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SYNTHESES OF ANIONIC DERIVATIVES OF $H_2Os_3(CO)_{10}$

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Summary

A number of anionic adducts of $H_2Os_3(CO)_{10}$ have been prepared. Potassium hydride reacts with $H_2Os_3(CO)_{10}$ in a 1 : 1 molar ratio in THF to yield $K[H_3Os_3(CO)_{10}]$. When a 2 : 1 molar ratio of KH to $H_2Os_3(CO)_{10}$ is employed, one mole of H_2 is given off and $K_2[H_2Os_3(CO)_{10}]$ is formed. Effectively two electrons have added to $H_2Os_3(CO)_{10}$. In the presence of an electron carrier, $(C_6H_5)_2CO$, potassium reacts with $H_2Os_3(CO)_{10}$ to give $K_2[H_2Os_3(CO)_{10}]$ which is spectroscopically identical to $K_2[H_2Os_3(CO)_{10}]$ obtained from the reaction of 2 KH with 1 $H_2Os_3(CO)_{10}$. Halide ions as $[(C_6H_5)_3P]_2N^+$ salts readily add to $H_2Os_3(CO)_{10}$, forming $[H_2Os_3(CO)_{10}X]^-$, where $X^- = Cl^-, Br^-$, and I^-. Metallocarbonylates react with $H_2Os_3(CO)_{10}$ in a manner analogous to the reaction of halide ions with this cluster. The following mixed metal ions have been prepared: $[H_2Os_3(CO)_{10}Mn(CO)_5]^-$, $[H_2Os_3(CO)_{10}Fe(CO)_4]^{2-}$, $[H_2Os_3(CO)_{10}Mo(\eta^5\text{-}C_5H_5)(CO)_3]^-$, $[H_2Os_3(CO)_{10}V(\eta^5\text{-}C_5H_5)(CO)_3]^{2-}$, and $[H_2Os_3(CO)_{10}Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$.

Introduction

The molecule $H_2Os_3(CO)_{10}$ is a triangular cluster in which two osmiums are doubly hydrogen bridged with a bridge above and a bridge below the Os_3 plane [1]. This compound is electronically unsaturated, containing 46 valence electrons instead of the usual 48 electrons associated with a triangular cluster of the iron triad [2]. A number of reactions are known which are based upon the unsaturated character of this compound [3].

One type of reaction is the addition of a neutral two-electron donor, L, to form $H_2Os_3(CO)_{10}L$ [4]. Upon adding to the cluster, the Lewis base L displaces a bridging hydrogen to a terminal site. In the present study we have examined reactions of anionic Lewis bases with $H_2Os_3(CO)_{10}$. These bases include hydride ion (H^-), halide ions (Cl^-, Br^-, and I^-), and metallocarbonylates $[Mn(CO)_5]^-$, $[Fe(CO)_4]^{2-}$, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$, and $[(\eta^5\text{-}C_5H_5)V(CO)_3]^{2-}$.

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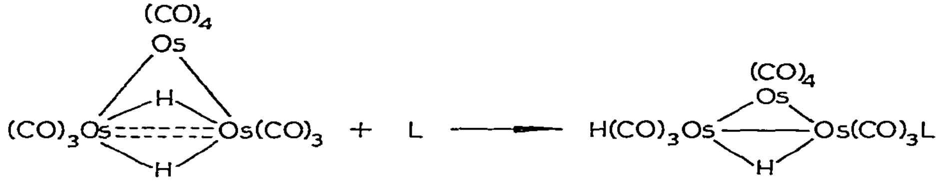


$L = CO, PR_3, CNR$ (1)

Results and discussion

A. Reactions of hydride ion with $H_2Os_3(CO)_{10}$

1. Formation of $K[H_2Os_3(CO)_{10}]$. Potassium hydride, KH, serves as a deprotonating agent for the hydrido metal carbonyl cluster, $H_4Ru_4(CO)_{12}$ [5], and boron hydrides in general [6]. In its reaction with $H_2Os_3(CO)_{10}$, the possibility was considered that KH might function similarly as a Brönsted base by abstracting a bridge proton from the cluster. On the other hand it could function as a Lewis base through the addition of hydride ion. Proton abstraction would generate an unsaturated anion, $HOs_3(CO)_{10}^-$, while hydride addition might occur at an osmium center to form $H_3Os_3(CO)_{10}^-$ the analogue of $H_2Os_3(CO)_{10}L$, or it could add to a carbon center to give $H_2Os_3(CO)_9(CHO)^-$, an anion which contains the formyl group. Examples of metal carbonyl clusters [7] and mono- and dinuclear carbonyl complexes [8] which contain the formyl group are known. We find that hydride ion adds to the cluster. A metal—hydrogen bond is formed. There is no spectroscopic evidence for the formation of a formyl group under the experimental conditions employed.

