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Mononuclear Hydrido Alkyl Carbonyl Complexes of Osmium and Their Polynuclear Derivatives

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Osmium hydrido alkyl carbonyl complexes *cis*-$Os(CO)_4(H)R$ (R = Me, Et) can be prepared by alkylation of $[Os(CO)_4H]^-$ with the corresponding alkyl fluorosulfates. The thermal decomposition of these complexes gives dinuclear and trinuclear derivatives $HOs_2(CO)_8R$ and $ROs_3(CO)_{12}R$. Other dinuclear complexes can be obtained from similar reactions of hydrides with alkyl carbonyl complexes. The course of the reaction of *cis*-$Os(CO)_4(H)CH_3$ with Ph_3P depends upon the reaction conditions: with complete exclusion of air $(Ph_3P)Os(CO)_4$ and CH_4 are obtained, whereas small amounts of air induce the rapid operation of a radical-chain substitution mechanism and the formation of $Os(CO)_3(PPh_3)(H)CH_3$.

Introduction

For an investigation of the elimination mechanisms of alkyl- and hydridoosmium carbonyl complexes,[2-7] convenient syntheses, amenable to isotopic labeling, of these materials in high purity were required. While *cis*-$Os(CO)_4H_2$ had been known since 1967,[8] and *cis*-$Os(CO)_4(CH_3)_2$ and *cis*-$Os(CO)_4(C_2H_5)_2$ since 1969,[9,10] *cis*-$Os(CO)_4(H)CH_3$ had only been reported as a spectroscopically observed minor byproduct of two reactions,[9,11] and the analogous hydrido ethyl complex was unknown. The required syntheses of these mononuclear complexes have now been developed, and in the process a number of polynuclear osmium alkyl complexes have been discovered.[12]

Results and Discussion

All of these materials ultimately arise from $Na_2[Os(CO)_4]$, prepared by the reduction of $Os_3(CO)_{12}$ with sodium in liquid ammonia (eq 1).[11,13] If the ratio of the reactants is carefully

$$Os_3(CO)_{12} + 6Na \xrightarrow{\text{liquid } NH_3} 3Na_2[Os(CO)_4] \qquad (1)$$

controlled, with just enough osmium carbonyl added to cause the disappearance of the blue color of the dissolved sodium, and the ammonia removed by prolonged pumping, it is possible to obtain $Na_2[Os(CO)_4]$ in sufficient purity to permit accurate control of stoichiometry in the reactions below.

The dianion is a cream-colored solid which is very air and water sensitive. Despite the reservations about its identity expressed by earlier workers[11] on the basis of the its behavior in water, it is now clear that the dianion formulation is correct. A Nujol mull of $Na_2[Os(CO)_4]$ shows a single broad carbonyl absorption at 1740 cm^{-1}, corresponding to the band at 1730 cm^{-1} reported[14] for $[Fe(CO)_4]^{2-}$ in DMF. Furthermore, the reactions to be reported herein are those which would be expected for $Na_2[Os(CO)_4]$.

The osmium dianion is both a powerful nucleophile and a very strong base. For example, even methyl chloride dialkylates it to *cis*-$Os(CO)_4(CH_3)_2$ (eq 2). Its basicity may

$$Na_2[Os(CO)_4] \xrightarrow[\text{tetraglyme}]{CH_3Cl} cis\text{-}Os(CO)_4(CH_3)_2 \qquad (2)$$

be estimated by comparison with known data for $[HOs(CO)_4]^-$ and the analogous iron carbonyl anions. The pK_1 of $Os(CO)_4H_2$ is 15.2 in methanol[15] and 20.8 in acetonitrile;[16] the pK_1 of $Fe(CO)_4H_2$ is 6.8 in methanol and its pK_2 is about 15 in the same solvent.[15,17] The assumption that the difference between the pK_1 and pK_2 of $Os(CO)_4H_2$ is about the same as that for $Fe(CO)_4H_2$ suggests that the pK_2 of $Os(CO)_4H_2$ in methanol is over 23.

Mononuclear Alkyls, Hydrides, and Hydrido Alkyls. These compounds can be made by alkylation and/or protonation of the dianion.[11] An ether solvent is helpful, and we found bis[2-(2-methoxyethoxy)ethyl] ether ("tetraglyme") particularly suitable because of its nonvolatility at room temperature even under high-vacuum conditions. (It does not dissolve the dianion but does dissolve its monoanionic derivatives, and it is not attacked by any of these species.) Similarly, methyl and ethyl tosylates (eq 3–5) are attractive alkylating agents because

$$Na_2[Os(CO)_4] + 2CH_3OTs \xrightarrow{\text{tetraglyme}} cis\text{-}Os(CO)_4(CH_3)_2 \qquad (3)$$

$$Na_2[Os(CO)_4] + 2C_2H_5OTs \xrightarrow{\text{tetraglyme}} cis\text{-}Os(CO)_4(C_2H_5)_2 \qquad (4)$$

$$Na_2[Os(CO)_4] + H_3PO_4 \xrightarrow{\text{tetraglyme}} cis\text{-}Os(CO)_4H_2 \qquad (5)$$

the resulting dialkylosmium complexes are the only components of the reaction mixture volatile at room temperature on a vacuum line and are thus easily obtained pure.

Difficulties arise with the straightforward extension of this approach to the synthesis of hydrido alkyls. The addition of 1 equiv of acid converts the $Na_2[Os(CO)_4]$ to $[Os(CO)_4H]^-$. However, methylation with methyl tosylate gives a mixture

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of $Os(CO)_4(CH_3)_2$, $Os(CO)_4(H)CH_3$, and $Os(CO)_4H_2$ in the approximate ratio 1:2:1. This apparently arises from deprotonation of the hydrido methyl product by unmethylated $[Os(CO)_4H]^-$ (reaction 7), followed by attack of the very nucleophilic[16] $[Os(CO)_4CH_3]^-$ on methyl tosylate (reaction 8). Such complications can be avoided by the use of a more

$$[Os(CO)_4H]^- + CH_3OTs \rightarrow Os(CO)_4(H)CH_3 + OTs^- \quad (6)$$

$$[Os(CO)_4H]^- + Os(CO)_4(H)CH_3 \rightarrow Os(CO)_4H_2 + [Os(CO)_4CH_3]^- \quad (7)$$

$$[Os(CO)_4CH_3]^- + CH_3OTs \rightarrow Os(CO)_4(CH_3)_2 \quad (8)$$

reactive methylating agent to increase the rate of the desired reaction, (6), as the rate of the proton-transfer side reaction (reaction 7) should remain constant.

