Journal of Organometallic Chemistry, 297 (1985) 349–359
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE REDUCTION OF CLUSTER-COORDINATED NITRIC OXIDE USING MOLECULAR HYDROGEN. SYNTHESIS AND CHARACTERIZATION OF $H_4Os_3(NH)(CO)_8$

JOANNE A. SMIEJA and WAYNE L. GLADFELTER *,*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455 (U.S.A.)

(Received March 11th, 1985)

Summary

The reaction of molecular hydrogen with $HOs_3(CO)_{10}(NO)$ leading to the reduction of the nitrosyl ligand has been studied. Four products have been isolated and a reasonable mass balance of osmium has been obtained. Two of the products, $H_2Os_3(NH)(CO)_9$ and the unusual hydrogen-rich cluster $H_4Os_3(NH)(CO)_8$ are new, and spectroscopic data for their formulations and proposed structures are presented. The other two products, $HOs_3(NH_2)(CO)_{10}$ and $H_4Os_4(CO)_{12}$, have been previously characterized. A new route to $HOs_3(NH_2)(CO)_{10}$ starting from the triazenido cluster, $HOs_3(HN_3H)(CO)_{10}$, has also been studied. Interconversions between the imido and amido clusters were investigated.

Introduction

There is much interest in using metal clusters to effect the stoichiometric and catalytic reduction of molecules that contain multiple bonds. In particular, the reduction of species containing triple bonds such as carbon monoxide [1], alkynes [2], isocyanides [3], and recently, nitric oxide [4], has been the focus of attention. Two recent reports have discussed the use of molecular hydrogen to reduce the bridging nitrosyl ligand in $HRu_3(CO)_{10}(NO)$ producing new clusters containing NH and NH_2 ligands [5,6].

We report here the reaction of $HOs_3(CO)_{10}(NO)$ with H_2 which leads to the reduction of the nitrosyl ligand and to the formation of an unusual hydrogen-rich species.

Experimental

$HOs_3(CO)_{10}(NO)$, [7] $H_2Os_3(CO)_{10}$, [8] and HN_3 [9] were prepared according to published procedures. Benzene, heptane, octane, and hexane were dried by distillation from sodium metal under nitrogen. The hydrogen and carbon monoxide used in

---

* Alfred P. Sloan Fellow.

0022-328X/85/$03.30

TABLE 1

SPECTROSCOPIC PROPERTIES

Compound	ν(CO) (cm^{-1}) (hexane)	ν(N–H), cm^{-1} (hexane)	$\delta(^1H)$	Ref.
$HOs_3(HN_3H)(CO)_{10}$	2111w, 2068s, 2061s, 2048w, 2025s, 2015s, 2001m, 1996m, 1982w	3363vw	8.38 (2H, s) (C_6D_6) −13.35 (1H, s)	this work
$H_2Os_3(NH)(CO)_9$	2115m, 2080s, 2052s, 2031s, 2008s, 1991m 1982m	3382vw	4.06 (1H, s(br)) (C_6D_6) −19.44 (2H, s) ($CDCl_3$)	this work
$H_4Os_3(NH)(CO)_8$	2120w, 2101s, 2080w, 2060m, 2040s, 2032s, 2021s, 1992w, 1962s	3390vw	4.42 (1H, s(br)) (C_6D_6) −12.74 (1H, d of d, J(H–H) 11.04, 3.18 Hz) −16.46 (1H, d of d, J(H–H) 11.04, 2.84 Hz) −18.47 (1H, t, J(H–H) 2.89 Hz) −20.40 (1H, t, J(H–H) 2.81 Hz)	this work
$HOs_3(NH_2)(CO)_{10}$	2108w, 2082w, 2070s 2053m, 2036w, 2023s, 2008s, 1998s, 1984w	$\left.\begin{matrix}3409vw\\3349vw\end{matrix}\right\}(CHCl_3)$	2.92 (1H, s(br)) 2.30 (1H, s(br)) −15.39 (1H, d, J(H–H) 3.4 Hz)	this work
$H_2Os_3(NCH_3)(CO)_9$	2112m, 2082s, 2078s, 2032s, 2005s, 1986s, 1974m		4.69 (CH_3)($CDCl_3$) −18.74	16
$HOs_3(HN_3Ph)(CO)_{10}$	2110w, 2069s, 2061s, 2047w, 2026s, 2015s, 2010sh, 2001m, 1990w, 1975w		8.35 ($CDCl_3$) −12.68	17
$H_4Os_3(NCH_2CF_3)(CO)_8$	2122w, 2104s, 2045m, 2043m, 2034vs, 2026sh, 2022m, 1964w, 1957m		4.77 (CH_2, q, J(H–F) 7.36)($CDCl_3$) −12.29 (1H, d, J(H–H) 9.81) −16.11 (1H, d, J(H–H) 10.99) 17.85 (1H, s) −19.01 (1H, s)	13