Equimolar amounts of KH and $H_2Os_3(CO)_{10}$ react at 0°C in tetrahydrofuran (THF) to form a dark brown-yellow solution. Over a period of approximately four hours, all traces of the relatively insoluble KH disappear, and only a trace amount (<5%) of non-condensible gas (CO/H_2) is evolved. Hydride ion adds to $H_2Os_3(CO)_{10}$ according to eq. 2.

$$H_2Os_3(CO)_{10} + KH \xrightarrow{THF, 0^\circ C} K[H_3Os_3(CO)_{10}] \qquad (2)$$

The formation of $K[H_3Os_3(CO)_{10}]$ appears to be quantitative by NMR spectroscopy; however, this compound is not readily isolated as a solid. It decomposes to a number of different species if it is allowed to remain in solution at room temperature.

Infrared and low temperature ^{13}C NMR spectra of $K[H_3Os_3(CO)_{10}]$ suggest that only terminal carbonyl groups are present. The ^{13}C NMR spectrum is too complicated to aid further in assigning a structure to $K[H_3Os_3(CO)_{10}]$. (See Experimental section.) At room temperature the proton NMR spectrum of $K[H_3Os_3(CO)_{10}]$ consists of a single signal at 23.56 τ. Coupled and selectivity decoupled ^1H NMR spectra obtained in THF at −80°C clearly indicate the presence of two isomers (See Fig. 1.)

One isomer contains a bridging hydrogen and two equivalent terminal hydrogens while the other isomer contains a bridging hydrogen and two non-equivalent terminal hydrogens. The ratio of isomers is about 2 : 1 with the isomer of higher symmetry being predominant. One of the several possible structures for

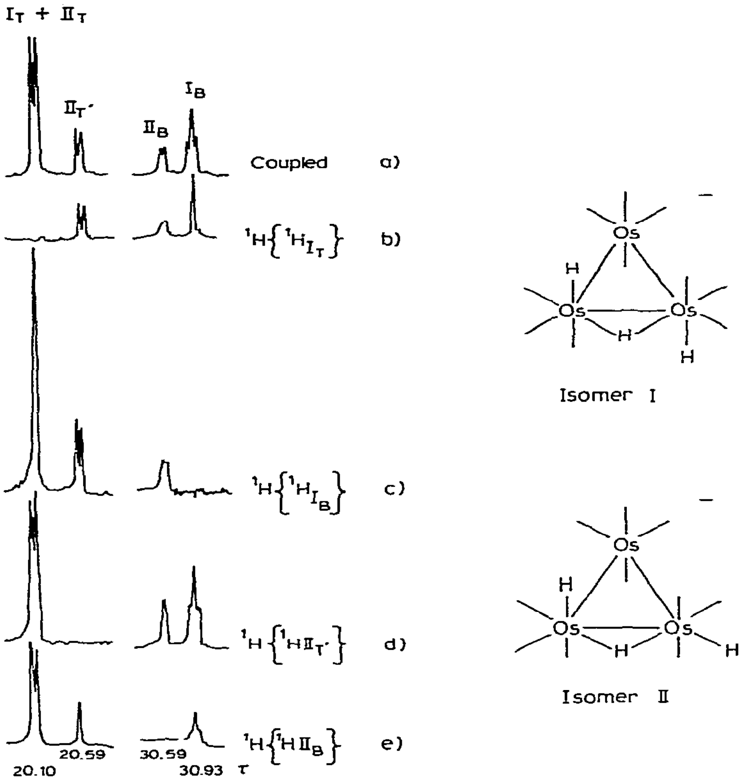


Fig. 1. Coupled and selectively decoupled ^1H NMR spectra of $K[H_3Os_3(CO)_{10}]$ in THF at —80°C. Possible structures of isomers I and II.

each isomer is shown in Fig. 1. Although the chemical shifts permit a distinction to be made between terminal and bridging hydrogens, axial and equatorial terminal hydrogens cannot be assigned on the basis of the available data.

