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Preparation and Characterization of Members of a Homologous Series of Dihydridocarbonyl Compounds of Osmium

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The carbonyl hydrides $H_2[Os(CO)_4]_n$ (n = 1, 2, or 3) have been prepared by the high-pressure carbonylation of osmium tetroxide in the presence of hydrogen. We also present evidence for the formation of $H_2Os_4(CO)_{16}$ in this reaction. The dihydrides $H_2Os_2(CO)_8$ and $H_2Os_3(CO)_{12}$ have also been obtained by the reduction of the dihalides $Os_2X_2(CO)_8$ and $Os_3X_2(CO)_{12}$ (X = Cl or Br). Ir, NMR, and mass spectra are reported and discussed for the compounds, with particular reference to the structures of these hydrides.

Introduction

The preparation of osmium carbonyls by carbonylation of osmium tetroxide was first reported by Hieber and Stallman in 1943.[2] In the preparation of osmium pentacarbonyl, they observed a more volatile component which they assumed to be $H_2Os(CO)_4$, although it was not fully characterized at the time. These reactions were reinvestigated by L'Eplattenier and Calderazzo, who prepared and characterized the pentacarbonyl[3] and later the dihydride, $H_2Os(CO)_4$.[4] More recently, trinuclear $H_2Os_3(CO)_{10}$,[5,6] $H_2Os_3(CO)_{11}$,[7,8] and $HOs_3(CO)_{12}^+$,[9,10] tetranuclear $H_4Os_4(CO)_{12}$[5,6] and $H_2Os_4(CO)_{13}$,[5] pentanuclear $H_2Os_5(CO)_{16}$[11] and $H_2Os_5(CO)_{15}$,[11] and hexanuclear $H_2Os_6(CO)_{18}$[11] have been prepared by a variety of synthetic routes, thus demonstrating the rich carbonyl–hydride chemistry of osmium.

We now report in detail on the preparation and characterization of the new dihydrides $H_2Os_2(CO)_8$ and $H_2Os_3(CO)_{12}$ and present evidence for $H_2Os_4(CO)_{16}$. These hydrides are members of the homologous series $H_2[Os(CO)_4]_n$. We have already reported briefly on these compounds in preliminary communications.[12,13]

Results and Discussion

L'Eplattenier and Calderazzo reported that almost quantitative yields of $H_2Os(CO)_4$ were obtained by the high-pressure carbonylation of osmium tetroxide in the presence of hydrogen.[4] Operating under conditions slightly different from those reported previously[4] and using a longer reaction time, we find that although $H_2Os(CO)_4$ is the main product of this reaction, other products are also formed. Thus after completion of the carbonylation reaction of osmium tetroxide in the presence of hydrogen, the heptane solution of the volatile products was collected in a liquid nitrogen trap. An ir spectrum of this solution in the ν(CO) region showed it to be mainly $H_2Os(CO)_4$ with traces of $Os(CO)_5$, as had been found previously.[4] However, we find an oily solid residue remains in the autoclave, the ir spectrum of which shows many bands in the ν(CO) region. Separation of this mixture by fractional sublimation and recrystallization (see Experimental Section) give the compounds $H_2Os_2(CO)_8$, $H_2Os_3(CO)_{12}$, and $Os_3(CO)_{12}$ and traces of $H_2Os_4(CO)_{16}$.

We also find that the dihydrides $H_2[Os(CO)_4]_n$ (n = 2 or 3) can be prepared by the reduction of the corresponding dihalides $X_2[Os(CO)_4]_n$ (X = Cl or Br). Although this route is of little preparative use for $H_2Os_2(CO)_8$, since the dihalide was itself prepared from the dihydride,[12] we find it to be a useful method for the preparation of the trinuclear hydride $H_2Os_3(CO)_{12}$, since the dihalides $Os_3X_2(CO)_{12}$ (X = Cl or Br) are readily available from the reactions of halogens with $Os_3(CO)_{12}$.[5] Using the reducing agent, sodium borohydride in methanol, only low yields of $H_2Os_3(CO)_{12}$ were obtained from $Os_3X_2(CO)_{12}$. This may be contrasted with the report of other workers who obtained low yields of $HOs_3Cl(CO)_{10}$ by the reduction of $Os_3Cl_2(CO)_{12}$ with sodium borohydride in tetrahydrofuran.[14] We find that use of the reducing system zinc dust/acetic acid/methanol results in good yields of the dihydrides. For example, reduction of $Os_3Br_2(CO)_{12}$ gives 90% yield of $H_2Os_3(CO)_{12}$. A modification of this reduction using acetic-d_4 acid and methanol-d was used to prepare the dideuterides $D_2[Os(CO)_4]_n$ (n = 2 or 3); in the case of $D_2Os_2(CO)_8$, a slightly impure product was obtained even after repeated distillations.