The use of methyl fluorosulfate is extremely successful in this regard. Somewhat surprisingly, there are no complications arising from attack on tetraglyme; the successful preparation of CD_3-labeled compounds[3,6,7] from CD_3OSO_2F in that solvent implies the absence of solvent attack. (As the tetraglyme is unlabeled, attack on its CH_3O oxygens would lead to eventual alkylation by CH_3^+ as well as CD_3^+.) Two equivalents of CH_3OSO_2F is required, as it also methylates the anion remaining from the acid used to protonate the $Na[Os(CO)_4]$. The acid must be chosen with a view to the easy separation of its methylated derivative from $Os(CO)_4(H)CH_3$; CF_3CO_2H is satisfactory, as $CF_3CO_2CH_3$ has a much higher vapor pressure than any organoosmium complex.

The preparation of *cis*-$Os(CO)_4(H)CH_3$ according to eq 9–11 gives good yields (>70%) of material without detectable

$$Na_2[Os(CO)_4] \xrightarrow[\text{tetraglyme}]{CF_3CO_2H} Na[Os(CO)_4H] + NaO_2CCF_3 \quad (9)$$

$$Na[Os(CO)_4H] \xrightarrow[\text{tetraglyme}]{CH_3OSO_2F} cis\text{-}Os(CO)_4(H)CH_3 \quad (10)$$

$$NaO_2CCF_3 \xrightarrow[\text{tetraglyme}]{CH_3OSO_2F} CH_3O_2CCF_3 \quad (11)$$

impurities if the stoichiometry is carefully controlled. The analogous hydrido ethyl complex *cis*-$Os(CO)_4(H)C_2H_5$ can be prepared by the corresponding reaction with $C_2H_5OSO_2F$ (eq 12) but invariably contains small amounts of $Os(CO)_4H_2$

$$Na[Os(CO)_4H] \xrightarrow[\text{tetraglyme}]{C_2H_5OSO_2F} cis\text{-}Os(CO)_4(H)C_2H_5 \quad (12a)$$

$$NaO_2CCF_3 \xrightarrow[\text{tetraglyme}]{C_2H_5OSO_2F} C_2H_5O_2CCF_3 \quad (12b)$$

and $Os(CO)_4(C_2H_5)_2$ as impurities (which can be removed by repeated trap-to-trap fractionation with considerable sacrifice in yield). Presumably the competition between alkylation and proton transfer is not as favorable in the ethyl case.

Reactions of Mononuclear Osmium Organometallics. The alkyl hydride complexes *cis*-$Os(CO)_4(H)R$ are colorless liquids, which decompose slowly at room temperature, the ethyl more rapidly than its methyl counterpart. In view of its instability and our inability to prepare it in high purity, the identity of *cis*-$Os(CO)_4(H)C_2H_5$ was confirmed by treating it with CCl_4 and converting it (reaction 13) to its chloro derivative, a crystalline white solid, which sublimes rapidly at room temperature. This reaction almost certainly proceeds by the type of radical-chain mechanism that will be discussed below in connection with $HOs_2(CO)_8R$.

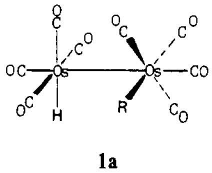
$$cis\text{-}Os(CO)_4(H)C_2H_5 \xrightarrow{CCl_4} cis\text{-}Os(CO)_4(Cl)C_2H_5 \quad (13)$$

The thermal decomposition of the alkyl hydride complexes gives, as primary products, dinuclear alkyl hydrides and 0.5 equiv of alkane (reaction 14). Trinuclear dialkyl complexes

$$cis\text{-}Os(CO)_4(H)R \xrightarrow{\Delta} HOs_2(CO)_8R + R\text{-}H + ROs_3(CO)_{12}R \quad (14)$$

$$R = CH_3, C_2H_5$$

are formed as secondary products, as well as (from $Os(CO)_4(H)C_2H_5$) a small amount of a third product tentatively identified as $HOs_3(CO)_{12}C_2H_5$. All of these polyosmium alkyl and hydride complexes, and their halide derivatives to be discussed, can be assigned the structures illustrated (see **1**)



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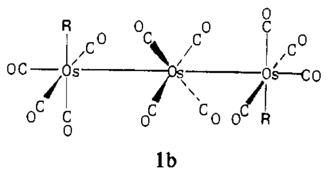
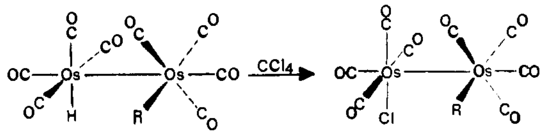


1b

for reasons that were discussed in detail earlier[18] and have been corroborated by a recent exhaustive spectroscopic study of $H_2Os_3(CO)_{12}$.[19] The structure of $CH_3Os_3(CO)_{12}CH_3$ has been verified by X-ray crystallography.[20]

The dinuclear alkyl hydrides are unstable colorless oils, which are (as above) converted to crystalline, air-stable chlorides by treatment with CCl_4 (eq 15). The reaction is



(15)

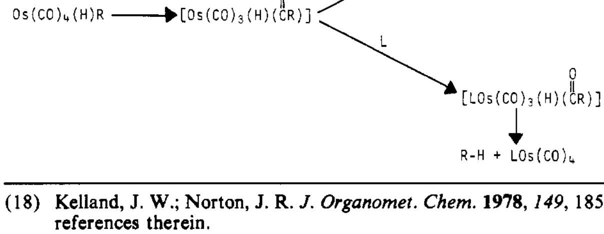
usually rapid at room temperature, but its rate is not reproducible—behavior indicative of a radical-chain mechanism (reactions 16–18) like those established by other workers for related reactions.[21-23]

$$\text{initiator In}\cdot + HOs(CO)_4Os(CO)_4R \rightarrow InH + \cdot Os(CO)_4Os(CO)_4R \quad (16)$$

$$\cdot Os(CO)_4Os(CO)_4R + CCl_4 \rightarrow ClOs(CO)_4Os(CO)_4R + \cdot CCl_3 \quad (17)$$

$$\cdot CCl_3 + HOs(CO)_4Os(CO)_4R \rightarrow CHCl_3 + \cdot Os(CO)_4Os(CO)_4R \quad (18)$$

Induced Radical-Chain Substitution. The formation of these dinuclear alkyl hydride complexes can be short-circuited by the presence of a nucleophile L other than the hydride ligand of the initial hydrido alkyl complex,[7] with resulting intramolecular alkane elimination and formation of an Os(O) complex (eq 19). For example, the addition of Et_3P to *cis*-Os-



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$(CO)_4(H)Me$ gives $(Et_3P)Os(CO)_4$ (eq 20). Even ethylene

$$cis\text{-}Os(CO)_4(H)CH_3 + Et_3P \rightarrow (Et_3P)Os(CO)_4 + CH_4 \tag{20}$$

$$cis\text{-}Os(CO)_4(H)CH_3 + C_2H_4 \rightarrow (C_2H_4)Os(CO)_4 + CH_4 \tag{21}$$

reacts in this fashion rather than by insertion (eq 21). As the alkyl migration reaction that triggers both this reaction and the competitive dinuclear alkane elimination is faster than carbonyl dissociation,[7] straightforward substitution for a carbonyl ligand on $Os(CO)_4(H)R$ ought not to be possible and has in fact not been observed under our high-vacuum line conditions even with a large excess of a variety of nucleophiles L.