this study were of chemically pure grade. Infrared spectra were recorded on a Mattson Cygnus 25 FTIR spectrometer equipped with a HgCdTe detector or a Beckman 4250 spectrophotometer. NMR spectra were obtained using a Nicolet NFT 300 MHz spectrometer. Table 1 contains a list of the clusters characterized in this study along with the spectral data of closely related compounds that have been characterized by single-crystal X-ray crystallography. The fast atom bombardment mass spectrum was obtained at the Midwest Center for Mass Spectrometry at the University of Nebraska.

Reduction of $HOs_3(CO)_{10}(NO)$

A solution of $HOs_3(CO)_{10}(NO)$ (101.7 mg, 0.115 mmol) in 20 ml of heptane was placed in a glass liner which was then sealed inside a rocking autoclave. The entire system was pressurized with N_2 and vented. This process was repeated several times with N_2 and then repeated four times with H_2. At this point the H_2 pressure was increased to 2000 p.s.i. while rocking and heating of the autoclave was initiated. The temperature, 140°C, was monitored with a thermocouple inserted in the autoclave and controlled with a proportional temperature controller. The reaction temperature of 140°C was maintained for 2 h, after which time the autoclave was cooled and, finally, depressurized. The cloudy, yellow reaction solution was filtered to remove the pale yellow solid identified as $H_4Os_4(CO)_{12}$ [10] (24.3 mg, 0.022 mmol, 26% yield). The clear yellow filtrate was chromatographed on silica gel using hexane as the eluent. Four yellow bands eluted from the column. The first band contained unreacted $HOs_3(CO)_{10}(NO)$ (3.1 mg, 0.0035 mmol).

The second band to elute contained the new imido cluster, $H_2Os_3(NH)(CO)_9$. The solvent was removed to yield pale yellow crystals in 10% yield (9.7 mg, 0.012 mmol). The electron impact mass spectrum exhibited a parent ion at 839 dalton (^{192}Os) which was followed by the loss of 8 carbonyls. Anal. Found: C, 12.89; H, 0.40; N, 1.61. $H_2Os_3(NH)(CO)_9$ calcd.: C, 12.87; H, 0.36; N, 1.67%.

The third yellow band was found to be $HOs_3(NH_2)(CO)_{10}$ [11] (25.9 mg, 0.030 mmol, 26% yield). Anal. Found: C, 13.99; H, 0.40; N, 1.59. $HOs_3(NH_2)(CO)_{10}$ calcd.: C, 13.82; H, 0.35; N, 1.61%.

The last band to elute contained another new imido cluster, $H_4Os_3(NH)(CO)_8$. This imido cluster was isolated in 30% yield (28.2 mg, 0.035 mmol) as a yellow-orange powder after the removal of the hexane. Routine electron impact mass spectrometry was of no value in the characterization of this cluster. However, fast atom bombardment mass spectrometry (FABS/MS) revealed an intense parent ion at 813 dalton (^{192}Os). Anal. Found: C, 12.61; H, 0.72; N, 1.69. $H_4Os_3(NH)(CO)_8$ calcd.: C, 11.80; H, 0.61; N, 1.72%.

General procedure for monitoring high pressure reactions by HPLC and/or infrared spectroscopy

The apparatus used in this study to monitor high pressure reactions has been described elsewhere [12]. Briefly, the desired reaction solution and a stir bar were placed in a glass liner which was then inserted into a 71 ml Parr autoclave equipped with a specially designed 0.01 inch I.D. diptube for removing small volumes (~ 0.2 ml) of liquid. The autoclave was maintained at constant pressure, agitated with a magnetic stirrer, and heated to the desired reaction temperature with an aluminum block containing heating rods controlled by a proportional temperature controller.