Several routes to the dihydrides $H_2[Os(CO)_4]_n$ (n = 2, 3, or 4) under the reaction conditions in the autoclave seem possible.

(1) Reaction of $H_2Os(CO)_4$ with the Coordinatively Unsaturated Intermediates $Os(CO)_4$ or $H_2Os(CO)_3$.

$$H_2Os(CO)_4 \xrightarrow{Os(CO)_4} H_2Os_2(CO)_8 \xrightarrow{Os(CO)_4} H_2Os_3(CO)_{12}, \text{etc.} \quad (1)$$

$$H_2Os(CO)_4 + H_2Os(CO)_3 \xrightarrow{CO} H_2Os_2(CO)_8 + H_2 \quad (2)$$

Equation 1 involves insertion of $Os(CO)_4$ into osmium–hydrogen bonds and represents the reverse of the reaction we suggested for the thermal decomposition of $H_2Os_3(CO)_{12}$.[13] Recently, it has been shown that the primary product of the thermal decomposition of $H_2Os(CO)_4$ is $H_2Os_2(CO)_8$, eq 2.[15] Under the conditions of the autoclave reaction, $H_2Os(CO)_3$ could be formed from the carbonylation of osmium tetroxide in the presence of hydrogen rather than dissociation of carbon monoxide from $H_2Os(CO)_4$, and $Os(CO)_4$ could be formed directly from the reaction of osmium tetroxide and carbon monoxide.

(2) Reaction of $Os_2(CO)_9$ with Hydrogen.

$$Os_2(CO)_9 + H_2 \rightarrow H_2Os_2(CO)_8 + CO \quad (3)$$

The dinuclear carbonyl $Os_2(CO)_9$ may have a fleeting existence in the autoclave reaction and is presumably an intermediate in the formation of $Os_3(CO)_{12}$ from $Os(CO)_5$. We have isolated $Os_2(CO)_9$[16] and shown that it reacts with hydrogen (30 atm) at room temperature to yield $H_2Os_2(CO)_8$.[17]

(3) Reaction of $Os_3(CO)_{12}$ with Hydrogen by Cleavage of Osmium–Osmium Bonds.

$$Os_3(CO)_{12} \xrightarrow{H_2} H_2Os_3(CO)_{12} \xrightarrow{H_2} H_2Os(CO)_4 + H_2Os_2(CO)_8 \qquad (4)$$

The first step in this reaction is similar to that observed for the reaction of halogens with $Os_3(CO)_{12}$.[5] In a separate experiment, we have shown that hydrogen (30 atm) reacts with $Os_3(CO)_{12}$ at 95 °C to yield $H_2Os_3(CO)_{10}$ but also $H_2Os(CO)_4$ and $H_2Os_2(CO)_8$ as minor products. The reaction of hydrogen (1 atm) at 120 °C has been shown[6] to yield $H_2Os_3(CO)_{10}$ as the main product (73%) and a mechanism has been suggested[8] involving initial dissociation of carbon monoxide from $Os_3(CO)_{12}$. Under a high pressure of carbon monoxide, cleavage of an osmium–osmium bond in $Os_3(CO)_{12}$ by hydrogen may be more favorable than dissociation of carbon monoxide. It is not surprising that neither $H_2Os_3(CO)_{11}$ nor $H_2Os_3(CO)_{10}$ was observed as a product in the autoclave reactions since it has been shown that these hydrides react with carbon monoxide to yield $Os_3(CO)_{12}$.[7,8] It is possible that more than one reaction pathway may lead to the observed dihydrides in the autoclave reactions.

