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SOME REACTIONS OF POLYNUCLEAR OSMIUM CARBONYL ALKYLS

J.W. KELLAND and J.R. NORTON *

Department of Chemistry, Princeton University, Princeton, New Jersey 08540 (U.S.A.)

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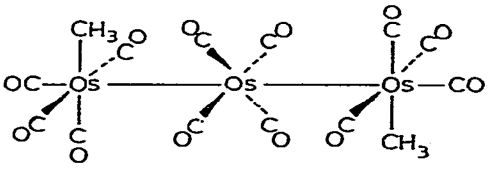
Summary

The trinuclear dimethyl cluster $Os_3(CO)_{12}(CH_3)_2$ (I) decomposes rapidly at 90°C to give largely $Os_3(CO)_{12}$ and CH_4, apparently from solvent attack by methyl radicals. Treatment of I with anhydrous HBr cleaves Os—C bonds, i.e. excess HBr converts it to $Os_3(CO)_{12}Br_2$. However, I undergoes rapid and selective cleavage of one Os—Os bond by I_2 to give *cis*-$Os(CO)_4(CH)_3I$ and $I(CH_3)Os_2(CO)_8$. Other halogen electrophiles give analogous results, although stronger electrophiles display less selectivity. The reaction of $HOs(CO)_4Os(CO)_4CH_3$ with PPh_3 gives exclusively $HOs(CO)_3(PPh_3)Os(CO)_4CH_3$ (two isomers) arising from substitution at the hydride end.

Introduction

We recently reported [1] the preparation of the first trinuclear dialkyl cluster, $Os_3(CO)_{12}(CH_3)_2$ (I) and of $HOs(CO)_4Os(CO)_4(CH_3)$ (II). (Each structure shown is only one of many conformers doubtless present in solution; the conformer shown for I is that found in the solid state by X-ray crystallography [2].) As they contain alkyl and hydride ligands on neighboring metal atoms, they offer a unique opportunity to explore the chemistry of such systems and to con-



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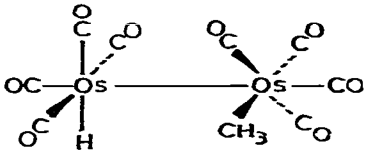

(II)

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* To whom correspondence should be addressed. Camille and Henry Dreyfus Foundation Teacher-Scholar, 1976, and Alfred P. Sloan Fellow, 1977—79.

trast the results with those for analogous mononuclear species. We report a study of some thermolysis, cleavage, and substitution reactions of $Os_3(CO)_{12}(CH_3)_2$ and $HOs(CO)_4Os(CO)_4CH_3$.

Results and discussion

Thermolysis of $Os_3(CO)_{12}(CH_3)_2$ (I)

The most thermodynamically desirable decomposition mode for this molecule is surely:

$$\underset{\text{(I)}}{Os_3(CO)_{12}(CH_3)_2} \rightarrow Os_3(CO)_{12} + C_2H_6$$

However, the mechanism of such a process would have to involve either one methyl migration and concerted elimination of ethane from adjacent osmium atoms, or the migration of two methyl groups. Both possibilities seem unlikely, but methyl migration finds some precedent in the "methyl transfer" process proposed by Bergman and coworkers [3] for the generation of acetone from $[(\eta^5\text{-}C_5H_5)Co(CO)CH_3]_2$. Similar mechanistic difficulties for I would arise in the elimination of acetone.

It is thus not surprising that, although $Os_3(CO)_{12}$ is the principal inorganic product when I is decomposed at 90°C in toluene, no acetone and relatively minor amounts of ethane (<5%) are observed. The principal organic product is methane (1.6 eq.), presumably by formation of methyl radicals and solvent attack. The principal reaction is therefore eq. 1.

$$\text{I} \xrightarrow[\text{solvent R—H}]{90^\circ\text{C}} Os_3(CO)_{12} + 2\ CH_4 \qquad (1)$$

Solvent attack was confirmed by the use of toluene-d_8 and consequent detection of CH_3D, and by the detection of CD_3H from normal toluene and I-d_6. The reaction is smoothly first-order: $d[\text{I}]/dt = -k_1[\text{I}]$, where $k_1 = 4.54(\pm 0.12) \times 10^{-6}$ sec^{-1} in toluene at 74°C.