We were therefore surprised by the report in the early paper by L'Eplattenier[9] that addition of PPh_3 to a mixture of $Os(CO)_4(H)CH_3$ and $Os(CO)_4(CH_3)_2$ in THF solution gave, in addition to $(Ph_3P)Os(CO)_4$,[24] a product spectroscopically identified as $Os(CO)_3(PPh_3)(H)CH_3$. It seemed possible that the latter product had arisen from a radical-chain mechanism induced by traces of oxygen. Such mechanisms, related to those discussed above for the reaction of transition-metal hydrides with CCl_4, have become well established the phosphine substitution on other metal carbonyl hydrides since the L'Eplattenier paper was written. The key features of such a mechanism are summarized in eq 22–25 for substitution of

$$In\cdot + HRe(CO)_5 \rightarrow InH + \cdot Re(CO)_5 \tag{22}$$

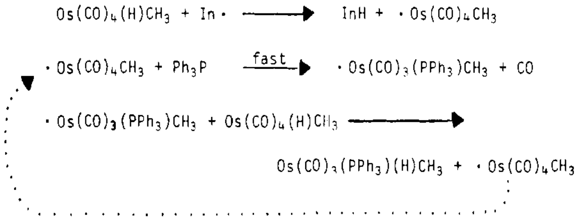
$$\cdot Re(CO)_5 \rightleftharpoons \cdot Re(CO)_4 + CO \tag{23}$$

$$\cdot Re(CO)_4 + L \rightleftharpoons \cdot Re(CO)_4L \tag{24}$$

$$\cdot Re(CO)_4L + HRe(CO)_5 \rightarrow HRe(CO)_4L + \cdot Re(CO)_5 \tag{25}$$

$HRe(CO)_5$[22]—a carbonyl hydride which is electronically very similar to the osmium carbonyl hydrides with which we are concerned here.

Such a mechanism does in fact operate for $cis\text{-}Os(CO)_4(H)CH_3$ (eq 26–28). Although no substitution is observed with careful exclusion of air, and very little substitution is observed in the presence of substantial amounts of air (known to inhibit substitution of $HRe(CO)_5$[22]), a small amount of air (0.1% oxygen) causes the reaction to proceed much more rapidly at room temperature than alkyl migration. (It is well-known that oxygen can either initiate or inhibit radical-chain reactions:[25] the reaction of tin hydrides with alkyl halides is accelerated by small amounts of O_2 but retarded by larger amounts,[26] apparently because O_2 combines with many initiating radicals to produce less reactive peroxy radicals.)



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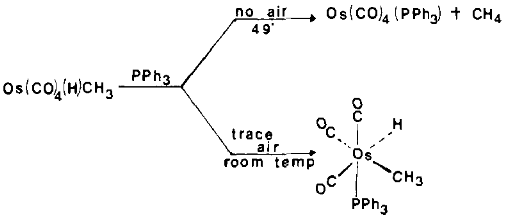
(28)

Thus, by increasing the concentration of initiating radicals, the addition of small amounts of air can change the chemistry of $Os(CO)_4(H)CH_3/PPh_3$ from $(Ph_3P)Os(CO)_4$ formation with methane elimination to carbonyl substitution by Ph_3P (eq 29). No disubstitution has been observed.



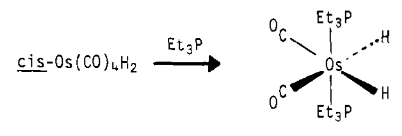
(29)

Substitution also occurs readily on photolysis (eq 30). It

$$cis\text{-}Os(CO)_4(H)CH_3 \xrightarrow[PPh_3]{h\nu} Os(CO)_3(PPh_3)(H)CH_3 \tag{30}$$

is not clear whether this represents photochemical CO dissociation or photochemical generation of initiators for radical-chain substitution.

Similar radical-chain substitution processess occur readily with $Os(CO)_4H_2$. A mixture of that compound and Et_3P formed the distribution product $Os(CO)_2(PEt_3)_2H_2$ (eq 31)



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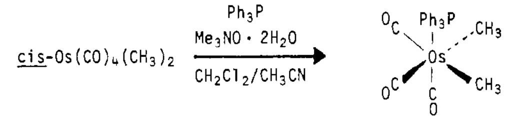
at temperatures far below that required[6] for carbonyl dissociation but with an induction period of variable length followed by extremely rapid reaction.

Substitution of $Os(CO)_4(CH_3)_2$ is of course not possible by a radical-chain mechanism, nor is thermal substitution successful; reaction between $Os(CO)_4(CH_3)_2$ and excess PPh_3 occurs only slowly,[9] yielding $Os(CO)_3(PPh_3)_2$ and acetone at elevated temperatures (eq 32). However, a carbonyl ligand



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is removed under mild conditions by trimethylamine oxide, a reagent that has been used by a number of authors for this purpose.[27–29] To our knowledge, this is the first time this reagent has been used in the presence of an alkyl ligand.