Reduction of $HOs_3(CO)_{10}(NO)$ monitored by HPLC

$HOs_3(CO)_{10}(NO)$ (60.0 mg, 0.068 mmol) dissolved in heptane (20 ml) was placed in a glass liner equipped with a stir bar. The liner was inserted into the autoclave described above, which was then filled with 400 p.s.i. N_2 and vented. This procedure was repeated four times with N_2, followed by four times with H_2. At this point, the autoclave was pressurized to 2000 p.s.i. H_2.

Stirring and heating of the small reaction autoclave was initiated. When the temperature reached 122°C, a small aliquot of reaction solution was removed, injected onto a HPLC equipped with a μ-Porasil column, and also examined by infrared spectroscopy. The temperature was increased to 140°C and the reaction was monitored in the above fashion for a further 245 min. Typical chromatograms are shown in Fig. 1. The peaks with retention times of 0.88 and 1.00 min are due to impurities in the solvent. Initially, there is a small peak at 1.20 min which disappears with time and which we have not been able to identify.

Reaction of $H_2Os_3(NH)(CO)_9$ with H_2

$H_2Os_3(NH)(CO)_9$ (9.1 mg, 0.011 mmol) dissolved in heptane (5 ml) was placed in a glass liner equipped with a stir bar. The glass liner was inserted into the Parr autoclave and the system was filled with N_2 and vented. This procedure was repeated several times with N_2, and then several times with H_2. At this point, the autoclave was pressurized to 2000 p.s.i. H_2 and mixing and heating was initiated. The reaction was allowed to run at 140°C for 2 h and then heating was terminated. When the bomb had cooled, it was depressurized and the clear yellow solution was chromatographed yielding two bands. The first band contained unreacted $H_2Os_3(NH)(CO)_9$ (5.9 mg, 0.007 mmol) in 65% yield. The second band contained $H_4Os_3(NH)(CO)_8$ (1.8 mg, 0.002 mmol) in 18% yield.

Reaction of $HOs_3(NH_2)(CO)_{10}$ with H_2

$HOs_3(NH_2)(CO)_{10}$ (7.4 mg, 0.009 mmol), dissolved in heptane (5 ml), was subjected to the same reaction conditions as described above for $H_2Os_3(NH)(CO)_9$ with H_2. After the autoclave was cooled and depressurized, the cloudy yellow reaction solution was filtered to yield a very small amount (< 1.0 mg) of $H_4Os_4(CO)_{12}$, identified by infrared spectroscopy, and a clear yellow filtrate. The filtrate was chromatographed and only one band eluted from the column. It contained unreacted $HOs_3(NH_2)(CO)_{10}$ (5.1 mg, 0.006 mmol) in 61% yield.

Reaction of $H_2Os_3(NH)(CO)_9$ with CO

$H_2Os_3(NH)(CO)_9$ (10.0 mg, 0.012 mmol) was placed in a glass liner with a stir bar and heptane (15 ml). The liner was placed inside the 71 ml Parr autoclave. The system was flushed with CO and pressurized to 300 p.s.i. The autoclave was agitated with a magnetic stirrer and heated to 140°C. Over a 23 h period small aliquots of reaction solution were removed and examined by infrared spectroscopy. The infrared absorptions due to $H_2Os_3(NH)(CO)_9$ completely disappeared as the new absorptions due to $HOs_3(NH_2)(CO)_{10}$ appeared. Absorptions at 2030 and 2000 cm^{-1} possibly indicated the presence of a small amount of $Os(CO)_5$. The reaction was continued for an additional 7 h, but no further changes were observed. After cooling and depressurizing, the clear yellow solution was chromatographed yielding one band which contained $HOs_3(NH_2)(CO)_{10}$.