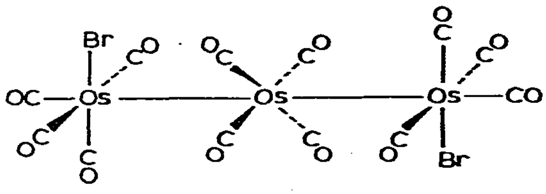
These results contrast with those obtained [4] in our study of the thermolysis of mononuclear $Os(CO)_4(CH_3)_2$. There $\cdot CH_3$ was formed only slowly even at 162°C and rapidly at 180°C. Assuming that the present case does involve $\cdot CH_3$ formation, there is thus a difference of about 100°C between the temperatures required for rapid loss of methyl radicals from the two compounds. The bond dissociation energy appears to be much smaller in the polynuclear I, presumably reflecting the stabilization of the dissociative transition state by delocalization of the unpaired electron along the metal chain.

Cleavage reactions of $Os_3(CO)_{12}(CH_3)_2$ (I)

It has been said that "the most general reaction" of mononuclear organometallic compounds is "cleavage by a proton source" [5]. We thus checked to see whether or not the same was true of the trinuclear $Os_3(CO)_{12}(CH_3)_2$. Not surprisingly, at room temperature anhydrous HBr in CH_2Cl_2 readily cleaved both methyl groups (reaction 2).

$$\text{I} + 2\ HBr \xrightarrow{CH_2Cl_2} Os_3(CO)_{12}Br_2\ (\text{III}) \qquad (2)$$

The product trinuclear dibromide III is well known [6,7] and apparently isostructural with I.



(III)

Although once again a variety of conformers are doubtless found in solution, the structure drawn for III is analogous to that recently found for $Os_3(CO)_{12}I_2$ in the solid state by an X-ray crystallographic study [8]. (Comparison of the IR spectra of $Os_3(CO)_{12}X_2$ [7a], $Os_3(CO)_{12}D_2$ [7b], $Os_3(CO)_{12}(CH_3)_2$, and related triosmium compounds (Table 1), allowing for the fact that the halides only dissolve in halocarbon solvents and hence give broader bands, strongly suggests that the entire series of compounds is isostructural. Particularly good examples are the spectra of $Os_3(CO)_{12}I_2$ and I in Fig. 1, and of $Os_3(CO)_{12}D_2$ in Fig. 1d of Ref. 7b.) The acid cleavage in reaction 2 thus proceeds with retention of stereochemistry about osmium.

Use of one equivalent of HBr permits isolation of the partial cleavage product $BrOs(CO)_4Os(CO)_4Os(CO)_4CH_3$ (IV). Its IR (Table 1) and NMR (Table 2) spectra, along with the presumption that the stereochemistry of partial cleavage is that eventually observed for complete cleavage, give IV the structure shown (and its conformers).

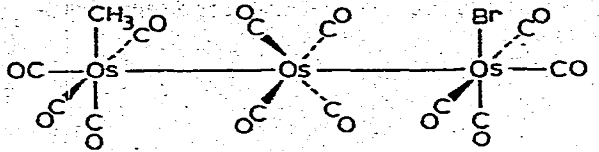
As cleavage by halogens, particularly iodine, of metal—carbon bonds in mononuclear species is a common and much investigated phenomenon [9], normally

TABLE 1

IR SPECTRA [a] (cm^{-1}, carbonyl region)