Formation of Other Dinuclear Complexes by Dinuclear Elimination. Just as 2 equiv of $Os(CO)_4(H)R$ can eliminate alkane to form $HOs_2(CO)_8R$ (eq 14), alkyl carbonyl complexes can undergo dinuclear alkane elimination with other hydride complexes. The principal inorganic product of the reaction of $Os(CO)_4(CH_3)_2$ and $Os(CO)_4H_2$, identified by NMR, is $HOs_2(CO)_8CH_3$ (eq 33). Furthermore, hydrido alkyl complexes such as $Os(CO)_4(H)CH_3$ can react both with other hydrides (eq 34 and 35) and with other alkyl carbonyl complexes (eq 36). In the last reaction, the dinuclear dimethyl

$$cis\text{-}Os(CO_4)(CH_3)_2 + cis\text{-}Os(CO)_4H_2 \rightarrow HOs_2(CO)_8CH_3 \tag{33}$$

$$cis\text{-}Os(CO)_4(H)CH_3 + cis\text{-}Os(CO)_4H_2 \rightarrow CH_4 + HOs_2(CO)_8H \tag{34}$$

$$cis\text{-}Os(CO)_4(H)CH_3 + HRe(CO)_5 \rightarrow CH_4 + HOs(CO)_4Re(CO)_5 \tag{35}$$

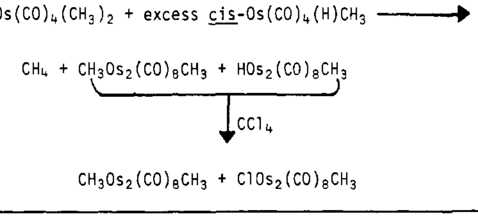

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Table I. Infrared Bands in the Carbonyl Stretching Region (cm^{-1})[a]

$Os(CO)_4H_2$[b]	2141 (w), 2066 (m), 2054 (s), 2047 (vs)
$Os(CO)_4(CH_3)_2$[b]	2130 (w), 2044 (vs), 2012 (s), 1979 (vw)
$Os(CO)_4(C_2H_5)_2$[c]	2125 (w), 2038 (vs), 2008 (s), 1975 (vw)
$Os(CO)_4(H)CH_3$[c]	2135 (w), 2063 (m), 2042 (vs), 2028 (s)
$Os(CO)_4(H)C_2H_5$	2133 (w), 2060 (s), 2043 (vs), 2030 (s)
$Os(CO)_4(Cl)C_2H_5$	2155 (w), 2078 (vs), 2023 (s)
$CH_3Os_3(CO)_{12}CH_3$	2132 (vw), 2094 (s), 2038 (vs), 2029 (s), 2013 (s), 2008 (m), 1988 (m)
$C_2H_5Os_3(CO)_{12}C_2H_5$	2132 (vw), 2093 (s), 2051 (m), 2034 (vs), 2025 (s), 2005 (m), 1989 (w)
$HOs_2(CO)_8C_2H_5$	2128 (vw), 2084 (m), 2053 (m), 2041 (s), 2036 (vs), 2030 (s), 2014 (w), 2003 (w)
$ClOs_2(CO)_8C_2H_5$	2139 (vw), 2098 (s), 2057 (vs), 2044 (m), 2030 (vs), 2018 (m), 2014 (m), 2008 (m)
$ClOs_2(CO)_8CH_3$	2103 (s), 2065 (s), 2060 (s), 2047 (m), 2034 (s), 2020 (m), 2013 (m), 2002 (w)
$Os(CO)_4(PEt_3)$	2060 (s), 1977 (m), 1936 (vs)
$Os(CO)_4(C_2H_4)$	2111 (w), 2023 (s), 1993 (s)
$Os(CO)_3(PPh_3)(H)CH_3$[d]	2078 (vs), 2028 (s), 1994 (s)
$Os(CO)_2(PEt_3)_2H_2$[b]	2001 (s), 1973 (s)
$Os(CO)_3(PPh_3)(CH_3)_2$[d]	2071 (vs), 1999 (vs), 1965 (s)
$HOs_2(CO)_8H$	2133 (vw), 2093 (s), 2056 (vs), 2039 (vs), 2032 (s), 2020 (s)
$HOs_2(CO)_8CH_3$	2130 (w), 2089 (s), 2056 (s), 2044 (s), 2039 (s), 2033 (s), 2025 (m), 2018 (m), 2007 (m), 2004 (w)
$CH_3Os_2(CO)_8CH_3$[d]	2124 (vw), 2084 (s), 2042 (vs), 2036 (vs), 2030 (vs), 2014 (m), 2002 (m), 2098 (sh), 1976 (vw)
$HOs(CO)_4Re(CO)_5$	2090 (m), 2084 (s), 2048 (s), 2041 (s), 2030 (vs), 2007 (s), 1996 (m), 1984 (s)

[a] All spectra run in pentane unless otherwise stated. [b] Methylcyclohexane. [c] THF. [d] Hexanes.

Table II. ^1H NMR Spectra of Alkyl- and Hydridoosmium Carbonyl Compounds[a]

compd	CH_3	CH_2	H	*J*, Hz
$Os(CO)_4H_2$			−8.58	
$Os(CO)_4(CH_3)_2$	0.15			
$Os(CO)_4(C_2H_5)_2$[b]	1.68	0.98		$J_{CH_2CH_3} = 7.7$
$Os(CO)_4(H)CH_3$	0.12		−7.75	$J_{CH_3\text{-}H} = 2.4$
$Os(CO)_4(H)C_2H_5$[c]	1.72	1.30	−7.90	$J_{CH_2CH_3} = 7$ $J_{CH_2\text{-}H} = 1.5$
$Os(CO)_4(Cl)C_2H_5$[d]	1.84	1.76		$J_{CH_2CH_3} = 7$
$CH_3Os_3(CO)_{12}CH_3$	0.29			
$HOs_2(CO)_8C_2H_5$	1.69	1.33	−10.11	$J_{CH_2CH_3} = 7$
$ClOs_2(CO)_8C_2H_5$[d]	1.86	1.53		$J_{CH_2CH_3} = 7$
$ClOs_2(CO)_8CH_3$	0.23			
$Os(CO)_4(C_2H_4)$		1.44		
$HOs_2(CO)_8H$			−10.08	
$HOs_2(CO)_8CH_3$	0.39		−10.01	
$CH_3Os_2(CO)_8CH_3$	0.21			
$HOs(CO)_4Re(CO)_5$[b]			−10.40	

[a] All spectra recorded in C_6D_6 unless otherwise stated. Chemical shifts reported in δ. [b] CH_2Cl_2. [c] CD_2Cl_2. [d] $CDCl_3$.

complex can only be separated from the major dinuclear product, $HOs_2(CO)_8CH_3$, by treatment of the mixture with CCl_4 to convert the latter to its chloro derivative. The resulting mixture of $CH_3Os_2(CO)_8CH_3$ and $ClOs_2(CO)_8CH_3$ is then readily separated by chromatography.

Experimental Section

General Procedures. Gas analysis was carried out with use of a 20-ft, $^1/_4$-in. diameter Porapak QS column installed in a Perkin-Elmer 3920 gas chromatograph fitted with a gas-switching valve connected to the vacuum-line Toepler pump. Mass spectra were obtained with an AEI MS9 mass spectrometer operating at 70 eV and equipped with direct-inlet and gas-inlet systems. Spectra were recorded with and without the standards heptacosafluorotributylamine and tris(perfluoroheptyl)-*s*-triazine in order to ensure that *m*/*e* values were accurate. All compounds exhibited parent ion enveloped with isotopic distributions that agreed with those calculated for the number of osmium and other polyisotopic atoms in the molecular formulas.