The hydrides of the series $H_2[Os(CO)_4]_n$ (n = 1–4) are all air stable and have high thermal stability. The great contrast between the thermal stability of $H_2Os(CO)_4$ and the instabilities of $H_2Fe(CO)_4$ and $H_2Ru(CO)_4$ has been noted.[18] Although no ruthenium analogue of $H_2Os_2(CO)_8$ has been prepared, the iron analogue $H_2Fe_2(CO)_8$ has been reported although not fully characterized.[19] In the trinuclear series, $H_2Fe_3(CO)_{12}$ and $H_2Ru_3(CO)_{12}$ have been suggested[18] as possible decomposition products of $H_2M(CO)_4$ (M = Fe[20] or Ru[18]). Both compounds are red, unstable, and not fully characterized. On the other hand, $H_2Os_3(CO)_{12}$ is air stable, can be heated to its melting point of 95 °C without appreciable decomposition, and can be sublimed unchanged.

Members of the series $H_2[Os(CO)_4]_n$ behave as expected for a homologous series; thus as n increases, the melting point increases and solubility decreases. At room temperature, $H_2Os(CO)_4$ is a volatile liquid, $H_2Os_2(CO)_8$ an oil, and $H_2Os_3(CO)_{12}$ a solid. The chemical properties, however, remain similar. Thus all readily react with carbon tetrahalides to give the corresponding dihalides.[4,12,13]

Mass Spectra of $H_2[Os(CO)_4]_n$. The mass spectra of the hydrides $H_2[Os(CO)_4]_n$ (n = 1–4) were recorded as part of their characterization. The value of n in this series of hydrides is readily found by comparison of calculated and observed mass spectra.[21]

The mass spectrum of $H_2Os(CO)_4$[22] shows no parent molecular ion. This contrasts with the mass spectra of other mononuclear hydrides, for example, $HRe(CO)_5$, $HMn(CO)_5$, and $HCo(CO)_4$,[23] and also other dihydrides of the series $H_2[Os(CO)_4]_n$ (n = 2–4), where a parent molecular ion is observed in every case. We have analyzed the highest m/e ion in the spectrum of $H_2Os(CO)_4$, nominally $Os(CO)_4$, with the aid of a computer program[24] and find that this peak is composed of 95.7% $Os(CO)_4$ and 4.3% $HOs(CO)_4$ (standard deviations are less than 1%). Doubly charged ions of the series $[Os(CO)_m]^{2+}$ (m = 0–4) were also observed in fairly high abundances in the mass spectrum of $H_2Os(CO)_4$.

As stated previously, a parent molecular ion was observed in every case for the polynuclear hydrides $H_2[Os(CO)_4]_n$ (n = 2–4). Nevertheless, there was significant hydrogen loss from the parent molecular ion which was not apparent from a visual comparison of observed and calculated intensities for the ion. However, a computer analysis[24] of the parent ions in the mass spectra made it possible to determine with reasonable accuracy the contributions of P^+, $[P - H]^+$, and $[P - 2H]^+$ to the observed patterns. A similar analysis has recently been made for some other metal carbonyl hydrides.[6] The difficulty associated with visual estimation of hydrogen loss in a complex pattern is shown in Figure A[33] for the parent ion of $H_2Os_2(CO)_8$. The extent of hydrogen loss from the parent ions of $H_2[Os(CO)_4]_n$ (n = 2–4) is shown in Table I. An analysis of the parent ion of the compound $H_2Os_3(CO)_{10}$, where the hydrogen atoms have been shown to occupy bridging positions,[25] was undertaken for comparison. The results of our analysis of this ion (see Table I) are in good agreement with those recently reported.[6] It can be seen that the hydrogen loss for the trinuclear compound with terminal Os–H bonds (i.e., $H_2Os_3(CO)_{12}$) is only slightly greater than the trinuclear compound with bridging hydrides (i.e., $H_2Os_3(CO)_{10}$). Thus in these polynuclear compounds it would appear difficult to differentiate between bridging and terminal hydrides merely on the basis of mass spectral data.

Table I. Computer Analysis[24] of the Patterns Observed for the Parent Molecular Ion of Some Polynuclear Osmium Carbonyl Hydrides[a]

Compd	% P	% P − H	% P − 2H
$H_2Os_2(CO)_8$	83.4 (0.4)	0.4 (0.4)	16.2 (0.5)
$H_2Os_3(CO)_{12}$	88 (2)	4 (2)	8 (2)
$H_2Os_3(CO)_{10}$	94 (1)	3 (1)	3 (1)
$H_2Os_4(CO)_{16}$	84 (4)	0	16 (4)

[a] Standard deviations are given in parentheses.