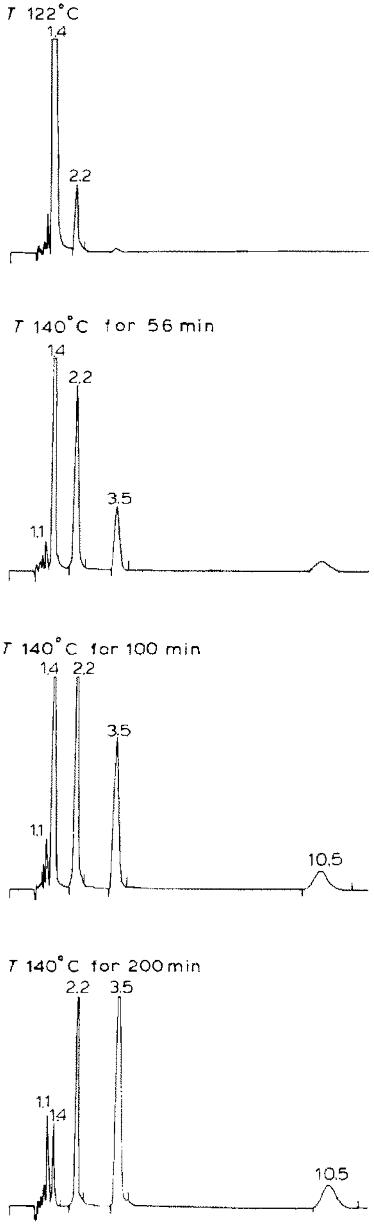


Fig. 1. HPLC chromatograms of the reaction of $HOs_3(CO)_{10}(NO)$ with molecular hydrogen in heptane. The HPLC eluent is hexane/CH_2Cl_2, 9/1. Retention times are given in minutes: $H_4Os_4(CO)_{12}$, 1.1; $HOs_3(CO)_{10}(NO)$, 1.4; $H_2Os_3(NH)(CO)_9$, 2.2; $HOs_3(NH_2)(CO)_{10}$, 3.5; $H_4Os_3(NH)(CO)_8$, 10.5 min.

Reaction of $H_4Os_3(NH)(CO)_8$ with CO

$H_4Os_3(NH)(CO)_8$ (13.3 mg, 0.016 mmol), dissolved in heptane (5 ml), was placed in a glass liner equipped with a stir bar. The glass liner was inserted into the Parr autoclave, flushed four times with N_2 and then four times with CO, and finally pressurized to 800 p.s.i. CO. The system was agitated by a magnetic stirrer and heated to 140°C for 0.5 h. After the autoclave had cooled, it was depressurized and the pale yellow solution was chromatographed yielding three bands. The first band contained $H_2Os_3(NH)(CO)_9$ (5.5 mg, 0.007 mmol) in 40% yield. The second band to elute contained a trace amount (< 0.5 mg) of $HOs_3(NH_2)(CO)_{10}$. The last band contained unreacted $H_4Os_3(NH)(CO)_8$ (4.0 mg, 0.005 mmol).

Preparation of $HOs_3(HN_3H)(CO)_{10}$

$H_2Os_3(CO)_{10}$ (63.1 mg, 0.074 mmol) was dissolved in 10 ml of deoxygenated benzene. A 10 ml deoxygenated benzene solution containing excess HN_3 was added, and the mixture was rapidly stirred. The purple solution turned yellow, indicating that immediate reaction had occurred. The benzene solution was extracted five times with 20 ml 5% HCl solution to remove excess HN_3. The solution was dried with $MgSO_4$, after which the benzene was removed using a rotary evaporator. The resulting yellow oil was dissolved in hexane and chromatographed giving two yellow bands. The first band formed an unidentified yellow oil after removal of the solvent. The second band contained $HOs_3(HN_3H)(CO)_{10}$ (36.1 mg, 0.040 mmol) corresponding to a 55% yield. The electron impact mass spectrum indicated a parent ion at 895 dalton, which was followed by a loss of 9 carbonyl ligands. Anal. Found: C, 13.93; H, 0.58; N, 4.15. $HOs_3(HN_3H)(CO)_{10}$ calcd.: C, 13.41; H, 0.34; N, 4.69%.

