr) together with an irreversible reduction occurring at potentials approaching the solvent limit ($E_{p,c}$ = –1.5 V)†. In the case of R = Et, the complex was reduced to $[(\eta^5\text{-}C_5H_5)_2Co][Os_2(O_2CEt)_4Br_2]$ by cobaltocene, but the resulting complex was extremely air sensitive. This reaction product is analogous to those that have been obtained upon reducing the chloro derivatives $Os_2(O_2CR)_4Cl_2$ with cobaltocene [8]. $[(\eta^5\text{-}C_5H_5)_2Co][Os_2(O_2CEt)_4Br_2]$ was characterized on the basis of its CV (recorded in 0.1 M $n\text{-}Bu_4NPF_6/CH_2Cl_2$), which showed a couple characteristic of the anion together with one at $E_{1/2}$ = –0.90 V versus Ag/AgCl that is due to the cobaltocenium cation.

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†Electrochemical and spectroscopic characterizations of these complexes were carried out using procedures described previously [10]. Note that in the CV measurements the potentials are quoted relative to the ferrocenium/ferrocene couple having $E_{1/2}$ = +0.47 V versus Ag/AgCl.

0020-1693/90/$3.50

The magnetic moments of these complexes (μ_{eff} = 1.9 μ_B and 1.4 μ_B for R = Et and n-Pr, respectively), as determined on dichloromethane solutions at room temperature by the Evans method [11], are similar to those reported for the chloro derivatives [8]. The paramagnetic nature of these $Os_2(O_2CR)_4Br_2$ complexes results in very characteristic contact-shifted ^1H NMR spectra. The propionate complex displays ^1H NMR resonances (measured in CD_2Cl_2) at δ −15.3 (quartet, CH_2) and δ +2.3 (triplet, CH_3), while the n-butyrate has signals at δ −16.6 (quartet, α-CH_2), δ +3.4 (sextet, β-CH_2), and δ +1.4 (triplet, CH_3). These features resemble the previously reported spectrum of $Os_2(O_2C\text{-n-Pr})_4Cl_2$ [5].

The electronic absorption spectra of these complexes are very similar to one another[†], and while detailed assignments are not readily made for all of these peaks, we suggest that the band at 457 nm in both complexes is a $Br(\pi) \rightarrow Os_2(\pi^*)$ charge-transfer transition. We have reported previously [8] that the addition of a large excess of $n\text{-}Bu_4NBr$ to a solution of $Os_2(O_2\text{-n-Pr})_4Cl_2$ reduces the intensity of the peak at 392 nm and introduces a new intense peak at 442 nm. We suggested [8] that halide exchange occurs and that some of the bromo complex is generated.

The complex $Os_2(hp)_4Br_2$ has properties similar to those of $Os_2(hp)_4Cl_2$ [5, 8] and the disomium(III) carboxylates. Its CV (recorded in 0.1 M $n\text{-}Bu_4NPF_6/CH_2Cl_2$) shows an oxidation at $E_{1/2}$ = +1.28 V and a one-electron reduction at $E_{1/2}$ = +0.11 V versus Ag/AgCl. Its paramagnetism is shown by a magnetic moment determination on a dichloromethane solution using the Evans method [11] (μ_{eff} = 1.5 μ_B), while its electronic absorption spectrum (recorded in CH_2Cl_2) shows λ_{max} values at 502 (ϵ = 4800), 420 (ϵ = 5250) and ≈390(sh) nm. These data agree well with the corresponding properties of $Os_2(hp)_4Cl_2$ [5, 8].

An additional feature of note is our observation that $Os_2(hp)_4Br_2$ is also formed upon the reaction of $(NH_4)_2OsBr_6$ (0.500 g, 0.71 mmol) [12] with an excess of molten 2-hydroxypyridine (1.00 g, 10.5 mmol) at 130 °C for *c.* 90 min under a nitrogen atmosphere. The melt was cooled to room temperature and then extracted several times with dichloromethane. The solvent was removed by evaporation, and the dark red oil that resulted was triturated with absolute ethanol to produce a dark red–brown solid; yield 0.25 g (77%). This product had electrochemical and spectroscopic properties (*vide supra*) that were in accord with its formulation as $Os_2(hp)_4Br_2$. Further studies are in progress.

Acknowledgement

We thank the National Science Foundation (grant No. CHE88-07444) for research support.

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[†] Electronic absorption spectra of $Os_2(O_2CR)_4Br_2$ were measured on dichloromethane solutions. For R = Et (900 - 300 nm): λ(nm) = 862 (ϵ = 230), 705(sh), 550 (ϵ = 640), 457 (ϵ = 18 600), 380(sh), 300 (ϵ = 5400). For R = n-Pr (2000–300 nm): λ(nm) = 1220 (ϵ = 20), 860 (ϵ = 250), 710(sh), 552 (ϵ = 680), 457 (ϵ = 19 100), 340(sh), 302 (ϵ = 5600).