of the mutual trans influence of the oxo ligands. The paramagnetism of $O_3Mo_2(TPP)_2$,[2,6,13] as contrasted to the diamagnetism of the other $Mo_2O_3^{4+}$ complexes, is easily understood from the structure differences. If the Mo=O (terminal) bond fixes the z direction and d_{xy} is the populated 4d orbital,[12a] overlap of the d_{xy} orbitals between the Mo atoms is inhibited in $O_3Mo_2(TPP)_2$ but not in the other $Mo_2O_3^{4+}$ complexes. The two skeletons are approximately staggered with NMoMo′N′ dihedral angles of ~30 and 60°.[14] The porphyrin interplanar separation in the Mo derivative is ~3.8 and ~4.9 Å in the Nb complex.

The large difference in the structures of $O_3Mo_2(TPP)_2$ and $O_3Nb_2(TPP)_2$ seems to result from the difference in the affinity of the two metals for the porphinato ligand. The structure observed for the Mo complex leads to strong interaction of each metal atom with its porphinato ligand and two oxo ligands. This arrangement concomitantly requires an energetically demanding radial expansion of the porphinato core (Ct···N = 2.092 Å),[17] a large number of tight O···N contacts, and a rather close intramolecular porphyrin interplanar spacing. The configuration of the Nb complex allows strong interaction of each metal atom with two oxo ligands and a weaker one with the third but also requires a decreased interaction of the metal atoms with the porphinato ligands. The decreased interaction is presumably partly counterbalanced by diminished radial strain of the porphinato ring (Ct···N = 2.006 Å), a smaller number of tight O···N contacts, and a substantially larger intramolecular interplanar spacing. We note that these different interactions of the metal atom with the porphinato ligand are also observed in the respective monomeric complexes. Thus in six-coordinate porphinatomolybdenum(V) derivatives,[18] the Mo atom is nearly centered in the prophinato plane, while in seven-coordinate acetatooxotetraphenylporphinatoniobium(V)[19] the Nb atom is displaced 1.0 Å out-of-plane and the oxo and the bidentate acetato ligands are on the same side of the porphinato plane.

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Supplementary Material Available: Tables of atomic coordinates (8 pages). Ordering information is given on any current masthead page.

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Mechanism of Reductive Elimination. 2.[1] Control of Dinuclear vs. Mononuclear Elimination of Methane from *cis*-Hydridomethyltetracarbonylosmium

Sir:

A general picture of the elimination of cis organic ligands from transition metal complexes must explain the rapid elimination of alkanes from almost all alkyl hydride complexes, the instability of which is particularly striking in comparison with the relative stability of dihydrido and dimethyl complexes.[2-7] This generalization is exemplified by the order of stability $Os(CO)_4(H)CH_3 \ll Os(CO)_4H_2 \ll Os(CO)_4(CH_3)_2$, to which we have called attention.[1] We have long felt the most likely explanation to be a mechanism unique to the combination of alkyl and hydride ligands.

We now report that elimination of methane from *cis*-$Os(CO)_4(H)CH_3$ (**1a**) to form $HOs(CO)_4Os(CO)_4CH_3$ (**2**)[3] proceeds by a dinuclear process, despite the presence of cis methyl and hydride ligands.[8-14] We further report that an external nucleophile, by intercepting an intermediate common to both reactions, can convert methane elimination from $Os(CO)_4(H)CH_3$ into a mononuclear process.

As with $Os(CO)_4H_2$,[1] the observation of the dinuclear **2** as primary decomposition product of $Os(CO)_4(H)CH_3$ (**1a**) suggests—but does not prove—that a dinuclear elimination is occurring. Fortunately, as we are dealing here with an *isolable* hydridomethyl complex,[15] the appropriate crossover experiment is feasible. Use of either CF_3COOD or CD_3OSO_2F in place of their nondeuterated analogues in the synthesis[3] of *cis*-$Os(CO)_4(H)CH_3$ allows preparation of $Os(CO)_4(D)CH_3$ (**1b**) and $Os(CO)_4(H)CD_3$ (**1c**), respectively.