The coupled spectrum (Fig. 1a) is resolved into four components reflecting conditions of slow exchange and indicating the presence of the two isomers. Signals with subscript B have chemical shifts in the region associated with bridging hydrogens while the signals with subscript T appear in the region usually associated with terminal hydrogens. Selective decoupling, $^1H\{^1H\}$, of the multiplets (J = 3.9 Hz) permits the hydrogens to be assigned to their respective isomers. The first set of decoupled spectra (Fig. 1b, c) corresponds to irradiation of the sample at the frequencies of the signals from isomer I which are labeled I_T and I_B respectively. It is apparent that this isomer has two equivalent terminal hydrogen signals which are coupled to the bridge hydrogen resonance. The ratio of areas of I_T to I_B being greater than 2 : 1 and the presence of only one terminal signal for isomer II imply that the second terminal signal of isomer II is obscured by I_T. Therefore the lowest field doublet is noted as $I_T + II_T$. The second set of decoupled spectra (Fig. 1d, e) represents irradiation at the frequencies II'_T, and II_B, respectively. These spectra show that these signals are indeed coupled to each other. The broad appearance of II_B may indicate that

II_T is coupled to II_B with a small coupling constant.

2. Formation of $K_2[H_2Os_3(CO)_{10}]$. When KH and $H_2Os_3(CO)_{10}$ are allowed to react in a 2 : 1 molar ratio at 0°C in THF only one hydride adds to the osmium cluster as indicated by eq. 2. On warming this system to room temperature, the second mole of KH reacts with $K[H_3Os_3(CO)_{10}]$ to give a red solution along with one mole of H_2 gas. The net reaction represented by eq. 3 is complete in 6—7 hours.

$$2\ KH + H_2Os_3(CO)_{10} \xrightarrow{THF, RT} K_2[H_2Os_3(CO)_{10}] + H_2 \qquad (3)$$

Hydrogen evolution is quanitative; its purity (95%) was determined by mass spectrometry. The overall reaction involves the addition of two electrons to $H_2Os_3(CO)_{10}$. This suggests that an alternate route to form $K_2[H_2Os_3(CO)_{10}]$ would be the reduction of $H_2Os_3(CO)_{10}$ by an alkali metal in the presence of an electron carrier. Such a reaction has been observed and is described below.

B. Two-electron reduction of $H_2Os_3(CO)_{10}$ by potassium to form $K_2[H_2Os_3(CO)_{10}]$

Benzophenone ketyl and $H_2Os_3(CO)_{10}$ react as shown in eq. 4.

$$2\ K[(C_6H_5)_2CO] + H_2Os_3(CO)_{10} \xrightarrow{THF, 0^\circ C} K_2[H_2Os_3(CO)_{10}] + 2(C_6H_5)_2CO \qquad (4)$$

This reaction occurs rapidly (approximately 10 min) in THF at 0°C. Infrared and NMR spectra show that the products formed by reactions 3 and 4 are identical.

Carbon-13 NMR spectra at —90°C and room-temperature infrared spectra of $K_2[H_2Os_3(CO)_{10}]$ imply that bridging carbonyls are present, as indicated by a pair of low-field signals (274.0 and 270.4 ppm) and by absorptions at 1660 and 1621 cm^{-1} (See Experimental section).

Proton NMR spectra of $K_2[H_2Os_3(CO)_{10}]$ taken over a range of temperatures are shown in Fig. 2. These spectra reveal that $K_2[H_2Os_3(CO)_{10}]$, like $K[H_3Os_3(CO)_{10}]$, exists in two isomeric forms under conditions of slow exchange. At 0°C, only one sharp resonance at 23.04 τ is observed. As the temperature is lowered, this signal broadens, and at —70°C two sharp signals of equal intensity at 22.57 and 24.05 τ rise from the baseline. These signals are assigned to two nonequivalent hydrogens in isomer I of $K_2[H_2Os_3(CO)_{10}]$. Additionally, as the temperature is lowered, a second set of equally intense signals at 21.39 and 24.30 τ rises from the baseline. These resonances do not sharpen as much as the first pair, even on cooling the sample to —95°C. These signals are assigned to isomer II of $K_2[H_2Os_3(CO)_{10}]$.

The substantial difference in temperature at which the exchange of hydrogens is slowed in the isomers is significant. For this reason, the general structures shown in Fig. 2 have been proposed. The greater separation of the hydrogens of isomer I could account for the fact that exchange of hydrogens within isomer I is slowed at a higher temperature. In the case of isomer II, which is suggested to have a terminal hydrogen on an osmium in the bridging system, exchange could be more facile.