Compound	No.	Spectrum
$Os_3(CO)_{12}(CH_3)_2$	I	2132vw, 2094s, 2038vs, 2029s, 2013s, 2008m, 1988m
$Os_3(CO)_{12}D_2$ [b]		2134vw, 2097s, 2068w, 2042vs, 2038(sh), 2031s, 2015s, 2002(sh), 1993m, 1989(sh)
$Os_3(CO)_{12}I_2$ [c]		2142w, 2111s, 2056vs(br), 2027s, 2022(sh), 2002w
$Os_3(CO)_{12}(CH_3)Br$	IV	2141w, 2104s, 2057vs, 2047m, 2036vs, 2022s, 2013m, 1994w
$Os_2(CO)_8(CH_3)H$	II	2130w, 2089s, 2056s, 2044s, 2039s, 2033s, 2025m, 2018m, 2007m, 2004w
$Os_2(CO)_8(CH_3)I$	V	2134vw, 2097s, 2058s, 2053s, 2043s, 2031s, 2017m, 2011m
$Os_2(CO)_8(CH_3)Cl$	VI	2098s, 2060s, 2054vs, 2044s, 2033vs, 2018m, 2013m
$Os_2(CO)_8(CH_3)Br$	VII	2103s, 2065s, 2059vs, 2047m, 2036s, 2020m, 2014w
$Os_2(CO)_8Cl_2$ [d]		2121s, 2082vs, 2069s, 2064s, 2054s, 2032s
$Os_2(CO)_8D_2$ [b]		2131vw, 2090s, 2048(sh), 2046s, 2039vs, 2033s, 2024s, 2022(sh), 2007s
$H(CH_3)Os_2(CO)_7PPh_3$	VIIIA	2103w, 2052m, 2024vs, 2018vs, 1992s, 1972m
	VIIIB	2110w, 2082m, 2062s, 2022s, 1982m, 1946vs

[a] All spectra run in pentane, unless otherwise stated. [b] Heptane, ref. [7b]. [c] CCl_4. [d] Heptane, ref. [7a].



(IV)

resulting in the formation of metal—iodine bonds [10], we have examined the halogen cleavage reactions of $Os_3(CO)_{12}(CH_3)_2$. We expected, and found, some competitive halogen cleavage of Os—Os bonds (as observed [6] with $Os_3(CO)_{12}$). What is remarkable is the selectivity with which halogen cleavage can be carried out.

For example, a solution of $Os_3(CO)_{12}(CH_3)_2$ (I) in CCl_4 can be titrated with I_2/CCl_4; the purple color is rapidly discharged until precisely 1 eq. has been added. The results are shown as reaction 3.

$$I + I_2 \xrightarrow{CCl_4} cis\text{-}Os(CO)_4(I)CH_3 + IOs(CO_4)Os(CO)_4CH_3 \qquad (3)$$

(V)

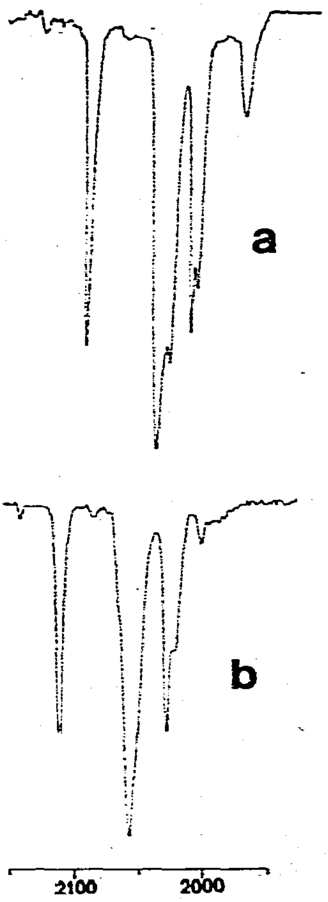


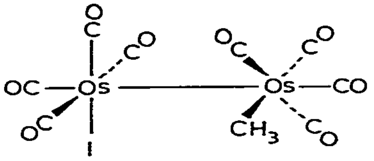
Fig. 1. Carbonyl region infrared spectra of (a) $Os_3(CO)_{12}(CH_3)_2$ in CCl_4 and (b) $Os_3(CO)_{12}I_3$ in pentane.