Reactions involving volatile mononuclear osmium complexes were (unless otherwise specified) performed on a high-vacuum line. The standard reaction vessel was a 25-mL glass bulb connected through a high-vacuum Teflon stopcock to an O-ring joint. Manipulations of $Na_2[Os(CO)_4]$ were carried out under nitrogen in a Vacuum Atmospheres inert-atmosphere box. Tetraglyme was predried over sodium metal and distilled under high vacuum (about 0.01 mm) from sodium/benzophenone, avoiding prolonged contact.

Carbonyl-region IR data for all compounds are in Table I, and ^1H NMR data are in Tables II and III.

Dodecacarbonyltriosmium, $Os_3(CO)_{12}$, was prepared by the method of Johnson, Lewis, and Kilty.[30]

Disodium Tetracarbonylosmate. Ammonia (25 mL) was passed through a column containing potassium hydroxide pellets and condensed in vacuo, with use of a dry ice/acetone bath, into a glass bulb containing metallic sodium (to remove moisture from the ammonia). During this and all subsequent operations, the system was open to a mercury manometer. The ammonia was then distilled, in vacuo, into a 250-mL three-necked round-bottom flask containing sodium (0.44 g) and equipped with a stopcock, dry ice/acetone condenser, glass stirring bar, and solid addition tube containing $Os_3(CO)_{12}$ (3.6 g). Roughly three-fourths of the $Os(CO)_{12}$ was then added to the sodium/ammonia solution and the mixture stirred. The pressure in the system was kept well below 1 atm by the condensation of the refluxing ammonia on the dry ice/acetone condenser. The bright yellow of unreacted $Os_3(CO)_{12}$ was readily discernible against both the dark blue of the sodium/ammonia solution and, later, the cream color of the product. When no unreacted $Os_3(CO)_{12}$ was visible at the bottom of the reaction vessel, further additions were carefully made until a pale green mixture (consisting of the product and a trace of sodium) was obtained. Sodium which splashed on the walls of the flask was washed down by cold spotting with glass wool drenched with liquid nitrogen. The ammonia was then allowed to bubble off through the mercury manometer by allowing the dry ice/acetone condenser to warm to room temperature. The flask was then evacuated and warmed slightly, to remove all the ammonia, and taken into an inert-atmosphere box for storage.

***cis*-Dihydridotetracarbonylosmium** was prepared from $Na_2[Os(CO)_4]$ and H_3PO_4 both by the method of Stone[11] (direct treatment of $Na_2[Os(CO)_4]$ with an excess of 85% H_3PO_4) and by the treatment of a suspension of $Na_2[Os(CO)_4]$ in tetraglyme with a few equivalents of H_3PO_4. It was dried over P_2O_5 on the vacuum line.

***cis*-Dimethyltetracarbonylosmium.** To $Na_2[Os(CO)_4]$ (0.369 g), suspended in tetraglyme (5 mL) under nitrogen, was added 2 equiv of methyl tosylate. While the system was left overnight at room temperature under high vacuum, $Os(CO)_4(CH_3)_2$ distilled into a −196 °C cold trap. Drying over P_2O_5 gave 0.32 g (91% yield) of $Os(CO)_4(CH_3)_2$, identified by comparison of its IR and NMR spectra with the literature data.[9-11] Significant amounts of $Os(CO)_4(CH_3)_2$ were identified by NMR analysis of all volatile material when 6 equiv of CH_3Cl was employed instead of methyl tosylate.

***cis*-Diethyltetracarbonylosmium.** Although L'Eplattenier prepared $Os(CO)_4(C_2H_5)_2$ by reacting a THF solution of $Na_2[Os(CO)_4]$ with ethyl iodide,[10] we find the following procedure more convenient. To $Na_2OsCO)_4$ (175 mg) suspended in tetraglyme (5 mL) under nitrogen was added 2 equiv of ethyl tosylate. Overnight at 40 °C under high vacuum, $Os(CO_4)(C_2H_5)_2$ distilled into a −196 °C cold trap. Drying over P_2O_5 gave 45 mg (25% yield). The IR and NMR spectra agreed with those reported.[10]

***cis*-Hydridomethyltetracarbonylosmium.** $Na_2[Os(CO)_4]$ (94 mg) was suspended in tetraglyme (5 mL) under vacuum, and 1 equiv (31 mg) of trifluoroacetic acid was distilled into the reaction vessel on the vacuum line. The mixture was then stirred at room temperature for 2 h, at which point all of the dianion had dissolved and produced a reddish orange solution. Methyl fluorosulfate (2 equiv, 62 mg) was then distilled into the reaction vessel and the mixture stirred for an additional 2 h at room temperature. At that point, a mixture of product and methyl trifluoroacetate was distilled under high vacuum at room temperature into a −196 °C cold trap. Redistillation through a −63 °C bath (which condensed the product but not methyl trifluoroacetate),

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(30) Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. A* **1968**, 2859.

Table III. ^1H NMR Spectra of Phosphine-Substituted Osmium Compounds[a]

compd	CH_3-Os	H-Os	other	J, Hz
$Os(CO)_3(PPh_3)(H)CH_3$[b]	−0.30	−7.14	7.53−7.31 (PPh_3)	$J_{CH_3\text{-}H} = 3.0$ $J_{CH_3\text{-}P} = 8.0$ $J_{H\text{-}P} = 24.0$
$Os(CO)_2(PEt_3)_2H_2$[c]		−9.1	0.95 (P-CH_2*CH_3*) 1.35 (P-*CH_2*CH_3)	$J_{H\text{-}P} = 22.5$
$Os(CO)_3(PPh_3)(CH_3)_2$[b]	−0.10		7.52−7.31 (PPh_3)	$J_{CH_3\text{-}P} = 8.0$

[a] Chemical shifts reported in δ. [b] $CDCl_3$. [c] C_6D_6.

followed by drying over P_2O_5, gave pure *cis*-$Os(CO)_4(H)CH_3$ (60 mg, 70% yield). The IR and NMR spectra in Tables I and II agree with those reported[9,11] when the compound was observed spectroscopically in solution.