Conversion of $HOs_3(HN_3H)(CO)_{10}$ to $HOs_3(NH_2)(CO)_{10}$

$HOs_3(HN_3H)(CO)_{10}$ (34.2 mg, 0.038 mmol) was dissolved in 30 ml hexane and was refluxed for 24 h under N_2. The cloudy yellow-orange solution was filtered and chromatographed yielding two yellow bands. The first to elute was $HOs_3(NH_2)(CO)_{10}$ (10.7 mg, 0.012 mmol) obtained in 33% yield and the second band contained unreacted $HOs_3(HN_3H)(CO)_{10}$ (10.8 mg, 0.012 mmol).

Attempted thermal conversion of $HOs_3(NH_2)(CO)_{10}$ to $H_2Os_3(NH)(CO)_9$

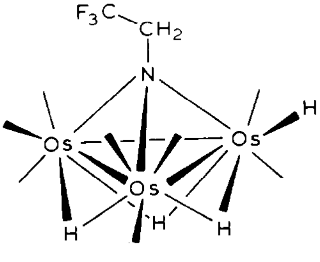
$HOs_3(NH_2)(CO)_{10}$ (17.5 mg, 0.020 mmol) was degassed in a Schlenk tube equipped with a condenser. Octane (8 ml) was added and the bright yellow solution was heated to reflux for 24 h. During this time the infrared absorptions for the carbonyls in $HOs_3(NH_2)(CO)_{10}$ slowly decreased, but no new carbonyl absorptions appeared. The bright yellow solution gradually turned brown and became cloudy. After 24 h at reflux, the solution was filtered to yield a hexane, Et_2O, and THF insoluble brown precipitate and a trace amount of starting material. The nitrogen containing product was not identified.

Results and discussion

The reduction of $HOs_3(CO)_{10}(NO)$ with molecular hydrogen produces two new species and two previously characterized compounds. During the course of this study, an alternate method of preparing one of these characterized compounds, $HOs_3(NH_2)(CO)_{10}$, from a new triazenido cluster, $HOs_3(HN_3H)(CO)_{10}$, was also investigated. The first section of this discussion will focus on the characterization of the three new species while the last section will concentrate on the reduction itself and on some of the reactivity of the compounds synthesized during this investigation.

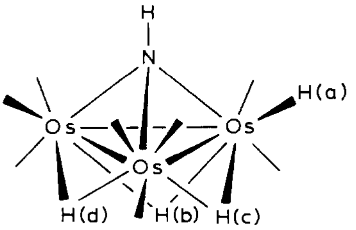
$H_4Os_3(NH)(CO)_8$

This unusual cluster is produced in the highest yield (30%) in the reduction of $HOs_3(NO)(CO)_{10}$. The formulation was based on the FABS/MS, which exhibited an intense parent ion at 813 dalton, elemental analysis, and spectroscopic comparison to the structurally characterized cluster $H_4Os_3(NCH_2CF_3)(CO)_8$ [13], (I). We were unable to obtain X-ray quality crystals and, in fact, the cluster was always isolated as a powder.



(I)

The proposed structure of $H_4Os_3(NH)(CO)_8$ is based on I, and is shown in II with each of the hydrogen atoms labelled. Figure 2 shows the ^1H NMR spectrum in



(II)

the hydride region of $H_4Os_3(NH)(CO)_8$ along with the assignments corresponding to II. Carbonyl metal clusters containing both terminal and bridging hydrides are uncommon. In the known examples, such as $H_2Os_3(CO)_{11}$, the terminal hydride resonance appears at −10.24 ppm, which is several ppm down field from the bridging hydride at −19.97 ppm [14]. The ^1H NMR spectrum of II exhibits a low field hydride resonance at −12.74 ppm which is separated from the group of three other resonances. This signal is assigned to the terminal hydride H(a). The assignment of the remaining resonances in the spectrum to the various hydrogens was possible using selective decoupling experiments. Since the resonance at −16.46 ppm