TABLE 2

^{1}H NMR DATA (τ, C_6D_6, 100 MHz)

Compound	No.	Me	H	PPh$_3$
$Br(Me)Os_3(CO)_{12}$	IV	9.67(s)		
$I(Me)Os_2(CO)_8$	V	9.71(s)		
$Cl(Me)Os_2(CO)_8$	VI	9.77(s)		
$H(Me)Os_2(CO)_7PPh_3$	VIIIA	9.72(s, 3H)	18.72 (d, J(P—H) 18Hz, 1H)	2.4—3.2(m)
	VIIIB	9.73(s, 3H)	17.55 (d, J(P—H) 24Hz, 1H)	2.4—3.2(m)

The dinuclear iodomethyl complex V is assigned the structure shown (and, as usual, its conformers) on the basis of the similarity of its IR spectrum (see Table 1) to that of the previously reported [1] $ClOs(CO)_4Os(CO)_4(CH_3)$ (VI). (By reasoning analogous to that used for the trinuclear compounds, comparison of the IR spectra of II, V, VI, VII (below), and all $Os_2(CO)_8X_2$ halides and hydrides [7] (see Table 1) suggests that all of these compounds have the same structure,



(V)

substituents *cis* to the Os—Os bond, confirmed crystallographically for $Os_2(CO)_8Cl_2$ [11].)

An Os—Os bond in I is thus cleaved more readily than the Os—Os bond in V and than the Os—C bonds in I. Precedent for the selective cleavage of a single Os—Os bond in a trinuclear system is offered by the previously reported [6] reaction 4.

$$Os_3(CO)_{12} + X_2 \xrightarrow{C_6H_6} XOs(CO)_4Os(CO)_4Os(CO)_4X \qquad (4)$$

The selective cleavage of Os—Os rather than Os—C is especially remarkable in view of the facile thermolysis of $Os—CH_3$, described above.

Considering that many of the same effects that favor electron-transfer mechanisms also favor electrophilic cleavages in general [12] it is not possible to reach any detailed mechanistic conclusions. An important effect does seem likely to be the increased ease of electron detachment from polyosmium systems of higher nuclearity.

Use of stronger electrophiles gives analogous results. ICl shows the same selectivity (Os—Os rather than Os—C) with considerably more iodine than chlorine going onto the diosmium fragment (reaction 5).

$$I + ICl \xrightarrow{CH_2Cl_2} cis\text{-}Os(CO)_4(CH_3)Cl + \underset{\text{(V) (major product)}}{Os_2(CO)_8(CH_3)I}$$

$$+\ cis\text{-}Os(CO)_4(CH_3)I + \underset{(VI)}{Os_2(CO)_8(CH_3)Cl} \qquad (5)$$

The even stronger electrophile Br_2 shows, as expected, less selectivity, giving both Os—Os and Os—C bond cleavage (reaction 6).

$$I + Br_2 \xrightarrow{CCl_4} cis\text{-}Os(CO)_4(CH_3)Br + \underset{(VII)}{Os_2(CO)_8(CH_3)Br} + Os_2(CO)_8Br_2 + cis\text{-}Os(CO)_4Br_2 \qquad (6)$$

As a result 1 eq. of bromine leaves some unreacted I. Additional equivalents of bromine are consumed rapidly.

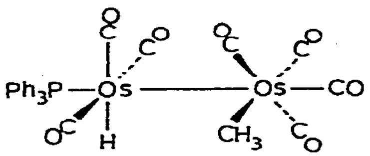
Phosphine substitutions of $HOs(CO)_4Os(CO)_4CH_3$ *(II)*

An investigation of the mechanism of formation of compounds such as I from *cis*-$Os(CO)_4(H)R$ (reported elsewhere [13] led to the surmise that the hydride end of polynuclear hydrides such as II was much more reactive than the alkyl end, and also much more reactive than the mononuclear hydride *cis*-$Os(CO)_4H_2$ [14]. In order to test this hypothesis we investigated phosphine substitution on II. At 50°C 1 eq. of triphenylphosphine reacted readily with II, converting it almost completely (reaction 7) into two isomers (VIIIA and VIIIB), both with Ph_3P substituted onto the hydride end.

$$II + Ph_3P \xrightarrow[\text{heptane}]{50^\circ C} \underset{(VIII)}{HOs(CO)_3(PPh_3)Os(CO)_4CH_3} \qquad (7)$$

No evidence was seen for any substitution at the methyl end (we assume such a species would have an observable $J(P—CH_3)$ and a much smaller $J(P—H)$ than that in VIII).