The chemical shifts of the hydrogens in $K_2[H_2Os_3(CO)_{10}]$ do not fall in

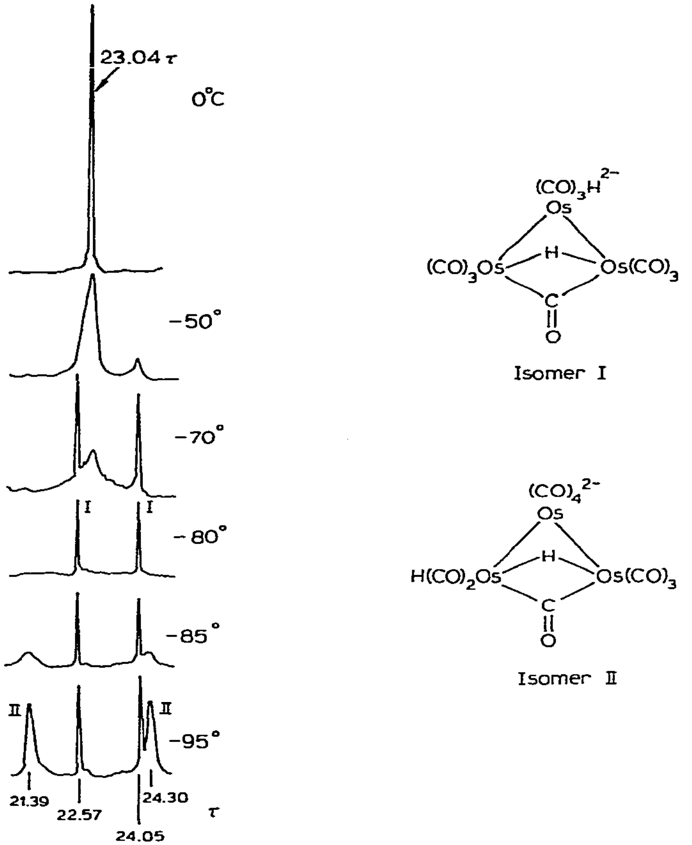
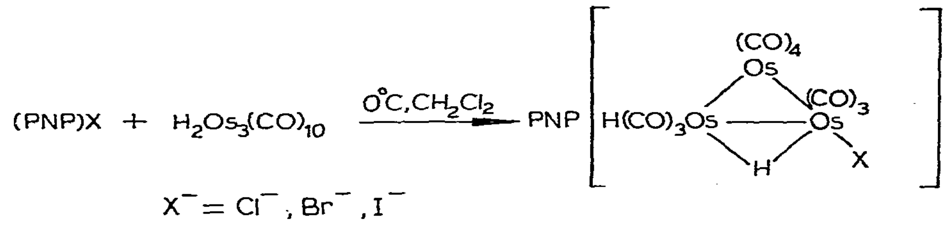


Fig. 2. Variable temperature ^1H NMR spectra of $K_2[H_2Os_3(CO)_{10}]$ in THF. Possible structures of isomers I and II.

regions where they can be clearly assigned at bridging or terminal sites. However, it seems reasonable to assume that the lower field signals correspond to the terminal hydrogens and the signals at higher field correspond to the bridging hydrogens. Preparation of $K_2[H_2Os_3(CO)_{10}]$ represents the first example of a triosmium cluster dianion. The salt $K_2[H_2Os_3(CO)_{10}]$ can be isolated as a solid in 80—85% yield, and represents a potentially important reagent in the formation of mixed-metal clusters. However, its chemistry must be approached with caution. When metathesis reactions with tetraphenylphosphonium bromide were attempted at 0°C in CH_2Cl_2/THF, $H_2Os_3(CO)_{10}^{2-}$ disproportionated into $H_2Os_4(CO)_{12}^{2-}$.

C. Reactions of halide ions with $H_2Os_3(CO)_{10}$

The halide ions, chloride, bromide, and iodide as bis-(triphenylphosphine)-iminium (PNP) salts, react readily with $H_2Os_3(CO)_{10}$ in dichloromethane at 0°C. In these reactions, eq. 5, halide ions add to the triosmium cluster in a fashion analogous to hydride ion. Adducts form in a period of about 15 minutes at 0°C. They can be isolated in high yield as yellow solids which precipitate from CH_2Cl_2 upon addition of Et_2O. These materials appear to be



(5)

stable in air for a period of approximately one hour. The colors of methylene chloride solutions range from bright yellow (X = Cl) to orange (X = I).