The thermolysis of a mixture of **1b** and **1c** under a wide variety of conditions (from 10^{-2} M in methylcyclohexane to a mixture of pure liquids) yields substantial quantities of CD_4, demonstrating dinuclear elimination.[16] From quantitative analysis of the isotopically labeled methanes (CD_4, CD_3H, CDH_3, and CH_4 a primary kinetic isotope effect k_H/k_D of 1.5 ± 0.2 can be obtained. This small effect is about the same as that (k_{HH}/k_{HD} of 1.4) seen with the $Os(CO)_4H_2/Os(CO)_4D_2$ system.[1]

A control experiment, the decomposition of $Os(CO)_4(H)CH_3$ in the presence of an equivalent of CD_4, gives only CH_4 and CD_4 and confirms that the dinuclear mechanism inferred from the preceding data is correct. In order to explore the details of this mechanism, rate studies on

$$2Os(CO)_4(H)CH_3 \rightarrow CH_4 + HOs(CO)_4Os(CO)_4CH_3 \quad (1)$$

have been carried out. The rate of disappearance[17] of **1** is *first order* in **1**

$$d[Os(CO)_4(H)CH_3]/dt = -k_1[Os(CO)_4(H)CH_3]$$

with $k_1 = (1.38 \pm 0.06) \times 10^{-4}\ s^{-1}$ at 49 °C, invariant between 10^{-2} and 10^{-3} M initial concentration in methylcyclohexane. The rate is not particularly solvent-sensitive: k_1 =

$(1.89 \pm 0.09) \times 10^{-4}\ s^{-1}$ at 49 °C in THF. Activation parameters, in methylcyclohexane, are $\Delta H^{\ddagger} = 21.9\ (\pm 0.5)$ kcal/mol and $\Delta S^{\ddagger} = -8\ (\pm 1)$ eu.

The negative value of $\Delta S^{\ddagger}$ suggests that, in contrast to the mechanism demonstrated for $Os(CO)_4H_2$, the dissociation of a carbonyl ligand is *not* rate determining in the present reaction.[18,19] This conclusion can be confirmed by carrying out the thermolysis in methylcyclohexane under ^{13}CO (3 equiv, 0.1 atm) and stopping the reaction before completion. Examination of the carbonyl region of the reaction mixture by IR shows that ^{13}CO has been incorporated neither into recovered starting material nor into product.

A desire to determine the nature of the species formed in the first-order process led us next to investigate the thermolysis of **1** in the presence of triethylphosphine. No simple substitution is observed,[20-22] confirming the absence of carbonyl dissociation from **1**. The reaction which does occur

$$Os(CO)_4(H)CH_3 + Et_3P \rightarrow Os(CO)_4(Et_3P)\ (\mathbf{3}) + CH_4 \qquad (2)$$

suggests the possibility of nucleophilic displacement of methane from osmium by entering phosphine, a phenomenon which would be an example of acceleration of simple intramolecular reductive elimination by an incoming nucleophile. Such acceleration has been predicted on theoretical grounds[13a] and reported in some Pt systems.[23]

However, *no rate acceleration is observed here.*[20] The rate of disappearance of **1a** in methylcyclohexane in the presence of Et_3P at 49 °C

$$d[Os(CO)_4(H)CH_3]/dt = k_2[Os(CO)_4(H)CH_3]$$

is $k_2 = 6.4\ (\pm 0.1) \times 10^{-5}\ s^{-1}$. This rate is *independent* of Et_3P concentration (from 7 to 110 equiv) and is about half that seen above for the disappearance of **1a** without added phosphine. Furthermore, the results of the crossover experiment are altered by the presence of Et_3P: a mixture of **1b**, **1c**, and 110 equiv of Et_3P in methylcyclohexane gives CD_3H and CH_3D, but none of the dinuclear elimination product CD_4.[24]

A general mechanism for the reactions of **1** must thus include rate-determining formation of an intermediate **4**, which *must contain* all of the *carbonyl* and *labeled* CH_3 and *H* ligands of **1** and can therefore only be an isomer of it. This intermediate must be common to the reactions of **1** in the presence and the absence of triethylphosphine in order to explain the first-order kinetics observed in both cases. The following scheme satisfies these requirements.