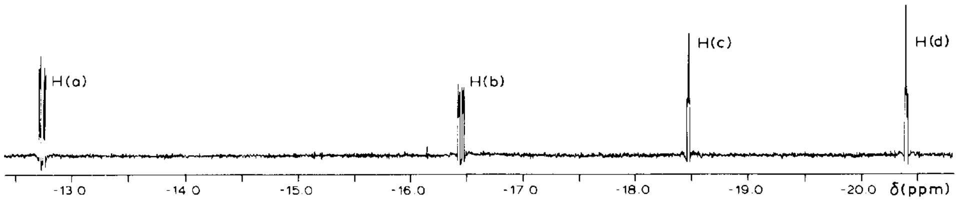


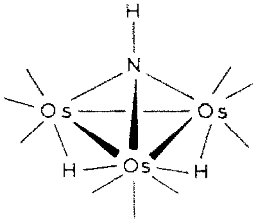
Fig. 2. ^1H NMR of the hydride region of $H_4Os_3(NH)(CO)_8$.

exhibits an 11.04 Hz coupling constant, this peak is assigned to H(b) which is *trans* to H(a). H(a) is also coupled to H(c) (−18.47 ppm) with a characteristic [15] *cis* coupling constant of 3.18 Hz. While H(b) is coupled to H(d) (−20.40 ppm, 2.82 Hz), the analogous J(H(b)–H(c)) is very small (< 1 Hz), probably because H(a) is exerting a *trans* labilizing influence on H(b) and weakening the H(b)–Os interaction. The coupling between H(c) and H(d) is 2.85 Hz which is similar to J(H(b)–H(d)).

The infrared spectrum of this unusual hydrogen-rich species is also interesting. In the carbonyl region, there is an intense absorption at high energy (2101 cm^{-1}), an intense absorption at low energy (1962 cm^{-1}), and a number of intense peaks centered around 2030 cm^{-1}. The high energy peak may be attributed to the relatively high formal oxidation states (+2) of the metals in this trinuclear cluster containing more hydrides than metals. Without isotopic labelling it is not possible to determine whether any of the absorptions are due to a ν(M–H) vibration.

$H_2Os_3(NH)(CO)_9$

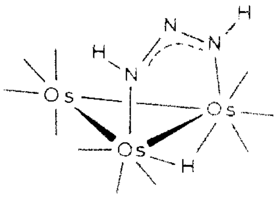
This species was obtained in low yield (10%) from the reaction of $HOs_3(CO)_{10}(NO)$ with molecular H_2. Higher yields (up to 14%) were obtained if the reaction time was decreased to 1.25 h. The formulation of this species was based on electron impact mass spectrometry, elemental analysis, and spectroscopic comparison to structurally characterized $H_2Os_3(NCH_3)(CO)_9$ [16] and $H_2Os_3(NPh)(CO)_9$ [17]. The similarities of the infrared spectrum exhibited by this new imido species and the previously characterized imido species leads to the proposed structure, III, for $H_2Os_3(NH)(CO)_9$.



(III)

$HOs_3(HN_3H)(CO)_{10}$

This cluster containing the μ_2-1,3-triazenido ligand was produced immediately upon addition of excess HN_3 to $H_2Os_3(CO)_{10}$. Electron impact mass spectrometry, elemental analysis, and spectroscopic comparison to the closely related structurally characterized analog $HOs_3(HN_3Ph)(CO)_{10}$, [17] is the basis for the formulation and proposed structure, IV, for $HOs_3(HN_3H)(CO)_{10}$.



(IV)

$HOs_3(CO)_{10}(NO) + H_2$

The reduction of $HOs_3(CO)_{10}(NO)$ with molecular hydrogen proceeded similarly to the reported reduction of $HRu_3(CO)_{10}(NO)$ with H_2. However, a few notable differences between these two reactions are worth mentioning. First, the temperature of the reaction for $HOs_3(CO)_{10}(NO)$ had to be raised to 140°C (compared to 75°C) to obtain rates similar to $HRu_3(CO)_{10}(NO)$. Second, the only precipitate that forms in the osmium reactions is $H_4Os_4(CO)_{12}$, while in the ruthenium reaction a carbonyl-containing species insoluble in hexane and soluble in THF forms along with $H_4Ru_4(CO)_{12}$. And finally, only in the reduction of $HOs_3(CO)_{10}(NO)$ does an unusual hydrogen-rich species form. Equation 1 shows the products formed in this reaction. Within the limitations normally found working with small samples, a reasonable mass balance of osmium is obtained.