Proton NMR and infrared spectra of these compounds are consistent with structures analogous to that of $K[H_3Os_3(CO)_{10}]$. Infrared spectra show carbonyl absorptions only in the terminal region. (See Experimental section.) Proton NMR spectra (Table 1) are similar to those observed for $K[H_3Os_3(CO)_{10}]$. At room temperature no signal is observed, but when the temperature is lowered two doublets of equal intensity arise from the baseline, which is attributed to the presence of one terminal and one bridging hydrogen under the condition of slow exchange. The chemical shift of the bridging hydrogen in these halogen adducts occurs at significantly lower field than in the hydride adduct $[H_3Os_3(CO)_{10}]^-$.

We have also used other halide salts to form adducts with $H_2Os_3(CO)_{10}$. For example $[(C_6H_5)_4P]Br$ reacts cleanly with $H_2Os_3(CO)_{10}$ in CH_2Cl_2 to form $[(C_6H_5)_4P]$ $[H_2Os_3(CO)_{10}Br]$ and KBr reacts very slowly with $H_2Os_3(CO)_{10}$ in THF to form $K[H_2Os_3(CO)_{10}Br]$.

D. Reactions of metallocarbonylates with $H_2Os(CO)_{10}$

The reactions of $H_2Os_3(CO)_{10}$ with metallocarbonylates occur in a manner analogous to the reactions of hydride and halide ions with the triosmium cluster. The carbonylates $K[Mn(CO)_5]$, $Na_2[Fe(CO)_4]$, $K[CpMo(CO)_3]$, $K_2[CpV(CO)_3]$, and $K[CpFe(CO)_2]$ (where Cp = η^5-C_5H_5) react smoothly with $H_2Os_3(CO)_{10}$ in THF at −78°C (eqs. 6—10).

Infrared and ^{1}H NMR data (Table 2) indicate the presence of only terminal carbonyls and the presence of one terminal and one bridging hydrogen at the slow exchange limit. The stabilities of these adducts vary greatly with the different carbonylates. In the case of $K_2[H_2CpVOs_3(CO)_{13}]$ decomposition occurs

TABLE 1

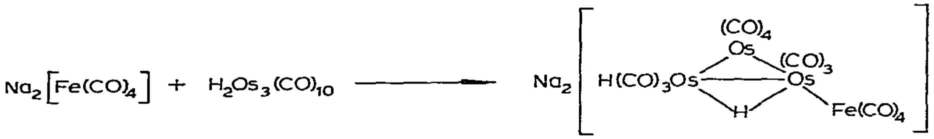
PROTON NMR SPECTRA OF $[PNP][H_2Os_3(CO)_{10}X]$ IN CD_2Cl_2 AT −70°C

Compound	Chemical Shift (τ)	
	$H_{terminal}$	H_{bridge}
$[PNP][H_2Os_3(CO)_{10}Cl]$	20.06(d)	26.25(d)
$[PNP][H_2Os_3(CO)_{10}Br]$	19.85(d)	27.14(d)
$[PNP][H_2Os_3(CO)_{10}I]$	19.46(d)	28.72(d)

d = doublet ($J \approx 4$ Hz)

in less than one hour at room temperature, while K[$H_2MnOs_3(CO)_{15}$] can remain in solution for weeks without appreciable amounts of decomposition. There is also large variation in the ease of isolation of these compounds. For example K[$H_2MnOs_3(CO)_{13}$] is readily isolated in 85% yield, but K[H_2-$CpMoOs_3(CO)_{13}$] rapidly reverts to starting materials under conditions used for isolation.

(6)



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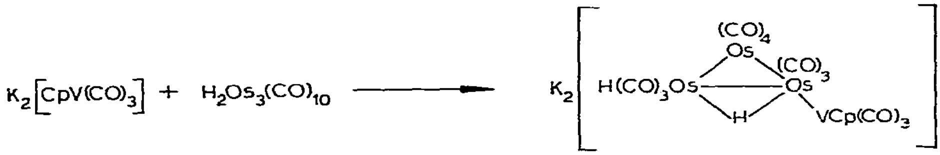

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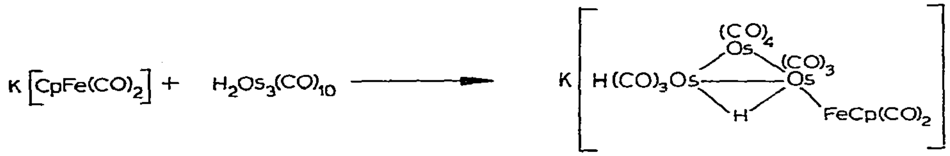