VIIIA (the principal product) and VIIIB are readily separated by TLC. Both show $J(P—H)$ (18 and 24 Hz respectively, Table 2) in the range usually associated (especially in the coordination shell of third-row transition elements) with *cis* hydride and phosphine ligands [15]. As steric factors produce axial substitution in $MnRe(CO)_{10} + PPh_3 \rightarrow (OC)_5MnRe(CO)_4(PPh_3)$ [16], it seems reasonable to suggest an axial substitution pattern here for the principal product VIIIA; the minor product VIIIB would on this basis be assigned the other *cis* structure as shown (with, as usual, other conformers present in solution).



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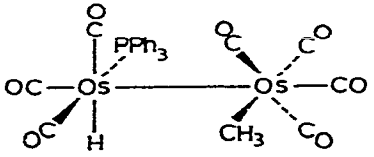

(VIII B)

These tentative assignments receive some support from the IR. The lowest frequency major $\nu(CO)$ is much lower in VIIIB (1946 cm^{-1}) than in VIIIA, reflecting the fact that only VIIIB has a carbonyl ligand *trans* to PPh_3. Similar observations can be made in comparing axially versus equatorially substituted $Re_2(CO)_8L_2$ [17,18]. Structures analogous to VIIIA and VIIIB have been proposed for the monosubstituted $Os_2(CO)_7H_2(PPh_3)$ derivative of $Os_2(CO)_8H_2$ [7a].

$HOs(CO)_4Os(CO)_4CH_3$ thus undergoes substitution much more rapidly than *cis*-$Os(CO)_4H_2$ [14] or *cis*-$Os(CO)_4(H)CH_3$ [19]. We plan a detailed investigation of the dinuclear substitution mechanism, paying particular attention to possible free radical processes [20].

Experimental

General

Mononuclear osmium complexes were handled by standard vacuum line techniques. The standard reaction vessel was a 25 ml glass bulb connected through a high-vacuum Teflon stopcock to an O-ring joint. Analytical reagent grade n-heptane, toluene, dichloromethane and toluene-d_8 were dried over P_2O_5 and then transferred into the reaction vessel.

Infrared spectra were obtained on a Perkin—Elmer Model 283 spectrometer, calibrated with $Os_3(CO)_{12}$. Proton NMR spectra were recorded on a Varian XL-100-FT using C_6D_6 as lock and solvent. Gas analysis was carried out on 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 mass spectrometer at 70 eV equipped with direct inlet and gas inlet systems. Spectra were recorded with and without the marking standards heptacosafluorotributylamine and tris(perfluoroheptyl)-s-triazine in order to ensure that *m/e* values were accurate. All compounds showed parent ion envelopes with isotopic distributions which agreed with those calculated for the number of osmium and other polyisotopic atoms in the molecular formulas.

Elemental analyses were performed by the microanalytical laboratory of Hoffmann—La Roche Inc., Nutley, New Jersey.

Preparation of $Os_3(CO)_{12}(CH_3)_2$ (I) and $HOs(CO)_4Os(CO)_4CH_3$ (II)

cis-$Os(CO)_4(H)CH_3$ [1] (200 mg) was transferred into a standard reaction bulb, which was then sealed and heated for 10 h at 49°C. After cooling, the bulb was opened to the air and the residue taken up in 3 ml CH_2Cl_2 and applied to silica gel TLC plates. (The products are sufficiently air-stable that TLC separation can be carried out in air if performed rapidly, less than $\frac{1}{2}$ hour. However, the products are quite light-sensitive, so the separation must be performed in the dark, and the resulting bands must be located by exposing only the edge of the plate to UV light.) Use of pentane as eluant produced two major bands. The top band ($R_f \sim 90\%$) yielded a colorloss oil II (28%) (which yellows rapidly in the presence of air and light but can be stored indefinitely in vacuo in a freezer). The lower band ($R_f \sim 75\%$) produced pale yellow, reasonably air-stable crystals of I (24%). Analysis: Found: C, 17.42; H, 0.68. $C_{14}H_6O_{12}Os_3$ calcd.: C, 17.95; H, 0.65%. Although spectroscopic data for these two complexes have been reported earlier [1], the IR spectra of highly purified samples of I and II are reported in Table 1 to facilitate comparison with the spectra of related tri- and dinuclear compounds. The IR spectrum of I is shown in Fig. 1.