$$HOs_3(CO)_{10}(NO) + H_2 \xrightarrow{140^\circ C} HOs_3(NH_2)(CO)_{10} + H_2Os_3(NH)(CO)_9 + H_4Os_3(NH)(CO)_8 + H_4Os_4(CO)_{12} \quad (1)$$

When this reaction was monitored by HPLC and infrared spectroscopy, some knowledge on the sequence of product formation and the disappearance of starting material was gained. The concentration of $HOs_3(CO)_{10}(NO)$ decreased steadily and only trace amounts remained after 245 min at 149°C. $H_2Os_3(NH)(CO)_9$ was the first product to be detected and its concentration increased during the first 80 min of reaction, remained approximately the same for the next 75 min, and then, slowly began to decrease. $HOs_3(NH_2)(CO)_{10}$ was detected shortly after $H_2Os_3(NH)(CO)_9$, and the concentration of this species, as well as $H_4Os_4(CO)_{12}$, increased steadily throughout the reaction. The HPLC peaks for $H_4Os_4(CO)_{12}$ were not reflective of the true concentration due to the low solubility of this species in heptane. However, the aliquots removed initially were clear and grew progressively more cloudy as the reaction proceeded. The precipitate was $H_4Os_4(CO)_{12}$. A very broad peak corresponding to $H_4Os_3(NH)(CO)_8$ was observed 10 min after the $HOs_3(NH_2)(CO)_{10}$ was first detected. The tetrahydrido cluster continued to form as long as some $HOs_3(CO)_{10}(NO)$ or $H_2Os_3(NH)(CO)_9$ remained.

Interconversion of the products under CO or H_2

Three products, $H_2Os_3(NH)(CO)_9$, $H_4Os_3(NH)(CO)_8$, and $HOs_3(NH_2)(CO)_{10}$, have empirical formulae which differ only by 1 molecule of H_2 and 1 or 2 molecules of CO. Interconversions between these products during the reduction are the most likely means for forming $HOs_3(NH_2)(CO)_{10}$ and $H_4Os_3(NH)(CO)_8$. When a pure sample of $H_2Os_3(NH)(CO)_9$ was reacted with 2000 p.s.i. H_2 at 140°C for 2 h, partial conversion to $H_4Os_3(NH)(CO)_8$ occurred, eq. 2.

$$H_2Os_3(NH)(CO)_9 + H_2 \rightleftharpoons H_4Os_3(NH)(CO)_8 + CO \quad (2)$$

The reverse reaction in eq. 2 was partially attained when the tetrahydrido imido species was subjected to 800 p.s.i. CO at 140°C for 0.5 h. Since $H_2Os_3(NH)(CO)_9$ reacts with CO (300 p.s.i.) in 23 h to completely convert to $HOs_3(NH_2)(CO)_{10}$, trace amounts of the amido species were also isolated in the reverse of eq. 2. Attempted conversion of $HOs_3(NH_2)(CO)_{10}$ to either of the imido species by reaction with 2000 p.s.i. H_2 at 140°C for 2 h, led only to partial conversion to $H_4Os_4(CO)_{12}$. A summary of the observed interconversions is shown in eq. 3.

$$H_4Os_3(NH)(CO)_8 \underset{H_2}{\overset{CO}{\rightleftharpoons}} H_2Os_3(NH)(CO)_9 \overset{CO}{\underset{\not\leftarrow}{\rightarrow}} HOs_3(NH_2)(CO)_{10} \qquad (3)$$

The amido species, $HOs_3(NH_2)(CO)_{10}$, can also be synthesized by refluxing the new 1,3-triazenido cluster, $HOs_3(HN_3H)(CO)_{10}$, in hexane, eq. 4.