***cis*-Hydridoethyltetracarbonylosmium.** One equivalent of trifluoroacetic acid (101 mg) was transferred, in vacuo, into a standard reaction bulb containing $Na_2[Os(CO)_4]$ (312 mg) suspended in tetraglyme (10 mL). The mixture was then stirred at room temperature for 2 h. Ethyl fluorosulfate (2 equiv, 232 mg) was then vacuum distilled into the reaction bulb and the mixture stirred for an additional 5 min at room temperature (if a longer stirring time is used, the ethyl fluorosulfate will begin ethylating the oxygens in the tetraglyme solvent). At that point, the system was evacuated and a mixture of osmium products and ethyl trifluoroacetate was distilled overnight at room temperature under high vacuum into a −196 °C cold trap. The products were freed of the more volatile ethyl trifluoroacetate by redistilling them into a −56 °C (octane slush) cold trap. This mixture was separated by trap-to-trap fractionation on the vacuum line. $Os(CO)_4(C_2H_5)_2$ was trapped in a −6 °C bath (aniline slush), the product, $Os(CO)_4(H)C_2H_5$, in a −23 °C bath (CCl_4 slush), and $Os(CO)_4H_2$ in a −196 °C trap. The usual purity of $Os(CO)_4(H)C_2H_5$ after four cycles was 90%. It was further purified by a final vacuum transfer, taking only the more volatile portion of the sample (162 mg, 54% yield). The compound was characterized by IR (Table I) and NMR (Table II) spectroscopy and by conversion to the chloro derivative.

***cis*-Chloroethyltetracarbonylosmium.** $Os(CO)_4(H)C_2H_5$ (30 mg) was combined with CCl_4 (5 mL) under a stream of N_2 in an open flask. After the mixture was stirred at room temperature for 2 h, CCl_4 was removed in vacuo, leaving a white solid. This was purified by sublimation at room temperature (<1 μm), giving $Os(CO)_4(Cl)C_2H_5$ (22.5 mg, 68% yield). This extremely volatile compound was identified by its IR (Table I) and NMR (Table II) spectra and by its mass spectrum run at 35 °C, which showed the parent ion at *m/e* 370 (^{192}Os, ^{37}Cl) with an isotopic distribution characteristic of OsCl. Anal. Calcd for $C_6H_5ClO_4Os$: C, 19.55; H, 1.36. Found: C, 19.63; H, 1.45.

Thermolysis of *cis*-$Os(CO)_4(H)CH_3$. A standard reaction bulb was charged with *cis*-$Os(CO)_4(H)CH_3$ (87.3 mg), closed, and heated for 10 h at 49 °C. After the compound was cooled, all −196 °C volatiles were pumped out and pressure–volume measurements showed that 0.5 equiv of gas/equiv of starting material had been evolved. Gas chromatographic analysis of these volatiles showed the gas to be entirely methane. No room-temperature volatiles were recoverable from the reaction mixture; the reaction had thus gone to completion. Chromatography of the remaining nonvolatile material, already described in detail,[18] yielded $HOs_2(CO)_8CH_3$ and $CH_3Os_3(CO)_{12}CH_3$.

Thermolysis of $Os(CO)_4(H)C_2H_5$. $Os(CO)_4(H)C_2H_5$ (53.4 mg, 0.16 mmol), containing about 5% $Os(CO)_4(C_2H_5)_2$ as impurity, was placed in a sealed NMR tube and kept at room temperature for 15 days. The tube was then opened on a vacuum line, and materials that were volatile were collected by a Toepler pump. Slightly less than 0.5 equiv of gas/equiv of $Os(CO)_4(H)C_2H_5$ was evolved. Gas chromatographic analysis of this gas showed it to be ethane with a very small amount (<1%) of methane (probably from traces of $Os(CO)_4(H)CH_3$ in the hydrido ethyl complex, arising from a very small amount of alkyl group exchange between $C_2H_5OSO_2F$ and tetraglyme during the preparation of $Os(CO)_4(H)C_2H_5$). No more volatile material evolved on heating to room temperature. The nonvolatile material was then removed from the vacuum line and separated by TLC (silica gel, pentane). IR spectra indicated $Os_2(CO)_8(H)C_2H_5$ and $Os_3(CO)_{12}(C_2H_5)_2$ (the identification of which is described in the next section) as products.

In a similar reaction, $Os(CO)_4(H)C_2H_5$ (12 mg) was transferred under vacuum into a standard reaction bulb containing 3 mL of methylcyclohexane. The bulb was then closed and heated for 16 h at 28 °C. After removal of volatiles in vacuo, the bulb was opened and the residue taken up in CH_2Cl_2, which was then applied to a silica gel TLC plate. Use of pentane as the eluant produced three bands. The top band (R_f ~0.9) yielded $HOs_2(CO)_8C_2H_5$ as a clear colorless oil (~3 mg). The compound was characterized by its IR (Table I) and NMR (Table II) spectra and by its mass spectrum recorded at 50 °C which showed a weak parent ion centered at *m/e* (^{192}Os) with the isotopic distribution characteristic of Os_2. It was further characterized by conversion (below) to the chloro derivative.

The second (R_f ~0.7) and third (R_f ~0.5) bands yielded <1 mg apiece of yellow solids. Both materials showed ethylosmium resonances in the FT ^1H NMR. The IR spectra (Table I), the method of preparation, and the TLC retention times all suggested that both complexes were trinuclear, and both showed isotopic patterns characteristic of Os_3 in their mass spectra. The second yellow complex (the third TLC band) was tentatively identified as $HOs_3(CO)_{12}C_2H_5$ on the basis of a peak at *m/e* 914 (^{192}Os) in its mass spectrum (recorded at 80 °C) assigned to $[P - 28]^+$; the first yellow complex (the second TLC band) was tentatively identified as $C_2H_5Os_3(CO)_{12}C_2H_5$ on the basis of a peak at *m/e* 942 (^{192}Os) in its mass spectrum (recorded at 120 °C) assigned to $[P - 28]^+$.

Chloroethyloctacarbonyldiosmium. $HOs_2(CO)_8C_2H_5$ was combined with CCl_4 under a stream of N_2 in an open flask. After several days at room temperture all volatiles were removed in vacuo, leaving behind a white solid. This was purified by TLC (silica gel, pentane with 20% CH_2Cl_2 as eluant, R_f 0.20), giving $ClOs_2(CO)_8C_2H_5$. The compound was identified by its IR (Table I) and NMR (Table II) spectra and by its mass spectrum recorded at 50 °C, which showed a parent ion at *m/e* 674 (^{192}Os, ^{37}Cl) with an isotopic distribution characteristic of Os_2Cl. Anal. Calcd for $C_{10}H_5ClO_8Os_2$: C, 17.94; H, 0.75; Cl, 5.31. Found: C, 18.36; H, 0.77; Cl, 5.05.