Table II. Nuclear Magnetic Resonance Data

Compd	τ for high-field protons	Solvent
$H_2Os(CO)_4$	18.70	Benzene
	18.73[a]	Heptane
$H_2Os_2(CO)_8$	20.11	Benzene
	20.05	Heptane
	20.15	CH_2Cl_2
$H_2Os_3(CO)_{12}$	19.85	Benzene
$H_2Os_4(CO)_{16}$	19.77	Benzene

[a] Data from ref 4.

In the mass spectrum of $H_2Os_2(CO)_8$, weak $[Os(CO)_m]^+$ (m = 0–4) ions and very weak doubly charged ions $[Os_2(CO)_m]^{2+}$ (m = 0–7) are observed; see Table A.[33] For $H_2Os_3(CO)_{12}$, mononuclear $[Os(CO)_m]^+$ (m = 0–4) and dinuclear $[Os_2(CO)_n]^+$ (n = 0–6) fragments are observed (Table B[33]) suggesting[5] that this compound does not have a triangulo structure. For $H_2Os_4(CO)_{16}$, there was again significant hydrogen loss from the parent ion. Due to the presence of $Os_3(CO)_{12}$ in the sample, the lower mass range of the spectrum was not studied in detail.

For these polynuclear carbonyl hydrides, there is a tendency for hydrogen to be lost in pairs (see Table I). This behavior has also been observed for some silyl–transition metal hydrides and $H_2Re_2(CO)_8$.[26]

NMR Spectra. The ^1H NMR spectra of the hydrides $H_2[Os(CO)_4]_n$ (n = 1–4) all show a sharp singlet in the high-field region (see Table II) in agreement with structures having equivalent hydride ligands. The possibility that some rapid exchange process makes the hydrogens appear equivalent at room temperature seems unlikely since the spectrum of $H_2Os_2(CO)_8$ remained as a sharp singlet at −80 °C. For the complex $H_2Os_3(CO)_{11}$, which has a bridging and a terminal hydride ligand, two high-field signals were observed at low temperature.[7,8] The hydrogen content of $H_2Os_2(CO)_8$ was confirmed by an integration of the high-field NMR signals of an equimolar mixture of $H_2Os_2(CO)_8$ and $H_2Re_2(CO)_8$[27] which showed the areas of the signals to be in the ratio 1:1.

Infrared Spectra. The ir spectra of $H_2Os_2(CO)_8$ and $H_2Os_3(CO)_{12}$ were examined in some detail in the region

Table III. Infrared Carbonyl and Metal–Hydrogen Stretching Vibrations (cm^{-1})[a]

Compd	Solvent	ν(CO)	ν(Os–H) or ν(Os–D)
$H_2Os_2(CO)_8$	Heptane	2132 vw, 2093 s, 2057 vs, 2039 vs, 2033 s, 2023 sh, 2020 s, 1998 vw, 1988 vw	1956 w, br
	C_6D_6	2131 w, 2092 s, 2055 vs, 2035 vs, 2015 s	1955 w, br
$D_2Os_2(CO)_8$	Heptane	2131 vw, 2090 s, 2048 sh, 2046 vs, 2039 vs, 2033 s, 2024 s, 2022 sh, 2007 s, 1987 vw, 1979 vw	
	C_6D_6	2130 vw, 2090 s, 2044 vs, 2033 vs, 2020 s, 2003 m	1428 vw, sh 1414 vw, br
$H_2Os_3(CO)_{12}$	Heptane	2135 vw, 2100 s, 2070 w, 2053 s, 2044 sh, 2038 s, 2030 vs, 2022 s, 2003 sh, 1995 m, 1991 sh	1955 w, br
	C_6D_6	2134 vw, 2100 s, 2069 w, 2052 s, 2028 vs, br, 1990 m	1957 w, br
	CH_2Cl_2	2134 vw, 2100 s, 2070 w, 2053 s, 2031 vs, br, 1992 m	
$D_2Os_3(CO)_{12}$	Heptane	2134 vw, 2097 s, 2068 w, 2042 vs, 2038 sh, 2031 s, 2015 s, 2002 sh, 1993 m, 1989 sh	
	C_6D_6	2134 vw, 2097 s, 2068 w, 2040 vs, 2029 sh, 2012 s, 1987 m	1424 vw, sh 1407 vw, br
	CH_2Cl_2	2134 vw, 2098 s, 2067 sh, 2040 vs, 2030 sh, 2011 s, 1988 m	

[a] Key: sh, shoulder; w, weak; m, medium; s, strong; v, very; br, broad.