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TABLE 2

PROTON NMR SPECTRA OF METALLOCARBONYLATE ADDUCTS OF $H_2Os_3(CO)_{10}$ IN THF-d_8

Carbonylate Used	−80°C		25°C
	$H_{terminal}$	H_{bridge}	
K[$Mn(CO)_5$]	20.4(d)	30.4(d)	25.2(s)
Na_2[$Fe(CO)_4$]	20.3(br)	30.9(br)	25.5(br)
K[$CpMo(CO)_3$]	20.2(d)	29.7(d)	24.8(s)
K[$CpFe(CO)_2$]	20.2(br)	30.9(br)	25.1(s)
K_2[$CpV(CO)_3$]	20.1(d)	29.9(d)	24.9(s)

d = doublet ($J \approx 4$ Hz), br = broad resonance, s = singlet.

Experimental

General

All manipulations were carried out under vacuum or under an atmosphere of prepurified nitrogen [9]. All solvents were dried and degassed by standard methods [10], and were stored in vessels fitted with teflon vacuum valves. Solvents were vacuum distilled into reaction mixtures as needed.

Osmium carbonyl (Strem Chemicals) was used as received to prepare $H_2Os_3(CO)_{10}$ by a standard literature method [11].

Potassium hydride (Research Organic/Inorganic Chemicals) was obtained as a mineral oil slurry and was washed repeatedly with dry pentane under vacuum. The free flowing white powder was determined to be ~95% hydride active by methanolysis and measurement of the hydrogen evolved.

Potassium metal (Mallinckrodt Inc.) was washed with several portions of dry pentane in a dry box to remove the hydrocarbons. Small pieces of potassium (3—10 mg) were cut just prior to use in a reaction. Benzophenone (J.T. Baker) was used as received.

Bis(triphenylphosphine)iminium chloride, [PNP]Cl, was purchased from Ventron Corp. and was recrystallized from CH_2Cl_2/Et_2O before use. The other PNP salts, [PNP]Br and [PNP]I, were prepared from [PNP]Cl by a literature method [12].

The metal carbonylate, $Na_2[Fe(CO)_4] \cdot 1.5\ C_4H_8O_2$, was purchased from Ventron Corp. and was used as received. The remaining carbonyl anions were prepared by reduction of the appropriate metal carbonyl by potassium benzophenone ketyl as previously described [13]. The metal carbonyls, $Mn_2(CO)_{10}$, $[CpMo(CO)_3]_2$, and $[CpFe(CO)_2]_2$ were obtained from Strem Chemicals and used as received, and $CpV(CO)_4$ (Strem) was sublimed prior to use.

Gaseous samples were analyzed on a modified AEI MS-10 mass spectrometer. The instrument was calibrated with known mixtures of H_2 and CO. Solution infrared spectra were obtained on a Perkin-Elmer 283B spectrometer in matched Perkin-Elmer cells with 0.1 mm teflon spacers and KBr windows. The spectra were calibrated with polystyrene film. NMR spectra were obtained on a Bruker HX90 spectrometer operating in the FT mode at 22.6 MHz (^{13}C) and 90 MHz (^1H). Chemical shifts are relative to Me_4Si. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

$K[H_3Os_3(CO)_{10}]$

In a drybox, 5.2 mg of 95% active KH (0.12 mmol) which had been weighed in a tared vessel was transferred into a small reaction flask which contained 107.4 mg of $H_2Os_3(CO)_{10}$ (0.126 mmol) and a teflon-covered magnetic stirring bar. A vacuum stopcock adapter was attached to the reaction vessel. The reaction system was removed from the dry box and connected to a vacuum line and evacuated. About 3 ml of THF was condensed onto the starting materials with —78°C bath. A water-ice bath was placed around the reaction flask, the contents of which were stirred by an external rotating magnet. The slightly soluble KH formed a slurry in the intensely violet solution of $H_2Os_3(CO)_{10}$. The mixture was allowed to stir for a period of 4 h at 0°C. During this time as the KH was used up, the color of the solution changed from deep violet to dark brown-yellow. The mixture was frozen to —196°C, and checked for non-condensible gas with a Toepler pump. Less than 0.01 mmol of non-condensible gas was given off during the reaction. Infrared spectrum (THF) cm^{-1}: 2070m, 2055m, 2018s, 2001s (sh), 1980m (sh), 1950m (sh). Carbon-13 NMR spectrum (THF, —90°C) 187.7, 184.4, 183.2, 178.4, 178.0, 177.3, 176.4, 174.9, 174.4, 173.8, 172.1 ppm.