Chloromethyloctacarbonyldiosmium. $HOs_2(CO)_8CH_3$ (20 mg) was combined with CCl_4 (1 mL) under nitrogen. After the mixture was stirred at room temperature for 1 h, all volatiles were removed in vacuo, leaving behind a white solid. Occasionally this reaction was not complete in 1 h, in which case CCl_4 was again added and the mixture stirred for an additional 1 h. This somewhat unpredictable behavior is consistent with the notion that the reaction of metal hydrides with CCl_4 occurs by a radical pathway.[21-23]

Purification by TLC with 20% CH_2Cl_2 in pentane as eluant gave $ClOs_2(CO)_8CH_3$ in virtually quantitative yield. Its mass spectrum, recorded at 100 °C, showed a parent ion at *m/e* 660 (^{192}Os, ^{37}Cl) with the isotopic distribution characteristic of Os_2Cl. Anal. Calcd for $C_9H_3ClO_8Os_2$: C, 16.50; H, 0.46; Cl, 5.42. Found: C, 16.68; H, 0.54; Cl, 5.13.

(Triethylphosphine)tetracarbonylosmium, $(Et_3P)Os(CO)_4$. A mixture of *cis*-$Os(CO)_4(H)CH_3$ (54 mg) and triethylphosphine (2 g) in methylcyclohexane (3 mL) was frozen, degassed, and then heated to 49 °C for 15 h. At that time, all −196 °C volatiles were Toepler-pumped into another bulb. Pressure–volume measurements indicated 1 equiv of gas/equiv of hydrido methyl complex had been evolved. Mass spectral analysis identified the gas as methane.

All room-temperature volatiles were then removed from the reaction mixture, leaving behind the white solid $(Et_3P)Os(CO)_4$ in virtually quantitative yield. Further purification was accomplished by TLC (10% methylene chloride in pentane as eluant, R_f 0.48). The mass spectrum, recorded at 120 °C, showed a parent ion at *m/e* 422 (^{192}Os) with the isotopic distribution characteristic of Os. Anal. Calcd for $C_{10}H_{15}O_4OsP$: C, 28.57; H, 3.59; P, 7.37. Found: C, 28.86; H, 3.74; P, 7.68.

(Ethylene)tetracarbonylosmium. $Os(CO)_4(H)CH_3$ (60 mg, 0.191 mmol) was transferred on the vacuum line into an evacuated standard reaction bulb. Into this was then distilled 15 mL of CH_2Cl_2. This solution was then saturated with ethylene gas (approximately a 10-fold excess). The flask was heated for 5 h at 40 °C in an oil bath. The product was isolated by vacuum transfer along with solvent at room temperature, followed by transfer through a −23 °C slush which condensed only $(C_2H_4)Os(CO)_4$. The product was identified by its IR (Table I) and NMR (Table II) spectra and by its mass spectrum, which showed a parent ion at *m/e* 332 (^{192}Os) (with an isotopic distribution characteristic of Os) and the subsequent loss of 5 units of 28 (1 C_2H_4 and 4 CO). The structure was further confirmed by the agreement of the observed IR spectrum with that of the iron analogue reported by Mardoch and Weiss.[31]

***cis*-Hydridomethyltricarbonyl(triphenylphosphine)osmium. Method A.** A standard reaction bulb was charged with 20.5 mg (0.06 mmol) of $Os(CO)_4(H)CH_3$, 51.1 mg (0.20 mmol) of PPh_3, and 2.8 mL of degassed hexanes. The bulb was opened to a vacuum line that had been filled with 6 mm of air and then pressured to 1012.8 mm with nitrogen. (The atmosphere thus contained 0.12% O_2, 0.03 equiv.) The bulb was closed, covered with aluminum foil, and stirred for a total of 36 h. An IR spectrum at that time showed no $Os(CO)_4(H)CH_3$ remaining. The product (16.9 mg, 48% yield) was isolated by preparative-layer chromatography (1 mm of silica gel, eluant 10% CH_2Cl_2 in hexanes) and recrystallization from hexanes at −30 °C. $Os(CO)_3(PPh_3)(H)CH_3$ was characterized by its IR (Table I) and NMR (Table III) spectra and by its mass spectrum (60 °C), which showed a parent ion at *m/e* 554 (^{192}Os) with the isotopic distribution characteristic of Os. Anal. Calcd for $C_{22}H_{19}O_3OsP$: C, 47.81; H, 3.64. Found: C, 48.04; H, 3.56.

Method B. A standard reaction bulb containing 45.0 mg (0.14 mmol) of $Os(CO)_4(H)CH_3$ and 121.0 mg (0.46 mmol) of PPh_3 dissolved in 3 mL of hexanes was irradiated (450-W Ace-Hanovia high-pressure Hg lamp) for ca. 10 min at 12 °C. At this time, the IR spectrum of the reaction mixture showed no $Os(CO)_4(H)CH_3$ remaining. The product (54.3 mg, 69% yield) was isolated as before.

Dihydridodicarbonylbis(triethylphosphine)osmium. At −196 °C $Os(CO)_4H_2$ (170 mg, 0.56 mmol) was condensed on a vacuum line into a standard reaction bulb containing methylcyclohexane (3 mL). Into this was transferred $(C_2H_5)_3P$ (1 mL). This mixture was allowed to stand for 1 h at 110 °C; then solvent and excess $(C_2H_5)_3P$ were removed in vacuo. The remaining oil was dissolved in dichloromethane and purified by TLC (silica gel, pentane with 10% CH_2Cl_2, R_f 0.30) to give $Os(CO)_2(PEt_3)_2H_2$ (105 mg, 0.336 mmol, 60% yield) as a colorless liquid. The product was identified by its IR (Table I) and NMR (Table III) spectra and by its mass spectrum (90 °C), which showed the parent ion at *m/e* 486 (^{192}Os) with an isotopic distribution characteristic of Os. Anal. Calcd for $C_{14}H_{32}O_2OsP_2$: C, 34.70; H, 6.67; P, 12.77. Found: C, 34.41; H, 6.67; P, 12.65.

***cis*-Dimethyl(triphenylphosphine)tricarbonylosmium.** A standard reaction bulb was charged with 68.1 mg (0.21 mmol) of $Os(CO)_4(CH_3)_2$, 102.3 mg (0.40 mmol) of PPh_3, and 2.6 mL of CH_2Cl_2. Next, 45.4 mg (0.41 mmol) of $Me_3NO{\cdot}2H_2O$ was dissolved in 20 mL of 1:1 CH_2Cl_2/CH_3CN. Over a period of 1 h, 10 mL of this solution was added in small aliquots to the $Os(CO)_4(CH_3)_2/PPh_3$ solution. The bulb was closed and covered with foil, and the reaction was stirred overnight. The solvent was removed in vacuo, and the resulting off-white solid was taken up in CH_2Cl_2. The product (88 mg, 76% yield) was isolated via preparative-layer chromatography on silica gel using 10% CH_2Cl_2 in hexanes as eluant, followed by recrystallization from hexanes. It was characterized by its IR (Table I) and NMR (Table III) spectra and by its mass spectrum (80 °C), which showed a parent ion at *m/e* 568 (^{192}Os) with the isotopic distribution characteristic of Os. Anal. Calcd for $C_{23}H_{21}O_3OsP$: C, 48.76; H, 3.74. Found: C, 49.27; H, 3.89. The $Os(CO)_3(PPh_3)(CH_3)_2$ previously reported,[9] to which a less symmetric structure was assigned on the basis of its complex NMR spectrum, appears to have been a mixture of $Os(CO)_3(PPh_3)(CH_3)_2$ (with spectra and structure as reported here) and $Os(CO)_4(CH_3)_2$.