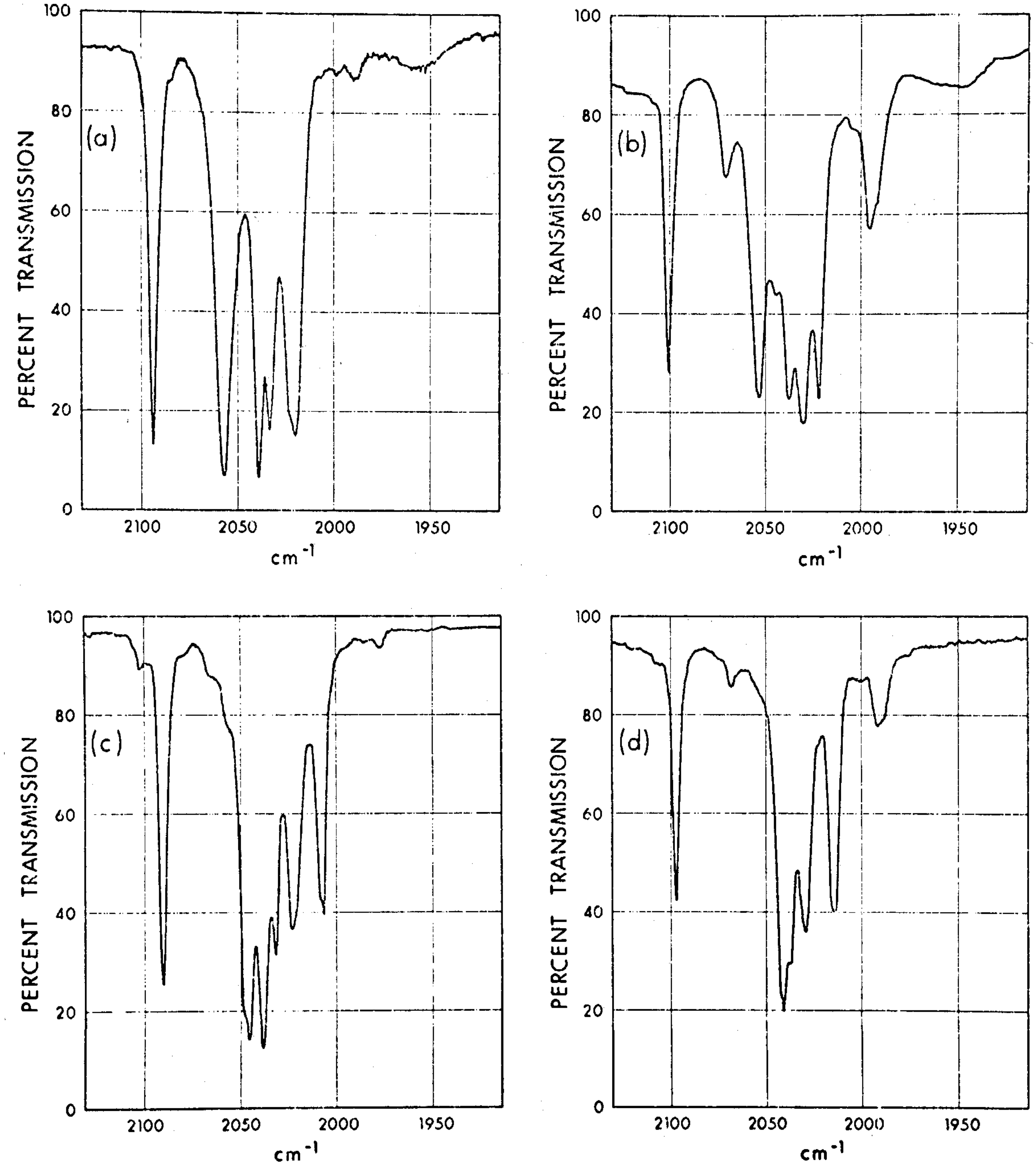
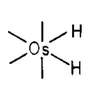


Figure 1. Infrared spectra in *n*-heptane solutions of (a) $H_2Os_2(CO)_8$, (b) $H_2Os_3(CO)_{12}$, (c) $D_2Os_2(CO)_8$, and (d) $D_2Os_3(CO)_{12}$.