$K_2[H_2Os_3(CO)_{10}]$

This compound was prepared by the addition of 11.5 mg of 95% KH (0.275 mmol) to 120.2 mg of $H_2Os_3(CO)_{10}$ (0.141 mmol) in the same manner performed in the preparation $K[H_3Os_3(CO)_{10}]$. Upon stirring at 0°C for 6 h, the mixture appeared to have the brown-yellow color of $K[H_3Os_3(CO)_{10}]$ along with a slurry of unreacted KH. The system was then warmed to room temperature and stirring was continued. Within a period of 3 h the solution was wine-red in color with no apparent sign of unreacted KH. Non-condensible gas given off was measured, 0.141 mmol (102% of theory) and analyzed, 95% H_2 by mass spectral analysis.

$K_2[H_2Os_3(CO)_{10}]$ was also prepared through the reaction of $H_2Os_3(CO)_{10}$ with potassium benzophenone ketyl. In a typical reaction, 8.7 mg of freshly cut potassium metal (0.22 mmol) was placed in a reaction flask with 41.9 mg of benzophenone (0.23 mmol) and a stir bar. The $H_2Os_3(CO)_{10}$ (95.4 mg, 0.11 mmol) was placed in a tip-tube and attached to a side-arm in the reaction vessel. The vessel was evacuated, and THF (4 ml) was condensed onto the benzophenone and potassium metal. This mixture was stirred at room temperature until all of the metal had been transformed into the ketyl. The deep-blue ketyl solution was then cooled and maintained at 0°C with an ice-water bath, and the $H_2Os_3(CO)_{10}$ was transferred into the solution through the tip-tube. The blue of the ketyl gave way to the wine-red of $K_2[H_2Os_3(CO)_{10}]$ in a period of 10 min. Isolation of $K_2[H_2Os_2(CO)_{10}]$ from the reaction mixture was accomplished by first pumping away THF at 0°C to leave a solvated residue. This residue was then dissolved in approximately 3 ml of $(CH_3)_2O$ at —78°C and an equal volume of CH_2Cl_2 was added, and the system was maintained at —78°C while open to a trap which was kept at —196°C. This resulted in the slow removal of ether. Orange $K_2[H_2Os_3(CO)_{10}]$ precipitated from the CH_2Cl_2. The reaction mixture was filtered to remove small amounts of suspended materials before the THF was removed. The final product was stored in a dry box. It is extremely sensitive to the atmosphere. A yield of 88 mg (86% of theory) was obtained. Anal. Found: K, 8.79; Os, 59.82; C, 14.85; H, 0.86. Calcd. for $K_2[H_2Os_2(CO)_{10}]$: K, 8.40; Os, 61.26; C, 12.20; H, 0.22%. Infrared spectrum (THF, cm^{-1}): 2013m, 1979s (br), 1951s (br), 1858m (sh), 1661w (br), 1621w (br). Carbon-13 NMR spectrum (THF, —90°C, ppm): 274.0, 270.4, 196.3 188.3, 185.4, 180.1, 179.5.

$[PNP][H_2Os_3(CO)_{10}X]$

Halide adducts of $H_2Os_3(CO)_{10}$ were prepared by the reactions of the triosmium cluster with the appropriate [PNP] halide. Equimolar amounts of [PNP] halide (ca. 0.030 mmol) and $H_2Os_3(CO)_{10}$ were employed. The halides were weighed in a dry box and were placed into a small reaction vessel with an equimolar amount of $H_2Os_3(CO)_{10}$. Approximately 2 ml of CH_2Cl_2 was vacuum distilled onto the starting materials at —78°C. The reaction mixtures were warmed and maintained at 0°C with a ice-water bath. Stirring was achieved by an external magnet which powered a teflon-covered spin bar within the reaction vessel. The reaction mixtures changed in color from the violet of $H_2Os_3(CO)_{10}$ to a shade of yellow in a period of 10—15 min. The color of the solution varied slightly with the halide. The chloride adduct produced a bright yellow solution, the bromide golden-yellow, while the iodide adduct produced an orange-yellow.