Thermolysis of $Os(CO)_4(CH_3)_2$ and $Os(CO)_4H_2$. $Os(CO)_4H_2$ (25.0 mg) was dissolved in C_6D_6 (0.6 mL) along with $Os(CO)_4(CH_3)_2$ (26.0 mg) and was held at 85 °C for 2.5 days. The −196 °C volatiles were removed by a Toepler pump and analyzed by gas chromatography; they were principally methane with a trace of carbon monoxide. All the room-temperature volatiles were then distilled into an NMR tube along with 12.7 mg of methylene chloride as an integration standard, and the tube was sealed under vacuum. The ^1H NMR spectrum showed the presence of unreacted $Os(CO)_4(CH_3)_2$ and $Os(CO)_4H_2$. Comparison of their concentrations, obtained by integration against the methylene chloride, with the pressure–volume measurements of the −196 °C volatiles indicated that 1 equiv of methane had formed per 1 equiv of $Os(CO)_4(CH_3)_2$ that had reacted. (Slightly more than 1 equiv of $Os(CO)_4H_2$ had reacted as this compound slowly decomposes at 85 °C.) The NMR spectrum of the residue nonvolatile at room temperature showed the presence of $HOs_2(CO)_8CH_3$.

Reaction of $Os(CO)_4(H)CH_3$ with $Os(CO)_4H_2$. $Os(CO)_4(H)CH_3$ (30.8 mg) was combined with $Os(CO)_4H_2$ (61.2 mg) and held at 49 °C for 6.5 h. At that time, all room-temperature volatiles were transferred out of the vial and an NMR spectrum of the nonvolatiles showed that substantial quantities of $H_2Os_2(CO)_8$ (identified by comparison of its ^1H NMR spectrum with that in the literature[32]) had formed.

Reaction of $Os(CO)_4(H)CH_3$ with $HRe(CO)_5$. A standard reaction bulb was charged with 52 mg (0.16 mmol) of $Os(CO)_4(H)CH_3$, 80 mg (0.25 mmol) of $HRe(CO)_5$, and 5 mL of methylcyclohexane. The bulb was closed and heated to 49 °C for 8 h. Preparative-layer chromatography (silica gel with pentane eluant) yielded a yellow oil as the major product. It was identified as $HOs(CO)_4Re(CO)_5$ by its IR spectrum (Table I), ^1H NMR spectrum (Table II), and mass spectrum; the last showed a parent ion at *m/e* 632 (^{192}Os, ^{187}Re) with the isotopic distribution characteristic of OsRe. The ^1H NMR chemical shift and mass spectrum agreed with those assigned in the literature[33] to $HOs(CO)_4Re(CO)_5$ as a component of a mixture.

Dimethyloctacarbonyldiosmium. A 500-mg sample of *cis*-$Os(CO)_4(H)CH_3$ containing 20 mg of *cis*-$Os(CO)_4(CH_3)_2$ was heated in a sealed, evacuated glass bulb at 49 °C for 12 h. After the bulb was cooled, the resulting yellow mixture was dissolved in 4 mL of CH_2Cl_2 and chromatographed on thin silica gel plates in the dark with pentane as eluant. Two major bands were located by UV spectroscopy (exposing only the edge of the plate to the UV radiation as the products are light sensitive). The top band (R_f ~90%) was extracted with 50 mL of CH_2Cl_2. To the resulting solution was added 1 mL of CCl_4 (to convert the $HOs_2(CO)_8Me$ to $ClOs_2(CO)_8Me$) in a glass bulb, which was then frozen, evacuated, and closed. The mixture was then warmed to room temperature and stirred overnight. After evaporation to dryness the residue was dissolved in 2 mL of CH_2Cl_2 and chromatographed on 1-mm silica gel plates in the dark with pentane as eluant. Two bands were found by exposing the edge of the plate to UV light. The top band (R_f ~90%) was extracted with 20 mL of CH_2Cl_2, which produced 10 mg of a colorless oil. The product was characterized as $MeOs(CO)_8Me$ by IR (Table I) and NMR (Table II) spectroscopy. Its mass spectrum (80 °C) showed a parent ion at *m/e* 638 (^{192}Os) with the isotopic distribution characteristic of Os_2. An analytical sample has been obtained by vacuum sublimation. Anal. Calcd for $C_{10}H_6O_8Os_2$: C, 18.93; H, 0.96. Found: C, 18.77; H, 1.01.

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Registry No. *cis*-$Os(CO)_4H_2$, 18972-42-2; *cis*-$Os(CO)_4(CH_3)_2$, 22639-01-6; *cis*-$Os(CO)_4(C_2H_5)_2$, 27882-33-3; *cis*-$Os(CO)_4(H)CH_3$, 22639-03-8; *cis*-$Os(CO)_4(H)C_2H_5$, 68568-90-1; *cis*-$Os(CO)_4(Cl)C_2H_5$, 68568-91-2; $CH_3Os_3(CO)_{12}CH_3$, 60442-72-0; $C_2H_5Os_3(CO)_{12}C_2H_5$, 68568-94-5; $HOs_2(CO)_8C_2H_5$, 82666-15-7; $ClOs_2(CO)_8C_2H_5$, 68568-93-4; $ClOs_2(CO)_8CH_3$, 68629-09-4; $Os(CO)_4(PEt_3)$, 21192-24-5; $Os(CO)_4(C_2H_4)$, 68569-22-2; $Os(CO)_3(PPh_3)(H)CH_3$, 82768-46-5; $Os(CO)_2(PEt_3)_2H_2$, 82666-16-8; $Os(CO)_3(PPh_3)(CH_3)_2$, 82729-21-3; $HOs_2(CO)_8H$, 25685-05-6; $HOs_2(CO)_8CH_3$, 60442-71-9; $CH_3Os_2(CO)_8CH_3$, 82666-17-9; $HOs(CO)_4Re(CO)_5$, 82666-18-0.

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