If the above thermolysis is performed for a shorter period of time, an impurity (apparently $HOs(CO)_4Os(CO)_4Os(CO)_4CH_3$) is present in the lower band. This can most easily be removed by treatment with methyl iodide (which presumably converts the hydride to an iodide) and further TLC.

Thermolysis of I

I (40 mg) was placed in a standard reaction bulb into which 2 ml of toluene were distilled. The bulb was heated at 94°C for 25 h. The gas evolved was analyzed on a 6′ Porapak QS column at room temperature; it proved to be largely methane with <5% ethane. The reaction was repeated and the volume of methane evolved measured as 1.6 ml at STP, or 0.073 m*M*. IR and TLC showed the osmium-containing residue to be largely $Os_3(CO)_{12}$.

The reaction was repeated in toluene-d_8 and the evolved methane was analyzed by mass spectroscopy. Spectra were recorded using resolution >1,000 so that the sample peaks were resolved away from the background ions (typically H_2O^+ at m/e 18 and OH^+ at m/e 17). After correction for CH_3D fragment contributions [21] at m/e 16, the methane was determined to be 60% CH_3D.

When 18 mg of $Os_3(CO)_{12}(CD_3)_2$ were pyrolysed in toluene, the methane evolved was 90% CD_3H and 10% CD_4, by the above mass spectroscopic technique.

Kinetics of thermolysis of I

The rate of decomposition of I in toluene was measured by infrared spectroscopy, monitoring the disappearance of the 2096 cm^{-1} carbonyl band. A solution of I in toluene, initially 0.0065 *M*, was frozen and degassed in a standard reaction bulb. The bulb was placed in a constant temperature bath and was removed at appropriate intervals and cooled with ice water in order to stop the reaction. An aliquot was removed under argon and its IR spectrum recorded.

Reaction of I with HBr

I (18 mg) was dissolved in 2 ml of CH_2Cl_2. This solution was frozen and degassed in a vial and then ca. 5 eq. of anhydrous HBr were transferred into the vial. The reaction mixture was allowed to warm to room temperature and the solvent and unreacted HBr were removed in vacuo. Analysis of the air-stable residue (TLC, silica gel, pentane with 10% CH_2Cl_2 as eluant) showed only one band, from which yellow crystals of $Os_3(CO)_{12}Br_2$ (III) were obtained in quantitative yield. The compound was identified by mass spectroscopy and IR [6,7].

Repeating the reaction with 1 eq. of HBr allowed the isolation by TLC of air-stable yellow crystals of $Br(CH_3)Os_3(CO)_{12}$ (IV) in about 50% yield. IV was characterized by its mass spectrum, recorded at 140°C, which showed a parent ion at m/e 1008 (^{192}Os, ^{81}Br) with the isotopic distribution characteristic of Os_3Br. Analysis: Found: C, 15.53; H, 0.58. $C_{13}H_3O_{12}BrOs_3$ calcd.: C, 15.59; H, 0.30%.

Reaction of I with I_2; preparation of V

A solution of I (16.4 mg, 0.018 mmol) in a few mol of CCl_4 was titrated under nitrogen with a 0.312 mg/ml (1.23 m*M*) solution of iodine in CCl_4. One equivalent (14.8 ml) was consumed before the purple iodine color persisted. After removal of solvent the reaction mixture gave rise to two bands on TLC (silica gel, pentane as eluant).

The reaction was carried out preparatively as follows. I (21 mg) was dissolved in 2 ml of CCl_4. This solution was frozen and degassed in a bulb and then 6 mg of I_2 (1 eq.) were transferred in. After warming and removal of solvent, TLC showed two bands as above. The upper band ($R_f \sim 90\%$) was identified as *cis*-$Os(CO)_4(CH_3)I$ by mass spectroscopy and by comparison with its reported IR [22]. Analysis: Found: C, 13.62; H, 0.73. $C_5H_3O_4IOs$ calcd.: C, 13.52; H, 0.68%. The lower band ($R_f \sim 50\%$) produced yellow crystals of $I(CH_3)Os_2(CO)_8$ (V). Analysis: Found: C, 14.74; H, 0.52; I, 17.18. $C_9H_3O_8IOs_2$ calcd.: C, 14.48; H, 0.40; I, 17.00%. The mass spectrum of V, recorded at 120°C, showed a parent ion at *m/e* 750 (^{192}Os) with the isotopic distribution characteristic of Os_2.