2200–1300 cm^{-1} (see Table III). Both complexes show many bands in the terminal ν(CO) region in *n*-heptane solution (Figure 1) consistent with structures of low symmetry. The ir spectra of the corresponding deuterides show large shifts for some of the carbonyl bands. Such shifts have also been observed for $H_2Os(CO)_4$,[4] $H_2Os_3(CO)_{11}$,[8] and the corresponding deuterides, and imply an interaction between ν(CO) and ν(M–H(or D)). This is further borne out by the weak, broad ν(Os–H(or D)) bands which are observed for these compounds (Table III and Figure 1).

General Structural Considerations. The cis configuration **1** for the first member of the series, $H_2Os(CO)_4$, has been established.[4] For higher homologues of the series $H_2[Os(CO)_4]_n$ (n = 2–4), the assumption that the hydride ligands are terminal is based on the following evidence.

(1) The high-field signals for the hydride ligands are observed in a position similar to that for $H_2Os(CO)_4$ (τ 18.70 in benzene). The signals for bridging hydrides often occur at considerably higher τ values,[28] although this is not always the case. For example the high-field signal for $H_2Os_3(CO)_{10}$ occurs at τ 21.6 (benzene)[5] and x-ray structural evidence suggests that the hydride ligands in this compound occupy bridging positions.[25]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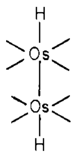
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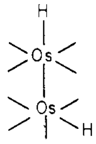
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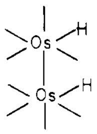
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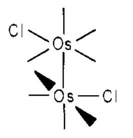
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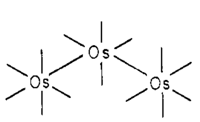
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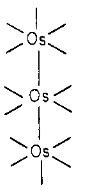
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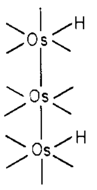
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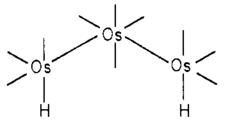
3d

(2) Osmium–hydrogen stretching frequencies are observed in the infrared region, in positions similar to those of $H_2Os(CO)_4$[4] and other mononuclear carbonyl hydrides.[28]

(3) The hydrides react rapidly and almost quantitatively with carbon tetrahalides to give the corresponding dihalides.[12,13] This reaction is characteristic of many terminal metal–hydrogen bonds.[29] These osmium carbonyl dihydrides are thus rare examples of a series of polynuclear carbonyl hydrides which contain terminal metal–hydrogen bonds.

For $H_2Os_2(CO)_8$, there are three possible structures.[30] **2a** and **2b** are unlikely on ir and NMR evidence respectively, which leaves **2c** or one of its conformers as the most probable structure. Further evidence for this structure is provided by an x-ray structural determination of $Os_2Cl_2(CO)_8$,[31] which has been shown to have structure **2d** in the crystal. Since the ir spectra of $H_2Os_2(CO)_8$ and $Os_2Cl_2(CO)_8$ in the ν(CO) region are similar and if we can assume that no configurational changes occur on reaction of $H_2Os_2(CO)_8$ with carbon tetrachloride, we might expect the dihydride to have a similar structure to the dichloride.

If we can disregard a triangulo structure for $H_2Os_3(CO)_{12}$ on the basis of the effective atomic number rule, two metal frameworks **3a** and **3b** remain as possibilities. If we then consider, on the NMR evidence, only those structures having two equivalent hydrogens, four possible structures remain. The structure based on the linear framework **3b** with axial hydrogens may be excluded on ir evidence. The structure based on framework **3a** with hydrogens trans to the osmium–osmium bonds is perhaps unlikely by analogy with $H_2Os_2(CO)_8$. Structures **3c** and **3d** are the most reasonable alternatives. An x-ray crystallographic determination of $Os_3I_2(CO)_{12}$ has shown that this compound has a structure which is a conformer of **3c**.[32]

Experimental Section

Osmium tetroxide was purchased from Engelhard Industries, Newark, N.J. The compounds $Os_3X_2(CO)_{12}$ (X = Cl or Br) were prepared by the methods of Johnson et al.[5] All solvents used were of reagent grade. All reactions, other than the high-pressure reactions, were carried out under an atmosphere of nitrogen. Melting points were determined on a Kofler hot-stage apparatus.

Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrophotometer and recorded in expanded form on a Hewlett-Packard 7127A recorder; spectra were calibrated with gaseous carbon monoxide. NMR measurements were made on Varian Associates A56/60 and HA100 instruments; chemical shifts are relative to tetramethylsilane (τ 10.00). Mass spectra were obtained using Associated Electrical Industries MS-9 and MS-12 instruments using an ionizing voltage of 70 eV. Samples were introduced by direct insertion of the solid sample at temperatures just sufficient to produce the spectrum, except where otherwise stated. Mass spectra were interpreted with the aid of a computer program which calculated exact masses and isotope combination patterns.[21] Exact masses were determined on the most abundant peak of the parent molecular ion.

Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany, by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and by the microanalytical laboratory of this department.

Carbonylation of Osmium Tetroxide in the Presence of Hydrogen. A 480-ml stainless steel rocking autoclave was charged with osmium tetroxide (5.0 g, 19.7 mmol), n-heptane (150 ml), hydrogen (37 atm), and carbon monoxide (140 atm). The autoclave was heated at 160–170 °C for 9 h and allowed to cool and the gases were vented. The volatile products and heptane were condensed in vacuo into a liquid nitrogen cooled trap and the colorless solution thus obtained was shown to contain mainly $H_2Os(CO)_4$ by its infrared spectrum.[3] Traces of osmium pentacarbonyl were also present. The yield of $H_2Os(CO)_4$ (2.2 g, 40%) was estimated after conversion by carbon tetrabromide of an aliquot of the $H_2Os(CO)_4$ solution to the solid $OsBr_2(CO)_4$[4] which was subsequently weighed.

The oily yellow solid and black residue remaining in the autoclave were transferred with hexane (30 ml) to a modified Hickman still. The hexane was removed under reduced pressure and the residue distilled (40 °C (0.01 mm)). The colorless oil which condensed on the probe was allowed to drip into the receiver to give dihydridooctacarbonyldiosmium, $H_2Os_2(CO)_8$ (1.24 g, 21%). The oil was purified by redistillation in the same apparatus. Anal. Calcd for $C_8H_2O_8Os_2$: C, 15.84; O, 21.10; Os, 62.71; mol wt 607.895. Found: C, 16.10; O, 20.54; Os, 60.99; mol wt (mass spectrometrically) 607.889.

The solid residue remaining after removal of $H_2Os_2(CO)_8$ was extracted with hexane (3 × 10 ml) and filtered. The hexane was removed under reduced pressure leaving a pale yellow solid (0.36 g; 6%) whose ir, NMR, and mass spectra were identical with those of an authentic sample of dihydridododecacarbonyltriosmium, $H_2Os_3(CO)_{12}$. The sample was purified by several recrystallizations from hexane. Traces of $H_2Os_4(CO)_{16}$ were detected in the hexane extracts by ir and mass spectroscopy.

The solid remaining after removal of the $H_2Os_3(CO)_{12}$ consisted of yellow crystals and a black residue. This was sublimed at 125 °C (0.01 mm) to give yellow $Os_3(CO)_{12}$ (0.89 g, 15%) leaving a black solid (0.53 g) which is presumably lower oxides of osmium and osmium metal.

Preparation of $H_2Os_3(CO)_{12}$ from $Os_3Br_2(CO)_{12}$. $Os_3Br_2(CO)_{12}$ (0.20 g) as a suspension in methanol (20 ml) was refluxed under nitrogen for 25 min with zinc dust (0.60 g) and glacial acetic acid (0.10 g). The solvent was removed under reduced pressure, the residue extracted with n-pentane (2 × 25 ml) and filtered, and the pentane was removed under reduced pressure leaving a very pale yellow crystalline solid (0.15 g, 90%). The product was purified by sublimation (80 °C (0.01 mm)) to give dihydridododecacarbonyltriosmium, $H_2Os_3(CO)_{12}$, mp 95–98 °C. Anal. Calcd for $C_{12}H_2O_{12}Os_3$: C, 15.86; H, 0.22; O, 21.13; mol wt 909.834. Found: C, 15.86; H, 0.83; O, 21.07; mol wt (mass spectrometrically) 909.828.