$$HOs_3(HN_3H)(CO)_{10} \xrightarrow{\Delta} HOs_3(NH_2)(CO)_{10} \qquad (4)$$

Presumably, loss of 1 mol of N_2 accompanies the reaction, although we have not determined this experimentally. In their work on closely related triazine clusters, Burgess et al. found that $HOs_3(HN_3R)(CO)_{10}$ (R = Ph, Me, cyclo-C_6H_{11}, CH_2Ph) converted to the corresponding imido species $H_2Os_3(NR)(CO)_9$ in refluxing DME. None of the amido species $HOs_3(HNR)(CO)_{10}$ was formed [17]. One possible pathway for this conversion is initial formation of an amido cluster followed by further reaction to give the imido cluster. This conversion has been observed for the osmium analogues by Kaesz and coworkers who reported that the pyrolysis of $HOs_3(HNCH_3)(CO)_{10}$ produces $H_2Os_3(NCH_3)(CO)_9$ [18]. An attempt to convert $HOs_3(NH_2)(CO)_{10}$ to $H_2Os_3(NH)(CO)_9$ by heating in refluxing octane for 24 h led only to the production of a hexane, Et_2O, and THF insoluble precipitate with no formation of the imido cluster being observed. It appears that the chemistry for μ_3-NR and μ_2-HNR containing clusters differs if R is a hydrogen or an organic moiety. This feature has also been observed in the analogous ruthenium clusters.

The cleavage of organoimido and organoamido ligands from carbonyl clusters has been reported to give the corresponding amine [19]. While the release of ammonia would appear to be reasonable, we currently have not positively identified it as an eventual reaction product in the reduction of $HOs_3(CO)_{10}(NO)$ with H_2.

Acknowledgement

We gratefully acknowledge the National Science Foundation for supporting this research (Grant No. CHE-8410999). J.A.S. is grateful for a Louise T. Dosdall Fellowship.

References

1 G.R. Steinmetz, E.D. Morrison, and G.L. Geoffroy, J. Am. Chem. Soc., 106 (1984) 2559.
2 M.G. Thomas, W.R. Pretzer, B.F. Beier, F.J. Hirsekorn, and E.L. Muetterties, J. Am. Chem. Soc., 99 (1977) 743.
3 E.L. Muetterties, E. Band, A. Kokorin, W.R. Pretzer, and M.G. Thomas, Inorg. Chem., 19 (1980) 1952.
4 P. Legzdins, C.R. Nurse, and S.J. Rettig, J. Am. Chem. Soc., 105 (1983) 3727.
5 W.L. Gladfelter, in B.L. Shapiro (Ed.), Organometallic Compounds: Synthesis, Structure, and Reactivity, Texas A & M University Press, 1983, p. 281.
6 B.F.G. Johnson, J. Lewis, and J.M. Mace, J. Chem. Soc., Chem. Commun., (1984) 186.
7 R.E. Stevens and W.L. Gladfelter, Inorg. Chem., 22 (1983) 2034.
8 S.A.R. Knox, J.W. Koepke, M.A. Andrews, and H.D. Kaesz, J. Am. Chem. Soc., 97 (1975) 3942.
9 L.F. Fieser and M. Fieser, Reagents for Organic Synthesis, John Wiley and Sons, Inc., 1967, p. 446.
10 H.D. Kaesz, S.A.R. Knox, J.W. Koepke, and R.B. Saillant, J. Chem. Soc., Chem. Commun., (1971) 477.

11 E.G. Bryan, B.F.G. Johnson, and J. Lewis, J. Chem. Soc., Dalton Trans., (1977) 1328.
12 J.A. Smieja, R.E. Stevens, D.E. Fjare, and W.L. Gladfelter, Inorg. Chem., in press.
13 Z. Dawoodi, M.J. Mays, and K. Henrick, J. Chem. Soc., Dalton Trans., (1984) 433.
14 A.J. Deeming and S. Hasso, J. Organomet. Chem., 114 (1976) 313.
15 A.P. Humphries and H.D. Kaesz, Prog. Inorg. Chem., 25 (1979) 145.
16 Y.C. Lin, C.B. Knobler, and H.D. Kaesz, J. Organomet. Chem., 213 (1981) C41.
17 K. Burgess, B.F.G. Johnson, J. Lewis, and P.R. Raithby, J. Organomet. Chem., 224 (1982) C40.
18 Y.C. Lin, C.B. Knobler, and H.D. Kaesz, J. Am. Chem. Soc., 103 (1981) 1216.
19 K. Bhaduri, K.S. Gopalkrishnan, W. Clegg, P.G. Jones, G.M. Sheldrick, and D. Stalke, J. Chem. Soc., Dalton Trans., (1984) 1765.