The reaction gave analogous results when carried out in pentane instead of CCl_4.

Reaction of I with ICl

I (24 mg) was dissolved in 2 ml of CH_2Cl_2. This solution was frozen and degassed in a bulb and then 4 mg of ICl (1 eq.) were distilled in. The resulting pale yellow solution, upon analysis by TLC in air (silica gel, pentane as eluant), produced four bands. Two were identified by IR and mass spectroscopy as the mononuclear complexes *cis*-$Os(CO)_4(CH_3)Cl$ ($R_f \sim 80\%$) and *cis*-$Os(CO)_4(CH_3)I$ ($R_f \sim 85\%$) [22]. The slower-moving bands contained the dinuclear complexes $I(CH_3)Os_2(CO)_8$ (V, characterized above) (50% yield) ($R_f \sim 50\%$) and $Cl(CH_3)Os_2(CO)_8$ (VI) [1] (10% yield) ($R_f \sim 40\%$).

The mass spectrum of VI, recorded at 100°C, showed a parent ion at *m/e* 660 (^{192}Os, ^{37}Cl) with the isotopic distribution characteristic of Os_2Cl.

Reaction of I with Br_2

I (22 mg) was dissolved in 2 ml of CCl_4. The solution was frozen and degassed in a bulb, and then Br_2 (4 mg, 1 eq.) was transferred in. Reaction occurred as the bulb warmed to room temperature. Removal of solvent in vacuo and analysis by TLC (silica gel, 10% CH_2Cl_2/90% pentane as eluant) gave five bands: unreacted I ($R_f \sim 100\%$), *cis*-$Os(CO)_4(CH_3)Br$ ($R_f \sim 90\%$) identified by its reported IR [22], $Br(CH_3)Os_2(CO)_8$ (VII) (pale yellow air-stable crystals) ($R_f \sim 85\%$) (45% yield), *cis*-$Os(CO)_4(CH_3)Br$ ($R_f \sim 20\%$) (identified by its reported IR [23] and $Os_2(CO)_8Br_2$ ($R_f \sim 10\%$) (identified by its reported IR [7]. VII was characterized by its mass spectrum, recorded at 120°C, which showed a parent ion at *m/e* 704 (^{192}Os, ^{81}Br) with the isotopic distribution characteristic of Os_2Br.

Analogous results are obtained when the reaction is run in pentane. Additional equivalents of bromine are readily consumed.

Reaction of triphenylphosphine with II; preparation of VIIIA and VIIIB

II (32 mg) was reacted with 13 mg (1 eq.) of triphenylphosphine in n-heptane solution in an evacuated, sealed bulb for 5 h at 50°C. Removal of the solvent produced a pale yellow sample of $HOs(CO)_3(PPh_3)Os(CO)_4CH_3$ (VIII). Separation of the two isomers (VIIIA, 70%, $R_f \sim 60\%$; VIIIB, 12%, $R_f \sim 50\%$) was achieved by TLC on silica gel plates using 10% CH_2Cl_2/90% pentane (v/v) as eluant. Both isomers were air-stable solids. Analysis for the major isomer VIIIA: Found: C, 35.95; H, 2.13; P, 3.53. $C_{26}H_{19}O_7Os_2P$ calcd.: C, 36.53; H, 2.24; P, 3.62%. The minor product, VIIIB, gave a mass spectrum identical to that of VIIIA, showing that the two compounds were in fact isomers; in both cases the spectra were obtained at 130°C and showed a parent ion P^+ at m/e 858 (^{192}Os) with the isotopic distribution characteristic of Os_2. $[P-16]^+$ was also observed, as well as peaks corresponding to the stepwise loss of seven carbonyl groups. The base peak was the $[P-Ph_3P]^+$ ion.

Acknowledgement

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