Scheme I

$$Os(CO)_4(H)CH_3 \xrightarrow[k]{\text{rate-determining step}} \mathbf{4} \qquad (3)$$

$$\mathbf{4} + Os(CO)_4(H)CH_3 \xrightarrow{\text{fast}} HOs(CO)_4Os(CO)_4CH_3 + CH_4 \qquad (4)$$

$$\mathbf{4} + Et_3P \xrightarrow{\text{fast}} Os(CO)_4(Et_3P) + CH_4 \qquad (5)$$

The dinuclear elimination path, reaction 4, consumes a second mole of **1** in addition to that which has isomerized in the rate-determining step (reaction 3), so that k_1 (rate of disappearance of **1** in the absence of external ligand) = $2k_2$ (rate of disappearance of **1** in the presence of additional nucleophile).

The overall process is then one of competition between Et_3P and additional **1** for the intermediate **4**. The outcome of this competition controls the mechanism of methane evolution. The coordination of Et_3P converts the original dinuclear methane elimination process into a mononuclear, intramolecular one.

The structure of the intermediate **4** must be conjectural. It is reasonable to suggest that it contains a vacant coordination site to facilitate interaction with **1** or Et_3P. Comparison of the activation parameters involved in its formation with those reported[25] for

$$PtX(CO)RL \rightarrow PtX(C(=O)R)L$$

and similar reactions[26] and consideration of the small solvent effect observed for reaction 1 suggest that **4** may be a five-coordinate unsolvated acyl hydride $Os(CO)_3(H)(C(=O)CH_3)$. Such an intermediate, available to $Os(CO)_4(H)CH_3$ but not to $Os(CO)_4H_2$, would explain the comparatively rapid decomposition of the former compound.[27] Attempts to trap **4**—by forming an adduct stable enough to be observed before methane evolution—have so far been unsuccessful ($(CH_3O)_3P$ gives results similar to Et_3P) but are continuing.

It is now clear that simple intramolecular reductive elimination of R-R′ does not occur from $Os(CO)_4RR'$ for R and R′ = CH_3 and H. The absence of this traditionally anticipated reaction no doubt reflects the high energy of the distorted tetrahedral $Os(CO)_4$ fragment[28] which such an elimination would leave. Instead $Os(CO)_4H_2$ and $Os(CO)_4(H)CH_3$ undergo dinuclear elimination, and $Os(CO)_4(CH_3)_2$, extraordinarily stable, eventually decomposes largely by metal-carbon bond homolysis and formation of methyl radicals.[29]

In such six-coordinate cases where simple reductive elimination is not possible, dinuclear elimination has thus far been found only when hydride is one of the ligands to be eliminated. This observation may be rationalized by noting that alkyl-bridged polynuclear transition metal complexes are unknown, whereas hydride-bridged ones are common in stable molecules.[30] If the ligand-bridged metal-metal interactions are important in dinuclear elimination, such interactions—and hence dinuclear elimination—would be expected to occur more readily when hydride is involved.

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(16) The fact that CD_4 is not observed in the presence of Et_3P (vide infra) demonstrates that scrambling of labels among different molecules of **1** does not occur prior to the rate-determining step in the dinuclear elimination.

(17) Monitored by observing the disappearance of the IR band at 2063 cm^{-1}.

(18) Such facile carbonyl dissociation would have been improbable on fundamental grounds. Exchange rate data[19] on $Os_3(CO)_{12}$, extrapolated to 126 °C and corrected statistically agree within a factor of 4 with the rate observed[1] for the thermolysis of $Os(CO)_4H_2$ at that temperature. As the trans effect of hydride is thus negligible in $Os(CO)_4H_2$, there is no plausible reason carbonyl dissociation from $Os(CO)_4(H)CH_3$ should be rapid enough to be rate-determining in its comparatively rapid thermal decomposition.

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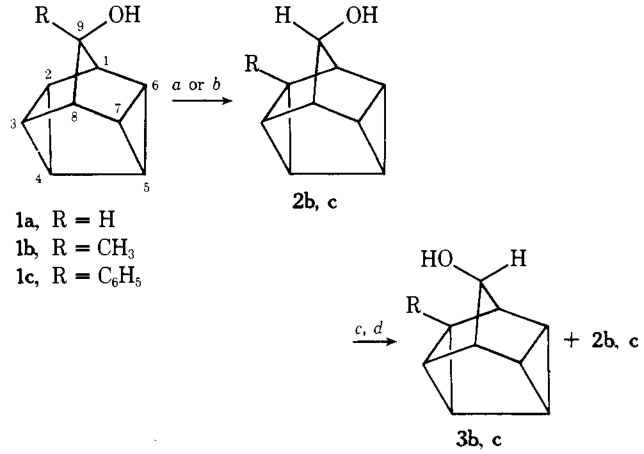
Remote and Proximate Substituent Effects on Trishomocyclopropenium Ion Formation in the Solvolysis of Methyl and Phenyl Substituted 9-Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl *p*-Nitrobenzoates