Dideuteriododecacarbonyltriosmium. $Os_3Br_2(CO)_{12}$ (0.16 g) as a suspension in C_2H_5OD (7.5 ml) was refluxed under nitrogen for 15 min with zinc dust (0.23 g) and CD_3COOD (0.05 g). The solvent was removed under reduced pressure, the residue was extracted with *n*-pentane (2 × 25 ml) and filtered, and the pentane was removed under reduced pressure to give $D_2Os_3(CO)_{12}$ as a pale yellow crystalline solid (0.086 g, 63%). The product was purified by sublimation (70 °C (0.01 mm)); mp 92–97 °C. Anal. Calcd for $C_{12}D_2O_{12}Os_3$: C, 15.83; D, 0.44; O, 21.09; mol wt 911.846. Found: C, 15.93; D, 0.83; O, 21.24; mol wt (mass spectrometrically) 911.843.

Dideuteriooctacarbonyldiosmium. $Os_2Cl_2(CO)_8$ (0.14 g) as a suspension in CH_3OD (8 ml) was refluxed under nitrogen for 10 min with zinc dust (0.23 g) and CH_3COOD (0.05 g). The solvent was removed under reduced pressure, the residue was extracted with pentane (2 × 30 ml) and filtered, and the pentane was removed under reduced pressure leaving the product as a pale yellow oil (0.06 g, 48%). The product was purified by condensation onto a water-cooled probe (30 °C (0.01 mm)) and identified mass spectrometrically (mol wt: calcd for $C_8D_2O_8Os_2$, 609.908; found, 609.909).

Reaction of $Os_3(CO)_{12}$ with Hydrogen. A 200-ml autoclave was charged with triosmium dodecacarbonyl (0.24 g), *n*-heptane (15 ml), and hydrogen (33 atm) and heated with magnetic stirring at 95 °C for 67 h. After the bomb was cooled and the gases were vented, the ir spectrum of the reaction solution showed the main product to be $H_2Os_3(CO)_{10}$ together with $H_2Os_2(CO)_8$, $H_2Os(CO)_4$, and unreacted $Os_3(CO)_{12}$. The solvent and $H_2Os(CO)_4$ were removed under reduced pressure and the residue was recrystallized several times from pentane to give a low yield of red crystals whose ir spectrum was identical with that of an authentic sample of $H_2Os_3(CO)_{10}$.[5,6] A molecular ion was observed in the mass spectrum.

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Registry No. $H_2Os_2(CO)_8$, 25685-05-6; $H_2Os_3(CO)_{12}$, 60645-64-9; $H_2Os_3(CO)_{10}$, 11063-23-3; $H_2Os_4(CO)_{16}$, 60645-65-0; $H_2Os(CO)_4$, 18972-42-4; $D_2Os_2(CO)_8$, 60645-66-1; $D_2Os_3(CO)_{12}$, 60645-67-2; OsO_4, 20816-12-0; $Os_3Br_2(CO)_{12}$, 21773-71-7; $Os_2Cl_2(CO)_8$, 25685-06-7; $Os_3(CO)_{12}$, 15696-40-9.

Supplementary Material Available: Tables A and B and Figure A, all showing mass spectra (4 pages). Ordering information is given on any current masthead page.

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Mass Spectra of Organometallic Compounds. 4. Electron-Impact Study of Some Cyclopentadienylmetal Carbonyl Dimers

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The mass spectra of the cyclopentadienylmetal carbonyl dimers $[QCr(CO)_2]_2$ ($Q = C_5H_5, C_5Me_5$), $[C_5H_5Fe(CO)_2]_2$, and $[C_5H_5Ni(CO)]_2$ have been examined and the appearance potentials of most of the metal-containing fragment ions, those with all ligands, determined. The primary fragmentations in the mass spectra of these complexes have been assigned and compared.

Introduction

Despite the large volume of mass spectral data on organometallic compounds,[1] relatively little has so far been done to confirm proposed fragmentation schemes. In general, metastable transitions, few of which are normally found in most mass spectra of organometallic compounds, do provide positive proof of specific fragmentations. However, these specific fragmentations are not necessarily the main sources of ions. Useful information for the assignment of fragmentations can be obtained from appearance potential data. Generally, under electron-impact conditions most organometallic ions exhibit one detectable appearance potential and this probably suggests the existence of a single primary precursor for each of the ions. Predominant processes by which fragment ions are produced will henceforth be referred to as primary fragmentations. In a primary fragmentation sequence,