Each of the adducts could be isolated as a yellow powder in moderately good yield (60—70%) by precipitation from CH_2Cl_2 solution through the addition of Et_2O. Anal. Found: C, 38.84; H, 2.28; P, 4.26; N, 1.13; Cl, 2.52. Calcd. for [PNP] [$H_2Os_3(CO)_{10}Cl$]: C, 38.73; H, 2.26; P, 4.34; N, 0.98; Cl, 2.48%. Infrared spectrum (CH_2Cl_2, cm^{-1}); 2090w (sh), 2075m (sh), 2058vs, 2040m, 2002vs (br), 1998vs (sh), 1963m, 1920w (sh). Anal. Found: C, 38.84; H, 2.27, P, 4.14; N, 1.17, Br, 5.51. Calcd. for [PNP] [$H_2Os_3(CO)_{10}Br$]: C, 37.56; H, 2.19; P, 4.21; N, 0.95; Br, 5.43%. Infrared spectrum (CH_2Cl_2, cm^{-1}): 2090w (sh), 2078m, 2058s, 2042m, 2012s (sh), 2001vs, 1995s (sh), 1963m, 1920w (sh). [PNP][$H_2Os_3(CO)_{10}I$] infrared spectrum (CH_2Cl_2, cm^{-1}): 2085w (sh), 2078m, 2055s, 2040m, 2010s, 2062vs, 1965m, 1922vw (sh).

Metallocarbonylate adducts of $H_2Os_3(CO)_{10}$

The adducts formed by $H_2Os_3(CO)_{10}$ and metallocarbonylates were readily prepared as described below. They were generally unstable in solution and decomposed at room temperature in a period of 5—60 min, making isolation of the pure product difficult. One notable exception was $K[H_2MnOs_3(CO)_{15}]$ which was stable in solution for a period of weeks and was isolated in high yield.

$K[H_2MnOs_3(CO)_{15}]$. Into a 30 ml reaction flask 275.1 mg (0.323 mmol) of $H_2Os_3(CO)_{10}$ and 71.4 mg (0.305 mmol) of $K[Mn(CO)_5]$ were placed. The reaction vessel was evacuated and 5 ml of THF was condensed onto the starting materials at —78°C and stirred for about 12 h. A light yellow solution formed and the product was isolated by removal of the THF, followed by dissolving in about 3 ml of Et_2O. Addition of 3—4 ml of CH_2Cl_2 caused the formation of a bright yellow precipitate which was vacuum filtered and washed with several portions of fresh CH_2Cl_2 to remove any remaining $H_2Os_3(CO)_{10}$. The yield of isolated product was 240 mg (75%). Anal. Found: K, 3.91; Mn, 4.99; Os, 53.88; C, 16.60; H, 0.30. Calcd. for $K[H_2MnOs_3(CO)_{15}]$: K, 3.60; Mn, 5.06; Os, 52.51; C, 16.58; H, 0.19%. Infrared spectrum (THF, cm^{-1}): 2058s, 2040s, 2020s (sh), 2005s, 1990vs, 1947m.

$Na_2[H_2FeOs_3(CO)_{14}]$. $H_2Os_3(CO)_{10}$ (76.0 mg, 0.089 mmol) and $Na_2[Fe(CO)_4] \cdot 1.5\ C_4H_6O_2$ (30.2 mg, 0.087 mmol) reacted in about 5 ml of THF at —78°C for 8 h to give a bright red adduct which decomposed rapidly when left in solution at room temperature.

$K[H_2CpMoOs_3(CO)_{13}]$. Reaction of $H_2Os_3(CO)_{10}$ (92.2 mg, 0.108 mmol) and $K[CpMo(CO)_3]$ (27.5 mg, 0.097 mmol) at —78°C in 5 ml of THF for 8 h gave a bright yellow-red adduct which decomposed slowly when warmed to room temperature.

$K[H_2CpFeOs_3(CO)_{12}]$. $H_2Os_3(CO)_{10}$ (82.6 mg, 0.097 mmol) and $K[CpFe(CO)_2]$ (19.8 mg, 0.093 mmol) reacted smoothly in 5 ml THF over a period of 8 h, at —78°C to form a dark red adduct which decomposed rapidly in solution at room temperature.

$K_2[H_2CpVOs_3(CO)_{13}]$. $H_2Os_3(CO)_{10}$ (74.3 mg, 0.087 mmol) and $K_2[CpV(CO)_3]$ (24.3 mg, 0.084 mmol) in 5 ml THF at −78°C for 8 h gave a yellow-brown adduct which decomposed rapidly at room temperature in solution.

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