Sir:

The significance of substituent effects upon the rate of formation of nonclassical carbonium ions in solvolysis reactions has been subject to considerable debate in spite of the large amount of kinetic data which has been obtained for this purpose.[1-5] Major uncertainties arise in many cases from the incursion of steric, conformational, and other extraneous effects which may accompany substituent changes and the troublesome possibility that the structure of the carbonium ion intermediate may be seriously altered as well. We wish to report the results of an investigation on the solvolysis of 9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl *p*-nitrobenzoates (**1**-OPNB and **2**-OPNB) bearing methyl and phenyl substituents at the 2 and 9 positions. Since the formation of nonclassical trishomocyclopropenium ions from compounds of this type is well established both under solvolytic[6a] and stable ion[6b] conditions and, in the case of the unsubstituted parent (**1a**-OPNB), is attended by a kinetic enhancement of 10^{10-12} from cyclopropane participation in the solvolysis,[6a] this seemed to be a propitious structural environment in which to evaluate remote and proximate substituent effects on trishomocyclopropenium ion formation.[7,8]



1a, R = H
1b, R = CH_3
1c, R = C_6H_5

2b, c

3b, c

[a] **1b** → **2b**: HCO_2H, 10 °C, 13 h; OH^- (~30%). [b] **1c** → **2c**: 0.1 M $HClO_4$, 80% aqueous dioxane, reflux, 8 h (73%). [c] $CrO_3 \cdot C_6H_5N$, CH_2Cl_2. [d] $LiAlH_4$, ether.

The secondary pentacyclic alcohols **2b** and **2c** were secured by means of acid-catalyzed homocyclopropylcarbinyl rearrangement of the previously reported tertiary isomers, **1b** and **1c**, respectively.[6b] The structures (**2b** and **2c**) assigned to the rearrangement products are supported by appropriate NMR spectral data, including in particular the appearance of a quartet for the carbinyl protons at C-9 (vicinal coupling to H_1 and H_8 and long range coupling to H_5)[6a] and the observation that kinetically controlled solvolyses of the corresponding *p*-nitrobenzoates regenerate the original tertiary alcohols as the major products (see below). Independent evidence which affirms the anti stereochemical relationship between the substituent and the hydroxyl group derives from the finding that lithium aluminum hydride reduction of the corresponding ketones affords epimeric alcohols as major products (**3b**:**2b** = 2:1; **3c**:**2c** = 3.4:1).

Solvolysis of either of the two methyl substituted *p*-nitrobenzoates **1b**-OPNB (mp 142–143.5 °C) and **2b**-OPNB (mp 115–116.5 °C) in 65% aqueous acetone at 100 °C furnishes the same 80:20 mixture of tertiary and secondary alcohols (70–75% isolated yield). In a similar manner, solvolysis of the tertiary phenyl substituted *p*-nitrobenzoate **1c**-OPNB at 80 °C produced a 94:6 mixture of tertiary and secondary alcohols. Since it was found that this product ratio varied with temperature, direct comparison of the product ratios for the solvolysis of the tertiary and secondary phenyl substituted *p*-nitrobenzoates, **1c**-OPNB (mp 162.5–164 °C) and **2c**-OPNB (mp 113–115 °C), was done at 125 °C. At this temperature, both isomers produced a 78:22 mixture of tertiary and secondary phenyl substituted alcohols. That these isomer ratios represent the kinetic product distributions was verified by GLC and/or LC analyses during the course of the solvolyses.[9]

The formation of the same product ratios from either tertiary or secondary *p*-nitrobenzoates in both the methyl and phenyl substituted pentacycles indicates common trishomocyclopropenium ions **4b** and **4c** as intermediates. Since these ions possess two enantiotopic secondary positions, the tertiary:secondary capture ratios for **4b** and **4c** are 8:1 at 100 °C and 7:1 at 125 °C, respectively.